

A Mechanistic Study of Oxinato Complexes of Rhodium(I)

by

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Preface

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**“By nature everyone wants to know everything but what is the purpose if you do not know and honour God”
(Thomas A Kempis)**

For my Parents: Inus and Erna

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Abbreviations and symbols

Label	Definitions
δ	Chemical shift
Δ	Heating
ν	Stretching frequency on IR
Ψ	Wave function of the system
ΔE	Energy difference
$\Delta H^\ddagger$	Enthalpy of activation
$\Delta S^\ddagger$	Entropy of activation
T	Temperature
d	Doublet
dd	Doublet of doublets
m	Multiplet
s	Singlet
<i>m</i>	Meta
<i>p</i>	Para
HF	Hartree-Fock method
UV	Ultraviolet
ppm	Part per million
^t Bu	Tertiary butyl
CO	Carbon monoxide
DCM	Dichloromethane
DFT	Density functional theory
DMF	N,N-Dimethylformamide
HP	High pressure
NMR	Nuclear magnetic resonance
PR ₃	Tertiary phosphine
RMS	Root mean square
STO	Slater type orbitals
Vis	Visible
ZPE	Zero potential energy
X-X	Single bonded atoms
X=X	Double bonded atoms
X...X	Non-bonded atomic interaction
LL'-Bid	Bidentate ligand
DMSO	Dimethyl sulfoxide
ox	8-Hydroxyquinoline
quinoline	8-Hydroxyquinoline
(Hox)	8-Hydroxyquinoline
(HoxCl)	5-Chloro-8-hydroxyquinoline
(HoxF)	5-Fluoro-8-hydroxyquinoline
(HoxBr)	5-Bromo-8-hydroxyquinoline
(HoxI)	5-Iodo-8-hydroxyquinoline
(HoxMe)	5-Methyl-8-hydroxyquinoline
(H ₂ oxCl.Br)	5-Chloro-8-hydroxyquinolinium bromide
(H ₂ oxCl.PF ₆)	5-Chloro-8-hydroxyquinolinium hexafluorophosphate hydrate
(HoxNO ₂)	5-Nitro-8-hydroxyquinoline
(H ₂ oxNO ₂ .NO ₃)	5-Nitro-8-hydroxyquinolinium nitrate
(HoxMeCl.HCl)	5-chloromethyl-8-hydroxyquinoline hydrochloric acid solvate
(HoxL)	5-phenylazo-8-hydroxyquinoline
(HoxL-Me ₂)	5-[(2,4-dimethyl)phenylazo]-8-hydroxyquinoline
(HoxL-Me ₃)	5-[(2,4,6-trimethyl)phenylazo]-8-hydroxyquinoline
PPh ₃	Triphenylphosphine
PPh ₂ Cy	Cyclohexyldiphenylphosphine
PPhCy ₂	di-cyclohexylphenylphosphine
PCy ₃	tricyclohexylphosphine
P(5FPh) ₃	tris(pentafluorophenyl)phosphine

$P(p\text{-ClPh})_3$	tris(para chloro phenyl)phosphine
$P(p\text{-FPh})_3$	tris(para fluoro phenyl)phosphine
$P(O\text{-}2,4\text{di}^t\text{BuPh})_3$	tris(2,4-di-tert-butylphenyl)phosphite
$P(O\text{-}4^t\text{BuPh})_3$	tris(4-tert-butylphenyl)phosphite
$P(O\text{-}2\text{MePh})_3$	tris(2-methylphenyl)phosphite

Summary

The aim of this study was to functionalize 8-hydroxyquinoline bidentate ligand systems and introduce these bidentate ligands as well as tertiary phosphine ligands in a systematic way into Rh(I) complexes, in an attempt to determine the complex solid state geometrical parameters and manipulate the metal electron density.

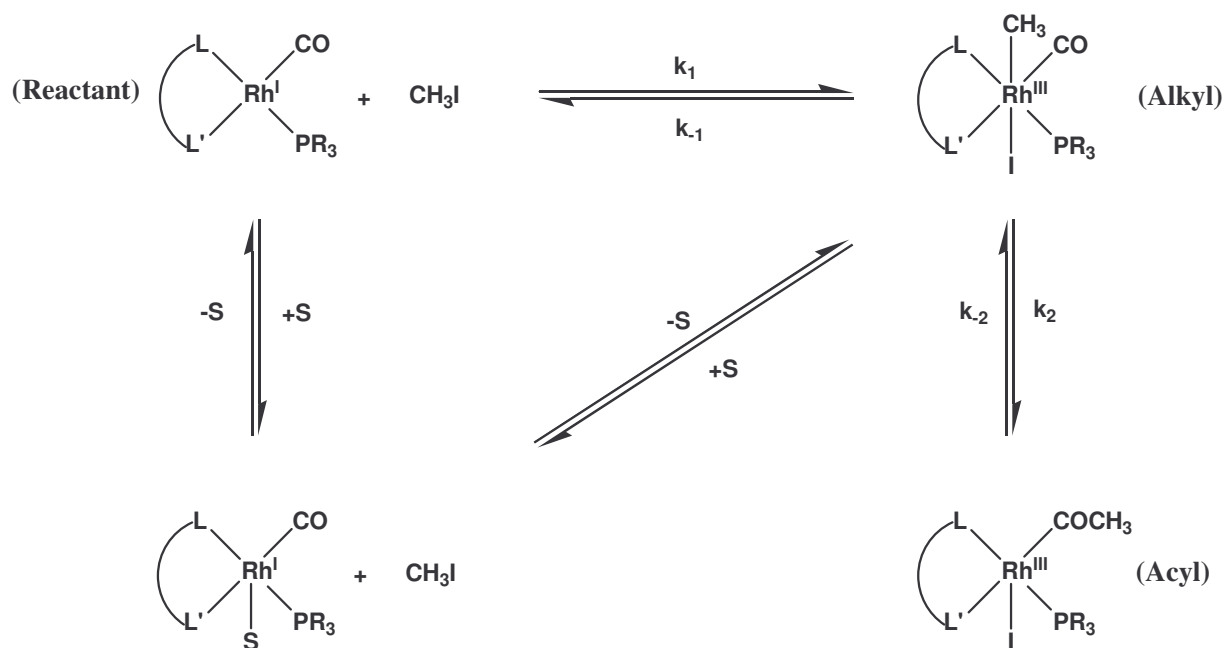
Functionalization of the oxine moiety was fairly easy and X-Ray crystallographic structure determinations are reported for a few ligand systems: 5-chloro-8-hydroxyquinoline (Orthorombic Fdd_2 , $R = 3.19\%$), 5-chloro-8-hydroxyquinolinium bromide (Monoclinic $P2_1/n$, $R = 4.50\%$), 5-chloro-8-hydroxyquinolinium hexafluorophosphate hydrate (Monoclinic $P2_1/n$, $R = 4.07\%$), 5-nitro-8-hydroxyquinoline (Orthorombic Fdd_2 , $R = 2.49\%$), 5-nitro-8-hydroxyquinolinium nitrate (Triclinic $P\bar{1}$, $R = 2.44\%$) and 5-chloromethyl-8-hydroxyquinoline hydrochloric acid solvate (Monoclinic $P2_1/c$, $R = 4.76\%$). From the solid state study it was established that for neutral ligands the *cis*-hydroxyl hydrogen configuration mostly leads to the formation of hydrogen bonded dimers and that the *trans*-hydroxyl hydrogen configuration will only occur in the presence of intermolecular soft contacts to neighbouring molecules. A theoretical investigation on functionalized 8-hydroxyquinoline compounds proved the *cis*-hydroxyl hydrogen configuration to be the energetically preferred isomer and that oxine functionalization influenced the molecular energy level.

Various phosphine and phosphite ligands were introduced onto the rhodium(I) complexes, to note different intermolecular interactions in the solid state. The reported X-Ray crystallographic structure determinations include the following complexes: $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3)]$ (Orthorombic $Pccn$, $R = 4.26\%$), $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2\text{MePh})_3)]$ (Monoclinic $P2_1/c$, $R = 4.63\%$), $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{5FPh})_3)]$ (Monoclinic C_2/c , $R = 6.39\%$), $[\text{Rh}(\text{ox})(\text{CO})(\text{PCy}_3)]$ (Monoclinic C_2/c , $R = 4.73\%$), $[\text{Rh}(\text{ox})(\text{CO})(\text{PCyPh}_2)]$ (Monoclinic $P2_1/n$, $R = 4.25\%$), $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ (Triclinic $P\bar{1}$, $R = 7.52\%$), $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-4^t\text{BuPh})_3]$ (Triclinic $P\bar{1}$, $R = 3.97\%$), $[\text{Rh}(\text{oxCl})(\text{CO})(\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3)]$ (Monoclinic $P2_1/n$, $R = 7.15\%$), $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-ClPh})_3]$ (Monoclinic $P2_1/n$, $R = 9.69\%$), $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-FPh})_3]$ (Triclinic $P\bar{1}$, $R = 4.14\%$), $[\text{Rh}(\text{oxL})(\text{CO})(\text{PPh}_3)]$ (Monoclinic $P2_1/c$, $R = 10.7\%$), $[\text{Rh}(\text{oxL})(\text{CO})(\text{PCy}_3)]$ (Monoclinic $P2_1/n$, $R = 6.74\%$) and $[\text{Rh}(\text{oxL-Me}_3)(\text{CO})(\text{PPh}_3)]$ (Triclinic $P\bar{1}$, $R = 4.70\%$). From these data sets the phosphorous ligands steric effect, in the solid state, was determined by calculating the ligands effective cone angle. In general the molecules pack with a

quinoline ligand to ligand's π -stacking in a "head to tail" fashion, influenced by 8-hydroxyquinoline functionalization.

A few phosphine substituted rhodium(I) complexes were selected to investigate the ligand's effect on the electron density of the rhodium metal centre, by determining the complex catalytic activity towards a methyl iodide oxidative addition reaction. The PPh_3 , PCyPh_2 , PCy_2Ph and PCy_3 ligated rhodium(I) complexes were selected to hopefully obtain a stepwise change in the steric and electronic properties of the metal centre. The influence from functionalized 8-hydroxyquinoline ligands on the metal's electron density was investigated in the same manner.

It was found that by altering the electron withdrawing properties of substituents on the 8-hydroxyquinolinato backbone, the rate of Rh(III) alkyl formation during methyl iodide oxidative addition can be manipulated. The activity of functionalized 8-hydroxyquinolinato metal complexes towards oxidative addition decrease in the following order: $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)] > [\text{Rh}(\text{oxCl})(\text{CO})(\text{PPh}_3)] > [\text{Rh}(\text{oxNO}_2)(\text{CO})(\text{PPh}_3)]$. Both 8-hydroxyquinolinato and 5-chloro-8-hydroxyquinolinato phosphine ligated rhodium complexes displayed the following order of activity towards Rh(III) alkyl formation: $[\text{Rh}(\text{oxY})(\text{CO})(\text{PCyPh}_2)] > [\text{Rh}(\text{oxY})(\text{CO})(\text{PPh}_3)] > [\text{Rh}(\text{oxY})(\text{CO})(\text{PCy}_3)] > [\text{Rh}(\text{oxY})(\text{CO})(\text{PCy}_2\text{Ph})]$ where Y = H or Cl respectively, demonstrating that neither the phosphine ligand steric nor electronic properties of the ligands are dominating influences on the rate of Rh(III) alkyl formation. The proposed mechanism for methyl iodide oxidative addition to complexes of the type $[\text{Rh}(\text{oxY})(\text{CO})(\text{PR}_3)]$, where Y = H, Cl or NO_2 and R = Ph_3 , CyPh_2 , Cy_2Ph or Cy_3 , is depicted in Scheme I.



Scheme I The reaction scheme for iodomethane oxidative addition to $[\text{Rh}(\text{oxY})(\text{CO})(\text{PR}_3)]$ complexes, where $\text{Y} = \text{H}, \text{Cl}$ or NO_2 and $\text{R} = \text{Ph}_3, \text{CyPh}_2, \text{Cy}_2\text{Ph}$ or Cy_3 , followed by migratory insertion. Two oxidative addition pathways are indicated, with the solvent denoted by S.

The $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ complex was also exploited as a catalytic precursor for the hydroformylation of 1-octene, to investigate ligand influences on a Rh(I) metal centre under hydroformylation reaction conditions.

Keywords: Rhodium

8-Hydroxyquinoline

Phosphine

Phosphite

Cone angle

π -Stacking

Iodomethane

Oxidative addition

Hydroformylation

Opsomming

Die mikpunt van die ondersoek was funksionalisering van die bidentate ligand 8-hidroksikinolien, gevolg deur sistematiese 8-hidroksikinolien en tertiere fosfien koördinasies tot 'n rhodium metaal kern. Om sodoende die geometriese kooördinasie van die komplekse in vastetoestand te kan bepaal en vas te stel hoe ligande die elektron digtheid van 'n metaal kern affekteer.

Funksionalisering van die 8-hidroksikinolien ligande was voor die hand liggend en X-Straal kristallografies struktuur bepaling vir van die ligand sisteme word gerapporteer: 5-chloro-8-hidroksikinolien (Orthorombies Fdd_2 , $R = 3.19\%$), 5-chloro-8-hidroksikinolinium bromide (Monoklien $P2_1/n$, $R = 4.50\%$), 5-chloro-8-hidroksikinolinium hexafluorophosphate hidraat (Monoklien $P2_1/n$, $R = 4.07\%$), 5-nitro-8-hidroksikinolien (Orthorombies Fdd_2 , $R = 2.49\%$), 5-nitro-8-hidroksikinolinium nitraat (Triklies $P\bar{1}$, $R = 2.44\%$) en 5-chlorometiel-8-hidroksikinolien hidrochloried suur oplosmiddel (Monoklien $P2_1/c$, $R = 4.76\%$). In die vastetoestand studie was daar bepaal dat die neutrale ligande waterstof gebinde dimere vorm met behulp van die *cis*-gekonfigureerde hidroksiel waterstof atome, die *trans*-gerigde hidroksiel waterstof atoom konfigurasie is slegs teenwoordig saam met intermolekulêre kontakte tussen die ligand en naburige molekules. Met 'n teoretiese studie van die gefunksionaliseerde 8-hidroksikinolien ligande was daar bepaal dat die *cis*-hidroksiel waterstof konfigurasie die laagste energie vlak beset en dat funksionalisering die molekulêre energie vlakke beïnvloed.

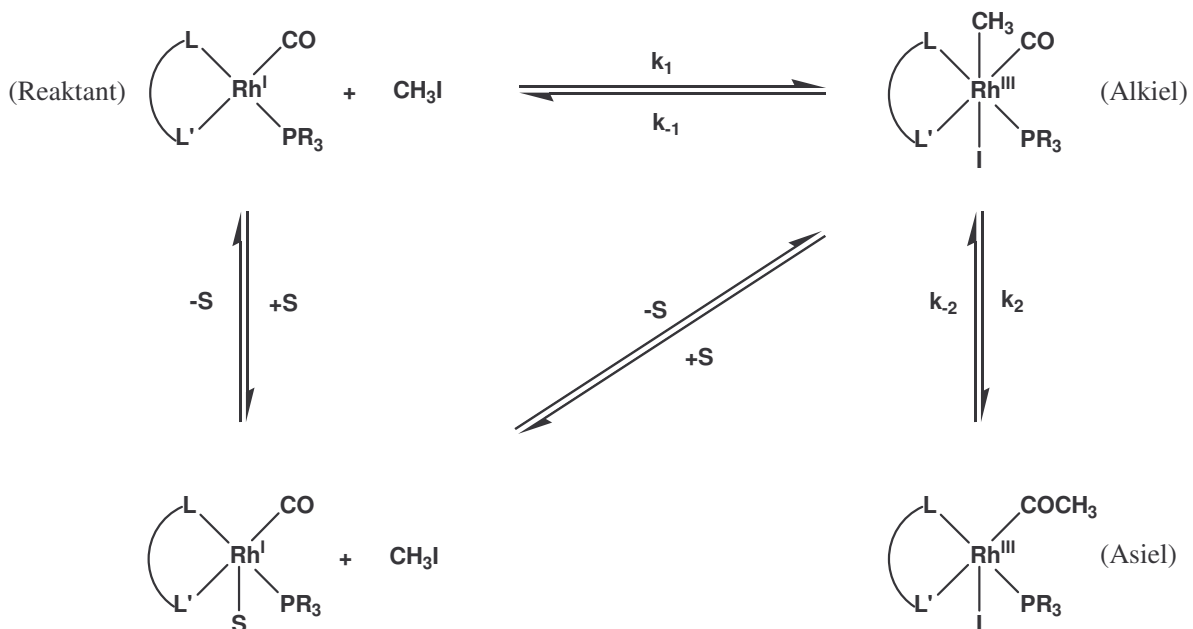
Verskeie fosfien en fosfiet rhodium(I) komplekse was gesintetiseer, om die moontlik verskillende intermolekulêre interaksies en pakking in die kristal sisteme te bestudeer. Gerapporteerde X-straal kristallografiese data van rhodium(I) fosfien en fosfiet komplekse sluit die volgende in: $[Rh(ox)(CO)(P(O-2,4di^tBuPh)_3)]$ (Orthorombies $Pccn$, $R = 4.26\%$), $[Rh(ox)(CO)(P(O-2MePh)_3)]$ (Monoklien $P2_1/c$, $R = 4.63\%$),

[Rh(ox)(CO)(P(5FPh)₃)] (Monoklien C_2/c , $R = 6.39\%$), [Rh(ox)(CO)(PCy₃)] (Monoklien C_2/c , $R = 4.73\%$), [Rh(ox)(CO)(PCyPh₂)] (Monoklien $P2_1/n$, $R = 4.25\%$), [Rh(ox)(CO)(PPh₃)] (Trikliesen $P\bar{1}$, $R = 7.52\%$), [Rh(oxCl)(CO)P(O-4^tBuPh)₃] (Trikliesen $P\bar{1}$, $R = 3.97\%$), [Rh(oxCl)(CO)P(O-2,4di^tBuPh)₃] (Monoklien $P2_1/n$, $R = 7.15\%$), [Rh(oxCl)(CO)P(p-ClPh)₃] (Monoklien $P2_1/n$, $R = 9.69\%$), [Rh(oxCl)(CO)P(p-FPh)₃] (Trikliesen $P\bar{1}$, $R = 4.14\%$), [Rh(oxL)(CO)(PPh₃)] (Monoklien $P2_1/c$, $R = 10.7\%$), [Rh(oxL)(CO)(PCy₃)] (Monoklien $P2_1/n$, $R = 6.74\%$) en [Rh(oxL-Me₃)(CO)(PPh₃)] (Trikliesen $P\bar{1}$, $R = 4.70\%$). Vanaf die datastelle kon onder andere die steriese invloed, in vaste toestand, van die fosfor ligande bepaal word. Dit deur die effektiewe keel hoek van die ligand te bereken. In die algemeen pak die molekules in 'n kinolien ligande tot ligand π -pakking met 'n "kop tot stert" rangskikking. Die pakking word wel beïnvloed deur die funksionaliserings groep op die kinolien basis.

Die invloed van ligande op die elektron digtheid van die metaal komplekse was getoets deur bepaling van die kompleks katalitiese aktiwiteit in 'n metiel jodied oksidatiewe addisie reaksie. Die gekose fosfien ligande sluit in: PPh₃, PCyPh₂, PCy₂Ph en PCy₃. Die ligande was gekies om onder andere 'n stapsgewyse verandering in hul steriese en elektroniese eienskappe te bewerkstellig, soos 'n feniel ring verplaas word met 'n sikloheksiel ring. So was die invloed van gefunksionaliseerde 8-hidroksiekinolien ligande op die rhodium(I) elektron digtheid is ook bepaal.

Met verandering van die elektron ontrekkings eienskappe van substituent op die 8-hidroksiekinolinato basis, kan die tempo van Rh(III)-alkiel spesie vorming tydens metiel jodied oksidatiewe addisie gemanipuleer word. Die gefunksionaliseerde 8-hidroksiekinolinato metaal komplekse kan as volg gerangskik word met afnemende aktiwiteit teenoor die oksidatiewe addisie: [Rh(ox)(CO)(PPh₃)] > [Rh(oxCl)(CO)(PPh₃)] > [Rh(oxNO₂)(CO)(PPh₃)].

Vir beide die 8-hidroksiekinolinato en 5-chloro-8-hidroksiekinolinato fosfien rhodium komplekse kan die aktiwiteit teenoor Rh(III) alkiel vorming tydens 'n metiel jodied oksidatiewe addisie as volg gerangskik word: $[\text{Rh}(\text{oxY})(\text{CO})(\text{PCyPh}_2)] > [\text{Rh}(\text{oxY})(\text{CO})(\text{PPh}_3)] > [\text{Rh}(\text{oxY})(\text{CO})(\text{PCy}_3)] > [\text{Rh}(\text{oxY})(\text{CO})(\text{PCy}_2\text{Ph})]$ waar Y = H of Cl respektiewelik is. Dit demonstreer dat nie die steriese of elektroniese invloed van die fosfien ligande dominerend is teenoor die tempo bepaling van Rh(III) alkiel vorming nie. Die voorgestelde algemeen aanvaarbare reaksie meganisme wat gevolg word in die betrokke oksidatiewe addisie reaksies is soos geïllustreer in Skema I.



Skema I. Die reaksie meganisme vir methieljodied oksidatiewe addisie $[\text{Rh}(\text{oxY})(\text{CO})(\text{PR}_3)]$ komplekse waar Y = H, Cl of NO_2 en R = Ph_3 , CyPh_2 , Cy_2Ph of Cy_3 , gevolg deur migrasie invoeging. Twee oksidatiewe addisie roetes word aangedui, met S wat 'n oplosmiddel voorstel.

Daar is bepaal dat die kompleks $[\text{Rh}(\text{oxY})(\text{CO})(\text{PPh}_3)]$ optree as 'n aktiewe katalis in die hidroformulering van 1-okteen. Dus is die bestudering van ligand invloed op 'n rhodium(I) kompleks in 'n tweede katalitiese reaksie moontlik.

Chapter 1

Introduction and Aim

1.1 Introduction

This study focus on 8-hydroxyquinolinatorrhodium(I) square planar systems, (Figure 1.1). As introduction to the various aims of the study; a brief explanation of the importance of rhodium in inorganic/organometallic chemistry, the influence of phosphorous ligands on a metal centre and the use of 8-hydroxyquinoline and its derivatives will follow.

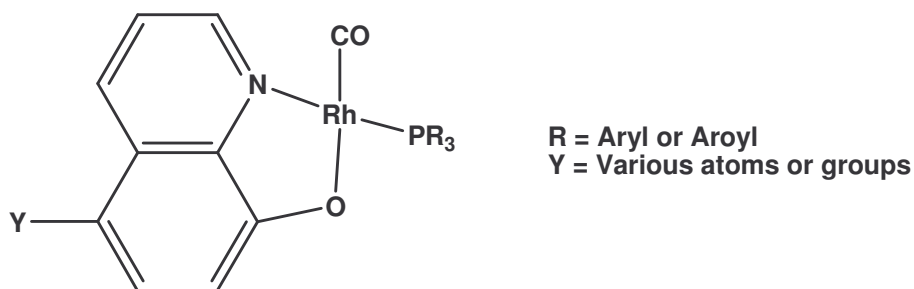


Figure 1.1 A line drawing of typical 8-hydroxyquinolinatorrhodium(I) systems.

1.2 Rhodium systems

Catalysis is a well known topic with a significant role in both academia and industry. To point out the role of rhodium in academia one can simply submit a search of a rhodium(I) square planar systems built from O:O or N:O donor bidentate ligands, a carbonyl ligand and a phosphorous ligand on the Crystal Structure Database (version 5.29, update August 2008), more than a hundred hits will be found¹. This is only a small contribution of research that is being done on these rhodium systems in academia. In industry, rhodium is used in various catalytic cycles, for example in the carbonylation of methanol to yield acetic acid in the Monsanto acetic acid process. As shown in (Section 2.3, Table 2.1), rhodium is used in various homogeneously catalysed industrial processes, i.e. Hydroformylation, the Acetic acid (Eastman Kodak and Tennessee-Eastman) and the Citronellal process. The use of rhodium as a homogeneous catalyst in hydrogenation of

¹ Allen, F. H. (2002). *Acta Cryst.* B58, 380.

alkenes and alkynes started with Wilkinson and his co-workers². In 1971 Roth *et al.*³ illustrated the catalytic importance of rhodium(I) complexes containing phosphine ligands.

1.3 Ligands in organo transition metal catalysis

Growth in organometallic chemistry over the past 20 years initiated ligand design and manipulation from an organic perspective and thus enriched the field of inorganic chemistry⁴.

Metal-ligand coordination with ligands such as H⁻ (hydride), CO and alkenes are allowed by the metal d-orbitals. Another reason for this coordination is the ability of transition metals to exist in various oxidation states and also being able to exhibit a range of coordination numbers. These ligands bind in such a way that they are active towards further reactions. Their reactivity towards such reactions is a way to measurement and explain the chemistry of organo transition metal catalysis⁵.

Coordination compounds can be classified into the group containing ionic ligands like: H⁻, Cl⁻, OH⁻, Alkyl⁻, Aryl⁻, CH₃CO⁻, etc. and neutral ligands such as: CO, alkenes, phosphines, phosphites, arsine, H₂O and amines. Neutral ligands like phosphines influence the metal centre electronically and sterically. Bidentate ligands like 8-hydroxyquinoline with differing donor atoms influence the coordination ability of the metal in such a way that secondary ligand substitution, for example the substitution of one CO to form the complex shown in Figure 1.1, will occur primarily *trans* to the stronger σ -donor atom *ea.* the N-atom. In Section 1.3.1 and Section 1.3.2 the mono- and bi-dentate ligands (of relevance to this study) and their influence on a metal centre in a coordination compound are discussed respectively.

² Young, J. F., Osborn, J. A., Jardine, F. H. & Wilkinson, G. (1965). *Chem. Commun.* 131.

³ Roth, J. F., Craddock, J.H., Hershman, A. & Paulik, F. E. (1971). *Chem. Technol.* 600.

⁴ McCleverty, J. A. & Meyer, T. J. (2003). *Comp. Coord. Chem.* 2.

⁵ Godwin, H. A., Hoffman, B. & James, K. B. (2001). *The Frontiers of Inorganic chemistry*. A report based on the workshop sponsored by the National Science Foundation. Held at Copper mountain, Colorado. September 8-10.

1.3.1 Tertiary phosphorous(III) ligands

Phosphine ligated systems are still receiving a significant amount of attention because of their widespread applications in organometallic chemistry and an important role in industrial catalysis⁶. These ligands significantly influence the metal centre *via* both electronic and steric properties. Section 1.3.1.1 and Section 1.3.1.2 discuss the steric and electronic effects of tertiary phosphorous ligands on a metal centre.

1.3.1.1 Steric effects

The most widely used method in defining a reliable steric parameter in a phosphorus based ligand system is the Tolman cone angle¹¹ (eq. 1.1). Tolman proposed the measurement of the steric bulk of a phosphine ligand by use of CPK models, as illustrated in Figure 1.2. Using a coordination distance to a metal centre of 2.28 Å and allowing all other groups on the phosphorus atom to be rotating freely, a cone can be constructed which embraces all substituent atoms. In the case of non-symmetrical phosphorous ligands this cone, (θ), can be calculated by equation 1.1.

$$\Theta = \left(\frac{2}{3}\right) \sum_{i=1}^3 \frac{\Theta_i}{2} \quad (1.1)$$

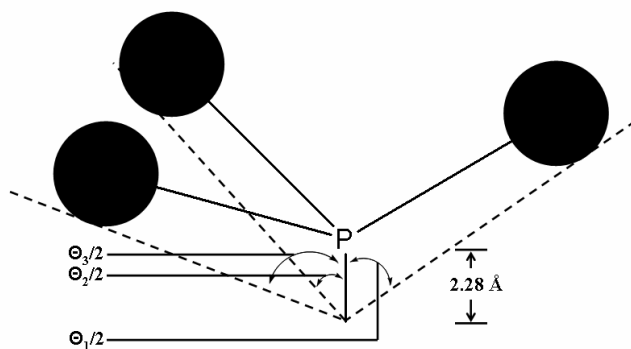


Figure 1.2 An illustration of the measurements needed for the calculation of the Tolman cone angle of a non-symmetrical phosphine ligand.

⁶ Van Leeuwen, P. W. N. M. (2004). *Homogenous Catalysis. Understanding the Art*. Kluwer academic publishers.

Another parameter being reported in the search of the ligand's steric influence is the effective cone angle. Determination of the effective cone angle is based on the Tolman cone angle, but the specific metal-phosphorous distance is used, as obtained from crystallographic data of the complex^{7,8}.

1.3.1.2 Electronic effects

With the inherent σ -donor and π -acceptor properties of phosphorous based ligands, they can form stable complexes with electron rich transition metals. The alkyl phosphines are better σ -electron donors compared to organophosphites which are in turn better π -electron acceptors. Please note that, in the case of a phosphine ligands the current view of orbitals responsible for π -back donation is the anti-bonding σ^* -orbitals of the phosphorus to carbon⁹.

By studying the change in carbonyl stretching frequencies on $\text{NiL}(\text{CO})_3$ or $\text{CrL}(\text{CO})_5$ complexes, where L is the phosphorus ligand, the different σ -basicity and π -acidity character of phosphorus ligands were determined and reported by Strohmeier and Harrocks for $\text{CrL}(\text{CO})_5$ complexes¹⁰. Remember that the electronic parameters of these ligands may differ from one metal to another. Tolman defined an electronic parameter χ (chi), using the $\text{NiL}(\text{CO})_3$ complex with $\text{L}=\text{P}(\text{t-Bu})_3$ as the reference¹¹. The χ (chi) values of other ligands are thus simply defined as the difference in the IR frequencies of the ligand in question and that of the reference ligand¹⁰. Other techniques for evaluating the electronic properties of phosphine ligands are described in literature e.g.: the quantitative analysis of ligand effects (QALE) that has been extended and developed significantly by Prock and co-workers¹².

⁷ Tolman, C.A. (1977). *Chem. Rev.* 77, 313.

⁸ Otto, S., Roodt, A. & Smith, J. (2000). *Inorg. Chim. Acta.* 303, 295.

⁹ Roodt, A., Otto, S. & Steyl, G. (2003). *Coord. Chem. Rev.* 245, 121.

¹⁰ Strohmeier, W. & Müller, F. J. (1967). *Chem. Ber.* 100, 2812.

¹¹ Tolman, C. A. (1977). *Chem. Rev.* 77, 313.

¹² Wilson, M. R., Prock, A., Geiring, W. P., Fernandez, A. L., Haar, C. M., Nolan, S. P. & Foxman, B. M. (2002). *Organometallics.* 21, 2758.

1.3.1.3 The Hammett parameter

Louis Hammett correlated electronic properties of organic acids and bases with their equilibrium constants and reactivity, noting the substituents' effect on the dissociation constant of organic acids and bases. Consider the dissociation constant of benzoic acid and that of *para*-nitro benzoic acid, being 6.27×10^{-5} and 37.0×10^{-5} , respectively. This indicates that electronic withdrawal by the nitro group increases the dissociation constant. The ability of a substituent to change the electron-donating or withdrawal properties of a phenyl ring can be defined by the Hammett equation 1.2, where k is the acidity constant for a substituted benzoic acid and k_H is the acidity constant of benzoic acid¹³.

$$\log \left(\frac{k}{k_H} \right) = \sigma \quad (1.2)$$

The Hammett equation is one of the earliest examples of a linear free energy relationship, between the equilibrium constant and reactivity of organic acids and bases. The Hammett equation thus describes the straight line correlation between a series of reactions with substituted aromatics and the hydrolysis of benzoic acids containing the same substituents as the aromatics¹⁴:

Kabachnik and Balueva reported the application of the Hammett equation to the basicity constants of phosphines and found a straight line relationship between the pKa and σ values of phosphines, See Figure 1.3¹⁵.

¹³ Hoffmann, R. V. (2004). *Organic chemistry: an intermediate text*. Wiley, New York.

¹⁴ Hammett, L. P. (1940). *Physical Organic Chemistry*. N.Y.

¹⁵ Kabachnik, M. I. & Balueva, G. A. (1962). *Translated from Izvestiya Akademii Nauk SSSR Otdelenie Khimicheskikh Nauk*. 3. 3, 536.

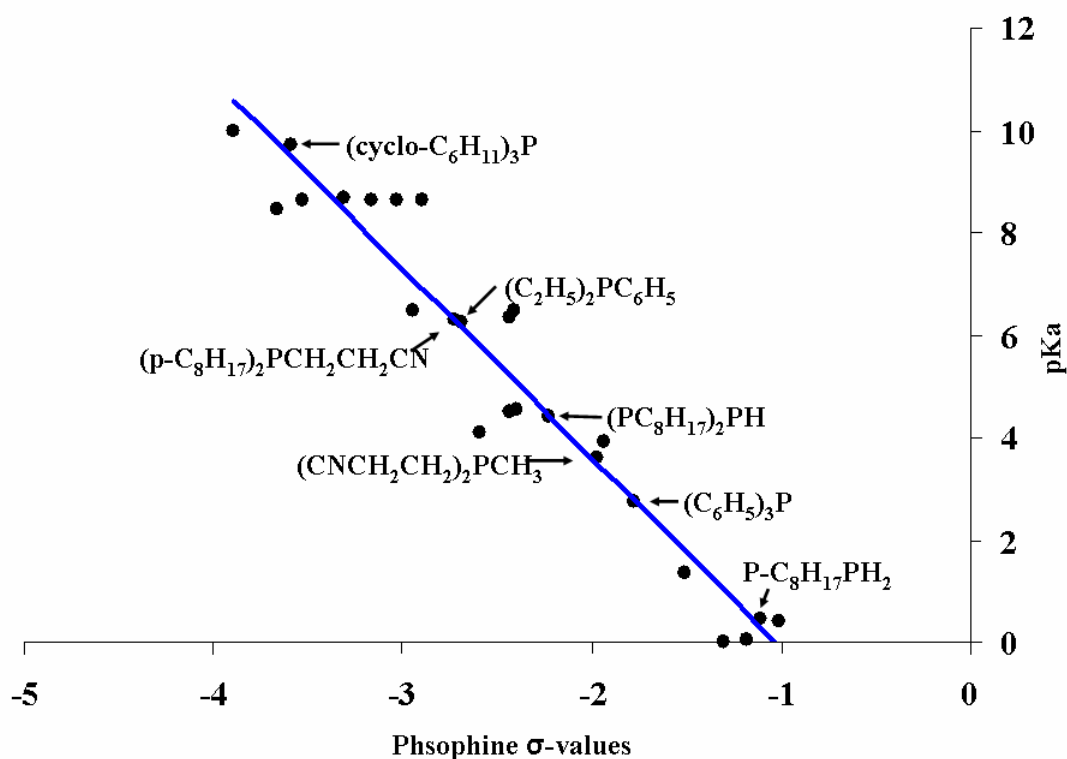


Figure 1.3 An indication of the straight line relationship between pKa and σ values of phosphines and the Hammett electronic parameter.

Also noted in this article is that the use of the Hammett equation for basicity constants (pKa) of the phosphines show the absence of a marked role of steric factors in a reaction.

1.3.2 8-Hydroxyquinoline

The bidentate ligand 8-hydroxyquinoline, Figure 1.4, can complex with metal ions as a neutral molecule¹⁶ and mostly as a deprotonated anion with the loss of the hydroxyl hydrogen¹⁷. In this complexation the pyridyl nitrogen and the phenyl oxygen act as N and O electron donors to the metal centre, resulting in the formation of a five-member chelate ring, (Figure 1.1). With the nitrogen donor atom being a stronger σ -electron donor than the phenyl oxygen, a secondary *mono*-ligand substitution on the metal centre results in

¹⁶ Huges, D. L. & Truter, M. R. (1979). *J. Chem. Soc. Dalton Trans.* 520.

¹⁷ Palenik, G. J. (1964). *Acta Cryst.* 17, 696.

the formation of one major isomer¹⁸ and an important application of, the *trans*-effect and *trans* influence. The *trans*-effect is defined as the labilization of ligands *trans* to other specific ligands, which can thus be regarded as *trans*-directing ligands¹⁹.

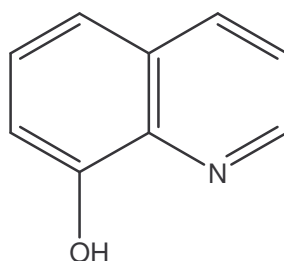


Figure 1.4 A line drawing of the molecule 8-hydroxyquinoline.

8-Hydroxyquinoline and some derivatives are well proven precipitation agents and complexants in chemical analysis which can form well defined chelate complexes with many ions of main groups and transition metals. 8-Hydroxyquinoline has also been used as a structural element to synthesise noncyclic crown-type compounds (podands) yielding crystalline complexes with alkali and alkaline earth metal ions. Lipophilic 8-hydroxyquinoline derivatives such as the commercial reagent Kelex 100 are promising extractants for metal extraction and decontamination of multimetal finishing wastes. These compounds have also been proposed as chemo luminescent probes for analytical determination of lanthanides²⁰. Here the *mono* Iodo-8-quinolines and 6-iodo-8-hydroxyquinoline proved to be the most active isomers.

In the field of organic light emitting devices (OLEDs) Tang and Van Slyke²¹ were the first to use tris-(8-hydroxyquinolinato) aluminium as an efficient green electroluminescent material. Since then it has been a workhorse material for use in OLED applications. These luminescent metal complexes are the most utilized materials for multilayer light emitting devices. 8-Hydroxyquinoline exhibits powerful chelating

¹⁸ Leipoldt, J. G., Basson, S.S. & Dennis, C.R. (1981). *Inorg. Chim. Acta*. 50, 121.

¹⁹ Basolo, F. & Pearson, R. G. (1962). *Prog. Inorg. Chem.* 4, 381.

²⁰ Marti, R., Meier, R., Nury, P., Roeder, M. & Zhang, K. (2004). *Org. Process Research and Development*. 8, No. 4, 663.

²¹ Tang, C. W. & VanSlyke, S. A. (1987). *Appl. Phys. Lett.* 51, 913-915.

capability and luminescence properties tuneable through appropriate substitutions. In OLEDs the metal coordinated compound also acts as the electron transport material and it has been suggested that such abilities arise from π - π interactions between adjacent molecules²².

The tris-(8-hydroxyquinolato) aluminium complex has low photoluminescence quenching in the solid state and has to be vapour deposited, the advantages are good electron mobility, good stability against recrystallisation as an amorphous thin film and good electron transport properties in both single and bi-layer devices. In the search to obtain easily spin-castable materials, Mishra *et al.*²³ synthesised 5-alkoxymethyl and 5-aminomethyl-substituted 8-hydroxyquinolines. They found that with the aluminium complexation, the complexes could be good candidates for electroluminescence devices. La Deda *et al.*²⁴ designed another range of 8-hydroxyquinoline derivatives to obtain materials with enhanced electron transport properties, this by substitution of penylazo groups on the 5-position of 8-hydroxyquinoline.

8-hydroxyquinoline has enhanced non-centrosymmetry due to the lack of rotational symmetry, an essential property to exhibit nonlinear optical activity (NLO). In the molecular design of new (NLO) materials, based on quinoline, the pyridine ring can function as an acceptor group and the benzene ring as the donor. The optical nonlinearities of this class of compounds can be improved by increasing the acceptor character of the pyridine ring and/or increasing the donor character of the benzene, *via* functionalization.

In the field of theoretical chemistry 8-hydroxyquinoline was not ignored but an extensive interest was rather shown towards 8-hydroxyquinoline. Li and Fang investigated

²² Sapochak, L. S., Burrows, E. P., Garbuzov, D., Ho, D. M., Forrest, S. R. & Thompson, M. E. (1996). *J. Phys. Chem.* 100, 161.

²³ Mishra, A., Nayak, P. K. & Periasamy, N. (2004). *Tetrahedron. Lett.* 45, 6265.

²⁴ La Deda, M., Grisolia, A., Aiello, I., Crispini, A., Ghedini, M., Belvisio, S., Amati, M. & Lelj, F. (2004). *Dalton Trans.* 2424.

combined CASSCF and density functional theory DFT calculations and did a MP2 study on the ground-and excited-state proton transfer processes of 8-hydroxyquinoline and it's one-water complex, to look into the relative importance of the intramolecular and intermolecular processes²⁵. Arici *et. al.*²⁶ reported the ab initio HF, DFT/B3LYP and BLYP calculation results on 8-hydroxyquinoline to give optimal molecular geometry, vibrational wavenumbers and modes of free 8-hydroxyquinoline.

²⁵ Li, Q. S. & Fang, W. H. (2003). *Chem. Phys. Lett.* 367, 637.

²⁶ Acrici, K., Yurdakul, M. & Yurdakul, S. (2005). *Spectrochim. Acta. A* 61, 37.

1.4 Aim

The numerous possibilities and applications of 8-hydroxyquinoline and 8-hydroxyquinolinato metal complexes are pointed out in the introduction as precipitation agents, organic light emitting devices and catalysts. Also note the effects of various ligands on the electronic properties of the metal centre, a known tool for tuning catalytic selectivity and reactivity.

These possibilities made the 8-hydroxyquinoline backbone a good choice as a basic ligand structure to exploit by chemical manipulation. The following aims were set for this study:

1. Functionalization of the 8-hydroxyquinoline backbone.
2. Solid state characterization of the functionalized 8-hydroxyquinoline compounds to determining the influence from *intra* and *inter* molecular interaction on the hydroxyl hydrogen position and molecular geometrical parameters.
3. Evaluation of the N-, O-donor atoms electronic properties, utilizing theoretical chemistry, combined with an investigation regarding the molecular energy levels of possible isomers.
4. Coordination of 8-hydroxyquinoline bidentate ligands to rhodium, obtaining the 8-hydroxyquinolinatorhodium(I) square planar complexes.
5. Solid state characterization of 8-hydroxyquinolinatorhodium(I) square planar complexes, to study the molecular geometrical parameters and solid state packing modes.
6. Investigate the influence from functionalized oxine moieties and various tertiary phosphorous ligands on the electron density of the metal centre, by determining the complex reaction rate in a methyl iodide oxidative addition reaction.

7. Investigate the viability of $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ as a catalytic precursor for hydroformylation reactions.

Chapter 2

Literature aspects of basic reactions associated with homogeneous catalysis

2.1 Introduction

The stipulated aims of this study include rhodium(I) square planar complex synthesis and catalytic investigations. A literature overview regarding ligand exchange and coordination, the “incipient carbonyl group”, complex formation, oxidative addition reactions, reductive elimination reactions and the application of rhodium as an industrial catalyst are topics that will be discussed.

The term “catalysis” is still defined as by Ostwald in 1895, “a catalyst accelerates a chemical reaction without affecting the position of equilibrium”. Apart from the reaction accelerating properties of catalysts, they can influence reaction selectivity. This means that different products can be obtained from a given starting material by the use of a different catalytic system. This type of reaction control is often more important in industry than the catalytic activity²⁷. Catalysis is typically divided into homogeneous, heterogeneous, and more recently biocatalysts. Considering a few of the stunning discoveries made in catalysis in recent years, five different types of chemical transformations can be pointed out.

1. Olefin Polymerizations
2. Olefin Metathesis
3. Carbonylation Reactions
4. Oxidation Catalysis
5. Asymmetric Catalysis

²⁷ Hagen, J. (1992). *Chemische Reaktionstechnik Eine Einführung mit Übungen*, VCH, Weinheim.

For the purpose of this study carbonylation reactions are discussed, an area of catalysis dominated by homogenous catalysts with almost endless applications.

2.2 Carbonylation reactions

Reactions involving a carbonyl attracted attention since the discovery of carbon-carbon bond formation reactions in the late nineteenth century²⁸. The carbonyl is one of the more versatile functionalities available, being susceptible to nucleophilic attack on the carbon and electrophilic attack on the oxygen. It also has the ability to stabilise an adjacent carbanion by charge delocalization onto the C=O double bond. For many synthetic purposes it can be regarded as an “incipient carbonyl group” that can be introduced directly onto a number of different sites in an organic molecule.

The numerous catalytic carbonylation reactions may be rationalized on the basis of a small number of “elementary reactions”. These reactions combine in a variety of ways to generate a series of catalytic cycles. Listed below are some of these “elementary reactions” followed by a short description of each²⁹.

1. Coordination and exchange of ligands
2. Complex formation
3. Acid–Base reactions
4. Redox reactions, oxidative addition and reductive elimination
5. Insertion and elimination reactions
6. Reactions at coordinated ligands

²⁸ Drury, D. J. (1984). *Aspects Homog. Catal.* 5, 197.

²⁹ Gates, B. C. (1992). *Catalytic Chemistry*, Wiley, New York.

2.2.1 Coordination and exchange of ligands

With the variable coordination number in many transition metals, especially when in solution, ligands can be released from the complex metal centre, undergo exchange or free coordination sites can be occupied by solvent molecules³⁰.

Many complexes do not react in their coordinatively saturated form, but *via* an intermediate of a lower coordination number with which they are in equilibrium. For ligand dissociation/association processes, Tolman⁷ introduced the 16/18 electron rule, being:

1. Under normal conditions, diamagnetic organometallic complexes of the transition metals exist in measurable concentrations only as 16- or 18-electron complexes.
2. Organometallic reactions, including catalytic processes, proceed by elemental steps involving intermediates with 16 or 18 valence electrons.

2.2.2 Complex formation

Complexation is governed by electron donating and accepting properties at the metal centre. In the catalytic reactions of alkenes substrate complexation at the metal centre is an important step.

The olefin ligands are bound to the transition metal through one or more double bonds, depending on the σ - and π -bonding capabilities of the transition metal. For softer metals the back bonding in the metal-olefin bond gets stronger the richer the metal centre in d-electrons, but there is a negligible influence from the lower d-electron species. The σ -acceptor property of the metal ion increases with the increasing positive charge, thus Rh(II) (d^7) is a stronger σ -acceptor than Rh(I) (d^8)²⁷. The π -bonding contribution of several metals can be arranged as depicted in Figure 2.1, showing the increase in the π -

³⁰ Taube, R. (1975). *Z. Chem.* 15, 11, 426.

bonding contribution and the stability of the metal olefin complex between the d^0 , d^8 and d^{10} metal species.

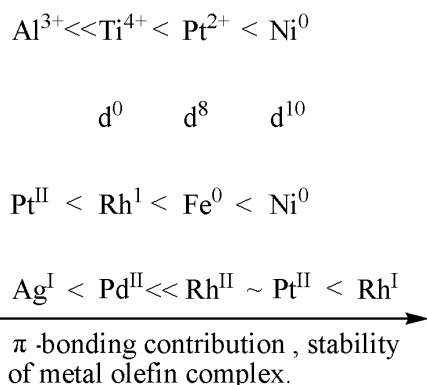


Figure 2.1 Arrangement of metals and their transition states, according to their contribution of π -bonding and their effect on the stability of the metal olefin complex.

2.2.3 Acid–Base reactions

Following the Brønsted and Lewis acid-base concept, transition metal cations can undergo addition of neutral or anionic nucleophiles to give cationic, anionic and π -acceptor complexes. An example of a Lewis acid is when a 16-electron species can add a ligand to result in the formation of an 18-electron complex, as shown in Scheme 2.1 for the complex $[\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2]$ (acac = acetyl acetone).



Scheme 2.1 An example of a Lewis acid where the 16e species accepts a ligand to form an 18 electron species.

Metal complexes acting as bases is a known concept; an example is the reaction of $[\text{Co}(\text{CO})_4]^-$ to form the cobalt carbonyl hydride, the true catalyst in many carbonylation reactions:

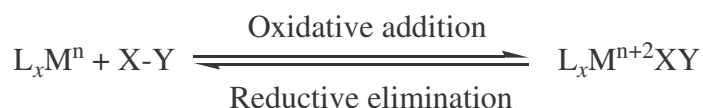


Scheme 2.2 A cobalt complex acting as a base to form the catalytic active cobalt carbonyl hydride.

The metal character of e.g. can be influenced by the donor character of ligands for example phosphines. Phosphine ligands that remove electron density from the metal centre lower the complex-formation constant and thus increase the metal basicity.

2.2.4 Redox reactions: oxidative addition and reductive elimination

The ability of transition metal complexes to access a number of different oxidation states, opens the possibility to add neutral or anionic nucleophiles, creating a field of endless synthetic possibilities³⁰. Transition metals can access these oxidation states *via* oxidative addition and its reverse, reductive elimination, as described by the following equilibrium.



Scheme 2.3 The equilibrium between transition metal oxidation states, accessed *via* oxidative addition and reductive elimination.

Bonds of small covalent molecules H-X, C-X, H-H, C-H, C-C, etc. (X = halogen) can add to low oxidation state transition metal complexes³¹. This increases both the coordination number and the oxidation number of the metal by two units. These reactions are mainly observed with complexes of d⁸ and d¹⁰ transition metals (e. g., Fe(0), Ru(0), Os(0), Rh(I), Ir(I), Ni(0), Pd(0), Pt(0), Pd(II), Pt(II)) and can take two possible courses:

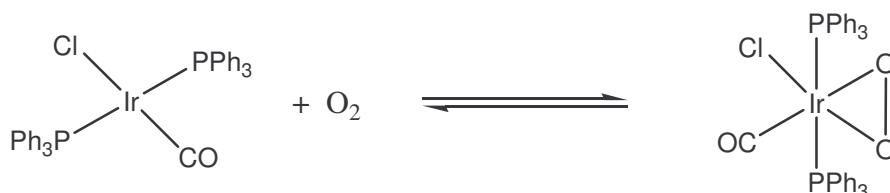
1. Molecules that are added split into two η^1 ligands, they are both formally anionically bound to the metal centre e.g. the square-planar iridium complex the central atom gives up two electrons and is oxidized to Ir(III).

³¹ Koga, N. & Morokama, K. (1991). *Chem. Rev.* 118, 91, 823.

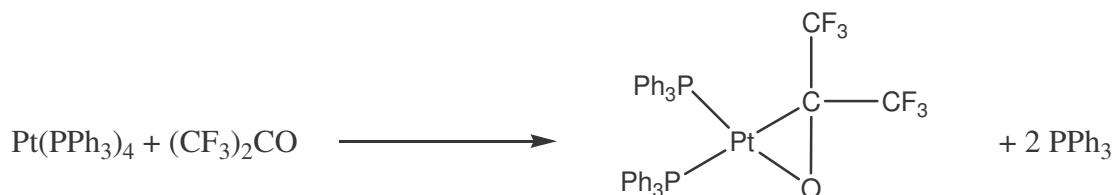


Scheme 2.4 An example of oxidation number increase: the Ir(I) complex (d^8) lose two electrons to form the Ir(III) complex (d^6).

2. Added molecules contain multiple bonds that are bound as η^2 ligands without bond cleavage resulting in a three-member ring system.



Scheme 2.5 An example of oxidative addition to an iridium complex, resulting in the formation of a three-member ring system



Scheme 2.6 An example of oxidative addition to a platinum complex, resulting in the formation of a three-member ring system

Oxidative addition is the initiating step for many catalytic carbonylation reactions, for example the C-X, (where X = halogen), addition to a rhodium(I) complex. The addition rate of these halogenated ligands to rhodium(I) complexes can be arranged in the order of $\text{C-I} > \text{C-Br} > \text{C-Cl} > \text{C-F}$. Considering the bond energy of the halogenated ligands, they show a bond energy increase in the same order. Summarised in Table 2.1 are some important molecules involved in oxidative addition reactions to transition metals and their influence on coordinating bonds.

Table 2.1 A short classification of important molecules in oxidative addition reactions on transition metal complexes.

Bond cleavage	No bond cleavage
H ₂	O ₂
X ₂	SO ₂
HX (X= Halogen, CN, RCOO, ClO ₄)	CS ₂
H ₂ S	CF ₂ =CF ₂
C ₆ H ₅ SH	(NC) ₂ C=C(CN) ₂
RX	R-C=C-R'
RCox	(CF ₃) ₂ CO
RSO ₂ X	RNCO
R ₃ SnX	R ₂ C=C=O
R ₃ SiX	
HgX ₂	
CH ₃ HgX	
SiCl ₄	
C ₆ H ₆	

R=alkyl, aryl, CF₃ etc.; X = Halogen

Presented in Figure 2.2 is a general layout of the various mechanisms found for oxidative addition reactions.

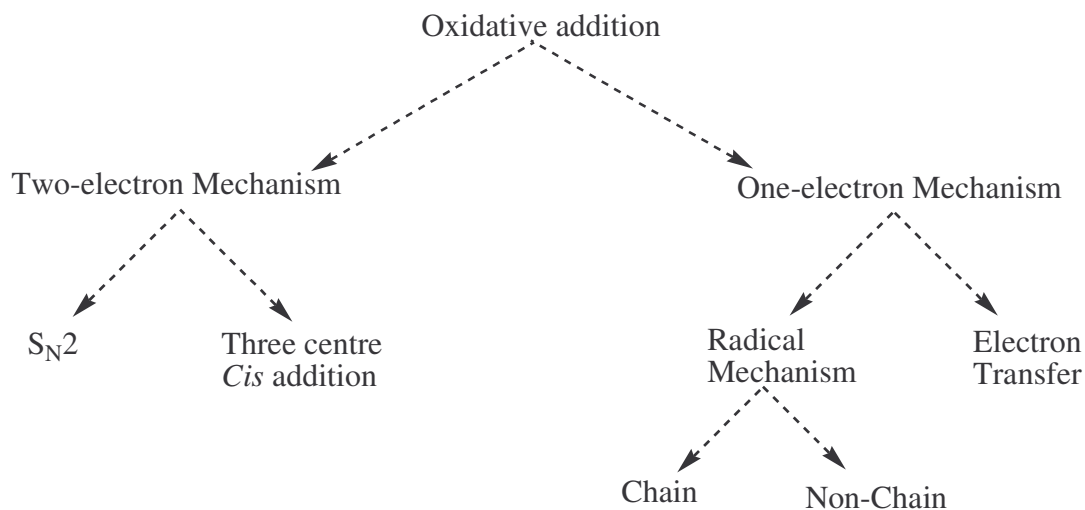


Figure 2.2 A General layout of the different mechanisms found for oxidative addition reactions.

Considering the order of metal reactivity towards oxidative addition, it can be depicted as in Figure 2.3³² the metals' tendency to undergo oxidative addition increases from top to bottom and from right to left during a period, as does the metal basicity³³.

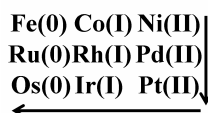


Figure 2.3 An illustration of the order of metal reactivity towards oxidative addition. Arrows indicate reactivity increase.

Coordinated ligands are of major importance to oxidative addition reactions. An increased σ -donor capability increases the electron density at the metal centre and favours oxidative addition. This means that electron-releasing (basic) ligands make the metal ligand bonds stronger, while electron-withdrawing (stronger π -acceptor) ligands weaken the metal ligand bonds.

The ligand steric effects should also be considered when for instance a low reaction rate is observed for the strong basic bulky ligand tri-*tert*-butylphosphine. Therefore solvent effects cannot be ignored and Parker³⁴ also made the conclusion that Hydrogen bond formation may have an important role in the reaction rate of oxidative addition. Polar solvents like acetone are less capable of hydrogen bond formation and decrease the reaction rate. On the other hand ions in a reaction solution can coordinate to the metal centre and enhance the reaction rate^{35,36}.

Reductive elimination, the reverse of oxidative addition, is often the last step in a catalytic cycle e.g. the alkane formation from an alkyl hydride complex. In the rhodium

³² Nyholm, R. S. & Vniece, K. (1965). *J. Chem. Soc.* 5337.

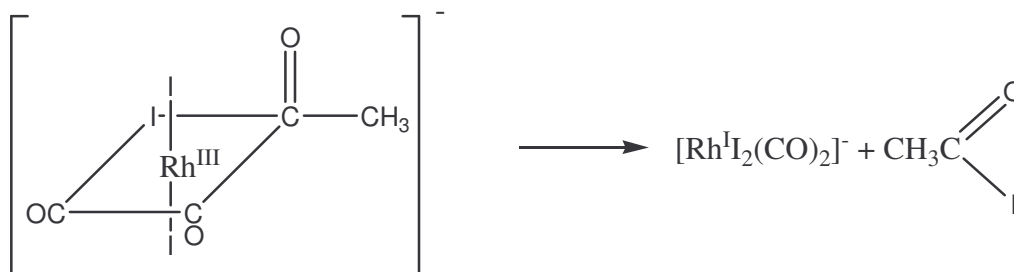
³³ Ittel, S. D., Johnson, L. K. & Brookhart, M. (2000). *Chem. Rev.* 100, 1169.

³⁴ Parker, A. J. (1969). *Chem. Rev.* 69, 1.

³⁵ Hichy, C. E. & Maitlis, P. M. (1984). *J. Chem. Soc. Chem. Comm.* 1609.

³⁶ Basson, S. S., Leipold, J. G., Roodt, A. & Venter, J. (1987). *A. Inorg Chim Acta.* 128, 31.

catalyzed carbonylation of methanol *via* methyl iodide, acetyl iodide is formed by reductive elimination from an anionic Rh(III) acyl complex³⁷.



Scheme 2.7 An example of reductive elimination of a rhodium acyl complex, present in the rhodium catalyzed carbonylation of methanol.

2.2.5 Insertion and elimination reactions

In the catalysis of C-C and C-H coupling, insertion reactions play an important role³⁸. In industry CO insertion into the metal-carbon bond is very important in the carbonylation reactions as described in 1957^{39,40}.



Scheme 2.8 Carbonyl insertion into the metal-carbon bond of a manganese complex.

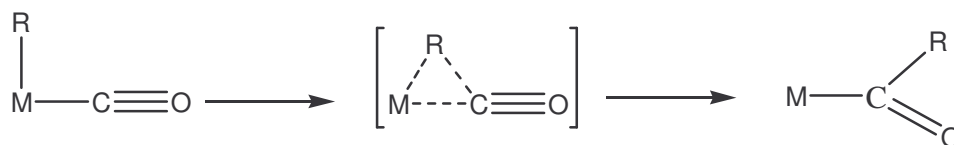
In carbonylation chemistry the migration of a one electron ligand from the metal centre to an unsaturated ligand is a known concept³⁴. In hydroformylation or hydroesterification reactions the migration of a hydride to a coordinated alkene generates an alkyl ligand that inserts carbon monoxide into the complex. These insertion reactions open the opportunity to create many different types of organic molecules. CO inserts into the polarized metal-carbon bond to give an acyl metal complex. However, it has been shown that an alkyl group rather migrates to the CO group, this migration then probably occurs *via* a three-centre transition state.

³⁷ Parshall, G.W. (1980). *Homogeneous Catalysis*. J. Wiley, New York.

³⁸ Berke, H. & Hoffmann, R. (1978). *J. Am. Chem. Soc.* 100, 7224.

³⁹ Calderazzo, F. (1977). *Angew. Chem.* 89, 305.

⁴⁰ Collman, J.P. (1978). *J. Am. Chem. Soc.* 100, 4766.

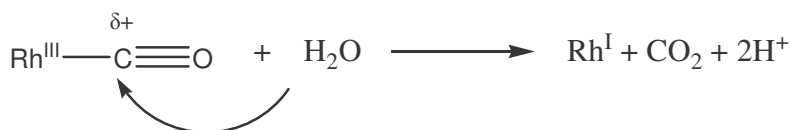


Scheme 2.9 An illustration of carbon monoxide migratory insertion *via* a three centre transition state.

The simplest carbonylation of all is perhaps the rhodium-catalysed conversion of iodomethane to an acetyl iodide, a crucial reaction for the success of the low pressure “Monsanto acetic acid process”. Enormous quantities of methanol are produced each year from the use of synthesis gas and the methanol is then converted to important chemicals such as acetic acid, formaldehyde and even gasoline.

2.2.6 Reactions at coordinated ligands

These reactions include the nucleophilic and electrophilic attack on coordinated ligands²⁷. An example of a nucleophilic attack is the carbonyl complexes that are readily attacked by various nucleophiles, including OH⁻, OR⁻, NR₃, NR₂⁻, H⁻ and CH₃⁻. By considering the ligand reactions of carbonyls, anionic rhodium complexes such as [Rh(CO)₂I₂]⁻ undergo nucleophilic attack by water to yield CO₂.



Scheme 2.10 An illustration of the nucleophilic attack of water on an anionic rhodium compound.

The resulting Rh(I) carbonyl complex can be proton oxidized to Rh(III), to form H₂.



Scheme 2.11 An illustration of the proton oxidation of a Rh(I) compound to yield a Rh(III) compound and H₂.

An electrophilic attack on a ligand is often observed for complexes of olefins and aromatic compounds.

2.3 Homogeneously catalyzed industrial processes

The most advances in industrial homogeneous catalysis are based on the development of organometallic complexes, these developments are driven by the potential industrial applications⁴¹. The chemical industry relies heavily on catalytic processes, resulting in a close relationship between catalytic development and the history of industrial chemistry. In Table 2.2 is a brief historical survey of a few selected catalytic reactions that were introduced to industry²⁷.

Table 2.2 A brief historic overview of selected industrial catalytic cycles.

Year of Discovery	Discoverer/company	Catalyst	Catalytic reaction
1906	Ostwald	Pt/Rh nets	Nitric acid by NH ₃ oxidation
1925	Fischer, Tropsch	Fe, Co, Ni	Hydrocarbons from CO/H ₂
1938	Roelen (Ruhrchemie)	Co	Hydroformylation of ethylene to propanal
1964	Banks, Bailey	Re, W, Mo	Olefin metathesis
1964	Wilkinson	Rh-, Ru complexes	Hydrogenation, isomerisation, hydroformylation
1966	Cativa-process, BP Chemicals	Ir, I, Ru	Acetic acid
1974	Knowles, L-Dopa (Monsanto)	Rh/chiral phosphine	Asymmetric hydrogenation
1974	General Motors, Ford	Pt, Rh/monolith	Three-way catalyst
1977	Shell (SHOP process)	Ni/chelate phosphine	α -olefins from ethylene
1984	Rhône-Poulenc/Ruhrchemie	Rh/phosphine/aqueous	Hydroformylation

Homogeneous transition metal catalyzed reactions are currently used in numerous areas and processes. Figure 2.4 illustrates the numerous areas where homogeneous catalytic systems are utilized⁴². Hydroformylation reactions are discussed in Chapter 9.

⁴¹ Johnson, L. K., Mecking, S. & Brookhart, M. (1996). *J. Am. Chem. Soc.* 118, 267.

⁴² Keim, W. (1984). *Chemisch Magazine*, 417.

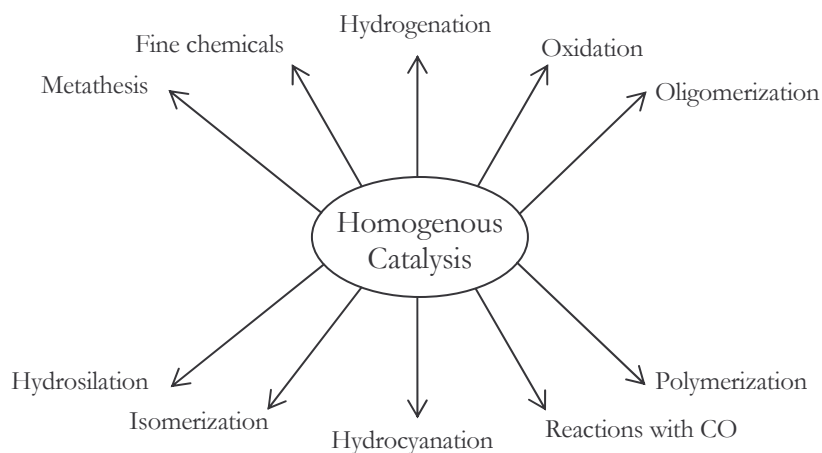


Figure 2.4 A graphical representation of the wide application and numerous areas where homogenous catalysis are used.

2.3.1 Industrial methanol-to-acetic acid processes

A description of metal catalysts used in the carbonylation of methanol to yield acetic acid follows⁴³. The original Monsanto conditions of 30-60 bar pressure and 150-200 °C spurred the search for new catalysts able to function under milder conditions. It was found that iridium complexes are normally more stable than the corresponding rhodium complexes and so the Cativa process was developed. The Cativa process is based on $[\text{Ir}(\text{CO})_2\text{I}_2]^-$ in combination with $[\text{Ru}(\text{CO})_4\text{I}_2]^-$, and is presently the most efficient process for the industrial manufacture of acetic acid⁴⁴.

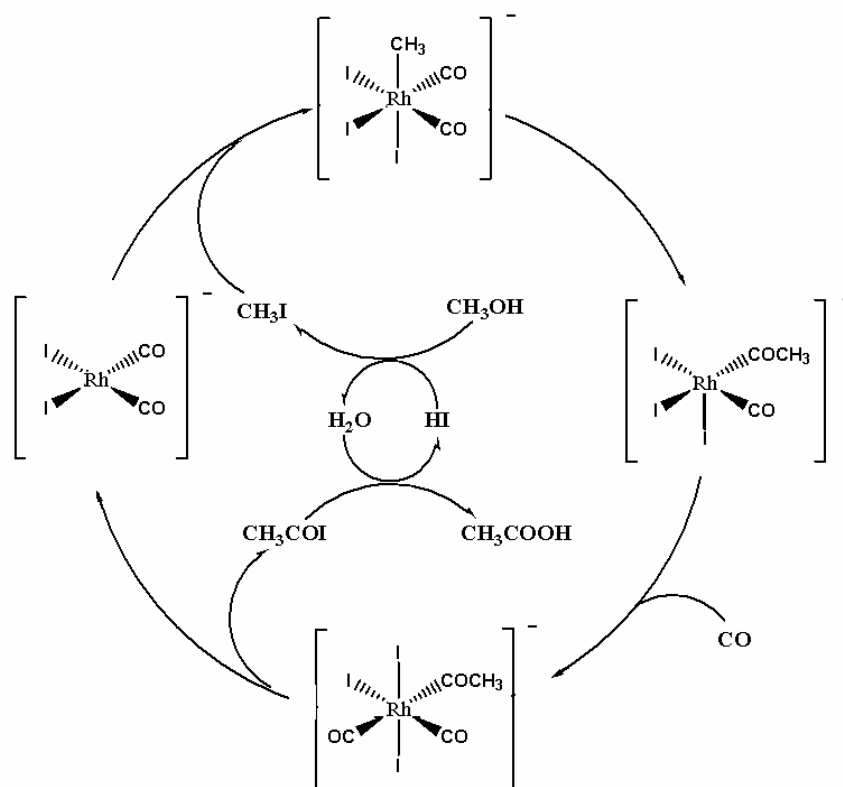
2.3.1.1 The Monsanto process

The Monsanto Acetic Acid process is a commercially important process producing a large amount of the annual world acetic acid capacity, by the homogeneous catalysed carbonylation of methanol. In the catalytic cycle, the rhodium metal centre facilitates both the oxidative addition and reductive elimination steps. Illustrated in Scheme 2.12 is an overview of the rhodium based Monsanto catalytic cycle, the key reaction being the facial oxidative addition of methyl iodide to the square planar rhodium(I) metal centre to

⁴³ Thomas, C. M. & Süß-Fink, G. (2003). *Coord. Chem. Rev.* 243, 125.

⁴⁴ Forster, D. (1976). *J. Am. Soc.* 98, 846.

form the octahedral rhodium(III) species. The second step involves carbon monoxide insertion into the *cis* Rh-CH₃ bond to yield a five-coordinated acyl intermediate, which undergoes carbon monoxide addition (Step 3). The fourth step is a reductive elimination of the acetyl iodide to yield the original rhodium(I) complex. The acetyl iodide undergoes hydrolysis, by water, in the aqueous methanol feed to give acetic acid and HI. HI reacts with methanol to regenerate methyl iodide and the cycle repeats^{45,46,47}.



Scheme 2.12 The Monsanto process, a rhodium based catalytic cycle for the synthesis of acetic acid from methanol.

⁴⁵ Haynes, A., Mann, B. E., Morris, G. E. & Maitlis, P. M. (1993). *J. Am. Chem. Soc.* 115, 4093.

⁴⁶ Forster, D. & Dekleva, T. W. (1986). *J. Chem. Edu.* 63, 204.

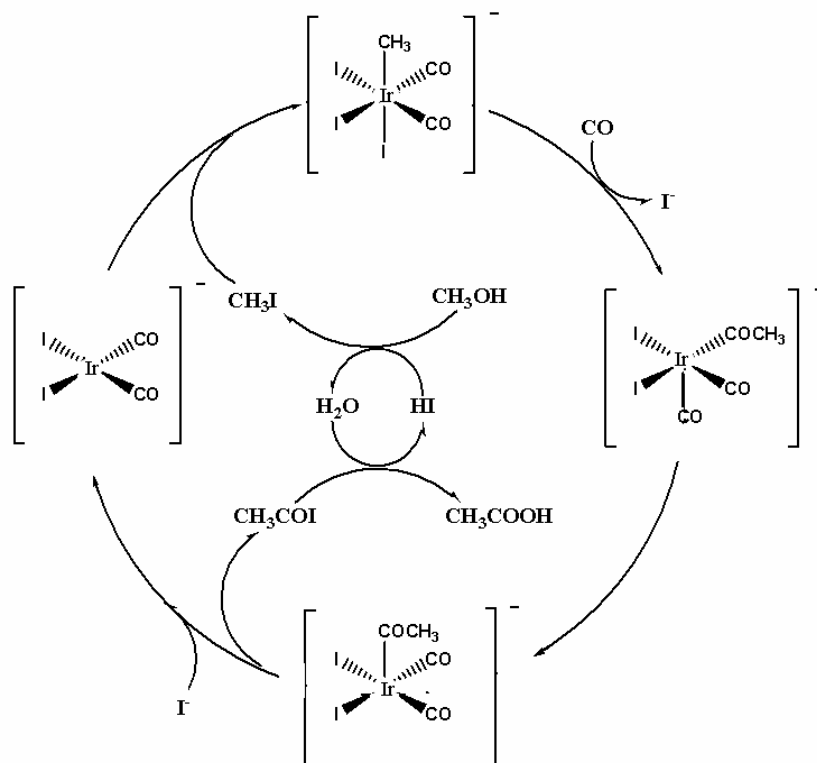
⁴⁷ Watson, D. J. (1998). *Catalysis of Organic reactions*, Marcel Dekker, New York.

2.3.1.2 The Iridium based Cativa process

The Monsanto group also noticed the effectiveness of iodide-promoted iridium catalysts⁴⁸ which was confirmed by other workers⁴⁴. Only with the combination of the iridium catalyst (at high concentrations) and a ruthenium promoter were a higher activity and selectivity could be obtained in relation to the rhodium catalyst system. The production of acetic acid using the iridium catalyst system was commercialized in 1996 by BP-Amoco, named the ‘Cativa™’ process. The Cativa process operates at reduced water levels, resulting in less by-product formation and improved carbon monoxide efficiency. The main difference between the rhodium- and iridium-based catalytic cycles has been pointed out by Maitlis *et al.* The rhodium based cycle involves anionic intermediates and the iridium-based cycle involves anionic as well as neutral intermediates⁴⁹. In the iridium catalytic cycle the methyl iodide oxidative addition step is about 150 times faster than in the rhodium cycle and thus no longer the rate determining step⁴⁹. The rate limiting step in the iridium-based cycle is a substitution of an iodo ligand by carbon monoxide. Presented in Scheme 2.13 is an illustration of the iridium Cativa process.

⁴⁸ Paulik, F. & Roth, J. E. (1968). *J. Chem. Soc. Chem. Commun.*, 1578.

⁴⁹ Maitlis, P. M., Haynes, A., Sunley, G. J. & Howard, M.J. (1996). *J. Chem. Soc. Dalton Trans.*, 2187.



Scheme 2.13 Illustration of the Iridium based catalytic cycle for the synthesis of acetic acid from methanol.

2.4 Iodomethane oxidative addition to monocarbonylphosphine complexes of Rhodium(I).

2.4.1 Summary

Iodomethane oxidative addition to square planar rhodium(I) complexes and subsequent CO insertion reactions is important in the Monsanto industrial process for production of acetic acid from methanol⁴⁹. As mentioned in Section 2.3.1.1 the rate determining step of the rhodium-based Monsanto process is the methyl iodide oxidative addition step.

Rhodium(I) complexes of the type $[\text{Rh}(\text{L}, \text{L}'\text{-Bid})(\text{CO})(\text{PR}_3)]$ (where $\text{L}, \text{L}'\text{-Bid}$ = mono anionic bidentate ligand and PR_3 = tertiary phosphine), containing either (O,O), (O,N), (O,S) or (N,S) donor atoms that can form an acyl species after the methyl iodide oxidative addition step^{50,51,52}. Conradie *et al.* Reported a summary of the reaction mechanisms found for these type of reactions which are dependant on the donor atoms, L and L'.

Summarized in Table 2.3 are the formed products obtainable with methyl iodide oxidative addition to rhodium(I) square planar complexes, with different bidentate ligands, by following different mechanistic pathways^{53,50,54}. Conradie *et al.* also reported the formation of a second rhodium(III) acyl species with the methyl iodide oxidative addition to $[\text{Rh}(\text{fctfa})(\text{CO})(\text{PPh}_3)]$ (where fctfa = ferrocenyltrifluoroacetato). Presented in Scheme 2.14 is a summary of the general reaction mechanism for the oxidative addition of iodo methane to square planar rhodium(I) complexes containing a monoanionic bidentate ligand^{54,53,55}.

⁵⁰ Conradie, J., Lamprecht, G. J., Roodt, A. & Swarts, J. C. (2007). *Polyhedron*, 26, 5075.

⁵¹ Basson, S. S., Leipoldt, J. G. & Nel, J. T. (1984). *Inorg. Chim. Acta*, 84, 167.

⁵² Steyn, G. J. J., Roodt, A. & Leipoldt, J. G. (1993). *Rhodium Ex.* 1, 25.

⁵³ Roodt, A. & Steyn, G. J. J. (2000). *Recent Res. Devel. Inorganic Chem.*, 2, 23.

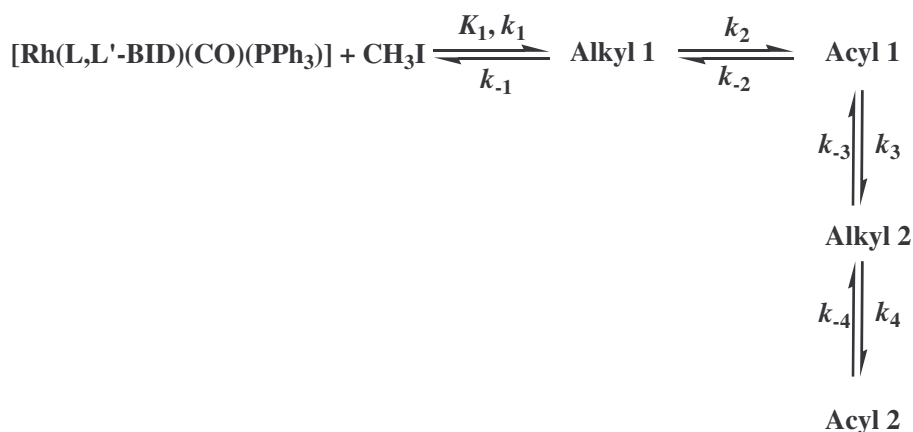
⁵⁴ Conradie, M. M. & Conradie, J. (2007). *Inorg. Chim. Acta*, 361, 2285.

⁵⁵ Steyl, G. (2005). *Ph.D. Thesis*. Rand Afrikaans University.

Table 2.3 A summary of the products obtainable with methyl iodide oxidative addition to rhodium(I) square planar complexes of the type $[\text{Rh}(\text{L}, \text{L}'\text{-Bid})(\text{CO})(\text{PR}_3)]$, where (L,L'-Bid) = different bidentate ligands. (Products are indicated in the table heading and bidentate ligands in the colour column directly below).

Acyl 1	Alkyl 2	Acyl 2
cacsm	acac	fctfa
acsm	tfaa	
macsm	tfdma	
macsh	hfaa	
cupf	sacac	
ox	tta	
anmeth		
dmavk		
trop		
pic		

(Note: See Scheme 2.14, cacsm = Methyl(2-cyclohexylamino-1-cyclopentene-1-dithiocarboxylato), acsm = Methyl(2-amino-1-cyclopentene-1-dithiocarboxylato), macsm = Methyl(2-methylamino-1-cyclopentene-1-dithiocarboxylato), macsh = Methyl(2-methylamino-1-cyclopentene-1-dithiocarboxylato), cupf = *N*-Hydroxy-*N*-nitroso-benzeneamino, ox = 8-Hydroxyquinolinato, anmeth = 4-Methoxy-*N*-methylbenzothiohydroxamato, dmavk = diMethylaminovinylketonato, trop = Troponolato, pic = Picolinato, acac = Acetylacetonato, tfaa = 1,1,1-Trifluoro-2,4-pentanedionato, tfdma = 1,1,1-Trifluoro-5-methyl-2,4-hexanedionato, hfaa = 1,1,1,5,5,5-Hexafluoro-2,4-pentanedionato, sacac = Thioacetylacetonato, tta = 2-Thenoyltrifluoroacetonoato, fctfa = Ferrocenyltrifluoroacetonoato).



Scheme 2.14 A general reaction mechanism for the oxidative addition of methyl iodide to square planar rhodium(I) complexes containing a monoanionic bidentate ligand.

The electron density on a metal centre can be manipulated by the use of different functionalized ligands and substituted tertiary phosphine ligands⁵³. Considering the electron donating capability of O-, N- and S-donor atoms, these ligands can be arranged with an increasing donor capability of: O < N < S. A higher electron density on the metal centre will increase the observed reactivity towards methyl iodide oxidative addition. In Table 2.4 a general increase in the reactivity is observed as the electron donating capability of the donor atoms increase the electron density on the rhodium metal centre, with no definite trend from the coordination number on the observed reactivity^{53,50,54,55,56}.

Table 2.4 Second order rate constants for selected [Rh(L,L'-Bid)(CO)(PPh₃)] complexes at 25 °C. Indicating the influence of donor atoms and coordination number on the observed reaction rate of methyl iodide oxidative addition.

L,L'-Bid	L	L'	CN	10 ² <i>k</i> ₁ (M ⁻¹ s ⁻¹)
cupf	O	O	5	0.12
trop	O	O	5	2.30
ox	N	O	5	3.00
pic	N	O	5	1.00
hpt	S	O	5	5.10
anmeth	S	O	5	2.4
acac	O	O	6	2.40
dmavk	N	O	6	11.4
sacac	S	O	6	4.00
hacsm	N	S	6	2.70

(Note: CN = Coordination number, L and L' indicate donor atoms. cupf = N-Hydroxy-N-nitrosobenzenaminato, trop = Troponolato, ox = 8-Hydroxyquinolinato, pic = Picolinato, hpt = 1-Hydroxy-2-pyridinethione, anmeth = 4-Methoxy-N-methylbenzothiohydroxamato, acac = Acetylacetonato, dmavk = diMethylaminovinylketonato, sacac = Thioacetylacetonato, acsm = Methyl(2-amino-1-cyclopentene-1-dithiocarboxylato).

As mentioned, different mono anionic bidentate ligands also influence the electron density on the metal centre. Note the reactivity difference between rhodium(I)triphenylphosphine systems containing different bidentate ligands, (Table 2.5). Also presented is the effect of bidentate ligand functionalization on the electron density of the metal centre and thus the observed reactivity towards methyl iodide oxidative addition^{55,56,53}.

⁵⁶ Brink, A. (2007). *M.Sc. Thesis*. University of the Free State.

Table 2.5 Second order rate constants for selected $[\text{Rh}(\text{L},\text{L}'\text{-Bid})(\text{CO})(\text{PPh}_3)]$ complexes at 25 °C. Indicating the influence of bidentate ligand functionalization on the observed reaction rate of methyl iodide oxidative addition.

L,L'-Bid	L	L'	CN	$10^2 k_1 (\text{M}^{-1} \text{s}^{-1})$
tropNO₂	O	O	5	0.273
tropBr₃	O	O	5	0.399
trop	O	O	5	2.300
tta	O	O	6	0.17
fctfa	O	O	6	0.611
macsm	S	N	6	3.4
cacsm	S	N	6	5.600
macsh	S	N	6	38

(Note: CN = Coordination number, L and L' indicate donor atoms. tropNO₂ = Nitrotropolonato, tropBr₃ = triBromotropolonato, trop = Troponolato, tta = 2-Thenoyltrifluoroacetonoato, fctfa = Ferrocenyltrifluoroacetonoato, macsm = Methyl(2-methylamino-1-cyclopentene-1-dithiocarboxylato), cacsm = Methyl(2-cyclohexylamino-1-cyclopentene-1-dithiocarboxylato), macsh = Methyl(2-methylamino-1-cyclopentene-1-dithiocarboxylato).

Apart from bidentate ligand influence, the metal centre can be manipulated by substitution of tertiary phosphine ligands. A study by Brink *et al.* indicate the steric and electronic influence from a range of phosphine ligands on the reactivity of the rhodium metal centre towards methyl iodide oxidative addition, summarized in Table 2.6⁵⁷.

Table 2.6 Second order rate constants for $[\text{Rh}(\text{acac})(\text{CO})(\text{PY})]$ complexes at 25 °C. Indicating the influence of phosphine ligands on the observed reaction rate of methyl iodide oxidative addition.

Complex	$10^2 k_1 (\text{M}^{-1} \text{s}^{-1})$
$[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$	3.90
$[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_2\text{Cy})]$	5.29
$[\text{Rh}(\text{acac})(\text{CO})(\text{PPhCy}_2)]$	0.69
$[\text{Rh}(\text{acac})(\text{CO})(\text{PCy}_3)]$	2.64

2.4.2 Conclusion

With the above in mind and the limited literature on 8-hydroxyquinolinorhodium(I)phosphine systems, the 8-hydroxyquinoline backbone was selected for this study and the subsequent functionalizations are described and presented in Chapter 3, 4 and 6. Electron donating capability of the N,O-donor atoms were investigated by the use of computational chemistry and presented in Chapter 5. Crystallographic data on metal complexation are presented in Chapter 6, 7 and 8. The influence from bidentate ligand functionalization and various tertiary phosphine ligands on the reactivity of the metal centre towards methyl iodide oxidative addition is reported in Chapter 9.

Chapter 3

Experimental

3.1 Introduction

Bidentate ligand coordination onto transition metals by means of oxygen, nitrogen or sulphur atoms is a well known concept, as described in Chapter 2. The following chapter discusses the synthetic routes used throughout this study, together with the product spectroscopic characterization. Figure 3.1 presents an overview of the synthetic routes used for ligand to metal coordination.

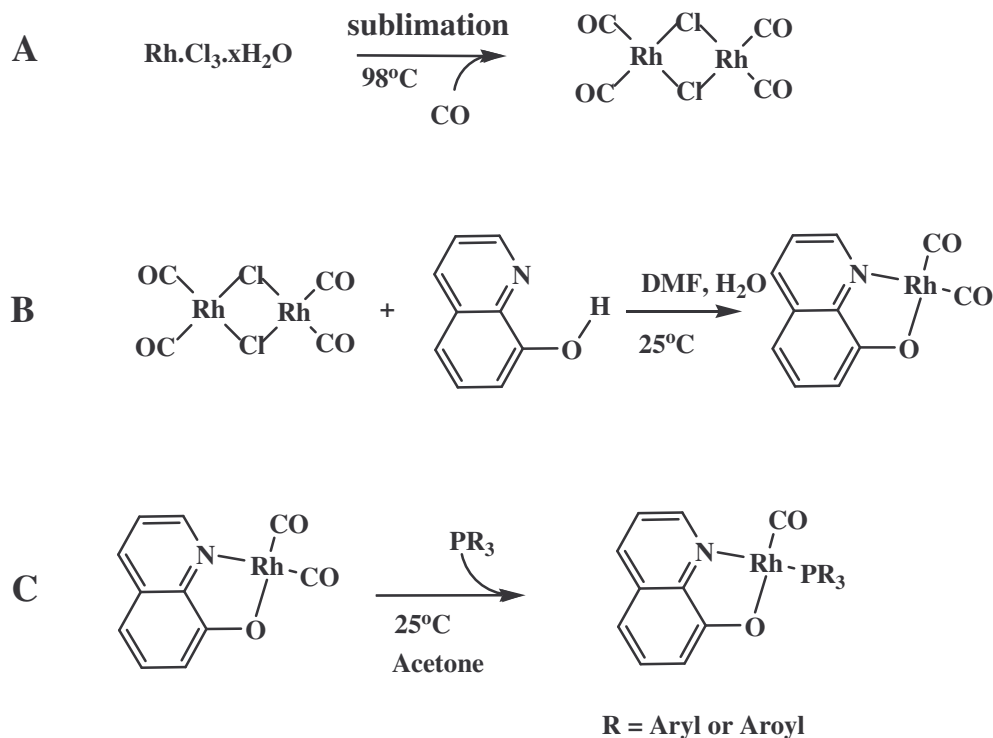


Figure 3.1 Summary of brief synthetic schemes for the preparation of: A = $[\text{Rh}_2\text{CO}_4\text{Cl}_2]$, B = $[\text{Rh}(\text{ox})(\text{CO})_2]$ and C = $[\text{Rh}(\text{ox})(\text{CO})(\text{PR}_3)]$.

3.2 Reagent and Apparatus detail

Unless otherwise stated in the individual procedures, all experiments were carried out in air, using analytical grade reagents. Rhodiumtrichloride hydrate ($\text{RhCl}_3 \cdot x\text{H}_2\text{O}$), was purchased from Next Chimica, South Africa. 8-Hydroxyquinoline and 5-chloro-8-hydroxyquinoline were obtained from Merck. Phosphorous ligands, PPh_3 , PPh_2Cy , PPhCy_2 , PCy_3 , $\text{P}(\text{5FPh})_3$, $\text{P}(\text{p-ClPh})_3$, $\text{P}(\text{p-FPh})_3$, and $\text{P}(\text{O-2,4di}^t\text{BuPh})_3$ were purchased from Sigma Aldrich. These reagents were used as received.

NMR spectroscopic data was acquired on a Bruker 300 MHz spectrometer. ^1H chemical shifts are reported relative to TMS using CDCl_3 as reference (7.24 ppm) and ^{31}P spectra relative to an 85% H_3PO_4 reference peak (0 ppm). All chemical shifts are reported in ppm and coupling constants in Hz.

A Varian 50 Cary Conc UV/Vis spectrophotometer was used for spectroscopic data collection, using quartz cuvette cells (1.000 ± 0.001 cm), equipped with a temperature cell regulator (Julabu F12mV temperature regulator accurate to 0.1 °C).

FT-IR spectra were recorded on a Bruker Tensor 27 spectrophotometer in the range of $3000\text{-}600\text{ cm}^{-1}$ for both the KBr pellets and in dry organic solvents, using a NaCl solvent cell. For the IR kinetic scans the solvent cell was equipped with a temperature regulated mantle, accurate to 0.3 °C.

3.3 Phosphite ligand synthesis

3.3.1 Tris(2-methylphenyl)phosphite ($\text{P}(\text{O}-2\text{MePh})_3$)

The tris(2-methylphenyl)phosphite ligand was obtained by addition of PCl_3 (10.0 ml, 114.6 mmol) and triethylamine (1.0 ml) to a solution of 2-methylphenol (39 g, 360 mmol) in xylene (40 ml). The reaction mixture was refluxed for 3 hours under a gentle nitrogen flow and then allowed to cool to room temperature. The product was filtered off (added pentane to wash) and the volatiles were removed in vacuo. Pentane was added to dissolve the solid material and the solution was left to crystallize in a refrigerator. $\text{P}(\text{O}-2\text{MePh})_3$ was isolated as fine white needles. (Yield: 60 g, 95 %). $\delta(^{31}\text{P}) = 130$ ppm.

3.3.2 Tris(4-tert-butylphenyl)phosphite ($\text{P}(\text{O}-4^t\text{BuPh})_3$)

The tris(4-tert-butylphenyl)phosphite ligand was obtained by addition of PCl_3 (10.0 ml, 114.6 mmol) and triethylamine (1.0 ml) to a solution of 4-tertbutylphenol (54 g; 360 mmol) in xylene (40 ml). The reaction mixture was refluxed for 3 hours under a gentle nitrogen flow and then allowed to cool to room temperature. The product was filtered off (added pentane to wash) and the volatiles were removed in vacuo. Pentane was added to dissolve the solid material and the solution was left to crystallize in a refrigerator. $\text{P}(\text{O}-4^t\text{BuPh})_3$ was isolated as fine white needles. (Yield: 59 g, 88 %). $\delta(^{31}\text{P}) = 128$ ppm.

3.4 Synthesis of functionalized Quinolines

3.4.1 5-Chloro-8-hydroxyquinoline (HoxCl)

(For the structure determination see Section 4.3)

Colourless needles suitable for single crystal X-Ray diffraction were obtained by recrystallizing HoxCl (20 mg) from acetone (8 ml).

3.4.2 5-Chloro-8-hydroxyquinolinium bromide (H₂oxCl.Br)

(For the structure determination see Section 4.4)

Yellow needles suitable for single crystal X-Ray diffraction were obtained by recrystallizing HoxCl (20 mg) from hydrobromic acid (8 ml).

3.4.3 5-Chloro-8-hydroxyquinolinium hexafluorophosphate hydrate (H₂oxCl.PF₆)

(For the structure determination see Section 4.5)

Hexafluorophosphoric acid (2 ml) was added drop wise to a solution of HoxCl (7 mg) in acetone (20 ml) and solvent evaporation to dryness yielded yellow cuboids suitable for single crystal X-Ray diffraction.

3.4.4 5-Nitro-8-hydroxyquinoline (HoxNO₂)

(For the structure determination see Section 4.6)

HoxNO₂ was synthesised with slight variation of a procedure previously described by Cook *et al.*⁵⁷ (this procedure is also used for the synthesis of 5-Nitrotropolone⁵⁵). The compound HoxNO₂ was prepared by drop wise addition of glacial acetic acid (3 ml) and nitric acid (0.6 ml, 55 %) to a solution of 8-hydroxyquinoline (725 mg, 0.005 mol) in glacial acetic acid (10 ml). The reaction mixture was stirred for an hour and evaporated to dryness. The resulting dark orange solid was extracted with hot benzene (4 x 50 ml) and recrystallization from acetone yielded orange needles. (Yield: 494 mg, 52 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 11.320 (dd, 1H), 10.348 (dd, 1H), 10.042 (m, 2H), 9.751 (d, 1H).

The ligand HoxNO₂ can also be synthesised by following the same procedure as described above using 5-Chloro-quinoline in place of 8-hydroxyquinoline.

3.4.5 5-Nitro-8-hydroxyquinolinium nitrate (H₂oxNO₂•NO₃)

(For the structure determination see Section 4.7)

Yellow cuboids suitable for single crystal X-Ray diffraction were obtained by recrystallizing HoxNO₂ (10 mg) from nitric acid (10 ml).

⁵⁷ Cook, W., London, J. D. & Steel, D. K. W. (1954). *J. Chem. Soc.*, 530.

3.4.6 5-chloromethyl-8-hydroxyquinoline hydrochloric acid solvate (HoxMeCl)

(For the structure determination see Section 4.8)

HoxMeCl was prepared *via* a procedure previously described by Bruckhalter and Leib⁵⁸. The product was obtained by treating a mixture of 8-hydroxyquinoline (7.3g, 0.05 mol) and formaldehyde (8ml, 0.05 mol) in HCl (30ml) with hydrogen chloride gas for 90 min. The yellow solid was filtered off and recrystallization from acetone yielded yellow crystals. (Yield: 7.84 mg, 81 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 8.709 (dd, 1H), 7.761 (dd, 1H), 7.415 (m, 2H), 7.103 (d, 1H), 4.683 (s, 2H).

3.4.7 5-phenylazo-8-hydroxyquinoline, (HoxL)

The compound HoxL was prepared *via* a slight variation of the procedure previously described by La Deda *et al.*²⁴. Hydrochloric acid (12M, 2 ml) was slowly added to a stirring solution of aniline (0.624 g, 6.687 mmol) in water (10 ml). The resulting solution was cooled in an ice bath and an aqueous sodium nitrite (0.5 g, 7.246 mmol) solution (10ml) was drop wise added. The formed diazonium chloride was then coupled with 8-hydroxyquinoline (0.97 g, 6.682 mmol) dissolved in ethanol (50 ml) and aqueous sodium hydroxide (50 ml, 15.401 mmol) and the reaction mixture was stirred for 1 h at 0 °C. The resulting yellow suspension was acidified with diluted hydrochloric acid (2 ml) and then allowed to reach room temperature. The dark red precipitate which formed was collected by filtration and washed with a water (40 ml) and ethanol (40 ml) mixture. The dark red product was recrystallized from a chloroform/ethanol mixture. (Yield: 1.43 g, 86 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 9.340 (dd, 1H), 8.882 (dd, 1H), 8.063 (d, 1H), 8.006 (m, 2H), 7.571 (m, 4H), 7.277 (d, 1H).

⁵⁸ Bruckhalter, J. H. & Leib, R. I. (1961). *J. Org. Chem.* 26(10), 4078.

3.4.8 5-[(2,4-dimethyl)phenylazo]-8-hydroxyquinoline, (HoxL-Me₂)

The compound HoxL-Me₂ was obtained according to the procedure described for preparation of the compound HoxL. By a reaction of 2,4-dimethyl aniline (0.81 g, 6.684 mmol) in place of aniline, the formed diazonium chloride was coupled with 8-hydroxyquinoline (0.97 g, 6.682 mmol). The orange precipitate was collected by filtration and washed with a water (40 ml) and ethanol (40 ml) mixture. The orange product was recrystallized from a chloroform/ethanol mixture. (Yield: 1.21 g, 64 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 9.278 (dd, 1H), 8.921 (dd, 1H), 8.118 (d, 1H), 7.834 (m, 1H), 7.425 (d, 1H), 7.138 (s, 2H), 2.592 (s, 3H), 2.453 (s, 3H).

3.4.9 5-[(2,4,6-trimethyl)phenylazo]-8-hydroxyquinoline, (HoxL-Me₃)

The compound HoxL-Me₃ was obtained according to the procedure described for preparation of the compound HoxL. By a reaction of 2,4,6-trimethyl aniline (0.99 g, 6.684 mmol) in place of aniline, the formed diazonium chloride was coupled with 8-hydroxyquinoline (0.97 g, 6.682 mmol). The reddish precipitate was collected by filtration and washed with a water (40 ml) and ethanol (40 ml) mixture. The reddish product was recrystallized from a chloroform/ethanol mixture. (Yield: 1.46 g, 73 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 9.213 (dd, 1H), 8.892 (dd, 1H), 7.998 (d, 1H), 7.636 (m, 1H), 7.328 (d, 1H), 6.989 (s, 2H), 2.494 (s, 6H), 2.351 (s, 3H).

3.5 Synthesis of tetracarbonyldichlorodirhodium, $[Rh_2CO_4Cl_2]$

The complex $[Rh_2CO_4Cl_2]$ was prepared by following a procedure proposed by McCleverty and Wilkinson⁵⁹. Pulverised $RhCl_3 \cdot xH_2O$ (1 g, 2.57 mmol) was flushed with carbon monoxide gas while kept at 96 °C. The sublimed red crystals were collected and washed with warm hexane. (Yield: 0.529 g, 53 %). IR _{KBr}: ν_{CO} = 1991 and 1967 cm^{-1} .

3.6 Synthesis of 5-phenylazo-8-hydroxyquinolinatorhodium(I) complexes

3.6.1 $[Rh(oxL)(CO)_2]$

The complex $[Rh(oxL)(CO)_2]$ was prepared by dissolving $[Rh_2CO_4Cl_2]$ (23 mg, 0.058 mmol) in DMF (10 ml) and drop wise addition of HoxL (30 mg, 0.121 mmol) in DMF (6 ml) to the stirring reaction mixture. The product was obtained as a brown precipitate by addition of ice water, collected by filtration and washed with water⁵⁹. (Yield: 39 mg, 84 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 9.4 (d, 1H), 8.8 (s, 1H), 8.1 (d, 2H), 7.67 – 7.560 (m, 1H), 7.1 (d, 1H), 6.8 (s, 2H). IR _{KBr}: ν_{CO} = 2084 and 2000 cm^{-1} .

3.6.2 $[Rh(oxL)(CO)(PPh_3)]$

(For the structure determination see Section 6.3.3)

The complex $[Rh(oxL)(CO)(PPh_3)]$ was prepared by the drop wise addition of PPh₃ (21 mg, 0.081 mmol) in acetone (10ml) to a stirring solution of $[Rh(oxL)(CO)_2]$ (30 mg, 0.074 mmol) in acetone (30 ml). Solvent evaporation to dryness yielded the product as a dark red solid. (Yield: 37 mg, 78 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 9.421 (d, 1H), 8.825 (d, 1H), 8.145 (d, 1H), 7.925 (d, 2H), 7.794-7.453 (m, 19H), 6.885 (d, 1H). ¹J(Rh-P) = 164 Hz. IR _{KBr}: ν_{CO} = 1970 cm^{-1} . $\lambda_{max}^{Acetone}$ = 474 nm (ϵ = 4400).

⁵⁹ McCleverty, J. A. & Wilkinson, G. (1990). *Inorg. Synth.*, 28, 84.

3.6.3 [Rh(oxL)(CO)(PCy₃)]

(For the structure determination see Section 6.3.4)

The complex [Rh(oxL)(CO)(PCy₃)] was synthesised according to the procedure described for synthesis of [Rh(oxL)(CO)(PPh₃)]. Addition of PCy₃ (17 mg, 0.059 mmol) to [Rh(oxL)(CO)₂] (22mg, 0.054 mmol) yielded the product as a red solid. (Yield: 27 mg, 69 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 9.421 (d, 1H), 8.764 (s, 1H), 8.144 (d, 1H), 7.910 (d, 2H), 7.506 – 7.369 (m, 4H), 6.859 (d, 1H), 1.824 – 1.232 (m, 33H). ¹J(Rh-P) = 154 Hz. IR _{KBr}: ν_{CO} = 1952 cm⁻¹. λ_{max}^{Acetone} = 474 nm (ε = 4320).

3.7 Synthesis of 5-(2,4,6-trimethyl)phenylazo - 8-hydroxyquinolinatorhodium(I) complexes

3.7.1 [Rh(oxL-Me₃)(CO)₂]

The complex [Rh(oxL-Me₃)(CO)₂] was prepared by dissolving [Rh₂CO₄Cl₂] (30 mg, 0.077 mmol) in DMF (10 ml) and by the drop wise addition of HoxL-Me₃ (48 mg, 0.162 mmol) in DMF (5 ml) to the stirring reaction mixture. The product was obtained as a brown precipitate by the addition of ice water, collected by filtration and washed with water. (Yield: 55 mg, 80 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 9.4 (d, 1H), 8.7 (s, 1H), 8.1 (d, 1H), 7.67 – 7.560 (m, 1H), 7.2 (d, 1H), 7.0 (s, 2H), 2.46 (s, 6H), 2.34 (s, 3H). IR_{KBr}: ν_{CO} = 2085 and 2004 cm⁻¹.

3.7.2 [Rh(oxL-Me₃)(CO)(PPh₃)]

(For the structure determination see Section 6.3.5)

The complex [Rh(oxL-Me₃)(CO)(PPh₃)] was prepared by the drop wise addition of PPh₃ (22 mg, 0.083 mmol) in acetone (10ml) to a stirring solution of [Rh(oxL-Me₃)(CO)₂] (34 mg, 0.075 mmol) in acetone (30 ml). Solvent evaporation to dryness yielded the product as a dark red solid. (Yield: 42 mg, 81 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 9.4 (d, 1H), 8.8 (d, 1H), 8.1 (d, 1H), 7.9 (d, 2H), 7.78-7.54 (m, 19H), 6.8 (d, 1H), 2.4 (s, 6H), 2.3 (s, 3H). ¹J(Rh-P) = 163 Hz. IR_{KBr}: ν_{CO} = 1972 cm⁻¹. λ_{max}^{Acetone} = 463 nm (ε = 4351).

3.8 Synthesis of 8-hydroxyquinolinatorhodium(I) complexes

3.8.1 [Rh(ox)(CO)₂]

The complex [Rh(ox)(CO)₂] was prepared by dissolving [Rh₂CO₄Cl₂] (100 mg, 0.257 mmol) in DMF (10 ml) and by the drop wise addition of 8-hydroxyquinoline (82.05 mg,

0.565 mmol) in DMF (5 ml) to the stirring reaction mixture. The product was obtained as a brown precipitate by addition of ice water, collected by filtration and washed with water. (Yield: 74.7 mg, 94 %). ^1H NMR (300 MHz, CDCl_3 , 25 °C): 8.653 (d, 1H), 8.374 (d, 1H), 7.502 (m, 2H), 7.134 (m, 2H). IR KBr : ν_{CO} = 2075 and 2005 cm^{-1} .

3.8.2 $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$

(For the structure determination see Section 7.8)

The complex $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ was prepared by drop wise addition of PPh_3 (30 mg, 0.114 mmol) in acetone (10ml) to a stirring solution of $[\text{Rh}(\text{ox})(\text{CO})_2]$ (31 mg, 0.103 mmol) in acetone (40 ml)¹⁸. Solvent evaporation to dryness yielded the product as yellow crystals. (Yield: 51 mg, 93 %). ^1H NMR (300 MHz, CDCl_3 , 25 °C): 8.771 (d, 1H), 8.248 (d, 1H), 7.806 – 7.646 (m, 8H), 7.482 – 7.373 (m, 9H), 6.963 (d, 1H), 6.88 (d, 1H). $^1\text{J}(\text{Rh-P})$ = 164 Hz. IR KBr : ν_{CO} = 1995 cm^{-1} . $\lambda_{\text{max}}^{\text{Acetone}}$ = 420 nm (ϵ = 3351).

3.8.3 $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_2\text{Cy})]$

(For the structure determination see Section 7.7)

The complex $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_2\text{Cy})]$ was prepared according to the procedure described for synthesis of $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$. By addition of PPh_2Cy (17.6 mg, 0.064 mmol) to $[\text{Rh}(\text{ox})(\text{CO})_2]$ (18 mg, 0.059 mmol), the product was obtained as a yellow crystalline solid. (Yield: 25 mg, 77 %). ^1H NMR (300 MHz, CDCl_3 , 25 °C): 8.717 (s, 1H), 8.225 (d, 1H), 7.866 – 7.417 (m, 12H), 6.918 (dd, 2H), 1.810 – 1.273 (m, 11H). $^1\text{J}(\text{Rh-P})$ = 163 Hz. IR KBr : ν_{CO} = 1959 cm^{-1} . $\lambda_{\text{max}}^{\text{Acetone}}$ = 420 nm (ϵ = 4512).

3.8.4 $[\text{Rh}(\text{ox})(\text{CO})(\text{PPhCy}_2)]$

The complex $[\text{Rh}(\text{ox})(\text{CO})(\text{PPhCy}_2)]$ was synthesised according to the procedure described for synthesis of $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$. By addition of PPhCy_2 (18 mg, 0.069 mmol) to $[\text{Rh}(\text{ox})(\text{CO})_2]$ (19 mg, 0.062 mmol), the product was obtained as a yellow

solid. (Yield: 28 mg, 82 %). ^1H NMR (300 MHz, CDCl_3 , 25 °C): 8.819 (s, 1H), 8.612 (d, 1H), 7.924 – 7.868 (m, 2H), 7.501 – 7.459 (m, 5H), 6.784 (d, 1H), 1.827 – 1.728 (M, 14H), 1.469 – 1.334 (m, 8H). $^1\text{J}(\text{Rh-P}) = 161$ Hz. IR_{KBr} : $\nu_{\text{CO}} = 1952$ cm^{-1} . $\lambda_{\text{max}}^{\text{Acetone}} = 420$ nm ($\epsilon = 5430$).

3.8.5 $[\text{Rh}(\text{ox})(\text{CO})(\text{PCy}_3)]$

(For the structure determination see Section 7.6)

The complex $[\text{Rh}(\text{ox})(\text{CO})(\text{PCy}_3)]$ was prepared according to the procedure described for synthesis of $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$. By addition of PCy_3 (20 mg, 0.072 mmol) to $[\text{Rh}(\text{ox})(\text{CO})_2]$ (19 mg, 0.059 mmol), the product was obtained as a yellow crystalline solid. (Yield: 20 mg, 62 %). ^1H NMR (300 MHz, CDCl_3 , 25 °C): 8.716 (s, 1H), 8.187 (d, 1H), 7.396 – 7.290 (m, 2H), 6.855 (dd, 2H), 2.163 – 1.311 (m, 33H). $^1\text{J}(\text{Rh-P}) = 156$ Hz. IR_{KBr} : $\nu_{\text{CO}} = 1946$ cm^{-1} . $\lambda_{\text{max}}^{\text{Acetone}} = 420$ nm ($\epsilon = 4224$).

3.8.6 $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{5FPh})_3)]$

(For the structure determination see Section 7.5)

The complex $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{5FPh})_3)]$ was prepared according to the procedure described for synthesis of $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$. By addition of $\text{P}(\text{5FPh})_3$ (43 mg, 0.081 mmol) to $[\text{Rh}(\text{ox})(\text{CO})_2]$ (22 mg, 0.073 mmol), the product was obtained as a yellow crystalline solid. (Yield: 51 mg, 87 %). ^1H NMR (300 MHz, CDCl_3 , 25 °C): 8.669 (s, 1H), 8.262 (dd, 1H), 7.559 – 7.352 (m, 2H), 6.972 (d, 1H), 6.688 (d, 1H). $^1\text{J}(\text{Rh-P}) = 177$ Hz. IR_{KBr} : $\nu_{\text{CO}} = 1983$ cm^{-1} .

3.8.7 $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O-2MePh})_3)]$

(For the structure determination see Section 7.4)

The complex $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O-2MePh})_3)]$ was prepared according to the procedure described for synthesis of $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$. By addition of $\text{P}(\text{O-2MePh})_3$ (65 mg,

0.119 mmol) to $[\text{Rh}(\text{ox})(\text{CO})_2]$ (33 mg, 0.108 mmol) the product was obtained as a yellow crystalline solid. (Yield: 57 mg, 64 %). ^1H NMR (300 MHz, CDCl_3 , 25 °C): 8.771 (d, 1H), 8.248 (d, 1H), 7.806 – 7.646 (m, 8H), 7.482 – 7.373 (m, 6H), 6.963 (d, 1H), 6.88 (d, 1H), 2.592 (s, 9H). $^1\text{J}(\text{Rh-P}) = 278$ Hz. IR $_{\text{KBr}}$: $\nu_{\text{CO}} = 1984$ cm^{-1} .

3.8.8 $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3)]$

(For the structure determination see Section 7.3)

The complex $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3)]$ was prepared according to the procedure described for synthesis of $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$. By addition of $\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3$ (40 mg, 0.061 mmol) to $[\text{Rh}(\text{ox})(\text{CO})_2]$ (17 mg, 0.056 mmol), the product was obtained as a yellow crystalline solid. (Yield: 39 mg, 76 %). ^1H NMR (300 MHz, CDCl_3 , 25 °C): 8.495 (m, 2H), 8.194 (d, 2H), 7.951 (d, 1H) 7.455 - 7.327 (m, 8H), 7.017 – 6.980 (m, 2H), 6.924 (d, 1H), 1.543 (d, 18H), 1.228 (s, 36H). $^1\text{J}(\text{Rh-P}) = 279$ Hz. IR $_{\text{KBr}}$: $\nu_{\text{CO}} = 1986$ cm^{-1} .

3.9 Synthesis of ***5-chloro-8-hydroxyquinolinatorhodium(I)*** ***complexes***

3.9.1 $[\text{Rh}(\text{oxCl})(\text{CO})_2]$

The complex $[\text{Rh}(\text{oxCl})(\text{CO})_2]$ was prepared by dissolving $[\text{Rh}_2\text{CO}_4\text{Cl}_2]$ (100 mg, 0.257 mmol) in DMF (10 ml) and by the drop wise addition of 5-chloro-8-hydroxyquinoline (60 mg, 0.338 mmol) in DMF (5 ml) to the stirring reaction mixture. The product was obtained as a brown precipitate by addition of ice water, collected by filtration and washed with water. (Yield: 91 mg, 88 %). ^1H NMR (300 MHz, CDCl_3 , 25 °C): 8.709 (d, 2H), 7.672 (dd, 2H), 7.027 (d, 1H). IR $_{\text{KBr}}$: $\nu_{\text{CO}} = 2079$ and 2002 cm^{-1} .

3.9.2 [Rh(oxCl)(CO)(PPh₃)]

The complex [Rh(oxCl)(CO)(PPh₃)] was prepared by drop wise addition of PPh₃ (20 mg, 0.079 mmol) in acetone (10ml) to a stirring solution of [Rh(oxCl)(CO)₂] (28 mg, 0.072 mmol) in acetone (40 ml). Evaporation to dryness yielded the yellow solid. (Yield: 32 mg, 78 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 8.795 (s, 1H), 8.681 (d, 1H), 7.792-7.7222 (m, 6H), 7.489 – 7.418 (m, 11H). 6.765 (d, 1H). ¹J(Rh-P) = 164 Hz. IR _{KBr}: ν_{CO} = 1967 cm⁻¹. λ_{max}^{Acetone} = 435 nm (ε = 4716).

3.9.3 [Rh(oxCl)(CO)(PPh₂Cy)]

The complex [Rh(oxCl)(CO)(PPh₂Cy)] was synthesised according to the procedure described for synthesis of [Rh(oxCl)(CO)(PPh₃)]. By addition of PPh₂Cy (23 mg, 0.085 mmol) to [Rh(oxCl)(CO)₂] (26 mg, 0.078 mmol), the product was obtained as a yellow solid. (Yield: 33 mg, 73 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 8.744 (s, 1H), 8.561 (d, 1H), 7.872 – 7.805 (m, 2H), 7.470 – 7.423 (m, 10H), 6.779 (d, 1H), 1.805 – 1.268 (m, 11H). ¹J(Rh-P) = 162 Hz. IR _{KBr}: ν_{CO} = 1961 cm⁻¹. λ_{max}^{Acetone} = 435 nm (ε = 4822).

3.9.4 [Rh(oxCl)(CO)(PPhCy₂)]

The complex [Rh(oxCl)(CO)(PPhCy₂)] was synthesised according to the procedure described for synthesis of [Rh(oxCl)(CO)(PPh₃)]. By addition of PPhCy₂ (16 mg, 0.059 mmol) to [Rh(oxCl)(CO)₂] (18 mg, 0.053 mmol) the product was obtained as a yellow solid. (Yield: 19 mg, 61 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 8.785 (s, 1H), 8.580 (d, 1H), 7.891 – 7.835 (m, 2H), 7.458 – 7.422 (m, 5H), 6.755 (d, 1H), 1.791 – 1.696 (M, 14H), 1.438 – 1.299 (m, 8H). ¹J(Rh-P) = 161 Hz. IR _{KBr}: ν_{CO} = 1958 cm⁻¹. λ_{max}^{Acetone} = 435 nm (ε = 3832).

3.9.5 [Rh(oxCl)(CO)(PCy₃)]

The complex [Rh(oxCl)(CO)(PCy₃)] was synthesised according to the procedure described for synthesis of [Rh(oxCl)(CO)(PPh₃)]. By addition of PCy₃ (24 mg, 0.085 mmol) to [Rh(oxCl)(CO)₂] (26 mg, 0.069 mmol), the product was obtained as a yellow solid. (Yield: 24 mg, 60 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 8.738 (s, 1H), 8.530 (d, 1H), 7.554 – 7.389 (m, 2H), 6.716 (d, 1H) 2.276 – 1.279 (m, 33H). ¹J(Rh-P) = 155 Hz. IR _{KBr}: ν_{CO} = 1948 cm⁻¹. λ_{max}^{Acetone} = 435 nm (ε = 2981).

3.9.6 [Rh(oxCl)(CO)(P(p-ClPh)₃)]

(For the structure determination see Section 8.5)

The complex [Rh(oxCl)(CO)(P(p-ClPh)₃)] was synthesised according to the procedure described for synthesis of [Rh(oxCl)(CO)(PPh₃)]. By addition of P(p-ClPh)₃ (12 mg, 0.033 mmol) to [Rh(oxCl)(CO)₂] (10 mg, 0.030 mmol), the product was obtained as a yellow crystalline solid. (Yield: 14 mg, 67 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 8.790 (s, 1H), 8.615 (d, 1H), 7.686 – 7.401 (m, 14H), 6.748 (d, 1H). ¹J(Rh-P) = 213 Hz. IR _{KBr}: ν_{CO} = 1965 cm⁻¹.

3.9.7 [Rh(oxCl)(CO)(P(p-FPh)₃)]

(For the structure determination see Section 8.6)

The complex [Rh(oxCl)(CO)(P(p-FPh)₃)] was synthesised according to the procedure described for synthesis of [Rh(oxCl)(CO)(PPh₃)]. By addition of P(p-FPh)₃ (23 mg, 0.727 mmol) to [Rh(oxCl)(CO)₂] (20 mg, 0.594 mmol), the product was obtained as an orange crystalline solid. (Yield: 30 mg, 83 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 8.786 (s, 1H), 8.616 (d, 1H), 7.772 – 7.103 (m, 14H), 6.753 (d, 1H). ¹J(Rh-P) = 166 Hz. IR _{KBr}: ν_{CO} = 2000 cm⁻¹.

3.9.8 [Rh(oxCl)(CO)(P(O-4^tBuPh)₃)]

(For the structure determination see Section 8.3)

The complex [Rh(oxCl)(CO)(P(O-4^tBuPh)₃)] was synthesised according to the procedure described for synthesis of [Rh(oxCl)(CO)(PPh₃)]. By addition of P(O-4^tBuPh)₃ (50 mg, 0.084 mmol) to [Rh(oxCl)(CO)₂] (26 mg, 0.077 mmol), the product was obtained as a yellow crystalline solid. (Yield: 43 mg, 62 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 8.512 (m, 2H), 7.987 (d, 2H), 7.776 – 7.414 (m, 8H), 7.125 – 7.034 (m, 2H), 6.841 (d, 1H), 1.26 (s, 27H). ¹J(Rh-P) = 265 Hz. IR _{KBr}: ν_{CO} = 1995 cm⁻¹.

3.9.9 [Rh(oxCl)(CO)(P(O-2,4di^tBuPh)₃)]

(For the structure determination see Section 8.4)

The complex [Rh(oxCl)(CO)(P(O-2,4di^tBuPh)₃)] was synthesised according to the procedure described for synthesis of [Rh(oxCl)(CO)(PPh₃)]. By addition of P(O-2,4di^tBuPh)₃ (32 mg, 0.049 mmol) to [Rh(oxCl)(CO)₂] (15 mg, 0.045 mmol) the product was obtained as a yellow crystalline solid. (Yield: 32 mg, 74 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 8.495 (m, 2H), 7.939 (d, 2H), 7.675 – 7.304 (m, 7H), 7.109 – 7.025 (m, 2H), 6.815 (d, 1H), 1.343 (d, 18H), 1.247 (s, 36H). ¹J(Rh-P) = 269 Hz. IR _{KBr}: ν_{CO} = 1996 cm⁻¹.

