Migration of Aryl and Methyl onto Carbonyl in Iodorhodium(III) Complexes

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The complexes $[(C_5Me_5)RhR(CO)I]$ [R = Me, (**1a**); Ph, (**1b**); p-MeC_6H_4, (**1c**); p-ClC_6H_4, (**1d**); p-$OHCC_6H_4$ (**1e**); p-NCC_6H_4, (**1f**) or p-$O_2NC_6H_4$, (**1g**)] were synthesised by the route $[(C_5Me_5)RhMe_2(Me_2SO)] + RCHO \longrightarrow [(C_5Me_5)RhR(CO)Me]$; $[(C_5Me_5)RhR(CO)Me] + I_2 \longrightarrow [(C_5Me_5)RhR(CO)I]$. The migration reaction, $[(C_5Me_5)RhR(CO)I]$ (**1**) + $PPh_3 \longrightarrow [(C_5Me_5)Rh(COR)(PPh_3)I]$ (**2**), proceeded easily and essentially quantitatively for (**1a**)—(**1d**) in a variety of solvents; in a side-reaction, (**1e**)—(**1g**) gave the substitution products $[(C_5Me_5)RhR(PPh_3)I]$ (**3e**)—(**3g**). The reactions of complexes (**1a**)—(**1g**) with PPh_3 in toluene obeyed second-order kinetics, rate = $k_3[(\mathbf{1})][PPh_3]$, implying a direct bimolecular attack by the triphenylphosphine on the metal complex. A Hammett plot of $k_{obs.}$ for the reaction of (**1b**)—(**1g**) to (**2b**)—(**2g**) against σ gave a good linear relationship ($\rho = -2.9$) indicating that migration is favoured by electron-releasing substituents, R = p-MeC_6H_4 > Ph > p-ClC_6H_4 > p-$OHCC_6H_4$ > p-NCC_6H_4 ≈ p-$O_2NC_6H_4$. Values of $\Delta G^‡$, $\Delta H^‡$, and $\Delta S^‡$ for the reactions of complexes (**1a**)—(**1d**) with PPh_3 were determined over the temperature range 286—343 K; $\Delta S^‡$ was smaller for (**1b**) than for the others, leading to the phenyl [in (**1b**)] migrating faster than methyl [in (**1a**)]. There were only small rate differences for the reactions of (**1a**) and (**1b**) between toluene, tetrahydrofuran, and dichloromethane, but they proceeded significantly faster in nitromethane or acetonitrile; for (**1b**) the migration in these solvents showed a first-order (unimolecular) as well as a second-order (bimolecular) path. Both the second-order rate constant, k_3, and the first-order rate constants, k_1, were several orders of magnitude larger than for any previously measured *unpromoted* migration reaction.

The migration of a co-ordinated organic group R onto a co-ordinated carbonyl of a metal promoted by an entering ligand (nucleophile)[1] has been extensively investigated for systems such as $[RMn(CO)_5]$,[2] $[(cp)FeR(CO)_2]$ (cp = η-C_5H_5),[3] or $[(cp)MoR(CO)_3]$.[4]

For d^6 metal systems,[3c] in *more polar* solvents, reactions generally proceed *via* two consecutive equilibria (1), the first,

$$RM(CO) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(\mathbf{A})}{M(COR)} \underset{k_{-2}}{\overset{+L,\,k_2}{\rightleftharpoons}} \underset{(\mathbf{B})}{LM(COR)} \qquad (1)$$

rate-determining step (k_1) forms (**A**), which may be either co-ordinatively unsaturated or stabilised by a solvent molecule. The second step (k_2), in which (**A**) is captured by the ligand, L, is fast. Assuming a steady-state concentration of (**A**) and that the overall reaction to (**B**) proceeds to completion, the overall rate constant, $k_{obs.}$, is given by $k_1k_2[L]/(k_{-1} + k_2[L])$.

In very *non-polar* solvents, relatively slow second-order kinetics have been observed, implying a direct bimolecular reaction of the complex with the incoming ligand to give the acyl in one step (2).[1b,2a,3a]

$$RM(CO) + L \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} LM(COR) \qquad (2)$$

Mechanisms (1) and (2) often occur concurrently, and for example in the reaction of $[MeMn(CO)_5]$ with L, first, second, parallel first and second order, and saturation [$k_2 \approx k_{-1}$ in (1)] kinetics have been observed, depending on the nucleophile and the solvent.[2a]

There have been numerous qualitative studies, but surprisingly few detailed rate measurements on platinum metal complexes, especially of Rh, which are most commonly used in carbonylation reactions. Migration rates and equilibria between five-co-ordinate acyls of Rh^{III} (ref. 5) or Ir^{III} (ref. 6) and the corresponding six-co-ordinate alkyl (or aryl) complexes, equation (3), and the analogous equilibria (4) between mono-nuclear platinum(II)[7] alkyl carbonyl complexes and dinuclear halogeno-bridged acyls have been examined.

$$[L_2M(COR)X_2] \rightleftharpoons [L_2MR(CO)X_2] \qquad (3)$$

$$2[LPtR(CO)X] \rightleftharpoons [L_2Pt_2(COR)_2(\mu\text{-}X)_2] \qquad (4)$$

Detailed measurements of the reactions of Ph_3As with $[PtEt(CO)(AsPh_3)Cl]$ and with $[PtMe(CO)(PPh_3)I]$,[8] and of the very complex reactions of CO with $[PtRL_2(X)]$ and with some analogues of Pd and Ni,[9] have been made. More recently Mawby and co-workers[10] studied the simpler reaction of t-butyl isocyanide (L) with $[(PMe_2Ph)_2RuR_2(CO)_2]$ to give $[(PMe_2Ph)_2RuR(CO)(COR)L]$ (R = phenyl or substituted phenyl), where the data were consistent with a rate-determining combination of R and CO, followed by *trans* attack by L.

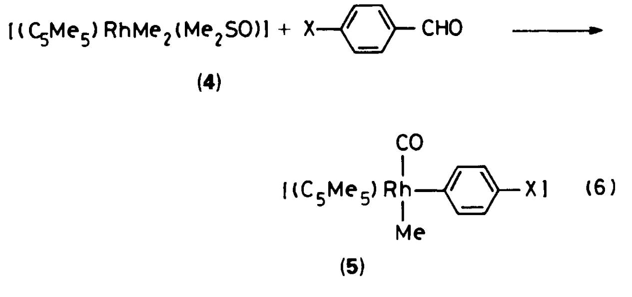
As models for the migration step in rhodium-catalysed carbonylations, we have investigated reactions of $[(C_5Me_5)RhR(CO)I]$ with PPh_3, which occur under mild conditions (20 °C) to give the acyls (**2**) [equation (5)], (R = Me, **a**; Ph, **b**; p-MeC_6H_4, **c**; p-ClC_6H_4, **d**; p-$OHCC_6H_4$, **e**; p-NCC_6H_4, **f**; or p-$O_2NC_6H_4$, **g**). Kinetic studies in a variety of solvents show that

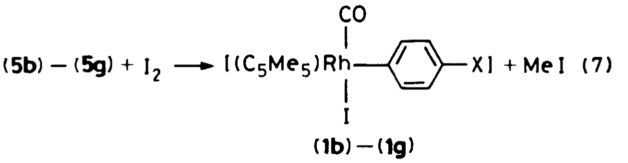
$$\underset{(\mathbf{1})}{[(C_5Me_5)RhR(CO)I]} + PPh_3 \longrightarrow \underset{(\mathbf{2})}{[(C_5Me_5)Rh(COR)(PPh_3)I]} \qquad (5)$$

