



## Data Article

# Density functional theory calculated data of the iodomethane oxidative addition to oligothiophene-containing rhodium complexes – Importance of dispersion correction



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## ARTICLE INFO

## Article history:

Received 8 February 2021

Revised 21 February 2021

Accepted 2 March 2021

Available online 3 March 2021

## Keywords:

Rhodium

Oxidative addition

DFT

Oligothiophene

## ABSTRACT

Electronic and free energy data of density functional theory calculated optimized geometries of the reactants, transition state of the oxidative addition reaction and different reaction products of the  $[\text{Rh}(\text{RCOCHCOCF}_3)(\text{CO})(\text{PPh}_3)] + \text{CH}_3\text{I}$  reactions ( $\text{R} = \text{C}_4\text{H}_3\text{S}$ ,  $\text{C}_4\text{H}_3\text{S}-\text{C}_4\text{H}_2\text{S}$  and  $\text{C}_4\text{H}_3\text{S}-\text{C}_4\text{H}_2\text{S}-\text{C}_4\text{H}_2\text{S}$ ) are presented to illustrate the influence of the amount of thiophene groups, the implicit solvent and dispersion correction on the calculated energies. All calculations were done with the B3LYP functional, in gas as well as in solvent phase, with and without dispersion correction. The data can save computational chemists time when choosing an appropriate method to calculate reaction energies of oxidative addition reactions. Detailed knowledge of energies involved in the oxidative addition reaction of methyl iodide to rhodium complexes have an important implication in catalysis, for example the Monsanto process where methanol is converted to acetic acid catalysed by a rhodium complex. For more insight in the reported data, see the related research article "Synthesis, characterization, electrochemistry, DFT and kinetic

DOI of original article: [10.1016/j.poly.2021.115095](https://doi.org/10.1016/j.poly.2021.115095)

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<https://doi.org/10.1016/j.dib.2021.106929>

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study of the oligothiophene-containing complex  $[\text{Rh}((\text{C}_4\text{H}_3\text{S}-\text{C}_4\text{H}_2\text{S})\text{COCHCOCF}_3)(\text{CO})(\text{PPh}_3)]$ , published in *Polyhedron* [1].

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## Specifications Table

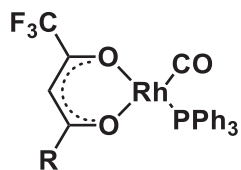
Subject	Physical and Theoretical Chemistry
Specific subject area	DFT calculations of chemical structures.
Type of data	Table Graph Figure
How data were acquired	Electronic structure calculations, using the Gaussian 16 program
Data format	Raw and Analyzed
Parameters for data collection	Geometry optimization and frequency calculations were done using the Gaussian 16 program, with and without the implicit solvent model IEF-PCM, using the B3LYP functional with and without D3 dispersion correction.
Description of data collection	Data were collected from DFT output files
Data source location	University of the Free State Bloemfontein South Africa
Data accessibility	With the article
Related research article	N G.S. Mateyise, M.M Conradie, Jeanet Conradie, Synthesis, Characterization, Electrochemistry, DFT and Kinetic Study of the Oligothiophene-containing Complex $[\text{Rh}((\text{C}_4\text{H}_3\text{S}-\text{C}_4\text{H}_2\text{S})\text{COCHCOCF}_3)(\text{CO})(\text{PPh}_3)]$ , <i>Polyhedron</i> , 115,095 (2021), <a href="https://doi.org/10.1016/j.poly.2021.115095">https://doi.org/10.1016/j.poly.2021.115095</a>

## Value of the Data

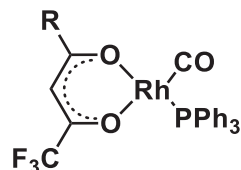
- Free energy data involved in oxidative addition reactions are important in the field of catalysis such as the oxidative addition reaction involved in the manufacturing of methanol from acetic acid (Monsanto process).
- Free energy data obtained by different computational chemistry approaches, namely in gas and solvent phase, with and without dispersion corrections helps computational chemistry researchers in the choice of method when calculating energies involved in oxidative addition reactions.
- Free energy data obtained by different computational chemistry approaches, indicates which method gives energies in agreement with experiment, making the theoretical prediction of energies involved in related oxidation addition reactions possible.

