

Supporting Information

Steric and electronic effects on the reactivity of Rh and Ir complexes containing P-S, P-P and P-O ligands; implications for the effects of chelate ligands in catalysis

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Kinetic data

Table 1. Observed pseudo first order rate constants, k_{obs} , for oxidative addition of MeI to Rh complexes **1a-c** and first order rate constants, k_2 , for migratory insertion in **2b**. (solvent CH₂Cl₂ except where stated).

Temp/°C	[MeI]/ M	[Bu ₄ NI]/ [Rh]	10 ³ $k_{\text{obs}}/\text{s}^{-1}$	10 ³ $k_{\text{obs}}/\text{s}^{-1}$	10 ³ $k_{\text{obs}}/\text{s}^{-1}$	10 ⁴ k_2/s^{-1}
			1a + MeI → 2a	1b + MeI → 2b	1c + MeI → 2c	2b → 3b
10	0.8	0	0.29	0.51		
10	0.8	0	0.38 ^a	0.58 ^a		
10	0.8	0	0.72 ^b	1.45 ^b		
10	0.8	0	0.82 ^c	1.41 ^c		
10	1.6	0	0.58	0.96	0.83	0.26
15	1.6	0	0.84	1.29	1.29	0.49
20	1.6	0	1.20	1.79	1.41	0.89
25	0.4	0	0.44	0.66		1.49
25	0.8	0	0.91	1.27		1.52
25	1.2	0	1.30	1.75	1.50	1.69
25	1.6	0	1.72	2.34	1.90	1.59
25	1.6	0			7.08 ^f	
25	1.6	1	2.21	2.65	4.55	
25	1.6	10	3.60	3.70	15.4	
25	2.4	0	2.80	3.42	2.71	1.66
25	3.2	0	3.98	4.40	3.55	1.58
30	1.6	0	2.32	3.11	2.40	2.86
35	1.6	0	3.19	4.07		5.08

^asolvent 2:1 CH₂Cl₂-THF ^bsolvent 2:1 CH₂Cl₂-MeCN ^csolvent 2:1 CH₂Cl₂-MeOH ^dsolvent MeCN

Table 2. Observed pseudo first order rate constants, k_{obs} , for the reaction of MeI (8 M) with **1a** in CH_2Cl_2 . Values of the steady state ratio of IR absorbances due to **2a** (2062 cm^{-1}) and **1a** (1987 cm^{-1}) are also given. Rate constants for migratory insertion in **2a** (k_2) were calculated from the data in columns 2 and 3 using the relationship $k_2 = k_{\text{obs}}(\epsilon_{2062}/\epsilon_{1987})/(A_{2062}/A_{1987})$. The ratio of extinction coefficients ($\epsilon_{2062}/\epsilon_{1987}$) was estimated as 0.6 based on data for model iridium complexes **4a** and **5a**.

Temp/ $^{\circ}\text{C}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$	A_{2062}/A_{1987}	k_2/s^{-1}
	1a + MeI \rightarrow 2a	2a \rightarrow 3a	
10	3.46	0.0111	0.19
15	4.93	0.0102	0.29
20	6.98	0.0095	0.44
25	8.9	0.0086	0.62

Table 3. Observed pseudo first order rate constants, k_{obs} , for reactions of MeI with iridium complexes **4a** and **4b** in CH_2Cl_2 .

Temp/ $^{\circ}\text{C}$	[MeI]/mol dm $^{-3}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$
		4a + MeI \rightarrow 5a	4b + MeI \rightarrow 5b
5	0.4		8.08
10	0.025	0.56	0.78
10	0.05	1.18	1.38
10	0.05	1.54 ^a	1.43 ^a
10	0.05	1.91 ^b	1.99 ^b
10	0.05	2.02 ^c	2.21 ^c
10	0.1	2.35	2.65
10	0.2	4.58	4.97
10	0.4		10.1
15	0.2	5.93	
20	0.2	7.70	
25	0.2	10.0	
15	0.4		13.1
20	0.4		16.6
25	0.4		20.7

^asolvent 2:1 CH_2Cl_2 -THF ^bsolvent 2:1 CH_2Cl_2 -MeCN ^csolvent 2:1 CH_2Cl_2 -MeOH

Crystallographic data

Crystallographic data for [Rh(dppe)I₂(COMe)] **3b**

Crystal data for C₂₈H₂₇I₂OP₂Rh; M = 798.15 Crystallises from dichloromethane/ether as colourless blocks; crystal dimensions 0.50 x 0.32 x 0.31 mm. Triclinic, *a* = 9.155(4), *b* = 10.436(4), *c* = 14.964(7) Å, α = 92.53(4) $^\circ$ β = 93.83(2) $^\circ$ γ = 100.34(3) $^\circ$, *U* = 1401.0(10) Å³, *Z* = 4, *D_C* = 1.892 Mg/m³, space group P $\overline{1}$ (C_i^1 , No. 2), Mo-K α radiation ($\bar{\lambda}$ = 0.71073 Å), μ (Mo-K α) = 2.947 mm⁻¹, *F*(000) = 768. Three-dimensional, room temperature X-ray data were collected in the range 3.5 < 2 θ < 50 $^\circ$ on a Siemens P4 diffractometer by the omega scan method. Of the 5918 reflections measured, all of which were corrected for Lorentz and polarisation effects but not for absorption, 3966 independent reflections exceeded the significance level |*F*|/ σ (|*F*|) > 4.0 The structure was solved by direct methods and refined by full matrix least squares methods on F². Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2(1.5 for methyl groups) times U_{eq} of the carrier atom. Refinement converged at a final R= 0.0456 (wR2=0.1659 for all 4906 unique data, 307 parameters, mean and maximum δ/σ 0.000, 0.009, with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -1.082 and 0.945e Å⁻³. A weighting scheme w = 1/[σ ²(F_o²) + (0.0607*P)²+2.19*P] where P=(F_o²+ 2 * F_c²)/3 was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL¹ as implemented on the Viglen Pentium computer.