(*a*) the chief mechanism is by direct bimolecular attack of triphenylphosphine on (**1**), both in non-polar as well as in moderately polar solvents, (*b*) the reactions are very fast, and (*c*) the migratory ability of phenyl can be greater than that of methyl, due to entropic factors, despite the enthalpic preference of methyl over phenyl. Part of this work has been published in a preliminary communication.[11]

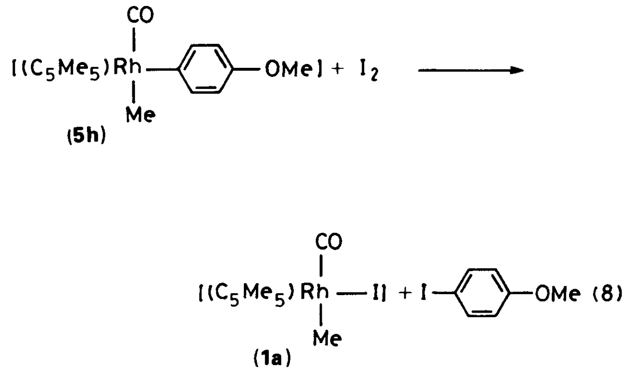
Results

Synthesis of Complexes (**1**), (**2**), *and* (**5**).—The complexes were made, in high yields, by the route shown in equations (6) and (7). The rhodium dimethyl complex (**4**) on reaction with the *p*-substituted benzaldehyde gave the appropriate methyl-carbonyl-aryl complexes (**5b**)—(**5g**);[12] these were treated with iodine to give (**1b**)—(**1g**).





When the *p*-substituent on the phenyl was H, Me, or strongly electron-withdrawing iodine cleavage of the Rh–Me bond occurred. However, complex (**5h**; X = OMe) reacted with iodine by cleavage of the aryl–rhodium rather than the methyl–rhodium bond, equation (8). This provided a useful route to the methyl complex (**1a**) and also gave *p*-iodoanisole. [Some 5% (**1a**) was also detected in the reaction of the *p*-tolyl complex (**5c**), but the major product was (**1c**).] Complex (**1a**) was also made



by reaction of the 4-pyridyl complex $[(C_5Me_5)RhMe(CO)(4\text{-}C_5H_4N)]$ with methyl iodide,[13] and by decarbonylation of $[(C_5Me_5)Rh(COMe)(CO)I]$, from the oxidative addition of methyl iodide to $[(C_5Me_5)Rh(CO)_2]$.[14] All the new complexes described were characterised by microanalysis and spectroscopy (Tables 1—3).

Reaction of (**1a**)—(**1d**) with triphenylphosphine gave the corresponding complexes (**2a**)—(**2d**) cleanly and in high yields. However, the migration reaction was substantially slowed by *p*-phenyl electron-withdrawing substituents, and a substitution directly at the metal [giving (**3**)] became competitive. Thus the *p*-formylphenyl, *p*-cyanophenyl, and *p*-nitrophenyl complexes (**1e**)—(**1g**) reacted to give mixtures in which the PPh_3-assisted migration was accompanied by some substitution with loss of CO giving (**3e**)—(**3g**) [equation (9) (R = *p*-$OHCC_6H_4$, **e**; *p*-NCC_6H_4, **f**; or *p*-$O_2NC_6H_4$, **g**)]. Although it was not possible to separate and individually isolate (**2f**) and (**3f**), or (**2g**) and (**3g**), the components of the mixtures (50:50 and 80:20, respectively) were identified by n.m.r. spectroscopy. Complex (**3e**) was also spectroscopically identified as a minor component (5%) of the total reaction mixture, from which pure (**2e**) was isolated by crystallisation.

$$\underset{(\mathbf{1})}{[(C_5Me_5)RhR(CO)I]} + PPh_3 \longrightarrow$$

$$\underset{(\mathbf{2})}{[(C_5Me_5)Rh(COR)(PPh_3)I]} + \underset{(\mathbf{3})}{[(C_5Me_5)RhR(PPh_3)I]} \quad (9)$$

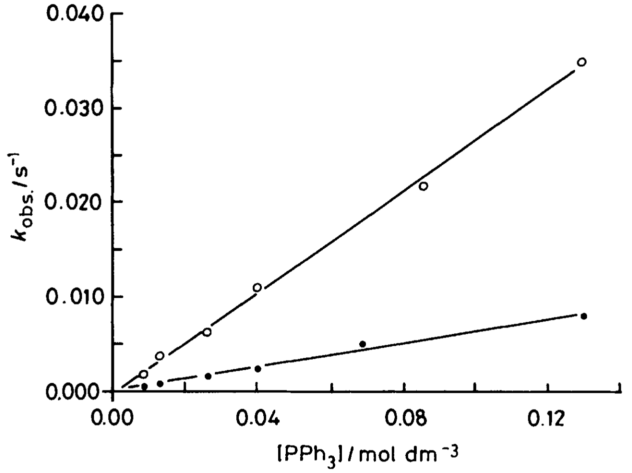


Figure 1. Dependence of observed rate constants ($k_{obs.}$) on PPh_3 concentration for the reaction of complexes (**1a**) (●) and (**1b**) (○) in tetrahydrofuran

Kinetics of Reactions of Complex (**1**) *with* PPh_3 *in Toluene, Tetrahydrofuran, or Dichloromethane.*—The reactions of complexes (**1a**)—(**1g**) with PPh_3, carried out in thermostatted cells, were monitored by following (*a*) the disappearance of the ν(CO) of (**1**) in the i.r. spectra, and (*b*) the absorbance increases, in the u.v.–visible spectra between 400 and 470 nm, with time. The two methods allowed a wide range of concentrations to be used; typically $[PPh_3]$ was varied from 9×10^{-4} to 9×10^{-2} mol dm^{-3}.

Plots of ln *A* (i.r. experiments, $A_\infty = 0$) or $\ln(A_\infty - A_t)$ (u.v.–visible) against time were linear for more than 90% completion of reaction. The $k_{obs.}$ were determined from the slopes of the lines by least-squares plots. Excellent agreement between the two methods was found (Table 4). Analysis of the data for complexes (**1a**) and (**1b**) (Table 5) showed that the reactions in toluene, dichloromethane, and tetrahydrofuran (thf) (Figure 1) were very cleanly first order in the complex concentration and first order in $[PPh_3]$, *i.e.* second order overall. The kinetics measurements were carried out under pseudo-first-order conditions, with a large excess ($> \times 10$) of PPh_3, such that $[PPh_3]$ remained sensibly constant throughout the reaction.

Since the reactions are quantitative and no equilibria are observed, $k_3 >>> k_{-3}$; under these conditions the overall rates and $k_{obs.}$ are given by, rate = $k_3[(\mathbf{1})][PPh_3]$ and $k_{obs.} = k_3[PPh_3]$.

