Isocyanide Complexes of Rhodium and Iridium. Part II.[1] Four- and Five-co-ordinate Complexes containing Tertiary Phosphines, and Some Oxidative Addition Reactions

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The synthesis of $[Rh(CNR)_2(PR'_3)_2][PF_6]$ (R′ = Ph, R = Me, Pr^i, or p-ClC_6H_4; $R'_3 = Ph_2Me$, R = Pr^i or p-ClC_6H_4), $[Rh(CNR)(PPh_2Me)_3][PF_6]$ (R = Pr^i or p-ClC_6H_4), $[M(CNR)_3(PR'_3)_2]X$ (M = Rh, X = PF_6, R = Pr^i, Bu^t, or p-ClC_6H_4; M = Ir, X = Cl, R = Pr^i, Bu^t, p-MeC_6H_4, or p-ClC_6H_4), $[Rh(CNR)_2(PR'_3)_3][PF_6]$ (R′ = Ph, R = Me or p-ClC_6H_4; $R'_3 = Ph_2Me$, R = Me, Pr^i, Bu^t, or p-ClC_6H_4), $[Ir(CO)(CNPr^i)_2(PPh_3)_2]Cl$, $[Rh(CNR)(CNR')_2(PPh_3)_2][PF_6]$ (R = Pr^i, R′ = p-ClC_6H_4; R = p-ClC_3H_4, R′ = Pr^i) and $[Rh(CNBu^t)_4(PPh_3)][PF_6]$, from $[M(CO)(PPh_3)_2Cl]$ (M = Rh or Ir), $[Rh(PPh_2Me)_3L][PF_6]$ (L = CO or PPh_2Me), or $[Rh(CNR)_4][PF_6]$, as precursors, is described. The hydrides, $[M(CNR)_3(PPh_3)_2H][PF_6]_2$ (M = Rh, R = Bu^t; M = Ir, R = Bu^t, p-MeC_6H_4 or p-ClC_6H_4) were obtained by protonation of $[M(CNR)_3(PPh_3)_2]^+$ using HPF_6. The complexes $\{[M(CNBu^t)_3(PPh_3)XY]Z\}_n$ (M = Rh; Z = PF_6; n = 1, X = Y = I; n = 2, X = PPh_3, Y = Cl, X = $CNBu^t$, Y = Me; M = Ir; Z = Cl, n = 1, X = PPh_3, Y = SO_2 or CS_2; Z = Cl, n = 2, X = PPh_3, Y = $SnPh_3$; Z = BPh_4, n = 2, X = PPh_3, Y = C_3H_5; Z = PF_6, n = 1, X = C_3H_5, Y = Cl, n = 2, X = PPh_3, Y = OMe), $[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_2Me)_2Cl_2][PF_6]$, $[Ir(CNPr^i)_2(PPh_3)_2XY]Cl$ (X = Cl, T = SnPh; X = I, Y = Me), $[Rh(CNBu^t)_3ClI_2]$, and $[Rh\{CN(p\text{-}ClC_6H_4)\}_2(C_2F_5)I_2]_2$ were prepared. The Rh^{II} complexes which are probably binuclear, *viz.*, $[Rh(CNBu^t)_3(PPh_3)I]_2[PF_6]_2$ and $[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_2Me)_2I]_2[PF_6]_2$, are also reported.

SOME structural analogies may be drawn between transition metal carbonyl and isocyanide complexes Thus $Ni(CO)_4$ and $Ni(CNR)_4$ are isostructural, and cobalt forms a series of isoelectronic cationic species $[Co(PPh_3)_2Q_3]^+$ (Q = CO [2] or CNR [3,4]). During our studies of rhodium and iridium isocyanide complexes [1] we noted that the co-ordinatively unsaturated species $[M(PPh_3)_2(CNR)_2]^+$ (M = Rh [5] or Ir) had no counterpart in cobalt chemistry, nor could we prepare such compounds. We also observed that, at that time, there were no rhodium or iridium analogues of $[Co(PPh_3)_2(CNR)_3]^+$, despite the fact that such species would be isoelectronic with the known $[Ir(PPh_3)_2(CO)_3]^+$.[6]