1. SHELXTL version, An integrated system for solving and refining crystal structures from diffraction data (Revision 5.1), Bruker AXS LTD

CIF file included in Supporting Information: “trial2”

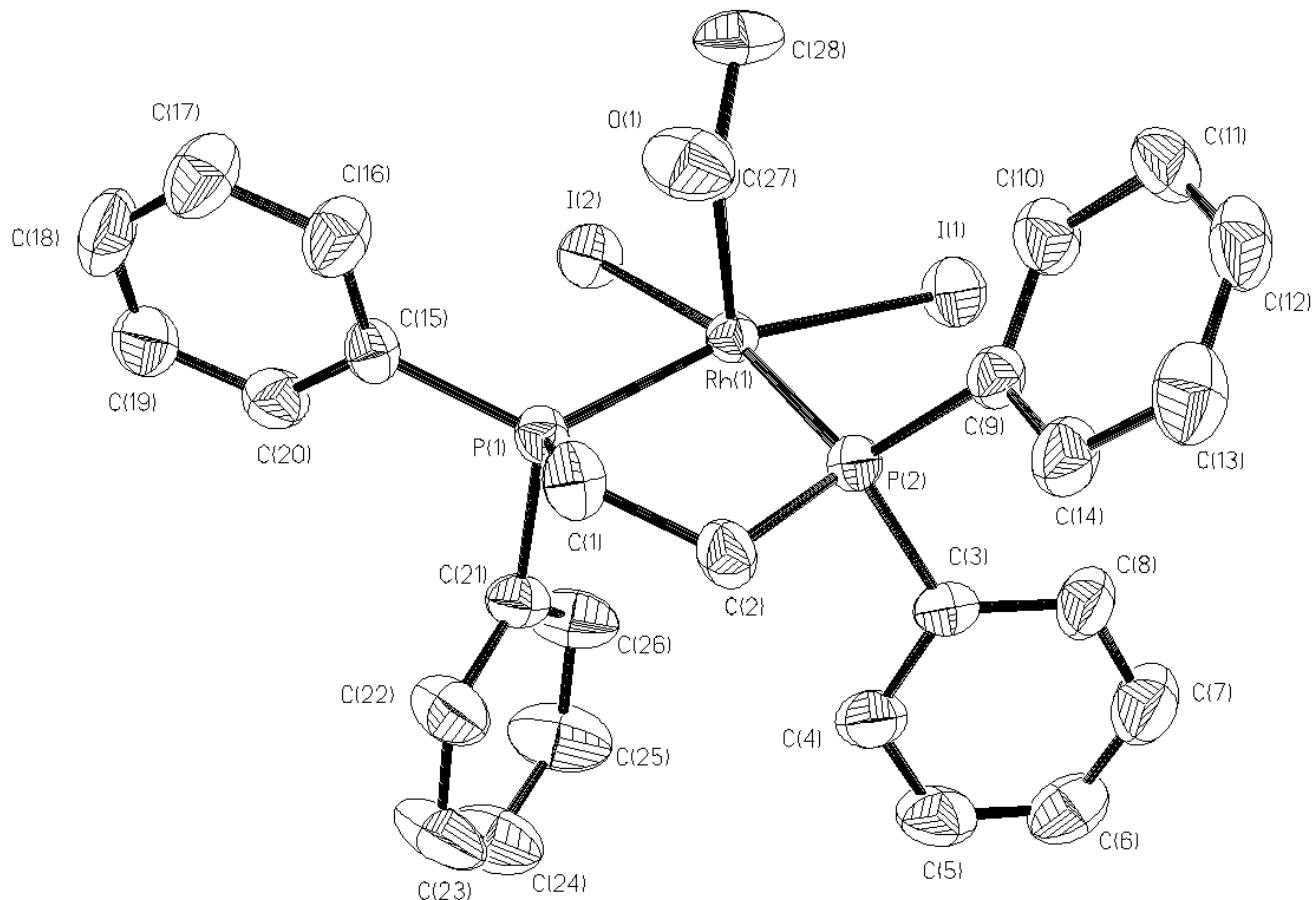


Figure S1. ORTEP plot for $[\text{Rh}(\text{dppe})\text{I}_2(\text{COMe})]$ **3b**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Crystallographic data for [Ir(CO)(dppms)I₂Et] **6**