3.10 Synthesis of ***5-nitro-8-hydroxyquinolinatorhodium(I)*** ***complexes***

3.10.1 [Rh(oxNO₂)(CO)₂]

The complex [Rh(oxNO₂)(CO)₂] was prepared by dissolving [Rh₂CO₄Cl₂] (22 mg, 0.062 mmol) in DMF (10 ml) and drop wise addition of HoxNO₂ (25 mg, 0.124 mmol) in DMF (5 ml) to the stirring reaction mixture. The product was obtained as a brown precipitate by addition of ice water, collected by filtration and washed with water. (Yield: 25 mg, 59 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 9.741 (d, 1H), 8.694 (d, 2H), 7.757 (dd, 1H), 6.998 (d, 1H). IR _{KBr}: ν_{CO} = 2084 and 2009 cm⁻¹.

3.10.2 [Rh(oxNO₂)(CO)(PPh₃)]

The complex [Rh(oxNO₂)(CO)(PPh₃)] was prepared by drop wise addition of PPh₃ (16 mg, 0.060 mmol) in acetone (10ml) to a stirring solution of [Rh(oxNO₂)(CO)₂] (18 mg, 0.055 mmol) in acetone (40 ml). Evaporation to dryness yielded the yellow solid. (Yield: 17 g, 54 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): 8.800 (s, 1H), 8.596 (d, 1H), 7.792 – 7.722 (m, 6H), 7.479 – 7.411 (m, 11H), 6.762 (d, 1H). ¹J(Rh-P) = 164 Hz. IR _{KBr}: ν_{CO} = 1966 cm⁻¹. λ_{max}^{Acetone} = 437 nm (ε = 4547).

3.11 Conclusion

Functionalization of the 8-hydroxyquinoline backbone with various phenylazo groups as well as nitro and methylchloride substituents were fairly easy and selective. The functionalized 8-hydroxyquinoline ligands were successfully coordinated to rhodium, forming stable rhodium(I) complexes.

Syntheses of the tris(2-methylphenyl)phosphite and tris(4-tert-butylphenyl)phosphite ligands as well as the *mono* phosphite ligand substitution on the 8-hydroxyquinolinatorhodium(I) and 5-chloro-8-hydroxyquinolinatorhodium(I) complexes were achieved with ease.

Phosphine ligand substitution on the 8-hydroxyquinolinato, 5-chloro-8-hydroxyquinolinato and 5-phenylazo-8-hydroxyquinolinatorhodium(I) complexes yielded a range of complexes with a systematic difference in the electron density of the metal centre, as a result of electronic influences from the bidentate and phosphine ligands.

Table 3.1 gives a summary of the spectroscopic data for the synthesised rhodium(I) complexes.

Experimental

Table 3.1 Summary of spectroscopic data for the synthesised rhodium(I) complexes.

	ν_{CO} (cm ⁻¹)	³¹ P-NMR Chemical shift (ppm)	³¹ P-NMR Coupling constant (Hz)
[Rh(oxL)(CO) ₂]	2084, 2000	-	-
[Rh(oxL)(CO)(PPh ₃)]	1970	41.5	164
[Rh(oxL)(CO)(PCy ₃)]	1952	56.2	154
[Rh(oxL-Me ₃)(CO) ₂]	2085, 2004	-	-
[Rh(oxL-Me ₃)(CO)(PPh ₃)]	1972	40.7	163
[Rh(ox)(CO) ₂]	2075, 2005	-	-
[Rh(ox)(CO)(PPh ₃)]	1995	41.2	164
[Rh(ox)(CO)(PPh ₂ Cy)]	1959	52.8	163
[Rh(ox)(CO)(PPhCy ₂)]	1952	53.6	161
[Rh(ox)(CO)(PCy ₃)]	1946	54.8	156
[Rh(ox)(CO)(P(5FPh) ₃)]	1983	56.1	177
[Rh(ox)(CO)(P(O-2MePh) ₃)]	1984	123.4	278
[Rh(ox)(CO)(P(O-2,4di ^t BuPh) ₃)]	1986	118.3	279
[Rh(oxCl)(CO) ₂]	2079, 2002	-	-
[Rh(oxCl)(CO)(PPh ₃)]	1967	40.7	164
[Rh(oxCl)(CO)(PPh ₂ Cy)]	1961	54.9	162
[Rh(oxCl)(CO)(PPhCy ₂)]	1958	47.9	161
[Rh(oxCl)(CO)(PCy ₃)]	1948	57.6	155
[Rh(oxCl)(CO)(P(p-ClPh) ₃)]	1965	40.5	213
[Rh(oxCl)(CO)(P(p-FPh) ₃)]	2000	39.5	166
[Rh(oxCl)(CO)(P(O-4 ^t BuPh) ₃)]	1995	122.4	265
[Rh(oxCl)(CO)(P(O-2,4di ^t BuPh) ₃)]	1996	117.8	162
[Rh(oxNO ₂)(CO) ₂]	2084, 2009	-	-
[Rh(oxNO ₂)(CO)(PPh ₃)]	1966	41.4	164

The solid state characterization of 8-hydroxyquinoline compounds, 8-hydroxyquinolinatorrhodium(I) complexes, 5-chloro-8-hydroxyquinolinatorrhodium(I) complexes and 5-phenylazo-8-hydroxyquinolinatorrhodium(I) complexes are discussed in Chapter 4, 6, 7 and 8 respectively.

Chapter 4

X-Ray crystallographic study of 8-hydroxyquinoline functionalities

4.1 Introduction

In the following chapter a series of 8-hydroxyquinoline compounds are presented with various guest molecules as ionic species, illustrating the different molecular interactions and various crystal packing modes.

The importance of bidentate ligand systems were briefly discussed in previous chapters. Their most important application is the ligand affect on a metal catalyst⁶⁰ and how they influence the reaction rate and selectivity. 8-Hydroxyquinoline forms part of the chelating ligands⁶¹, not only attracting interest in industrial application, but also showing potential as extracting agents of metal ions in diluted solutions⁶².

As part of the study on different bidentate ligand systems various 8-hydroxyquinoline compounds were synthesised by substituting several molecules and groups on the 5-position of the 8-hydroxyquinoline backbone. These functionalizations were done to change the donor and acceptor character of the pyridine and benzene rings. Functionalization of the quinoline backbone might also influence the electronic properties of the ring system or the coordination behaviour towards metal centres.

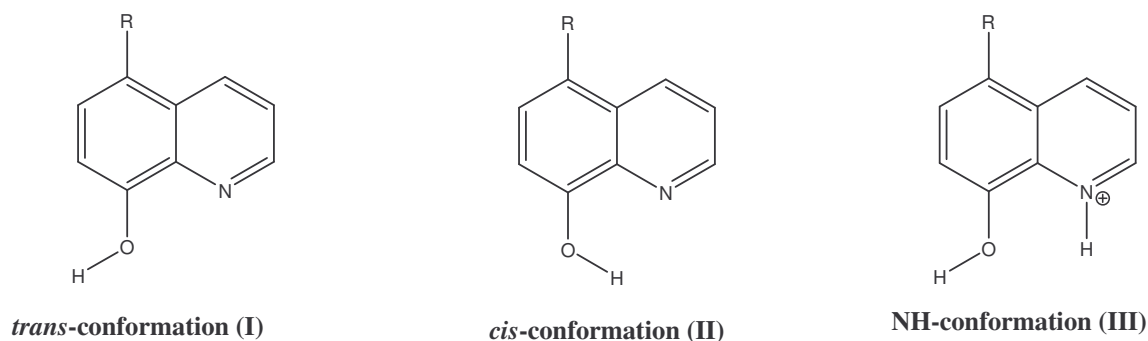
Illustrated in Scheme 4.1 are the 8-hydroxyquinoline isomers discussed in this solid state crystallographic study: The *trans*-conformation (I), a *trans* orientated hydroxyl hydrogen, in relation to the nitrogen atom. The *cis*-conformation (II), a *cis* orientated hydroxyl

⁶⁰ Van Leeuwen, P. W. N. M., Zuideveld, M. A., Swennenhuis, B. H. G., Freixa, Z., Kramer, P. C. J., Groubitz, K., Fraanje, J., Lutz, M., Spek, A. L. (2003). *J. Am. Chem. Soc.* 125, 5523.

⁶¹ McCleverty, J. A. & Meyer, T. J. (2004). *Comprehensive Coordination Chemistry II*. V1, 97.

⁶² Huges, D. L. & Truter, M. R. (1979). *J. Chem. Soc. Dalton Trans.* 520.

hydrogen and the NH-conformation (III), a cationic species with protonation on the nitrogen atom. Crystallized NH-conformation is in the presence of an anionic species, to form a neutral crystal system. The crystallographic details described in this chapter are correlated with results obtained from computational studies as described in Chapter 5.



Scheme 4.1 Line drawings of the three 8-hydroxyquinoline isomers found during this solid state study, the *trans*-conformation (I), *cis*- conformation (II) and the NH- conformation.
R = Cl, NO₂ or MeCl.

Solid state data on the following molecules are reported:

1. 5-Chloro-8-hydroxyquinoline (HoxCl).
2. 5-Chloro-8-hydroxyquinolinium bromide (H₂oxCl.Br).
3. 5-Chloro-8-hydroxyquinolinium hexafluorophosphate hydrate (H₂oxCl.PF₆).
4. 5-Nitro-8-hydroxyquinoline (HoxNO₂).
5. 5-Nitro-8-hydroxyquinolinium nitrate (H₂oxNO₂.NO₃).
6. 5-chloromethyl-8-hydroxyquinoline hydrochloric acid solvate (HoxMeCl).

4.2 *Experimental*

The above mentioned compounds were analysed by single crystal X-ray diffraction. The initial unit cell and data collections were performed on a Bruker X8 Apex II 4K Kappa CCD diffractometer using the Apex2 software package⁶³. The optimum measurement method to collect more than a hemisphere of reciprocal space was predicted by COSMO⁶⁴. Frame integration and data reductions were performed using the SAINT-Plus and XPREP⁶⁵ software packages, and a multi-scan absorption correction was performed on the data using SADABS⁶⁶. The structures were solved by the direct methods package SIR97⁶⁷, and refinement using the WinGX software package⁶⁸ incorporating SHELXL⁶⁹. All non H-atoms were refined anisotropically. Except for the hydrogens riding on nitrogen atoms, that were refined, all other H-atoms were positioned geometrically and refined using a riding model with fixed C-H distances of 0.93 Å (CH) [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$] and 0.82 Å (OH) [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}$]. Molecular diagrams were drawn using the DIAMOND⁷⁰ package with a 30% thermal envelope probability for non-hydrogen atoms. General crystal data and refinement parameters are presented in Table 4.1. A complete list of atomic coordinates, equivalent isotropic parameters, bond distances and angles, anisotropic displacement parameters and hydrogen coordinates for each individual dataset is given in Appendix A.

⁶³ Bruker (2005). Apex2 (Version 1.0-27). Bruker AXS Inc., Madison, Wisconsin, USA.

⁶⁴ Bruker (2003). COSMO (Version 1.48). Bruker AXS Inc., Madison, Wisconsin, USA.

⁶⁵ Bruker (2004a). SAINT-Plus. Version 7.12 (including XPREP). Bruker AXS Inc., Madison, Wisconsin, USA.

⁶⁶ Bruker (2004b). SAINT-Plus. Version 7.12 (including XPREP). Bruker AXS Inc., Madison, Wisconsin, USA.

⁶⁷ Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* 32, 115.

⁶⁸ Farrugia, L. J. (1999). WinGX, *J. Appl. Cryst.* 32, 837.

⁶⁹ Sheldrick, G.M. (1997). SHELXL97. *Program for crystal structure refinement*. University of Göttingen, Germany.

⁷⁰ Brandenburg, K. & Putz, H. (2005). DIAMOND, Release 3.1b. Crystal Impact GbR, Bonn, Germany.

Table 4.1 General crystal data for the following compounds, HoxCl, H₂oxCl.Br, H₂oxCl.PF₆, HoxNO₂, H₂oxNO₂.NO₃ and HoxMeCl. For label definition see section 4.1.

Identification code	(HoxCl)	(H ₂ oxCl.Br)	(H ₂ oxCl.PF ₆)	(HoxNO ₂)	(H ₂ oxNO ₂ .NO ₃)	(HoxMeCl)
Empirical formula	C36 H24 Br Cl4 N4 O4	C9 H7 Br Cl N O	C9 H9 Cl F3 N O2 P	C12 H8 N2.67 O4	C9 H7 N3 O6	C10 H9 Cl2 N O
Formula weight	718.39	260.52	271.11	253.54	253.18	230.08
Crystal system, space group	Orthorhombic, <i>Fdd</i> ₂	Monoclinic, <i>P2</i> ₁ / <i>n</i>	Monoclinic, <i>P2</i> ₁ / <i>n</i>	Orthorhombic, <i>Fdd</i> ₂	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>P2</i> ₁ / <i>c</i>
Unit cell dimensions						
<i>a</i> = (Å)	27.356(5)	4.738(5)	7.1691(3)	28.0015(7)	4.8518(4)	8.4517(5)
<i>b</i> = (Å)	29.564(5)	10.090(5)	12.3595(6)	30.7746(8)	8.3590(8)	14.8350(7)
<i>c</i> = (Å)	3.738(5)	19.237(5)	11.5380(6)	3.64710(10)	12.5393(13)	8.0843(4)
<i>a</i> = (°).	90.0.	90.0	90.0	90	100.497(3)	90.0
<i>β</i> = (°).	90.0	95.633(5)	93.507(2)	90	96.977(3)	97.338(2)
<i>γ</i> = (°)	90.0	90.0	90.0	90	102.390(3)	90.0
Volume (Å ³)	3023(4)	915.2(11)	1020.43(8)	3142.83(14)	481.52(8)	1005.32(9)
<i>Z</i>	4	4	4	12	2	4
Density (calculated) (Mg/m ³)	1.578	1.891	1.765	1.608	1.746	1.520
Absorption coefficient (mm ⁻¹)	0.443	4.737	0.483	0.124	0.150	0.608
<i>F</i> (000)	1472	512	550	1568	260	472
Crystal size (mm ³)	0.40 x 0.08 x 0.07	0.15 x 0.03 x 0.02	0.32 x 0.14 x 0.14	0.38 x 0.10 x 0.07	0.23 x 0.13 x 0.08	0.25 x 0.14 x 0.08
Theta range for data collection (°)/ completeness for collection (%)	2.76 to 27.98 / 97.0	2.28 to 25.00./ 96.3	2.42 to 28.29 / 99.3	1.97 to 27.99 / 100	2.55 to 28.29 / 99.8	2.43 to 28.31 / 99.9
Index ranges	-35<= <i>h</i> <=35, -37<= <i>k</i> <=37, -4<= <i>l</i> <=2	-3<= <i>h</i> <=5, -12<= <i>k</i> <=10, -22<= <i>l</i> <=22	-9<= <i>h</i> <=9, -16<= <i>k</i> <=16, -12<= <i>l</i> <=15	-36<= <i>h</i> <=36, -37<= <i>k</i> <=40, -4<= <i>l</i> <=4	-6<= <i>h</i> <=6, -11<= <i>k</i> <=11, -16<= <i>l</i> <=15	-11<= <i>h</i> <=11, -19<= <i>k</i> <=19, -10<= <i>l</i> <=10
Reflections collected	4943	3932	15856	15017	5942	18323
Independent reflections	1435	1554	2521	1096	2394	2502
	[<i>R</i> _{int} = 0.0319]	[<i>R</i> _{int} = 0.0450]	[<i>R</i> _{int} = 0.0407]	[<i>R</i> _{int} = 0.0249]	[<i>R</i> _{int} = 0.0244]	[<i>R</i> _{int} = 0.0476]
Absorption correction	Multiscan	Multiscan	Multiscan	Multiscan	Multiscan	Multiscan
Max. and min. transmission	0.9696 and 0.8427	0.9112 and 0.5368	0.9355 and 0.8609	0.9914 and 0.9543	0.9881 and 0.9663	0.9530 and 0.8628
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	1435 / 1 / 110	1554 / 0 / 117	2521 / 0 / 164	1096 / 1 / 128	2394 / 0 / 171	2502 / 1 / 132
Goodness-of-fit on <i>F</i> ²	1.080	1.089	1.057	1.077	1.045	1.106
Final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> 1 = 0.0283, <i>wR</i> 2 = 0.0661	<i>R</i> 1 = 0.0449, <i>wR</i> 2 = 0.0793	<i>R</i> 1 = 0.0317, <i>wR</i> 2 = 0.0806	<i>R</i> 1 = 0.0357, <i>wR</i> 2 = 0.0979	<i>R</i> 1 = 0.0398, <i>wR</i> 2 = 0.1059	<i>R</i> 1 = 0.0659, <i>wR</i> 2 = 0.1911
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0328, <i>wR</i> 2 = 0.0680	<i>R</i> 1 = 0.0580, <i>wR</i> 2 = 0.0838	<i>R</i> 1 = 0.0398, <i>wR</i> 2 = 0.0855	<i>R</i> 1 = 0.0376, <i>wR</i> 2 = 0.0999	<i>R</i> 1 = 0.0495, <i>wR</i> 2 = 0.1138	<i>R</i> 1 = 0.0899, <i>wR</i> 2 = 0.2089
Largest diff. peak and hole (e.Å ⁻³)	0.279 and -0.190	0.702 and -0.578	0.368 and -0.581	0.365 and -0.160	0.416 and -0.462	0.695 and -0.938

4.3 Crystal structure of 5-chloro-8-hydroxyquinoline (HoxCl)

4.3.1 Results and Discussion

(Supplementary data A1)

The compound 5-chloro-8-hydroxyquinoline, HoxCl, crystallized in the orthorhombic space group Fdd_2 ($Z=4$). The numbering scheme of HoxCl is presented in Figure 4.1 and the most important bond distances and angles are reported in Table 4.2.

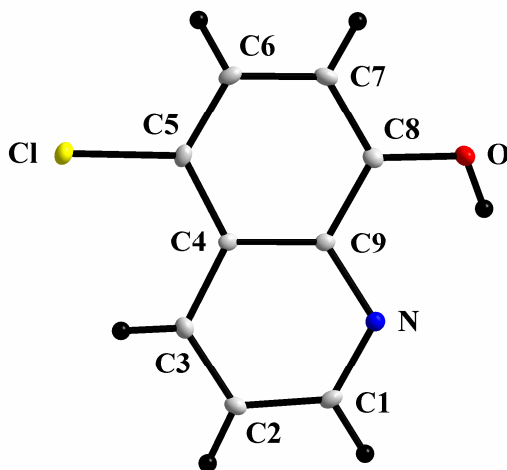


Figure 4.1 A diamond drawing of 5-chloro-8-hydroxyquinoline, HoxCl, indicating atom labels.
Hydrogen atom labels are omitted for clarity.

Table 4.2 Selected bond distances and angles (Å, °) for the compound HoxCl.

Atoms	Distance	Atoms	Angle
O-H	0.820*	N...O (Bite distance)	2.765(6)
C8-O	1.349(2)	C8-O-H	109.5*
C5-Cl	1.747(2)	N-C9-C8	117.5(2)
N-C1	1.314(3)	C4-C9-C8	120.0(2)
C1-C2	1.408(3)	C9-C8-C7	119.7(2)
C2-C3	1.365(3)	C8-C7-C6	120.6(2)
C3-C4	1.413(3)	C2-C1-N	123.9(2)
C4-C5	1.416(3)	C4-C5-Cl	118.7(2)
C5-C6	1.362(3)	C7-C8-C9-C4	1.8(4)
C6-C7	1.407(3)	C1-C2-C3-C4	0.3(4)
C7-C8	1.373(3)		
C8-C9	1.426(3)		
C9-C4	1.420(2)		
C9-N	1.366(2)		

* No e.s.d. H-atoms were placed as riding.

The fused ring system, atoms C1-C9 and N, yields a r.m.s. deviation from planarity of 0.0088 Å. A dihedral angle of 0.79(14)° between the benzene and pyridine ring and the torsion angles C7-C8-C9-C4 and C1-C2-C3-C4 is 1.8(4)° and 0.3(4)°, respectively, indicates the planarity of this compound. Both the hydroxyl O atom and the pyridine N atom lie in the plane of the fused ring system, the out-of-plane distances for O and N are 0.040(3) and -0.010(2) Å, respectively. The 5-chloro moiety and the *cis*-conformational hydroxyl hydrogen are displaced at 0.032(3) and 0.13(3) Å respectively above the fused ring system plane.

Non-planar hydrogen bonded dimer formations in these systems is usually achieved by soft contacts between the aromatic rings of two neighbouring quinoline molecules⁷¹. More specifically, the hydroxyl hydrogen of one molecule interacts with the pyridine ring N-atom of the next molecule. Presented in Figure 4.2 is a hydrogen bonded dimeric unit, is formed *via* two soft N...O contacts. With N...H-O forming an angle of 146.9(1)° and a N...H distance of 2.094(2) Å, the dihedral angle formed by the least-squares planes through the two separate fused ring systems in a dimeric unit, is 50.32(4)°. The direct intermolecular soft contacts are most likely responsible for the twist in these dimeric units (see Sections 4.4 for planar hydrogen bonded dimer formation). If the neighbouring

⁷¹ Banerjee, T. & Saha, N. N., (1986). *Acta Cryst.* C42, 1408.

quinoline rings were in plane the interacting atoms might be too far apart or a steric hindrance between the hydroxyl hydrogen atoms might prohibit an in plane stacking.

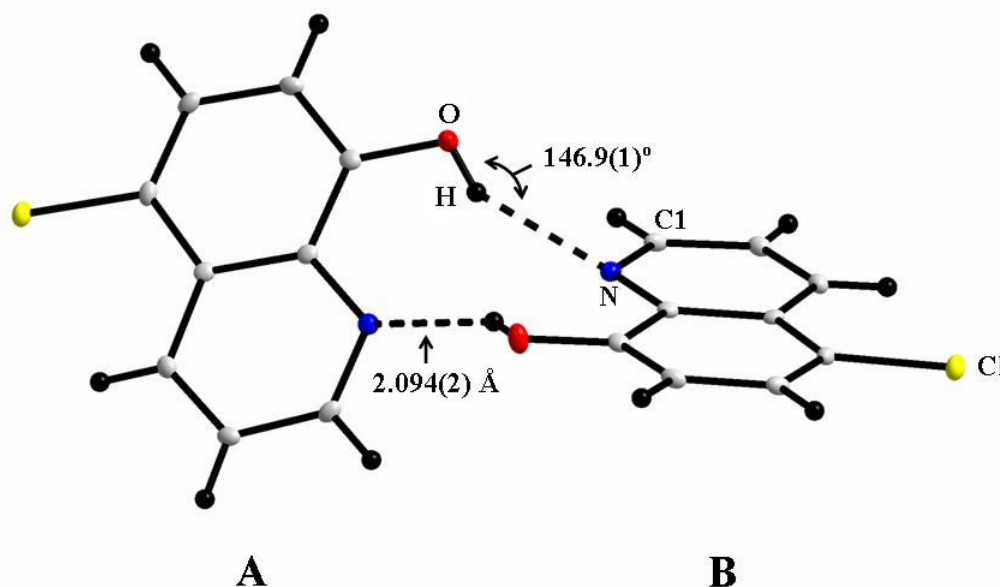


Figure 4.2 An illustration of a typical hydrogen bonded dimeric unit between the molecules of HoxCl. The dimeric unit forms *via* soft contacts between the N-atom of the donor molecule, (A), and the associated acceptor OH-atoms of the neighbour molecule (B). The N...OH distance is 2.094(2) Å and the N...O-H angle is 146.9(1)°.

Molecular packing is not only stabilized by the formation of hydrogen bonded dimers, but also by a ligand π -stacking with an interplanar distance of 3.383 Å (Figure 4.3). This π -stacking is in a “head-to-head” mode acting as stabilizers which are not only between neighbouring molecules but also between the molecular layers. The molecules form hatched layers along the *ab*-axis, roughly parallel to the molecular plane. Each molecule in this layer π - π interaction is shared with either the up- or downstairs neighbouring molecule, operating as an interlayer stabilizer.

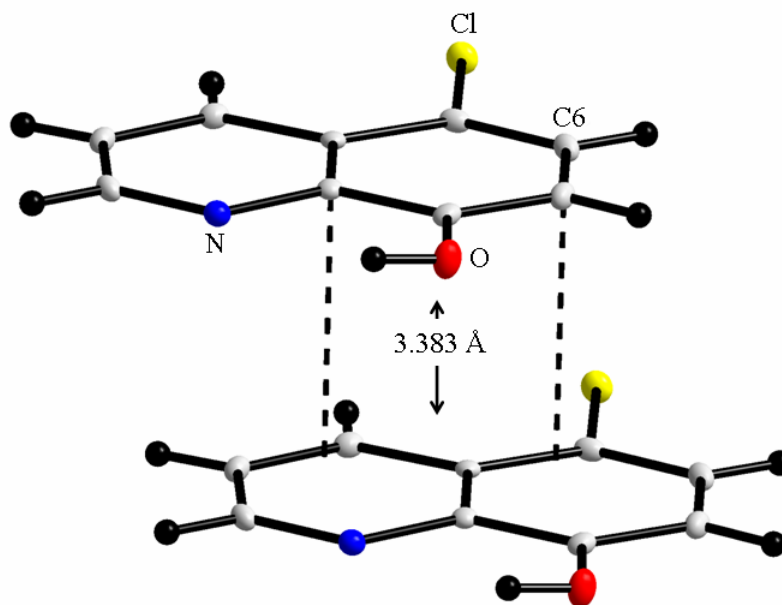


Figure 4.3 An illustration of the ligand to ligand π -stacking along the c -axis in a “head-to-head” mode as found in the crystal packing of the compound, HoxCl, with an interplanar distance of 3.383 Å.

As mentioned above molecular packing, forms hatched layers in the (0 0 h) plane. In this plane a molecule is surrounded by six neighbouring molecules. Some of the stabilizing soft contacts between the centre molecule and neighbouring molecules are illustrated by the use of hashed lines in Figure 4.4 labelled 1-7. The contacts labelled 1 and 2 are the mentioned hydrogen bonding contacts, resulting in the formation of a dimeric unit. Contacts 3 to 7 are Cl...C contacts with the Cl...H distance ranging between 3.067 and 4.145 Å and the Cl...H-C angles between 94.57 and 124.08°.

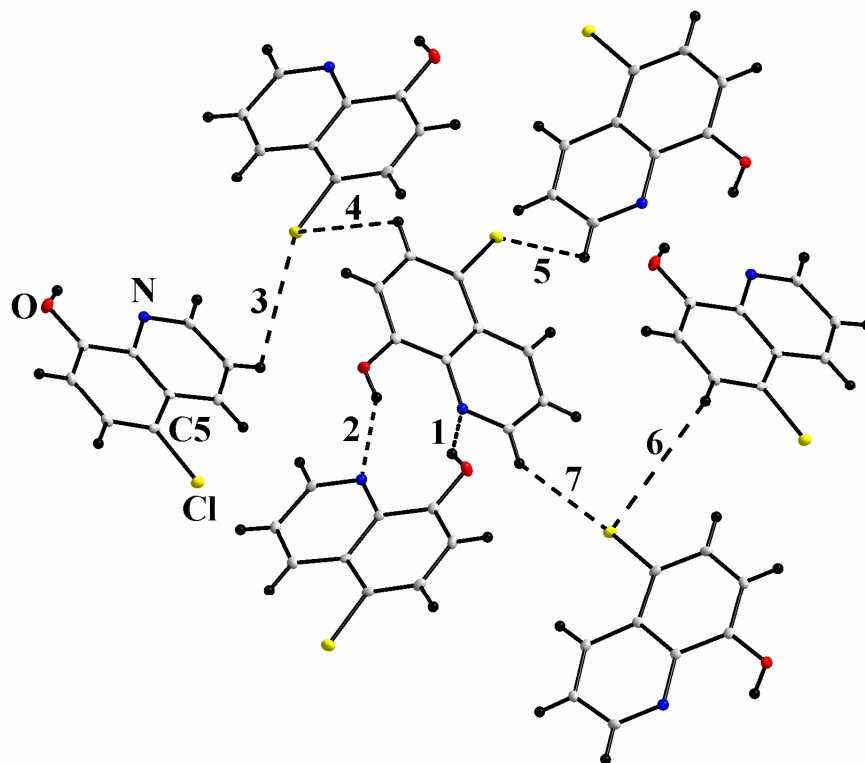


Figure 4.4 An illustration of molecular packing of the compound HoxCl. Hashed lines 1 and 2 indicate the hydrogen bonding dimer contacts, 3-7 indicate soft contacts present between neighbouring molecules stabilizing the crystal packing mode, with contact distances ranging from 3.067 – 4.145 Å and Cl...H-C angles between 94.57 and 124.08°.

Bond distances and angles observed for the fused ring system do not differ significantly from typical quinoline ligands. The structure comparisons and illustrative overlays are discussed in Section 4.9.

4.4 Crystal structure of 5-chloro-8-hydroxyquinolinium bromide (H₂oxCl.Br)

4.4.1 Results and Discussion

(Supplementary data A2)

The compound 5-chloro-8-hydroxyquinolinium bromide, H₂oxCl.Br, crystallized with four molecules in a unit cell of the monoclinic space group *P*2₁/*n*. The atom labelling of this compound is as presented in Figure 4.5 and a few selected geometrical parameters are tabulated in Table 4.3.

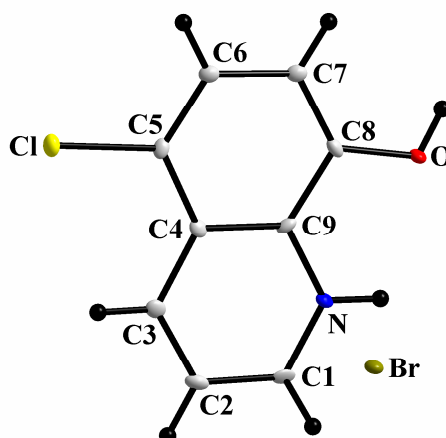


Figure 4.5 A diamond drawing of 5-chloro-8-hydroxyquinolinium bromide, H₂oxCl.Br, presenting the atom numbering scheme of the system. Hydrogen atom labels are omitted for clarity.

Table 4.3 Selected bond distances and angles (Å, °) for the compound H₂oxCl.Br.

Atoms	Distance	Atoms	Angle
O-H	0.82*	H...Br	2.389(3)
N-H	0.882(6)	N...O (Bite distance)	2.641(1)
C8-O	1.358(6)	C8-O-H	109.5*
C5-Cl	1.742(5)	C9-N-H	118(5)
N-C1	1.332(7)	N-C9-C8	119.3(4)
C1-C2	1.399(7)	C4-C9-C8	122.2(5)
C2-C3	1.368(7)	C9-C8-C7	119.1(5)
C3-C4	1.403(7)	C8-C7-C6	120.1(5)
C4-C5	1.420(7)	C2-C1-N	119.9(5)
C5-C6	1.364(8)	C4-C5-Cl	119.1(4)
C6-C7	1.368(7)	C7-C8-C9-C4	2.3(8)
C7-C8	1.407(7)	C1-C2-C3-C4	0.4(8)
C8-C9	1.420(7)		
C9-C4	1.417(7)		
C9-N	1.367(6)		

* No e.s.d. H-atoms were placed as riding.

The fused ring system is fairly planar, with a r.m.s. deviation for atoms C1-C9 and N of 0.0082 Å. Molecular planarity is further emphasized by a dihedral angle of 0.58(27)° between the benzene and pyridine ring and the torsion angles C7-C8-C9-C4 and C1-C2-C3-C4 of 2.3(8)° and 0.4(8)°, respectively. Both the hydroxyl O atom and the pyridine N atom lie in the plane of the fused ring system with out-of-plane distance for O and N of 0.029(6) and 0.009(4) Å. The 5-chloro moiety and the *trans*-conformational hydroxyl hydrogen are slightly displaced from the fused ring system plane at 0.1168(51) and 0.0356(3) Å, respectively.

Figure 4.6 shows the molecular interaction as found in H₂oxCl.Br. The formation of direct hydrogen bonded dimers between two neighbouring quinoline molecules is disrupted by soft intermolecular contacts *via* the bromide atom. These contacts include a O...Br contact, O-H...Br = 170.54(3)° and H...Br = 2.389(3) Å and an N...Br contact, N-H...Br = 150.66(1)° and H...Br = 2.393(7) Å. These neighbouring molecules display no twist between the molecular planes, but pack in parallel planes separated by a distance of 0.265(1) Å.

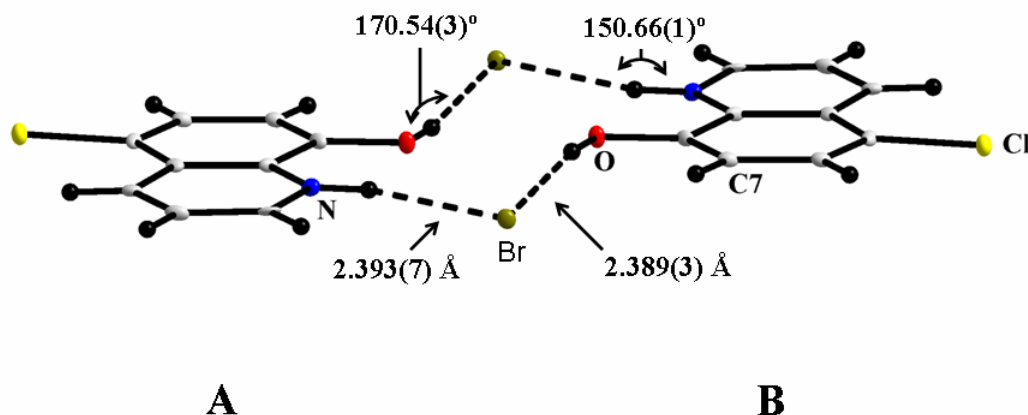


Figure 4.6 An illustration of soft contacts between molecules of $\text{H}_2\text{oxCl.Br}$. With distances of 2.393(7) and 2.389(3) Å and contact angles of 150.66(1) and 170.54(3)°.

The molecular packing forms a puckered pseudo-hexagonal close packed layer along the b-axis. Along this plane a molecule is surrounded by six neighbouring molecules. Some of the stabilizing soft contacts between the centre molecule and surrounding neighbour molecules are illustrated by hashed lines in Figure 4.7 (labelled 1-3). The contacts labelled 1 and 2 are the mentioned hydrogen bonding contacts (Figure 4.6) resulting in the ligand pairing. Contacts 3 are $\text{H}\dots\text{Br}$ contacts with $\text{H}\dots\text{Br} = 2.792(5)$ Å and $\text{C-H}\dots\text{Br} = 143.47(2)^\circ$. Considering the close packing angles (determined from the molecular centres) a variation from 104-129° is observed. With soft contacts between a quinolinium molecule and three bromide atoms on the same side, one would expect the close packing angles to increase (to accommodate the bromide atoms) this is however not the case. This is probably due to the dominating influence from quinoline...quinoline and inter layer contacts.

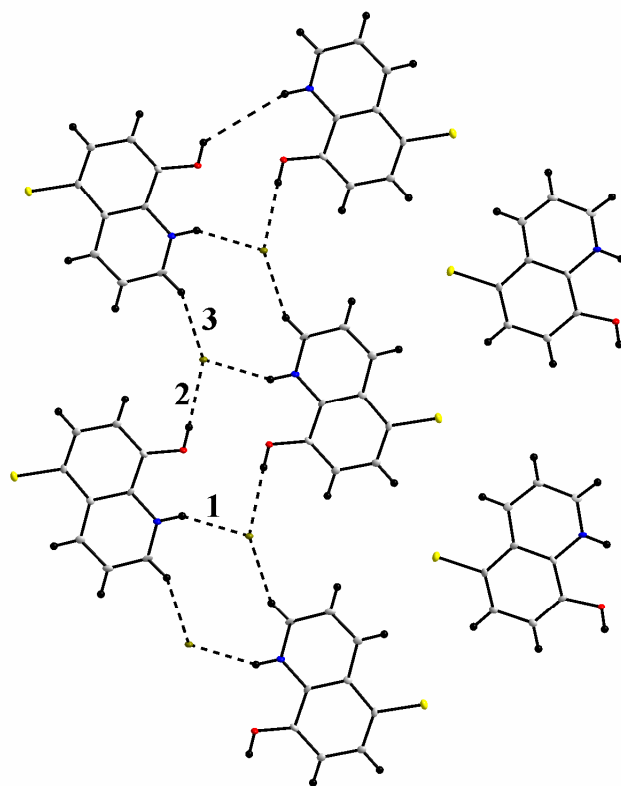


Figure 4.7 An illustration of molecular packing of the compound $\text{H}_2\text{oxCl.Br}$. Hashed lines 1 and 2 indicate the non-direct hydrogen bonding dimer contacts and 3 the soft $\text{Br}\cdots\text{H}$ contact with a distance of $2.792(5)$ Å and an $\text{Br}\cdots\text{H-C}$ angle of $143.47(2)^\circ$.

Bond distances and angles observed for the fused ring system do not significantly differ from typical quinoline ligands and further structure comparisons are discussed in Section 4.9.

***4.5 Crystal structure of
5-Chloro-8-hydroxyquinolinium
hexafluorophosphate hydrate ($H_2oxCl.PF_6$)***

4.5.1 Results and Discussion

(Supplementary data A3)

The compound 5-Chloro-8-hydroxyquinolinium hexafluorophosphate hydrate, $H_2oxCl:PF_6$, crystallized in the monoclinic space group $P2_1/n$, ($Z=4$). Presented in Figure 4.8 is a molecular drawing of the compound $H_2oxCl.PF_6$ displaying the numbering scheme of the system. The most important bond distances and angles are summarized in Table 4.4.

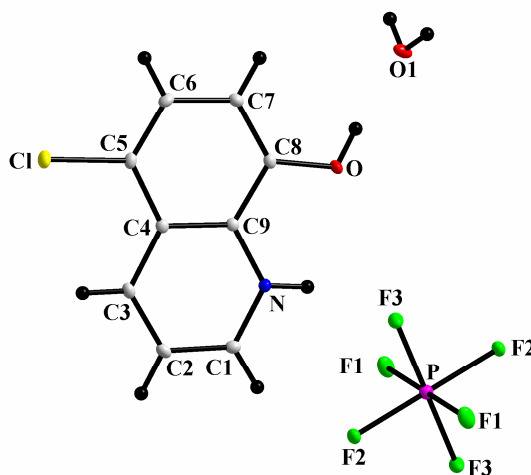


Figure 4.8 A diamond drawing of the hydrated compound 5-chloro-8-hydroxyquinolinium hexafluorophosphate, $H_2oxCl.PF_6$, in the asymmetric unit, showing the atom numbering scheme of the system. Hydrogen atom labels are omitted for clarity.

Table 4.4 Selected bond distances and angles (Å, °) for the compound H₂oxCl.PF₆.

Atoms	Distance	Atoms	Angle
O-H	0.82*	N...O (Bite distance)	2.671(2)
N-H	0.86(3)	C8-O-H	109.5
C8-O	1.343(2)	N-C9-C8	119.26(14)
C5-Cl	1.731(2)	C4-C9-C8	121.99(14)
N-C1	1.327(2)	C9-C8-C7	118.32(14)
C1-C2	1.390(2)	C8-C7-C6	120.86(15)
C2-C3	1.371(2)	C2-C1-N	120.53(15)
C3-C4	1.409(2)	C4-C5-Cl	119.00(12)
C4-C5	1.421(2)	C7-C8-C9-C4	0.3(2)
C5-C6	1.365(2)	C1-C2-C3-C4	1.1(2)
C6-C7	1.411(2)		
C7-C8	1.373(2)		
C8-C9	1.418(2)		
C9-C4	1.416(2)		
C9-N	1.363(2)		

* No e.s.d. H-atoms were placed as riding.

The fused ring system is planar, with a r.m.s. deviation from planarity of 0.0114 Å. A dihedral angle of 1.33(6)° between the benzene and pyridine ring and the torsion angles C7-C8-C9-C4 and C1-C2-C3-C4 of 0.3(2)° and 1.1(2)°, respectively, display molecular planarity. Both the hydroxyl O atom and the pyridine N atom lie in the plane of the fused ring system. The out-of-plane distances for O and N are 0.001(2) and 0.012(1) Å each. The 5-chloro moiety and the *trans*-conformational hydroxyl hydrogen are slightly displaced from the fused ring system plane in the same direction by 0.1050(67) and 0.093(21) Å respectively.

As presented in Figure 4.9, the quinoline molecule is surrounded by four hexafluorophosphate molecules and four neighbouring quinoline molecules. There are no direct H-bonded dimeric units formed between the quinoline moieties of this structure, but intermolecular soft contacts are present. The hydroxyl hydrogen is directed towards the oxygen atom of the water guest molecule, H...O = 1.750(1) Å and O-H...O = 174.97(9)°. Other stabilizing soft contacts are N...F and C...F contacts with N-H...F = 159.86(22)°, H...F = 1.845(22) Å and C-H...F = 147.86(11)° and H...F = 2.236(2) Å.

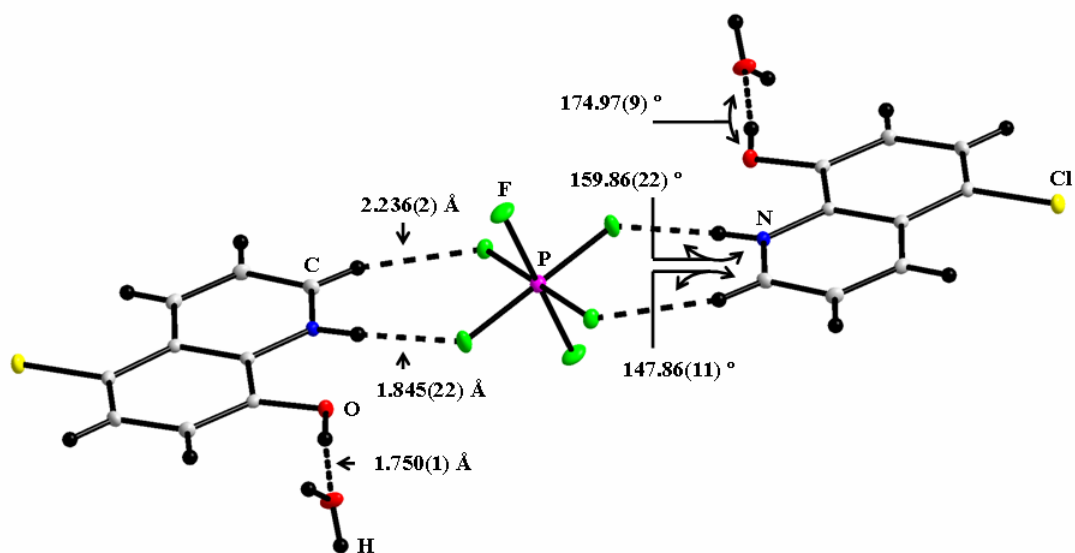


Figure 4.9 An illustration of intermolecular contacts as found in the crystal structure of the compound $\text{H}_2\text{oxCl} \cdot \text{PF}_6$. These contact distances range from 1.750 to 2.236 Å with contact angles between 147.8 and 174.7°.

Structure comparisons to relative structures and illustrative overlays are discussed in Section 4.9.

4.6 Crystal structure of 5-nitro-8-hydroxyquinoline (HoxNO₂)

4.6.1 Results and Discussion

(Supplementary data A4)

The compound 5-nitro-8-hydroxyquinoline, HoxNO₂, crystallized in the orthorhombic space group *Fdd*₂, (*Z*=12). The numbering scheme of HoxNO₂ is presented in Figure 4.10. The most important bond distances and angles are reported in Table 4.5.

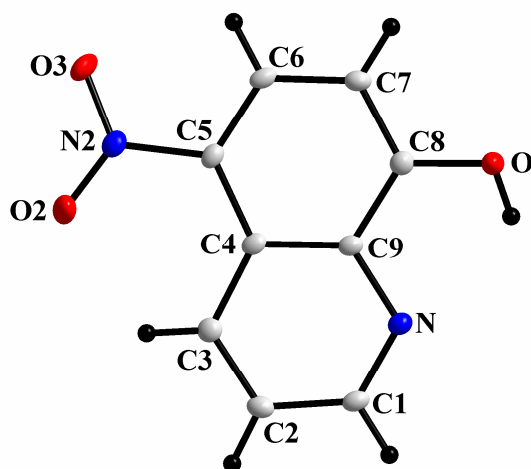


Figure 4.10 A diamond drawing of 5-nitro-8-hydroxyquinoline, HoxNO₂, in the asymmetric unit, showing the atom numbering scheme of the system. Hydrogen atom labels are omitted for clarity.

Table 4.5 Selected bond distances and angles (Å, °) for the compound HoxNO₂.

Atoms	Distance	Atoms	Angle
O-H	0.82*	N...O (Bite distance)	2.728(2)
C8-O	1.337(2)	N2-O2	1.220(3)
C5-N2	1.457(2)	N2-O3	1.232(2)
N-C1	1.317(3)	C8-O-H	109.5*
C1-C2	1.405(3)	N-C9-C8	115.94(17)
C2-C3	1.363(3)	C4-C9-C8	120.93(17)
C3-C4	1.425(3)	C9-C8-C7	120.17(18)
C4-C5	1.434(3)	C8-C7-C6	119.68(19)
C5-C6	1.372(3)	C2-C1-N	123.19(18)
C6-C7	1.393(3)	C4-C5-N2	122.07(18)
C7-C8	1.379(3)	C7-C8-C9-C4	0.8(3)
C8-C9	1.430(3)	C1-C2-C3-C4	0.2(3)
C9-C4	1.422(3)	C6-C5-N2-O3	7.5(3)
C9-N	1.364(2)		

* No e.s.d. H-atoms were placed as riding.

The fused ring system is planar, with a r.m.s. deviation from planarity of 0.0073 Å, for atoms C1-C9 and N. A dihedral angle of 0.75(9)° between the benzene and pyridine ring and the torsion angles C7-C8-C9-C4 and C1-C2-C3-C4 of 0.8(3)° and 0.2(3)°, exists. This emphasizes the planarity of this compound. Both the hydroxyl O atom and the pyridine N atom lie in the plane of the fused ring system and the out-of-plane distances for O and N are -0.025(3) and 0.010(2) Å. The N-atom of the 5-Nitro moiety and the *cis*-conformational hydroxyl hydrogen are displaced, 0.0196(21) and -0.031(3) Å, above the fused ring system plane. The O-atoms of the 5-nitro moiety is twisted out of the molecular plane which is shown by the torsion angle, C6-C5-N2-O3 = 7.5(3)°.

Presented in Figure 4.11 is the hydrogen bonded dimeric unit, formed *via* direct contacts between the donor atoms of the quinoline molecules. This dimeric unit consist of two N...O contacts with N...H = 2.109(2) Å and O-H...N = 141.19(11)°. As mentioned in Section 4.3.1, the neighbouring molecules of such a dimeric unit are twisted towards one another, in this case to form a dihedral angle of 46.87(4)°.

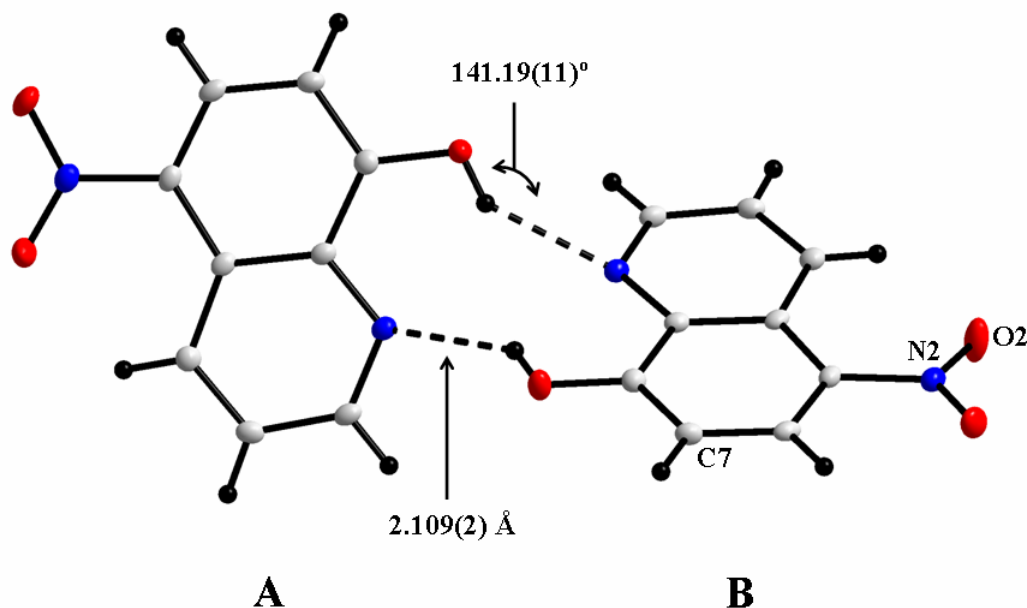


Figure 4.11 4.12 An illustration of a typical hydrogen bonded dimeric unit between the molecules of compound HoxNO_2 . The dimeric unit form *via* soft contacts between the N-atom of the donor molecule, (A), and the associated acceptor OH-atoms of the neighbour molecule (B). The $\text{N}\cdots\text{OH}$ distance is $2.109(2) \text{ \AA}$ and the $\text{N}\cdots\text{O-H}$ angle is $141.19(11)^\circ$.

The molecular packing is also stabilized by the ligand π -stacking with an interplanar distance of $3.346 \text{ \AA}$ (Figure 4.13). This π -stacking is in a “head-to-head” mode which also acts as stabilizers between neighbouring molecules and molecular layers. The molecules form hacked layers along the *ab*-axis, approximately parallel to the molecular plane. For each molecule in this layer π - π interaction is shared with either the up- or downstairs neighbouring molecule, operating as an interlayer stabilizer.

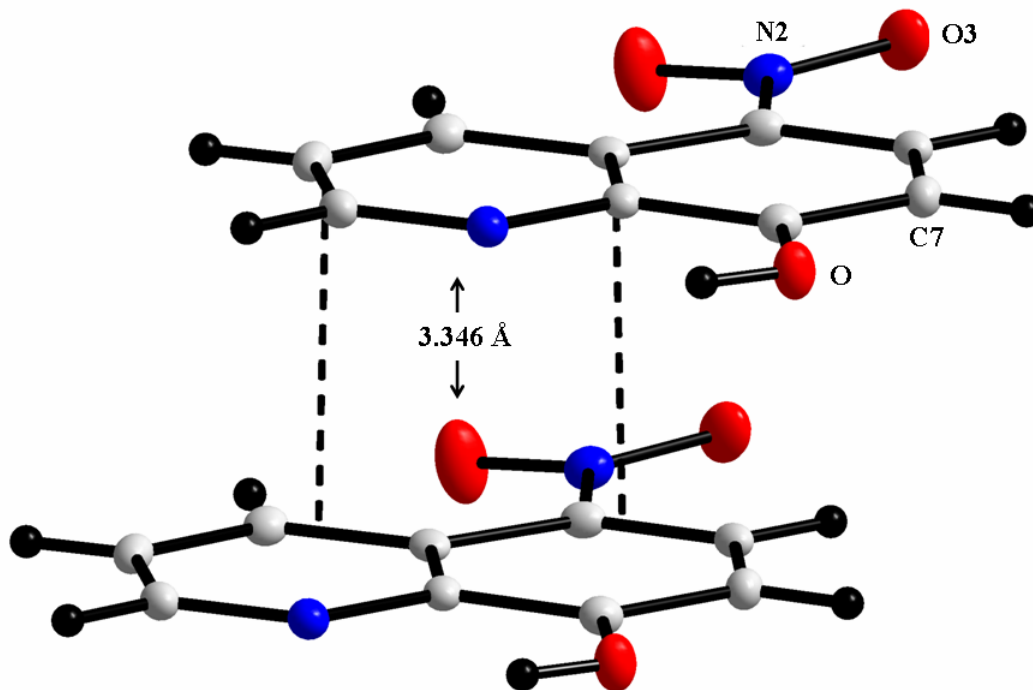


Figure 4.13 An illustration of the ligand to ligand π -stacking in a “head to head” mode as found in the crystal packing of the compound, HoxNO_2 , with an inter planar distance of 3.346 Å.

As mentioned above molecular packing forms, hatched layers in the (0 0 h) plane and molecules is thus surrounded by six other molecules. Some of the stabilizing soft contacts between the centre molecule and surrounding neighbour molecules are illustrated in Figure 4.14. The contacts labelled 1 and 2 are the hydrogen bonding contacts, forming the dimeric unit. Contacts 3 and 4 are C...O contacts, 3, with $\text{H}\cdots\text{O} = 2.748(2)$ Å and $\text{C}\cdots\text{H}\cdots\text{O} = 110.04(13)^\circ$ and (4), with $\text{H}\cdots\text{O} = 2.440(2)$ Å and $\text{C}\cdots\text{H}\cdots\text{O} = 149.34(13)^\circ$.

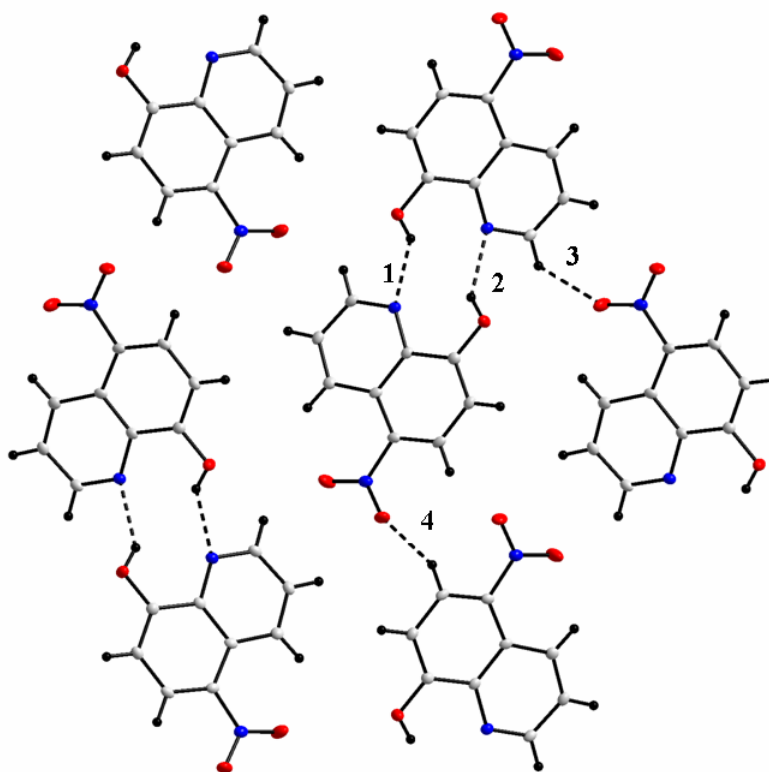


Figure 4.14 An illustration of molecular packing for the compound HoxNO₂. Hashed lines 1 and 2 indicate the hydrogen bonding dimer contacts, 3 and 4 indicate soft contacts present between neighbouring molecules, stabilizing the crystal packing mode, with contact distances ranging from 2.440(2) – 2.748(2) Å and soft contact angles between 110.04(13) and 149.34(13)°.

A geometrical and molecular packing comparison of the discussed compound HoxNO₂ and other relative 8-hydroxyquinoline compounds is presented in Section 4.9.

4.7 *Crystal structure of* *5-nitro-8-hydroxyquinolinium nitrate* *(H₂oxNO₂.NO₃)*

4.7.1 Results and Discussion

(Supplementary data A5)

The compound 5-nitro-8-hydroxyquinolinium nitrate, H₂oxNO₂.NO₃, crystallized in the triclinic space group *P* $\bar{1}$ with two independent molecules in a unit cell. The molecular numbering scheme is as presented in Figure 4.15 and some important bond distances and angles are reported in Table 4.6.

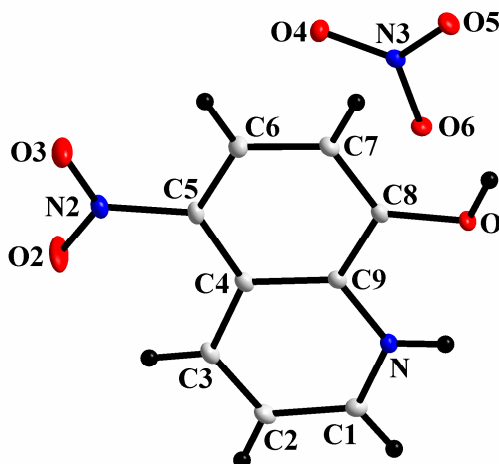


Figure 4.15 A diamond drawing of 5-nitro-8-hydroxyquinolinium nitrate, H₂oxNO₂.NO₃, in the asymmetric unit, showing the atom numbering scheme of the system. Hydrogen atom labels are omitted for clarity.

Table 4.6 Selected geometrical parameters (Å, °) for the compound $\text{H}_2\text{oxNO}_2\cdot\text{NO}_3$.

Atoms	Distance	Atoms	Angle
O-H	0.84(2)	N...O (Bite distance)	2.647(2)
C8-O	1.332(2)	N2-O2	1.2193(17)
C5-N2	1.460(2)	N2-O3	1.2197(18)
N-C1	1.3225(18)	C8-O-H	112.3(16)
C1-C2	1.395(2)	N-C9-C8	117.89(12)
C2-C3	1.367(2)	C4-C9-C8	122.37(13)
C3-C4	1.4232(19)	C9-C8-C7	118.75(13)
C4-C5	1.425(2)	C8-C7-C6	119.89(13)
C5-C6	1.3754(19)	C2-C1-N	19.88(13)
C6-C7	1.390(2)	C4-C5-N2	122.80(12)
C7-C8	1.377(2)	C7-C8-C9-C4	2.1(2)
C8-C9	1.4262(18)	C1-C2-C3-C4	0.8(2)
C9-C4	1.4154(19)	C6-C5-N2-O3	169.56(14)
C9-N	1.3681(18)		

An indication of molecular planarity is the dihedral angle of $1.82(9)^\circ$ between the benzene and pyridine ring. Both the hydroxyl O atom and the pyridine N atom lie essentially in the fused ring system plane, with out-of-plane distances of 0.068(2) and 0.027(2) Å, respectively. The N-atom of the 5-Nitro moiety and the *trans*-conformational hydroxyl hydrogen are displaced at 0.027(1) and -0.08(2) Å, above the fused ring system plane. The O-atoms of the 5-nitro moiety is twisted out of the molecular plane, shown by the torsion angle of $\text{C6-C5-N2-O3} = 10.6(2)^\circ$.

Figure 4.16 illustrates the molecular interaction as found in the crystal packing of the compound $\text{H}_2\text{oxNO}_2\cdot\text{NO}_3$. Formation of direct hydrogen bonded dimers between two neighbouring quinoline molecules is disrupted and soft intermolecular contacts *via* the nitric molecule are present. These contacts include a N...O contact, $\text{N-H}\cdots\text{O} = 169.8(22)^\circ$, $\text{H}\cdots\text{O} = 1.98(2)$ Å and an O...O contact, $\text{O-H}\cdots\text{O} = 162.8(24)^\circ$ and $\text{H}\cdots\text{O} = 1.79(3)$ Å. These neighbouring molecules display no twist between them and do not pack in exactly the same plane, but pack in parallel planes separated by a distance of 0.595 Å.

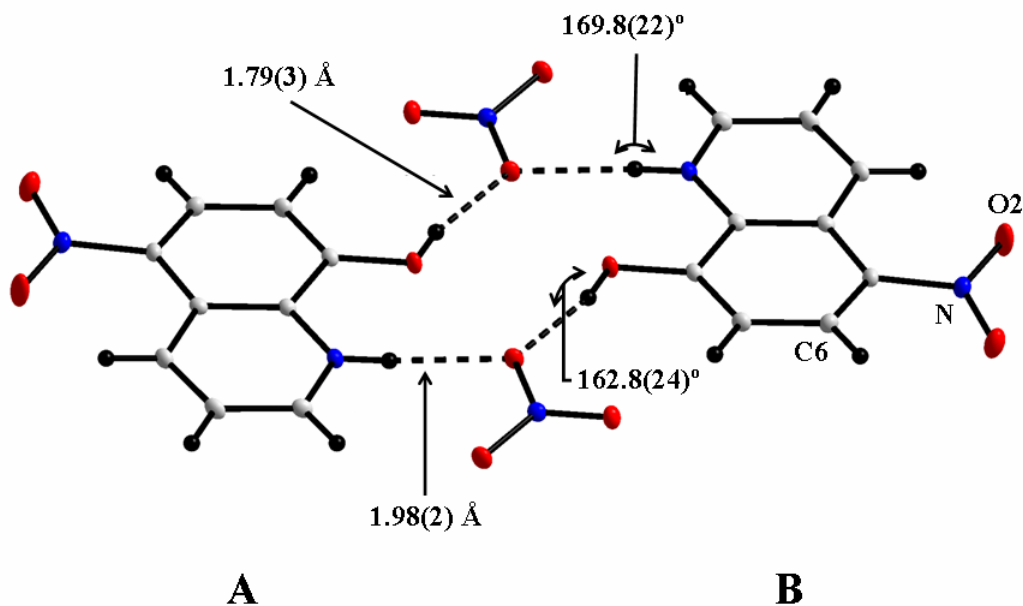


Figure 4.16 An illustration of soft contacts between molecules of the compound $\text{H}_2\text{oxNO}_2\cdot\text{NO}_3$. With contact distances of 1.79(3) and 1.98(2) Å and contact angles of 169.8(22) and 162.8(24)°.

The molecular packing, forms a puckered pseudo-hexagonal close packed layer. Some of the stabilizing soft contacts between the centre molecule and neighbouring molecules are illustrated in Figure 4.17. The contacts labelled 1 and 2 are the mentioned hydrogen bonding contacts (see Figure 4.16), results in the ligand pairing. Contacts 3 are $\text{H}\dots\text{O} = 2.690(6)$ Å and $\text{C-H}\dots\text{O} = 151.79(10)^\circ$, 4, with $\text{H}\dots\text{O} = 2.310(3)$ Å and $\text{C-H}\dots\text{O} = 132.53(10)^\circ$, 5, with $\text{H}\dots\text{O} = 2.287(4)$ Å and $\text{C-H}\dots\text{O} = 161.34(10)^\circ$, 6, with $\text{H}\dots\text{O} = 2.551(5)$ Å and $\text{C-H}\dots\text{O} = 129.36(10)^\circ$, 7, with $\text{H}\dots\text{O} = 2.435(4)$ Å and $\text{C-H}\dots\text{O} = 142.83(10)^\circ$ and 8, with $\text{H}\dots\text{O} = 2.319(5)$ Å and $\text{C-H}\dots\text{O} = 137.08(10)^\circ$. Considering the close packing angles measured from the molecular centres, a variation of 102 -134° is observed. One would expect an angle increase from the ideal 120° with the one sided presence of NO_3^- anions, this is however not the case, indicating the influence from quinoline...quinoline and inter layer contacts

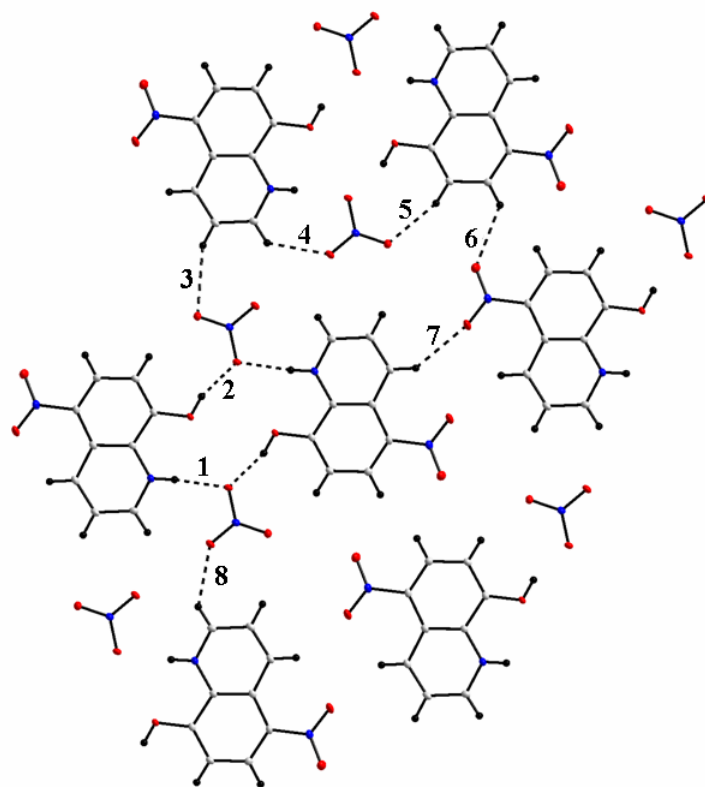


Figure 4.17 An illustration of molecular packing of the compound $\text{H}_2\text{oxNO}_2 \cdot \text{NO}_3^-$. Hashed lines 1 and 2 indicate the non-direct hydrogen bonding dimer contacts, 3-8 indicate soft contacts present between neighbouring molecules, stabilizing the crystal packing mode, with contact distances of ranging between 2.287 and 2.690 Å and contact angles between 129.36 and 161.34°.

Structure comparison and illustrative overlays between the HoxNO_2 and $\text{HoxNO}_2 \cdot \text{NO}_3$ compounds are discussed in Section 4.9.

4.8 Crystal structure of 5-chloromethyl-8-hydroxyquinoline hydrochloric acid solvate (HoxMeCl)

4.8.1 Results and Discussion

(Supplementary data A6)

As reported in Table 4.1, an electron density of $0.695 \text{ e.}\text{\AA}^{-3}$ is present $0.8 \text{ \AA}$ from the N-atom with a goodness of fit on F^2 of 1.106. A refinement of 5-chloromethyl-8-hydroxyquinoline chloride results in a $0.871 \text{ e.}\text{\AA}^{-3}$ electron density, $0.78 \text{ \AA}$ from Cl2 with a goodness of fit on F^2 of 1.128. Based on these values, the structure was refined as 5-chloromethyl-8-hydroxyquinoline hydrochloric acid solvate. To date there are 53 structures on the CSD (version 5.29, update August 2008) with refined hydrochloric acid molecules¹.

The compound 5-chloromethyl-8-hydroxyquinoline hydrochloric acid solvate, HoxMeCl, crystallized in the monoclinic space group $P2_1/c$, ($Z=4$). In Figure 4.18 we present the numbering scheme of HoxMeCl and in Table 4.7 the most important bond distances and angles are reported.

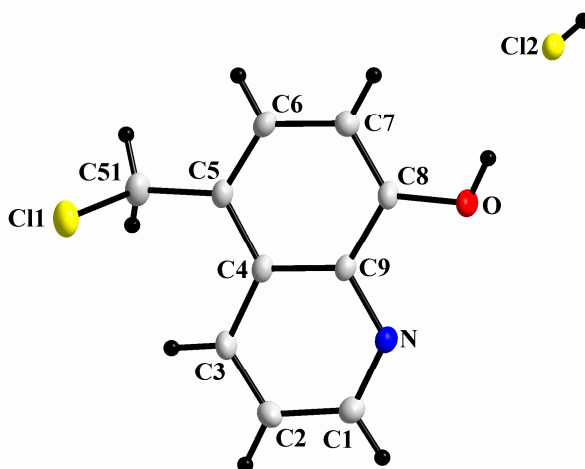


Figure 4.18 A diamond drawing of 5-chloromethyl-8-hydroxyquinoline hydrochloric acid solvate, HoxMeCl, in the asymmetric unit, showing the atom numbering scheme of the system. Hydrogen atom labels are omitted for clarity.

Table 4.7 Selected geometrical parameters (Å, °) for the compound HoxMeCl.

Atoms	Distance	Atoms	Angle
O-H	0.82*	N...O (Bite distance)	2.662(4)
C8-O	1.344(4)	C8-O-H	109.5
C5-C51	1.495(5)	N-C9-C8	119.1(3)
C51-Cl	1.807(5)	C4-C9-C8	121.8(3)
N-C1	1.316(5)	C9-C8-C7	118.6(3)
C1-C2	1.396(6)	C8-C7-C6	119.8(4)
C2-C3	1.363(6)	C2-C1-N	120.2(4)
C3-C4	1.412(6)	C4-C5-C51	121.2(4)
C4-C5	1.425(6)	C7-C8-C9-C4	0.3(5)
C5-C6	1.366(6)	C1-C2-C3-C4	0.1(7)
C6-C7	1.408(5)		
C7-C8	1.373(6)		
C8-C9	1.414(5)		
C9-C4	1.418(5)		
C9-N	1.369(5)		

* No e.s.d. H-atoms were placed as riding.

The fused ring system is planar with a r.m.s. deviation from planarity of 0.0179 Å for atoms C1-C9 and N. A dihedral angle of 2.05(22) between the benzene and pyridine ring and the torsion angles C7-C8-C9-C4 and C1-C2-C3-C4 of 0.3(5)° and 0.1(7)° respectively emphasizes the planarity of this compound. Both the hydroxyl O atom and the pyridine N atom lie in the plane of the fused ring system, the out-of-plane distances for O and N are 0.023(3) and 0.006(3) Å. The chloromethyl moiety is almost perpendicular to the quinoline plane which results in a C4-C5-C51-Cl1 torsion angle of 75.6(1)°. The 5-carbon atom C51 and the *trans*-conformational hydroxyl hydrogen are displaced to 0.185(5) and 0.101(1) Å, above the fused ring system plane.

Figure 4.19 shows the intra-molecular interaction between HoxMeCl molecules. The formation of direct hydrogen bonded dimers between neighbouring quinoline molecules is disrupted by soft intermolecular contacts *via* the chlorine atom of the guest molecule. These include a soft N...Cl contact = 3.074(3) Å and an O...Cl contact, with O-H...Cl = 147.9(2) ° and H...Cl = 2.145(2) Å (Figure 4.19). These neighbouring molecules display no twist between them, but pack in parallel planes separated by a distance of 0.698(1) Å.

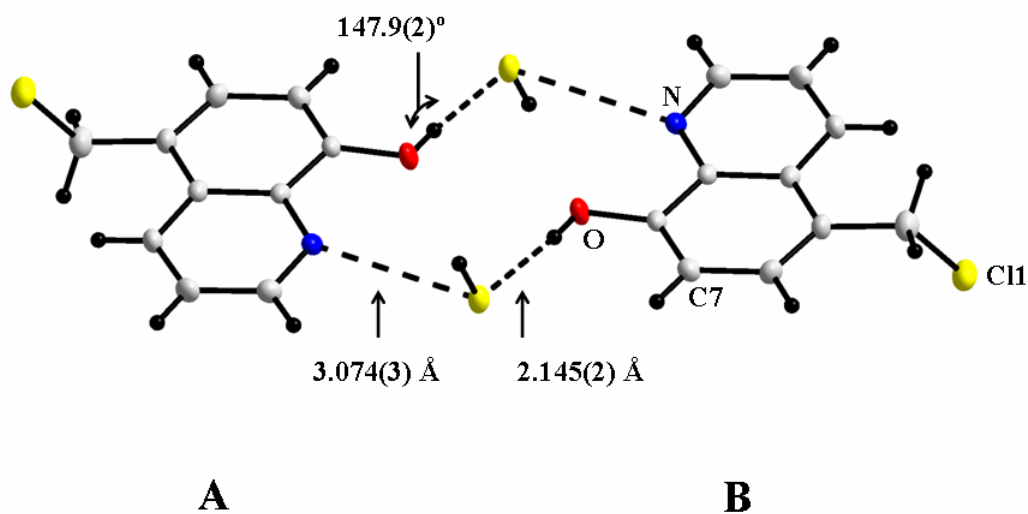


Figure 4.19 An illustration of soft contacts between molecules of compound HoxMeCl. With contact distances of 2.145(2) and 3.074(3) Å and a contact angle of 150.66(1) and 147.9(2)°.

Molecular packing is not only stabilized by the formation of hydrogen bonded dimers, but also by a ligand to ligand π -stacking with a distance of 3.344 Å (Figure 4.20). This π -stacking is in a “head to tail” mode and also acts as an interlayer stabilizer.

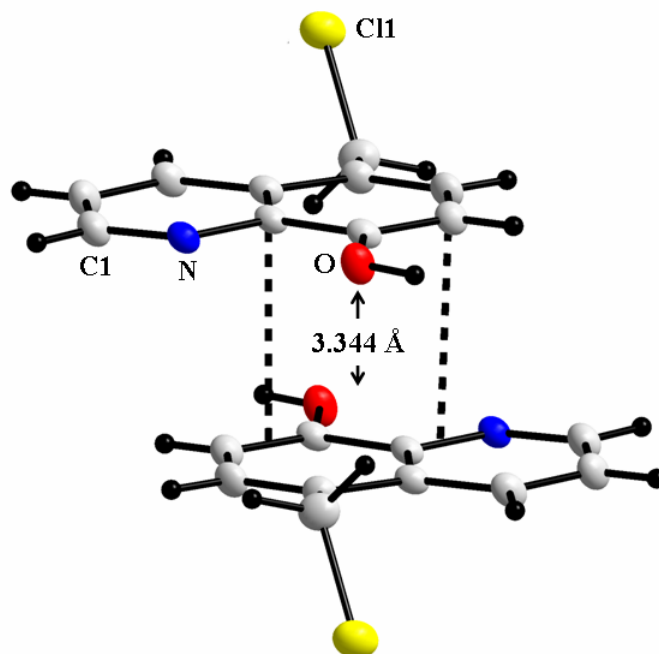


Figure 4.20 An illustration of the ligand to ligand π -stacking in a “head-to-tail” mode as found in the crystal packing of the compound, HoxMeCl, with an interplanar distance of 3.344 Å.

The molecular packing, forms hatched layers in the (0 0 h) plane. In this plane a molecule is surrounded by six neighbouring molecules. Some of the stabilizing soft contacts between the centre molecule and neighbouring molecules are illustrated, by the use of hashed lines in Figure 4.21 (labelled 1-4). The contacts labelled 1 and 2 are the mentioned hydrogen bonding contacts, resulting in the formation of a non direct hydrogen bonded dimeric unit. Contact number 3 is Cl...H contacts with $\text{C-H}\cdots\text{Cl} = 125.34(27)^\circ$ and $\text{H}\cdots\text{Cl} = 2.993(2) \text{ \AA}$ and 4 is Cl...H contact with $\text{C-H}\cdots\text{Cl} = 103.44(27)^\circ$ and $\text{H}\cdots\text{Cl} = 3.075(2) \text{ \AA}$.

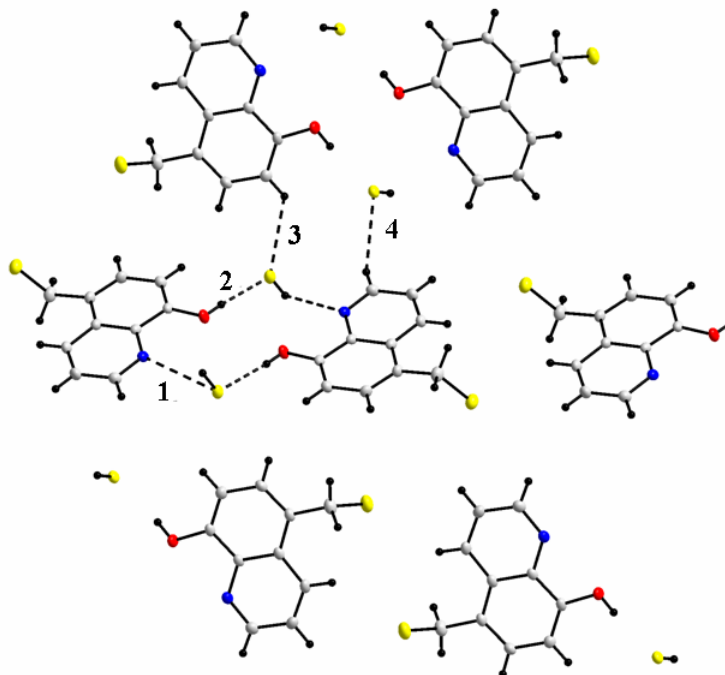


Figure 4.21 An illustration of molecular packing of the compound HoxMeCl. Hashed lines 1 and 2 indicate the non-direct hydrogen bonding dimer contacts, lines 3 and 4 indicate soft contacts present between neighbouring molecules, stabilizing the crystal packing mode, with contact distances of 2.993(2) and 3.075(2) Å and contact angles of 125.34(27) and 103.44(27)°

Additional molecular comparisons and illustrative overlays are discussed in Section 4.9.

4.9 Interpretation and correlation of structural characteristics

The following subsection correlates structural data from the different quinoline compounds as described above. Further correlation to structures from literature and DFT calculations are presented in Chapter 5.

4.9.1 Molecular geometry

Table 4.8 gives the general bond distances and angles of the discussed crystal structures.

Table 4.8 Selected geometrical parameters (Å, °) of the presented 8-hydroxyquinoline derivatives, tabulated for comparison.
For label definition see section 4.1.

	(HoxCl)	(H ₂ oxCl.Br)	(H ₂ oxCl.PF ₆)	(HoxNO ₂)	(H ₂ oxNO ₂ .NO ₃)	(HoxMeCl)
Bonds (Å)						
O-H*	0.82*	0.82*	0.82*	0.82*	0.84(2)	0.82*
N-H		0.88(6)	0.86(3)		0.86(2)	
C4-C5	1.416(3)	1.420(7)	1.421(2)	1.434(3)	1.425(2)	1.425(6)
C5-C6	1.362(3)	1.364(8)	1.365(2)	1.372(3)	1.375(2)	1.366(6)
C7-C8	1.373(3)	1.368(7)	1.373(2)	1.379(3)	1.377(2)	1.373(6)
C8-C9	1.426(3)	1.407(7)	1.418(2)	1.430(3)	1.426(2)	1.414(5)
C1-N	1.314(3)	1.332(7)	1.327(2)	1.317(3)	1.323(2)	1.316(5)
C9-N	1.366(2)	1.367(6)	1.363(2)	1.364(2)	1.368(2)	1.369(5)
C8-O	1.349(2)	1.358(6)	1.343(2)	1.337(2)	1.333(2)	1.344(4)
C5-5'	1.747(2)	1.742(5)	1.731(2)	1.457(2)	1.460(2)	1.495(5)
N..O _(Bite)	2.765(6)	2.641(1)	2.671(2)	2.728(2)	2.647(2)	2.662(4)
Angles (°)						
C4-C5-C6	121.73(17)	121.3(5)	121.08(15)	121.99(18)	121.07(13)	118.8(3)
C9-C8-C7	119.63(17)	119.1(5)	118.32(14)	120.17(18)	118.75(13)	118.6(3)
C8-O-H*	109.5*	109.5*	109.5*	109.5*	112.3(16)	109.5*
C9-N-H		118(5)	121.7(17)		122.6(14)	
C4-C5-R	118.66(16)	119.1(4)	119.00(12)	122.07(18)	122.80(12)	121.2(4)
N-C9-C8	117.56(16)	119.3(4)	119.26(14)	115.94(17)	117.89(12)	119.1(3)

*No e.s.d when H-atoms were placed as riding on the parent atom. R = various substituted atoms, directly bound to atom C5.

This discussion starts by focusing on the differences between the bond distances and angles of cationic and neutral compounds, by comparing the three structures of 5-chloro-8-hydroxyquinoline. It must be noted that the distribution of C-C and C-N bond distances of the aromatic ring moieties (Table 4.8) corresponds with literary values.⁷⁴ The structural geometry of the HoxCl and H₂oxCl.Br ligands are very similar, as determined by structural overlay, (r.m.s of fitted atoms N, C1, C2, C3, C4 and C9 = 4.5654×10^{-7} Å). Whereas in the overlay, Figure 4.22, of the compound HoxCl (shown in blue) and H₂oxCl.PF₆ (shown in red) the dihedral angle difference between the benzene and the pyridine rings are noted. The bite angle difference between these two structures, Figure 4.22, (r.m.s of fitted atoms, N, C1, C2, C3, C4 and C9 = 0.0309 Å).

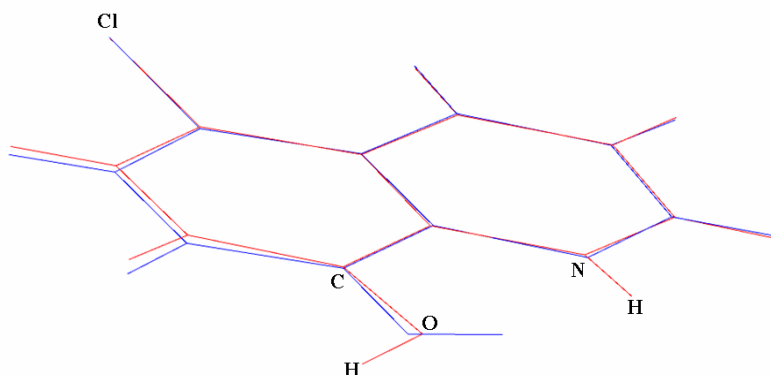


Figure 4.22 Structural overlay of the compounds HoxCl drawn in blue and H₂oxCl.PF₆ drawn in red, showing small differences in the bite distance and the fused ring systems planarity.

The N-H bond of the H₂oxCl.Br structure is 0.02 Å longer than that of the H₂oxCl.PF₆ structure. As shown in Figure 4.6 and Figure 4.9 the intermolecular interaction of the N...H atoms for each of the compounds H₂oxCl.Br and H₂oxCl.PF₆ are 2.393(7) and 1.845(22) Å, thus the difference in bond distance might be described to intermolecular interaction and various electron densities of the Br- and F-atoms. The same effects could be responsible for the small variations in the C8-O and C5-Cl bond distances, Table 4.8.

Other variations include the N...O bite distance decrease from 2.765, 2.671 and 2.641 Å, for the compounds HoxCl, H₂oxCl.PF₆ and H₂oxCl.Br, respectively. The same decreasing order is noted for the endo-cyclic ring angle C4-C5-C6, 121.73(17)° and 121.3(5)° to 121.08(15)°, respectively. The endo-cyclic ring angle C9-C8-C7 of the H₂oxCl.PF₆ structure is almost 1° smaller than that of the other two structures. The much larger C9-N-H angle which is present in the structure of the compound H₂oxCl.PF₆, is once again responsible for the intermolecular interaction between this hydrogen and the atom F1 (Figure 4.9). The C4-C5-Cl angles show some variation, also described to possible inter molecular interaction with neighbouring molecules (as shown in Figure 4.4, Figure 4.7 and Figure 4.14). Finally note that for the neutral HoxCl complex, the N-C9-C8 ring angle is smaller than those for the solvated structures, with a value of 117.56(16)°.

It therefore seems that various anions influence the molecular geometry *via* inter molecular interact, both directly and indirectly. Directly because the electron density of the anions differ and indirectly by the hydroxyl hydrogen conformations, which in turn have a significant effect on for example the N...O bite distance.

Considering the difference between the HoxNO₂ and H₂oxNO₂.NO₃ compounds, distribution of the C-C and C-N bond distances of the aromatic ring moiety's is in the general range and the C8-O and C5-N2 bond distances are corresponds well. A 0.081 Å decrease is noted in the N...O bite distance when a solvate is introduced into the system. The C4-C5-C6 and C9-C8-C7 endo cyclic ring angles are smaller in the solvated structure at 0.92° and 1.42° respectively. The C8-O-H angle of the solvated structure is 2.8° larger than that of the non-refined hydroxyl hydrogen atom. The small difference between the C4-C5-N2 angles is probably due to inter molecular interaction. As noted in the HoxCl structures, the smallest N-C9-C8 angle is present in the structure with the larger N...O bite distance. Presented in Figure 4.23 is the overlay between structures HoxNO₂ (shown in blue) and H₂oxNO₂.NO₃ (shown in red). These show small

differences in the bite distance, fused ring systems planarity and twist of the NO₂ group, being in the opposite direction (r.m.s of fitted atoms, N, C1, C2, C3, C4 and C9 = 0.0304 Å).

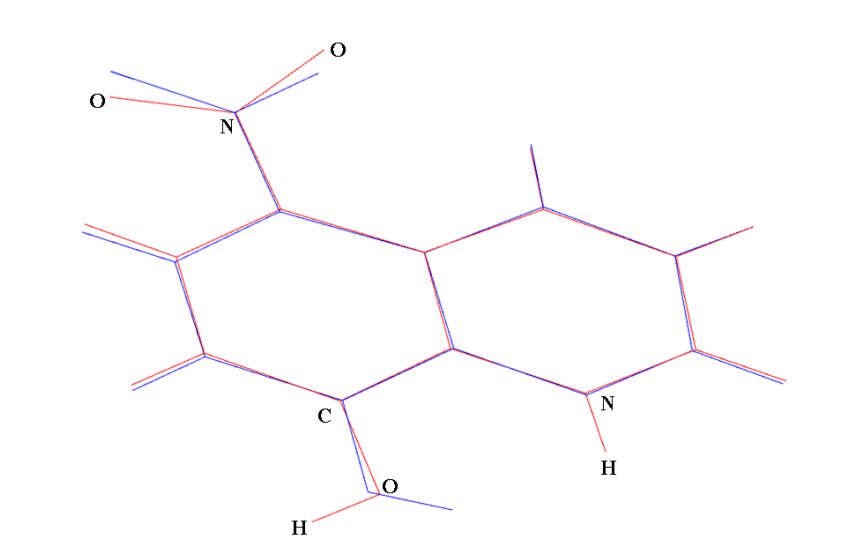


Figure 4.23 An overlay of the compounds: HoxNO₂ drawn in blue and H₂oxNO₂.NO₃ drawn in red. Showing small differences in the bite distance, fused ring systems planarity and twist of the NO₂ group, in opposite direction.

Powder diffraction data for the ligand HoxNO₂ were found in literature.⁷² Apart for the fact that the powder diffraction data can only provide isotropic displacement parameters the data is comparable with that of the presented single crystal diffraction, as shown in Figure 4.24 with the overlay of the single crystal diffraction data (shown in blue) and the powder diffraction data (shown in red) (r.m.s of fitted atoms, N, C1, C2, C3, C4 and C9 = 0.0152 Å).

⁷² Yatsenko, A. V., Paseshnichenko, K. A., Chernyshev, V. V. & Schenk. H. (2002). *Acta Cryst.* C58, o19.

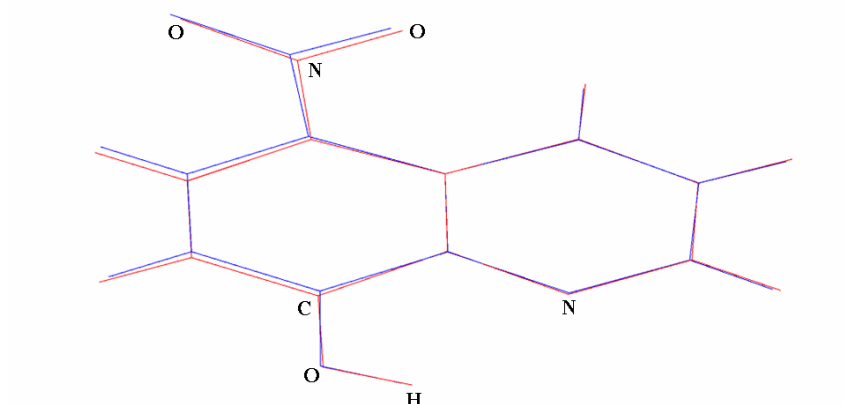


Figure 4.24 An overlay of 5-nitro-8-hydroxyquinoline single crystal structural data, (Section 4.6) in blue, and powder data⁷², in red. Showing the molecular geometrical similarity as obtained via different techniques.

For the complex, HoxMeCl, small variations are present, but bond distances and angles corresponds with all other 8-hydroxyquinoline structures. Presented in Figure 4.25 is the overlay between the structures of HoxCl, shown in blue, and that of HoxMeCl, shown in red. This shows the variation between the dihedral angles of the benzene and the pyridine ring. It is a general occurrence (as mentioned) and so the difference in the molecular bite angle is probably from the hydroxyl hydrogen orientation and intermolecular interaction, (r.m.s of fitted atoms, N, C1, C2, C3, C4 and C9 = 0.0316 Å).

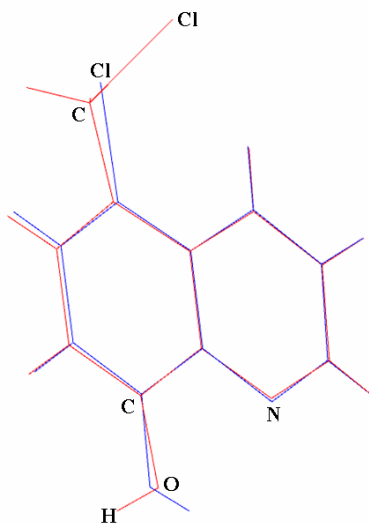


Figure 4.25 An overlay between the discussed compounds HoxCl, drawn in blue, and HoxMeCl, drawn in red. Showing small difference in the bite distances and the fused ring systems planarity.

4.9.2 Molecular packing

Neutral and non-solvated 8-hydroxyquinoline type systems most frequently crystallize in the orthorhombic space group, Fdd_2 and the packed molecules form H-bonded dimers.⁷³ For the crystal systems discussed in this chapter only neutral compounds crystallized in the orthorhombic Fdd_2 space group, summarized in Table 4.9. Note that structures of the compounds HoxCl and HoxNO₂ are not isomorphous.

Table 4.9 Space group comparison between the 8-hydroxyquinoline derivatives presented in this chapter.

Compound	Space group
HoxCl	Fdd_2 , Z=4
H ₂ oxCl.Br	$P2_1/c$, Z=4
H ₂ oxCl.PF ₆	$P2_1/n$, Z=4
HoxNO ₂	Fdd_2 , Z=12
H ₂ oxNO ₂ .NO ₃	$P\bar{1}$, Z=2
HoxMeCl	$P2_1/c$, Z=4

Presented in Figure 4.26 is an overview of the molecular packing in the unit cell, for the six discussed structures. Molecular packing in the orthorhombic unit cell for the

⁷³ Allen, F. H. (2002). *Acta Cryst.* B58, 380.

structures of HoxCl and HoxNO₂ clearly exhibit ligand “head to head” orientation for the formation of the hydrogen bonded dimers. For these two structures the six neighbouring molecules around a molecule form a hatched layer. The molecular packing of the structures H₂oxCl.Br and H₂oxNO₂.NO₃, where a molecule is surrounded by six neighbouring molecules and three guest molecules, all in the same plane, forming a *pseudo*-hexagonal close packing layer. The molecular packing of HoxMeCl exhibits packing properties found in both of the previous mentioned cases. When a single molecule is surrounded by six neighbouring molecules and three guest molecules, with no direct hydrogen bonded dimer formation. One would suspect that these molecules would be in plane, this is not the case, seen that they stack in a hatched layer.

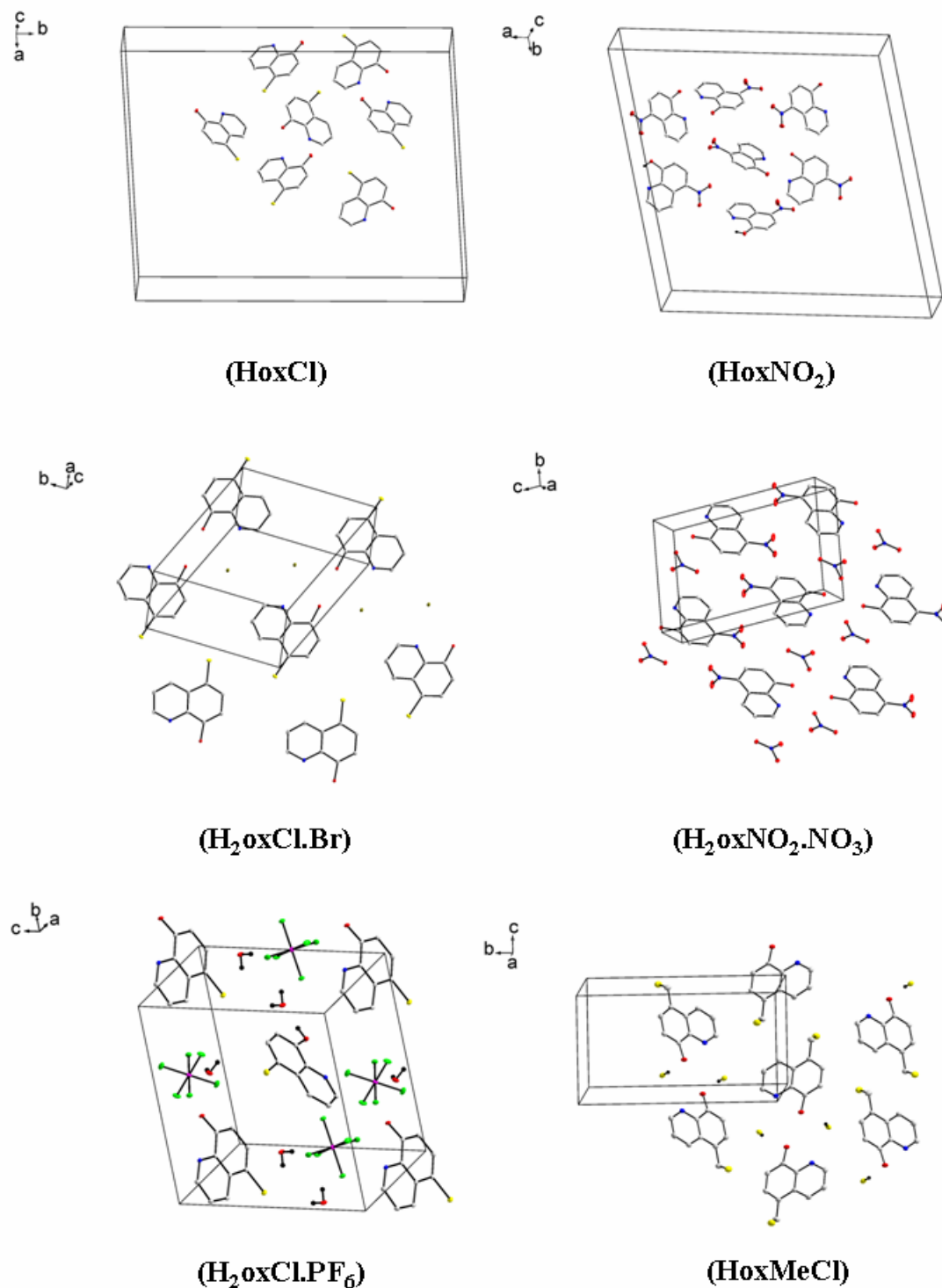


Figure 4.26 Diamond illustrations of molecular packing in and around the unit cell for the presented compounds: HoxCl, H₂oxCl.Br, H₂oxCl.PF₆, HoxNO₂, HoxNO₂.NO₃ and HoxMeCl. A view of six molecules is presented for comparison between *pseudo*-hexagonal and non *pseudo*-hexagonal packing modes. Note the various unit cells and packing modes found for different solvates and co-crystals of 8-hydroxyquinoline functionalities.

4.10 Conclusion

In the crystal structures of 8-hydroxyquinoline and its derivatives, the formation of bifurcated hydrogen bonds is a well known concept,⁷⁴ forming between the charge densities of the O- and N-atoms. This study shows that guest molecules influence the molecular packing in such a way that direct hydrogen dimer formation is prevented.

As mentioned, neutral compounds HoxCl and HoxNO₂ display molecular packing stabilized by the formation of hydrogen bonded dimers and a “head to head” ligand π -stacking. The only other structure in this study exhibiting π -stacking is the compound HoxMeCl, where the ligand to ligand π -stacking is in a “head to tail” manner. In the case of ligand to ligand π -stacking between 8-hydroxyquinolinato-metal complexes, π -stacking is usually in a “head to tail” manner: (Chapter 6, 7 and 8). For metal complexes this can be described to the steric hindrance of ligands coordinated to the metal centre, for example the tertiary phosphine systems. Considering 8-hydroxyquinoline ligand structures it seems that formation of hydrogen bonded dimers are essential for molecular π -stacking. In the structure of HoxMeCl the out of molecular plane 5-MeCl moiety might be responsible for the “head to tail” π -stacking mode through either steric or inter-molecular interaction. It is worth noting a study by Badger & Moritz⁷⁵, indicated that both intramolecular and intermolecular H-bonding patterns for quinoline ligands are maintained in solution⁷⁴.

Various 8-hydroxyquinoline configurations are found in the solid state, as discussed in this chapter, while Badger & Moritz⁷⁶ reported molecular interactions in solution. For the purpose of this study, the obtained solid state data is sufficient and compound recrystallizations from a larger range of acids was not pursued. It was deemed necessary to conduct a study of intramolecular interaction of 8-hydroxyquinoline compounds in the

⁷⁴ Banerjee, T. & Saha, N. N., (1986). *Acta Cryst.* C42, 1408.

⁷⁵ Badger, G. M. & Moritz, A. G. (1958). *J. Chem. Soc.* 3437.

⁷⁶ Badger, G. M. & Moritz, A. G. (1958). *J. Chem. Soc.* 3437.

gas phase, and thus a computational study was conducted. Computational data from this gas phase study is reported and discussed in Chapter 5.

Chapter 5

Theoretical study of quinoline functionalities

5.1 Introduction

The following chapter is based on a theoretical investigation regarding the behaviour of 8-hydroxyquinoline compounds in respect to: functionalization, hydrogen bond formation and hydroxyl hydrogen configuration. Electronic effects were included in the study to determine the influence of halogens and electron withdrawing groups on the 8-hydroxyquinoline fused ring system.

5.2 Theoretical Background

Computational chemistry can be described as using a set of techniques for the investigation of chemical problems on a computer, for example the determination of molecular geometry, energies of molecules, transition states and chemical reactivity. Various methods exist for solving these problems and these can be classified into five broad classes:⁷⁷.

1. Molecular mechanics (MM)
2. Ab initio calculations
3. Semiempirical (SE) calculations
4. Density functional calculations (DFT)
5. Molecular dynamics

The presented study is based on DFT calculations and thus the focus will be on this specific model of computational chemistry. Seen that the goal of DFT calculations is

⁷⁷Lewars, E. (2004). *Computational Chemistry, Introduction to the theory and Application of molecular and quantum mechanics*. Kluwer academic publishers New York, Boston, Dordrecht, London, Moscow.

implemented to design functionals connecting the electron density with the molecular energy⁷⁸.

DFT calculations are not based on the wavefunction, but rather on the electron density function, this theorem originated with a theorem by Hohenberg and Kohn⁷⁹. In this formulation the electron density is expressed as a linear combination of basis functions similar in mathematical form to HF orbitals. A determinant is formed from these functions called Kohn-Sham orbitals and the electron density of these orbitals is used to compute the energy⁸⁰. Although these orbitals describe electron behaviour they are not mathematically equivalent to either HF or natural orbitals. Subsequently a density functional is used to obtain the energy for the electron density (remember a functional is a function of a function). Density functionals can be broken down into several classes, with the simplest called the $X\alpha$ method, introduced by J. C. Slater in an attempt to make an approximation to Hartree-Fock. Some of the more widely used functionals are listed in Table 5.1^{81,82,83,84}.

Table 5.1 Some functionals used in calculatorial chemistry.

Acronyms	Name	Type
Xα	X alpha	Exchange only
HFS	Hartree-Fock Slater	HF with LDA exchange
VWN	Vosko, Wilks and Nusair	LDA
BLYP	Becke correlation functional with Lee, Yang and Parr exchange	Gradient corrected
B3LYP	Becke 3 term with Lee, Yang and Parr exchange	Hybrid

DFT calculations must use a basis set and each unique pairing of a method with a basis set represents a different approximation to the Schrödinger equation. A basis set is a set of mathematical functions (basis functions), linear combinations which yield molecular

⁷⁸ Parr, R. G. & Yang, W. (1989). *Density Functional Theory*. Oxford University Press.

⁷⁹ Hohenberg, P. & Kohn, W. (1964). *Phys. Rev.* 136, B864.

⁸⁰ Kohn, W. & Sham, J. L. (1965). *Phys. Rev.* 140, A1133.

⁸¹ Young, D. C. (2001). *Computational Chemistry: A Practical Guide for Applying Techniques to Real-World Problems*. John Wiley & Sons, Inc.

⁸² Jensen, F. (1999). *Introduction to Computational Chemistry*. John Wiley & Sons, New York.

⁸³ Koch, W. & Holthausen, M. C. (2000). *A Chemist's Guide to Density Functional Theory*. Wiley-VCH, Weinheim.

⁸⁴ Dobson, J. F., Vignale, G. & Das, M. P. (1998). *Electronic Density Functional Theory Recent Progress and New Directions*. Plenum, New York.

orbitals. The functions are usually but not invariably centred on atomic nuclei, as presented in Figure 5.1⁷⁷.

As presented in Figure 5.1 the basis functions ϕ are one-electron functions, usually centered on atomic nuclei. R_1 , and R_2 are vectors representing the x, y and z coordinates of the nuclei and r is a vector representing the x, y and z coordinates of an electron. The distance of the electron from the centers of the various basis functions are the absolute values of the various vector differences: $|r - R_1|$ and $|r - R_2|$. For a particular molecular geometry, R_1 and R_2 are fixed and the functions ϕ_1 and ϕ_2 are only parametrically entered to denote where the ϕ 's are centered. The variable in these functions is r which is thus $\phi(x, y, z)$. Several basis functions may centre on each nucleus.

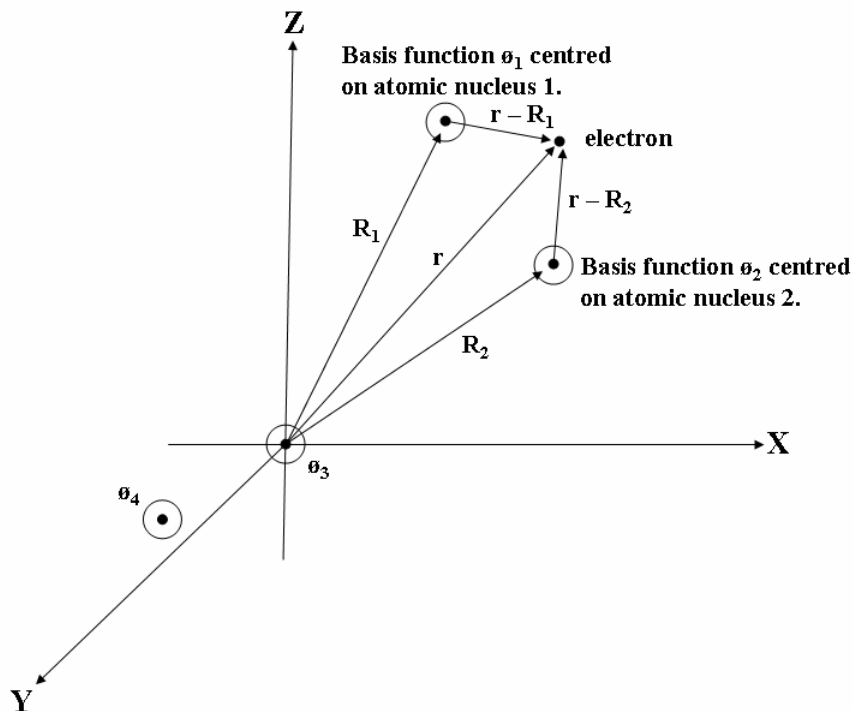


Figure 5.1 A Four atom molecule in a coordinate system, showing one of the many possible electrons.

The basis set that were used in this study is 6-31G(d,p) or 6-31G**. This basis set adds p-functions to hydrogens and d-functions to heavy atoms⁸².

5.3 Experimental

All molecules and transition states were fully optimized with the density functional theory (DFT) using the Becke3-Lee-Yang-Parr (B3LYP)⁸⁵ functionals supplemented with the standard 6-31G(d,p) and LANL2DZ basis sets. Analytical frequency calculations were done at the same level to confirm the optimized structures, to be either a minimum or a first-order saddle point, as well as to obtain the zero-point energy (ZPE) correction. All calculations were carried out using the Gaussian 03 software suite⁸⁶.

5.4 Theoretical Calculations on Halogenated 8-hydroxyquinolines

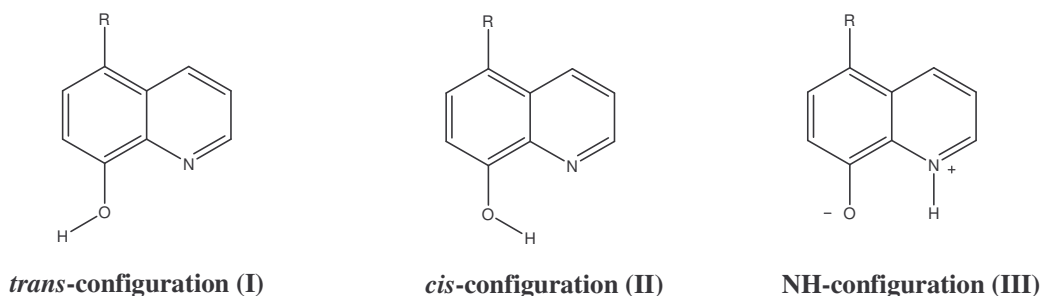
5.4.1 Results and Discussion

(Supplementary data B2-B5)

This part of the computational study was conducted to determine the electronic and geometrical influence that halogen substituents have on the 8-hydroxyquinoline backbone. By varying the halide on the 5th position of the oxine moiety from F, Cl, Br to I. The data herein is for the three possible configurations that can form: the *trans*-configuration (I) and the *cis*-configuration (II), and the NH-configuration (III), (Scheme 5.1). Please note: configuration labels (I), (II) and (III) extend compound labels to be indicative of a specific molecular configuration.

⁸⁵ Lee, C., Yang, W. & Parr, R. G. (1988). *Phys. Rev. B*, 37, 785.

⁸⁶ Gaussian 03, Revision C.01, Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Montgomery, Jr., J. A., Vreven, T., Kudin, K. N., Burant, J. C., Millam, J. M., Iyengar, S. S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G. A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J. E., Hratchian, H. P., Cross, J. B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Ayala, P. Y., Morokuma, K., Voth, G. A., Salvador, P., Dannenberg, J. J., Zakrzewski, V. G., Dapprich, S., Daniels, A. D., Strain, M. C., Farkas, O., Malick, D. K., Rabuck, A. D., Raghavachari, K., Foresman, J. B., Ortiz, J. V., Cui, Q., Baboul, A. G., Clifford, S., Cioslowski, J., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R. L., Fox, D. J., Keith, T., Al-Laham, M. A., Peng, C. Y., Nanayakkara, N., Challacombe, M., Gill, P. M. W., Johnson, B., Chen, W., Wong, M. W., Gonzalez, C., & Pople, J. A., Gaussian, Inc., Pittsburgh PA, 2003.

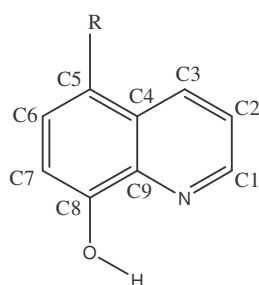


Scheme 5.1 Diagrams of the three possible 8-hydroxyquinoline configurations. R = Halogen for section 5.4.

Firstly the variations are between halogenated quinoline ligands is discussed:

1. 5-Fluoro-8-hydroxyquinoline (HoxF)
2. 5-Chloro-8-hydroxyquinoline (HoxCl)
3. 5-Bromo-8-hydroxyquinoline (HoxBr)
4. 5-Iodo-8-hydroxyquinoline (HoxI)

The general atom labelling is shown in Scheme 5.2. The bond lengths and bond angles determined at the DFT level of theory are listed in Table 5.2 with the relative energy components presented in Table 5.3. Supplementary data is provided in Appendix B.



Scheme 5.2 Diagram showing the general numbering scheme of an 8-hydroxyquinoline system.

Table 5.2 Selected bond distances and angles, (Å, °), for the possible configurations of the halogenated 8-hydroxyquinoline compounds.
For label definition see section 5.4.1.

Compound	(HoxF)			(HoxCl)			(HoxBr)			(HoxI)		
Configuration	<i>trans</i> (I)	<i>cis</i> (II)	NH(III)	<i>trans</i> (I)	<i>cis</i> (II)	NH(III)	<i>trans</i> (I)	<i>cis</i> (II)	NH(III)	<i>trans</i> (I)	<i>cis</i> (II)	NH(III)
O-H	0.966	0.976	-	0.966	0.977	-	0.966	0.977	-	0.966	0.977	-
N-O	2.708	2.701	2.627	2.695	2.684	2.624	2.692	2.682	2.673	2.685	2.673	2.612
N-H	-	-	1.032	-	-	1.052	-	-	1.032	-	-	1.032
H...N	-	2.121	-	-	2.099	-	-	2.098	-	-	2.087	-
O-C8	1.360	1.354	1.264	1.359	1.351	1.262	1.358	1.351	1.262	1.357	1.349	1.259
N-C1	1.318	1.320	1.335	1.318	1.320	1.335	1.318	1.320	1.335	1.314	1.316	1.332
C1-C2	1.418	1.417	1.403	1.416	1.416	1.402	1.416	1.415	1.402	1.413	1.413	1.400
C2-C3	1.375	1.378	1.387	1.375	1.378	1.386	1.375	1.377	1.385	1.375	1.375	1.383
C3-C4	1.419	1.417	1.420	1.414	1.418	1.421	1.418	1.418	1.420	1.417	1.417	1.419
C4-C5	1.421	1.414	1.407	1.423	1.422	1.406	1.422	1.420	1.406	1.422	1.420	1.405
C5-C6	1.377	1.371	1.399	1.374	1.378	1.396	1.374	1.378	1.396	1.373	1.377	1.396
C6-C7	1.415	1.416	1.400	1.413	1.413	1.398	1.412	1.413	1.398	1.411	1.412	1.396
C7-C8	1.383	1.380	1.424	1.381	1.379	1.423	1.381	1.379	1.423	1.378	1.376	1.420
C8-C9	1.433	1.420	1.463	1.433	1.430	1.464	1.433	1.429	1.464	1.431	1.427	1.463
C9-N	1.361	1.360	1.352	1.359	1.359	1.351	1.358	1.359	1.351	1.356	1.357	1.349
C9-C4	1.433	1.428	1.431	1.436	1.436	1.431	1.436	1.430	1.436	1.436	1.429	1.430
C5-R	1.350	1.364	1.350	1.762	1.761	1.761	1.911	1.910	1.910	2.138	2.136	2.130
O-H...N	-	116.388	-	-	116.651	-	-	116.629	-	-	116.826	-
H-O-C8	109.350	106.388	-	109.516	106.281	-	109.484	106.283	-	109.748	106.212	-
O-C8-C9	117.062	121.272	118.281	117.006	118.827	118.319	117.027	118.840	118.342	117.015	118.781	118.324
C8-C9-N	118.849	116.971	114.577	118.288	116.275	114.379	118.202	116.241	114.312	118.044	116.029	114.009
C9-N-H	-	-	110.747	-	-	110.665	-	-	110.694	-	-	110.534
C4-C5-R	119.316	117.872	120.382	120.027	119.786	120.069	120	120	120.361	121.495	121.176	121.387
C7-C8-O-H	0	180	-	0	180	-	0	180	-	0	180	-

R = Halogens bonded to C5.

Variations between bond distances of carbon-carbon and carbon-nitrogen bonds of the ring moieties are very comparable to literature and self determined crystallographic values¹. A difference of 0.01 Å between the *cis*- and *trans*-configurations of all compounds is noted in the hydroxyl hydrogen distance. A possible influence could come from the soft contact between the hydroxyl hydrogen and the nitrogen atom of the *cis*-configuration, this increasing the hydroxyl bond distance but with no significant difference between the hydroxyl bonds of the different quinoline compounds. In general the N...O bite distance is larger for the *trans*- than for the *cis*-configuration.

Except for the NH-configuration of the compound HoxBr, the bidentate bite distance N...O decreases as the electronegativity of the substituted atom increases. This might be due to the richer electron density on the O-atom. As presented in Table 5.3 and Figure 5.2 note that for the NH-configuration, the higher the electronegativity of the substituent on the fused ring system the lower the occupied energy level. Meaning, the higher the electron negativity of the substituted atom, the higher the electron density on the O-atom and the stronger the N...H soft contact and the lower the energy barrier of the proton transfer transition state.

Excluding the compound HoxCl the general N-H distance is 1.032 Å. The C8-O_(hydroxyl) bond distance for *cis*- and *trans*-configurations is in the 1.3 Å range while the NH-configuration displays a shorter bond distance of *ca.* 1.25 Å.

The H-O-C8 bond angles are close to 106° for the *cis*-configuration and 109° for the *trans*-configuration. The O-C8-C9 bond angles are generally larger for the *cis*- and smaller for the *trans*-configurations see Table 5.2. The C8-C9-N bond angles show a common decrease from the *trans*- to *cis*- to NH-configuration of *ca.* 118°>116°>114°. The only exception is for the *cis*-configuration of the HoxF compound, with a value of 121.27°. The C9-N-H bond angle for all NH-configurations is in the order of 110°. The C4-C5-Halogen bond angles increases from the *cis*-, to *trans*- and to NH-configuration

but the overall effect on this angles indicates a decrease as the electronegativity on the donor atom increases. The torsion angle, C7-C8-O-H, indicates that the hydroxyl hydrogen is in plane with the ring system.

The relative energy components of the halogenated 8-hydroxyquinoline configurations are presented in Table 5.3 and Figure 5.2. Small energy variations are noted between configurations of the different 8-hydroxyquinoline ligands, except for the 5-Fluoro-8-hydroxyquinoline that displays a much higher energy level in the NH-configuration state, Table 5.3.

Table 5.3 Relative energy components of halogenated 8-hydroxyquinoline configurations.
For label definition see section 5.4.1.