Similar kinetic data were obtained for the complexes (**1c**)—(**1g**), the more electron-releasing *p*-substituted phenyls

Table 1. Microanalytical, f.a.b.m.s., and i.r. spectroscopic data[a]

Complex	Yield (%)	Found (Calc.) (%) C	H	I[b]	Other	F.a.b.m.s. $[M + H]^+$	ν(C=O) (cm^{-1})
(1a)	83	36.2	4.9	30.8	—	—	2 028
		(35.3)	(4.5)	(31.1)			
(1b)	90	43.0	4.2	26.8	—	—	2 040
		(43.4)	(4.3)	(27.0)			
(1c)	90	45.2	4.9	27.7	—	—	2 039
		(44.6)	(4.6)	(26.6)			
(1d)	73	41.1	4.3	23.6	Cl, 6.6	—	2 043
		(40.5)	(3.8)	(25.2)	(7.0)		
(1e)	90	43.4	4.3	26.0	—	—	2 044
		(43.4)	(4.0)	(25.5)			(1 687, CHO)
(1f)	95	43.9	4.1	25.8	N, 2.6	—	2 045
		(43.7)	(3.9)	(25.6)	(2.8)		(2 225, CN)
(1g)	69	39.8	4.0	24.5	N, 2.3	—	2 046
		(39.6)	(3.7)	(24.6)	(2.7)		
(2a)	70	53.9	4.9	18.6	—	671	1 631
		(53.8)	(5.0)	(18.9)			1 652 (sh)
(2b)	97	57.9	5.2	17.8	—	733	1 606
		(57.4)	(4.8)	(17.3)			
(2c)	91	57.7	5.4	16.0	—	747	1 608
		(57.9)	(5.0)	(17.0)			
(2d)	97	55.5	4.9	16.2	Cl, 4.5	767	1 607
		(54.8)	(4.5)	(16.6)	(4.6)	769	
(2e)	80	57.1	4.9	16.1	—	—	1 613
		(56.9)	(4.6)	(16.7)			(1 703, CHO)
(2f)[c]						758	1 611
(2g)[c]						778	1 609
(3f)[c]						730	
(3g)[c]						750	
(5d)	77	55.8	5.9	—	Cl, 8.5	—	2 006
		(55.1)	(5.7)		(9.0)		
(5e)	80	58.8	6.1	—	—	—	2 010
		(59.1)	(6.0)				
(5f)	90	59.9	5.7	—	N, 3.7	—	2 010
		(59.4)	(5.8)		(3.7)		
(5g)	68	53.8	5.7	—	N, 3.3	—	2 012
		(53.6)	(5.4)		(3.5)		
(5h)	45	59.4	6.2	—	—	—	2 001
		(58.8)	(6.5)				

[a] I.r. spectra measured in dichloromethane, except for complexes **(1a)**—**(1g)** measured in toluene. [b] Iodine microanalyses for compounds with higher amounts of iodine were occasionally unreliable owing to difficulties in combustion. [c] Not isolated, these are mixtures of $[(C_5Me_5)Rh(COR)(PPh_3)I]$ and $[(C_5Me_5)RhR(PPh_3)I]$, see text.

migrating faster (p-XC_6H_4, X = Me > H > Cl > CHO > NO_2 ≈ CN). For the complexes **(1e)**—**(1g)** where substitution as well as migration reactions were observed, the kinetic data were modified appropriately to obtain k_3, using the relationship $k_{overall} = k_{migration} + k_{substitution}$, where $k_{migration} = k_{overall} \times$ (fractional yield$_{migration}$) $= k_3$ and $k_{substitution} = k_{overall} \times$ (fractional yield$_{substitution}$).

A Hammett plot of the rate constants (k_3) for the reactions **(1b)**—**(1g)** $\longrightarrow$ **(2b)**—**(2g)** against the appropriate σ exhibited good linearity [ρ −2.9, correlation coefficient $r = 0.991$ for **(1b)**—**(1g)**; *cf.* ρ −3.1, $r = 0.993$ for **(1b)**—**(1f)**[11]], indicating no change in the migration mechanism from the most to the least reactive substrate.

The rate constants, k_3, showed that the methyl complex **(1a)** reacted more slowly with PPh_3 than the phenyl **(1b)** (Table 6). This was further investigated by measurements at different temperatures. Plots of $\ln(k_3/T)$ against $(1/T)$ over the temperature range 285—333 K for complexes **(1a)**—**(1d)** in toluene gave good straight lines and allowed evaluation of activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (Table 7) using the Eyring equation $k_3 = (k_b T/h)e^{-\Delta H^{\ddagger}/RT}e^{-\Delta S^{\ddagger}/R}$.

Kinetics of Reactions of Complex **(1)** *with* PPh_3 *in Nitromethane or Acetonitrile.*—Reaction (5) showed some significant differences in nitromethane and in acetonitrile solvent. Thus the benzoyl complex **(2b)** was only stable in these solvents in the absence of excess of triphenylphosphine. In the presence of an excess, further reaction occurred, to give a complicated mixture. There was no similar reaction with the methyl complex in these solvents.

More involved kinetic behaviour was observed in these solvents. A plot of $k_{obs.}$ against $[PPh_3]$ exhibited good linearity for **(1a)** (up to *ca.* 0.08 mol dm^{-3} in nitromethane, Figure 2), and corresponding to a second-order process, with $k_3 = 0.68$ (MeCN) and 0.70 $dm^3\ mol^{-1}\ s^{-1}$ ($MeNO_2$) (Table 5).

The plots were also linear up to 0.05 mol dm^{-3} PPh_3 for complex **(1b)**, but in that case the graph of $k_{obs.}$ against $[PPh_3]$ did not go through the origin (Figure 2). This can be accounted

Table 2. Proton and ^{31}P n.m.r. data (δ/p.p.m.) for [(C_5Me_5)Rh(COR)(PPh_3)I] and [(C_5Me_5)MR(L)I] complexes[a]

Complex	^{1}H C_5Me_5	 Aromatics	 Other	 ^{31}P
(1a)	1.93	—	Me 1.05(d) [2]	—
(1b)	1.85	6.99(m)[b] 7.45(m)[b]	—	—
(1c)	1.85	6.84(m)[b] 7.31(m)[b]	Me 2.24	—
(1d)	1.85	6.99(m)[b] 7.38(m)[b]	—	—
(1e)	1.87	7.47(m)[b] 7.71(m)[b]	CHO 9.87	—
(1f)	1.87	7.23(m)[b] 7.63(m)[b]	—	—
(1g)	1.89	7.70(m)[b] 7.83(m)[b]	—	—
(2a)	1.54(d) {2.5}	7.42(m, br) 7.90(m, br)	COMe 2.69(d) {0.5}	35.7(d) [168]
(2b)	1.61(dd) {3} [1]	7.65(m) 7.40(m) 7.08—7.38(m)	—	34.5(d) [164]
(2c)	1.60(dd) {3} [1]	7.65(m) 6.98—7.49(m)	*p*-Me 2.31	34.8(d) [165]
(2d)	1.59(d) {2.5}	7.64(m) 7.45(m) 7.08—7.40(m)	—	34.4(d) [163]
(2e)[c]	1.63(d) {3}	7.05—7.80(m)	CHO 9.97	—
(2f)	1.60(d) {3}	6.6—7.8(m)	—	41.2[d] 36.4
(2g)	1.64(d) {2.5}	6.6—8.0(m)	—	33.3(d) [160]
(3f)	1.46(d) {2.5}			35.9[d] 30.9
(3g)	1.49(d) {3}			38.7(d) [156]
(5d)	1.68	6.98(m)[b] 7.08(m)[b]	Me 0.48 (d) [2.5]	
(5e)	1.70	7.40(m)[b] 7.48(m)[b]	Me 0.54 (d) [2]	
(5f)	1.67	7.21(m)[b] 7.30(m)[b]	Me 0.49(d) [2.5]	
(5g)	1.70	7.35(m)[b] 7.82(m)[b]	Me 0.50(d) [2]	
(5h)	1.69	6.68(m)[b] 7.02(m)[b]	Me 0.50(d) [2.5] MeO 3.75	

[a] All spectra measured in $CDCl_3$; solvent as internal standard. Coupling constants in Hz to the nearest 0.5 Hz: [ ] = *J*(Rh–H) or *J*(Rh–P) and { } = *J*(P–H). [b] Multiplet of an AA′BB′ system. [c] N.m.r. spectrum of the crude product indicates the presence of 5% of complex **(3e)** [C_5Me_5 at δ 1.48 (d) {2.5} and CHO at δ 9.82]. [d] ^{31}P N.m.r. spectrum of the mixture of complexes **(2f)** and **(3f)** clearly shows two sets of doublets, but the middle two signals are very close and similar in intensity, and it is difficult to assign the chemical shift of each doublet.

