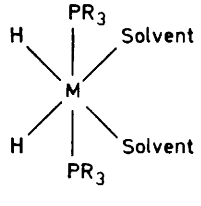
Rates and Activation Parameters for Solvent Exchange with $[M(PR_3)_2(solvent)_2H_2]^+$ ($M = Rh^{III}$ or Ir^{III}, R = cyclohexyl or phenyl) Cations

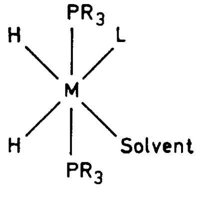
By **Oliver W. Howarth, Colin H. McAteer, Peter Moore,* and George E. Morris,** Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL

Using ^1H n.m.r. line-broadening and, where possible, stopped-flow Fourier-transform n.m.r., rates and activation parameters have been determined for solvent exchange with complexes of the type $[M(PR_3)_2(solvent)_2H_2]^+$ ($M = Rh^{III}$ or Ir^{III}; R = phenyl, solvent = MeCN or Me_2CO; R = cyclohexyl, solvent = MeCN) in $[^2H_2]$-dichloromethane solution. In all cases the co-ordinated solvent molecules are in *trans* positions with respect to the hydride ligands, and at 298 K the various complexes have rate constants for solvent exchange (k_1) which differ almost by a factor of 10^7; $k_1(Rh) > k_1(Ir)$ because for analogous species $\Delta H^‡(Rh) < \Delta H^‡(Ir)$, and the acetone solvates are much more labile than the acetonitrile complexes because of lower $\Delta H^‡$ values. Values of $\Delta S^‡$ are significantly positive (8—32 J K^{-1} mol^{-1} when $M = Rh^{III}$, 25—30 J K^{-1} mol^{-1} when $M = Ir^{III}$) in line with a dissociative, *D* mechanism. Hydrogen-1 n.m.r. spectra of $[M(PR_3)_2(solvent)_2H_2]^+$ and $[Ir(PR_3)_2(OCMe_2)(L)H_2]^+$ ions (L = MeOH, MeCN, pyridine, styrene, or cyclo-octene) are reported and compared.

CATIONS of the type $[M(PR_3)_2(solvent)_2H_2]^+$ ($M = Rh^{III}$ or Ir^{III}; R = alkyl or aryl) having structure (A) are known to be catalysts for the hydrogenation of alkenes, alkynes, and ketones,[1-3] and for the isomerisation [4] and hydroformylation [5] of alkenes. Recently their potential for the activation of C–H bonds in alkanes (*e.g.* cyclo-octane) [6] or unsaturated rings (*e.g.* cyclopentadienyl) [7] has also been demonstrated.



(A)



(B)

Since a primary step in all of these catalytic processes is substrate binding, and because this is expected to be related to the rate of solvent exchange, in this study we have measured the rates and activation parameters for solvent exchange when the solvent is a weakly co-ordinating ligand (acetone), and a more strongly bound solvent molecule (acetonitrile). The effect of changing the R groups of the non-exchanging phosphine ligands from phenyl to the bulkier cyclohexyl has also been investigated for both rhodium(III) and iridium(III) complexes with the solvent MeCN.

Recently we have shown how stopped-flow Fourier-transform n.m.r. can be used to obtain the rates of solvent exchange for moderately labile metal ions by following the release of co-ordinated proteo-solvent molecules after mixing metal solvates with an excess of the same deuteriated solvent.[8,9] This direct approach markedly extends the temperature range over which rates of such processes can be measured, and by combining the results with conventional n.m.r. line-broadening studies at higher temperatures, it is often possible to measure rates over a temperature range of more than 100 K. In this way more accurate activation parameters can be obtained, and the values of $\Delta S^‡$ are significantly more reliable than results obtained from line-broadening studies alone. It was possible to apply stopped-flow Fourier-transform n.m.r. to most of the acetonitrile solvates studied here, but the acetone complexes were too labile and could only be investigated by the line-broadening method.