## 1. Data Description

Electronic and free energy data of the reactants, first transition state (TS) and the possible reaction products of  $[\text{Rh}(\text{RCOCHCOCF}_3)(\text{CO})(\text{PPh}_3)] + \text{CH}_3\text{I}$  reaction ( $\text{R} = \text{C}_4\text{H}_3\text{S}$  (tta) [2],  $\text{C}_4\text{H}_3\text{S}-\text{C}_4\text{H}_2\text{S}$  (di-tta) [1] and  $\text{C}_4\text{H}_3\text{S}-\text{C}_4\text{H}_2\text{S}-\text{C}_4\text{H}_2\text{S}$  (tri-tta)) shown in *Scheme 1*, are specified in the graphs in *Figs. 1–5*. The influence of dispersion correction to the energy data of the  $\text{Rh}(\text{I})$ -di-tta +  $\text{CH}_3\text{I}$  reaction ( $\text{R} = \text{C}_4\text{H}_3\text{S}-\text{C}_4\text{H}_2\text{S}$ ) is illustrated in *Fig. 1* (gas phase data), *Fig. 2* (data in chloroform as solvent) and *Fig. 3* (data in methanol as solvent). The influence of the phase (gas, chloroform or methanol) to the energy data of the  $\text{Rh}(\text{I})$ -di-tta +  $\text{CH}_3\text{I}$  reaction ( $\text{R} = \text{C}_4\text{H}_3\text{S}-\text{C}_4\text{H}_2\text{S}$ ) is illustrated in *Fig. 4* (B3LYP-D3 data). The influence of the amount of thienyl groups to the energy data of the  $\text{Rh}(\text{I}) + \text{CH}_3\text{I}$  reaction ( $\text{R} = \text{C}_4\text{H}_3\text{S}$  (tta),  $\text{C}_4\text{H}_3\text{S}-\text{C}_4\text{H}_2\text{S}$  (di-tta) and  $\text{C}_4\text{H}_3\text{S}-\text{C}_4\text{H}_2\text{S}-\text{C}_4\text{H}_2\text{S}$  (tri-tta)) is illustrated in *Fig. 5* (B3LYP-D3 data in chloroform as



Rh(I) A

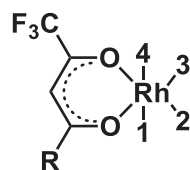


Rh(I) B

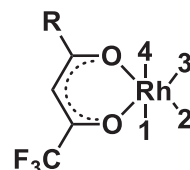
R = C<sub>4</sub>H<sub>3</sub>S (tta)

R = C<sub>4</sub>H<sub>3</sub>S-C<sub>4</sub>H<sub>2</sub>S (di-tta)

R = C<sub>4</sub>H<sub>3</sub>S-C<sub>4</sub>H<sub>2</sub>S-C<sub>4</sub>H<sub>2</sub>S (tri-tta)



Rh(III)-alkyl A



Rh(III)-alkyl B

Alkyl 1: 1 = I, 2 = PPh<sub>3</sub>, 3 = CO, 4 = CH<sub>3</sub>

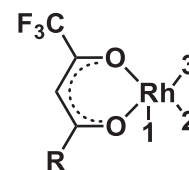
Alkyl 2: 1 = I, 2 = CH<sub>3</sub>, 3 = CO, 4 = PPh<sub>3</sub>

Alkyl 3: 1 = PPh<sub>3</sub>, 2 = I, 3 = CO, 4 = CH<sub>3</sub>

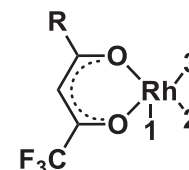
Alkyl 4: 1 = CO, 2 = CH<sub>3</sub>, 3 = PPh<sub>3</sub>, 4 = I

