

Supplementary Material

Kinetic Data

Table S1. Observed pseudo first order rate constants (k_{obs}) and calculated second order rate constants (k_1) for oxidative addition of MeI to $[\text{Rh}(\text{C}_5\text{H}_4(\text{CH}_2)_2\text{PET}_2)(\text{CO})]$ in CH_2Cl_2 .

$T / ^\circ\text{C}$	$[\text{MeI}] / \text{mol dm}^{-3}$	$10^3 k_{\text{obs}} / \text{s}^{-1}$	$10^2 k_1 / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
11	0.08	2.62	3.28
16	0.08	3.57	4.46
16	0.16	7.79	4.87
16	0.24	10.6	4.42
16	0.32	15.3	4.78
21	0.08	4.88	6.10
25	0.08	6.24	7.80
29	0.08	8.11	10.1

Table S2. Observed pseudo first order rate constants (k_{obs}) and calculated second order rate constants (k_1) for oxidative addition of MeI to $[\text{Rh}(\text{C}_5\text{Me}_4(\text{CH}_2)_2\text{PPh}_2)(\text{CO})]$ in CH_2Cl_2 .

$T / ^\circ\text{C}$	$[\text{MeI}] / \text{mol dm}^{-3}$	$10^2 k_{\text{obs}} / \text{s}^{-1}$	$k_1 / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
10	0.08	7.91	0.989
16	0.08	8.55	1.07
21	0.08	14.0	1.75
25	0.08	17.8	2.23
29	0.08	20.4	2.54

Table S3. Rate constants (k_2) for methyl migration in complexes $[\text{Rh}(\text{C}_5\text{R}_4(\text{CH}_2)_2\text{PR}'_2)(\text{CO})\text{Me}]^+\text{T}^-$ (measured in CH_2Cl_2 containing 2.0 mol dm^{-3} MeI).

T/°C	$10^3 k_2 / \text{s}^{-1}$		
	R = H, R' = Et	R = Me, R' = Ph	R = Me, R' = Et
11	3.38	3.75	1.34
16	6.25	7.36	2.51
20		11.0	4.11
21	9.87		
25	14.7	17.5	6.76
29		27.1	10.7
30	21.1		

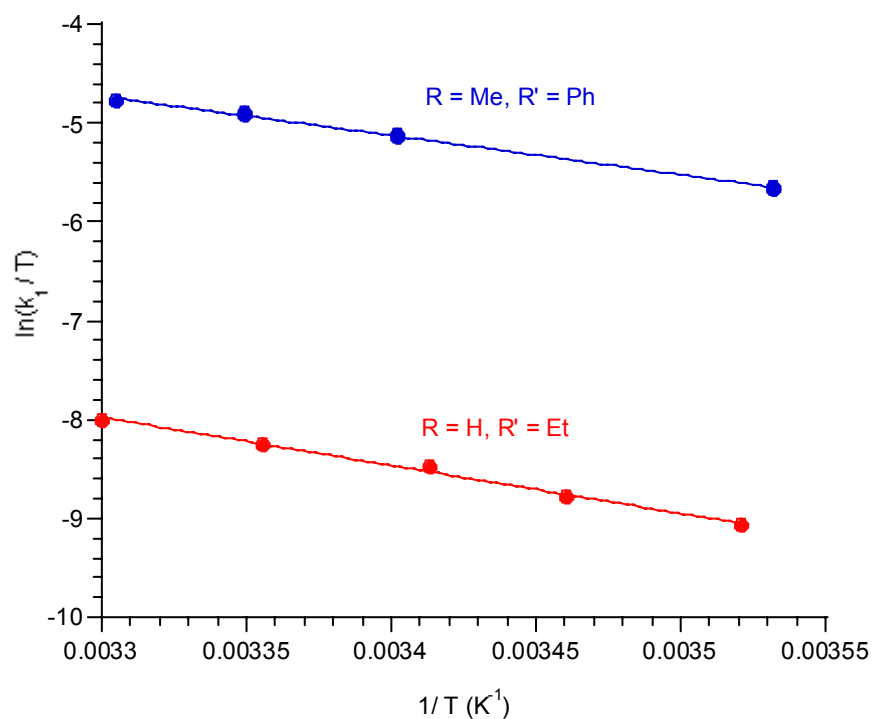


Figure S1. Eyring plots for oxidative addition of MeI to $[\text{Rh}(\text{C}_5\text{R}_4(\text{CH}_2)_2\text{PR}'_2)(\text{CO})]$.