RESULTS

Synthesis and Hydrogen-1 *N.M.R. Spectra.*—The solvates $[M(PPh_3)_2(OCMe_2)_2H_2][PF_6]$ (1a, M = Ir; 2a, M = Rh) were prepared by hydrogenation of $[M(PPh_3)_2(cod)][PF_6]$ (cod = cyclo-octa-1,5-diene) in acetone as described by Schrock and Osborn.[1] They generally crystallise with approximately one molecule of lattice acetone as shown by integration of 220 or 90 MHz ^1H n.m.r. spectra of solutions in $[^2H_2]$dichloromethane (co-ordinated acetone at $\delta = 1.41$ p.p.m., free acetone at $\delta = 2.16$ p.p.m.). The corresponding bis(acetonitrile) solvates [(1b),(2b)] were obtained without lattice solvent molecules by adding a slight excess of acetonitrile to the respective acetone solution of (1a) or (2a) followed by precipitation with hexane. The tricyclohexylphosphine $[P(C_6H_{11})_3]$ complexes [(1c),(2c)] were prepared by hydrogenation of $[M(cod)_2][PF_6]$ in acetone in the presence of two moles of $P(C_6H_{11})_3$ followed by recrystallisation in the presence of acetonitrile.

The purity of the complexes was confirmed by ^1H n.m.r. and the spectra were also consistent with the previously proposed structure (A) in all cases. For the PPh_3 complexes, the methyl resonance of the co-ordinated solvent molecules is generally *ca.* 0.4—0.8 p.p.m. upfield of the unco-ordinated solvent methyl resonance, whereas in the $P(C_6H_{11})_3$ complexes, the free and bound solvent resonances are in the reverse order and separated by *ca.* 0.35 p.p.m. Presumably the ring currents of the phenyl groups in $[M(PPh_3)_2(solvent)_2H_2]^+$ ions cause the shift of the co-ordinated solvent methyl resonance to high field.

Further evidence for the structure (A) was provided by mixing (1a) with other ligands, L, in $[^2H_2]$dichloromethane solution. The ^1H n.m.r. data (Table 1) indicate the presence of mixed species of structure (B). At temperatures below 253 K, the high-field hydride region consists of two resonances of equal area, each being a doublet of triplets due to coupling with two equivalent phosphorus atoms

TABLE 1

Hydrogen-1 n.m.r. shifts and coupling constants of the hydride resonances of $[M(PR_3)_2L(solvent)H_2]^+$ ions in $[^2H_2]$dichloromethane solution at 243 K

	M	R	Solvent	L	$\delta(H_{solv.})$ [a]/ p.p.m.	^2J(P–H)/ Hz	$\delta(H_L)$ [b]/ p.p.m.	^2J(P–H)/ Hz	^2J(H–H)/ Hz	^1J(Rh–H)/ Hz	Conditions
(1a)	Ir	Ph	Me_2CO	Me_2CO	−27.6	15.4					*c*
	Ir	Ph	MeOH	MeOH	−29.6	19.0					*c*
(1b)	Ir	Ph	MeCN	MeCN	−20.5	16.2					*c*
	Ir	Ph	py	py	−21.4	17.0					*c*
	Ir	Ph	Me_2CO	MeOH	−27.1	15.0	−29.4	18.0	8		*c*, *d*
	Ir	Ph	Me_2CO	MeCN	−27.3	15.0	−20.4	17.0	8		*c*, *e*
	Ir	Ph	Me_2CO	py	−27.5	15.0	−21.2	19.0	8		*c*, *e*
	Ir	Ph	Me_2CO	Styrene	−29.5	16.5	−11.5	19.3	6.6		*c*, *d*
	Ir	Ph	Me_2CO	Cyclooctene	−30.1	17.0	−12.3	19.2	6.6		*c*, *d*
(1c)	Ir	C_6H_{11}	MeCN	MeCN	−22.2	14.8					*c*
(2a)	Rh	Ph	Me_2CO	Me_2CO	−20.2	15.0				26.0	*c*
(2b)	Rh	Ph	MeCN	MeCN	−16.9	12.6				16.5	*c*
(2c)	Rh	C_6H_{11}	MeCN	MeCN	−18.9	13.4				17.6	*c*