Alkyl 5: 1 = PPh<sub>3</sub>, 2 = CH<sub>3</sub>, 3 = I, 4 = CO

Alkyl 6: 1 = CO, 2 = PPh<sub>3</sub>, 3 = I, 4 = CH<sub>3</sub>



Rh(III)-acyl A



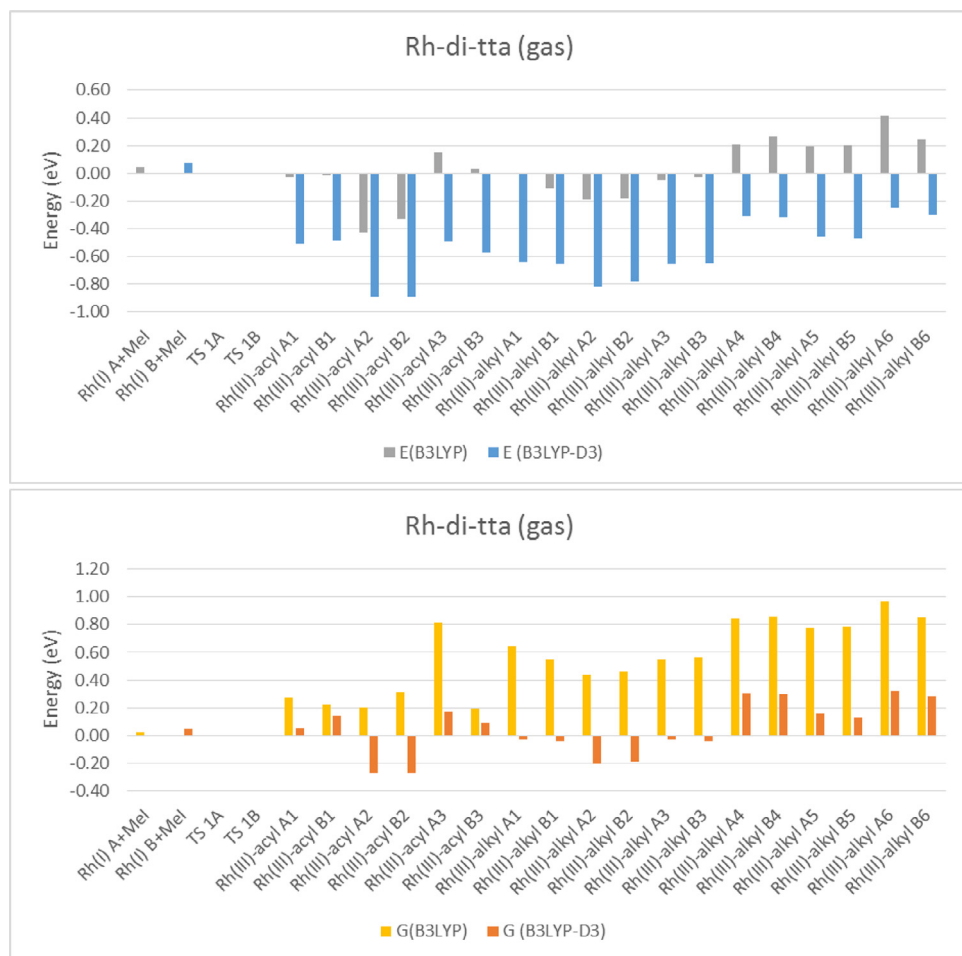
Rh(III)-acyl B

Acyl 1: 1 = I, 2 = PPh<sub>3</sub>, 3 = COCH<sub>3</sub>

Acyl 2: 1 = COCH<sub>3</sub>, 2 = I, 3 = PPh<sub>3</sub>

Acyl 3: 1 = PPh<sub>3</sub>, 2 = COCH<sub>3</sub>, 3 = I

**Scheme 1.** Rhodium(I) and (III) complexes of this study. For each Rh(I), Rh(III)-alkyl and Rh(III)-acyl, two geometrical isomers are possible, namely A and B.

