Electronic Supplementary Information for Dalton Transactions

Supporting Information

Steric *vs*. electronic anomaly observed from iodomethane oxidative addition to tertiary phosphine modified rhodium(I) acetylacetonato complexes following progressive phenyl replacement by cyclohexyl [PR_3 = PPh_3; PPh_2Cy, $PPhCy_2$ and PCy_3]

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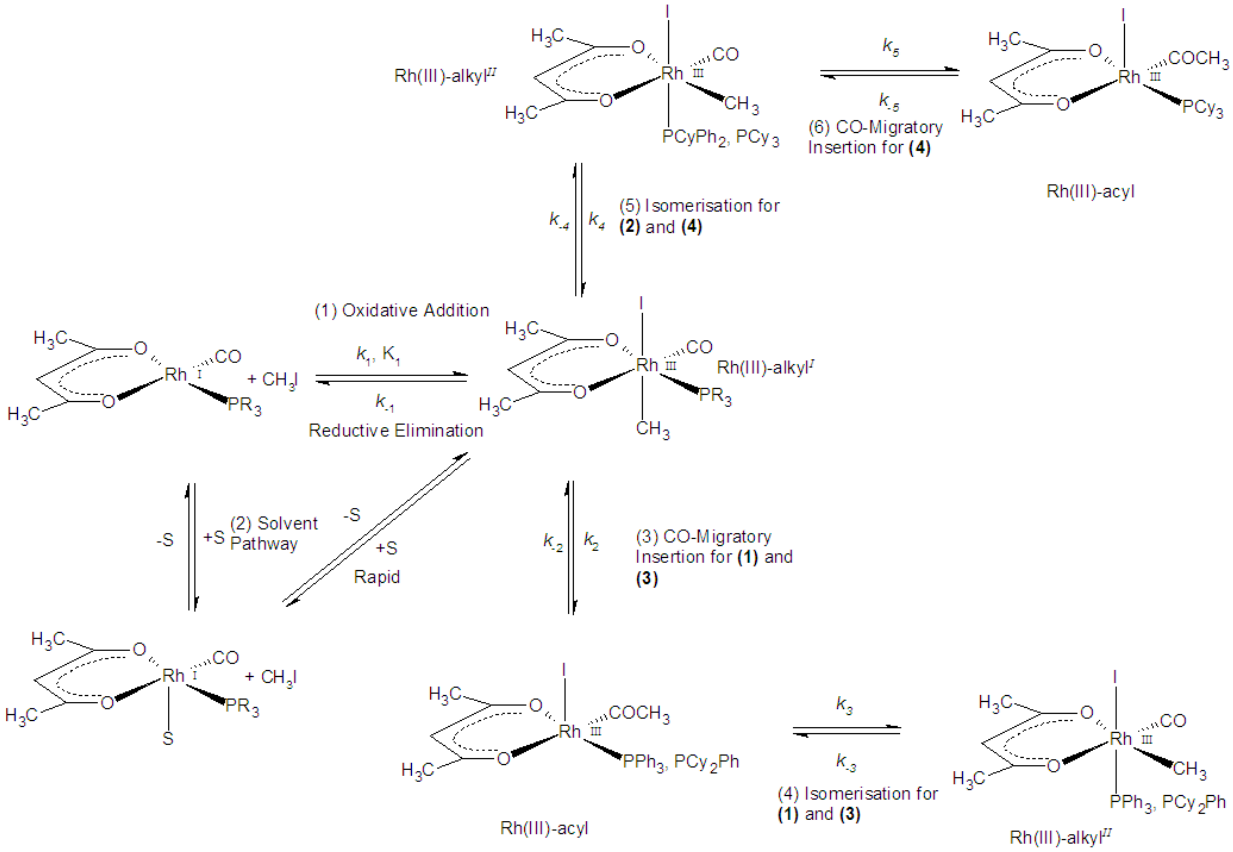
Contents:

S. Table 1: General X-ray crystallographic data and refinement parameters for [Rh(acac)(CO)(PR_3)].

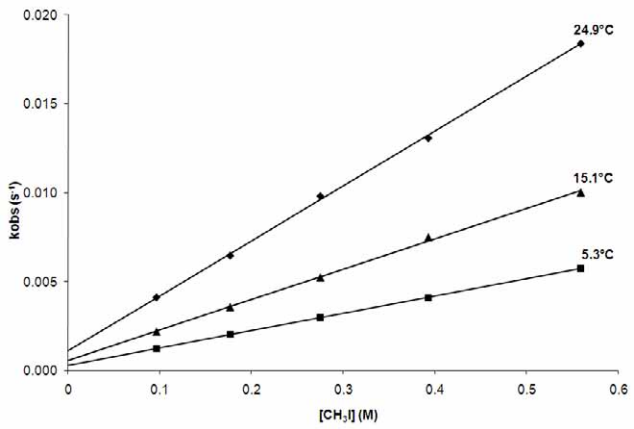
Compound	(**1**)	(**2**)	(**3**)	(**4**)
Effective cone angle /θ_E	149.3	151.2	163.5	169.5
Empirical Formula	$C_{24}H_{22}O_3PRh$	$C_{24}H_{28}O_3PRh$	$C_{24}H_{34}O_3PRh$	$C_{24}H_{40}O_3PRh$
Formula weight	492.30	498.34	504.39	510.44
Temperature /K	100(2)	100(2)	100(2)	100(2)
Wavelength /Å	0.71069	0.71073	0.71069	0.71073
Crystal System	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space Group	$P\bar{1}$	$P2_12_12_1$	$P2_1/n$	$P2_1/n$
Unit Cell Dimensions				
a /Å	8.856(5)	9.4682(5)	10.076(5)	10.3418(5)
b /Å	10.314(5)	12.7534(6)	12.990(5)	13.0644(6)
c /Å	12.844(5)	18.4602(9)	17.937(5)	17.9301(8)
α /°	71.298(5)	90	90	90
β /°	70.143(5)	90	90.576(5)	90.612(2)
γ /°	82.775(5)	90	90	90
Volume /Å^3	1045.0(9)	2229.10(19)	2347.6(16)	2422.39(19)
Z	2	4	4	4
Density$_{calc.}$ /g.cm^{-1}	1.565	1.485	1.427	1.400
μ /mm^{-1}	0.916	0.860	0.817	0.792
F(000)	500	1024	1048	1072
Crystal Colour	Yellow	Yellow	Yellow	Yellow
Crystal Morphology	Plate	Plate	Cuboid	Cuboid
Crystal Size /mm	0.20x0.11x0.04	0.42x0.27x0.06	0.18x0.09x0.05	0.22x0.18x0.17
Theta Range /°	2.45 - 27.00	2.21 - 27.00	2.31 - 26.75	2.26 - 27.00
Completeness	99.7 %	100.0 %	98.0 %	100.0 %
Index Ranges	h = -11 to 11	h = -11 to 12	h = -12 to 9	h = -13 to 10
	k = -13 to 13	k = -16 to 16	k = -16 to 16	k = -16 to 16
	l = -16 to 16	l = -23 to 12	l = -22 to 22	l = -22 to 22
Reflections Collected	23869	12624	25476	27734
Independent Reflections	4564	4825	4885	5288
R_{int}	0.0400	0.0233	0.0370	0.0304
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Semi-empirical from equivalents	Full-matrix least-squares on F^2
Data / restraints / parameters	4564 / 0 / 264	4825 / 3 / 264	4885 / 0 / 264	5288 / 0 / 264
Goodness-of-fit on F^2	1.041	1.061	1.049	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0243, wR2 = 0.0541	R1 = 0.0226, wR2 = 0.0567	R1 = 0.0273, wR2 = 0.0656	R1 = 0.0202, wR2 = 0.0503
R indices (all data)	R1 = 0.0287, wR2 = 0.0562	R1 = 0.0239, wR2 = 0.0573	R1 = 0.0355, wR2 = 0.0698	R1 = 0.0236, wR2 = 0.0523
ρ_{max} and ρ_{min} /e.Å^{-3}	0.546 and -0.429	0.543 and -0.332	0.469 and -0.315	0.454 and -0.297

