Electronic Supplementary Information for Dalton Transactions

Supplementary Information

A Mechanistic Study into the Interconversion of Rhodium Alkyne, Alkynyl-Hydride and Vinylidene Complexes

Michael J. Cowley, Jason M. Lynam and John M. Slattery

Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK. Fax +44(0)1904 432516, Tel +44(0)1904 4332534, E-mail jml12@york.ac.uk.

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1. Experimental

1.1. General Considerations

All experimental procedures were performed under an atmosphere of either dinitrogen or argon using standard Schlenk line techniques or an MBraun Unilab glovebox. General solvents for synthetic chemistry were dried using an Innovative Technology anhydrous solvent engineering system or were distilled from an appropriate drying agent under Ar as necessary. d_8-THF for NMR spectroscopy was dried over potassium metal and degassed with three freeze-pump-thaw cycles, the solvent was then vacuum transferred prior to use. $[Rh(coe)_2(\mu\text{-}Cl)]_2$ was prepared by the published procedure.[111] PhC_2H for kinetic studies was purchased from Aldrich and passed through a short plug of alumina immediately prior to use. $PhC{\equiv}^{13}CH$ and Bu^nC_2H were purchased from Aldrich and used as supplied.

1.2. Synthesis of $[Rh(PPr^i_3)_2(\mu\text{-}Cl)]_2$

$[Rh(coe)_2(\mu\text{-}Cl)]_2$ (100mg, 0.139 mmol) was placed in a schlenk tube and suspended in THF(10 mL). 4 equivalents PPr^i_3 (110 µl, 0.55 mmol) was rapidly added to the solution, causing a colour change from orange to dark violet. The solution was stirred for 10 minutes and then the solvent removed in vacuo. The purple residue was washed with hexane (2 x 5ml) and dried under vacuum.

^{1}H NMR: (d_8-THF) δ 2.14 (m, 6H, PC***H***), 1.37 (dvt, 36 H, PCH{C***H***$_3$}$_2$).
^{31}P{^{1}H} NMR: (d_8-THF) δ 56.40 (d, $^1J_{Rh\text{-}P}$ = 197.7 Hz).

1.3. NMR studies

NMR spectra were acquired on a Bruker Avance 500 spectrometer (Operating Frequencies ^{1}H 500.23 MHz, ^{31}P 202.50 MHz, ^{13}C 125.77)

In a typical experiment, $[Rh(PPr^i_3)_2Cl]_2$ (24 mg, 0.026 mmol) was placed in an NMR tube fitted with a PTFE Young's tap. To the tube was added 0.5 mL of d_8-THF and the tube shaken until the $[Rh(PPr^i_3)_2Cl]_2$ was fully dissolved. The sample was placed in the spectrometer and the instrument was locked and shimmed. The sample was removed from the machine and PhC_2H (5.8 µL, 0.052 mmol, 2 equivalents) and a small amount of triphenylphosphine oxide (for use as an internal standard) were added to the sample, which

was then shaken briefly, and immediately changed from deep purple to an orange/brown colour. The sample was placed into the spectrometer, and after a short period of time for shimming, experiments were begun.

Experiments with Bu^nC_2H were performed in an identical manner to that detailed above by replacement of the PhC_2H. Studies in hexane was also performed as described above and a small amount of C_6D_6 was added to enable locking of the spectrometer.

The concentrations of the various species were monitored by $^{31}P\{^1H\}$ spectroscopy. The *zgig* pulse program, with 32 scans was used to acquire the spectra. A 30 degree pulse was used followed by a ten second recycle delay to ensure complete relaxation of all nuclei after each scan (measurements revealed that the maximum t_1 for the phosphorus resonances for all three species was 3.6 seconds). Spectra were acquired every 10 minutes. After collection, the spectra were batch processed. For the kinetic modelling, the raw integrals were used.

NMR data for complex **2**, **3** and **4** are presented below. The $^{13}C\{^1H\}$ data were obtained using samples prepared from $H^{13}C{\equiv}CPh$, therefore only the resonance from the enriched carbon atom are presented. These data are in agreement with those reported by Werner for **2a**,[2] **3a**[2] and **4a**[3]. In some cases unequivocal assignments could not be made due to overlap with the other components of the reaction mixture or free alkyne.

2a **^{1}H NMR:** (d_8-THF) δ = 4.31 (d, $^2J_{Rh\text{-}H}$ = 2.37 Hz, ***H***C≡CPh), 2.35 (m, 6H, PC***H***), 1.31 (dvt $^3J_{H\text{-}H}$ = 6.6, *N* = 13.2 Hz, 36 H, PCH(C***H***$_3$)$_2$).
^{31}P{^{1}H} NMR: (d_8-THF) δ 32.13 (d, $^1J_{Rh\text{-}P}$ = 117.1 Hz).
^{13}C{^{1}H} NMR (d_8-THF) δ 102.20, (dt, $^1J_{Rh\text{-}C}$ = 47.1 Hz, $^2J_{P\text{-}C}$ = 15.3, H***C***≡CPh).

3a **^{1}H NMR:** (d_8-THF) δ = 2.97 (m, 6H, PC***H***), 1.39 (m, 36H, PCH(C***H***$_3$)$_2$), δ -27.97 (dt, $^1J_{Rh\text{-}H}$ = 42.9, $^2J_{P\text{-}H}$ = 12.8, Rh-***H***).
^{31}P{^{1}H} NMR: (d_8-THF) δ = 49.31 (d, $^1J_{P\text{-}Rh}$ = 98.7 Hz, $^2J_{P\text{-}H}$ = 12.4 Hz).
^{13}C{^{1}H} NMR (d_8-THF) δ = 75.31 (dt $^1J_{Rh\text{-}C}$ = 228.7 Hz, $^2J_{P\text{-}C}$ = 14.3, Rh-***C***≡CPh).

4a **^{1}H NMR:** (d_8-THF) δ = 7.10-7.05 (m, 4H, *Ph*), 6.87 (tt, *J* = 6.6, 2.0, 1H, phenyl ring para-*H*), 2.80 (m, 6H, PC***H***), 1.35 (m, 36H, PCH(C***H***$_3$)$_2$).
^{31}P{^{1}H} NMR: (d_8-THF) δ = 42.38 (d, $^1J_{P\text{-}Rh}$ = 135.1 Hz).

^{13}C{^{1}H} NMR (d_8-THF) δ = 296.10 (dt, $^{1}J_{Rh-C}$ = 58.7, $^{2}J_{P-C}$ 15.9 Hz).

2b **^{1}H NMR:** (d_8-THF) δ = 2.92 (m, 6H, PC***H***), δ 1.32 (m, 36H, PCH(C***H***$_3$)$_2$).
^{31}P{^{1}H} NMR: (d_8-THF) δ = 33.61 (d, $^{1}J_{Rh-P}$ = 119.9 Hz).

3b **^{1}H NMR:** (d_8-THF) δ = 2.35 (m, 6H, PC***H***) δ 1.32 (m, 36H, PCH(C***H***$_3$)$_2$) δ -28.51 (dt, $^{1}J_{Rh-H}$ = 42.6 Hz, $^{2}J_{H-P}$ = 13.1 Hz, Rh-***H***).
^{31}P{^{1}H} NMR: (d_8-THF) δ = 48.94 (dd, $^{1}J_{Rh-P}$ = 100.4 Hz, $^{2}J_{H-P}$ 6.4 Hz).

4b **^{1}H NMR:** (d_8-THF) δ = 2.84 (m, 6H, PC***H***), 1.34 (dvt, $^{3}J_{H-H}$ = 6.8 Hz, *N* = 13.6 Hz, 36H, PCH(C***H***$_3$)$_2$), 0.44 (m, 1H, Rh=C=C(***H***)Bu).
^{31}P{^{1}H} NMR: (d_8-THF) δ = 41.92 (d, $^{1}J_{Rh-P}$ = 136.7 Hz).

2. Kinetic Modeling.

Data were simulated using either the chemical kinetics programme *Dynafit*,[4] or the direct solutions of the relevant rate equations (see below) for the postulated model were used. In this latter instance, a series of trial rate constants were used to generate a series of calculated concentrations to, which were compared to experimentally observed values. . The Solver module in Microsoft *Excel* was then used to vary the rate constants to optimise the fit between the calculated and experimental concentrations.

For the reaction:

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_3} C$$

in this context of this manuscript

A = $RhCl(PPr^i_3)_2(\eta^2\text{-}PhC{\equiv}CH)$,

B = $Rh(H)Cl(PPr^i_3)_2(\text{-}C{\equiv}CPh)$

C = $RhCl(PPr^i_3)_2(=C{=}CPhH)$

The rate equations used were:

$$\frac{dA}{dT} = -k_1A + k_2B$$
$$\frac{dB}{dT} = k_1A - (k_2 + k_3)B$$
$$\frac{dC}{dT} = k_3B$$

The direct solution of the rate equations is[5]

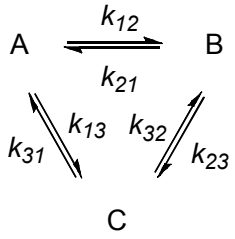
$$A = A_0(\lambda_2 - \lambda_1)^{-1}\left[(\lambda_2 - \lambda_1)e^{-\lambda_1 t} - (\lambda_1 - k_1)e^{-\lambda_2 t}\right]$$
$$B = A_0k_1(\lambda_2 - \lambda_1)^{-1}\left[e^{-\lambda_1 t} - e^{-\lambda_2 t}\right]$$
$$C = A_0\left[1 - \lambda_2(\lambda_2 - \lambda_1)^{-1}e^{-\lambda_1 t} + \lambda_1(\lambda_2 - \lambda_1)^{-1}e^{-\lambda_2 t}\right]$$

where:

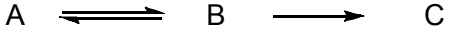
$$\lambda_1 = \tfrac{1}{2}(p - q)$$
$$\lambda_2 = \tfrac{1}{2}(p + q)$$
$$p = k_1 + k_2 + k_3$$
$$q = \sqrt{(p^2 - 4k_1k_2)}$$

when at t = 0, A = A_0 and B = C = 0.

An alternative approach for modelling the η^2-alkyne/alkynyl hydride/vinylidene system, which was useful for investigating alternate reaction pathways was to use the integrated rate equations (below) for the system:



the value of the rate constants can be varied to create several permutations, for example, for:



the constants k_{13}, k_{31} and k_{32} can be set to zero. Other reaction pathways, for example:

are also easily modelled. In this example, k_{31}, k_{32} and k_{23} are set to zero.

The relevant equations used were:[6]

$$[A]_0-[A]=\frac{1}{\lambda_1-\lambda_2}\left\{\frac{\lambda_2 T'}{\theta_1}(e^{-\theta_1 t}-1)-\frac{\lambda_1 T''}{\theta_2}(e^{-\theta_2 t}-1)\right\}$$

$$[B]_0-[B]=\frac{1}{\lambda_1-\lambda_2}\left\{-\frac{T'}{\theta_1}(e^{-\theta_1 t}-1)+\frac{T''}{\theta_2}(e^{-\theta_2 t}-1)\right\}$$

$$[C]_0-[C]=\frac{1}{\lambda_1-\lambda_2}\left\{-(\lambda_2-1)\frac{T'}{\theta_1}(e^{-\theta_1 t}-1)+(\lambda_1-1)\frac{T''}{\theta_2}(e^{-\theta_2 t}-1)\right\}$$

where:

$$\theta_{1(2)}=\frac{S_1+S_2}{2}(\pm)\sqrt{\frac{(S_1+S_2)^2}{4}+(k_{12}-k_{32})(k_{21}-k_{31)}}$$

$$S_1=k_{12}+k_{31}+k_{13}$$

$$S_2=k_{21}+k_{23}+k_{32}$$

$$\lambda_1=\frac{k_{21}-k_{31}}{S_2-\theta_1}$$

$$\lambda_2=\frac{k_{21}-k_{31}}{S_2-\theta_2}$$

$$T'=T_1+\lambda_1 T_2$$

$$T''=T_1+\lambda_2 T_2$$

$$T_1=(k_{12}+k_{13})[A]_0-k_{21}[B]_0-k_{31}[C]_0$$

$$T_2=-k_{12}[A]_0+(k_{21}+k_{23})[B]_0-k_{32}[C]_0$$

with the initial conditions $[A]=[A]_0$, $[B]=[B]_0$, $[C]=[C]_0$.

Both approaches (modelling either of the two sets of equations using Excel, or using Dynafit) yielded very similar results. In all cases the best fit to the experimental data was based on the model

Errors in the measured integrals were calculated from the standard deviation of the integrals for the internal standard (triphenylphosphine oxide) throughout the experiment.

Activation parameters at 298 K were calculated using the Eyring equation and the errors in the data from the *Dynafit* programme propagated appropriately.

The fits for the conversion of **2a** to **4a** in hexane, and for the conversion of **2b** to **4b** in THF are shown in **Figures S1** and **S2** respectivty.

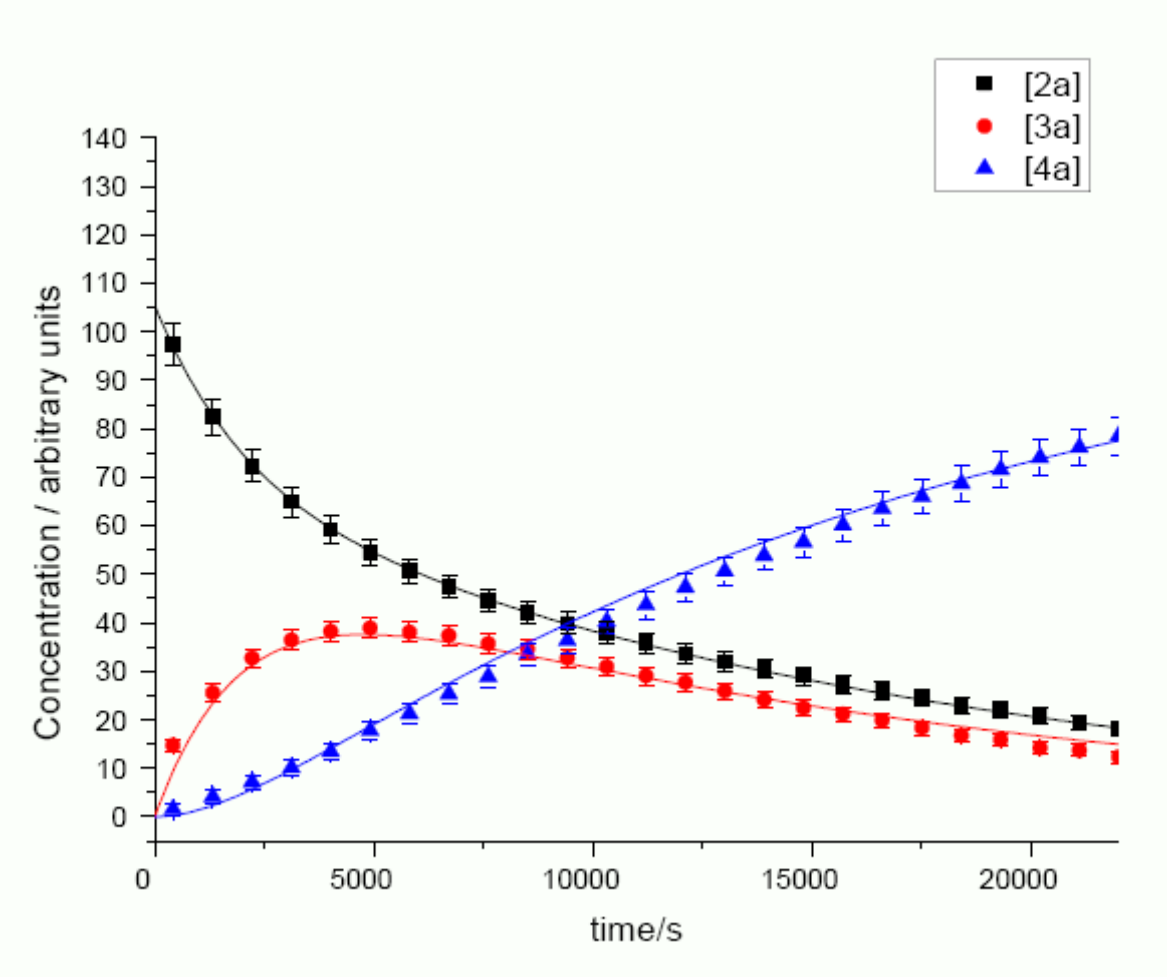


Figure S1 Reaction Profile for the formation of complex **4a** from **2a** with theoretical fit in hexane solution.

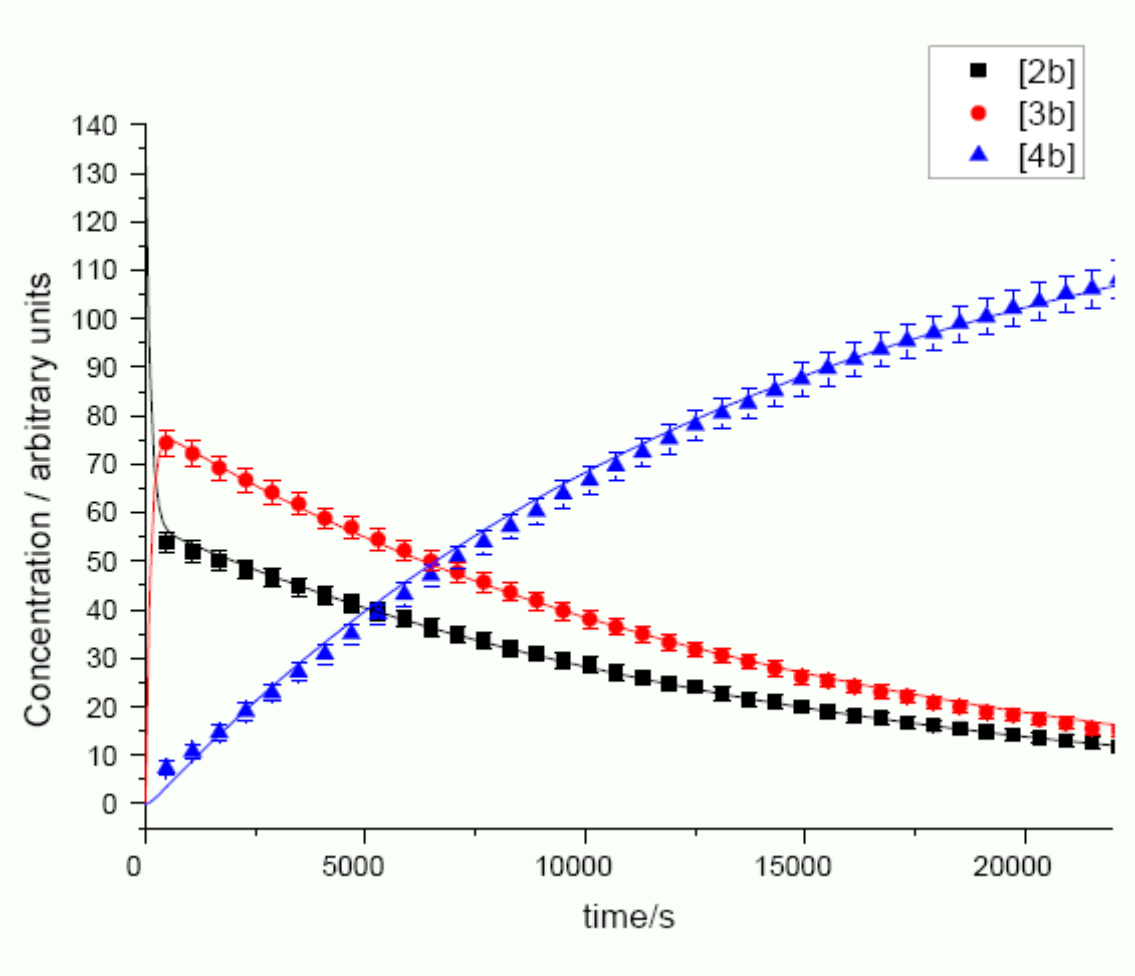


Figure S2 Reaction Profile for the formation of complex **4b** from **2b** with theoretical fit in THF solution.