Crystal data for C₂₈H₂₇I₂IrOP₂S; M = 919.50, crystallises from dichloromethane as yellow blocks; crystal dimensions 0.08 x 0.06 x 0.04mm. Monoclinic, $a = 10.2276(10)$, $b = 16.9486(17)$, $c = 17.2942(16)$ Å, $\beta = 102.196(2)$ °, $U = 2930.2(5)$ Å³, $Z = 4$, $D_C = 2.084$ g Mg/m³, space group P2₁/n (a non-standard setting of P2₁/c C_h No.14), Mo-K α radiation (= 0.71073 Å), $\mu(\text{Mo-K}\alpha) = 6.864$ mm⁻¹, $F(000) = 1728$. Data collected were measured on a Bruker Smart CCD area detector with Oxford Cryosystems low temperature system. Cell parameters were refined from the setting angles of 160 reflections (θ range 1.25 < 22.50). Reflections were measured from a hemisphere of data collected of frames each covering 0.3 degrees in omega. Of the 12552 reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by semi empirical methods based on symmetry -equivalent and repeated reflections(minimum and maximum transmission coefficients 0.7708 and 0.6097) 3711 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full matrix least squares methods on F². Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2(1.5 for methyl groups) times U_{eq} of the carrier atom. Refinement converged at a final R= 0.0405(wR₂=0.1074, for all 4226 data, 316 parameters, mean and maximum δ/σ 0.000, 0.000) with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -1.469 and 1.668e Å⁻³. A weighting scheme $w = 1/[\sigma^2(Fo^2) + (0.0474*P)^2 + 12.0906 * P]$ where $P=(Fo^2 + 2 * Fc^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL¹ as implemented on the Viglen 486dx computer.

1. SHELXTL version, An integrated system for solving and refining crystal structures from diffraction data (Revision 5.1), Bruker AXS LTD

CIF file included in Supporting Information: “iah1ta”

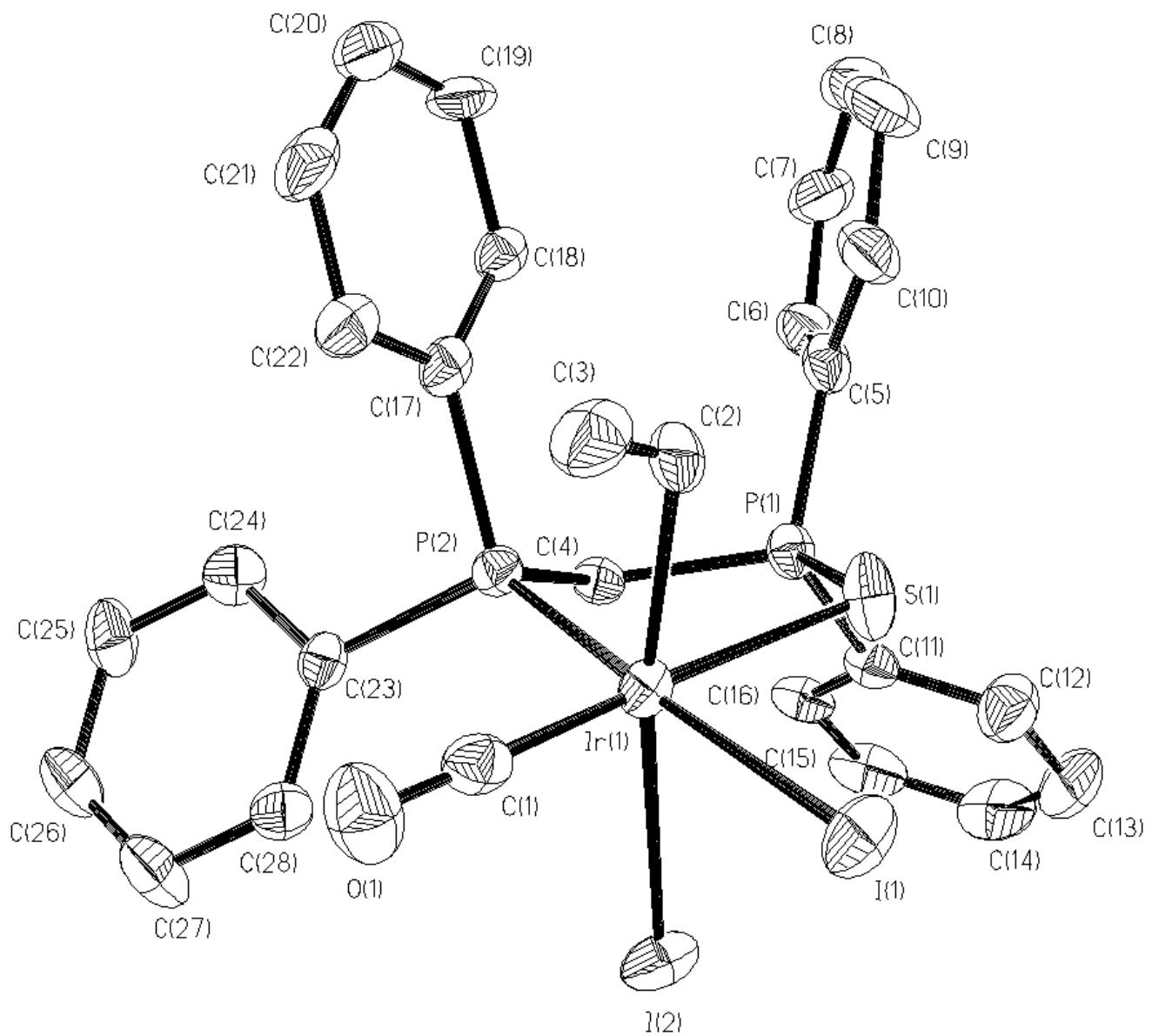


Figure S2. ORTEP plot for $[\text{Ir}(\text{CO})(\text{dppms})\text{I}_2\text{Et}]$ **6**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Crystallographic data for $\{[\text{Ir}(\text{CO})(\text{dppms})\text{IMe}]_2\}^{2+}[\text{CF}_3\text{SO}_3]_2 \cdot 2 \text{CH}_2\text{Cl}_2$ **7**