TABLE 1

Cationic isocyanide complexes of rhodium(I) or iridium(I) containing CO or tertiary phosphines, $[Mi_{4-n}L_n]^+$ or $[Mi_{5-n}L_n]^+$

Metal complex [a]	Isocyanide ligand substituent, CNR						
Type	R = Me	Pr^i	Bu^t	Ph	p-MeC_6H_4	p-$MeOC_6H_4$	p-ClC_6H_4
i_4 [b]	R, I	R	R, I	R	R	R	R, I
i_3L							
i_2L_2	R	R, R′		R [c]	R′ [d]		R,[d] R′
iL_3		R′					R′
i_4L	I [d]		R				
i_3L_2	R	R, I	R, I		I		R, I
i_2L_3	R, R′	R′, I″	R′				R, R′
iL_4	I–I [e]						

[a] R = Rh complex containing PPh_3; R′ = Rh complex containing PPh_2Me; I = Ir complex containing PPh_3; I″ = Ir complex containing CO and PPh_3; I–I; Ir complex containing $Ph_2PCH_2CH_2PPh_2$; i = isocyanide; L = tertiary phosphine or CO. [b] Ref. 1 and references therein. [c] Ref. 9. [d] Ref. 7. [e] Ref. 8.

During our investigation of routes to tetrakis(isocyanide) complexes of rhodium(I) and iridium(I), we found that while $[M(CO)(PPh_3)_2Cl]$ would indeed furnish $[M(CNR)_4]^+$ under appropriate conditions, mixed isocyanide–phosphine species, *e.g.* $[Rh(CNR)_2(PR'_3)_2]^+$ and $[M(CNR)_3(PR'_3)_2]^+$, could also be obtained. Accordingly, we began an investigation of the formation of five-co-ordinate isocyanide complexes of rhodium and iridium.

Like their carbonyl analogues, the new five-co-ordinate isocyanide complexes undergo a variety of oxidative addition reactions, and a report of some of these is given here. A preliminary account of our work has been presented.[7]

RESULTS AND DISCUSSION

The rhodium(I) and iridium(I) compounds prepared and described in this paper are summarised in Table 1 together with some related species reported by other workers.[5,8,9] All complexes were obtained as crystalline solids and, when ionic, were usually isolated as PF_6^- salts (some iridium complexes were obtained as Cl^- salts); all were satisfactorily characterised by elemental

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TABLE 2

Analytical, conductivity, and infrared data obtained from rhodium and iridium isocyanide complexes