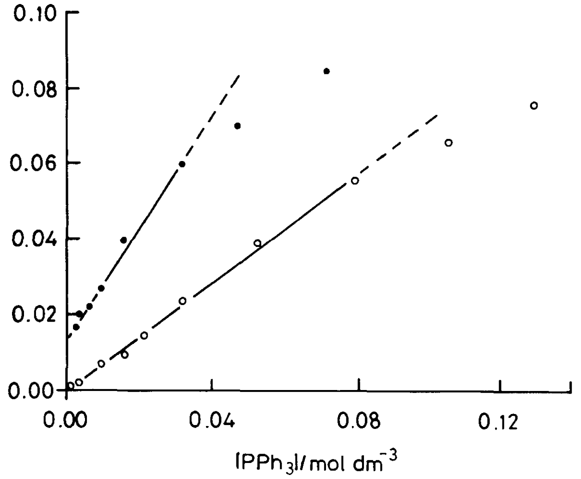


Figure 2. Dependence of observed rate constants ($k_{obs.}$) on PPh_3 concentration for the reaction of complexes **(1a)** (○) and **(1b)** (●) in nitromethane

for by parallel first and second order paths, rate = $k_{obs.}$[**(1b)**] = k_1[**(1b)**] + k_3[**(1b)**][PPh_3] or $k_{obs.} = k_1 + k_3$[PPh_3], with k_1 = 0.013 s^{-1} and k_3 = 1.48 dm^3 mol^{-1} s^{-1} in nitromethane, and k_1 = 0.009 s^{-1} and k_3 = 1.25 dm^3 mol^{-1} s^{-1} in acetonitrile. These second-order rate constants are some 4—5 times higher than in the less polar solvents, but at low [PPh_3] the first-order process predominates here.

Deviations from linearity were observed for the reactions of both **(1a)** and **(1b)** in nitromethane and of **(1a)** in acetonitrile at very high [PPh_3], the reactions becoming slower than expected. These situations have not yet been analysed further.

Discussion

The Second-order Kinetics Regime.—(*i*) *The effect of* p*-phenyl substituents.* The novel features of the reaction **(1)** ⟶ **(2)** in toluene and other less polar solvents are the clean second-order kinetics and the very fast rates. We interpret these data to imply a direct attack by the triphenylphosphine on the complex *via* a transition state [(C_5Me_5)RhR(CO)(PPh_3)I]‡, with simultaneous migration of R. The absence of a first-order pathway (in the less polar solvents) is unexpected, since bimolecular paths are normally of relatively minor significance.[2c,8] In most previously investigated systems the rate-determining step is the migration, independent of incoming nucleophile concentration, and bimolecular paths are very slow.

The good linearity of the Hammett plot of the rate constants for the reactions of the phenyl complexes **(1b)**—**(1g)** ⟶ **(2b)**—**(2g)** in toluene implies no change in the migration mechanism from the most to the least reactive substrate. The sign and the absolute value of ρ (−2.9) would imply, for a purely organic reaction such as the pinacol rearrangement, that positive charge is built up (or, equivalently, that negative charge is dissipated) in going to the transition state.[15,16] In both cases, the relative migratory aptitude increases with increasing electron-releasing ability of the phenyl substituents; in both, phenyl also migrates faster than methyl.

Ab initio calculations for the conversion of [PdMe(H)(CO)PH_3] into [Pd(H)(COMe)PH_3] have been carried out by Koga and Morokuma;[17] they find it proceeds by methyl migration and give reasons why CO insertion is not favoured. They also find that the three-centre transition state is stabilised by interaction between the methyl *sp*^{3}, the CO π*, and the Pd (*d* + *p*) orbitals, and that the methyl loses negative charge to the CO as the reaction proceeds. Replacement of methyl by ethyl lowers the calculated activation energy, while replacement of methyl hydrogens by one or more electron-withdrawing fluorines raises it substantially. Although the metal, the oxidation state, the *d*-electron count, the co-ligands, and the geometries are all very

Table 3. ^{13}C-{^{1}H} N.m.r. data^a

Complex	C_5Me_5	Aromatics	Other	CO
(1a)	9.9 103.3 (d) [4]	—	Me −5.9(d) [19]	189.5(d) [78]
(1b)	10.0 104.7(d) [4]	C(1) 147.8 [28] C(2) 142.2 C(3) 128.8 C(4) 124.0		188.6(d) [76]
(1c)	10.1 104.6(d) [4]	C(1) 142.6 C(2) 141.8 C(3) 129.9 C(4) 133.3	Me 20.6	188.7(d) [75]
(1d)	10.1 104.8(d) [4]	C(1) 145.4 (d) [29] C(2) 143.1 C(3) 128.4 C(4) 130.7		188.2(d) [76]
(1e)	10.1 104.9(d) [4]	C(1) 162.9(d) [30] C(2) 143.0 C(3) 128.7 C(4) 124.0	CHO 192.8	187.8(d) [76]
(1f)	10.1 105.0(d) [4]	C(1) 159.3(d) [29] C(2) 143.2 C(3) 130.7 C(4) 107.7	CN 119.6	187.7(d) [75]
(1g)	10.1 105.1 [n.o.]	C(1) 163.5(d) [29] C(2) 142.7 C(3) 121.9 C(4) 146.0		187.5(d) [75]
(2a)	9.8 101.9(m)	C(1) 133.5(d) {89} C(2) 134.1(d) {30} C(3) 127.6(d) {10} C(4) 129.8	*Me*CO 52.4	247.6(dd) [28] {13}
(2b)	9.9 101.8	C(1) 146.2 126.3—136.0 (mm)	—	247.5(dd) [3] {14}
(2c)	9.8 101.8(m)	C(1) 143.5 C(4) 140.2 127.1—135.9 (mm)	*p*-Me 21.4	246.7(dd) [31] {15}
(2d)	9.8 101.8(m)	C(1) 144.3 126.6—136.2 (mm)	—	247.0(dd) [31] {14}
(2e)	9.9 102.0(dd) [3] {3}	C(1) 150.8 127.5—136.2 (mm)	CHO 192.2	248.8(dd) [32] {15}
(2f)^b	9.8		—	248.3(dd)^e [30] {18}
+	100.8^c			
(3f)	102.0^c	C(1) 168.5(dd)^d [32] {18}		
(2g)^b	9.9		—	248.8(dd)^e [32] {16}
+	100.9(m)^c			
(3g)	102.0(m)^c	C(1) 174.7(dd)^d [33] {18}		
(5d)	9.1 101.7(d) [3]	C(1) 150.3(d) [35] C(2) 140.0 C(3) 127.5 C(4) 129.5	Me −2.7(d) [24]	192.5(d) [78]
(5e)	9.0 101.9(d) [3]	C(1) 169.2(d) [35] C(2) 139.8 C(3) 127.7 C(4) 137.5	Me −2.6(d) [24] CHO 192.9	192.2(d) [75]
(5f)	9.0 101.9(d) [3]	C(1) 165.1(d) [35] C(2) 139.9 C(3) 129.7 C(4) 120.3	Me −2.5(d) [25] CN 106.3	192.1(d) [78]
(5g)	9.0 102.0(d) [3]	C(1) 107.2(d) [35] C(2) 139.4 C(3) 120.9 C(4) 145.2	Me −2.4(d) [25] CHO 192.9	191.9(d) [75]
(5h)	9.1 101.6	C(1) 139.7(d) [34] C(3) 114.1 C(2) 138.9 C(4) 156.7	MeO 55.0	—