[a] Hydride in a *trans* position with respect to solvent. [b] Hydride in a *trans* position with respect to ligand L. [c] [M] = *ca.* 5×10^{-2} mol dm^{-3}. [d] Equilibrium with acetone more strongly bound, 5—10-fold excess of L. [e] (1a) with one equivalent of L.

TABLE 2

Rates of exchange of a single solvent molecule from $[M(PR_3)_2(solvent)_2H_2]^+$ ions of structure (A)

(*a*) $[Ir(PPh_3)_2(OCMe_2)_2H_2]^+$, (1a) [a]						
T/K	263.5	274.2	278.9	284.5		
$k_{ex.}{}^{I}/s^{-1}$	9.60 ± 0.09	33.14 ± 0.14	59.67 ± 0.65	106.4 ± 0.3		
T/K	295.1	299.7	304.3			
$k_{ex.}{}^{I}/s^{-1}$	287.9 ± 0.8	448.8 ± 1.7	696.2 ± 4.6			
(*b*) $[Ir(PPh_3)_2(NCMe)_2H_2]^+$, (1b)						
T/K	269.2	278.7	288.6	298.3		*b*
$10^5k_{ex.}{}^{I}/s^{-1}$	3.91 ± 0.08	18.59 ± 0.43	82.1 ± 1.8	628.7 ± 22.2		
T/K	370.8	381.0	391.3			*a*
$k_{ex.}{}^{I}/s^{-1}$	5.83 ± 0.02	19.56 ± 0.05	45.40 ± 0.20			
(*c*) $[Rh(PPh_3)_2(OCMe_2)_2H_2]^+$, (2a) [a]						
T/K	219.9	231.2	236.8	241.9	247.3	
$k_{ex.}{}^{I}/s^{-1}$	7.18 ± 0.36	22.12 ± 0.50	39.98 ± 0.16	64.75 ± 0.29	124.9 ± 0.9	
T/K	252.5	263.3	274.0	284.5		
$k_{ex.}{}^{I}/s^{-1}$	247.1 ± 1.3	855.9 ± 4.9	2 166.5 ± 60.4	5 584 ± 385		
(*d*) $[Rh(PPh_3)_2(NCMe)_2H_2]^+$, (2b)						
T/K	232.6	243.0	253.4	263.5		*b*
$10^3k_{ex.}{}^{I}/s^{-1}$	1.29 ± 0.04	6.99 ± 0.11	37.2 ± 1.1	135 ± 4		
T/K	288.8	299.4	309.3	320.0		*a*
$k_{ex.}{}^{I}/s^{-1}$	5.39 ± 0.11	12.4 ± 0.1	32.36 ± 0.03	86.4 ± 0.4		
T/K	330.5	340.7				*a*
$k_{ex.}{}^{I}/s^{-1}$	235.7 ± 0.5	558.5 ± 3.6				
(*e*) $[Ir\{P(C_6H_{11})_3\}_2(NCMe)_2H_2]^+$, (1c)						
T/K	254.2	264.4	274.7	284.4		*b*
$10^3k_{ex.}{}^{I}/s^{-1}$	3.25 ± 0.21	15.4 ± 0.5	59.6 ± 1.8	216.1 ± 18.3		
T/K	350.8	360.6	370.1			*a*
$k_{ex.}{}^{I}/s^{-1}$	157.0 ± 2.8	380.0 ± 11.1	659.5 ± 25.5			
(*f*) $[Rh\{P(C_6H_{11})_3\}_2(NCMe)_2H_2]^+$, (2c) [a]						
T/K	253.9	264.1				
$k_{ex.}{}^{I}/s^{-1}$	9.81 ± 0.6	18.6 ± 0.6				
T/K	284.7	295.2	304.0	314.7		
$k_{ex.}{}^{I}/s^{-1}$	166.1 ± 3.6	489.9 ± 17.7	987 ± 33	1 754 ± 70		

[a] Hydrogen-1 n.m.r. line broadening studies. [b] Stopped-flow Fourier-transform ^1H n.m.r.