	Elemental analyses									I.r. spectral data [a] ν(CN) stretching frequency	
	Found				Calc.						
Complex	C	H	N	X [b]	C	H	N	X [b]	Λ [a]	CH_2Cl_2 Soln.	KBr disc
$[Rh(CNMe)_2(PPh_3)_2][PF_6]$	55·1	4·7	3·7		56·2	4·2	3·3		87	2182s	
$[Rh(CNPr^i)_2(PPh_3)_2][PF_6]$	57·2	5·1	3·2		57·8	4·8	3·1		100	2164s	
$[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_3)_2][PF_6]$	57·1	4·0	2·7	7·2 [c]	57·5	3·8	2·8	6·8 [c]	78	2121s	
$[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_2Me)_2][PF_6]$	51·9	3·9	3·1	7·4 [c]	51·4	3·6	2·9	7·5 [c]	87	2115s	
$[Rh(CNPr^i)(PPh_2Me)_3][PF_6]$	55·1	5·0	1·9		56·3	5·0	1·5		83	2183s	
$[Rh\{CN(p\text{-}ClC_6H_4)\}(PPh_2Me)_3][PF_6]$	56·0	4·9	0·9	3·1 [c]	56·0	4·4	1·4	3·6 [c]	76	2152s	
$[Rh(CNPr^i)_3(PPh_3)_2][PF_6]$	58·3	4·7	4·3		58·8	5·2	4·3		85	2153s	
$[Rh(CNBu^t)_3(PPh_3)_2][PF_6]$	59·3	5·6	4·1		59·9	5·6	4·1		87	2184s, 2208s, 2228w	
$[Rh\{CN(p\text{-}ClC_6H_4)\}_3(PPh_3)_2][PF_6]$	57·6	4·0	3·7	9·1 [c]	57·7	3·6	3·6	9·0	89	2082sbr, 2121w, 2135w	
$[Ir(CNPr^i)_3(PPh_3)_2]Cl$	59·8	5·3	3·8	3·5 [c]	59·1	5·5	4·5	3·8 [c]	84		2112s, 2160w, 2190w
$[Ir(CNBu^t)_3(PPh_3)_2]Cl$	60·7	5·9	3·9	3·7 [c]	60·2	5·7	4·2	3·6	72		2110s, 2115w, 2190w
$[Ir\{CN(p\text{-}MeC_6H_4)\}_3(PPh_3)_2][PF_6]$	58·6	4·4	3·7		59·4	4·2	3·5		76		2020s, 2075w, 2085w
$[Ir\{CN(p\text{-}ClC_6H_4)\}_3(PPh_3)_2]Cl$	48·0	3·9	3·9	12·1 [c]	48·2	3·6	3·6	12·2	72		2020s, 2070m, 2090w
$[Ir(CO)(CNPr^i)_2(PPh_3)_2]Cl$	59·0	5·0	2·9	4·0 [c]	58·9	4·8	3·1	3·9	78		2150s, 2190m; 1920s [ν(CO)]
$[Rh(CNMe)_2(PPh_3)_3][PF_6]$	62·4	5·0	2·4		62·4	4·6	2·5		83	2175s, 2210sh	
$[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_3)_3][PF_6]$	61·9	4·5	2·2	5·7 [c]	62·3	4·0	2·1	5·4	87	2121s, 2137sh	
$[Rh(CNMe)_2(PPh_2Me)_3][PF_6]$	56·6	5·3	2·9		56·4	4·8	3·0		90	2169sbr, 2205sh	
$[Rh(CNPr^i)_2(PPh_2Me)_3][PF_6]$	57·0	5·5	2·5		57·6	5·2	2·8		85	2147sbr, 2030w	
$[Rh(CNBu^t)_2(PPh_2Me)_3][PF_6]$	58·0	5·9	2·7		58·0	5·6	2·7		85	2148sbr	
$[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_3Me)_3][PF_7]$	56·8	4·4	2·6	6·2 [c]	56·6	4·2	2·5	6·3	83	2108sbr, 2145sh	
$[Rh(CNBu^t)_4(PPh_3)][PF_6]$	54·1	6·1	6·0		54·2	6·1	6·7		81	2105sh, 2168s, 2212sh	
$[Rh(CNPr^i)_2\{CN(p\text{-}ClC_6H_4)\}(PPh_3)_2][PF_6]$	58·1	4·3	4·0	3·7 [c]	58·4	4·6	4·0	3·5 [c]	80	2072sbr, 2098sh, 2130sbr, 2151s, 2162sh, 2205w	
$[Rh(CNPr^i)\{CN(p\text{-}ClC_6H_4)\}_2(PPh_3)_2][PF_6]$	58·0	4·2	3·9	6·3 [c]	58·1	4·0	3·8	6·4 [c]	76	2080sbr, 2132m, 2150m	
$[Rh(CNBu^t)_3(PPh_3)_2H][PF_6]_2$	52·6	5·3	3·4		52·4	5·0	3·6		182		2220s, 2250sh
$[Ir(CNBu^t)_3(PPh_3)_2H][PF_6]_2$	53·8	5·4	3·4		53·7	5·1	3·7		186		2210s, 2250sh
$[Ir\{CN(p\text{-}MeC_6H_4)\}_3(PPh_3)_2H][PF_6]_2$	53·7	4·2	3·3		53·0	3·8	3·1		154		2180s
$[Ir\{CN(p\text{-}ClC_6H_4)\}_3(PPh_3)_2H][PF_6]_2$	48·3	2·8	2·8	7·1 [c]	48·2	3·0	3·0	7·5 [c]	160		2179s, 2208s
$[Rh(CNBu^t)_3(PPh_3)I_2][PF_6]_2$	40·7	4·1	4·1	26·6 [d]	39·1	4·1	4·2	25·1 [d]	*e*		2220s, 2250sh
$[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_3)_2I_2][PF_6]$	45·8	2·9	2·1	6·0 [c,f]	46·1	2·9	2·2	5·5 [c,f]	74		2200s, 2250w
$[Rh(CNBu^t)_3(PPh_3)_2Cl][PF_6]_2$	50·7	5·5	3·3	2·6 [c]	50·8	4·8	3·5	2·7 [c]	188		2200sbr, 2218sbr
$[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_2Me)_2Cl_2][PF_6]$	48·9	3·7	2·9	*e*	48·3	3·4	2·8	*e*	*e*		2220s
$[Rh(CNBu^t)_3I_2Cl]$	28·3	4·5	6·1	5·5 [c,g]	28·1	4·2	6·6	5·5 [c,g]	*h*		2230s
$[Rh(CNBu^t)_3(PPh_3)I]_2[PF_6]_2$	44·1	4·8	4·5	14·2 [d]	44·7	4·7	4·7	14·3 [d]	*g*		2240s
$[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_3)_2I_2][PF_6]_2$	51·2	3·9	2·5	6·1 [c,i]	51·1	3·2	2·4	7·0 [c,i]	82		2086s, 2208s
$[Rh(CNBu^t)_4(PPh_3)Me][PF_6]_2$	47·2	5·4	5·3		46·8	5·4	5·6		178		2226s
$[Ir(CNBu^t)_3(PPh_3)(Me)I]Cl$	46·8	4·9	4·6	*e*	46·3	5·1	4·8	*e*	75		2230s