(HoxF)	Energy (Hartrees)	ZPE (Hartrees)	ΔE (kJ/mole)
(I)	-576.4154376	0.131403	13.3
(II)	-576.4282074	0.132093	0.0
(III)	-576.401466	0.131786	29.0
(HoxCl)			
(I)	-936.7699914	0.130033	13.7
(II)	-936.7831593	0.130757	0.0
(III)	-936.758931	0.130527	26.3
(HoxBr)			
(I)	-3048.31	0.131697	13.7
(II)	-3048.318685	0.132173	0.0
(III)	-3048.295644	0.132916	26.1
(HoxI)			
(I)	-488.0410228	0.128645	13.8
(II)	-488.054484	0.129526	0.0
(III)	-488.0304716	0.129226	26.0

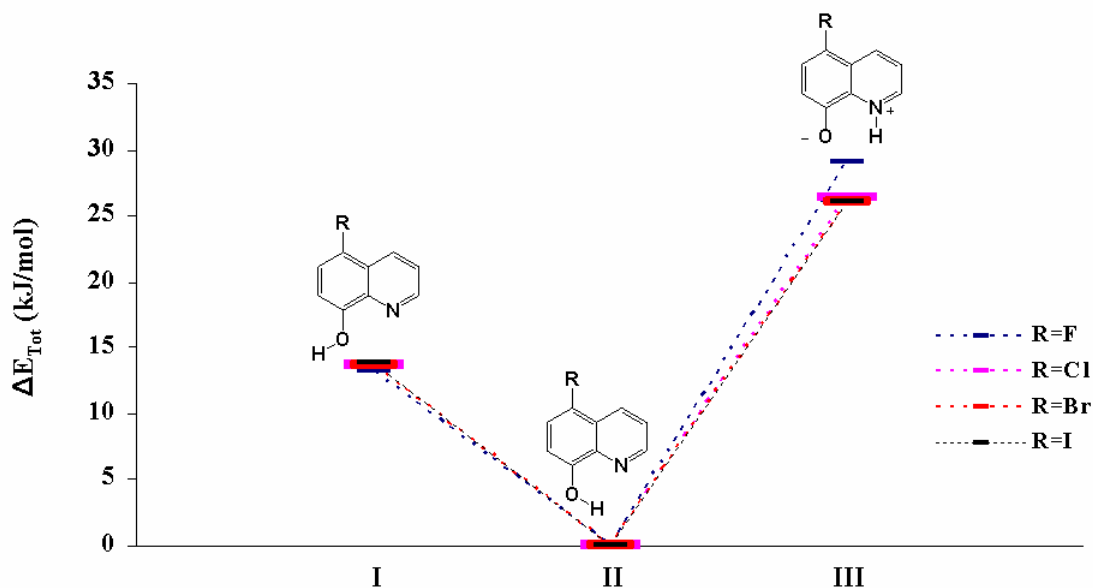


Figure 5.2 Relative energy profile of halogenated 8-hydroxyquinoline configurations. Displaying the influence from halides on the 5th position of the oxine moiety.

In addition, previous reports regarding other bidentate ligand systems indicate that the *cis*-configuration is favoured over the *trans*, a suspected stabilization effect from intramolecular hydrogen interaction between the donor atoms OH and N⁸⁷. Thus, the stability of the *cis*-configuration can be largely attributed to the formation of a hydrogen bond between the hydroxyl group and the nitrogen atom.

Even through a small alteration, the relative energy levels of the *trans*-configuration increases as the electronegativity of the atom on the 5th position of the oxine moiety increases. The reverse influence is seen in the relative energy levels of the NH-configurations, as presented in Figure 5.3.

⁸⁷ Steyl, G. (2004), *Ph.D. Thesis*, Rand Afrikaans University.

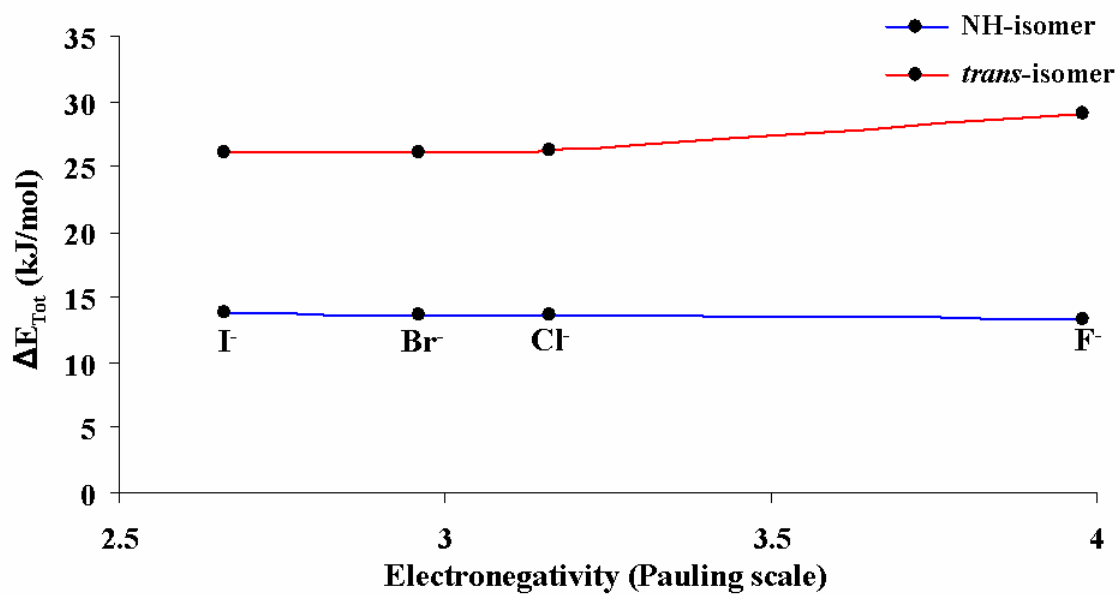


Figure 5.3 Illustration of the influence from halogens on the 5th position of the oxine moiety. As the electron negativity of the halide increases, the relative energy levels of the *trans*-configuration increase and that of the NH-configuration slightly decrease.

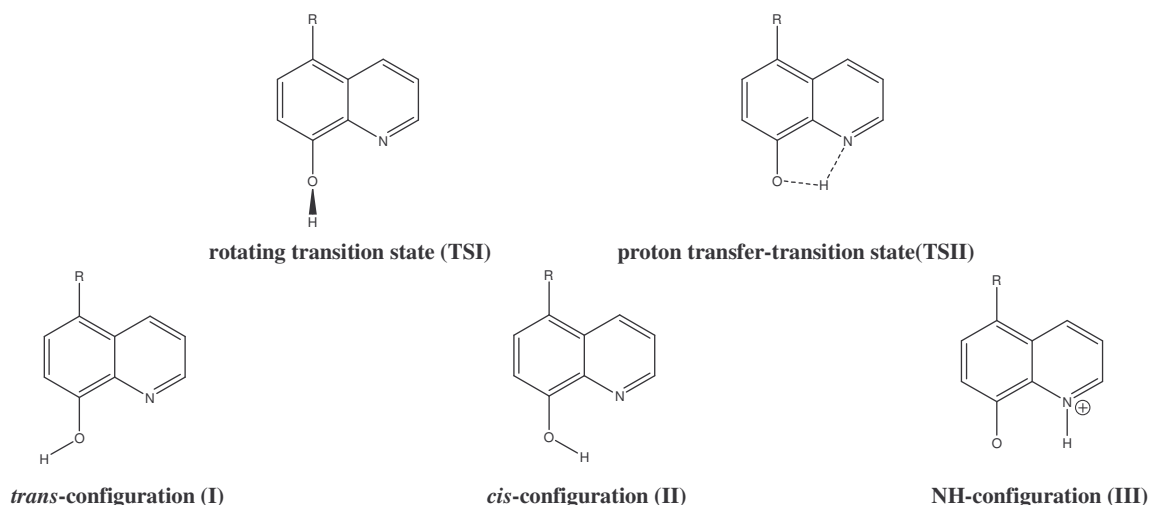
5.5 Theoretical Calculations on Functionalised 8-hydroxyquinolines

5.5.1 Results and Discussion

(Supplementary data B3, B6-B9)

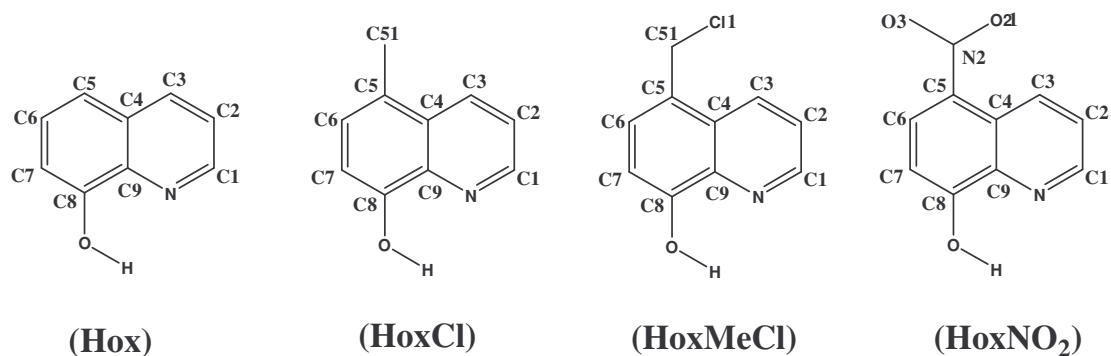
The following section of the computational study was conducted to determine the electronic and geometrical influence of various functionalities on the 5th-position of the 8-hydroxyquinoline backbone. The data herein is for the three possible configurations and two transition states that can form; the *trans*-configuration (I), rotating transition state (TSI), *cis*-configuration (II), proton transfer-transition state (TSII) and the NH-configuration (III) (Scheme 5.3). Please note: configuration labels (I), (TSI), (II), (TSII) and (III) extend compound labels which are indicative of a specific molecular configuration or transition state. The selected range of functionalized compounds are:

1. 8-Hydroxyquinoline (Hox)
2. 5-Chloro-8-hydroxyquinoline (HoxCl)
3. 5-Chloromethyl-8-hydroxyquinoline (HoxMeCl)
4. 5-Nitro-8-hydroxyquinoline (HoxNO₂)



Scheme 5.3 Diagrams of the three possible 8-hydroxyquinoline configurations and the two transition states.

The general atom labelling is as depicted in Scheme 5.4. The bond lengths and bond angles determined at the DFT level of theory are listed in Table 5.4 with the relative energy components summarized in Table 5.5. Supplementary data is provided in Appendix B.



Scheme 5.4 Illustrations of the general atom labelling as for the 8-hydroxyquinoline systems.

Table 5.4 Selected bond distances and angles, (Å, °), for possible configurations of the compounds Hox, HoxMe, HoxMeCl and HoxNO₂.
For label definition see section 5.5.1.

Compound	(Hox)			(HoxMe)			(HoxMeCl)			(HoxNO ₂)		
Configuration	<i>trans</i> (I)	<i>cis</i> (II)	NH(III)	<i>trans</i> (I)	<i>cis</i> (II)	NH(III)	<i>trans</i> (I)	<i>cis</i> (II)	NH(III)	<i>trans</i> (I)	<i>cis</i> (II)	NH(III)
O-H	0.966	0.977	-	0.966	0.977	-	0.966	0.978	-	0.967	0.981	-
N-O	2.708	2.692	2.627	2.698	2.684	2.619	2.690	2.675	2.620	2.660	2.638	2.603
N-H	-	-	1.036	-	-	1.033	-	-	1.032	-	-	1.031
H...N	-	2.13105	-	-	2.09756	-	-	2.67504	-	3.622	2.038	1.253
O-C8	1.360	1.353	1.298	1.362	1.354	1.265	1.357	1.349	1.260	1.348	1.339	1.335
N-C1	1.318	1.320	1.347	1.318	1.321	1.335	1.318	1.320	1.335	1.317	1.320	1.396
C1-C2	1.418	1.417	1.414	1.415	1.415	1.402	1.415	1.419	1.400	1.412	1.411	1.389
C2-C3	1.375	1.378	1.397	1.376	1.379	1.387	1.376	1.379	1.387	1.376	1.379	1.424
C3-C4	1.419	1.419	1.431	1.420	1.420	1.422	1.420	1.420	1.421	1.423	1.424	1.427
C4-C5	1.421	1.420	1.414	1.432	1.430	1.413	1.433	1.432	1.418	1.435	1.436	1.410
C5-C6	1.377	1.380	1.411	1.380	1.389	1.402	1.382	1.386	1.407	1.382	1.388	1.383
C6-C7	1.415	1.415	1.410	1.414	1.415	1.401	1.410	1.411	1.395	1.400	1.401	1.426
C7-C8	1.383	1.380	1.430	1.378	1.377	1.420	1.381	1.379	1.423	1.385	1.383	1.476
C8-C9	1.433	1.430	1.67	1.433	1.429	1.462	1.435	1.432	1.487	1.437	1.436	1.351
C9-N	1.361	1.361	1.366	1.360	1.360	1.350	1.359	1.359	1.351	1.357	1.357	1.423
C9-C4	1.433	1.427	1.439	1.435	1.429	1.433	1.433	1.426	1.427	1.437	1.429	1.434
C5-R	1.086	1.086	1.084	1.510	1.510	1.510	1.493	1.492	1.480	1.464	1.461	-
O-H...N	-	115.142	-	-	116.882	-	-	116.987	-	-	117.466	-
H-O-C8	250.649	106.190	-	250.752	106.053	-	250.485	106.151	-	109.887	106.071	118.087
O-C8-C9	117.003	118.700	117.872	117.183	118.846	118.332	117.028	118.679	118.227	116.911	118.454	113.240
C8-C9-N	118.849	116.706	114.601	118.223	116.216	114.183	117.997	115.940	114.157	116.808	114.540	111.138
C9-N-H	-	-	110.687	-	-	110.479	-	-	110.886	-	-	122.684
C4-C5-R	119.337	119.407	118.947	121.197	121.039	121.618	121.930	121.727	122.018	123.085	122.913	-
C7-C8-O-H	0	180	-	0	180	-	0.435	179.891	-	0.077	179.910	-

R = various substituted atoms, directly bound to atom C5.

Bond distances of the ring moieties are in agreement with literature values¹. The *cis*-configuration of the compound HoxNO₂ all O-H_(Hydroxyl) bond distances are in the 0.97Å range with a 0.01Å reduction in this bond as the *trans*-configuration is occupied. Small differences are present in the N-H bond distances of differing moieties.

In general the N...O bite distance is larger for the *cis*-configurations and smaller for the NH-configurations. A notable bite distance decrease between substituted 8-hydroxyquinoline ligands in the order of: Hox > HoxMe > HoxMeCl > HoxNO₂.

The C5-R bond distances (as in Table 5.4) of the *cis*-configurations decrease in the order: HoxMe > HoxMeCl > HoxNO₂ > Hox. The O-C8-C9 bond angle is larger in the *cis*-configurations than in the *trans*-configurations. Except for the NH-configuration of the compound HoxNO₂, the C8-C9-N bond angles show a decrease from the *trans*- to *cis*- to NH-configuration of ca. 118°>116°>114°. The C9-N-H bond angles for all NH-configurations are in the 110° range. The C4-C5-R bond angles for all configurations show an increase in the order: Hox > HoxMe > HoxMeCl > HoxNO₂. The torsion angles C7-C8-O-H indicate that the hydroxyl hydrogens are in plane with the respective fused ring systems.

Considering the relative energy difference between the configurations of these 8-hydroxyquinoline derivatives (see Table 5.5 and Figure 5.4) it is clear that the compound HoxNO₂ does not follow the general energy level trend. Earlier reported data proved the *cis*-configuration to be the more stable configuration and other datasets from this study also verifies this. In the relative energy profile the rotating transition-state has a much lower energy level than that of the proton transfer transition-state.

Table 5.5. Relative energy components of halogenated 8-hydroxyquinoline configurations and transition states.

For label definition see section 5.5.1.

(Hox)	Energy (Hartree)	ZPE (Hartree)	ΔE (kJ/mol)
(I)	-477.17771	0.13959	13.5
(TSI)	-477.17232	0.13861	18.3
(II)	-477.19077	0.14034	0.0
(TSII)	-477.15881	0.13620	30.5
(III)	-477.16639	0.14003	26.4
(HoxMe)			
(I)	-516.49712	0.16735	13.7
(TSI)	-516.49202	0.16638	18.2
(II)	-516.51029	0.16802	0.0
(TSII)	-516.47812	0.16372	30.6
(III)	-516.48504	0.16763	27.3
(HoxCl)			
(I)	-936.76999	0.13003	13.7
(TSI)	-936.76474	0.12905	18.3
(II)	-936.78315	0.13075	0.0
(TSII)	-936.75140	0.13003	34.0
(III)	-936.75893	0.13052	26.3
(HoxMeCl)			
(I)	-976.09012	0.15901	14.1
(TSI)	-976.08426	0.15794	19.3
(II)	-976.10361	0.15965	0.0
(TSII)	-976.07377	0.15543	28.1
(III)	-976.08426	0.15794	19.4
(HoxNO ₂)			
(I)	-681.69751	0.14289	-15.0
(TSI)	-681.67549	0.14094	6.9
(II)	-681.68311	0.14220	0.0
(TSII)	-681.67328	0.13871	6.9
(III)	-681.68317	0.14269	0.5

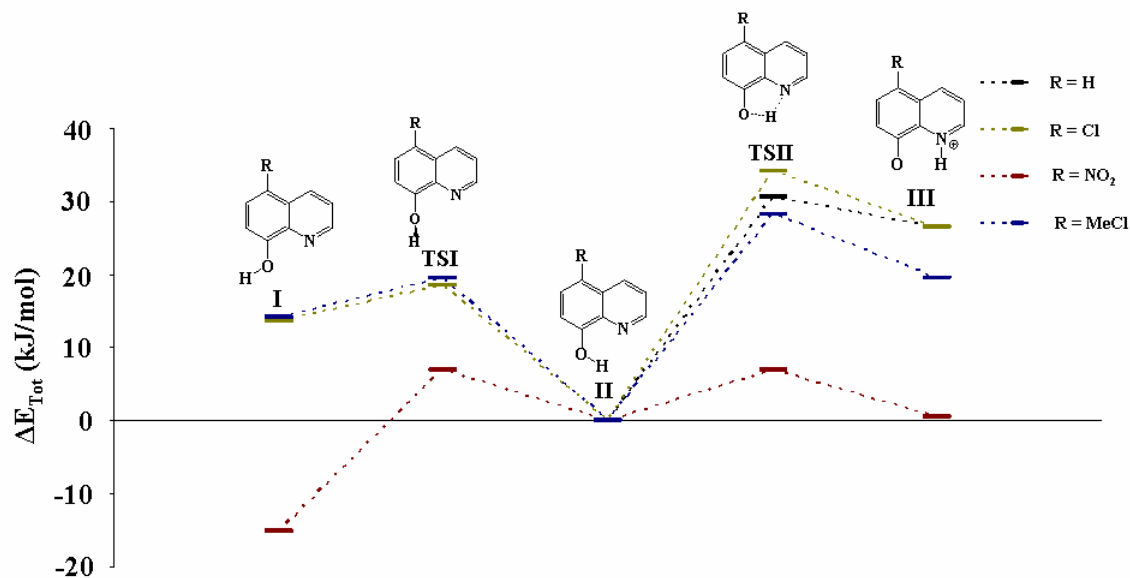


Figure 5.4 Relative energy profile of functionalized 8-hydroxyquinoline configurations.

Between these 8-hydroxyquinoline functionalities, the overall energy levels of the compound HoxNO₂ are much lower and as mentioned for this compound, the *trans*-configuration occupies the lowest energy level and not the *cis*-configuration.

The derivatives Hox, HoxMe, HoxMeCl and HoxCl have general energy levels of 13 kJ/mol for the *cis*-configuration and 18 kJ/mol for the rotating transition state. The proton transfer transition states show some variation in the energy level of around 30 kJ/mol. The energy levels of the NH-configuration increases in the order of HoxMeCl < Hox < HoxCl < HoxMe.

To summarize: functionalities on the fused ring system change the electronic properties of the accepting nitrogens lone pair, the O-H σ* orbital and the bond lengths and angles of the molecule. The effect of a stronger electron donating group should thus lower the

energy of the proton transfer transition state. In effect, the stronger the electron donating group on the 5-position of 8-hydroxyquinoline, the higher the electrondensity on the O-atom. This strengthens the intramolecular hydrogen interaction and shortens the N...O bite distance and a shorter N...O bite distance lowers the energy barrier for the tautomerization pathway from the *cis*- to the NH-configuration.

Presented in Figure 5.5 is the relationship of the N...O bite distance of the *cis*-configuration and the electronegativity of the substituted group or atom. Apart from the Hox, HoxMe and HoxNO₂ derivatives, the other compounds seem to follow the trend of the higher the electronegativity of the 5-substituent the larger the N...O bite distance.

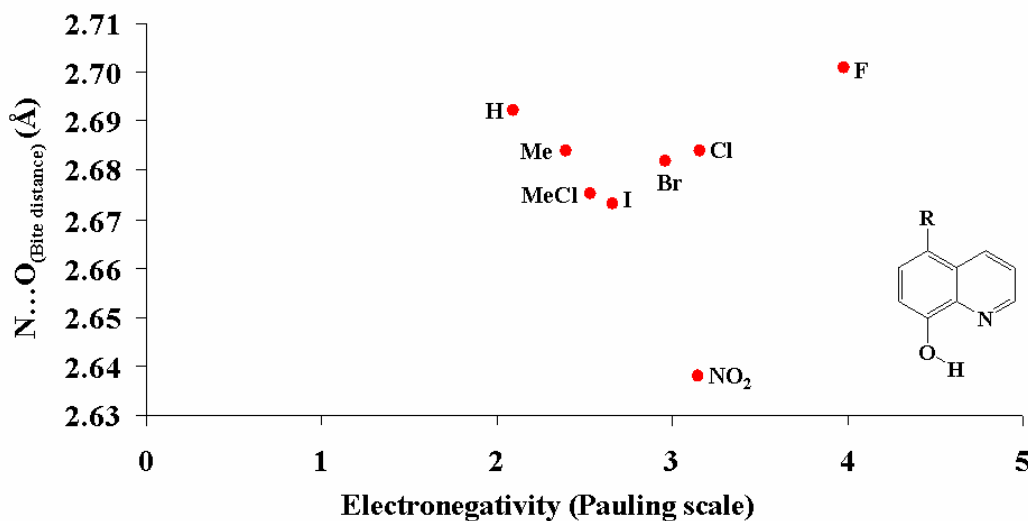


Figure 5.5 Correlation of the N...O bite distance to the electronegativity of the substituted group (Pauling scale). Labels are indicative of the substituent R.

Considering the valence bond theory, the lone pair of the accepting nitrogen atom and the O-H σ^* orbital is one of the main reasons for proton transfer²⁵. Li and Fang also proposed

that the N-H and N...O distances play an important role in the proton transfer mechanism. Based on this assumption by Li and Fang a plot of the N-H bond distance and the N...O bite distance against the relative energy values of the proton transfer transition state is shown in Figure 5.6 and Figure 5.7.

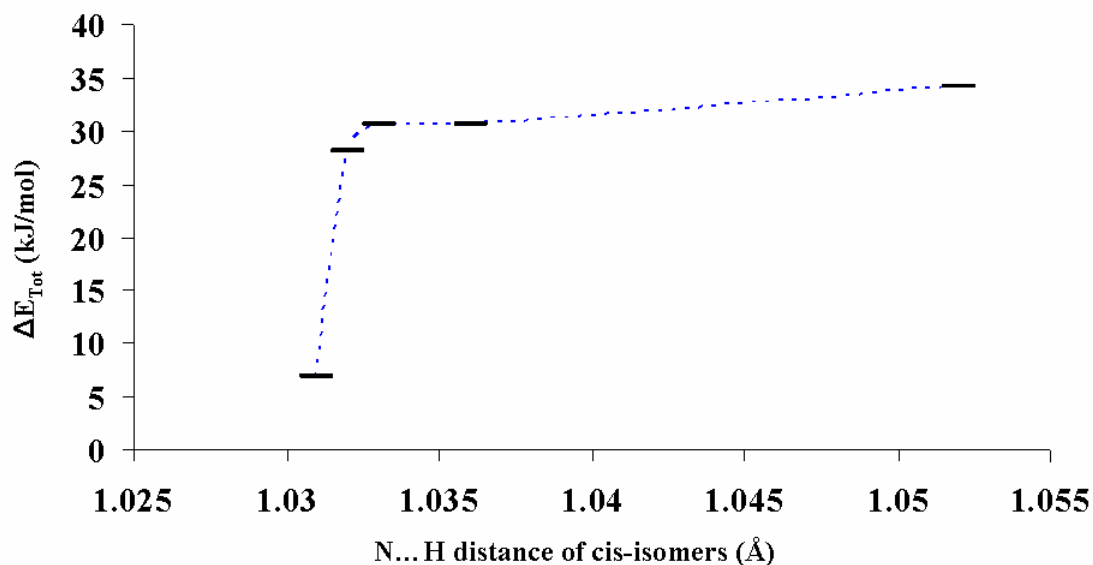


Figure 5.6 Energy levels of calculated proton transfer transition states for the 8-hydroxyquinoline compounds, relative to the N...H distances of these configurations (data as from Table 5.5).

Figure 5.6 shows an exponential increase in the bond distances as the energy level of the configuration increases. Thus the longer the N-H bond distance the higher the energy level of the proton transfer transition state. Noted in Figure 5.7 is a linear increase in the energy levels as the bite distances increases. A larger distance between the N...O donor atoms requires a higher energy level to obtain successful proton transfer.

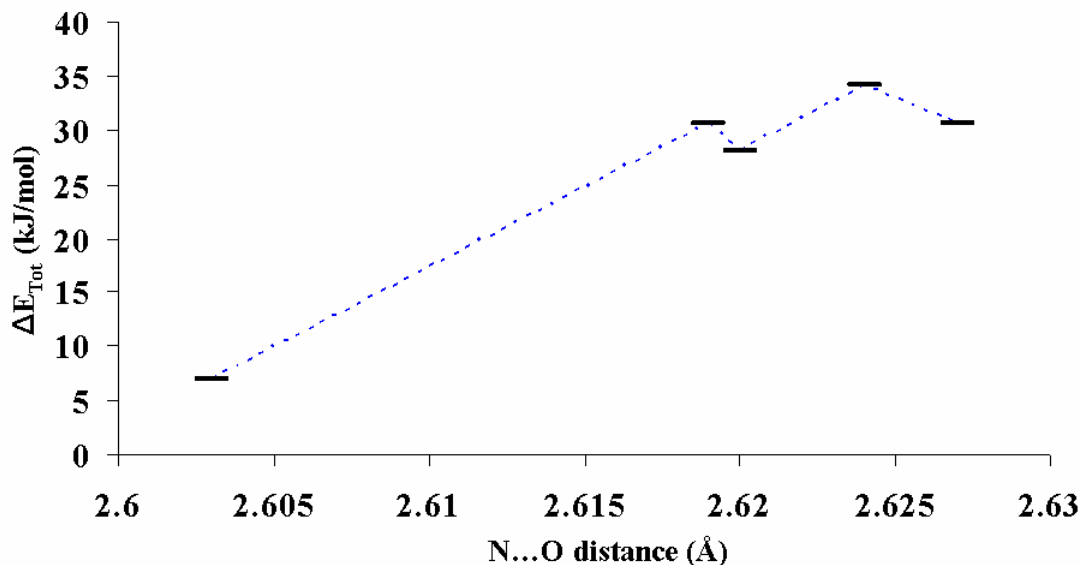


Figure 5.7 Energy levels of calculated proton transfer transition states for the 8-hydroxyquinoline compounds, relative to the N...O bite distances of these configurations.

5.6 Comparison of literature, crystallographic and theoretical data

As mentioned in the crystallographic discussion of the 8-hydroxyquinoline compounds, the neutral compounds crystallize out in such a way that the hydroxyl hydrogen is in the *cis*-configuration. In the solid state other hydroxyl hydrogen configurations were only found in the presence of anions accompanied by intermolecular interactions. Shown in this theoretical study is the stability of the *cis*-configured hydroxyl hydrogen compared to other possible configurations and transition states. Compared in the following subsections are the geometrical parameters of the *cis*-configurations of the calculated data to those of single crystal data and where present as found in literature.

5.6.1 Comparison between literature and calculated data for the compound 8-hydroxyquinoline (Hox)

Presented in Table 5.6 and Figure 5.8 are the geometrical differences between the structural data for the compound 8-hydroxyquinoline, as found in crystal data literature and calculated DFT data. With a good correlation between these data sets, small differences are noted in the N...O bite distances, N...H distances and the C5-H distances. Other differences are between the O-H...N contact angle and the H-O-C8 bond angles. The crystal data collection by Zhang and Wu was done at room temperature⁸⁸. Similarity of the geometrical parameters are emphasized by a structural overlay, depicted in Figure 5.8 with the r.m.s of fitted atoms = 0.03108 Å.

⁸⁸ J. Zhang & L. Wu. (2005). *Private communication*. Cambridge, 1078.

Table 5.6 Selected bond distances and angles, (Å, °), for the compound Hox, from single crystal data in literature and DFT calculation data from this study.

(Hox)	Literature values, (XRD) ⁸⁸	DFT ^a
O-H	0.955	0.977
N-O	2.753	2.692
H...N	2.285	2.131
O-C8	1.347	1.353
N-C1	1.312	1.320
C1-C2	1.405	1.417
C2-C3	1.359	1.378
C3-C4	1.409	1.419
C4-C5	1.407	1.420
C5-C6	1.361	1.380
C6-C7	1.406	1.415
C7-C8	1.366	1.380
C8-C9	1.420	1.430
C9-N	1.361	1.361
C9-C4	1.417	1.427
C5-H	0.971	1.086
O-H---N	109.26	115.14
H-O-C8	111.54	106.19
O-C8-C9	120.81	118.70
C8-C9-N	118.16	116.71
C4-C5-H	118.13	119.41
C7-C8-O-H	177.24	180.00

a= Values as reported in Section 5.5 and Table 5.4.

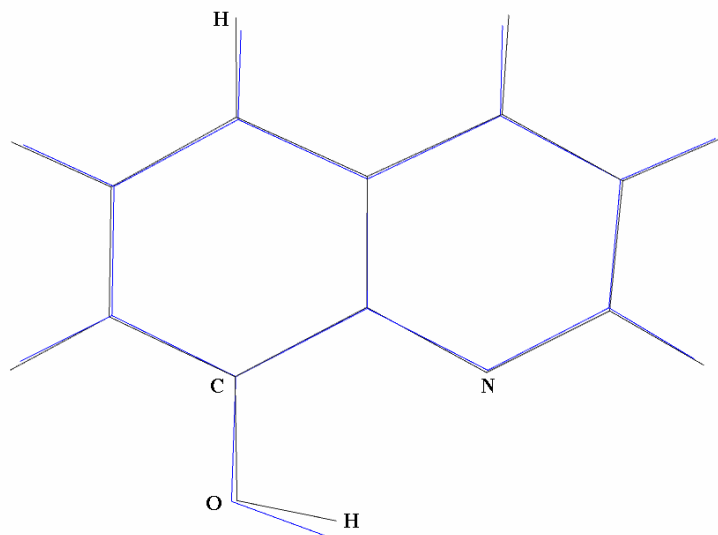


Figure 5.8 An overlay of the Hox structures from literature crystal data (drawn in blue) and calculated DFT data (drawn in black), as summarized in Table 5.6. With an r.m.s value between all non-hydrogen atoms of 0.03108 Å.

5.6.2 Comparison between literature, crystallographic and theoretical data for the compound 5-chloro-8-hydroxyquinoline (HoxCl)

Single crystal data which was found in literature and those determined by us (see Chapter 4) is compared to the DFT calculated data, summarized in Table 5.7 and graphically presented in Figure 5.9. A good correlation between the geometrical parameters from literature and from self determined crystal data are observed. When considering all three data sets, small differences is present between the following distances; O-H, N...O and H...N. The molecular angles also show variation in the following atom groups, O-H...N, H-O-C8 and O-C8-C9. There is a significant difference between the torsion angles of the hydroxyl hydrogen (C7-C8-O-H) ranging from 169 - 180°. Keep in mind that the HoxCl structure taken from literature⁷¹ was collected in 1986, at room temperature in the range of 283-303K, compared to the collection presented in this study, done at 100 K. Both these compounds crystallized in the orthorhombic space group Fdd_2 ($Z=16$). Apart from the position of hydrogen atoms, the general geometry of the structures are very comparable, as previously mentioned. But no anisotropic displacement parameters are available for the earlier collection of Banerjee and Saha⁷¹.

Table 5.7 Selected bond distances and angles, (Å, °), for the compound HoxCl, as found for single crystal data in literature, single crystal data collected by us and DFT calculation data.

(HoxCl)	Literature values ⁷¹	XRD ^a	DFT ^b
O-H	0.774	0.820	0.977
N-O	2.748	2.765	2.684
H...N	2.347	2.328	2.099
O-C8	1.346	1.349	1.351
N-C1	1.325	1.314	1.320
C1-C2	1.395	1.408	1.416
C2-C3	1.360	1.365	1.378
C3-C4	1.399	1.413	1.418
C4-C5	1.406	1.416	1.422
C5-C6	1.381	1.362	1.378
C6-C7	1.403	1.407	1.413
C7-C8	1.368	1.373	1.379
C8-C9	1.424	1.426	1.430
C9-N	1.358	1.366	1.359
C9-C4	1.426	1.420	1.436
C5-Cl	1.721	1.747	1.761
O-H...N	113.38	113.93	116.65
H-O-C8	110.20	109.50	106.28
O-C8-C9	121.19	121.51	118.82
C8-C9-N	117.42	117.50	116.27
C4-C5-Cl	120.67	118.70	119.78
C7-C8-O-H	169.98	174.07	180.00

a= Values as reported in Section 4.3. b= Values as reported in Section 5.5 and Table 5.4.

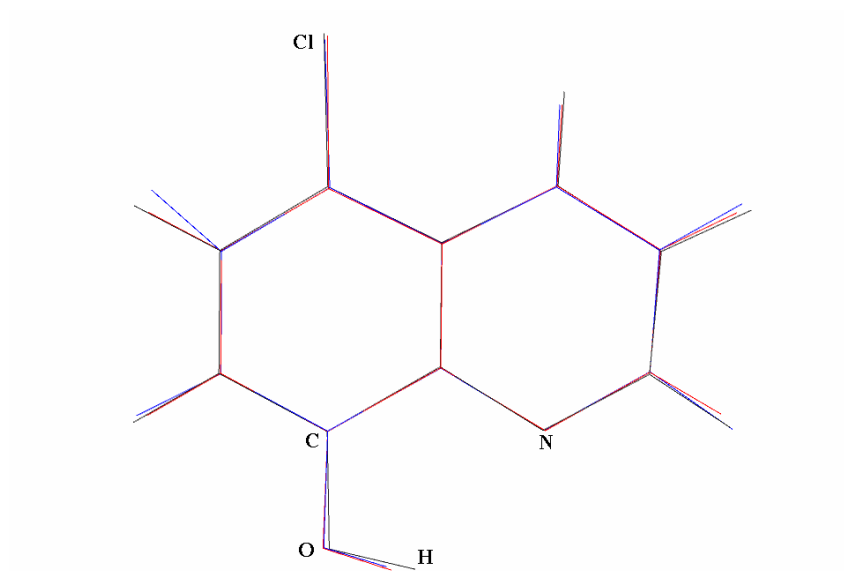


Figure 5.9 An overlay of the HoxCl structures from literature crystal data (drawn in blue), determined crystal data (drawn in red) and calculated DFT data (drawn in black), as summarized in Table 5.7. With a r.m.s. value between all non-hydrogen atoms of the two crystal data sets of 0.0232804 Å and a r.m.s. value of 0.03439639 Å between the crystal data as determined by us and the DFT calculated data.

5.6.3 Comparison between powder diffraction⁷², single crystal diffraction (this study) and DFT calculated geometrical parameters for the compound 5-nitro-8-hydroxyquinoline (HoxNO₂)

Presented in Table 5.8 and Figure 5.10 is the comparison of geometrical data for the compound 5-nitro-8-hydroxyquinoline. The structural data was obtained from powder diffraction (from applicable literature)⁷², from single crystal x-ray diffraction and computational chemistry using DFT techniques. The differences between atomic distances are present between the O-H, N...O and H...N atoms. Molecular angle differences occur between the O-H...N, H-O-C8 and O-C8-C9 angles. Please note that for the calculated data (Figure 5.10) the molecule drawn in black and the orientation of the NO₂ moiety is clearly in a different direction.

Table 5.8 Selected bond distances and angles, (Å, °), for the compound HoxNO₂, as found for single crystal data in literature, single crystal data collected by us and DFT calculation data.

(HoxNO ₂)	Literature ⁷²	XRD ^b	DFT ^a
O-H	0.90	0.82	0.981
N-O	2.695	2.728	2.638
H...N	2.232	2.275	2.038
O-C8	1.318	1.337	1.339
N-C1	1.348	1.317	1.320
C1-C2	1.410	1.405	1.411
C2-C3	1.367	1.363	1.379
C3-C4	1.436	1.425	1.424
C4-C5	1.406	1.434	1.436
C5-C6	1.399	1.372	1.388
C6-C7	1.408	1.393	1.401
C7-C8	1.360	1.379	1.383
C8-C9	1.461	1.430	1.436
C9-N	1.373	1.364	1.357
C9-C4	1.403	1.422	1.429
C5-N2	1.468	1.457	1.461
O-H...N	111.47	115.05	117.46
H-O-C8	112.28	109.50	106.07
O-C8-C9	120.80	121.56	118.45
C8-C9-N	113.88	115.94	114.54
C4-C5-N2	120.42	122.07	122.91
C7-C8-O-H	178.88	179.94	179.91

a= Values as reported in Section 4.6. b= Values as reported in Section 5.5 and Table 5.4.

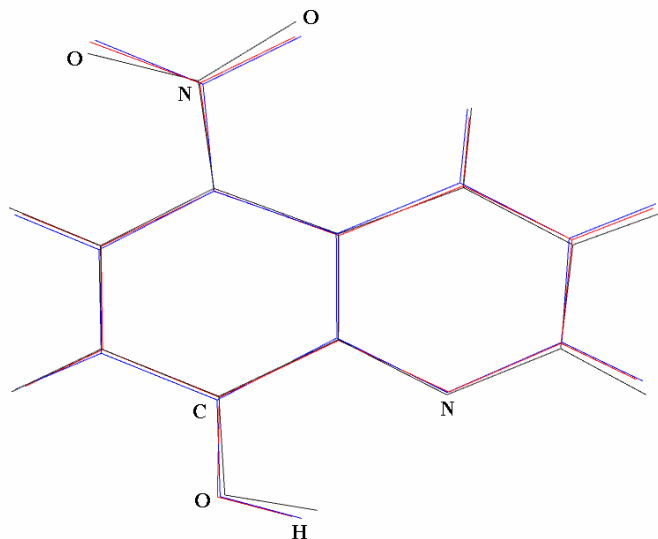


Figure 5.10 An overlay of the HoxNO_2 structures from literature crystal data (drawn in blue), determined crystal data (drawn in red) and calculated DFT data (drawn in black), as summarized in Table 5.8. With an r.m.s value between all non-hydrogen atoms of the two crystal data sets of $0.04325 \text{ \AA}$ and a r.m.s. value of $0.08708 \text{ \AA}$ between the crystal data as determined by us and the DFT calculated data.

5.6.4 Conclusion

The theoretical calculations presented in this chapter show that the hydroxyl hydrogen position has a significant affect on the energy level of the molecule, preferring the *cis*-configuration. The electronegativity of substituted atoms or groups on the 5th position of an oxine moiety influences the molecular energy level and the charge density of the nitrogen and oxygen atoms. In the solid state neutral 8-hydroxyquinoline compounds crystallize with a *cis*-configured hydroxyl hydrogen (Chapter 4) unless intermolecular interaction disrupts the energetically preferred configuration.

Comparison of solid state and theoretical data showed small geometrical differences, typically at the hydroxyl position, the N...O bite distance and around the functionalized position. This was suspected, seen that these positions allow the highest possibility for movement or vibration.

With theoretical establishment that functionalization on the 5th position of the oxine moiety has an influence on the charge densities of the donor atoms, a range of functionalized 8-hydroxyquinoline ligands were synthesized (as described in Chapter 3) and coordinated to rhodium in a square planar fashion. This was to investigate the influence from functionalized 8-hydroxyquinoline ligands on the metal centre and these results are discussed in the following chapters. Chapter 6 presents a theoretical investigation on the phenylazo configuration of 5-phenylazo-8-hydroxyquinoline, with the hydroxyl hydrogen in a *cis*-configuration. This theoretical investigation is combined with a crystallographic solid state characterization of selected 5-phenylazo-8-hydroxyquinolinatorrhodium(I) systems.

Chapter 6

X-Ray crystallographic and theoretical study of 5-Phenylazo-8-hydroxyquinoline as free ligand and in rhodium(I) complexes

6.1 Introduction

Aromatic diazo compounds were discovered in 1858 by Peter Griess. Griess named these new compounds 'diazo', because he initially thought that two benzene hydrogen atoms were replaced by two nitrogen atoms that they were basic and could form salts of the type $(C_6H_4)_2(N_2)$ and (HX) . The great success of Griess is partly due to the fact that most aromatic amines readily convert into diazo compounds⁸⁹.

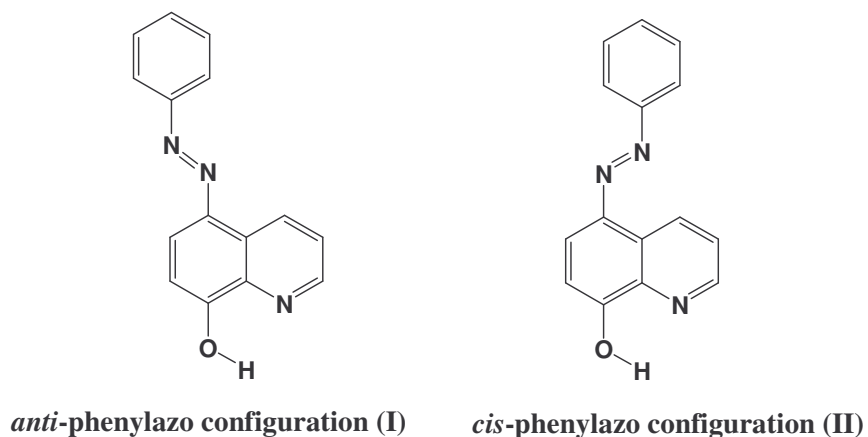
With this study, interest in the electronic influence of substituted groups and atoms on 8-hydroxyquinoline the work of La Deda *et. al.* was encountered²⁴ and as mentioned in Chapter 1, La Deda investigated the electronic transport properties along the electron delocalized ring systems of various 5-phenylazo-8-hydroxyquinoline compounds. It was thus decided to synthesise a range of 5-phenylazo-8-hydroxyquinoline compounds. The molecular energy levels of the various compounds and their possible conformers were investigated by utilizing DFT calculations and solid state characterization of 5-phenylazo-8-hydroxyquinolinorhodium(I) complex.

6.2 Theoretical calculations on 5-phenylazo-8-hydroxyquinoline compounds.

6.2.1 Introduction

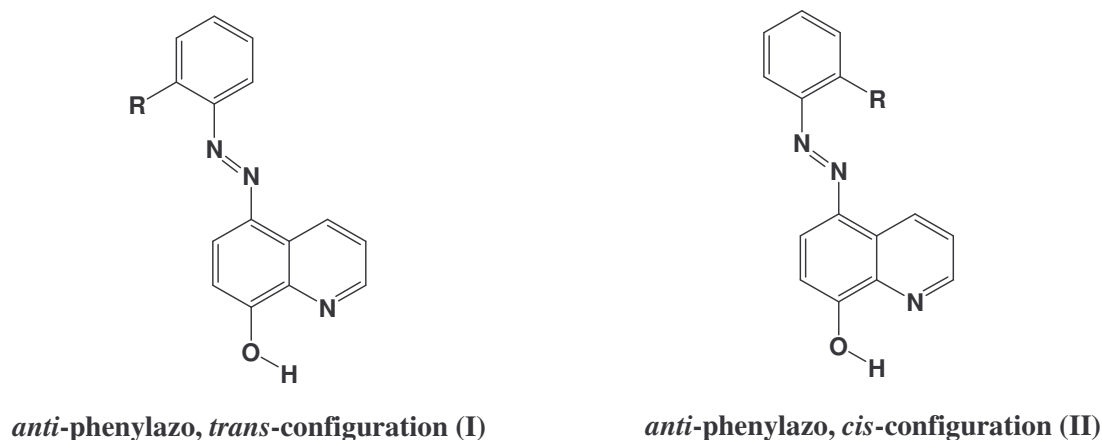
It was established in Chapter 5 that the *cis*-hydroxyl hydrogen configuration is energetically preferred by 8-hydroxyquinoline type compounds. After synthesizing the 5-phenylazo-8-hydroxyquinoline compounds there was an interest in the configuration of the phenylazo group, and the value difference of the energy barrier between possible configurations of a planar ring system. These questions were investigated by utilizing DFT calculations to determine the various energy levels of the possible conformers. Presented in Scheme 6.1 are line drawings of the *anti*-phenylazo configuration (I) and the *cis*-phenylazo configuration (II). Supplementary data is provided in Appendix C.

⁸⁹ Zollinger, H. (1994). *Diazo Chemistry I, Aromatic and Heteroaromatic compounds*. VCH Verlagsgesellschaft mbh.



Scheme 6.1 Line drawing of the two possible 5-phenylazo-8-hydroxyquinoline conformers. (I) *anti*-phenylazo configuration and (II) the *cis*-phenylazo configuration.

The possibility to synthesize various phenylazo ligands, increases the number of possible conformers (Scheme 6.2). After determining the energetically favoured ring configuration, this investigation continued only with this most stable conformer, to further investigate the influence of substitutions on the phenylazo ring as presented in Scheme 6.2 (where these substitutions might be *cis*- or *trans* directed in relation to the quinoline fused ring system). Supplementary data is provided in Appendix C.



Scheme 6.2 Line drawings of the two possible *anti*-phenylazo ring positioned conformers for 5-phenylazo-8-hydroxyquinoline systems.

6.2.2 Experimental

All molecules and transition states were fully optimized using density functional theory (DFT) by using the Becke3-Lee-Yang-Parr (B3LYP)⁷⁸ functionals, supplemented with the standard 6-31G(d,p) and LANL2DZ basis sets. Analytical frequency calculations were done at the same level, to confirm the optimized structures to be either a minimum or a first-order saddle point, as well as to obtain the zero-point energy (ZPE) correction. All calculations were carried out using the Gaussian 03 software suite⁸⁶.

6.2.3 Results and Discussion

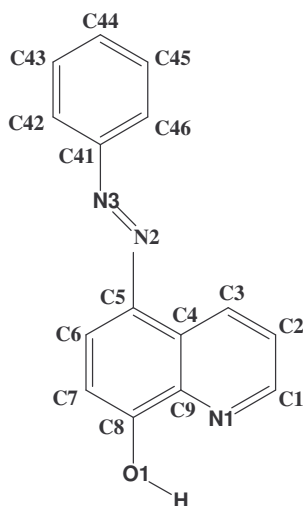
(Supplementary data C2)

The different energy levels of the *cis*- and *anti*-configured phenylazo ring positions, in relation to the 8-hydroxyquinoline fused ring system, were determined. As allocated in Table 6.1, the *anti*-configuration (I), is at a 2.53 kJ/mole lower energy state than the *cis*-configuration (II).

Table 6.1 Relative energy components of the two planar 5-phenylazo-8-hydroxyquinoline conformers.

(HoxL)	Energy (Hartrees)	ZPE (Hartrees)	ΔE (kJ/mole)
(I)	-817.7230658	0.230306	0.00
(II)	-817.7209327	0.230481	2.53

Scheme 6.3 presents the atom labelling for the 5-phenylazo-8-hydroxyquinoline compounds and summarized in Table 6.2 are the selected geometrical parameters of the two 5-phenylazo-8-hydroxyquinoline conformers.



Scheme 6.3 The general atom numbering scheme of the 5-phenylazo-8-hydroxyquinoline system.

Table 6.2 Selected bond distances and angles, ($\text{\AA}$, $^\circ$), for the possible conformers, *anti*- and *cis*-phenylazo-8-hydroxyquinoline as found from theoretical calculations. For label definition see Section 6.2.1.

Compound	(HoxL)	
Configuration	(I)	(II)
O1-H	0.979	0.980
N1...O1	2.678	2.646
H...N	2.088	2.044
O1-C8	1.347	1.345
N1-C1	1.320	1.322
C1-C2	1.417	1.410
C2-C3	1.379	1.381
C3-C4	1.419	1.421
C4-C5	1.434	1.445
C5-C6	1.395	1.396
C6-C7	1.403	1.403
C7-C8	1.387	1.381
C8-C9	1.430	1.437
C9-N1	1.361	1.358
C9-C4	1.424	1.429
C5-N2	1.407	1.403
N2=N3	1.262	1.264
N3-C41	1.417	1.421
C41-C42	1.403	1.407
C42-C43	1.395	1.392
C43-C44	1.397	1.402
C44-C45	1.402	1.397
C45-C46	1.392	1.395
C46-C41	1.408	1.403
O1-H...N1	116.976	117.677
H-O1-C8	106.137	105.872
O1-C8-C9	118.755	118.381
C8-C9-N1	116.133	114.786
C6-C5-N2	124.630	112.561
C5-N2=N3	115.743	118.603
N2=N3-C41	115.412	114.581
N3-C41-C42	115.297	124.760
C6-C5-N2=N3	0.0	-180.0
C5-N2=N3-C41	180.0	180.0
N2=N3-C41-C42	-180.0	0.0

A significant difference in the N1...O1 bite distance ($0.032 \text{ \AA}$) is observed when comparing the bond distances and angles of the *cis*- and *anti*- configured phenylazo ring. This leads to a decrease in the H...N1 distance of $0.044 \text{ \AA}$ when moving from the *anti*- to the *cis*-configuration. Parallel to this is a decrease in the C8-C9-N1 bond angle of the *cis*-configuration of 1.552° . The C-C and C-N bond distances in both the quinoline fused ring system and the phenylazo ring are very comparable between the conformers and literary values¹. The bond angle decrease continues in the C6-C5-N2 angle with a value of 12.069° . There is a 2.638° difference in the C5-N2=N3 bond angle together with the conformation difference around the C5-N2 bond. The difference in the N2=N3-C41 angle is not as dominant as that in the N3-C41-C42 bond angle. Considering the tabulated torsion angles it is clear that the phenylazo ring is in plane with the quinoline ring system.

Establishing that the *anti*- configuration is the preferred conformer, methyl groups were introduced onto the phenyl ring to determine the preferred configuration of *ortho*-substituents on the phenylazo ring (see Scheme 6.2). The relative energy components for the possible conformers of the functionalized 5-phenylazo-8-hydroxyquinoline compounds are summarized in Table 6.3 and in Figure 6.1 are the energy differences (in Hartrees) between the conformers (I), of the functionalized 5-phenylazo-8-hydroxyquinoline compounds, graphically presented. See supplementary data C3-C5.

Table 6.3 Relative energy components of the possible anti-phenylazo configuration (*trans*- and *cis*- functionalized 5-phenylazo-8-hydroxyquinoline conformers). For label definition see Section 6.2.1.

(HoxL-Me)	Energy (Hartrees)	ZPE (Hartrees)	ΔE (kJ/mole)
(I)	-857.042713	0.257816	0.00
(II)	-857.0389735	0.258054	4.36
(HoxL-Me ₂)			
(I)	-896.3641505	0.284938	0.00
(II)	-896.3605435	0.28526	4.31
(HoxL-Me ₃)			
(I) _(sole conformer)	-935.6790036	0.312735	0.00

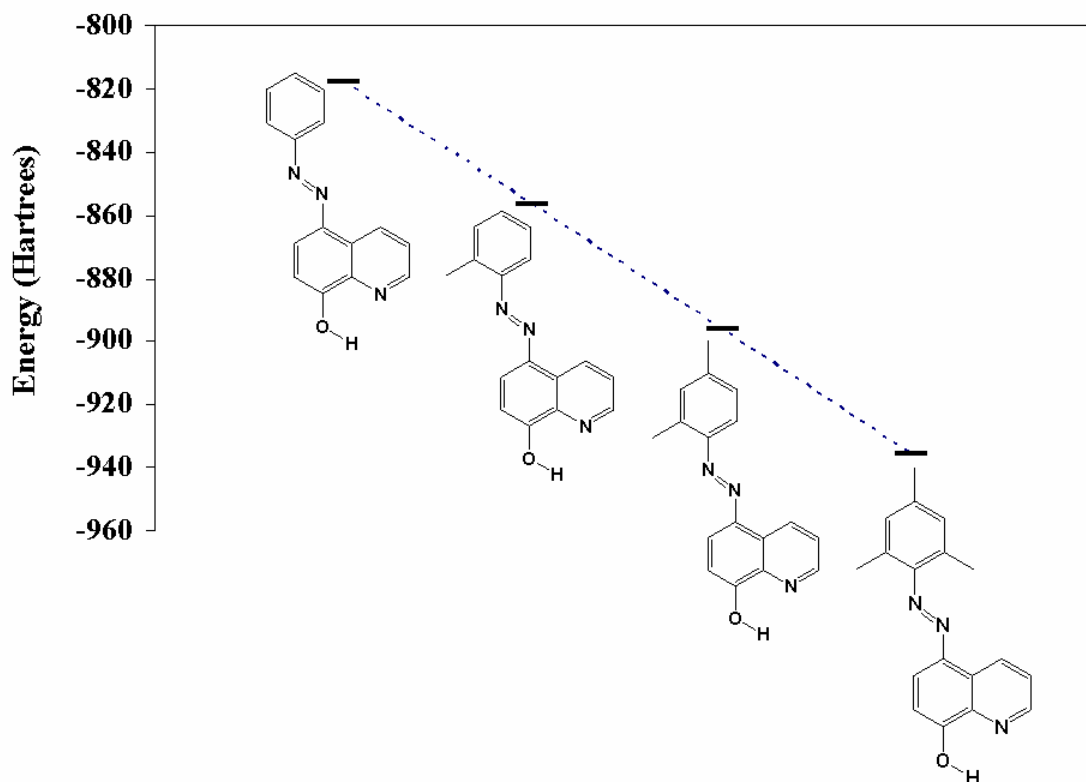
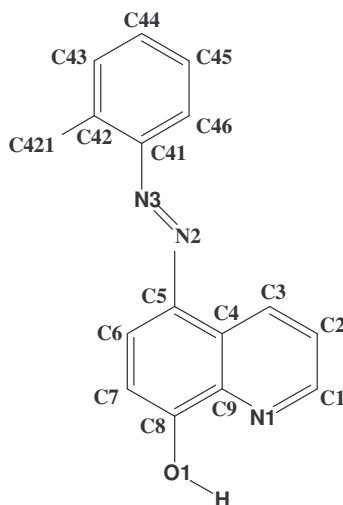


Figure 6.1 Illustration of the energy level decrease as methyl groups are introduced to the phenyl ring of the compound 5-phenylazo-8-hydroxyquinoline, (data from Table 6.3).

From Table 6.3 it was concluded that the energetically preferred conformer is the *trans*-orientation of the phenyl substituent with a *ca.* 4.3 kJ/mole difference between these conformers. In Figure 6.1 it is noted that the energy level decreases linearly as methyl groups are added onto the phenylazo ring. This might be due to the methyl group's electronic influence. The atom labelling for the functionalized 5-phenylazo-8-hydroxyquinoline compounds are presented in Scheme 6.4 with selected geometrical parameters summarized in Table 6.4.



Scheme 6.4 The general atom numbering scheme of the functionalized 5-phenylazo-8-hydroxyquinoline system. Numbering of phenyl ring substituents indicate the ring number, the second digit the position on the ring and finally the number of C-atoms on this position.

Table 6.4 Selected bond distances and angles, (Å, °), for possible conformers of functionalized 5-phenylazo-8-hydroxyquinoline, from theoretical calculations.

Compound	(HoxL-Me)		(HoxL-Me2)		(HoxL-Me3)
Configuration	(I)	(II)	(I)	(II)	(I)
O1-H	0.979	0.978	0.979	0.979	0.979
N1...O1	2.679	2.678	2.679	2.679	2.679
H...N	2.088	2.088	2.088	2.099	2.090
O1-C8	1.347	1.348	1.348	1.348	1.348
N1-C1	1.320	1.320	1.320	1.320	1.320
C1-C2	1.417	1.417	1.417	1.417	1.417
C2-C3	1.379	1.379	1.379	1.379	1.378
C3-C4	1.419	1.419	1.420	1.419	1.419
C4-C5	1.434	1.433	1.434	1.433	1.433
C5-C6	1.394	1.394	1.394	1.394	1.394
C6-C7	1.404	1.404	1.404	1.404	1.404
C7-C8	1.386	1.386	1.386	1.385	1.386
C8-C9	1.430	1.430	1.430	1.430	1.430
C9-N1	1.361	1.361	1.361	1.361	1.361
C9-C4	1.424	1.425	1.425	1.425	1.425
C5-N2	1.407	1.411	1.407	1.412	1.412
N2=N3	1.263	1.264	1.264	1.264	1.270
N3-C41	1.415	1.412	1.413	1.410	1.407
C41-C42	1.415	1.425	1.413	1.424	1.423
C42-C43	1.401	1.401	1.401	1.400	1.395
C43-C44	1.396	1.397	1.399	1.402	1.399
C44-C45	1.340	1.396	1.407	1.401	1.400
C45-C46	1.390	1.390	1.387	1.389	1.399
C46-C41	1.407	1.410	1.409	1.409	1.426
C42-C421	1.510	1.508	1.510	1.508	1.512
C44-C441	---	---	1.510	1.510	1.510
C46-C461	---	---	---	---	1.509
O1-H---N1	116.990	116.970	117.001	116.999	116.977
H-O1-C8	106.123	106.123	106.094	106.089	106.088
O1-C8-C9	118.751	118.773	118.775	118.775	118.804
C8-C9-N1	116.164	116.138	116.152	116.159	116.149
C6-C5-N2	124.644	124.708	124.789	124.754	124.843
C5-N2=N3	115.775	115.019	115.721	114.967	114.920
N2=N3-C41	115.431	118.044	115.722	118.102	118.597
N3-C41-C42	116.193	128.329	116.220	128.553	112.923
C6-C5-N2=N3	-8.274	0.016	-0.228	0.570	0.570
C5-N2=N3-C41	177.249	179.992	179.991	-179.948	-179.840
N2=N3-C41-C42	167.152	0.044	179.617	1.264	-177.573

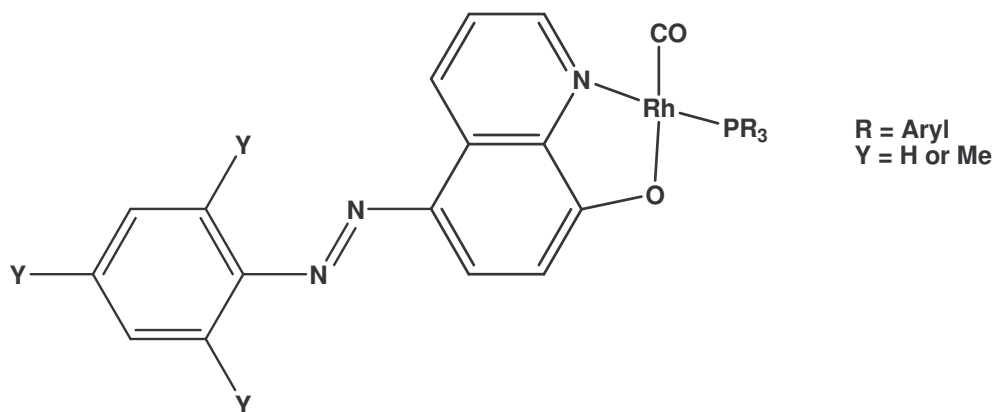
Very similar bond distances and bond angles are found between the differing compounds and conformers, (Table 6.4). Some changes show up in the bond angles around the phenylazo moiety, especially the N2=N3-C41 and N3-C41-C42 bond angle. It is also possible from a secondary effect from the twist between the phenylazo and quinoline rings. The torsion angles C6-C5-N2=N3, C5-N2=N3-C41 and N2=N3-C41-C42 specify this ring twist.

6.3 Crystallographic characterisation of 5-phenylazo-8-hydroxyquinolinatorhodium(I) square planar complexes.

6.3.1 Introduction

A few of the synthesized *mono*-phosphine substituted 5-phenylazo-8-hydroxyquinolinatorhodium(I) complexes yielded crystals suitable for single crystal X-ray diffraction. Illustrated in Scheme 6.5, as a line drawing, is a typical rhodium(I) complex as investigated during this study. The identification codes for complexes that are discussed in this chapter follow:

1. $[\text{Rh}(\text{C}_{15}\text{H}_{11}\text{N}_3\text{O})(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}]/[\text{Rh}(\text{oxL})(\text{CO})(\text{PPh}_3)]$
= Carbonyl[triphenylphosphine](5-phenylazo-8-hydroxyquinolinato)rhodium(I).
2. $[\text{Rh}(\text{C}_{15}\text{H}_{11}\text{N}_3\text{O})(\text{CO})\{\text{P}(\text{C}_6\text{H}_{11})_3\}]/[\text{Rh}(\text{oxL})(\text{CO})(\text{PCy}_3)]$
= Carbonyl[tricyclohexylphosphine](5-phenylazo-8-hydroxyquinolinato)rhodium(I)
3. $[\text{Rh}(\text{C}_{18}\text{H}_{17}\text{N}_3\text{O})(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}]/[\text{Rh}(\text{oxL-Me}_3)(\text{CO})(\text{PPh}_3)]$
= Carbonyl[triphenylphosphine](5-phenylazo-8-hydroxyquinolinato)rhodium(I).



Scheme 6.5 Line drawing of the typical 5-phenylazo-8-hydroxyquinolinatorhodium(I) complexes that were investigated in this study and reflected in this chapter.

6.3.2 Experimental

The reflection data for the following datasets were collected on a Bruker X8 Apex II 4K Kappa CCD diffractometer using the Apex2 software package⁶³. The optimum measurement method to collect more than a hemisphere of reciprocal space was predicted by COSMO⁶⁴. Frame integration and data reduction were performed using the SAINT-Plus and XPREP⁶⁵ software packages. A multi-scan absorption correction was performed on the data using SADABS⁶⁶. The structures were solved by the direct methods package SIR97⁶⁷. For refinement the WinGX⁶⁸ software package incorporating SHELXL⁶⁹ were used. All non-H atoms were refined anisotropically. H atoms were positioned geometrically and refined using a riding model with fixed C-H distances of 0.93 Å (CH) [Uiso(H) = 1.2Ueq]. Molecular diagrams were drawn using the DIAMOND⁷⁰ package with a 30% thermal envelope probability for non-hydrogen atoms.

General crystal data and refinement parameters are presented in Table 6.5. A complete list of atomic coordinates, equivalent isotopic parameters, bond distances and angles, anisotropic displacement parameters and hydrogen coordinates are given in Appendix C.

Table 6.5 General crystal data for the complexes, [Rh(oxL)(CO)(PPh₃)], [Rh(oxL)(CO)(PCy₃)] and [Rh(oxL-Me₃)(CO)(PPh₃)]

Identification code	[Rh(oxL)(CO)(PPh ₃)]	[Rh(oxL)(CO)(PCy ₃)]	[Rh(oxL-Me ₃)(CO)(PPh ₃)]
Empirical formula	C34 H25 N3 O2 P Rh	C37 H49 N3 O3 P Rh	C37 H31 N3 O2 P Rh
Formula weight	641.45	717.67	683.53
Collection Temperature (K)	100(2)	100(2)	100(2)
Crystal system, space group	Monoclinic, P2 ₁ /c	Monoclinic, P2 ₁ /n	Triclinic, $P\bar{1}$
Unit cell dimensions			
<i>a</i> = (Å)	9.358(5)	9.564(5)	8.313(5)
<i>b</i> = (Å)	13.287(5)	14.033(5)	8.811(5)
<i>c</i> = (Å)	22.336(5)	25.967(5)	24.083(5)
<i>a</i> = (°).	90.0	90.0	88.164(5)
<i>β</i> = (°).	97.985(5)	91.032(5)	90.0
<i>γ</i> = (°)	90.0	90.0	61.852(5)
Volume (Å ³)	2750.3(19)	3485(2)	1554.3(13)
<i>Z</i>	4	4	2
Density (calculated) (Mg/m ³)	1.549	1.368	1.460
Absorption coefficient (mm ⁻¹)	0.717	0.575	0.639
<i>F</i> (000)	1304	1504	700
Crystal size (mm ³)	0.15 x 0.10 x 0.02	0.45 x 0.11 x 0.06	0.40 x 0.32 x 0.02
Theta range for data collection (°)/ completeness for collection (%)	1.79 to 28.29 / 98.8	1.57 to 28.35 / 99.6	0.85 to 28.49 / 57
Index ranges	-12<= <i>h</i> <=12, -17<= <i>k</i> <=17, -29<= <i>l</i> <=26	-12<= <i>h</i> <=12, -17<= <i>k</i> <=18, -34<= <i>l</i> <=34	-11<= <i>h</i> <=10, -11<= <i>k</i> <=8, -32<= <i>l</i> <=32
Reflections collected	25374	48687	12191
Independent reflections	6763 [R(int) = 0.1070]	8690 [R(int) = 0.0674]	4493 [R(int) = 0.0470]
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan
Max. and min. transmission	0.9858 and 0.9001	0.9663 and 0.7818	0.9873 and 0.7840
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	6763 / 0 / 370	8690 / 0 / 396	4493 / 0 / 370
Goodness-of-fit on F ²	1.001	1.114	0.974
Final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	R1 = 0.0542, wR2 = 0.0903	R1 = 0.0399, wR2 = 0.0961	R1 = 0.0447, wR2 = 0.0896
<i>R</i> indices (all data)	R1 = 0.1092, wR2 = 0.1103	R1 = 0.0578, wR2 = 0.1120	R1 = 0.0606, wR2 = 0.0945
Largest diff. peak and hole (e.Å ⁻³)	0.952 and -0.744	1.065 and -0.707	1.062 and -0.597

6.3.3 Crystal structure of Carbonyl[triphenylphosphine] (5-Phenylazo-8-hydroxyquinolinato)rhodium(I), [Rh(oxL)(CO)(PPh₃)]

6.3.3.1 Results and Discussion

(Supplementary data C6)

Molecules of the complex [Rh(oxL)(CO)(PPh₃)], where L= phenyl azo, crystallized in the Monoclinic *P*₂₁/*c* space group with four molecules in the unit cell. The stacking motifs displayed are quinoline ligand to ligand stacking and phosphine to phosphine orientated stacking. An in depth discussion of the molecular packing is presented in Section 6.4, combined with the stacking patterns of the structures reported in Section 6.3.4 and Section 6.3.5. The general atom numbering scheme and important geometrical parameters are presented in Figure 6.2 and Table 6.6.

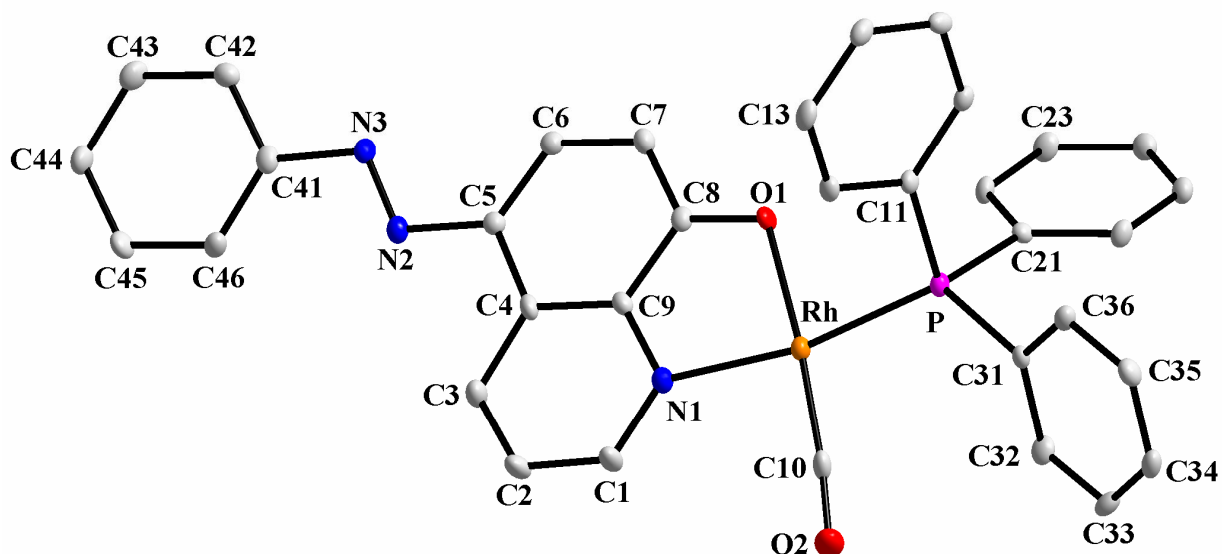


Figure 6.2 Diamond drawing of Carbonyl[triphenylphosphine](5-phenylazo-8-hydroxyquinolinato)rhodium(I), [Rh(oxL)(CO)(PPh₃)], in the asymmetric unit, showing the atom numbering scheme of the molecule. Hydrogen atoms are omitted for clarity. For the phenyl C-atoms, the first digit indicates ring number and the second digit the position of the atom in the ring

Table 6.6 Selected bond distances and angles (Å, °) for the complex [Rh(oxL)(CO)(PPh₃)].

Atoms	Distance (Å)	Atoms	Angle (°)
Rh-O1	2.052(3)	O1-Rh-N1 _(Bite angle)	80.03(13)
Rh-N1	2.089(3)	N1-Rh-C10	95.27(17)
Rh-P	2.2626(12)	C10-Rh-P	94.49(14)
Rh-C10	1.794(5)	P-Rh-O1	90.30(8)
C10-O2	1.161(5)	Rh-C10-O2	175.0(4)
C8-O1	1.311(4)	C1-N1-C9	118.7(4)
P-C11	1.825(4)	N1-C9-C8	115.3(3)
P-C21	1.834(4)	C9-C8-C7	116.7(4)
P-C31	1.835(4)	C6-C5-N2	125.0(4)
C5-N2	1.424(5)	C5-N2=N3	113.6(4)
N2=N3	1.263(5)	N2=N3-C41	112.5(4)
N3-C41	1.441(5)	C6-C5-N2=N3	5.9(6)
N1...O1 _(Bite distance)	2.663(5)	C5-N2=N3-C41	179.3(3)
		N2=N3-C41-C42	177.7(4)

The phenylazo group is in an *anti* conformation in relation to the quinoline backbone, this conformation ensures minimal interaction / hinderance between the H atoms on the pyridine ring and the N=N azo forming atoms, choosing the molecular plane to be formed by the quinoline atoms C1-C9 and N1 (r.m.s. of fitted atoms = 0.009 Å). A slight molecular bend is formed by the upwards lift of the phenyl azo ring and the P-atom. The phenylazo centre is lifted 0.3615(4) Å from the molecular plane and the P-atom by 0.278(1) Å. The torsion angle C5-N2=N3-C41 = 179.3(3)° and is partly responsible for the phenyl lift from the quinolinato ring plane. A modest twist, mainly in the C5-N2 bond, results in a dihedral angle of 10.15(1)° between the phenyl azo and quinoline backbone. This twist is influenced by the rotation around the C5-N2 bond, since the torsion angle C6-C5-N2=N3 = 5.9(6)°. The N2=N3-C41-C42 torsion angle, 177.7(4)°, also contributes to this ring twist.

A dihedral angle of 4.82(8)° is observed between the defined molecular plane and the metal coordination plane. The Rh-atom is displaced from the metal coordination plane by 0.0626(5) Å. The quinoline bite angle is 80.03(13)° compared to the ideal 90° for a perfect metal coordination polyhedron, pointing out slight distortion. This is however, a constant observation in the 8-hydroxyquinoline bidentate ligands, that forms 5-membered chelating moieties, note the bite angles for rhodium complexes reported in Chapter 7 and 8. The N...O bite distance for this ligand was found to be 2.663(5) Å.

The molecular packing of the complex [Rh(oxL)(CO)(PPh₃)] is reported in Section 6.4 and geometrical correlation is discussed in Section 6.5.

6.3.4 Crystal structure of Carbonyl[tricyclohexylphosphine] (5-Phenylazo-8-hydroxyquinolinato)rhodium(I), acetone solvate [Rh(oxL)(CO)(PCy₃)]

6.3.4.1 Results and Discussion

(Supplementary data C7)

The complex [Rh(oxL)(CO)(PCy₃)], where L= phenyl azo, crystallized with a acetone solvate molecule in the Monoclinic $P2_1/n$ space group ($Z = 4$). *Mono* phosphine substitution on the metal centre occurred *trans* to the nitrogen atom and the effective cone angle of the phosphine ligand was calculated to be 167°, (Rh-P = 2.2631(9) Å). Atom labelling of the molecule is as depicted in Figure 6.3 and the most important bond distances and angles are tabulated in Table 6.7.

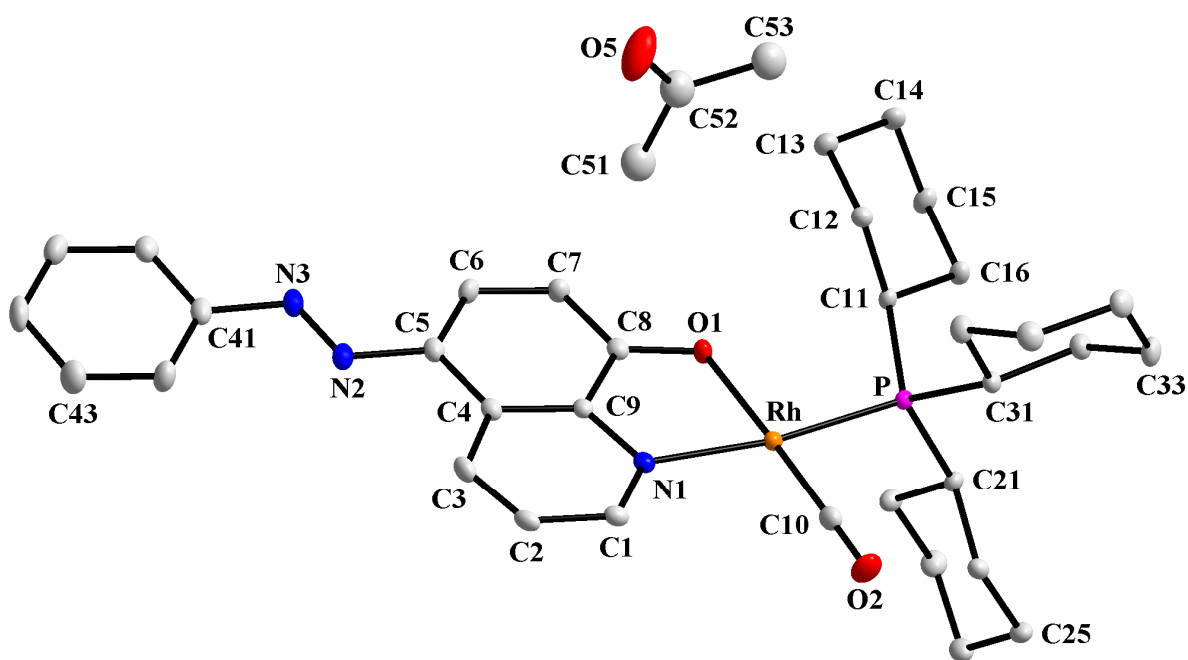


Figure 6.3 A graphical illustration of the complex Carbonyl[tricyclohexylphosphine](5-phenylazo-8-hydroxyquinolinato)rhodium(I), [Rh(oxL)(CO)(PCy₃)], in the asymmetric units showing the atom numbering scheme of the molecule. Hydrogen atoms are omitted for clarity. For the cyclohexyl C-atoms, the first digit indicates ring number and the second digit the position of the atom in the ring

Table 6.7 Selected bond distances and angles (Å, °) for the complex [Rh(oxL)(CO)(PCy₃)].

Atoms	Distance (Å)	Atoms	Angle (°)
Rh-O1	2.052(2)	O1-Rh-N1 _(Bite angle)	79.76(8)
Rh-N1	2.099(2)	N1-Rh-C10	97.95(11)
Rh-P	2.2631(9)	C10-Rh-P	89.82(9)
Rh-C10	1.794(3)	P-Rh-O1	92.44(5)
C10-O2	1.159(4)	Rh-C10-O2	178.2(3)
C8-O1	1.307(3)	C1-N1-C9	118.1(2)
P-C11	1.846(3)	N1-C9-C8	115.4(2)
P-C21	1.847(3)	C9-C8-C7	117.6(2)
P-C31	1.844(3)	C6-C5-N2	124.5(3)
C5-N2	1.410(3)	C5-N2=N3	114.3(2)
N2=N3	1.265(3)	N2=N3-C41	114.2(2)
N3-C41	1.424(4)	C6-C5-N2=N3	0.9(4)
N1...O1 _(Bite distance)	2.662(3)	C5-N2=N3-C41	178.6(2)
		N2=N3-C41-C42	4.7(4)

The molecular plane formed by the quinoline atoms C1-C9 and N1 yields a r.m.s. of 0.0201 Å. Also present is the dihedral angle of 2.2(2)° between the benzene and the pyridine ring. In relation to the quinoline backbone, the phenylazo group is in an *anti* conformation and a 7.33(7)° dihedral angle is present between the planes of these two ring systems. Slight molecular buckling is present because the phenylazo ring centre is lifted from the molecular plane by 0.2778(3) Å and the P-atom is displaced by 0.1167(8) Å in the opposite direction. The N...O bite distance was measured to be 2.662(3) Å and the O1-Rh-N1 bite angle is 79.76(8)°. A slight distortion is displayed by the 7.26(7)° dihedral angle between the molecular plane and the metal coordination plane, while the Rh-atom is slightly displaced from the metal coordination plane by 0.0333(3) Å.

The hydrogen interactions (as found between neighbouring acetone molecules) is illustrated in Figure 6.4. This interaction is between the donor O5 and acceptor C53 of the next molecule with a O5...H distance of 2.711(8) Å and a O5...H-C53 angle of 132.3(2)°. The symmetry operator on O5 is (2-x, 1-y, 1-z) and that on O5ⁱ = (1+x, 1+y, z).

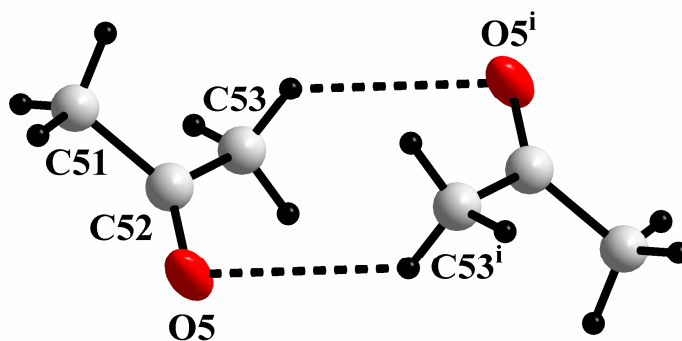


Figure 6.4 An illustration of the hydrogen interaction between adjacent acetone molecules. The interacting distance and angle are 2.711(8) Å and 132.3(2)° respectively. The symmetry operators on O5 is (2-x, 1-y, 1-z) and that on O5ⁱ = (1+x, 1+y, z).

The molecular packing of the complex [Rh(oxL)(CO)(PCy₃)] is reported in Section 6.4 and the geometrical correlation discussed in Section 6.5.

6.3.5 Crystal structure of Carbonyl[triphenylphosphine] (5-[(2,4,6-trimethyl)phenylazo]-8-hydroxyquinolinato)rhodium(I), [Rh(oxL-Me₃)(CO)(PPh₃)]

6.3.5.1 Results and Discussion

(Supplementary data C8)

The single crystal X-ray data collection of the complex [Rh(oxL-Me₃)(CO)(PPh₃)], where (oxL-Me₃) = 5-[(2,4,6-trimethyl)phenylazo]-8-hydroxyquinolinato, is at a very low level of completeness (57%). Even at this level of completeness the data was solved with a R_{int} value of 4.7% and a goodness of fit on $F^2 = 0.974$. The complex crystallized in the Triclinic space group $P\bar{1}$ ($Z = 2$) with a general positioned rhodium metal centre. The atom labelling is presented in Figure 6.5 and the most important bond distances and angles are tabulated in Table 6.8.

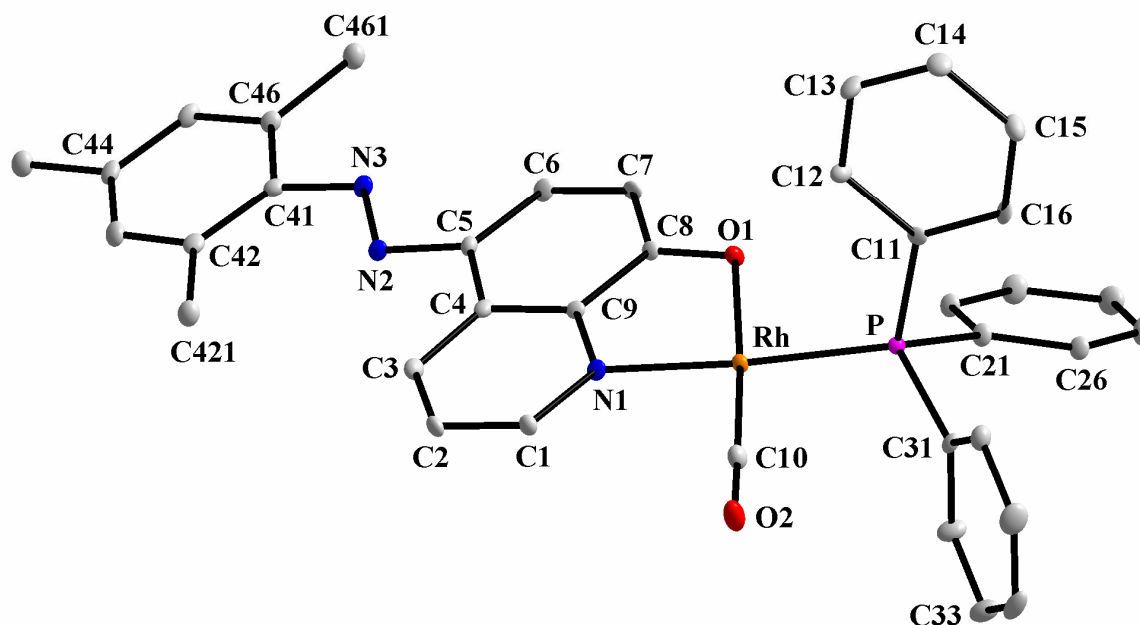


Figure 6.5 Illustration of the complex Carbonyl[triphenylphosphine](5-[(2,4,6-trimethyl)phenylazo]-8-hydroxyquinolino)rhodium(I), $[\text{Rh}(\text{oxL-Me}_3)(\text{CO})(\text{PPh}_3)]$, in the asymmetric unit, showing the atom numbering scheme of the molecule, hydrogen atoms are omitted for clarity. For the phenyl C-atoms, the first digit indicates ring number and the second digit the position of the atom in the ring

Table 6.8 Selected bond distances and angles ($\text{\AA}$, $^\circ$) for the complex $[\text{Rh}(\text{oxL-Me}_3)(\text{CO})(\text{PPh}_3)]$.

Atoms	Distance ($\text{\AA}$)	Atoms	Angle ($^\circ$)
Rh-O1	2.062(3)	O1-Rh-N1 _(Bite angle)	79.95(13)
Rh-N1	2.103(4)	N1-Rh-C10	96.80(17)
Rh-P	2.2831(15)	C10-Rh-P	87.38(14)
Rh-C10	1.805(4)	P-Rh-O1	95.85(9)
C10-O2	1.151(5)	Rh-C10-O2	179.0(4)
C8-O1	1.340(4)	C1-N1-C9	118.3(4)
P-C11	1.846(3)	N1-C9-C8	115.4(4)
P-C21	1.839(5)	C9-C8-C7	117.0(4)
P-C31	1.837(4)	C6-C5-N2	125.8(4)
C5-N2	1.431(5)	C5-N2=N3	114.0(3)
N2=N3	1.272(4)	N2=N3-C41	117.3(3)
N3-C41	1.434(5)	C6-C5-N2=N3	10.9(6)
N1...O1 _(Bite distance)	2.676(5)	C5-N2=N3-C41	178.3(3)
		N2=N3-C41-C42	9.1(6)

The quinoline backbone, atoms C1-C9 and N were selected to form the molecular plane (r.m.s. of fitted atoms = 0.015 $\text{\AA}$). The phenylazo group is in an *anti* conformation to the quinoline backbone and is displaced from the molecular plane by 0.0819(4) $\text{\AA}$ (phenylazo centre to plane distance). Rotation in the C5-N2 bond form the C6-C5-N2=N3 torsion angle of 10.9(6) $^\circ$ that contributes to the twist between

the phenylazo group and the molecular plane, resulting in the dihedral angle of $4.6(1)^\circ$ between these two planes. Displacement from the molecular plane by the P-atom, $0.355(1) \text{ \AA}$, and the mentioned phenylazo centre, $0.0819(4) \text{ \AA}$, show the molecular bending, further emphasized by the dihedral angle of $6.67(6)^\circ$ formed between the phenylazo plane and the metal coordination plane. The rhodium atom is displaced by $0.0176(5) \text{ \AA}$ from the coordination plane. The N...O bite distance is $2.676(5) \text{ \AA}$ with a O1-Rh-N1 bite angle of $79.95(13)^\circ$. The rhodium carbonyl bond is almost linear with a Rh-C10-O2 angle of $179.0(4)^\circ$.

The molecular packing of the complex $[\text{Rh}(\text{oxL-Me}_3)(\text{CO})(\text{PPh}_3)]$ is reported in the following section and geometrical correlations is discussed in Section 6.5.

6.4 Crystal packing modes of the ***[(5-phenylazo-8-hydroxyquinolinato)rhodium(I)] type*** ***complexes.***

6.4.1 Discussion

Figure 6.6 to Figure 6.8 presents the crystal packing modes between neighbouring molecules for the discussed 5-phenylazo-8-hydroxyquinolinatorhodium(I) type complexes.

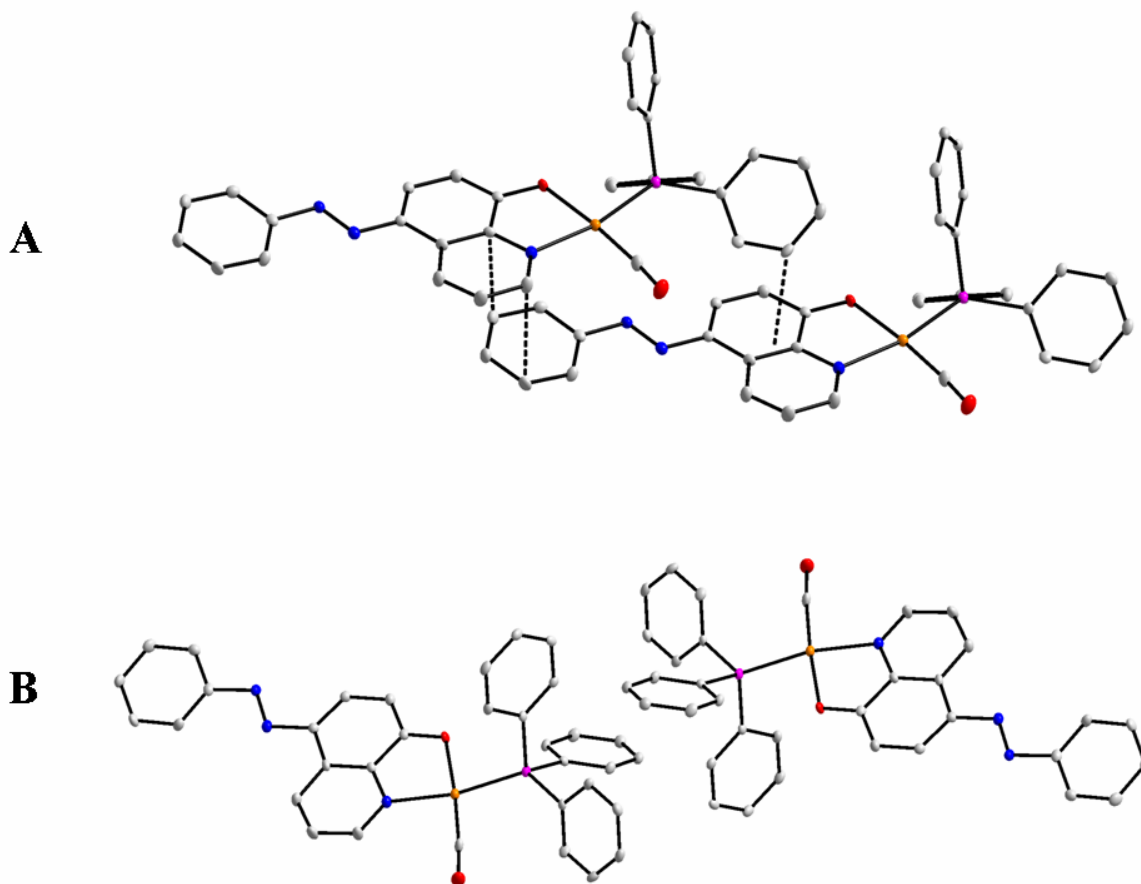


Figure 6.6 An illustration of two different molecular orientations towards neighbour molecules, in the crystal packing of the complex $[\text{Rh}(\text{oxL})(\text{CO})(\text{PPh}_3)]$. Shown in (A) is the ligand “head to head” stacking with two different π -stacking interactions and (B) a phosphine to phosphine mode. H-atoms were omitted for clarity.

The molecules of the complex, $[\text{Rh}(\text{oxL})(\text{CO})(\text{PPh}_3)]$, did not stack in the usual ligand to ligand π -stacking mode. In this case a ligand to ligand π -stacking in a “head to head” fashion, (Figure 6.6 (A)) was observed. This is quite surprising, considering the fact that steric influences from the phosphine ligand usually prohibits a “head to tail” mode. The reason for this type of stacking is, however, partly possible due to the phosphine phenyl ring orientation, since a point to plane π -stacking ($3.421(4) \text{ \AA}$) is present between the phosphine phenyl and quinoline fused ring system. With the elongation of the quinoline ligand by the phenylazo group, ligand to ligand π -stacking is still achieved, between the pyridine ring of one molecule and a phenylazo ring of the next ($3.202(1) \text{ \AA}$). (B) is an additional molecular stacking with the direction of phosphine phenyl rings towards those of a neighbour molecule. It is a stacking mode also found in the crystal packing of the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$, Section 7.8.

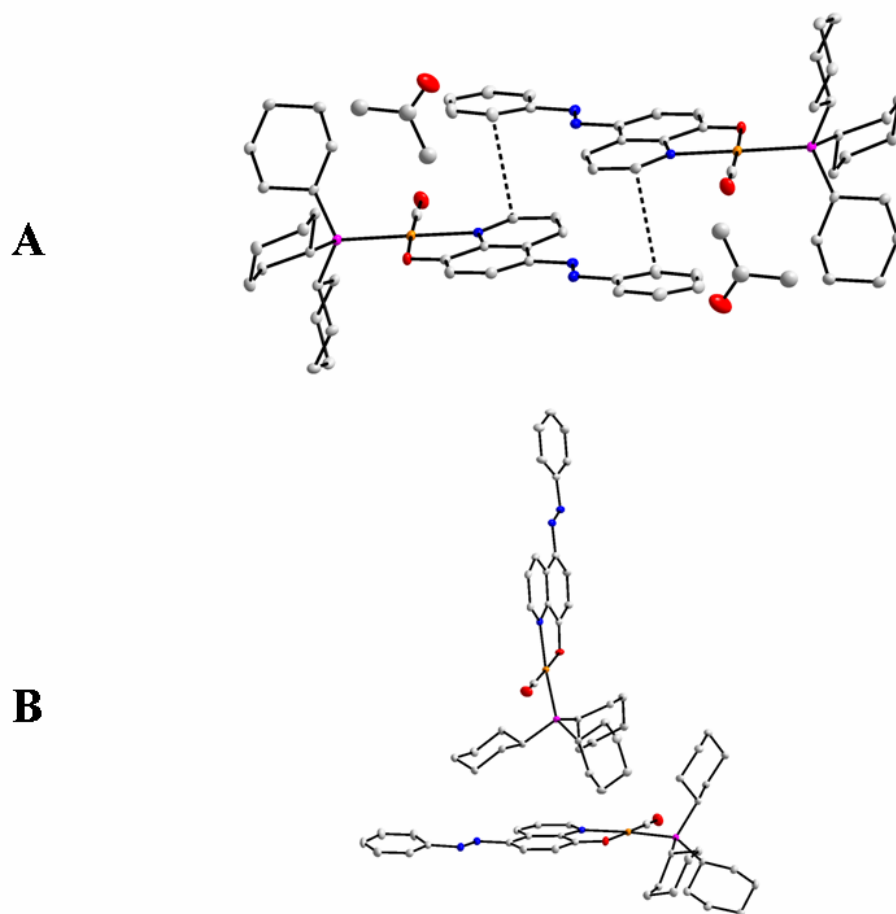


Figure 6.7 Crystal packing modes as found for the complex $[\text{Rh}(\text{oxL})(\text{CO})(\text{PCy}_3)]$. Displaying the ligand to ligand “head to tail” mode (A) and the phosphine aryl ring towards the quinoline backbone mode (B). H-atoms are omitted for clarity.

It is clear from Figure 6.7 that the molecular crystal packing of the complex $[\text{Rh}(\text{oxL})(\text{CO})(\text{PCy}_3)]$ is in the general mode of the quinolinatorhodium(I) complexes; displaying the ligand to ligand “head to tail” mode Figure 6.7 (A), but with much less π -orbital overlap than suspected and separated by a distance of 3.326(1) Å. The limited ring overlap might be due to the position of the acetone guest molecule. The guest molecule might have influenced the crystal packing with a steric influence to prevent a “head to head” mode as in Figure 6.6 (A). Figure 6.7 (B) displays the phosphine aryl ring orientation towards the quinoline backbone also found in the crystal packing.

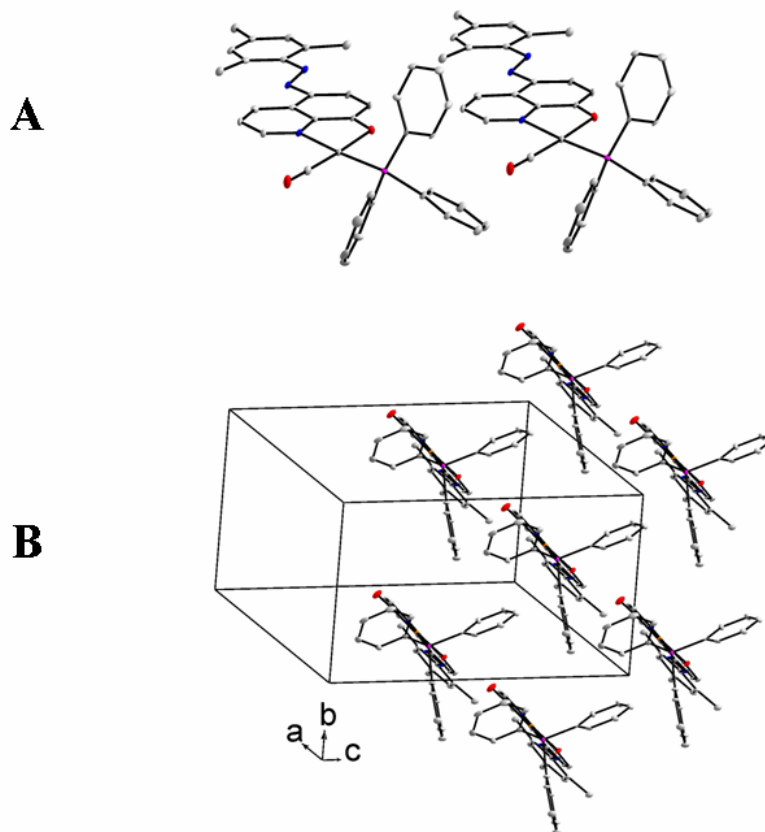


Figure 6.8 Diamond drawings indicating the molecular alignment (A) in the crystal packing of the complex $[\text{Rh}(\text{oxL-Me}_3)(\text{CO})(\text{PPh}_3)]$ and the *pseudo*-hexagonal close packing between the molecules (B). H-atoms are omitted for clarity.

Crystal packing of the complex $[\text{Rh}(\text{oxL-Me}_3)(\text{CO})(\text{PPh}_3)]$ does not display the expected stabilizing interactions or stacking modes. Neighbouring molecules pack next to one another with almost parallel molecular planes, (Figure 6.8 (A)). As presented in Figure 6.8 (B) these molecules stack as rods in a *pseudo*-hexagonal close packing mode.

6.5 Comparison between the theoretical data on 5-phenylazo-8-hydroxyquinoline compounds and X-Ray data of the [(5-phenylazo-8-hydroxyquinolinato)rhodium(I)] complexes

Presented in Table 6.9 is a summary of the 5-phenylazo-8-hydroxyquinolinatorhodium(I) solid state geometrical data, (Section 6.3), and summarized in Table 6.10 are geometrical parameters of the oxine moieties as from theoretical calculations, (Section 6.2).

5-phenylazo-8-hydroxyquinoline compounds and rhodium(I) complexes

Table 6.9 Comparative geometrical data for 5-phenylazo-8-hydroxyquinolinorhodium(I) and 8-hydroxyquinolinorhodium(I) complexes.
For label definition see Section 6.3.

	Rh-P (Å)	Rh-N (Å)	Rh-O (Å)	Rh-C (Å)	O-Rh-N (°)	θ _F (°)	π-stacking (Å)	¹ J _(Rh-P) (Hz)	ν _(CO) (cm ⁻¹)
[Rh(oxL)(CO)(PPh ₃)]	2.2626(12)	2.089(3)	2.052(3)	1.794(5)	80.03(13)	161	3.202(1)	164	1970
[Rh(oxL)(CO)(PCy ₃)]	2.2631(9)	2.099(2)	2.052(2)	1.794(3)	79.76(8)	167	3.326(1)	154	1952
[Rh(oxL-Me ₃)(CO)(PPh ₃)]	2.2831(15)	2.103(4)	2.062(3)	1.805(4)	79.95(13)	162	---	163	1972

Table 6.10 Comparative geometrical data for 5-phenylazo-8-hydroxyquinoline compounds and 5-phenylazo-8-hydroxyquinolinorhodium(I) complexes.
For label definition see Section 6.2.

Atoms	(HoxL)(I) ^a	[Rh(oxL)(CO)(PPh ₃)] ^b	(HoxL-Me ₃)(II) ^a	[Rh(oxL-Me ₃)(CO)(PPh ₃)] ^b
N1...O1 (Å)	2.678	2.663(5)	2.679	2.676(5)
C5-N2 (Å)	1.407	1.424(5)	1.412	1.431(5)
N2=N3 (Å)	1.262	1.263(5)	1.270	1.272(4)
N3-C41 (Å)	1.417	1.441(5)	1.407	1.434(5)
O1-C8-C9 (°)	118.755	119.5(3)	118.804	111.8(2)
C8-C9-N1 (°)	116.133	115.3(3)	116.149	115.4(4)
C5-N2=N3 (°)	115.743	113.6(4)	114.920	114.0(3)
N2=N3-C41 (°)	115.412	112.5(4)	118.597	117.3(3)
O1-C8-C9-N1 (°)	0.0	-2.3(5)	0.0	-5.6(4)
C5-N2=N3-C41 (°)	180.0	179.3(3)	-179.840	178.3(3)

Note: a= DFT data from this study (no esd), b = X-Ray data from this study.

Apart from the Rh-P bond distance of the complex $[\text{Rh}(\text{oxL-Me}_3)(\text{CO})(\text{PPh}_3)]$ that is 0.02 Å longer than that of the $[\text{Rh}(\text{oxL})(\text{CO})(\text{PR}_3)]$ complexes, other metal coordinating bonds and molecular bite angles, O-Rh-N, are comparable to one another. As presented in Table 6.10 the geometrical parameters of the coordinated oxL and oxL-Me₃ ligands display the largest difference in the O1-C8-C9 and N2-N3-C41 angles and the O1-C8-C9-N1 torsion angles. The theoretical and solid state geometrical data are very comparable, (Table 6.10), with the differences probably due to metal coordination.

6.6 Conclusion

The energetically preferred phenylazo configuration on a 8-hydroxyquinoline backbone was determined by utilizing DFT theoretical calculations. Establishing that the anti-phenylazo configuration is the energetically preferred isomer, the influence from substituents on the phenylazo ring were determined, noting an energy decrease as methyl substituents are introduced into the system. Single crystal X-Ray diffraction data on 5-phenylazo-8-hydroxyquinolinorhodium(I) complexes proved to be in an *anti*-phenylazo mode and that these rhodium(I) square planar complexes display various molecular packing modes including a strong ligand to ligand π - π overlap due to the electron delocalization over the 5-phenylazo-8-hydroxyquinolinato rings. A more detailed crystallographic study regarding functionalized 8-hydroxyquinolinorhodium(I) complexes containing different phosphorous ligands follows in the next two chapters, including a comparison between the geometrical parameters of the $[\text{Rh}(\text{oxY})(\text{CO})(\text{PR}_3)]$ type complexes, where Y = various substituents and R = Aryl or Aroyl.

Chapter 7

X-Ray crystallographic study of 8-hydroxyquinolinorhodium(I) square planar complexes

7.1 Introduction

The following chapter presents the solid state and theoretical characterisation of selected 8-hydroxyquinolinorhodium(I) complexes. Forming part of the study on complexes of the type $[\text{Rh}(\text{ox})(\text{CO})(\text{PR}_3)]$, where ox = 8-hydroxyquinolinato and R = alkyl, aryl, alkoyl or aroyl. This work is part of an investigation aimed at determining the factors influencing molecular packing of rhodium(I) non-symmetrical bidentate ligand complexes.

The bidentate ligand used in this study is the well known 8-hydroxyquinoline, containing a pyridine and a benzene ring with donor atoms nitrogen and oxygen. The rhodium(I) compounds were prepared by addition of a phosphorous ligand to $[\text{Rh}(\text{ox})(\text{CO})_2]$ (ox is 8-hydroxyquinolate, $(\text{C}_9\text{H}_6\text{NO})$) which leads to carbonyl substitution from the rhodium coordination sphere. The trans-influence from differing donor atoms in square-planar rhodium(I) complexes, as manifested with the Rh-P bond distances is a well known phenomenon⁹⁰. The better σ -electron donor capability of nitrogen compared to that of oxygen, leads to selective carbonyl displacement (*trans* to the nitrogen atom), forming the most stable isomer. Rhodium(I) complexes, containing bulky phosphite ligands, are useful in catalysed hydroformylation of alkenes⁹¹, while the rhodium(I) phosphine ligand complexes are just as important in catalysis, as illustrated by Roth *et al.*⁹².

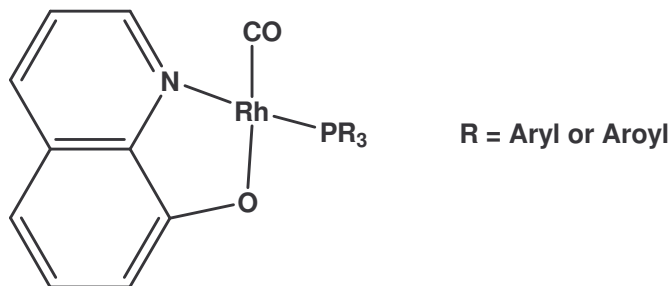
Illustrated in Scheme 7.1 (as a line drawing) are the typical rhodium(I) complexes as investigated in this study. The identification codes for complexes that will be discussed in this chapter are as follows:

⁹⁰ Steyn, G.J.J., Roodt, A., Poletaeva, I. & Varshavsky, Y.S. (1997). *J. Organomet. Chem.* 536.

⁹¹ Crous, R., Datt, M., Foster, D., Bennie, L., Steenkamp, C., Huyser, J., Kirsten, L., Steyl, G. & Roodt, A. (2005). *J. Chem. Soc., Dalton Trans.* 1108.

⁹² Roth, J. F., Craddock, J.H & Hershman, A. (1971). *Chem. Technol.* 600.

1. $[\text{Rh}(\text{C}_9\text{H}_6\text{NO})(\text{CO})\{\text{P}(\text{OC}_{14}\text{H}_{21})_3\}]/[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3)]$
= Carbonyl[tris(2,4-di-tert-butylphenyl)phosphite](8-hydroxyquinolinato)rhodium(I).
2. $[\text{Rh}(\text{C}_9\text{H}_6\text{NO})(\text{CO})\{\text{P}(\text{OC}_7\text{H}_7)_3\}]/[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2\text{MePh})_3)]$
= Carbonyl[tris(2-methylphenyl)phosphite] (8-hydroxyquinolinato)rhodium(I).
3. $[\text{Rh}(\text{C}_9\text{H}_6\text{NO})(\text{CO})\{\text{P}(\text{C}_6\text{F}_5)_3\}]/[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{5FPh})_3)]$
= Carbonyl[tris(pentafluorophenyl)phosphine](8-hydroxyquinolinato)rhodium(I).
4. $[\text{Rh}(\text{C}_9\text{H}_6\text{NO})(\text{CO})\{\text{P}(\text{C}_6\text{H}_{11})_3\}]/[\text{Rh}(\text{ox})(\text{CO})(\text{PCy}_3)]$
= Carbonyl[tricyclohexylphosphine](8-hydroxyquinolinato)rhodium(I)
5. $[\text{Rh}(\text{C}_9\text{H}_6\text{NO})(\text{CO})\{\text{P}(\text{C}_6\text{H}_{11})(\text{C}_6\text{H}_5)_2\}]/[\text{Rh}(\text{ox})(\text{CO})(\text{PCyPh}_2)]$
= Carbonyl(cyclohexyldiphenylphosphine)(8-hydroxyquinolinato)rhodium(I).
6. $[\text{Rh}(\text{C}_9\text{H}_6\text{NO})(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}]/[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$
= Carbonyl[triphenylphosphine](8-hydroxyquinolinato)rhodium(I).



Scheme 7.1 Line drawing of the typical 8-hydroxyquinolinato-rhodium(I) complexes that were investigated in this study.

7.2 *Experimental*

The above mentioned complexes were analysed by single crystal X-ray diffraction, although two different diffractometers were used. For complexes $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{5FPh})_3)]$ and $[\text{Rh}(\text{ox})(\text{CO})(\text{PCyPh}_2)]$ the reflection data was collected on a Bruker SMART CCD 1K area detector⁹³ diffractometer, using graphite monochromated Mo-K α radiation ($\lambda=0.71073 \text{ \AA}$)⁹⁴. For all other structures the reflection data was collected on a Bruker X8 Apex II 4K Kappa CCD diffractometer using the Apex2 software package⁶³. The optimum measurement method to collect more than a hemisphere of reciprocal space was predicted by COSMO⁶⁴.

Once all six data sets was acquired, the frame integration and data reduction was performed using the SAINT-Plus and XPREP⁶⁵ software packages. A multi-scan absorption correction was performed on the data using SADABS⁶⁶. The structures were solved by the direct methods package SIR97⁶⁷. For refinement the WinGX software package⁶⁸ incorporating SHELXL⁶⁹ were used. All non-H atoms were refined anisotropically and H atoms were positioned geometrically and refined using a riding model with fixed C-H distances of $0.93 \text{ \AA}$ (CH) [$\text{Uiso}(\text{H}) = 1.2\text{Ueq}$]. Molecular diagrams were drawn using the DIAMOND⁷⁰ package with a 30% thermal envelope probability for non-hydrogen atoms.

General crystal data and refinement parameters are presented in Table 7.1 and Table 7.2. A complete list of the atomic coordinates, equivalent isotopic parameters, bond distances and angles, anisotropic displacement parameters and hydrogen coordinates are provided in the Appendix D.

⁹³ Bruker (1998). SMART-NT. Version 5.050. Bruker AXS Inc. Area-Detector Software Package; Madison, WI, USA.

⁹⁴ We thank Prof. Dave Billing and The University of the Witwatersrand for the use of their diffractometer.

Table 7.1 General crystal data for the complexes, [Rh(ox)(CO)(P(O-2,4di^tBuPh)₃)], [Rh(ox)(CO)(P(O-2MePh)₃)] and [Rh(ox)(CO)(P(5FPh)₃)].

Identification code	[Rh(ox)(CO)(P(O-2,4di ^t BuPh) ₃)]	[Rh(ox)(CO)(P(O-2MePh) ₃)]	[Rh(ox)(CO)(P(5FPh) ₃)]
Empirical formula	C107 H144 N2 O11 P2 Rh2	C31 H27 N O5 P Rh	C28 H6 F15 N O2 P Rh
Formula weight	1902.00	627.42	807.22
Collection temperature (K)	100(2)	100(2)	293(2)
Crystal system, space group	Orthorhombic, <i>Pccn</i>	Monoclinic, <i>P2₁/c</i>	Monoclinic, <i>C2/c</i>
Unit cell dimensions			
<i>a</i> = (Å)	34.945(5)	7.652(5)	19.975(5)
<i>b</i> = (Å)	17.307(5)	20.370(5)	12.764(5)
<i>c</i> = (Å)	17.778(5)	18.173(5)	22.241(5)
<i>α</i> = (°)	90.0	90.0	90.0
<i>β</i> = (°)	90.0	101.546(5)	104.930(5)
<i>γ</i> = (°)	90.0	90.0	90.0
Volume (Å ³)	10752(5)	2775(2)	5479(3)
<i>Z</i>	4	4	8
Density (calculated) (Mg/m ³)	1.175	1.502	1.957
Absorption coefficient (mm ⁻¹)	0.391	0.714	0.815
<i>F</i> (000)	4032	1280	3136
Crystal size (mm ³)	0.30 x 0.28 x 0.21	0.22 x 0.13 x 0.13	0.24 x 0.08 x 0.08
Theta range for data collection (°)/ completeness for collection (%)	1.17 to 28.29/99.8	2.72 to 28.28/99.8	1.90 to 28.0/99.6
Index ranges	-45<= <i>h</i> <=46, -20<= <i>k</i> <=23, -23<= <i>l</i> <=23	-9<= <i>h</i> <=10, -7<= <i>k</i> <=27, -9<= <i>l</i> <=24	-26<= <i>h</i> <=13, -16<= <i>k</i> <=16, -6<= <i>l</i> <=29
Reflections collected	86538	15688	18540
Independent reflections	13332 [<i>R</i> (int) = 0.0426]	6869 [<i>R</i> (int) = 0.0463]	6595 [<i>R</i> (int) = 0.0639]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9223 and 0.8916	0.9129 and 0.8587	0.9377 and 0.8284
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	13332/6/600	6869/0/355	6595/0/433
Goodness-of-fit on <i>F</i> ²	1.069	1.019	0.937
Final <i>R</i> indices [<i>I</i> >2sigma(<i>I</i>)]	<i>R</i> 1 = 0.0389, w <i>R</i> 2 = 0.1163	<i>R</i> 1 = 0.0418, w <i>R</i> 2 = 0.0802	<i>R</i> 1 = 0.0386, w <i>R</i> 2 = 0.0668
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0524, w <i>R</i> 2 = 0.1295	<i>R</i> 1 = 0.0758, w <i>R</i> 2 = 0.0942	<i>R</i> 1 = 0.0935, w <i>R</i> 2 = 0.0791
Largest diff. peak and hole (e.Å ⁻³)	1.142 and -0.484	0.545 and -0.974	0.385 and -0.443

Table 7.2 General crystal data for the complexes, [Rh(ox)(CO)(PCy₃)], [Rh(ox)(CO)(PCyPh₂)] and [Rh(ox)(CO)(PPh₃)].

Identification code	[Rh(ox)(CO)(PCy ₃)]	[Rh(ox)(CO)(PCyPh ₂)]	[Rh(ox)(CO)(PPh ₃)]
Empirical formula	C28 H39 N O2 P Rh	C28 H27 N O2 P Rh	C56 H42 N2 O4 P2 Rh2
Formula weight	555.48	543.39	1074.68
Collection temperature (K)	100(2)	293(2)	100(2)
Crystal system, space group	Monoclinic, C2/c	Monoclinic, P2 ₁ /n	Triclinic; P $\bar{1}$
Unit cell dimensions			
<i>a</i> = (Å)	18.391(5)	10.559(2)	9.927(5)
<i>b</i> = (Å)	8.018(5)	13.296(3)	14.899(5)
<i>c</i> = (Å)	35.458(5)	17.658(4)	16.942(5)
<i>a</i> = (°).	90.0	90.0	78.340(5)
<i>β</i> = (°).	102.388(5)	90.99(3)	84.842(5)
<i>γ</i> = (°)	90.0	90.0	76.043(5)
Volume (Å ³)	5107(4)	2478.7(9)	2379.4(16)
<i>Z</i>	8	4	2
Density (calculated) (Mg/m ³)	1.445	1.456	1.500
Absorption coefficient (mm ⁻¹)	0.757	0.778	0.810
<i>F</i> (000)	2320	1112	1088
Crystal size (mm ³)	0.77 x 0.47 x 0.16	0.20 x 0.18 x 0.14	0.068 x 0.038 x 0.025
Theta range for data collection (°)/ completeness for collection (%)	1.18 to 25.0/95.9	1.92 to 28.0/99.9	1.43 to 25.0/95.0
Index ranges	-21<= <i>h</i> <=21, -8<= <i>k</i> <=9, -40<= <i>l</i> <=36	-13<= <i>h</i> <=13, -16<= <i>k</i> <=17, -14<= <i>l</i> <=23	-9<= <i>h</i> <=11, -11<= <i>k</i> <=17, -19<= <i>l</i> <=20
Reflections collected	11919	16521	10318
Independent reflections	4298 [R(int) = 0.0473]	5979 [R(int) = 0.0425]	7970 [R(int) = 0.0752]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.8885 and 0.5934	0.8988 and 0.8599	0.9800 and 0.9470
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	4298/0/238	5979/0/299	7970/199/335
Goodness-of-fit on <i>F</i> ²	1.126	0.998	0.718
Final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> 1 = 0.0693, <i>wR</i> 2 = 0.1740	<i>R</i> 1 = 0.0357, <i>wR</i> 2 = 0.0722	<i>R</i> 1 = 0.0607, <i>wR</i> 2 = 0.0872
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0864, <i>wR</i> 2 = 0.1988	<i>R</i> 1 = 0.0714, <i>wR</i> 2 = 0.0833	<i>R</i> 1 = 0.1547, <i>wR</i> 2 = 0.1107
Largest diff. peak and hole (e.Å ⁻³)	1.876 and -1.995	0.461 and -0.363	0.843 and -0.994

***7.3 Crystal structure of
Carbonyl[tris(2,4-di-tert-butylphenyl)phosphite]
(8-hydroxyquinolinato)rhodium(I),
[Rh(ox)(CO)(P(O-2,4di^tBuPh)₃)]⁹⁵***

7.3.1 Results and Discussion

(Supplementary data D1)

The compound [Rh(C₉H₆NO)(CO){P(OC₁₄H₂₁)₃}] crystallized in the orthorhombic space group *Pccn* (*Z*=8) with a solvent molecule incorporated in the crystal lattice, found to be disordered over two positions. The general atom numbering scheme is illustrated in Figure 7.1 and the most important bond distances and angles are reported in Table 7.3. The fused ring system of the bidentate ligand is bending slightly, with a r.m.s. deviation from planarity of 0.0263 Å and a dihedral angle of 3.4(1)° between the two aromatic rings. Further distortion is observed between the bidentate oxinate backbone and the metal coordination plane, yielding a dihedral angle of 7.09(8)°. The N...O bite distance is 2.668(1) Å, the C8-O4 bond distance is 1.322(3) Å and the endocyclic angle at C7-C8-C9 = 117.4(2)°. In the five membered chelate ring, the oxinate ligand has a small bite angle of 81.00(8)° and a C10-Rh-P bond angle of 89.88(7)°, which illustrates the distorted square-planar metal coordination polyhedron. The rhodium atom lies in a general position and is slightly displaced out of the coordination plane by 0.043(1) Å (r.m.s. displacement of fitted atoms = 0.005 Å). The carbonyl ligand is almost linear with a Rh-C10-O5 angle of 177.0(2)°. The significant steric demand of the tris(2,4-di-tert-butylphenyl)phosphite ligand, in the solid state, was determined to be 192°, by calculating the effective cone angle (θ_E), using the actual Rh-P bond distance as described previously⁹⁶.