Crystal data for $\text{C}_{29}\text{H}_{27}\text{Cl}_2\text{F}_3\text{IrO}_4\text{P}_2\text{S}_2$; $M = 1012.57$, crystallises from dichloromethane as yellow blocks; crystal dimensions $0.30 \times 0.20 \times 0.17\text{mm}$. Monoclinic, $a = 10.7366(9)$, $b = 15.6551(13)$, $c = 20.1261(16) \text{\AA}$, $\beta = 94.248(2)^\circ$, $U = 3373.6(5) \text{\AA}^3$, $Z = 4$, $D_c = 1.994 \text{ Mg/m}^3$, space group $\text{P}2_1/\text{n}$ (a non-standard setting of $\text{P}2_1/\text{c}$ C_2^5 h' No.14), Mo-K α radiation ($\bar{\lambda} = 0.71073 \text{\AA}$), $\mu(\text{Mo-K}\alpha) = 5.301 \text{ mm}^{-1}$, $F(000) = 1944$. Data collected were measured on a Bruker Smart CCD area detector with Oxford Cryosystems low temperature system. Cell parameters were refined from the setting angles of 46 reflections (θ range $1.65 < 28.30$). Reflections were measured from a hemisphere of data collected of frames each covering 0.3 degrees in omega. Of the 21933 reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections (minimum and maximum transmission coefficients 0.2992 and 0.4660) 6617 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full matrix least squares methods on F^2 . Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. Refinement converged at a final $R = 0.0413$ ($wR_2 = 0.1098$, for all 8078 data, 397 parameters, mean and maximum δ/σ 0.000, 0.000) with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -4.864 and 2.981 e \AA^{-3} (the latter being 0.3 \AA from Ir1). A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0695*P)^2 + 0.00*P]$ where $P = (F_o^2 + 2 * F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL¹ as implemented on the Viglen Pentium computer.

1. SHELXTL version, An integrated system for solving and refining crystal structures from diffraction data (Revision 5.1), Bruker AXS LTD

CIF file included in Supporting Information: “iah46s”