3. DFT Calculations

The potential energy surfaces for the alkyne to vinylidene isomerisation involving the four model complexes described in **Figure S3** were investigated using density functional theory (DFT). Initial optimisations were performed at the (RI-)BP86/SV(P) level, followed by frequency calculations at the same level. Transition states were located by performing an initial constrained minimisation (by freezing internal coordinates that change most during the reaction) of a structure close to the anticipated transition state. This was followed by a frequency calculation to identify the transition vector to follow during a subsequent transition state optimisation. A frequency calculation was then performed on the optimised transition-state-structure. All minima were confirmed as such by the absence of imaginary frequencies and all transition states were identified by the presence of only one imaginary frequency.

Single-point calculations on the (RI-)BP86/SV(P) optimised geometries were performed using the hybrid PBE0 functional and the TZVP basis set in order to obtain more reliable energies. For the simplest system (**model *i***) the minima were also re-optimised at the (RI-)PBE0/TZVP level. The energies determined at this level of theory were almost indistinguishable from those obtained from the (RI-)PBE0/TZVP single point calculations on the (RI-)BP86/SV(P) optimised geometries suggesting that this less expensive methodology was sufficient for the system.

The (RI-)PBE0/TZVP SCF energies were corrected for their zero point energies, thermal energies and entropies (obtained from the (RI-)BP86/SV(P)-level frequency calculations) and the resulting Gibbs energies are shown below and in the main section of the publication. In all calculations a 28 electron quasi-relativistic ECP replaced the core electrons of Rh. No symmetry constraints were applied during optimisations. All calculations were performed using the TURBOMOLE package using the resolution of identity (RI) approximation.[7], [8], [9]

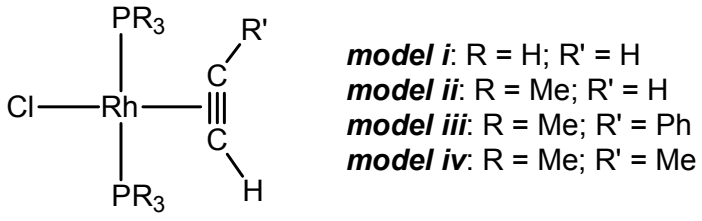


Figure S3 - Model structures used for DFT calculations. **Models *iii*** and ***iv*** were chosen as slightly simplified models of the experimental systems **a** and **b** respectively – see main section for details.

In previous theoretical studies, an alkyne σ-complex as shown in **Figure S4** was found on the potential energy surface in addition to structures **2**, **3** and **4** described in the main section.[10] This was also found in our studies of **model *i*** and is described below as **model 3*_i_**. The transition states connecting this to **models 2i** and **3i** are denoted **TS_{23}*_i_** and **TS_3*$_3$_i_** respectively. Attempts to locate a similar σ-complex in the **model *ii, iii*** and ***iv*** systems were unsuccessful, with all optimisation attempts converging to structure **3**. In view of this, and the very flat potential energy surface around **model 3*_i_**, which is unlikely to significantly affect the kinetics, this structure was not discussed in the main section.

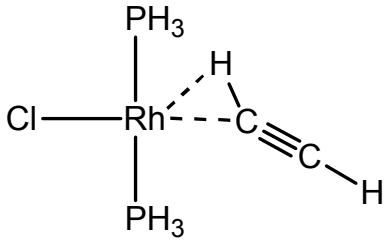


Figure S4 – schematic representation of the alkyne σ-complex found in previous work and in this study for the **model *i*** system.

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Table S1 – Breakdown of individual contributions to the reported Gibbs energies at the different levels used during this work.

	BP86/SV(P) (optimisation)						PBE0/TZVP (single point)			PBE0/TZVP (optimisation)		
Structure	**ZPE (a.u.)**	**H corr. (kJ/mol)**	**S (kJ/mol)**	**SCF energy (a.u.)**	**Rel. H^{298} (kJ/mol)**	**Rel. G^{298} (kJ/mol)**	**SCF energy (a.u.)**	**Rel. H^{298} (kJ/mol)**	**Rel. G^{298} (kJ/mol)**	**SCF energy (a.u.)**	**Rel. H^{298} (kJ/mol)**	**Rel. G^{298} (kJ/mol)**
model *i* ClRh(PH3)2(C2H2)												
model 2i	0.082682	248.1	0.4533	-1334.324477	0	0	-1334.807662	0	0	-1334.808281	0	0
ts23*i	0.079622	240.9	0.4668	-1334.279579	111	107	-1334.766093	102	98			
model 3*i	0.080228	242.1	0.4607	-1334.300952	56	54	-1334.787275	47	45	-1334.787863	48	45
ts3*3i	0.079013	238.4	0.4586	-1334.300636	53	51	-1334.786976	45	43			
model 3i	0.080416	243.5	0.4800	-1334.304894	47	39	-1334.791225	39	31	-1334.791784	39	31
ts34i	0.078021	236.8	0.4639	-1334.273191	123	120	-1334.759265	116	113			
model 4i	0.083100	249.4	0.4630	-1334.336506	-30	-33	-1334.819186	-29	-32	-1334.819707	-29	-32
model *ii* ClRh(PMe3)2(C2H2)												
model 2ii	0.251392	716.1	0.6316	-1570.067684	0	0	-1569.727671	0	0			
ts23ii	0.248298	708.5	0.6366	-1570.023349	109	107	-1569.682044	112	111			
model 3ii	0.249192	711.3	0.6448	-1570.057623	22	18	-1569.718892	18	14			
ts34ii	0.246580	704.4	0.6378	-1570.016679	122	120	-1569.673521	130	129			
model 4ii	0.251845	717.6	0.6433	-1570.081642	-35	-39	-1569.736249	-21	-25			
model *iii* ClRh(PMe3)2(CHCPh)												
model 2iii	0.331079	937.9	0.7406	-1800.974478	0	0	-1800.587049	0	0			
ts23iii	0.328997	932.0	0.7444	-1800.936767	93	92	-1800.544111	107	106			
model 3iii	0.328995	933.5	0.7682	-1800.963252	25	17	-1800.575542	26	18			
ts34iii	0.326710	927.2	0.7584	-1800.924751	120	115	-1800.534225	128	123			
model 4iii	0.331831	939.8	0.7695	-1800.979911	-12	-21	-1800.587526	1	-8			
model *iv* ClRh(PMe3)2(CHCMe)												
model 2iv	0.278792	792.8	0.6687	-1609.358508	0	0	-1609.013451	0	0			
ts23iv	0.275895	785.6	0.6807	-1609.319764	95	91	-1608.972497	100	97			
model 3iv	0.276584	788.2	0.6919	-1609.347764	24	17	-1609.002603	24	17			
ts34iv	0.274395	781.9	0.6797	-1609.310361	116	112	-1608.962322	123	120			
model 4iv	0.279724	795.0	0.6786	-1609.364536	-14	-17	-1609.014378	0	-3			

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ZPE = zero point energy, H corr = combined thermal and ZPE correction to the SCFenergies.

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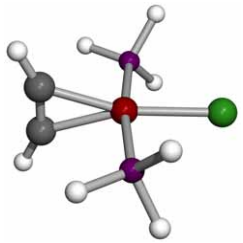
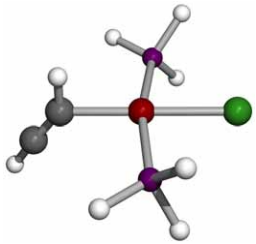
Optimised structures for the model *i* system – Gibbs energies in kJ mol^{-1} (relative to structure 2) are shown below each structure.



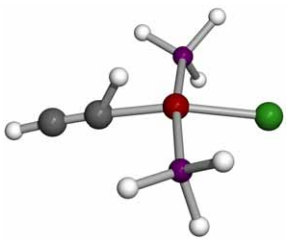
Model 2i

0



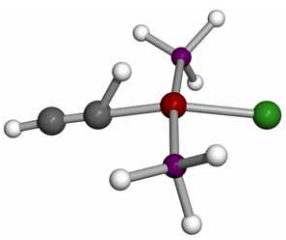
TS_{23}*i

98



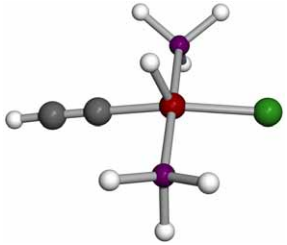
Model 3*i

45



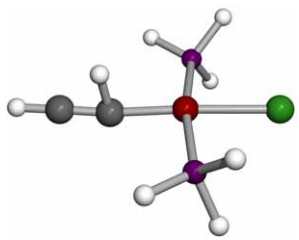
TS_3*$_3$i

43



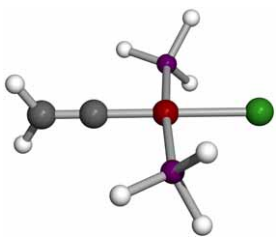
Model 3i

31



TS_{34}i

113



Model 4i

-32

Table S2 – Solvation energy corrections (COSMO model, BP86/SV(P) level) to the gas phase energies for each stationary point and relative Gibbs energies (in solution) at 298.15 K.

Structure	PBE0/TZVP (gas phase)		Solvation corrections (COSMO)			
	Rel. H^{298} (kJ/mol)	Rel. G^{298} (kJ/mol)	Solvation correction hexane (ε 2.02) (a.u.)	Rel. G^{298} (hexane) (kJ/mol)	Solvation correction thf (ε 7.52) (a.u.)	Rel. G^{298} (thf) (kJ/mol)
model *i* ClRh(PH3)2(C2H2)						
model2i	0	0	-0.005393	0	-0.012840	0
ts23i	102	98	-0.006276	96	-0.015172	92
model3i	39	31	-0.006181	29	-0.014341	27
ts34i	116	113	-0.007010	108	-0.017341	101
model4i	-29	-32	-0.005659	-33	-0.013470	-33
model *ii* ClRh(PMe3)2(C2H2)						
model2ii	0	0	-0.004676	0	-0.011191	0
ts23ii	112	111	-0.005315	109	-0.012996	106
model3ii	18	14	-0.005699	12	-0.013023	9
ts34ii	130	129	-0.005879	125	-0.014630	120
model4ii	-21	-25	-0.004743	-25	-0.011327	-25
model *iii* ClRh(PMe3)2(CHCPh)						
model2iii	0	0	-0.004846	0	-0.011476	0
ts23iii	107	106	-0.005906	103	-0.014605	98
model3iii	26	18	-0.006163	14	-0.014152	11
ts34iii	128	123	-0.006511	118	-0.016131	111
model4iii	1	-8	-0.005383	-9	-0.012600	-11
model *iv* ClRh(PMe3)2(CHCMe)						
model2iv	0	0	-0.004737	0	-0.011473	0
ts23iv	100	97	-0.005708	94	-0.014393	89
model3iv	24	17	-0.005362	15	-0.012367	15
ts34iv	123	120	-0.006443	116	-0.016428	107
model4iv	0	-3	-0.004584	-3	-0.011063	-2

Electronic Supplementary Information for Dalton Transactions

Model 2i (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	0.72596	-2.37830	0.02888
Cl	2.33063	-0.67821	0.37749
C	-1.06143	-3.39823	-0.45070
C	-0.20028	-4.27118	-0.09970
P	0.14619	-2.09239	2.23635
P	1.50963	-2.44124	-2.13277
H	-2.04691	-3.07254	-0.79538
H	0.13976	-5.29112	0.10433
H	1.14433	-2.34362	3.23672
H	-0.24127	-0.78306	2.67645
H	-0.93125	-2.84288	2.82660
H	1.40780	-1.24749	-2.92276
H	2.90706	-2.69160	-2.33983
H	0.98215	-3.37400	-3.09464

Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	63.85	4.15856	YES YES
8	a	93.85	0.57485	YES YES
9	a	97.00	0.50975	YES YES
10	a	108.30	0.66197	YES YES
11	a	115.09	2.50859	YES YES
12	a	118.19	11.52647	YES YES
13	a	147.96	0.00309	YES YES
14	a	180.20	0.61973	YES YES
15	a	275.64	7.15147	YES YES
16	a	308.24	9.58721	YES YES
17	a	328.91	10.22718	YES YES
18	a	425.68	0.00316	YES YES
19	a	433.28	0.00097	YES YES
20	a	459.80	1.37643	YES YES
21	a	484.99	0.57279	YES YES
22	a	511.37	1.22385	YES YES
23	a	548.03	16.97780	YES YES
24	a	643.95	47.81005	YES YES
25	a	664.56	0.33866	YES YES
26	a	773.03	13.18050	YES YES
27	a	789.28	35.91804	YES YES
28	a	987.08	447.14098	YES YES
29	a	1016.20	2.59816	YES YES
30	a	1090.92	0.71888	YES YES
31	a	1091.50	1.00537	YES YES
32	a	1093.79	4.24573	YES YES
33	a	1095.33	11.75277	YES YES
34	a	1745.31	50.31795	YES YES
35	a	2332.66	226.99694	YES YES
36	a	2337.98	27.94029	YES YES
37	a	2368.77	46.70221	YES YES
38	a	2371.45	29.12911	YES YES
39	a	2376.80	22.15595	YES YES
40	a	2376.90	15.83510	YES YES
41	a	3188.34	10.82969	YES YES
42	a	3248.96	3.93853	YES YES

Model 2i (RI-)PBE0/TZVP optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	0.73011	-2.37628	0.02921
Cl	2.34334	-0.67254	0.38153
C	-1.06047	-3.40624	-0.44976
C	-0.20823	-4.27059	-0.10199
P	0.14590	-2.09219	2.24116
P	1.51164	-2.44307	-2.13819
H	-2.03247	-3.07810	-0.78995
H	0.13413	-5.27571	0.09897
H	1.14066	-2.33937	3.23431
H	-0.23947	-0.78866	2.67460
H	-0.92605	-2.84009	2.82475
H	1.41066	-1.25338	-2.92016
H	2.90174	-2.69173	-2.34163
H	0.98323	-3.37045	-3.09207

Vibrational frequencies

#	mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	64.86	4.09914	YES	YES
8	a	100.44	0.37167	YES	YES
9	a	103.91	0.84384	YES	YES
10	a	110.09	1.51397	YES	YES
11	a	114.23	0.79046	YES	YES
12	a	121.01	10.94067	YES	YES
13	a	143.24	0.00257	YES	YES
14	a	177.65	0.49452	YES	YES
15	a	275.10	5.53976	YES	YES
16	a	297.92	19.83764	YES	YES
17	a	317.31	4.91559	YES	YES
18	a	414.52	0.01279	YES	YES
19	a	426.43	0.00150	YES	YES
20	a	449.94	1.56977	YES	YES
21	a	477.83	0.63914	YES	YES
22	a	504.71	1.46515	YES	YES
23	a	540.39	17.16919	YES	YES
24	a	648.66	57.17670	YES	YES
25	a	655.40	0.00012	YES	YES
26	a	774.82	13.89637	YES	YES
27	a	777.54	32.53791	YES	YES
28	a	965.97	410.70384	YES	YES
29	a	995.29	1.84620	YES	YES
30	a	1081.22	0.35908	YES	YES
31	a	1083.13	2.34680	YES	YES
32	a	1084.75	8.32764	YES	YES
33	a	1086.09	2.96532	YES	YES
34	a	1749.07	63.20388	YES	YES
35	a	2335.78	208.00493	YES	YES
36	a	2340.27	22.33691	YES	YES
37	a	2368.43	45.95550	YES	YES
38	a	2370.29	18.69977	YES	YES
39	a	2373.80	27.45343	YES	YES
40	a	2374.16	12.24447	YES	YES
41	a	3210.35	13.70236	YES	YES
42	a	3270.61	5.36389	YES	YES

TS_{23}*i (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	-0.15203	0.16546	0.00086
Cl	2.23835	0.00658	-0.01596
C	-2.20645	0.30257	0.01413
C	-3.04351	-0.62911	0.02178
P	0.10712	0.09948	2.27357
P	0.07556	0.07140	-2.27416
H	-2.08275	1.41372	0.01255
H	-3.70993	-1.48497	0.02723
H	0.71589	-1.08025	2.81740
H	0.96284	1.06931	2.89464
H	-0.99922	0.18927	3.19370
H	0.93236	1.02388	-2.91925
H	0.66432	-1.12162	-2.81038
H	-1.04263	0.15990	-3.18005

Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1	a	-494.98	0.00000	YES YES
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7		0.00	0.52868	- -
8	a	53.58	2.88031	YES YES
9	a	72.05	0.52157	YES YES
10	a	79.77	0.91856	YES YES
11	a	82.27	1.21943	YES YES
12	a	100.29	1.13414	YES YES
13	a	104.98	2.18778	YES YES
14	a	115.96	12.40946	YES YES
15	a	195.51	0.08837	YES YES
16	a	296.15	13.07058	YES YES
17	a	298.79	11.45050	YES YES
18	a	328.44	0.06996	YES YES
19	a	367.60	5.33168	YES YES
20	a	439.84	14.61200	YES YES
21	a	448.50	0.48207	YES YES
22	a	473.54	3.24122	YES YES
23	a	491.65	11.55514	YES YES
24	a	527.15	0.63410	YES YES
25	a	558.44	20.07066	YES YES
26	a	620.28	49.56307	YES YES
27	a	672.79	35.20806	YES YES
28	a	992.44	467.31220	YES YES
29	a	1020.65	13.34287	YES YES
30	a	1087.99	3.20348	YES YES
31	a	1090.38	2.91272	YES YES
32	a	1094.32	0.20039	YES YES
33	a	1097.80	11.82635	YES YES
34	a	1799.17	40.23998	YES YES
35	a	2320.62	228.18381	YES YES
36	a	2324.29	25.76095	YES YES
37	a	2368.71	72.52403	YES YES
38	a	2372.86	35.23152	YES YES
39	a	2374.42	10.62600	YES YES
40	a	2376.33	19.02969	YES YES
41	a	2944.52	30.98536	YES YES
42	a	3357.81	90.30985	YES YES

Model 3*i (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	-0.11072	0.10299	0.00068
Cl	2.22445	-0.23244	-0.01433
C	-2.08094	-0.13234	0.01350
C	-3.30041	-0.37199	0.02155
P	0.05355	0.05214	2.29538
P	0.02334	0.05213	-2.29593
H	-1.48674	1.05238	0.00972
H	-4.34608	-0.65229	0.02863
H	0.47069	-1.19012	2.87633
H	1.00251	0.91606	2.93221
H	-1.08464	0.30809	3.13293
H	0.96381	0.91574	-2.94565
H	0.43286	-1.19027	-2.88192
H	-1.12581	0.30770	-3.11834

Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	67.06	6.12093	YES YES
8	a	71.27	0.18623	YES YES
9	a	80.55	0.91970	YES YES
10	a	88.80	0.01172	YES YES
11	a	102.40	4.40193	YES YES
12	a	104.47	1.05428	YES YES
13	a	118.09	9.24384	YES YES
14	a	290.08	5.60392	YES YES
15	a	313.61	17.98334	YES YES
16	a	325.70	16.99726	YES YES
17	a	334.62	9.35573	YES YES
18	a	392.59	0.20798	YES YES
19	a	419.46	8.68657	YES YES
20	a	446.66	0.78445	YES YES
21	a	492.75	0.23332	YES YES
22	a	521.15	0.58351	YES YES
23	a	549.93	42.10992	YES YES
24	a	554.16	13.07873	YES YES
25	a	565.54	25.35295	YES YES
26	a	646.45	39.44970	YES YES
27	a	841.43	279.98240	YES YES
28	a	985.19	425.39643	YES YES
29	a	1015.85	0.57142	YES YES
30	a	1089.29	0.14512	YES YES
31	a	1091.64	6.92092	YES YES
32	a	1095.45	0.30811	YES YES
33	a	1098.12	9.53101	YES YES
34	a	1844.82	17.91586	YES YES
35	a	2019.62	15.92931	YES YES
36	a	2360.66	185.79674	YES YES
37	a	2363.81	5.91061	YES YES
38	a	2383.71	9.81905	YES YES
39	a	2385.38	31.09668	YES YES
40	a	2392.40	3.55595	YES YES
41	a	2392.97	24.89715	YES YES
42	a	3370.50	82.29771	YES YES

Model 3*i (RI-)PBE0/TZVP optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	-0.10790	0.09603	-0.00012
Cl	2.23772	-0.21877	0.00224
C	-2.07979	-0.13070	-0.00203
C	-3.29180	-0.35030	-0.00312
P	0.02308	0.05093	2.30221
P	0.02761	0.05092	-2.30223
H	-1.46727	1.03326	-0.00140
H	-4.32732	-0.62269	-0.00403
H	0.43013	-1.18339	2.88848
H	0.96133	0.91333	2.93960
H	-1.12329	0.31132	3.11239
H	0.96787	0.91286	-2.93731
H	0.43533	-1.18369	-2.88741
H	-1.11654	0.31189	-3.11535

Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	66.87	6.16183	YES YES
8	a	68.40	0.11727	YES YES
9	a	77.42	0.69097	YES YES
10	a	85.90	0.03027	YES YES
11	a	98.78	3.29857	YES YES
12	a	109.68	1.15836	YES YES
13	a	118.95	9.47495	YES YES
14	a	287.26	4.49539	YES YES
15	a	304.13	26.88068	YES YES
16	a	313.13	15.66559	YES YES
17	a	322.84	7.18723	YES YES
18	a	382.70	0.19737	YES YES
19	a	417.47	9.47480	YES YES
20	a	436.56	0.37540	YES YES
21	a	483.77	0.00003	YES YES
22	a	512.27	0.87167	YES YES
23	a	544.78	16.96167	YES YES
24	a	547.18	34.80042	YES YES
25	a	558.29	57.01984	YES YES
26	a	634.53	40.93485	YES YES
27	a	846.53	299.50543	YES YES
28	a	962.28	396.68221	YES YES
29	a	993.99	0.23751	YES YES
30	a	1080.08	0.02386	YES YES
31	a	1082.87	6.63217	YES YES
32	a	1084.08	0.27190	YES YES
33	a	1086.46	7.53669	YES YES
34	a	1841.22	20.84217	YES YES
35	a	2023.22	30.60961	YES YES
36	a	2362.22	168.67049	YES YES
37	a	2365.03	4.13981	YES YES
38	a	2380.48	4.56229	YES YES
39	a	2381.61	28.06091	YES YES
40	a	2387.73	4.10560	YES YES
41	a	2388.37	23.61625	YES YES
42	a	3389.81	98.61748	YES YES

$TS_{23}i$ (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	-0.12068	0.11843	0.00127
Cl	2.21415	-0.25846	-0.00843
C	-2.07469	-0.11224	0.00987
C	-3.30498	-0.26815	0.01551
P	0.00806	0.08162	2.30002
P	-0.01269	0.08142	-2.29870
H	-1.32536	1.18528	0.00677
H	-4.36605	-0.48291	0.02066
H	0.35025	-1.17453	2.89974
H	0.98782	0.90427	2.94395
H	-1.13456	0.40379	3.10593
H	0.97729	0.88513	-2.95076
H	0.30001	-1.18109	-2.90140
H	-1.15588	0.42484	-3.09500

Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1	a	-466.36	0.00000	YES YES
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7		0.00	0.05172	- -
8	a	66.11	0.33469	YES YES
9	a	66.59	6.30151	YES YES
10	a	77.40	1.47076	YES YES
11	a	90.00	0.05202	YES YES
12	a	102.62	2.02525	YES YES
13	a	103.69	3.63992	YES YES
14	a	124.20	23.51251	YES YES
15	a	291.23	4.33818	YES YES
16	a	315.16	11.27909	YES YES
17	a	332.21	8.87602	YES YES
18	a	361.11	6.81190	YES YES
19	a	387.86	0.01315	YES YES
20	a	448.05	0.34709	YES YES
21	a	487.49	12.05777	YES YES
22	a	498.14	0.05517	YES YES
23	a	523.39	1.04313	YES YES
24	a	551.35	52.60474	YES YES
25	a	558.38	7.84340	YES YES
26	a	567.54	29.52455	YES YES
27	a	683.40	38.84460	YES YES
28	a	984.22	417.76027	YES YES
29	a	1013.14	4.33571	YES YES
30	a	1088.91	0.02167	YES YES
31	a	1091.41	6.70459	YES YES
32	a	1095.69	0.45808	YES YES
33	a	1098.02	8.26795	YES YES
34	a	1947.18	13.69149	YES YES
35	a	2053.13	13.11813	YES YES
36	a	2366.78	178.13219	YES YES
37	a	2370.01	1.54922	YES YES
38	a	2386.54	2.39631	YES YES
39	a	2387.73	29.44594	YES YES
40	a	2396.43	4.69183	YES YES
41	a	2397.15	23.08322	YES YES
42	a	3370.49	69.51978	YES YES

Model 3i (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	-0.04832	-0.07350	-0.00105
Cl	0.18100	2.29974	0.01486
P	-0.08182	-0.09584	2.30058
P	-0.08154	-0.06773	-2.30150
H	1.19130	-0.13814	2.96054
H	-0.65971	1.01417	2.99659
H	-0.71886	-1.18194	2.98200
H	-0.65009	1.05546	-2.98387
H	1.19076	-0.11405	-2.96222
H	-0.72786	-1.14048	-2.99461
C	0.14835	-2.02960	-0.01367
C	0.27580	-3.26027	-0.01659
H	-1.52732	-0.48695	-0.00422
H	0.43379	-4.33128	-0.02060

Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	24.38	0.26188	YES YES
8	a	39.07	3.66161	YES YES
9	a	56.49	3.66277	YES YES
10	a	85.93	0.13930	YES YES
11	a	103.40	2.78085	YES YES
12	a	103.83	5.95048	YES YES
13	a	117.13	15.06598	YES YES
14	a	245.79	7.53997	YES YES
15	a	293.28	1.31400	YES YES
16	a	319.44	18.01689	YES YES
17	a	326.38	3.63238	YES YES
18	a	377.22	0.53665	YES YES
19	a	446.40	0.22313	YES YES
20	a	466.49	10.43978	YES YES
21	a	487.62	1.42715	YES YES
22	a	518.37	0.05220	YES YES
23	a	535.60	1.99669	YES YES
24	a	566.87	33.37680	YES YES
25	a	570.53	10.36378	YES YES
26	a	580.07	48.82275	YES YES
27	a	704.10	38.27061	YES YES
28	a	984.26	409.89489	YES YES
29	a	1014.78	1.97191	YES YES
30	a	1088.66	2.26713	YES YES
31	a	1091.70	7.51058	YES YES
32	a	1094.48	0.21127	YES YES
33	a	1096.12	5.28990	YES YES
34	a	2004.59	11.29610	YES YES
35	a	2242.80	1.14559	YES YES
36	a	2369.59	118.06448	YES YES
37	a	2372.53	12.89474	YES YES
38	a	2394.53	28.18648	YES YES
39	a	2395.72	20.57475	YES YES
40	a	2405.03	6.59118	YES YES
41	a	2406.37	19.31205	YES YES
42	a	3369.18	48.83833	YES YES

Model 3i (RI-)PBE0/TZVP optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	-0.04120	-0.07621	0.00025
Cl	0.17216	2.30925	-0.00186
P	-0.08419	-0.08249	2.30782
P	-0.08437	-0.08469	-2.30699
H	1.17595	-0.11998	2.97573
H	-0.66529	1.03215	2.97727
H	-0.72626	-1.15850	2.98353
H	-0.65887	1.03323	-2.97647
H	1.17557	-0.12943	-2.97478
H	-0.73286	-1.15710	-2.98204
C	0.14446	-2.03346	0.00095
C	0.26281	-3.25470	0.00000
H	-1.50580	-0.47642	0.00045
H	0.41476	-4.31468	-0.00061

Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	31.93	0.09605	YES YES
8	a	41.84	2.28542	YES YES
9	a	60.09	4.94189	YES YES
10	a	83.54	0.30906	YES YES
11	a	102.00	6.34772	YES YES
12	a	109.63	1.01037	YES YES
13	a	118.41	16.58671	YES YES
14	a	243.34	6.40987	YES YES
15	a	289.59	0.62007	YES YES
16	a	302.89	27.83932	YES YES
17	a	320.47	0.16745	YES YES
18	a	368.68	0.22023	YES YES
19	a	441.14	0.56072	YES YES
20	a	460.22	12.57970	YES YES
21	a	480.22	0.39294	YES YES
22	a	510.27	0.18138	YES YES
23	a	528.56	1.91416	YES YES
24	a	542.27	48.79763	YES YES
25	a	561.72	19.68417	YES YES
26	a	563.07	54.93778	YES YES
27	a	696.19	34.00377	YES YES
28	a	962.66	387.89097	YES YES
29	a	993.64	1.62998	YES YES
30	a	1079.76	2.01690	YES YES
31	a	1082.54	6.17769	YES YES
32	a	1083.64	0.41202	YES YES
33	a	1085.66	4.80561	YES YES
34	a	2003.02	24.78345	YES YES
35	a	2261.54	0.37384	YES YES
36	a	2368.83	104.34390	YES YES
37	a	2370.97	6.75158	YES YES
38	a	2390.61	27.26157	YES YES
39	a	2391.52	18.08149	YES YES
40	a	2401.43	6.13227	YES YES
41	a	2402.32	18.85102	YES YES
42	a	3387.70	63.48009	YES YES

$TS_{34}i$ (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	-0.04390	-0.17744	-0.00100
Cl	0.02748	2.20310	0.01755
P	0.00286	-0.00445	2.28418
P	0.00116	0.02798	-2.28343
C	0.00736	-2.09384	-0.01540
C	-0.12788	-3.36131	-0.02493
H	1.20116	0.53146	2.86440
H	-0.93784	0.87339	2.91650
H	-0.14738	-1.13610	3.16050
H	-0.93204	0.92369	-2.90195
H	1.20355	0.56028	-2.85806
H	-0.16081	-1.08979	-3.17540
H	-1.19245	-2.25258	-0.01608
H	-0.22700	-4.44251	-0.03275

Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1	a	-1087.55	0.00000	YES YES
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7		0.00	1.36680	- -
8	a	56.33	2.28121	YES YES
9	a	77.46	0.58772	YES YES
10	a	84.79	6.40459	YES YES
11	a	95.34	0.47537	YES YES
12	a	96.82	2.78798	YES YES
13	a	110.72	0.77804	YES YES
14	a	122.10	9.25859	YES YES
15	a	293.86	31.18799	YES YES
16	a	303.56	9.46476	YES YES
17	a	306.46	33.33802	YES YES
18	a	319.42	1.08666	YES YES
19	a	332.87	0.82594	YES YES
20	a	396.93	51.11414	YES YES
21	a	436.85	0.78368	YES YES
22	a	444.93	0.01664	YES YES
23	a	482.16	5.74310	YES YES
24	a	503.04	0.51648	YES YES
25	a	516.01	0.72096	YES YES
26	a	554.78	22.56212	YES YES
27	a	606.35	46.18820	YES YES
28	a	990.74	436.56574	YES YES
29	a	1015.95	17.34089	YES YES
30	a	1089.23	2.04827	YES YES
31	a	1090.96	3.43474	YES YES
32	a	1097.94	0.74290	YES YES
33	a	1101.08	11.95106	YES YES
34	a	1817.10	240.05634	YES YES
35	a	2338.78	226.28356	YES YES
36	a	2342.03	15.27723	YES YES
37	a	2368.04	37.55433	YES YES
38	a	2370.52	35.14875	YES YES
39	a	2380.51	13.70156	YES YES
40	a	2381.77	31.32249	YES YES
41	a	2384.26	2.75661	YES YES
42	a	3337.51	180.24557	YES YES

Model 4i (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	-0.00081	-0.10340	-0.00052
Cl	0.00244	2.27477	0.00730
P	-0.00111	-0.01394	2.30263
P	-0.00097	0.00001	-2.30299
H	1.09168	0.66033	2.94087
H	-1.07536	0.68982	2.94021
H	-0.01644	-1.20370	3.10576
H	-1.08641	0.69049	-2.93638
H	1.08076	0.69544	-2.93727
H	0.00118	-1.18504	-3.11318
C	0.00081	-1.92772	-0.00567
C	0.00385	-3.25193	-0.00874
H	-0.94296	-3.82790	-0.01039
H	0.95325	-3.82363	-0.01003

Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	52.03	3.13291	YES YES
8	a	72.71	0.00968	YES YES
9	a	74.83	1.46631	YES YES
10	a	89.97	1.52962	YES YES
11	a	93.68	3.82250	YES YES
12	a	103.43	0.15329	YES YES
13	a	111.94	13.11494	YES YES
14	a	290.74	8.87855	YES YES
15	a	300.00	0.00052	YES YES
16	a	311.76	10.55921	YES YES
17	a	326.67	13.05819	YES YES
18	a	362.01	0.70803	YES YES
19	a	438.79	0.00013	YES YES
20	a	461.75	0.93475	YES YES
21	a	506.48	0.18429	YES YES
22	a	510.17	3.73982	YES YES
23	a	527.70	3.98690	YES YES
24	a	569.95	4.74259	YES YES
25	a	685.63	60.80214	YES YES
26	a	850.08	0.70342	YES YES
27	a	986.41	409.15639	YES YES
28	a	1010.14	11.99873	YES YES
29	a	1090.89	0.24702	YES YES
30	a	1092.01	4.41473	YES YES
31	a	1098.18	0.00838	YES YES
32	a	1101.27	11.66272	YES YES
33	a	1284.70	0.01741	YES YES
34	a	1688.29	232.26284	YES YES
35	a	2360.77	213.02844	YES YES
36	a	2364.20	0.96033	YES YES
37	a	2381.11	3.56763	YES YES
38	a	2382.66	34.82957	YES YES
39	a	2384.40	7.69086	YES YES
40	a	2384.76	18.52828	YES YES
41	a	3028.92	6.28741	YES YES
42	a	3097.81	1.56442	YES YES

Model 4i (RI-)PBE0/TZVP optimisation (symmetry: C_1)

XYZ coordinates (Å)

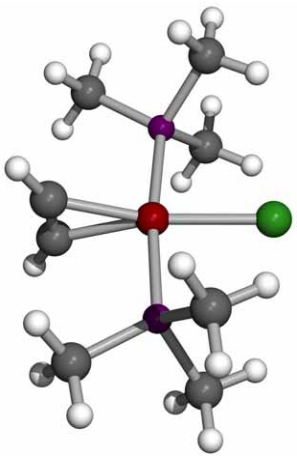
	x	y	z
Rh	-0.00026	-0.10274	0.00014
Cl	0.00121	2.28704	-0.00282
P	-0.00078	-0.01400	2.30762
P	-0.00068	-0.01968	-2.30754
H	1.08484	0.66200	2.93872
H	-1.07278	0.68418	2.93760
H	-0.01240	-1.20013	3.10137
H	-1.08099	0.66403	-2.93934
H	1.07678	0.66770	-2.94021
H	0.00091	-1.20786	-3.09828
C	0.00045	-1.92649	0.00233
C	0.00187	-3.24068	0.00381
H	-0.93390	-3.80825	0.00436
H	0.93902	-3.80600	0.00452

Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	52.64	2.89014	YES YES
8	a	84.43	4.11058	YES YES
9	a	94.79	0.02210	YES YES
10	a	98.02	1.83913	YES YES
11	a	102.71	0.09761	YES YES
12	a	103.04	0.63792	YES YES
13	a	116.08	12.99808	YES YES
14	a	289.51	7.52044	YES YES
15	a	296.81	0.00119	YES YES
16	a	300.47	28.02231	YES YES
17	a	314.93	2.53824	YES YES
18	a	360.72	1.13127	YES YES
19	a	433.92	0.00012	YES YES
20	a	456.92	0.33470	YES YES
21	a	502.14	0.34885	YES YES
22	a	504.56	3.84145	YES YES
23	a	520.87	3.58641	YES YES
24	a	561.98	4.92595	YES YES
25	a	698.45	64.93219	YES YES
26	a	850.46	0.17412	YES YES
27	a	966.10	376.63489	YES YES
28	a	990.15	9.64313	YES YES
29	a	1083.22	0.18633	YES YES
30	a	1084.83	3.15060	YES YES
31	a	1088.67	0.00730	YES YES
32	a	1091.72	10.26629	YES YES
33	a	1297.85	0.06236	YES YES
34	a	1672.34	271.68378	YES YES
35	a	2362.28	192.45134	YES YES
36	a	2365.35	1.16814	YES YES
37	a	2379.63	3.01628	YES YES
38	a	2380.77	22.99809	YES YES
39	a	2381.11	11.48779	YES YES
40	a	2381.37	21.09525	YES YES
41	a	3043.60	6.03877	YES YES
42	a	3114.65	0.82947	YES YES

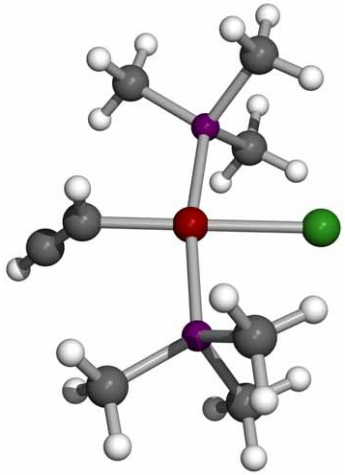
Electronic Supplementary Information for Dalton Transactions

Optimised structures for the model *ii* system – Gibbs energies in kJ mol^{-1} (relative to structure 2) are shown below each structure.



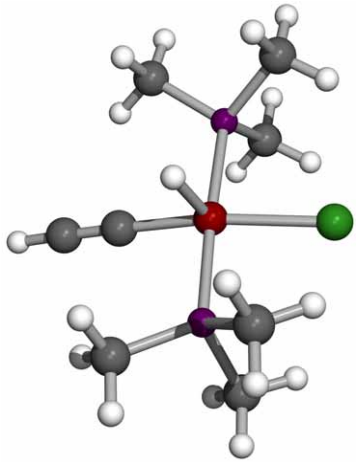
Model 2ii

0



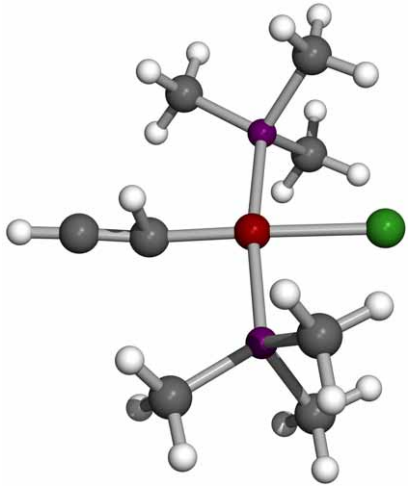
TS_{23}ii

111



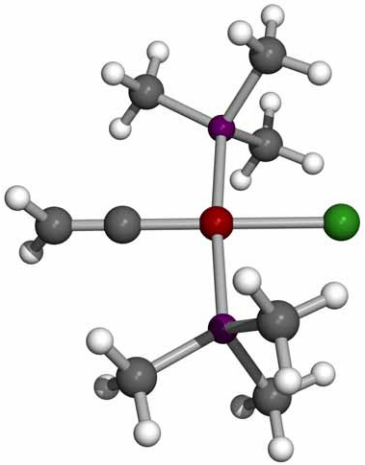
Model 3ii

14



TS_{34}ii

129



Model 4ii

-25

Model 2ii (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	0.04016	-0.00011	-0.00000
Cl	1.69401	1.68065	0.38835
C	-1.75389	-0.97132	-0.49482
C	-0.90479	-1.86538	-0.15569
P	-0.57855	0.28174	2.23185
P	0.84077	-0.07278	-2.18930
H	-2.74411	-0.64969	-0.83341
H	-0.60189	-2.90294	0.01956
C	0.77925	-0.07558	3.43884
C	-1.04374	2.02214	2.65733
C	-1.99941	-0.70423	2.89922
C	0.73303	1.55158	-3.07056
C	2.64282	-0.47903	-2.31303
C	0.06357	-1.25259	-3.39000
H	-1.24503	2.14565	3.74523
H	-1.94446	2.31518	2.07628
H	-0.20197	2.67645	2.34603
H	-2.91369	-0.48479	2.30772
H	-2.18676	-0.46758	3.96982
H	-1.78314	-1.78853	2.79276
H	0.47367	0.14552	4.48630
H	1.65037	0.55233	3.15584
H	1.07644	-1.14297	3.35601
H	0.53547	-1.17638	-4.39452
H	-1.02251	-1.03524	-3.47521
H	0.16892	-2.29156	-3.01134
H	1.19548	1.50646	-4.08210
H	1.25638	2.30461	-2.44393
H	-0.33283	1.85240	-3.16196
H	3.19198	0.24036	-1.66926
H	3.01250	-0.41575	-3.36117
H	2.81839	-1.50334	-1.91984

Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	36.39	0.19911	YES YES
8	a	40.73	2.78191	YES YES
9	a	49.31	0.01825	YES YES
10	a	84.85	2.50157	YES YES
11	a	98.68	0.05184	YES YES
12	a	128.32	3.60198	YES YES
13	a	136.20	0.14869	YES YES
14	a	151.75	0.00313	YES YES
15	a	159.48	0.10864	YES YES
16	a	174.92	1.55983	YES YES
17	a	175.27	0.96497	YES YES
18	a	181.92	0.37299	YES YES
19	a	186.23	0.04114	YES YES
20	a	195.14	1.05487	YES YES
21	a	198.77	5.74108	YES YES
22	a	209.50	0.13710	YES YES
23	a	212.77	0.61347	YES YES
24	a	216.14	0.06393	YES YES
25	a	223.05	0.33085	YES YES
26	a	225.08	0.07142	YES YES
27	a	242.79	0.00596	YES YES
28	a	254.55	0.73672	YES YES
29	a	256.05	2.45598	YES YES
30	a	258.18	10.85586	YES YES
31	a	306.22	8.09011	YES YES
32	a	316.68	16.67491	YES YES
33	a	338.74	0.26235	YES YES
34	a	425.00	0.01604	YES YES
35	a	477.72	3.84358	YES YES
36	a	631.69	11.48136	YES YES
37	a	640.79	64.80275	YES YES
38	a	644.00	0.61418	YES YES
39	a	660.91	0.08667	YES YES
40	a	703.38	3.02169	YES YES
41	a	704.34	12.16779	YES YES
42	a	704.42	2.67307	YES YES
43	a	705.59	23.15792	YES YES
44	a	774.19	0.07010	YES YES
45	a	775.22	0.06697	YES YES
46	a	777.46	9.16427	YES YES
47	a	796.71	28.88374	YES YES
48	a	823.96	1.04394	YES YES
49	a	829.70	0.15125	YES YES
50	a	834.73	18.33555	YES YES
51	a	841.05	8.24587	YES YES
52	a	934.64	2.30207	YES YES
53	a	935.50	59.51963	YES YES
54	a	938.69	423.38167	YES YES
55	a	940.56	37.32957	YES YES
56	a	943.04	50.50581	YES YES
57	a	957.69	1.47942	YES YES
58	a	1255.64	23.09353	YES YES
59	a	1255.93	9.88781	YES YES
60	a	1257.95	6.52822	YES YES
61	a	1259.82	27.81655	YES YES
62	a	1277.42	13.91438	YES YES
63	a	1280.66	0.42955	YES YES
64	a	1385.84	0.09415	YES YES
65	a	1386.14	0.30010	YES YES
66	a	1397.18	1.33189	YES YES
67	a	1398.81	1.94110	YES YES

68	a	1400.45	1.24038	YES	YES
69	a	1401.24	4.60911	YES	YES
70	a	1401.58	5.06960	YES	YES
71	a	1402.54	20.54863	YES	YES
72	a	1408.40	2.87506	YES	YES
73	a	1409.76	15.91332	YES	YES
74	a	1422.64	10.02184	YES	YES
75	a	1424.65	0.57464	YES	YES
76	a	1731.60	52.03172	YES	YES
77	a	2943.66	39.60190	YES	YES
78	a	2943.77	10.46941	YES	YES
79	a	2943.98	28.68706	YES	YES
80	a	2944.12	2.13566	YES	YES
81	a	2950.37	15.26112	YES	YES
82	a	2951.14	11.58427	YES	YES
83	a	3044.05	6.09273	YES	YES
84	a	3044.25	10.12985	YES	YES
85	a	3044.37	7.05293	YES	YES
86	a	3044.49	5.40981	YES	YES
87	a	3048.55	9.91512	YES	YES
88	a	3049.44	7.10059	YES	YES
89	a	3060.22	2.30479	YES	YES
90	a	3060.70	2.07597	YES	YES
91	a	3063.79	0.44248	YES	YES
92	a	3064.02	0.42983	YES	YES
93	a	3064.38	0.39314	YES	YES
94	a	3065.33	0.41976	YES	YES
95	a	3171.10	3.63464	YES	YES
96	a	3229.60	0.53210	YES	YES

Electronic Supplementary Information for Dalton Transactions

TS_{23}ii (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	-0.14314	0.15309	-0.00096
Cl	2.28244	-0.00520	-0.01966
C	-2.15987	0.30037	0.01538
C	-3.02344	-0.61624	0.02814
P	0.07807	0.10010	2.30954
P	0.04024	0.07459	-2.31416
H	-2.07728	1.42004	0.00787
H	-3.71336	-1.45247	0.03884
C	0.88610	-1.45149	2.91233
C	1.16258	1.43030	3.00276
C	-1.44094	0.21350	3.36916
C	1.12495	1.38667	-3.04057
C	0.82479	-1.49120	-2.91119
C	-1.49470	0.18936	-3.35055
H	1.05833	-1.42951	4.01192
H	1.85150	-1.55017	2.37190
H	0.24756	-2.32306	2.65311
H	-2.15013	-0.59208	3.08363
H	-1.94647	1.18762	3.19326
H	-1.19105	0.12296	4.44967
H	0.70100	2.42189	2.80627
H	2.13053	1.38095	2.46054
H	1.32346	1.30642	4.09729
H	0.67504	2.38463	-2.84937
H	1.26757	1.24773	-4.13580
H	2.10071	1.33560	-2.51267
H	-1.26366	0.08198	-4.43372
H	-1.98708	1.17112	-3.17961
H	-2.20743	-0.60484	-3.04272
H	1.79844	-1.59187	-2.38614
H	0.97859	-1.48419	-4.01370
H	0.18336	-2.35394	-2.63050

Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1	a	-491.48	0.00000	YES YES
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7		0.00	1.42146	- -
8	a	37.73	1.01271	YES YES
9	a	43.35	0.01226	YES YES
10	a	45.36	2.26581	YES YES
11	a	85.93	2.65006	YES YES
12	a	92.01	0.40426	YES YES
13	a	95.47	0.54119	YES YES
14	a	133.33	3.52921	YES YES
15	a	141.74	0.00003	YES YES
16	a	156.21	0.15753	YES YES
17	a	177.91	0.42803	YES YES
18	a	187.80	0.61980	YES YES
19	a	189.02	0.21591	YES YES
20	a	194.95	4.15363	YES YES
21	a	197.07	1.03724	YES YES
22	a	198.60	2.44551	YES YES
23	a	211.24	0.17592	YES YES
24	a	214.03	0.85180	YES YES
25	a	221.13	0.12458	YES YES
26	a	222.69	0.00624	YES YES
27	a	225.32	0.13465	YES YES
28	a	244.10	0.00072	YES YES
29	a	251.67	0.72354	YES YES
30	a	256.14	8.46485	YES YES
31	a	258.98	4.91750	YES YES
32	a	285.37	2.22885	YES YES
33	a	325.63	22.11013	YES YES
34	a	341.31	2.58848	YES YES
35	a	400.60	7.35630	YES YES
36	a	436.24	21.06712	YES YES
37	a	479.18	8.34666	YES YES
38	a	619.24	43.20389	YES YES
39	a	625.90	34.11671	YES YES
40	a	639.06	34.85899	YES YES
41	a	645.11	0.11655	YES YES
42	a	702.82	0.51625	YES YES
43	a	704.26	23.72352	YES YES
44	a	704.65	0.45026	YES YES
45	a	705.72	19.46585	YES YES
46	a	777.33	0.06430	YES YES
47	a	777.62	0.06660	YES YES
48	a	827.13	0.74636	YES YES
49	a	829.54	0.05155	YES YES
50	a	839.76	15.28031	YES YES
51	a	841.81	6.96856	YES YES
52	a	937.05	52.90973	YES YES
53	a	938.24	51.48547	YES YES
54	a	938.83	202.83063	YES YES
55	a	940.83	240.36928	YES YES
56	a	943.04	46.75625	YES YES
57	a	957.64	7.74851	YES YES
58	a	1252.41	38.27942	YES YES
59	a	1252.73	0.09906	YES YES
60	a	1257.86	5.03887	YES YES
61	a	1260.48	34.18519	YES YES
62	a	1277.39	13.96241	YES YES
63	a	1280.10	0.14831	YES YES
64	a	1384.12	0.02726	YES YES
65	a	1384.32	0.05626	YES YES
66	a	1398.10	0.91934	YES YES
67	a	1400.14	22.36761	YES YES

68	a	1400.77	0.79092	YES	YES
69	a	1401.80	1.45195	YES	YES
70	a	1403.54	0.01947	YES	YES
71	a	1403.92	6.29637	YES	YES
72	a	1410.46	0.00165	YES	YES
73	a	1411.47	18.41941	YES	YES
74	a	1423.90	10.34562	YES	YES
75	a	1425.86	0.19653	YES	YES
76	a	1766.46	62.49368	YES	YES
77	a	2886.21	21.72430	YES	YES
78	a	2942.88	22.71685	YES	YES
79	a	2943.00	13.42402	YES	YES
80	a	2943.20	39.85876	YES	YES
81	a	2943.45	5.20031	YES	YES
82	a	2947.12	26.97994	YES	YES
83	a	2947.41	8.50900	YES	YES
84	a	3043.61	0.25138	YES	YES
85	a	3043.64	0.91814	YES	YES
86	a	3044.23	8.75959	YES	YES
87	a	3044.32	6.41246	YES	YES
88	a	3044.52	23.34099	YES	YES
89	a	3044.64	7.06206	YES	YES
90	a	3059.10	2.15265	YES	YES
91	a	3059.39	2.56677	YES	YES
92	a	3063.26	0.80299	YES	YES
93	a	3063.31	0.41559	YES	YES
94	a	3064.21	0.63702	YES	YES
95	a	3064.34	0.40242	YES	YES
96	a	3356.96	86.92437	YES	YES

Model 3ii (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	-0.04347	-0.11493	-0.00003
Cl	0.24721	2.28743	0.00065
P	-0.07772	-0.04381	2.33383
P	-0.07781	-0.04335	-2.33383
C	1.56676	0.44325	3.02458
C	-1.23288	1.21869	3.02564
C	-0.50690	-1.59216	3.23948
C	-1.22962	1.22217	-3.02597
C	1.56811	0.43951	-3.02430
C	-0.51079	-1.59051	-3.23959
C	0.18223	-2.05204	-0.00048
C	0.37125	-3.27757	-0.00085
H	-1.52652	-0.50942	0.00001
H	0.56909	-4.34181	-0.00106
H	1.53601	0.53130	4.13347
H	1.85147	1.41865	2.57562
H	2.32487	-0.31598	2.73560
H	-1.12962	1.30656	4.12985
H	-2.27716	0.93603	2.77245
H	-1.00502	2.18840	2.53409
H	-1.54723	-1.88497	2.98301
H	-0.41859	-1.45730	4.34016
H	0.16368	-2.40624	2.89294
H	1.85503	1.41452	-2.57591
H	1.53805	0.52694	-4.13324
H	2.32415	-0.32145	-2.73440
H	-0.42248	-1.45561	-4.34027
H	-1.55170	-1.88097	-2.98282
H	0.15805	-2.40623	-2.89348
H	-1.12548	1.30990	-4.13011
H	-0.99968	2.19121	-2.53407
H	-2.27472	0.94201	-2.77339

Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	25.62	0.42531	YES YES
8	a	30.07	0.03618	YES YES
9	a	45.41	4.71155	YES YES
10	a	73.18	1.56969	YES YES
11	a	90.63	3.74886	YES YES
12	a	107.28	0.02969	YES YES
13	a	116.99	2.39643	YES YES
14	a	141.10	1.76568	YES YES
15	a	164.65	0.17053	YES YES
16	a	176.20	1.42342	YES YES
17	a	183.39	0.59795	YES YES
18	a	184.74	0.17236	YES YES
19	a	192.04	5.70342	YES YES
20	a	199.42	2.70485	YES YES
21	a	203.76	2.84165	YES YES
22	a	206.40	0.38584	YES YES
23	a	210.22	1.12695	YES YES
24	a	218.03	0.17855	YES YES
25	a	219.42	0.03472	YES YES
26	a	241.47	0.02947	YES YES
27	a	248.69	0.35945	YES YES
28	a	251.74	10.33596	YES YES
29	a	261.30	0.46877	YES YES
30	a	262.41	11.57138	YES YES
31	a	300.50	9.92877	YES YES
32	a	328.37	6.82442	YES YES
33	a	340.23	0.33122	YES YES
34	a	405.75	0.04416	YES YES
35	a	473.85	4.08833	YES YES
36	a	532.66	43.01884	YES YES
37	a	536.66	0.84566	YES YES
38	a	562.94	40.67163	YES YES
39	a	641.30	44.05045	YES YES
40	a	645.76	0.16819	YES YES
41	a	648.71	0.40228	YES YES
42	a	712.83	19.58895	YES YES
43	a	713.56	1.01137	YES YES
44	a	716.94	2.70192	YES YES
45	a	717.01	22.46108	YES YES
46	a	781.82	0.05953	YES YES
47	a	781.95	0.07199	YES YES
48	a	829.91	6.17339	YES YES
49	a	837.79	5.67407	YES YES
50	a	840.67	10.19062	YES YES
51	a	846.22	17.27183	YES YES
52	a	942.43	74.12698	YES YES
53	a	943.98	155.46020	YES YES
54	a	944.49	57.36440	YES YES
55	a	947.72	56.43010	YES YES
56	a	949.16	223.65313	YES YES
57	a	963.46	4.83809	YES YES
58	a	1256.55	23.27472	YES YES
59	a	1256.70	11.08686	YES YES
60	a	1262.38	2.38603	YES YES
61	a	1264.67	32.20596	YES YES
62	a	1282.57	15.34570	YES YES
63	a	1285.37	0.71807	YES YES
64	a	1383.95	0.05608	YES YES
65	a	1384.32	0.96572	YES YES
66	a	1397.74	5.03513	YES YES
67	a	1398.89	11.51904	YES YES

68	a	1400.15	0.15216	YES	YES
69	a	1401.39	2.66759	YES	YES
70	a	1402.22	1.12944	YES	YES
71	a	1403.46	22.31002	YES	YES
72	a	1408.29	0.07893	YES	YES
73	a	1409.42	13.14424	YES	YES
74	a	1423.35	16.83804	YES	YES
75	a	1425.01	0.09513	YES	YES
76	a	1988.44	28.60910	YES	YES
77	a	2246.59	3.75818	YES	YES
78	a	2947.10	17.21317	YES	YES
79	a	2947.23	6.53085	YES	YES
80	a	2948.04	22.76012	YES	YES
81	a	2948.19	5.32222	YES	YES
82	a	2952.82	29.32833	YES	YES
83	a	2952.92	3.13562	YES	YES
84	a	3047.61	6.19129	YES	YES
85	a	3047.71	3.88629	YES	YES
86	a	3050.14	5.02129	YES	YES
87	a	3050.23	2.12012	YES	YES
88	a	3053.58	9.76159	YES	YES
89	a	3053.67	0.82992	YES	YES
90	a	3063.96	1.25614	YES	YES
91	a	3064.08	0.51503	YES	YES
92	a	3064.35	0.07493	YES	YES
93	a	3064.40	0.23803	YES	YES
94	a	3068.80	0.18757	YES	YES
95	a	3068.89	0.26989	YES	YES
96	a	3366.54	49.45308	YES	YES

TS_{34}ii (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	-0.02116	-0.18290	-0.00199
Cl	0.15857	2.22221	0.01259
P	0.01535	-0.02837	2.31799
P	0.02574	-0.00121	-2.31979
C	-0.07771	-2.08066	-0.01340
C	-0.35378	-3.32893	-0.02124
C	1.57331	0.73938	2.95606
C	-1.30269	1.06630	3.01880
C	-0.13501	-1.56444	3.34464
C	-1.29031	1.10034	-3.01364
C	1.58573	0.77531	-2.94234
C	-0.11864	-1.52536	-3.36486
H	-1.30024	-2.14266	-0.01616
H	-0.52766	-4.40016	-0.02775
H	-1.16517	1.25500	-4.10898
H	-1.22621	2.06999	-2.47608
H	-2.28804	0.65448	-2.81297
H	1.70578	1.74586	-2.41583
H	1.55690	0.93543	-4.04362
H	2.44887	0.12611	-2.68224
H	-0.06468	-1.27979	-4.44878
H	-1.08426	-2.03368	-3.15485
H	0.69935	-2.22959	-3.10370
H	-2.29991	0.62366	2.80883
H	-1.23553	2.04196	2.49259
H	-1.18200	1.20835	4.11632
H	-0.08510	-1.33175	4.43160
H	0.68309	-2.26670	3.07845
H	-1.10047	-2.06893	3.12482
H	1.69634	1.71602	2.44164
H	2.43703	0.09262	2.69185
H	1.54000	0.88638	4.05902

Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1	a	-1161.28	0.00000	YES YES
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7		0.00	0.23374	- -
8	a	37.93	1.32788	YES YES
9	a	41.96	0.01676	YES YES
10	a	45.04	2.62493	YES YES
11	a	85.11	1.89555	YES YES
12	a	90.91	1.13582	YES YES
13	a	102.15	1.45724	YES YES
14	a	133.62	2.82391	YES YES
15	a	142.37	0.09147	YES YES
16	a	160.61	0.01722	YES YES
17	a	177.92	0.57634	YES YES
18	a	188.06	0.34300	YES YES
19	a	188.72	0.25824	YES YES
20	a	193.76	1.42611	YES YES
21	a	193.95	5.80452	YES YES
22	a	207.99	0.00050	YES YES
23	a	211.38	0.07978	YES YES
24	a	213.02	0.84994	YES YES
25	a	222.35	0.19116	YES YES
26	a	223.83	0.00596	YES YES
27	a	243.78	0.00281	YES YES
28	a	249.02	0.88697	YES YES
29	a	252.95	2.73727	YES YES
30	a	257.96	9.24464	YES YES
31	a	296.39	17.49827	YES YES
32	a	316.25	83.13802	YES YES
33	a	322.36	6.91341	YES YES
34	a	325.31	5.60704	YES YES
35	a	341.71	1.28488	YES YES
36	a	350.02	15.89707	YES YES
37	a	461.79	9.02302	YES YES
38	a	504.78	18.57969	YES YES
39	a	582.00	48.79282	YES YES
40	a	640.96	28.00433	YES YES
41	a	646.74	0.37833	YES YES
42	a	704.13	0.06734	YES YES
43	a	704.44	16.55827	YES YES
44	a	706.64	1.56191	YES YES
45	a	707.55	24.75576	YES YES
46	a	777.38	0.06153	YES YES
47	a	777.66	0.05723	YES YES
48	a	831.17	1.04245	YES YES
49	a	831.78	3.78717	YES YES
50	a	840.73	14.46512	YES YES
51	a	842.17	6.03160	YES YES
52	a	938.00	20.36924	YES YES
53	a	938.78	50.47739	YES YES
54	a	940.00	151.75226	YES YES
55	a	941.44	292.30179	YES YES
56	a	943.37	44.84610	YES YES
57	a	957.42	9.26897	YES YES
58	a	1253.74	34.38349	YES YES
59	a	1254.07	2.87406	YES YES
60	a	1258.68	4.15130	YES YES
61	a	1261.02	32.81408	YES YES
62	a	1278.08	13.58172	YES YES
63	a	1280.71	0.06706	YES YES
64	a	1384.70	0.01499	YES YES
65	a	1384.72	0.07344	YES YES
66	a	1398.65	1.22274	YES YES
67	a	1400.69	23.86105	YES YES

68	a	1400.88	1.61153	YES	YES
69	a	1401.59	0.46827	YES	YES
70	a	1403.38	0.52568	YES	YES
71	a	1403.72	5.86600	YES	YES
72	a	1410.30	0.05690	YES	YES
73	a	1411.27	18.64598	YES	YES
74	a	1423.88	11.76755	YES	YES
75	a	1425.62	0.02140	YES	YES
76	a	1802.35	258.30198	YES	YES
77	a	2299.19	9.78933	YES	YES
78	a	2943.49	29.34288	YES	YES
79	a	2943.67	16.32447	YES	YES
80	a	2943.88	30.05484	YES	YES
81	a	2944.12	9.30677	YES	YES
82	a	2948.11	25.26149	YES	YES
83	a	2948.29	5.42289	YES	YES
84	a	3044.62	1.60638	YES	YES
85	a	3044.72	0.29601	YES	YES
86	a	3045.23	22.08271	YES	YES
87	a	3045.33	3.23564	YES	YES
88	a	3045.64	13.06571	YES	YES
89	a	3045.79	6.59908	YES	YES
90	a	3060.76	2.18094	YES	YES
91	a	3060.83	2.29117	YES	YES
92	a	3065.15	1.18089	YES	YES
93	a	3065.21	0.29944	YES	YES
94	a	3065.25	0.32367	YES	YES
95	a	3065.35	0.46550	YES	YES
96	a	3338.04	155.76421	YES	YES