⁹⁵ Janse van Rensburg, J. M., Roodt, A. & Muller, A. (2006). *Acta Cryst.* E62, m2978.

⁹⁶ Otto, S., Roodt, A. & Smith, J. (2000). *Inorg. Chim. Acta.* 303, 295

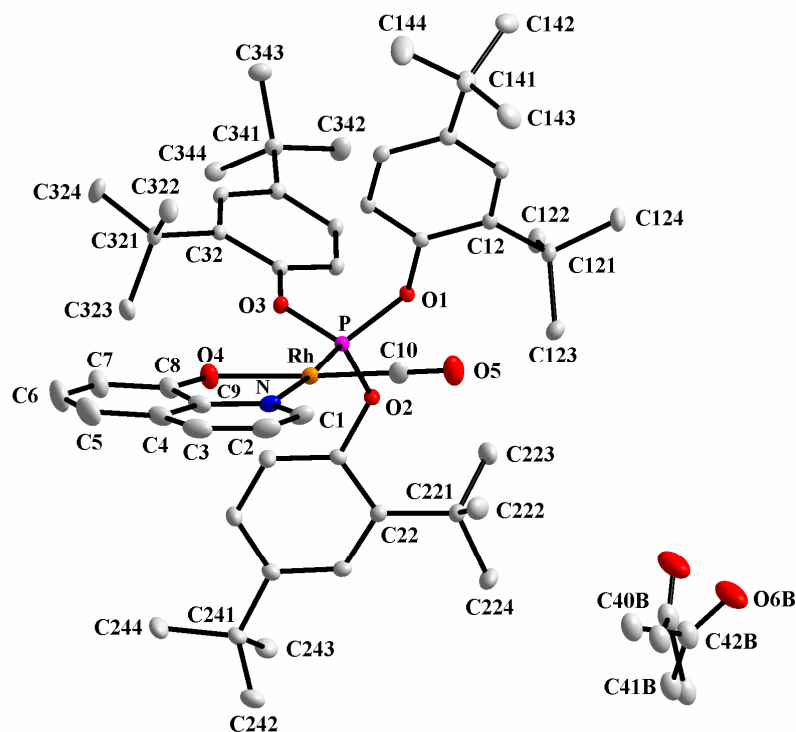


Figure 7.1 Diamond drawing of Carbonyl[tris(2,4-di-tert-butylphenyl)phosphite](8-hydroxyquinolinato)rhodium(I), acetone solvate, $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3)]$, in the asymmetric unit, showing the atom numbering scheme of the system, hydrogen atom labels are omitted for clarity. For the phenyl C-atoms, the first digit indicates ring number and the second digit the position of the atom in the ring.

Table 7.3 Selected bond distances and angles ($\text{\AA}$, $^\circ$) for the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3)]$.

Atoms	Distance ($\text{\AA}$)	Atoms	Angle ($^\circ$)
Rh-O4	2.023(2)	O4-Rh-N _(Bite angle)	81.00(8)
Rh-N	2.084(2)	N-Rh-C10	95.37(9)
Rh-P	2.182(1)	C10-Rh-P	89.88(7)
Rh-C10	1.818(3)	P-Rh-O4	93.64(5)
P-O1	1.604(2)	Rh-C10-O5	177.0(2)
P-O2	1.603(2)	C1-N-C9	119.3(2)
P-O3	1.597(2)	N-C9-C8	115.9(2)
C8-O4	1.322(3)	C9-C8-C7	117.4(2)
N...O(Bite distance)	2.668(1)		

The molecular packing is stabilized by two distinctive packing modes between neighboring molecules. One of these intermolecular interactions is the familiar quinoline ligand to ligand π -stacking, the second is the formation of intermolecular soft contacts between the quinoline ligand of one molecule and the aryl substituted rings of a phosphorous ligand. The quinoline ligand to ligand π -stacking is in a “head to tail” mode with an inter-planar distance of 3.271(1) $\text{\AA}$ (Figure 7.2). Other soft contacts, present between these molecules are C...H contacts with distances of 2.782(2) $\text{\AA}$ and 2.812(2) $\text{\AA}$ as illustrated in Figure 7.2.

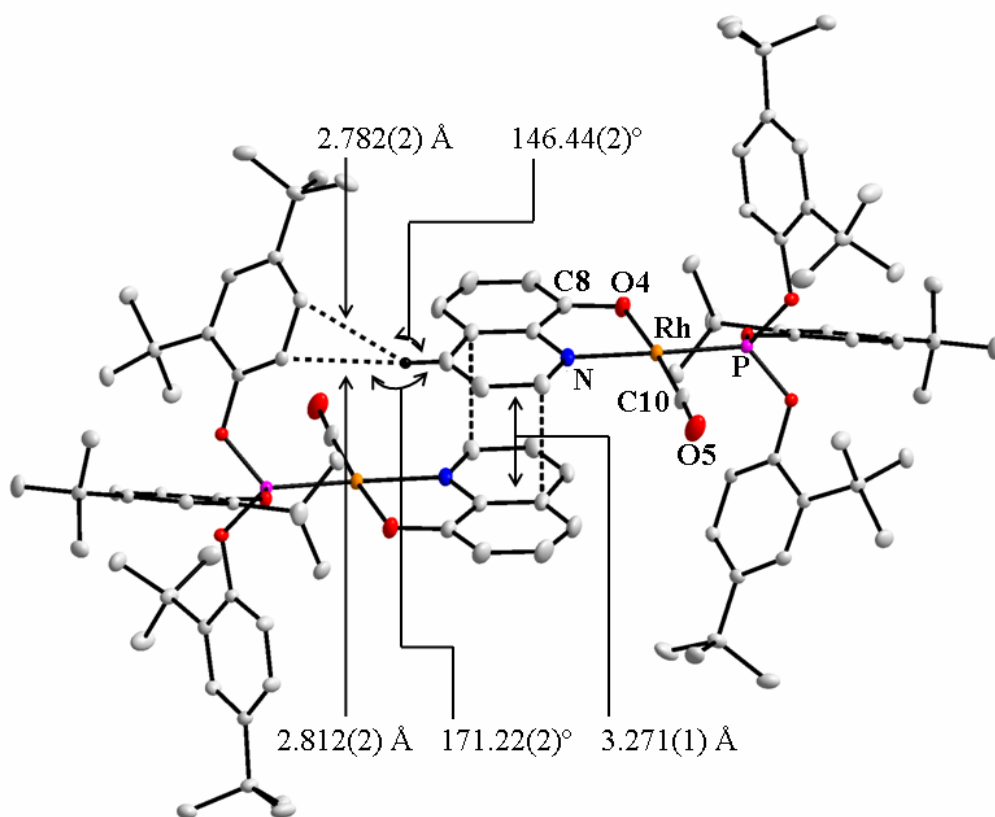


Figure 7.2 An illustration of the ligand to ligand π -stacking in a “head to tail” mode as found in the crystal packing of the complex, $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3)]$, with an inter planar distance of 3.271(1) Å. Also indicated are the C...H stabilizing soft contacts. Hydrogen atoms were omitted for clarity.

The configuration of one of the *para*-tertiarybutyl moieties takes place in such a way that an intermolecular soft contact is present between this moiety and the quinolinato ligand of the next molecule. These C...C soft contacts range from 2.825 – 3.005 Å and 125.85 – 148.59°, as presented in Figure 7.3.

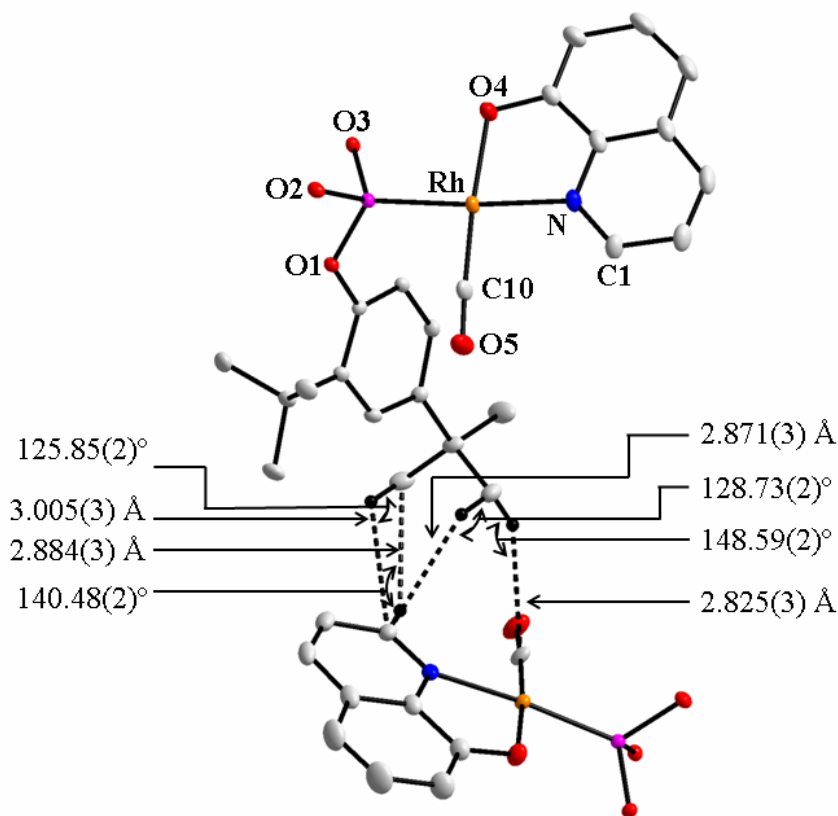


Figure 7.3 An illustration of the aroyl ligands tertiary butyl group to quinolinato ligand stabilizing C...C soft contacts. As found in the crystal packing of the complex, $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3)]$. Only interacting molecular fragments are shown.

A comparison between geometrical parameters and molecular packing modes of the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3)]$ to relative structures are discussed and presented in Sections 7.9 and 8.7.

7.4 Crystal structure of Carbonyl- [tris(2-methylphenyl)phosphite] (8-hydroxyquinolinato)rhodium(I), [Rh(ox)(CO)(P(O-2MePh)₃)]⁹⁷

7.4.1 Results and Discussion

(Supplementary data D2)

The compound $[\text{Rh}(\text{C}_9\text{H}_6\text{NO})(\text{CO})\{\text{P}(\text{OC}_7\text{H}_7)_3\}]$, crystallized in the monoclinic space group $P2_1/c$, ($Z=4$). In Figure 7.4 a diamond drawing of a $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2\text{MePh})_3)]$ molecule is presented with thermal ellipsoids at a 30% probability level. The fused ring system of the 8-hydroxyquinolinato

⁹⁷ Janse van Rensburg, J. M., Roodt, A., Muller, A. & Meijboom. R. (2005). *Acta Cryst.* E61, m2743.

ligand is almost planar, with a r.m.s. deviation from planarity of 0.0055 Å and a dihedral angle of 0.7(2)° between the two aromatic rings. A slight distortion is observed between the bidentate oxinate backbone and the metal coordination plane, yielding a dihedral angle of 1.07(15)°. In the five member chelate ring, the oxinate ligand has a small bite angle of 81.27(11)° and a C10-Rh-P bond angle of 91.21(12)°, this illustrates the distorted square-planar metal coordination polyhedron. The rhodium atom lies in a general position and is slightly displaced out of the coordination plane by 0.014(1) Å (r.m.s. displacement of fitted atoms = 0.006 Å). The carbonyl ligand is almost linear with a Rh-C10-O5 angle of 177.5(3)°.

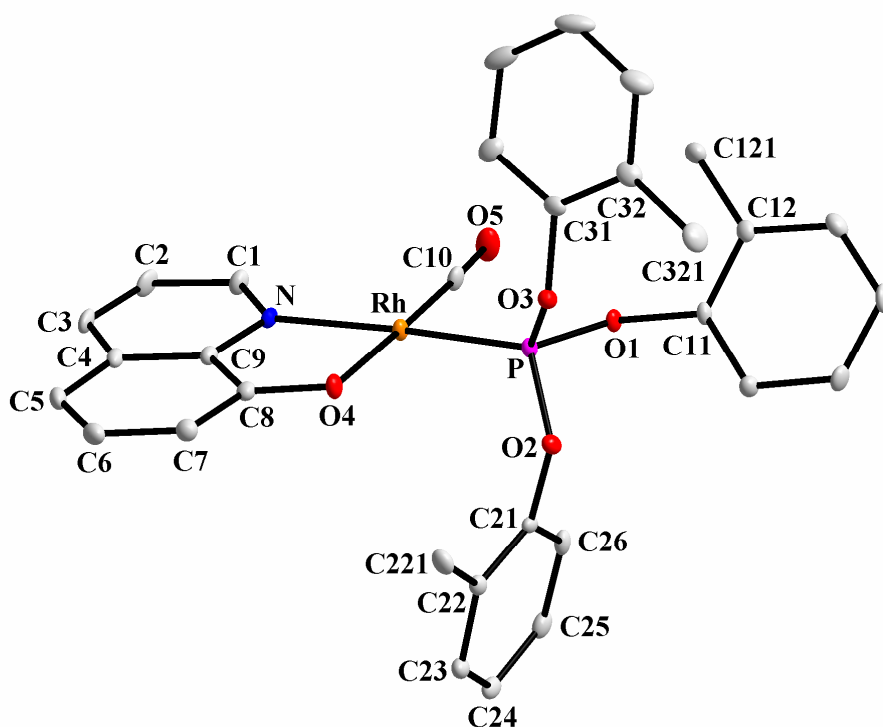


Figure 7.4 Diamond drawing of Carbonyl[tris(2-methylphenyl)phosphite] (8-hydroxyquinolinato)rhodium(I), [Rh(ox)(CO)(P(O-2MePh)₃)], in the asymmetric unit, showing the atom numbering scheme of the system, hydrogen atoms are omitted for clarity. For the phenyl C-atoms, the first digit indicates ring number and the second digit the position of the atom in the ring.

The significant steric demand of the tris(2-methylphenyl)phosphite ligand (in the solid state) was determined to be 168°, by calculating the effective cone angle (θ_E), using the actual Rh-P bond distance of 2.189(1) Å. Some of the important bond distances and angles are tabulated in Table 7.4.

Table 7.4 Selected bond distances and angles (Å, °) for the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2\text{MePh})_3)]$.

Atoms	Distance (Å)	Atoms	Angle (°)
Rh-O4	2.030(2)	O4-Rh-N _(Bite angle)	81.27(11)
Rh-N	2.086(2)	N-Rh-C10	96.78(12)
Rh-P	2.189(1)	C10-Rh-P	91.21(12)
Rh-C10	1.810(4)	P-Rh-O4	91.05(6)
P-O1	1.596(2)	Rh-C10-O5	177.5(3)
P-O2	1.603(2)	C1-N-C9	119.0(3)
P-O3	1.611(2)	N-C9-C8	116.0(3)
C8-O4	1.326(4)	C9-C8-C7	117.1(3)
N...O _(Bite distance)	2.678(3)		

The molecular packing exhibits a quinoline ligand to ligand π -stacking that is in a “head to tail” mode with an inter-planar distance of 3.459(1) Å, (Figure 7.5). The other stabilizing contacts in the π -stacked units are Rh...H contacts, 5.154(3) Å, and C...H contacts with C-H...C being 168.22(2)° and 147.58(2)° and C...H being 2.827(3) Å and 2.720(3) Å.

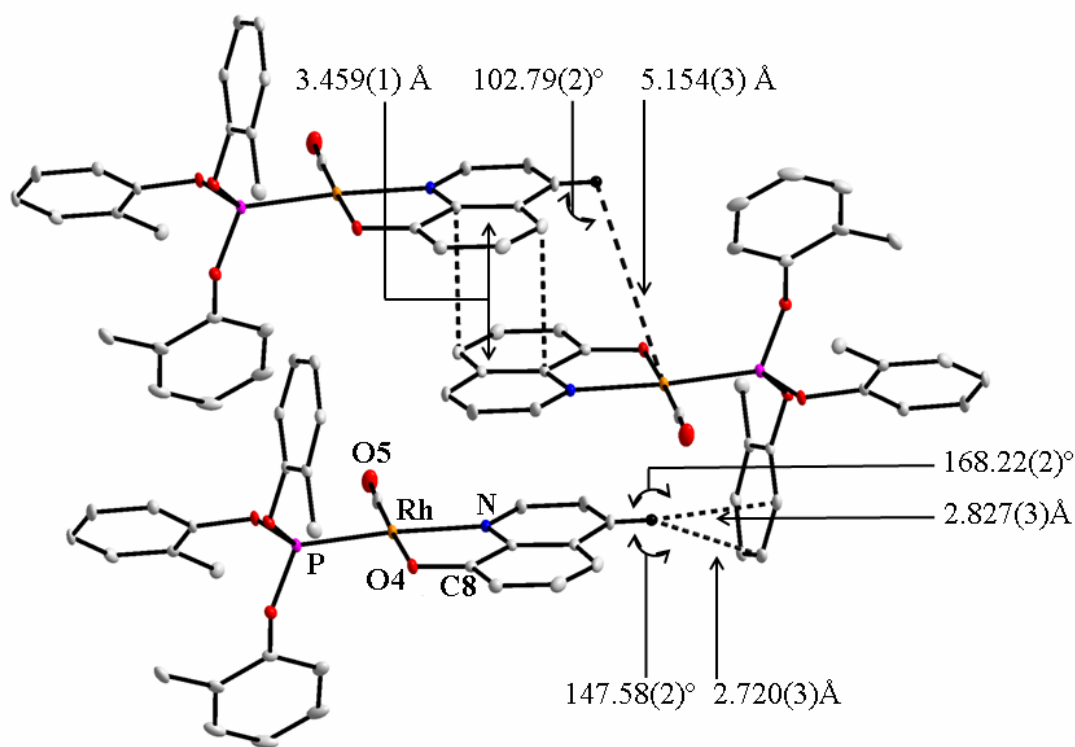


Figure 7.5 An illustration of the ligand to ligand π -stacking in a “head to tail” mode and intermolecular stabilizing soft contacts in the crystal packing of the complex, $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2\text{MePh})_3)]$.

A comparison between geometrical parameters and molecular packing modes of the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2\text{MePh})_3)]$, to relative structures is discussed and presented in Sections 7.9 and 8.7.

***7.5 Crystal structure of
Carbonyl[tris(pentafluorophenyl)phosphine]
 (8-hydroxyquinolato)rhodium(I),
 [Rh(ox)(CO)(P(5FPh)₃)]⁹⁸***

7.5.1 Results and Discussion

(Supplementary data D3)

The compound [Rh(C₉H₆NO)(CO){P(C₆F₅)₃}] crystallized in the monoclinic space group *C2/c* (*Z*=8). In Figure 7.6 is a diamond drawing of a [Rh(ox)(CO)(P(5FPh)₃)] molecule is presented with the system numbering. The fused ring system of the bidentate ligand is bending slightly, with a r.m.s. deviation from planarity of 0.0137 Å and a dihedral angle of 1.4(1)° between the two aromatic rings of the oxinate ligand, indicating a slight distortion in the ligand backbone. Further distortion is observed between the bidentate oxinate backbone and the metal coordination plane, yielding a dihedral angle of 3.2(1)°. In the five member chelate ring, the oxinate ligand has a small bite angle of 80.77(10)° and a C10-Rh-P bond angle of 90.89(11)°, which illustrates the distorted square-planar metal coordination polyhedron. The rhodium atom lies in a general position, slightly displaced out of the coordination plane by 0.032 (1) Å (r.m.s. displacement of fitted atoms = 0.034). The carbonyl ligand is almost linear with a Rh-C10-O5 angle of 179.2(4)°.

⁹⁸ Janse van Rensburg, J. M. & Roodt, A. (2006). *Acta Cryst.* E62, m2981.

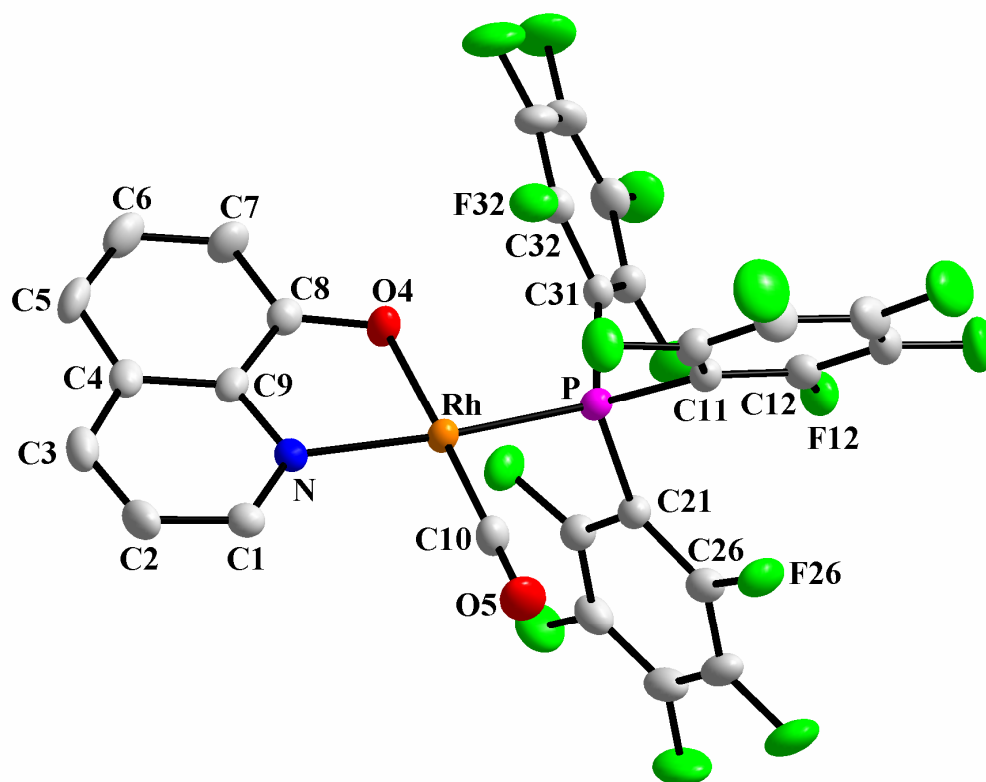


Figure 7.6 7 Diamond drawing of Carbonyl[tris(pentafluorophenyl)phosphine](8-hydroxyquinolinato)rhodium(I), $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{5FPh})_3)]$, showing the atom numbering scheme of the system, hydrogen atoms are omitted for clarity. For the phenyl C-atoms, the first digit indicates ring number and the second digit the position of the atom in the ring. The F-atoms are numbered according to the parent carbon atom.

The significant steric demand of the tris(penta-fluorophenyl)phosphine ligand (in the solid state) was determined to be 163° , by calculating the effective cone angle (θ_E), using the actual Rh-P bond distance of $2.2145(11) \text{ \AA}$. The most important bond distances and angles are reported in Table 7.5.

Table 7.5 Selected bond distances and angles ($\text{\AA}$, $^\circ$) for the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{5FPh})_3)]$.

Atoms	Distance ($\text{\AA}$)	Atoms	Angle ($^\circ$)
Rh-O4	2.018(2)	O4-Rh-N _(Bite angle)	80.77(10)
Rh-N	2.077(3)	N-Rh-C10	97.53(13)
Rh-P	2.2145(11)	C10-Rh-P	90.89(11)
Rh-C10	1.817(4)	P-Rh-O4	90.82(7)
C8-O4	1.320(4)	Rh-C10-O5	179.2(4)
N...O _(Bite distance)	2.653(4)	C1-N-C9	118.2(3)
		N-C9-C8	115.5(3)
		C9-C8-C7	117.2(3)

The molecular packing is stabilized by two distinctive packing modes between neighboring molecules on opposite sides. One is the quinoline ligand to ligand π -stacking and the other molecular soft contacts between the quinoline ligand of one molecule and the aryl substituted rings of a phosphorous ligand. The quinoline ligand to ligand π -stacking is in a “head to tail” mode with an inter-planar distance of 3.364(2) $\text{\AA}$, (Figure 7.8). Other stabilizing contacts are Rh...H contacts with Rh...H = 3.416(7) $\text{\AA}$ and Rh...H-C = 102.07(2) $^\circ$.

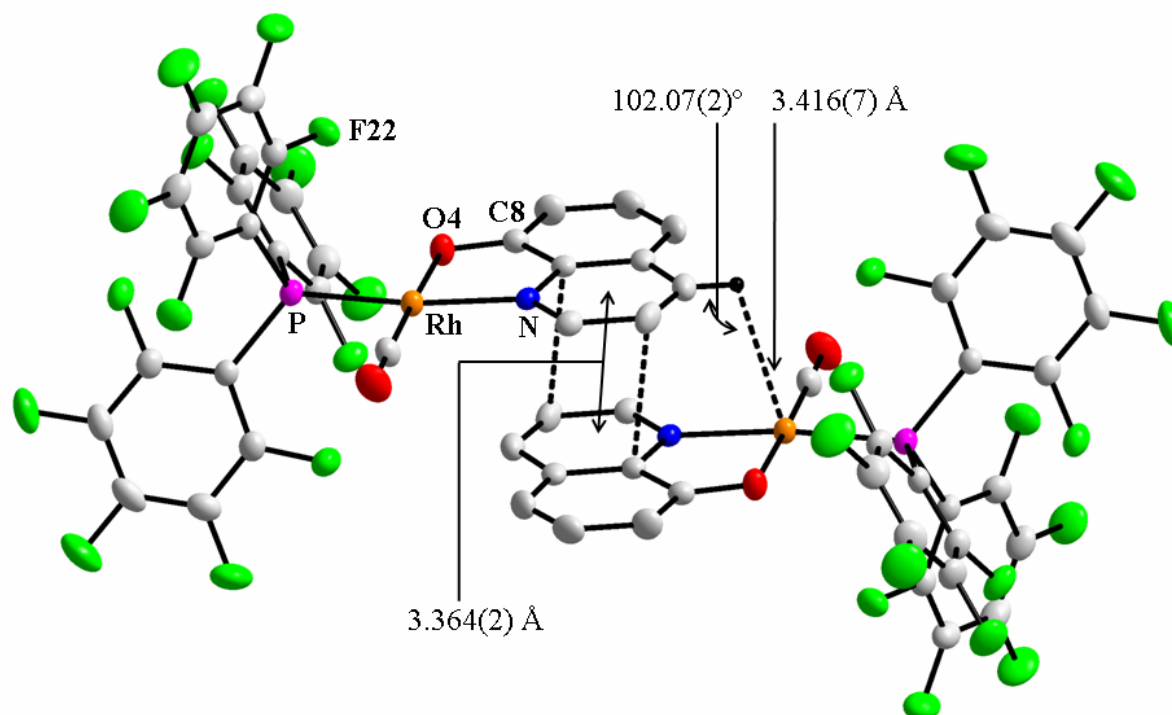


Figure 7.8 An illustration of the ligand to ligand π -stacking in a “head to tail” mode as found in the crystal packing of the complex, $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{5FPh})_3)]$, with an inter planar distance of 3.364(2) $\text{\AA}$. Hydrogen atoms were omitted for clarity.

Also present in the crystal packing are the soft contacts between the aryl substituted rings of the phosphorous ligand of one molecule and the quinoline ligand of the next. These are soft C...F contacts ranging from 3.013 – 3.103 Å and 140.08–146.54° and C...C soft contact = 3.859(6) Å (as shown in Figure 7.9).

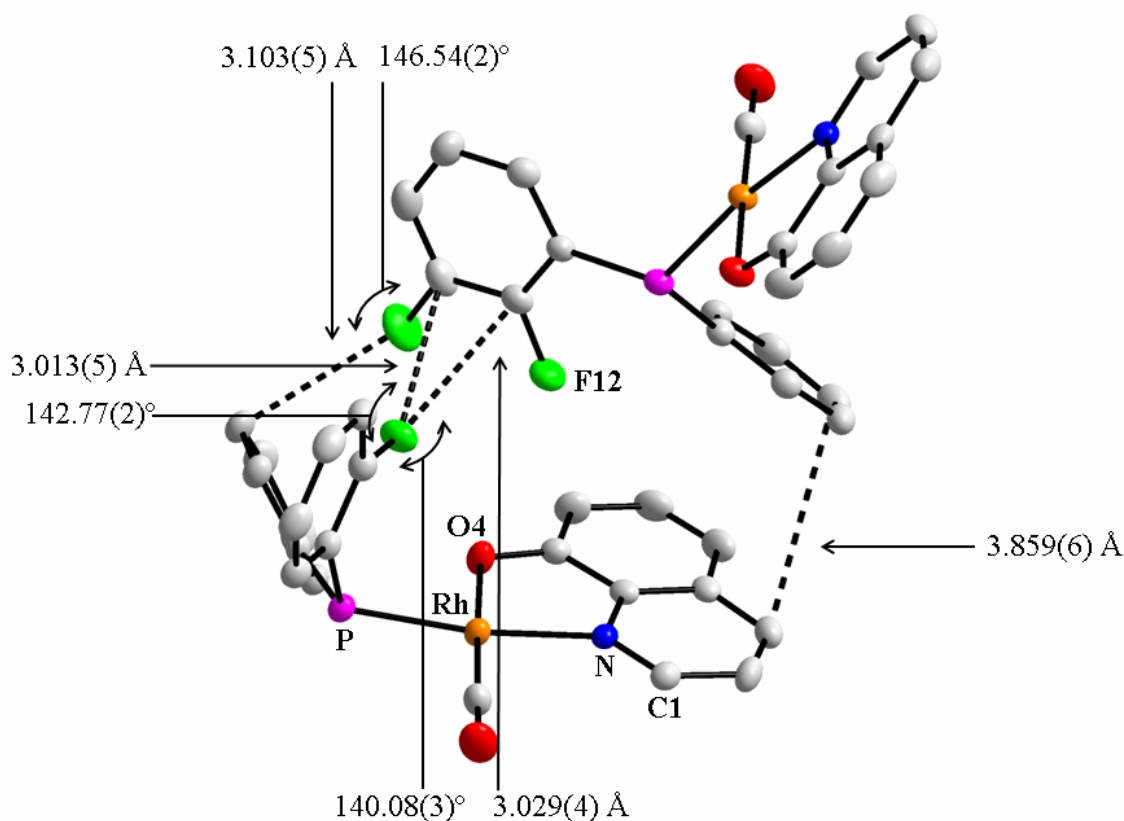


Figure 7.9 An illustration of the soft contacts between neighbouring molecules of the complex, $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{5FPh})_3)]$. Only interacting molecular fragments are shown and all hydrogen atoms were omitted for clarity.

A comparison between geometrical parameters and molecular packing modes of the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{5FPh})_3)]$ to relative structures is discussed and presented in Sections 7.9 and 8.7.

7.6 Crystal structure of Carbonyl[tricyclohexylphosphine] (8-hydroxyquinolinato)rhodium(I), $[\text{Rh}(\text{ox})(\text{CO})(\text{PCy}_3)]$

7.6.1 Results and Discussion

(Supplementary data D4)

The compound $[\text{Rh}(\text{C}_9\text{H}_6\text{NO})(\text{CO})\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$ crystallized with eight molecules in a unit cell ($Z=8$) in the monoclinic space group C2/c . In Figure 7.10 the general numbering scheme of the complex

$[\text{Rh}(\text{C}_9\text{H}_6\text{NO})(\text{CO})\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$ is presented and reported in Table 7.6 are the most important bond distances and angles. The fused ring system of the bidentate ligand is almost planar, with a r.m.s deviation between atoms C1-C9 and N of 0.0139 Å, this is further emphasized by the dihedral angle between the two aromatic rings of 1.54(31)°. The distorted square-planar metal coordination polyhedron is illustrated by the small oxinate ligand bite angle of 80.65(16)° and a C10-Rh-P bond angle of 90.89(18)°. The carbonyl ligand is almost linear with a Rh-C10-O2 angle of 176.5(5)°. A slight molecular bending is displayed by the dihedral angle of 7.18(10)° which formed between the fused ring system plane and the metal coordination plane. the rhodium metal centre is displaced 0.170(5) Å from the fused ring system plane and 0.0118(5) Å out of the metal coordination plane. By calculating the effective cone angle (θ_E) 167° and using the actual Rh-P bond distance of 2.256(2) Å the tricyclohexylphosphine ligands steric demand in the solid state, could be determined.

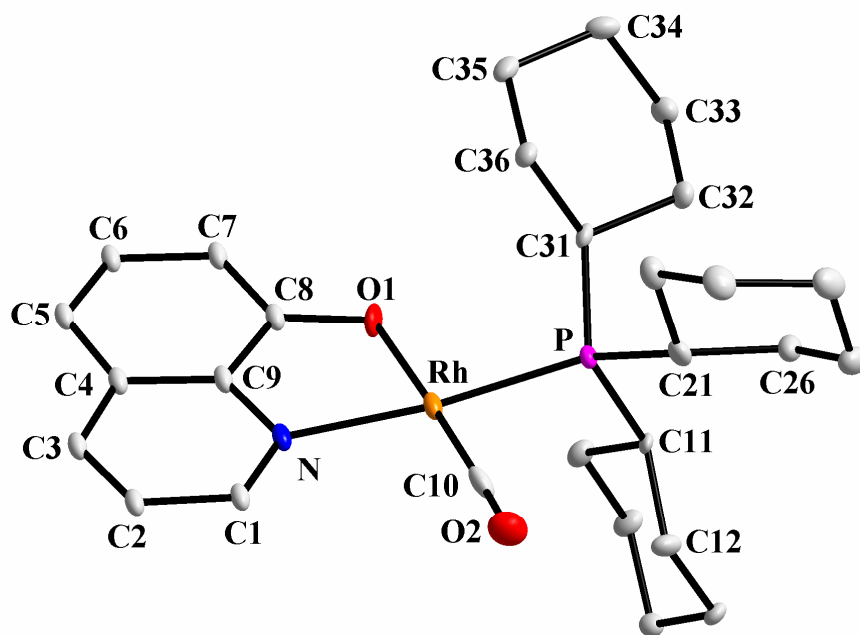


Figure 7.10 Diamond drawing of Carbonyl[tricyclohexylphosphine](8-hydroxyquinolinato)rhodium(I), $[\text{Rh}(\text{ox})(\text{CO})(\text{PCy}_3)]$, in the asymmetric unit, showing the atom numbering scheme of the system, hydrogen atoms are omitted for clarity. For the cyclohexyl C-atoms, the first digit indicates ring number and the second digit the position of the atom in the ring.

Table 7.6 Selected bond distances and angles (Å, °) for the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{PCy}_3)]$.

Atoms	Distance (Å)	Atoms	Angle (°)
Rh-O1	2.036(4)	O1-Rh-N _(Bite angle)	80.65(16)
Rh-N	2.091(4)	N-Rh-C10	97.3(2)
Rh-P	2.2557(15)	C10-Rh-P	90.89(18)
Rh-C10	1.817(6)	P-Rh-O1	91.14(11)
C8-O1	1.321(7)	Rh-C10-O2	176.5(5)
N...O _(Bite distance)	2.671(5)	C1-N-C9	119.9(5)
		N-C9-C8	116.0(5)
		C9-C8-C7	117.0(5)

The molecular crystal packing is stabilized by a ligand π - π stacking and soft contacts between the aryl substituted rings of the phosphorous ligand and the quinoline ligand of the next molecule. Presented in Figure 7.11 is the ligand π - π stacking in a “head to tail” mode with a stacking distance of 3.269(3) Å. Another soft contact present in this type of stacking mode is the Rh-H soft contact with a distance of 3.223(1) Å and a C3-H-Rh angle of 102.39°.

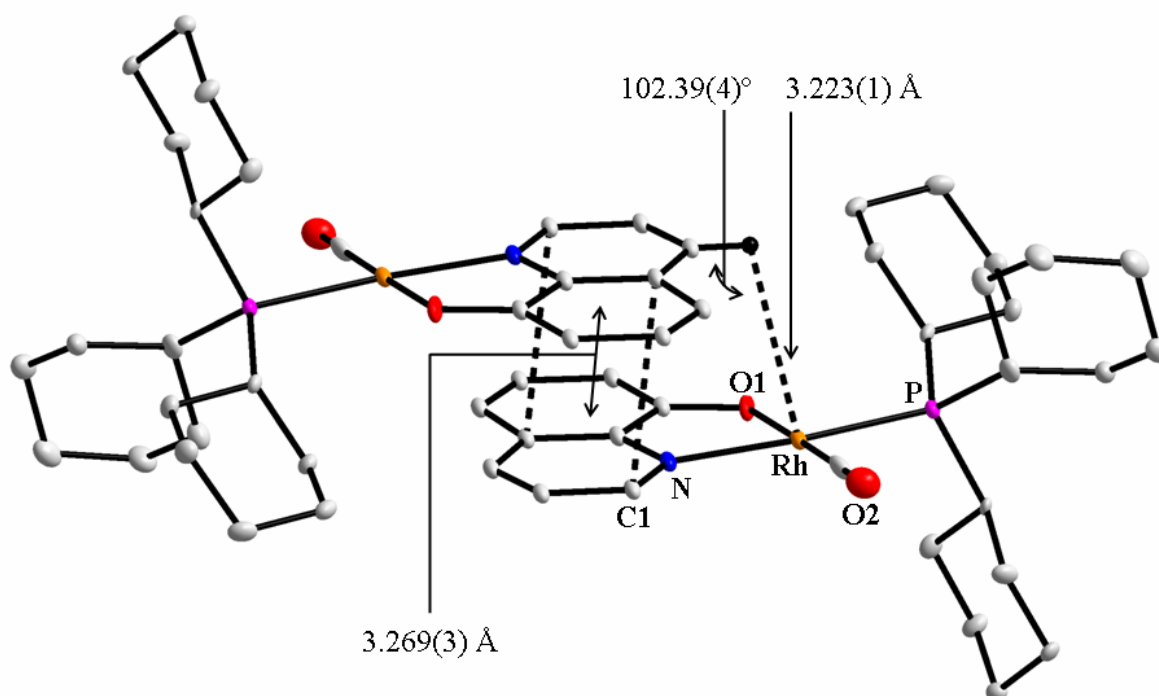


Figure 7.11 An illustration of the ligand to ligand π -stacking in a “head to tail” mode as found in the crystal packing of the complex, $[\text{Rh}(\text{ox})(\text{CO})(\text{PCy}_3)]$, with an inter planar distance of 3.269(3) Å. Also indicated is the Rh...H interaction. Other hydrogen atoms were omitted for clarity.

The mentioned aryl ring to quinoline ligand contacts are as indicated in Figure 7.12, with C...C soft contacts in the range of 2.8 Å and a C...O soft contact with a distance of 2.692(5) Å.

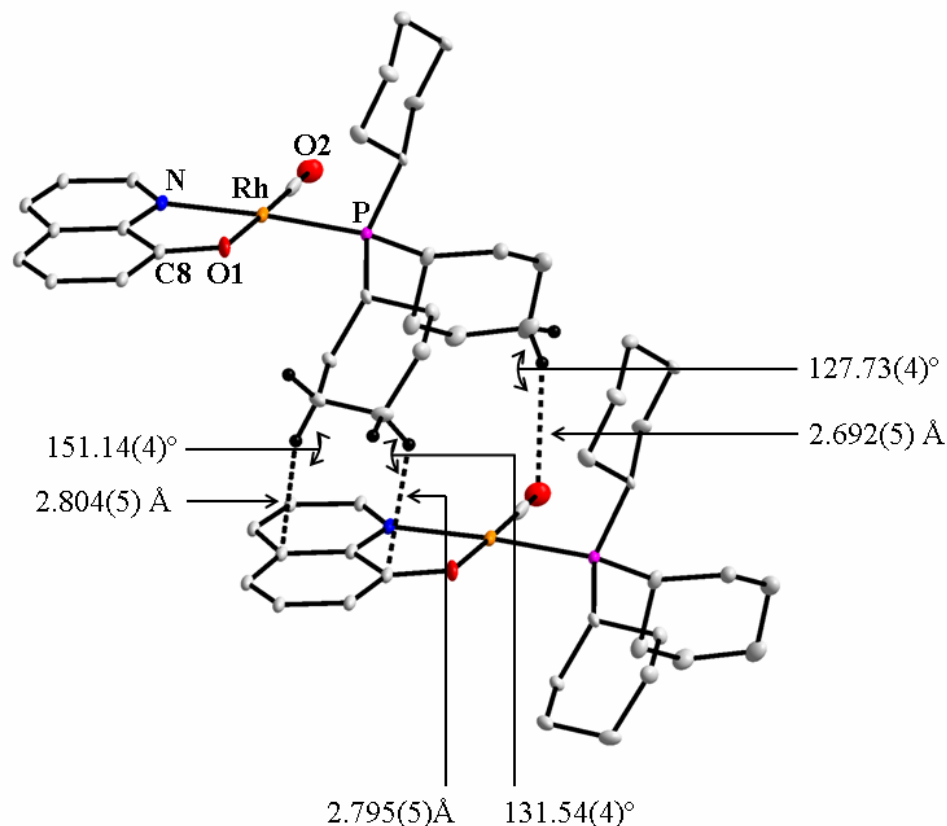


Figure 7.12 An illustration of the soft contacts found between the cyclohexyl ring C-atoms and quinolinato ligand atoms in the crystal packing of the complex, $[\text{Rh}(\text{ox})(\text{CO})(\text{PCy}_3)]$.

A comparison between the geometrical parameters and molecular packing modes of the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{PCy}_3)]$, to relative structures are discussed and presented in Sections 7.9 and 8.7.

7.7 Crystal structure of *Carbonyl(cyclohexyldiphenylphosphine)* *(8-hydroxyquinolinato)rhodium(I),* *$[\text{Rh}(\text{ox})(\text{CO})(\text{PCyPh}_2)]$* ⁹⁹

7.7.1 Results and Discussion

(Supplementary data D5)

The compound $[\text{Rh}(\text{C}_9\text{H}_6\text{NO})(\text{CO})\{\text{P}(\text{C}_6\text{H}_{11})(\text{C}_6\text{H}_5)_2\}]$ crystallized in the monoclinic space group $P2_1/n$, ($Z=4$). Figure 7.13 the general atom numbering used for the $[\text{Rh}(\text{ox})(\text{CO})(\text{PCyPh}_2)]$ molecules is presented. The fused ring system of the bidentate ligand is bending slightly, with a r.m.s. deviation

⁹⁹ Janse van Rensburg, J. M., Roodt, A. & Muller, A. (2006). *Acta Cryst.* E62, m1040.

from planarity of 0.0214 Å and a dihedral angle of 2.0(1)° between the two aromatic rings of the oxinate ligand, indicating a slight distortion in the ligand backbone. A further distortion is observed between the bidentate oxinate backbone and the metal coordination plane, yielding a dihedral angle of 11.3(1)°. In the five membered chelate ring, the oxinate ligand has a small bite angle of 79.41(9)° and a C10-Rh-P bond angle of 88.70(10)°, which illustrates the distorted square-planar metal coordination polyhedron. The rhodium atom lies in a general position and is slightly displaced out of the coordination plane by 0.062 (1) Å (r.m.s. displacement of fitted atoms = 0.098 Å). The carbonyl ligand is almost linear with an Rh-C10-O2 angle of 179.6(3)°.

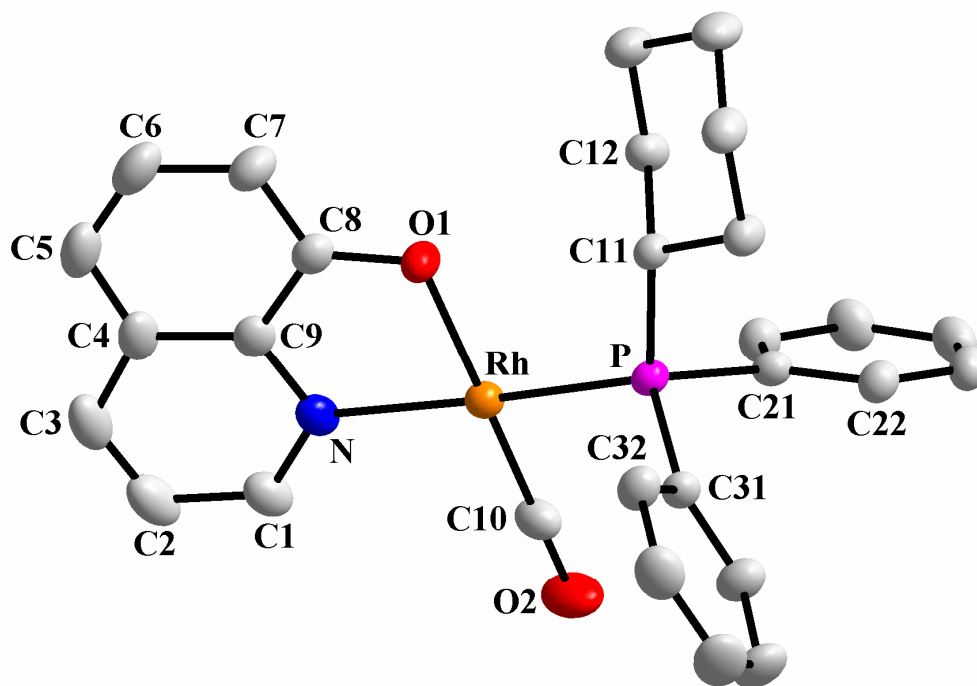


Figure 7.13 Diamond drawing of Carbonyl(cyclohexyldiphenylphosphine)(8-hydroxyquinolinato)rhodium(I), [Rh(ox)(CO)(PCyPh₂)], showing the atom labelling of the system, hydrogen atoms are omitted for clarity. For the cyclohexyl C-atoms, the first digit indicates ring number and the second digit the position of the atom in the ring.

The significant steric demand of the cyclohexyldiphenylphosphine ligand (in the solid state) was determined to be 151°. This was done by calculating the effective cone angle (θ_E) using the actual Rh-P bond distance of 2.2798(8) Å. The most important bond distances and angles are reported in Table 7.7.

Table 7.7 Selected bond distances and angles (Å, °) for the complex [Rh(ox)(CO)(PCyPh₂)].

Atoms	Distance (Å)	Atoms	Angle (°)
Rh-O1	2.060(2)	O1-Rh-N _(Bite angle)	79.41(9)
Rh-N	2.128(2)	N-Rh-C10	99.10(12)
Rh-P	2.2798(8)	C10-Rh-P	88.70(10)
Rh-C10	1.803(3)	P-Rh-O1	93.11(6)
C8-O1	1.328(3)	Rh-C10-O2	179.6(3)
N...O _(Bite distance)	2.676(3)	C1-N-C9	118.8(3)
		N-C9-C8	115.7(3)
		C9-C8-C7	117.5(3)

The molecules pack with the phenyl and cyclohexyl rings of the phosphine ligand directed towards the neighboring oxine ligand, forming an infinite stacking chain along the b-axis, see Figure 7.14 for the soft intermolecular contacts present in this stacking mode.

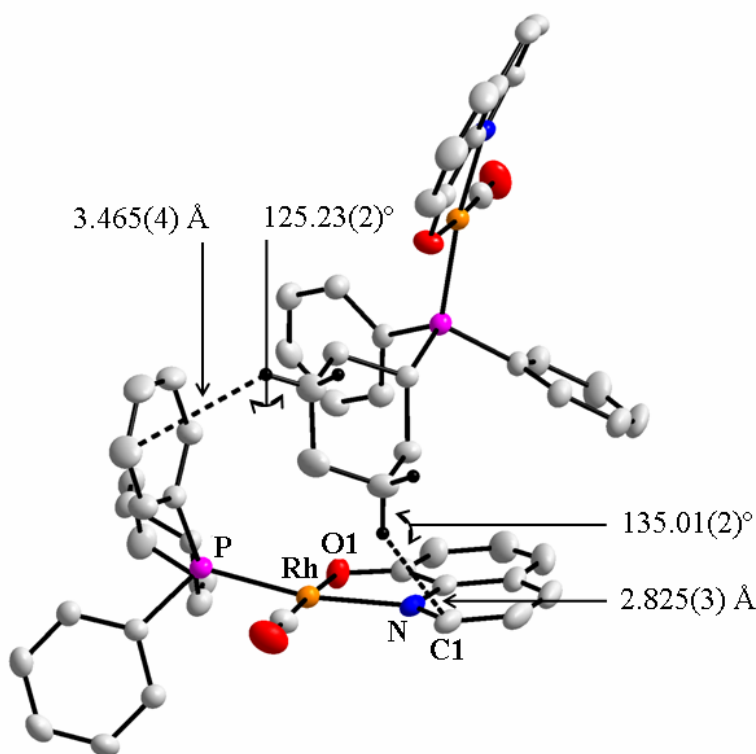


Figure 7.14 An illustration of the soft contacts found between the cyclohexyl and phenyl ring C-atoms of neighbouring molecules in the crystal packing of the complex, [Rh(ox)(CO)(PCyPh₂)].

A comparison between the geometrical parameters and molecular packing modes of the complex [Rh(ox)(CO)(PCyPh₂)] to relative structures is discussed and presented in Sections 7.9 and 8.7.

7.8 Crystal structure of Carbonyl[triphenylphosphine](8-hydroxyquinolinato)rhodium(I), [Rh(ox)(CO)(PPh₃)]

7.8.1 Results and Discussion

(Supplementary data D6)

The compound [Rh(C₉H₆NO)(CO){P(C₆H₅)₃}] crystallized with two independent molecules in the triclinic space group $P\bar{1}$ ($Z=2$), with a disordered toluene molecule incorporated as a solvent. The general numbering scheme is as indicated in Figure 7.15. Molecule **A** is indicative of the molecule where the rhodium centre is numbered Rh1, and so molecule **B** is indicative of the molecule where the rhodium centre is numbered Rh2.

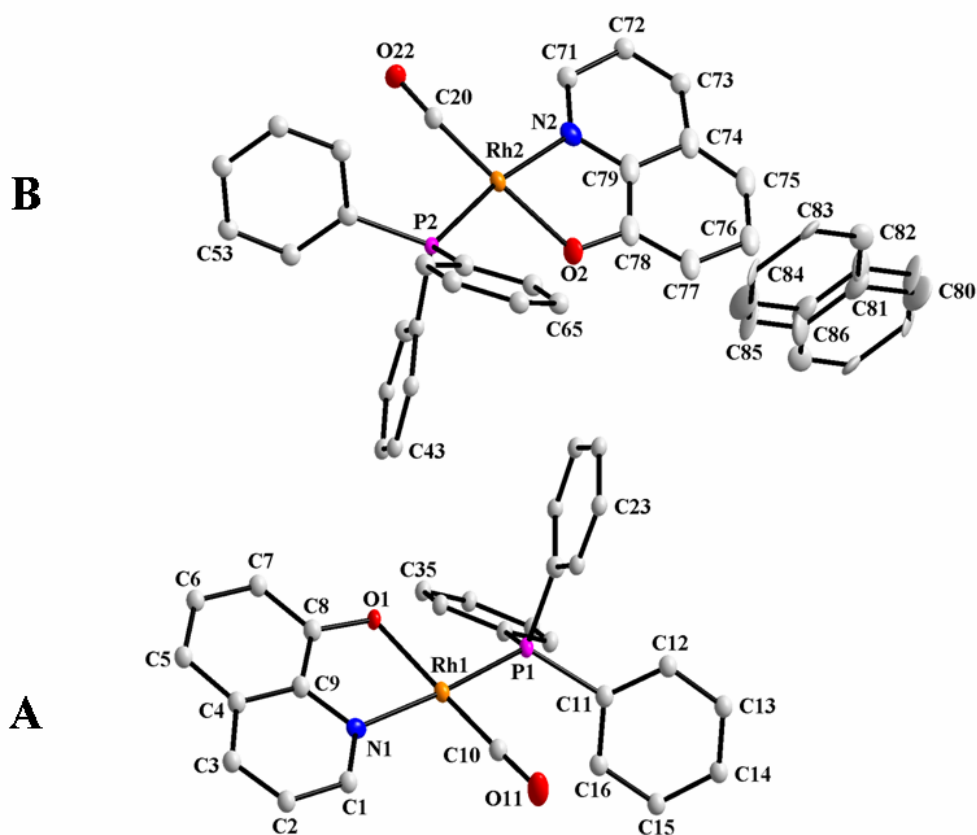


Figure 7.15 Diamond drawing of the two independent molecules of Carbonyl[triphenylphosphine](8-hydroxyquinolinato)rhodium(I), [Rh(ox)(CO)(PPh₃)], in the asymmetric unit, showing the atom numbering scheme of the system of molecules A and B. Hydrogen atoms are omitted for clarity. For the phenyl C-atoms, the first digit indicates ring number and the second digit the position of the atom in the ring

Tabulated in Table 7.8 are the general dihedral angles for each molecule as calculated for the fused ring system plane and the metal coordination plane. The fused ring systems in both molecules are fairly planar with r.m.s of fitted atoms (C1-C9 and N1) and (C71-C79 and N2) being 0.0118 and

0.0198 Å respectively. The dihedral angles between the benzene and pyridine rings of both molecules are *ca.* 1°. The molecular bending for both molecules is displayed by the dihedral angle between the fused ring system and the metal coordination plane, being 4.4(1) and 4.7(1)° respectively.

Table 7.8 Selected geometrical parameters, (Å, °), indicating disorder in the fused ring system and metal coordination plane of the complex [Rh(ox)(CO)(PPh₃)].

	Molecule A	Molecule B
The r.m.s. of fitted atoms (C1-C9 and N1)/(C71-C79 and N2)	0.0118 Å	0.0198 Å
Dihedral angle between the Benzene ring plane and the pyridine ring plane	0.8(4)°	1.1(4)°
Dihedral angle between the fused ring system and the metal coordination plane	4.4(1)°	4.7(1)°
Metal displacement from the metal coordination plane.	0.003(1) Å	0.002(1) Å

The selected bond distances and angles for both molecules **A** and **B** are mentioned in Table 7.9. The metal coordinating bond distances to O- and N-atoms are approximately 2 Å of which the metal carbonyl bond is the shorter coordinating bond, 1.7 and 1.8 Å, and the metal phosphorous bond the longest (in the 2.2 Å range). The distorted metal coordinating polyhedron is displayed by the small O-Rh-N bite angles $\pm 80^\circ$ and the other coordinating bond angles varying from an ideal 90° . The effective cone angles (θ_E), for molecules **A** and **B** were calculated to be 155.92° and 157.35° respectively, yielding an average effective cone angle of 156.64° and an indication of the ligand steric effect in the solid state.

Table 7.9 Selected bond distances and angles (Å, °) for independent molecules (A) and (B) of the complex [Rh(ox)(CO)(PPh₃)].

Molecule	A	Molecule	B
Atoms	Distance (Å)	Atoms	Distance (Å)
Rh1-O1	2.041(4)	Rh2-O2	2.038(4)
Rh1-N1	2.089(5)	Rh2-N2	2.079(5)
Rh1-P1	2.2459(18)	Rh2-P2	2.2557(18)
Rh1-C10	1.721(6)	Rh2-C20	1.806(6)
C8-O1	1.344(6)	C78-O2	1.324(7)
N1...O1_(Bite distance)	2.663(7)	N2...O2_(Bite distance)	2.668(7)
Atoms	Angle (°)	Atoms	Angle (°)
O1-Rh1-N1_(Bite angle)	80.25(17)	O2-Rh2-N2_(Bite angle)	80.78(19)
N1-Rh1-C10	97.1(2)	N2-Rh2-C20	95.9(2)
C10-Rh1-P1	88.8(2)	C20-Rh2-P2	93.4(2)
P1-Rh1-O1	94.07(12)	P2-Rh2-O2	89.85(13)
Rh1-C10-O11	176.7(5)	Rh2-C20-O22	175.4(5)
C1-N1-C9	118.6(5)	C71-N2-C79	119.7(6)
N1-C9-C8	115.9(5)	N2-C79-C78	117.0(6)
C9-C8-C7	118.3(5)	C79-C78-C77	117.2(6)

Ligand π - π stacking in a “head to tail” mode is present between molecules **A** and **B** and not between symmetrical equivalent molecules, separated by a distance of 3.358(5) Å, (Figure 7.16). Molecular packing also displays phosphine ligand “head to head” stacking, between symmetrically equivalent molecules as presented in Figure 7.17 and Figure 7.18. The phosphine ligand “head to head” soft contacts between molecules **A** are C...C soft contact with C...H distances in the range of 2.8 Å and C-H...C angles ranging from 137 to 145°. The phosphine ligand “head to head” arrangement between molecules **B** is also a C...C soft contact with a distance 2.791(6) Å and a C-H...C angle of 137.26(4)°.

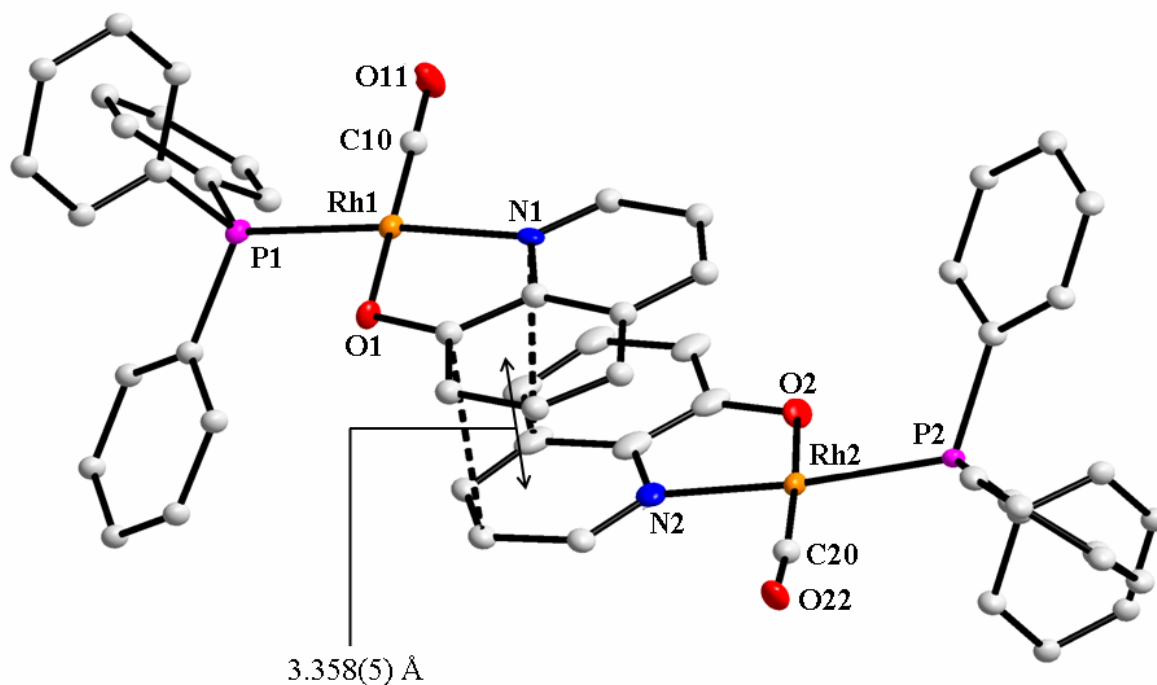


Figure 7.16 An illustration of the ligand to ligand π -stacking in a “head to tail” mode as found in the crystal packing of the complex, $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$, with an inter planar distance of 3.358(5) Å. Hydrogen atoms were omitted for clarity.

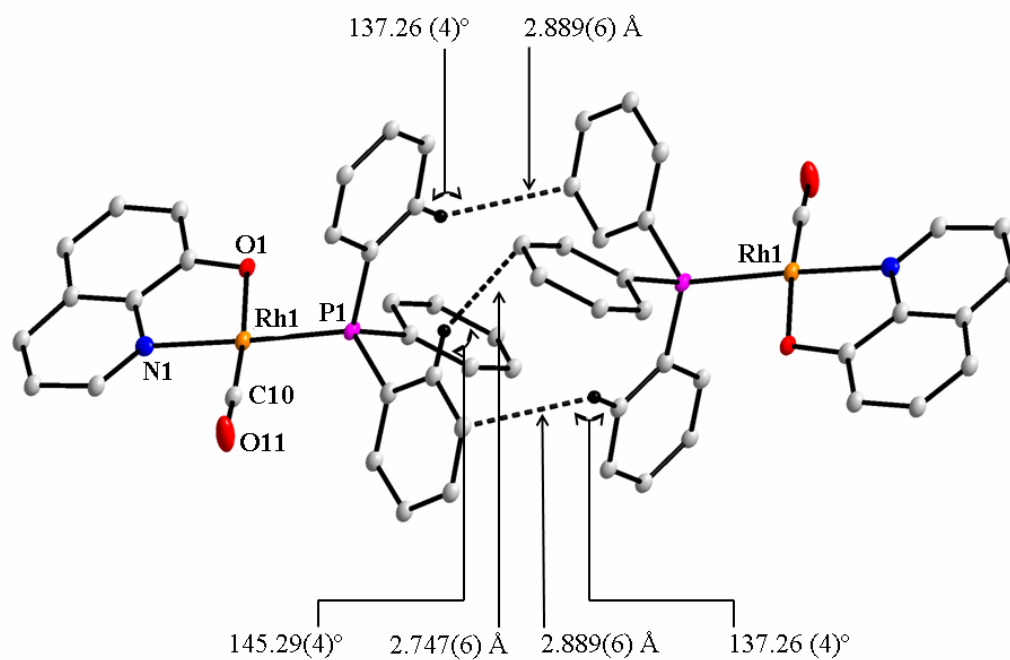


Figure 7.17 An illustration of the phosphine ligand to ligand stacking mode, “head to head”, between molecules (A) as found in the crystal packing of the complex, $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$.

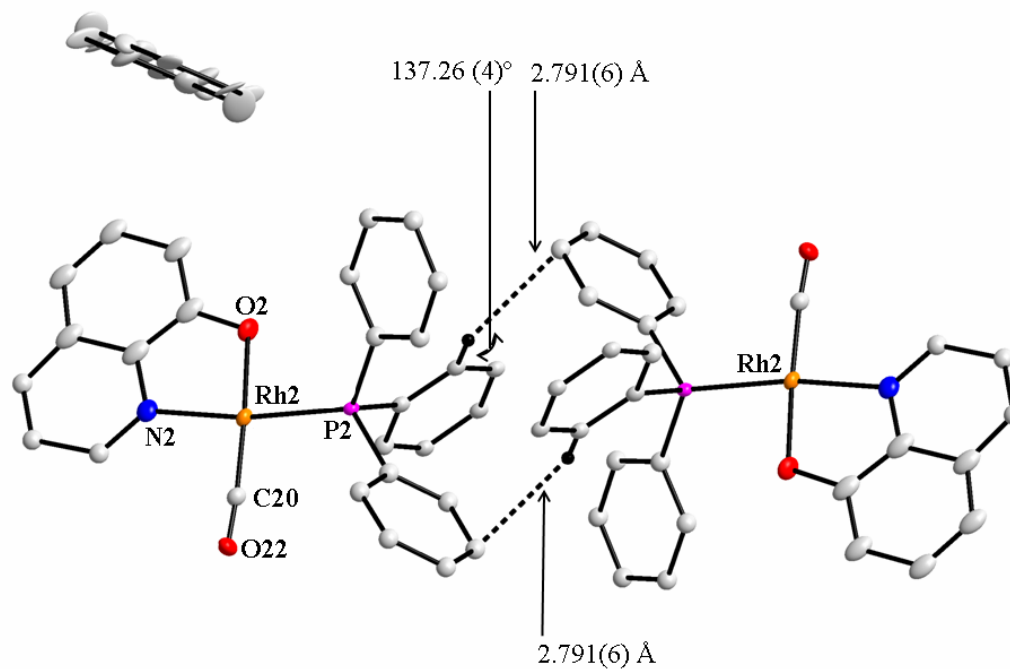


Figure 7.18 An illustration of the phosphine ligand to ligand stacking mode, “head to head”, between molecules (B) as found in the crystal packing of the complex, $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$.

A comparison between the geometrical parameters and molecular packing modes of the complex [Rh(ox)(CO)(PPh₃)] to relative structures is discussed and presented in Sections 7.9 and 8.7.

7.9 Correlation of structural parameters between 8-hydroxyquinoline neutral ligand systems and 8-hydroxyquinolinatorhodium(I) complexes

The structures presented in this chapter will be discussed in relation to each other and to other relevant structures from literature. Data for these complexes are summarized in Table 7.10. The current chapter reports the effects of phosphorous ligands on the 8-hydroxyquinolinatorhodium(I) system, focusing on the steric and electronic influences that these phosphorous ligands have on the metal centre. As mentioned in Chapter 2, by manipulating the electronic and steric parameters of a metal centre *via* different ligands, one can alter the selectivity and reactivity of a catalyst and so also in a catalytic cycle. With the solid state crystallographic data both from this chapter and literature as well as considering the various solid state cone angles, coordinating bond distances, several packing modes and intermolecular interactions, one can investigate the influence of steric and electronic differing phosphorous ligands.

8-Hydroxyquinolinorhodium(I) square planar complexes

Table 7.10 Comparative spectroscopic and crystallographic data for relevant 8-hydroxyquinolinorhodium(I) complexes.

	Rh-P (Å)	Rh-N (Å)	Rh-O (Å)	Rh-C (Å)	O-Rh-N (°)	θ_F (°)	π -stacking (Å)	$^1J_{\text{Rh-P}}$ (Hz)	ν_{CO} (cm ⁻¹)
PHOSPHITE COMPLEXES									
[Rh(ox)(CO)(P(O-2,4di ^t BuPh) ₃)] ⁹⁹	2.182(1)	2.084(2)	2.023(2)	1.818(3)	81.00(8)	192	3.271(1)	279	1986
[Rh(ox)(CO)(P(O-2,6dimePh) ₃)] ¹⁰⁰	2.198(1)	2.091(3)	2.029(3)	1.805(5)	80.3(1)	183	3.76(6)	280	1980
[Rh(ox)(CO)(P(O-2MePh) ₃)] ⁹⁷	2.189(1)	2.086(2)	2.030(2)	1.810(4)	81.27(11)	168	3.459(1)	278	1984
[Rh(ox)(CO)(P(OPh) ₃)] ¹⁰¹	2.186(1)	2.097(2)	2.022(2)		80.8	154		279	1991
PHOSPHINE COMPLEXES									
[Rh(ox)(CO)(P(SFPh) ₃)] ⁹⁸	2.215(1)	2.077(3)	2.018(2)	1.817(4)	80.77(10)	163	3.364(2)	177	1983
[Rh(ox)(CO)(PCy ₃)]	2.256(2)	2.091(4)	2.036(4)	1.817(6)	80.65(16)	167	3.269(3)	156	1946
[Rh(ox)(CO)(PCyPh ₂)] ⁹⁹	2.280(1)	2.128(2)	2.060(2)	1.803(3)	79.41(9)	151	---	163	1959
[Rh(ox)(CO)(PPh ₃)] (A)	2.246(2)	2.089(5)	2.041(4)	1.721(6)	80.25(17)	155	3.358(5)	164	1995
(B)	2.256(2)	2.079(5)	2.038(4)	1.806(6)	80.78(19)	157	3.358(5)	164	1995
[Rh(ox)(CO)(PPh ₃)] ¹⁰²	2.261(2)	2.098(9)	2.042(5)		80.0(3)	153		164	-
[Rh(ox)(CO)(I)(Me)(PPh ₃)] ¹⁰³	2.317(2)	2.084(7)	2.037(4)		81.2(2)	153		163	-

¹⁰⁰ Janse van Rensburg, J. M., Roodt, A., Muller, A. & Meijboom, R. (2005). *Acta Cryst.* E61, m1741.

¹⁰¹ Simanko, W., Meretier, K., Schmid, R., Kirchner, K., Trzeciak, A. M. & Ziolkowski, J. J. (2000). *J. Organomet. Chem.* 602, 59.

¹⁰² Leipoldt, J. G., Basson, S. S. & Dennis, C. R. (1981). *Inorg. Chim. Acta.* 50, 121.

¹⁰³ Van Aswegen, K. G., Leipoldt, J. G., Potgieter, I. M., Lamprecht, G. J., Roodt, A. & Van Zyl, G. J. (1991). *Transition Met. Chem.* 16, 369.

The shorter Rh-P bonds in the phosphite complexes are due to the phosphite being a weaker σ -donor but better π -acceptor than the phosphine ligand, leading to a stronger bond. This influence is also seen in the significant increase of ca. 120 Hz in coupling constants between phosphine and phosphite complexes. The comparable $^1J_{(\text{Rh-P})}$ values of the phosphite complexes are an indication that the methyl and tertiary butyl groups on the phenyl ring have negligible electronic influence on the P donor atom. Apart from the hexafluorophosphate and the tricyclohexylphosphine systems, the $^1J_{(\text{Rh-P})}$ values of the phosphine ligand systems illustrate small electronic differences. This is also manifested in the $\nu_{(\text{CO})}$ values, see Table 7.10. The net influence of the fluoro atoms result in a shorter Rh-P bond, also reflected in the increase of the $^1J_{(\text{Rh-P})}$ value. The additional Rh-P bond distance increase from the last entry in Table 7.10 is due to the change from Rh(I) to Rh(III) following CH_3I oxidative addition.

In general larger effective cone angles are observed for the phosphite complexes, indicating that the oxygen atom between the phosphorous atom and the substituted ring allows more ring movement. Considering the phosphite systems, the effect of various ring substituents on the steric parameter is clear with the cone angle ranging from 154° to 192° , while the difference between the phenyl and cyclohexyl rings systems of the phosphine ligands are not so prominent. It is to be remembered that intermolecular interaction might also influence ring orientation. In solution, ligand substituent orientation might also differ, as observed by Ferguson *et al.*¹⁰⁴, resulting in variation in cone angle size. Therefore, the solid state cone angle might not always necessarily be a true indication of the ligand steric properties as in solution.

As summarized in Table 7.1, these complexes crystallized in the orthorhombic, monoclinic or triclinic space groups. Except for the $[\text{Rh}(\text{ox})(\text{CO})(\text{PCyPh}_2)]$ complex, the molecular packing displays a ligand π - π stacking between the quinoline rings in such a way that the molecules stack in a “head to tail” mode with an average plane to plane distance of 3.4 Å.

¹⁰⁴ Ferguson, G., Roberts, P. J., Alyea, E. C. & Khan, M. (1978). *Inorg. Chem.* 17, 2965.

In order to note the geometrical difference between an 8-hydroxyquinoline ligand and a metal coordinated 8-hydroxyquinolinato ligand, selected data was noted in Table 7.11. Usually the N...O bite distance and the C-O_(hydroxyl bond) distance decreases with metal coordination, a possible effect of the higher electron density in the metal complex. The N-C9-C8 and the C7-C8-C9 endocyclic ring angles also decrease.

Table 7.11 Comparative data for relevant 8-hydroxyquinoline compounds (from literature and as reported in Chapter 4) and 8-hydroxyquinolinatorrhodium complexes (discussed in this chapter).

	N...O (Bite distance)	C8-O	N-C9-C8	C7-C8-C9
RHODIUM PHOSPHITE COMPLEXES				
[Rh(ox)(CO)(P(O-2,4di ^t BuPh) ₃)] ⁹⁵	2.668(1)	1.322(3)	115.9(2)	117.4(2)
[Rh(ox)(CO)(P(O-2MePh) ₃)] ⁹⁷	2.678(3)	1.326(4)	116.0(3)	117.1(3)
RHODIUM PHOSPHINE COMPLEXES				
[Rh(ox)(CO)(P(5FPh) ₃)] ⁹⁸	2.653(4)	1.320(4)	115.5(3)	117.2(3)
[Rh(ox)(CO)(PCy ₃)]	2.671(5)	1.321(7)	116.0(5)	117.0(5)
[Rh(ox)(CO)(PCyPh ₂)] ⁹⁹	2.676(3)	1.328(3)	115.7(3)	117.5(3)
[Rh(ox)(CO)(PPh ₃)] (A)	2.663(7)	1.344(6)	115.9(5)	118.3(5)
(B)	2.668(7)	1.324(7)	117.0(6)	117.2(6)
NEUTRAL QUINOLINE LIGANDS				
(Hox)*, ⁸⁸	2.753	1.347	118.16	119.89
(HoxCl)	2.765(6)	1.349(2)	117.5(2)	119.7(2)
(HoxNO ₂)	2.728(2)	1.337(2)	115.9(2)	120.2(2)
(HoxMeCl)	2.662(4)	1.344(4)	119.1(3)	118.6(3)

No e.s.d. data from CSD.

7.10 Conclusion

Chapter 7 reports the successful single crystal X-Ray characterization of six 8-hydroxyquinolinatorrhodium(I) complexes, substituted with a range of phosphite and phosphine ligands. Summarized in Table 7.10 are the geometrical and spectroscopic differences between these metal complexes, as a result of different phosphorous ligands. The largest differences are between the Rh-P bond distances and the effective cone angles of the phosphorous ligands.

The solid state study on functionalized 8-hydroxyquinoline ligands, Chapter 4, and the theoretical results presented in Chapter 5 it was established that functionalization on the 5th position of the oxine moiety influences the electron properties of the donor atoms. In order to determine the influence of a functionalized oxine moiety on a metal centre, 5-chloro-8-hydroxyquinoinerhodium(I) square planar complexes were synthesised and characterized *via* single crystal X-Ray diffraction, these results are reported in Chapter 8.

Chapter 8

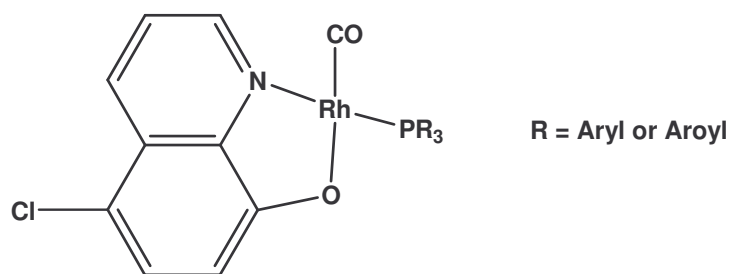
X-Ray crystallographic study of 5-chloro-8-hydroxyquinolinatorhodium(I) square planar complexes

8.1 Introduction

The following chapter discusses the solid state characterisation of selected 5-chloro-8-hydroxyquinolinatorhodium(I) complexes containing either a phosphine or a phosphite ligand, utilizing single crystal X-Ray diffraction. Attention is specifically focused on the effects of the 5-chloro moiety and the phosphorous ligand on the molecular geometry, intra/inter-molecular interaction and the molecular packing modes.

Various 5-chloro-8-hydroxyquinolinatorhodium(I) phosphine/phosphite complexes were prepared in order to investigate the electronic influence of the 5-chloro moiety on the metal complex and molecular packing. In chapter 4 and 5 it was noted that functionalization of the 8-hydroxyquinoline backbone does have an influence on the donor atoms. In Scheme 8.1 a line drawing is presented of typical 5-chloro-8-hydroxyquinolinatorhodium(I) complexes, as studied in this chapter, while identification codes for these complexes follow:

1. $[\text{Rh}(\text{C}_9\text{H}_6\text{NOCl})(\text{CO})\{\text{P}(\text{OC}_{10}\text{H}_{13})_3\}]/[\text{Rh}(\text{oxCl})(\text{CO})(\text{P}(\text{O}-4^t\text{BuPh})_3)]$
= Carbonyl[tris(4-tert-butylphenyl)phosphite](5-chloro-8-hydroxyquinolinato)rhodium(I).
2. $[\text{Rh}(\text{C}_9\text{H}_6\text{NOCl})(\text{CO})\{\text{P}(\text{OC}_{14}\text{H}_{21})_3\}]/[\text{Rh}(\text{oxCl})(\text{CO})(\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3)]$
= Carbonyl[tris(2,4-di-tert-butylphenyl)phosphite] (5-chloro-8-hydroxyquinolinato)rhodium(I).
3. $[\text{Rh}(\text{C}_9\text{H}_6\text{NOCl})(\text{CO})\{\text{P}(\text{ClC}_6\text{H}_4)_3\}]/[\text{Rh}(\text{oxCl})(\text{CO})(\text{P}(\text{p-ClPh})_3)]$
= Carbonyl[tris(para chloro phenyl)phosphine](5-chloro-8-hydroxyquinolinato)rhodium(I).
4. $[\text{Rh}(\text{C}_9\text{H}_6\text{NOCl})(\text{CO})\{\text{P}(\text{FC}_6\text{H}_4)_3\}]/[\text{Rh}(\text{oxCl})(\text{CO})(\text{P}(\text{p-FPh})_3)]$
= Carbonyl[tris(para fluoro phenyl)phosphine](5-chloro-8-hydroxyquinolinato)rhodium(I).



Scheme 8.1 Line drawing of typical 5-chloro-8-hydroxyquinolinorhodium(I) complexes.

8.2 *Experimental*

The reflection data for the following data sets was collected on a Bruker X8 Apex II 4K Kappa CCD diffractometer, using the Apex2 software package⁶³. The optimum measurement method to collect more than a hemisphere of reciprocal space was predicted by COSMO⁶⁴. Frame integration and data reduction was performed using the SAINT-Plus and XPREP⁶⁵ software packages. A multi-scan absorption correction was performed on the data using SADABS⁶⁶. The structures were solved by the direct methods package, SIR97⁶⁷. For refinement the WinGX⁶⁸ software package incorporating SHELXL⁶⁹ was used. All non-H atoms were refined anisotropically. H atoms were positioned geometrically and refined using a riding model with fixed C-H distances of 0.93 Å (CH) [Uiso(H) = 1.2Ueq]. Molecular diagrams were drawn using the DIAMOND⁷⁰ package with a 30% thermal envelope probability for non-hydrogen atoms.

General crystal data and refinement parameters are presented in Table 8.1. A complete list of atomic coordinates, equivalent isotopic parameters, bond distances and angles, anisotropic displacement parameters and hydrogen coordinates are given in Appendix E.

X-Ray crystallographic study of 5-chloro-8-hydroxyquinolinorhodium(I)

Table 8.1 General crystal data for the complexes, [Rh(oxCl)(CO)P(O-4'BuPh)₃], [Rh(oxCl)(CO)P(O-2,4di'BuPh)₃], [Rh(oxCl)(CO)P(p-ClPh)₃] and [Rh(oxCl)(CO)P(p-FPh)₃].

Identification code	[Rh(oxCl)(CO)P(O-4'BuPh) ₃]	[Rh(oxCl)(CO)P(O-2,4di'BuPh) ₃]	[Rh(oxCl)(CO)P(p-ClPh) ₃]	[Rh(oxCl)(CO)P(p-FPh) ₃]
Empirical formula	C40 H44 Cl N O5 P Rh	C52 H68 Cl N O5 P Rh	C28 H17 Cl4 N O2 P Rh	C28 H17 Cl F3 N O2 P Rh
Formula weight	788.09	956.40	675.11	625.76
Collection Temperature (K)	100(2)	100(2)	100(2)	100(2)
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Triclinic, <i>P</i> $\bar{1}$
Unit cell dimensions				
<i>a</i> = (Å)	11.612(5)	17.325(5)	9.558(5)	13.465(5)
<i>b</i> = (Å)	12.289(5)	16.103(5)	19.788(5)	14.055(5)
<i>c</i> = (Å)	14.022(5)	18.563(5)	14.608(5)	14.217(5)
<i>a</i> = (°).	74.959(5)	90.0	90.0	88.117(5)
<i>β</i> = (°).	75.559(5)	90.0(5)	103.670(5)	81.124(5)
<i>γ</i> = (°)	79.950(5)	90.0	90.0	74.812(5)
Volume (Å ³)	1858.4(13)	5179(3)	2684.6(18)	2565.4(16)
<i>Z</i>	2	4	4	4
Density (calculated) (Mg/m ³)	1.408	1.227	1.670	1.620
Absorption coefficient (mm ⁻¹)	0.619	0.456	1.122	0.881
<i>F</i> (000)	816	2016	1344	1248
Crystal size (mm ³)	0.12 x 0.08 x 0.06	0.27 x 0.14 x 0.06	0.12 x 0.08 x 0.06	0.04 x 0.06 x 0.33
Theta range for data collection (°)/ completeness for collection (%)	1.82 to 28.39 / 99.0	1.61 to 25.00 / 82.2	1.77 to 28.36 / 99.7	1.45 to 27.10 / 99.8
Index ranges	-15<= <i>h</i> <=15, -16<= <i>k</i> <=16, -18<= <i>l</i> <=18	-20<= <i>h</i> <=19, -19<= <i>k</i> <=19, -22<= <i>l</i> <=22	12<= <i>h</i> <=12, -26<= <i>k</i> <=26, -19<= <i>l</i> <=19	-17<= <i>h</i> <=17, -17<= <i>k</i> <=18, -18<= <i>l</i> <=18
Reflections collected	22397	63146	39703	41073
Independent reflections	9232 [R(int) = 0.0397]	7501 [R(int) = 0.0715]	6708 [R(int) = 0.0969]	11292 [R(int) = 0.0414]
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	0.9638 and 0.9295	0.9732 and 0.8868	0.9409 and 0.8762	1.45 to 27.10
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	9232 / 12 / 479	7501 / 0 / 568	6708 / 0 / 334	11292 / 0 / 667
Goodness-of-fit on F ²	1.021	0.871	0.881	1.025
Final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> 1 = 0.0426, <i>wR</i> 2 = 0.0962	<i>R</i> 1 = 0.0492, <i>wR</i> 2 = 0.1343	<i>R</i> 1 = 0.0362, <i>wR</i> 2 = 0.0604	<i>R</i> 1 = 0.0324, <i>wR</i> 2 = 0.0642
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0622, <i>wR</i> 2 = 0.1057	<i>R</i> 1 = 0.0786, <i>wR</i> 2 = 0.1531	<i>R</i> 1 = 0.0766, <i>wR</i> 2 = 0.0679	<i>R</i> 1 = 0.0568, <i>wR</i> 2 = 0.0784
Largest diff. peak and hole (e.Å ⁻³)	1.065 and -0.891	0.329 and -0.727	0.684 and -0.739	0.347 and -0.250

8.3 Crystal structure of Carbonyl[tris(4-tert-butylphenyl)phosphite] (5-chloro-8-hydroxyquinolinato)rhodium(I), [Rh(oxCl)(CO)P(O-4^tBuPh)₃]

8.3.1 Results and Discussion

(Supplementary data E1)

The compound [Rh(oxCl)(CO)P(O-4^tBuPh)₃], crystallized in the triclinic space group $P\bar{1}$ ($Z=2$). The numbering scheme of [Rh(oxCl)(CO)P(O-4^tBuPh)₃] is presented in Figure 8.1. The most important bond distances and angles are reported (see Table 8.2). The fused ring system of the bidentate ligand is bending slightly, with a r.m.s. deviation from planarity of 0.0214 Å and a dihedral angle of 2.45(13)° between the benzene and pyridine rings. The N...O bite distance is 2.671(4) Å and the N-Rh-O bite angle is at 80.59(9)°. The C8-O4 bond distance is 1.311(3) Å and the endocyclic angle at C7-C8-C9 = 117.1(3)°. The 5-chloro moiety, the O-donor atom and the metal centre is essentially in the fused ring system plane, displaced by 0.072(1) Å, 0.042(2) Å and 0.095(1) Å respectively.

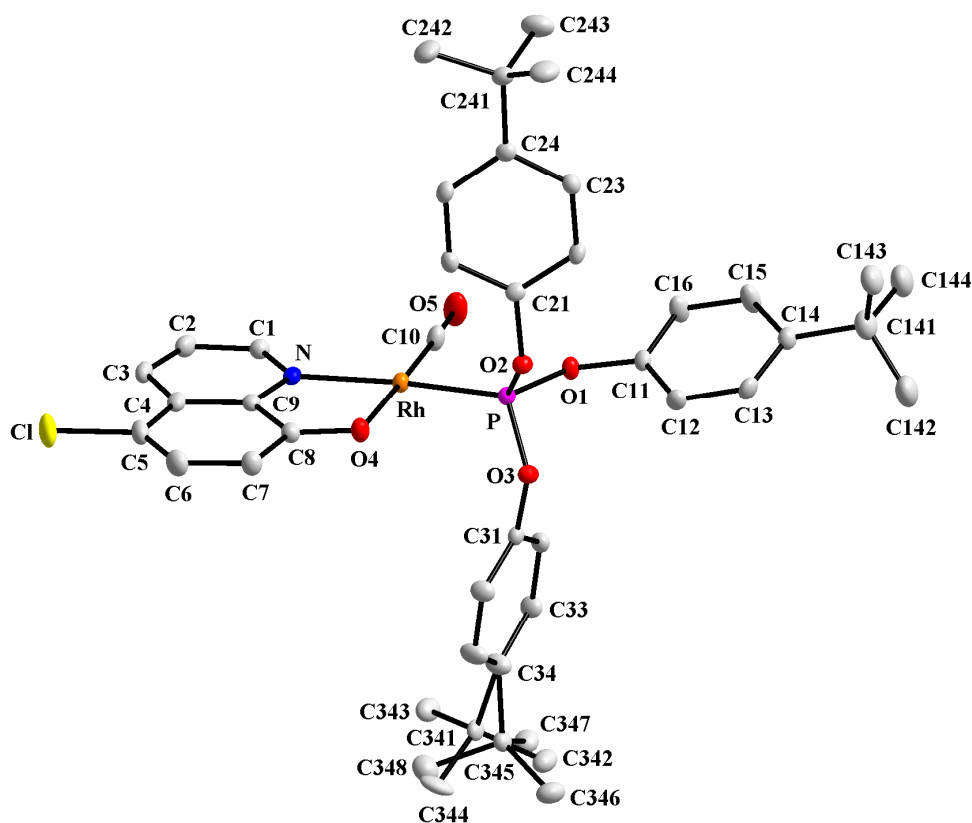


Figure 8.1 Diamond drawing of a [Rh(oxCl)(CO)P(O-4^tBuPh)₃] molecule as in the asymmetric unit, showing the numbering scheme. Hydrogen atoms are omitted for clarity. For the phenyl rings, the first digit refers to the ring number and the second digit to the atom number in the ring.

The rhodium metal centre is slightly displaced from the coordination plane by 0.023(1) Å (r.m.s of fitted atoms = 0.0108 Å). The four metal coordinating bond distances are: the Rh-N bond = 2.098(2) Å, the Rh-O bond = 2.030(2) Å, the Rh-P bond = 2.1811(11) Å and the Rh-C10 bond = 1.821(3) Å, Table 8.2.

The metal-carbonyl moiety is slightly bent with a Rh-C10-O5 bond angle of 177.6(3) °, and a C10-O5 bond distance of 1.148(4) Å. Phosphine ligand substitution occurred *trans* to the N-donor atom, the stronger σ -electron donor. Phosphine substituent arrangement is in such a way that one of the phosphite O-atoms is *cis* to the carbonyl, reflected by the C10-Rh-P-O1 torsion angle of 2.02(14)°. The steric behaviour of the ligand at the metal centre was determined by calculating the cone angle. A value of 172° was obtained.

Table 8.2 Selected bond distances and angles (Å, °) for the complex [Rh(oxCl)(CO)P(O-4^tBuPh)₃].

Atoms	Distance (Å)	Atoms	Distance (Å)
Rh-C10	1.821(3)	C10-O5	1.148(4)
Rh-N	2.098(2)	C8-O4	1.311(3)
Rh-O4	2.030(2)	N...O4 _(Bite distance)	2.671(4)
Rh-P	2.1811(11)		
Atoms	Angle (°)	Atoms	Angle (°)
C10-Rh-P	92.33(9)	Rh-C10-O5	177.6(3)
Rh-P-O1	115.37(7)	C7-C8-C9	117.1(3)
Rh-P-O2	118.63(8)	C8-C9-N	115.2(2)
Rh-P-O3	117.02(8)	O4-Rh-N _(Bite angle)	80.59(9)

Neighboring molecules display three different arrangements with intermolecular soft contacts. One arrangement is the familiar quinoline ligand to ligand π -stacking, the other a molecular soft contact between the quinoline ligand of one molecule and the aryl substituted ring of a phosphorous ligand and the third arrangement is the formation of soft contacts between the carbonyl moiety and the aryl substituted ring of a phosphorous ligand. The quinoline ligand to ligand π -stacking is in a “head to tail” mode with an inter-planar distance of 3.2706(4) Å, Figure 8.2, and a stabilizing Rh...H contact with a distance of 3.389(1) Å and a Rh...H-C angle of 92.0(2)°.

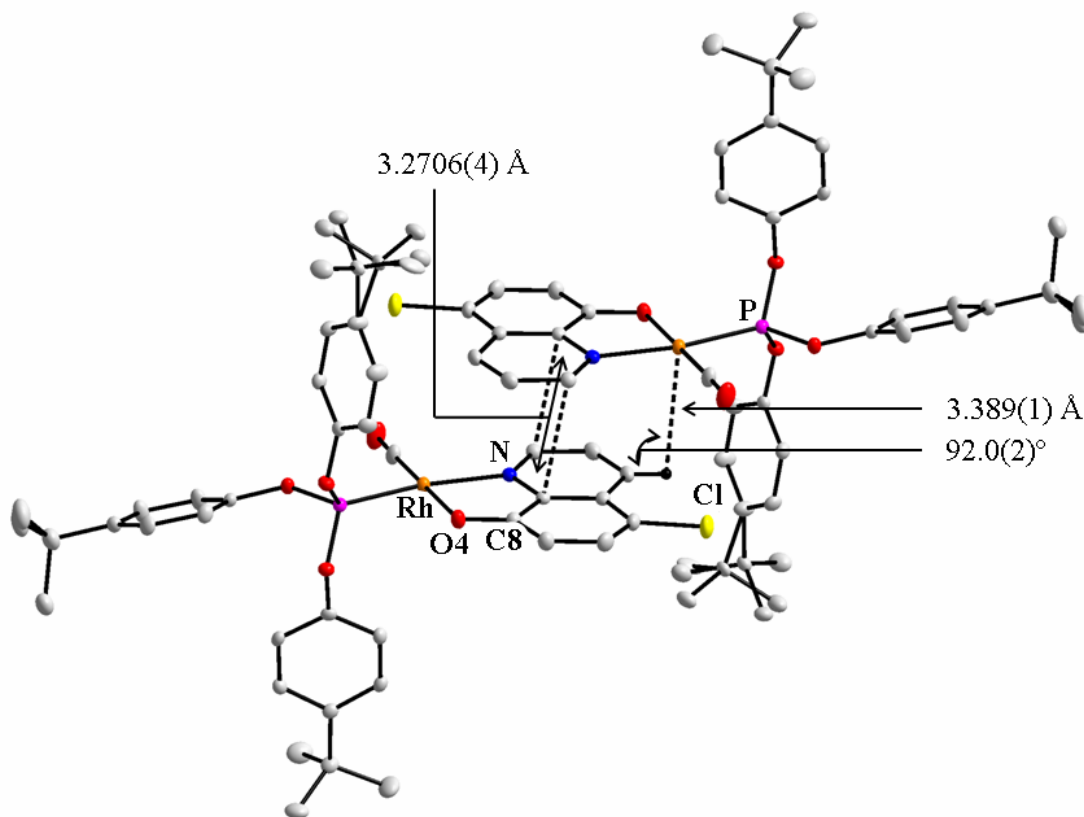


Figure 8.2 An illustration of the ligand to ligand π -stacking in a “head to tail” mode as found in the crystal packing of the complex, $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-4^t\text{BuPh})_3]$, with an inter planar distance of 3.2706(4) Å. Also indicated is the $\text{Rh}\cdots\text{H}$ stabilizing soft contact. Hydrogen atoms were omitted for clarity.

A soft intermolecular contact is present between the tertiary butyl group of the phosphite ligand and the quinoline backbone of the next molecule, (Figure 8.3). This contact is between C8 of the quinoline backbone and C342 of the tertiary butyl group, with a $\text{C}\cdots\text{H}$ distance of 2.649(2) Å and a $\text{C}\cdots\text{H}-\text{C}$ angle of 131.1(1)°.

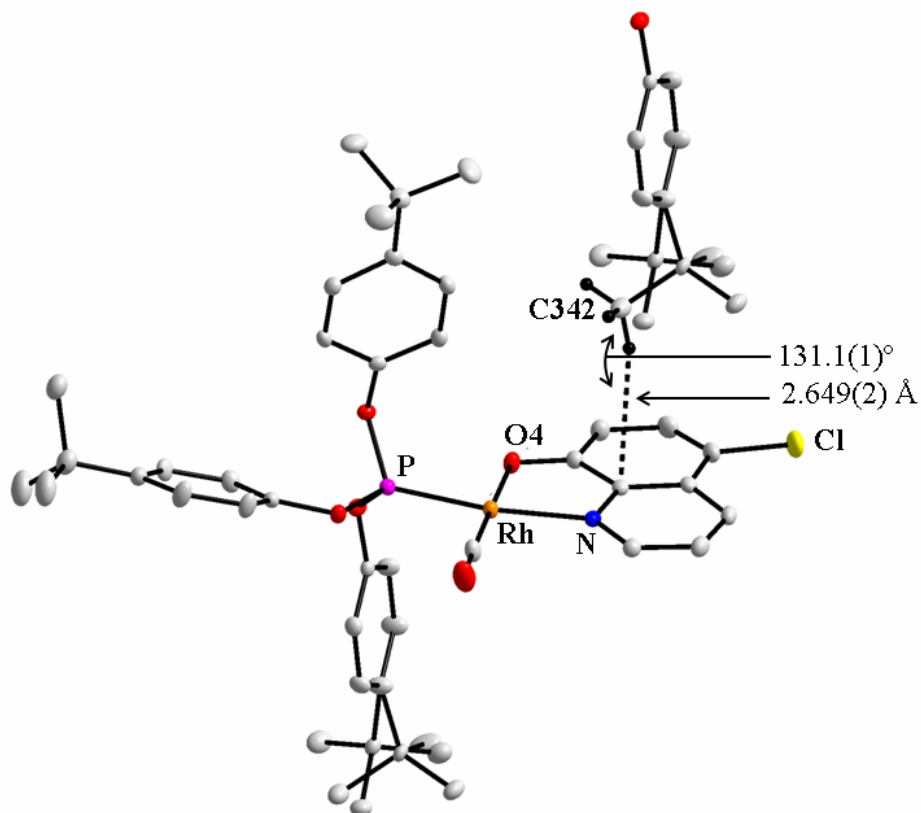


Figure 8.3 An illustration of the aroyl ligand to quinoline backbone hydrogen interaction, as found in the crystal packing of the complex, $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-4^t\text{BuPh})_3]$, with a distance of 2.649(2) Å and an angle of 131.1(1)°. Only interacting molecular fragment are displayed.

Even with the above mentioned intermolecular interaction, this tertiary butyl group exhibits some disorder, (Figure 8.4). The disorder is over two positions with a 5 and 95% distribution, forming a C345...C34...C341 angle of 23.6(4)° and a C345...C341 distance of 0.63(1) Å. This indicates a variation between the two positions. Disorder in tertiary butyl groups is a well know occurrence, surprisingly enough the intermolecular interaction shown in Figure 8.3 did not stabilise the orientation of this tertiary butyl group.

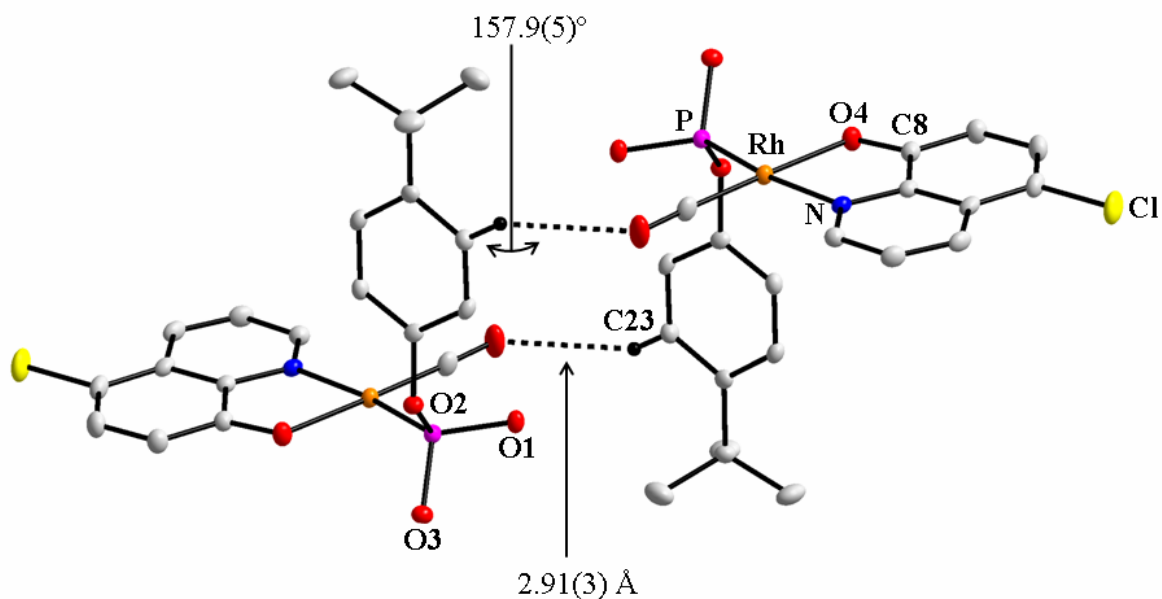


Figure 8.5 An illustration of two molecular fragments of the complex, $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-4^t\text{BuPh})_3]$, indicating molecular soft contacts between neighbouring carbonyl oxygen atoms and aromatic carbon atoms.

Crystal data of the complex $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-4^t\text{BuPh})_3]$ is further discussed and compared to relative 8-hydroxyquinolinatorhodium(I) complexes in Section 8.7.

8.4 Crystal structure of Carbonyl[tris(2,4-di-tert-butylphenyl)phosphite] (5-chloro-8-hydroxyquinolinato)rhodium(I), $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3]$

8.4.1 Results and Discussion

(Supplementary data E2)

Although the single crystal X-Ray data is at a low level of completeness, 82.2%, the data is acceptable for the purpose of this study. The compound $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3]$ crystallized in the monoclinic space group $P2_1/n$ ($Z=4$). The numbering scheme of $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3]$ is presented in Figure 8.6, with a summary of the most important bond distances and angles reported in Table 8.3. The fused ring system of the bidentate ligand is bending slightly, with a r.m.s. deviation from planarity of 0.0111 Å and a dihedral angle of $1.22(34)^\circ$ between the benzene and pyridine rings.

The N...O bite distance is 2.658(5) Å and the N-Rh-O bite angle is 80.15(16)°. The C8-O4 bond distance is 1.328(6) Å and the endocyclic angle at C7-C8-C9 = 117.5(5)°. The 5-chloro moiety, the O-donor atom and the metal centre is essentially in the fused ring system plane, displaced by 0.029(2) Å, 0.019(3) Å and 0.1678(4) Å respectively.

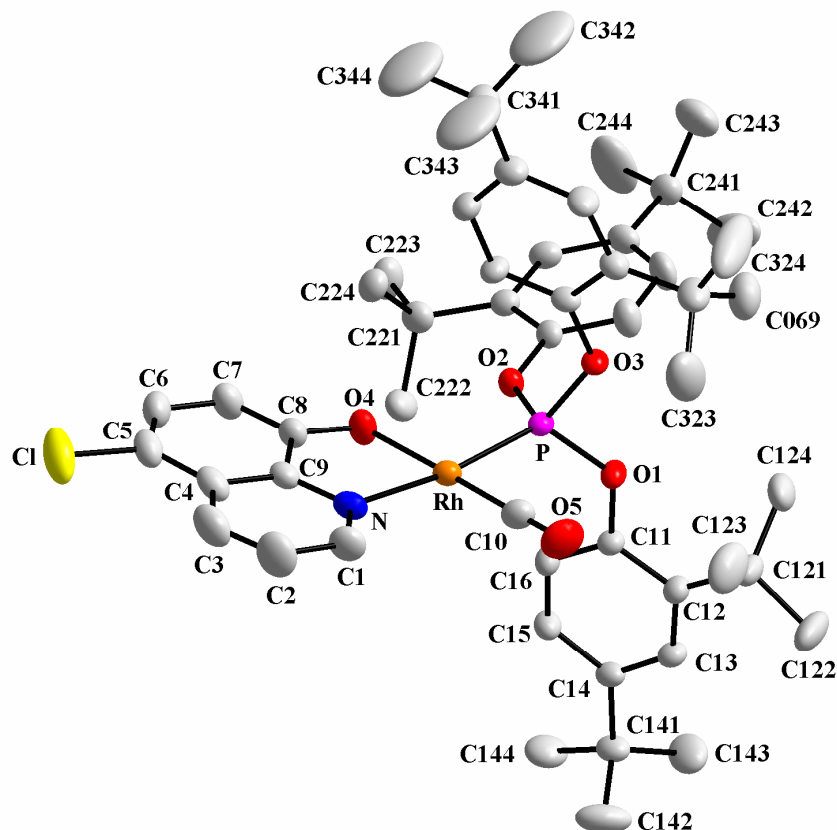


Figure 8.6 Diamond drawing of a $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-2,4\text{di}'\text{BuPh})_3]$ molecule as in the asymmetric unit, showing the numbering scheme. Hydrogen atoms are omitted for clarity. For the phenyl rings, the first digit refers to the ring number and the second digit to the atom number in the ring. For tertiary butyl groups the first digit indicates ring number, the second the position on the phenyl ring.

The rhodium metal centre is slightly displaced from the coordination plane by 0.0723(2) Å (r.m.s of fitted atoms = 0.0365 Å). The four metal coordinating bond distances are: the Rh-N bond = 2.101(4) Å, the Rh-O bond = 2.026(4) Å, the Rh-P bond = 2.1918(13) Å and the Rh-C10 bond = 1.817(6) Å. The metal-carbonyl moiety is slightly bent with a Rh-C10-O5 bond angle of 177.8(6)° and a C10-O5 bond distance of 1.161(7) Å. Phosphite ligand substitution occurred *trans* to the N-donor atom which is the stronger σ -electron donor. Phosphite substituent arrangement is in such a way that one of the phosphite O-atoms is *cis* to the carbonyl, reflected by the C10-Rh-P-O1 torsion angle of 48.7(2)°. The steric effect of the ligand at the metal centre was determined by calculating the cone angle, which was found to be 170°.

Table 8.3 Selected bond distances and angles (Å, °) for the complex [Rh(oxCl)(CO)P(O-2,4di^tBuPh)₃].

Atoms	Distance (Å)	Atoms	Distance (Å)
Rh-C10	1.817(6)	C10-O5	1.161(7)
Rh-N	2.101(4)	C8-O4	1.328(6)
Rh-O4	2.026(4)	N...O4 _(Bite distance)	2.657(5)
Rh-P	2.1918(13)		
Atoms	Angle (°)	Atoms	Angle (°)
C10-Rh-P	89.34(18)	Rh-C10-O5	177.8(6)
Rh-P-O1	121.51(14)	C7-C8-C9	117.5(5)
Rh-P-O2	112.78(12)	C8-C9-N	115.8(4)
Rh-P-O3	115.52(13)	O4-Rh-N _(Bite angle)	80.15(16)

Neighboring molecules display three different arrangements with intermolecular soft contacts that help to stabilize the molecular packing. One arrangement is the familiar quinoline ligand to ligand π -stacking, the other molecular soft contacts between the rhodium metal centre of one ligand with the *para*-tertiary butyl groups of the next, lastly are the soft contacts between the *ortho* and *para*-tertiary butyl groups of neighbouring molecules. The quinoline ligand to ligand π -stacking is in a “head to tail” mode with an inter-planar distance of 3.2753(3) Å, (Figure 8.7) and a stabilizing Rh...Cl contact with a distance of 4.225(2) Å and a Rh...Cl-C angle of 102.9(2)°.

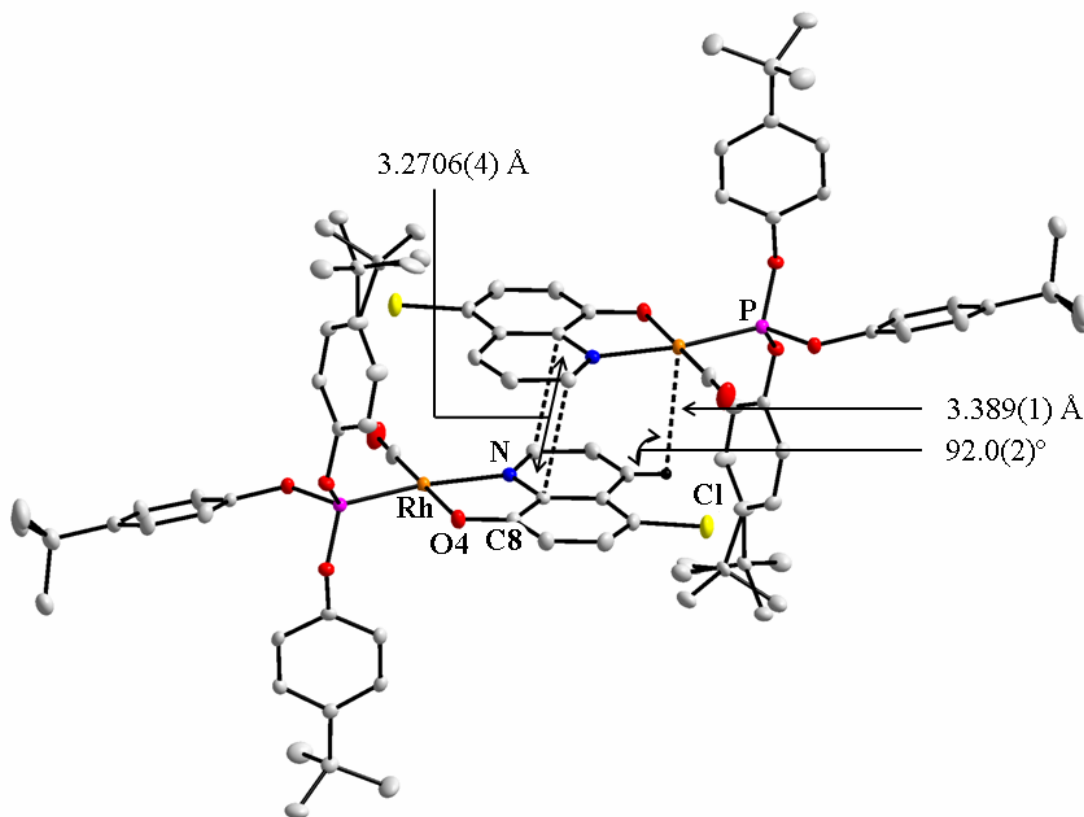


Figure 8.7 An illustration of the ligand to ligand π -stacking in a “head to tail” mode as found in the crystal packing of the complex, $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3]$, with an inter planar distance of 3.2753(3) Å. Also indicated is the $\text{Rh}\cdots\text{Cl}$ stabilizing soft contact. Hydrogen atoms were omitted for clarity.

Soft intermolecular contacts are present between the aroyl tertiary butyl group of one molecule and the rhodium metal centre of the next, Figure 8.8. This contact is between C144 and the neighbouring metal centre, with a $\text{Rh}\cdots\text{H}$ distance of 3.061(1) Å and a $\text{Rh}\cdots\text{H}-\text{C}$ angle of 151.7(4)°.

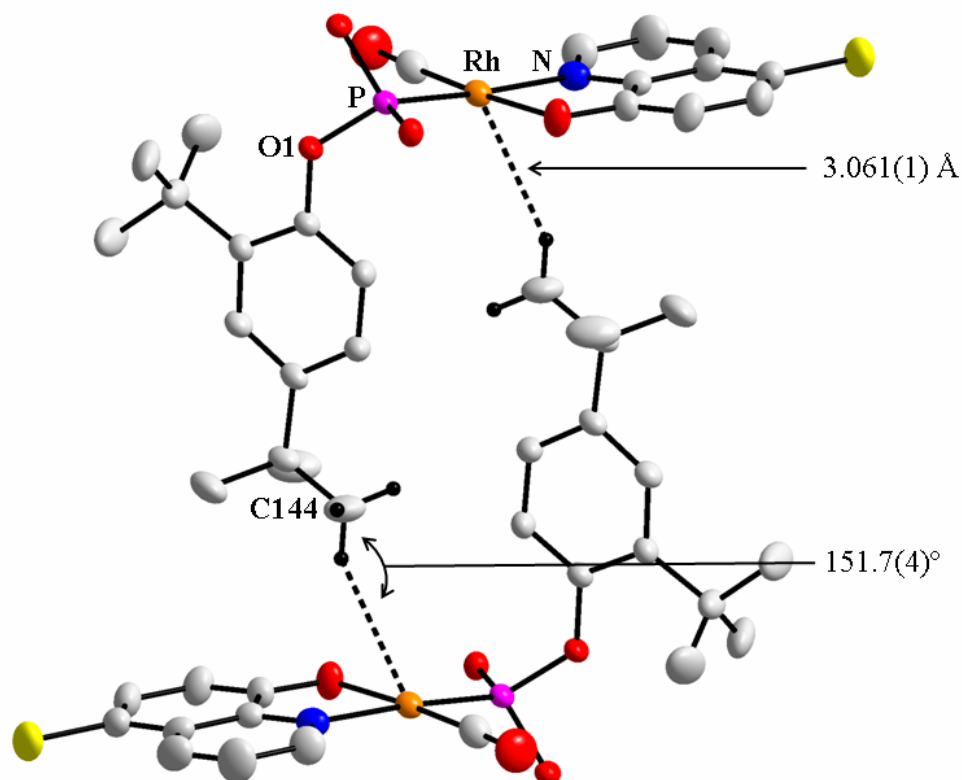


Figure 8.8 An illustration of the aryl ligand tertiary butyl group to rhodium metal centre stabilizing contact, as found in the crystal packing of the complex, $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3]$, with a distance of 3.061(1) Å and an angle of 151.7(4)°. Only interacting molecular fragment are shown and all hydrogen atoms were omitted, this for clarity.

The third kind of soft intermolecular contacts stabilizing molecular packing, is between the aryl tertiary butyl groups of neighbouring molecules (Figure 8.9). With two contacts stabilizing this arrangement, a C...H contact with a C...H distance of 2.90(2) Å and C...H-C angles of 173.8(5)°. The other contact is a H...H contact with a distance of 2.295(1) Å.

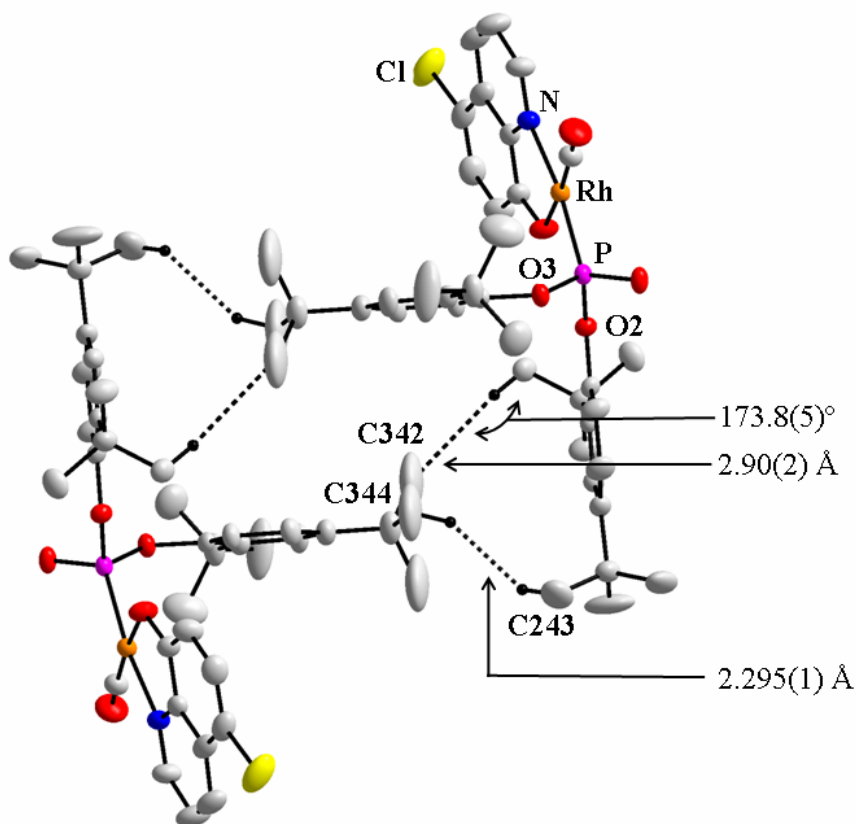


Figure 8.9 An illustration of two partially molecules of the complex, $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3]$, indicating molecular soft contacts between neighbouring aryl tertiary butyl groups.

The crystal data for the complex $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3]$ is compared relative to 8-hydroxyquinolinatorhodium(I) complexes in Section 8.7.

8.5 Crystal structure of Carbonyl[tris(*para* chloro phenyl)phosphine] (5-chloro-8-hydroxyquinolinato)rhodium(I), $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(p\text{-ClPh})_3]$ ¹⁰⁵

8.5.1 Results and Discussion

(Supplementary data E3)

The compound $[\text{Rh}(\text{C}_9\text{H}_7\text{ClNO})(\text{CO})\{\text{P}(\text{C}_6\text{H}_4\text{Cl})_3\}]$ crystallized in the monoclinic space group $P2_1/c$ ($Z=4$), with the Belsky notation as $P2_1/c$, $Z=4(1) : [(-1^4)]$,^{106,107}. The numbering scheme of

¹⁰⁵ Janse van Rensburg, J. M., Muller, A. & Roodt, A. (2007). *Acta Cryst.* E63, m3015.

¹⁰⁶ Belsky, V. K. (1995). *Acta Cryst.* A51, 473.