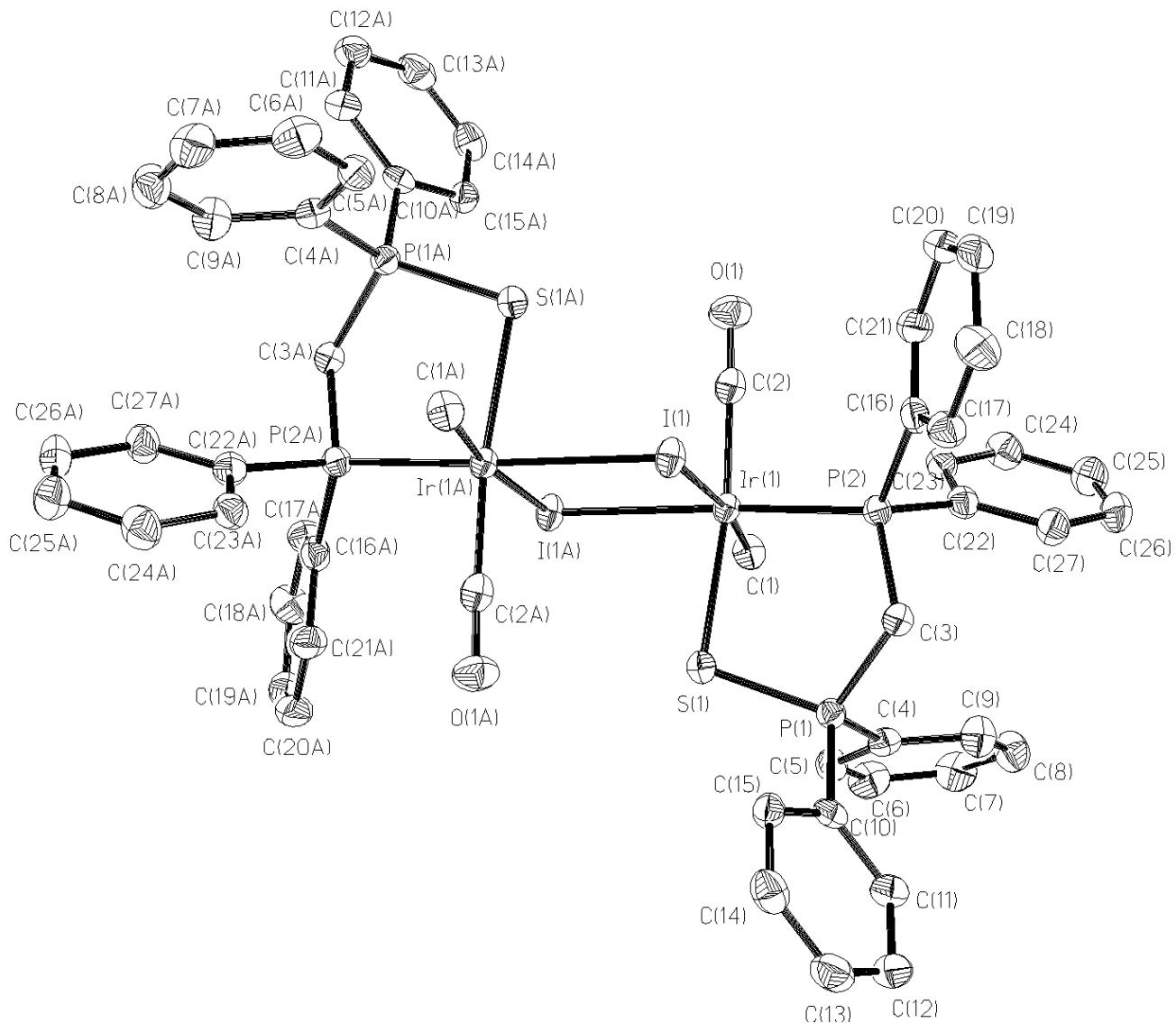


Figure S3. ORTEP plot for $\{[\text{Ir}(\text{CO})(\text{dppms})\text{IMe}]_2\}^{2+}$ 7. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms , trifltae counterions and CH_2Cl_2 solvent molecules are omitted for clarity.

Crystallographic data for [Rh(dppmo)(NCMe)I₂(COMe)] 3c-MeCN

Crystal data for C₂₉H₂₈I₂NO₂P₂Rh; M = 841.17, crystallises from dichloromethane as yellow blocks; crystal dimensions 0.48 x 0.32 x 0.21 mm. Monoclinic, $a = 10.096(2)$, $b = 14.489(3)$, $c = 20.967(4)$ Å, $\beta = 99.76(3)^\circ$ $U = 3022.7(10)$ Å³, $Z = 4$, $D_C = 1.848$ Mg/m³, space group P2₁/c (C_{2h}^5 , No.14), Mo-K α radiation ($\bar{\lambda} = 0.71073$ Å), $\mu(\text{Mo-K}\alpha) = 2.740$ mm⁻¹, F(000) = 1624. Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 50^\circ$ on a Siemens P4 diffractometer by the omega scan method. Of the 6824 reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections (minimum and maximum transmission coefficients 0.3530 and 0.5969), 2870 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full matrix least squares methods on F². Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. Refinement converged at a final R = 0.0740 (wR₂ = 0.1899, for all 5305 data, 335 parameters, mean and maximum δ / σ 0.000, 0.000) with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -1.312 and 1.471e Å⁻³. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0770 * P)^2 + 7.04 * P]$ where $P = (F_o^2 + 2 * F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL¹ as implemented on the Viglen pentium computer.

1. SHELXTL version, An integrated system for solving and refining crystal structures from diffraction data (Revision 5.1), Bruker AXS LTD

CIF file included in Supporting Information: “sarp2”