Model 4ii (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	-0.00133	-0.14314	-0.00003
Cl	0.00380	2.26622	-0.00036
P	-0.00166	-0.02847	2.33547
P	-0.00076	-0.02867	-2.33542
C	1.46091	0.88211	3.01050
C	-1.43524	0.92429	3.01412
C	-0.02293	-1.58715	3.33096
C	-1.45188	0.89930	-3.01144
C	1.44476	0.90664	-3.01288
C	0.00309	-1.58747	-3.33087
C	0.00127	-1.95722	0.00022
C	0.00543	-3.28589	0.00040
H	-0.94022	-3.86369	0.00208
H	0.95448	-3.85811	-0.00108
H	-1.38108	1.02784	-4.11482
H	-1.47927	1.89024	-2.51087
H	-2.38662	0.35365	-2.76028
H	1.46868	1.89695	-2.51095
H	1.37133	1.03609	-4.11597
H	2.38241	0.36488	-2.76410
H	0.90099	-2.18837	-3.07472
H	0.00182	-1.36686	-4.42122
H	-0.89089	-2.19367	-3.07356
H	-2.37960	0.39352	2.76701
H	-1.44837	1.91426	2.51111
H	-1.35880	1.05367	4.11700
H	-0.01255	-1.36689	4.42134
H	0.86034	-2.20657	3.06838
H	-0.93123	-2.17462	3.08005
H	1.49947	1.87307	2.51065
H	2.38893	0.32572	2.75802
H	1.39270	1.01088	4.11399

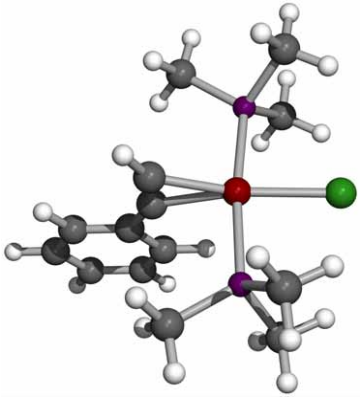
Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	24.57	0.00061	YES YES
8	a	28.81	0.03776	YES YES
9	a	39.89	3.45627	YES YES
10	a	81.70	0.05671	YES YES
11	a	84.42	3.12827	YES YES
12	a	108.93	0.95389	YES YES
13	a	126.96	3.47539	YES YES
14	a	139.57	0.00188	YES YES
15	a	163.28	0.27668	YES YES
16	a	171.24	0.02703	YES YES
17	a	172.79	0.26201	YES YES
18	a	175.28	1.05517	YES YES
19	a	191.18	1.24794	YES YES
20	a	193.01	5.83030	YES YES
21	a	206.59	0.07678	YES YES
22	a	206.79	0.33256	YES YES
23	a	209.09	1.03788	YES YES
24	a	220.42	0.19990	YES YES
25	a	221.94	0.00120	YES YES
26	a	244.53	0.00874	YES YES
27	a	246.80	0.35341	YES YES
28	a	253.70	2.00293	YES YES
29	a	255.34	10.75881	YES YES
30	a	273.10	0.00336	YES YES
31	a	303.13	11.66402	YES YES
32	a	322.92	17.44024	YES YES
33	a	337.30	1.08286	YES YES
34	a	365.90	0.54304	YES YES
35	a	482.48	4.42811	YES YES
36	a	564.29	0.37081	YES YES
37	a	642.79	18.44373	YES YES
38	a	647.73	0.77373	YES YES
39	a	662.47	69.89802	YES YES
40	a	705.99	0.04631	YES YES
41	a	706.45	16.25818	YES YES
42	a	711.06	3.10154	YES YES
43	a	711.71	22.43201	YES YES
44	a	778.36	0.06500	YES YES
45	a	778.44	0.08663	YES YES
46	a	832.77	0.00014	YES YES
47	a	834.82	7.22979	YES YES
48	a	841.91	12.40192	YES YES
49	a	842.79	5.74305	YES YES
50	a	858.09	0.00183	YES YES
51	a	941.52	1.33395	YES YES
52	a	941.80	47.46536	YES YES
53	a	942.17	87.51022	YES YES
54	a	943.28	355.77492	YES YES
55	a	944.34	45.71376	YES YES
56	a	958.55	7.41972	YES YES
57	a	1256.44	34.85634	YES YES
58	a	1256.59	0.00566	YES YES
59	a	1262.12	3.42293	YES YES
60	a	1264.30	31.92241	YES YES
61	a	1283.22	12.42979	YES YES
62	a	1284.83	0.30724	YES YES
63	a	1290.80	0.00008	YES YES
64	a	1386.31	0.01839	YES YES
65	a	1386.38	0.14965	YES YES
66	a	1396.54	2.92031	YES YES
67	a	1397.36	0.28065	YES YES

68	a	1400.73	0.80937	YES	YES
69	a	1402.33	0.03317	YES	YES
70	a	1402.48	26.57085	YES	YES
71	a	1402.70	5.96125	YES	YES
72	a	1409.26	0.00713	YES	YES
73	a	1410.20	18.86089	YES	YES
74	a	1422.49	13.66571	YES	YES
75	a	1424.12	0.02312	YES	YES
76	a	1672.30	235.65562	YES	YES
77	a	2945.08	56.22450	YES	YES
78	a	2945.19	3.77212	YES	YES
79	a	2945.27	10.04476	YES	YES
80	a	2945.34	4.03230	YES	YES
81	a	2952.91	20.77731	YES	YES
82	a	2953.05	5.48069	YES	YES
83	a	3026.11	2.36287	YES	YES
84	a	3045.97	2.74630	YES	YES
85	a	3045.99	17.63193	YES	YES
86	a	3046.08	0.31177	YES	YES
87	a	3046.16	5.38864	YES	YES
88	a	3052.26	12.60579	YES	YES
89	a	3052.48	2.68792	YES	YES
90	a	3065.50	0.58988	YES	YES
91	a	3065.70	0.70363	YES	YES
92	a	3065.80	0.87980	YES	YES
93	a	3065.88	0.12714	YES	YES
94	a	3066.85	0.75253	YES	YES
95	a	3066.97	0.59892	YES	YES
96	a	3093.90	0.26130	YES	YES

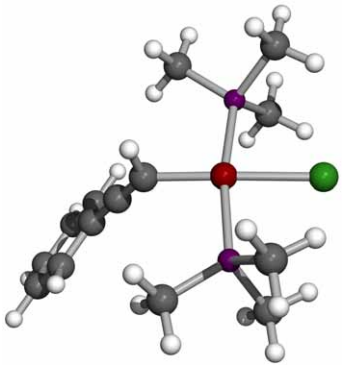
Electronic Supplementary Information for Dalton Transactions

Optimised structures for the model *iii* system – Gibbs energies in kJ mol^{-1} (relative to structure 2) are shown below each structure.



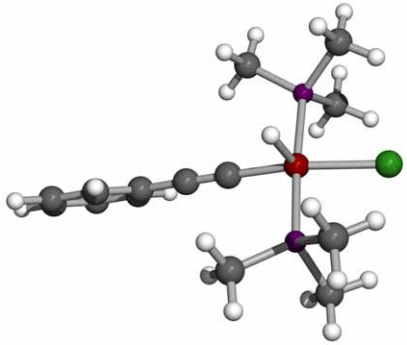
Model 2iii

0



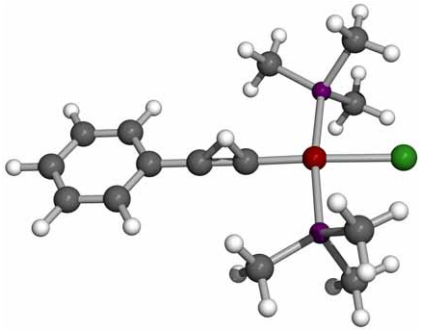
TS_{23}iii

106



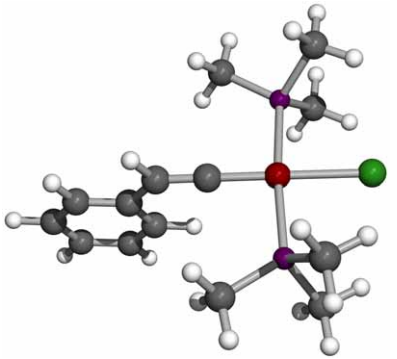
Model 3iii

18



TS_{34}iii

123



Model 4iii

-8

Model 2iii (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	0.77467	-0.21478	-0.01084
Cl	2.68706	1.21772	-0.05926
C	-1.22556	-0.89595	0.03575
C	-0.41839	-1.90032	0.02372
P	0.93857	-0.12164	2.31671
P	0.81683	-0.12853	-2.34494
C	-2.52022	-0.26132	0.05093
H	-0.23399	-2.98021	0.02736
C	2.55983	-0.73288	2.96721
C	0.84394	1.59424	3.00464
C	-0.30270	-1.04882	3.33242
C	0.68864	1.58439	-3.03474
C	2.39993	-0.74663	-3.07797
C	-0.47901	-1.05634	-3.28958
H	1.01590	1.60958	4.10444
H	-0.15565	2.02484	2.78066
H	1.61366	2.20647	2.48882
H	-1.32480	-0.68958	3.08649
H	-0.11522	-0.91386	4.42068
H	-0.25405	-2.12979	3.08144
H	2.64097	-0.60107	4.06952
H	3.36274	-0.16260	2.45377
H	2.67821	-1.80780	2.71196
H	-0.34690	-0.92984	-4.38696
H	-1.48532	-0.68992	-2.99411
H	-0.42316	-2.13582	-3.03367
H	0.80424	1.59464	-4.14197
H	1.48366	2.19892	-2.56172
H	-0.29835	2.01605	-2.76232
H	3.23090	-0.17797	-2.60937
H	2.42284	-0.61774	-4.18341
H	2.52802	-1.82145	-2.82683
C	-5.07173	0.98514	0.07280
C	-4.96835	-0.41984	0.07821
C	-3.71227	-1.03892	0.06771
C	-2.64066	1.15367	0.04695
C	-3.90232	1.76642	0.05800
H	-6.06300	1.46829	0.08046
H	-5.88102	-1.03929	0.09006
H	-3.63401	-2.13847	0.07117
H	-1.71584	1.75467	0.03413
H	-3.97504	2.86707	0.05344

Vibrational frequencies

#	mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR	RAMAN
	1		0.00	0.00000	- -
	2		0.00	0.00000	- -
	3		0.00	0.00000	- -
	4		0.00	0.00000	- -
	5		0.00	0.00000	- -
	6		0.00	0.00000	- -
	7	a	23.40	0.04149	YES YES
	8	a	29.53	0.10122	YES YES
	9	a	38.48	1.87603	YES YES
	10	a	41.04	0.70785	YES YES
	11	a	45.02	0.06568	YES YES
	12	a	62.96	0.20994	YES YES
	13	a	83.68	2.74520	YES YES
	14	a	115.77	0.56328	YES YES
	15	a	124.79	2.25820	YES YES
	16	a	134.59	0.01532	YES YES
	17	a	140.62	1.60705	YES YES
	18	a	161.34	0.06400	YES YES
	19	a	170.16	0.28040	YES YES
	20	a	173.97	1.85558	YES YES
	21	a	176.04	0.83380	YES YES
	22	a	182.12	2.75231	YES YES
	23	a	185.67	0.62569	YES YES
	24	a	196.49	2.77655	YES YES
	25	a	207.13	0.03868	YES YES
	26	a	209.43	0.79362	YES YES
	27	a	215.79	0.21790	YES YES
	28	a	221.72	1.61231	YES YES
	29	a	223.42	1.14878	YES YES
	30	a	226.34	0.52041	YES YES
	31	a	243.72	0.00301	YES YES
	32	a	252.33	0.14232	YES YES
	33	a	257.47	12.06284	YES YES
	34	a	258.10	3.97083	YES YES
	35	a	314.93	10.68512	YES YES
	36	a	317.53	15.18335	YES YES
	37	a	337.44	2.96844	YES YES
	38	a	367.16	1.96988	YES YES
	39	a	405.11	0.00293	YES YES
	40	a	442.59	1.19004	YES YES
	41	a	498.49	18.08655	YES YES
	42	a	531.27	0.50661	YES YES
	43	a	569.21	30.32769	YES YES
	44	a	616.05	7.35969	YES YES
	45	a	631.04	10.52619	YES YES
	46	a	639.92	33.13254	YES YES
	47	a	645.32	0.05449	YES YES
	48	a	694.58	27.25189	YES YES
	49	a	703.79	4.30041	YES YES
	50	a	705.01	10.66048	YES YES
	51	a	706.51	0.42529	YES YES
	52	a	707.75	26.14289	YES YES
	53	a	758.89	20.63882	YES YES
	54	a	771.59	0.46000	YES YES
	55	a	776.15	0.07542	YES YES
	56	a	777.24	0.06106	YES YES
	57	a	805.25	11.41641	YES YES
	58	a	826.75	1.69570	YES YES
	59	a	826.81	0.13255	YES YES
	60	a	833.57	0.04186	YES YES
	61	a	837.06	22.37707	YES YES
	62	a	838.47	6.06861	YES YES
	63	a	905.01	0.80027	YES YES
	64	a	936.91	2.91440	YES YES
	65	a	937.86	65.51221	YES YES
	66	a	939.06	399.47812	YES YES
	67	a	940.22	31.67684	YES YES

68	a	942.88	50.47928	YES	YES
69	a	956.00	19.63623	YES	YES
70	a	958.09	0.18795	YES	YES
71	a	979.33	0.41552	YES	YES
72	a	980.67	0.48011	YES	YES
73	a	1021.65	5.89602	YES	YES
74	a	1066.09	6.38061	YES	YES
75	a	1137.79	0.00296	YES	YES
76	a	1147.95	0.83458	YES	YES
77	a	1185.22	1.25452	YES	YES
78	a	1252.82	17.87214	YES	YES
79	a	1254.12	17.57244	YES	YES
80	a	1258.77	1.59072	YES	YES
81	a	1260.64	28.50728	YES	YES
82	a	1278.37	15.34644	YES	YES
83	a	1280.98	1.20578	YES	YES
84	a	1282.80	2.91694	YES	YES
85	a	1357.92	2.13003	YES	YES
86	a	1384.99	0.07030	YES	YES
87	a	1385.61	0.15205	YES	YES
88	a	1399.82	3.15445	YES	YES
89	a	1400.02	1.00447	YES	YES
90	a	1400.83	7.12804	YES	YES
91	a	1401.68	20.99264	YES	YES
92	a	1402.02	1.39729	YES	YES
93	a	1402.82	2.48267	YES	YES
94	a	1408.19	1.01616	YES	YES
95	a	1409.42	15.81939	YES	YES
96	a	1423.17	10.74254	YES	YES
97	a	1424.86	0.33736	YES	YES
98	a	1437.01	6.64865	YES	YES
99	a	1472.16	21.13907	YES	YES
100	a	1574.22	3.85249	YES	YES
101	a	1606.12	30.91008	YES	YES
102	a	1832.99	102.53481	YES	YES
103	a	2943.61	31.44397	YES	YES
104	a	2943.79	8.88998	YES	YES
105	a	2944.41	20.86289	YES	YES
106	a	2944.83	15.62827	YES	YES
107	a	2950.18	21.47699	YES	YES
108	a	2950.32	3.51638	YES	YES
109	a	3043.49	8.24614	YES	YES
110	a	3043.68	6.09376	YES	YES
111	a	3044.78	7.57118	YES	YES
112	a	3045.19	6.32522	YES	YES
113	a	3048.22	15.24313	YES	YES
114	a	3048.34	1.61102	YES	YES
115	a	3061.01	0.93765	YES	YES
116	a	3061.04	1.38095	YES	YES
117	a	3064.40	0.18027	YES	YES
118	a	3064.45	0.52671	YES	YES
119	a	3065.01	0.29550	YES	YES
120	a	3065.17	0.38230	YES	YES
121	a	3083.97	3.52757	YES	YES
122	a	3090.53	2.17580	YES	YES
123	a	3099.30	6.59121	YES	YES
124	a	3105.66	23.51135	YES	YES
125	a	3113.32	23.16481	YES	YES
126	a	3188.56	4.30253	YES	YES

TS_{23}iii (RI-)BP86/SV(P) Optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	-0.13834	0.16282	-0.02663
Cl	2.29832	-0.01474	-0.06166
C	-2.14156	0.20421	-0.00976
C	-2.99382	-0.74818	0.01370
P	0.09149	0.03784	2.27869
P	0.03479	0.21130	-2.34224
H	-2.31173	1.30966	-0.07944
C	-3.90150	-1.82635	0.05760
C	0.91745	-1.52118	2.83819
C	1.17468	1.35901	2.99194
C	-1.41322	0.11368	3.36161
C	1.14571	1.54227	-2.99054
C	0.78624	-1.32982	-3.03778
C	-1.49749	0.42623	-3.36859
H	1.10109	-1.52302	3.93621
H	1.87768	-1.59917	2.28532
H	0.28274	-2.39153	2.56552
H	-2.10856	-0.70477	3.07870
H	-1.93892	1.07970	3.20206
H	-1.14595	0.01619	4.43740
H	0.70566	2.35230	2.82327
H	2.13702	1.32678	2.43842
H	1.34780	1.21080	4.08168
H	0.71568	2.53557	-2.73912
H	1.28560	1.46610	-4.09224
H	2.11959	1.43979	-2.46646
H	-1.27167	0.38019	-4.45722
H	-1.96437	1.40795	-3.13639
H	-2.23087	-0.36618	-3.10790
H	1.76053	-1.47889	-2.52518
H	0.93578	-1.26016	-4.13865
H	0.13173	-2.19689	-2.80485
C	-5.74323	-3.98933	0.14599
C	-5.56924	-3.16355	1.27404
C	-4.65753	-2.10383	1.23985
C	-4.10431	-2.66970	-1.07986
C	-5.00363	-3.73839	-1.02696
H	-6.45630	-4.82944	0.18031
H	-6.15124	-3.35451	2.19090
H	-4.51839	-1.45810	2.12162
H	-3.52674	-2.47015	-1.99645
H	-5.13601	-4.38518	-1.91010

Vibrational frequencies

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1	a	-289.99	0.00000	YES YES
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7		0.00	0.17642	- -
8	a	21.01	0.23513	YES YES
9	a	25.72	0.32500	YES YES
10	a	33.05	0.03678	YES YES
11	a	39.50	2.04044	YES YES
12	a	43.82	0.91988	YES YES
13	a	66.75	1.24005	YES YES
14	a	83.15	2.43462	YES YES
15	a	93.33	0.10012	YES YES
16	a	102.71	0.96307	YES YES
17	a	132.70	4.18790	YES YES
18	a	141.23	0.03926	YES YES
19	a	155.22	0.22572	YES YES
20	a	177.57	0.57241	YES YES
21	a	184.97	0.75752	YES YES
22	a	189.99	0.89297	YES YES
23	a	192.27	0.50247	YES YES
24	a	198.06	3.96237	YES YES
25	a	199.82	2.53608	YES YES
26	a	213.43	0.20293	YES YES
27	a	214.09	0.97945	YES YES
28	a	222.06	0.04965	YES YES
29	a	226.65	0.13653	YES YES
30	a	230.80	7.88959	YES YES
31	a	243.42	0.11770	YES YES
32	a	247.70	13.99791	YES YES
33	a	252.78	0.97606	YES YES
34	a	255.99	11.08679	YES YES
35	a	262.96	3.53838	YES YES
36	a	306.44	2.46463	YES YES
37	a	326.24	21.94137	YES YES
38	a	332.50	1.00382	YES YES
39	a	340.88	15.03861	YES YES
40	a	399.33	0.86617	YES YES
41	a	469.51	2.68258	YES YES
42	a	506.48	6.50008	YES YES
43	a	510.53	47.19791	YES YES
44	a	608.91	0.85310	YES YES
45	a	632.84	9.51368	YES YES
46	a	638.79	28.45906	YES YES
47	a	644.52	4.68988	YES YES
48	a	680.81	25.90779	YES YES
49	a	689.65	36.34197	YES YES
50	a	701.53	1.26973	YES YES
51	a	703.48	6.96534	YES YES
52	a	703.98	9.05315	YES YES
53	a	704.87	15.89312	YES YES
54	a	759.65	9.62453	YES YES
55	a	766.67	11.96448	YES YES
56	a	774.15	0.01611	YES YES
57	a	779.15	0.10404	YES YES
58	a	821.25	0.26600	YES YES
59	a	826.19	1.38134	YES YES
60	a	829.39	0.00979	YES YES
61	a	839.41	16.33657	YES YES
62	a	841.64	6.01534	YES YES
63	a	903.31	1.27268	YES YES
64	a	934.97	28.46140	YES YES
65	a	938.83	290.73148	YES YES
66	a	940.04	69.67438	YES YES