TABLE 2 (*Continued*)

	Elemental analyses									I.r. spectral data [a] ν(CN) stretching frequency
	Found				Calc.					
Complex	C	H	N	X [b]	C	H	N	X [b]	Λ [a]	KBr disc
$[Ir(CNPr^i)_2(PPh_3)_2(Me)I]Cl$	52·3	4·9	2·5	*e*	52·4	4·6	2·7	*e*	87	2225s
$[Rh\{CN(p\text{-}ClC_6H_4)\}_2(C_2F_5)I_2]_2$	26·2	1·3	3·0	9·3 [c,j]	25·6	1·7	3·7	9·5 [c,j]	*h*	2002s [k]
$[Ir(CNBu^t)_3(PPh_3)_2(C_3H_5)][BPh_4]_2$	74·9	6·9	2·4		74·6	6·3	2·6		140	2219s
$[Ir(CNBu^t)_3(PPh_3)(C_3H_5)Cl][PF_6]$	46·2	4·9	4·8	3·4 [c]	46·6	5·3	4·5	3·8 [c]	76	2235s
$[Ir(CNBu^t)_3(PPh_3)_2(SnPh_3)]Cl_2$	59·7	5·6	2·9	5·3 [c]	59·8	5·2	3·0	5·1 [c]	151	2219s
$[Ir(CNBu^t)_2(PPh_3)_2(SnPh_3)Cl]Cl$	59·0	5·1	2·0	5·1 [c]	59·0	4·8	2·2	5·5 [c]	80	2230s
$[Ir(CNBu^t)_3(PPh_3)_2(CS_2)]Cl$ [l]	58·5	5·6	4·2	3·0 [c]	58·0	5·3	3·9	3·3 [c]	89	2235s
$[Ir(CNBu^t)_3(PPh_3)_2(SO_2)]Cl$ [m]	57·0	5·5	3·9	3·9 [c]	44·5	5·4	4·0	3·3 [c]	75	2200sh, 2240s
$[Ir(CNBu^t)_3(PPh_3)_2(OMe)][PF_6]_2$	48·7	5·0	3·6		48·5	4·7	3·3		151	2220s