TABLE 3

Rates and activation parameters at 298.2 K for the exchange of a single solvent molecule from $[M(PR_3)_2(solvent)_2H_2]^+$ ions of structure (A)

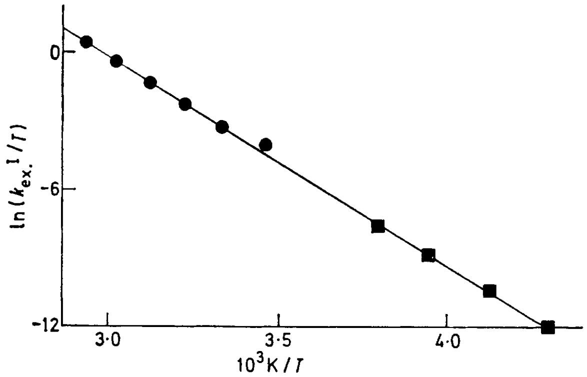
Complex	M	PR_3	Solvent	$k_{ex.}{}^{I}/s^{-1}$ *	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	T range/K
(1a)	Ir	PPh_3	Me_2CO	395 ± 7	67.3 ± 0.7	30.4 ± 2.3	41
(1b)	Ir	PPh_3	MeCN	(3.34 ± 0.46) × 10^{-3}	95.6 ± 2.3	28.2 ± 7.1	122
(1c)	Ir	$P(C_6H_{11})_3$	MeCN	1.05 ± 0.03	80.3 ± 0.4	24.7 ± 1.2	116
(2a)	Rh	PPh_3	Me_2CO	(1.95 ± 0.27) × 10^4	57.6 ± 1.6	30.4 ± 6.5	65
(2b)	Rh	PPh_3	MeCN	10.24 ± 0.13	76.7 ± 0.6	31.7 ± 1.8	108
(2c)	Rh	$P(C_6H_{11})_3$	MeCN	552 ± 43	59.9 ± 2.6	8.3 ± 9.0	61

* $k_{ex.}{}^{I} = k_1$ (Scheme).

($^2J_{PH}$ *cis* in the range 15—20 Hz) and between inequivalent hydrides ($^2J_{HH}$ *cis*,5—8 Hz) which is only consistent with the structure shown. Furthermore, as would be expected, the chemical shifts of the hydride resonances show a very strong dependence on the nature of the *trans* ligand. When one equivalent of a strongly complexing ligand L, such as pyridine (py) or acetonitrile, is added to a solution of (1a), only the mixed species is observed, while complete displacement of acetone occurs with two equivalents of L. However, with weakly co-ordinating monoenes such as styrene and cyclo-octene, temperature-dependent equilibria are observed between (1a) and the mixed species (B), even in the presence of a ten-fold excess of monoene, and no bis(monoene) complex could be detected. In addition, on mixing equimolar amounts of (1a) with either (1b) or [Ir$(PPh_3)_2(py)_2H_2]^+$, disproportionation occurs and eventually only the mixed species (B) are observed.

Also, it is of interest to note that the $^2J_{HH}$ *cis* coupling in the mixed species (B) is eventually lost as the temperature increases above 253 K, due to acetone exchange ' averaging out ' both L and solvent sites on the metal.