¹⁰⁷ Oskarsson, 2007, *ecm* 24, Marrakech, abstract, 198.

$[\text{Rh}(\text{C}_9\text{H}_7\text{ClNO})(\text{CO})\{\text{P}(\text{C}_6\text{H}_4\text{Cl})_3\}]$ is as presented in Figure 8.10. The most important bond distances and angles are reported in Table 8.4. The fused ring system of the bidentate ligand is bending slightly, with a r.m.s. deviation from planarity of 0.0423 Å and a dihedral angle of 4.87(16)° between the benzene and pyridine rings. The N...O bite distance is 2.659(9) Å and the N-Rh-O bite angle is 80.15(9)°. The C8-O1 bond distance is 1.326(3) Å and the endocyclic angle at C7-C8-C9 = 117.8(3)°. The 5-chloro moiety, the O-donor atom and the metal centre is essentially in the fused ring system plane, displaced by 0.124(3) Å, 0.081(3) Å and 0.065(3) Å respectively.

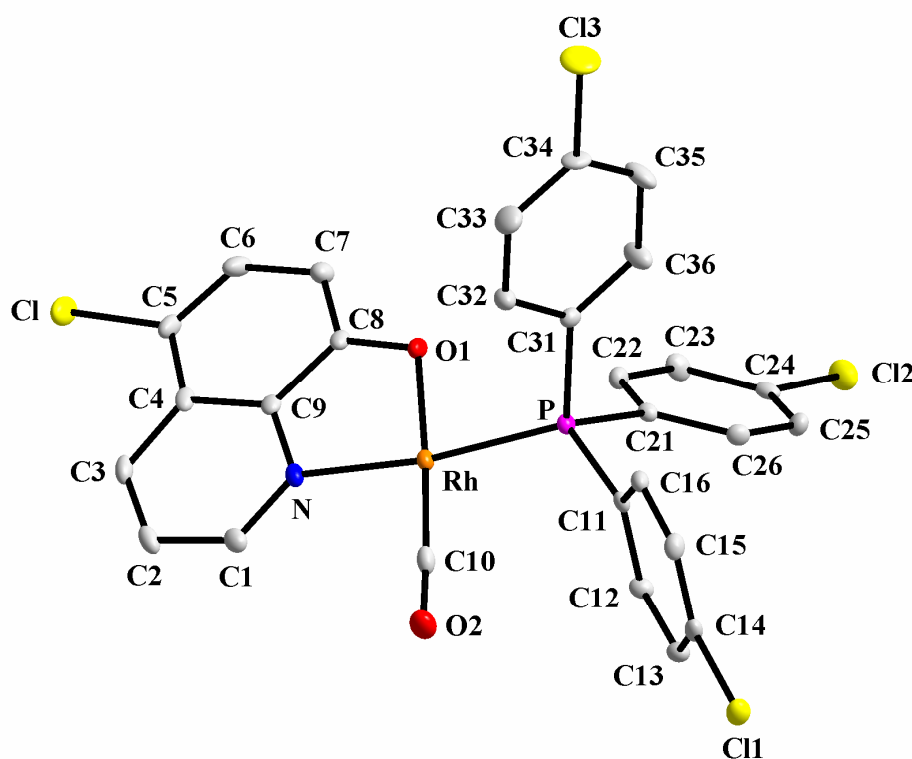


Figure 8.10 Diamond drawing of a $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-ClPh})_3]$ molecule as in the asymmetric unit, showing the numbering scheme. Hydrogen atoms are omitted for clarity. For the phenyl rings, the first digit refers to the ring number and the second digit to the atom number in the ring.

The rhodium metal centre is slightly displaced from the coordination plane by 0.014(1) Å (r.m.s of fitted atoms = 0.0007 Å). The four metal coordinating bonds distances are: the Rh-N bond = 2.093(2) Å, the Rh-P bond = 2.2478(9) Å and the Rh-C10 bond = 1.803(4) Å. The metal-carbonyl moiety is slightly bended with an Rh-C10-O2 bond angle of 177.4(3)°, and a C10-O2 bond distance of 1.154(4) Å. The phosphine ligand substitution occurred *trans* to the N-donor atom, which is the stronger σ -electron donor. The phosphine substituent arrangement is in such a way that one of the phenyl rings is *cis* to the carbonyl, reflected by the C10-Rh-P-C11 torsion angle of 1.86(14)°. The steric behaviour of

the ligand at the metal centre was determined by calculating the cone angle as described previously. A value of 165° was obtained. The most important bond distances and angles are reported in Table 8.4.

Table 8.4 Selected bond distances and angles (Å, °) for the complex [Rh(oxCl)(CO)P(p-ClPh)₃].

Atoms	Distance (Å)	Atoms	Distance (Å)
Rh-C10	1.803(4)	C10-O2	1.154(4)
Rh-N	2.093(2)	C8-O1	1.326(3)
Rh-O1	2.038(2)	N...O1 _(Bite distance)	2.659(3)
Rh-P	2.2478(9)		
Atoms	Angle (°)	Atoms	Angle (°)
C10-Rh-P	91.62(10)	Rh-C10-O2	177.4(3)
Rh-P-C11	116.73(10)	C7-C8-C9	117.8(3)
Rh-P-C21	114.94(10)	C8-C9-N	115.9(3)
Rh-P-C31	112.33(10)	O1-Rh-N _(Bite angle)	80.15(9)

The molecular packing is stabilized by two distinctive packing modes between neighboring molecules. One is the familiar quinoline ligand to ligand π -stacking and the other molecular soft contacts between the quinoline ligand of one molecule and the aryl substituted rings of the phosphorous ligand. The quinoline ligand to ligand π -stacking is in a “head to tail” mode with an inter-planar distance of 3.261(1) Å, (Figure 8.11). Other stabilizing contacts are two Rh...H contacts (3.388(1) Å) and two Cl...O contacts (3.489(3) Å).

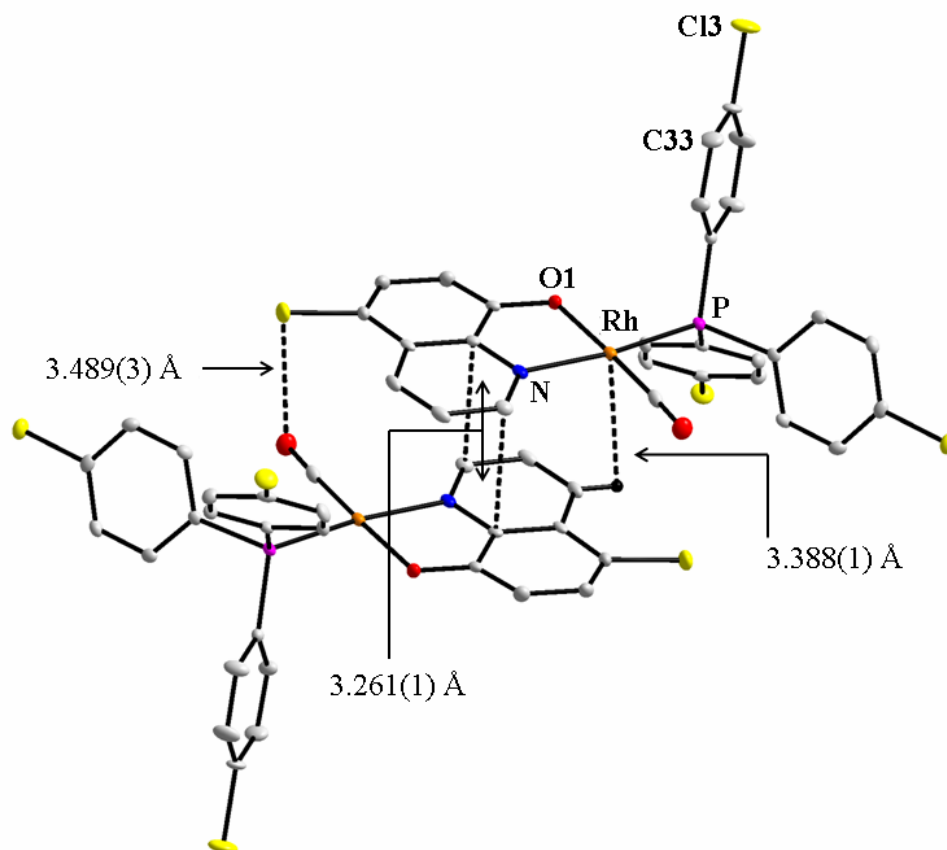


Figure 8.11 An illustration of the ligand to ligand π -stacking in a “head to tail” mode as found in the crystal packing of the complex, $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-ClPh})_3]$, with an inter planar distance of 3.261(1) Å. Also indicated is the Rh...H stabilizing soft contact. Hydrogen atoms were omitted for clarity.

Also present in the crystal packing are the soft contacts between the aryl substituted rings of the phosphorous ligand of one molecule and the quinoline ligand of the next, Figure 8.12. These contact sinclude a Rh-H contact with $\text{C-H}\dots\text{Rh} = 130.4(2)^\circ$ and $\text{Rh}\dots\text{H} = 2.608(7) \text{ \AA}$, a Cl...H contact with $\text{C-H}\dots\text{Cl} = 117.4(1)^\circ$ and $\text{Cl}\dots\text{H} = 2.943(10) \text{ \AA}$ and lastly a C...C soft contact with a distance of 3.314(10) Å.

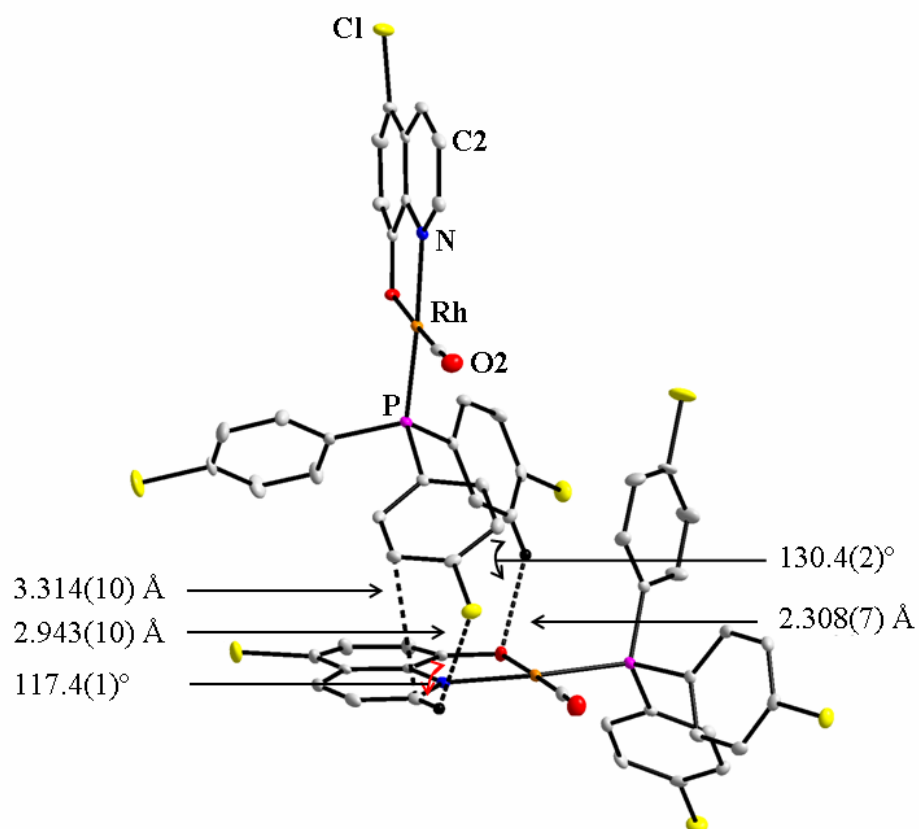


Figure 8.12 An illustration of the aryl ligand to quinoline backbone interactions, as found in the crystal packing of the complex, $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-ClPh})_3]$. Hydrogen atoms were omitted, this for clarity.

A comparison between the presented crystal data of the complex $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-ClPh})_3]$ and relative to 8-hydroxyquinolinatorhodium(I) complexes is discussed in Section 8.7.

8.6 Crystal structure of Carbonyl[tris(para fluoro phenyl)phosphine] (5-chloro-8-hydroxyquinolinato)rhodium(I), [Rh(oxCl)(CO)P(p-FPh)₃]

8.6.1 Results and Discussion

(Supplementary data E4)

The molecules of the compound, [[Rh(oxCl)(CO)P(p-FPh)₃], crystallized as two independent molecules in the triclinic space group *P* $\bar{1}$ (*Z*=4). When referring to molecule **A**, consider the molecule with the rhodium centre numbered Rh1, and molecule **B** refers to the Rh2 numbered system, (Figure 8.13). As mentioned in Table 8.5 and Table 8.6 a few selected dihedral angles are noted as well as important bond distances and angles for each independent molecule.

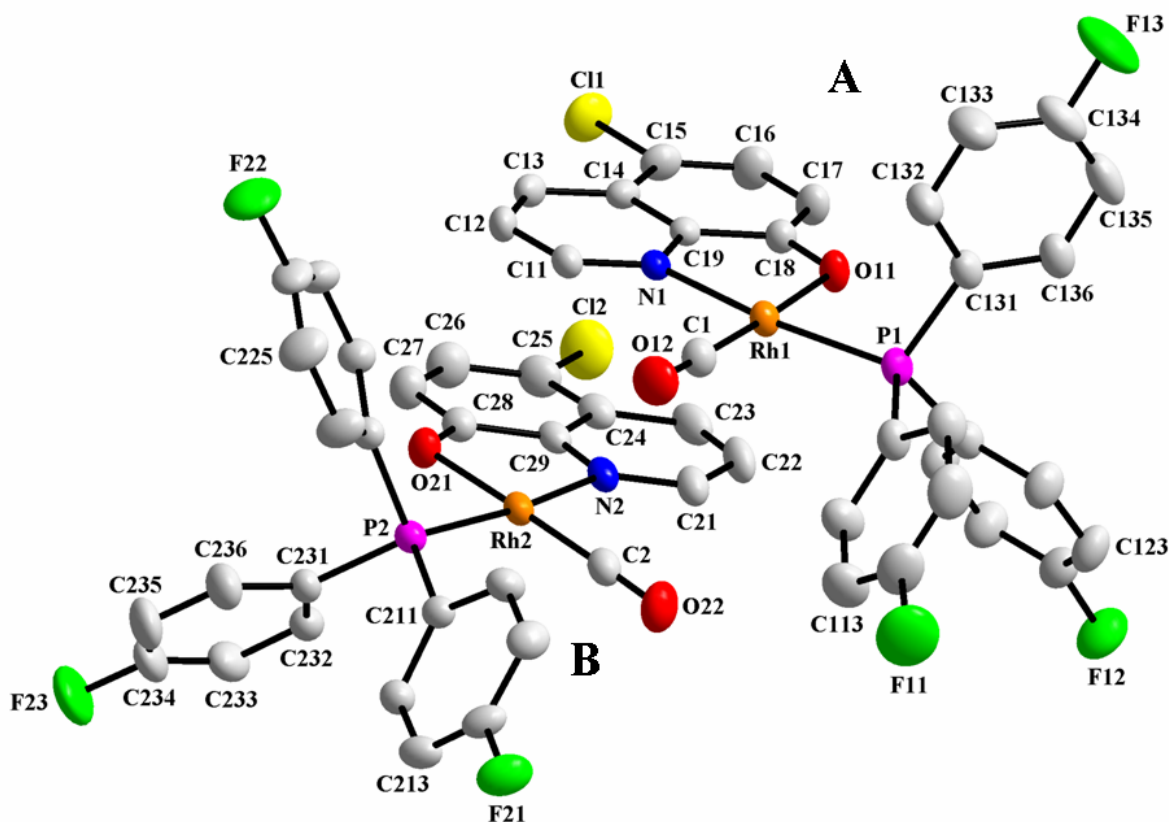


Figure 8.13 Diamond drawing of the two independent Carbonyl[tris(para fluoro phenyl)phosphine](5-chloro-8-hydroxyquinolinato)rhodium(I), [Rh(oxCl)(CO)P(p-FPh)₃], molecules in the asymmetric unit, showing the atom numbering scheme of the molecules A and B. Hydrogen atoms are omitted for clarity. For the phenyl C-atoms, the first digit indicates ring number and the second digit the position of the atom in the ring

Table 8.5 Selected geometrical parameters, (Å, °), indicating disorder in the fused ring system and metal coordination plane of the complex [Rh(oxCl)(CO)P(p-FPh)₃].

	Molecule A	Molecule B
The r.m.s. of fitted atoms (C11-C19 and N1)/(C21-C29 and N2)	0.0095 Å	0.0204 Å
Dihedral angle between the Benzene ring plane and the pyridine ring plane	0.44(6)°	1.90(8)°
Dihedral angle between the fused ring system and the metal coordination plane	2.44(6)°	5.39(6)°
Metal displacement from the metal coordination plane.	0.0149(3) Å	0.0217(3) Å

Table 8.6 Selected bond distances and angles (Å, °) for independent molecules (A) and (B) of the complex [Rh(oxCl)(CO)P(p-FPh)₃].

Molecule	A	Molecule	B
Atoms	Distance (Å)	Atoms	Distance (Å)
Rh1-O11	2.040(2)	Rh2-O21	2.043(2)
Rh1-N1	2.088(2)	Rh2-N2	2.084(2)
Rh1-P1	2.2497(11)	Rh2-P2	2.2559(10)
Rh1-C1	1.803(3)	Rh2-C2	1.802(4)
C18-O11	1.316(3)	C28-O21	1.325(3)
N1...O11 _(Bite distance)	2.661(4)	N2...O21 _(Bite distance)	2.656(4)
Atoms	Angle (°)	Atoms	Angle (°)
O11-Rh1-N1 _(Bite angle)	80.27(8)	O21-Rh2-N2 _(Bite angle)	80.12(9)
N1-Rh1-C1	97.45(12)	N2-Rh2-C2	97.17(12)
C1-Rh1-P1	92.09(10)	C2-Rh2-P2	91.21(10)
P1-Rh1-O11	90.18(6)	P2-Rh2-O21	91.48(6)
Rh1-C1-O12	178.4(3)	Rh2-C2-O22	176.7(3)
C11-N1-C19	118.8(2)	C21-N2-C29	118.7(3)
N1-C19-C18	115.8(2)	N2-C29-C28	115.8(3)
C19-C18-C17	117.4(3)	C29-C28-C27	117.5(3)

It is clear from Table 8.5 that both fused ring systems are approximately planar, even though larger ring distortion is present in molecule **B** and the dihedral angle between the benzene and pyridine rings. Molecule **B** also displays larger molecular bending, with a dihedral angle of 5.39(6)° between the fused ring system and metal coordination plane. The higher distortion in molecule **B** is further emphasized by the rhodium metal displacement from the metal coordination plane, with a distance of 0.0217(3) Å. Comparing metal coordination bonds and angles between molecules **A** and **B** (see Table 8.6) the largest differences are noted in the Rh-P bond and bond angles. The C28-O21 bond distance of molecule **B** is larger than the C18-O11 bond distance of molecule **A**. It was noted that a decrease takes place in both the bite distance and bite angle of molecule **B** which might have resulted in the C28-O21 bond elongation.

The two ligand to ligand π -stacking modes present in the crystal packing are illustrated in Figure 8.14 and Figure 8.15. Even with the steric hindrance of the phosphine ligand, in a “skew head to head” packing mode is still present between molecules **A** and **B**. This might be a result from the stabilising soft contacts between the 5-chloro atoms of the quinoline and the Rh...H contacts. Also present in the

crystal packing is the known “head to tail” stacking mode, (Figure 8.15). This is, however, between symmetrical equivalent molecules A.

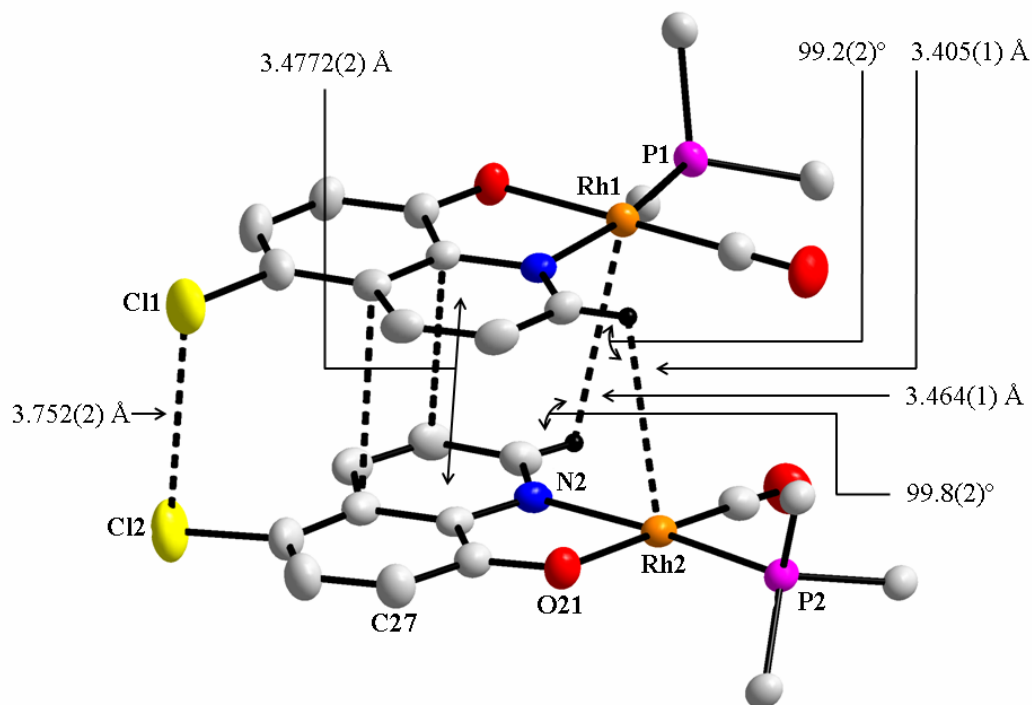


Figure 8.14 An illustration of the ligand to ligand π -stacking in a “skew head to head” mode between molecules (A) and (B) as found in the crystal packing of the complex, $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-FPh})_3]$, with an inter planar distance of 3.4772(2) Å. Also indicated are the Cl...Cl and Rh...H stabilizing soft contacts. Non interacting hydrogen atoms were omitted for clarity.

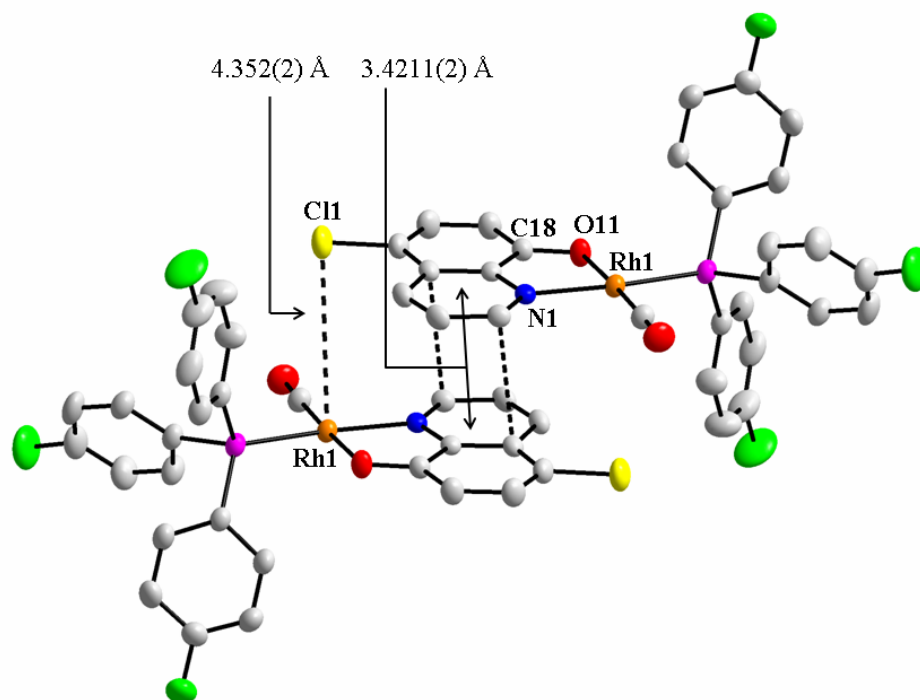


Figure 8.15 An illustration of the ligand to ligand π -stacking in a “head to tail” mode between molecules (A) as found in the crystal packing of the complex, $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-FPh})_3]$, with an inter planar distance of 3.4211(2) Å. Also indicated is a Rh...Cl stabilizing soft contact. Hydrogen atoms were omitted for clarity.

The above presented 5-chloro-8-hydroxyquinolinatorhodium(I) complexes are compared in Section 8.7.

8.7 Correlation between the structural parameters of 8-hydroxyquinolinatorhodium(I) and functionalized 8-hydroxyquinolinatorhodium(I) complexes

As in the case of 8-hydroxyquinolinatorhodium(I) complexes the phosphine and phosphite ligands have the same geometrical effects on the 5-chloro-8-hydroxyquinolinatorhodium(I) complexes (see Table 7.10 and Table 8.7). The phosphine complexes have longer Rh-P bonds and display a much smaller first order coupling constant for the phosphorous NMR spectra. This is due to the phosphite being a weaker σ -donor but better π -acceptor than the phosphine ligand, leading to a stronger bond. The small influence from different substituents on the phosphorous ligand rings can be noted in the very similar $^1J_{(\text{Rh-P})}$ values.

The carbonyl[tris(2,4-di-tert-butylphenyl)phosphite]rhodium(I) complexes of 8-hydroxyquinolinato and 5-chloro-8-hydroxyquinolinato is compared in Table 8.8. There are some variation on the Rh-P and Rh-N coordinating bonds and a smaller bite angle is displayed in the 5-chloro-8-hydroxyquinolinato complex. There is a definite electronic influence on the metal centre, observed from the 10 Hz difference in the $^1J_{(\text{Rh-P})}$ values. The *ca.* 20° difference in the effective cone angle, θ_E , can be ascribed to the different inter and intra molecular interactions present in the crystal packing. This emphasizes the possible difference between the solid state cone angle and ligand steric influence in solution. There is a 0.5 Å difference in the ligand to ligand π -stacking distance, with the shorter distance for the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3)]$, which has the larger cone angle. This indicates that the ligand to ligand π -stacking in a “head to tail” mode experiences no influence from the phosphorous ligand. The “head to tail” orientation already cancels out the phosphorous ligands’ steric effect. In a precise “head to head” stacking the phosphorous ligands will definitely have a steric influence on the ligand to ligand π -stacking distance.

Banerjee and Saha reported the effects on bond lengths and angles of the free 5-chloro moiety *vs* that of the free 8-hydroxyquinoline ligand⁷¹. A comparison of these molecular distances to the rhodium bonded 5-chloro-8-hydroxyquinoline compound, $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-ClPh})_3]$ was also reported¹⁰⁵. There is a *ca.* 0.1 Å decrease in the (N...O) bite distance upon complexation, as noted for the compound $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-ClPh})_3]$, 2.659(9) Å compared to the larger bite distance of the free ligand. Chelation of 5-chloro-8-hydroxyquinoline to the metal centre shortens the C8-O1 bond distance by *ca.* 0.04 Å, compared to the neutral 8-hydroxyquinolines¹⁶.

Table 8.9 summarizes the comparative geometrical data for 5-phenylazo-8-hydroxyquinolinatorrhodium(I) and 8-hydroxyquinolinatorrhodium(I) complexes. The Rh-P bonds, $^1J_{(\text{Rh-P})}$ coupling constants and the ν_{CO} stretching frequencies increase in the order of $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)] < [\text{Rh}(\text{oxL})(\text{CO})(\text{PPh}_3)] < [\text{Rh}(\text{oxL-Me}_3)(\text{CO})(\text{PPh}_3)]$ and from $[\text{Rh}(\text{ox})(\text{CO})(\text{PCy}_3)] < [\text{Rh}(\text{oxL})(\text{CO})(\text{PCy}_3)]$.

Table 8.7 Comparative data for the reported 5-chloro-8-hydroxyquinolinorhodium(I) complexes.

PHOSPHITE COMPLEXES	Rh-P (Å)	Rh-N (Å)	Rh-O (Å)	Rh-C (Å)	O-Rh-N (°)	θ_E (°)	π -stacking (Å) “Head to Tail”	$^1J_{(Rh-P)}$ (Hz)	$\nu_{(CO)}$ (cm ⁻¹)
[Rh(oxCl)(CO)P(O-4 ^t BuPh) ₃]	2.181(11)	2.098(2)	2.030(2)	1.821(3)	80.59(9)	172	3.271(1)	265	1995
[Rh(oxCl)(CO)P(O-2,4di ^t BuPh) ₃]	2.1918(13)	2.101(4)	2.026(4)	1.817(6)	80.15(16)	170	3.753(3)	269	1996
PHOSPHINE COMPLEXES									
[Rh(oxCl)(CO)P(p-ClPh) ₃] ¹⁰⁵	2.2478(9)	2.093(2)	2.038(2)	1.803(4)	80.15(9)	165	3.489(3)	213	1965
[Rh(oxCl)(CO)P(p-FPh) ₃] (A)	2.2497(11)	2.088(2)	2.040(2)	1.803(3)	80.27(8)	159	3.421(1)	166	2000
(B)	2.2559(10)	2.084(2)	2.043(2)	1.802(4)	80.12(9)	160			

Table 8.8 Comparative data for 5-chloro-8-hydroxyquinolinorhodium(I) and 8-hydroxyquinolinorhodium(I) complexes.

PHOSPHITE COMPLEXES	Rh-P (Å)	Rh-N (Å)	Rh-O (Å)	Rh-C (Å)	O-Rh-N (°)	θ_E (°)	π -stacking (Å) “Head to Tail”	$^1J_{(Rh-P)}$ (Hz)	$\nu_{(CO)}$ (cm ⁻¹)
[Rh(ox)(CO)P(O-2,4di ^t BuPh) ₃]	2.1819(6)	2.0842(19)	2.0234(18)	1.818(3)	81.00(8)	192	3.271(1)	279	1986
[Rh(oxCl)(CO)P(O-2,4di ^t BuPh) ₃]	2.1918(13)	2.101(4)	2.026(4)	1.817(6)	80.15(16)	170	3.753(3)	269	1996

Table 8.9 Comparative geometrical data for 5-phenylazo-8-hydroxyquinolinorhodium(I) and 8-hydroxyquinolinorhodium(I) complexes.

	Rh-P (Å)	Rh-N (Å)	Rh-O (Å)	Rh-C (Å)	O-Rh-N (°)	θ_E (°)	π -stacking (Å)	$^1J_{(Rh-P)}$ (Hz)	$\nu_{(CO)}$ (cm ⁻¹)
[Rh(oxL)(CO)(PPh ₃)]	2.2626(12)	2.089(3)	2.052(3)	1.794(5)	80.03(13)	161	3.202(1)	164	1970
[Rh(oxL)(CO)(PCy ₃)]	2.2631(9)	2.099(2)	2.052(2)	1.794(3)	79.76(8)	167	3.326(1)	154	1952
[Rh(oxL-Me ₃)(CO)(PPh ₃)]	2.2831(15)	2.103(4)	2.062(3)	1.805(4)	79.95(13)	162	---	163	1972
[Rh(ox)(CO)(PPh ₃)] (A)	2.2459(18)	2.089(5)	2.041(4)	1.721(6)	80.25(17)	155	3.358(5)	164	1995
(B)	2.2557(18)	2.079(5)	2.038(4)	1.806(6)	80.78(19)	157	3.358(5)	164	1995
[Rh(ox)(CO)(PCy ₃)]	2.2557(15)	2.091(4)	2.036(4)	1.817(6)	80.65(16)	167	3.269(3)	138	1946

A summary of the molecular packing of the four 5-chloro-8-hydroxyquinolinorhodium(I) complexes discussed in this chapter is presented in Figure 8.16. For the complexes, $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-4^t\text{BuPh})_3]$, $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-ClPh})_3]$ and $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-FPh})_3]$, it was noted that a “head to tail” π -stacking unit repeats itself to display a *pseudo* hexagonal close packing. Also note the clear phosphine ligand to quinoline backbone packing mode displayed for the $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-ClPh})_3]$ complex, forming a “beehive” around the ligand to ligand π -stacked unit. This happens even though the $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3]$ complex does display the ligand to ligand π -stacking, Figure 8.7, and the effective cone angle for this phosphite ligand is 170° compared to the 172° effective cone angle of the phosphite ligand of the complex, $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-4^t\text{BuPh})_3]$. The absence of a *pseudo* hexagonal close packing mode is probably due to differing intermolecular interactions which also forms the large voids noted between neighbouring molecules along the bc-axis.

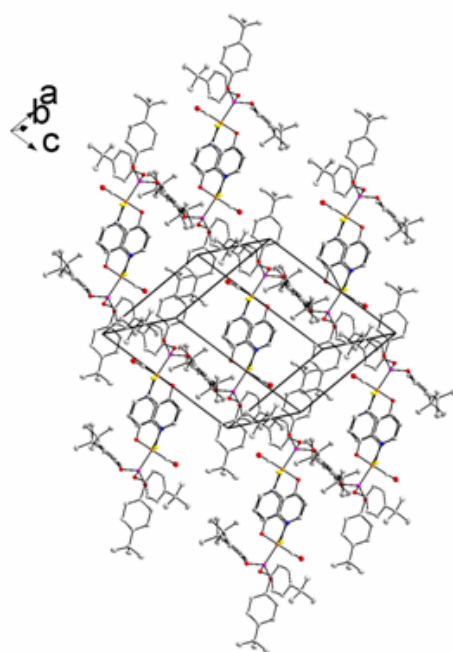
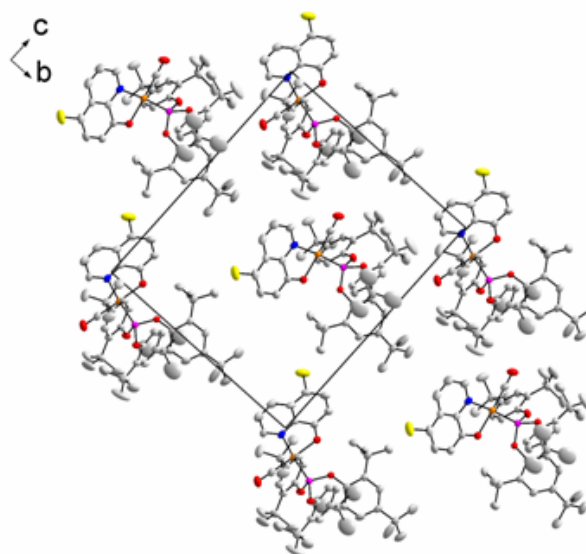
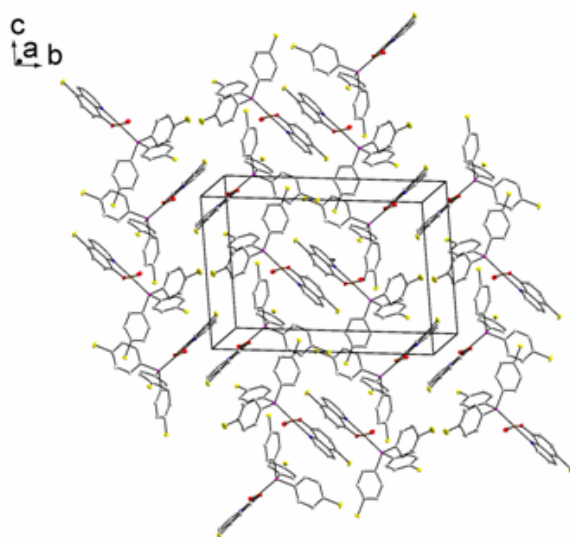
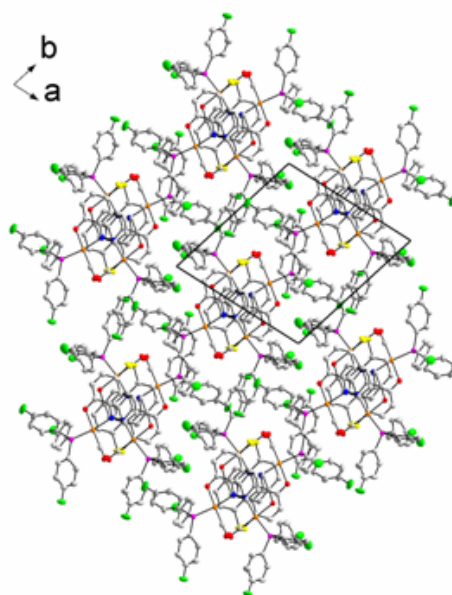
 $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-4^t\text{BuPh})_3]$  $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3]$  $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p}-\text{ClPh})_3]$  $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p}-\text{FPh})_3]$

Figure 8.16 Illustration of the unit cell and molecular packing for each of the 5-chloro-8-hydroxyquinoline complexes reported in this chapter

The ligand to ligand π -stacking for the quinolinatorhodium(I) complexes presented in Chapter 7 and 8 is summarized in Table 8.10 and Figure 8.17. It was noted that for the 5-chloro-8-hydroxyquinolinato complexes it was noted that the pyridine rings overlap and in the case of ring glide as for the $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-4^t\text{BuPh})_3]$ and $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-ClPh})_3]$ complexes, the glide will be in the direction of the neighbouring molecules rhodium centre and not towards the benzene ring. This gliding might be a result of the $\text{Cl}\dots\text{O}_{(\text{carbonyl})}$ soft contacts. The skew “head to head” stacking for the complex, $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-FPh})_3]$, displays the pyridine-pyridine overlap, probably stabilized by the halogen...halogen and oxygen...oxygen soft contacts.

In the π -stacking of the 8-hydroxyquinolinato complexes the pyridine-pyridine ring overlap is also found, but ring glide is towards the benzene ring. This might be from the $\text{Rh}\dots\text{H}$ soft contacts, however in the case of a 5-chloro atom on the quinoline backbone the $\text{Cl}\dots\text{O}$ contacts are probably stronger and more dominating, thus not allowing ring glide towards the benzene ring.

Table 8.10 π -Stacking distances for quinolinatorhodium(I) complexes

π -Stacking Distance	Plane to Plane (Å)	Centroid to Centroid (Å)
8-Hydroxyquinolinato complexes		
$[\text{Rh}(\text{ox})(\text{CO})\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3]$	3.271(1)	3.820(1)
$[\text{Rh}(\text{ox})(\text{CO})\text{P}(\text{O}-2\text{MePh})_3]$	3.459(1)	3.720(2)
$[\text{Rh}(\text{ox})(\text{CO})\text{P}(\text{5FPh})_3]$	3.364(2)	3.669(1)
$[\text{Rh}(\text{ox})(\text{CO})\text{P}(\text{PCy}_3)_3]$	3.269(3)	3.724(1)
$[\text{Rh}(\text{ox})(\text{CO})\text{P}(\text{PPh}_3)_3]$	3.358(5)	3.628(1)
5-Chloro-8-hydroxyquinolinato complexes		
$[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-4^t\text{BuPh})_3]$	3.270(1)	3.966(1)
$[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3]$	3.275(1)	4.043(1)
$[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-ClPh})_3]$	3.261(1)	4.270(1)
$[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-FPh})_3]$ “Head to Tail”	3.421(1)	4.087(11)
$[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-FPh})_3]$ “Head to Head”	3.477(1)	3.564(1)

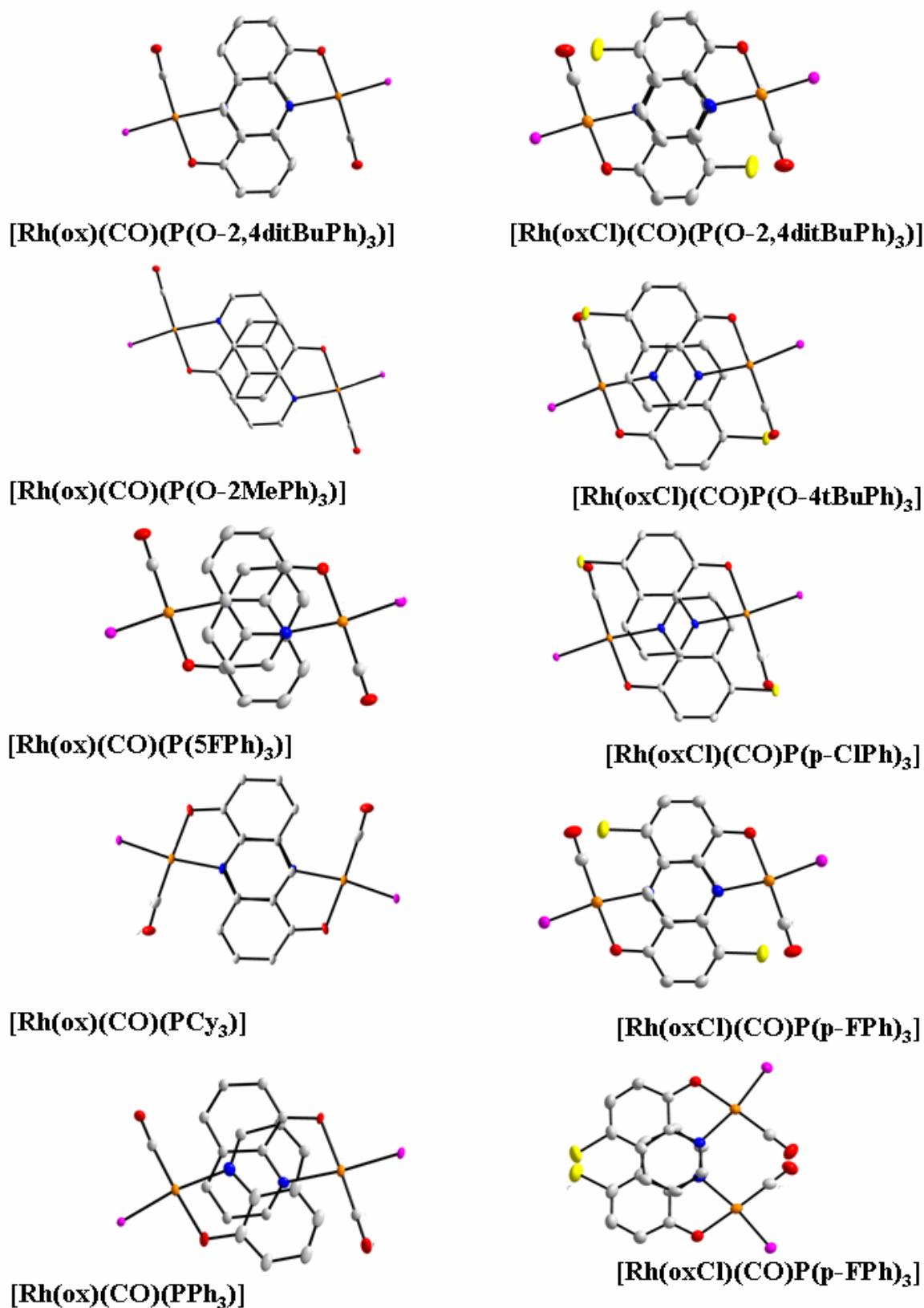


Figure 8.17 Illustration of the ligand to ligand π -stacking found for the presented 8-hydroxyquinolinato and 5-chloro-8-hydroxyquinolinato complexes. Note: each illustration is a perpendicular view onto the oxine plane of a single π -stacked unit. Thus two quinoline moieties and two metal centres, with the phosphine ligands omitted for clarity.

8.8 Conclusion

From the solid state data presented in Chapter 8, the geometrical and packing differences between various rhodium(I) complexes of the type $[\text{Rh}(\text{oxCl})(\text{CO})(\text{PPR}_3)]$, where R = Aryl or Aroyl, could be determined, (Table 8.7). The phosphite and phosphine ligands influenced the 5-chloro-8-hydroxyquinolinorhodium(I) complexes in the same manner as for the 8-hydroxyquinolinorhodium(I) complexes, even though the electronic properties of the metal centre vary between the functionalized quinoline complexes, as seen in the $^1\text{J}(\text{Rh-P})$ values for the $(\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3)$ substituted metal complexes (Table 8.8).

Chapter 7 and 8 reported influences from phosphorous ligands and functionalized quinoline ligands in the solid state. To determine the ligand influence on the electron density of the metal centre in solution, the reactivity of the complexes towards methyl iodide oxidative addition under *pseudo*-first order conditions were investigated, these results are reported in Chapter 9.

Chapter 9

Kinetic study of iodomethane oxidative addition to $[Rh(oxY)(CO)(PR_3)]$ type complexes

9.1 Introduction

Kinetic studies involving iodomethane oxidative addition reactions to rhodium(I) square planar complexes is no new concept. For example the various investigations on complexes of the type $[Rh(L,L'\text{-Bid})(CO)(PR_3)]$, where $L,L'\text{-Bid}$ = mono anionic bidentate ligand and PR_3 = tertiary phosphine ligand. These investigations utilised techniques such as X-ray crystallography, infra-red, UV/Vis and NMR (^1H and ^{31}P) spectroscopy^{108,109,110,111}. See further discussion in Chapter 2.

The general reaction scheme for the overall reaction of iodomethane addition to $[Rh(oxY)(CO)(PR_3)]$ complexes, as in previous conducted studies, is postulated to occur as presented in Scheme 9.1. Oxidative addition of methyl iodide to the complex $[Rh(ox)(CO)(PPh_3)]$ has been investigated in the past¹¹². van Aswegen *et. al.* were also able to isolate and do a crystal structure determination of the formed rhodium(III) alkyl complex¹¹³. The iodomethane oxidative addition to rhodium(I) reaction is thus an ideal way to evaluate the influence and effects of phosphorous ligands and single point ligand functionalities on the catalytic activity and effectivity of the rhodium(I) metal centre.

¹⁰⁸ Roodt, A. & Steyn, G. J. J. (2000). *Recent Res. Devel. Inorg. Chem.* 2, 1.

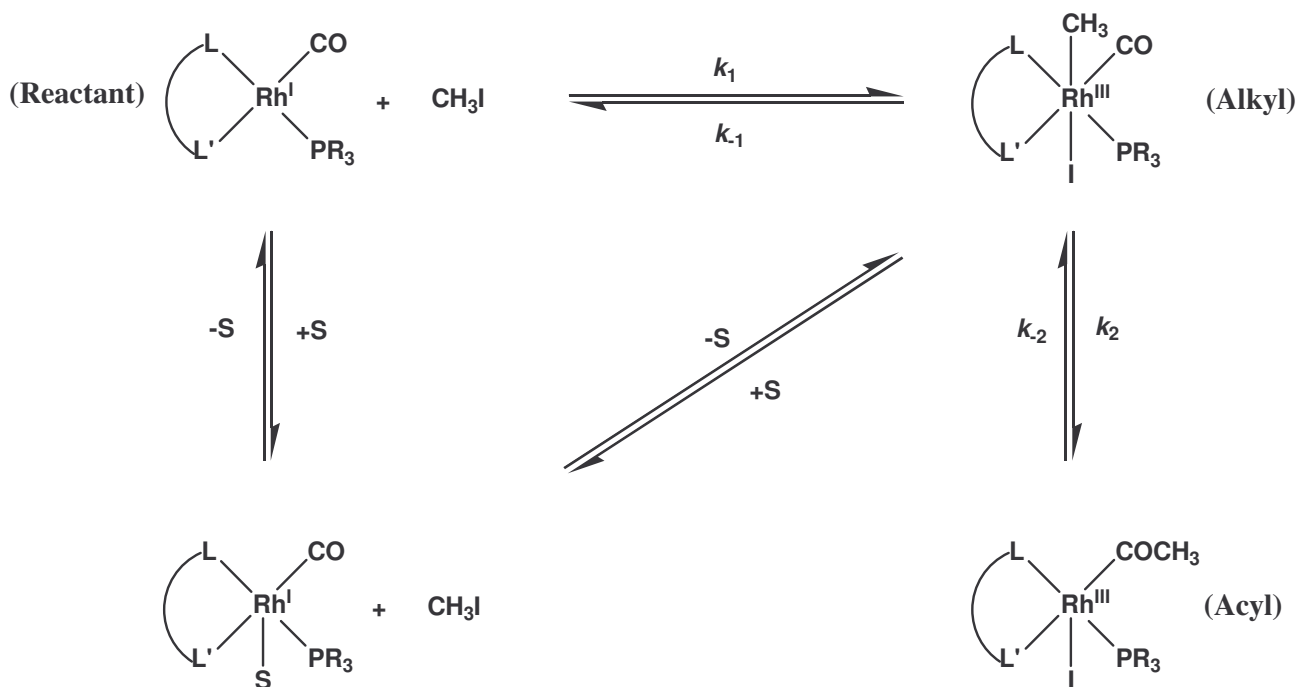
¹⁰⁹ Basson, S.S., Leipoldt, J. G. & Nel, J. T. (1984). *Inorg. Chim. Acta.* 86, 167.

¹¹⁰ Basson, S.S., Leipoldt, J. G., Roodt, A. & Venter, J. A. (1987). *Inorg. Chim. Acta.* 128, 31.

¹¹¹ Leipoldt, J. G., Steynberg, E. C. & Van Eldik, R. (1987). *Inorg. Chem.* 26, 3068.

¹¹² van Aswegen, K. G. M.Sc Thesis, UOVS.

¹¹³ van Aswegen, K. G., Leipoldt, J. G., Potgieter, I.M., Lampbrecht, J.G., Roodt, A. & van Zyl, G.J. (1991). *Trans. Met. Chem.* 16, 369.



Scheme 9.1 The reaction scheme for iodomethane oxidative addition to $[\text{Rh}(\text{L},\text{L}'\text{-Bid})(\text{CO})(\text{PR}_3)]$ complexes followed by migratory insertion. Two oxidative addition pathways are indicated, with the solvent denoted by S.

Being interested in ligand influences in catalytic cycles and the fact that ligands may influence different catalytic cycles in various ways, very basic and preliminary investigations on the $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ complex under hydroformylation reaction conditions were conducted.

9.2 *Experimental*

All kinetic experiments were carried out in air and all solvents were pre-dried over aluminiumoxide and distilled. The rhodium metal complexes were synthesised, characterized and purified as described in Chapter 3.

^{31}P NMR spectra were recorded on a 300 MHz Bruker spectrometer, collecting 1024 scans per spectra, ^{31}P chemical shifts are reported relative to 85 % H_3PO_4 (0 ppm);

positive shifts are downfield. The FT-IR spectra were recorded as liquid samples in dry organic solvents (acetone) in a NaCl cell on a Bruker Tensor 27 spectrometer in the range of $3000\text{--}600\text{ cm}^{-1}$, equipped with a temperature cell regulator accurate within $0.3\text{ }^{\circ}\text{C}$. The HP-IR spectra were recorded by positioning an HP-IR spectroscopic cell¹¹⁴ on a Bruker Tensor 27 spectrometer. UV/Vis absorbance spectra were collected on a Varian Cary 50 Conc spectrophotometer in a $1.000 \pm 0.001\text{ cm}$ quartz cuvette, which was equipped with a temperature cell regulator accurate within $0.1\text{ }^{\circ}\text{C}$.

Kinetic data was analyzed with the Scientist¹¹⁵ software package. Rate laws and kinetic activation parameters are given in Appendix F.

9.3 Results and discussion

9.3.1 Reaction mechanism

An advantage of investigating the activity of 8-hydroxyquinolinorhodium(I) complexes by means of the methyl iodide oxidative reaction is that these complexes form one major isomer¹⁰⁸. This simplifies the mechanistic interpretation and limits side reactions, increasing the viability of studying ligand and functionality influences.

To confirm methyl iodide oxidative addition to the 8-hydroxyquinolinorhodium(I) complexes, FT-IR studies were conducted on all kinetically investigated complexes. These FT-IR spectra illustrates the conversion of a Rh(I)-carbonyl peak to a Rh(III)-alkyl peak, as suggested in Scheme 9.1. Presented in Figure 9.1 are the FT-IR spectra of the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$, illustrating carbonyl stretching frequency change as methyl iodide oxidative addition occurs (Figure 9.2 illustrates the carbonyl peak change over time). These spectra were obtained in acetone at 25°C , displaying a decrease in the

¹¹⁴ We would like to express our gratitude towards SASOL for the use of their HP-IR cell.

¹¹⁵ Scientist for Windows (32), Micromath Inc., Version 2.01, 1986-1995.

Rh(I)-carbonyl signal ($\nu_{\text{CO}} = 1965 \text{ cm}^{-1}$) with a simultaneous increase in the signal of the Rh(III)-alkyl compound ($\nu_{\text{CO}} = 2057 \text{ cm}^{-1}$).

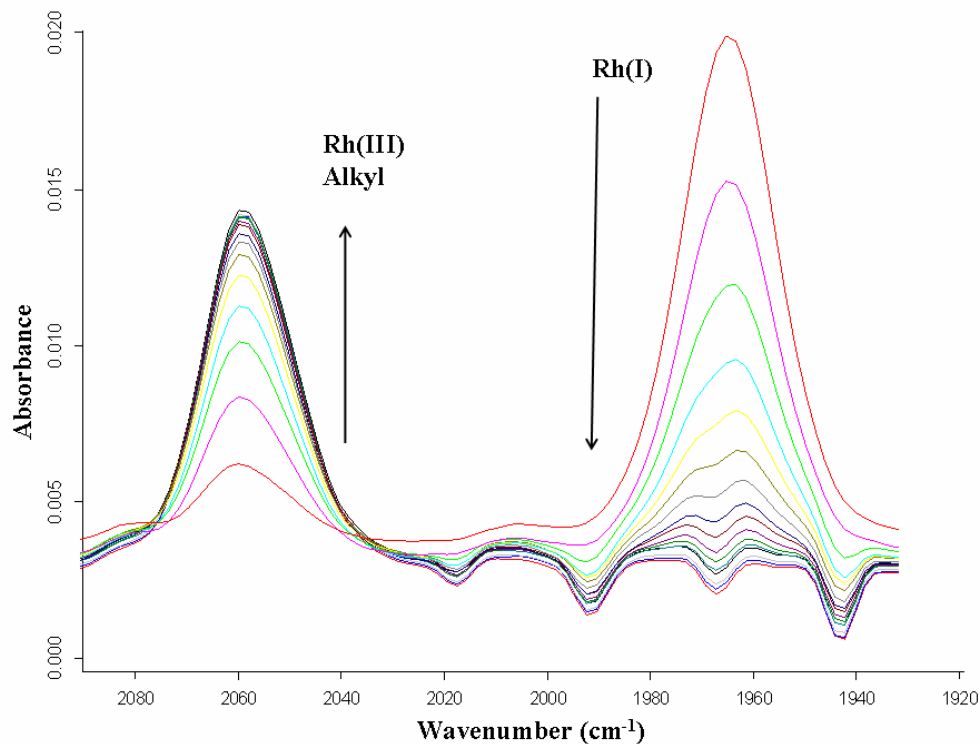


Figure 9.1 Infra red spectra change of $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ by means of MeI oxidative addition.

Illustrating the conversion of the Rh(I) starting complex (1965 cm^{-1}) to the Rh(III) alkyl species (2057 cm^{-1}) in acetone at 25°C . Scans were recorded with 2 min intervals, $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)] = 1.1 \times 10^{-3} \text{ M}$ and $[\text{MeI}] = 9.82 \times 10^{-2} \text{ M}$. $\text{Rh(I)} \text{ } k_{\text{obs}} = 3.8(2) \times 10^{-3} \text{ s}^{-1}$ and $\text{Rh(III)} \text{ } k_{\text{obs}} = 4.0(2) \times 10^{-3} \text{ s}^{-1}$.

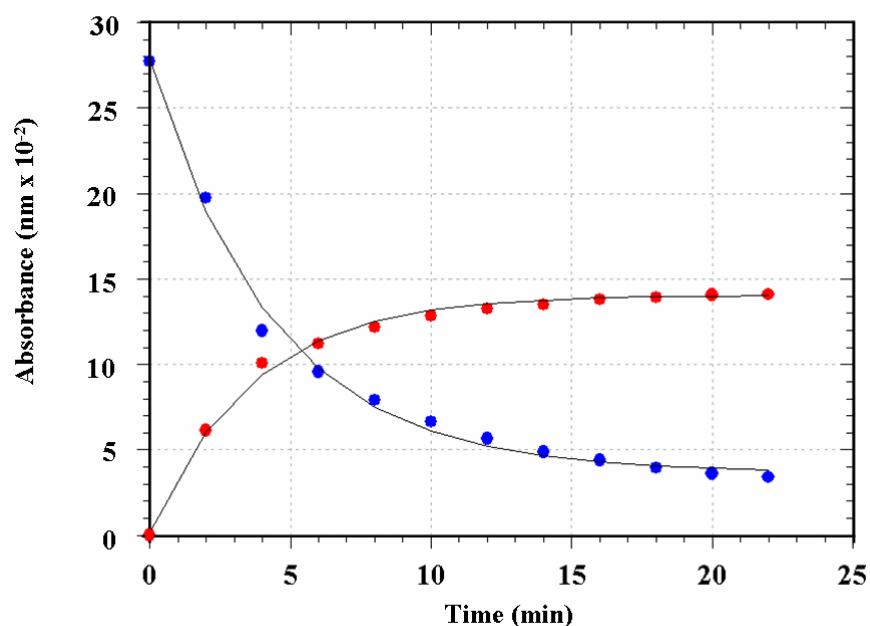


Figure 9.2 Illustration of the carbonyl peak change over time with the methyl iodide oxidative addition to the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$, in acetone at 25°C. Scans collected in 2 min intervals, $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)] = 1.1 \times 10^{-3} \text{ M}$ and $[\text{MeI}] = 9.82 \times 10^{-2} \text{ M}$. $\text{Rh(I)} \ k_{\text{obs}} = 3.8(2) \times 10^{-3} \text{ s}^{-1}$ and $\text{Rh(III)} \ k_{\text{obs}} = 4.0(2) \times 10^{-3} \text{ s}^{-1}$.

The observed change in the ^{31}P -NMR spectra with methyl iodide oxidative addition to the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ is presented in Figure 9.3, a summary of the first order coupling constants is given in Table 9.1. Due to low sensitivity the collected spectra were obtained by 1024 scans, $\pm 51 \text{ min}$. Hence the recorded spectra were not obtained from a reaction mixture under *pseudo*-first order conditions monitoring the observed rate constant of the first reaction step.

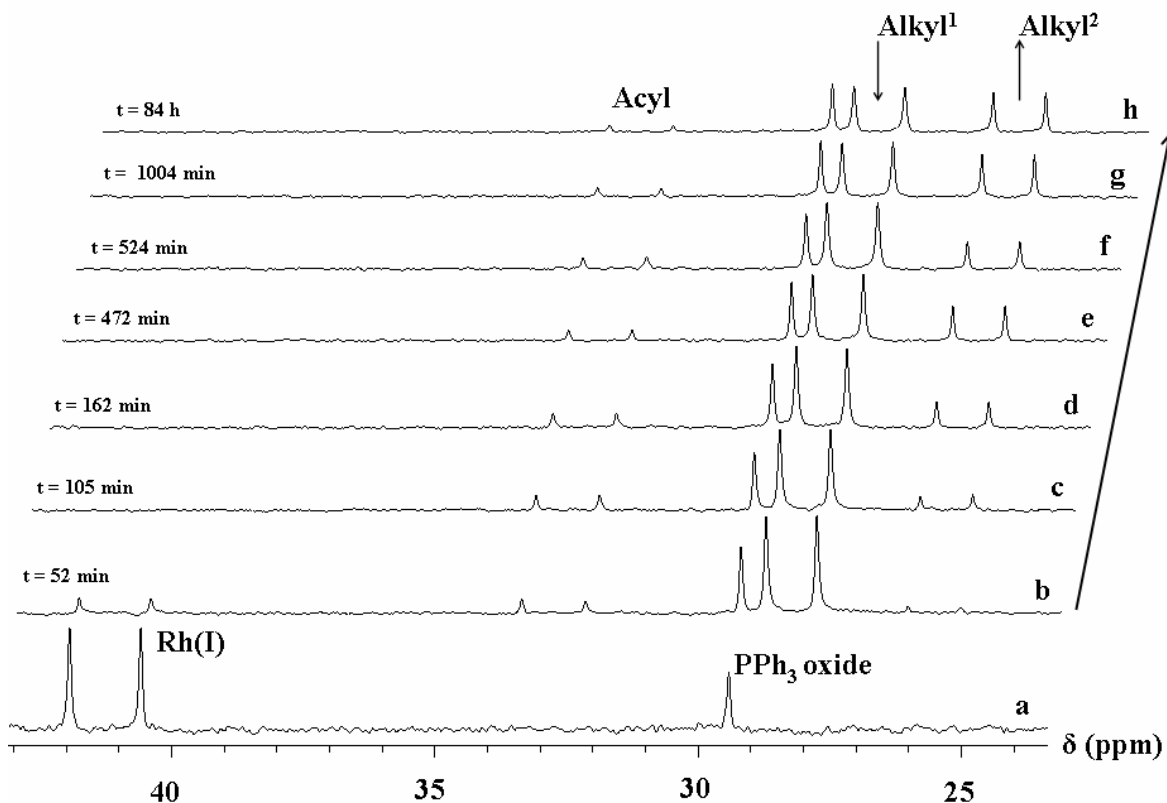


Figure 9.3 Observed ^{31}P -NMR spectra as the $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ complex undergoes methyl iodide oxidative addition to form Alkyl intermediates $[\text{Rh}(\text{ox})(\text{CH}_3)(\text{I})(\text{CO})(\text{PPh}_3)]$ and migratory insertion to form the Acyl product, in acetone at 25°C . a) $[\text{Rh}] = 1.44 \times 10^{-2} \text{ M}$. b) $[\text{Rh}] = 1.34 \times 10^{-1} \text{ M}$, $[\text{MeI}] = 1.05 \times 10^{-1} \text{ M}$. c) $[\text{Rh}] = 1.26 \times 10^{-1} \text{ M}$, $[\text{MeI}] = 2.04 \times 10^{-1} \text{ M}$. d) $[\text{Rh}] = 1.06 \times 10^{-1} \text{ M}$, $[\text{MeI}] = 4.24 \times 10^{-1} \text{ M}$. e-h) $[\text{Rh}] = 7.71 \times 10^{-2} \text{ M}$, $[\text{MeI}] = 7.52 \times 10^{-1} \text{ M}$.

Table 9.1 Summary of chemical shifts and coupling constants for rhodium species present during methyl iodide oxidative addition to the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$, data as from Figure 9.3.

	Chemical shift (ppm)	Coupling constant (Hz)
$[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$	41.2	164
Alkyl ¹	28.4	116
Alkyl ²	25.7	120
Acyl	32.9	146

As observed in Figure 9.3 spectrum **a** is a doublet signal as expected for one major isomer of the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ and a singlet from the internal standard PPh_3 oxide. As illustrated in spectrum **b**, the addition of methyl iodide (0.78 eq) results in a

decrease of the Rh(I) signal and the formation of an Alkyl species, Alkyl^1 , also present is the formation of an Alkyl^2 and an Acyl species. Observed in spectra **c** is the total conversion from the Rh(I) to the Rh(III) species after the addition of 1.6 eq of methyl iodide. Spectra **c** – **h** illustrate the slow formation of the second alkyl species, Alkyl^2 .

From the spectra presented in Figure 9.3 the following conclusions can be made:

1. The complex $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ exists as one major isomer ($\delta = 41.2$ ppm).
2. The first reaction step of methyl iodide oxidative addition to the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ is the formation of an alkyl species, Alkyl^1 ($\delta = 28.4$ ppm), followed by a much slower formation of a second alkyl species, Alkyl^2 ($\delta = 25.7$ ppm).
3. The alkyl species undergoes migratory insertion to form the Acyl product ($\delta = 32.9$ ppm).

The FT-IR and ^{31}P -NMR studies confirmed methyl iodide oxidative addition to the 8-hydroxyquinolinatrhodium(I) complexes, with the first reaction step being the formation of an Rh(III) alkyl species. Being interested in the manipulation of the metals electron density *via* oxine ligand functionalization and phosphine ligand substitution, reaction rates for the Rh(III) Alkyl^1 formation was determined for a range of rhodium complexes, presented in Section 9.3.2 to 9.3.4.

9.3.2 The effect of backbone functionalized 8-hydroxyquinoline on the oxidative addition rate of iodomethane to $[\text{Rh}(\text{oxY})(\text{CO})(\text{PPh}_3)]$ ($\text{Y} = \text{H}, \text{Cl}, \text{NO}_2$)

Apart from studying the influence of 8-hydroxyquinoline functionalities on the nitrogen and oxygen donor atoms, Chapter 5, the influence of these functionalities on the metal centre was investigated. With the aim of investigating electron density variation on the metal centre, it was decided to compare the 8-hydroxyquinolinato-, 5-chloro-8-

hydroxyquinolinato- and 5-nitro-8-hydroxyquinolinato-rhodium(I) systems, expecting that functionalization on the quinoline moiety would influence the electron density on the metal centre and thus the complex activity towards methyl iodide oxidative addition.

The influence of functionalized 8-hydroxyquinolinato ligands on the metal centre was investigated by reacting different CH_3I concentrations with the backbone functionalized rhodium(I)-triphenylphosphine systems. The data was fitted to equation 9.1, incorporating a possible reductive elimination and/or a solvent pathway as an intercept.

$$k_{\text{obs}} = k_f[\text{MeI}] + k_{\text{int}} \quad (9.1)$$

The results are illustrated in Figure 9.4 and summarized in Table 9.2. With no significant intercepts and no trace of a reductive elimination step, all data was handled assuming a negligible contribution from the reductive elimination or solvent steps for the overall observed rate constant.

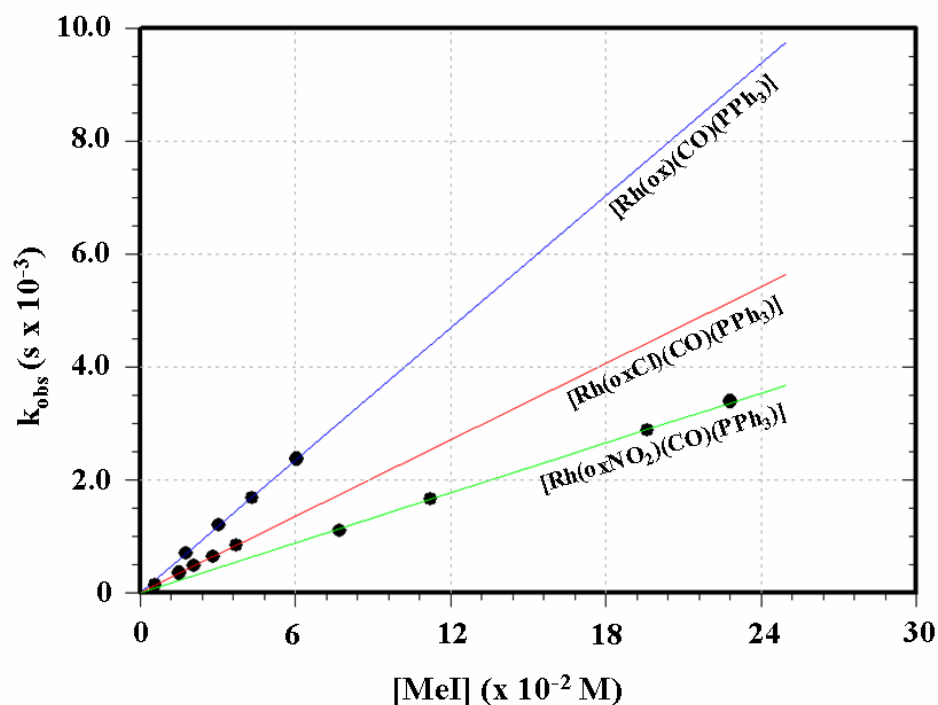


Figure 9.4 Effect of functionalized 8-hydroxyquinolinato rhodium(I) complexes and $[\text{MeI}]$ dependence on the *pseudo*-first order rate constant for the formation of $[\text{Rh}(\text{oxY})(\text{CH}_3)(\text{I})(\text{CO})(\text{PPh}_3)]$, in acetone at 25°C. $[\text{Rh}(\text{ox})(\text{CH}_3)(\text{PPh}_3)] = 2.394 \times 10^{-4} \text{ M}$, $[\text{Rh}(\text{oxCl})(\text{CH}_3)(\text{PPh}_3)] = 2.078 \times 10^{-4} \text{ M}$, $[\text{Rh}(\text{oxNO}_2)(\text{CH}_3)(\text{PPh}_3)] = 1.935 \times 10^{-4} \text{ M}$, $\lambda = 380 \text{ nm}$ for all complexes.

Table 9.2 Kinetic data (2nd order rate constants from Figure 9.4) for the iodomethane oxidative addition to functionalized 8-hydroxyquinolinato rhodium(I) complexes in acetone at 25°C.

Complex	$k_I (\text{M}^{-1} \cdot \text{s}^{-1})$	$t_{1/2} (\text{s})$	$\nu_{\text{CO}} (\text{cm}^{-1})^a$	$^1J_{(\text{Rh-P})} (\text{Hz})^a$
$[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$	0.039(1)	17.8	1965	169
$[\text{Rh}(\text{oxCl})(\text{CO})(\text{PPh}_3)]$	0.023(1)	30.8	1967	164
$[\text{Rh}(\text{oxNO}_2)(\text{CO})(\text{PPh}_3)]$	0.015(1)	46.2	1966	164

a) Data as reported in Table 3.1.

It is clear from Figure 9.4 that there is a decrease in complex activity towards oxidative addition, moving from the basic system $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ to the $[\text{Rh}(\text{oxCl})(\text{CO})(\text{PPh}_3)]$ and finally the $[\text{Rh}(\text{oxNO}_2)(\text{CO})(\text{PPh}_3)]$ complex. The introduction of an electron withdrawing substituent on the quinolinato ligand, decreases the rate of Rh(III)-alkyl species formation. A nitro group on the quinoline backbone

decreases the reaction rate even further than a single substituted atom. On the Pauling scale, the electron negativity values of a Cl-atom and a NO₂ group are 3.16 and 3.15 respectively. Considering these values, one would suspect that their effect on the electron density of the metal centre will be fairly similar or at least comparable. In contrast to this, the kinetic results show a two fold decrease from a 5-NO₂ group compared to that of a 5-Cl atom. This is probably due to electron delocalization over the NO₂ moiety.

9.3.3 The effect of tertiary aryl phosphine ligands on the oxidative addition rate of iodomethane to $[\text{Rh}(\text{ox})(\text{CO})(\text{PR}_3)]$ ($\text{R} = \text{PPh}_3, \text{PPh}_2\text{Cy}, \text{PPhCy}_2, \text{PCy}_3$)

Phosphine ligands can influence a catalytic metal centre in various ways. To investigate the electronic and steric influence from such ligands, a range of tertiary aryl phosphine ligands were introduced to the rhodium(I) complexes. The following phosphine ligands were selected for this evaluation: PPh₃, PPh₂Cy, PPhCy₂ and PCy₃, this on the basis of obtaining a gradual influence from both the electronic and steric parameter, starting with a tri-phenyl ligand and stepwise replacing a phenyl ring with a cyclohexyl ring, up to the tri-cyclohexyl ligand system.

The oxidative addition and reductive elimination steps were investigated for each 8-hydroxyquinolinerhodium(I) ligand system, using different CH₃I concentrations. From the initial data fits with no significant intercepts and no trace of a reductive elimination step. All data were handled assuming a negligible contribution from the reductive elimination or solvent steps for the overall observed rate constant. The *pseudo*-first order rate constants were obtained by the data plotting as illustrated in Figure 9.5 and summarised in Table 9.3.

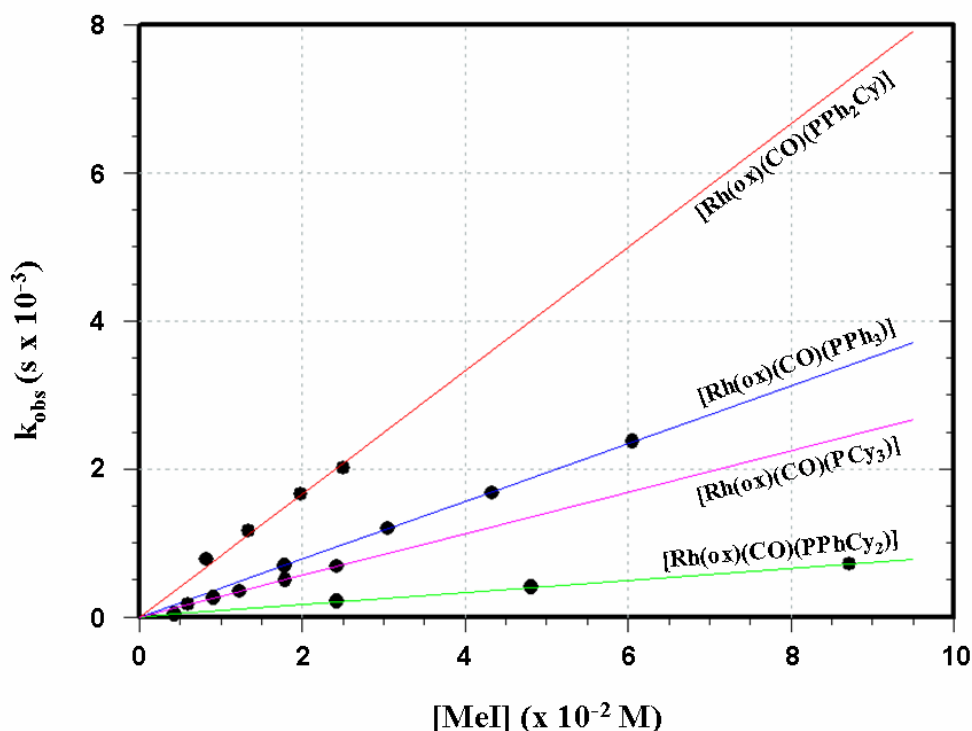


Figure 9.5 Effect of phosphine ligands on 8-hydroxyquinolinorhodium(I) complexes and $[\text{MeI}]$ dependence on the *pseudo*-first order rate constant for the formation of $[\text{Rh}(\text{ox})(\text{CH}_3)(\text{I})(\text{CO})(\text{PR}_3)]$, in acetone at 25°C. $[\text{Rh}(\text{ox})(\text{CH}_3)(\text{PPh}_3)] = 2.394 \times 10^{-4} \text{ M}$, $[\text{Rh}(\text{ox})(\text{CH}_3)(\text{PPh}_2\text{Cy})] = 2.119 \times 10^{-4} \text{ M}$, $[\text{Rh}(\text{ox})(\text{CH}_3)(\text{PPhCy}_2)] = 2.230 \times 10^{-4} \text{ M}$, $[\text{Rh}(\text{ox})(\text{CH}_3)(\text{PCy}_3)] = 2.276 \times 10^{-4} \text{ M}$, $\lambda = 380 \text{ nm}$ for all complexes.

Table 9.3 Kinetic data (2nd order rate constants from Figure 9.5) for the iodomethane oxidative addition to $[\text{Rh}(\text{ox})(\text{CO})(\text{PY})]$ ($\text{Y} = \text{PPh}_3, \text{PPh}_2\text{Cy}, \text{PPhCy}_2, \text{PCy}_3$) complexes, in acetone at 25°C.

Complex	$k_I (\text{M}^{-1} \cdot \text{s}^{-1})$	$t_{1/2} (\text{s})$	$\nu_{\text{CO}} (\text{cm}^{-1})^a$	$^1J_{(\text{Rh-P})} (\text{Hz})^a$	$\theta_E (^\circ)^b$
$[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$	0.039(1)	17.8	1995	164	156
$[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_2\text{Cy})]$	0.083(2)	8.4	1968	163	151
$[\text{Rh}(\text{ox})(\text{CO})(\text{PPhCy}_2)]$	0.008(1)	86.6	1952	161	---
$[\text{Rh}(\text{ox})(\text{CO})(\text{PCy}_3)]$	0.028(1)	24.8	1946	156	167

Data as reported in a) Table 3.1. b) Table 7.1.

When replacing a phenyl ring of a phosphine ligand with the larger cyclohexyl ring, one suspects that the steric influence of the ligand will increase accordingly. If the ligands steric properties are dominating and the assumption is made that the ligands steric factor increase as the number of cyclohexyl rings increases, one would suspect a decrease in the

reaction rate. If the electronic properties of the ligands are dominating, one assumes that the electronic increase from a cyclohexyl ring will increase the electron density on the metal centre and increase the reaction rate. The available ligand effective cone angles, $^1J_{(\text{Rh-P})}$ coupling constants and the *pseudo*-first order reaction rates of the metal complexes are presented in Table 9.3. In Figure 9.5 a reaction rate decrease is noted in the order of $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_2\text{Cy})] > [\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)] > [\text{Rh}(\text{ox})(\text{CO})(\text{PCy}_3)] > [\text{Rh}(\text{ox})(\text{CO})(\text{PPhCy}_2)]$ (further discussed in Section 9.3.4).

By considering the *pseudo*-first order reaction rates and the $^1J_{(\text{Rh-P})}$ coupling constants, it seems that the complex activity is not dominated by the ligands electronic influence. Quite surprisingly, the effective cone angle decreases by 5° with the first phenyl ring replacement by a cyclohexyl ring, (Section 7.7). The $[\text{Rh}(\text{ox})(\text{CO})(\text{PCy}_3)]$ complex however, shows an 11° larger effective cone angle than that of the $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ complex, (Section 7.6). Even though the phosphine ligands effective cone angles do not illustrate the stepwise steric increase, the *pseudo*-first order reaction rates are influenced by the phosphine ligand cone angle. A graphical illustration of the decreasing reaction rate as the effective cone angles increase is presented in Figure 9.6. This suggests that intermolecular soft contacts influencing the ligands effective cone angle are present in the solid state and in solution.

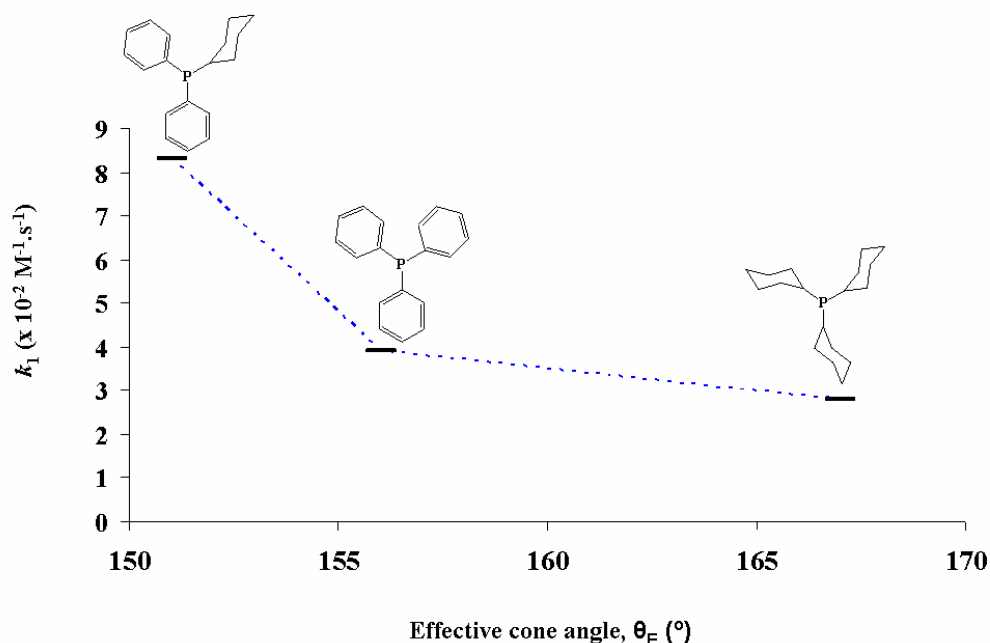


Figure 9.6 Illustrate the relation between the phosphine ligand cone angle (θ_E) and the 2nd order rate constant, for methyl iodide oxidative addition to $[\text{Rh}(\text{ox})(\text{CO})(\text{PR}_3)]$ complexes, data from Table 9.3.

9.3.4 The effect of tertiary aryl phosphine ligands on the oxidative addition rate of iodomethane to $[\text{Rh}(\text{oxCl})(\text{CO})(\text{PR}_3)]$ ($\text{R} = \text{PPh}_3, \text{PPh}_2\text{Cy}, \text{PPhCy}_2, \text{PCy}_3$)

The influence of a Cl-atom on the 5-position of the quinoline backbone was reported in Section 9.3.2. The selected range of phosphine ligated complexes, as reported in Section 9.3.3, yielded an unsuspected influence on the metal complex rate towards methyl iodide oxidative addition. It was thus decided to investigate the influence of phosphine ligands on a 5-chloro-8-hydroxyquinolinorhodium(I) system, an electron poorer rhodium metal centre.

The oxidative addition and reductive elimination steps were investigated for each 5-chloro-8-hydroxyquinolinorhodium(I) ligand system, using different CH_3I concentrations. From the initial data fits, with no significant intercepts and no trace of a reductive elimination step. All data was handled assuming a negligible contribution from the reductive elimination or solvent steps for the overall observed rate constant.

The *pseudo*-first order rate constants were obtained by the data plotting as illustrated in Figure 9.7 and summarised in Table 9.4.

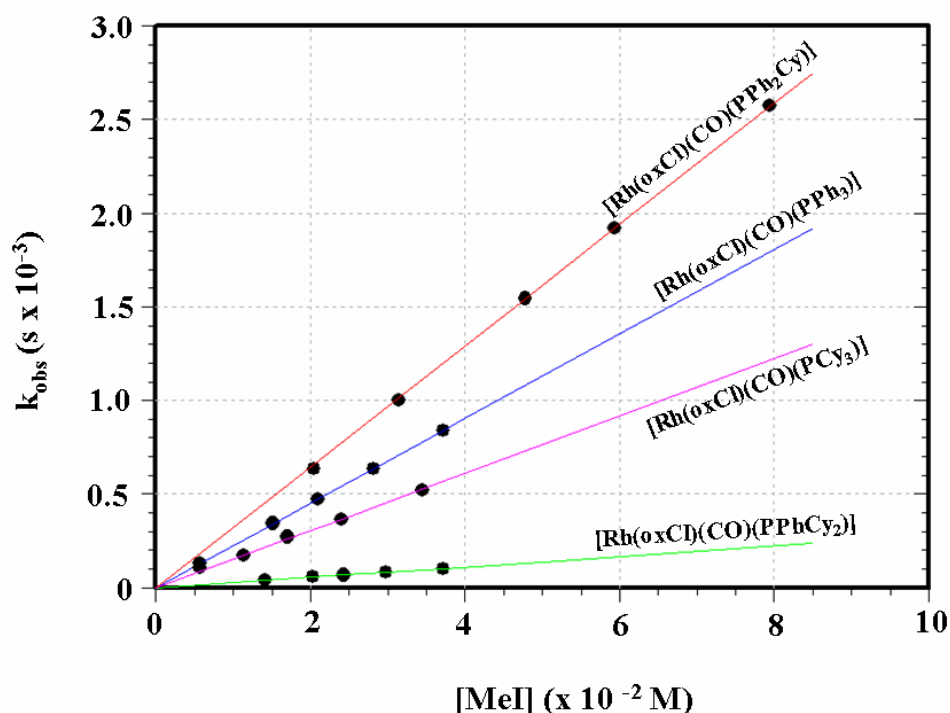


Figure 9.7 Effect of phosphine ligands on 5-chloro-8-hydroxyquinolinorhodium(I) complexes and [MeI] dependence on the *pseudo*-first order rate constant for the formation of $[\text{Rh}(\text{oxCl})(\text{CH}_3)(\text{I})(\text{CO})(\text{PR}_3)]$, in acetone at 25°C. $[\text{Rh}(\text{oxCl})(\text{CH}_3)(\text{PPh}_3)] = 2.078 \times 10^{-4} \text{ M}$, $[\text{Rh}(\text{oxCl})(\text{CH}_3)(\text{PPh}_2\text{Cy})] = 1.291 \times 10^{-4} \text{ M}$, $[\text{Rh}(\text{oxCl})(\text{CH}_3)(\text{PPhCy}_2)] = 1.281 \times 10^{-4} \text{ M}$, $[\text{Rh}(\text{oxCl})(\text{CH}_3)(\text{PCy}_3)] = 2.181 \times 10^{-4} \text{ M}$, $\lambda = 380 \text{ nm}$ for all complexes.

Table 9.4 Kinetic data (2nd order rate constants from Figure 9.7) for the iodomethane oxidative addition to $[\text{Rh}(\text{oxCl})(\text{CO})(\text{PY})]$ (Y = PPh₃, PPh₂Cy, PPhCy₂, PCy₃) complexes in acetone at 25°C, (constants from Figure 9.7).

Complex	$k_I (\text{M}^{-1} \cdot \text{s}^{-1})$	$t_{1/2} (\text{s})$	$\nu_{\text{CO}} (\text{cm}^{-1})^a$	$^1J_{(\text{Rh-P})} (\text{Hz})^a$	Hammett σ value ^b
$[\text{Rh}(\text{oxCl})(\text{CO})(\text{PPh}_3)]$	0.0225(1)	30.8	1967	164	-1.776
$[\text{Rh}(\text{oxCl})(\text{CO})(\text{PPh}_2\text{Cy})]$	0.0323(1)	21.5	1961	162	-2.380
$[\text{Rh}(\text{oxCl})(\text{CO})(\text{PPhCy}_2)]$	0.0027(1)	256.7	1961	162	-2.984
$[\text{Rh}(\text{oxCl})(\text{CO})(\text{PCy}_3)]$	0.0153(2)	45.3	1948	155	-3.588

Data as reported in a) Table 3.1. b) Calculated as described in Chapter 1.

As for the 8-hydroxyquinolinato rhodium complexes, the 5-chloro-8-hydroxyquinolinato rhodium(I) complexes are influenced by the phosphine ligands, in such a way that the metal activity towards oxidative addition decreases in the order of $[\text{Rh}(\text{oxCl})(\text{CO})(\text{PPhCy}_2)] > [\text{Rh}(\text{oxCl})(\text{CO})(\text{PPh}_3)] > [\text{Rh}(\text{oxCl})(\text{CO})(\text{PCy}_3)] > [\text{Rh}(\text{oxCl})(\text{CO})(\text{PPh}_2\text{Cy})]$. The range of phosphine ligands influenced the activity of the different bidentate metal complexes in the same manner, but the strength and effectiveness of these influences changed. To compare the ligand influences between the different bidentate metal complexes each triphenylphosphine complex was selected and the rate constant set to zero, the rate constants of other phosphines were determined as to yield an effective ligand influence. Presented in Figure 9.8 is a graphic illustration of the effective influence of phosphine ligands on the metal activity towards oxidative addition.

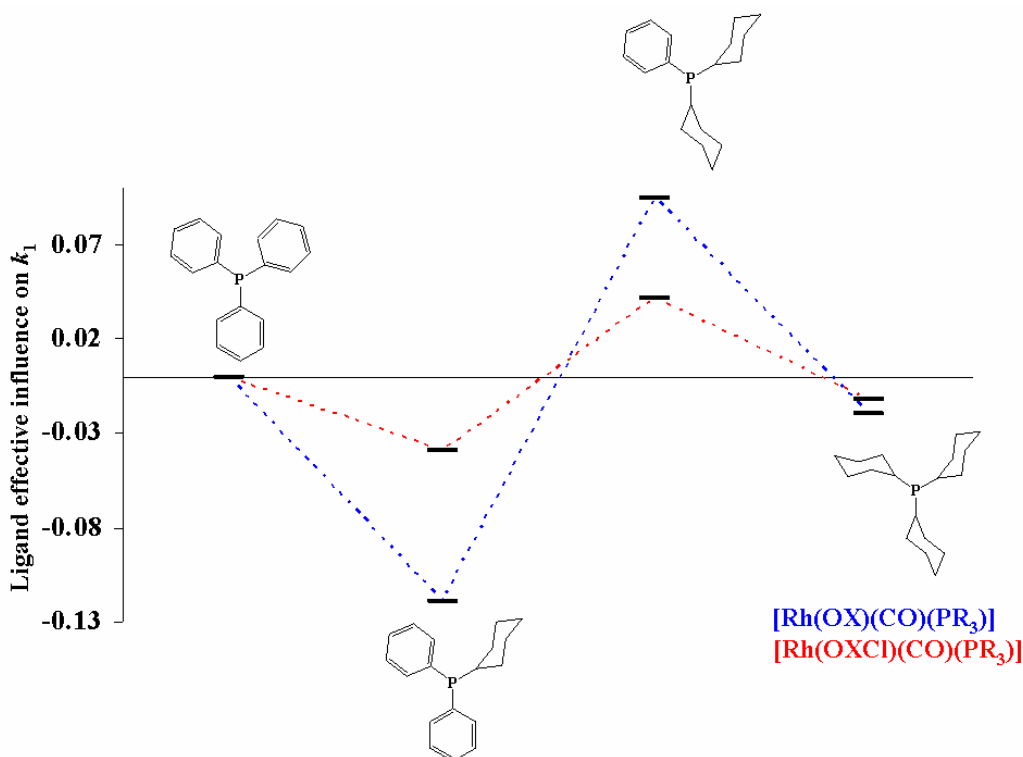


Figure 9.8 Effective activity influence of phosphine ligands on the 8-hydroxyquinolinato and 5-chloro-8-hydroxyquinolinato rhodium(I) complexes towards oxidative addition, selecting the activity of triphenylphosphine complexes as zero and plotting other phosphine ligands relative to zero.

It is concluded from Figure 9.8 that the phosphine ligands influence on the 5-chloro-8-hydroxyquinolinato systems are much smaller, compared to those of the 8-hydroxyquinolinato systems. The functionalized oxine moiety decreases the electron density of the metal centre, Table 9.2, limiting the possibility of electronic influence on the metal centre from a phosphine ligand, (Figure 9.8). The PCy₃ ligand influenced both bidentate metal complexes in the same manner, indicating that the phosphine ligands have a combined steric and electronic effect on the metal centre, up to a point where the ligand cone angle is large enough to dominate all electronic influences in the system. This also points out that for the PPh₃ and PPh₂Cy ligand systems a combined electronic and steric influence is noted.

9.3.5 Temperature dependence of methyl iodide oxidative addition to $[\text{Rh}(\text{oxY})(\text{CO})(\text{PPh}_3)]$ type complexes (Y = H, Cl, NO_2)

Activation parameters for the oxidative addition reaction were determined by a temperature study on the complexes, $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$, $[\text{Rh}(\text{oxCl})(\text{CO})(\text{PPh}_3)]$ and $[\text{Rh}(\text{oxNO}_2)(\text{CO})(\text{PPh}_3)]$. These parameters were calculated by plotting the collected kinetic data to equation 9.2:

$$\ln(k_1/T) = \ln(k_B/h) + \Delta S/R - \Delta H/RT \quad (9.2)$$

The temperature study was utilized by reacting a range of CH_3I concentrations with the rhodium(I) complexes, at four different temperatures. A reductive elimination step was ignored since no experimental evidence suggested its presence. The Gibbs free energy of activation for the oxidative addition reaction was calculated by using the equation 9.3:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (9.3)$$

The obtained and fitted results are illustrated in Figure 9.9 and summarized in Table 9.5.

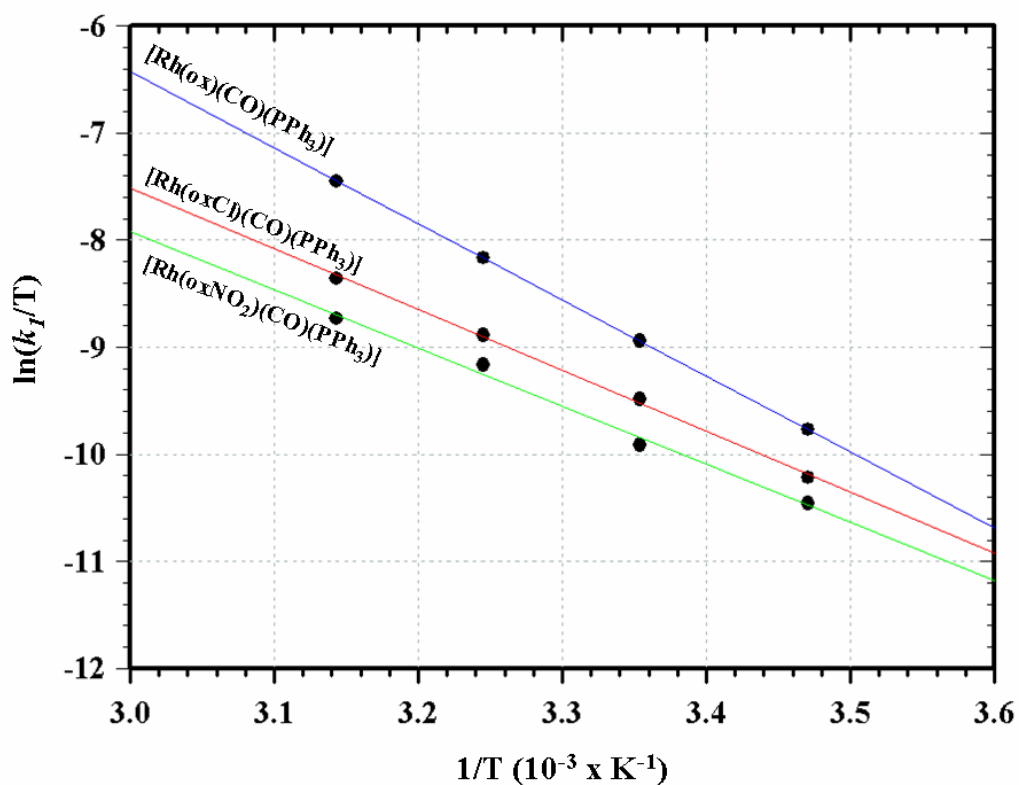


Figure 9.9 Eyring plots of the *pseudo*-first order rate constants, (k_i), for the formation of $[\text{Rh}(\text{oxY})(\text{CH}_3)(\text{I})(\text{CO})(\text{PPh}_3)]$ (where $\text{Y} = \text{H}, \text{Cl}$ or NO_2), in acetone.

Table 9.5 Summary of the activation parameters as obtained from the Eyring equation for the reaction of functionalized 8-hydroxyquinolinatorrhodium(I) complexes with methyl iodide.

Complex	$\Delta H^\ddagger (k_i)$ ($\text{kJ}\cdot\text{mol}^{-1}$)	$\Delta S^\ddagger (k_i)$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	% $T\Delta S^\ddagger$ at 25°C	$\Delta G^\ddagger (k_i)$ ($\text{kJ}\cdot\text{mol}^{-1}$) at 25°C
$[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$	58.9(2)	-74.1(6)	27	81(6)
$[\text{Rh}(\text{oxCl})(\text{CO})(\text{PPh}_3)]$	47(1)	-118(4)	43	82(3)
$[\text{Rh}(\text{oxNO}_2)(\text{CO})(\text{PPh}_3)]$	45(2)	-127(9)	46	83(4)

The oxidative addition reactions proceeded with the characteristic negative values of $\Delta S^\ddagger$ usually observed for associative reactions. As electron withdrawing properties of functionalized quinoline rings increase, the activation parameters decreases, indicating that the lower the electron density of the metal centre, the weaker the formed atomic bonds and the slower the reaction rate.

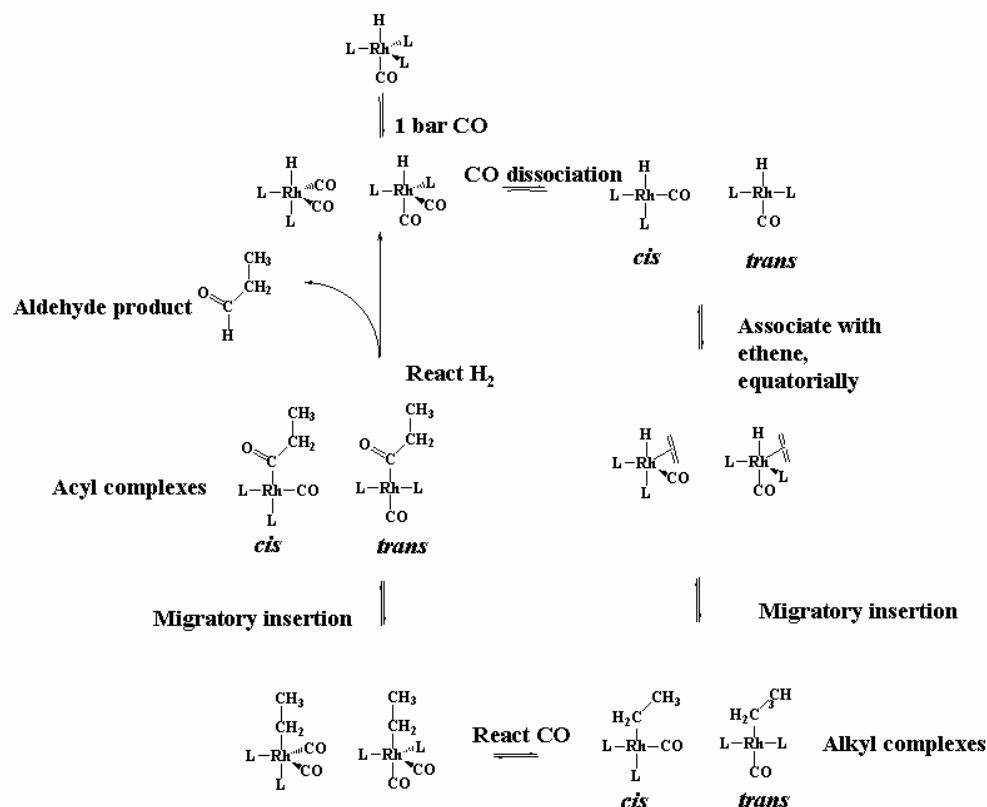
One can observed from Table 9.5 is that the slower the reaction, the larger the contribution of the $-\text{T}\Delta S^\ddagger$ term (between 27 and 46%), thus a larger contribution of entropic effects. Consequently the larger the contribution from the entropy term to the overall free energy of activation, the slower the reaction. At 251 K the $\Delta G^\ddagger$ values of all three complexes are equal, with a value of 77 kJ.mol^{-1} . Although the complex activity towards methyl iodide oxidative addition differ, it is assumed that these complexes probably react with the same reaction mechanism.

9.4 $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ catalyzed hydroformylation

9.4.1 Introduction

Cobalt and rhodium catalysed hydroformylation reactions are known because of the Oxo process discovered in 1938 by O. Roelen. Depicted in Scheme 9.2 is the well known mechanism as first proposed by Heck¹¹⁶. This mechanism corresponds to the dissociative mechanism of Wilkinson.

¹¹⁶ Heck, R. F. (1969). *Acc. Chem. Res.* 2, 10.

Scheme 9.2 Simplified mechanism for rhodium catalysed hydroformylation of ethane⁶.

Without going into a detailed discussion of the mechanism, note the CO insertion under 1 bar of CO pressure and various isomer formations, as well as the formation of a five coordinated rhodium complex before the second migratory insertion step takes place. These facts were important in our preliminary characterization of possible metal species that can form when the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ is treated with syngas under hydroformylation reaction conditions. Section 9.4.2 presents the metal species characterization for $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ catalyzed hydroformylation.

9.4.2 $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ under hydroformylation reaction conditions

The investigation started by determining the effect of CO gas on the dicarbonyl complex $[\text{Rh}(\text{ox})(\text{CO})_2]$. In Figure 9.10 the bottom spectra (blue) displays two stretching frequencies (2077 and 2000 cm^{-1}), the known carbonyl stretching frequencies of the

complex $[\text{Rh}(\text{ox})(\text{CO})_2]$. As CO gas is introduced to the system in 10 bar increments up to 50 bar, a new carbonyl stretching frequency appears at 2020 cm^{-1} , this is most likely a tricarbonyl species that is being formed. The peak at 2020 cm^{-1} is stable as the CO gas is released from the system, but does disappear over time.

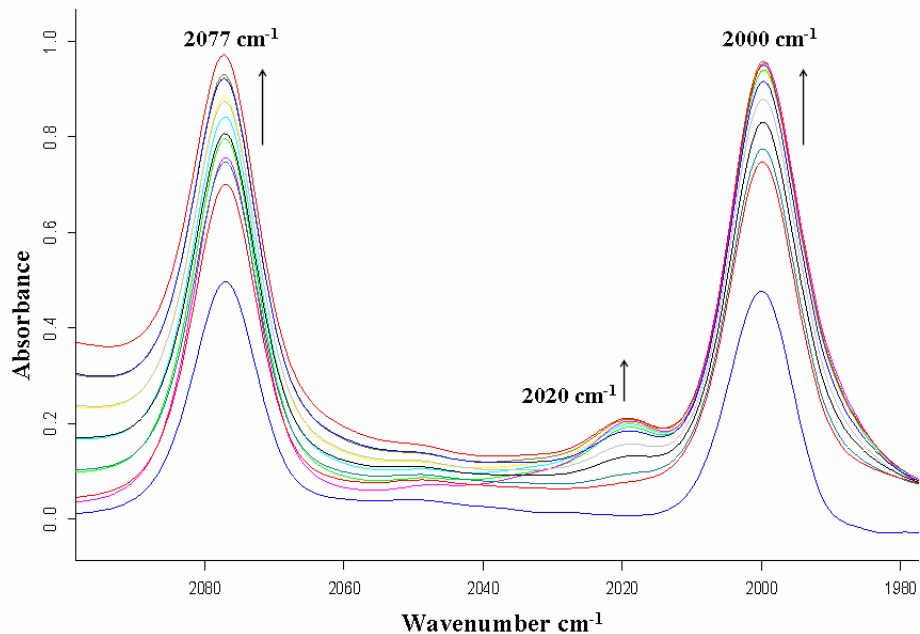


Figure 9.10 HP-IR spectrum indicating carbonyl peak formation at 2020 cm^{-1} , as CO gas pressure are increased in 10 bar increments up to 50 bar. $[\text{Rh}] = 3.8\text{mM}$, using toluene as solvent at 25°C .

After determining that a tricarbonyl species might form under CO gas pressure, triphenylphosphine was added to the rhodiumdicarbonyl complex. The spectra presented in Figure 9.11 were analyzed as follow: spectrum 1 indicates the carbonyl stretching frequencies of the $[\text{Rh}(\text{ox})(\text{CO})_2]$ complex under CO gas pressure. Only after addition of two equivalents of PPh_3 formation of a *mono*-phosphine rhodium complex was observed, indicated by spectrum 2, with no stretching frequency in the 2080 cm^{-1} region. Spectrum 2 does display three carbonyl stretching frequencies, the peak at 1962 cm^{-1} is from the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$. With a 50 bar increase in the CO gas pressure an increase

in the intensities of 2020 and 2000 cm^{-1} peaks was noted, as shown by spectrum 3. With the intensity of the peak at 1962 cm^{-1} staying constant, meaning that the peaks at 2020 and 2000 cm^{-1} are [CO] dependant. Thus the possibility arises of three isomers in the system at this stage. Postulated illustrations are presented in Scheme 9.3, assuming that the phosphine ligand stays in the metal coordination plane, based on the fact that the peak at 1962 cm^{-1} does not decrease as the peaks at 2020 and 2000 cm^{-1} increase.

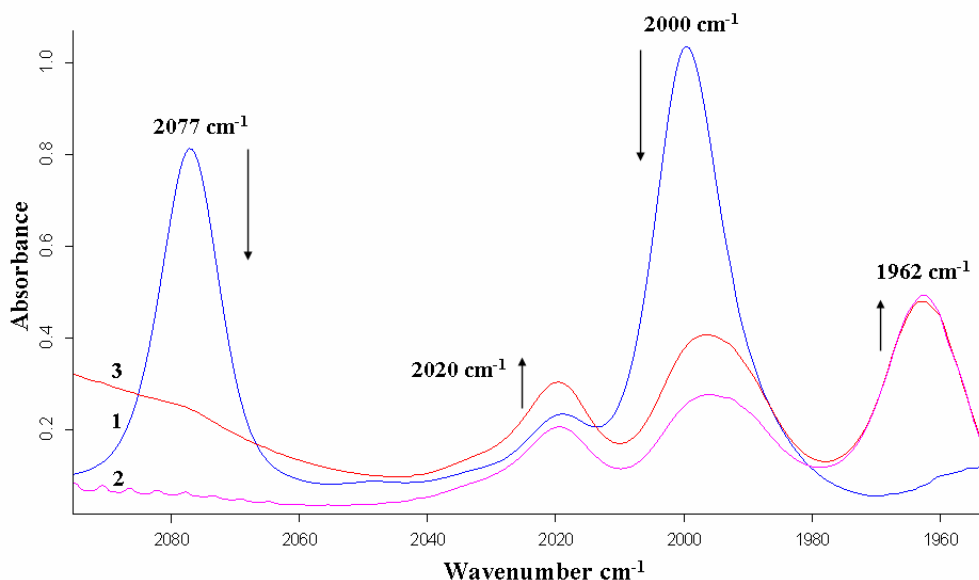
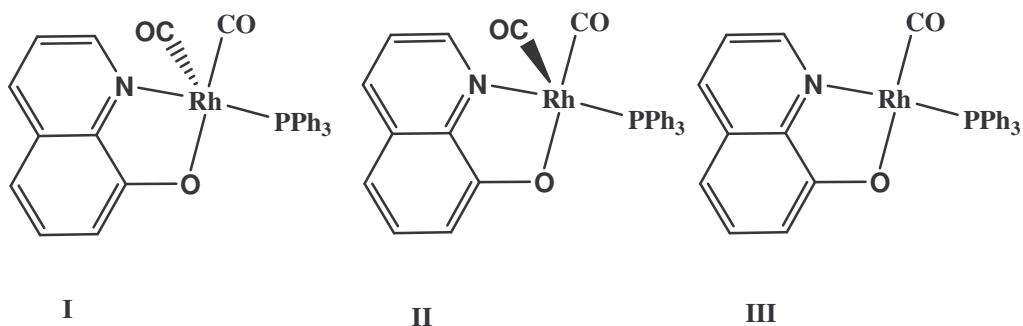


Figure 9.11 HP-IR spectra showing $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ species formation, 1962 cm^{-1} , from $[\text{Rh}(\text{ox})(\text{CO})_2]$, 2077 and 2000 cm^{-1} , after addition of 2.5eq of PPh_3 at 10bar CO pressure. CO pressure increase to 50 bar indicate two CO dependant peaks, 2020 and 2000 cm^{-1} . $[\text{Rh}] = 3.8\text{mM}$, using toluene as solvent.



Scheme 9.3 Line drawing of the possible rhodium species formed under CO gas pressure.

Figure 9.12 presents the obtained IR-spectra after introducing 1-octene to the catalytic system, at 20 bar syngas pressure and 50 °C, scanning for 30 minutes. The intensity of the 1-octene decreases, with a rapid peak formation and growth was observed in the mid 1700 cm^{-1} range in the region for the aldehyde product frequency. In the carbonyl stretching frequency range, five peaks are observed. Together with the information obtained from spectra presented in Figure 9.10 and Figure 9.11, the peaks were labeled as follows: Peak (1) and (3) represents the complex $[\text{Rh}(\text{ox})(\text{CO})_2]$ and peak (5) the complex $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$. Peak (2) presents a CO pressure dependant peak for the $[\text{Rh}(\text{ox})(\text{CO})_2(\text{PPh}_3)]$ species. The stretching frequency of another $[\text{Rh}(\text{ox})(\text{CO})_2(\text{PPh}_3)]$ species will also be at peak (3), a possible explanation for the peak height difference between (1) and (3), while peak (4) possibly represents a catalytic intermediate.

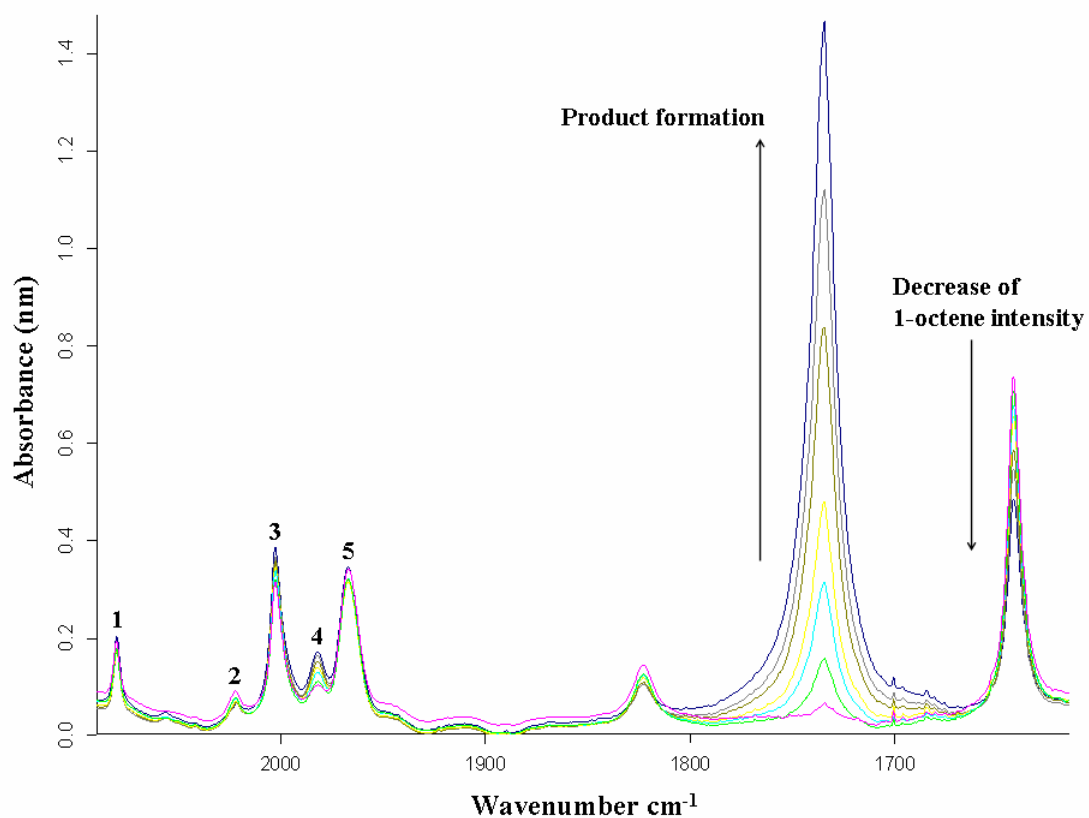


Figure 9.12 Illustrates catalytic activity of $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$ under hydroformylation reaction conditions, displaying a decrease in the 1-octene intensity and a product formation in the aldehyde stretching frequency range. Peaks 1-5 are carbonyl stretching frequencies of metal species and intermediates. $[\text{Rh}] = 3.3 \text{ mM}$ using Octane as solvent at 50°C and 20bar syngas, scan time = 30min.

9.5 Conclusion

In this chapter the influences of functionalized bidentate ligands and phosphine ligands on a rhodium metal centre were determined utilizing methyl iodide oxidative addition to the metal complex, summarized in Table 9.6.

Table 9.6 Summary of the kinetic data (2nd order rate constants), for the reactions of 8-hydroxyquinolinatorrhodium(I) complexes with methyl iodide.

Complex	k_I ($\text{M}^{-1} \cdot \text{s}^{-1}$)	$t_{1/2}$ (s)	$^1J_{(\text{Rh-P})}$ (Hz) ^a
$[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$	0.039(1)	17.8	164
$[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_2\text{Cy})]$	0.083(2)	8.4	163
$[\text{Rh}(\text{ox})(\text{CO})(\text{PPhCy}_2)]$	0.008(1)	86.6	161
$[\text{Rh}(\text{ox})(\text{CO})(\text{PCy}_3)]$	0.028(1)	24.8	156
$[\text{Rh}(\text{oxCl})(\text{CO})(\text{PPh}_3)]$	0.0225(1)	30.8	164
$[\text{Rh}(\text{oxCl})(\text{CO})(\text{PPh}_2\text{Cy})]$	0.0323(1)	21.5	162
$[\text{Rh}(\text{oxCl})(\text{CO})(\text{PPhCy}_2)]$	0.0027(1)	256.7	162
$[\text{Rh}(\text{oxCl})(\text{CO})(\text{PCy}_3)]$	0.0153(2)	45.3	155
$[\text{Rh}(\text{oxNO}_2)(\text{CO})(\text{PPh}_3)]$	0.015(1)	46.2	164

Specific electron density manipulation was achieved by single point functionalization on the 8-hydroxyquinoline backbone. Functionalization on the quinoline backbone ensured sole electronic influence, seen that an atom or group on the 5-position is too far away from the metal centre to have a steric contribution.

Phosphine ligands influence the metal centre *via* combined electronic and steric properties. The selected range of phosphines decrease 8-hydroxyquinolinatorrhodium(I) complex activity towards methyl iodide oxidative addition in the order of: $\text{PPh}_2\text{Cy} > \text{PPh}_3 > \text{PPhCy}_2 > \text{PCy}_3$. A study on acetylacetonate based systems showed the same order of activity for the phosphine ligated complexes¹¹⁷. A solid state study on $[\text{Rh}(\text{acac})(\text{CO})(\text{PR}_3)]$ complexes indicated an increasing effective cone angle from the PPh_3 to the PCy_3 ligand system¹¹⁷, in contrast with the kinetic results, (Table 2.6). The $[\text{Rh}(\text{ox})(\text{CO})(\text{PR}_3)]$ complexes yielded a cone angle increase in the ligand order of:

¹¹⁷ Brink, A. (2007). *M.Sc. Thesis*. University of the Free State.

$\text{PPh}_2\text{Cy} < \text{PPh}_3 < \text{PCy}_3$, corresponding with the kinetic results, as illustrated in Figure 9.6.

To clarify the phosphine ligand influences, the 5-chloro-8-hydroxyquinolinato complexes were catalytically investigated and a comparison of the quinolinato kinetic data showed the following:

1. Phosphine ligands influence the metal centre in the same manner, as illustrated in Figure 9.5 and Figure 9.7.
2. With an electron withdrawing influence from the bidentate ligand, Figure 9.4, the electronic influence from a phosphine ligand is limited but still present, (Figure 9.8). This Emphasizes that phosphine ligands with relative small cone angles do have an electronic influence and not a sole steric influence.
3. At some point the phosphine ligands steric influence will be large enough to overwhelm all electronic influences in the system, both phosphine and quinoline affiliated (as illustrated in Figure 9.8) where both PCy_3 ligand complexes have the same influence on the complex activity towards methyl iodide oxidative addition.

The preliminary investigation of 8-hydroxyquinolinatorhodium(I) complexes under hydroformylation reaction conditions showed catalytic activity towards aldehyde formation, making a study regarding the ligand influences on catalysed hydroformylation reactions viable, however, species characterization utilizing HP-NMR experiments should be conducted to propose a reaction mechanism.

An overview and evaluation of the results obtained throughout this study is presented Chapter 10.