[a] Conductivity measurements in Ω^{-1} cm^2 mol^{-1} on 10^{-4}M-$MeNO_2$ solutions. Infrared data in cm^{-1}, other frequencies listed where appropriate. [b] Halogen analysis, as specified. [c] Cl Analysis. [d] Iodine analysis. [e] Not determined. [f] I analysis: found 21·6, calc. 19·5%. [g] I analysis: found 39·2, calc. 39·6%. [h] Non-electrolyte. [i] I Analysis: found 12·5, calc. 10·8%. [j] I Analysis: found: 33·1, calc. 33·8%. [k] ν(CF): 1300m, 1200mbr, 1180m, 1150mbr, 918m cm^{-1}. [l] S Analvsis: found 2·8, calc. 3·0%. [m] S Analysis: found 6·0, calc. 5·9%.

TABLE 3

^{1}H N.m.r. spectral data obtained from rhodium and iridium isocyanide complexes

Complex [a]	Solvent	τ	Relative area	Assignments and remarks
$[Rh(CNMe)_2(PPh_3)_2][PF_6]$	$CDCl_3$	2·70	10	(m) $P(C_6\mathit{H}_5)_3$
		7·61	1	(s) } $C\mathit{H}_3NC$
		7·81	1	(s)
$[Rh(CNPr^i)_2(PPh_3)_2][PF_6]$	$CDCl_3$	2·53	15	(m) $P(C_6\mathit{H}_5)_3$
		6·90	1	(m) $Me_2C\mathit{H}NC$
		9·47	6	(d) $(C\mathit{H}_3)_2CHNC$; *J*(HH) 7·0 Hz
$[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_3)_2][PF_6]$	$(CD_3)_2CO$	2·33	15	(m) $P(C_6\mathit{H}_5)_3$
		3·20	4	(dd) A_2B_2 pair; $ClC_6\mathit{H}_4NC$; *J*(AB) 8·5 Hz
$[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_2Me)_2][PF_6]$	$CDCl_3$	2·60	10	(m) br ($W_{\frac{1}{2}}$ 35 Hz); $P(C_6\mathit{H}_5)_2Me$
		3·35	4	(dd) A_2B_2 pair; $ClC_6\mathit{H}_4NC$; *J*(AB) 8·4 Hz
		7·86	3	(asym. t) $PPh_2(C\mathit{H}_3)$; *J*(PH) 4·0 Hz
$[Rh(CNPr^i)(PPh_2Me)_3][PF_6]$	$CDCl_3$	2·72	30	(m) $P(C_6\mathit{H}_5)_2Me$
		5·82	1	(sept) $Me_2C\mathit{H}NC$; *J*(HH) 7·0 Hz
		8·13	3	(d) $PPh_2(C\mathit{H}_3)$ *trans* to RNC; *J*(PH) 9·0 Hz
		8·36	6	(t) $PPh_2(C\mathit{H}_3)$ mutually *trans*; *J*(PH) 4·3 Hz
$[Rh\{CN(p\text{-}ClC_6H_4)\}(PPh_2Me)_3][PF_6]$	$(CD_3)_2CO$	2·50	16	(m) br ($W_{\frac{1}{2}}$ 28 Hz); overlapping signals due to $P(C_6\mathit{H}_5)_2Me$ are $ClC_6\mathit{H}_4NC$
		3·16	1	(d) part of A_2B_2 pair; $ClC_6\mathit{H}_5NC$; *J*(AB) 8·5 Hz