67	a	940.32	103.28979	YES	YES
68	a	943.09	52.83578	YES	YES
69	a	954.76	73.31438	YES	YES
70	a	956.41	8.05493	YES	YES
71	a	976.46	1.76886	YES	YES
72	a	979.59	0.08289	YES	YES
73	a	1020.28	4.35061	YES	YES
74	a	1071.00	5.71152	YES	YES
75	a	1141.04	0.03931	YES	YES
76	a	1153.02	0.49034	YES	YES
77	a	1196.55	1.39091	YES	YES
78	a	1252.27	31.08626	YES	YES
79	a	1252.91	6.55542	YES	YES
80	a	1255.76	10.83901	YES	YES
81	a	1259.66	28.53516	YES	YES
82	a	1275.14	13.97268	YES	YES
83	a	1279.89	2.73409	YES	YES
84	a	1281.70	0.72158	YES	YES
85	a	1352.27	0.17825	YES	YES
86	a	1384.20	0.01804	YES	YES
87	a	1384.68	0.07245	YES	YES
88	a	1398.31	1.40257	YES	YES
89	a	1400.17	11.93224	YES	YES
90	a	1400.76	11.82394	YES	YES
91	a	1402.53	1.88030	YES	YES
92	a	1403.32	0.65511	YES	YES
93	a	1404.57	3.09955	YES	YES
94	a	1410.24	3.08303	YES	YES
95	a	1411.85	14.07827	YES	YES
96	a	1424.26	8.82677	YES	YES
97	a	1426.45	0.81743	YES	YES
98	a	1437.06	4.70739	YES	YES
99	a	1466.86	21.66597	YES	YES
100	a	1560.17	1.95955	YES	YES
101	a	1599.02	17.44602	YES	YES
102	a	1898.03	18.40608	YES	YES
103	a	2915.34	35.35248	YES	YES
104	a	2942.08	14.79412	YES	YES
105	a	2942.37	41.51536	YES	YES
106	a	2942.79	7.70315	YES	YES
107	a	2943.00	23.97515	YES	YES
108	a	2946.48	20.75164	YES	YES
109	a	2947.54	13.90319	YES	YES
110	a	3042.70	5.67468	YES	YES
111	a	3042.89	4.14734	YES	YES
112	a	3043.92	8.05445	YES	YES
113	a	3044.19	2.08794	YES	YES
114	a	3044.39	22.05723	YES	YES
115	a	3044.63	12.55803	YES	YES
116	a	3057.81	3.21019	YES	YES
117	a	3060.28	2.71493	YES	YES
118	a	3062.39	0.78987	YES	YES
119	a	3063.16	0.71365	YES	YES
120	a	3063.46	0.76346	YES	YES
121	a	3063.55	0.28965	YES	YES
122	a	3091.70	5.88617	YES	YES
123	a	3099.16	3.72342	YES	YES
124	a	3110.34	10.98056	YES	YES
125	a	3116.35	16.84485	YES	YES
126	a	3121.04	13.44313	YES	YES

Model 3iii (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	-0.06110	1.08413	0.00201
Cl	0.47222	3.44280	-0.03240
P	-0.01484	1.19330	2.33591
P	-0.18757	1.16331	-2.33163
C	1.67052	1.60284	2.97546
C	-1.08089	2.53184	3.02836
C	-0.50462	-0.31040	3.28489
C	-1.30964	2.48867	-2.95759
C	1.44280	1.57302	-3.10103
C	-0.73957	-0.35452	-3.22239
C	-0.07942	-0.85983	0.01481
C	-0.05554	-2.10585	0.01560
H	-1.58263	0.89951	0.06088
C	0.01649	-3.53318	0.01050
H	1.67053	1.71820	4.08223
H	1.99687	2.54973	2.49508
H	2.37914	0.79589	2.68953
H	-0.94534	2.63409	4.12786
H	-2.14570	2.30497	2.80621
H	-0.80936	3.47797	2.51371
H	-1.55619	-0.56888	3.03836
H	-0.40819	-0.14675	4.38099
H	0.13214	-1.16245	2.96753
H	1.79584	2.53019	-2.66168
H	1.36082	1.66910	-4.20654
H	2.17722	0.77661	-2.85372
H	-0.72259	-0.20592	-4.32468
H	-1.76939	-0.61349	-2.89725
H	-0.07924	-1.20067	-2.93966
H	-1.25420	2.58184	-4.06478
H	-1.00810	3.44121	-2.47231
H	-2.35411	2.25690	-2.65774
C	0.15668	-6.37953	-0.00357
C	1.16501	-5.61509	-0.61855
C	1.09873	-4.21506	-0.61483
C	-0.99293	-4.32383	0.62924
C	-0.92095	-5.72368	0.61901
H	0.21037	-7.48079	-0.00977
H	2.01577	-6.11766	-1.10958
H	1.89194	-3.62049	-1.09644
H	-1.84026	-3.81520	1.11684
H	-1.71840	-6.31183	1.10440

Vibrational frequencies

#	mode	symmetry	wave number	IR intensity	selection rules
#			cm**(-1)	km/mol	IR RAMAN
	1		0.00	0.00000	- -
	2		0.00	0.00000	- -
	3		0.00	0.00000	- -
	4		0.00	0.00000	- -
	5		0.00	0.00000	- -
	6		0.00	0.00000	- -
	7	a	13.63	0.19225	YES YES
	8	a	16.30	0.02205	YES YES
	9	a	23.81	0.00995	YES YES
	10	a	26.40	0.05424	YES YES
	11	a	41.81	3.34150	YES YES
	12	a	55.94	1.48652	YES YES
	13	a	80.37	4.44817	YES YES
	14	a	89.86	2.13819	YES YES
	15	a	104.54	0.32139	YES YES
	16	a	119.36	3.15608	YES YES
	17	a	139.74	1.87167	YES YES
	18	a	162.71	0.27546	YES YES
	19	a	173.16	2.63345	YES YES
	20	a	175.70	0.85173	YES YES
	21	a	180.45	0.57585	YES YES
	22	a	183.40	0.45779	YES YES
	23	a	198.09	1.53557	YES YES
	24	a	203.07	3.44504	YES YES
	25	a	205.79	0.33515	YES YES
	26	a	208.49	0.92658	YES YES
	27	a	220.81	0.41539	YES YES
	28	a	221.69	1.31039	YES YES
	29	a	224.43	4.58888	YES YES
	30	a	236.65	2.25257	YES YES
	31	a	240.87	0.36384	YES YES
	32	a	245.23	0.59873	YES YES
	33	a	254.10	20.84545	YES YES
	34	a	259.62	2.55956	YES YES
	35	a	296.93	2.48474	YES YES
	36	a	316.83	12.64201	YES YES
	37	a	329.71	4.55256	YES YES
	38	a	338.73	3.34576	YES YES
	39	a	402.88	0.09028	YES YES
	40	a	417.17	0.96155	YES YES
	41	a	478.20	1.47998	YES YES
	42	a	528.94	6.40636	YES YES
	43	a	548.27	1.99570	YES YES
	44	a	561.58	10.67072	YES YES
	45	a	614.31	0.05852	YES YES
	46	a	625.75	32.46045	YES YES
	47	a	644.50	10.13215	YES YES
	48	a	648.26	1.40848	YES YES
	49	a	692.88	27.05765	YES YES
	50	a	711.96	16.58003	YES YES
	51	a	712.65	1.91600	YES YES
	52	a	716.05	5.51067	YES YES
	53	a	716.68	21.64334	YES YES
	54	a	756.60	25.87854	YES YES
	55	a	778.19	0.04798	YES YES
	56	a	778.30	0.01408	YES YES
	57	a	800.87	0.13037	YES YES
	58	a	826.51	0.08760	YES YES
	59	a	830.30	6.37430	YES YES
	60	a	835.38	3.80523	YES YES
	61	a	841.13	10.51983	YES YES
	62	a	843.97	18.71767	YES YES
	63	a	895.33	1.71529	YES YES
	64	a	941.32	25.66491	YES YES
	65	a	942.65	57.84773	YES YES
	66	a	943.65	127.83732	YES YES
	67	a	945.43	283.60261	YES YES

68	a	946.36	59.11544	YES	YES
69	a	951.26	0.07920	YES	YES
70	a	960.72	29.96711	YES	YES
71	a	972.93	0.26394	YES	YES
72	a	980.02	0.40816	YES	YES
73	a	1024.77	5.72747	YES	YES
74	a	1066.68	6.64364	YES	YES
75	a	1137.50	0.03836	YES	YES
76	a	1156.01	1.62916	YES	YES
77	a	1224.51	22.69654	YES	YES
78	a	1255.04	18.53336	YES	YES
79	a	1257.16	16.94969	YES	YES
80	a	1261.05	3.95883	YES	YES
81	a	1263.25	27.67975	YES	YES
82	a	1281.13	12.44410	YES	YES
83	a	1283.02	0.50157	YES	YES
84	a	1283.94	1.27165	YES	YES
85	a	1349.45	0.28161	YES	YES
86	a	1384.22	0.15584	YES	YES
87	a	1384.48	0.23279	YES	YES
88	a	1396.30	6.06868	YES	YES
89	a	1397.94	9.55335	YES	YES
90	a	1399.41	0.37585	YES	YES
91	a	1400.27	4.35146	YES	YES
92	a	1401.77	1.63822	YES	YES
93	a	1403.14	26.44619	YES	YES
94	a	1407.85	0.78160	YES	YES
95	a	1409.00	13.25098	YES	YES
96	a	1422.58	16.38732	YES	YES
97	a	1424.35	0.21604	YES	YES
98	a	1437.09	1.73895	YES	YES
99	a	1479.98	46.11715	YES	YES
100	a	1572.47	2.80077	YES	YES
101	a	1610.44	68.52152	YES	YES
102	a	2106.40	178.21741	YES	YES
103	a	2249.33	4.99577	YES	YES
104	a	2947.17	12.65732	YES	YES
105	a	2947.66	11.06297	YES	YES
106	a	2948.24	15.97911	YES	YES
107	a	2948.63	11.92151	YES	YES
108	a	2954.03	13.52522	YES	YES
109	a	2954.57	11.14592	YES	YES
110	a	3047.51	4.82930	YES	YES
111	a	3048.20	4.74859	YES	YES
112	a	3049.92	4.10930	YES	YES
113	a	3050.40	3.58212	YES	YES
114	a	3054.43	6.11245	YES	YES
115	a	3055.19	4.54306	YES	YES
116	a	3064.43	0.20740	YES	YES
117	a	3064.67	0.48527	YES	YES
118	a	3064.74	0.60498	YES	YES
119	a	3064.98	0.47898	YES	YES
120	a	3070.72	0.17045	YES	YES
121	a	3071.24	0.21353	YES	YES
122	a	3081.62	7.52870	YES	YES
123	a	3088.53	7.09414	YES	YES
124	a	3103.40	19.38439	YES	YES
125	a	3108.03	28.11396	YES	YES
126	a	3113.89	15.77070	YES	YES

Electronic Supplementary Information for Dalton Transactions

TS_{34}iii (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	-0.03832	-0.16561	-0.01285
Cl	0.16191	2.23643	0.05454
P	-0.10005	-0.05594	2.30707
P	0.09782	0.05721	-2.32126
C	-0.08000	-2.06417	-0.05824
C	-0.17990	-3.34810	-0.07932
C	1.43768	0.68079	3.02684
C	-1.43339	1.04211	2.97398
C	-0.31188	-1.60463	3.30552
C	-1.20696	1.15564	-3.04252
C	1.66743	0.86447	-2.87970
C	0.00969	-1.44523	-3.40503
H	-1.26564	-2.40213	-0.10856
C	-0.24731	-4.77512	-0.12341
H	-1.04813	1.32913	-4.13077
H	-1.17083	2.11777	-2.48910
H	-2.20595	0.69673	-2.88126
H	1.75982	1.82397	-2.32805
H	1.67053	1.04895	-3.97766
H	2.52986	0.21930	-2.60724
H	0.10343	-1.17600	-4.48067
H	-0.95866	-1.96604	-3.24371
H	0.82652	-2.14499	-3.12771
H	-2.42597	0.61642	2.71345
H	-1.33266	2.02667	2.47016
H	-1.35705	1.16223	4.07808
H	-0.29450	-1.39020	4.39734
H	0.50290	-2.31705	3.05595
H	-1.28006	-2.08503	3.04592
H	1.59608	1.66382	2.53462
H	2.30396	0.02695	2.78990
H	1.35786	0.81083	4.12955
C	-0.37577	-7.60730	-0.21427
C	-0.55592	-6.93127	1.00750
C	-0.49033	-5.53365	1.05801
C	-0.06931	-5.47507	-1.35145
C	-0.12981	-6.87350	-1.39015
H	-0.42497	-8.70813	-0.24936
H	-0.74524	-7.50285	1.93162
H	-0.62424	-5.00247	2.01398
H	0.12262	-4.89845	-2.26971
H	0.01559	-7.39991	-2.34804

Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1	a	-961.74	0.00000	YES YES
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7		0.00	0.15409	- -
8	a	13.76	0.02945	YES YES
9	a	25.26	0.00584	YES YES
10	a	25.88	0.42049	YES YES
11	a	38.70	2.30296	YES YES
12	a	42.60	0.70568	YES YES
13	a	65.90	0.11894	YES YES
14	a	79.92	1.43374	YES YES
15	a	89.50	0.05475	YES YES
16	a	106.12	0.58211	YES YES
17	a	133.78	3.43468	YES YES
18	a	141.68	0.11635	YES YES
19	a	159.16	0.02120	YES YES
20	a	174.92	1.48252	YES YES
21	a	180.24	0.01337	YES YES
22	a	186.91	1.14314	YES YES
23	a	192.48	0.81463	YES YES
24	a	194.73	1.19318	YES YES
25	a	206.52	2.16801	YES YES
26	a	212.54	2.85346	YES YES
27	a	215.15	4.62071	YES YES
28	a	221.84	0.51755	YES YES
29	a	223.32	16.34860	YES YES
30	a	225.92	2.84155	YES YES
31	a	227.85	7.39095	YES YES
32	a	243.57	0.17174	YES YES
33	a	248.03	2.27922	YES YES
34	a	248.83	0.48079	YES YES
35	a	258.53	20.57730	YES YES
36	a	266.66	3.12029	YES YES
37	a	318.66	9.96367	YES YES
38	a	324.35	19.56740	YES YES
39	a	341.40	11.09415	YES YES
40	a	389.01	14.05116	YES YES
41	a	404.25	24.44759	YES YES
42	a	405.70	0.07623	YES YES
43	a	470.21	13.31155	YES YES
44	a	532.99	35.31479	YES YES
45	a	567.18	21.63715	YES YES
46	a	611.54	0.16718	YES YES
47	a	640.47	27.17147	YES YES
48	a	646.26	3.73358	YES YES
49	a	688.36	29.12501	YES YES
50	a	702.90	5.26939	YES YES
51	a	703.41	11.56385	YES YES
52	a	704.21	2.17855	YES YES
53	a	705.31	24.16942	YES YES
54	a	760.11	26.21996	YES YES
55	a	775.78	0.05151	YES YES
56	a	779.27	0.12177	YES YES
57	a	798.17	8.92738	YES YES
58	a	827.42	0.03603	YES YES
59	a	830.03	3.98199	YES YES
60	a	831.26	0.62618	YES YES
61	a	840.42	13.41513	YES YES
62	a	841.78	5.48939	YES YES
63	a	906.97	2.09480	YES YES
64	a	937.33	45.64705	YES YES
65	a	939.71	162.55197	YES YES
66	a	940.19	107.70803	YES YES
67	a	940.65	148.59895	YES YES

68	a	942.95	50.53496	YES	YES
69	a	955.33	63.87371	YES	YES
70	a	958.21	0.13807	YES	YES
71	a	981.22	1.26905	YES	YES
72	a	982.46	0.04313	YES	YES
73	a	1022.09	4.15850	YES	YES
74	a	1068.82	5.40456	YES	YES
75	a	1141.38	0.02975	YES	YES
76	a	1153.26	0.10824	YES	YES
77	a	1202.30	0.45316	YES	YES
78	a	1253.08	24.45700	YES	YES
79	a	1254.12	11.69082	YES	YES
80	a	1256.45	12.09884	YES	YES
81	a	1260.41	27.39816	YES	YES
82	a	1276.28	11.95542	YES	YES
83	a	1280.64	2.98767	YES	YES
84	a	1283.53	0.19117	YES	YES
85	a	1353.52	0.21029	YES	YES
86	a	1384.66	0.00499	YES	YES
87	a	1385.06	0.07295	YES	YES
88	a	1398.67	1.86881	YES	YES
89	a	1400.77	29.82155	YES	YES
90	a	1401.05	1.99126	YES	YES
91	a	1402.62	3.28306	YES	YES
92	a	1403.79	1.43726	YES	YES
93	a	1405.34	2.61423	YES	YES
94	a	1410.12	3.11891	YES	YES
95	a	1411.62	16.54393	YES	YES
96	a	1424.16	12.76992	YES	YES
97	a	1426.01	0.59875	YES	YES
98	a	1436.99	4.75644	YES	YES
99	a	1472.99	23.47646	YES	YES
100	a	1569.97	2.05453	YES	YES
101	a	1604.21	39.06888	YES	YES
102	a	1944.19	284.20470	YES	YES
103	a	2297.36	2.43922	YES	YES
104	a	2942.85	7.53198	YES	YES
105	a	2942.97	49.37978	YES	YES
106	a	2943.50	14.32595	YES	YES
107	a	2943.84	22.23054	YES	YES
108	a	2945.95	16.59406	YES	YES
109	a	2946.89	11.32265	YES	YES
110	a	3042.11	9.69378	YES	YES
111	a	3043.66	0.30241	YES	YES
112	a	3044.12	13.94370	YES	YES
113	a	3044.68	17.36342	YES	YES
114	a	3045.01	5.57067	YES	YES
115	a	3045.48	11.95151	YES	YES
116	a	3058.45	2.52368	YES	YES
117	a	3058.91	2.62831	YES	YES
118	a	3064.95	0.65342	YES	YES
119	a	3065.18	1.01816	YES	YES
120	a	3065.21	0.11543	YES	YES
121	a	3065.34	0.54814	YES	YES
122	a	3090.86	5.50348	YES	YES
123	a	3098.82	4.61111	YES	YES
124	a	3110.46	13.15181	YES	YES
125	a	3116.38	16.42427	YES	YES
126	a	3122.33	9.29772	YES	YES

Model 4iii (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	0.13200	0.95453	-0.00017
Cl	-0.75342	3.19194	-0.00145
P	0.08692	1.05770	2.33985
P	0.08809	1.05489	-2.34046
C	1.10595	2.44261	3.02153
C	-1.59981	1.40618	3.01383
C	0.64258	-0.40751	3.32141
C	-1.59947	1.39714	-3.01570
C	1.10284	2.44209	-3.02388
C	0.64889	-0.41021	-3.31916
C	0.77776	-0.73306	0.00128
C	1.24624	-1.98839	0.00245
C	0.45678	-3.23156	0.00166
H	2.35145	-2.09762	0.00420
H	-1.57729	1.53883	-4.11931
H	-1.98311	2.31303	-2.51868
H	-2.27522	0.55195	-2.76382
H	0.77082	3.37924	-2.52915
H	0.98754	2.52972	-4.12746
H	2.17245	2.27396	-2.77459
H	1.70498	-0.64154	-3.06605
H	0.56265	-0.22119	-4.41220
H	0.03522	-1.29455	-3.04623
H	-2.27740	0.56164	2.76464
H	-1.98134	2.32133	2.51384
H	-1.57748	1.55137	4.11699
H	0.55598	-0.21614	4.41400
H	1.69812	-0.64254	3.06946
H	0.02657	-1.29053	3.04952
H	0.77631	3.38034	2.52631
H	2.17493	2.27123	2.77171
H	0.99157	2.53154	4.12511
C	-1.02058	-5.66563	0.00015
C	0.38477	-5.68728	0.00283
C	1.11371	-4.48808	0.00379
C	-0.96385	-3.22583	-0.00126
C	-1.68759	-4.42545	-0.00177
H	-1.59360	-6.60748	-0.00038
H	0.92284	-6.65047	0.00435
H	2.21697	-4.51834	0.00583
H	-1.49491	-2.25872	-0.00293
H	-2.79039	-4.39342	-0.00396