S. Table 2: ^{31}P NMR spectral parameters of rhodium acetylacetonato phosphine complexes.

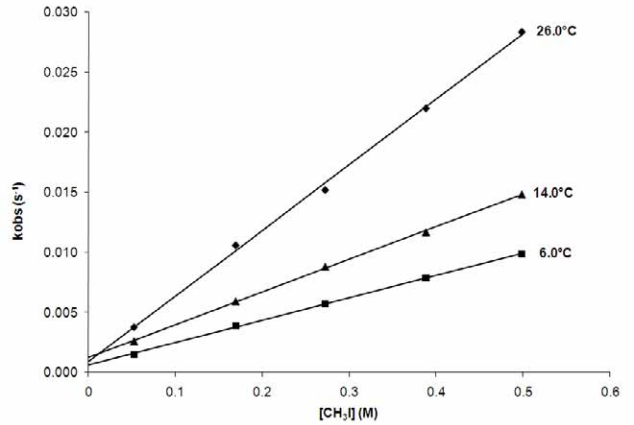
Complex	Isomer	ν(CO) (cm^{-1})	δ ^{31}P NMR (ppm)	$^{1}J_{Rh-P}$ (Hz)
[Rh(acac)(CO)(PPh_3)]	Rh(I)	1977.6	48.6	176.9
(1)	Rh(III)-alkyl^{I}	2071.5	32.8	124.6
	Rh(III)-acyl	1720.5	37.7	153.3
	Rh(III)-alkyl^{II}	-	29.5	118.3
[Rh(acac)(CO)($PCyPh_2$)]	Rh(I)	1959.3	53.3	171.3
(2)	Rh(III)-alkyl^{I}	2067.0	35.8	123.2
	Rh(III)-alkyl^{II}	-	46.3	118.5
[Rh(acac)(CO)(PCy_2Ph)]	Rh(I)	1948.8	58.8	168.3
(3)	Rh(III)-alkyl^{I}	2052.3	43.0	122.1
	Rh(III)-acyl	-	38.1	146.3
	Rh(III)-alkyl^{II}	-	41.7	117.9
[Rh(acac)(CO)(PCy_3)]	Rh(I)	1945.3	59.3	164.3
(4)	Rh(III)-alkyl^{I}	2052.3	50.2	118.1
	Rh(III)-alkyl^{II}	-	45.0	116.4
	Rh(III)-acyl	1720.5	40.2	144.4



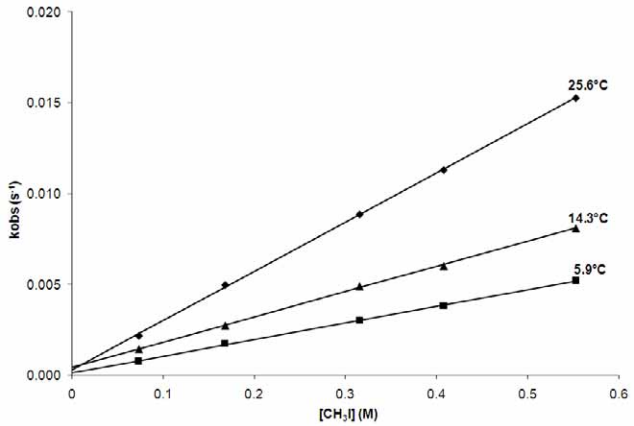
S. Figure 1: General reaction pathway for the reaction of [Rh(acac)(CO)(PR_3)] complexes with iodomethane (CH_3I).



S. Figure 2: Temperature and $[CH_3I]$ dependence of the pseudo-first order rate constant for the formation of $[Rh(acac)I(CH_3)(CO)(PPh_3)]$ in dichloromethane, UV/vis; (λ = 322 nm) $[Rh(acac)(CO)(PPh_3)] = 1.01 \times 10^{-4}$ M.



S. Figure 3: Temperature and $[CH_3I]$ dependence of the pseudo-first order rate constant for the formation of $[Rh(acac)I(CH_3)(CO)(PCyPh_2)]$ in dichloromethane, UV/vis; (λ = 315 nm) $[Rh(acac)(CO)(PCyPh_2)] = 9.61 \times 10^{-5}$ M.



S. Figure 4: Temperature and $[CH_3I]$ dependence of the pseudo-first order rate constant for the formation of $[Rh(acac)I(CH_3)(CO)(PCy_3)]$ in dichloromethane, UV/vis; (λ = 322 nm) $[Rh(acac)(CO)(PCy_3)] = 9.38 \times 10^{-5}$ M.