		8·18	3	(asymm. t) $PPh_2(C\mathit{H}_3)$
		Remainder of spectrum mixed with Me_2CO		
	$CDCl_3$	2·70	30	(m) br $P(C_6\mathit{H}_5)_2Me$
		3·22	4	(dd) A_2B_2 pair; $ClC_6\mathit{H}_4NC$; *J*(AB) 8·5 Hz
		8·05	3	(d) $PPh_2(C\mathit{H}_3)$ *trans* to RNC; *J*(PH) 8·9 Hz
		8·26	6	(asymm. t) $PPh_2(C\mathit{H}_3)$ mutually *trans*; *J*(PH) 4·5 Hz
$[Rh(CNPr^i)_3(PPh_3)_2][PF_6]$	$CDCl_3$	2·55	5	(m) $P(C_6H_5)_3$
		9·62	3	(d) $(C\mathit{H}_3)_2CHNC$; *J*(HH) 7·0 Hz
				Unique proton not resolved
$[Rh(CNBu^t)_3(PPh_3)_2][PF_6]$	$CDCl_3$	2·55	10	(m) $P(C_6\mathit{H}_5)_3$
		8·97	9	(s) $(C\mathit{H}_3)_3CNC$
$[Rh\{CN(p\text{-}MeC_6H_4)\}_3(PPh_3)_2][PF_6]$	$(CD_3)_2CO$	2·49	10	(s) $P(C_6\mathit{H}_5)_3$
		3·28	4	(dd) A_2B_2 pair; $MeC_6\mathit{H}_4NC$; *J*(AB) 8·0 Hz
		7·74	3	(s) $C\mathit{H}_3C_6H_4NC$
$[Ir(CNPr^i)_3(PPh_3)_2]Cl$	$(CD_3)_2CO$	2·60	10	(m) $P(C_6\mathit{H}_5)_3$
		7·10	1	(m) $Me_2C\mathit{H}NC$
		9·00	6	(d) $(C\mathit{H}_3)_2CHNC$; *J*(HH) 6·0 Hz
$[Ir(CNBu^t)_3(PPh_3)_2]Cl$	$(CD_3)_2CO$	2·35	10	(m) $P(C_6\mathit{H}_5)_3$
		8·90	9	(s) $(C\mathit{H}_3)_3CNC$
$[Ir\{CN(p\text{-}MeC_6H_4)\}_3(PPh_3)_2]Cl$	$(CD_3)_2CO$	2·72	10	(m) $P(C_6\mathit{H}_5)_3$
		3·57	4	(dd) A_2B_2 pair; $MeC_6\mathit{H}_4NC$; *J*(AB) 8·0 Hz
		7·78	3	(s) $C\mathit{H}_3C_6H_4NC$
$[Ir\{CN(p\text{-}ClC_6H_4)\}_3(PPh_3)_2]Cl$	$(CD_3)_2CO$	2·44	10	(m) $P(C_6\mathit{H}_5)_3$
		3·35	4	(dd) A_2B_2 pair; $ClC_6\mathit{H}_4NC$; *J*(AB) 8·5 Hz
$[Ir(CO)(CNPr^i)_2(PPh_3)_2]Cl$	$(CD_3)_2CO$	2·46	15	(m) $P(C_6\mathit{H}_5)_3$
		6·40	1	(m) $Me_2C\mathit{H}NC$
		8·85	6	(d) $(C\mathit{H}_3)_2CHNC$; *J*(HH) 6·0 Hz
$[Rh(CNMe)_2(PPh)_{23}][PF_6]$	$CDCl_3$	2·70	15	$P(C_6\mathit{H}_5)_3$
		7·63	2	(s) $C\mathit{H}_3NC$
$[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_3)_3][PF_6]$	$(CD_3)_2CO$	2·44	45	(m) $P(C_6\mathit{H}_5)_3$
		3·22	8	(dd) A_2B_2 pair; $ClC_6\mathit{H}_4NC$; *J*(AB) 8·2 Hz

TABLE 3 (*Continued*)