^{a} δ/p.p.m. All spectra measured in $CDCl_3$ on a Bruker AM250 instrument, except for complex **(2b)** measured on a Bruker WH400; solvent as internal standard; [ ] = *J*(Rh–C) and { } = *J*(P–C) in Hz to the nearest 1 Hz. ^{b} Spectrum measured as a mixture of the two products. ^{c} Arbitrary assignment. ^{d} Signal due to aromatic C(1) in complex **(3)**; the rest of the aromatic region is very complex. ^{e} Signal due to Rh*C*OR in complex **(2)**.

Table 4. First-order rate constants ($k_{obs.}$) for the reactions of complexes (**1a**) (*a*) and (**1b**) (*b*) with PPh_3 in different solvents

Solvent	[Complex]/mol dm^{-3}	[PPh_3]/mol dm^{-3}	$k_{obs.}^{-1}/s^{-1}$	Method */λ (nm) or ν (cm^{-1})
(*a*) Complex (**1a**)				
Toluene	5.1×10^{-4}	9.15×10^{-3}	8.0×10^{-4}	(*b*)/400 nm
	5.1×10^{-4}	1.75×10^{-2}	1.7×10^{-3}	(*b*)/400 nm
	1.5×10^{-3}	1.75×10^{-2}	1.6×10^{-3}	(*a*)/2 027 cm^{-1}
	5.1×10^{-4}	8.75×10^{-2}	8.4×10^{-3}	(*b*)/400 nm
Dichloromethane	9.5×10^{-4}	1.2×10^{-2}	1.7×10^{-3}	(*b*)/430 nm
	9.5×10^{-4}	7.0×10^{-2}	1.05×10^{-2}	(*b*)/430 nm
	9.5×10^{-4}	1.0×10^{-1}	1.7×10^{-2}	(*b*)/430 nm
Acetonitrile	1.8×10^{-4}	2.15×10^{-3}	1.5×10^{-3}	(*b*)/460 nm
	1.1×10^{-3}	2.15×10^{-2}	1.4×10^{-2}	(*b*)/460 nm
	7.3×10^{-4}	7.10×10^{-2}	4.8×10^{-2}	(*b*)/460 nm
	1.4×10^{-3}	1.02×10^{-1}	5.9×10^{-2}	(*b*)/460 nm
	1.1×10^{-3}	1.54×10^{-1}	7.6×10^{-2}	(*b*)/460 nm
(*b*) Complex (**1b**)				
Toluene	7.0×10^{-5}	9.1×10^{-4}	3.0×10^{-4}	(*b*)/450 nm
	3.5×10^{-4}	9.1×10^{-3}	3.5×10^{-3}	(*b*)/450 nm
	9.7×10^{-4}	9.1×10^{-3}	3.1×10^{-3}	(*a*)/2 040 cm^{-1}
	3.7×10^{-4}	1.7×10^{-2}	5.9×10^{-3}	(*b*)/450 nm
	3.7×10^{-4}	8.7×10^{-2}	3.2×10^{-2}	(*b*)/450 nm
Dichloromethane	5.0×10^{-4}	6.2×10^{-3}	2.2×10^{-3}	(*b*)/450 nm
	9.0×10^{-4}	1.2×10^{-2}	4.3×10^{-3}	(*b*)/450 nm
	1.2×10^{-3}	6.6×10^{-2}	2.2×10^{-2}	(*b*)/455 nm
Acetonitrile	1.6×10^{-4}	2.1×10^{-3}	9.0×10^{-3}	(*b*)/450 nm
	6.0×10^{-4}	8.6×10^{-3}	2.0×10^{-2}	(*b*)/450 nm
	1.3×10^{-3}	1.4×10^{-2}	2.9×10^{-2}	(*b*)/450 nm
	1.3×10^{-3}	2.1×10^{-2}	3.8×10^{-2}	(*b*)/450 nm
	1.3×10^{-3}	4.0×10^{-2}	6.0×10^{-2}	(*b*)/470 nm
	4.2×10^{-4}	5.1×10^{-2}	7.1×10^{-2}	(*b*)/470 nm
	1.3×10^{-3}	6.1×10^{-2}	8.5×10^{-2}	(*b*)/470 nm

* See Experimental section.

Table 5. Rate constants[a] for the reaction of complexes (**1**), [$(C_5Me_5)RhR(CO)I$], with PPh_3 at 25 °C in different solvents

	Complex (**1a**)	Complex (**1b**)			
Solvent	k_3/dm^3 mol^{-1} s^{-1}	k_1/s^{-1}	k_3/dm^3 mol^{-1} s^{-1}	Donor number[b]	Dielectric constant
Toluene	0.092(5)	—	0.35(2)	0.1	2.4
CH_2Cl_2	0.15(2)	—	0.35(2)	2	9.1
thf	0.064(4)	—	0.25(3)	20	7.6
$MeNO_2$	0.70(5)	0.013(1)	1.48(7)	2.7	35.9
MeCN	0.68(3)	0.009(1)	1.25(6)	14.1	37.5

[a] Standard deviations in parentheses, thus 0.092(5) ≡ 0.092 ± 0.005.
[b] Ref. 19.

Table 6. Relative rates of migratory insertion for complexes (**1**) in toluene at 25 °C*

Complex	k_3/dm^3 mol^{-1} s^{-1}	$k_{rel.}$	k(substitution)/ dm^3 mol^{-1} s^{-1}
(**1a**)	0.092(5)	0.26	—
(**1b**)	0.35(2)	1	—
(**1c**)	0.95(4)	2.8	—
(**1d**)	0.11(2)	0.31	—
(**1e**)	0.012(1)	0.034	$6.5(5) \times 10^{-4}$
(**1f**)	$2.8(2) \times 10^{-3}$	0.008	$2.8(2) \times 10^{-3}$
(**1g**)	$2.6(1) \times 10^{-3}$	0.007	$6.6(3) \times 10^{-4}$

* See Table 5, footnote *a*.

different in the system studied here, and although no calculations have been made for migrating aryls, the main conclusion agrees with experimental data for a number of systems: that electron-releasing substituents on the organic group will promote its migration from the metal onto CO.

Such *p*-phenyl substituent effects have been observed, both in the carbonylation of σ-aryls (*e.g.* MeO > Me > H > Cl)[9,10] and of σ-benzyls.[4d] Reverse migration (decarbonylation) reactions are expected to be promoted by electron-withdrawing substituents on the organic group,[1] and examples are known for rhodium, such as the reaction of [$Rh(p\text{-}XC_6H_4CO)(PPh_3)_2Cl_2$] to [$Rh(p\text{-}XC_6H_4)(CO)(PPh_3)_2Cl_2$].[5b] However in some cases electron-releasing substituents on σ-benzyls give higher rates for the reverse migration.[5b,6a]

The value of ρ (−2.9, toluene, 298 K) found for reaction (**1**) ⟶ (**2**) is close to that for the aryl migration step in the carbonylation of [$PtR(PPh_3)_2I$] (−3.6, $C_2Cl_4H_2$ solution, 303 K),[9b] and for the combination of aryl and carbonyl in the reaction of Bu^{t}NC with [$RuR_2(CO)_2(PPhMe_2)_2$] to give [$RuR(CO)(COR)(PPhMe_2)_2(Bu^tNC)$] (−3.75, $CHCl_3$ solution, 298 K).[10] This may indicate considerable mechanistic similarity between the reactions, and that in each case an anionoid centre migrates onto a co-ordinated CO, thus dissipating the charge, during the rate-limiting step. The numerically somewhat larger ρ values for the platinum(II) and ruthenium(II) systems possibly imply a slightly larger dissipation of negative charge during the migration there than from Rh^{III}.