Kinetics.—Hydrogen-1 n.m.r. line-broadening studies of the solvent-exchange processes in [$^2H_2$]dichloromethane solution were carried out by monitoring the solvent methyl resonances as a function of temperature. Concentrations of complex of *ca*. 5×10^{-2} mol dm^{-3} were used with the free solvent concentration adjusted so that the populations of free and bound solvent were approximately equal, as shown by the ^{1}H n.m.r. spectra in the slow-exchange limit. A complete line-shape analysis of the exchange-broadened spectra was carried out with a modified version [8] of the nonlinear least-squares program described previously.[10] A small variation of the chemical-shift separation, $\delta\omega$, with temperature was allowed for as in our previous studies.[8] The rate constants for the exchange of a single solvent molecule, $k_{ex.}{}^{I}$, were calculated from the equation $k_{ex.}{}^{I} = P_a/\tau$, where P_a is the fractional population of the free solvent resonance ($P_a + P_b = 1$, where P_b is the fractional population of the bound solvent resonance), and τ is the estimated relaxation time.[11] The results are collected in Table 2.



Eyring plot for $[Rh(PPh_3)_2(NCMe)_2H_2]^+$ ion. Line-broadening data (●), stopped-flow n.m.r. data (■)

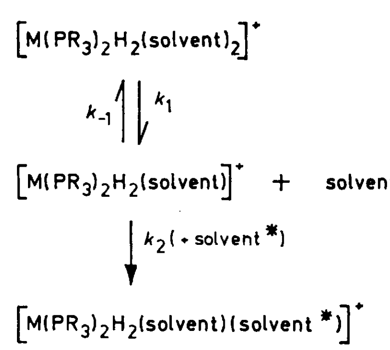
Whenever possible the results were extended to lower temperatures using stopped-flow Fourier-transform n.m.r. as described previously.[8,9,12] This was possible for all of the $[M(PR_3)_2(NCMe)_2H_2]^+$ ions except (2c). The results are collected with those from the line-broadening studies in Table 2. Where both stopped-flow Fourier-transform n.m.r. and n.m.r. line-broadening studies were possible, data were obtained over a temperature range of $\geqslant$108 K, and values of $\Delta S^{\ddagger}$ are usually more reliable in these cases.

Activation parameters were calculated from the data in Table 2 using a weighted linear least-squares analysis from a plot of ln($k_{ex.}{}^{I}/T$) against ($1/T$). The results, with standard deviations, are shown in Table 3. Very good agreement was observed between the data obtained by stopped-flow Fourier-transform n.m.r. and n.m.r. line-broadening, as shown by a typical Eyring plot in the Figure.

DISCUSSION

Rhodium(III) and iridium(III) complexes are often very inert because of the $t_{2g}{}^6$ electronic configurations of the metal ions, and their high effective nuclear charge, both of which contribute to the very high activation energies for ligand exchange. Previous studies of solvent exchange with $[Rh(NH_3)_5(solvent)]^{3+}$ ions [solvent = H_2O or dimethylformamide (dmf)] have indicated a degree of associativity in their substitution reactions. For example, values of $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$ are somewhat negative in line with an I_a mechanism for solvent exchange.[13-17] In contrast, the $[Rh(OH_2)_6]^{3+}$ ion is believed to anate with a dissociative mechanism.[18]