Complex [a]	Solvent	τ	Relative area	Assignments and remarks
$\mathrm{[Rh(CNMe)_2(PPh_2Me)_3][PF_6]}$	$\mathrm{CDCl_3}$	2·62	10	(s) br ($W_{\frac{1}{2}}$ 8·0 Hz); $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_2Me}$
		7·23	2	(s) $\mathrm{C}\mathit{H}_3\mathrm{NC}$
		8·05	3	(s) br ($W_{\frac{1}{2}}$ 9·0 Hz); $\mathrm{PPh_2(C}\mathit{H}_3)$
$\mathrm{[Rh(CNPr^i)_2(PPh_2Me)_3][PF_6]}$	$\mathrm{CDCl_3}$	2·71	30	(s) $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_2Me}$
		6·63	2	(sept) $\mathrm{Me_2C}\mathit{H}\mathrm{NC}$; J(HH) 7·0 Hz
		8·14	9	(s) br ($W_{\frac{1}{2}}$ 7·0 Hz); $\mathrm{PPh_2(C}\mathit{H}_3)$
		9·31	12	(d) $\mathrm{(C}\mathit{H}_3\mathrm{)_2CHNC}$; J(HH) 7·0 Hz
$\mathrm{[Rh(CNBu^t)_2(PPh_2Me)_3][PF_6]}$	$\mathrm{CDCl_3}$	2·66	10	(m) $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_2Me}$
		8·06	3	(s) br ($W_{\frac{1}{2}}$ 7·0 Hz); $\mathrm{PPh_2(C}\mathit{H}_3)$
		9·19	6	(s) $\mathrm{(C}\mathit{H}_3\mathrm{)_3CNC}$
$\mathrm{[Rh\{CN(\mathit{p}\text{-}ClC_6H_4)\}_2(PPh_2Me)_3][PF_6]}$	$\mathrm{(CD_3)_2CO}$	2·60	34	(m) br overlapping signals of $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_2Me}$ and $\mathrm{ClC_6}\mathit{H}_4\mathrm{NC}$
		3·45	4	(d) part of $\mathrm{A_2B_2}$ pair; $\mathrm{ClC_6}\mathit{H}_4\mathrm{NC}$; J(AB) 8·5 Hz
		7·86	9	(s) br $\mathrm{PPh_2(C}\mathit{H}_3)$
$\mathrm{[Rh\{CN(Bu^t)\}_4(PPh_3)][PF_6]}$	$\mathrm{CDCl_3}$	2·60	5	(m) $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_3}$
		8·66	12	(s) $\mathrm{(CH_3)_3CNC}$
$\mathrm{[Rh(CNPr^i)\{CN(\mathit{p}\text{-}ClC_6H_4)\}_2(PPh_3)_2][PF_6]}$	$\mathrm{CDCl_3}$	2·49	15	(m) $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_3}$
		3·30	4	(dd) $\mathrm{A_2B_2}$ multiplet; $\mathrm{ClC_6}\mathit{H}_4\mathrm{NC}$; J(AB) 8·0 Hz
		9·08	3	(d) $\mathrm{(C}\mathit{H}_3\mathrm{)_2CHNC}$; J(HH) 7·0 Hz
				Unique proton not resolved
$\mathrm{[Rh(CNPr^i)_2\{CN(\mathit{p}\text{-}ClC_6H_4)\}(PPh_3)_2][PF_6]}$	$\mathrm{CDCl_3}$	2·63	15	(m) $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_3}$
		3·41	2	(dd) $\mathrm{A_2B_2}$ multiplet; $\mathrm{ClC_6}\mathit{H}_4\mathrm{NC}$; J(AB) 8·2 Hz
		6·40	1	(sept) $\mathrm{Me_2C}\mathit{H}\mathrm{NC}$; J(HH) 7·0 Hz
		9·17	6	(d) $\mathrm{(C}\mathit{H}_3\mathrm{)_2CHNC}$; J(HH) 7·0 Hz
$\mathrm{[Rh(CNBu^t)_3(PPh_3)_2H][PF_6]_2}$	$\mathrm{(CD_3)_2CO}$	2·54	10	(m) $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_3}$