Chapter 10

Evaluation of Study

10.1 Introduction

The successes of this study is discussed in the following section, in terms of the aims as described in Chapter 1, followed by some future aspects.

10.2 Evaluation

10.2.1 8-Hydroxyquinoline compounds

The fact that the 5-position on an 8-hydroxyquinoline molecule is the most reactive site towards substitution reactions, makes single point ligand functionalization viable, fairly easy and selective, (Chapter 3). This leads to the successful synthesis and characterization of a range of bidentate ligands with electronic and steric differing substituents on the 5-position of the quinoline backbone, (Chapter 4).

By using computational chemistry at a DFT level to study the non-complexed ligands, it was determined that the energetically preferred isomer is the *cis*-hydroxyl hydrogen configuration, (Chapter 5). The electronic influence from the substituents on the quinoline backbone affects the hydroxyl hydrogen rotation and proton transfer transition states. It however does not change the nitrogen and oxygen order of σ -electron donor capability. Configuration studies on the 5-phenylazo substituted compounds seem to indicate that orientations are sterically determined. The phenylazo ring prefers an *anti*-configuration in relation to the quinoline ring system and substituents on the *ortho*-position of the phenylazo ring also prefer to be *trans*-directed in relation to the quinoline rings, (Chapter 6).

A few 8-hydroxyquinoline type compounds were characterized by single crystal X-ray diffraction. The importance of the hydroxyl hydrogen configuration was clear in this

study by noting specifically how the intermolecular interaction *via* a hydroxyl hydrogen influences the crystal packing. A neutral 8-hydroxyquinoline system with a *cis*-configured hydroxyl hydrogen forms hydrogen bonded dimers in the solid state, while a *trans*-configured hydroxyl hydrogen prohibits the formation of direct hydrogen bonded dimers, (Chapter 4).

10.2.2 Rhodium(I) square planar complexes

The bidentate ligands donor atoms play a significant role in phosphine ligand substitution on square planar metal complexes. Being interested in the σ -donor and π -acceptor properties of the N- and O-atoms and the influence that quinoline ligand functionalities will have on these donor atoms. Complexation of a range of 8-hydroxyquinoline bidentate ligands to a rhodium metal centre, forming the dicarbonyl complex, was successful. With all 8-hydroxyquinolinorhodium(I) compounds the electron density was distributed over the fused ring system in such a way that the N-atom always remains as the stronger σ -electron donor. This leads to phosphine and phosphite ligand substitution *trans* to the N-atom of the bidentate ligand, also confirmed by the solid state characterization.

Thirteen metal complexes were characterized by single crystal X-ray diffraction (see Chapter 6, 7 and 8). As the neutral 8-hydroxyquinoline ligands stack in pairs by the formation of hydrogen bonded dimers, the metal complexes stack in pairs, however, by the stabilization of a ligand to ligand π - π stacking. This π -stacking is also influenced by the steric properties of the phosphorous ligand. The quinoline ligands need to be relatively close to one another, 3.4 Å, for π -orbital overlapping a distance that in most cases could only be gained by a “head to tail” orientation to prevent phosphorous ligand overlap. The π -stacking is also an indication of the electron delocalization over the fused ring system and the electronic strength present in these orbitals. Cases where no ligand to ligand π - π stacking are present are found in the crystal packing of the complexes, [Rh(ox)(CO)(PCyPh₂)] and [Rh(oxL-Me₃)(CO)(PPh₃)], probably due to other dominating intermolecular interactions. On the other hand for the complexes [Rh(oxCl)(CO)P(p-FPh)₃] and [Rh(oxL)(CO)(PPh₃)] ligand to ligand π -stacking is present but not in the

usual fashion. For the complex $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-FPh})_3]$, this is probably due to the two independent molecules in the unit cell. For the complexes $[\text{Rh}(\text{oxL})(\text{CO})(\text{PPh}_3)]$, it is probably the ligand elongation by the phenylazo ring that allows the molecules to pack in a “head to head” fashion and achieve significant π -orbital overlap between one quinoline and one phenylazo ring without steric hindrance from the phosphine ligand. Functionalization thus influences the complex ligand to ligand π -stacking *via* additional intermolecular interaction and bidentate ligand elongation. Another interaction between the ligand to ligand π -stacking is the interaction between the metal carbonyl moiety and the substituent on the 5-position of the quinoline backbone.

10.2.3 Oxidative addition activity of the rhodium(I) complexes

A number of rhodium(I) complexes were prepared by introducing functionalized 8-hydroxyquinoline ligands and selected phosphine ligands. The effect in basic catalytic substitution reactions of the rhodium metal centre towards, for example a MeI oxidative addition reaction, was investigated. Methyl iodide oxidative addition to a range of 8-hydroxyquinolinorhodium(I) complexes containing the following phosphines, PPh_3 , PPh_2Cy , PPhCy_2 and PCy_3 , has show that the complex oxidative addition activity decreases in the following order: $[\text{Rh}(\text{ox})(\text{CO})(\text{PPhCy}_2)] > [\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)] > [\text{Rh}(\text{ox})(\text{CO})(\text{PCy}_3)] > [\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_2\text{Cy})]$. The same decreasing order in oxidative addition activity was observed for the 5-chloro-8-hydroxyquinolinorhodium(I) complexes: $[\text{Rh}(\text{oxCl})(\text{CO})(\text{PPhCy}_2)] > [\text{Rh}(\text{oxCl})(\text{CO})(\text{PPh}_3)] > [\text{Rh}(\text{oxCl})(\text{CO})(\text{PCy}_3)] > [\text{Rh}(\text{oxCl})(\text{CO})(\text{PPh}_2\text{Cy})]$. Considering the phosphine ligands effective cone angle, (θ_E), and the Rh-P coupling constants (as given in Table 9.3 and Table 9.4) it was concluded that the phosphines have a combined steric and electronic influence on the metal's electron density. Thus was observed in the oxidative addition activity where the phosphine ligands steric influence becomes large enough to dominate all electronic influences on the metal centre, as illustrated in Figure 9.8.

The influence of bidentate ligand functionalization on the complex oxidative addition activity was investigated by comparing the electronic influences from a H, Cl and a NO_2 moiety on the 5-position of the quinoline backbone. The complex oxidative addition activity decreased in the following order: $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)] > [\text{Rh}(\text{oxCl})(\text{CO})(\text{PPh}_3)] > [\text{Rh}(\text{oxNO}_2)(\text{CO})(\text{PPh}_3)]$. A decrease in the oxidative addition activity was noticed as the electron accepting property of the substituent on the 5th position of the oxine backbone increased, decreasing the electron density on the metal centre. Determination of activation parameters for the complexes $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$, $[\text{Rh}(\text{oxCl})(\text{CO})(\text{PPh}_3)]$ and $[\text{Rh}(\text{oxNO}_2)(\text{CO})(\text{PPh}_3)]$ displayed low positive activation enthalpy values and high negative activation entropy values, indicating no significant bond breaking and a possible associative mechanism. This also indicates similar reaction pathways with comparable activation barriers for these complexes, although their activity varies significantly.

Investigations of the complex $[\text{Rh}(\text{oX})(\text{CO})(\text{PPh}_3)]$ as a catalytic precursor in hydroformylation reactions showed reactivity towards aldehyde formation. Before investigations regarding ligand influence on aldehyde formation activity commences, the various catalytic species and intermediates present in the catalytic cycle should be characterized by HP-NMR.

10.3 Future work

As mentioned, the possibilities arising from this study is quite abundant with 8-hydroxyquinoline ligand functionalization alone. Not even considering different metal systems, the range of complexes that one can synthesize with commercially available phosphines, arsines, stibines, etc. is quite significant.

The presented investigation on methyl iodide oxidative addition to complexes of the type $[\text{Rh}(\text{oXY})(\text{CO})(\text{PR}_3)]$ were $\text{Y} = \text{H}, \text{Cl}$ or NO_2 and $\text{R} = \text{Aryl}$, (Chapter 9) should be expanded to include mechanistic investigations on the Alky^2 and Acyl species formation and ligand influence on the formation rate of these species.

As mentioned, after characterization of the catalytic species and intermediates present in $[\text{Rh}(\text{oX})(\text{CO})(\text{PPh}_3)]$ catalysed hydroformylation reactions, this study should continue by investigating ligand effects on the rate of aldehyde formation.

Appendix A Crystal data of Quinoline ligands

A1. Crystal data of 5-chloro-8-hydroxyquinoline, (HoxCl)

Table A1. 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (HoxCl). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2185(1)	1667(1)	2492(7)	15(1)
C(2)	1808(1)	1356(1)	1750(7)	14(1)
C(3)	1338(1)	1469(1)	2581(7)	14(1)
C(4)	1240(1)	1893(1)	4176(8)	12(1)
C(5)	770(1)	2048(1)	5196(7)	14(1)
C(6)	704(1)	2459(1)	6763(8)	15(1)
C(7)	1106(1)	2745(1)	7398(7)	15(1)
C(8)	1568(1)	2616(1)	6411(7)	14(1)
C(9)	1644(1)	2183(1)	4822(7)	12(1)
N	2113(1)	2063(1)	3997(6)	14(1)
O	1943(1)	2903(1)	7006(6)	20(1)
Cl	265(1)	1701(1)	4359(2)	18(1)

Table A1. 2. Bond lengths ($\text{\AA}$) and angles ($^\circ$) for (HoxCl)

C(1)-N	1.314(3)	C(1)-C(2)-H(2)	120.5
C(1)-C(2)	1.408(3)	C(2)-C(3)-C(4)	119.44(17)
C(1)-H(1)	0.9300	C(2)-C(3)-H(3)	120.3
C(2)-C(3)	1.365(3)	C(4)-C(3)-H(3)	120.3
C(2)-H(2)	0.9300	C(3)-C(4)-C(5)	124.91(17)
C(3)-C(4)	1.413(3)	C(3)-C(4)-C(9)	117.33(17)
C(3)-H(3)	0.9300	C(5)-C(4)-C(9)	117.75(18)
C(4)-C(5)	1.416(3)	C(6)-C(5)-C(4)	121.73(17)
C(4)-C(9)	1.420(2)	C(6)-C(5)-Cl	119.60(15)
C(5)-C(6)	1.362(3)	C(4)-C(5)-Cl	118.66(16)
C(5)-Cl	1.7473(19)	C(5)-C(6)-C(7)	120.27(17)
C(6)-C(7)	1.407(3)	C(5)-C(6)-H(6)	119.9
C(6)-H(6)	0.9300	C(7)-C(6)-H(6)	119.9
C(7)-C(8)	1.373(3)	C(8)-C(7)-C(6)	120.60(19)
C(7)-H(7)	0.9300	C(8)-C(7)-H(7)	119.7
C(8)-O	1.349(2)	C(6)-C(7)-H(7)	119.7
C(8)-C(9)	1.426(3)	O-C(8)-C(7)	118.86(18)
C(9)-N	1.366(2)	O-C(8)-C(9)	121.50(17)
O-H(0)	0.8200	C(7)-C(8)-C(9)	119.63(17)
		N-C(9)-C(4)	122.45(17)
N-C(1)-C(2)	123.83(18)	N-C(9)-C(8)	117.56(16)
N-C(1)-H(1)	118.1	C(4)-C(9)-C(8)	119.99(17)

C(2)-C(1)-H(1)	118.1	C(1)-N-C(9)	117.89(16)
C(3)-C(2)-C(1)	119.04(18)	C(8)-O-H(0)	109.5
C(3)-C(2)-H(2)	120.5		

Table A1. 3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (HoxCl). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	13(1)	17(1)	15(2)	4(1)	2(1)	4(1)
C(2)	19(1)	13(1)	12(1)	0(1)	2(1)	1(1)
C(3)	17(1)	13(1)	13(2)	2(1)	0(1)	-2(1)
C(4)	13(1)	14(1)	8(1)	2(1)	-1(1)	2(1)
C(5)	12(1)	16(1)	14(2)	5(1)	-1(1)	-3(1)
C(6)	13(1)	17(1)	15(1)	5(1)	3(1)	3(1)
C(7)	21(1)	12(1)	13(2)	0(1)	2(1)	3(1)
C(8)	18(1)	14(1)	10(1)	1(1)	1(1)	0(1)
C(9)	15(1)	14(1)	9(1)	3(1)	1(1)	1(1)
N	14(1)	14(1)	14(1)	1(1)	0(1)	0(1)
O	18(1)	16(1)	26(1)	-5(1)	5(1)	-3(1)
Cl	12(1)	21(1)	22(1)	0(1)	0(1)	-3(1)

Table A1. 4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (HoxCl).

	x	y	z	U(eq)
H(1)	2503	1587	1882	18
H(2)	1879	1078	709	17
H(3)	1084	1269	2102	17
H(6)	391	2551	7416	18
H(7)	1057	3023	8496	18
H(0)	2194	2800	6116	30

A2. Crystal data of 5-Chloro-8-hydroxyquinolinium bromide, (H₂oxCl.Br)

Table A2. 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (H₂oxCl.Br). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5460(10)	1030(6)	9222(3)	14(1)
C(2)	3238(10)	594(6)	8745(3)	15(1)
C(3)	1652(10)	1512(6)	8356(3)	14(1)
C(4)	2219(10)	2873(6)	8423(2)	12(1)
C(5)	701(10)	3900(6)	8046(2)	12(1)
C(6)	1375(10)	5201(6)	8163(3)	13(1)
C(7)	3638(10)	5569(6)	8659(3)	13(1)
C(8)	5201(10)	4616(5)	9026(3)	13(1)
C(9)	4467(10)	3275(5)	8919(2)	12(1)
N	6010(9)	2320(4)	9290(2)	12(1)
O	7450(7)	4825(4)	9508(2)	14(1)
Cl	-1972(3)	3483(2)	7395(1)	18(1)
Br	982(1)	2092(1)	10529(1)	13(1)

Table A2. 2. Bond lengths ($\text{\AA}$) and angles ($^\circ$) for (H₂oxCl.Br)

C(1)-N	1.332(7)	C(1)-C(2)-H(2)	120.5
C(1)-C(2)	1.399(7)	C(2)-C(3)-C(4)	121.5(5)
C(1)-H(1)	0.9300	C(2)-C(3)-H(3)	119.3
C(2)-C(3)	1.368(7)	C(4)-C(3)-H(3)	119.3
C(2)-H(2)	0.9300	C(3)-C(4)-C(9)	117.9(5)
C(3)-C(4)	1.403(7)	C(3)-C(4)-C(5)	125.8(5)
C(3)-H(3)	0.9300	C(9)-C(4)-C(5)	116.4(5)
C(4)-C(9)	1.417(7)	C(6)-C(5)-C(4)	121.3(5)
C(4)-C(5)	1.420(7)	C(6)-C(5)-Cl	119.5(4)
C(5)-C(6)	1.364(8)	C(4)-C(5)-Cl	119.1(4)
C(5)-Cl	1.742(5)	C(5)-C(6)-C(7)	120.9(5)
C(6)-C(7)	1.413(7)	C(5)-C(6)-H(6)	119.5
C(6)-H(6)	0.9300	C(7)-C(6)-H(6)	119.5
C(7)-C(8)	1.368(7)	C(8)-C(7)-C(6)	120.1(5)
C(7)-H(7)	0.9300	C(8)-C(7)-H(7)	120.0
C(8)-O	1.358(6)	C(6)-C(7)-H(7)	120.0
C(8)-C(9)	1.407(7)	O-C(8)-C(7)	126.4(5)
C(9)-N	1.367(6)	O-C(8)-C(9)	114.5(5)
N-H(600)	0.88(6)	C(7)-C(8)-C(9)	119.1(5)
O-H(0)	0.8200	N-C(9)-C(8)	119.3(4)
		N-C(9)-C(4)	118.5(5)
N-C(1)-C(2)	119.9(5)	C(8)-C(9)-C(4)	122.2(5)
N-C(1)-H(1)	120.0	C(1)-N-C(9)	123.3(5)
C(2)-C(1)-H(1)	120.0	C(1)-N-H(600)	119(4)
C(3)-C(2)-C(1)	118.9(5)	C(9)-N-H(600)	118(5)
C(3)-C(2)-H(2)	120.5	C(8)-O-H(0)	109.5

Table A2. 3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ($\text{H}_2\text{oxCl.Br}$). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	20(3)	13(3)	11(3)	6(2)	10(2)	2(2)
C(2)	18(3)	10(3)	19(3)	2(3)	10(2)	0(2)
C(3)	16(3)	15(3)	12(3)	1(2)	8(2)	-2(2)
C(4)	12(2)	13(3)	11(2)	-3(3)	6(2)	0(2)
C(5)	8(2)	18(3)	11(3)	-2(2)	2(2)	2(2)
C(6)	13(2)	14(2)	15(2)	2(2)	5(1)	1(2)
C(7)	13(2)	14(2)	15(2)	2(2)	5(1)	1(2)
C(8)	13(2)	12(3)	13(3)	-5(2)	4(2)	-3(2)
C(9)	10(2)	15(3)	12(2)	5(2)	3(2)	4(2)
N	16(2)	8(3)	13(2)	-2(2)	2(2)	1(2)
O	15(2)	8(2)	18(2)	-1(2)	-3(2)	0(2)
Cl	16(1)	22(1)	17(1)	-2(1)	-3(1)	-4(1)
Br	15(1)	8(1)	17(1)	1(1)	0(1)	0(1)

Table A2. 4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ($\text{H}_2\text{oxCl.Br}$).

	x	y	z	U(eq)
H(1)	6553	419	9493	17
H(2)	2845	-306	8692	19
H(3)	164	1227	8040	17
H(6)	331	5855	7912	16
H(7)	4064	6460	8735	16
H(0)	7764	5622	9544	21
H(600)	7350(130)	2580(70)	9610(30)	40(20)

A3. Crystal data of 5-Chloro-8-hydroxyquinolinium hexafluorophosphate hydrate, (H₂oxCl.PF₆)

Table A3. 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (H₂oxCl.PF₆). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P	5000	5000	10000	14(1)
F(2)	4356(1)	6239(1)	9542(1)	16(1)
F(1)	2716(1)	4646(1)	9997(1)	24(1)
F(3)	5041(2)	4580(1)	8615(1)	23(1)
O(1)	4691(2)	1350(1)	5730(1)	19(1)
O	3877(2)	3295(1)	6295(1)	15(1)
N	3320(2)	5396(1)	6693(1)	12(1)
C(6)	1923(2)	4177(1)	3418(2)	15(1)
C(3)	1841(2)	6795(1)	5043(2)	14(1)
C(4)	2107(2)	5703(1)	4743(1)	12(1)
C(8)	3147(2)	3877(1)	5395(1)	12(1)
C(2)	2302(2)	7150(1)	6149(2)	15(1)
C(9)	2863(2)	4993(1)	5613(1)	11(1)
C(5)	1657(2)	5252(1)	3629(1)	13(1)
C(1)	3064(2)	6426(1)	6969(2)	14(1)
C(7)	2659(2)	3485(1)	4305(2)	14(1)
Cl	712(1)	6080(1)	2535(1)	19(1)

Table A3. 2. Bond lengths ($\text{\AA}$) and angles ($^\circ$) for (H₂oxCl.PF₆)

P-F(2)#1	1.6758(9)	F(3)#1-P-F(1)	90.48(5)
P-F(2)	1.6758(9)	F(2)#1-P-F(1)#1	89.28(5)
P-F(3)	1.6817(10)	F(2)-P-F(1)#1	90.72(5)
P-F(3)#1	1.6817(10)	F(3)-P-F(1)#1	90.48(5)
P-F(1)	1.6946(10)	F(3)#1-P-F(1)#1	89.52(5)
P-F(1)#1	1.6946(10)	F(1)-P-F(1)#1	180.0
O(1)-H(11)	0.82(3)	H(11)-O(1)-H(12)	106(2)
O(1)-H(12)	0.79(3)	C(8)-O-H(0)	109.5
O-C(8)	1.3431(19)	C(1)-N-C(9)	122.80(14)
O-H(0)	0.8200	C(1)-N-H(10)	115.4(17)
N-C(1)	1.327(2)	C(9)-N-H(10)	121.7(17)
N-C(9)	1.363(2)	C(5)-C(6)-C(7)	120.74(15)
N-H(10)	0.86(3)	C(5)-C(6)-H(6)	119.6
C(6)-C(5)	1.365(2)	C(7)-C(6)-H(6)	119.6
C(6)-C(7)	1.411(2)	C(2)-C(3)-C(4)	120.48(15)
C(6)-H(6)	0.9300	C(2)-C(3)-H(3)	119.8
C(3)-C(2)	1.371(2)	C(4)-C(3)-H(3)	119.8
C(3)-C(4)	1.409(2)	C(3)-C(4)-C(9)	118.13(14)
C(3)-H(3)	0.9300	C(3)-C(4)-C(5)	124.87(14)
C(4)-C(9)	1.416(2)	C(9)-C(4)-C(5)	117.00(14)
C(4)-C(5)	1.421(2)	O-C(8)-C(7)	125.81(14)
C(8)-C(7)	1.373(2)	O-C(8)-C(9)	115.87(14)
C(8)-C(9)	1.418(2)	C(7)-C(8)-C(9)	118.32(14)
C(2)-C(1)	1.390(2)	C(3)-C(2)-C(1)	119.31(15)
C(2)-H(2)	0.9300	C(3)-C(2)-H(2)	120.3

C(5)-Cl	1.7312(16)	C(1)-C(2)-H(2)	120.3
C(1)-H(1)	0.9300	N-C(9)-C(4)	118.75(14)
C(7)-H(7)	0.9300	N-C(9)-C(8)	119.26(14)
		C(4)-C(9)-C(8)	121.99(14)
F(2)#1-P-F(2)	180.0	C(6)-C(5)-C(4)	121.08(15)
F(2)#1-P-F(3)	89.82(5)	C(6)-C(5)-Cl	119.91(13)
F(2)-P-F(3)	90.18(5)	C(4)-C(5)-Cl	119.00(12)
F(2)#1-P-F(3)#1	90.18(5)	N-C(1)-C(2)	120.53(15)
F(2)-P-F(3)#1	89.82(5)	N-C(1)-H(1)	119.7
F(3)-P-F(3)#1	180.000(1)	C(2)-C(1)-H(1)	119.7
F(2)#1-P-F(1)	90.72(5)	C(8)-C(7)-C(6)	120.86(15)
F(2)-P-F(1)	89.28(5)	C(8)-C(7)-H(7)	119.6
F(3)-P-F(1)	89.52(5)	C(6)-C(7)-H(7)	119.6

Table A3. 3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{H}_2\text{oxCl.PF}_6)$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U¹¹	U²²	U³³	U²³	U¹³	U¹²
P	14(1)	13(1)	16(1)	1(1)	-1(1)	-1(1)
F(2)	20(1)	11(1)	18(1)	2(1)	-2(1)	0(1)
F(1)	12(1)	19(1)	40(1)	6(1)	0(1)	-3(1)
F(3)	35(1)	20(1)	12(1)	-1(1)	-2(1)	9(1)
O(1)	14(1)	13(1)	30(1)	-7(1)	2(1)	0(1)
O	21(1)	10(1)	14(1)	1(1)	-1(1)	4(1)
N	13(1)	11(1)	10(1)	2(1)	1(1)	0(1)
C(6)	14(1)	20(1)	11(1)	-3(1)	1(1)	0(1)
C(3)	13(1)	12(1)	17(1)	3(1)	1(1)	1(1)
C(4)	10(1)	12(1)	13(1)	1(1)	2(1)	0(1)
C(8)	10(1)	13(1)	14(1)	2(1)	2(1)	1(1)
C(2)	16(1)	11(1)	19(1)	0(1)	2(1)	1(1)
C(9)	10(1)	12(1)	12(1)	0(1)	2(1)	0(1)
C(5)	12(1)	16(1)	11(1)	4(1)	1(1)	1(1)
C(1)	15(1)	14(1)	14(1)	-2(1)	2(1)	-1(1)
C(7)	16(1)	12(1)	16(1)	-1(1)	2(1)	1(1)
Cl	22(1)	20(1)	13(1)	4(1)	-2(1)	4(1)

Table A3. 4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{H}_2\text{oxCl.PF}_6)$.

	x	y	z	U(eq)
H(11)	3860(40)	940(20)	5490(20)	36(7)
H(12)	5640(40)	1090(20)	5540(20)	35(7)
H(10)	3760(30)	4990(20)	7250(20)	36(7)
H(0)	4122	2684	6074	22
H(6)	1616	3899	2682	18
H(3)	1350	7277	4487	16
H(2)	2106	7868	6349	18
H(1)	3398	6664	7718	17
H(7)	2815	2754	4149	17

A4. Crystal data of 5-Nitro-8-hydroxyquinoline, (HoxNO₂)

Table A4. 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (HoxNO₂). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N	4604(1)	421(1)	1463(6)	21(1)
O(2)	2868(1)	1035(1)	1746(8)	46(1)
C(5)	3305(1)	425(1)	3398(6)	20(1)
O(3)	2508(1)	534(1)	4760(7)	36(1)
O	4465(1)	-394(1)	4216(6)	28(1)
C(2)	4304(1)	1117(1)	-363(7)	22(1)
N(2)	2869(1)	683(1)	3283(6)	25(1)
C(9)	4151(1)	307(1)	2468(6)	19(1)
C(6)	3261(1)	15(1)	4835(6)	20(1)
C(8)	4096(1)	-120(1)	3937(6)	21(1)
C(3)	3850(1)	1011(1)	656(6)	22(1)
C(4)	3754(1)	592(1)	2139(6)	18(1)
C(1)	4672(1)	811(1)	70(6)	21(1)
C(7)	3654(1)	-261(1)	5103(7)	22(1)

Table A4. 2. Bond lengths ($\text{\AA}$) and angles ($^\circ$) for (HoxNO₂)

N-C(1)	1.317(3)	C(3)-C(2)-C(1)	119.63(19)
N-C(9)	1.364(2)	C(3)-C(2)-H(2)	120.2
O(2)-N(2)	1.220(3)	C(1)-C(2)-H(2)	120.2
C(5)-C(6)	1.372(3)	O(2)-N(2)-O(3)	122.02(18)
C(5)-C(4)	1.434(3)	O(2)-N(2)-C(5)	119.89(18)
C(5)-N(2)	1.457(2)	O(3)-N(2)-C(5)	118.09(18)
O(3)-N(2)	1.232(2)	N-C(9)-C(4)	123.13(18)
O-C(8)	1.337(2)	N-C(9)-C(8)	115.94(17)
O-H(0)	0.8200	C(4)-C(9)-C(8)	120.93(17)
C(2)-C(3)	1.363(3)	C(5)-C(6)-C(7)	121.21(17)
C(2)-C(1)	1.405(3)	C(5)-C(6)-H(6)	119.4
C(2)-H(2)	0.9300	C(7)-C(6)-H(6)	119.4
C(9)-C(4)	1.422(3)	O-C(8)-C(7)	118.28(19)
C(9)-C(8)	1.430(3)	O-C(8)-C(9)	121.56(17)
C(6)-C(7)	1.393(3)	C(7)-C(8)-C(9)	120.17(18)
C(6)-H(6)	0.9300	C(2)-C(3)-C(4)	119.66(18)
C(8)-C(7)	1.379(3)	C(2)-C(3)-H(3)	120.2
C(3)-C(4)	1.425(3)	C(4)-C(3)-H(3)	120.2
C(3)-H(3)	0.9300	C(9)-C(4)-C(3)	116.26(17)
C(1)-H(1)	0.9300	C(9)-C(4)-C(5)	116.02(18)
C(7)-H(7)	0.9300	C(3)-C(4)-C(5)	127.72(18)
		N-C(1)-C(2)	123.19(18)
C(1)-N-C(9)	118.13(17)	N-C(1)-H(1)	118.4
C(6)-C(5)-C(4)	121.99(18)	C(2)-C(1)-H(1)	118.4
C(6)-C(5)-N(2)	115.93(17)	C(8)-C(7)-C(6)	119.68(19)
C(4)-C(5)-N(2)	122.07(18)	C(8)-C(7)-H(7)	120.2
C(8)-O-H(0)	109.5	C(6)-C(7)-H(7)	120.2

Table A4. 3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (HoxNO_2) . The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N	19(1)	23(1)	20(1)	-1(1)	1(1)	-2(1)
O(2)	27(1)	43(1)	68(2)	25(1)	7(1)	10(1)
C(5)	16(1)	25(1)	19(1)	-5(1)	-1(1)	0(1)
O(3)	19(1)	36(1)	53(1)	-5(1)	11(1)	-1(1)
O	22(1)	23(1)	38(1)	6(1)	5(1)	2(1)
C(2)	26(1)	21(1)	19(1)	-1(1)	-2(1)	-6(1)
N(2)	20(1)	28(1)	27(1)	-5(1)	-1(1)	0(1)
C(9)	20(1)	21(1)	15(1)	-2(1)	0(1)	-4(1)
C(6)	19(1)	26(1)	16(1)	-5(1)	3(1)	-7(1)
C(8)	22(1)	23(1)	19(1)	-2(1)	0(1)	0(1)
C(3)	22(1)	24(1)	19(1)	-2(1)	-3(1)	-1(1)
C(4)	17(1)	25(1)	13(1)	-4(1)	-2(1)	-4(1)
C(1)	21(1)	25(1)	19(1)	-3(1)	3(1)	-6(1)
C(7)	24(1)	21(1)	21(1)	0(1)	2(1)	-6(1)

Table A4. 4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (HoxNO_2) .

	x	y	z	U(eq)
H(0)	4707	-275	3442	42
H(2)	4369	1389	-1340	26
H(6)	2964	-80	5644	24
H(3)	3604	1212	385	26
H(1)	4979	887	-662	26
H(7)	3617	-539	6063	26

A5. Crystal data of 5-Nitro-8-hydroxyquinolinium nitrate, (H₂oxNO₂.NO₃)

Table A5. 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (H₂oxNO₂.NO₃). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2011(3)	-2366(2)	1529(1)	17(1)
C(2)	787(3)	-2103(2)	2477(1)	19(1)
C(3)	1917(3)	-683(2)	3276(1)	18(1)
C(4)	4313(3)	548(2)	3151(1)	15(1)
C(5)	5670(3)	2103(2)	3892(1)	16(1)
C(6)	7940(3)	3197(2)	3650(1)	18(1)
C(7)	9086(3)	2816(2)	2698(1)	17(1)
C(8)	7906(3)	1320(2)	1957(1)	14(1)
C(9)	5486(3)	201(2)	2179(1)	14(1)
N	4282(3)	-1252(2)	1414(1)	15(1)
N(2)	4755(3)	2637(2)	4939(1)	20(1)
N(3)	5059(3)	3891(2)	967(1)	16(1)
O	8835(2)	804(1)	1027(1)	17(1)
O(2)	2512(3)	1859(2)	5134(1)	43(1)
O(3)	6266(3)	3861(2)	5596(1)	34(1)
O(4)	4344(2)	4722(1)	1754(1)	21(1)
O(5)	7356(2)	4374(1)	647(1)	21(1)
O(6)	3421(2)	2454(1)	459(1)	18(1)

Table A5. 2. Bond lengths ($\text{\AA}$) and angles ($^\circ$) for (H₂oxNO₂.NO₃)

C(1)-N	1.3225(18)	C(2)-C(3)-C(4)	120.92(13)
C(1)-C(2)	1.395(2)	C(2)-C(3)-H(3)	119.5
C(1)-H(1)	0.9300	C(4)-C(3)-H(3)	119.5
C(2)-C(3)	1.367(2)	C(9)-C(4)-C(3)	116.67(13)
C(2)-H(2)	0.9300	C(9)-C(4)-C(5)	115.95(12)
C(3)-C(4)	1.4232(19)	C(3)-C(4)-C(5)	127.38(13)
C(3)-H(3)	0.9300	C(6)-C(5)-C(4)	121.07(13)
C(4)-C(9)	1.4154(19)	C(6)-C(5)-N(2)	116.12(13)
C(4)-C(5)	1.425(2)	C(4)-C(5)-N(2)	122.80(12)
C(5)-C(6)	1.3754(19)	C(5)-C(6)-C(7)	121.92(14)
C(5)-N(2)	1.4600(18)	C(5)-C(6)-H(6)	119.0
C(6)-C(7)	1.390(2)	C(7)-C(6)-H(6)	119.0
C(6)-H(6)	0.9300	C(8)-C(7)-C(6)	119.89(13)
C(7)-C(8)	1.377(2)	C(8)-C(7)-H(7)	120.1
C(7)-H(7)	0.9300	C(6)-C(7)-H(7)	120.1
C(8)-O	1.3329(17)	O-C(8)-C(7)	125.45(12)
C(8)-C(9)	1.4262(18)	O-C(8)-C(9)	115.80(13)
C(9)-N	1.3681(18)	C(7)-C(8)-C(9)	118.75(13)
N-H	0.86(2)	N-C(9)-C(4)	119.74(12)
N(2)-O(2)	1.2193(17)	N-C(9)-C(8)	117.89(12)
N(2)-O(3)	1.2197(18)	C(4)-C(9)-C(8)	122.37(13)
N(3)-O(4)	1.2311(16)	C(1)-N-C(9)	122.94(13)
N(3)-O(5)	1.2414(15)	C(1)-N-H	114.5(14)
N(3)-O(6)	1.2918(15)	C(9)-N-H	122.6(14)

O-H(8)	0.84(2)	O(2)-N(2)-O(3)	121.64(13)
		O(2)-N(2)-C(5)	119.61(13)
N-C(1)-C(2)	119.88(13)	O(3)-N(2)-C(5)	118.75(12)
N-C(1)-H(1)	120.1	O(4)-N(3)-O(5)	122.03(12)
C(2)-C(1)-H(1)	120.1	O(4)-N(3)-O(6)	119.95(11)
C(3)-C(2)-C(1)	119.82(13)	O(5)-N(3)-O(6)	118.01(12)
C(3)-C(2)-H(2)	120.1	C(8)-O-H(8)	112.3(16)
C(1)-C(2)-H(2)	120.1		

Table A5. 3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{H}_2\text{oxNO}_2.\text{NO}_3)$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	15(1)	15(1)	22(1)	4(1)	3(1)	1(1)
C(2)	15(1)	18(1)	24(1)	8(1)	8(1)	2(1)
C(3)	16(1)	21(1)	18(1)	8(1)	7(1)	4(1)
C(4)	12(1)	18(1)	16(1)	7(1)	4(1)	4(1)
C(5)	16(1)	22(1)	13(1)	4(1)	5(1)	5(1)
C(6)	17(1)	19(1)	16(1)	2(1)	3(1)	1(1)
C(7)	14(1)	17(1)	18(1)	5(1)	5(1)	1(1)
C(8)	14(1)	17(1)	15(1)	6(1)	5(1)	5(1)
C(9)	13(1)	14(1)	16(1)	5(1)	4(1)	3(1)
N	15(1)	16(1)	16(1)	4(1)	6(1)	4(1)
N(2)	20(1)	24(1)	15(1)	4(1)	6(1)	3(1)
N(3)	15(1)	15(1)	18(1)	5(1)	4(1)	2(1)
O	16(1)	16(1)	18(1)	2(1)	9(1)	0(1)
O(2)	35(1)	50(1)	29(1)	-8(1)	22(1)	-16(1)
O(3)	37(1)	33(1)	22(1)	-5(1)	11(1)	-7(1)
O(4)	22(1)	19(1)	20(1)	1(1)	9(1)	3(1)
O(5)	16(1)	22(1)	25(1)	6(1)	9(1)	-2(1)
O(6)	15(1)	15(1)	22(1)	2(1)	6(1)	-2(1)

Table A5. 4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{H}_2\text{oxNO}_2.\text{NO}_3)$.

	x	y	z	U(eq)
H	4940(50)	-1510(30)	816(18)	29(5)
H(8)	10260(50)	1500(30)	936(19)	40(6)
H(1)	1231	-3323	978	21
H(2)	-793	-2892	2565	22
H(3)	1109	-519	3911	21
H(6)	8732	4222	4137	22
H(7)	10647	3570	2563	20

A6. Crystal data of 5-chloromethyl-8-hydroxyquinoline hydrochloric acid solvate, (HoxMeCl)

Table A6. 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (HoxMeCl). $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1517(5)	-1350(3)	674(5)	36(1)
C(2)	972(5)	-1236(3)	-1017(5)	37(1)
C(3)	1416(5)	-489(3)	-1824(5)	35(1)
C(4)	2419(5)	171(3)	-980(4)	29(1)
C(5)	3005(5)	946(3)	-1746(5)	32(1)
C(6)	3974(5)	1531(3)	-782(5)	34(1)
C(7)	4449(5)	1393(3)	932(5)	33(1)
C(8)	3936(5)	642(3)	1702(4)	29(1)
C(9)	2913(4)	30(2)	743(4)	27(1)
C(51)	2694(6)	1085(4)	-3590(5)	44(1)
N	2432(4)	-735(2)	1484(4)	29(1)
Cl(1)	664(2)	1443(1)	-4226(1)	50(1)
Cl(2)	6744(1)	1643(1)	5097(1)	38(1)
O	4342(4)	415(2)	3309(3)	37(1)

Table A6. 2. Bond lengths ($\text{\AA}$) and angles ($^\circ$) for (HoxMeCl)

C(1)-N	1.316(5)	C(2)-C(3)-C(4)	121.1(4)
C(1)-C(2)	1.396(6)	C(2)-C(3)-H(3)	119.4
C(1)-H(1)	0.9300	C(4)-C(3)-H(3)	119.4
C(2)-C(3)	1.363(6)	C(3)-C(4)-C(9)	117.1(3)
C(2)-H(2)	0.9300	C(3)-C(4)-C(5)	124.8(3)
C(3)-C(4)	1.412(6)	C(9)-C(4)-C(5)	118.1(3)
C(3)-H(3)	0.9300	C(6)-C(5)-C(4)	118.8(3)
C(4)-C(9)	1.418(5)	C(6)-C(5)-C(51)	119.8(4)
C(4)-C(5)	1.425(6)	C(4)-C(5)-C(51)	121.2(4)
C(5)-C(6)	1.366(6)	C(5)-C(6)-C(7)	122.9(4)
C(5)-C(51)	1.495(5)	C(5)-C(6)-H(6)	118.5
C(6)-C(7)	1.408(5)	C(7)-C(6)-H(6)	118.5
C(6)-H(6)	0.9300	C(8)-C(7)-C(6)	119.8(4)
C(7)-C(8)	1.373(6)	C(8)-C(7)-H(7)	120.1
C(7)-H(7)	0.9300	C(6)-C(7)-H(7)	120.1
C(8)-O	1.344(4)	O-C(8)-C(7)	125.8(4)
C(8)-C(9)	1.414(5)	O-C(8)-C(9)	115.6(3)
C(9)-N	1.369(5)	C(7)-C(8)-C(9)	118.6(3)
C(51)-Cl(1)	1.807(5)	N-C(9)-C(8)	119.1(3)
C(51)-H(51A)	0.9700	N-C(9)-C(4)	119.0(3)
C(51)-H(51B)	0.9700	C(8)-C(9)-C(4)	121.8(3)
Cl(2)-H(9)	1.28(2)	C(5)-C(51)-Cl(1)	111.3(3)
O-H(0)	0.8200	C(5)-C(51)-H(51A)	109.4
		Cl(1)-C(51)-H(51A)	109.4
N-C(1)-C(2)	120.2(4)	C(5)-C(51)-H(51B)	109.4
N-C(1)-H(1)	119.9	Cl(1)-C(51)-H(51B)	109.4

C(2)-C(1)-H(1)	119.9	H(51A)-C(51)-H(51B)	108.0
C(3)-C(2)-C(1)	119.4(4)	C(1)-N-C(9)	123.1(3)
C(3)-C(2)-H(2)	120.3	C(8)-O-H(0)	109.5
C(1)-C(2)-H(2)	120.3		

Table A6. 3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (HoxMeCl). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	48(2)	29(2)	31(2)	-1(2)	6(2)	1(2)
C(2)	46(2)	31(2)	33(2)	-5(2)	-4(2)	-1(2)
C(3)	48(2)	33(2)	21(2)	-3(1)	-2(2)	5(2)
C(4)	37(2)	29(2)	21(2)	1(1)	5(1)	7(2)
C(5)	41(2)	34(2)	22(2)	2(2)	2(2)	4(2)
C(6)	45(2)	29(2)	28(2)	6(2)	4(2)	1(2)
C(7)	41(2)	31(2)	26(2)	-4(2)	4(2)	1(2)
C(8)	39(2)	29(2)	19(2)	-2(1)	2(1)	8(2)
C(9)	36(2)	26(2)	20(2)	1(1)	6(1)	7(2)
C(51)	48(3)	53(3)	29(2)	4(2)	6(2)	4(2)
N	40(2)	27(2)	22(1)	-1(1)	5(1)	4(1)
Cl(1)	55(1)	57(1)	37(1)	2(1)	-4(1)	11(1)
Cl(2)	52(1)	35(1)	25(1)	5(1)	-2(1)	-5(1)
O	56(2)	36(2)	18(1)	-1(1)	0(1)	-5(1)

Table A6. 4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (HoxMeCl).

	x	y	z	U(eq)
H(1)	1233	-1863	1229	43
H(2)	312	-1666	-1587	45
H(3)	1051	-412	-2950	41
H(6)	4335	2044	-1281	41
H(7)	5109	1809	1541	40
H(51A)	2892	526	-4153	52
H(51B)	3423	1537	-3919	52
H(0)	4996	777	3753	55
H(9)	8210(40)	1440(50)	5060(100)	110(30)

Appendix B Computational data on Quinoline ligands

B1. Introduction

Appendix B lists the .out/.log files of the computational data on the quinoline ligand systems. This information can be accessed directly *via* the folder Appendix B. For label definition see Chapter 5.

B2. 5-Fluoro-8-hydroxyquinoline

[\(HoxF\)\(I\).out](#)

[\(HoxF\)\(II\).out](#)

[\(HoxF\)\(III\).out](#)

B3. 5-Chloro-8-hydroxyquinoline

[\(HoxCl\)\(I\).out](#)

[\(HoxCl\)\(II\).out](#)

[\(HoxCl\)\(III\).out](#)

B4. 5-Bromo-8-hydroxyquinoline

[\(HoxBr\)\(I\).out](#)

[\(HoxBr\)\(II\).out](#)

[\(HoxBr\)\(III\).out](#)

B5. 5-Iodo-8-hydroxyquinoline

[\(HoxI\)\(I\).out](#)

[\(HoxI\)\(II\).log](#)

[\(HoxI\)\(III\).out](#)

B6. 8-Hydroxyquinoline

[\(Hox\)\(I\).out](#)

[\(Hox\)\(TSI\).log](#)

[\(Hox\)\(II\).out](#)

[\(Hox\)\(TSII\).log](#)

[\(Hox\)\(III\).out](#)

B7. 5-Methyl-8-hydroxyquinoline

[\(HoxMe\)\(I\).out](#)

[\(HoxMe\)\(TSI\).out](#)

[\(HoxMe\)\(II\).out](#)

[\(HoxMe\)\(TSII\).out](#)

[\(HoxMe\)\(III\).out](#)

B8. 5-Methylchloride-8-hydroxyquinoline

[\(HoxMeCl\)\(I\).out](#)

[\(HoxMeCl\)\(TSI\).out](#)

[\(HoxMeCl\)\(II\).out](#)

[\(HoxMeCl\)\(TSII\).out](#)

[\(HoxMeCl\)\(III\).out](#)

B9. 5-Nitro-8-hydroxyquinoline

[\(HoxNO2\)\(I\).out](#)

[\(HoxNO2\)\(TSI\).log](#)

[\(HoxNO2\)\(II\).out](#)

[\(HoxNO2\)\(TSII\).log](#)

[\(HoxNO2\)\(III\).out](#)

Appendix C Crystallographic and computational data of 5-phenylazo- 8-hydroxyquinolinatorhodium(I) systems

C1. Introduction

Appendix C lists the .out files of the computational results, these data files can be accessed in the folder Appendix C. Also presented are the supplementary crystallographic results on complexes of the type $[\text{Rh}(\text{oxY})(\text{CO})(\text{PR}_3)]$, where Y = phenylazo derivative and R = Aryl. For further label definition see Chapter 6.

C2. 5-phenylazo-8-hydroxyquinolate

[\(HoxL\)\(I\).out](#)

[\(HoxL\)\(II\).out](#)

C3. 5-(2-methylphenylazo)-8-hydroxyquinolate

[\(HoxL-Me\)\(I\).out](#)

[\(HoxL-Me\)\(II\).out](#)

C4. 5-[(2,4-dimethyl)phenylazo]-8-hydroxyquinolato

[\(HoxL-Me2\)\(I\).out](#)

[\(HoxL-Me2\)\(II\).out](#)

C5. 5-[(2,4,6-trimethyl)phenylazo]-8-hydroxyquinolinato

[\(HoxL-Me3\)\(I\).out](#)

C6. Crystal data of Carbonyl[triphenylphosphine](5-phenylazo-8-hydroxyquinolinato)rhodium(I), [Rh(oxL)(CO)(PPh₃)]

Table C6. 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Rh(oxL)(CO)(PPh₃)]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh	1076(1)	2687(1)	3542(1)	19(1)
P	2738(1)	1685(1)	4080(1)	17(1)
O(1)	-87(3)	2736(2)	4256(1)	20(1)
N(2)	-5299(3)	4746(3)	3619(2)	22(1)
C(11)	1829(4)	544(3)	4283(2)	17(1)
N(3)	-6172(3)	4730(3)	4002(2)	22(1)
N(1)	-735(3)	3486(3)	3146(2)	21(1)
C(8)	-1296(4)	3241(3)	4136(2)	19(1)
O(2)	2500(3)	2790(3)	2444(2)	40(1)
C(41)	-7516(4)	5224(3)	3787(2)	22(1)
C(31)	4281(4)	1200(3)	3743(2)	17(1)
C(4)	-3020(4)	4158(3)	3379(2)	21(1)
C(5)	-3954(4)	4273(3)	3824(2)	19(1)
C(3)	-3320(4)	4489(4)	2773(2)	27(1)
C(45)	-9150(4)	6166(3)	3076(2)	28(1)
C(22)	2826(4)	2791(3)	5143(2)	20(1)
C(6)	-3546(4)	3909(3)	4399(2)	20(1)
C(46)	-7820(4)	5710(3)	3236(2)	25(1)
C(26)	5012(4)	1916(3)	5044(2)	21(1)
C(10)	1992(4)	2725(4)	2888(2)	24(1)
C(21)	3605(4)	2170(3)	4810(2)	17(1)
C(25)	5623(4)	2258(3)	5607(2)	23(1)
C(42)	-8533(4)	5196(3)	4180(2)	23(1)
C(16)	2168(4)	72(3)	4838(2)	20(1)
C(7)	-2241(4)	3401(3)	4551(2)	23(1)
C(33)	6258(4)	1504(3)	3187(2)	25(1)
C(13)	89(4)	-765(3)	3985(2)	25(1)
C(12)	761(4)	123(3)	3860(2)	20(1)
C(36)	4739(4)	212(3)	3829(2)	22(1)
C(23)	3437(4)	3126(3)	5707(2)	24(1)
C(14)	452(4)	-1228(3)	4538(2)	24(1)
C(15)	1483(4)	-809(3)	4971(2)	21(1)

C(32)	5054(4)	1847(3)	3421(2)	23(1)
C(24)	4833(4)	2861(3)	5942(2)	24(1)
C(35)	5949(4)	-135(3)	3593(2)	26(1)
C(2)	-2343(5)	4324(4)	2392(2)	33(1)
C(9)	-1706(4)	3642(3)	3543(2)	19(1)
C(1)	-1054(4)	3821(4)	2585(2)	29(1)
C(43)	-9861(4)	5662(3)	4021(2)	27(1)
C(34)	6709(4)	518(4)	3280(2)	26(1)
C(44)	-10160(4)	6147(3)	3472(2)	28(1)

Table C6. 2 Bond lengths (Å) and angles (°) for [Rh(oxL)(CO)(PPh₃)]

Rh-C(10)	1.794(5)	C(7)-C(8)-C(9)	116.7(4)
Rh-O(1)	2.052(3)	C(42)-C(41)-C(46)	120.2(4)
Rh-N(1)	2.089(3)	C(42)-C(41)-N(3)	114.9(4)
Rh-P	2.2626(12)	C(46)-C(41)-N(3)	124.9(4)
P-C(11)	1.825(4)	C(36)-C(31)-C(32)	119.0(4)
P-C(21)	1.834(4)	C(36)-C(31)-P	121.4(3)
P-C(31)	1.835(4)	C(32)-C(31)-P	119.5(3)
O(1)-C(8)	1.311(4)	C(9)-C(4)-C(3)	116.8(4)
N(2)-N(3)	1.263(5)	C(9)-C(4)-C(5)	118.0(4)
N(2)-C(5)	1.424(5)	C(3)-C(4)-C(5)	125.2(4)
C(11)-C(16)	1.386(6)	C(6)-C(5)-C(4)	119.9(4)
C(11)-C(12)	1.394(5)	C(6)-C(5)-N(2)	125.0(4)
N(3)-C(41)	1.441(5)	C(4)-C(5)-N(2)	115.1(4)
N(1)-C(1)	1.324(5)	C(2)-C(3)-C(4)	119.4(4)
N(1)-C(9)	1.370(5)	C(2)-C(3)-H(3)	120.3
C(8)-C(7)	1.383(6)	C(4)-C(3)-H(3)	120.3
C(8)-C(9)	1.430(6)	C(44)-C(45)-C(46)	119.7(4)
O(2)-C(10)	1.161(5)	C(44)-C(45)-H(45)	120.1
C(41)-C(42)	1.382(6)	C(46)-C(45)-H(45)	120.1
C(41)-C(46)	1.384(6)	C(23)-C(22)-C(21)	119.9(4)
C(31)-C(36)	1.386(6)	C(23)-C(22)-H(22)	120.0
C(31)-C(32)	1.388(6)	C(21)-C(22)-H(22)	120.0
C(4)-C(9)	1.411(5)	C(5)-C(6)-C(7)	121.1(4)
C(4)-C(3)	1.413(6)	C(5)-C(6)-H(6)	119.4
C(4)-C(5)	1.420(6)	C(7)-C(6)-H(6)	119.4
C(5)-C(6)	1.375(6)	C(41)-C(46)-C(45)	120.0(4)
C(3)-C(2)	1.352(6)	C(41)-C(46)-H(46)	120.0
C(3)-H(3)	0.9300	C(45)-C(46)-H(46)	120.0
C(45)-C(44)	1.382(6)	C(25)-C(26)-C(21)	120.8(4)
C(45)-C(46)	1.385(5)	C(25)-C(26)-H(26)	119.6
C(45)-H(45)	0.9300	C(21)-C(26)-H(26)	119.6
C(22)-C(23)	1.383(6)	O(2)-C(10)-Rh	175.0(4)
C(22)-C(21)	1.384(6)	C(22)-C(21)-C(26)	119.0(4)
C(22)-H(22)	0.9300	C(22)-C(21)-P	119.0(3)
C(6)-C(7)	1.396(5)	C(26)-C(21)-P	121.9(3)
C(6)-H(6)	0.9300	C(24)-C(25)-C(26)	119.9(4)
C(46)-H(46)	0.9300	C(24)-C(25)-H(25)	120.0
C(26)-C(25)	1.385(6)	C(26)-C(25)-H(25)	120.0
C(26)-C(21)	1.388(5)	C(41)-C(42)-C(43)	119.7(4)
C(26)-H(26)	0.9300	C(41)-C(42)-H(42)	120.1
C(25)-C(24)	1.379(6)	C(43)-C(42)-H(42)	120.1
C(25)-H(25)	0.9300	C(11)-C(16)-C(15)	121.3(4)

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C(42)-C(43)	1.389(5)	C(11)-C(16)-H(16)	119.4
C(42)-H(42)	0.9300	C(15)-C(16)-H(16)	119.4
C(16)-C(15)	1.387(6)	C(8)-C(7)-C(6)	122.1(4)
C(16)-H(16)	0.9300	C(8)-C(7)-H(7)	119.0
C(7)-H(7)	0.9300	C(6)-C(7)-H(7)	119.0
C(33)-C(32)	1.383(6)	C(32)-C(33)-C(34)	120.3(4)
C(33)-C(34)	1.383(6)	C(32)-C(33)-H(33)	119.9
C(33)-H(33)	0.9300	C(34)-C(33)-H(33)	119.9
C(13)-C(14)	1.379(6)	C(14)-C(13)-C(12)	119.9(4)
C(13)-C(12)	1.384(6)	C(14)-C(13)-H(13)	120.0
C(13)-H(13)	0.9300	C(12)-C(13)-H(13)	120.0
C(12)-H(12)	0.9300	C(13)-C(12)-C(11)	120.6(4)
C(36)-C(35)	1.392(6)	C(13)-C(12)-H(12)	119.7
C(36)-H(36)	0.9300	C(11)-C(12)-H(12)	119.7
C(23)-C(24)	1.384(5)	C(31)-C(36)-C(35)	120.9(4)
C(23)-H(23)	0.9300	C(31)-C(36)-H(36)	119.5
C(14)-C(15)	1.385(6)	C(35)-C(36)-H(36)	119.5
C(14)-H(14)	0.9300	C(22)-C(23)-C(24)	120.9(4)
C(15)-H(15)	0.9300	C(22)-C(23)-H(23)	119.5
C(32)-H(32)	0.9300	C(24)-C(23)-H(23)	119.5
C(24)-H(24)	0.9300	C(13)-C(14)-C(15)	120.5(4)
C(35)-C(34)	1.374(6)	C(13)-C(14)-H(14)	119.7
C(35)-H(35)	0.9300	C(15)-C(14)-H(14)	119.7
C(2)-C(1)	1.394(6)	C(14)-C(15)-C(16)	119.1(4)
C(2)-H(2)	0.9300	C(14)-C(15)-H(15)	120.4
C(1)-H(1)	0.9300	C(16)-C(15)-H(15)	120.4
C(43)-C(44)	1.380(6)	C(33)-C(32)-C(31)	120.1(4)
C(43)-H(43)	0.9300	C(33)-C(32)-H(32)	119.9
C(34)-H(34)	0.9300	C(31)-C(32)-H(32)	119.9
C(44)-H(44)	0.9300	C(25)-C(24)-C(23)	119.3(4)
		C(25)-C(24)-H(24)	120.3
C(10)-Rh-O(1)	175.15(15)	C(23)-C(24)-H(24)	120.3
C(10)-Rh-N(1)	95.27(17)	C(34)-C(35)-C(36)	119.3(4)
O(1)-Rh-N(1)	80.03(13)	C(34)-C(35)-H(35)	120.3
C(10)-Rh-P	94.49(14)	C(36)-C(35)-H(35)	120.3
O(1)-Rh-P	90.30(8)	C(3)-C(2)-C(1)	121.0(5)
N(1)-Rh-P	168.95(11)	C(3)-C(2)-H(2)	119.5
C(11)-P-C(21)	103.6(2)	C(1)-C(2)-H(2)	119.5
C(11)-P-C(31)	103.33(19)	N(1)-C(9)-C(4)	122.5(4)
C(21)-P-C(31)	102.20(18)	N(1)-C(9)-C(8)	115.3(3)
C(11)-P-Rh	108.13(13)	C(4)-C(9)-C(8)	122.2(4)
C(21)-P-Rh	116.89(13)	N(1)-C(1)-C(2)	121.7(4)
C(31)-P-Rh	120.71(15)	N(1)-C(1)-H(1)	119.2
C(8)-O(1)-Rh	113.2(3)	C(2)-C(1)-H(1)	119.2
N(3)-N(2)-C(5)	113.6(4)	C(44)-C(43)-C(42)	120.0(4)
C(16)-C(11)-C(12)	118.5(4)	C(44)-C(43)-H(43)	120.0
C(16)-C(11)-P	122.8(3)	C(42)-C(43)-H(43)	120.0
C(12)-C(11)-P	118.7(3)	C(35)-C(34)-C(33)	120.3(4)
N(2)-N(3)-C(41)	112.5(4)	C(35)-C(34)-H(34)	119.8
C(1)-N(1)-C(9)	118.7(4)	C(33)-C(34)-H(34)	119.8
C(1)-N(1)-Rh	129.4(3)	C(43)-C(44)-C(45)	120.3(4)
C(9)-N(1)-Rh	112.0(3)	C(43)-C(44)-H(44)	119.8
O(1)-C(8)-C(7)	123.8(4)	C(45)-C(44)-H(44)	119.8
O(1)-C(8)-C(9)	119.5(4)		

Table C6. 3 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{oxL})(\text{CO})(\text{PPh}_3)]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U11	U22	U33	U23	U13	U12
Rh	15(1)	20(1)	20(1)	2(1)	0(1)	2(1)
P	13(1)	19(1)	19(1)	-1(1)	1(1)	2(1)
O(1)	18(1)	22(2)	19(2)	5(2)	1(1)	8(1)
N(2)	18(2)	21(2)	25(3)	0(2)	-1(2)	1(2)
C(11)	13(2)	17(2)	21(3)	2(2)	1(2)	4(2)
N(3)	17(2)	21(2)	27(3)	5(2)	2(2)	2(2)
N(1)	18(2)	23(2)	22(2)	1(2)	0(2)	2(2)
C(8)	17(2)	15(2)	24(3)	1(2)	1(2)	0(2)
O(2)	30(2)	66(3)	25(2)	5(2)	7(2)	6(2)
C(41)	19(2)	17(2)	29(3)	-1(2)	-1(2)	0(2)
C(31)	13(2)	21(2)	15(3)	1(2)	-1(2)	2(2)
C(4)	16(2)	21(2)	23(3)	5(2)	-4(2)	1(2)
C(5)	18(2)	18(2)	21(3)	2(2)	2(2)	0(2)
C(3)	19(2)	38(3)	24(3)	4(2)	1(2)	7(2)
C(45)	25(2)	29(3)	29(3)	11(2)	0(2)	9(2)
C(22)	13(2)	21(2)	26(3)	-1(2)	0(2)	1(2)
C(6)	19(2)	18(2)	22(3)	0(2)	4(2)	1(2)
C(46)	17(2)	37(3)	20(3)	0(2)	3(2)	1(2)
C(26)	15(2)	22(2)	27(3)	-3(2)	4(2)	3(2)
C(10)	15(2)	33(3)	23(3)	-2(2)	-4(2)	5(2)
C(21)	17(2)	16(2)	17(3)	4(2)	2(2)	3(2)
C(25)	16(2)	26(2)	26(3)	2(2)	-1(2)	-2(2)
C(42)	25(2)	24(2)	21(3)	2(2)	2(2)	-1(2)
C(16)	13(2)	22(2)	24(3)	-1(2)	3(2)	2(2)
C(7)	19(2)	25(2)	23(3)	3(2)	-1(2)	2(2)
C(33)	17(2)	33(3)	26(3)	-2(2)	7(2)	-6(2)
C(13)	15(2)	29(3)	30(3)	-6(2)	-1(2)	-2(2)
C(12)	16(2)	26(2)	17(3)	-3(2)	-1(2)	1(2)
C(36)	16(2)	30(3)	19(3)	-1(2)	2(2)	1(2)
C(23)	22(2)	22(2)	29(3)	-9(2)	3(2)	-2(2)
C(14)	16(2)	21(2)	35(3)	3(2)	6(2)	3(2)
C(15)	20(2)	21(2)	23(3)	7(2)	7(2)	8(2)
C(32)	19(2)	19(2)	28(3)	-5(2)	-1(2)	-3(2)
C(24)	22(2)	23(3)	25(3)	-2(2)	-1(2)	-3(2)
C(35)	24(2)	26(2)	25(3)	5(2)	-1(2)	7(2)
C(2)	29(2)	48(3)	22(3)	14(3)	5(2)	11(2)
C(9)	18(2)	18(2)	19(3)	4(2)	-2(2)	0(2)
C(1)	23(2)	47(3)	18(3)	7(2)	4(2)	11(2)
C(43)	24(2)	25(3)	33(3)	-4(2)	10(2)	4(2)
C(34)	14(2)	40(3)	22(3)	-3(2)	0(2)	2(2)
C(44)	17(2)	32(3)	36(3)	6(2)	4(2)	6(2)

Table C6. 4 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{oxL})(\text{CO})(\text{PPh}_3)]$.

	x	y	z	U(eq)
H(3)	-4182	4817	2638	33
H(45)	-9361	6484	2703	34
H(22)	1892	2982	4987	24
H(6)	-4151	4003	4691	24
H(46)	-7132	5731	2973	29
H(26)	5551	1512	4819	25
H(25)	6565	2080	5760	28
H(42)	-8330	4866	4549	28
H(16)	2869	351	5126	24
H(7)	-1998	3163	4943	27
H(33)	6766	1938	2967	30
H(13)	-606	-1050	3697	30
H(12)	497	442	3490	24
H(36)	4231	-224	4048	26
H(23)	2903	3534	5931	29
H(14)	1	-1826	4621	28
H(15)	1712	-1115	5347	25
H(32)	4761	2513	3361	27
H(24)	5235	3088	6322	28
H(35)	6240	-802	3648	31
H(2)	-2534	4549	1994	40
H(1)	-400	3719	2313	35
H(43)	-10547	5646	4285	32
H(34)	7531	296	3129	31
H(44)	-11047	6463	3368	34

C7. Crystal data of
Carbonyl[tricyclohexylphosphine](5-phenylazo-
8-hydroxyquinolinato)rhodium(I),
[Rh(oxL)(CO)(PCy₃)]

Table C7. 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Rh(oxL)(CO)(PCy₃)]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh	8102(1)	2759(1)	6637(1)	17(1)
P	8326(1)	1529(1)	7196(1)	17(1)
O(2)	11054(2)	2541(2)	6344(1)	37(1)
O(1)	6031(2)	2945(1)	6804(1)	21(1)
N(2)	3630(3)	5828(2)	5619(1)	23(1)
N(3)	2346(3)	5995(2)	5685(1)	25(1)
C(10)	9901(3)	2624(2)	6467(1)	25(1)
C(45)	-256(4)	7670(2)	5169(1)	33(1)
C(4)	5605(3)	4861(2)	5854(1)	20(1)
C(16)	6490(3)	553(2)	7911(1)	21(1)
C(32)	9356(3)	-395(2)	7241(1)	24(1)
N(1)	7589(2)	3873(2)	6128(1)	18(1)
C(21)	9338(3)	1787(2)	7792(1)	19(1)
C(34)	9975(3)	-1335(2)	6446(1)	27(1)
C(12)	5649(3)	760(2)	6995(1)	20(1)
C(8)	5414(3)	3605(2)	6527(1)	20(1)
C(9)	6216(3)	4132(2)	6161(1)	18(1)
C(6)	3395(3)	4535(2)	6260(1)	22(1)
C(2)	7849(3)	5041(2)	5466(1)	23(1)
C(41)	1813(3)	6779(2)	5394(1)	25(1)
C(35)	9809(3)	-430(2)	6122(1)	30(1)
C(11)	6586(3)	1174(2)	7425(1)	18(1)
C(1)	8372(3)	4316(2)	5786(1)	21(1)
C(25)	11663(3)	2221(2)	8196(1)	25(1)
C(36)	8782(3)	257(2)	6366(1)	25(1)
C(5)	4168(3)	5065(2)	5915(1)	22(1)
C(7)	3999(3)	3820(2)	6561(1)	23(1)
C(24)	10980(3)	3000(2)	8514(1)	28(1)
C(15)	4984(3)	510(2)	8090(1)	25(1)
C(46)	390(3)	6935(2)	5438(1)	28(1)
C(52)	3693(4)	1051(3)	5333(2)	51(1)
C(42)	2611(3)	7378(2)	5088(1)	31(1)
C(13)	4134(3)	727(2)	7170(1)	24(1)
C(31)	9255(3)	506(2)	6916(1)	20(1)
C(26)	10870(3)	2042(2)	7691(1)	22(1)
C(23)	9450(3)	2779(2)	8607(1)	29(1)
C(44)	532(4)	8263(2)	4861(1)	35(1)
O(5)	3263(3)	1024(3)	4896(1)	74(1)
C(22)	8664(3)	2597(2)	8096(1)	23(1)
C(33)	10370(3)	-1108(2)	7003(1)	28(1)
C(3)	6492(3)	5320(2)	5499(1)	24(1)
C(43)	1960(4)	8122(2)	4824(1)	36(1)

C(51)	4010(4)	1954(3)	5613(2)	51(1)
C(14)	3985(3)	149(2)	7664(1)	25(1)
C(53)	3957(4)	157(3)	5626(2)	51(1)

Table C7. 2 Bond lengths (Å) and angles (°) for [Rh(oxL)(CO)(PCy₃)]

Rh-C(10)	1.794(3)		
Rh-O(1)	2.052(2)	C(5)-C(4)-C(9)	118.3(2)
Rh-N(1)	2.099(2)	C(33)-C(34)-H(34B)	109.3
Rh-P	2.2631(9)	C(35)-C(34)-H(34B)	109.3
P-C(31)	1.844(3)	H(34A)-C(34)-H(34B)	107.9
P-C(11)	1.846(3)	C(13)-C(12)-C(11)	109.9(2)
P-C(21)	1.847(3)	C(13)-C(12)-H(12A)	109.7
O(2)-C(10)	1.159(4)	C(11)-C(12)-H(12A)	109.7
O(1)-C(8)	1.307(3)	C(13)-C(12)-H(12B)	109.7
N(2)-N(3)	1.265(3)	C(11)-C(12)-H(12B)	109.7
N(2)-C(5)	1.410(3)	H(12A)-C(12)-H(12B)	108.2
N(3)-C(41)	1.424(4)	O(1)-C(8)-C(7)	123.2(3)
C(45)-C(46)	1.385(4)	O(1)-C(8)-C(9)	119.2(2)
C(45)-C(44)	1.386(5)	C(7)-C(8)-C(9)	117.6(2)
C(45)-H(45)	0.9300	N(1)-C(9)-C(4)	123.0(2)
C(4)-C(5)	1.416(4)	N(1)-C(9)-C(8)	115.4(2)
C(4)-C(9)	1.417(4)	C(4)-C(9)-C(8)	121.6(3)
C(4)-C(3)	1.417(4)	C(5)-C(6)-C(7)	121.9(3)
C(16)-C(15)	1.523(4)	C(5)-C(6)-H(6)	119.0
C(16)-C(11)	1.537(4)	C(7)-C(6)-H(6)	119.0
C(16)-H(16A)	0.9700	C(3)-C(2)-C(1)	120.2(3)
C(16)-H(16B)	0.9700	C(3)-C(2)-H(2)	119.9
C(32)-C(31)	1.521(4)	C(1)-C(2)-H(2)	119.9
C(32)-C(33)	1.532(4)	C(46)-C(41)-C(42)	120.1(3)
C(32)-H(32A)	0.9700	C(46)-C(41)-N(3)	115.0(3)
C(32)-H(32B)	0.9700	C(42)-C(41)-N(3)	125.0(3)
N(1)-C(1)	1.328(3)	C(36)-C(35)-C(34)	111.0(2)
N(1)-C(9)	1.366(3)	C(36)-C(35)-H(35A)	109.4
C(21)-C(22)	1.532(4)	C(34)-C(35)-H(35A)	109.4
C(21)-C(26)	1.535(4)	C(36)-C(35)-H(35B)	109.4
C(21)-H(21)	0.9800	C(34)-C(35)-H(35B)	109.4
C(34)-C(33)	1.522(4)	H(35A)-C(35)-H(35B)	108.0
C(34)-C(35)	1.530(4)	C(12)-C(11)-C(16)	109.9(2)
C(34)-H(34A)	0.9700	C(12)-C(11)-P	112.70(19)
C(34)-H(34B)	0.9700	C(16)-C(11)-P	119.03(18)
C(12)-C(13)	1.527(4)	C(12)-C(11)-H(11)	104.6
C(12)-C(11)	1.534(4)	C(16)-C(11)-H(11)	104.6
C(12)-H(12A)	0.9700	P-C(11)-H(11)	104.6
C(12)-H(12B)	0.9700	N(1)-C(1)-C(2)	122.5(3)
C(8)-C(7)	1.391(4)	N(1)-C(1)-H(1)	118.7
C(8)-C(9)	1.437(4)	C(2)-C(1)-H(1)	118.7
C(6)-C(5)	1.388(4)	C(26)-C(25)-C(24)	111.9(2)
C(6)-C(7)	1.391(4)	C(26)-C(25)-H(25A)	109.2
C(6)-H(6)	0.9300	C(24)-C(25)-H(25A)	109.2
C(2)-C(3)	1.360(4)	C(26)-C(25)-H(25B)	109.2
C(2)-C(1)	1.400(4)	C(24)-C(25)-H(25B)	109.2
C(2)-H(2)	0.9300	H(25A)-C(25)-H(25B)	107.9
C(41)-C(46)	1.384(4)	C(35)-C(36)-C(31)	110.6(2)
C(41)-C(42)	1.393(4)	C(35)-C(36)-H(36A)	109.5

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C(35)-C(36)	1.522(4)	C(31)-C(36)-H(36A)	109.5
C(35)-H(35A)	0.9700	C(35)-C(36)-H(36B)	109.5
C(35)-H(35B)	0.9700	C(31)-C(36)-H(36B)	109.5
C(11)-H(11)	0.9800	H(36A)-C(36)-H(36B)	108.1
C(1)-H(1)	0.9300	C(6)-C(5)-N(2)	124.5(3)
C(25)-C(26)	1.524(4)	C(6)-C(5)-C(4)	119.6(2)
C(25)-C(24)	1.525(4)	N(2)-C(5)-C(4)	115.9(2)
C(25)-H(25A)	0.9700	C(8)-C(7)-C(6)	121.0(3)
C(25)-H(25B)	0.9700	C(8)-C(7)-H(7)	119.5
C(36)-C(31)	1.531(4)	C(6)-C(7)-H(7)	119.5
C(36)-H(36A)	0.9700	C(23)-C(24)-C(25)	111.3(2)
C(36)-H(36B)	0.9700	C(23)-C(24)-H(24A)	109.4
C(7)-H(7)	0.9300	C(25)-C(24)-H(24A)	109.4
C(24)-C(23)	1.520(4)	C(23)-C(24)-H(24B)	109.4
C(24)-H(24A)	0.9700	C(25)-C(24)-H(24B)	109.4
C(24)-H(24B)	0.9700	H(24A)-C(24)-H(24B)	108.0
C(15)-C(14)	1.534(4)	C(16)-C(15)-C(14)	111.9(2)
C(15)-H(15A)	0.9700	C(16)-C(15)-H(15A)	109.2
C(15)-H(15B)	0.9700	C(14)-C(15)-H(15A)	109.2
C(46)-H(46)	0.9300	C(16)-C(15)-H(15B)	109.2
C(52)-O(5)	1.201(5)	C(14)-C(15)-H(15B)	109.2
C(52)-C(53)	1.486(6)	H(15A)-C(15)-H(15B)	107.9
C(52)-C(51)	1.490(5)	C(41)-C(46)-C(45)	120.5(3)
C(42)-C(43)	1.391(4)	C(41)-C(46)-H(46)	119.8
C(42)-H(42)	0.9300	C(45)-C(46)-H(46)	119.8
C(13)-C(14)	1.526(4)	O(5)-C(52)-C(53)	120.6(4)
C(13)-H(13A)	0.9700	O(5)-C(52)-C(51)	123.4(4)
C(13)-H(13B)	0.9700	C(53)-C(52)-C(51)	116.0(4)
C(31)-H(31)	0.9800	C(43)-C(42)-C(41)	119.2(3)
C(26)-H(26A)	0.9700	C(43)-C(42)-H(42)	120.4
C(26)-H(26B)	0.9700	C(41)-C(42)-H(42)	120.4
C(23)-C(22)	1.534(4)	C(14)-C(13)-C(12)	111.7(2)
C(23)-H(23A)	0.9700	C(14)-C(13)-H(13A)	109.3
C(23)-H(23B)	0.9700	C(12)-C(13)-H(13A)	109.3
C(44)-C(43)	1.385(5)	C(14)-C(13)-H(13B)	109.3
C(44)-H(44)	0.9300	C(12)-C(13)-H(13B)	109.3
C(22)-H(22A)	0.9700	H(13A)-C(13)-H(13B)	107.9
C(22)-H(22B)	0.9700	C(32)-C(31)-C(36)	110.0(2)
C(33)-H(33A)	0.9700	C(32)-C(31)-P	117.0(2)
C(33)-H(33B)	0.9700	C(36)-C(31)-P	114.16(18)
C(3)-H(3)	0.9300	C(32)-C(31)-H(31)	104.8
C(43)-H(43)	0.9300	C(36)-C(31)-H(31)	104.8
C(51)-H(51A)	0.9600	P-C(31)-H(31)	104.8
C(51)-H(51B)	0.9600	C(25)-C(26)-C(21)	110.7(2)
C(51)-H(51C)	0.9600	C(25)-C(26)-H(26A)	109.5
C(14)-H(14A)	0.9700	C(21)-C(26)-H(26A)	109.5
C(14)-H(14B)	0.9700	C(25)-C(26)-H(26B)	109.5
C(53)-H(53A)	0.9600	C(21)-C(26)-H(26B)	109.5
C(53)-H(53B)	0.9600	H(26A)-C(26)-H(26B)	108.1
C(53)-H(53C)	0.9600	C(24)-C(23)-C(22)	110.9(3)
		C(24)-C(23)-H(23A)	109.5
C(10)-Rh-O(1)	177.62(10)	C(22)-C(23)-H(23A)	109.5
C(10)-Rh-N(1)	97.95(11)	C(24)-C(23)-H(23B)	109.5
O(1)-Rh-N(1)	79.76(8)	C(22)-C(23)-H(23B)	109.5
C(10)-Rh-P	89.82(9)	H(23A)-C(23)-H(23B)	108.1
O(1)-Rh-P	92.44(5)	C(43)-C(44)-C(45)	120.1(3)

N(1)-Rh-P	171.90(6)	C(43)-C(44)-H(44)	119.9
C(31)-P-C(11)	111.13(13)	C(45)-C(44)-H(44)	119.9
C(31)-P-C(21)	103.56(12)	C(21)-C(22)-C(23)	111.4(2)
C(11)-P-C(21)	104.15(12)	C(21)-C(22)-H(22A)	109.4
C(31)-P-Rh	112.47(9)	C(23)-C(22)-H(22A)	109.4
C(11)-P-Rh	109.70(8)	C(21)-C(22)-H(22B)	109.4
C(21)-P-Rh	115.44(9)	C(23)-C(22)-H(22B)	109.4
C(8)-O(1)-Rh	113.70(17)	H(22A)-C(22)-H(22B)	108.0
N(3)-N(2)-C(5)	114.3(2)	C(34)-C(33)-C(32)	111.8(2)
N(2)-N(3)-C(41)	114.2(2)	C(34)-C(33)-H(33A)	109.3
O(2)-C(10)-Rh	178.2(3)	C(32)-C(33)-H(33A)	109.3
C(46)-C(45)-C(44)	119.7(3)	C(34)-C(33)-H(33B)	109.3
C(46)-C(45)-H(45)	120.2	C(32)-C(33)-H(33B)	109.3
C(44)-C(45)-H(45)	120.2	H(33A)-C(33)-H(33B)	107.9
C(5)-C(4)-C(3)	125.1(2)	C(2)-C(3)-C(4)	119.6(3)
C(9)-C(4)-C(3)	116.6(3)	C(2)-C(3)-H(3)	120.2
C(15)-C(16)-C(11)	110.1(2)	C(4)-C(3)-H(3)	120.2
C(15)-C(16)-H(16A)	109.6	C(44)-C(43)-C(42)	120.4(3)
C(11)-C(16)-H(16A)	109.6	C(44)-C(43)-H(43)	119.8
C(15)-C(16)-H(16B)	109.6	C(42)-C(43)-H(43)	119.8
C(11)-C(16)-H(16B)	109.6	C(52)-C(51)-H(51A)	109.5
H(16A)-C(16)-H(16B)	108.2	C(52)-C(51)-H(51B)	109.5
C(31)-C(32)-C(33)	110.7(2)	H(51A)-C(51)-H(51B)	109.5
C(31)-C(32)-H(32A)	109.5	C(52)-C(51)-H(51C)	109.5
C(33)-C(32)-H(32A)	109.5	H(51A)-C(51)-H(51C)	109.5
C(31)-C(32)-H(32B)	109.5	H(51B)-C(51)-H(51C)	109.5
C(33)-C(32)-H(32B)	109.5	C(13)-C(14)-C(15)	111.4(2)
H(32A)-C(32)-H(32B)	108.1	C(13)-C(14)-H(14A)	109.4
C(1)-N(1)-C(9)	118.1(2)	C(15)-C(14)-H(14A)	109.4
C(1)-N(1)-Rh	129.94(19)	C(13)-C(14)-H(14B)	109.4
C(9)-N(1)-Rh	111.94(17)	C(15)-C(14)-H(14B)	109.4
C(22)-C(21)-C(26)	109.1(2)	H(14A)-C(14)-H(14B)	108.0
C(22)-C(21)-P	110.98(18)	C(52)-C(53)-H(53A)	109.5
C(26)-C(21)-P	112.90(19)	C(52)-C(53)-H(53B)	109.5
C(22)-C(21)-H(21)	107.9	H(53A)-C(53)-H(53B)	109.5
C(26)-C(21)-H(21)	107.9	C(52)-C(53)-H(53C)	109.5
P-C(21)-H(21)	107.9	H(53A)-C(53)-H(53C)	109.5
C(33)-C(34)-C(35)	111.7(2)	H(53B)-C(53)-H(53C)	109.5
C(33)-C(34)-H(34A)	109.3		
C(35)-C(34)-H(34A)	109.3		

Table C7. 3 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{oxL})(\text{CO})(\text{PCy}_3)]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U11	U22	U33	U23	U13	U12
Rh	16(1)	15(1)	20(1)	1(1)	0(1)	0(1)
P	14(1)	15(1)	20(1)	1(1)	-1(1)	1(1)
O(2)	18(1)	51(1)	42(1)	9(1)	7(1)	1(1)
O(1)	20(1)	19(1)	23(1)	6(1)	2(1)	3(1)
N(2)	29(1)	21(1)	19(1)	-2(1)	-3(1)	5(1)
N(3)	31(1)	20(1)	23(1)	-1(1)	-4(1)	6(1)
C(10)	29(2)	22(1)	23(1)	5(1)	-3(1)	-2(1)
C(45)	32(2)	31(2)	37(2)	-4(1)	-8(1)	9(1)
C(4)	25(1)	16(1)	18(1)	-1(1)	-2(1)	0(1)

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C(16)	19(1)	23(1)	23(1)	6(1)	1(1)	1(1)
C(32)	27(2)	20(1)	26(2)	0(1)	0(1)	3(1)
N(1)	22(1)	16(1)	17(1)	-2(1)	-1(1)	-1(1)
C(21)	15(1)	19(1)	23(1)	1(1)	-3(1)	1(1)
C(34)	28(2)	23(1)	31(2)	-4(1)	3(1)	6(1)
C(12)	20(1)	19(1)	22(1)	1(1)	0(1)	-1(1)
C(8)	24(2)	17(1)	19(1)	-2(1)	-2(1)	-1(1)
C(9)	20(1)	15(1)	19(1)	-1(1)	-3(1)	-1(1)
C(6)	19(1)	23(1)	25(1)	-1(1)	-1(1)	6(1)
C(2)	29(2)	19(1)	20(1)	1(1)	1(1)	-8(1)
C(41)	33(2)	20(1)	22(1)	-3(1)	-7(1)	5(1)
C(35)	35(2)	28(2)	25(2)	-2(1)	5(1)	3(1)
C(11)	16(1)	17(1)	22(1)	3(1)	-1(1)	2(1)
C(1)	22(1)	19(1)	23(1)	-3(1)	2(1)	-3(1)
C(25)	22(2)	23(1)	29(2)	2(1)	-8(1)	-3(1)
C(36)	29(2)	24(1)	22(1)	0(1)	1(1)	5(1)
C(5)	27(2)	18(1)	20(1)	-1(1)	-3(1)	2(1)
C(7)	21(1)	22(1)	24(1)	3(1)	2(1)	1(1)
C(24)	33(2)	23(1)	28(2)	-1(1)	-11(1)	-2(1)
C(15)	18(1)	31(2)	27(2)	6(1)	2(1)	2(1)
C(46)	31(2)	23(1)	30(2)	-3(1)	-4(1)	3(1)
C(52)	50(1)	50(1)	53(1)	-3(1)	9(1)	6(1)
C(42)	30(2)	34(2)	30(2)	6(1)	-3(1)	9(1)
C(13)	19(1)	26(2)	28(2)	2(1)	0(1)	-1(1)
C(31)	19(1)	15(1)	26(1)	0(1)	-2(1)	2(1)
C(26)	20(1)	17(1)	27(2)	1(1)	-1(1)	-1(1)
C(23)	32(2)	27(2)	26(2)	-7(1)	-4(1)	3(1)
C(44)	49(2)	27(2)	28(2)	2(1)	-9(1)	16(2)
O(5)	75(2)	102(3)	46(2)	1(2)	-8(2)	43(2)
C(22)	20(1)	22(1)	28(2)	-6(1)	-2(1)	3(1)
C(33)	28(2)	25(2)	30(2)	2(1)	-2(1)	10(1)
C(3)	36(2)	17(1)	19(1)	3(1)	-3(1)	-2(1)
C(43)	43(2)	36(2)	31(2)	9(1)	-2(2)	5(2)
C(51)	50(1)	50(1)	53(1)	-3(1)	9(1)	6(1)
C(14)	18(1)	27(2)	31(2)	6(1)	2(1)	-3(1)
C(53)	50(1)	50(1)	53(1)	-3(1)	9(1)	6(1)

Table C7. 4 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{oxL})(\text{CO})(\text{PCy}_3)]$.

	x	y	z	U(eq)
H(45)	-1214	7766	5195	40
H(16A)	6819	-85	7837	26
H(16B)	7081	818	8182	26
H(32A)	8438	-683	7265	29
H(32B)	9677	-233	7586	29
H(21)	9329	1214	8008	23
H(34A)	9104	-1689	6436	33
H(34B)	10693	-1734	6298	33
H(12A)	5715	1152	6689	24
H(12B)	5961	122	6910	24
H(6)	2446	4661	6291	27
H(2)	8431	5332	5230	28
H(35A)	10711	-121	6091	35

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H(35B)	9476	-597	5779	35
H(11)	6135	1775	7519	22
H(1)	9304	4138	5757	25
H(25A)	12617	2406	8122	30
H(25B)	11698	1636	8394	30
H(36A)	7861	-32	6372	30
H(36B)	8720	834	6162	30
H(7)	3449	3481	6789	27
H(24A)	11472	3059	8843	33
H(24B)	11053	3604	8335	33
H(15A)	4693	1141	8197	30
H(15B)	4930	90	8385	30
H(46)	-135	6543	5649	34
H(42)	3569	7281	5062	38
H(13A)	3805	1371	7228	29
H(13B)	3555	446	6900	29
H(31)	10223	723	6884	24
H(26A)	11310	1524	7507	26
H(26B)	10908	2607	7477	26
H(23A)	9022	3310	8784	34
H(23B)	9381	2221	8825	34
H(44)	102	8756	4679	42
H(22A)	7700	2434	8166	28
H(22B)	8664	3174	7891	28
H(33A)	11309	-847	7017	33
H(33B)	10370	-1692	7203	33
H(3)	6148	5809	5291	29
H(43)	2486	8526	4620	44
H(51A)	3885	2484	5382	76
H(51B)	4960	1941	5739	76
H(51C)	3391	2020	5897	76
H(14A)	4183	-515	7594	30
H(14B)	3030	194	7781	30
H(53A)	3528	-369	5447	76
H(53B)	3568	212	5963	76
H(53C)	4947	50	5657	76

***C8. Crystal data of Carbonyl[triphenylphosphine]
(5-[(2,4,6-trimethyl)phenylazo]-8-hydroxyquinoli
nato)rhodium(I), [Rh(oxL-Me₃)(CO)(PPh₃)]***

Table C8. 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Rh(oxL-Me₃)(CO)(PPh₃)]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh	675(1)	6977(1)	7133(1)	10(1)
P	-1773(1)	7503(1)	6579(1)	11(1)
C(10)	1438(5)	7886(5)	6576(2)	18(1)
O(1)	-92(3)	5956(3)	7802(1)	14(1)
N(3)	5145(4)	2733(4)	9904(1)	13(1)
N(2)	5454(4)	3356(4)	9458(1)	12(1)
C(9)	2737(5)	5584(5)	8170(2)	11(1)
O(2)	1941(4)	8470(4)	6226(1)	28(1)
C(1)	4233(5)	6775(5)	7641(2)	14(1)
C(6)	2442(5)	3781(5)	9092(2)	15(1)
C(14)	-6982(5)	11996(5)	7283(2)	21(1)
C(4)	4149(5)	4961(5)	8591(2)	14(1)
C(5)	3973(5)	4017(5)	9063(2)	13(1)
C(7)	1052(5)	4428(5)	8685(2)	15(1)
C(461)	4392(5)	1076(5)	10773(2)	20(1)
C(8)	1169(5)	5352(5)	8211(2)	11(1)
C(421)	8763(6)	3039(5)	9886(2)	20(1)
C(16)	-5548(5)	10068(5)	6537(2)	15(1)
C(11)	-3876(5)	9322(5)	6830(2)	11(1)
C(43)	9474(6)	1227(5)	10762(2)	18(1)
C(46)	6199(5)	1125(5)	10753(2)	14(1)
C(44)	9152(5)	324(5)	11193(2)	16(1)
C(42)	8252(5)	2078(5)	10322(2)	16(1)
C(15)	-7085(5)	11412(5)	6761(2)	20(1)
C(3)	5629(5)	5293(5)	8513(2)	16(1)
C(41)	6585(5)	2001(5)	10314(2)	14(1)
N(1)	2826(4)	6461(4)	7694(1)	12(1)
C(24)	-3711(6)	3384(6)	6484(2)	25(1)
C(2)	5667(5)	6217(5)	8044(2)	15(1)
C(45)	7501(6)	295(5)	11185(2)	17(1)
C(21)	-2442(5)	5801(5)	6513(2)	15(1)
C(22)	-1898(5)	4488(5)	6929(2)	15(1)
C(23)	-2524(6)	3289(5)	6909(2)	23(1)
C(25)	-4236(6)	4679(6)	6065(2)	23(1)
C(13)	-5322(6)	11267(5)	7583(2)	20(1)
C(441)	10534(6)	-583(5)	11667(2)	20(1)
C(12)	-3774(5)	9915(5)	7357(2)	16(1)
C(26)	-3601(5)	5852(5)	6080(2)	15(1)
C(31)	-1568(5)	7979(5)	5842(2)	14(1)
C(36)	-2579(6)	9596(5)	5568(2)	19(1)
C(32)	-152(6)	6644(5)	5558(2)	22(1)
C(33)	210(7)	6918(6)	5010(2)	27(1)
C(35)	-2189(7)	9832(6)	5014(2)	27(1)
C(34)	-803(7)	8507(6)	4736(2)	26(1)

Table C8. 2 Bond lengths (Å) and angles (°) for [Rh(oxL-Me₃)(CO)(PPh₃)]

Rh-C(10)	1.805(4)	C(13)-C(14)-H(14)	119.8
Rh-O(1)	2.062(3)	C(3)-C(4)-C(9)	118.2(4)
Rh-N(1)	2.103(4)	C(3)-C(4)-C(5)	123.8(4)
Rh-P	2.2831(15)	C(9)-C(4)-C(5)	118.0(4)
P-C(31)	1.837(4)	C(6)-C(5)-N(2)	125.8(4)
P-C(21)	1.839(5)	C(6)-C(5)-C(4)	118.3(4)
P-C(11)	1.846(3)	N(2)-C(5)-C(4)	115.9(4)
C(10)-O(2)	1.151(5)	C(6)-C(7)-C(8)	120.6(4)
O(1)-C(8)	1.340(4)	C(6)-C(7)-H(7)	119.7
N(3)-N(2)	1.272(4)	C(8)-C(7)-H(7)	119.7
N(3)-C(41)	1.434(5)	C(46)-C(461)-H(46A)	109.5
N(2)-C(5)	1.431(5)	C(46)-C(461)-H(46B)	109.5
C(9)-N(1)	1.383(5)	H(46A)-C(461)-H(46B)	109.5
C(9)-C(8)	1.415(6)	C(46)-C(461)-H(46C)	109.5
C(9)-C(4)	1.435(5)	H(46A)-C(461)-H(46C)	109.5
C(1)-N(1)	1.329(6)	H(46B)-C(461)-H(46C)	109.5
C(1)-C(2)	1.422(5)	O(1)-C(8)-C(7)	123.1(4)
C(1)-H(1)	0.9300	O(1)-C(8)-C(9)	119.8(3)
C(6)-C(5)	1.385(6)	C(7)-C(8)-C(9)	117.0(4)
C(6)-C(7)	1.402(5)	C(42)-C(421)-H(42A)	109.5
C(6)-H(6)	0.9300	C(42)-C(421)-H(42B)	109.5
C(14)-C(15)	1.392(6)	H(42A)-C(421)-H(42B)	109.5
C(14)-C(13)	1.404(6)	C(42)-C(421)-H(42C)	109.5
C(14)-H(14)	0.9300	H(42A)-C(421)-H(42C)	109.5
C(4)-C(3)	1.403(6)	H(42B)-C(421)-H(42C)	109.5
C(4)-C(5)	1.436(6)	C(15)-C(16)-C(11)	120.2(4)
C(7)-C(8)	1.410(5)	C(15)-C(16)-H(16)	119.9
C(7)-H(7)	0.9300	C(11)-C(16)-H(16)	119.9
C(461)-C(46)	1.524(6)	C(16)-C(11)-C(12)	119.5(3)
C(461)-H(46A)	0.9600	C(16)-C(11)-P	123.8(3)
C(461)-H(46B)	0.9600	C(12)-C(11)-P	116.7(3)
C(461)-H(46C)	0.9600	C(44)-C(43)-C(42)	124.1(4)
C(421)-C(42)	1.510(6)	C(44)-C(43)-H(43)	118.0
C(421)-H(42A)	0.9600	C(42)-C(43)-H(43)	118.0
C(421)-H(42B)	0.9600	C(45)-C(46)-C(41)	119.6(4)
C(421)-H(42C)	0.9600	C(45)-C(46)-C(461)	119.2(4)
C(16)-C(15)	1.393(5)	C(41)-C(46)-C(461)	121.2(4)
C(16)-C(11)	1.404(5)	C(45)-C(44)-C(43)	117.4(4)
C(16)-H(16)	0.9300	C(45)-C(44)-C(441)	120.5(4)
C(11)-C(12)	1.407(5)	C(43)-C(44)-C(441)	122.0(4)
C(43)-C(44)	1.389(6)	C(43)-C(42)-C(41)	117.7(4)
C(43)-C(42)	1.396(5)	C(43)-C(42)-C(421)	118.5(4)
C(43)-H(43)	0.9300	C(41)-C(42)-C(421)	123.8(4)
C(46)-C(45)	1.412(5)	C(14)-C(15)-C(16)	120.1(4)
C(46)-C(41)	1.413(6)	C(14)-C(15)-H(15)	119.9
C(44)-C(45)	1.385(7)	C(16)-C(15)-H(15)	119.9
C(44)-C(441)	1.530(5)	C(2)-C(3)-C(4)	119.3(4)
C(42)-C(41)	1.420(7)	C(2)-C(3)-H(3)	120.4
C(15)-H(15)	0.9300	C(4)-C(3)-H(3)	120.4

Appendix C

C(3)-C(2)	1.381(6)	C(46)-C(41)-C(42)	119.6(4)
C(3)-H(3)	0.9300	C(46)-C(41)-N(3)	112.5(4)
C(24)-C(23)	1.394(7)	C(42)-C(41)-N(3)	127.9(4)
C(24)-C(25)	1.402(6)	C(1)-N(1)-C(9)	118.3(4)
C(24)-H(24)	0.9300	C(1)-N(1)-Rh	129.8(3)
C(2)-H(2)	0.9300	C(9)-N(1)-Rh	111.8(3)
C(45)-H(45)	0.9300	C(23)-C(24)-C(25)	119.7(5)
C(21)-C(26)	1.406(6)	C(23)-C(24)-H(24)	120.2
C(21)-C(22)	1.407(5)	C(25)-C(24)-H(24)	120.2
C(22)-C(23)	1.382(7)	C(3)-C(2)-C(1)	119.5(4)
C(22)-H(22)	0.9300	C(3)-C(2)-H(2)	120.2
C(23)-H(23)	0.9300	C(1)-C(2)-H(2)	120.2
C(25)-C(26)	1.366(7)	C(44)-C(45)-C(46)	121.6(4)
C(25)-H(25)	0.9300	C(44)-C(45)-H(45)	119.2
C(13)-C(12)	1.401(5)	C(46)-C(45)-H(45)	119.2
C(13)-H(13)	0.9300	C(26)-C(21)-C(22)	119.0(4)
C(441)-H(44A)	0.9600	C(26)-C(21)-P	121.5(3)
C(441)-H(44B)	0.9600	C(22)-C(21)-P	119.3(3)
C(441)-H(44C)	0.9600	C(23)-C(22)-C(21)	119.7(4)
C(12)-H(12)	0.9300	C(23)-C(22)-H(22)	120.1
C(26)-H(26)	0.9300	C(21)-C(22)-H(22)	120.1
C(31)-C(32)	1.408(5)	C(22)-C(23)-C(24)	120.6(4)
C(31)-C(36)	1.408(5)	C(22)-C(23)-H(23)	119.7
C(36)-C(35)	1.404(6)	C(24)-C(23)-H(23)	119.7
C(36)-H(36)	0.9300	C(26)-C(25)-C(24)	119.9(4)
C(32)-C(33)	1.393(6)	C(26)-C(25)-H(25)	120.1
C(32)-H(32)	0.9300	C(24)-C(25)-H(25)	120.1
C(33)-C(34)	1.390(6)	C(12)-C(13)-C(14)	119.4(4)
C(33)-H(33)	0.9300	C(12)-C(13)-H(13)	120.3
C(35)-C(34)	1.385(6)	C(14)-C(13)-H(13)	120.3
C(35)-H(35)	0.9300	C(44)-C(441)-H(44A)	109.5
C(34)-H(34)	0.9300	C(44)-C(441)-H(44B)	109.5
		H(44A)-C(441)-H(44B)	109.5
C(10)-Rh-O(1)	176.62(18)	C(44)-C(441)-H(44C)	109.5
C(10)-Rh-N(1)	96.80(17)	H(44A)-C(441)-H(44C)	109.5
O(1)-Rh-N(1)	79.95(13)	H(44B)-C(441)-H(44C)	109.5
C(10)-Rh-P	87.38(14)	C(13)-C(12)-C(11)	120.2(4)
O(1)-Rh-P	95.85(9)	C(13)-C(12)-H(12)	119.9
N(1)-Rh-P	175.70(10)	C(11)-C(12)-H(12)	119.9
C(31)-P-C(21)	100.1(2)	C(25)-C(26)-C(21)	121.1(4)
C(31)-P-C(11)	107.11(17)	C(25)-C(26)-H(26)	119.5
C(21)-P-C(11)	102.73(19)	C(21)-C(26)-H(26)	119.5
C(31)-P-Rh	115.52(15)	C(32)-C(31)-C(36)	119.0(4)
C(21)-P-Rh	118.87(13)	C(32)-C(31)-P	115.6(3)
C(11)-P-Rh	111.03(14)	C(36)-C(31)-P	125.1(3)
O(2)-C(10)-Rh	179.0(4)	C(35)-C(36)-C(31)	119.6(4)
C(8)-O(1)-Rh	112.5(2)	C(35)-C(36)-H(36)	120.2
N(2)-N(3)-C(41)	117.3(3)	C(31)-C(36)-H(36)	120.2
N(3)-N(2)-C(5)	114.0(3)	C(33)-C(32)-C(31)	120.1(4)
N(1)-C(9)-C(8)	115.4(4)	C(33)-C(32)-H(32)	119.9
N(1)-C(9)-C(4)	121.7(4)	C(31)-C(32)-H(32)	119.9
C(8)-C(9)-C(4)	122.9(4)	C(34)-C(33)-C(32)	120.9(4)
N(1)-C(1)-C(2)	122.9(4)	C(34)-C(33)-H(33)	119.6
N(1)-C(1)-H(1)	118.6	C(32)-C(33)-H(33)	119.6
C(2)-C(1)-H(1)	118.6	C(34)-C(35)-C(36)	121.0(4)
C(5)-C(6)-C(7)	123.2(4)	C(34)-C(35)-H(35)	119.5

C(5)-C(6)-H(6)	118.4	C(36)-C(35)-H(35)	119.5
C(7)-C(6)-H(6)	118.4	C(35)-C(34)-C(33)	119.4(4)
C(15)-C(14)-C(13)	120.4(3)	C(35)-C(34)-H(34)	120.3
C(15)-C(14)-H(14)	119.8	C(33)-C(34)-H(34)	120.3

Table C8. 3 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{oxL-Me}_3)(\text{CO})(\text{PPh}_3)]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U11	U22	U33	U23	U13	U12
Rh	12(1)	10(1)	13(1)	1(1)	0(1)	-7(1)
P	12(1)	10(1)	12(1)	0(1)	0(1)	-6(1)
C(10)	17(2)	20(2)	19(2)	2(2)	-3(2)	-11(2)
O(1)	13(1)	17(1)	14(1)	3(1)	-1(1)	-9(1)
N(3)	20(2)	11(2)	14(2)	2(1)	-1(1)	-11(1)
N(2)	18(1)	10(1)	14(1)	1(1)	0(1)	-11(1)
C(9)	15(2)	8(2)	13(2)	-2(1)	2(1)	-7(1)
O(2)	29(2)	46(2)	22(2)	11(1)	-7(1)	-28(2)
C(1)	15(2)	16(2)	16(2)	-1(2)	0(1)	-11(2)
C(6)	22(2)	11(2)	17(2)	1(2)	-1(2)	-13(2)
C(14)	20(2)	13(2)	27(2)	-6(2)	3(2)	-5(2)
C(4)	14(2)	11(2)	13(2)	-4(1)	1(1)	-4(2)
C(5)	14(2)	14(2)	13(2)	-2(1)	-1(1)	-7(2)
C(7)	17(2)	18(2)	17(2)	-2(2)	4(1)	-16(2)
C(461)	25(1)	21(1)	21(1)	0(1)	-2(1)	-15(1)
C(8)	14(2)	8(2)	15(2)	-3(1)	1(1)	-8(1)
C(421)	25(1)	21(1)	21(1)	0(1)	-2(1)	-15(1)
C(16)	20(2)	12(2)	18(2)	-5(2)	-2(2)	-13(2)
C(11)	14(2)	8(2)	16(2)	-1(1)	4(1)	-9(1)
C(43)	21(2)	17(2)	22(2)	-5(2)	-2(2)	-12(2)
C(46)	19(2)	11(2)	15(2)	-1(2)	0(1)	-9(2)
C(44)	20(2)	12(2)	16(2)	-5(2)	-3(2)	-7(2)
C(42)	18(2)	11(2)	18(2)	-6(2)	1(2)	-5(2)
C(15)	15(2)	15(2)	30(2)	-4(2)	-3(2)	-7(2)
C(3)	14(2)	14(2)	17(2)	-1(2)	-2(1)	-5(2)
C(41)	16(2)	12(2)	14(2)	-3(1)	3(1)	-6(2)
N(1)	18(1)	10(1)	14(1)	1(1)	0(1)	-11(1)
C(24)	33(2)	22(2)	31(2)	-5(2)	2(2)	-21(2)
C(2)	12(2)	17(2)	20(2)	-3(2)	1(1)	-11(2)
C(45)	25(2)	13(2)	13(2)	1(2)	-2(2)	-9(2)
C(21)	19(1)	11(1)	18(1)	0(1)	-1(1)	-11(1)
C(22)	19(1)	11(1)	18(1)	0(1)	-1(1)	-11(1)
C(23)	32(2)	15(2)	26(2)	4(2)	-3(2)	-15(2)
C(25)	27(2)	24(2)	22(2)	-1(2)	-6(2)	-16(2)
C(13)	25(2)	15(2)	17(2)	-7(2)	0(2)	-7(2)
C(441)	25(1)	21(1)	21(1)	0(1)	-2(1)	-15(1)
C(12)	15(2)	15(2)	14(2)	-1(2)	1(1)	-5(2)
C(26)	19(1)	11(1)	18(1)	0(1)	-1(1)	-11(1)
C(31)	19(2)	17(2)	12(2)	-5(2)	1(1)	-12(2)
C(36)	23(2)	21(2)	18(2)	1(2)	-3(2)	-14(2)
C(32)	31(2)	16(2)	21(2)	-5(2)	8(2)	-12(2)
C(33)	38(2)	29(3)	23(2)	-12(2)	12(2)	-23(2)
C(35)	42(3)	27(2)	21(2)	9(2)	-4(2)	-23(2)
C(34)	48(3)	40(3)	12(2)	-1(2)	2(2)	-38(2)

Table C8. 4 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{oxL-Me}_3)(\text{CO})(\text{PPh}_3)]$.

	x	y	z	U(eq)
H(1)	4283	7388	7325	17
H(6)	2330	3163	9397	18
H(14)	-8019	12875	7435	25
H(7)	43	4246	8727	17
H(46A)	3402	2231	10750	30
H(46B)	4328	520	11115	30
H(46C)	4307	447	10466	30
H(42A)	9890	3010	9993	30
H(42B)	7819	4214	9853	30
H(42C)	8904	2506	9536	30
H(16)	-5630	9663	6191	18
H(43)	10572	1268	10767	22
H(15)	-8183	11920	6561	24
H(3)	6574	4894	8775	19
H(24)	-4152	2591	6478	30
H(2)	6623	6472	7992	18
H(45)	7243	-287	11471	21
H(22)	-1120	4426	7217	18
H(23)	-2150	2412	7181	28
H(25)	-5015	4740	5779	27
H(13)	-5249	11677	7928	24
H(44A)	10179	127	11985	30
H(44B)	11720	-781	11552	30
H(44C)	10570	-1665	11763	30
H(12)	-2677	9409	7557	19
H(26)	-3941	6698	5798	18
H(36)	-3499	10501	5752	23
H(32)	543	5576	5737	27
H(33)	1143	6027	4825	32
H(35)	-2873	10894	4831	33
H(34)	-552	8678	4370	31

Appendix D Crystallographic data of 8-Hydroxyquinolinatorhodium(I) complexes

D1. Crystal data of Carbonyl[tris(2,4-di-tert-butylphenyl)phosphi te] (8-hydroxyquinolinato)rhodium(I), [Rh(ox)(CO)(P(O-2,4di^tBuPh)₃)]

Table D1. 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Rh(ox)(CO)(P(O-2,4di^tBuPh)₃)]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh	4244(1)	333(1)	1440(1)	20(1)
P	3697(1)	-21(1)	1925(1)	17(1)
N	4739(1)	670(1)	873(1)	26(1)
O(1)	3679(1)	-781(1)	2440(1)	18(1)
O(2)	3490(1)	502(1)	2549(1)	20(1)
O(3)	3388(1)	-160(1)	1278(1)	18(1)
O(4)	4002(1)	740(1)	485(1)	32(1)
O(5)	4663(1)	-317(1)	2743(1)	47(1)
C(1)	5100(1)	607(2)	1077(2)	32(1)
C(2)	5404(1)	809(2)	598(2)	38(1)
C(3)	5324(1)	1070(2)	-97(2)	39(1)
C(4)	4943(1)	1143(2)	-350(2)	36(1)
C(5)	4832(1)	1371(2)	-1081(2)	49(1)
C(6)	4452(1)	1382(2)	-1261(2)	55(1)
C(7)	4161(1)	1177(2)	-748(2)	44(1)
C(8)	4256(1)	953(2)	-25(2)	32(1)
C(9)	4652(1)	939(1)	166(2)	30(1)
C(10)	4492(1)	-65(2)	2251(1)	29(1)
C(11)	3886(1)	-1454(1)	2282(1)	17(1)
C(12)	4001(1)	-1918(1)	2892(1)	19(1)
C(13)	4225(1)	-2556(1)	2706(1)	22(1)
C(14)	4325(1)	-2761(1)	1969(1)	22(1)
C(15)	4182(1)	-2309(1)	1396(1)	21(1)
C(16)	3962(1)	-1658(1)	1550(1)	19(1)
C(21)	3396(1)	1283(1)	2460(1)	20(1)
C(22)	3384(1)	1750(1)	3106(1)	22(1)
C(23)	3262(1)	2506(1)	2994(1)	24(1)
C(24)	3154(1)	2812(1)	2298(1)	25(1)
C(25)	3180(1)	2329(1)	1679(1)	29(1)
C(26)	3302(1)	1569(1)	1760(1)	27(1)

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C(31)	3019(1)	-477(1)	1312(1)	17(1)
C(32)	2832(1)	-608(1)	626(1)	18(1)
C(33)	2470(1)	-939(1)	680(1)	20(1)
C(34)	2294(1)	-1144(1)	1356(1)	19(1)
C(35)	2490(1)	-991(1)	2015(1)	20(1)
C(36)	2850(1)	-654(1)	1994(1)	19(1)
C(121)	3875(1)	-1758(1)	3705(1)	23(1)
C(122)	3435(1)	-1756(2)	3743(1)	31(1)
C(123)	4033(1)	-979(2)	3984(1)	32(1)
C(124)	4016(1)	-2383(2)	4244(1)	33(1)
C(141)	4582(1)	-3466(2)	1830(1)	29(1)
C(142)	4389(1)	-4193(2)	2142(2)	36(1)
C(143)	4969(1)	-3322(2)	2224(2)	37(1)
C(144)	4659(1)	-3592(2)	992(2)	50(1)
C(221)	3500(1)	1449(1)	3887(1)	28(1)
C(222)	3925(1)	1237(2)	3880(2)	40(1)
C(223)	3253(1)	753(2)	4114(1)	37(1)
C(224)	3445(1)	2067(2)	4501(2)	43(1)
C(241)	3009(1)	3648(1)	2248(1)	28(1)
C(242)	3329(1)	4202(2)	2488(2)	37(1)
C(243)	2664(1)	3749(2)	2773(2)	33(1)
C(244)	2883(1)	3861(2)	1444(2)	43(1)
C(321)	3004(1)	-382(1)	-139(1)	22(1)
C(322)	3391(1)	-780(2)	-272(1)	32(1)
C(323)	3055(1)	498(2)	-179(1)	31(1)
C(324)	2739(1)	-612(2)	-791(1)	34(1)
C(341)	1900(1)	-1533(1)	1342(1)	23(1)
C(342)	1754(1)	-1715(2)	2132(1)	32(1)
C(343)	1929(1)	-2297(1)	903(2)	30(1)
C(344)	1609(1)	-998(2)	957(1)	28(1)
C(40A)	4759(2)	1840(6)	5904(6)	38(1)
C(41A)	4215(5)	2420(9)	6470(7)	38(1)
C(42A)	4326(3)	1669(7)	6129(6)	38(1)
O(6A)	4130(3)	1122(5)	6087(5)	68(2)
C(40B)	4641(4)	1836(10)	5621(8)	38(1)
C(41B)	4205(7)	2424(14)	6645(12)	38(1)
C(42B)	4431(4)	1767(10)	6348(8)	38(1)
O(6B)	4375(4)	1196(7)	6694(8)	68(2)

Table D1. 2 Bond lengths (Å) and angles (°) for [Rh(ox)(CO)(P(O-2,4di^tBuPh)₃]

Rh-C(10)	1.818(3)	C(14)-C(13)-H(13)	117.9
Rh-O(4)	2.0234(18)	C(15)-C(14)-C(13)	117.2(2)
Rh-N	2.0842(19)	C(15)-C(14)-C(141)	122.9(2)
Rh-P	2.1819(6)	C(13)-C(14)-C(141)	119.9(2)
P-O(3)	1.5965(16)	C(14)-C(15)-C(16)	120.9(2)
P-O(2)	1.6030(16)	C(14)-C(15)-H(15)	119.5
P-O(1)	1.6042(16)	C(16)-C(15)-H(15)	119.5
N-C(1)	1.320(3)	C(11)-C(16)-C(15)	120.0(2)
N-C(9)	1.374(3)	C(11)-C(16)-H(16)	120.0
O(1)-C(11)	1.401(2)	C(15)-C(16)-H(16)	120.0
O(2)-C(21)	1.402(3)	C(26)-C(21)-O(2)	120.27(19)
O(3)-C(31)	1.402(2)	C(26)-C(21)-C(22)	121.7(2)
O(4)-C(8)	1.322(3)	O(2)-C(21)-C(22)	117.99(19)
O(5)-C(10)	1.145(3)	C(23)-C(22)-C(21)	115.6(2)

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C(1)-C(2)	1.404(4)	C(23)-C(22)-C(221)	122.0(2)
C(1)-H(1)	0.9300	C(21)-C(22)-C(221)	122.4(2)
C(2)-C(3)	1.344(4)	C(22)-C(23)-C(24)	124.5(2)
C(2)-H(2)	0.9300	C(22)-C(23)-H(23)	117.7
C(3)-C(4)	1.409(4)	C(24)-C(23)-H(23)	117.7
C(3)-H(3)	0.9300	C(25)-C(24)-C(23)	117.2(2)
C(4)-C(5)	1.413(4)	C(25)-C(24)-C(241)	123.0(2)
C(4)-C(9)	1.415(3)	C(23)-C(24)-C(241)	119.8(2)
C(5)-C(6)	1.364(5)	C(24)-C(25)-C(26)	120.6(2)
C(5)-H(5)	0.9300	C(24)-C(25)-H(25)	119.7
C(6)-C(7)	1.413(4)	C(26)-C(25)-H(25)	119.7
C(6)-H(6)	0.9300	C(21)-C(26)-C(25)	120.4(2)
C(7)-C(8)	1.382(4)	C(21)-C(26)-H(26)	119.8
C(7)-H(7)	0.9300	C(25)-C(26)-H(26)	119.8
C(8)-C(9)	1.426(4)	C(36)-C(31)-O(3)	121.12(19)
C(11)-C(16)	1.375(3)	C(36)-C(31)-C(32)	121.78(19)
C(11)-C(12)	1.407(3)	O(3)-C(31)-C(32)	117.10(18)
C(12)-C(13)	1.392(3)	C(33)-C(32)-C(31)	115.55(19)
C(12)-C(121)	1.537(3)	C(33)-C(32)-C(321)	121.40(19)
C(13)-C(14)	1.402(3)	C(31)-C(32)-C(321)	123.02(19)
C(13)-H(13)	0.9300	C(32)-C(33)-C(34)	124.42(19)
C(14)-C(15)	1.379(3)	C(32)-C(33)-H(33)	117.8
C(14)-C(141)	1.535(3)	C(34)-C(33)-H(33)	117.8
C(15)-C(16)	1.392(3)	C(35)-C(34)-C(33)	117.45(19)
C(15)-H(15)	0.9300	C(35)-C(34)-C(341)	122.94(19)
C(16)-H(16)	0.9300	C(33)-C(34)-C(341)	119.60(19)
C(21)-C(26)	1.379(3)	C(34)-C(35)-C(36)	120.5(2)
C(21)-C(22)	1.406(3)	C(34)-C(35)-H(35)	119.7
C(22)-C(23)	1.391(3)	C(36)-C(35)-H(35)	119.7
C(22)-C(221)	1.536(3)	C(31)-C(36)-C(35)	120.25(19)
C(23)-C(24)	1.398(3)	C(31)-C(36)-H(36)	119.9
C(23)-H(23)	0.9300	C(35)-C(36)-H(36)	119.9
C(24)-C(25)	1.385(3)	C(124)-C(121)-C(12)	111.68(19)
C(24)-C(241)	1.536(3)	C(124)-C(121)-C(123)	107.6(2)
C(25)-C(26)	1.390(3)	C(12)-C(121)-C(123)	110.93(19)
C(25)-H(25)	0.9300	C(124)-C(121)-C(122)	107.3(2)
C(26)-H(26)	0.9300	C(12)-C(121)-C(122)	109.15(18)
C(31)-C(36)	1.384(3)	C(123)-C(121)-C(122)	110.1(2)
C(31)-C(32)	1.402(3)	C(121)-C(122)-H(12D)	109.5
C(32)-C(33)	1.390(3)	C(121)-C(122)-H(12E)	109.5
C(32)-C(321)	1.538(3)	H(12D)-C(122)-H(12E)	109.5
C(33)-C(34)	1.397(3)	C(121)-C(122)-H(12F)	109.5
C(33)-H(33)	0.9300	H(12D)-C(122)-H(12F)	109.5
C(34)-C(35)	1.383(3)	H(12E)-C(122)-H(12F)	109.5
C(34)-C(341)	1.532(3)	C(121)-C(123)-H(12G)	109.5
C(35)-C(36)	1.388(3)	C(121)-C(123)-H(12H)	109.5
C(35)-H(35)	0.9300	H(12G)-C(123)-H(12H)	109.5
C(36)-H(36)	0.9300	C(121)-C(123)-H(12I)	109.5
C(121)-C(124)	1.527(3)	H(12G)-C(123)-H(12I)	109.5
C(121)-C(123)	1.538(3)	H(12H)-C(123)-H(12I)	109.5
C(121)-C(122)	1.540(3)	C(121)-C(124)-H(12A)	109.5
C(122)-H(12D)	0.9600	C(121)-C(124)-H(12B)	109.5
C(122)-H(12E)	0.9600	H(12A)-C(124)-H(12B)	109.5
C(122)-H(12F)	0.9600	C(121)-C(124)-H(12C)	109.5
C(123)-H(12G)	0.9600	H(12A)-C(124)-H(12C)	109.5
C(123)-H(12H)	0.9600	H(12B)-C(124)-H(12C)	109.5