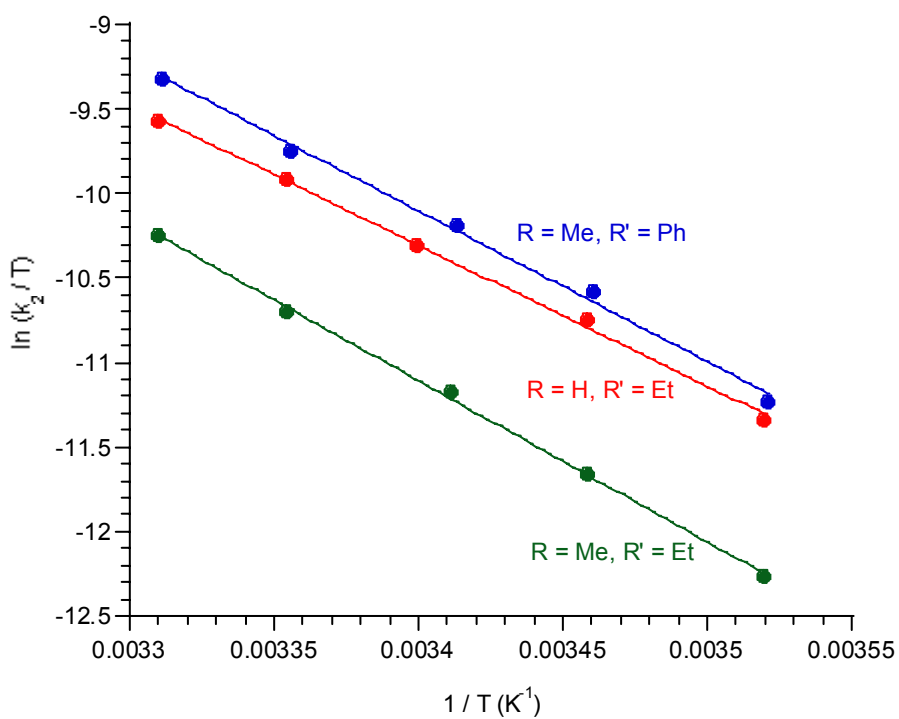


Figure S2. Eyring plots for methyl migration in $[\text{Rh}(\text{C}_5\text{R}_4(\text{CH}_2)_2\text{PR}'_2)(\text{CO})\text{Me}]^+\text{T}^-$.

Crystal Structures

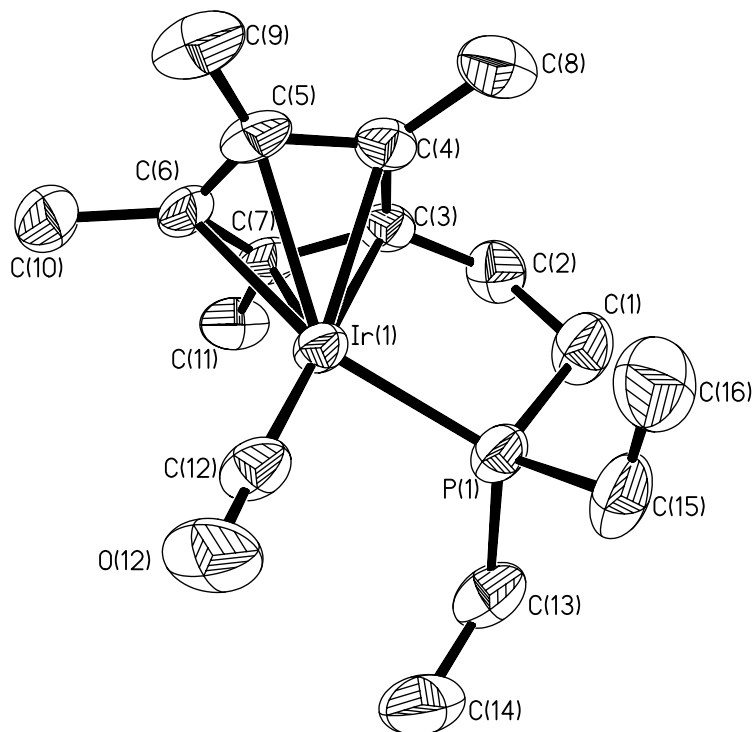


Figure S3 Molecular structure and numbering scheme for [Ir(Cp'(CH₂)₂PEt₂)CO]