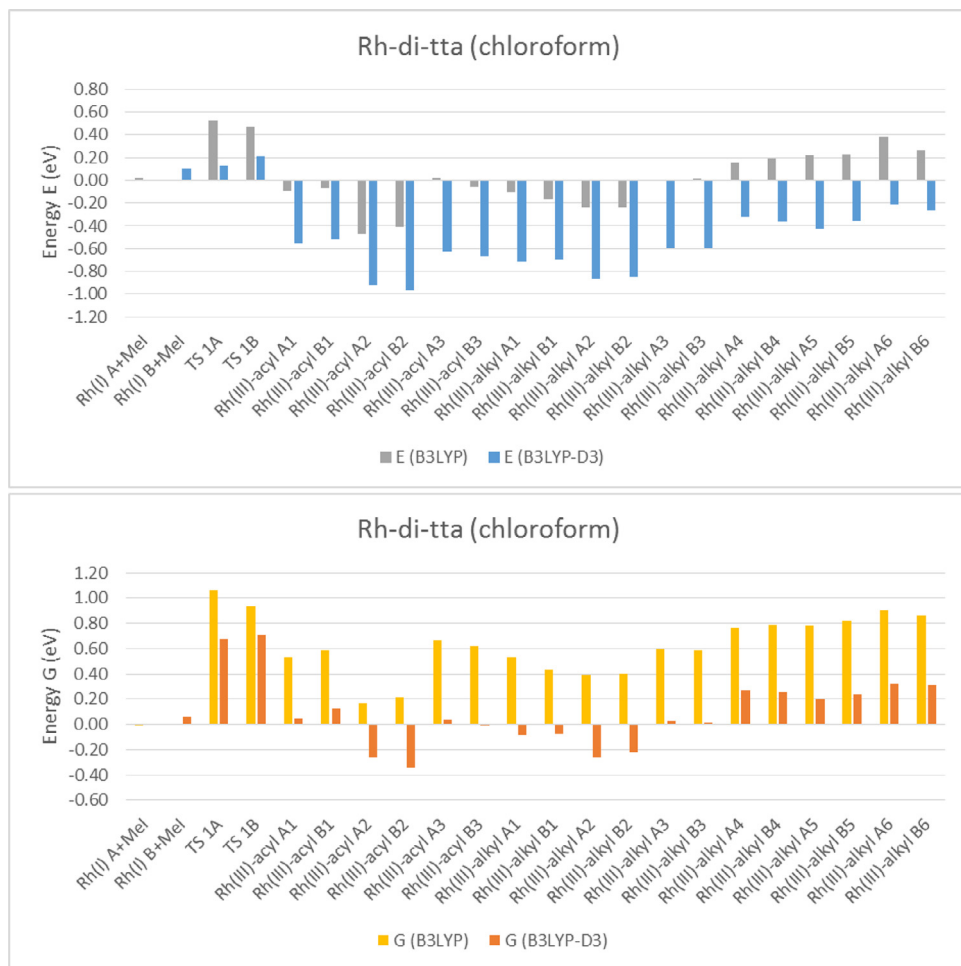


**Fig. 1.** B3LYP and B3LYP-D3 gas phase relative electronic (E) and free (G) energies of Rh(III)-di-tta complexes compared to the lowest energy reactant isomer Rh(I) + CH<sub>3</sub>I (MeI), illustrating the influence of the dispersion correction on the gas phase calculated energy. No oxidative addition TS could be located in the gas phase.

solvent). The energies of the products, relative to the energy of the reactants, show if a reaction product is thermodynamically favoured. The electronic and free energy data presented in Figs. 1–5 are provided in Table 1. The B3LYP-D3 data in chloroform as solvent of [Rh((C<sub>4</sub>H<sub>3</sub>S-C<sub>4</sub>H<sub>2</sub>S)COCHCOFC<sub>3</sub>)(CO)(PPh<sub>3</sub>)] + CH<sub>3</sub>I is from the related research article [1]. Experimental and theoretical data of reaction involving the mother complex, [Rh(CH<sub>3</sub>COCHCOCH<sub>3</sub>)(CO)(PPh<sub>3</sub>)], and related complexes, [Rh(RCOCHCOCH<sub>3</sub>H<sub>3</sub>S)(CO)(PPh<sub>3</sub>)] (R = C<sub>6</sub>H<sub>5</sub> and C<sub>4</sub>H<sub>3</sub>333S), can be found in references [3–5].