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C(123)-H(12I)	0.9600	C(144)-C(141)-C(142)	108.2(2)
C(124)-H(12A)	0.9600	C(144)-C(141)-C(14)	111.9(2)
C(124)-H(12B)	0.9600	C(142)-C(141)-C(14)	109.8(2)
C(124)-H(12C)	0.9600	C(144)-C(141)-C(143)	108.1(2)
C(141)-C(144)	1.529(4)	C(142)-C(141)-C(143)	110.7(2)
C(141)-C(142)	1.530(4)	C(14)-C(141)-C(143)	108.0(2)
C(141)-C(143)	1.543(4)	C(141)-C(142)-H(14G)	109.5
C(142)-H(14G)	0.9600	C(141)-C(142)-H(14H)	109.5
C(142)-H(14H)	0.9600	H(14G)-C(142)-H(14H)	109.5
C(142)-H(14I)	0.9600	C(141)-C(142)-H(14I)	109.5
C(143)-H(14A)	0.9600	H(14G)-C(142)-H(14I)	109.5
C(143)-H(14B)	0.9600	H(14H)-C(142)-H(14I)	109.5
C(143)-H(14C)	0.9600	C(141)-C(143)-H(14A)	109.5
C(144)-H(14D)	0.9600	C(141)-C(143)-H(14B)	109.5
C(144)-H(14E)	0.9600	H(14A)-C(143)-H(14B)	109.5
C(144)-H(14F)	0.9600	C(141)-C(143)-H(14C)	109.5
C(221)-C(222)	1.530(4)	H(14A)-C(143)-H(14C)	109.5
C(221)-C(223)	1.535(4)	H(14B)-C(143)-H(14C)	109.5
C(221)-C(224)	1.541(3)	C(141)-C(144)-H(14D)	109.5
C(222)-H(22G)	0.9600	C(141)-C(144)-H(14E)	109.5
C(222)-H(22H)	0.9600	H(14D)-C(144)-H(14E)	109.5
C(222)-H(22I)	0.9600	C(141)-C(144)-H(14F)	109.5
C(223)-H(22A)	0.9600	H(14D)-C(144)-H(14F)	109.5
C(223)-H(22B)	0.9600	H(14E)-C(144)-H(14F)	109.5
C(223)-H(22C)	0.9600	C(222)-C(221)-C(223)	111.0(2)
C(224)-H(22D)	0.9600	C(222)-C(221)-C(22)	109.2(2)
C(224)-H(22E)	0.9600	C(223)-C(221)-C(22)	110.8(2)
C(224)-H(22F)	0.9600	C(222)-C(221)-C(224)	107.0(2)
C(241)-C(242)	1.533(4)	C(223)-C(221)-C(224)	106.8(2)
C(241)-C(243)	1.536(4)	C(22)-C(221)-C(224)	111.9(2)
C(241)-C(244)	1.540(4)	C(221)-C(222)-H(22G)	109.5
C(242)-H(24G)	0.9600	C(221)-C(222)-H(22H)	109.5
C(242)-H(24H)	0.9600	H(22G)-C(222)-H(22H)	109.5
C(242)-H(24I)	0.9600	C(221)-C(222)-H(22I)	109.5
C(243)-H(24A)	0.9600	H(22G)-C(222)-H(22I)	109.5
C(243)-H(24B)	0.9600	H(22H)-C(222)-H(22I)	109.5
C(243)-H(24C)	0.9600	C(221)-C(223)-H(22A)	109.5
C(244)-H(24D)	0.9600	C(221)-C(223)-H(22B)	109.5
C(244)-H(24E)	0.9600	H(22A)-C(223)-H(22B)	109.5
C(244)-H(24F)	0.9600	C(221)-C(223)-H(22C)	109.5
C(321)-C(323)	1.534(3)	H(22A)-C(223)-H(22C)	109.5
C(321)-C(322)	1.535(3)	H(22B)-C(223)-H(22C)	109.5
C(321)-C(324)	1.535(3)	C(221)-C(224)-H(22D)	109.5
C(322)-H(32D)	0.9600	C(221)-C(224)-H(22E)	109.5
C(322)-H(32E)	0.9600	H(22D)-C(224)-H(22E)	109.5
C(322)-H(32F)	0.9600	C(221)-C(224)-H(22F)	109.5
C(323)-H(32A)	0.9600	H(22D)-C(224)-H(22F)	109.5
C(323)-H(32B)	0.9600	H(22E)-C(224)-H(22F)	109.5
C(323)-H(32C)	0.9600	C(242)-C(241)-C(243)	109.4(2)
C(324)-H(32G)	0.9600	C(242)-C(241)-C(24)	109.5(2)
C(324)-H(32H)	0.9600	C(243)-C(241)-C(24)	109.3(2)
C(324)-H(32I)	0.9600	C(242)-C(241)-C(244)	108.5(2)
C(341)-C(342)	1.526(3)	C(243)-C(241)-C(244)	108.2(2)
C(341)-C(344)	1.536(3)	C(24)-C(241)-C(244)	111.9(2)
C(341)-C(343)	1.539(3)	C(241)-C(242)-H(24G)	109.5
C(342)-H(34G)	0.9600	C(241)-C(242)-H(24H)	109.5

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C(342)-H(34H)	0.9600	H(24G)-C(242)-H(24H)	109.5
C(342)-H(34I)	0.9600	C(241)-C(242)-H(24I)	109.5
C(343)-H(34A)	0.9600	H(24G)-C(242)-H(24I)	109.5
C(343)-H(34B)	0.9600	H(24H)-C(242)-H(24I)	109.5
C(343)-H(34C)	0.9600	C(241)-C(243)-H(24A)	109.5
C(344)-H(34D)	0.9600	C(241)-C(243)-H(24B)	109.5
C(344)-H(34E)	0.9600	H(24A)-C(243)-H(24B)	109.5
C(344)-H(34F)	0.9600	C(241)-C(243)-H(24C)	109.5
C(40A)-C(42A)	1.592(11)	H(24A)-C(243)-H(24C)	109.5
C(40A)-H(40A)	0.9600	H(24B)-C(243)-H(24C)	109.5
C(40A)-H(40B)	0.9600	C(241)-C(244)-H(24D)	109.5
C(40A)-H(40C)	0.9600	C(241)-C(244)-H(24E)	109.5
C(41A)-C(42A)	1.487(13)	H(24D)-C(244)-H(24E)	109.5
C(41A)-H(41A)	0.9600	C(241)-C(244)-H(24F)	109.5
C(41A)-H(41B)	0.9600	H(24D)-C(244)-H(24F)	109.5
C(41A)-H(41C)	0.9600	H(24E)-C(244)-H(24F)	109.5
C(42A)-O(6A)	1.171(14)	C(323)-C(321)-C(322)	109.5(2)
C(40B)-C(42B)	1.491(15)	C(323)-C(321)-C(324)	107.0(2)
C(40B)-H(40D)	0.9600	C(322)-C(321)-C(324)	107.3(2)
C(40B)-H(40E)	0.9600	C(323)-C(321)-C(32)	109.81(18)
C(40B)-H(40F)	0.9600	C(322)-C(321)-C(32)	111.51(18)
C(41B)-C(42B)	1.482(16)	C(324)-C(321)-C(32)	111.48(19)
C(41B)-H(41D)	0.9600	C(321)-C(322)-H(32D)	109.5
C(41B)-H(41E)	0.9600	C(321)-C(322)-H(32E)	109.5
C(41B)-H(41F)	0.9600	H(32D)-C(322)-H(32E)	109.5
C(42B)-O(6B)	1.18(2)	C(321)-C(322)-H(32F)	109.5
		H(32D)-C(322)-H(32F)	109.5
C(10)-Rh-O(4)	175.38(10)	H(32E)-C(322)-H(32F)	109.5
C(10)-Rh-N	95.37(9)	C(321)-C(323)-H(32A)	109.5
O(4)-Rh-N	81.00(8)	C(321)-C(323)-H(32B)	109.5
C(10)-Rh-P	89.88(7)	H(32A)-C(323)-H(32B)	109.5
O(4)-Rh-P	93.64(5)	C(321)-C(323)-H(32C)	109.5
N-Rh-P	174.30(6)	H(32A)-C(323)-H(32C)	109.5
O(3)-P-O(2)	106.10(8)	H(32B)-C(323)-H(32C)	109.5
O(3)-P-O(1)	105.13(8)	C(321)-C(324)-H(32G)	109.5
O(2)-P-O(1)	92.81(8)	C(321)-C(324)-H(32H)	109.5
O(3)-P-Rh	110.51(6)	H(32G)-C(324)-H(32H)	109.5
O(2)-P-Rh	120.66(6)	C(321)-C(324)-H(32I)	109.5
O(1)-P-Rh	119.36(6)	H(32G)-C(324)-H(32I)	109.5
C(1)-N-C(9)	119.3(2)	H(32H)-C(324)-H(32I)	109.5
C(1)-N-Rh	129.74(18)	C(342)-C(341)-C(34)	111.98(19)
C(9)-N-Rh	110.80(16)	C(342)-C(341)-C(344)	108.3(2)
C(11)-O(1)-P	123.20(13)	C(34)-C(341)-C(344)	109.66(19)
C(21)-O(2)-P	124.90(14)	C(342)-C(341)-C(343)	108.2(2)
C(31)-O(3)-P	130.60(14)	C(34)-C(341)-C(343)	109.11(19)
C(8)-O(4)-Rh	113.06(16)	C(344)-C(341)-C(343)	109.57(19)
N-C(1)-C(2)	122.4(3)	C(341)-C(342)-H(34G)	109.5
N-C(1)-H(1)	118.8	C(341)-C(342)-H(34H)	109.5
C(2)-C(1)-H(1)	118.8	H(34G)-C(342)-H(34H)	109.5
C(3)-C(2)-C(1)	119.0(3)	C(341)-C(342)-H(34I)	109.5
C(3)-C(2)-H(2)	120.5	H(34G)-C(342)-H(34I)	109.5
C(1)-C(2)-H(2)	120.5	H(34H)-C(342)-H(34I)	109.5
C(2)-C(3)-C(4)	121.3(2)	C(341)-C(343)-H(34A)	109.5
C(2)-C(3)-H(3)	119.3	C(341)-C(343)-H(34B)	109.5
C(4)-C(3)-H(3)	119.3	H(34A)-C(343)-H(34B)	109.5
C(3)-C(4)-C(5)	125.4(3)	C(341)-C(343)-H(34C)	109.5

C(3)-C(4)-C(9)	116.6(3)	H(34A)-C(343)-H(34C)	109.5
C(5)-C(4)-C(9)	117.9(3)	H(34B)-C(343)-H(34C)	109.5
C(6)-C(5)-C(4)	119.3(3)	C(341)-C(344)-H(34D)	109.5
C(6)-C(5)-H(5)	120.4	C(341)-C(344)-H(34E)	109.5
C(4)-C(5)-H(5)	120.4	H(34D)-C(344)-H(34E)	109.5
C(5)-C(6)-C(7)	123.0(3)	C(341)-C(344)-H(34F)	109.5
C(5)-C(6)-H(6)	118.5	H(34D)-C(344)-H(34F)	109.5
C(7)-C(6)-H(6)	118.5	H(34E)-C(344)-H(34F)	109.5
C(8)-C(7)-C(6)	119.9(3)	O(6A)-C(42A)-C(41A)	125.4(11)
C(8)-C(7)-H(7)	120.1	O(6A)-C(42A)-C(40A)	133.7(11)
C(6)-C(7)-H(7)	120.1	C(41A)-C(42A)-C(40A)	100.9(10)
O(4)-C(8)-C(7)	123.7(3)	C(42B)-C(40B)-H(40D)	109.5
O(4)-C(8)-C(9)	119.0(2)	C(42B)-C(40B)-H(40E)	109.5
C(7)-C(8)-C(9)	117.4(2)	H(40D)-C(40B)-H(40E)	109.5
N-C(9)-C(4)	121.4(2)	C(42B)-C(40B)-H(40F)	109.5
N-C(9)-C(8)	115.9(2)	H(40D)-C(40B)-H(40F)	109.5
C(4)-C(9)-C(8)	122.6(3)	H(40E)-C(40B)-H(40F)	109.5
O(5)-C(10)-Rh	177.0(2)	C(42B)-C(41B)-H(41D)	109.5
C(16)-C(11)-O(1)	120.15(19)	C(42B)-C(41B)-H(41E)	109.5
C(16)-C(11)-C(12)	121.9(2)	H(41D)-C(41B)-H(41E)	109.5
O(1)-C(11)-C(12)	117.87(19)	C(42B)-C(41B)-H(41F)	109.5
C(13)-C(12)-C(11)	115.4(2)	H(41D)-C(41B)-H(41F)	109.5
C(13)-C(12)-C(121)	121.81(19)	H(41E)-C(41B)-H(41F)	109.5
C(11)-C(12)-C(121)	122.7(2)	O(6B)-C(42B)-C(41B)	111.7(14)
C(12)-C(13)-C(14)	124.3(2)	O(6B)-C(42B)-C(40B)	126.9(16)
C(12)-C(13)-H(13)	117.9	C(41B)-C(42B)-C(40B)	120.6(14)

Table D1. 3 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2,4\text{di}^i\text{BuPh})_3)]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Rh	19(1)	22(1)	20(1)	0(1)	2(1)	-5(1)
P	17(1)	17(1)	16(1)	1(1)	0(1)	-1(1)
N	27(1)	24(1)	26(1)	-5(1)	6(1)	-9(1)
O(1)	20(1)	18(1)	17(1)	2(1)	1(1)	1(1)
O(2)	27(1)	18(1)	17(1)	0(1)	2(1)	2(1)
O(3)	17(1)	22(1)	16(1)	1(1)	0(1)	-4(1)
O(4)	28(1)	42(1)	28(1)	11(1)	1(1)	-4(1)
O(5)	34(1)	63(2)	43(1)	19(1)	-12(1)	-13(1)
C(1)	28(1)	33(1)	34(1)	-8(1)	4(1)	-10(1)
C(2)	30(1)	34(1)	50(2)	-10(1)	9(1)	-12(1)
C(3)	38(1)	28(1)	51(2)	-6(1)	22(1)	-10(1)
C(4)	45(2)	25(1)	38(1)	1(1)	17(1)	-6(1)
C(5)	61(2)	45(2)	42(2)	16(1)	23(2)	0(2)
C(6)	73(2)	56(2)	34(2)	22(2)	11(2)	5(2)
C(7)	52(2)	46(2)	34(2)	14(1)	4(1)	2(1)
C(8)	38(1)	28(1)	29(1)	5(1)	7(1)	-2(1)
C(9)	37(1)	21(1)	32(1)	0(1)	11(1)	-6(1)
C(10)	22(1)	37(1)	29(1)	6(1)	-1(1)	-12(1)
C(11)	15(1)	16(1)	21(1)	1(1)	-1(1)	-1(1)
C(12)	20(1)	20(1)	17(1)	1(1)	-2(1)	-2(1)
C(13)	24(1)	22(1)	20(1)	4(1)	-3(1)	2(1)
C(14)	21(1)	22(1)	22(1)	0(1)	-1(1)	2(1)
C(15)	22(1)	23(1)	18(1)	-2(1)	1(1)	-1(1)

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C(16)	17(1)	21(1)	17(1)	2(1)	-1(1)	-2(1)
C(21)	23(1)	16(1)	21(1)	0(1)	2(1)	0(1)
C(22)	25(1)	22(1)	19(1)	0(1)	1(1)	-2(1)
C(23)	32(1)	20(1)	22(1)	-4(1)	3(1)	-1(1)
C(24)	31(1)	19(1)	25(1)	2(1)	3(1)	0(1)
C(25)	45(1)	24(1)	19(1)	2(1)	2(1)	6(1)
C(26)	41(1)	22(1)	19(1)	-2(1)	2(1)	4(1)
C(31)	16(1)	17(1)	19(1)	1(1)	0(1)	0(1)
C(32)	21(1)	16(1)	16(1)	1(1)	-1(1)	1(1)
C(33)	22(1)	21(1)	16(1)	-2(1)	-3(1)	-1(1)
C(34)	18(1)	19(1)	21(1)	0(1)	-1(1)	1(1)
C(35)	20(1)	25(1)	16(1)	2(1)	2(1)	-1(1)
C(36)	20(1)	23(1)	15(1)	0(1)	-1(1)	-1(1)
C(121)	27(1)	25(1)	15(1)	2(1)	-1(1)	1(1)
C(122)	32(1)	42(2)	20(1)	4(1)	5(1)	2(1)
C(123)	43(1)	31(1)	21(1)	-3(1)	-3(1)	-2(1)
C(124)	45(2)	35(1)	18(1)	6(1)	-1(1)	5(1)
C(141)	31(1)	29(1)	28(1)	-1(1)	-2(1)	11(1)
C(142)	38(1)	26(1)	43(2)	-3(1)	-10(1)	7(1)
C(143)	27(1)	36(1)	48(2)	9(1)	0(1)	8(1)
C(144)	66(2)	52(2)	33(2)	-3(1)	9(1)	33(2)
C(221)	41(1)	23(1)	18(1)	0(1)	-2(1)	1(1)
C(222)	43(2)	37(2)	40(2)	1(1)	-16(1)	1(1)
C(223)	55(2)	32(1)	23(1)	5(1)	7(1)	-2(1)
C(224)	77(2)	33(2)	20(1)	-5(1)	-5(1)	4(1)
C(241)	39(1)	19(1)	26(1)	2(1)	3(1)	4(1)
C(242)	47(2)	22(1)	42(2)	1(1)	5(1)	-3(1)
C(243)	37(1)	26(1)	37(1)	-1(1)	1(1)	7(1)
C(244)	71(2)	25(1)	31(1)	3(1)	-6(1)	14(1)
C(321)	26(1)	26(1)	14(1)	1(1)	-1(1)	-1(1)
C(322)	36(1)	39(1)	21(1)	1(1)	10(1)	6(1)
C(323)	41(1)	28(1)	22(1)	8(1)	0(1)	-3(1)
C(324)	39(1)	48(2)	16(1)	0(1)	-2(1)	-10(1)
C(341)	20(1)	24(1)	24(1)	0(1)	-1(1)	-4(1)
C(342)	26(1)	42(2)	29(1)	3(1)	3(1)	-12(1)
C(343)	26(1)	25(1)	37(1)	-5(1)	0(1)	-5(1)
C(344)	21(1)	30(1)	33(1)	-4(1)	-4(1)	1(1)
C(40A)	28(2)	47(2)	39(4)	13(3)	2(2)	1(2)
C(41A)	28(2)	47(2)	39(4)	13(3)	2(2)	1(2)
C(42A)	28(2)	47(2)	39(4)	13(3)	2(2)	1(2)
O(6A)	100(6)	36(3)	66(5)	8(4)	40(4)	11(4)
C(40B)	28(2)	47(2)	39(4)	13(3)	2(2)	1(2)
C(41B)	28(2)	47(2)	39(4)	13(3)	2(2)	1(2)
C(42B)	28(2)	47(2)	39(4)	13(3)	2(2)	1(2)
O(6B)	100(6)	36(3)	66(5)	8(4)	40(4)	11(4)

Table D1. 4 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3)]$.

	x	y	z	U(eq)
H(1)	5157	422	1556	38
H(2)	5656	764	758	46
H(3)	5523	1205	-417	47
H(5)	5015	1512	-1435	59

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H(6)	4382	1531	-1745	66
H(7)	3906	1192	-896	53
H(13)	4313	-2866	3096	26
H(15)	4234	-2441	899	25
H(16)	3866	-1360	1157	22
H(23)	3251	2830	3411	29
H(25)	3117	2516	1204	35
H(26)	3319	1251	1340	33
H(33)	2337	-1029	236	24
H(35)	2380	-1116	2476	24
H(36)	2978	-546	2441	23
H(12D)	3338	-2242	3564	47
H(12E)	3337	-1346	3434	47
H(12F)	3354	-1678	4254	47
H(12G)	3952	-893	4493	47
H(12H)	3940	-571	3669	47
H(12I)	4308	-989	3965	47
H(12A)	3915	-2875	4091	49
H(12B)	3930	-2268	4744	49
H(12C)	4290	-2400	4234	49
H(14G)	4339	-4125	2668	54
H(14H)	4556	-4629	2072	54
H(14I)	4153	-4282	1880	54
H(14A)	5086	-2867	2018	56
H(14B)	5133	-3758	2146	56
H(14C)	4927	-3250	2753	56
H(14D)	4423	-3711	741	75
H(14E)	4835	-4013	930	75
H(14F)	4767	-3131	780	75
H(22G)	3972	869	3487	60
H(22H)	3994	1016	4356	60
H(22I)	4074	1693	3792	60
H(22A)	2987	891	4086	55
H(22B)	3315	601	4618	55
H(22C)	3303	330	3777	55
H(22D)	3602	2508	4389	65
H(22E)	3517	1858	4980	65
H(22F)	3181	2222	4517	65
H(24G)	3411	4076	2989	55
H(24H)	3235	4723	2477	55
H(24I)	3541	4154	2148	55
H(24A)	2463	3403	2622	50
H(24B)	2574	4272	2745	50
H(24C)	2739	3634	3280	50
H(24D)	3097	3809	1108	64
H(24E)	2793	4385	1436	64
H(24F)	2681	3521	1287	64
H(32D)	3575	-585	80	48
H(32E)	3476	-675	-775	48
H(32F)	3363	-1327	-204	48
H(32A)	3250	654	170	46
H(32B)	2818	746	-52	46
H(32C)	3129	642	-679	46
H(32G)	2851	-451	-1259	51
H(32H)	2495	-366	-728	51
H(32I)	2706	-1162	-793	51

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H(34G)	1929	-2063	2376	49
H(34H)	1506	-1950	2100	49
H(34I)	1737	-1245	2418	49
H(34A)	2026	-2196	407	44
H(34B)	1680	-2528	866	44
H(34C)	2099	-2642	1161	44
H(34D)	1587	-526	1237	42
H(34E)	1364	-1249	937	42
H(34F)	1694	-885	455	42
H(40A)	4901	1365	5905	57
H(40B)	4869	2191	6261	57
H(40C)	4767	2065	5411	57
H(41A)	4044	2688	6137	57
H(41B)	4439	2728	6552	57
H(41C)	4089	2330	6942	57
H(40D)	4717	1332	5453	57
H(40E)	4864	2152	5692	57
H(40F)	4477	2069	5251	57
H(41D)	3967	2236	6847	57
H(41E)	4153	2783	6245	57
H(41F)	4347	2679	7034	57

D2. Crystal data of
Carbonyl[tris(2-methylphenyl)phosphite]
(8-hydroxyquinolinato)rhodium(I),
[Rh(ox)(CO)(P(O-2MePh)₃)]

Table D2. 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Rh(ox)(CO)(P(O-2MePh)₃)]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh	568(1)	675(1)	3264(1)	14(1)
P	-50(1)	643(1)	2036(1)	14(1)
N	1378(3)	594(1)	4427(1)	15(1)
O(1)	-1307(3)	1230(1)	1666(1)	16(1)
O(2)	-890(3)	-20(1)	1639(1)	16(1)
O(3)	1552(3)	634(1)	1580(1)	16(1)
O(4)	1849(3)	-201(1)	3309(1)	18(1)
O(5)	-1252(4)	1958(1)	3286(1)	32(1)
C(1)	1149(4)	999(2)	4966(2)	19(1)
C(2)	1748(5)	848(2)	5732(2)	23(1)
C(3)	2600(4)	272(2)	5932(2)	23(1)
C(4)	2914(4)	-173(2)	5376(2)	18(1)
C(5)	3786(5)	-781(2)	5524(2)	23(1)
C(6)	3987(5)	-1174(2)	4937(2)	24(1)
C(7)	3357(4)	-990(2)	4184(2)	20(1)
C(8)	2481(4)	-399(2)	4007(2)	16(1)
C(9)	2252(4)	10(2)	4618(2)	15(1)
C(10)	-562(5)	1457(2)	3261(2)	20(1)
C(11)	-1745(4)	1395(2)	896(2)	14(1)
C(12)	-1348(4)	2031(2)	708(2)	16(1)
C(13)	-1887(5)	2209(2)	-45(2)	22(1)
C(14)	-2765(5)	1774(2)	-574(2)	22(1)
C(15)	-3154(5)	1148(2)	-366(2)	21(1)
C(16)	-2633(4)	952(2)	380(2)	17(1)
C(21)	-2194(4)	-383(2)	1908(2)	14(1)
C(22)	-1789(4)	-1042(2)	2056(2)	16(1)
C(23)	-3114(4)	-1418(2)	2279(2)	20(1)
C(24)	-4719(5)	-1148(2)	2361(2)	21(1)
C(25)	-5064(5)	-489(2)	2216(2)	21(1)
C(26)	-3794(4)	-101(2)	1978(2)	18(1)
C(31)	2679(4)	1172(2)	1567(2)	17(1)
C(32)	2959(5)	1363(2)	854(2)	21(1)
C(33)	4075(5)	1897(2)	843(2)	30(1)
C(34)	4892(5)	2219(2)	1488(3)	34(1)
C(35)	4639(5)	2003(2)	2177(2)	30(1)
C(36)	3531(4)	1475(2)	2220(2)	22(1)
C(121)	-418(5)	2508(2)	1288(2)	21(1)
C(221)	-26(5)	-1322(2)	1985(2)	21(1)
C(321)	2116(5)	998(2)	153(2)	28(1)

Table D2. 2 Bond lengths (Å) and angles (°) for [Rh(ox)(CO)(P(O-2MePh)₃)]

Rh-C(10)	1.810(4)	C(1)-C(2)-H(2)	120.1
Rh-O(4)	2.030(2)	C(2)-C(3)-C(4)	120.3(3)
Rh-N	2.086(2)	C(2)-C(3)-H(3)	119.9
Rh-P	2.1890(10)	C(4)-C(3)-H(3)	119.9
P-O(1)	1.596(2)	C(5)-C(4)-C(3)	124.6(3)
P-O(2)	1.603(2)	C(5)-C(4)-C(9)	118.7(3)
P-O(3)	1.611(2)	C(3)-C(4)-C(9)	116.6(3)
N-C(1)	1.318(4)	C(6)-C(5)-C(4)	119.3(3)
N-C(9)	1.375(4)	C(6)-C(5)-H(5)	120.3
O(1)-C(11)	1.413(3)	C(4)-C(5)-H(5)	120.3
O(2)-C(21)	1.406(4)	C(5)-C(6)-C(7)	122.1(3)
O(3)-C(31)	1.397(4)	C(5)-C(6)-H(6)	119.0
O(4)-C(8)	1.326(4)	C(7)-C(6)-H(6)	119.0
O(5)-C(10)	1.155(4)	C(8)-C(7)-C(6)	120.9(3)
C(1)-C(2)	1.410(4)	C(8)-C(7)-H(7)	119.5
C(1)-H(1)	0.9300	C(6)-C(7)-H(7)	119.5
C(2)-C(3)	1.357(5)	O(4)-C(8)-C(7)	123.6(3)
C(2)-H(2)	0.9300	O(4)-C(8)-C(9)	119.3(3)
C(3)-C(4)	1.413(5)	C(7)-C(8)-C(9)	117.1(3)
C(3)-H(3)	0.9300	N-C(9)-C(4)	122.2(3)
C(4)-C(5)	1.407(5)	N-C(9)-C(8)	116.0(3)
C(4)-C(9)	1.419(4)	C(4)-C(9)-C(8)	121.8(3)
C(5)-C(6)	1.367(5)	O(5)-C(10)-Rh	177.5(3)
C(5)-H(5)	0.9300	C(16)-C(11)-C(12)	123.0(3)
C(6)-C(7)	1.409(5)	C(16)-C(11)-O(1)	120.4(3)
C(6)-H(6)	0.9300	C(12)-C(11)-O(1)	116.4(3)
C(7)-C(8)	1.385(5)	C(11)-C(12)-C(13)	116.6(3)
C(7)-H(7)	0.9300	C(11)-C(12)-C(121)	121.8(3)
C(8)-C(9)	1.426(4)	C(13)-C(12)-C(121)	121.7(3)
C(11)-C(16)	1.377(4)	C(14)-C(13)-C(12)	121.5(3)
C(11)-C(12)	1.390(4)	C(14)-C(13)-H(13)	119.2
C(12)-C(13)	1.396(4)	C(12)-C(13)-H(13)	119.2
C(12)-C(121)	1.505(4)	C(15)-C(14)-C(13)	120.3(3)
C(13)-C(14)	1.380(5)	C(15)-C(14)-H(14)	119.8
C(13)-H(13)	0.9300	C(13)-C(14)-H(14)	119.8
C(14)-C(15)	1.378(5)	C(14)-C(15)-C(16)	119.7(3)
C(14)-H(14)	0.9300	C(14)-C(15)-H(15)	120.1
C(15)-C(16)	1.393(4)	C(16)-C(15)-H(15)	120.1
C(15)-H(15)	0.9300	C(11)-C(16)-C(15)	118.8(3)
C(16)-H(16)	0.9300	C(11)-C(16)-H(16)	120.6
C(21)-C(26)	1.381(5)	C(15)-C(16)-H(16)	120.6
C(21)-C(22)	1.393(4)	C(26)-C(21)-C(22)	123.4(3)
C(22)-C(23)	1.394(5)	C(26)-C(21)-O(2)	121.2(3)
C(22)-C(221)	1.494(5)	C(22)-C(21)-O(2)	115.3(3)
C(23)-C(24)	1.382(5)	C(21)-C(22)-C(23)	116.1(3)
C(23)-H(23)	0.9300	C(21)-C(22)-C(221)	121.4(3)
C(24)-C(25)	1.383(5)	C(23)-C(22)-C(221)	122.5(3)
C(24)-H(24)	0.9300	C(24)-C(23)-C(22)	121.8(3)
C(25)-C(26)	1.388(5)	C(24)-C(23)-H(23)	119.1
C(25)-H(25)	0.9300	C(22)-C(23)-H(23)	119.1
C(26)-H(26)	0.9300	C(23)-C(24)-C(25)	120.4(3)
C(31)-C(36)	1.380(5)	C(23)-C(24)-H(24)	119.8
C(31)-C(32)	1.410(4)	C(25)-C(24)-H(24)	119.8

C(32)-C(33)	1.386(5)	C(24)-C(25)-C(26)	119.6(3)
C(32)-C(321)	1.506(5)	C(24)-C(25)-H(25)	120.2
C(33)-C(34)	1.379(6)	C(26)-C(25)-H(25)	120.2
C(33)-H(33)	0.9300	C(21)-C(26)-C(25)	118.7(3)
C(34)-C(35)	1.376(6)	C(21)-C(26)-H(26)	120.6
C(34)-H(34)	0.9300	C(25)-C(26)-H(26)	120.6
C(35)-C(36)	1.381(5)	C(36)-C(31)-O(3)	121.6(3)
C(35)-H(35)	0.9300	C(36)-C(31)-C(32)	122.2(3)
C(36)-H(36)	0.9300	O(3)-C(31)-C(32)	116.1(3)
C(121)-H(12A)	0.9600	C(33)-C(32)-C(31)	116.0(3)
C(121)-H(12B)	0.9600	C(33)-C(32)-C(321)	122.4(3)
C(121)-H(12C)	0.9600	C(31)-C(32)-C(321)	121.6(3)
C(221)-H(22A)	0.9600	C(34)-C(33)-C(32)	122.4(4)
C(221)-H(22B)	0.9600	C(34)-C(33)-H(33)	118.8
C(221)-H(22C)	0.9600	C(32)-C(33)-H(33)	118.8
C(321)-H(32A)	0.9600	C(35)-C(34)-C(33)	119.9(4)
C(321)-H(32B)	0.9600	C(35)-C(34)-H(34)	120.0
C(321)-H(32C)	0.9600	C(33)-C(34)-H(34)	120.0
		C(34)-C(35)-C(36)	120.0(4)
C(10)-Rh-O(4)	177.93(11)	C(34)-C(35)-H(35)	120.0
C(10)-Rh-N	96.78(12)	C(36)-C(35)-H(35)	120.0
O(4)-Rh-N	81.16(9)	C(31)-C(36)-C(35)	119.3(3)
C(10)-Rh-P	91.02(10)	C(31)-C(36)-H(36)	120.3
O(4)-Rh-P	91.05(6)	C(35)-C(36)-H(36)	120.3
N-Rh-P	172.11(8)	C(12)-C(121)-H(12A)	109.5
O(1)-P-O(2)	106.78(12)	C(12)-C(121)-H(12B)	109.5
O(1)-P-O(3)	104.40(12)	H(12A)-C(121)-H(12B)	109.5
O(2)-P-O(3)	92.13(12)	C(12)-C(121)-H(12C)	109.5
O(1)-P-Rh	113.28(8)	H(12A)-C(121)-H(12C)	109.5
O(2)-P-Rh	117.97(9)	H(12B)-C(121)-H(12C)	109.5
O(3)-P-Rh	119.60(9)	C(22)-C(221)-H(22A)	109.5
C(1)-N-C(9)	119.0(3)	C(22)-C(221)-H(22B)	109.5
C(1)-N-Rh	130.2(2)	H(22A)-C(221)-H(22B)	109.5
C(9)-N-Rh	110.79(19)	C(22)-C(221)-H(22C)	109.5
C(11)-O(1)-P	126.67(19)	H(22A)-C(221)-H(22C)	109.5
C(21)-O(2)-P	122.34(19)	H(22B)-C(221)-H(22C)	109.5
C(31)-O(3)-P	122.4(2)	C(32)-C(321)-H(32A)	109.5
C(8)-O(4)-Rh	112.7(2)	C(32)-C(321)-H(32B)	109.5
N-C(1)-C(2)	122.2(3)	H(32A)-C(321)-H(32B)	109.5
N-C(1)-H(1)	118.9	C(32)-C(321)-H(32C)	109.5
C(2)-C(1)-H(1)	118.9	H(32A)-C(321)-H(32C)	109.5
C(3)-C(2)-C(1)	119.7(3)	H(32B)-C(321)-H(32C)	109.5
C(3)-C(2)-H(2)	120.1		

Table D2. 3 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2\text{MePh})_3)]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh	19(1)	16(1)	8(1)	0(1)	2(1)	2(1)
P	18(1)	14(1)	9(1)	0(1)	3(1)	1(1)
N	14(1)	20(2)	9(1)	-1(1)	1(1)	-1(1)
O(1)	21(1)	18(1)	7(1)	-1(1)	2(1)	2(1)
O(2)	21(1)	16(1)	12(1)	0(1)	6(1)	-2(1)

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O(3)	18(1)	16(1)	14(1)	0(1)	4(1)	-1(1)
O(4)	22(1)	22(1)	10(1)	1(1)	3(1)	4(1)
O(5)	43(2)	27(1)	22(1)	-5(1)	2(1)	13(1)
C(1)	20(2)	26(2)	12(2)	-3(1)	2(1)	2(2)
C(2)	24(2)	36(2)	9(1)	-8(1)	2(1)	-2(2)
C(3)	21(2)	36(2)	9(1)	2(2)	-2(1)	-6(2)
C(4)	14(2)	26(2)	12(1)	5(1)	2(1)	-5(1)
C(5)	21(2)	28(2)	18(2)	10(2)	-2(1)	-5(2)
C(6)	21(2)	20(2)	28(2)	7(2)	0(2)	-1(2)
C(7)	19(2)	21(2)	19(2)	0(1)	4(1)	0(2)
C(8)	13(2)	20(2)	14(2)	1(1)	3(1)	-2(1)
C(9)	14(2)	21(2)	10(1)	1(1)	3(1)	-3(1)
C(10)	23(2)	25(2)	9(1)	-2(1)	-1(1)	1(2)
C(11)	15(2)	18(2)	9(1)	2(1)	4(1)	5(1)
C(12)	13(2)	19(2)	15(1)	2(1)	4(1)	3(1)
C(13)	24(2)	22(2)	21(2)	7(2)	10(1)	2(2)
C(14)	24(2)	32(2)	8(1)	5(1)	2(1)	5(2)
C(15)	26(2)	28(2)	9(1)	-4(1)	1(1)	0(2)
C(16)	21(2)	17(2)	13(1)	-1(1)	4(1)	0(1)
C(21)	16(2)	17(2)	8(1)	0(1)	1(1)	-5(1)
C(22)	20(2)	17(2)	10(1)	-1(1)	3(1)	-2(1)
C(23)	23(2)	23(2)	12(2)	3(1)	1(1)	-5(2)
C(24)	22(2)	31(2)	10(1)	0(1)	3(1)	-8(2)
C(25)	19(2)	32(2)	11(1)	-4(1)	2(1)	2(2)
C(26)	22(2)	22(2)	10(1)	-1(1)	1(1)	5(2)
C(31)	15(2)	15(2)	23(2)	2(1)	6(1)	1(1)
C(32)	19(2)	23(2)	26(2)	1(2)	13(1)	6(2)
C(33)	30(2)	25(2)	42(2)	2(2)	23(2)	-1(2)
C(34)	26(2)	19(2)	63(3)	-8(2)	24(2)	-7(2)
C(35)	16(2)	27(2)	45(2)	-16(2)	5(2)	-1(2)
C(36)	16(2)	26(2)	25(2)	-5(2)	4(1)	4(2)
C(121)	23(2)	16(2)	22(2)	3(1)	2(1)	0(2)
C(221)	27(2)	16(2)	22(2)	4(1)	7(1)	6(2)
C(321)	33(2)	35(2)	19(2)	2(2)	14(2)	2(2)

Table D2. 4 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{O}-2\text{MePh})_3)]$.

	x	y	z	U(eq)
H(1)	574	1397	4836	23
H(2)	1559	1143	6099	28
H(3)	2978	168	6437	27
H(5)	4222	-913	6016	27
H(6)	4558	-1577	5039	29
H(7)	3531	-1269	3800	24
H(13)	-1650	2631	-194	26
H(14)	-3096	1903	-1074	26
H(15)	-3762	858	-723	25
H(16)	-2881	531	527	20
H(23)	-2912	-1863	2374	24
H(24)	-5573	-1410	2516	25
H(25)	-6140	-307	2278	25
H(26)	-4017	341	1866	22
H(33)	4281	2044	383	36
H(34)	5613	2582	1458	41

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H(35)	5215	2212	2613	35
H(36)	3360	1326	2684	27
H(12A)	-823	2443	1750	31
H(12B)	-683	2949	1114	31
H(12C)	847	2437	1372	31
H(22A)	886	-1154	2381	32
H(22B)	236	-1199	1508	32
H(22C)	-65	-1792	2019	32
H(32A)	2708	1113	-247	42
H(32B)	877	1114	15	42
H(32C)	2224	534	244	42

D3. Crystal data of
Carbonyl[tris(pentafluorophenyl)phosphine]
(8-hydroxyquinolinato)rhodium(I),
[Rh(ox)(CO)(P(5FPh)₃)]

Table D3. 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Rh(ox)(CO)(P(5FPh)₃)]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh	8075(1)	1126(1)	6462(1)	34(1)
P	8101(1)	-342(1)	6998(1)	35(1)
F(32)	7177(1)	-951(2)	5821(1)	57(1)
F(22)	7411(1)	965(2)	7739(1)	57(1)
F(12)	8439(1)	-2310(2)	7790(1)	57(1)
F(26)	9524(1)	-857(2)	7995(1)	58(1)
F(16)	8712(1)	-907(2)	5906(1)	64(1)
F(36)	7198(1)	-1072(2)	7947(1)	61(1)
F(23)	7824(1)	1625(2)	8916(1)	72(1)
F(34)	5161(1)	-1728(2)	6419(1)	92(1)
F(25)	9929(1)	-156(2)	9155(1)	76(1)
C(11)	8570(2)	-1527(3)	6873(2)	35(1)
F(14)	9504(1)	-4272(2)	6527(1)	93(1)
F(13)	9085(1)	-4062(2)	7587(1)	83(1)
F(15)	9318(1)	-2678(2)	5701(1)	91(1)
F(35)	5866(1)	-1574(2)	7634(1)	77(1)
O(4)	7030(1)	1109(2)	6218(1)	46(1)
N	7894(1)	2534(2)	5980(1)	33(1)
C(32)	6857(2)	-1052(3)	6279(2)	42(1)
F(33)	5829(1)	-1412(2)	5515(1)	88(1)
C(1)	8331(2)	3234(3)	5867(2)	40(1)
C(12)	8670(2)	-2364(3)	7277(2)	43(1)
F(24)	9100(1)	1096(2)	9629(1)	81(1)
C(26)	9079(2)	-261(3)	8201(2)	43(1)
C(10)	9016(2)	1176(3)	6668(2)	45(1)
C(24)	8887(2)	744(3)	9045(2)	54(1)
C(16)	8799(2)	-1659(3)	6341(2)	45(1)
C(22)	8033(2)	652(3)	8087(2)	42(1)
C(31)	7235(2)	-915(2)	6892(2)	35(1)
C(21)	8425(2)	-20(3)	7826(2)	37(1)
C(7)	6046(2)	2039(3)	5615(2)	52(1)
C(8)	6751(2)	1915(3)	5871(2)	39(1)
C(33)	6164(2)	-1313(3)	6113(2)	53(1)
C(36)	6880(2)	-1137(3)	7337(2)	45(1)
C(15)	9120(2)	-2570(3)	6225(2)	58(1)
O(5)	9608(1)	1214(2)	6792(1)	68(1)
C(35)	6189(2)	-1404(3)	7186(2)	50(1)
C(13)	8991(2)	-3278(3)	7178(2)	53(1)
C(34)	5834(2)	-1487(3)	6577(2)	56(1)
C(3)	7430(2)	4297(3)	5252(2)	50(1)
C(2)	8113(2)	4133(3)	5507(2)	50(1)
C(25)	9302(2)	106(3)	8810(2)	51(1)

C(9)	7197(2)	2700(3)	5734(1)	36(1)
C(4)	6937(2)	3577(3)	5355(2)	40(1)
C(6)	5792(2)	2902(3)	5236(2)	56(1)
C(23)	8242(2)	1014(3)	8685(2)	49(1)
C(5)	6220(2)	3642(3)	5105(2)	52(1)
C(14)	9210(2)	-3372(3)	6639(2)	62(1)

Table D3. 2 Bond lengths (Å) and angles (°) for [Rh(ox)(CO)(P(5FPh)₃)]

Rh-C(10)	1.817(4)	F(32)-C(32)-C(33)	117.4(3)
Rh-O(4)	2.018(2)	F(32)-C(32)-C(31)	119.3(3)
Rh-N	2.077(3)	C(33)-C(32)-C(31)	123.3(3)
Rh-P	2.2145(11)	N-C(1)-C(2)	122.7(3)
P-C(21)	1.835(3)	N-C(1)-H(1)	118.7
P-C(31)	1.836(3)	C(2)-C(1)-H(1)	118.7
P-C(11)	1.838(3)	F(12)-C(12)-C(13)	117.3(3)
F(32)-C(32)	1.342(4)	F(12)-C(12)-C(11)	119.5(3)
F(22)-C(22)	1.343(4)	C(13)-C(12)-C(11)	123.2(4)
F(12)-C(12)	1.337(4)	F(26)-C(26)-C(21)	121.6(3)
F(26)-C(26)	1.339(4)	F(26)-C(26)-C(25)	116.7(3)
F(16)-C(16)	1.341(4)	C(21)-C(26)-C(25)	121.6(4)
F(36)-C(36)	1.344(4)	O(5)-C(10)-Rh	179.2(4)
F(23)-C(23)	1.339(4)	F(24)-C(24)-C(25)	120.1(4)
F(34)-C(34)	1.335(4)	F(24)-C(24)-C(23)	120.0(4)
F(25)-C(25)	1.332(4)	C(25)-C(24)-C(23)	119.9(4)
C(11)-C(12)	1.378(4)	F(16)-C(16)-C(11)	121.2(3)
C(11)-C(16)	1.384(5)	F(16)-C(16)-C(15)	116.6(4)
F(14)-C(14)	1.342(4)	C(11)-C(16)-C(15)	122.2(4)
F(13)-C(13)	1.334(4)	F(22)-C(22)-C(23)	117.7(3)
F(15)-C(15)	1.331(4)	F(22)-C(22)-C(21)	118.8(3)
F(35)-C(35)	1.338(4)	C(23)-C(22)-C(21)	123.5(3)
O(4)-C(8)	1.320(4)	C(32)-C(31)-C(36)	115.2(3)
N-C(1)	1.318(4)	C(32)-C(31)-P	115.6(2)
N-C(9)	1.375(4)	C(36)-C(31)-P	128.8(3)
C(32)-C(33)	1.378(5)	C(22)-C(21)-C(26)	115.5(3)
C(32)-C(31)	1.388(4)	C(22)-C(21)-P	117.9(3)
F(33)-C(33)	1.332(4)	C(26)-C(21)-P	125.9(3)
C(1)-C(2)	1.402(5)	C(8)-C(7)-C(6)	120.6(4)
C(1)-H(1)	0.9300	C(8)-C(7)-H(7)	119.7
C(12)-C(13)	1.377(5)	C(6)-C(7)-H(7)	119.7
F(24)-C(24)	1.335(4)	O(4)-C(8)-C(7)	124.0(3)
C(26)-C(21)	1.390(5)	O(4)-C(8)-C(9)	118.8(3)
C(26)-C(25)	1.393(5)	C(7)-C(8)-C(9)	117.2(3)
C(10)-O(5)	1.144(4)	F(33)-C(33)-C(32)	120.3(4)
C(24)-C(25)	1.359(5)	F(33)-C(33)-C(34)	121.1(3)
C(24)-C(23)	1.374(5)	C(32)-C(33)-C(34)	118.6(3)
C(16)-C(15)	1.384(5)	F(36)-C(36)-C(35)	116.4(3)
C(22)-C(23)	1.367(5)	F(36)-C(36)-C(31)	120.8(3)
C(22)-C(21)	1.386(5)	C(35)-C(36)-C(31)	122.8(3)
C(31)-C(36)	1.388(5)	F(15)-C(15)-C(14)	119.9(4)
C(7)-C(8)	1.385(4)	F(15)-C(15)-C(16)	120.4(4)
C(7)-C(6)	1.400(5)	C(14)-C(15)-C(16)	119.6(4)
C(7)-H(7)	0.9300	F(35)-C(35)-C(34)	120.0(4)
C(8)-C(9)	1.424(5)	F(35)-C(35)-C(36)	120.4(4)
C(33)-C(34)	1.379(5)	C(34)-C(35)-C(36)	119.7(4)

C(36)-C(35)	1.376(5)	F(13)-C(13)-C(12)	121.0(4)
C(15)-C(14)	1.357(6)	F(13)-C(13)-C(14)	120.5(4)
C(35)-C(34)	1.364(5)	C(12)-C(13)-C(14)	118.5(4)
C(13)-C(14)	1.383(6)	F(34)-C(34)-C(35)	120.7(4)
C(3)-C(2)	1.351(5)	F(34)-C(34)-C(33)	119.0(4)
C(3)-C(4)	1.408(5)	C(35)-C(34)-C(33)	120.3(3)
C(3)-H(3)	0.9300	C(2)-C(3)-C(4)	120.2(3)
C(2)-H(2)	0.9300	C(2)-C(3)-H(3)	119.9
C(9)-C(4)	1.416(4)	C(4)-C(3)-H(3)	119.9
C(4)-C(5)	1.400(5)	C(3)-C(2)-C(1)	119.9(3)
C(6)-C(5)	1.355(5)	C(3)-C(2)-H(2)	120.1
C(6)-H(6)	0.9300	C(1)-C(2)-H(2)	120.1
C(5)-H(5)	0.9300	F(25)-C(25)-C(24)	120.3(4)
		F(25)-C(25)-C(26)	119.6(4)
C(10)-Rh-O(4)	178.29(13)	C(24)-C(25)-C(26)	120.1(4)
C(10)-Rh-N	97.53(13)	N-C(9)-C(4)	122.4(3)
O(4)-Rh-N	80.77(10)	N-C(9)-C(8)	115.5(3)
C(10)-Rh-P	90.89(11)	C(4)-C(9)-C(8)	122.0(3)
O(4)-Rh-P	90.82(7)	C(5)-C(4)-C(3)	125.7(3)
N-Rh-P	170.84(8)	C(5)-C(4)-C(9)	117.6(3)
C(21)-P-C(31)	107.20(16)	C(3)-C(4)-C(9)	116.6(3)
C(21)-P-C(11)	105.95(15)	C(5)-C(6)-C(7)	121.8(4)
C(31)-P-C(11)	98.85(15)	C(5)-C(6)-H(6)	119.1
C(21)-P-Rh	107.67(11)	C(7)-C(6)-H(6)	119.1
C(31)-P-Rh	112.17(11)	F(23)-C(23)-C(22)	120.4(4)
C(11)-P-Rh	123.80(11)	F(23)-C(23)-C(24)	120.4(4)
C(12)-C(11)-C(16)	116.1(3)	C(22)-C(23)-C(24)	119.2(4)
C(12)-C(11)-P	122.2(3)	C(6)-C(5)-C(4)	120.7(3)
C(16)-C(11)-P	121.6(3)	C(6)-C(5)-H(5)	119.6
C(8)-O(4)-Rh	113.6(2)	C(4)-C(5)-H(5)	119.6
C(1)-N-C(9)	118.2(3)	F(14)-C(14)-C(15)	120.5(4)
C(1)-N-Rh	130.5(2)	F(14)-C(14)-C(13)	119.0(4)
C(9)-N-Rh	111.3(2)	C(15)-C(14)-C(13)	120.5(4)

Table D3. 3 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{5FPh})_3)]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Rh	29(1)	36(1)	37(1)	6(1)	7(1)	1(1)
P	30(1)	39(1)	34(1)	6(1)	7(1)	-1(1)
F(32)	60(1)	68(2)	43(1)	-6(1)	14(1)	-13(1)
F(22)	51(1)	64(2)	55(1)	0(1)	10(1)	18(1)
F(12)	67(2)	52(1)	52(1)	14(1)	18(1)	-2(1)
F(26)	32(1)	75(2)	63(1)	-5(1)	4(1)	3(1)
F(16)	85(2)	63(2)	55(1)	12(1)	35(1)	12(1)
F(36)	54(1)	85(2)	44(1)	15(1)	12(1)	-17(1)
F(23)	99(2)	62(2)	62(2)	-16(1)	34(1)	3(1)
F(34)	41(2)	117(2)	111(2)	1(2)	10(1)	-32(1)
F(25)	48(2)	107(2)	58(2)	2(1)	-13(1)	-17(1)
C(11)	31(2)	36(2)	38(2)	4(2)	8(2)	-1(2)
F(14)	85(2)	61(2)	131(2)	-15(2)	26(2)	26(2)
F(13)	86(2)	50(2)	104(2)	28(1)	9(2)	16(1)
F(15)	107(2)	95(2)	90(2)	-13(2)	58(2)	22(2)
F(35)	52(2)	102(2)	85(2)	20(2)	36(1)	-13(1)
O(4)	35(1)	46(2)	55(2)	15(1)	10(1)	1(1)

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N	38(2)	33(2)	30(2)	-1(1)	12(1)	-1(1)
C(32)	43(2)	39(2)	46(2)	3(2)	15(2)	-6(2)
F(33)	70(2)	120(2)	61(2)	-14(2)	-8(1)	-36(2)
C(1)	43(2)	41(2)	37(2)	-3(2)	11(2)	-4(2)
C(12)	38(2)	43(2)	46(2)	4(2)	9(2)	-7(2)
F(24)	98(2)	92(2)	44(1)	-21(1)	4(1)	-29(2)
C(26)	37(2)	45(2)	46(2)	0(2)	12(2)	-7(2)
C(10)	42(2)	39(2)	54(2)	7(2)	12(2)	4(2)
C(24)	66(3)	54(3)	38(2)	-3(2)	6(2)	-20(2)
C(16)	39(2)	48(2)	47(2)	7(2)	9(2)	1(2)
C(22)	43(2)	42(2)	41(2)	3(2)	9(2)	-2(2)
C(31)	32(2)	31(2)	43(2)	6(2)	10(2)	0(1)
C(21)	37(2)	36(2)	35(2)	4(2)	7(2)	-2(2)
C(7)	29(2)	67(3)	59(3)	7(2)	9(2)	4(2)
C(8)	38(2)	43(2)	38(2)	-1(2)	13(2)	4(2)
C(33)	44(2)	54(3)	53(3)	-9(2)	-3(2)	-12(2)
C(36)	39(2)	45(2)	49(2)	9(2)	10(2)	-3(2)
C(15)	54(3)	59(3)	66(3)	-7(2)	22(2)	8(2)
O(5)	31(2)	69(2)	102(2)	5(2)	12(2)	-1(1)
C(35)	47(2)	48(3)	62(3)	11(2)	24(2)	-6(2)
C(13)	45(2)	39(2)	68(3)	9(2)	0(2)	2(2)
C(34)	36(2)	54(3)	76(3)	-1(2)	12(2)	-15(2)
C(3)	68(3)	39(2)	43(2)	6(2)	17(2)	11(2)
C(2)	66(3)	41(2)	45(2)	6(2)	17(2)	-12(2)
C(25)	42(2)	60(3)	45(2)	5(2)	-1(2)	-15(2)
C(9)	38(2)	41(2)	28(2)	-1(2)	9(2)	7(2)
C(4)	52(2)	39(2)	29(2)	-2(2)	13(2)	8(2)
C(6)	39(2)	74(3)	54(3)	3(2)	8(2)	20(2)
C(23)	67(3)	38(2)	47(2)	-3(2)	22(2)	-5(2)
C(5)	55(3)	59(3)	37(2)	10(2)	4(2)	24(2)
C(14)	43(3)	45(3)	95(4)	-7(3)	14(2)	9(2)

Table D3. 4 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{ox})(\text{CO})(\text{P}(\text{5FPh})_3)]$.

	x	y	z	U(eq)
H(1)	8803	3127	6032	48
H(7)	5739	1544	5696	62
H(3)	7286	4888	5008	59
H(2)	8437	4615	5444	60
H(6)	5317	2969	5071	68
H(5)	6034	4198	4845	62

D4. Crystal data of
Carbonyl[tricyclohexylphosphine]
(8-hydroxyquinolinato)rhodium(I),
[Rh(ox)(CO)(PCy₃)]

Table D4. 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Rh(ox)(CO)(PCy₃)]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N	5268(2)	-840(5)	5555(1)	20(1)
C(1)	4697(3)	-1840(6)	5423(2)	20(1)
C(2)	4671(3)	-2849(6)	5089(2)	20(1)
C(3)	5243(3)	-2781(6)	4911(2)	20(1)
C(4)	5868(3)	-1739(6)	5040(2)	20(1)
C(5)	6475(3)	-1528(6)	4862(2)	20(1)
C(6)	7026(3)	-504(6)	5009(2)	20(1)
C(7)	7022(3)	489(6)	5345(2)	20(1)
C(8)	6441(3)	352(6)	5534(2)	20(1)
C(9)	5849(3)	-766(6)	5371(2)	20(1)
C(10)	4498(3)	606(7)	6124(2)	29(2)
C(11)	6157(3)	1946(6)	6937(1)	17(1)
C(12)	5624(3)	862(7)	7105(2)	25(1)
C(13)	6011(3)	154(7)	7494(2)	21(1)
C(14)	6690(3)	-858(6)	7464(2)	21(1)
C(15)	7226(3)	176(7)	7289(2)	25(1)
C(16)	6845(3)	928(7)	6901(2)	25(1)
C(21)	4905(3)	4082(6)	6573(2)	25(1)
C(22)	4527(3)	5173(7)	6229(2)	28(2)
C(23)	3800(3)	5928(8)	6303(2)	35(2)
C(24)	3924(3)	6841(8)	6684(2)	36(2)
C(25)	4302(3)	5765(7)	7012(2)	33(2)
C(26)	5047(3)	5070(7)	6948(2)	28(1)
C(31)	6424(3)	4301(6)	6349(1)	18(1)
C(32)	6724(3)	5643(7)	6645(2)	23(1)
C(33)	7421(3)	6422(7)	6556(2)	27(1)
C(34)	7277(3)	7128(7)	6148(2)	27(1)
C(35)	6937(3)	5811(7)	5851(2)	25(1)
C(36)	6237(3)	5032(7)	5946(2)	22(1)
O(1)	6396(2)	1201(5)	5847(1)	26(1)
O(2)	3916(2)	412(6)	6179(1)	41(1)
P	5702(1)	2873(2)	6464(1)	17(1)
Rh	5401(1)	903(1)	6003(1)	20(1)

Table D4. 2 Bond lengths ($\text{\AA}$) and angles ($^\circ$) for [Rh(ox)(CO)(PCy₃)]

N-C(1)	1.324(6)	C(13)-C(12)-C(11)	110.7(4)
N-C(9)	1.368(7)	C(13)-C(12)-H(12A)	109.5
N-Rh	2.091(4)	C(11)-C(12)-H(12A)	109.5
C(1)-C(2)	1.424(7)	C(13)-C(12)-H(12B)	109.5

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C(1)-H(1)	0.9300	C(11)-C(12)-H(12B)	109.5
C(2)-C(3)	1.339(8)	H(12A)-C(12)-H(12B)	108.1
C(2)-H(2)	0.9300	C(14)-C(13)-C(12)	111.6(5)
C(3)-C(4)	1.416(7)	C(14)-C(13)-H(13A)	109.3
C(3)-H(3)	0.9300	C(12)-C(13)-H(13A)	109.3
C(4)-C(5)	1.406(8)	C(14)-C(13)-H(13B)	109.3
C(4)-C(9)	1.416(7)	C(12)-C(13)-H(13B)	109.3
C(5)-C(6)	1.321(7)	H(13A)-C(13)-H(13B)	108.0
C(5)-H(5)	0.9300	C(13)-C(14)-C(15)	110.7(4)
C(6)-C(7)	1.434(7)	C(13)-C(14)-H(14A)	109.5
C(6)-H(6)	0.9300	C(15)-C(14)-H(14A)	109.5
C(7)-C(8)	1.384(8)	C(13)-C(14)-H(14B)	109.5
C(7)-H(7)	0.9300	C(15)-C(14)-H(14B)	109.5
C(8)-O(1)	1.321(7)	H(14A)-C(14)-H(14B)	108.1
C(8)-C(9)	1.432(7)	C(14)-C(15)-C(16)	111.8(4)
C(10)-O(2)	1.140(7)	C(14)-C(15)-H(15A)	109.2
C(10)-Rh	1.817(6)	C(16)-C(15)-H(15A)	109.2
C(11)-C(12)	1.524(7)	C(14)-C(15)-H(15B)	109.2
C(11)-C(16)	1.533(7)	C(16)-C(15)-H(15B)	109.2
C(11)-P	1.859(5)	H(15A)-C(15)-H(15B)	107.9
C(11)-H(11)	0.9800	C(15)-C(16)-C(11)	111.2(5)
C(12)-C(13)	1.521(7)	C(15)-C(16)-H(16A)	109.4
C(12)-H(12A)	0.9700	C(11)-C(16)-H(16A)	109.4
C(12)-H(12B)	0.9700	C(15)-C(16)-H(16B)	109.4
C(13)-C(14)	1.514(7)	C(11)-C(16)-H(16B)	109.4
C(13)-H(13A)	0.9700	H(16A)-C(16)-H(16B)	108.0
C(13)-H(13B)	0.9700	C(26)-C(21)-C(22)	111.1(4)
C(14)-C(15)	1.518(8)	C(26)-C(21)-P	117.2(4)
C(14)-H(14A)	0.9700	C(22)-C(21)-P	111.9(4)
C(14)-H(14B)	0.9700	C(26)-C(21)-H(21)	105.2
C(15)-C(16)	1.527(7)	C(22)-C(21)-H(21)	105.2
C(15)-H(15A)	0.9700	P-C(21)-H(21)	105.2
C(15)-H(15B)	0.9700	C(21)-C(22)-C(23)	110.5(5)
C(16)-H(16A)	0.9700	C(21)-C(22)-H(22A)	109.5
C(16)-H(16B)	0.9700	C(23)-C(22)-H(22A)	109.5
C(21)-C(26)	1.522(8)	C(21)-C(22)-H(22B)	109.5
C(21)-C(22)	1.540(8)	C(23)-C(22)-H(22B)	109.5
C(21)-P	1.864(6)	H(22A)-C(22)-H(22B)	108.1
C(21)-H(21)	0.9800	C(24)-C(23)-C(22)	111.8(5)
C(22)-C(23)	1.541(8)	C(24)-C(23)-H(23A)	109.3
C(22)-H(22A)	0.9700	C(22)-C(23)-H(23A)	109.3
C(22)-H(22B)	0.9700	C(24)-C(23)-H(23B)	109.3
C(23)-C(24)	1.511(9)	C(22)-C(23)-H(23B)	109.3
C(23)-H(23A)	0.9700	H(23A)-C(23)-H(23B)	107.9
C(23)-H(23B)	0.9700	C(25)-C(24)-C(23)	111.9(5)
C(24)-C(25)	1.496(9)	C(25)-C(24)-H(24A)	109.2
C(24)-H(24A)	0.9700	C(23)-C(24)-H(24A)	109.2
C(24)-H(24B)	0.9700	C(25)-C(24)-H(24B)	109.2
C(25)-C(26)	1.542(8)	C(23)-C(24)-H(24B)	109.2
C(25)-H(25A)	0.9700	H(24A)-C(24)-H(24B)	107.9
C(25)-H(25B)	0.9700	C(24)-C(25)-C(26)	111.9(5)
C(26)-H(26A)	0.9700	C(24)-C(25)-H(25A)	109.2
C(26)-H(26B)	0.9700	C(26)-C(25)-H(25A)	109.2
C(31)-C(36)	1.515(7)	C(24)-C(25)-H(25B)	109.2
C(31)-C(32)	1.521(7)	C(26)-C(25)-H(25B)	109.2
C(31)-P	1.865(5)	H(25A)-C(25)-H(25B)	107.9

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C(31)-H(31)	0.9800	C(21)-C(26)-C(25)	109.0(5)
C(32)-C(33)	1.519(8)	C(21)-C(26)-H(26A)	109.9
C(32)-H(32A)	0.9700	C(25)-C(26)-H(26A)	109.9
C(32)-H(32B)	0.9700	C(21)-C(26)-H(26B)	109.9
C(33)-C(34)	1.525(8)	C(25)-C(26)-H(26B)	109.9
C(33)-H(33A)	0.9700	H(26A)-C(26)-H(26B)	108.3
C(33)-H(33B)	0.9700	C(36)-C(31)-C(32)	110.6(4)
C(34)-C(35)	1.527(8)	C(36)-C(31)-P	114.6(3)
C(34)-H(34A)	0.9700	C(32)-C(31)-P	116.9(4)
C(34)-H(34B)	0.9700	C(36)-C(31)-H(31)	104.4
C(35)-C(36)	1.533(8)	C(32)-C(31)-H(31)	104.4
C(35)-H(35A)	0.9700	P-C(31)-H(31)	104.4
C(35)-H(35B)	0.9700	C(33)-C(32)-C(31)	110.2(5)
C(36)-H(36A)	0.9700	C(33)-C(32)-H(32A)	109.6
C(36)-H(36B)	0.9700	C(31)-C(32)-H(32A)	109.6
O(1)-Rh	2.036(4)	C(33)-C(32)-H(32B)	109.6
P-Rh	2.2557(15)	C(31)-C(32)-H(32B)	109.6
		H(32A)-C(32)-H(32B)	108.1
C(1)-N-C(9)	119.9(5)	C(32)-C(33)-C(34)	111.5(4)
C(1)-N-Rh	128.9(4)	C(32)-C(33)-H(33A)	109.3
C(9)-N-Rh	110.9(3)	C(34)-C(33)-H(33A)	109.3
N-C(1)-C(2)	121.3(5)	C(32)-C(33)-H(33B)	109.3
N-C(1)-H(1)	119.3	C(34)-C(33)-H(33B)	109.3
C(2)-C(1)-H(1)	119.3	H(33A)-C(33)-H(33B)	108.0
C(3)-C(2)-C(1)	118.6(5)	C(33)-C(34)-C(35)	111.1(5)
C(3)-C(2)-H(2)	120.7	C(33)-C(34)-H(34A)	109.4
C(1)-C(2)-H(2)	120.7	C(35)-C(34)-H(34A)	109.4
C(2)-C(3)-C(4)	122.5(5)	C(33)-C(34)-H(34B)	109.4
C(2)-C(3)-H(3)	118.7	C(35)-C(34)-H(34B)	109.4
C(4)-C(3)-H(3)	118.7	H(34A)-C(34)-H(34B)	108.0
C(5)-C(4)-C(3)	126.5(5)	C(34)-C(35)-C(36)	111.6(5)
C(5)-C(4)-C(9)	118.0(5)	C(34)-C(35)-H(35A)	109.3
C(3)-C(4)-C(9)	115.4(5)	C(36)-C(35)-H(35A)	109.3
C(6)-C(5)-C(4)	120.9(5)	C(34)-C(35)-H(35B)	109.3
C(6)-C(5)-H(5)	119.6	C(36)-C(35)-H(35B)	109.3
C(4)-C(5)-H(5)	119.6	H(35A)-C(35)-H(35B)	108.0
C(5)-C(6)-C(7)	122.2(5)	C(31)-C(36)-C(35)	109.5(4)
C(5)-C(6)-H(6)	118.9	C(31)-C(36)-H(36A)	109.8
C(7)-C(6)-H(6)	118.9	C(35)-C(36)-H(36A)	109.8
C(8)-C(7)-C(6)	120.1(5)	C(31)-C(36)-H(36B)	109.8
C(8)-C(7)-H(7)	120.0	C(35)-C(36)-H(36B)	109.8
C(6)-C(7)-H(7)	120.0	H(36A)-C(36)-H(36B)	108.2
O(1)-C(8)-C(7)	124.1(5)	C(8)-O(1)-Rh	112.9(3)
O(1)-C(8)-C(9)	118.9(5)	C(11)-P-C(21)	104.1(2)
C(7)-C(8)-C(9)	117.0(5)	C(11)-P-C(31)	103.8(2)
N-C(9)-C(4)	122.2(5)	C(21)-P-C(31)	110.8(2)
N-C(9)-C(8)	116.0(5)	C(11)-P-Rh	111.47(17)
C(4)-C(9)-C(8)	121.8(5)	C(21)-P-Rh	115.65(17)
O(2)-C(10)-Rh	176.5(5)	C(31)-P-Rh	110.28(17)
C(12)-C(11)-C(16)	109.9(4)	C(10)-Rh-O(1)	177.8(2)
C(12)-C(11)-P	112.1(3)	C(10)-Rh-N	97.3(2)
C(16)-C(11)-P	111.0(4)	O(1)-Rh-N	80.65(16)
C(12)-C(11)-H(11)	107.9	C(10)-Rh-P	90.89(18)
C(16)-C(11)-H(11)	107.9	O(1)-Rh-P	91.14(11)
P-C(11)-H(11)	107.9	N-Rh-P	171.78(13)

Table D4. 3 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{ox})(\text{CO})(\text{PCy}_3)]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N	30(1)	15(1)	15(1)	-3(1)	0(1)	7(1)
C(1)	30(1)	15(1)	15(1)	-3(1)	0(1)	7(1)
C(2)	30(1)	15(1)	15(1)	-3(1)	0(1)	7(1)
C(3)	30(1)	15(1)	15(1)	-3(1)	0(1)	7(1)
C(4)	30(1)	15(1)	15(1)	-3(1)	0(1)	7(1)
C(5)	30(1)	15(1)	15(1)	-3(1)	0(1)	7(1)
C(6)	30(1)	15(1)	15(1)	-3(1)	0(1)	7(1)
C(7)	30(1)	15(1)	15(1)	-3(1)	0(1)	7(1)
C(8)	30(1)	15(1)	15(1)	-3(1)	0(1)	7(1)
C(9)	30(1)	15(1)	15(1)	-3(1)	0(1)	7(1)
C(10)	39(3)	15(3)	28(3)	-8(2)	-6(3)	4(2)
C(11)	31(2)	14(2)	8(2)	-2(2)	8(2)	0(2)
C(12)	27(2)	21(3)	31(3)	7(2)	15(2)	2(2)
C(13)	30(2)	22(3)	13(3)	3(2)	10(2)	1(2)
C(14)	26(2)	18(3)	18(3)	2(2)	3(2)	1(2)
C(15)	25(2)	33(3)	17(3)	5(2)	2(2)	0(2)
C(16)	24(2)	31(3)	21(3)	1(2)	9(2)	-1(2)
C(21)	30(2)	18(3)	27(3)	-7(2)	8(2)	-6(2)
C(22)	26(2)	27(3)	31(3)	-7(3)	5(2)	3(2)
C(23)	35(3)	29(3)	40(4)	1(3)	4(3)	10(3)
C(24)	37(3)	27(3)	49(4)	-1(3)	20(3)	6(2)
C(25)	41(3)	28(3)	35(4)	2(3)	20(3)	3(2)
C(26)	42(3)	20(3)	23(3)	0(2)	12(2)	5(2)
C(31)	25(2)	19(2)	10(3)	0(2)	6(2)	6(2)
C(32)	30(2)	24(3)	15(3)	-3(2)	4(2)	-1(2)
C(33)	33(3)	24(3)	23(3)	-2(2)	3(2)	-5(2)
C(34)	26(2)	25(3)	32(3)	10(2)	8(2)	-1(2)
C(35)	33(3)	25(3)	18(3)	6(2)	10(2)	8(2)
C(36)	31(3)	22(3)	13(3)	1(2)	5(2)	2(2)
O(1)	33(2)	28(2)	19(2)	-7(2)	9(2)	12(2)
O(2)	27(2)	41(2)	52(3)	1(2)	7(2)	-4(2)
P	25(1)	13(1)	14(1)	-2(1)	5(1)	3(1)
Rh	30(1)	15(1)	15(1)	-3(1)	0(1)	7(1)

Table D4. 4 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{ox})(\text{CO})(\text{PCy}_3)]$.

	x	y	z	U(eq)
H(1)	4305	-1886	5550	24
H(2)	4266	-3540	4997	24
H(3)	5228	-3444	4695	24
H(5)	6489	-2116	4637	24
H(6)	7430	-425	4890	24
H(7)	7411	1225	5435	24
H(11)	6323	2862	7118	20
H(12A)	5199	1524	7135	30
H(12B)	5444	-44	6928	30
H(13A)	6159	1062	7675	25

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H(13B)	5665	-548	7593	25
H(14A)	6538	-1833	7304	25
H(14B)	6939	-1237	7719	25
H(15A)	7637	-521	7253	30
H(15B)	7427	1067	7466	30
H(16A)	6698	41	6714	30
H(16B)	7194	1643	6808	30
H(21)	4532	3244	6601	30
H(22A)	4419	4502	5996	34
H(22B)	4862	6062	6191	34
H(23A)	3596	6696	6095	42
H(23B)	3439	5045	6301	42
H(24A)	4226	7823	6671	43
H(24B)	3448	7209	6730	43
H(25A)	3976	4844	7042	39
H(25B)	4391	6413	7249	39
H(26A)	5388	5980	6935	33
H(26B)	5271	4353	7162	33
H(31)	6853	3576	6349	21
H(32A)	6348	6497	6640	28
H(32B)	6838	5157	6901	28
H(33A)	7811	5585	6585	33
H(33B)	7594	7308	6740	33
H(34A)	7742	7521	6092	33
H(34B)	6941	8072	6129	33
H(35A)	7302	4944	5844	29
H(35B)	6811	6320	5597	29
H(36A)	5854	5876	5930	26
H(36B)	6049	4163	5760	26

D5. Crystal data of
Carbonyl(cyclohexyldiphenylphosphine)
(8-hydroxyquinolinato)rhodium(I),
[Rh(ox)(CO)(PCyPh₂)]

Table D5. 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Rh(ox)(CO)(PCyPh₂)]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh	477(1)	2721(1)	3246(1)	38(1)
P	1985(1)	1531(1)	3037(1)	36(1)
N	-778(2)	3973(2)	3249(1)	45(1)
O(1)	-129(2)	2727(2)	2131(1)	51(1)
O(2)	1215(3)	2703(2)	4873(1)	81(1)
C(1)	-1074(3)	4589(2)	3819(2)	55(1)
C(2)	-1781(3)	5476(3)	3697(3)	70(1)
C(3)	-2204(3)	5708(3)	2984(3)	69(1)
C(4)	-1957(3)	5067(2)	2368(2)	56(1)
C(5)	-2383(3)	5222(3)	1617(3)	73(1)
C(6)	-2099(3)	4536(3)	1067(2)	75(1)
C(7)	-1359(3)	3666(3)	1224(2)	62(1)
C(8)	-879(3)	3496(2)	1952(2)	46(1)
C(9)	-1216(2)	4196(2)	2531(2)	44(1)
C(10)	931(3)	2711(2)	4235(2)	50(1)
C(11)	1920(2)	1110(2)	2041(2)	37(1)
C(12)	678(3)	515(2)	1897(2)	51(1)
C(13)	482(3)	312(3)	1052(2)	62(1)
C(14)	1608(3)	-248(3)	727(2)	65(1)
C(15)	2841(3)	316(3)	887(2)	57(1)
C(16)	3044(3)	509(2)	1735(2)	48(1)
C(21)	1936(2)	360(2)	3589(2)	39(1)
C(22)	2971(3)	-305(2)	3646(2)	47(1)
C(23)	2868(3)	-1201(2)	4032(2)	54(1)
C(24)	1741(3)	-1463(2)	4367(2)	59(1)
C(25)	706(3)	-832(2)	4305(2)	59(1)
C(26)	808(3)	84(2)	3926(2)	49(1)
C(31)	3601(2)	2017(2)	3206(2)	41(1)
C(32)	4207(3)	2564(2)	2644(2)	52(1)
C(33)	5417(3)	2954(3)	2766(2)	68(1)
C(34)	6009(3)	2820(3)	3452(3)	77(1)
C(35)	5414(3)	2311(3)	4027(2)	76(1)
C(36)	4205(3)	1902(3)	3903(2)	58(1)

Table D5. 2 Bond lengths (Å) and angles (°) for [Rh(ox)(CO)(PCyPh₂)]

Rh-C(10)	1.803(3)	C(5)-C(4)-C(3)	125.3(3)
Rh-O(1)	2.060(2)	C(5)-C(4)-C(9)	118.3(3)
Rh-N	2.128(2)	C(3)-C(4)-C(9)	116.4(3)
Rh-P	2.2798(8)	C(6)-C(5)-C(4)	120.0(3)
P-C(21)	1.838(3)	C(6)-C(5)-H(5)	120.0
P-C(31)	1.844(3)	C(4)-C(5)-H(5)	120.0
P-C(11)	1.846(3)	C(5)-C(6)-C(7)	122.0(4)
N-C(1)	1.338(4)	C(5)-C(6)-H(6)	119.0
N-C(9)	1.375(4)	C(7)-C(6)-H(6)	119.0
O(1)-C(8)	1.328(3)	C(8)-C(7)-C(6)	120.2(3)
O(2)-C(10)	1.161(4)	C(8)-C(7)-H(7)	119.9
C(1)-C(2)	1.410(5)	C(6)-C(7)-H(7)	119.9
C(1)-H(1)	0.9300	O(1)-C(8)-C(7)	123.4(3)
C(2)-C(3)	1.364(5)	O(1)-C(8)-C(9)	119.1(3)
C(2)-H(2)	0.9300	C(7)-C(8)-C(9)	117.5(3)
C(3)-C(4)	1.410(5)	N-C(9)-C(4)	122.5(3)
C(3)-H(3)	0.9300	N-C(9)-C(8)	115.7(3)
C(4)-C(5)	1.408(5)	C(4)-C(9)-C(8)	121.8(3)
C(4)-C(9)	1.424(4)	O(2)-C(10)-Rh	179.6(3)
C(5)-C(6)	1.369(5)	C(16)-C(11)-C(12)	109.4(2)
C(5)-H(5)	0.9300	C(16)-C(11)-P	118.41(19)
C(6)-C(7)	1.421(5)	C(12)-C(11)-P	109.19(19)
C(6)-H(6)	0.9300	C(16)-C(11)-H(11)	106.4
C(7)-C(8)	1.392(4)	C(12)-C(11)-H(11)	106.4
C(7)-H(7)	0.9300	P-C(11)-H(11)	106.4
C(8)-C(9)	1.432(4)	C(13)-C(12)-C(11)	110.6(3)
C(11)-C(16)	1.536(4)	C(13)-C(12)-H(12A)	109.5
C(11)-C(12)	1.549(4)	C(11)-C(12)-H(12A)	109.5
C(11)-H(11)	0.9800	C(13)-C(12)-H(12B)	109.5
C(12)-C(13)	1.527(4)	C(11)-C(12)-H(12B)	109.5
C(12)-H(12A)	0.9700	H(12A)-C(12)-H(12B)	108.1
C(12)-H(12B)	0.9700	C(14)-C(13)-C(12)	111.1(2)
C(13)-C(14)	1.523(4)	C(14)-C(13)-H(13A)	109.4
C(13)-H(13A)	0.9700	C(12)-C(13)-H(13A)	109.4
C(13)-H(13B)	0.9700	C(14)-C(13)-H(13B)	109.4
C(14)-C(15)	1.525(4)	C(12)-C(13)-H(13B)	109.4
C(14)-H(14A)	0.9700	H(13A)-C(13)-H(13B)	108.0
C(14)-H(14B)	0.9700	C(13)-C(14)-C(15)	111.1(3)
C(15)-C(16)	1.532(4)	C(13)-C(14)-H(14A)	109.4
C(15)-H(15A)	0.9700	C(15)-C(14)-H(14A)	109.4
C(15)-H(15B)	0.9700	C(13)-C(14)-H(14B)	109.4
C(16)-H(16A)	0.9700	C(15)-C(14)-H(14B)	109.4
C(16)-H(16B)	0.9700	H(14A)-C(14)-H(14B)	108.0
C(21)-C(26)	1.390(4)	C(14)-C(15)-C(16)	111.5(3)
C(21)-C(22)	1.408(4)	C(14)-C(15)-H(15A)	109.3
C(22)-C(23)	1.378(4)	C(16)-C(15)-H(15A)	109.3
C(22)-H(22)	0.9300	C(14)-C(15)-H(15B)	109.3
C(23)-C(24)	1.383(4)	C(16)-C(15)-H(15B)	109.3
C(23)-H(23)	0.9300	H(15A)-C(15)-H(15B)	108.0
C(24)-C(25)	1.381(4)	C(15)-C(16)-C(11)	109.6(2)
C(24)-H(24)	0.9300	C(15)-C(16)-H(16A)	109.8
C(25)-C(26)	1.395(4)	C(11)-C(16)-H(16A)	109.8
C(25)-H(25)	0.9300	C(15)-C(16)-H(16B)	109.8

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C(26)-H(26)	0.9300	C(11)-C(16)-H(16B)	109.8
C(31)-C(36)	1.385(4)	H(16A)-C(16)-H(16B)	108.2
C(31)-C(32)	1.395(4)	C(26)-C(21)-C(22)	118.3(3)
C(32)-C(33)	1.393(4)	C(26)-C(21)-P	118.9(2)
C(32)-H(32)	0.9300	C(22)-C(21)-P	122.7(2)
C(33)-C(34)	1.364(5)	C(23)-C(22)-C(21)	120.7(3)
C(33)-H(33)	0.9300	C(23)-C(22)-H(22)	119.7
C(34)-C(35)	1.380(6)	C(21)-C(22)-H(22)	119.7
C(34)-H(34)	0.9300	C(22)-C(23)-C(24)	120.3(3)
C(35)-C(36)	1.402(4)	C(22)-C(23)-H(23)	119.8
C(35)-H(35)	0.9300	C(24)-C(23)-H(23)	119.8
C(36)-H(36)	0.9300	C(25)-C(24)-C(23)	120.0(3)
		C(25)-C(24)-H(24)	120.0
C(10)-Rh-O(1)	177.29(11)	C(23)-C(24)-H(24)	120.0
C(10)-Rh-N	99.10(12)	C(24)-C(25)-C(26)	120.0(3)
O(1)-Rh-N	79.41(9)	C(24)-C(25)-H(25)	120.0
C(10)-Rh-P	88.70(10)	C(26)-C(25)-H(25)	120.0
O(1)-Rh-P	93.11(6)	C(21)-C(26)-C(25)	120.7(3)
N-Rh-P	168.64(7)	C(21)-C(26)-H(26)	119.7
C(21)-P-C(31)	104.24(12)	C(25)-C(26)-H(26)	119.7
C(21)-P-C(11)	104.35(12)	C(36)-C(31)-C(32)	118.7(3)
C(31)-P-C(11)	106.25(13)	C(36)-C(31)-P	121.1(2)
C(21)-P-Rh	118.42(9)	C(32)-C(31)-P	120.1(2)
C(31)-P-Rh	112.15(9)	C(33)-C(32)-C(31)	121.0(3)
C(11)-P-Rh	110.48(9)	C(33)-C(32)-H(32)	119.5
C(1)-N-C(9)	118.8(3)	C(31)-C(32)-H(32)	119.5
C(1)-N-Rh	129.4(2)	C(34)-C(33)-C(32)	119.7(3)
C(9)-N-Rh	111.47(18)	C(34)-C(33)-H(33)	120.2
C(8)-O(1)-Rh	113.83(18)	C(32)-C(33)-H(33)	120.2
N-C(1)-C(2)	121.8(3)	C(33)-C(34)-C(35)	120.6(3)
N-C(1)-H(1)	119.1	C(33)-C(34)-H(34)	119.7
C(2)-C(1)-H(1)	119.1	C(35)-C(34)-H(34)	119.7
C(3)-C(2)-C(1)	119.6(3)	C(34)-C(35)-C(36)	120.1(4)
C(3)-C(2)-H(2)	120.2	C(34)-C(35)-H(35)	120.0
C(1)-C(2)-H(2)	120.2	C(36)-C(35)-H(35)	120.0
C(2)-C(3)-C(4)	120.8(3)	C(31)-C(36)-C(35)	120.0(3)
C(2)-C(3)-H(3)	119.6	C(31)-C(36)-H(36)	120.0
C(4)-C(3)-H(3)	119.6	C(35)-C(36)-H(36)	120.0

Table D5. 3 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{ox})(\text{CO})(\text{PCyPh}_2)]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Rh	36(1)	42(1)	37(1)	-2(1)	3(1)	-1(1)
P	32(1)	41(1)	36(1)	1(1)	-2(1)	-1(1)
N	32(1)	48(2)	55(2)	-7(1)	9(1)	-4(1)
O(1)	53(1)	56(1)	43(1)	-6(1)	-6(1)	16(1)
O(2)	117(2)	85(2)	40(2)	1(1)	-4(1)	-19(2)
C(1)	41(2)	57(2)	67(2)	-15(2)	14(2)	-5(2)
C(2)	47(2)	63(2)	101(3)	-28(2)	22(2)	-2(2)
C(3)	37(2)	50(2)	120(4)	-10(2)	9(2)	5(2)
C(4)	28(2)	51(2)	89(3)	2(2)	-2(2)	1(1)
C(5)	46(2)	64(2)	108(4)	14(2)	-16(2)	9(2)
C(6)	53(2)	90(3)	81(3)	18(2)	-21(2)	4(2)
C(7)	53(2)	79(2)	53(2)	1(2)	-10(2)	8(2)

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C(8)	36(2)	52(2)	51(2)	0(2)	-2(1)	-2(1)
C(9)	29(1)	47(2)	57(2)	0(2)	3(1)	-5(1)
C(10)	60(2)	46(2)	45(2)	-3(2)	7(2)	-8(2)
C(11)	34(1)	41(2)	37(2)	-1(1)	-3(1)	3(1)
C(12)	42(2)	56(2)	56(2)	-10(2)	-3(2)	2(1)
C(13)	54(2)	72(2)	59(2)	-11(2)	-15(2)	6(2)
C(14)	68(2)	79(2)	49(2)	-18(2)	-15(2)	10(2)
C(15)	58(2)	69(2)	45(2)	-4(2)	5(2)	13(2)
C(16)	41(2)	57(2)	45(2)	-4(1)	0(1)	8(1)
C(21)	38(1)	42(2)	38(2)	0(1)	-2(1)	-5(1)
C(22)	44(2)	51(2)	45(2)	3(1)	0(1)	3(1)
C(23)	61(2)	50(2)	52(2)	4(2)	-5(2)	12(2)
C(24)	78(2)	43(2)	56(2)	6(2)	4(2)	-3(2)
C(25)	60(2)	52(2)	65(2)	8(2)	16(2)	-7(2)
C(26)	43(2)	50(2)	55(2)	2(2)	5(1)	1(1)
C(31)	35(1)	41(2)	47(2)	-1(1)	-4(1)	-3(1)
C(32)	44(2)	52(2)	59(2)	8(2)	-4(2)	-4(1)
C(33)	50(2)	59(2)	94(3)	8(2)	11(2)	-12(2)
C(34)	38(2)	74(3)	119(4)	3(2)	-12(2)	-17(2)
C(35)	55(2)	85(3)	86(3)	5(2)	-31(2)	-12(2)
C(36)	50(2)	66(2)	57(2)	7(2)	-7(2)	-10(2)

Table D5. 4 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{ox})(\text{CO})(\text{PCyPh}_2)]$.

	x	y	z	U(eq)
H(1)	-807	4428	4308	66
H(2)	-1958	5899	4101	84
H(3)	-2662	6298	2903	83
H(5)	-2858	5790	1494	87
H(6)	-2399	4643	575	90
H(7)	-1195	3209	840	74
H(11)	1856	1721	1731	45
H(12A)	717	-119	2169	61
H(12B)	-33	897	2085	61
H(13A)	-281	-85	974	74
H(13B)	369	945	786	74
H(14A)	1486	-325	185	78
H(14B)	1660	-914	950	78
H(15A)	2824	953	619	68
H(15B)	3545	-74	698	68
H(16A)	3823	882	1819	57
H(16B)	3116	-127	2002	57
H(22)	3732	-138	3420	56
H(23)	3561	-1631	4068	65
H(24)	1680	-2064	4633	70
H(25)	-60	-1018	4517	71
H(26)	115	515	3899	59
H(32)	3796	2670	2181	62
H(33)	5820	3303	2383	81
H(34)	6821	3075	3533	93
H(35)	5816	2240	4496	91
H(36)	3809	1553	4289	69

D6. Crystal data of
Carbonyl[triphenylphosphine]
(8-hydroxyquinolinato)rhodium(I),
[Rh(ox)(CO)(PPh₃)]

Table D6. 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Rh(ox)(CO)(PPh₃)]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	9360(5)	9349(4)	7805(4)	26(1)
C(2)	9838(5)	10044(4)	7241(3)	26(1)
C(3)	9533(5)	10153(4)	6458(3)	26(1)
C(4)	8783(6)	9586(4)	6217(4)	26(1)
C(5)	8409(5)	9631(4)	5421(3)	26(1)
C(6)	7701(5)	9023(4)	5264(4)	26(1)
C(7)	7231(5)	8367(4)	5862(3)	26(1)
C(8)	7566(6)	8305(4)	6669(4)	26(1)
C(9)	8337(6)	8904(4)	6823(4)	26(1)
C(10)	8549(6)	7770(4)	9242(4)	26(1)
C(11)	6653(5)	6482(4)	10166(3)	26(1)
C(12)	6821(5)	5590(4)	10645(3)	26(1)
C(13)	6643(5)	5529(4)	11471(3)	26(1)
C(14)	6280(5)	6284(4)	11824(4)	26(1)
C(15)	6148(5)	7183(4)	11367(3)	26(1)
C(16)	6312(5)	7275(4)	10527(3)	26(1)
C(20)	6631(6)	2062(4)	5024(4)	26(1)
C(21)	7485(6)	5499(4)	8847(4)	26(1)
C(22)	8920(5)	5124(4)	8967(3)	23(1)
C(23)	9539(6)	4249(4)	8816(3)	23(1)
C(24)	8793(5)	3735(4)	8523(3)	23(1)
C(25)	7385(5)	4102(4)	8375(3)	23(1)
C(26)	6745(6)	4978(4)	8555(3)	23(1)
C(31)	4871(5)	6898(4)	8860(3)	23(1)
C(32)	3908(5)	6708(4)	9464(3)	23(1)
C(33)	2517(5)	6876(4)	9281(3)	23(1)
C(34)	2098(6)	7213(4)	8500(3)	23(1)
C(35)	3065(5)	7407(4)	7893(3)	23(1)
C(36)	4467(5)	7245(4)	8063(3)	23(1)
C(41)	7395(6)	4281(4)	6011(3)	23(1)
C(42)	8110(6)	4855(4)	6247(3)	23(1)
C(43)	7453(5)	5699(4)	6475(3)	23(1)
C(44)	6025(5)	5985(4)	6451(3)	23(1)
C(45)	5288(6)	5438(4)	6210(3)	23(1)
C(46)	5941(5)	4578(4)	6009(3)	27(1)
C(51)	8489(6)	3615(4)	4567(4)	27(1)
C(52)	8264(5)	4561(4)	4214(4)	27(1)
C(53)	8547(5)	4822(4)	3397(3)	27(1)
C(54)	9059(5)	4169(4)	2936(4)	27(1)
C(55)	9308(5)	3235(4)	3274(4)	27(1)
C(56)	9026(5)	2954(4)	4086(3)	27(1)
C(61)	9980(5)	2935(4)	5978(4)	27(1)

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C(62)	11093(5)	3150(4)	5498(4)	27(1)
C(63)	12405(6)	2944(4)	5790(3)	27(1)
C(64)	12629(6)	2536(4)	6597(4)	27(1)
C(65)	11538(5)	2311(4)	7087(4)	27(1)
C(66)	10210(6)	2503(4)	6796(3)	27(1)
C(71)	5209(5)	612(4)	6282(4)	27(1)
C(72)	4590(5)	-125(4)	6752(4)	27(1)
C(73)	4706(5)	-277(4)	7536(3)	27(1)
C(74)	5422(6)	176(5)	7925(4)	41(1)
C(75)	5615(6)	55(5)	8727(4)	41(1)
C(76)	6380(6)	534(4)	9060(4)	41(1)
C(77)	6967(6)	1246(5)	8538(4)	41(1)
C(78)	6768(6)	1457(5)	7721(4)	41(1)
C(79)	6050(6)	904(5)	7412(4)	41(1)
N(1)	8661(4)	8799(3)	7623(3)	23(2)
N(2)	5925(5)	1079(3)	6602(3)	31(2)
O(1)	7142(4)	7691(3)	7278(2)	24(1)
O(2)	7260(4)	2117(3)	7216(2)	33(1)
O(11)	9140(4)	7752(3)	9848(3)	53(2)
O(22)	6350(4)	2001(3)	4405(2)	34(1)
P(1)	6715(2)	6668(1)	9063(1)	21(1)
P(2)	8211(2)	3216(1)	5642(1)	17(1)
Rh(1)	7804(1)	7759(1)	8366(1)	23(1)
Rh(2)	6979(1)	2102(1)	6043(1)	22(1)
C(86)	9912(7)	587(5)	9865(5)	59(5)
C(85)	10785(8)	880(5)	9228(5)	52(5)
C(84)	11837(8)	221(6)	8923(4)	36(4)
C(83)	12016(8)	-730(6)	9257(5)	33(4)
C(82)	11143(8)	-1023(5)	9894(5)	36(4)
C(81)	10091(8)	-364(5)	10198(5)	46(5)
C(80)	9108(18)	-717(13)	10940(10)	74(6)

Table D6. 2 Bond lengths (Å) and angles (°) for [Rh(ox)(CO)(PPh₃)]

C(1)-N(1)	1.291(7)	C(22)-C(23)-C(24)	120.5(5)
C(1)-C(2)	1.401(7)	C(22)-C(23)-H(23)	119.7
C(1)-H(1)	0.9300	C(24)-C(23)-H(23)	119.7
C(2)-C(3)	1.356(8)	C(23)-C(24)-C(25)	120.2(5)
C(2)-H(2)	0.9300	C(23)-C(24)-H(24)	119.9
C(3)-C(4)	1.390(8)	C(25)-C(24)-H(24)	119.9
C(3)-H(3)	0.9300	C(26)-C(25)-C(24)	119.1(6)
C(4)-C(9)	1.413(8)	C(26)-C(25)-H(25)	120.4
C(4)-C(5)	1.415(8)	C(24)-C(25)-H(25)	120.4
C(5)-C(6)	1.350(8)	C(21)-C(26)-C(25)	121.0(5)
C(5)-H(5)	0.9300	C(21)-C(26)-H(26)	119.5
C(6)-C(7)	1.390(7)	C(25)-C(26)-H(26)	119.5
C(6)-H(6)	0.9300	C(32)-C(31)-C(36)	120.4(5)
C(7)-C(8)	1.416(8)	C(32)-C(31)-P(1)	121.2(4)
C(7)-H(7)	0.9300	C(36)-C(31)-P(1)	118.4(4)
C(8)-O(1)	1.344(6)	C(31)-C(32)-C(33)	119.4(5)
C(8)-C(9)	1.382(8)	C(31)-C(32)-H(32)	120.3
C(9)-N(1)	1.390(7)	C(33)-C(32)-H(32)	120.3
C(10)-O(11)	1.220(7)	C(34)-C(33)-C(32)	121.2(5)
C(10)-Rh(1)	1.721(6)	C(34)-C(33)-H(33)	119.4
C(11)-C(12)	1.390(7)	C(32)-C(33)-H(33)	119.4

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C(11)-C(16)	1.394(8)	C(35)-C(34)-C(33)	119.5(5)
C(11)-P(1)	1.832(6)	C(35)-C(34)-H(34)	120.3
C(12)-C(13)	1.383(8)	C(33)-C(34)-H(34)	120.3
C(12)-H(12)	0.9300	C(34)-C(35)-C(36)	120.3(5)
C(13)-C(14)	1.338(8)	C(34)-C(35)-H(35)	119.8
C(13)-H(13)	0.9300	C(36)-C(35)-H(35)	119.8
C(14)-C(15)	1.387(7)	C(35)-C(36)-C(31)	119.3(5)
C(14)-H(14)	0.9300	C(35)-C(36)-H(36)	120.4
C(15)-C(16)	1.400(8)	C(31)-C(36)-H(36)	120.4
C(15)-H(15)	0.9300	C(42)-C(41)-C(46)	117.4(5)
C(16)-H(16)	0.9300	C(42)-C(41)-P(2)	124.0(4)
C(20)-O(22)	1.135(7)	C(46)-C(41)-P(2)	118.4(5)
C(20)-Rh(2)	1.806(6)	C(41)-C(42)-C(43)	122.4(5)
C(21)-C(26)	1.372(8)	C(41)-C(42)-H(42)	118.8
C(21)-C(22)	1.415(7)	C(43)-C(42)-H(42)	118.8
C(21)-P(1)	1.822(6)	C(44)-C(43)-C(42)	119.0(6)
C(22)-C(23)	1.365(7)	C(44)-C(43)-H(43)	120.5
C(22)-H(22)	0.9300	C(42)-C(43)-H(43)	120.5
C(23)-C(24)	1.370(8)	C(45)-C(44)-C(43)	120.0(5)
C(23)-H(23)	0.9300	C(45)-C(44)-H(44)	120.0
C(24)-C(25)	1.398(7)	C(43)-C(44)-H(44)	120.0
C(24)-H(24)	0.9300	C(44)-C(45)-C(46)	121.0(5)
C(25)-C(26)	1.388(7)	C(44)-C(45)-H(45)	119.5
C(25)-H(25)	0.9300	C(46)-C(45)-H(45)	119.5
C(26)-H(26)	0.9300	C(45)-C(46)-C(41)	120.1(6)
C(31)-C(32)	1.372(8)	C(45)-C(46)-H(46)	120.0
C(31)-C(36)	1.402(7)	C(41)-C(46)-H(46)	120.0
C(31)-P(1)	1.829(6)	C(56)-C(51)-C(52)	118.3(6)
C(32)-C(33)	1.394(7)	C(56)-C(51)-P(2)	118.9(4)
C(32)-H(32)	0.9300	C(52)-C(51)-P(2)	122.6(5)
C(33)-C(34)	1.382(7)	C(53)-C(52)-C(51)	120.0(6)
C(33)-H(33)	0.9300	C(53)-C(52)-H(52)	120.0
C(34)-C(35)	1.379(7)	C(51)-C(52)-H(52)	120.0
C(34)-H(34)	0.9300	C(54)-C(53)-C(52)	120.9(6)
C(35)-C(36)	1.400(7)	C(54)-C(53)-H(53)	119.5
C(35)-H(35)	0.9300	C(52)-C(53)-H(53)	119.5
C(36)-H(36)	0.9300	C(53)-C(54)-C(55)	120.0(6)
C(41)-C(42)	1.371(8)	C(53)-C(54)-H(54)	120.0
C(41)-C(46)	1.404(7)	C(55)-C(54)-H(54)	120.0
C(41)-P(2)	1.803(6)	C(54)-C(55)-C(56)	120.3(6)
C(42)-C(43)	1.382(7)	C(54)-C(55)-H(55)	119.8
C(42)-H(42)	0.9300	C(56)-C(55)-H(55)	119.8
C(43)-C(44)	1.380(7)	C(55)-C(56)-C(51)	120.3(5)
C(43)-H(43)	0.9300	C(55)-C(56)-H(56)	119.8
C(44)-C(45)	1.357(8)	C(51)-C(56)-H(56)	119.8
C(44)-H(44)	0.9300	C(62)-C(61)-C(66)	118.1(5)
C(45)-C(46)	1.383(8)	C(62)-C(61)-P(2)	124.1(5)
C(45)-H(45)	0.9300	C(66)-C(61)-P(2)	117.7(4)
C(46)-H(46)	0.9300	C(61)-C(62)-C(63)	121.7(6)
C(51)-C(56)	1.383(8)	C(61)-C(62)-H(62)	119.1
C(51)-C(52)	1.388(8)	C(63)-C(62)-H(62)	119.1
C(51)-P(2)	1.815(6)	C(62)-C(63)-C(64)	120.3(5)
C(52)-C(53)	1.381(8)	C(62)-C(63)-H(63)	119.8
C(52)-H(52)	0.9300	C(64)-C(63)-H(63)	119.8
C(53)-C(54)	1.346(8)	C(65)-C(64)-C(63)	119.1(5)
C(53)-H(53)	0.9300	C(65)-C(64)-H(64)	120.4

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C(54)-C(55)	1.365(7)	C(63)-C(64)-H(64)	120.4
C(54)-H(54)	0.9300	C(64)-C(65)-C(66)	121.1(5)
C(55)-C(56)	1.380(8)	C(64)-C(65)-H(65)	119.5
C(55)-H(55)	0.9300	C(66)-C(65)-H(65)	119.5
C(56)-H(56)	0.9300	C(65)-C(66)-C(61)	119.6(5)
C(61)-C(62)	1.374(8)	C(65)-C(66)-H(66)	120.2
C(61)-C(66)	1.420(8)	C(61)-C(66)-H(66)	120.2
C(61)-P(2)	1.820(6)	N(2)-C(71)-C(72)	123.2(6)
C(62)-C(63)	1.376(7)	N(2)-C(71)-H(71)	118.4
C(62)-H(62)	0.9300	C(72)-C(71)-H(71)	118.4
C(63)-C(64)	1.393(7)	C(73)-C(72)-C(71)	116.3(6)
C(63)-H(63)	0.9300	C(73)-C(72)-H(72)	121.8
C(64)-C(65)	1.369(8)	C(71)-C(72)-H(72)	121.8
C(64)-H(64)	0.9300	C(72)-C(73)-C(74)	124.7(6)
C(65)-C(66)	1.394(7)	C(72)-C(73)-H(73)	117.7
C(65)-H(65)	0.9300	C(74)-C(73)-H(73)	117.7
C(66)-H(66)	0.9300	C(75)-C(74)-C(73)	128.8(6)
C(71)-N(2)	1.320(8)	C(75)-C(74)-C(79)	114.9(7)
C(71)-C(72)	1.450(8)	C(73)-C(74)-C(79)	116.3(6)
C(71)-H(71)	0.9300	C(74)-C(75)-C(76)	124.5(7)
C(72)-C(73)	1.312(8)	C(74)-C(75)-H(75)	117.8
C(72)-H(72)	0.9300	C(76)-C(75)-H(75)	117.8
C(73)-C(74)	1.374(9)	C(75)-C(76)-C(77)	118.8(6)
C(73)-H(73)	0.9300	C(75)-C(76)-H(76)	120.6
C(74)-C(75)	1.359(9)	C(77)-C(76)-H(76)	120.6
C(74)-C(79)	1.473(9)	C(78)-C(77)-C(76)	121.2(7)
C(75)-C(76)	1.380(9)	C(78)-C(77)-H(77)	119.4
C(75)-H(75)	0.9300	C(76)-C(77)-H(77)	119.4
C(76)-C(77)	1.440(9)	O(2)-C(78)-C(77)	123.7(7)
C(76)-H(76)	0.9300	O(2)-C(78)-C(79)	119.0(6)
C(77)-C(78)	1.376(9)	C(77)-C(78)-C(79)	117.2(6)
C(77)-H(77)	0.9300	N(2)-C(79)-C(78)	117.0(6)
C(78)-O(2)	1.324(7)	N(2)-C(79)-C(74)	119.8(7)
C(78)-C(79)	1.410(10)	C(78)-C(79)-C(74)	123.2(6)
C(79)-N(2)	1.355(8)	C(1)-N(1)-C(9)	118.6(5)
N(1)-Rh(1)	2.089(5)	C(1)-N(1)-Rh(1)	130.0(4)
N(2)-Rh(2)	2.079(5)	C(9)-N(1)-Rh(1)	111.3(4)
O(1)-Rh(1)	2.041(4)	C(71)-N(2)-C(79)	119.7(6)
O(2)-Rh(2)	2.038(4)	C(71)-N(2)-Rh(2)	129.6(4)
P(1)-Rh(1)	2.2459(18)	C(79)-N(2)-Rh(2)	110.7(5)
P(2)-Rh(2)	2.2557(18)	C(8)-O(1)-Rh(1)	112.5(4)
C(86)-C(81)#1	0.370(16)	C(78)-O(2)-Rh(2)	112.2(4)
C(86)-C(82)#1	1.177(13)	C(21)-P(1)-C(31)	105.8(3)
C(86)-C(85)	1.3900	C(21)-P(1)-C(11)	103.5(3)
C(86)-C(81)	1.3900	C(31)-P(1)-C(11)	101.4(3)
C(86)-C(80)#1	1.609(19)	C(21)-P(1)-Rh(1)	112.2(2)
C(86)-C(86)#1	1.686(15)	C(31)-P(1)-Rh(1)	114.11(19)
C(85)-C(80)#1	0.40(2)	C(11)-P(1)-Rh(1)	118.3(2)
C(85)-C(84)	1.3900	C(41)-P(2)-C(51)	104.0(3)
C(85)-C(81)#1	1.470(15)	C(41)-P(2)-C(61)	103.9(3)
C(84)-C(80)#1	1.084(19)	C(51)-P(2)-C(61)	100.9(3)
C(84)-C(83)	1.3900	C(41)-P(2)-Rh(2)	111.2(2)
C(83)-C(82)	1.3900	C(51)-P(2)-Rh(2)	118.2(2)
C(82)-C(86)#1	1.177(13)	C(61)-P(2)-Rh(2)	116.8(2)
C(82)-C(81)	1.3900	C(10)-Rh(1)-O(1)	173.5(2)
C(81)-C(86)#1	0.370(16)	C(10)-Rh(1)-N(1)	97.1(2)

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C(81)-C(81)#1	1.138(14)	O(1)-Rh(1)-N(1)	80.25(17)
C(81)-C(85)#1	1.470(14)	C(10)-Rh(1)-P(1)	88.8(2)
C(81)-C(80)	1.602(17)	O(1)-Rh(1)-P(1)	94.07(12)
C(80)-C(85)#1	0.40(2)	N(1)-Rh(1)-P(1)	173.80(14)
C(80)-C(84)#1	1.08(2)	C(20)-Rh(2)-O(2)	176.4(2)
C(80)-C(86)#1	1.609(19)	C(20)-Rh(2)-N(2)	95.9(2)
		O(2)-Rh(2)-N(2)	80.78(19)
N(1)-C(1)-C(2)	123.9(6)	C(20)-Rh(2)-P(2)	93.4(2)
N(1)-C(1)-H(1)	118.1	O(2)-Rh(2)-P(2)	89.85(13)
C(2)-C(1)-H(1)	118.1	N(2)-Rh(2)-P(2)	170.61(16)
C(3)-C(2)-C(1)	118.2(6)	C(81)#1-C(86)-C(82)#1	118(3)
C(3)-C(2)-H(2)	120.9	C(81)#1-C(86)-C(85)	95(2)
C(1)-C(2)-H(2)	120.9	C(82)#1-C(86)-C(85)	128.2(10)
C(2)-C(3)-C(4)	121.1(6)	C(81)#1-C(86)-C(81)	41(2)
C(2)-C(3)-H(3)	119.4	C(82)#1-C(86)-C(81)	110.7(10)
C(4)-C(3)-H(3)	119.4	C(85)-C(86)-C(81)	120.0
C(3)-C(4)-C(9)	117.2(5)	C(81)#1-C(86)-C(80)#1	82(2)
C(3)-C(4)-C(5)	126.2(5)	C(82)#1-C(86)-C(80)#1	135.2(12)
C(9)-C(4)-C(5)	116.6(6)	C(85)-C(86)-C(80)#1	12.9(9)
C(6)-C(5)-C(4)	120.3(5)	C(81)-C(86)-C(80)#1	109.8(7)
C(6)-C(5)-H(5)	119.9	C(81)#1-C(86)-C(86)#1	32.9(18)
C(4)-C(5)-H(5)	119.9	C(82)#1-C(86)-C(86)#1	113.3(12)
C(5)-C(6)-C(7)	123.2(6)	C(85)-C(86)-C(86)#1	115.6(5)
C(5)-C(6)-H(6)	118.4	C(81)-C(86)-C(86)#1	8.3(5)
C(7)-C(6)-H(6)	118.4	C(80)#1-C(86)-C(86)#1	104.4(9)
C(6)-C(7)-C(8)	118.4(6)	C(80)#1-C(85)-C(84)	35(3)
C(6)-C(7)-H(7)	120.8	C(80)#1-C(85)-C(86)	117(3)
C(8)-C(7)-H(7)	120.8	C(84)-C(85)-C(86)	120.0
O(1)-C(8)-C(9)	120.0(5)	C(80)#1-C(85)-C(81)#1	102(3)
O(1)-C(8)-C(7)	121.7(6)	C(84)-C(85)-C(81)#1	107.8(5)
C(9)-C(8)-C(7)	118.3(5)	C(86)-C(85)-C(81)#1	14.5(6)
C(8)-C(9)-N(1)	115.9(5)	C(80)#1-C(84)-C(85)	12.1(12)
C(8)-C(9)-C(4)	123.2(6)	C(80)#1-C(84)-C(83)	120.1(11)
N(1)-C(9)-C(4)	121.0(6)	C(85)-C(84)-C(83)	120.0
O(11)-C(10)-Rh(1)	176.7(5)	C(84)-C(83)-C(82)	120.0
C(12)-C(11)-C(16)	119.7(6)	C(86)#1-C(82)-C(83)	128.2(7)
C(12)-C(11)-P(1)	122.3(5)	C(86)#1-C(82)-C(81)	13.6(8)
C(16)-C(11)-P(1)	117.8(4)	C(83)-C(82)-C(81)	120.0
C(13)-C(12)-C(11)	117.8(6)	C(86)#1-C(81)-C(81)#1	126(3)
C(13)-C(12)-H(12)	121.1	C(86)#1-C(81)-C(82)	48(2)
C(11)-C(12)-H(12)	121.1	C(81)#1-C(81)-C(82)	113.3(7)
C(14)-C(13)-C(12)	123.1(6)	C(86)#1-C(81)-C(86)	139(2)
C(14)-C(13)-H(13)	118.4	C(81)#1-C(81)-C(86)	12.4(8)
C(12)-C(13)-H(13)	118.4	C(82)-C(81)-C(86)	120.0
C(13)-C(14)-C(15)	120.5(6)	C(86)#1-C(81)-C(85)#1	70(2)
C(13)-C(14)-H(14)	119.8	C(81)#1-C(81)-C(85)#1	134.4(12)
C(15)-C(14)-H(14)	119.8	C(82)-C(81)-C(85)#1	107.8(9)
C(14)-C(15)-C(16)	118.0(6)	C(86)-C(81)-C(85)#1	131.5(9)
C(14)-C(15)-H(15)	121.0	C(86)#1-C(81)-C(80)	85(2)
C(16)-C(15)-H(15)	121.0	C(81)#1-C(81)-C(80)	126.6(11)
C(11)-C(16)-C(15)	120.7(5)	C(82)-C(81)-C(80)	119.1(8)
C(11)-C(16)-H(16)	119.6	C(86)-C(81)-C(80)	120.9(8)
C(15)-C(16)-H(16)	119.6	C(85)#1-C(81)-C(80)	14.2(9)
O(22)-C(20)-Rh(2)	175.4(5)	C(85)#1-C(80)-C(84)#1	133(4)
C(26)-C(21)-C(22)	118.7(5)	C(85)#1-C(80)-C(81)	64(3)
C(26)-C(21)-P(1)	122.9(4)	C(84)#1-C(80)-C(81)	117.4(14)

C(22)-C(21)-P(1)	118.3(5)	C(85)#1-C(80)-C(86)#1	51(2)
C(23)-C(22)-C(21)	120.3(6)	C(84)#1-C(80)-C(86)#1	125.6(16)
C(23)-C(22)-H(22)	119.8	C(81)-C(80)-C(86)#1	13.2(6)
C(21)-C(22)-H(22)	119.8		

Table D6. 3 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	19(1)	29(1)	26(1)	0(1)	1(1)	-4(1)
C(2)	19(1)	29(1)	26(1)	0(1)	1(1)	-4(1)
C(3)	19(1)	29(1)	26(1)	0(1)	1(1)	-4(1)
C(4)	19(1)	29(1)	26(1)	0(1)	1(1)	-4(1)
C(5)	19(1)	29(1)	26(1)	0(1)	1(1)	-4(1)
C(6)	19(1)	29(1)	26(1)	0(1)	1(1)	-4(1)
C(7)	19(1)	29(1)	26(1)	0(1)	1(1)	-4(1)
C(8)	19(1)	29(1)	26(1)	0(1)	1(1)	-4(1)
C(9)	19(1)	29(1)	26(1)	0(1)	1(1)	-4(1)
C(10)	19(1)	29(1)	26(1)	0(1)	1(1)	-4(1)
C(11)	19(1)	29(1)	26(1)	0(1)	1(1)	-4(1)
C(12)	19(1)	29(1)	26(1)	0(1)	1(1)	-4(1)
C(13)	19(1)	29(1)	26(1)	0(1)	1(1)	-4(1)
C(14)	19(1)	29(1)	26(1)	0(1)	1(1)	-4(1)
C(15)	19(1)	29(1)	26(1)	0(1)	1(1)	-4(1)
C(16)	19(1)	29(1)	26(1)	0(1)	1(1)	-4(1)
C(20)	19(1)	29(1)	26(1)	0(1)	1(1)	-4(1)
C(21)	19(1)	29(1)	26(1)	0(1)	1(1)	-4(1)
C(22)	20(1)	27(1)	19(1)	0(1)	0(1)	-4(1)
C(23)	20(1)	27(1)	19(1)	0(1)	0(1)	-4(1)
C(24)	20(1)	27(1)	19(1)	0(1)	0(1)	-4(1)
C(25)	20(1)	27(1)	19(1)	0(1)	0(1)	-4(1)
C(26)	20(1)	27(1)	19(1)	0(1)	0(1)	-4(1)
C(31)	20(1)	27(1)	19(1)	0(1)	0(1)	-4(1)
C(32)	20(1)	27(1)	19(1)	0(1)	0(1)	-4(1)
C(33)	20(1)	27(1)	19(1)	0(1)	0(1)	-4(1)
C(34)	20(1)	27(1)	19(1)	0(1)	0(1)	-4(1)
C(35)	20(1)	27(1)	19(1)	0(1)	0(1)	-4(1)
C(36)	20(1)	27(1)	19(1)	0(1)	0(1)	-4(1)
C(41)	20(1)	27(1)	19(1)	0(1)	0(1)	-4(1)
C(42)	20(1)	27(1)	19(1)	0(1)	0(1)	-4(1)
C(43)	20(1)	27(1)	19(1)	0(1)	0(1)	-4(1)
C(44)	20(1)	27(1)	19(1)	0(1)	0(1)	-4(1)
C(45)	20(1)	27(1)	19(1)	0(1)	0(1)	-4(1)
C(46)	17(1)	29(1)	31(1)	-4(1)	2(1)	-2(1)
C(51)	17(1)	29(1)	31(1)	-4(1)	2(1)	-2(1)
C(52)	17(1)	29(1)	31(1)	-4(1)	2(1)	-2(1)
C(53)	17(1)	29(1)	31(1)	-4(1)	2(1)	-2(1)
C(54)	17(1)	29(1)	31(1)	-4(1)	2(1)	-2(1)
C(55)	17(1)	29(1)	31(1)	-4(1)	2(1)	-2(1)
C(56)	17(1)	29(1)	31(1)	-4(1)	2(1)	-2(1)
C(61)	17(1)	29(1)	31(1)	-4(1)	2(1)	-2(1)
C(62)	17(1)	29(1)	31(1)	-4(1)	2(1)	-2(1)
C(63)	17(1)	29(1)	31(1)	-4(1)	2(1)	-2(1)
C(64)	17(1)	29(1)	31(1)	-4(1)	2(1)	-2(1)
C(65)	17(1)	29(1)	31(1)	-4(1)	2(1)	-2(1)

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C(66)	17(1)	29(1)	31(1)	-4(1)	2(1)	-2(1)
C(71)	17(1)	29(1)	31(1)	-4(1)	2(1)	-2(1)
C(72)	17(1)	29(1)	31(1)	-4(1)	2(1)	-2(1)
C(73)	17(1)	29(1)	31(1)	-4(1)	2(1)	-2(1)
C(74)	28(2)	39(2)	39(2)	6(2)	10(1)	12(1)
C(75)	28(2)	39(2)	39(2)	6(2)	10(1)	12(1)
C(76)	28(2)	39(2)	39(2)	6(2)	10(1)	12(1)
C(77)	28(2)	39(2)	39(2)	6(2)	10(1)	12(1)
C(78)	28(2)	39(2)	39(2)	6(2)	10(1)	12(1)
C(79)	28(2)	39(2)	39(2)	6(2)	10(1)	12(1)
N(1)	11(2)	24(3)	32(3)	-4(3)	-4(2)	2(2)
N(2)	19(3)	26(3)	43(4)	-2(3)	1(3)	3(3)
O(1)	29(2)	25(2)	15(2)	3(2)	3(2)	-9(2)
O(2)	22(2)	40(3)	32(3)	3(2)	10(2)	-10(2)
O(11)	47(3)	67(3)	47(3)	18(3)	-16(2)	-36(3)
O(22)	32(2)	41(3)	32(3)	-1(2)	-8(2)	-18(2)
P(1)	21(1)	22(1)	17(1)	2(1)	3(1)	-2(1)
P(2)	14(1)	19(1)	16(1)	0(1)	-2(1)	-2(1)
Rh(1)	21(1)	22(1)	22(1)	2(1)	2(1)	-4(1)
Rh(2)	18(1)	21(1)	24(1)	2(1)	2(1)	-4(1)
C(86)	57(9)	61(9)	37(9)	20(8)	-15(8)	7(9)
C(85)	20(7)	94(11)	19(7)	13(8)	12(6)	2(8)
C(84)	40(7)	42(8)	9(6)	6(6)	-8(6)	19(7)
C(83)	45(7)	43(7)	12(6)	-11(6)	-8(6)	-2(7)
C(82)	17(6)	44(8)	46(8)	-4(7)	-8(6)	-6(6)
C(81)	43(8)	73(10)	25(8)	-12(7)	6(7)	-19(8)
C(80)	82(11)	106(13)	34(9)	-15(9)	40(8)	-37(11)

Table D6. 4 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$.