Different ρ have been found, though the underlying order of *p*-phenyl substituent reactivities remains similar. Cotton *et al.*[4d] found a ρ of −0.97 for benzylic migrations in the reaction of PPh_3 with [$(cp)Mo(p\text{-}XC_6H_4CH_2)(CO)_3$] in acetonitrile to give [$(cp)Mo(CO)_2(p\text{-}XC_6H_4CH_2CO)(PPh_3)$] (X = MeO > Me > F > H > CF_3). For a wider range of sub-

Table 7. Activation parameters for the reaction of complexes (**1**) with triphenylphosphine in toluene*

Complex	Temp. (°C)	k_3 ($dm^3\ mol^{-1}\ s^{-1}$)	$\Delta H^\ddagger$ ($kJ\ mol^{-1}$)	$\Delta S^\ddagger$ ($J\ K^{-1}\ mol^{-1}$)
(**1a**)	13.0	0.034	55.6 ± 0.5	−79 ± 2
	25.0	0.093		
	40.0	0.295		
	56.0	0.82		
	70.0	2.0		
(**1b**)	13.0	0.14	62.3 ± 1.3	−43 ± 4
	25.0	0.35		
	40.0	1.35		
	56.0	4.83		
	70.0	11.9		
(**1c**)	12.0	0.40	48.5 ± 0.8	−82 ± 3
	25.0	1.10		
	42.0	3.14		
	59.0	8.6		
(**1d**)	13.0	0.04	59.0 ± 1.7	−66 ± 6
	25.0	0.11		
	40.0	0.40		
	55.0	1.04		

* Correlation coefficient, >0.996.

stituents, Cawse *et al.*[2c] reported a ρ^* of −8.7 for the reaction of $[Mn(RCH_2)(CO)_5]$ and CO to give $[Mn(RCH_2CO)(CO)_5]$ (where R = n-alkyl > cyclohexyl > H > phenyl).

Analysis of the activation data for the reactions of complexes (**1a**)—(**1d**) showed that $\Delta H^\ddagger$ decreased in the order R = *p*-tolyl < methyl < *p*-chlorophenyl < phenyl, while $\Delta S^\ddagger$ decreased in the opposite order, R = *p*-tolyl > methyl > *p*-chlorophenyl > phenyl. As a consequence, the $\Delta G^\ddagger$ values and the rate constants (k_3) vary more randomly. At 25 °C the k_3 values follow the order *p*-tolyl (1.1) > phenyl (0.35) > *p*-chlorophenyl (0.11) ⩾ methyl (0.09 $dm^3\ mol^{-1}\ s^{-1}$). A result of the low $\Delta S^\ddagger$ for the phenyl complex (**1b**) is that at above *ca.* 340 K the phenyl is predicted to migrate faster than the other R investigated, while it should become the slowest at very low temperatures (<130 K), were the reaction possible there, since $\Delta H^\ddagger$ becomes dominant.

(*ii*) *The migratory ability of methyl compared to phenyl.* Comparison of reactions of complexes (**1a**) and (**1b**) shows, apparently for the first time, that phenyl can migrate faster than methyl in a direct and quantitative transformation, $MR(CO) + L \longrightarrow L\text{-}M(COR)$. No change in rate for the phenyl complex (**1b**), and little for the methyl complex (**1a**), was observed (Table 5) between toluene, dichloromethane (which has weak acceptor properties), and tetrahydrofuran (which is a donor solvent), and there is no correlation with the donor number.[18] Thus a contribution to the migratory insertion process from the solvent acting as nucleophile is unlikely. There is a small correlation with the dielectric constant of the solvent, suggesting that the solvent may help to stabilise the transition state, but since the ratios $(k_3{}^{1a}):(k_3{}^{1b})$ are similar in the various solvents, differential solvation is unlikely to explain the entropy differences between their reactions.

The rates of reactions (**1**) ⟶ (**2**) only show a factor of 12 for (**1a**) and 6 for (**1b**) between nitromethane and thf, the two ends of the solvent spectrum. Much larger solvent effects are typical for the more common situation, showing first-order kinetics, in which migration precedes nucleophilic attack; *e.g.* a factor of 168 has been found for $k_{obs.}$ between thf and mesitylene for the reaction of $[MeMn(CO)_5]$ and cyclohexylamine.[2a]

Early data indicated that methyl migrated onto CO faster than phenyl, by a factor of *ca.* 8 for $[MnR(CO)_5]$.[1a,b] A thermodynamic preference of 50-fold in rate for phenyl over methyl for the reverse migration from RCO–Re to R–Re(CO), and a kinetic preference of *ca.* 28-fold in rate for methyl migration from the five-co-ordinate intermediate $[Re(CO)_3(COMe)(COPh)]^-$ have also been noted.[19]

In the reactions $[RhR(CO)(PPh_3)_2Cl_2] \rightleftharpoons [Rh(COR)(PPh_3)_2Cl_2]$ the acyl form is favoured for R = Me, while the equilibrium is strongly to the left for R = Ph.[5a,c] By contrast, the acyl form is favoured in the order R = Et > Ph > Me > $PhCH_2$, in the equilibria[7b] $2[PtR(PPh_2Me)(CO)Cl] \rightleftharpoons [Pt_2(PPh_2Me)_2(COR)_2(\mu\text{-}Cl)_2]$.

Most of these measurements were made at a single temperature, and in some cases relate only to equilibria; such limited data make structure–reactivity correlations difficult to draw. For example, in the reactions (**1**) ⟶ (**2**), although phenyl migrates faster than methyl at all reasonable temperatures, the comparison between phenyl and *p*-tolyl is more complex since the $\Delta G^\ddagger$ are the same at 354 K. Above that temperature phenyl will migrate faster, below, *p*-tolyl is faster.

(*iii*) *Comparative reaction rates.* Comparisons with published data (Table 8) indicate that the bimolecular rate constants, k_3, for (**1**) ⟶ (**2**) *are substantially larger, by ca. 3 orders of magnitude*, than for the related reactions of PR_3 with $[(C_5H_5)MoMe(CO)_3]$[3a,4b] or of $[MnMe(CO)_5]$ with cyclohexylamine.[3a] Fast migratory rates are common in rhodium(III) carbonyl chemistry. Thus, in the reaction of MeI with $[Rh(CO)_2I_2]^-$ the product is the acetyl complex $[Rh(CO)(COMe)I_3]^-$, and $[RhMe(CO)_2I_3]^-$ is not detected because it is converted into the acetyl faster than it is formed.[20,21] Different ligands at the rhodium centre offer a range of rates: $[Rh(COMe)(PPh_3)_2Cl_2]$ and $[RhMe(CO)(PPh_3)_2Cl_2]$ interconverted slowly on the n.m.r. time-scale ($\Delta H^\ddagger$ −8 kJ mol^{-1} and $\Delta S^\ddagger$ −35 J K^{-1} mol^{-1}),[5c] while the rates of migration between the cations $[Rh(COMe)(PMe_2Ph)_3Cl]^+$ and $[RhMe(CO)(PMe_2Ph)_3Cl]^+$ were much faster.[5d]

Although limited, these data suggest that very fast migrations on rhodium are facilitated by either a cationic centre or an iodide on the rhodium. The first can be understood from the theoretical interpretations of migration reactions,[17,22] and many other examples are known. Thus, substantial enhancement of migration onto CO results from the co-ordination of Lewis acids, ranging from 10^2 for $[WPh(CO)_5]^-$ and $AlPh_3$, to 10^8 for $[MnMe(CO)_5]$ and $AlCl_3$,[23] an extreme manifestation of the accelerating effect of a positive charge.