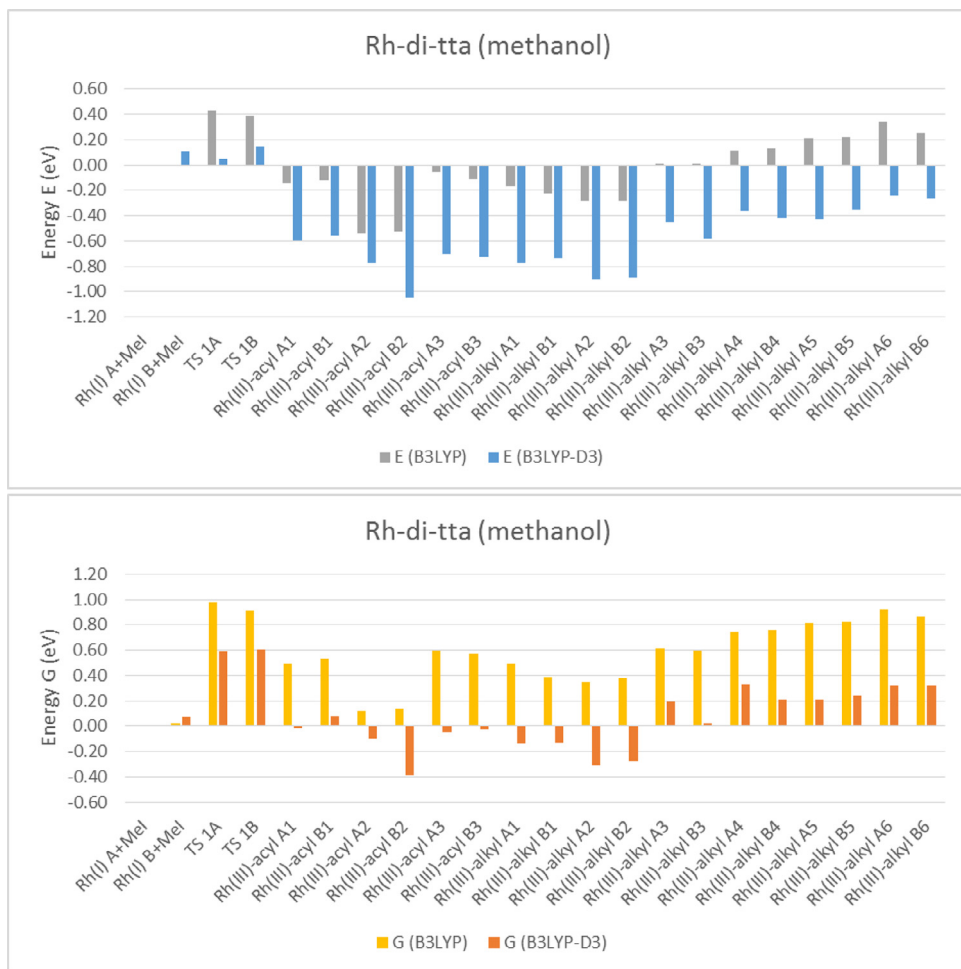
## 2. Experimental Design, Materials and Methods

Density functional theory (DFT) calculations using the Gaussian 16 package [6], were used to determine the optimized geometry and energy of the specified molecules. The input coordinates for the compounds were constructed using Chemcraft [7]. The coordinates were specified in the input files of the DFT calculations. DFT calculations were performed using the hybrid functional B3LYP functional [8,9] applying the GTO (Gaussian type orbital) triple- $\zeta$  basis set