	x	y	z	U(eq)
H(1)	9560	9281	8343	31
H(2)	10349	10420	7399	31
H(3)	9832	10615	6075	31
H(5)	8653	10082	5003	31
H(6)	7519	9044	4731	31
H(7)	6709	7979	5734	31
H(12)	7045	5052	10417	31
H(13)	6783	4935	11798	31
H(14)	6115	6206	12380	31
H(15)	5956	7708	11611	31
H(16)	6193	7871	10206	31
H(22)	9443	5476	9149	27
H(23)	10476	4000	8913	27
H(24)	9224	3139	8423	27
H(25)	6883	3764	8158	27
H(26)	5801	5215	8478	27
H(32)	4179	6469	9991	27
H(33)	1860	6760	9693	27
H(34)	1170	7307	8384	27
H(35)	2785	7647	7367	27
H(36)	5123	7366	7652	27
H(42)	9074	4670	6255	27
H(43)	7965	6068	6641	27

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H(44)	5568	6552	6600	27
H(45)	4329	5645	6179	27
H(46)	5417	4196	5873	32
H(52)	7923	5020	4526	32
H(53)	8380	5457	3163	32
H(54)	9244	4355	2387	32
H(55)	9668	2786	2954	32
H(56)	9199	2316	4312	32
H(62)	10958	3442	4963	32
H(63)	13145	3077	5447	32
H(64)	13507	2418	6799	32
H(65)	11687	2026	7623	32
H(66)	9477	2350	7137	32
H(71)	5096	764	5728	32
H(72)	4136	-470	6511	32
H(73)	4273	-723	7851	32
H(75)	5205	-380	9075	50
H(76)	6514	400	9611	50
H(77)	7490	1569	8756	50

Appendix E Crystallographic data of 5-Chloro- 8-hydroxyquinolinatorhodium(I) complexes

E1. Crystal data of Carbonyl[tris(4-tert-butylphenyl)phosphite] (5-chloro-8-hydroxyquinolinato)rhodium(I), [Rh(oxCl)(CO)P(O-4^tBuPh)₃]

Table E1. 1 Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for [Rh(oxCl)(CO)P(O-4^tBuPh)₃]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh	2336(1)	5101(1)	6751(1)	23(1)
P	524(1)	4628(1)	7328(1)	21(1)
Cl	5730(1)	8269(1)	2503(1)	49(1)
O(2)	-582(2)	5608(2)	7278(1)	24(1)
O(3)	41(2)	3978(2)	6675(1)	25(1)
O(1)	256(2)	3907(2)	8465(1)	25(1)
O(4)	1881(2)	5864(2)	5406(2)	29(1)
N	3950(2)	5746(2)	5955(2)	23(1)
C(21)	-743(2)	6513(2)	7756(2)	23(1)
C(22)	-1674(2)	6529(2)	8594(2)	25(1)
C(31)	705(2)	3077(2)	6268(2)	22(1)
O(5)	3062(2)	4045(2)	8702(2)	51(1)
C(11)	-853(2)	3621(2)	9087(2)	23(1)
C(23)	-1931(2)	7468(2)	9011(2)	26(1)
C(14)	-2967(2)	2997(2)	10453(2)	27(1)
C(24)	-1286(2)	8401(2)	8619(2)	24(1)
C(13)	-2865(3)	3208(3)	9414(2)	30(1)
C(9)	3856(2)	6366(2)	5000(2)	23(1)
C(33)	1759(3)	1219(3)	6420(2)	29(1)
C(36)	777(3)	3161(3)	5259(2)	30(1)
C(26)	-66(2)	7400(2)	7354(2)	26(1)
C(141)	-4131(3)	2685(3)	11200(3)	46(1)
C(25)	-336(2)	8333(2)	7786(2)	26(1)
C(8)	2740(2)	6378(2)	4737(2)	26(1)
C(34)	1846(3)	1263(3)	5401(2)	35(1)
C(6)	3567(3)	7508(3)	3090(2)	37(1)
C(32)	1198(2)	2115(2)	6859(2)	25(1)
C(16)	-931(3)	3444(3)	10107(2)	34(1)
C(5)	4620(3)	7514(3)	3358(2)	33(1)
C(4)	4808(3)	6924(2)	4326(2)	27(1)

C(12)	-1821(3)	3518(3)	8726(2)	29(1)
C(35)	1346(3)	2261(3)	4838(2)	36(1)
C(241)	-1635(3)	9429(3)	9092(2)	30(1)
C(1)	4973(2)	5664(2)	6240(2)	27(1)
C(3)	5878(3)	6827(3)	4672(2)	30(1)
C(15)	-1973(3)	3130(3)	10776(2)	37(1)
C(143)	-5027(3)	3771(3)	11231(3)	46(1)
C(10)	2760(3)	4441(3)	7955(2)	33(1)
C(244)	-2956(3)	9879(3)	9081(3)	44(1)
C(7)	2626(3)	6950(3)	3768(2)	32(1)
C(2)	5950(3)	6201(3)	5619(2)	32(1)
C(242)	-880(4)	10386(3)	8518(3)	51(1)
C(243)	-1489(4)	9075(3)	10190(3)	50(1)
C(144)	-3942(4)	2213(4)	12287(3)	66(1)
C(142)	-4708(4)	1859(4)	10918(3)	66(1)
C(341)	2717(7)	337(6)	4901(6)	26(2)
C(344)	2745(10)	570(11)	3784(9)	45(3)
C(342)	2219(8)	-779(7)	5449(7)	41(2)
C(343)	4020(5)	231(6)	5035(6)	38(2)
C(345)	2196(7)	206(6)	4943(6)	25(2)
C(347)	2785(7)	-779(6)	5646(6)	35(2)
C(348)	3143(10)	569(11)	3975(9)	42(2)
C(346)	1176(6)	-218(6)	4681(5)	42(2)

Table E1. 2 Bond lengths (Å) and angles (°) for [Rh(oxCl)(CO)P(O-4^tBuPh)₃]

Rh-C(10)	1.821(3)	C(23)-C(24)-C(25)	116.7(3)
Rh-O(4)	2.030(2)	C(23)-C(24)-C(241)	119.9(3)
Rh-N	2.098(2)	C(25)-C(24)-C(241)	123.4(3)
Rh-P	2.1811(11)	C(14)-C(13)-C(12)	122.3(3)
P-O(1)	1.594(2)	C(14)-C(13)-H(13)	118.9
P-O(2)	1.602(2)	C(12)-C(13)-H(13)	118.9
P-O(3)	1.6070(19)	N-C(9)-C(4)	122.1(2)
Cl-C(5)	1.741(3)	N-C(9)-C(8)	115.2(2)
O(2)-C(21)	1.405(3)	C(4)-C(9)-C(8)	122.7(3)
O(3)-C(31)	1.398(3)	C(32)-C(33)-C(34)	122.1(3)
O(1)-C(11)	1.408(3)	C(32)-C(33)-H(33)	119.0
O(4)-C(8)	1.311(3)	C(34)-C(33)-H(33)	119.0
N-C(1)	1.324(3)	C(31)-C(36)-C(35)	119.0(3)
N-C(9)	1.378(4)	C(31)-C(36)-H(36)	120.5
C(21)-C(26)	1.372(4)	C(35)-C(36)-H(36)	120.5
C(21)-C(22)	1.386(4)	C(21)-C(26)-C(25)	119.2(3)
C(22)-C(23)	1.381(4)	C(21)-C(26)-H(26)	120.4
C(22)-H(22)	0.9300	C(25)-C(26)-H(26)	120.4
C(31)-C(36)	1.374(4)	C(142)-C(141)-C(14)	113.0(3)
C(31)-C(32)	1.380(4)	C(142)-C(141)-C(144)	109.1(3)
O(5)-C(10)	1.148(4)	C(14)-C(141)-C(144)	111.9(3)
C(11)-C(16)	1.372(4)	C(142)-C(141)-C(143)	107.7(3)
C(11)-C(12)	1.379(4)	C(14)-C(141)-C(143)	108.9(3)
C(23)-C(24)	1.395(4)	C(144)-C(141)-C(143)	105.9(3)
C(23)-H(23)	0.9300	C(26)-C(25)-C(24)	121.9(3)
C(14)-C(15)	1.389(4)	C(26)-C(25)-H(25)	119.1
C(14)-C(13)	1.390(4)	C(24)-C(25)-H(25)	119.1
C(14)-C(141)	1.529(4)	O(4)-C(8)-C(7)	123.1(3)

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C(24)-C(25)	1.401(4)	O(4)-C(8)-C(9)	119.8(3)
C(24)-C(241)	1.525(4)	C(7)-C(8)-C(9)	117.1(3)
C(13)-C(12)	1.390(4)	C(35)-C(34)-C(33)	116.7(3)
C(13)-H(13)	0.9300	C(35)-C(34)-C(345)	118.6(4)
C(9)-C(4)	1.412(4)	C(33)-C(34)-C(345)	123.3(4)
C(9)-C(8)	1.430(4)	C(35)-C(34)-C(341)	122.8(4)
C(33)-C(32)	1.385(4)	C(33)-C(34)-C(341)	119.1(4)
C(33)-C(34)	1.396(4)	C(345)-C(34)-C(341)	23.6(2)
C(33)-H(33)	0.9300	C(5)-C(6)-C(7)	121.7(3)
C(36)-C(35)	1.378(4)	C(5)-C(6)-H(6)	119.1
C(36)-H(36)	0.9300	C(7)-C(6)-H(6)	119.1
C(26)-C(25)	1.385(4)	C(31)-C(32)-C(33)	118.7(3)
C(26)-H(26)	0.9300	C(31)-C(32)-H(32)	120.6
C(141)-C(142)	1.487(5)	C(33)-C(32)-H(32)	120.6
C(141)-C(144)	1.540(6)	C(11)-C(16)-C(15)	119.8(3)
C(141)-C(143)	1.546(5)	C(11)-C(16)-H(16)	120.1
C(25)-H(25)	0.9300	C(15)-C(16)-H(16)	120.1
C(8)-C(7)	1.386(4)	C(6)-C(5)-C(4)	120.6(3)
C(34)-C(35)	1.394(4)	C(6)-C(5)-Cl	119.6(3)
C(34)-C(345)	1.543(7)	C(4)-C(5)-Cl	119.8(2)
C(34)-C(341)	1.570(8)	C(9)-C(4)-C(5)	117.2(3)
C(6)-C(5)	1.367(5)	C(9)-C(4)-C(3)	117.1(3)
C(6)-C(7)	1.405(4)	C(5)-C(4)-C(3)	125.7(3)
C(6)-H(6)	0.9300	C(11)-C(12)-C(13)	118.8(3)
C(32)-H(32)	0.9300	C(11)-C(12)-H(12)	120.6
C(16)-C(15)	1.379(4)	C(13)-C(12)-H(12)	120.6
C(16)-H(16)	0.9300	C(36)-C(35)-C(34)	122.3(3)
C(5)-C(4)	1.412(4)	C(36)-C(35)-H(35)	118.8
C(4)-C(3)	1.419(4)	C(34)-C(35)-H(35)	118.8
C(12)-H(12)	0.9300	C(242)-C(241)-C(24)	112.0(3)
C(35)-H(35)	0.9300	C(242)-C(241)-C(243)	109.3(3)
C(241)-C(242)	1.522(5)	C(24)-C(241)-C(243)	109.4(3)
C(241)-C(243)	1.531(4)	C(242)-C(241)-C(244)	108.1(3)
C(241)-C(244)	1.540(5)	C(24)-C(241)-C(244)	109.1(2)
C(1)-C(2)	1.396(4)	C(243)-C(241)-C(244)	108.8(3)
C(1)-H(1)	0.9300	N-C(1)-C(2)	122.6(3)
C(3)-C(2)	1.366(4)	N-C(1)-H(1)	118.7
C(3)-H(3)	0.9300	C(2)-C(1)-H(1)	118.7
C(15)-H(15)	0.9300	C(2)-C(3)-C(4)	119.5(3)
C(143)-H(14A)	0.9600	C(2)-C(3)-H(3)	120.2
C(143)-H(14B)	0.9600	C(4)-C(3)-H(3)	120.2
C(143)-H(14C)	0.9600	C(16)-C(15)-C(14)	122.1(3)
C(244)-H(24A)	0.9600	C(16)-C(15)-H(15)	118.9
C(244)-H(24B)	0.9600	C(14)-C(15)-H(15)	118.9
C(244)-H(24C)	0.9600	C(141)-C(143)-H(14A)	109.5
C(7)-H(7)	0.9300	C(141)-C(143)-H(14B)	109.5
C(2)-H(2)	0.9300	H(14A)-C(143)-H(14B)	109.5
C(242)-H(24D)	0.9600	C(141)-C(143)-H(14C)	109.5
C(242)-H(24E)	0.9600	H(14A)-C(143)-H(14C)	109.5
C(242)-H(24F)	0.9600	H(14B)-C(143)-H(14C)	109.5
C(243)-H(24G)	0.9600	O(5)-C(10)-Rh	177.6(3)
C(243)-H(24H)	0.9600	C(241)-C(244)-H(24A)	109.5
C(243)-H(24I)	0.9600	C(241)-C(244)-H(24B)	109.5
C(144)-H(14D)	0.9600	H(24A)-C(244)-H(24B)	109.5
C(144)-H(14E)	0.9600	C(241)-C(244)-H(24C)	109.5
C(144)-H(14F)	0.9600	H(24A)-C(244)-H(24C)	109.5

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C(142)-H(14G)	0.9600	H(24B)-C(244)-H(24C)	109.5
C(142)-H(14H)	0.9600	C(8)-C(7)-C(6)	120.6(3)
C(142)-H(14I)	0.9600	C(8)-C(7)-H(7)	119.7
C(341)-C(344)	1.511(13)	C(6)-C(7)-H(7)	119.7
C(341)-C(342)	1.521(11)	C(3)-C(2)-C(1)	120.0(3)
C(341)-C(343)#1	1.550(10)	C(3)-C(2)-H(2)	120.0
C(341)-C(343)	1.550(10)	C(1)-C(2)-H(2)	120.0
C(344)-H(34A)	0.9600	C(241)-C(242)-H(24D)	109.5
C(344)-H(34B)	0.9600	C(241)-C(242)-H(24E)	109.5
C(344)-H(34C)	0.9600	H(24D)-C(242)-H(24E)	109.5
C(342)-H(34D)	0.9600	C(241)-C(242)-H(24F)	109.5
C(342)-H(34E)	0.9600	H(24D)-C(242)-H(24F)	109.5
C(342)-H(34F)	0.9600	H(24E)-C(242)-H(24F)	109.5
C(343)-H(34G)	0.9600	C(241)-C(243)-H(24G)	109.5
C(343)-H(34H)	0.9600	C(241)-C(243)-H(24H)	109.5
C(343)-H(34I)	0.9600	H(24G)-C(243)-H(24H)	109.5
C(345)-C(347)	1.527(11)	C(241)-C(243)-H(24I)	109.5
C(345)-C(346)	1.530(10)	H(24G)-C(243)-H(24I)	109.5
C(345)-C(348)	1.537(14)	H(24H)-C(243)-H(24I)	109.5
C(347)-H(34J)	0.9600	C(141)-C(144)-H(14D)	109.5
C(347)-H(34K)	0.9600	C(141)-C(144)-H(14E)	109.5
C(347)-H(34L)	0.9600	H(14D)-C(144)-H(14E)	109.5
C(348)-H(34M)	0.9600	C(141)-C(144)-H(14F)	109.5
C(348)-H(34N)	0.9600	H(14D)-C(144)-H(14F)	109.5
C(348)-H(34O)	0.9600	H(14E)-C(144)-H(14F)	109.5
C(346)-H(34P)	0.9600	C(141)-C(142)-H(14G)	109.5
C(346)-H(34Q)	0.9600	C(141)-C(142)-H(14H)	109.5
C(346)-H(34R)	0.9600	H(14G)-C(142)-H(14H)	109.5
		C(141)-C(142)-H(14I)	109.5
C(10)-Rh-O(4)	178.88(11)	H(14G)-C(142)-H(14I)	109.5
C(10)-Rh-N	98.56(11)	H(14H)-C(142)-H(14I)	109.5
O(4)-Rh-N	80.59(9)	C(344)-C(341)-C(342)	110.5(8)
C(10)-Rh-P	92.33(9)	C(344)-C(341)-C(343)#1	108.1(7)
O(4)-Rh-P	88.49(6)	C(342)-C(341)-C(343)#1	108.0(7)
N-Rh-P	168.95(7)	C(344)-C(341)-C(343)	108.1(7)
O(1)-P-O(2)	104.42(10)	C(342)-C(341)-C(343)	108.0(7)
O(1)-P-O(3)	106.35(11)	C(343)#1-C(341)-C(343)	0.0(5)
O(2)-P-O(3)	91.94(10)	C(344)-C(341)-C(34)	111.2(7)
O(1)-P-Rh	115.37(7)	C(342)-C(341)-C(34)	105.3(6)
O(2)-P-Rh	118.63(8)	C(343)#1-C(341)-C(34)	113.6(5)
O(3)-P-Rh	117.02(8)	C(343)-C(341)-C(34)	113.6(5)
C(21)-O(2)-P	122.90(16)	C(347)-C(345)-C(346)	108.0(7)
C(31)-O(3)-P	124.08(16)	C(347)-C(345)-C(348)	108.0(7)
C(11)-O(1)-P	128.45(17)	C(346)-C(345)-C(348)	109.6(6)
C(8)-O(4)-Rh	113.31(17)	C(347)-C(345)-C(34)	110.8(5)
C(1)-N-C(9)	118.7(2)	C(346)-C(345)-C(34)	115.7(6)
C(1)-N-Rh	130.3(2)	C(348)-C(345)-C(34)	104.4(7)
C(9)-N-Rh	110.99(17)	C(345)-C(347)-H(34J)	109.5
C(26)-C(21)-C(22)	121.1(3)	C(345)-C(347)-H(34K)	109.5
C(26)-C(21)-O(2)	120.9(2)	H(34J)-C(347)-H(34K)	109.5
C(22)-C(21)-O(2)	117.8(2)	C(345)-C(347)-H(34L)	109.5
C(23)-C(22)-C(21)	118.8(3)	H(34J)-C(347)-H(34L)	109.5
C(23)-C(22)-H(22)	120.6	H(34K)-C(347)-H(34L)	109.5
C(21)-C(22)-H(22)	120.6	C(345)-C(348)-H(34M)	109.5
C(36)-C(31)-C(32)	121.2(3)	C(345)-C(348)-H(34N)	109.5
C(36)-C(31)-O(3)	116.6(2)	H(34M)-C(348)-H(34N)	109.5

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C(32)-C(31)-O(3)	122.0(2)	C(345)-C(348)-H(34O)	109.5
C(16)-C(11)-C(12)	120.4(3)	H(34M)-C(348)-H(34O)	109.5
C(16)-C(11)-O(1)	115.7(2)	H(34N)-C(348)-H(34O)	109.5
C(12)-C(11)-O(1)	123.9(2)	C(345)-C(346)-H(34P)	109.5
C(22)-C(23)-C(24)	122.3(3)	C(345)-C(346)-H(34Q)	109.5
C(22)-C(23)-H(23)	118.9	H(34P)-C(346)-H(34Q)	109.5
C(24)-C(23)-H(23)	118.9	C(345)-C(346)-H(34R)	109.5
C(15)-C(14)-C(13)	116.6(3)	H(34P)-C(346)-H(34R)	109.5
C(15)-C(14)-C(141)	121.7(3)	H(34Q)-C(346)-H(34R)	109.5
C(13)-C(14)-C(141)	121.7(3)		

Table E1. 3 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-4^t\text{BuPh})_3]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh	21(1)	23(1)	22(1)	-2(1)	-4(1)	-5(1)
P	21(1)	21(1)	21(1)	-4(1)	-4(1)	-3(1)
Cl	41(1)	50(1)	42(1)	9(1)	7(1)	-16(1)
O(2)	24(1)	22(1)	27(1)	-7(1)	-7(1)	0(1)
O(3)	23(1)	27(1)	28(1)	-11(1)	-5(1)	-2(1)
O(1)	20(1)	28(1)	23(1)	1(1)	-6(1)	-4(1)
O(4)	23(1)	36(1)	27(1)	-1(1)	-5(1)	-7(1)
N	21(1)	20(1)	28(1)	-8(1)	-3(1)	-3(1)
C(21)	22(1)	20(1)	26(1)	-5(1)	-9(1)	2(1)
C(22)	22(1)	20(1)	29(2)	1(1)	-5(1)	-6(1)
C(31)	17(1)	23(1)	25(1)	-5(1)	-2(1)	-5(1)
O(5)	51(2)	64(2)	35(1)	14(1)	-20(1)	-21(1)
C(11)	20(1)	19(1)	26(1)	-1(1)	-2(1)	-3(1)
C(23)	24(1)	27(2)	23(1)	-5(1)	-2(1)	-3(1)
C(14)	22(1)	27(2)	31(2)	-4(1)	-4(1)	-3(1)
C(24)	27(1)	23(1)	22(1)	-3(1)	-9(1)	-2(1)
C(13)	25(1)	35(2)	35(2)	-7(1)	-9(1)	-13(1)
C(9)	23(1)	20(1)	25(1)	-7(1)	-2(1)	-2(1)
C(33)	36(2)	23(2)	26(2)	0(1)	-9(1)	-1(1)
C(36)	34(2)	29(2)	26(2)	-5(1)	-12(1)	4(1)
C(26)	25(1)	28(2)	21(1)	-1(1)	-2(1)	-5(1)
C(141)	32(1)	54(2)	46(2)	-8(1)	0(1)	-7(1)
C(25)	27(1)	22(2)	27(2)	0(1)	-5(1)	-7(1)
C(8)	25(1)	25(2)	26(1)	-5(1)	-3(1)	-3(1)
C(34)	45(2)	28(2)	29(2)	-8(1)	-9(1)	6(1)
C(6)	42(2)	35(2)	28(2)	2(1)	-5(1)	-6(1)
C(32)	28(1)	27(2)	20(1)	-3(1)	-4(1)	-6(1)
C(16)	21(1)	53(2)	27(2)	-2(1)	-9(1)	-8(1)
C(5)	32(2)	28(2)	32(2)	-2(1)	5(1)	-7(1)
C(4)	26(1)	19(1)	34(2)	-8(1)	0(1)	-4(1)
C(12)	33(2)	34(2)	22(1)	-4(1)	-8(1)	-10(1)
C(35)	51(2)	34(2)	22(2)	-7(1)	-13(1)	5(2)
C(241)	36(2)	27(2)	29(2)	-10(1)	-7(1)	-6(1)
C(1)	26(1)	28(2)	28(2)	-8(1)	-4(1)	-4(1)
C(3)	23(1)	27(2)	38(2)	-11(1)	3(1)	-8(1)
C(15)	26(2)	60(2)	23(2)	0(2)	-6(1)	-7(2)
C(143)	32(1)	54(2)	46(2)	-8(1)	0(1)	-7(1)
C(10)	28(2)	35(2)	35(2)	0(1)	-6(1)	-13(1)

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C(244)	45(2)	33(2)	58(2)	-23(2)	-13(2)	5(2)
C(7)	28(2)	36(2)	31(2)	-3(1)	-6(1)	-5(1)
C(2)	24(1)	35(2)	41(2)	-13(1)	-5(1)	-6(1)
C(242)	61(2)	35(2)	62(3)	-21(2)	0(2)	-18(2)
C(243)	68(2)	50(2)	41(2)	-19(2)	-20(2)	0(2)
C(144)	53(2)	88(2)	54(2)	-18(2)	11(1)	-33(2)
C(142)	53(2)	88(2)	54(2)	-18(2)	11(1)	-33(2)
C(341)	14(3)	28(4)	33(4)	-9(3)	0(3)	-3(3)
C(344)	49(7)	52(5)	34(5)	-29(4)	-9(5)	21(6)
C(342)	31(4)	35(4)	57(5)	-21(4)	-3(4)	-3(3)
C(343)	23(3)	39(4)	53(4)	-20(3)	-4(3)	1(3)
C(345)	19(4)	28(4)	29(3)	-9(3)	-1(3)	-3(3)
C(347)	33(4)	26(4)	43(4)	-11(3)	-5(3)	3(3)
C(348)	38(6)	42(5)	42(6)	-9(4)	-6(4)	5(4)
C(346)	40(4)	43(4)	51(4)	-23(3)	-15(3)	-2(3)

Table E1. 4 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{O}-4^t\text{BuPh})_3]$.

	x	y	z	U(eq)
H(22)	-2119	5918	8870	29
H(23)	-2555	7478	9574	31
H(13)	-3518	3138	9171	36
H(33)	2088	568	6818	35
H(36)	447	3816	4866	36
H(26)	565	7376	6799	31
H(25)	127	8932	7515	31
H(6)	3472	7882	2442	44
H(32)	1154	2070	7540	30
H(16)	-283	3535	10346	40
H(12)	-1776	3654	8035	35
H(35)	1398	2321	4154	43
H(1)	5043	5232	6879	33
H(3)	6526	7187	4257	36
H(15)	-2011	3004	11466	45
H(14A)	-5220	4075	10579	69
H(14B)	-4674	4323	11406	69
H(14C)	-5744	3590	11728	69
H(24A)	-3085	9987	8411	65
H(24B)	-3148	10589	9283	65
H(24C)	-3460	9340	9542	65
H(7)	1919	6964	3564	39
H(2)	6649	6132	5851	39
H(24D)	-51	10123	8516	77
H(24E)	-1124	11014	8841	77
H(24F)	-988	10625	7835	77
H(24G)	-1982	8486	10558	75
H(24H)	-1726	9717	10494	75
H(24I)	-666	8798	10205	75
H(14D)	-4696	2058	12737	98
H(14E)	-3612	2762	12487	98
H(14F)	-3400	1525	12315	98
H(14G)	-4944	2198	10287	98
H(14H)	-5402	1654	11434	98

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H(14I)	-4152	1193	10852	98
H(34A)	3207	-52	3514	67
H(34B)	3104	1254	3444	67
H(34C)	1943	657	3683	67
H(34D)	1395	-716	5412	61
H(34E)	2278	-950	6144	61
H(34F)	2671	-1375	5136	61
H(34G)	4025	53	5743	57
H(34H)	4343	936	4714	57
H(34I)	4499	-362	4732	57
H(34J)	3137	-1372	5295	52
H(34K)	2192	-1065	6229	52
H(34L)	3395	-519	5854	52
H(34M)	3784	832	4141	64
H(34N)	2784	1169	3510	64
H(34O)	3452	-67	3670	64
H(34P)	1482	-871	4400	63
H(34Q)	834	370	4197	63
H(34R)	572	-419	5283	63

E2. Crystal data of
Carbonyl[tris(2,4-di-tert-butylphenyl)phosphite] (5-chloro-8-
hydroxyquinolinato)rhodium(I),
[Rh(oxCl)(CO)(P(O-2,4di^tBuPh)₃)]

Table E2. 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Rh(oxCl)(CO)(P(O-2,4di^tBuPh)₃)]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh	2039(1)	3919(1)	4389(1)	42(1)
P	2608(1)	2742(1)	4123(1)	38(1)
Cl	-70(1)	6029(2)	6953(1)	109(1)
O(1)	3355(2)	2711(2)	3613(2)	47(1)
O(4)	1958(2)	3665(2)	5455(2)	58(1)
O(2)	2827(2)	2213(2)	4820(2)	41(1)
C(10)	2042(3)	4191(4)	3439(3)	59(1)
O(3)	2120(2)	2122(2)	3603(2)	43(1)
N	1387(2)	4948(2)	4729(3)	52(1)
C(15)	4978(3)	3778(3)	4524(3)	53(1)
O(5)	2018(3)	4365(3)	2833(3)	91(2)
C(26)	3224(4)	889(4)	4296(3)	61(1)
C(13)	5255(3)	3606(3)	3285(3)	49(1)
C(33)	165(3)	1348(4)	3304(3)	60(1)
C(4)	705(3)	5476(3)	5769(3)	60(1)
C(31)	1358(2)	1892(3)	3733(3)	42(1)
C(35)	304(3)	1671(3)	4546(3)	57(1)
C(32)	913(3)	1594(3)	3135(3)	49(1)
C(321)	1214(3)	1541(4)	2371(4)	73(1)
C(7)	1323(4)	4105(4)	6531(4)	68(2)
C(23)	3460(3)	260(3)	5648(3)	52(1)
C(223)	3252(5)	1117(4)	6967(4)	76(2)
C(121)	4343(3)	2890(4)	2370(3)	65(2)
C(224)	2190(3)	1831(4)	6334(3)	58(1)
C(9)	1197(3)	4892(3)	5436(3)	47(1)
C(5)	536(3)	5345(4)	6510(4)	67(2)
C(122)	5008(5)	3056(6)	1847(4)	109(3)
C(030)	1061(3)	1919(3)	4418(3)	49(1)
C(21)	3090(3)	1386(3)	4896(3)	42(1)
C(12)	4552(3)	3217(3)	3136(3)	47(1)
C(242)	4669(6)	-1227(5)	4710(8)	132(5)
C(11)	4055(2)	3131(3)	3728(3)	42(1)
C(141)	6289(3)	4309(3)	4053(3)	54(1)
C(16)	4269(3)	3411(3)	4409(3)	52(1)
C(34)	-159(3)	1372(4)	3989(3)	60(1)
C(8)	1512(3)	4188(3)	5819(3)	51(1)
C(341)	-978(4)	1099(4)	4101(4)	73(1)
C(342)	-1097(6)	246(11)	3798(8)	201(4)
C(24)	3621(3)	-247(3)	5062(3)	54(1)
C(6)	846(4)	4678(4)	6871(3)	70(2)

C(143)	6918(4)	3797(5)	3701(6)	93(3)
C(244)	4081(8)	-1362(5)	5912(6)	135(4)
C(22)	3199(3)	1085(3)	5599(3)	43(1)
C(241)	3938(4)	-1138(3)	5140(4)	59(1)
C(123)	3620(5)	3328(6)	2096(4)	105(3)
C(124)	4224(5)	1942(5)	2414(4)	98(3)
C(344)	-1177(7)	1042(10)	4888(10)	201(4)
C(221)	3038(3)	1603(3)	6286(3)	59(1)
C(14)	5494(3)	3893(3)	3958(3)	47(1)
C(324)	619(6)	1197(8)	1852(5)	167(6)
C(142)	6251(4)	5177(4)	3720(5)	98(3)
C(222)	3536(4)	2411(4)	6285(3)	69(2)
C(25)	3489(4)	88(4)	4390(3)	68(2)
C(323)	1390(7)	2430(6)	2099(4)	125(4)
C(069)	1933(5)	1006(5)	2346(5)	99(3)
C(144)	6501(4)	4420(4)	4858(4)	78(2)
C(2)	609(5)	6174(4)	4651(5)	91(2)
C(1)	1097(4)	5566(3)	4337(4)	69(2)
C(3)	426(4)	6126(4)	5344(5)	80(2)
C(243)	3355(5)	-1755(4)	4847(6)	108(3)
C(343)	-1515(6)	1687(11)	3762(9)	201(4)

Table E2. 2 Bond lengths (Å) and angles (°) for [Rh(oxCl)(CO)(P(O-2,4di^tBuPh)₃]

Rh-C(10)	1.817(6)	C(22)-C(23)-H(23)	117.6
Rh-O(4)	2.026(4)	C(221)-C(223)-H(22A)	109.5
Rh-N	2.101(4)	C(221)-C(223)-H(22B)	109.5
Rh-P	2.1918(13)	H(22A)-C(223)-H(22B)	109.5
P-O(2)	1.594(3)	C(221)-C(223)-H(22C)	109.5
P-O(1)	1.605(3)	H(22A)-C(223)-H(22C)	109.5
P-O(3)	1.627(3)	H(22B)-C(223)-H(22C)	109.5
Cl-C(5)	1.729(6)	C(123)-C(121)-C(122)	109.0(6)
O(1)-C(11)	1.406(5)	C(123)-C(121)-C(124)	111.5(6)
O(4)-C(8)	1.328(6)	C(122)-C(121)-C(124)	107.8(6)
O(2)-C(21)	1.414(6)	C(123)-C(121)-C(12)	109.8(5)
C(10)-O(5)	1.161(7)	C(122)-C(121)-C(12)	110.1(5)
O(3)-C(31)	1.391(5)	C(124)-C(121)-C(12)	108.5(5)
N-C(1)	1.332(7)	C(221)-C(224)-H(22D)	109.5
N-C(9)	1.356(7)	C(221)-C(224)-H(22E)	109.5
C(15)-C(16)	1.379(7)	H(22D)-C(224)-H(22E)	109.5
C(15)-C(14)	1.390(8)	C(221)-C(224)-H(22F)	109.5
C(15)-H(15)	0.9300	H(22D)-C(224)-H(22F)	109.5
C(26)-C(25)	1.381(8)	H(22E)-C(224)-H(22F)	109.5
C(26)-C(21)	1.390(8)	N-C(9)-C(4)	121.9(5)
C(26)-H(26)	0.9300	N-C(9)-C(8)	115.8(4)
C(13)-C(14)	1.395(7)	C(4)-C(9)-C(8)	122.3(5)
C(13)-C(12)	1.398(7)	C(6)-C(5)-C(4)	120.5(5)
C(13)-H(13)	0.9300	C(6)-C(5)-Cl	120.2(5)
C(33)-C(34)	1.390(9)	C(4)-C(5)-Cl	119.4(5)
C(33)-C(32)	1.391(7)	C(121)-C(122)-H(12A)	109.5
C(33)-H(33)	0.9300	C(121)-C(122)-H(12B)	109.5
C(4)-C(3)	1.398(9)	H(12A)-C(122)-H(12B)	109.5
C(4)-C(9)	1.411(7)	C(121)-C(122)-H(12C)	109.5
C(4)-C(5)	1.421(9)	H(12A)-C(122)-H(12C)	109.5

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C(31)-C(030)	1.371(7)	H(12B)-C(122)-H(12C)	109.5
C(31)-C(32)	1.434(6)	C(31)-C(030)-C(35)	120.2(5)
C(35)-C(030)	1.391(7)	C(31)-C(030)-H(030)	119.9
C(35)-C(34)	1.395(8)	C(35)-C(030)-H(030)	119.9
C(35)-H(35)	0.9300	C(26)-C(21)-C(22)	121.5(5)
C(32)-C(321)	1.515(9)	C(26)-C(21)-O(2)	121.0(5)
C(321)-C(069)	1.515(11)	C(22)-C(21)-O(2)	117.5(4)
C(321)-C(324)	1.515(9)	C(13)-C(12)-C(11)	115.1(4)
C(321)-C(323)	1.549(11)	C(13)-C(12)-C(121)	122.3(4)
C(7)-C(8)	1.370(9)	C(11)-C(12)-C(121)	122.5(4)
C(7)-C(6)	1.390(9)	C(241)-C(242)-H(24A)	109.5
C(7)-H(7)	0.9300	C(241)-C(242)-H(24B)	109.5
C(23)-C(24)	1.387(8)	H(24A)-C(242)-H(24B)	109.5
C(23)-C(22)	1.407(7)	C(241)-C(242)-H(24C)	109.5
C(23)-H(23)	0.9300	H(24A)-C(242)-H(24C)	109.5
C(223)-C(221)	1.533(8)	H(24B)-C(242)-H(24C)	109.5
C(223)-H(22A)	0.9600	C(16)-C(11)-C(12)	121.0(4)
C(223)-H(22B)	0.9600	C(16)-C(11)-O(1)	121.6(4)
C(223)-H(22C)	0.9600	C(12)-C(11)-O(1)	117.3(4)
C(121)-C(123)	1.524(10)	C(143)-C(141)-C(142)	110.8(6)
C(121)-C(122)	1.530(8)	C(143)-C(141)-C(14)	110.9(5)
C(121)-C(124)	1.543(10)	C(142)-C(141)-C(14)	108.1(5)
C(121)-C(12)	1.559(7)	C(143)-C(141)-C(144)	108.0(6)
C(224)-C(221)	1.516(7)	C(142)-C(141)-C(144)	107.2(5)
C(224)-H(22D)	0.9600	C(14)-C(141)-C(144)	111.8(5)
C(224)-H(22E)	0.9600	C(15)-C(16)-C(11)	121.1(5)
C(224)-H(22F)	0.9600	C(15)-C(16)-H(16)	119.5
C(9)-C(8)	1.445(7)	C(11)-C(16)-H(16)	119.5
C(5)-C(6)	1.375(9)	C(33)-C(34)-C(35)	117.1(5)
C(122)-H(12A)	0.9600	C(33)-C(34)-C(341)	120.0(5)
C(122)-H(12B)	0.9600	C(35)-C(34)-C(341)	122.8(6)
C(122)-H(12C)	0.9600	O(4)-C(8)-C(7)	124.6(5)
C(030)-H(030)	0.9300	O(4)-C(8)-C(9)	117.9(5)
C(21)-C(22)	1.405(7)	C(7)-C(8)-C(9)	117.5(5)
C(12)-C(11)	1.403(7)	C(343)-C(341)-C(342)	110.1(9)
C(242)-C(241)	1.504(11)	C(343)-C(341)-C(34)	110.4(7)
C(242)-H(24A)	0.9600	C(342)-C(341)-C(34)	110.3(7)
C(242)-H(24B)	0.9600	C(343)-C(341)-C(344)	108.1(10)
C(242)-H(24C)	0.9600	C(342)-C(341)-C(344)	106.1(10)
C(11)-C(16)	1.392(7)	C(34)-C(341)-C(344)	111.7(7)
C(141)-C(143)	1.514(9)	C(341)-C(342)-H(34A)	109.5
C(141)-C(142)	1.530(8)	C(341)-C(342)-H(34B)	109.5
C(141)-C(14)	1.543(7)	H(34A)-C(342)-H(34B)	109.5
C(141)-C(144)	1.548(9)	C(341)-C(342)-H(34C)	109.5
C(16)-H(16)	0.9300	H(34A)-C(342)-H(34C)	109.5
C(34)-C(341)	1.502(8)	H(34B)-C(342)-H(34C)	109.5
C(341)-C(343)	1.469(17)	C(25)-C(24)-C(23)	116.5(5)
C(341)-C(342)	1.498(17)	C(25)-C(24)-C(241)	120.5(5)
C(341)-C(344)	1.503(18)	C(23)-C(24)-C(241)	123.1(5)
C(342)-H(34A)	0.9600	C(5)-C(6)-C(7)	122.0(6)
C(342)-H(34B)	0.9600	C(5)-C(6)-H(6)	119.0
C(342)-H(34C)	0.9600	C(7)-C(6)-H(6)	119.0
C(24)-C(25)	1.379(9)	C(141)-C(143)-H(14A)	109.5
C(24)-C(241)	1.544(7)	C(141)-C(143)-H(14B)	109.5
C(6)-H(6)	0.9300	H(14A)-C(143)-H(14B)	109.5
C(143)-H(14A)	0.9600	C(141)-C(143)-H(14C)	109.5

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C(143)-H(14B)	0.9600	H(14A)-C(143)-H(14C)	109.5
C(143)-H(14C)	0.9600	H(14B)-C(143)-H(14C)	109.5
C(244)-C(241)	1.498(12)	C(241)-C(244)-H(24D)	109.5
C(244)-H(24D)	0.9600	C(241)-C(244)-H(24E)	109.5
C(244)-H(24E)	0.9600	H(24D)-C(244)-H(24E)	109.5
C(244)-H(24F)	0.9600	C(241)-C(244)-H(24F)	109.5
C(22)-C(221)	1.549(8)	H(24D)-C(244)-H(24F)	109.5
C(241)-C(243)	1.518(10)	H(24E)-C(244)-H(24F)	109.5
C(123)-H(12D)	0.9600	C(21)-C(22)-C(23)	115.4(5)
C(123)-H(12E)	0.9600	C(21)-C(22)-C(221)	123.6(4)
C(123)-H(12F)	0.9600	C(23)-C(22)-C(221)	121.0(5)
C(124)-H(12G)	0.9600	C(244)-C(241)-C(242)	110.2(8)
C(124)-H(12H)	0.9600	C(244)-C(241)-C(243)	107.2(7)
C(124)-H(12I)	0.9600	C(242)-C(241)-C(243)	108.0(7)
C(344)-H(34D)	0.9600	C(244)-C(241)-C(24)	111.8(5)
C(344)-H(34E)	0.9600	C(242)-C(241)-C(24)	109.8(5)
C(344)-H(34F)	0.9600	C(243)-C(241)-C(24)	109.7(5)
C(221)-C(222)	1.561(8)	C(121)-C(123)-H(12D)	109.5
C(324)-H(32A)	0.9600	C(121)-C(123)-H(12E)	109.5
C(324)-H(32B)	0.9600	H(12D)-C(123)-H(12E)	109.5
C(324)-H(32C)	0.9600	C(121)-C(123)-H(12F)	109.5
C(142)-H(14D)	0.9600	H(12D)-C(123)-H(12F)	109.5
C(142)-H(14E)	0.9600	H(12E)-C(123)-H(12F)	109.5
C(142)-H(14F)	0.9600	C(121)-C(124)-H(12G)	109.5
C(222)-H(22G)	0.9600	C(121)-C(124)-H(12H)	109.5
C(222)-H(22H)	0.9600	H(12G)-C(124)-H(12H)	109.5
C(222)-H(22I)	0.9600	C(121)-C(124)-H(12I)	109.5
C(25)-H(25)	0.9300	H(12G)-C(124)-H(12I)	109.5
C(323)-H(32D)	0.9600	H(12H)-C(124)-H(12I)	109.5
C(323)-H(32E)	0.9600	C(341)-C(344)-H(34D)	109.5
C(323)-H(32F)	0.9600	C(341)-C(344)-H(34E)	109.5
C(069)-H(06A)	0.9600	H(34D)-C(344)-H(34E)	109.5
C(069)-H(06B)	0.9600	C(341)-C(344)-H(34F)	109.5
C(069)-H(06C)	0.9600	H(34D)-C(344)-H(34F)	109.5
C(144)-H(14G)	0.9600	H(34E)-C(344)-H(34F)	109.5
C(144)-H(14H)	0.9600	C(224)-C(221)-C(223)	108.0(5)
C(144)-H(14I)	0.9600	C(224)-C(221)-C(22)	110.7(5)
C(2)-C(3)	1.327(12)	C(223)-C(221)-C(22)	111.1(4)
C(2)-C(1)	1.419(10)	C(224)-C(221)-C(222)	109.5(5)
C(2)-H(2)	0.9300	C(223)-C(221)-C(222)	107.0(5)
C(1)-H(1)	0.9300	C(22)-C(221)-C(222)	110.4(5)
C(3)-H(3)	0.9300	C(15)-C(14)-C(13)	116.2(4)
C(243)-H(24G)	0.9600	C(15)-C(14)-C(141)	123.1(5)
C(243)-H(24H)	0.9600	C(13)-C(14)-C(141)	120.7(5)
C(243)-H(24I)	0.9600	C(321)-C(324)-H(32A)	109.5
C(343)-H(34G)	0.9600	C(321)-C(324)-H(32B)	109.5
C(343)-H(34H)	0.9600	H(32A)-C(324)-H(32B)	109.5
C(343)-H(34I)	0.9600	C(321)-C(324)-H(32C)	109.5
		H(32A)-C(324)-H(32C)	109.5
C(10)-Rh-O(4)	175.6(2)	H(32B)-C(324)-H(32C)	109.5
C(10)-Rh-N	95.9(2)	C(141)-C(142)-H(14D)	109.5
O(4)-Rh-N	80.15(16)	C(141)-C(142)-H(14E)	109.5
C(10)-Rh-P	89.34(18)	H(14D)-C(142)-H(14E)	109.5
O(4)-Rh-P	94.37(10)	C(141)-C(142)-H(14F)	109.5
N-Rh-P	172.07(12)	H(14D)-C(142)-H(14F)	109.5
O(2)-P-O(1)	105.63(17)	H(14E)-C(142)-H(14F)	109.5

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O(2)-P-O(3)	106.09(18)	C(221)-C(222)-H(22G)	109.5
O(1)-P-O(3)	92.80(16)	C(221)-C(222)-H(22H)	109.5
O(2)-P-Rh	112.78(12)	H(22G)-C(222)-H(22H)	109.5
O(1)-P-Rh	121.51(14)	C(221)-C(222)-H(22I)	109.5
O(3)-P-Rh	115.52(13)	H(22G)-C(222)-H(22I)	109.5
C(11)-O(1)-P	126.2(3)	H(22H)-C(222)-H(22I)	109.5
C(8)-O(4)-Rh	114.1(3)	C(24)-C(25)-C(26)	122.3(5)
C(21)-O(2)-P	131.4(3)	C(24)-C(25)-H(25)	118.9
O(5)-C(10)-Rh	177.8(6)	C(26)-C(25)-H(25)	118.9
C(31)-O(3)-P	123.5(3)	C(321)-C(323)-H(32D)	109.5
C(1)-N-C(9)	119.0(5)	C(321)-C(323)-H(32E)	109.5
C(1)-N-Rh	129.0(4)	H(32D)-C(323)-H(32E)	109.5
C(9)-N-Rh	111.7(3)	C(321)-C(323)-H(32F)	109.5
C(16)-C(15)-C(14)	120.9(5)	H(32D)-C(323)-H(32F)	109.5
C(16)-C(15)-H(15)	119.6	H(32E)-C(323)-H(32F)	109.5
C(14)-C(15)-H(15)	119.6	C(321)-C(069)-H(06A)	109.5
C(25)-C(26)-C(21)	119.5(6)	C(321)-C(069)-H(06B)	109.5
C(25)-C(26)-H(26)	120.2	H(06A)-C(069)-H(06B)	109.5
C(21)-C(26)-H(26)	120.2	C(321)-C(069)-H(06C)	109.5
C(14)-C(13)-C(12)	125.7(5)	H(06A)-C(069)-H(06C)	109.5
C(14)-C(13)-H(13)	117.2	H(06B)-C(069)-H(06C)	109.5
C(12)-C(13)-H(13)	117.2	C(141)-C(144)-H(14G)	109.5
C(34)-C(33)-C(32)	125.0(5)	C(141)-C(144)-H(14H)	109.5
C(34)-C(33)-H(33)	117.5	H(14G)-C(144)-H(14H)	109.5
C(32)-C(33)-H(33)	117.5	C(141)-C(144)-H(14I)	109.5
C(3)-C(4)-C(9)	117.4(6)	H(14G)-C(144)-H(14I)	109.5
C(3)-C(4)-C(5)	125.9(6)	H(14H)-C(144)-H(14I)	109.5
C(9)-C(4)-C(5)	116.8(5)	C(3)-C(2)-C(1)	120.0(6)
C(030)-C(31)-O(3)	120.6(4)	C(3)-C(2)-H(2)	120.0
C(030)-C(31)-C(32)	121.7(4)	C(1)-C(2)-H(2)	120.0
O(3)-C(31)-C(32)	117.6(4)	N-C(1)-C(2)	121.1(7)
C(030)-C(35)-C(34)	121.0(5)	N-C(1)-H(1)	119.4
C(030)-C(35)-H(35)	119.5	C(2)-C(1)-H(1)	119.4
C(34)-C(35)-H(35)	119.5	C(2)-C(3)-C(4)	120.6(6)
C(33)-C(32)-C(31)	115.0(5)	C(2)-C(3)-H(3)	119.7
C(33)-C(32)-C(321)	121.0(5)	C(4)-C(3)-H(3)	119.7
C(31)-C(32)-C(321)	124.0(4)	C(241)-C(243)-H(24G)	109.5
C(32)-C(321)-C(069)	110.1(6)	C(241)-C(243)-H(24H)	109.5
C(32)-C(321)-C(324)	112.4(6)	H(24G)-C(243)-H(24H)	109.5
C(069)-C(321)-C(324)	109.4(7)	C(241)-C(243)-H(24I)	109.5
C(32)-C(321)-C(323)	108.7(5)	H(24G)-C(243)-H(24I)	109.5
C(069)-C(321)-C(323)	110.7(7)	H(24H)-C(243)-H(24I)	109.5
C(324)-C(321)-C(323)	105.3(8)	C(341)-C(343)-H(34G)	109.5
C(8)-C(7)-C(6)	121.0(6)	C(341)-C(343)-H(34H)	109.5
C(8)-C(7)-H(7)	119.5	H(34G)-C(343)-H(34H)	109.5
C(6)-C(7)-H(7)	119.5	C(341)-C(343)-H(34I)	109.5
C(24)-C(23)-C(22)	124.8(5)	H(34G)-C(343)-H(34I)	109.5
C(24)-C(23)-H(23)	117.6	H(34H)-C(343)-H(34I)	109.5

Table E2. 3 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{oxCl})(\text{CO})(\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3)]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh	40(1)	36(1)	51(1)	2(1)	3(1)	-1(1)
P	32(1)	40(1)	41(1)	-2(1)	3(1)	-3(1)
Cl	78(1)	141(2)	109(2)	-62(1)	-6(1)	41(1)
O(1)	33(2)	61(2)	47(2)	-13(2)	7(1)	-9(1)
O(4)	77(3)	46(2)	52(2)	-1(2)	6(2)	20(2)
O(2)	45(2)	38(2)	41(2)	-2(1)	2(1)	6(1)
C(10)	59(3)	46(3)	72(4)	6(3)	9(3)	2(2)
O(3)	35(2)	49(2)	47(2)	-7(1)	3(1)	-9(1)
N	51(2)	37(2)	69(3)	3(2)	-5(2)	2(2)
C(15)	41(3)	59(3)	57(3)	-18(2)	6(2)	-9(2)
O(5)	113(4)	93(4)	68(3)	32(3)	4(3)	-2(3)
C(26)	73(4)	58(3)	53(3)	-9(3)	-3(3)	19(3)
C(13)	39(3)	52(3)	56(3)	-3(2)	10(2)	-9(2)
C(33)	42(3)	72(3)	66(4)	-18(3)	-2(3)	-15(3)
C(4)	53(3)	51(3)	75(4)	-20(3)	-14(3)	6(2)
C(31)	29(2)	39(2)	57(3)	-3(2)	-3(2)	-2(2)
C(35)	49(3)	63(3)	60(3)	-10(3)	16(2)	-11(2)
C(32)	44(3)	48(3)	55(3)	-7(2)	-3(2)	-3(2)
C(321)	51(2)	88(3)	79(3)	-26(3)	7(2)	-17(2)
C(7)	92(5)	52(3)	61(4)	-6(3)	3(3)	8(3)
C(23)	44(3)	43(3)	67(3)	7(2)	6(2)	1(2)
C(223)	99(5)	74(4)	55(4)	5(3)	7(3)	23(3)
C(121)	57(3)	88(4)	50(3)	-17(3)	16(3)	-24(3)
C(224)	55(3)	58(3)	62(3)	-1(3)	15(2)	8(2)
C(9)	42(2)	39(2)	59(3)	-8(2)	-3(2)	-3(2)
C(5)	52(3)	75(4)	74(4)	-31(3)	-1(3)	4(3)
C(122)	103(5)	166(9)	59(4)	-29(5)	35(4)	-59(6)
C(030)	37(2)	59(3)	50(3)	-4(2)	7(2)	-11(2)
C(21)	34(2)	41(2)	52(3)	-6(2)	6(2)	5(2)
C(12)	41(2)	52(3)	48(3)	-7(2)	10(2)	-5(2)
C(242)	98(6)	56(4)	241(14)	24(6)	60(7)	33(4)
C(11)	35(2)	44(3)	48(3)	-3(2)	6(2)	-4(2)
C(141)	37(3)	49(3)	77(4)	-4(3)	4(2)	-8(2)
C(16)	44(3)	63(3)	48(3)	-15(2)	11(2)	-8(2)
C(34)	42(3)	59(3)	79(4)	-7(3)	4(3)	-6(2)
C(8)	53(3)	41(3)	58(3)	-6(2)	5(2)	6(2)
C(341)	51(2)	88(3)	79(3)	-26(3)	7(2)	-17(2)
C(342)	76(4)	311(12)	216(9)	10(8)	38(5)	-64(6)
C(24)	45(3)	38(3)	81(4)	-6(3)	8(3)	5(2)
C(6)	73(4)	76(4)	61(4)	-21(3)	13(3)	-3(3)
C(143)	44(3)	103(6)	132(7)	-30(5)	16(4)	-5(3)
C(244)	218(12)	63(4)	124(8)	1(5)	-29(8)	68(7)
C(22)	33(2)	42(3)	54(3)	2(2)	3(2)	1(2)
C(241)	59(2)	45(2)	73(3)	-1(2)	10(2)	8(2)
C(123)	92(5)	172(9)	51(4)	-1(5)	-12(4)	-1(6)
C(124)	109(6)	103(6)	82(5)	-51(4)	35(4)	-35(5)
C(344)	76(4)	311(12)	216(9)	10(8)	38(5)	-64(6)
C(221)	59(2)	45(2)	73(3)	-1(2)	10(2)	8(2)
C(14)	36(2)	40(3)	65(3)	-5(2)	10(2)	-5(2)
C(324)	81(6)	339(19)	80(6)	-78(8)	1(5)	-56(8)
C(142)	85(5)	73(5)	137(7)	36(5)	-30(5)	-33(4)

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C(222)	77(4)	71(4)	58(3)	-16(3)	2(3)	-21(3)
C(25)	78(4)	51(3)	76(4)	-22(3)	10(3)	18(3)
C(323)	205(11)	108(7)	63(5)	5(5)	14(6)	3(7)
C(069)	97(6)	116(7)	85(5)	-28(4)	17(4)	13(5)
C(144)	61(4)	83(5)	91(5)	-3(4)	-17(3)	-24(3)
C(2)	106(6)	64(4)	102(6)	4(4)	-6(5)	37(4)
C(1)	82(4)	46(3)	79(4)	10(3)	1(3)	12(3)
C(3)	74(4)	60(4)	105(6)	-21(4)	-16(4)	25(3)
C(243)	110(6)	55(4)	160(9)	-25(5)	19(6)	-1(4)
C(343)	76(4)	311(12)	216(9)	10(8)	38(5)	-64(6)

Table E2. 4 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{oxCl})(\text{CO})(\text{P}(\text{O}-2,4\text{di}^t\text{BuPh})_3)]$.

	x	y	z	U(eq)
H(15)	5113	3950	4985	63
H(26)	3135	1095	3836	74
H(13)	5594	3679	2902	59
H(33)	-142	1152	2930	72
H(35)	105	1704	5010	68
H(7)	1517	3658	6792	82
H(23)	3530	38	6105	62
H(22A)	3191	1468	7381	114
H(22B)	3779	936	6934	114
H(22C)	2920	643	7012	114
H(22D)	2063	2211	5953	88
H(22E)	2089	2089	6790	88
H(22F)	1882	1339	6288	88
H(12A)	5449	2735	1988	164
H(12B)	5137	3636	1857	164
H(12C)	4854	2902	1368	164
H(030)	1367	2103	4797	58
H(24A)	5059	-870	4908	197
H(24B)	4572	-1074	4218	197
H(24C)	4843	-1792	4730	197
H(16)	3928	3350	4792	62
H(34A)	-1069	-156	4179	302
H(34B)	-703	131	3448	302
H(34C)	-1595	216	3572	302
H(6)	733	4609	7357	84
H(14A)	6918	3248	3902	140
H(14B)	7410	4053	3785	140
H(14C)	6825	3765	3192	140
H(24D)	3622	-1259	6189	203
H(24E)	4496	-1031	6098	203
H(24F)	4215	-1939	5945	203
H(12D)	3551	3208	1594	158
H(12E)	3674	3916	2162	158
H(12F)	3179	3134	2361	158
H(12G)	3835	1819	2765	147
H(12H)	4700	1681	2551	147
H(12I)	4065	1736	1952	147
H(34D)	-1728	1051	4945	302
H(34E)	-955	1504	5140	302

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H(34F)	-976	533	5082	302
H(32A)	450	662	2017	250
H(32B)	844	1144	1382	250
H(32C)	185	1568	1829	250
H(14D)	6212	5130	3206	147
H(14E)	6709	5481	3842	147
H(14F)	5807	5465	3903	147
H(22G)	3366	2770	5903	103
H(22H)	4068	2270	6212	103
H(22I)	3479	2691	6738	103
H(25)	3581	-238	3985	82
H(32D)	914	2720	2014	188
H(32E)	1679	2400	1658	188
H(32F)	1685	2722	2455	188
H(06A)	2343	1278	2602	149
H(06B)	2084	923	1853	149
H(06C)	1828	479	2566	149
H(14G)	6085	4695	5103	117
H(14H)	6962	4747	4897	117
H(14I)	6586	3885	5072	117
H(2)	417	6607	4371	109
H(1)	1215	5600	3849	83
H(3)	109	6529	5548	96
H(24G)	3565	-2306	4873	162
H(24H)	3239	-1621	4355	162
H(24I)	2891	-1728	5129	162
H(34G)	-1274	1930	3346	302
H(34H)	-1645	2116	4099	302
H(34I)	-1975	1399	3618	302

E3. Crystal data of
Carbonyl[tris(para chloro phenyl)phosphine]
(5-chloro-8-hydroxyquinolino)rhodium(I),
[Rh(oxCl)(CO)P(p-ClPh)₃]

Table E3. 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Rh(oxCl)(CO)P(p-ClPh)₃]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-1624(4)	428(2)	-917(2)	21(1)
C(2)	-1670(4)	-81(2)	-1592(2)	25(1)
C(3)	-468(4)	-222(2)	-1899(2)	24(1)
C(4)	823(4)	128(1)	-1526(2)	21(1)
C(5)	2164(4)	5(2)	-1737(2)	26(1)
C(6)	3369(4)	336(2)	-1267(2)	29(1)
C(7)	3318(4)	833(2)	-591(2)	26(1)
C(8)	2036(4)	1005(1)	-387(2)	19(1)
C(9)	780(4)	635(2)	-846(2)	18(1)
C(10)	-1950(4)	1606(2)	567(2)	21(1)
C(11)	-802(3)	2758(1)	2006(2)	14(1)
C(12)	-1370(3)	2343(2)	2598(2)	19(1)
C(13)	-2469(3)	2558(2)	2985(2)	22(1)
C(14)	-3032(3)	3192(2)	2759(2)	19(1)
C(15)	-2514(3)	3616(2)	2172(2)	21(1)
C(16)	-1378(3)	3403(2)	1807(2)	19(1)
C(21)	2029(3)	2205(1)	2481(2)	15(1)
C(22)	3095(3)	1762(1)	2356(2)	19(1)
C(23)	4229(3)	1599(2)	3101(2)	24(1)
C(24)	4294(3)	1880(2)	3974(2)	20(1)
C(25)	3261(3)	2325(2)	4116(2)	20(1)
C(26)	2132(3)	2486(2)	3365(2)	18(1)
C(31)	1206(3)	3143(1)	928(2)	17(1)
C(32)	440(4)	3353(2)	45(2)	25(1)
C(33)	851(4)	3930(2)	-367(2)	34(1)
C(34)	2040(4)	4277(2)	99(2)	27(1)
C(35)	2825(4)	4074(2)	963(2)	36(1)
C(36)	2384(4)	3509(2)	1379(2)	31(1)
N	-451(3)	780(1)	-558(2)	18(1)
O(1)	1899(2)	1485(1)	218(1)	21(1)
O(2)	-3131(2)	1613(1)	630(2)	33(1)
P	560(1)	2412(1)	1464(1)	15(1)
Cl(1)	-4442(1)	3463(1)	3227(1)	27(1)
Cl	2285(1)	-575(1)	-2615(1)	39(1)
Cl(2)	5746(1)	1690(1)	4909(1)	32(1)
Cl(3)	2588(1)	4992(1)	-421(1)	51(1)
Rh	-125(1)	1563(1)	433(1)	16(1)

Table E3. 2 Bond lengths (Å) and angles (°) for [Rh(oxCl)(CO)P(p-ClPh)₃]

C(1)-N	1.319(4)	C(8)-C(7)-H(7)	119.7
C(1)-C(2)	1.401(4)	C(6)-C(7)-H(7)	119.7
C(1)-H(1)	0.9300	O(1)-C(8)-C(7)	123.8(3)
C(2)-C(3)	1.357(5)	O(1)-C(8)-C(9)	118.4(3)
C(2)-H(2)	0.9300	C(7)-C(8)-C(9)	117.8(3)
C(3)-C(4)	1.408(4)	N-C(9)-C(4)	122.1(3)
C(3)-H(3)	0.9300	N-C(9)-C(8)	115.9(3)
C(4)-C(5)	1.409(5)	C(4)-C(9)-C(8)	121.9(3)
C(4)-C(9)	1.420(4)	O(2)-C(10)-Rh	177.4(3)
C(5)-C(6)	1.361(5)	C(12)-C(11)-C(16)	118.5(3)
C(5)-Cl	1.745(3)	C(12)-C(11)-P	118.3(2)
C(6)-C(7)	1.403(4)	C(16)-C(11)-P	123.0(2)
C(6)-H(6)	0.9300	C(13)-C(12)-C(11)	121.4(3)
C(7)-C(8)	1.370(5)	C(13)-C(12)-H(12)	119.3
C(7)-H(7)	0.9300	C(11)-C(12)-H(12)	119.3
C(8)-O(1)	1.326(3)	C(12)-C(13)-C(14)	118.6(3)
C(8)-C(9)	1.430(4)	C(12)-C(13)-H(13)	120.7
C(9)-N	1.370(4)	C(14)-C(13)-H(13)	120.7
C(10)-O(2)	1.154(4)	C(15)-C(14)-C(13)	121.9(3)
C(10)-Rh	1.803(4)	C(15)-C(14)-Cl(1)	119.1(2)
C(11)-C(12)	1.392(4)	C(13)-C(14)-Cl(1)	119.0(2)
C(11)-C(16)	1.393(4)	C(14)-C(15)-C(16)	119.1(3)
C(11)-P	1.811(3)	C(14)-C(15)-H(15)	120.4
C(12)-C(13)	1.372(4)	C(16)-C(15)-H(15)	120.4
C(12)-H(12)	0.9300	C(15)-C(16)-C(11)	120.4(3)
C(13)-C(14)	1.376(4)	C(15)-C(16)-H(16)	119.8
C(13)-H(13)	0.9300	C(11)-C(16)-H(16)	119.8
C(14)-C(15)	1.373(4)	C(22)-C(21)-C(26)	118.9(3)
C(14)-Cl(1)	1.734(3)	C(22)-C(21)-P	118.7(2)
C(15)-C(16)	1.383(4)	C(26)-C(21)-P	122.4(2)
C(15)-H(15)	0.9300	C(23)-C(22)-C(21)	120.5(3)
C(16)-H(16)	0.9300	C(23)-C(22)-H(22)	119.7
C(21)-C(22)	1.387(4)	C(21)-C(22)-H(22)	119.7
C(21)-C(26)	1.389(4)	C(24)-C(23)-C(22)	119.3(3)
C(21)-P	1.833(3)	C(24)-C(23)-H(23)	120.4
C(22)-C(23)	1.381(4)	C(22)-C(23)-H(23)	120.4
C(22)-H(22)	0.9300	C(25)-C(24)-C(23)	121.4(3)
C(23)-C(24)	1.379(4)	C(25)-C(24)-Cl(2)	119.2(2)
C(23)-H(23)	0.9300	C(23)-C(24)-Cl(2)	119.4(2)
C(24)-C(25)	1.375(4)	C(24)-C(25)-C(26)	118.8(3)
C(24)-Cl(2)	1.744(3)	C(24)-C(25)-H(25)	120.6
C(25)-C(26)	1.382(4)	C(26)-C(25)-H(25)	120.6
C(25)-H(25)	0.9300	C(25)-C(26)-C(21)	121.1(3)
C(26)-H(26)	0.9300	C(25)-C(26)-H(26)	119.5
C(31)-C(36)	1.371(4)	C(21)-C(26)-H(26)	119.5
C(31)-C(32)	1.388(4)	C(36)-C(31)-C(32)	118.7(3)
C(31)-P	1.820(3)	C(36)-C(31)-P	122.5(2)
C(32)-C(33)	1.390(4)	C(32)-C(31)-P	118.7(2)
C(32)-H(32)	0.9300	C(31)-C(32)-C(33)	120.6(3)
C(33)-C(34)	1.364(5)	C(31)-C(32)-H(32)	119.7
C(33)-H(33)	0.9300	C(33)-C(32)-H(32)	119.7
C(34)-C(35)	1.368(4)	C(34)-C(33)-C(32)	119.0(3)
C(34)-Cl(3)	1.746(3)	C(34)-C(33)-H(33)	120.5
C(35)-C(36)	1.384(4)	C(32)-C(33)-H(33)	120.5

C(35)-H(35)	0.9300	C(33)-C(34)-C(35)	121.6(3)
C(36)-H(36)	0.9300	C(33)-C(34)-Cl(3)	119.4(3)
N-Rh	2.093(2)	C(35)-C(34)-Cl(3)	118.9(3)
O(1)-Rh	2.038(2)	C(34)-C(35)-C(36)	118.9(3)
P-Rh	2.2478(9)	C(34)-C(35)-H(35)	120.5
		C(36)-C(35)-H(35)	120.5
N-C(1)-C(2)	122.8(3)	C(31)-C(36)-C(35)	121.2(3)
N-C(1)-H(1)	118.6	C(31)-C(36)-H(36)	119.4
C(2)-C(1)-H(1)	118.6	C(35)-C(36)-H(36)	119.4
C(3)-C(2)-C(1)	119.5(3)	C(1)-N-C(9)	118.6(3)
C(3)-C(2)-H(2)	120.2	C(1)-N-Rh	129.8(2)
C(1)-C(2)-H(2)	120.2	C(9)-N-Rh	111.65(19)
C(2)-C(3)-C(4)	120.2(3)	C(8)-O(1)-Rh	113.82(19)
C(2)-C(3)-H(3)	119.9	C(11)-P-C(31)	103.86(14)
C(4)-C(3)-H(3)	119.9	C(11)-P-C(21)	102.88(13)
C(3)-C(4)-C(5)	126.2(3)	C(31)-P-C(21)	104.69(14)
C(3)-C(4)-C(9)	116.8(3)	C(11)-P-Rh	116.73(10)
C(5)-C(4)-C(9)	117.0(3)	C(31)-P-Rh	112.33(10)
C(6)-C(5)-C(4)	120.8(3)	C(21)-P-Rh	114.94(10)
C(6)-C(5)-Cl	119.5(3)	C(10)-Rh-O(1)	176.92(11)
C(4)-C(5)-Cl	119.8(3)	C(10)-Rh-N	96.90(12)
C(5)-C(6)-C(7)	121.8(3)	O(1)-Rh-N	80.15(9)
C(5)-C(6)-H(6)	119.1	C(10)-Rh-P	91.62(10)
C(7)-C(6)-H(6)	119.1	O(1)-Rh-P	91.33(6)
C(8)-C(7)-C(6)	120.5(3)	N-Rh-P	171.45(8)

Table E3. 3 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-ClPh})_3]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U¹¹	U²²	U³³	U²³	U¹³	U¹²
C(1)	22(2)	19(2)	20(2)	4(1)	-1(1)	0(2)
C(2)	32(2)	15(2)	21(2)	1(1)	-5(2)	-5(2)
C(3)	42(2)	13(2)	14(2)	-2(1)	2(2)	-2(2)
C(4)	38(2)	9(2)	14(2)	2(1)	6(1)	-4(2)
C(5)	45(2)	14(2)	25(2)	-4(1)	20(2)	-3(2)
C(6)	38(2)	19(2)	39(2)	-4(2)	25(2)	-5(2)
C(7)	30(2)	23(2)	28(2)	-5(1)	13(2)	-9(2)
C(8)	31(2)	12(2)	16(2)	1(1)	9(1)	-6(1)
C(9)	29(2)	12(2)	14(1)	3(1)	7(1)	-4(1)
C(10)	30(2)	15(2)	16(2)	-3(1)	-1(1)	1(2)
C(11)	14(2)	13(2)	14(1)	-2(1)	-1(1)	-2(1)
C(12)	17(2)	14(2)	24(2)	3(1)	4(1)	1(1)
C(13)	22(2)	22(2)	20(2)	2(1)	5(1)	-6(2)
C(14)	15(2)	26(2)	16(2)	-6(1)	2(1)	-2(1)
C(15)	26(2)	15(2)	19(2)	-2(1)	3(1)	4(1)
C(16)	25(2)	17(2)	14(1)	-2(1)	3(1)	-6(2)
C(21)	16(2)	11(2)	15(2)	2(1)	2(1)	-1(1)
C(22)	23(2)	15(2)	19(2)	-3(1)	6(1)	0(1)
C(23)	23(2)	14(2)	32(2)	-3(1)	4(1)	5(2)
C(24)	17(2)	18(2)	22(2)	8(1)	2(1)	-6(1)
C(25)	23(2)	23(2)	14(2)	0(1)	4(1)	0(2)
C(26)	17(2)	16(2)	23(2)	0(1)	6(1)	2(1)
C(31)	22(2)	13(2)	18(2)	0(1)	9(1)	1(1)

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C(32)	30(2)	24(2)	20(2)	0(1)	5(1)	-9(2)
C(33)	46(3)	34(2)	21(2)	10(2)	5(2)	-5(2)
C(34)	36(2)	16(2)	32(2)	10(1)	16(2)	-4(2)
C(35)	33(2)	28(2)	41(2)	7(2)	-4(2)	-16(2)
C(36)	32(2)	27(2)	28(2)	11(2)	-7(2)	-9(2)
N	26(2)	12(1)	14(1)	1(1)	0(1)	-2(1)
O(1)	29(1)	17(1)	20(1)	-6(1)	11(1)	-7(1)
O(2)	24(1)	39(2)	34(1)	-6(1)	4(1)	-2(1)
P	19(1)	11(1)	15(1)	-1(1)	3(1)	-1(1)
Cl(1)	21(1)	34(1)	27(1)	-7(1)	8(1)	2(1)
Cl	58(1)	25(1)	41(1)	-16(1)	27(1)	-9(1)
Cl(2)	28(1)	34(1)	28(1)	8(1)	-5(1)	4(1)
Cl(3)	68(1)	30(1)	56(1)	21(1)	18(1)	-13(1)
Rh	22(1)	12(1)	14(1)	-1(1)	3(1)	-3(1)

Table E3. 4 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-ClPh})_3]$.

	x	y	z	U(eq)
H(1)	-2456	520	-713	25
H(2)	-2516	-319	-1827	30
H(3)	-498	-551	-2358	29
H(6)	4249	230	-1398	35
H(7)	4162	1048	-278	31
H(12)	-998	1910	2733	23
H(13)	-2825	2280	3391	26
H(15)	-2921	4040	2021	25
H(16)	-996	3692	1427	23
H(22)	3046	1575	1765	23
H(23)	4941	1301	3016	28
H(25)	3321	2514	4707	24
H(26)	1430	2788	3454	22
H(32)	-355	3106	-273	29
H(33)	324	4077	-952	41
H(35)	3643	4312	1267	43
H(36)	2896	3376	1975	38

E4. Crystal data of
Carbonyl[tris(para fluoro phenyl)phosphine]
(5-chloro-8-hydroxyquinolinato)rhodium(I),
[Rh(oxCl)(CO)P(p-FPh)₃]

Table E4. 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Rh(oxCl)(CO)P(p-FPh)₃]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh(2)	5419(1)	2425(1)	1637(1)	41(1)
Rh(1)	2904(1)	1530(1)	3802(1)	42(1)
P(2)	5962(1)	3775(1)	1873(1)	42(1)
P(1)	1183(1)	2092(1)	3777(1)	45(1)
Cl(1)	6877(1)	-2750(1)	3486(1)	82(1)
Cl(2)	7085(1)	-2595(1)	826(1)	100(1)
N(1)	4457(2)	775(2)	3826(2)	39(1)
F(12)	-213(2)	957(2)	347(2)	92(1)
C(12)	6262(2)	500(2)	3897(2)	52(1)
F(21)	3133(2)	7716(1)	1424(2)	79(1)
O(21)	6871(2)	1524(1)	1690(2)	52(1)
O(11)	2802(2)	116(1)	3695(2)	52(1)
C(221)	6278(2)	3843(2)	3062(2)	43(1)
C(24)	6046(3)	-676(2)	1187(2)	52(1)
F(22)	7297(2)	3855(2)	5633(2)	101(1)
C(231)	7183(2)	3797(2)	1125(2)	46(1)
C(18)	3705(2)	-544(2)	3645(2)	44(1)
C(1)	3044(2)	2759(2)	3919(2)	52(1)
C(211)	5103(2)	4987(2)	1711(2)	43(1)
C(134)	-589(4)	1387(3)	6594(3)	86(1)
C(15)	5668(3)	-1895(2)	3557(2)	56(1)
C(131)	453(2)	1773(2)	4868(2)	50(1)
N(2)	5143(2)	1062(2)	1424(2)	44(1)
C(19)	4609(2)	-226(2)	3716(2)	38(1)
C(121)	713(2)	1643(2)	2785(2)	47(1)
O(22)	3328(2)	3632(2)	1395(2)	79(1)
C(232)	7535(2)	3185(2)	342(2)	54(1)
C(11)	5266(2)	1117(2)	3909(2)	45(1)
C(111)	618(2)	3409(2)	3646(2)	51(1)
C(22)	4209(3)	-111(3)	1176(2)	62(1)
C(216)	4163(3)	5291(2)	2315(2)	56(1)
C(222)	6769(2)	2973(2)	3467(2)	51(1)
C(14)	5606(2)	-889(2)	3680(2)	45(1)
F(11)	-778(2)	6232(2)	2935(2)	128(1)
C(2)	4137(3)	3174(2)	1515(2)	52(1)
C(214)	3777(3)	6801(2)	1510(2)	55(1)
C(29)	6030(2)	316(2)	1363(2)	43(1)
C(16)	4807(3)	-2200(2)	3478(3)	63(1)
C(233)	8457(3)	3184(3)	-244(3)	72(1)
C(212)	5341(2)	5611(2)	983(2)	49(1)
F(23)	9928(2)	3781(2)	-580(2)	126(1)
C(124)	88(3)	1159(3)	1164(3)	62(1)

C(28)	6944(2)	588(2)	1502(2)	48(1)
C(223)	7103(3)	2979(3)	4337(2)	64(1)
C(17)	3831(3)	-1540(2)	3518(2)	55(1)
C(224)	6937(3)	3855(3)	4789(2)	65(1)
C(122)	-296(3)	2035(2)	2599(3)	64(1)
C(21)	4259(3)	851(2)	1326(2)	53(1)
C(116)	-273(3)	3939(2)	4208(3)	63(1)
C(136)	-326(3)	1293(2)	4917(3)	61(1)
C(234)	9009(3)	3796(4)	-18(3)	83(1)
O(12)	3154(2)	3533(2)	4003(2)	79(1)
C(215)	3494(3)	6211(3)	2217(2)	61(1)
C(25)	7011(3)	-1378(2)	1111(3)	62(1)
C(235)	8699(3)	4412(3)	749(4)	89(1)
F(13)	-1109(2)	1216(2)	7449(2)	132(1)
C(125)	1074(3)	739(3)	1312(3)	69(1)
C(126)	1386(3)	979(3)	2134(2)	61(1)
C(23)	5081(3)	-857(3)	1099(2)	61(1)
C(213)	4667(3)	6529(2)	884(2)	56(1)
C(236)	7777(3)	4417(3)	1324(3)	72(1)
C(13)	6438(2)	-491(2)	3783(2)	51(1)
C(225)	6446(3)	4724(3)	4432(3)	75(1)
C(112)	1047(3)	3862(2)	2868(3)	67(1)
C(27)	7857(3)	-146(2)	1439(3)	61(1)
C(26)	7889(3)	-1120(3)	1230(3)	70(1)
C(123)	-616(3)	1787(3)	1793(3)	69(1)
C(132)	708(3)	2035(3)	5714(3)	73(1)
C(226)	6126(3)	4715(2)	3559(3)	67(1)
C(115)	-733(3)	4909(3)	3969(3)	81(1)
C(114)	-293(3)	5304(3)	3191(4)	82(1)
C(113)	592(3)	4821(3)	2636(3)	82(1)
C(135)	-848(3)	1087(3)	5793(3)	77(1)
C(133)	179(4)	1850(3)	6586(3)	92(1)

Table E4. 2 Bond lengths (Å) and angles (°) for [Rh(oxCl)(CO)P(p-FPh)₃]

Rh(2)-C(2)	1.802(4)	C(232)-C(231)-P(2)	119.6(2)
Rh(2)-O(21)	2.043(2)	C(236)-C(231)-P(2)	121.8(3)
Rh(2)-N(2)	2.084(2)	O(11)-C(18)-C(17)	123.5(3)
Rh(2)-P(2)	2.2559(10)	O(11)-C(18)-C(19)	119.0(2)
Rh(1)-C(1)	1.803(3)	C(17)-C(18)-C(19)	117.4(3)
Rh(1)-O(11)	2.040(2)	O(12)-C(1)-Rh(1)	178.4(3)
Rh(1)-N(1)	2.088(2)	C(212)-C(211)-C(216)	118.5(3)
Rh(1)-P(1)	2.2497(11)	C(212)-C(211)-P(2)	122.2(2)
P(2)-C(221)	1.817(3)	C(216)-C(211)-P(2)	119.2(2)
P(2)-C(211)	1.822(3)	C(135)-C(134)-F(13)	119.1(4)
P(2)-C(231)	1.823(3)	C(135)-C(134)-C(133)	123.1(4)
P(1)-C(131)	1.812(3)	F(13)-C(134)-C(133)	117.8(5)
P(1)-C(111)	1.823(3)	C(16)-C(15)-C(14)	121.1(3)
P(1)-C(121)	1.825(3)	C(16)-C(15)-Cl(1)	120.0(3)
Cl(1)-C(15)	1.743(3)	C(14)-C(15)-Cl(1)	118.9(3)
Cl(2)-C(25)	1.745(3)	C(136)-C(131)-C(132)	118.1(3)
N(1)-C(11)	1.323(3)	C(136)-C(131)-P(1)	125.2(3)
N(1)-C(19)	1.377(3)	C(132)-C(131)-P(1)	116.7(2)
F(12)-C(124)	1.350(4)	C(21)-N(2)-C(29)	118.7(3)

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C(12)-C(13)	1.360(4)	C(21)-N(2)-Rh(2)	129.3(2)
C(12)-C(11)	1.391(4)	C(29)-N(2)-Rh(2)	111.97(18)
C(12)-H(12)	0.9300	N(1)-C(19)-C(14)	121.7(3)
F(21)-C(214)	1.362(3)	N(1)-C(19)-C(18)	115.8(2)
O(21)-C(28)	1.325(3)	C(14)-C(19)-C(18)	122.5(3)
O(11)-C(18)	1.316(3)	C(126)-C(121)-C(122)	117.7(3)
C(221)-C(222)	1.383(4)	C(126)-C(121)-P(1)	120.6(2)
C(221)-C(226)	1.388(4)	C(122)-C(121)-P(1)	121.4(2)
C(24)-C(25)	1.402(5)	C(231)-C(232)-C(233)	121.3(3)
C(24)-C(23)	1.412(5)	C(231)-C(232)-H(232)	119.4
C(24)-C(29)	1.418(4)	C(233)-C(232)-H(232)	119.4
F(22)-C(224)	1.361(4)	N(1)-C(11)-C(12)	122.3(3)
C(231)-C(232)	1.374(4)	N(1)-C(11)-H(11)	118.9
C(231)-C(236)	1.390(4)	C(12)-C(11)-H(11)	118.9
C(18)-C(17)	1.380(4)	C(116)-C(111)-C(112)	118.9(3)
C(18)-C(19)	1.421(4)	C(116)-C(111)-P(1)	123.7(3)
C(1)-O(12)	1.148(3)	C(112)-C(111)-P(1)	116.9(2)
C(211)-C(212)	1.388(4)	C(23)-C(22)-C(21)	120.0(3)
C(211)-C(216)	1.388(4)	C(23)-C(22)-H(22)	120.0
C(134)-C(135)	1.351(6)	C(21)-C(22)-H(22)	120.0
C(134)-F(13)	1.354(4)	C(215)-C(216)-C(211)	120.8(3)
C(134)-C(133)	1.356(6)	C(215)-C(216)-H(216)	119.6
C(15)-C(16)	1.358(5)	C(211)-C(216)-H(216)	119.6
C(15)-C(14)	1.409(4)	C(223)-C(222)-C(221)	120.7(3)
C(131)-C(136)	1.380(4)	C(223)-C(222)-H(222)	119.6
C(131)-C(132)	1.388(5)	C(221)-C(222)-H(222)	119.6
N(2)-C(21)	1.328(4)	C(13)-C(14)-C(15)	126.1(3)
N(2)-C(29)	1.361(4)	C(13)-C(14)-C(19)	117.3(3)
C(19)-C(14)	1.414(4)	C(15)-C(14)-C(19)	116.6(3)
C(121)-C(126)	1.379(4)	O(22)-C(2)-Rh(2)	176.7(3)
C(121)-C(122)	1.388(4)	C(213)-C(214)-C(215)	123.3(3)
O(22)-C(2)	1.146(4)	C(213)-C(214)-F(21)	118.2(3)
C(232)-C(233)	1.384(5)	C(215)-C(214)-F(21)	118.4(3)
C(232)-H(232)	0.9300	N(2)-C(29)-C(24)	122.4(3)
C(11)-H(11)	0.9300	N(2)-C(29)-C(28)	115.8(3)
C(111)-C(116)	1.381(4)	C(24)-C(29)-C(28)	121.8(3)
C(111)-C(112)	1.382(4)	C(15)-C(16)-C(17)	121.7(3)
C(22)-C(23)	1.346(5)	C(15)-C(16)-H(16)	119.1
C(22)-C(21)	1.396(4)	C(17)-C(16)-H(16)	119.1
C(22)-H(22)	0.9300	C(234)-C(233)-C(232)	117.9(4)
C(216)-C(215)	1.386(4)	C(234)-C(233)-H(233)	121.0
C(216)-H(216)	0.9300	C(232)-C(233)-H(233)	121.0
C(222)-C(223)	1.380(4)	C(213)-C(212)-C(211)	120.5(3)
C(222)-H(222)	0.9300	C(213)-C(212)-H(212)	119.8
C(14)-C(13)	1.405(4)	C(211)-C(212)-H(212)	119.8
F(11)-C(114)	1.362(4)	F(12)-C(124)-C(125)	118.9(3)
C(214)-C(213)	1.352(5)	F(12)-C(124)-C(123)	118.0(3)
C(214)-C(215)	1.356(5)	C(125)-C(124)-C(123)	123.1(3)
C(29)-C(28)	1.425(4)	O(21)-C(28)-C(27)	123.7(3)
C(16)-C(17)	1.390(4)	O(21)-C(28)-C(29)	118.8(3)
C(16)-H(16)	0.9300	C(27)-C(28)-C(29)	117.5(3)
C(233)-C(234)	1.351(6)	C(224)-C(223)-C(222)	118.7(3)
C(233)-H(233)	0.9300	C(224)-C(223)-H(223)	120.6
C(212)-C(213)	1.387(4)	C(222)-C(223)-H(223)	120.6
C(212)-H(212)	0.9300	C(18)-C(17)-C(16)	120.7(3)
F(23)-C(234)	1.361(4)	C(18)-C(17)-H(17)	119.6

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C(124)-C(125)	1.350(5)	C(16)-C(17)-H(17)	119.6
C(124)-C(123)	1.353(5)	C(225)-C(224)-C(223)	122.9(3)
C(28)-C(27)	1.375(4)	C(225)-C(224)-F(22)	118.9(3)
C(223)-C(224)	1.359(5)	C(223)-C(224)-F(22)	118.2(4)
C(223)-H(223)	0.9300	C(123)-C(122)-C(121)	121.7(3)
C(17)-H(17)	0.9300	C(123)-C(122)-H(122)	119.2
C(224)-C(225)	1.351(5)	C(121)-C(122)-H(122)	119.2
C(122)-C(123)	1.370(5)	N(2)-C(21)-C(22)	122.1(3)
C(122)-H(122)	0.9300	N(2)-C(21)-H(21)	118.9
C(21)-H(21)	0.9300	C(22)-C(21)-H(21)	118.9
C(116)-C(115)	1.396(5)	C(111)-C(116)-C(115)	119.6(4)
C(116)-H(116)	0.9300	C(111)-C(116)-H(116)	120.2
C(136)-C(135)	1.393(5)	C(115)-C(116)-H(116)	120.2
C(136)-H(136)	0.9300	C(131)-C(136)-C(135)	120.8(4)
C(234)-C(235)	1.358(6)	C(131)-C(136)-H(136)	119.6
C(215)-H(215)	0.9300	C(135)-C(136)-H(136)	119.6
C(25)-C(26)	1.359(5)	C(233)-C(234)-C(235)	123.2(4)
C(235)-C(236)	1.377(5)	C(233)-C(234)-F(23)	118.1(4)
C(235)-H(235)	0.9300	C(235)-C(234)-F(23)	118.7(4)
C(125)-C(126)	1.381(5)	C(214)-C(215)-C(216)	118.2(3)
C(125)-H(125)	0.9300	C(214)-C(215)-H(215)	120.9
C(126)-H(126)	0.9300	C(216)-C(215)-H(215)	120.9
C(23)-H(23)	0.9300	C(26)-C(25)-C(24)	121.2(3)
C(213)-H(213)	0.9300	C(26)-C(25)-Cl(2)	119.7(3)
C(236)-H(236)	0.9300	C(24)-C(25)-Cl(2)	119.1(3)
C(13)-H(13)	0.9300	C(234)-C(235)-C(236)	118.6(4)
C(225)-C(226)	1.375(5)	C(234)-C(235)-H(235)	120.7
C(225)-H(225)	0.9300	C(236)-C(235)-H(235)	120.7
C(112)-C(113)	1.380(5)	C(124)-C(125)-C(126)	118.4(3)
C(112)-H(112)	0.9300	C(124)-C(125)-H(125)	120.8
C(27)-C(26)	1.400(4)	C(126)-C(125)-H(125)	120.8
C(27)-H(27)	0.9300	C(121)-C(126)-C(125)	121.0(3)
C(26)-H(26)	0.9300	C(121)-C(126)-H(126)	119.5
C(123)-H(123)	0.9300	C(125)-C(126)-H(126)	119.5
C(132)-C(133)	1.383(5)	C(22)-C(23)-C(24)	120.4(3)
C(132)-H(132)	0.9300	C(22)-C(23)-H(23)	119.8
C(226)-H(226)	0.9300	C(24)-C(23)-H(23)	119.8
C(115)-C(114)	1.347(6)	C(214)-C(213)-C(212)	118.6(3)
C(115)-H(115)	0.9300	C(214)-C(213)-H(213)	120.7
C(114)-C(113)	1.350(6)	C(212)-C(213)-H(213)	120.7
C(113)-H(113)	0.9300	C(235)-C(236)-C(231)	120.4(4)
C(135)-H(135)	0.9300	C(235)-C(236)-H(236)	119.8
C(133)-H(133)	0.9300	C(231)-C(236)-H(236)	119.8
		C(12)-C(13)-C(14)	119.6(3)
C(2)-Rh(2)-O(21)	175.99(11)	C(12)-C(13)-H(13)	120.2
C(2)-Rh(2)-N(2)	97.17(12)	C(14)-C(13)-H(13)	120.2
O(21)-Rh(2)-N(2)	80.12(9)	C(224)-C(225)-C(226)	118.2(3)
C(2)-Rh(2)-P(2)	91.21(10)	C(224)-C(225)-H(225)	120.9
O(21)-Rh(2)-P(2)	91.48(6)	C(226)-C(225)-H(225)	120.9
N(2)-Rh(2)-P(2)	171.60(7)	C(113)-C(112)-C(111)	121.3(3)
C(1)-Rh(1)-O(11)	177.56(12)	C(113)-C(112)-H(112)	119.4
C(1)-Rh(1)-N(1)	97.45(12)	C(111)-C(112)-H(112)	119.4
O(11)-Rh(1)-N(1)	80.27(8)	C(28)-C(27)-C(26)	121.2(3)
C(1)-Rh(1)-P(1)	92.09(10)	C(28)-C(27)-H(27)	119.4
O(11)-Rh(1)-P(1)	90.18(6)	C(26)-C(27)-H(27)	119.4
N(1)-Rh(1)-P(1)	170.42(6)	C(25)-C(26)-C(27)	121.0(3)

C(221)-P(2)-C(211)	103.63(13)	C(25)-C(26)-H(26)	119.5
C(221)-P(2)-C(231)	102.06(14)	C(27)-C(26)-H(26)	119.5
C(211)-P(2)-C(231)	104.07(13)	C(124)-C(123)-C(122)	118.0(3)
C(221)-P(2)-Rh(2)	113.12(9)	C(124)-C(123)-H(123)	121.0
C(211)-P(2)-Rh(2)	118.84(10)	C(122)-C(123)-H(123)	121.0
C(231)-P(2)-Rh(2)	113.30(10)	C(133)-C(132)-C(131)	121.3(4)
C(131)-P(1)-C(111)	104.27(14)	C(133)-C(132)-H(132)	119.4
C(131)-P(1)-C(121)	107.52(15)	C(131)-C(132)-H(132)	119.4
C(111)-P(1)-C(121)	98.69(14)	C(225)-C(226)-C(221)	121.6(3)
C(131)-P(1)-Rh(1)	110.50(11)	C(225)-C(226)-H(226)	119.2
C(111)-P(1)-Rh(1)	119.42(10)	C(221)-C(226)-H(226)	119.2
C(121)-P(1)-Rh(1)	115.12(10)	C(114)-C(115)-C(116)	118.8(4)
C(11)-N(1)-C(19)	118.8(2)	C(114)-C(115)-H(115)	120.6
C(11)-N(1)-Rh(1)	129.9(2)	C(116)-C(115)-H(115)	120.6
C(19)-N(1)-Rh(1)	111.29(17)	C(115)-C(114)-C(113)	123.6(4)
C(13)-C(12)-C(11)	120.3(3)	C(115)-C(114)-F(11)	118.3(4)
C(13)-C(12)-H(12)	119.8	C(113)-C(114)-F(11)	118.1(4)
C(11)-C(12)-H(12)	119.8	C(114)-C(113)-C(112)	117.8(4)
C(28)-O(21)-Rh(2)	113.03(18)	C(114)-C(113)-H(113)	121.1
C(18)-O(11)-Rh(1)	113.48(17)	C(112)-C(113)-H(113)	121.1
C(222)-C(221)-C(226)	117.9(3)	C(134)-C(135)-C(136)	118.5(4)
C(222)-C(221)-P(2)	117.6(2)	C(134)-C(135)-H(135)	120.8
C(226)-C(221)-P(2)	124.3(2)	C(136)-C(135)-H(135)	120.8
C(25)-C(24)-C(23)	126.4(3)	C(134)-C(133)-C(132)	118.2(4)
C(25)-C(24)-C(29)	117.3(3)	C(134)-C(133)-H(133)	120.9
C(23)-C(24)-C(29)	116.3(3)	C(132)-C(133)-H(133)	120.9
C(232)-C(231)-C(236)	118.6(3)		

Table E4. 3 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-FPh})_3]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh(2)	43(1)	45(1)	41(1)	-1(1)	-3(1)	-20(1)
Rh(1)	35(1)	40(1)	49(1)	-1(1)	-2(1)	-11(1)
P(2)	44(1)	41(1)	43(1)	2(1)	-7(1)	-16(1)
P(1)	35(1)	43(1)	55(1)	-3(1)	-1(1)	-9(1)
Cl(1)	65(1)	59(1)	109(1)	2(1)	-22(1)	10(1)
Cl(2)	114(1)	52(1)	135(1)	-25(1)	-21(1)	-20(1)
N(1)	36(1)	45(1)	36(1)	4(1)	-3(1)	-14(1)
F(12)	97(2)	100(2)	83(2)	-24(1)	-35(1)	-17(1)
C(12)	39(2)	67(2)	56(2)	11(2)	-11(2)	-25(2)
F(21)	99(2)	52(1)	73(1)	-6(1)	-23(1)	9(1)
O(21)	48(1)	46(1)	66(1)	-2(1)	-13(1)	-18(1)
O(11)	38(1)	42(1)	78(2)	2(1)	-10(1)	-14(1)
C(221)	46(2)	43(2)	43(2)	2(1)	-8(1)	-17(1)
C(24)	67(2)	53(2)	40(2)	-5(1)	-2(2)	-28(2)
F(22)	121(2)	133(2)	50(1)	-7(1)	-33(1)	-26(2)
C(231)	43(2)	48(2)	50(2)	7(1)	-8(1)	-17(1)
C(18)	40(2)	44(2)	48(2)	4(1)	-8(1)	-13(1)
C(1)	48(2)	51(2)	58(2)	-2(2)	-5(2)	-14(2)
C(211)	48(2)	43(2)	42(2)	2(1)	-9(1)	-16(1)
C(134)	91(3)	76(3)	80(3)	11(2)	26(3)	-28(2)
C(15)	54(2)	47(2)	60(2)	4(2)	-12(2)	0(2)

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C(131)	38(2)	47(2)	61(2)	1(2)	0(2)	-9(1)
N(2)	47(2)	51(1)	39(1)	-4(1)	0(1)	-25(1)
C(19)	38(2)	43(2)	33(2)	5(1)	-3(1)	-12(1)
C(121)	39(2)	44(2)	55(2)	-3(1)	-2(1)	-9(1)
O(22)	48(2)	87(2)	102(2)	-4(2)	-14(2)	-15(1)
C(232)	49(2)	64(2)	52(2)	9(2)	-10(2)	-20(2)
C(11)	45(2)	50(2)	46(2)	5(1)	-6(1)	-21(1)
C(111)	40(2)	44(2)	65(2)	-5(2)	-2(2)	-8(1)
C(22)	62(2)	71(2)	62(2)	-14(2)	3(2)	-42(2)
C(216)	60(2)	56(2)	51(2)	10(2)	-6(2)	-17(2)
C(222)	56(2)	49(2)	48(2)	0(1)	-9(2)	-14(2)
C(14)	41(2)	53(2)	38(2)	8(1)	-7(1)	-8(1)
F(11)	126(2)	54(1)	187(3)	13(2)	-35(2)	13(1)
C(2)	51(2)	60(2)	47(2)	-3(2)	-1(2)	-24(2)
C(214)	72(2)	45(2)	46(2)	-2(2)	-23(2)	-5(2)
C(29)	53(2)	50(2)	33(2)	-2(1)	-1(1)	-26(2)
C(16)	66(2)	39(2)	84(3)	-1(2)	-18(2)	-11(2)
C(233)	61(2)	91(3)	57(2)	7(2)	6(2)	-18(2)
C(212)	52(2)	50(2)	48(2)	3(1)	-7(2)	-18(2)
F(23)	73(2)	179(3)	130(2)	24(2)	22(2)	-62(2)
C(124)	65(2)	61(2)	64(2)	-4(2)	-19(2)	-19(2)
C(28)	51(2)	51(2)	45(2)	0(1)	-7(2)	-19(2)
C(223)	67(2)	71(2)	52(2)	14(2)	-18(2)	-14(2)
C(17)	51(2)	44(2)	75(2)	2(2)	-15(2)	-17(2)
C(224)	69(2)	94(3)	36(2)	-4(2)	-13(2)	-25(2)
C(122)	48(2)	62(2)	77(3)	-16(2)	-9(2)	-1(2)
C(21)	51(2)	64(2)	49(2)	-7(2)	1(2)	-28(2)
C(116)	53(2)	55(2)	75(3)	-9(2)	2(2)	-9(2)
C(136)	48(2)	51(2)	81(3)	1(2)	-1(2)	-14(2)
C(234)	52(2)	112(3)	88(3)	28(3)	2(2)	-37(2)
O(12)	97(2)	53(1)	96(2)	-7(1)	-18(2)	-33(1)
C(215)	59(2)	66(2)	49(2)	-8(2)	-2(2)	-5(2)
C(25)	79(3)	45(2)	63(2)	-9(2)	-6(2)	-20(2)
C(235)	72(3)	110(3)	105(4)	10(3)	-7(3)	-61(3)
F(13)	150(3)	130(2)	102(2)	13(2)	55(2)	-58(2)
C(125)	59(2)	75(2)	65(2)	-21(2)	-5(2)	-3(2)
C(126)	43(2)	68(2)	63(2)	-8(2)	-3(2)	-2(2)
C(23)	85(3)	57(2)	52(2)	-11(2)	0(2)	-42(2)
C(213)	77(2)	46(2)	48(2)	7(2)	-15(2)	-19(2)
C(236)	71(3)	78(2)	78(3)	-1(2)	-7(2)	-42(2)
C(13)	35(2)	66(2)	50(2)	13(2)	-7(1)	-11(2)
C(225)	93(3)	69(2)	64(2)	-17(2)	-25(2)	-15(2)
C(112)	58(2)	54(2)	77(3)	5(2)	4(2)	-4(2)
C(27)	55(2)	56(2)	73(2)	-4(2)	-11(2)	-16(2)
C(26)	67(3)	54(2)	82(3)	-7(2)	-8(2)	-7(2)
C(123)	50(2)	72(2)	84(3)	-10(2)	-23(2)	-8(2)
C(132)	67(3)	95(3)	63(2)	6(2)	-2(2)	-40(2)
C(226)	92(3)	47(2)	64(2)	-5(2)	-29(2)	-12(2)
C(115)	60(2)	55(2)	113(4)	-22(2)	-4(2)	5(2)
C(114)	78(3)	43(2)	118(4)	-3(2)	-25(3)	-1(2)
C(113)	80(3)	59(2)	101(3)	19(2)	-10(3)	-12(2)
C(135)	58(2)	56(2)	110(4)	6(2)	20(2)	-21(2)
C(133)	108(4)	115(4)	59(3)	4(2)	0(2)	-50(3)

Table E4. 4 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{oxCl})(\text{CO})\text{P}(\text{p-FPh})_3]$.

	x	y	z	U(eq)
H(12)	6811	766	3968	62
H(232)	7146	2764	203	65
H(11)	5166	1792	3977	54
H(22)	3574	-236	1129	74
H(216)	3980	4871	2791	67
H(222)	6875	2378	3151	61
H(16)	4872	-2869	3394	76
H(233)	8689	2774	-777	86
H(212)	5957	5412	560	59
H(223)	7434	2393	4608	76
H(17)	3257	-1772	3460	66
H(122)	-766	2477	3032	77
H(21)	3653	1361	1358	64
H(116)	-564	3652	4742	76
H(136)	-505	1104	4358	73
H(215)	2867	6417	2625	73
H(235)	9102	4822	882	107
H(125)	1533	299	870	83
H(126)	2059	689	2251	73
H(23)	5047	-1495	986	73
H(213)	4824	6949	397	67
H(236)	7550	4838	1849	87
H(13)	7105	-901	3774	61
H(225)	6327	5310	4766	90
H(112)	1654	3513	2494	80
H(27)	8465	8	1537	73
H(26)	8520	-1599	1172	84
H(123)	-1298	2042	1682	82
H(132)	1245	2341	5696	87
H(226)	5800	5308	3297	80
H(115)	-1333	5276	4341	97
H(113)	885	5126	2115	98
H(135)	-1362	751	5826	93
H(133)	344	2037	7151	110

Appendix F

Supplementary data for the oxidative addition of iodomethane to complexes of the type $[\text{Rh}(\text{oxY})(\text{CO})(\text{PR}_3)]$

F1. Supplementary data for the oxidative addition of iodomethane to $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)]$

Table F1. 1 Absorbance data for a infra-red spectra illustrating the conversion of the Rh(I) starting complex (1965 cm^{-1}) to the Rh(III) alkyl species (2057 cm^{-1}) in acetone at 25°C . $[\text{Rh}(\text{ox})(\text{CO})(\text{PPh}_3)] = 1.1 \times 10^{-3}\text{ M}$ and $[\text{MeI}] = 9.82 \times 10^{-2}\text{ M}$. $\text{Rh(I)}\ k_{\text{obs}} = 3.8(2) \times 10^{-3}\text{ s}^{-1}$ and $\text{Rh(III)}\ k_{\text{obs}} = 4.0(2) \times 10^{-3}\text{ s}^{-1}$.

Time (s)	Rh(I) (Abs)	Rh(III) (Abs)
0	0.027728	0.006135
120	0.019728	0.010056
240	0.011956	0.011197
360	0.009571	0.012181
480	0.00792	0.01284
600	0.006652	0.013248
720	0.005654	0.0135
840	0.00487	0.013791
960	0.004396	0.013908
1080	0.003962	0.014044
1200	0.003625	0.014087
1320	0.00339	0.014279
		0.014133
		0.014098
		0.014095
		0.014357
		0.01414

F2. Supplementary data for the oxidative addition of iodomethane to $[\text{Rh}(\text{oxY})(\text{CO})(\text{PR}_3)]$ type complexes ($Y = \text{H}, \text{Cl}, \text{NO}_2$), ($R = \text{PPh}_3, \text{PPh}_2\text{Cy}, \text{PPhCy}_2, \text{PCy}_3$)

Appendix F

Table F2. 1 Effect of functionalized 8-hydroxyquinolinorhodium(I) complexes and [MeI] dependence on the *pseudo*-first order rate constant for the formation of $[\text{Rh}(\text{oxY})(\text{CH}_3)(\text{I})(\text{CO})(\text{PPh}_3)]$, in acetone at 25°C. $[\text{Rh}(\text{ox})(\text{CH}_3)(\text{CH}_3)(\text{PPh}_3)] = 2.394 \times 10^{-4} \text{ M}$, $[\text{Rh}(\text{oxCl})(\text{CH}_3)(\text{PPh}_3)] = 2.078 \times 10^{-4} \text{ M}$, $[\text{Rh}(\text{oxNO}_2)(\text{CH}_3)(\text{PPh}_3)] = 1.935 \times 10^{-4} \text{ M}$, $\lambda = 380 \text{ nm}$ for all complexes.

$[\text{Rh}(\text{ox})(\text{CH}_3)(\text{PPh}_3)]$	$[\text{Rh}(\text{oxCl})(\text{CH}_3)(\text{PPh}_3)]$	$[\text{Rh}(\text{oxNO}_2)(\text{CH}_3)(\text{PPh}_3)]$
$[\text{CH}_3\text{I}] (10^{-3} \text{ M})$	$10^3 k_{\text{obs}} (s^{-1})$	$10^3 k_{\text{obs}} (s^{-1})$
4.086	5.706	77.215
17.824	15.147	112.230
30.505	20.924	164.243
43.328	28.180	196.068
60.518	37.198	228.265

Table F2. 2 Effect of phosphine ligands on 8-hydroxyquinolinorhodium(I) complexes and [MeI] dependence on the *pseudo*-first order rate constant for the formation of $[\text{Rh}(\text{ox})(\text{CH}_3)(\text{I})(\text{CO})(\text{PR}_3)]$, in acetone at 25°C. $[\text{Rh}(\text{ox})(\text{CH}_3)(\text{PPh}_3)] = 2.394 \times 10^{-4} \text{ M}$, $[\text{Rh}(\text{ox})(\text{CH}_3)(\text{PPh}_2\text{Cy})] = 2.119 \times 10^{-4} \text{ M}$, $[\text{Rh}(\text{ox})(\text{CH}_3)(\text{PPhCy}_2)] = 2.230 \times 10^{-4} \text{ M}$, $[\text{Rh}(\text{ox})(\text{CH}_3)(\text{PCy}_3)] = 2.276 \times 10^{-4} \text{ M}$, $\lambda = 380 \text{ nm}$ for all complexes.

$[\text{Rh}(\text{ox})(\text{CH}_3)(\text{PPh}_3)]$	$[\text{Rh}(\text{ox})(\text{CH}_3)(\text{PPh}_2\text{Cy})]$	$[\text{Rh}(\text{ox})(\text{CH}_3)(\text{PPhCy}_2)]$	$[\text{Rh}(\text{ox})(\text{CH}_3)(\text{PCy}_3)]$
$[\text{CH}_3\text{I}] (10^{-3} \text{ M})$	$10^3 k_{\text{obs}} (s^{-1})$	$10^3 k_{\text{obs}} (s^{-1})$	$10^3 k_{\text{obs}} (s^{-1})$
4.086	8.242	0.779	5.988
17.824	13.420	1.168	9.088
30.505	19.790	1.660	12.329
43.328	25.010	2.016	17.894
60.518	3.0	95.0	24.235

$$[\text{Rh}(\text{oxCl})(\text{CH}_3)(\text{I})(\text{CO})(\text{PR}_3)], \text{ in acetone at } 25^\circ\text{C. } [\text{Rh}(\text{oxCl})(\text{CH}_3)(\text{PPh}_3)] = 2.078 \times 10^{-4} \text{ M, } [\text{Rh}(\text{oxCl})(\text{CH}_3)(\text{PPh}_2\text{Cy})] = 1.291 \times 10^{-4} \text{ M, } [\text{Rh}(\text{oxCl})(\text{CH}_3)(\text{PPhC}_2\text{Y})] = 1.281 \times 10^{-4} \text{ M, } [\text{Rh}(\text{oxCl})(\text{CH}_3)(\text{PCy}_3)] = 2.181 \times 10^{-4} \text{ M, } \lambda = 380 \text{ nm for all complexes.}$$

[Rh(oxCl)(CH ₃)(PPH ₃)]		[Rh(oxCl)(CH ₃)(PPh ₂ Cy)]		[Rh(oxCl)(CH ₃)(PPhC ₆ H ₄) ₂]		[Rh(oxCl)(CH ₃)(PCy ₃)]	
[CH ₃ I] (10 ⁻³ M)	10 ³ k _{obs} (s ⁻¹)	[CH ₃ I] (10 ⁻³ M)	10 ³ k _{obs} (s ⁻¹)	[CH ₃ I] (10 ⁻³ M)	10 ³ k _{obs} (s ⁻¹)	[CH ₃ I] (10 ⁻³ M)	10 ³ k _{obs} (s ⁻¹)
5.706	0.129	20.431	0.634	14.090	0.040	5.706	0.105
15.147	0.344	31.421	1.001	20.290	0.057	11.342	0.172
20.924	0.473	47.766	1.544	24.278	0.067	17.049	0.270
28.180	0.635	59.320	1.918	29.730	0.082	24.024	0.364
37.198	0.838	79.399	2.575	37.198	0.101	34.451	0.520

Table F2. 4 Temperature effect and $[\text{CH}_3\text{I}]$ dependence of the *pseudo*-first order rate constant for the formation of $[\text{Rh}(\text{ox})(\text{CH}_3)(\text{I})(\text{CO})(\text{PPh}_3)]$ in acetone at 15, 25, 35 and 45 °C.

15 °C	25 °C	35 °C	45 °C		
[CH ₃ I] (10 ⁻³ M)	10 ³ k _{obs} (s ⁻¹)	[CH ₃ I] (10 ⁻³ M)	10 ³ k _{obs} (s ⁻¹)	[CH ₃ I] (10 ⁻³ M)	10 ³ k _{obs} (s ⁻¹)
23.249	0.408	4.086	0.391	4.368	0.808
40.510	0.670	17.824	0.853	9.229	1.746
51.571	0.854	30.505	1.377	10.356	2.917
65.661	1.086	43.328	1.919	15.640	4.061
80.527	1.304	60.518		22.192	

Table F2.5 Temperature effect and $[\text{CH}_3\text{I}]$ dependence of the *pseudo*-first order rate constant for the formation of $[\text{Rh}(\text{oxCl})(\text{CH}_3)(\text{I})(\text{CO})(\text{PPh}_3)_3]$ in acetone at 15, 25, 35 and 45 °C.

$$[\text{Rh}(\text{oxCl})(\text{CO})(\text{PPh}_3)_3] = 22.078 \times 10^{-4} \text{ M.}$$

15 °C	25 °C	35 °C	45 °C
$[\text{CH}_3\text{I}]$ (10^{-3} M)	$[\text{CH}_3\text{I}]$ (10^{-3} M)	$[\text{CH}_3\text{I}]$ (10^{-3} M)	$[\text{CH}_3\text{I}]$ (10^{-3} M)
20.149	5.706	16.063	9.299
25.996	15.147	21.769	22.262
33.887	20.924	32.196	29.026
40.157	28.180	39.101	41.144
48.400	37.198	46.428	50.021
$10^3 k_{\text{obs}}$ (s^{-1})	$10^3 k_{\text{obs}}$ (s^{-1})	$10^3 k_{\text{obs}}$ (s^{-1})	$10^3 k_{\text{obs}}$ (s^{-1})
0.165	0.129	0.836	0.345
0.215	0.344	1.135	0.700
0.282	0.473	1.639	0.951
0.334	0.635	2.003	1.344
0.395	0.838	2.381	1.587

Appendix F

Table F2. 6 Temperature effect and $[\text{CH}_3\text{I}]$ dependence of the *pseudo*-first order rate constant for the formation of $[\text{Rh}(\text{oxNO}_2)(\text{CH}_3)(\text{I})(\text{CO})(\text{PPh}_3)]$ in acetone at 15, 25, 35 and 45 °C. $[\text{Rh}(\text{oxNO}_2)(\text{CO})(\text{PPh}_3)] = 1.935 \times 10^{-4} \text{ M}$.

15 °C		25 °C		35 °C		45 °C	
$[\text{CH}_3\text{I}] (10^{-3} \text{ M})$	$10^3 k_{\text{obs}} (\text{s}^{-1})$	$[\text{CH}_3\text{I}] (10^{-3} \text{ M})$	$10^3 k_{\text{obs}} (\text{s}^{-1})$	$[\text{CH}_3\text{I}] (10^{-3} \text{ M})$	$10^3 k_{\text{obs}} (\text{s}^{-1})$	$[\text{CH}_3\text{I}] (10^{-3} \text{ M})$	$10^3 k_{\text{obs}} (\text{s}^{-1})$
83.908	0.884	77.215	0.109	82.992	3.563	0.083.085938	0.649
107.792	1.146	112.230	0.165	119.416	5.213	107.792	0.827
150.486	1.597	164.243	-	162.674	6.956	150.486	1.137
191.700	2.023	196.068	0.287	204.452	8.695	191.700	1.392
232.140	2.418	228.265	0.339	251.726	10.56	232.140	1.730

Table F2. 7 Eyring plots of the *pseudo*-first order rate constants, (k_1) , for the formation of $[\text{Rh}(\text{oxY})(\text{CH}_3)(\text{I})(\text{CO})(\text{PPh}_3)]$ (where $\text{Y} = \text{H}, \text{Cl}$ or NO_2), in acetone.

$10^3 \times 1/T (\text{K}^{-1})$	$(\text{Y}=\text{H}) \ln (k_1/T)$	$(\text{Y}=\text{Cl}) \ln (k_1/T)$	$(\text{Y}=\text{NO}_2) \ln (k_1/T)$
3.470	-9.771	-10.218	-10.460
3.354	-8.941	-9.488	-9.9153
3.245	-8.165	-8.889	-9.1653
3.143	-7.451	-8.358	-8.7322

F3. Rate laws and kinetic activation parameters

Rate constant

The rate of a reaction can be defined as the change in the concentration of a reactant or product per unit time. Denoted by the rate constant, k , that relates to the change of the reagent concentration per unit time. For a simple reaction, as given below:



The rate can be expressed by the equation:

$$\text{Rate} = \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{d[C]}{dt} = k[A]^m[B]^n \quad (F2)$$

Where $[]$ denotes concentration and the negative signs indicates the disappearance of A and B. The values m and n represent the order of the reaction with regard to the concentrations of A and B, the sum of m and n is equal to the total order of the reaction. The reaction order is the way in which the rate of the reaction will vary as the concentration of both of one of the reacting species is changed. The order of the reaction can be determined experimentally, but with a lot of difficulty. This is overcome by forcing the reaction to *pseudo*-first order conditions, where one of the species concentration stays constant by having the concentration of the second species much higher. With this the rate equation simplifies to:

$$\text{Rate} = k_{\text{obs}}[A]^m \quad (F3)$$

The pseudo-first order rate constant can now be given as

$$k_{\text{obs}} = k[B]^n \quad (F4)$$

By varying the concentration of B, as in the equation above, the rate constant, k , can be determined. If a second reaction occurs, the rate law is extended to (under *pseudo*-first order conditions):

$$\text{Rate} = k_1[A][B] + k_2[A] \quad (F5)$$

$$k_{\text{obs}} = k_1[B] + k_2 \quad (F6)$$

Integration of the rate equation:

$$\text{Rate} = \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{d[C]}{dt} = k[A]^m[B]^n \quad (F7)$$

With boundaries of $t = 0$ and t , yields an expression on terms of C, where C denotes the concentration change of the reactants at time t and the initial time is obtained.

$$[C]_t = [C]_0 e^{k_{\text{obs}} t} \quad (\text{F8})$$

$$\text{where } \frac{[C]_t}{[C]_0} = \frac{A_{\infty} - A_t}{A_{\infty} - A_0} \quad (\text{F9})$$

Substitution of this equation into the Beer-Lambert law;

$$A = \varepsilon \cdot l \cdot C \quad (\text{F10})$$

Where A = absorbance, ε = molar extinction coefficient, C = concentration and l = light path length. Gives the following equation:

$$A_t = A_{\infty} - (A_{\infty} - A_0) e^{k_{\text{obs}} t} \quad (\text{F11})$$

Where A_t and A_{∞} are the absorbance after time t and at the time of reaction completeness, respectively. A least-squares fit utilising absorbance vs. time data for a first order reaction, would yield k_{obs} for the reaction. Data plotting were done utilizing the computer software Scientist, with the following model for k_{obs} determination.

MicroMath Scientist Model File

IndVars: l

DepVars: Kobs

Params: k1 kn1

Kobs=k1*l+kn1

Reaction half-life

The reaction half-life is the required time to convert 50% of the reactant, for first order reactions the half-life are determined by the equation:

$$t_{1/2} = \frac{\ln(2)}{k_{\text{obs}}} = \frac{0.6932}{k_{\text{obs}}} \quad (\text{F12})$$

Activation enthalpy and entropy

The Transition State Theory states that an activated complex or transition state is in equilibrium with the reagents before the reaction occurs, and that the rate is given by the decomposition rate, k, of the activated complex to yield the products:



Where $K_c^\ddagger$ = equilibrium constant

The exponential form of the Eyring equation is given as:

$$k = \frac{k_B T}{h} e^{\left[\frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \right]} \quad (F14)$$

That can be rewritten into a logarithmic form:

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \left(\frac{\Delta S^\ddagger}{R}\right) - \left(\frac{\Delta H^\ddagger}{RT}\right) \quad (F15)$$

A graph of $\ln\left(\frac{k}{T}\right)$ versus $\frac{1}{T}$ will have a slope of $\frac{-\Delta H^\ddagger}{R}$, with $\Delta H^\ddagger$ = standard enthalpy change of activation and the Y-axis intercept $\frac{\Delta S^\ddagger}{R} + \ln\left(\frac{k_B}{h}\right)$, with $\Delta S^\ddagger$ = standard enthalpy change of activation.

Chapter 11