There have been no systematic studies of solvent-exchange processes at Rh^{III} and Ir^{III} centres analogous to those investigated here. The rates observed are very much greater than those found for classical co-ordination compounds of the type studied previously.[13-18] This is understandable because of the presence of the hydride ions in *trans* positions to the exchanging solvent molecules as well as the presence of the bulky *cis* phosphine molecules, and the low overall charge. The most labile solvate studied, $[Rh(PPh_3)_2(OCMe_2)_2H_2]^+$ is a factor of 10^{10} more labile at 298 K than a complex such as $[Rh(NH_3)_5(dmf)]^{3+}$ for which $10^6 k_{ex.}{}^{I} = 2.44$ s^{-1}, $\Delta H^{\ddagger} =$ 99 kJ mol^{-1}, $\Delta S^{\ddagger} = -20$ J K^{-1} mol^{-1}.[15] This remarkably increased reactivity is seen to arise from a large decrease in $\Delta H^{\ddagger}$ (to 58 kJ mol^{-1}) and a marked increase in $\Delta S^{\ddagger}$ (to +30 J K^{-1} mol^{-1}). Values of $\Delta S^{\ddagger}$ are significantly positive for all of the systems studied, in line with a dissociative, *D* mechanism (Scheme, M = Rh or Ir; k_1 = rate constant for solvent exchange). In support of this mechanism we have observed rate-law retardation by added acetone during the reaction of $[Ir(PPh_3)_2(OCMe_2)_2H_2]^+$ ion with 1,10-phenanthroline (phen) in



SCHEME

dichloromethane solution: $d\{\ln[Ir(PPh_3)_2(phen)H_2^+]\}/dt = k_1k_2[phen]/(k_{-1}[solvent] + k_2[phen])$ (Scheme with phen replacing solvent*; $k_2/k_{-1} = 6.2 \pm 0.2$ at 280.2 K).

A good *trans*-labilising ligand is often present in systems found to react with a *D* mechanism, for example, *S*-bonded sulphite ion in *trans*-$[Co(NH_3)_4(SO_3)L]^+$ (L = unidentate leaving group), and CN^- ion in $[Co(CN)_5L]^{2-}$ ions.[19,20] Iodide ion is known to have a *trans* effect in rhodium(III) complexes,[21] and there can be no doubt that hydride ions exert an even greater *trans*-labilising effect.

The complexes in this present investigation show a wide range of lability at 298 K, with the least reactive ion (1b) being a factor of 10^7 less labile than the most reactive ion (2a). Since values of $\Delta S^\ddagger$ in Table 3 are not too dissimilar, expecially if we disregard the rather imprecise value obtained for the ion (2c), then the considerable reactivity range can be seen to arise primarily from the differing $\Delta H^\ddagger$ values (58 to 96 kJ mol^{-1}). Further, as all ions studied are believed to undergo solvent exchange by a *D* mechanism, then the values of $\Delta H^\ddagger$ for this process can be expected to reflect the metal–solvent bond strength.

It can be seen from Table 3 that all of the iridium complexes are less labile than the analogous rhodium species, with $\Delta H^\ddagger$ being 10—20 kJ mol^{-1} larger in all cases. This behaviour also parallels that found in classical complexes such as $[M(NH_3)_5(OH_2)]^{3+}$ ions, where for water exchange, $\Delta H^\ddagger$ is 15 kJ mol^{-1} larger for M = Ir than for M = Rh.[13,14]

Major $\Delta H^\ddagger$ differences are evident in Table 3 between acetone and acetonitrile solvates of both metals (*ca.* 28 kJ mol^{-1}, M = Ir; 19 kJ mol^{-1}, M = Rh). The catalytically active acetone solvates are *ca.* 10^5 (Ir) and 2×10^3 (Rh) times as labile as their acetonitrile analogues at 298 K. This readily explains why the acetonitrile solvates show very little catalytic activity.

The experiments involving the mixing of (1a) with monoenes in $[^2H_2]$dichloromethane solution show that under such conditions acetone competes well with monoenes for the labile metal sites. However, with a similar molar excess of a chelating diene such as cycloocta-1,5-diene or bicyclo[2.2.1]hepta-2,5-diene, acetone is readily displaced to give initially a diene–dihydride species [equation (1), P atoms in *trans* positions].[22] This reacts smoothly in stages involving hydrogen transfers and a further diene molecule to give ultimately free monoene and the iridium(I)–diene complex [equation (2)]. This observation highlights a marked chelate effect in diene substrate binding, and the involvement of an excess of diene in the subsequent hydrogenation step.