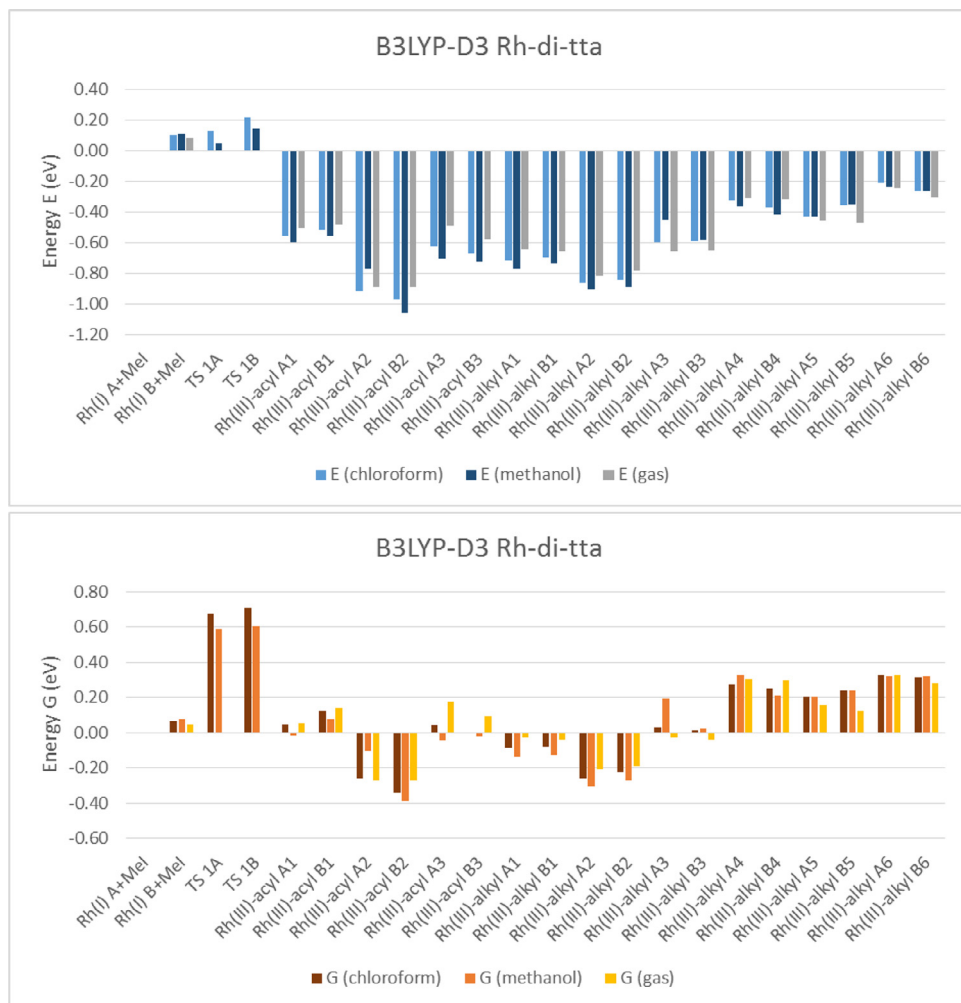


**Fig. 2.** B3LYP and B3LYP-D3 solvent (chloroform) phase relative electronic (E) and free (G) energies of Rh(III)-di-tta complexes compared to the lowest energy reactant isomer Rh(I) + CH<sub>3</sub>I (Mel), illustrating the influence of the dispersion correction on the solvent (chloroform) phase calculated energy.

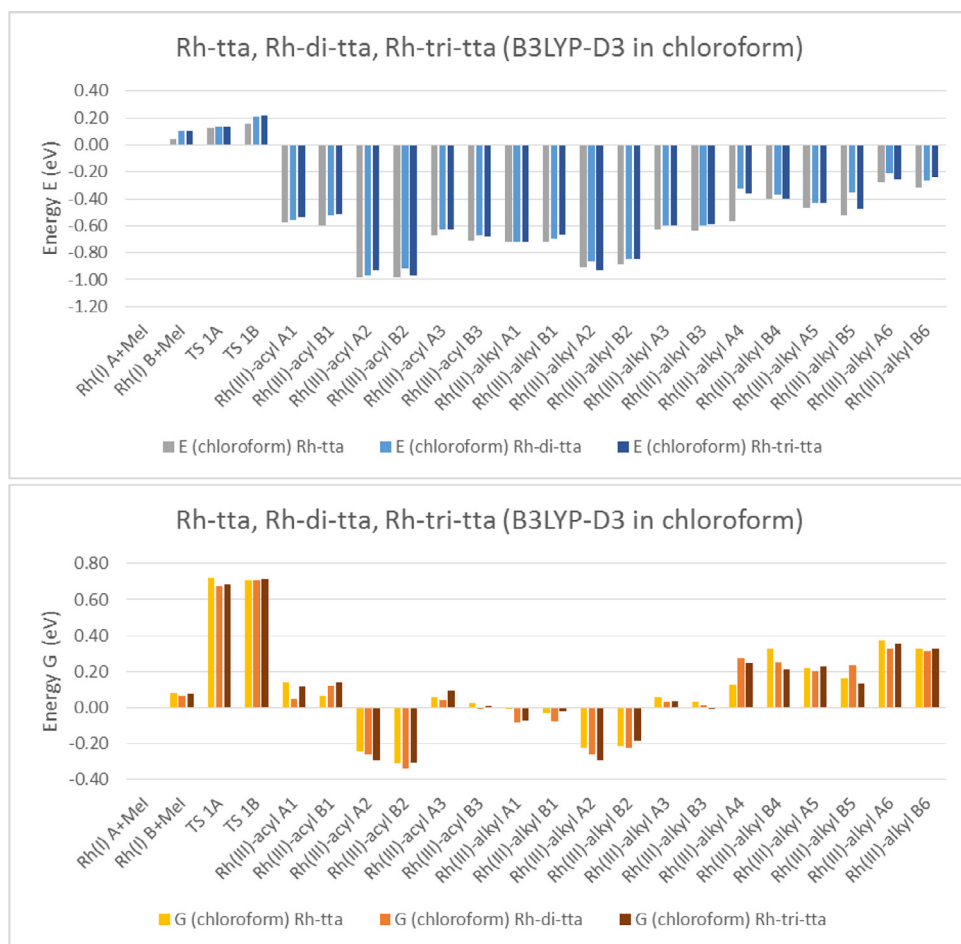
6–311G(d,p) for the lighter atoms (C, H, O, F) and the LanL2dz basis set [10], that corresponds to the Los Alamos ECP plus DZ, for Rh and I. The optimization is performed using Bery algorithm using GEDIIS [11] as implemented in Gaussian 16. The convergence is reached when the root mean square force, the maximum force, the root mean square displacement and the maximum displacement are within the threshold of 0.00030, 0.00045, 0.0012 and 0.0018 atomic units, respectively. The requested convergence on energy is 1.0D-8 atomic unit. Calculations were done with and without Grimme's D3 dispersion correction [12], in gas and solvent phase, using either chloroform or methanol as solvent. For solvent calculations, the integral equation formalism polarizable continuum model (IEFPCM) of solvation to describe the dielectric continuum medium, was used [13,14]. Frequency calculations were done on all molecules to ensure true minimum energy (no imaginary frequency) or transition state structure (one imaginary frequency), and to provide the free energies of the molecules. The free energies were obtained from the output files searching for "Sum of electronic and thermal Free Energies=". The electronic energies were obtained from the output files at the final optimization step, searching for "SCF Done" from the bottom of the output file.