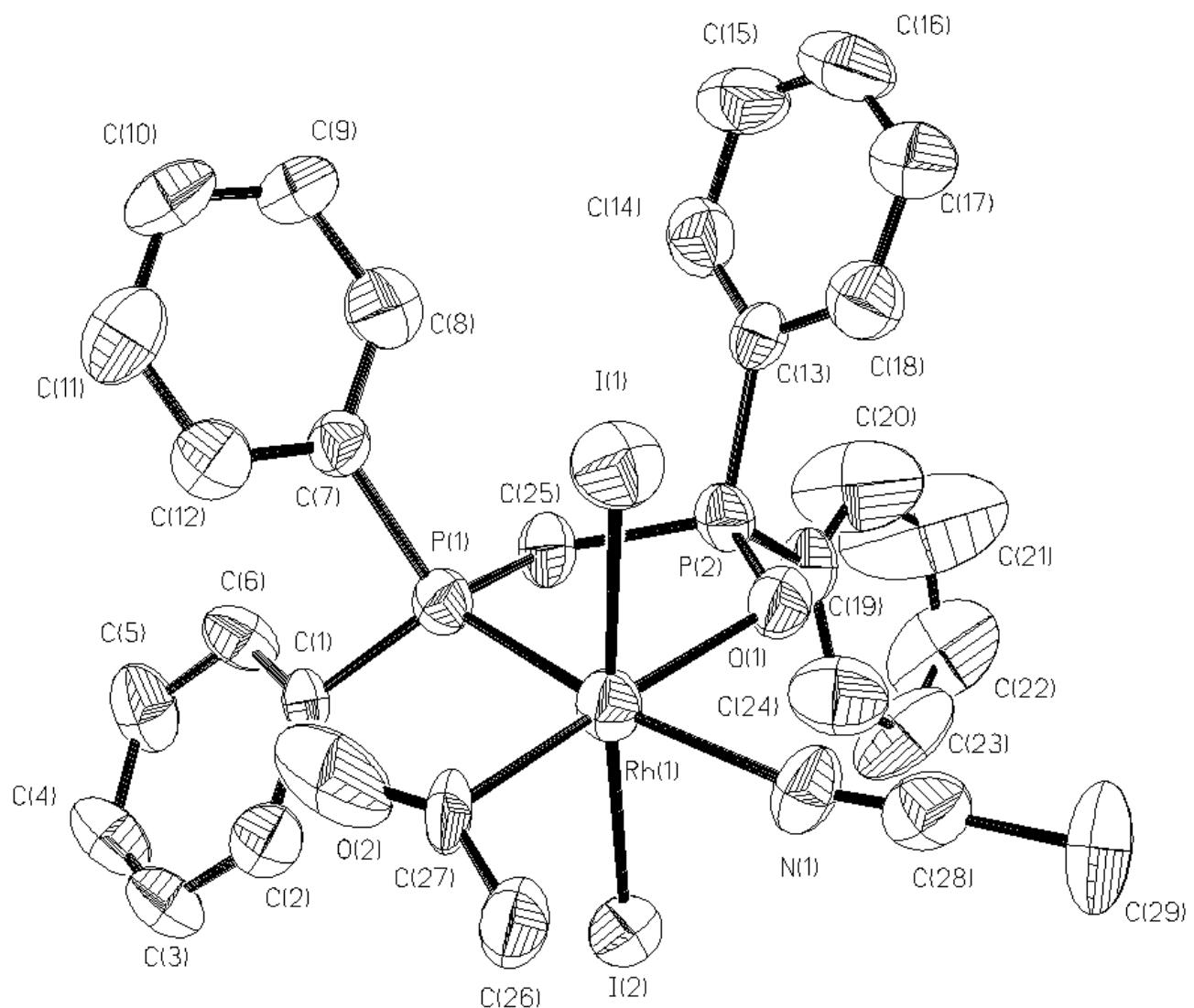


Figure S4. ORTEP plot for $[\text{Rh}(\text{dppmo})(\text{NCMe})\text{I}_2(\text{COMe})] \textbf{3c-MeCN}$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Ab initio structures

Cartesian coordinates (Å) and energies for *ab initio* optimized structures of stationary states (Gaussian94, MP2, LANL2DZ basis). Ligand abbreviations used in formulae as given in text.

[Rh(CO)(dhpms)I₂Me] (CO *trans* to S)

	x	y	z
Rh	0.211909	-0.429018	0.572540
I	2.540598	-0.016909	-0.725058
S	-0.486686	-1.886878	-1.339986
P	-1.906604	-0.936270	1.599823
C	0.933264	0.560220	1.961141
H	-2.091317	-2.217460	2.212480
H	-2.484896	-0.081672	2.583767
O	1.394048	1.191437	2.865890
P	-2.571538	-1.248170	-1.442386
C	-3.302671	-0.943654	0.277288
H	-2.797079	-0.077788	-2.198217
H	-3.385708	-2.250295	-2.028062
H	-4.045344	-1.726500	0.505902
H	-3.780953	0.048341	0.284460
C	1.142021	-2.229672	1.378697
H	2.015375	-1.951760	1.990398
H	0.385961	-2.766622	1.979842
H	1.459226	-2.822512	0.507370
I	-1.099846	1.946266	-0.353318

Energy = -347.98968183737 Hartrees

[Rh(CO)(dhpms)I₂Me] (CO *trans* to S)
migratory insertion TS

	x	y	z
Rh	0.120647	-0.548666	0.421588
I	2.384918	0.044859	-0.910124
S	-0.895285	-1.695288	-1.747576
P	-2.026930	-0.966404	1.425629
C	1.126228	-0.542081	2.025875
H	-2.389106	-2.295181	1.821036
H	-2.474338	-0.230152	2.562595
O	1.612674	-0.102140	3.048943
P	-2.799874	-0.680687	-1.601521
C	-3.434394	-0.556304	0.182753
H	-2.785932	0.646065	-2.089174
H	-3.847700	-1.317525	-2.314043
H	-4.282155	-1.248297	0.320456
H	-3.766251	0.477468	0.370382
C	1.338019	-2.324525	1.534747
H	2.436958	-2.338939	1.498287
H	0.909532	-2.825735	2.416639
H	0.932036	-2.755123	0.599587
I	-0.696543	2.026140	0.147682

Energy = -347.95194219675 Hartrees
Imaginary frequency -350.4431 cm⁻¹

[Rh(dhpms)I₂(COMe)]

	x	y	z
Rh	0.192402	-0.011925	-0.190703
I	-1.584253	2.003538	-0.241274
I	-1.701366	-1.931073	-0.154150
S	1.865005	1.787246	-0.529610
P	1.754177	-1.803233	-0.528398
C	0.607385	-0.082047	1.779105
H	1.916398	-2.744729	0.526750
H	1.669997	-2.670644	-1.656754
O	1.772186	-0.393241	2.143366
P	3.672984	0.612864	-0.039524
C	3.552403	-1.133748	-0.731232
H	3.961747	0.491909	1.337923
H	4.843505	1.168244	-0.614618
H	3.772301	-1.069290	-1.811498
H	4.293723	-1.792718	-0.247543
C	-0.510807	0.298905	2.764807
H	-0.565193	1.401054	2.795546
H	-0.251999	-0.101271	3.761677
H	-1.479596	-0.079690	2.417219

Energy = -347.98498242981 Hartrees

[Rh(CO)(dhpms)I₂Me] (CO *trans* to P)

	x	y	z
Rh	-0.170900	-0.601940	0.383503
I	-2.589048	0.106633	-0.588409
S	1.967524	-1.655995	1.198422
P	0.589718	-0.952350	-1.861613
C	-0.782767	-0.214088	2.118503
H	0.473064	-2.249641	-2.451795
H	0.119252	-0.117923	-2.910946
O	-1.162739	0.043265	3.218517
P	3.295921	-0.733887	-0.269332
C	2.490717	-0.648101	-1.977322
H	3.744980	0.564450	0.053748
H	4.461896	-1.522438	-0.438858
H	2.961547	-1.395865	-2.637902
H	2.648641	0.363405	-2.384858
C	-1.018154	-2.604706	0.502559
H	-1.272151	-2.926105	-0.522146
H	-0.247746	-3.253096	0.953080
H	-1.932079	-2.573956	1.116614
I	0.931147	2.014937	0.119433