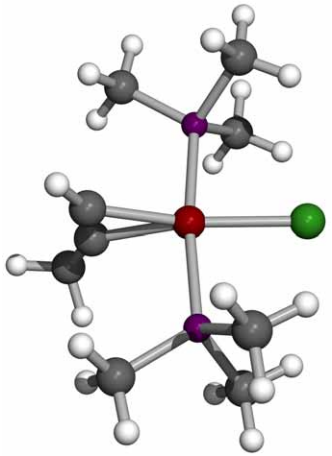
Vibrational frequencies

#	mode	symmetry	wave number	IR intensity	selection rules
#			cm**(-1)	km/mol	IR RAMAN
	1		0.00	0.00000	- -
	2		0.00	0.00000	- -
	3		0.00	0.00000	- -
	4		0.00	0.00000	- -
	5		0.00	0.00000	- -
	6		0.00	0.00000	- -
	7	a	5.28	0.18830	YES YES
	8	a	15.13	0.09300	YES YES
	9	a	21.75	0.00107	YES YES
	10	a	35.45	3.44788	YES YES
	11	a	37.07	0.01114	YES YES
	12	a	49.47	0.10358	YES YES
	13	a	77.56	3.12148	YES YES
	14	a	98.07	0.76785	YES YES
	15	a	98.63	0.04088	YES YES
	16	a	125.02	4.00085	YES YES
	17	a	136.08	0.04584	YES YES
	18	a	158.21	0.48153	YES YES
	19	a	173.48	1.45554	YES YES
	20	a	176.16	0.93723	YES YES
	21	a	177.85	0.10006	YES YES
	22	a	185.40	4.18306	YES YES
	23	a	192.11	1.61192	YES YES
	24	a	203.96	1.06409	YES YES
	25	a	205.97	0.03885	YES YES
	26	a	208.26	0.75569	YES YES
	27	a	225.83	0.33813	YES YES
	28	a	226.51	0.07430	YES YES
	29	a	236.40	1.61312	YES YES
	30	a	241.01	0.08548	YES YES
	31	a	246.81	0.02791	YES YES
	32	a	247.64	0.00024	YES YES
	33	a	250.34	2.24649	YES YES
	34	a	258.08	22.10762	YES YES
	35	a	317.48	10.31858	YES YES
	36	a	322.44	15.71630	YES YES
	37	a	334.83	4.87440	YES YES
	38	a	396.27	0.53993	YES YES
	39	a	404.34	0.00129	YES YES
	40	a	461.97	0.07219	YES YES
	41	a	482.76	18.51622	YES YES
	42	a	576.43	19.41284	YES YES
	43	a	613.26	1.95372	YES YES
	44	a	642.95	19.11136	YES YES
	45	a	647.11	2.78533	YES YES
	46	a	663.34	5.20897	YES YES
	47	a	694.26	25.53967	YES YES
	48	a	700.94	0.25333	YES YES
	49	a	706.10	0.01547	YES YES
	50	a	706.50	14.87817	YES YES
	51	a	710.31	0.86827	YES YES
	52	a	711.04	23.94563	YES YES
	53	a	762.94	31.92049	YES YES
	54	a	775.71	0.02175	YES YES
	55	a	775.84	0.04229	YES YES
	56	a	814.90	0.24823	YES YES
	57	a	826.97	0.51786	YES YES
	58	a	829.94	0.02030	YES YES
	59	a	832.12	6.19424	YES YES
	60	a	839.13	14.55667	YES YES
	61	a	840.00	5.72730	YES YES
	62	a	891.91	2.61559	YES YES
	63	a	938.35	3.57239	YES YES
	64	a	939.08	50.17346	YES YES
	65	a	941.35	253.75491	YES YES
	66	a	942.26	165.95557	YES YES
	67	a	944.16	49.46949	YES YES

68	a	949.67	0.19205	YES	YES
69	a	955.71	39.92506	YES	YES
70	a	972.30	0.50671	YES	YES
71	a	980.90	0.47527	YES	YES
72	a	1026.41	4.97717	YES	YES
73	a	1068.86	8.56221	YES	YES
74	a	1135.90	11.79791	YES	YES
75	a	1140.10	16.36844	YES	YES
76	a	1161.52	1.04272	YES	YES
77	a	1233.55	4.36933	YES	YES
78	a	1254.89	35.14723	YES	YES
79	a	1255.05	0.10605	YES	YES
80	a	1259.32	2.53481	YES	YES
81	a	1261.18	31.12502	YES	YES
82	a	1280.17	12.63614	YES	YES
83	a	1282.47	0.45630	YES	YES
84	a	1303.09	4.70440	YES	YES
85	a	1365.00	2.91446	YES	YES
86	a	1385.10	0.01632	YES	YES
87	a	1385.20	0.16304	YES	YES
88	a	1396.85	2.91169	YES	YES
89	a	1397.76	1.54187	YES	YES
90	a	1399.92	0.39887	YES	YES
91	a	1400.97	14.15698	YES	YES
92	a	1401.32	0.73940	YES	YES
93	a	1402.18	23.36998	YES	YES
94	a	1407.95	0.18132	YES	YES
95	a	1409.03	17.14976	YES	YES
96	a	1422.58	14.42344	YES	YES
97	a	1424.18	0.21378	YES	YES
98	a	1444.04	11.81060	YES	YES
99	a	1484.49	37.83263	YES	YES
100	a	1581.64	4.79054	YES	YES
101	a	1610.57	175.28051	YES	YES
102	a	1661.36	382.02149	YES	YES
103	a	2945.87	28.71844	YES	YES
104	a	2946.02	10.55723	YES	YES
105	a	2946.73	22.10120	YES	YES
106	a	2946.86	7.07057	YES	YES
107	a	2952.05	18.86660	YES	YES
108	a	2952.19	4.57496	YES	YES
109	a	3008.72	2.44296	YES	YES
110	a	3046.55	7.66272	YES	YES
111	a	3046.64	4.63118	YES	YES
112	a	3047.71	7.45940	YES	YES
113	a	3047.80	4.70868	YES	YES
114	a	3051.20	11.30645	YES	YES
115	a	3051.41	3.88968	YES	YES
116	a	3066.31	0.08844	YES	YES
117	a	3066.35	1.54585	YES	YES
118	a	3066.69	0.46899	YES	YES
119	a	3066.74	0.38762	YES	YES
120	a	3067.13	0.11051	YES	YES
121	a	3067.15	0.12147	YES	YES
122	a	3078.26	9.71374	YES	YES
123	a	3082.88	1.35175	YES	YES
124	a	3093.37	5.08265	YES	YES
125	a	3098.56	32.52678	YES	YES
126	a	3112.05	26.24254	YES	YES

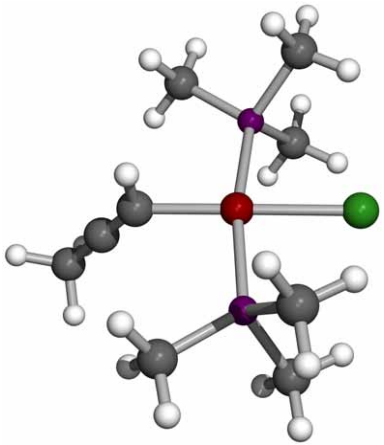
Electronic Supplementary Information for Dalton Transactions

Optimised structures for the model *iv* system – Gibbs energies in kJ mol^{-1} (relative to structure 2) are shown below each structure.



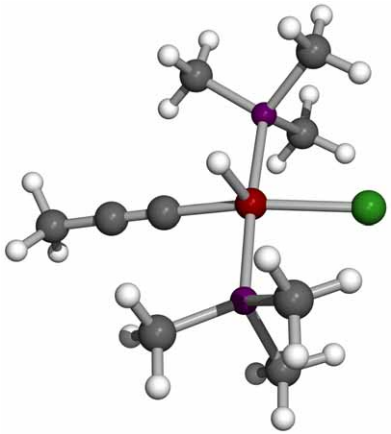
Model 2iv

0



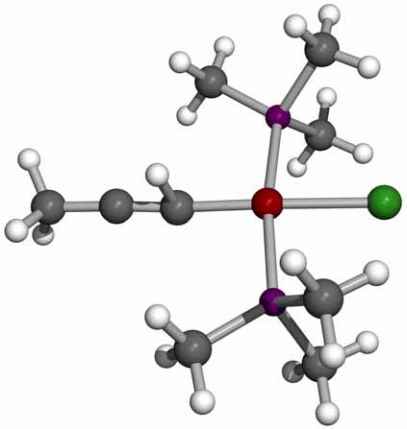
TS_{23}iv

97



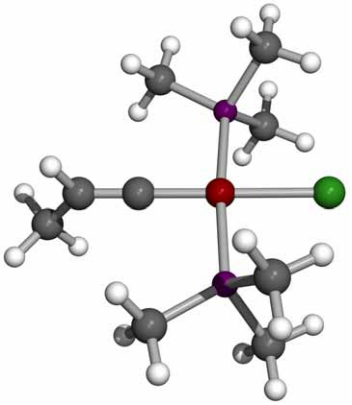
Model 3iv

17



TS_{34}iv

120



Model 4iv

-3

Note: The methyl group of the coordinated alkyne exhibits an eclipsed-like conformation in **model 2iv** and **TS_{23}iv**. Staggered conformations were not found to be minima, The conformation switches at **model 3iv** to a staggered-like conformation with respect to the hydride hydrogen.

Model 2iv (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	0.04032	-0.01402	0.00133
Cl	1.72427	1.63979	0.40193
C	-1.75609	-0.96526	-0.49614
C	-0.93373	-1.88745	-0.16492
P	-0.57936	0.27636	2.22867
P	0.83995	-0.07955	-2.18546
H	-2.73983	-0.62551	-0.83351
C	-0.48547	-3.27280	0.08313
C	0.77945	-0.07388	3.43772
C	-1.04787	2.01763	2.65071
C	-2.00131	-0.70337	2.90746
C	0.72988	1.54773	-3.06225
C	2.64300	-0.48173	-2.31677
C	0.06348	-1.24896	-3.39809
H	-1.24894	2.14111	3.73894
H	-1.95089	2.30739	2.07133
H	-0.20833	2.67440	2.33873
H	-2.91554	-0.48840	2.31444
H	-2.18796	-0.45640	3.97618
H	-1.78777	-1.78943	2.81508
H	0.47799	0.15654	4.48436
H	1.65224	0.54781	3.14572
H	1.07434	-1.14246	3.36355
H	0.53319	-1.15941	-4.40253
H	-1.02311	-1.03292	-3.47787
H	0.17384	-2.29323	-3.03559
H	1.19522	1.50665	-4.07252
H	1.24737	2.30200	-2.43259
H	-0.33671	1.84430	-3.15596
H	3.18982	0.23700	-1.67049
H	3.01118	-0.41332	-3.36532
H	2.82353	-1.50654	-1.92720
H	-0.18938	-3.42038	1.14761
H	0.41275	-3.52594	-0.52594
H	-1.28639	-4.01043	-0.15734

Vibrational frequencies

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	37.30	0.31969	YES	YES
8	a	41.11	1.55811	YES	YES
9	a	44.02	0.89028	YES	YES
10	a	68.69	0.11574	YES	YES
11	a	82.69	1.47926	YES	YES
12	a	86.61	0.94771	YES	YES
13	a	121.06	0.30900	YES	YES
14	a	128.86	3.35726	YES	YES
15	a	136.04	0.00951	YES	YES
16	a	158.79	0.09335	YES	YES
17	a	173.43	0.95191	YES	YES
18	a	175.81	0.89521	YES	YES
19	a	176.70	0.90836	YES	YES
20	a	181.28	0.26985	YES	YES
21	a	185.41	0.55100	YES	YES
22	a	197.98	4.71725	YES	YES
23	a	206.79	0.50360	YES	YES
24	a	208.53	0.60050	YES	YES
25	a	214.43	0.21204	YES	YES
26	a	221.90	0.46499	YES	YES
27	a	223.03	0.05893	YES	YES
28	a	223.61	0.88451	YES	YES
29	a	243.34	0.01101	YES	YES
30	a	252.99	0.20418	YES	YES
31	a	258.11	11.61169	YES	YES
32	a	258.65	2.33834	YES	YES
33	a	306.12	9.06309	YES	YES
34	a	316.72	19.55255	YES	YES
35	a	339.23	0.65334	YES	YES
36	a	345.91	4.56729	YES	YES
37	a	414.28	5.71156	YES	YES
38	a	472.59	2.11136	YES	YES
39	a	626.14	10.33873	YES	YES
40	a	638.17	36.08390	YES	YES
41	a	643.81	0.01466	YES	YES
42	a	702.07	4.26737	YES	YES
43	a	702.16	4.36428	YES	YES
44	a	703.33	11.55141	YES	YES
45	a	704.02	21.59698	YES	YES
46	a	773.58	0.19469	YES	YES
47	a	774.65	0.29060	YES	YES
48	a	780.04	15.58755	YES	YES
49	a	823.43	0.75853	YES	YES
50	a	829.51	0.18102	YES	YES
51	a	833.92	16.58635	YES	YES
52	a	840.85	6.45280	YES	YES
53	a	920.23	6.41428	YES	YES
54	a	933.91	4.65048	YES	YES
55	a	934.89	53.95866	YES	YES
56	a	937.97	370.80104	YES	YES
57	a	939.63	77.05298	YES	YES
58	a	942.12	51.23444	YES	YES
59	a	956.39	6.00382	YES	YES
60	a	1008.91	33.28474	YES	YES
61	a	1016.88	2.04345	YES	YES
62	a	1255.28	23.53019	YES	YES
63	a	1255.59	11.02134	YES	YES
64	a	1257.76	4.86427	YES	YES
65	a	1259.47	27.47684	YES	YES
66	a	1277.14	15.70109	YES	YES
67	a	1280.33	0.58780	YES	YES

68	a	1352.13	2.38875	YES	YES
69	a	1385.75	0.03692	YES	YES
70	a	1385.83	0.14367	YES	YES
71	a	1397.09	2.90156	YES	YES
72	a	1399.02	3.25142	YES	YES
73	a	1399.97	1.02936	YES	YES
74	a	1401.48	12.06071	YES	YES
75	a	1401.95	5.63908	YES	YES
76	a	1402.40	9.84084	YES	YES
77	a	1405.09	7.16184	YES	YES
78	a	1408.73	4.19405	YES	YES
79	a	1409.72	8.00911	YES	YES
80	a	1414.46	15.23087	YES	YES
81	a	1422.76	7.83706	YES	YES
82	a	1424.74	0.68585	YES	YES
83	a	1882.48	29.93515	YES	YES
84	a	2913.70	47.76069	YES	YES
85	a	2942.23	27.90812	YES	YES
86	a	2942.65	17.69873	YES	YES
87	a	2943.52	20.36663	YES	YES
88	a	2945.18	19.35436	YES	YES
89	a	2950.16	20.33136	YES	YES
90	a	2950.41	8.35016	YES	YES
91	a	2988.27	11.18422	YES	YES
92	a	2995.70	13.11508	YES	YES
93	a	3042.42	7.63486	YES	YES
94	a	3042.97	6.52348	YES	YES
95	a	3043.89	8.47160	YES	YES
96	a	3045.78	7.31630	YES	YES
97	a	3047.62	11.69399	YES	YES
98	a	3048.03	7.18797	YES	YES
99	a	3060.54	2.52840	YES	YES
100	a	3061.36	2.71960	YES	YES
101	a	3064.02	0.35349	YES	YES
102	a	3064.12	0.49773	YES	YES
103	a	3064.64	0.57006	YES	YES
104	a	3065.76	0.36712	YES	YES
105	a	3204.85	2.87575	YES	YES

TS_{23}iv (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	-0.13817	0.12177	-0.00078
Cl	2.28795	-0.03680	-0.01940
C	-2.16477	0.23676	0.01538
C	-3.03040	-0.68159	0.02672
P	0.08276	0.09036	2.30524
P	0.04542	0.06446	-2.30963
H	-2.13098	1.35630	0.00966
C	-3.98649	-1.77505	0.03876
C	0.90266	-1.44516	2.93607
C	1.16127	1.43575	2.98091
C	-1.43145	0.21123	3.37388
C	1.11934	1.39635	-3.01834
C	0.84743	-1.48235	-2.93577
C	-1.48535	0.18094	-3.35496
H	1.07869	-1.40253	4.03456
H	1.86696	-1.54657	2.39404
H	0.27037	-2.32630	2.69431
H	-2.13216	-0.61055	3.11477
H	-1.95036	1.17414	3.17676
H	-1.17430	0.15081	4.45490
H	0.69399	2.42215	2.77231
H	2.12769	1.38439	2.43606
H	1.32624	1.32693	4.07657
H	0.66027	2.38752	-2.81411
H	1.26615	1.27361	-4.11509
H	2.09406	1.34661	-2.48830
H	-1.24644	0.10568	-4.43925
H	-1.99517	1.14943	-3.16139
H	-2.18665	-0.63324	-3.07423
H	1.82042	-1.58207	-2.40921
H	1.00486	-1.45355	-4.03752
H	0.21536	-2.35754	-2.67279
H	-3.89952	-2.42751	-0.86146
H	-5.02835	-1.37108	0.04422
H	-3.88668	-2.41915	0.94362

Vibrational frequencies

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1	a	-395.40	0.00000	YES	YES
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7		0.00	5.73913	-	-
8	a	31.87	0.22599	YES	YES
9	a	41.03	0.29754	YES	YES
10	a	42.15	2.87479	YES	YES
11	a	44.18	0.01757	YES	YES
12	a	59.53	0.70345	YES	YES
13	a	83.17	1.00449	YES	YES
14	a	85.65	2.06936	YES	YES
15	a	132.81	3.73338	YES	YES
16	a	141.60	0.00402	YES	YES
17	a	153.07	0.01689	YES	YES
18	a	165.68	0.14214	YES	YES
19	a	178.08	0.63365	YES	YES
20	a	185.26	0.63793	YES	YES
21	a	187.77	0.05995	YES	YES
22	a	193.85	1.57168	YES	YES
23	a	195.09	9.23787	YES	YES
24	a	210.84	2.36182	YES	YES
25	a	211.49	0.46456	YES	YES
26	a	212.31	0.73689	YES	YES
27	a	222.75	0.42134	YES	YES
28	a	223.28	6.32562	YES	YES
29	a	224.51	0.10739	YES	YES
30	a	243.51	0.02021	YES	YES
31	a	250.13	1.58636	YES	YES
32	a	255.81	6.80725	YES	YES
33	a	260.82	3.12768	YES	YES
34	a	283.02	3.68189	YES	YES
35	a	299.46	3.53509	YES	YES
36	a	325.89	28.62162	YES	YES
37	a	342.33	5.14362	YES	YES
38	a	373.97	16.76486	YES	YES
39	a	527.63	4.16161	YES	YES
40	a	578.55	14.89190	YES	YES
41	a	637.85	31.73277	YES	YES
42	a	644.26	0.84530	YES	YES
43	a	700.52	0.56349	YES	YES
44	a	701.93	24.03591	YES	YES
45	a	702.56	0.15412	YES	YES
46	a	703.48	19.60064	YES	YES
47	a	776.41	0.07696	YES	YES
48	a	776.45	0.04510	YES	YES
49	a	825.97	0.52931	YES	YES
50	a	829.50	0.01016	YES	YES
51	a	838.72	16.17731	YES	YES
52	a	841.65	6.21326	YES	YES
53	a	924.13	32.38030	YES	YES
54	a	935.88	13.20078	YES	YES
55	a	936.83	52.93876	YES	YES
56	a	937.98	302.50449	YES	YES
57	a	939.58	168.26663	YES	YES
58	a	942.22	48.88775	YES	YES
59	a	957.88	6.34953	YES	YES
60	a	985.05	5.74675	YES	YES
61	a	1013.47	5.02865	YES	YES
62	a	1251.55	38.15301	YES	YES
63	a	1251.90	0.56420	YES	YES
64	a	1256.72	4.84889	YES	YES
65	a	1259.27	33.02840	YES	YES
66	a	1275.85	14.58247	YES	YES
67	a	1278.64	0.07140	YES	YES