**Fig. 3.** B3LYP and B3LYP-D3 solvent (methanol) phase relative electronic (E) and free (G) energies of Rh(III)-di-tta complexes compared to the lowest energy reactant isomer Rh(I) + CH<sub>3</sub>I (Mel), illustrating the influence of the dispersion correction on the solvent (methanol) phase calculated energy.



**Fig. 4.** B3LYP-D3 relative electronic (E) and free (G) energies of Rh(III)-di-tta complexes compared to the lowest energy reactant isomer Rh(I) + CH<sub>3</sub>I (Mel), illustrating the influence of the phase (gas, chloroform or methanol) on the calculated energy. No oxidative addition TS could be located in the gas phase.



**Fig. 5.** B3LYP-D3 solvent (chloroform) phase relative electronic (E) and free (G) energies of Rh(III)-tta, Rh(III)-di-tta and Rh(III)-tri-tta complexes compared to the lowest energy reactant isomer Rh(I) + Rh(I) + CH<sub>3</sub>I (Mel), illustrating the influence of the amount of thienyl groups on the calculated energy.



**Table 1**

Electronic (E (eV)) and free energy (G (eV)) data of the indicated reaction products of the  $[\text{Rh}(\text{RCOCHCOCF}_3)(\text{CO})(\text{PPh}_3)] + \text{CH}_3\text{I}$  (Mel), reaction (R =  $\text{C}_4\text{H}_3\text{S}$  (tta),  $\text{C}_4\text{H}_3\text{S}-\text{C}_4\text{H}_2\text{S}$  (di-tta) and  $\text{C}_4\text{H}_3\text{S}-\text{C}_4\text{H}_2\text{S}-\text{C}_4\text{H}_2\text{S}$  (tri-tta)) calculated with B3LYP (with and without dispersion correction) and the indicated phase (gas, chloroform or methanol).