Energy = -347.99277635111 Hartrees

[Rh(CO)(dhpms)I₂Me] (CO *trans* to P)
migratory insertion TS

	x	y	z
Rh	-0.052813	-0.608685	0.239705
I	-2.473927	0.028633	-0.747595
S	2.178798	-1.366068	1.160730
P	0.841136	-0.664712	-2.115191
C	-0.875341	-1.013820	1.913149
H	0.618007	-1.640748	-3.141686
H	0.664716	0.522621	-2.886884
O	-1.294853	-0.832127	3.038245
P	3.390668	-0.348913	-0.329294
C	2.776600	-0.752077	-2.064758
H	3.390226	1.058718	-0.192448
H	4.746452	-0.758231	-0.285985
H	3.085172	-1.790353	-2.277753
H	3.246382	-0.078810	-2.801931
C	-0.995965	-2.676913	1.098452
H	-0.414088	-3.281788	1.811001
H	-2.085455	-2.809465	1.169020
H	-0.663159	-2.877959	0.061998
I	0.518787	2.035937	0.480925

Energy = -347.95086248372 Hartrees
Imaginary frequency -319.4647 cm⁻¹

[Rh(CO)(dhpmo)I₂Me] (CO *trans* to O)

	x	y	z
Rh	0.184842	-0.571958	0.453291
I	2.471377	0.183713	-0.709339
O	-0.443829	-1.426124	-1.426486
P	-1.999308	-1.358143	1.201892
C	0.859482	0.038329	2.035250
H	-2.192616	-2.726516	1.579156
H	-2.795957	-0.690353	2.175168
O	1.290438	0.429424	3.081632
P	-2.009236	-1.134277	-1.876316
C	-3.133452	-1.237987	-0.355442
H	-2.250789	0.097420	-2.527860
H	-2.438407	-2.150822	-2.767302
H	-3.793357	-2.118240	-0.432741
H	-3.732040	-0.317106	-0.277642
C	1.100767	-2.497542	0.776208
H	2.147742	-2.389332	1.096473
H	0.509105	-3.053571	1.526434
H	1.025621	-2.932625	-0.233645
I	-1.233692	1.883502	-0.015133

Energy = -413.00989638200 Hartrees

[Rh(CO)(dhpmo)I₂Me] (CO *trans* to O)
migratory insertion TS

	x	y	z
Rh	0.078714	0.679705	-0.171751
I	2.330403	-0.405364	0.794375
O	-0.842351	0.882256	1.963309
P	-2.138478	1.460812	-0.776374
C	1.056544	1.357636	-1.631620
H	-2.504517	2.841887	-0.662053
H	-2.786269	1.123137	-2.000587
O	1.517878	1.376726	-2.756969
P	-2.361122	0.258229	2.066975
C	-3.347702	0.660570	0.494443
H	-2.441673	-1.146252	2.244427
H	-3.113023	0.809650	3.139685
H	-4.184408	1.339249	0.730049
H	-3.737022	-0.271884	0.055438
C	1.270268	2.742825	-0.447727
H	2.369180	2.762410	-0.412008
H	0.824737	3.578675	-1.009037
H	0.874346	2.706522	0.588334
I	-0.832824	-1.797538	-0.765049

Energy = -412.97020052030 Hartrees
Imaginary frequency -330.6889 cm⁻¹

[Rh(dhpmo)I₂(COMe)]

	x	y	z
Rh	-0.262308	0.002375	-0.241082
I	1.503672	-1.989366	-0.253916
I	1.593060	1.908890	-0.125484
O	-1.812142	-1.473348	-0.649726
P	-1.973911	1.709140	-0.484806
C	-0.682452	-0.060493	1.712243
H	-2.156733	2.659393	0.559232
H	-2.115622	2.547061	-1.631754
O	-1.906465	0.026695	2.027102
P	-3.366722	-1.053952	-0.245973
C	-3.680898	0.797207	-0.459927
H	-4.279953	-1.713938	-1.107135
H	-3.775368	-1.401076	1.063631
H	-4.301127	1.166491	0.373248
H	-4.209252	0.962871	-1.414404
C	0.421470	-0.278946	2.756807
H	0.572676	-1.369626	2.846146
H	0.084798	0.136194	3.723798
H	1.367308	0.169799	2.432084

Energy = -412.99386264507 Hartrees

[Rh(CO)(dhpe)I₂Me]

	x	y	z
Rh	0.024421	-0.442681	0.514794
I	2.490059	-0.005806	-0.532758
P	-0.533202	-1.420333	-1.590330
P	-2.197647	-1.037033	1.162352
C	0.570008	0.370061	2.133373
H	-2.396985	-2.245287	1.905523
H	-3.025125	-0.121974	1.873870
O	0.930419	0.887852	3.146573
C	-2.291045	-2.186430	-1.449122
C	-3.172117	-1.373243	-0.450564
H	-2.157522	-3.224061	-1.089794
H	-2.771677	-2.219231	-2.443123
H	-3.432403	-0.385983	-0.867152
H	-4.097867	-1.929491	-0.218533
C	0.804599	-2.374389	1.192043
H	1.054019	-2.982472	0.305185
H	0.045086	-2.871271	1.823647
H	1.721638	-2.176428	1.768577
H	0.246631	-2.517759	-2.058812
H	-0.588707	-0.574400	-2.730045
I	-1.124876	1.973932	-0.386909