The beneficial influence of co-ordinated iodide has been noted before,[7b,8] and the vital role which iodide (halide) plays in the reactions studied here can be gauged from the fact that no migration (or substitution) could be effected when non-halide-containing complexes such as $[(C_5Me_5)RhMe(Ph)(CO)]$ were treated with triphenylphosphine under the conditions used to effect (**1**) ⟶ (**2**).

The Mixed Kinetics Regime.—Kinetics corresponding to mixed first- and second-order processes were found for the reactions of the phenyl complex (**1b**) in the highly polar solvents acetonitrile or nitromethane [dielectric constants 35.9 ($MeNO_2$) and 37.5. (MeCN)]. This path is absent for the methyl complex (**1a**). Since nitromethane is a poor ligand for Rh^{III} it is unlikely that the solvent acts in this way; however it is possible that reaction proceeds by ionisation of the iodide, followed by attack by PPh_3.

Reaction of complex (**1b**) with $AgBF_4$ in acetonitrile gave a solution the i.r. spectrum of which suggested the presence of both $[(C_5Me_5)Rh(COPh)(MeCN)_2]^+$ [ν(CO) 1 641 cm^{-1}] and $[(C_5Me_5)Rh(CO)(MeCN)]^+$ [ν(CO) 2 077 cm^{-1}]. Rather similar cationic complexes have previously been isolated and characterised,[5d,e] and it is plausible that related species may play a role in the migration reactions.

Table 8. Comparison of rate constants for migratory insertion in different systems

Compound	Nucleophile	k_1 (s^{-1})	k_3 ($dm^3\ mol^{-1}\ s^{-1}$)	Solvent	Temp. (°C)
$[(C_5Me_5)RhMe(CO)I]$	PPh_3	—	9.2×10^{-2}	Toluene	25.0
$[(C_5H_5)MoMe(CO)_3]$[a]	PPh_2Me	7.8×10^{-4}	1.7×10^{-4}	thf	59.9
$[(C_5H_5)MoMe(CO)_3]$[b]	PPh_3	—	3.2×10^{-5}	Toluene	50.7
$[(C_5H_5)FeMe(CO)_2]$[b]	PPh_3	4.2×10^{-6}	—	Toluene	50.7
$[MnMe(CO)_5]$[c]	$C_6H_{11}NH_2$	—	1.1×10^{-4}	Mesitylene	25.5
$[MnMe(CO)_5]$[c]	PPh_3	9.0×10^{-4}	—	thf	25.5

[a] Ref. 4*b*. [b] Ref. 3*a*. [c] Ref. 2*b*.

Mixed first- and second-order kinetics were previously observed, but in *less polar* solvents, for the reactions of $[MnMe(CO)_5]$ with cyclohexylamine in mesitylene,[2a] and of $[(C_5H_5)MoMe(CO)_3]$ with PR_3 in toluene and in thf.[3a,4b] Values of k_3 for these reactions are some 10^3—10^5 times *lower* than for (**1b**) $\longrightarrow$ (**2b**).

Experimental

Unless otherwise indicated all reactions were carried out under nitrogen or argon using standard Schlenk-line techniques. Solvents were thoroughly degassed before use; toluene was distilled under nitrogen from sodium–benzophenone, and dichloromethane and acetonitrile were distilled under nitrogen from calcium hydride. Nitromethane was washed with $NaHCO_3$ solution, dried, and distilled. Chemicals and all other solvents were reagent grade. Typical experimental procedures are given below. Elemental analyses were performed by the Sheffield University Microanalysis Service (Table 1). Alumina (neutral, activated Brockmann I) was used for chromatography.

Infra-red [Nujol mulls, KBr discs, or solution (CaF_2 cell, with computerised subtraction of the solvent) on Perkin-Elmer PE-1710 F-T and PE-157 spectrometers], ^1H n.m.r. [PE R12B spectrometer (60 MHz, continuous wave), Bruker AM-250, WP-80 SY, or WH-400 FT spectrometers using the solvent or tetramethylsilane as an internal standard], ^{13}C n.m.r. (Bruker AM-250 and WH-400 spectrometers using solvent as an internal standard), and ^{31}P n.m.r. spectra (Bruker WP-80 SY, orthophosphoric acid as an external reference) are collected in Tables 1—3. Fast-atom bombardment mass spectra (f.a.b.m.s.) were recorded in *p*-nitrobenzyl alcohol matrices on a Kratos MS80RF mass spectrometer.

$[(C_5Me_5)RhMe(p\text{-}MeC_6H_4)(CO)]$ (**5c**).—*p*-Tolualdehyde (0.21 cm^3, 1.80 mmol) was added to a solution of $[(C_5Me_5)RhMe_2(Me_2SO)]$ (**4**) (0.31 g, 0.92 mmol) in cyclohexane (10 cm^3) in a Schlenk tube, and the solution was stirred (80 °C, 3.5 h). The solvent was removed *in vacuo* and the resultant residue chromatographed. A pale yellow band eluted with hexane–diethyl ether (9:1) gave yellow crystals of $[(C_5Me_5)RhMe(p\text{-}MeC_6H_4)(CO)]$ (**5c**) (0.20 g, 58%) from hexane.

$[(C_5Me_5)RhMe(p\text{-}O_2NC_6H_4)(CO)]$ (**5g**).—*p*-Nitrobenzaldehyde (0.23 g, 1.49 mmol) was added to a solution of $[(C_5Me_5)RhMe_2(Me_2SO)]$ (**4**) (0.26 g, 0.75 mmol) in cyclohexane (10 cm^3) and the solution stirred (60 °C, 3 h). The solvent was removed on a rotary evaporator and the resultant residue chromatographed. A yellow band was eluted with diethyl ether to give yellow crystals of $[(C_5Me_5)RhMe(p\text{-}O_2NC_6H_4)(CO)]$ (**5g**) (0.24 g, 78%).

Reaction of $[(C_5Me_5)RhMe(p\text{-}NCC_6H_4)(CO)]$ (**5f**) *with Iodine to give Complex* (**1f**).—$[(C_5Me_5)RhMe(p\text{-}NCC_6H_4)(CO)]$ (**5f**) (0.17 g, 0.43 mmol) was added, with stirring, to a solution of iodine (0.11 g, 0.43 mmol) dissolved in dichloromethane at −5 °C. A bright orange solution formed almost instantaneously. Alumina was then added and the solvent removed *in vacuo*. The impregnated powder was placed on top of an alumina column, and was eluted with diethyl ether. Orange crystals of $[(C_5Me_5)Rh(p\text{-}NCC_6H_4)(CO)I]$ (**1f**) (0.20 g, 91%) were obtained from the orange eluate.