	Rh-tta B3LYP-D3		Rh-di-tta B3LYP		B3LYP-D3								Rh-tri-tta B3LYP-D3			
	CHCl <sub>3</sub>		Gas		CHCl <sub>3</sub>		MeOH		Gas		CHCl <sub>3</sub>		MeOH		CHCl <sub>3</sub>	
	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG
Rh(I) A + CH <sub>3</sub> I	0.00	0.00	0.05	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Rh(I) B + CH <sub>3</sub> I	0.04	0.08	0.00	0.00	0.00	0.00	0.00	0.02	0.08	0.05	0.10	0.06	0.11	0.07	0.10	0.08
TS 1A	0.13	0.72	-	-	0.53	1.06	0.43	0.98	-	-	0.13	0.67	0.05	0.59	0.13	0.68
TS 1B	0.16	0.71	-	-	0.47	0.94	0.39	0.91	-	-	0.21	0.71	0.14	0.60	0.21	0.72
Rh(III)-acyl A1	-0.58	0.14	-0.03	0.28	-0.09	0.53	-0.14	0.49	-0.51	0.05	-0.56	0.04	-0.60	-0.02	-0.54	0.11
Rh(III)-acyl B1	-0.60	0.06	-0.01	0.22	-0.07	0.58	-0.12	0.53	-0.48	0.14	-0.52	0.12	-0.55	0.08	-0.51	0.14
Rh(III)-acyl A2	-0.99	-0.24	-0.43	0.20	-0.47	0.16	-0.54	0.12	-0.89	-0.27	-0.92	-0.26	-0.77	-0.10	-0.93	-0.29
Rh(III)-acyl B2	-0.99	-0.31	-0.33	0.31	-0.41	0.21	-0.53	0.14	-0.89	-0.27	-0.97	-0.34	-1.05	-0.39	-0.97	-0.31
Rh(III)-acyl A3	-0.67	0.06	0.15	0.81	0.02	0.67	-0.06	0.60	-0.49	0.17	-0.63	0.04	-0.70	-0.05	-0.63	0.09
Rh(III)-acyl B3	-0.71	0.02	0.03	0.20	-0.06	0.62	-0.12	0.57	-0.58	0.09	-0.67	-0.01	-0.72	-0.02	-0.68	0.01
Rh(III)-alkyl A1	-0.72	-0.01	0.00	0.64	-0.10	0.53	-0.17	0.49	-0.64	-0.03	-0.72	-0.09	-0.77	-0.14	-0.72	-0.08
Rh(III)-alkyl B1	-0.72	-0.03	-0.11	0.55	-0.17	0.44	-0.22	0.39	-0.66	-0.04	-0.70	-0.08	-0.74	-0.13	-0.66	-0.02
Rh(III)-alkyl A2	-0.91	-0.23	-0.19	0.44	-0.24	0.39	-0.28	0.35	-0.81	-0.21	-0.86	-0.26	-0.90	-0.31	-0.93	-0.29
Rh(III)-alkyl B2	-0.89	-0.22	-0.18	0.46	-0.24	0.40	-0.28	0.37	-0.78	-0.19	-0.85	-0.23	-0.89	-0.27	-0.85	-0.19
Rh(III)-alkyl A3	-0.63	0.06	-0.05	0.55	0.00	0.60	0.01	0.61	-0.66	-0.03	-0.60	0.03	-0.45	0.19	-0.60	0.04
Rh(III)-alkyl B3	-0.63	0.03	-0.03	0.56	0.01	0.58	0.01	0.59	-0.65	-0.04	-0.59	0.01	-0.58	0.02	-0.59	-0.01
Rh(III)-alkyl A4	-0.56	0.13	0.21	0.84	0.16	0.77	0.11	0.74	-0.31	0.30	-0.32	0.27	-0.36	0.33	-0.36	0.25
Rh(III)-alkyl B4	-0.40	0.33	0.26	0.86	0.19	0.79	0.13	0.76	-0.32	0.30	-0.37	0.25	-0.42	0.21	-0.40	0.21
Rh(III)-alkyl A5	-0.47	0.22	0.19	0.78	0.22	0.78	0.21	0.81	-0.46	0.16	-0.43	0.20	-0.43	0.20	-0.43	0.23
Rh(III)-alkyl B5	-0.52	0.16	0.20	0.78	0.22	0.82	0.22	0.82	-0.47	0.12	-0.36	0.24	-0.35	0.24	-0.48	0.13
Rh(III)-alkyl A6	-0.28	0.37	0.41	0.97	0.38	0.90	0.34	0.92	-0.25	0.32	-0.21	0.32	-0.24	0.32	-0.26	0.36
Rh(III)-alkyl B6	-0.32	0.33	0.25	0.85	0.26	0.86	0.25	0.87	-0.30	0.28	-0.27	0.31	-0.26	0.32	-0.24	0.33

## Ethics Statement

This work does not require any ethical statement.

## CRedit Author Statement

**Nandisiwe Ghandi Sibongile Mateyise:** DFT calculations, Data curation; **Marrigje M. Conradie:** Conceptualization, Supervision, Methodology, Reviewing and Editing; **Jeanet Conradie:** Supervision, Methodology, DFT calculations, Data curation, Writing - Reviewing and Editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships which have or could be perceived to have influenced the work reported in this article.

## Acknowledgments

This work has received support from the South African National Research Foundation (Grant numbers [129270](#), [113327](#), [96111](#), [132504](#) (JC) and [108960](#) (MMC)) and the Central Research Fund of the University of the Free State, Bloemfontein, South Africa. The CHPC of South Africa, the High Performance Computing facility of the UFS and the Norwegian Supercomputing Program (UNINETT Sigma2, Grant No. [NN9684K](#)) are acknowledged for computer time.

## Supplementary Materials

Supplementary material associated with this article can be found in the online version at doi:[10.1016/j.dib.2021.106929](#).

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