68	a	1346.39	5.17418	YES	YES
69	a	1384.18	0.03058	YES	YES
70	a	1384.36	0.08276	YES	YES
71	a	1391.30	12.05757	YES	YES
72	a	1398.04	0.71309	YES	YES
73	a	1400.06	21.55426	YES	YES
74	a	1400.91	0.16788	YES	YES
75	a	1401.72	2.06829	YES	YES
76	a	1403.56	0.57029	YES	YES
77	a	1403.91	5.12003	YES	YES
78	a	1410.59	0.03856	YES	YES
79	a	1411.36	17.12013	YES	YES
80	a	1412.76	20.79898	YES	YES
81	a	1424.00	8.88514	YES	YES
82	a	1425.95	0.16086	YES	YES
83	a	1948.80	11.25684	YES	YES
84	a	2900.57	31.57167	YES	YES
85	a	2919.05	64.83276	YES	YES
86	a	2941.59	22.34885	YES	YES
87	a	2941.72	16.50619	YES	YES
88	a	2941.88	46.97658	YES	YES
89	a	2942.16	5.87168	YES	YES
90	a	2946.19	30.96060	YES	YES
91	a	2946.44	6.69918	YES	YES
92	a	2971.12	5.49403	YES	YES
93	a	2985.45	5.75480	YES	YES
94	a	3042.61	0.62254	YES	YES
95	a	3042.62	0.11163	YES	YES
96	a	3043.04	2.57664	YES	YES
97	a	3043.07	0.23737	YES	YES
98	a	3043.32	41.09849	YES	YES
99	a	3043.47	8.96717	YES	YES
100	a	3058.14	2.91410	YES	YES
101	a	3058.26	4.25131	YES	YES
102	a	3062.20	0.75975	YES	YES
103	a	3062.28	0.63700	YES	YES
104	a	3063.61	0.73010	YES	YES
105	a	3063.72	0.41202	YES	YES

Model 3iv (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	-0.05285	0.08750	0.00011
Cl	0.35215	2.47818	0.00066
P	-0.09216	0.16994	2.33045
P	-0.09222	0.17120	-2.33015
C	1.55411	0.63405	3.03382
C	-1.22906	1.45812	3.00669
C	-0.55511	-1.36238	3.24812
C	-1.22932	1.45957	-3.00573
C	1.55398	0.63602	-3.03326
C	-0.55480	-1.36070	-3.24874
C	0.05441	-1.86502	-0.00040
C	0.15040	-3.10245	-0.00114
H	-1.55864	-0.20788	0.00005
C	0.30130	-4.55961	-0.00251
H	1.51553	0.73031	4.14180
H	1.85753	1.60132	2.57955
H	2.30286	-0.13873	2.75633
H	-1.13129	1.55342	4.11084
H	-2.27682	1.19295	2.74886
H	-0.97929	2.41938	2.50909
H	-1.59264	-1.64882	2.97423
H	-0.48652	-1.21467	4.34864
H	0.11476	-2.18689	2.92624
H	1.85705	1.60325	-2.57866
H	1.51544	0.73258	-4.14122
H	2.30295	-0.13660	-2.75594
H	-0.48579	-1.21245	-4.34915
H	-1.59246	-1.64725	-2.97544
H	0.11494	-2.18538	-2.92701
H	-1.13155	1.55541	-4.10984
H	-0.97969	2.42062	-2.50767
H	-2.27704	1.19413	-2.74805
H	-0.16779	-5.03312	0.89258
H	1.37381	-4.86796	-0.00265
H	-0.16751	-5.03131	-0.89870

Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	26.28	0.15335	YES YES
8	a	30.61	0.04796	YES YES
9	a	37.52	0.00020	YES YES
10	a	44.01	4.09129	YES YES
11	a	59.94	0.01730	YES YES
12	a	67.01	1.01898	YES YES
13	a	86.78	3.30353	YES YES
14	a	116.67	2.46226	YES YES
15	a	138.51	1.01325	YES YES
16	a	162.43	0.05379	YES YES
17	a	167.21	10.00105	YES YES
18	a	176.38	1.97657	YES YES
19	a	180.59	0.23887	YES YES
20	a	183.28	1.31269	YES YES
21	a	191.72	5.68242	YES YES
22	a	196.89	0.02646	YES YES
23	a	199.73	1.37034	YES YES
24	a	205.92	0.11062	YES YES
25	a	209.22	0.41180	YES YES
26	a	219.23	0.00487	YES YES
27	a	220.75	0.00770	YES YES
28	a	227.25	10.13263	YES YES
29	a	241.20	0.61291	YES YES
30	a	248.47	2.04057	YES YES
31	a	251.79	11.00940	YES YES
32	a	260.32	4.15389	YES YES
33	a	290.83	11.68683	YES YES
34	a	319.89	1.06968	YES YES
35	a	328.94	5.07650	YES YES
36	a	340.57	0.64968	YES YES
37	a	384.16	2.77080	YES YES
38	a	416.07	0.98230	YES YES
39	a	520.77	4.35567	YES YES
40	a	627.12	34.07656	YES YES
41	a	644.23	10.56660	YES YES
42	a	648.33	0.49087	YES YES
43	a	711.67	19.41822	YES YES
44	a	712.32	0.69221	YES YES
45	a	715.47	1.80349	YES YES
46	a	715.76	23.80411	YES YES
47	a	780.21	0.09838	YES YES
48	a	780.26	0.06705	YES YES
49	a	829.94	6.98221	YES YES
50	a	835.76	3.54694	YES YES
51	a	840.33	10.89566	YES YES
52	a	844.56	16.52554	YES YES
53	a	941.22	53.02531	YES YES
54	a	943.16	56.93297	YES YES
55	a	943.60	192.45291	YES YES
56	a	947.02	57.35029	YES YES
57	a	947.11	200.21957	YES YES
58	a	961.14	8.65547	YES YES
59	a	1004.14	0.63090	YES YES
60	a	1016.47	0.99593	YES YES
61	a	1020.36	1.73899	YES YES
62	a	1255.35	34.39780	YES YES
63	a	1255.40	0.05498	YES YES
64	a	1260.93	1.97779	YES YES
65	a	1263.06	30.18786	YES YES
66	a	1280.28	15.38239	YES YES
67	a	1283.16	0.74247	YES YES

68	a	1367.23	26.49766	YES	YES
69	a	1383.78	0.11059	YES	YES
70	a	1384.09	0.85519	YES	YES
71	a	1396.49	4.73931	YES	YES
72	a	1397.71	10.95710	YES	YES
73	a	1399.70	0.00001	YES	YES
74	a	1400.89	1.41225	YES	YES
75	a	1401.74	0.93950	YES	YES
76	a	1403.03	24.23025	YES	YES
77	a	1408.49	0.12976	YES	YES
78	a	1409.62	13.04256	YES	YES
79	a	1417.29	3.86885	YES	YES
80	a	1418.44	5.53084	YES	YES
81	a	1423.31	17.89618	YES	YES
82	a	1425.00	0.03351	YES	YES
83	a	2138.90	5.33533	YES	YES
84	a	2244.84	3.99231	YES	YES
85	a	2900.49	118.81146	YES	YES
86	a	2946.39	19.86899	YES	YES
87	a	2946.51	6.00136	YES	YES
88	a	2947.34	24.42279	YES	YES
89	a	2947.49	5.98621	YES	YES
90	a	2952.84	29.53938	YES	YES
91	a	2952.94	2.24611	YES	YES
92	a	2968.47	14.25655	YES	YES
93	a	2970.22	14.50857	YES	YES
94	a	3046.92	9.16791	YES	YES
95	a	3046.95	1.54311	YES	YES
96	a	3049.35	5.99037	YES	YES
97	a	3049.43	2.22286	YES	YES
98	a	3053.53	11.05345	YES	YES
99	a	3053.63	0.55304	YES	YES
100	a	3063.50	1.19077	YES	YES
101	a	3063.59	0.61466	YES	YES
102	a	3063.70	0.14624	YES	YES
103	a	3063.76	0.23412	YES	YES
104	a	3069.75	0.05135	YES	YES
105	a	3069.81	0.37596	YES	YES

TS_{34}iv (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	-0.02727	-0.18483	-0.00250
Cl	0.15776	2.22378	0.01246
P	0.00905	-0.02889	2.31202
P	0.02378	-0.00071	-2.31468
C	-0.07876	-2.09301	-0.01397
C	-0.25627	-3.36119	-0.02167
C	1.56945	0.73373	2.95326
C	-1.30211	1.07227	3.01790
C	-0.14682	-1.56040	3.34806
C	-1.29575	1.09450	-3.01448
C	1.57897	0.78672	-2.93858
C	-0.10922	-1.52127	-3.36971
H	-1.28561	-2.25652	-0.01929
C	-0.36290	-4.81863	-0.02925
H	-1.16842	1.25089	-4.10947
H	-1.23731	2.06393	-2.47579
H	-2.29209	0.64436	-2.81648
H	1.69297	1.75563	-2.40756
H	1.54852	0.95120	-4.03931
H	2.44651	0.14228	-2.68114
H	-0.04692	-1.27208	-4.45250
H	-1.07647	-2.03096	-3.16988
H	0.70868	-2.22451	-3.10495
H	-2.30214	0.63461	2.81083
H	-1.23139	2.04668	2.48972
H	-1.17770	1.21542	4.11499
H	-0.08771	-1.32511	4.43415
H	0.66418	-2.27002	3.07916
H	-1.11897	-2.05615	3.13696
H	1.69649	1.70834	2.43577
H	2.43129	0.08350	2.69132
H	1.53564	0.88421	4.05588
H	-0.87341	-5.21040	-0.93935
H	-0.89165	-5.21803	0.86705
H	0.66387	-5.25681	-0.02054

Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1	a	-1053.74	0.00000	YES YES
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7		0.00	0.11861	- -
8	a	32.65	0.16704	YES YES
9	a	41.20	3.25501	YES YES
10	a	43.07	0.22904	YES YES
11	a	53.95	1.40772	YES YES
12	a	71.94	0.00551	YES YES
13	a	80.48	0.04120	YES YES
14	a	84.37	2.15316	YES YES
15	a	132.08	2.87069	YES YES
16	a	142.20	0.02526	YES YES
17	a	160.42	0.04120	YES YES
18	a	169.43	3.82925	YES YES
19	a	178.47	0.66673	YES YES
20	a	183.61	2.85726	YES YES
21	a	191.86	0.56051	YES YES
22	a	192.63	3.74583	YES YES
23	a	192.86	0.30559	YES YES
24	a	210.36	0.26267	YES YES
25	a	213.41	0.45150	YES YES
26	a	214.82	1.35387	YES YES
27	a	220.76	0.16342	YES YES
28	a	223.43	0.15338	YES YES
29	a	224.95	0.00941	YES YES
30	a	243.81	0.00081	YES YES
31	a	249.48	1.48185	YES YES
32	a	256.03	3.60921	YES YES
33	a	257.93	6.85718	YES YES
34	a	286.36	28.64250	YES YES
35	a	325.39	9.45423	YES YES
36	a	328.41	33.76402	YES YES
37	a	340.52	19.94790	YES YES
38	a	348.29	18.33417	YES YES
39	a	412.45	0.14951	YES YES
40	a	436.66	20.63819	YES YES
41	a	639.83	30.43993	YES YES
42	a	645.81	1.33455	YES YES
43	a	702.24	0.67010	YES YES
44	a	702.42	15.89892	YES YES
45	a	704.08	1.55333	YES YES
46	a	705.01	25.28831	YES YES
47	a	776.47	0.05279	YES YES
48	a	777.32	0.06613	YES YES
49	a	830.54	2.57318	YES YES
50	a	831.17	2.03530	YES YES
51	a	840.13	13.95081	YES YES
52	a	841.80	5.79799	YES YES
53	a	937.17	28.45014	YES YES
54	a	938.08	45.15067	YES YES
55	a	939.11	147.30018	YES YES
56	a	940.37	284.25764	YES YES
57	a	941.84	9.81282	YES YES
58	a	945.74	115.83208	YES YES
59	a	963.20	6.92479	YES YES
60	a	1000.80	5.43810	YES YES
61	a	1025.28	0.72719	YES YES
62	a	1252.53	33.17450	YES YES
63	a	1252.95	4.30670	YES YES
64	a	1257.13	4.74634	YES YES
65	a	1259.51	30.68422	YES YES
66	a	1276.18	14.26038	YES YES
67	a	1279.01	0.52449	YES YES

68	a	1350.11	15.86562	YES	YES
69	a	1384.56	0.00080	YES	YES
70	a	1384.58	0.07544	YES	YES
71	a	1397.43	9.24895	YES	YES
72	a	1398.36	0.76250	YES	YES
73	a	1400.45	24.88799	YES	YES
74	a	1402.00	0.87987	YES	YES
75	a	1402.92	0.22377	YES	YES
76	a	1403.79	1.56274	YES	YES
77	a	1404.24	4.35321	YES	YES
78	a	1410.59	0.20856	YES	YES
79	a	1411.54	18.79777	YES	YES
80	a	1417.01	10.50146	YES	YES
81	a	1424.24	11.26386	YES	YES
82	a	1426.08	0.11037	YES	YES
83	a	1960.96	203.85611	YES	YES
84	a	2338.33	12.72414	YES	YES
85	a	2908.97	72.83566	YES	YES
86	a	2942.08	21.49587	YES	YES
87	a	2942.22	38.84938	YES	YES
88	a	2942.29	24.96549	YES	YES
89	a	2942.57	9.75661	YES	YES
90	a	2945.83	24.57630	YES	YES
91	a	2946.13	9.33491	YES	YES
92	a	2982.74	7.25634	YES	YES
93	a	2991.02	6.29548	YES	YES
94	a	3042.22	7.84503	YES	YES
95	a	3042.58	3.84195	YES	YES
96	a	3043.50	11.23205	YES	YES
97	a	3043.73	8.81553	YES	YES
98	a	3044.16	14.40937	YES	YES
99	a	3044.32	8.32519	YES	YES
100	a	3058.32	2.92450	YES	YES
101	a	3058.49	3.06543	YES	YES
102	a	3064.01	0.78825	YES	YES
103	a	3064.10	0.58139	YES	YES
104	a	3064.48	0.76797	YES	YES
105	a	3064.55	0.50035	YES	YES

Model 4iv (RI-)BP86/SV(P) optimisation (symmetry: C_1)

XYZ coordinates (Å)

	x	y	z
Rh	0.04888	0.04484	-0.00017
Cl	-0.23463	2.43810	-0.00115
P	0.03514	0.15703	2.33337
P	0.03601	0.15562	-2.33379
C	1.37249	1.24280	3.01038
C	-1.50419	0.92221	3.01736
C	0.20982	-1.39358	3.32808
C	-1.51191	0.90323	-3.01790
C	1.36091	1.25561	-3.01201
C	0.22769	-1.39363	-3.32734
C	0.27257	-1.76038	0.00182
C	0.43481	-3.08100	0.00712
C	-0.68503	-4.10377	-0.00191
H	1.48003	-3.45811	0.02170
H	-1.45263	1.03646	-4.12130
H	-1.65833	1.88561	-2.52075
H	-2.37677	0.25232	-2.76789
H	1.26613	2.24246	-2.51170
H	1.27440	1.37399	-4.11543
H	2.35599	0.83029	-2.76087
H	1.18411	-1.88978	-3.05823
H	0.21544	-1.17631	-4.41841
H	-0.59673	-2.09507	-3.07990
H	-2.37576	0.27843	2.77209
H	-1.64210	1.90376	2.51621
H	-1.44137	1.05933	4.12013
H	0.19930	-1.17532	4.41895
H	1.16089	-1.90034	3.05978
H	-0.62206	-2.08619	3.08069
H	1.28612	2.23156	2.51235
H	2.36268	0.80820	2.75591
H	1.28959	1.35990	4.11422
H	-1.67928	-3.60917	-0.03195
H	-0.65304	-4.75258	0.90472
H	-0.61150	-4.77846	-0.88653

Vibrational frequencies

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	25.61	0.12211	YES YES
8	a	34.15	0.02210	YES YES
9	a	38.03	3.31719	YES YES
10	a	51.51	0.07035	YES YES
11	a	69.99	0.05070	YES YES
12	a	82.25	2.76386	YES YES
13	a	114.28	0.68644	YES YES
14	a	124.73	3.47961	YES YES
15	a	137.46	0.00016	YES YES
16	a	159.42	0.11367	YES YES
17	a	160.97	0.95256	YES YES
18	a	164.40	0.21820	YES YES
19	a	175.56	1.17641	YES YES
20	a	179.98	0.31542	YES YES
21	a	181.02	0.01111	YES YES
22	a	191.59	5.16641	YES YES
23	a	198.90	2.70681	YES YES
24	a	208.40	0.37124	YES YES
25	a	209.94	0.05706	YES YES
26	a	212.61	0.90213	YES YES
27	a	224.37	0.23705	YES YES
28	a	225.83	0.09880	YES YES
29	a	241.53	0.00118	YES YES
30	a	248.01	0.36780	YES YES
31	a	251.71	1.98383	YES YES
32	a	255.48	11.34361	YES YES
33	a	301.04	11.64249	YES YES
34	a	322.95	17.40972	YES YES
35	a	337.90	1.78158	YES YES
36	a	459.78	1.79005	YES YES
37	a	474.37	1.29067	YES YES
38	a	610.08	34.71991	YES YES
39	a	614.93	1.66720	YES YES
40	a	642.08	22.23935	YES YES
41	a	647.07	1.31824	YES YES
42	a	705.01	0.39521	YES YES
43	a	705.41	15.42668	YES YES
44	a	710.03	1.56038	YES YES
45	a	710.82	23.05730	YES YES
46	a	776.88	0.02348	YES YES
47	a	777.41	0.03579	YES YES
48	a	831.39	5.06673	YES YES
49	a	831.56	0.08918	YES YES
50	a	838.64	12.90459	YES YES
51	a	841.77	5.93973	YES YES
52	a	934.34	21.04232	YES YES
53	a	938.72	2.56670	YES YES
54	a	939.43	51.28858	YES YES
55	a	941.51	392.12763	YES YES
56	a	941.90	37.75767	YES YES
57	a	944.18	45.08156	YES YES
58	a	957.64	8.27724	YES YES
59	a	1004.22	0.07451	YES YES
60	a	1039.89	0.50451	YES YES
61	a	1183.93	36.29798	YES YES
62	a	1256.21	31.29456	YES YES
63	a	1256.42	3.71899	YES YES
64	a	1259.09	1.94910	YES YES
65	a	1260.70	29.47530	YES YES
66	a	1278.22	14.12089	YES YES
67	a	1281.03	0.65498	YES YES

68	a	1349.85	18.79896	YES	YES
69	a	1385.56	0.07925	YES	YES
70	a	1385.69	0.26478	YES	YES
71	a	1397.75	2.90611	YES	YES
72	a	1398.48	2.56364	YES	YES
73	a	1400.54	0.68433	YES	YES
74	a	1401.09	0.66667	YES	YES
75	a	1401.55	6.97242	YES	YES
76	a	1402.26	26.02854	YES	YES
77	a	1408.94	0.07541	YES	YES
78	a	1410.02	17.44430	YES	YES
79	a	1421.60	2.91739	YES	YES
80	a	1423.04	15.58290	YES	YES
81	a	1424.45	0.15653	YES	YES
82	a	1429.73	4.68074	YES	YES
83	a	1705.70	171.97526	YES	YES
84	a	2919.21	80.20567	YES	YES
85	a	2945.34	46.38296	YES	YES
86	a	2945.48	8.87660	YES	YES
87	a	2945.60	15.87942	YES	YES
88	a	2945.70	4.92515	YES	YES
89	a	2951.48	19.95362	YES	YES
90	a	2951.67	7.04746	YES	YES
91	a	2981.92	16.99615	YES	YES
92	a	3008.69	1.96433	YES	YES
93	a	3036.18	10.68312	YES	YES
94	a	3046.51	10.58097	YES	YES
95	a	3046.60	1.64072	YES	YES
96	a	3046.70	9.29934	YES	YES
97	a	3046.89	4.73881	YES	YES
98	a	3050.65	13.61509	YES	YES
99	a	3050.87	3.50192	YES	YES
100	a	3064.89	0.63690	YES	YES
101	a	3064.93	2.80921	YES	YES
102	a	3065.29	0.21505	YES	YES
103	a	3065.32	0.23701	YES	YES
104	a	3066.87	0.34225	YES	YES
105	a	3067.12	0.29725	YES	YES

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