Reaction of $[(C_5Me_5)Rh(p\text{-}MeC_6H_4)(CO)I]$ (**1c**) *with Triphenylphosphine to give Complex* (**2c**).—Toluene (5 cm^3) was added to a mixture of complex $[(C_5Me_5)Rh(p\text{-}MeC_6H_4)(CO)I]$ (**1c**) (0.04 g, 0.087 mmol) and triphenylphosphine (0.02 g, 0.095 mmol) in a Schlenk tube. The resultant solution turned from orange to dark red on stirring (24 h, 20 °C), and the i.r. spectrum showed that all the starting material had reacted. The solution was filtered, the solvent removed *in vacuo*, and the residue was crystallised from dichloromethane and n-heptane (−20 °C) to give $[(C_5Me_5)Rh(p\text{-}MeC_6H_4CO)(PPh_3)I]$ (**2c**) (0.06 g, 91%).

Reaction of $[(C_5Me_5)RhMe(CO)I]$ (**1a**) *with Triphenylphosphine to give Complex* (**2a**).—Toluene (5 cm^3) was added to the complex $[(C_5Me_5)RhMe(CO)I]$ (**1a**) (0.08 g, 0.20 mmol) and triphenylphosphine (0.06 g, 0.21 mmol) in a Schlenk tube. The resultant solution was stirred (24 h, 20 °C), turning quickly from orange-red to dark red; it was then filtered, the solvent removed *in vacuo*, and the resultant residue was chromatographed. Red-brown crystals of pure $[(C_5Me_5)Rh(COMe)(PPh_3)I]$ (**2a**) (0.09 g, 70%) were obtained.

The reaction was repeated using $[^2H_8]$toluene (1 cm^3) as solvent, $[(C_5Me_5)RhMe(CO)I]$ (0.02 g, 0.049 mmol), and triphenylphosphine (0.02 g, 0.098 mmol). The ^1H n.m.r. spectrum (250 MHz) of the crude reaction solution (20 °C, 15 h) showed the presence of essentially one product [C_5Me_5 at δ 1.39(d), *J*(H–P) 3 Hz; COMe at δ 2.87(s)] and no starting material or other products. Impurities arising from other reactions were negligible, indicating that only one reaction pathway exists under these conditions.

Reaction of $[(C_5Me_5)Rh(p\text{-}NCC_6H_4)(CO)I]$ (**1f**) *with Triphenylphosphine to give Complexes* (**2f**) *and* (**3f**).—Toluene (10 cm^3) was added to the complex $[(C_5Me_5)Rh(p\text{-}NCC_6H_4)(CO)I]$ (0.11 g, 0.23 mmol) and triphenylphosphine (0.07 g, 0.25 mmol) in a Schlenk tube. The resultant solution was stirred (72 h, 15 °C), turning from orange to dark red-brown. The solvent was removed *in vacuo* and the resultant oil triturated in n-pentane to give a red powder, yield 0.14 g. This powder was shown by ^1H n.m.r. spectroscopy to contain $[(C_5Me_5)Rh(p\text{-}NCC_6H_4CO)(PPh_3)I]$ (**2f**) and $[(C_5Me_5)Rh(p\text{-}NCC_6H_4)(PPh_3)I]$ (**3f**), ratio 1:1.

Reaction of $[(C_5Me_5)RhMe(p\text{-}MeOC_6H_4)(CO)]$ *with Iodine to give Complex* (**1a**).—A solution of iodine (0.12 g, 0.46 mmol) in dichloromethane (100 cm^3) at -20 °C was added, with stirring, to the solution of complex [(C_5Me_5)RhMe(p-MeOC_6H_4)(CO)] (0.18 g, 0.46 mmol) in dichloromethane (50 cm^3) at -20 °C, the resultant solution quickly turning bright orange. The solution was allowed to stand with occasional stirring (-20 °C, 2 h) and the solvent was then removed *in vacuo*. The ^{1}H n.m.r. spectrum (in C_6D_6) of the residue showed that the reaction had gone to completion giving essentially one organometallic product. The residue was then chromatographed. A colourless band eluted with n-pentane; this was collected and gave a white residue, which was crystallised from n-hexane to give p-MeOC_6H_4I (0.08 g, 70%). Further elution of the column with n-pentane–diethyl ether (1:1) gave an orange band, which yielded pure red crystals of [(C_5Me_5)RhMe(CO)I] (**1a**) (0.16 g, 83%).

Kinetics Measurements of the Rates of Reaction of Complexes (**1a**)—(**1g**) *with Triphenylphosphine.*—Kinetics measurements [ν(CO)] were carried out using a Perkin-Elmer 684 i.r. spectrometer, equipped with a thermostatted cell holder and connected to a PE-3600 data station. A program was used to record automatically and subtract signals of the solvent from spectra of the reaction solution. A Perkin-Elmer 559 u.v.–visible spectrophotometer was equipped with an electrically thermostatted cell holder and was used in the time drive mode to record changes in the absorbance in the 400—450 nm region during kinetics runs.

Experiments were carried out under pseudo-first-order conditions, using a ten-fold or larger excess of triphenylphosphine, by mixing standard solutions of triphenylphosphine and of the complex (**1**) made up anaerobically in the solvent.

Method (*a*). Measured volumes of thermostatted solutions of the reagents were mixed and a portion of the resulting solution was introduced into a 1-mm CaF_2 cell. Rates were measured by following the disappearance of the ν(CO) band of the complexes, in the i.r. region between 2 100 and 2 000 cm^{-1}. The magnitudes of the bands were computed as peak heights (or areas) from the difference spectra recorded at defined time intervals.

Method (*b*). A quartz cell (length 1 cm), containing the complex solution (1 cm^3) under nitrogen, was placed in the thermostatted cell holder of the u.v.–visible spectrometer and allowed to equilibrate. The triphenylphosphine solution (1 cm^3) was added, and the cell was shaken to ensure mixing. The increase of absorbance associated with the reaction was followed between 470 and 400 nm.

For slow reacting substrates, absorbances at infinity time were calculated by the Mangelsdorf method. All the reactions were characterised by a change in colour from orange to reddish orange, as indicated by the increases in absorbance between 650 and 350 nm. The largest variation was at 450 nm for complex (**1b**) (R = phenyl) and at 400 nm for (**1a**) (R = methyl).

Plots of ln A for the i.r. experiments ($A_\infty = 0$) and of $\ln(A_\infty - A_t)$ for the u.v.–visible experiments *versus* time were linear for more than 90% completion of the reaction. Values of $k_{\text{obs.}}$ were determined from the slopes of the lines by application of the least-squares method (correlation coefficients > 0.998). Agreement between the methods (*a*) and (*b*) was excellent. For the reactions in nitromethane and acetonitrile, the second-order rate constants were obtained from the straight line plots of $k_{\text{obs.}}$ *versus* triphenylphosphine concentrations, while the rate constants for the first-order process were obtained from the non-zero intercepts in the same plots, according to the equation $k_{\text{obs.}} = k_1 + k_3[\text{PPh}_3]$. The observed rate constants ($k_{\text{obs.}}$) for complexes (**1a**) and (**1b**), obtained from duplicate runs, are reported graphically (Figures 1 and 2) for reactions in thf and nitromethane, and in Table 4 for the other solvents. Typical errors in rate measurements were ±4%, but larger scatter was found for the reactions of (**1b**) in nitromethane due to the interference of the second reaction. Second-order rate constants (Tables 5—7) are the averaged mean values of the runs carried out under the conditions specified in Table 4. The variations indicated in the Tables are standard deviations of the derived rate constants.

Activation parameters were obtained by method (*b*), between 12 and 70 °C, in toluene.

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