Energy = -377.20051530578 Hartrees

[Rh(CO)(dhpe)I₂Me] migratory insertion TS

	x	y	z
Rh	-0.08378	-0.50038	0.40002
I	2.38307	-0.21714	-0.67816
P	-0.93643	-1.40219	-1.77161
P	-2.37149	-0.67599	1.08599
C	0.66703	-0.32926	2.15354
H	-2.80335	-1.83143	1.81826
H	-2.99651	0.36513	1.83146
O	1.01228	0.23899	3.17305
C	-2.80769	-1.79074	-1.51645
C	-3.43940	-0.78824	-0.49928
H	-2.87494	-2.82510	-1.12881
H	-3.35173	-1.74499	-2.47636
H	-3.47345	0.23079	-0.92265
H	-4.46520	-1.10322	-0.23646
C	0.87024	-2.12935	1.94417
H	1.96004	-2.18945	2.08012
H	0.28715	-2.50934	2.79748
H	0.59517	-2.66473	1.01460
H	-0.50218	-2.59118	-2.44116
H	-0.96971	-0.49920	-2.87739
I	-0.64450	2.09197	-0.17188

Energy = -377.15638125108 Hartrees

Imaginary frequency -347.3916 cm⁻¹

[Rh(dhpe)I₂(COMe)]

	x	y	z
Rh	-0.316202	0.001013	-0.138114
I	1.509952	-1.978457	-0.292785
I	1.457679	2.036107	-0.206902
P	-2.033618	-1.639688	-0.407975
P	-2.066421	1.617070	-0.378652
C	-0.648432	-0.049500	1.870372
H	-2.465551	2.336701	0.785167
H	-1.988335	2.659291	-1.346688
O	-1.811324	0.003025	2.326396
C	-3.713345	-0.735692	-0.207288
C	-3.659949	0.668633	-0.887321
H	-3.883684	-0.633667	0.877710
H	-4.526948	-1.339335	-0.647425
H	-3.625762	0.563480	-1.988316
H	-4.554971	1.257809	-0.619442
C	0.617658	-0.191636	2.744436
H	0.782440	-1.272599	2.901288
H	0.420406	0.306260	3.711248
H	1.496643	0.227982	2.246427
H	-2.139475	-2.728738	0.505608
H	-2.154525	-2.313939	-1.659963

Energy = -377.18771059488 Hartrees

[Rh(CO)(PH₃)₂I₂Me]

	x	y	z
Rh	0.000000	0.785563	0.000000
I	1.978184	-1.231241	0.000000
I	-2.134981	-0.929870	0.000000
P	-0.093207	0.604603	2.372193
P	-0.093207	0.604603	-2.372193
C	1.373747	2.070456	0.000000
H	-0.136360	-0.719231	2.877070
H	0.993348	1.166444	3.103161
H	-1.210044	1.217385	3.011316
H	-0.136360	-0.719231	-2.877070
H	0.993348	1.166444	-3.103161
H	-1.210044	1.217385	-3.011316
C	-1.511725	2.376611	0.000000
H	-2.130255	2.241005	0.902052
H	-1.015546	3.362976	0.000000
H	-2.130255	2.241005	-0.902052
O	2.239563	2.899231	0.000000

Energy = -300.12437692224 Hartrees

[Rh(CO)(PH₃)₂I₂Me] migratory insertion TS

	x	y	z
Rh	0.000000	0.593878	0.000000
I	2.372934	-0.904747	0.000000
I	-2.182823	-1.020415	0.000000
P	0.033984	0.306159	2.367173
P	0.033984	0.306159	-2.367173
C	-0.906560	2.274804	0.000000
H	1.117692	0.914206	3.065361
H	-1.082153	0.786921	3.112978
H	0.117904	-1.039883	2.804209
H	1.117692	0.914206	-3.065361
H	-1.082153	0.786921	-3.112978
H	0.117904	-1.039883	-2.804209
C	0.880448	2.902750	0.000000
H	0.837912	3.509927	-0.917235
H	1.765817	2.244850	0.000000
H	0.837912	3.509927	0.917235
O	-1.835911	3.058978	0.000000

Energy = -300.08556171570 Hartrees

Imaginary frequency -361.2855 cm⁻¹

[Rh(PH₃)₂I₂(COMe)]

	x	y	z
Rh	0.000000	0.140292	0.000000
C	-0.240367	-1.895665	0.000000
O	-1.384893	-2.377600	0.000000
I	0.014207	0.333259	2.696442
I	0.014207	0.333259	-2.696442
P	-2.381118	0.445690	0.000000
P	2.409653	0.289790	0.000000
C	1.061133	-2.730449	0.000000
H	0.795189	-3.801783	0.000000
H	1.644522	-2.488239	-0.902667
H	1.644522	-2.488239	0.902667
H	-3.103032	-0.080745	1.104698
H	-2.813068	1.803818	0.000000
H	-3.103032	-0.080745	-1.104698
H	3.168581	-0.206289	-1.100165
H	2.818311	1.655215	0.000000
H	3.168581	-0.206289	1.100165

Energy = -300.12015277349 Hartrees