$$(1a) + \text{diene} \longrightarrow [Ir(PPh_3)_2(\text{diene})H_2]^+ + 2Me_2CO \quad (1)$$

$$[Ir(PPh_3)_2(\text{diene})H_2]^+ + \text{diene} \longrightarrow cis\text{-}[Ir^I(PPh_3)_2(\text{diene})]^+ + \text{monoene} \quad (2)$$

Finally, we note that $[M\{P(C_6H_{11})_3\}_2(NCMe)_2H_2]^+$ ions show increased solvent lability compared with the PPh_3 counterparts, by a factor of *ca.* 10^2 (Rh) and 10^3 (Ir), due to a lowering of $\Delta H^\ddagger$ by 15—17 kJ mol^{-1}. However, with the present data, one cannot distinguish between steric and electronic effects, both of which are likely to contribute to this increased lability.

EXPERIMENTAL

Syntheses.—The complexes (1a), (1b), (2a), and (2b) were prepared by a method similar to that described previously,[1] and (1c), (2c) as described below.[23]

$[Ir(PPh_3)_2(acetone)_2H_2][PF_6]$ (1a). The complex $[Ir(PPh_3)_2(cod)][PF_6]$ (0.570 g, 0.56 mmol; cod = cyclo-octa-1,5-diene) in acetone (20 cm^3) was stirred under hydrogen at 1 atmosphere pressure and room temperature to give a colourless solution. The solution was concentrated under reduced pressure to a volume of *ca.* 5 cm^3 then light petroleum (b.p. 40—60 °C) added until the solution became turbid, readily depositing well formed colourless crystals on standing. The crystals were isolated, washed with light petroleum, and dried at room temperature *in vacuo*; yield 0.465 g (80%). The acetonitrile analogues were prepared in a similar manner with prior addition of acetonitrile (1 cm^3) to the initial acetone solution.

Preparation of $[Ir\{P(C_6H_{11})_3\}_2(NCMe)_2H_2][PF_6]$ (1c).—A solution of $[Ir(cod)_2][PF_6]$ (0.55 g) and $P(C_6H_{11})_3$ (0.56 g) in acetone (20 cm^3) was stirred at room temperature under hydrogen to give a pale yellow solution and a white precipitate. Light petroleum (20 cm^3) was added and the solution concentrated under reduced pressure to give an amorphous white solid (0.75 g). Hydrogen-1 n.m.r. and i.r. suggested that this contained significant quantities of $[Ir\{P(C_6H_{11})_3\}_2H_5]$.[2] The solid was dissolved in acetonitrile–ethanol (15 cm^3 : 1 cm^3) and triphenylcarbonium hexafluorophosphate (0.45 g) added to generate HPF_6 *in situ*, giving a colourless solution which was concentrated to a small volume under reduced pressure. Diethyl ether was added to give a microcrystalline precipitate which was recrystallised from CH_2Cl_2–light petroleum to give white crystals (0.45 g; 46%) (Found: C, 49.1; H, 7.55; N, 2.90. Calc. for $C_{40}H_{74}F_6IrN_2P_3$: C, 48.9; H, 7.60; N, 2.85%). The rhodium analogue (2c) was prepared in a similar manner, and in good yield, but addition of HPF_6 was not necessary since the intermediate $[Rh\{P(C_6H_{11})_3\}_2(OCMe_2)_2H_2][PF_6]$ appeared reasonably pure from ^1H n.m.r. and i.r. evidence (Found: C, 53.1; H, 8.15; N, 3.10. Calc. for $C_{40}H_{74}F_6N_2P_3Rh$: C, 53.8; H, 8.35, N, 3.15%).

Spectra.—90 MHz Bruker WH90 and 220 MHz Perkin-Elmer R34 spectrometers were used to obtain ^1H n.m.r. spectra. Flow n.m.r. spectra were recorded as described previously.[9] Line-broadening studies were carried out upon samples sealed *in vacuo* at 77 K in 5 mm n.m.r. tubes.

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