		9·04	9	(s) $\mathrm{(C}\mathit{H}_3\mathrm{)_3CNC}$
				Hydride resonance not resolved
$\mathrm{[Ir(CNBu^t)_3(PPh_3)_2H][PF_6]_2}$	$\mathrm{(CD_3)_2CO}$	2·40	30	(m) $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_3}$
		8·54	27	(s) $\mathrm{(C}\mathit{H}_3\mathrm{)_3CNC}$
		20·90	1	(c) Ir-H; J(PH) 11·0 Hz
$\mathrm{[Ir\{CN(\mathit{p}\text{-}MeC_6H_4)\}_3(PPh_3)_2H][PF_6]_2}$	$\mathrm{(CD_3)_2CO}$	2·32	30	(m) $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_3}$
		2·79	4	(dd) $\mathrm{A_2B_2}$ multiplet; $\mathrm{MeC_6}\mathit{H}_4\mathrm{NC}$; J(AB) 8·0 Hz; RNC *trans* to H
		3·36	8	(dd) $\mathrm{A_2B_2}$ multiplet; $\mathrm{MeC_6}\mathit{H}_4\mathrm{NC}$; J(AB) 8·0 Hz
		7·67	9	(s) $\mathrm{C}\mathit{H}_3\mathrm{C_6H_4NC}$
		27·04	1	(t) Ir-H; J(PH) 11·0 Hz
$\mathrm{[Ir\{CN(\mathit{p}\text{-}ClC_6H_4)\}_3(PPh_3)_2H][PF_6]_2}$	$\mathrm{(CD_3)_2CO}$	2·30	30	(m) br $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_3}$
		2·74	4	(dd) $\mathrm{A_2B_2}$ multiplet; $\mathrm{ClC_6}\mathit{H}_4\mathrm{NC}$; J(AB) 4·0 Hz; RNC *trans* to H
		2·92	8	(dd) $\mathrm{A_2B_2}$ multiplet; $\mathrm{ClC_6}\mathit{H}_4\mathrm{NC}$; J(AB) 9·0 Hz
		19·71	1	(t) Ir-H; J(PH) 10·0 Hz
$\mathrm{[Rh(CNBu^t)_3(PPh_3)I_2][PF_6]}$	$\mathrm{(CD_3)_2CO}$	2·40	5	(m) $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_3}$
		8·54	6	(s) $\mathrm{(C}\mathit{H}_3\mathrm{)_3CNC}$; *cis* to $\mathrm{PPh_3}$
		8·64	3	(s) $\mathrm{(C}\mathit{H}_3\mathrm{)_3CNC}$; *trans* to $\mathrm{PPh_3}$
$\mathrm{[Rh(CNBu^t)_3(PPh_3)I_2][PF_6]_2}$	$\mathrm{(CD_3)_2CO}$	2·18	5	(m) $\mathrm{P(C_6H_5)_3}$
		8·48	9	(s) $\mathrm{(CH_3)_3CNC}$
$\mathrm{[Rh(CNBu^t)_3(PPh_3)_2Cl][PF_6]_2}$	$\mathrm{(CD_3)_2CO}$	2·58	10	(m) $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_3}$
		9·05	9	(m) $\mathrm{(C}\mathit{H}_3\mathrm{)_3CNC}$
$\mathrm{[Rh(CNBu^t)_4(PPh_3)(Me)][PF_6]_2}$	$\mathrm{CDCl_3}$	2·55	5	(m) $\mathrm{P(C_6H_5)_3}$
		9·01	12	(s) br $\mathrm{(C}\mathit{H}_3\mathrm{)_3CNC}$
		9·22	1	(dd) Rh-CH_3; J(PH) 5·0 Hz; J(RhH) 2·0 Hz
$\mathrm{[Ir(CNPr^i)_2(PPh_3)_2(Me)I]Cl}$	$\mathrm{(CD_3)_2CO}$	2·27	30	(m) $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_3}$
		6·30	2	(m) $\mathrm{Me_2C}\mathit{H}\mathrm{NC}$
		8·92	12	(d) $\mathrm{(C}\mathit{H}_3\mathrm{)_2CHNC}$; J(HH) 6·5 Hz
		9·00	3	(d) Ir-CH_3; J(PH) 2·1 Hz
$\mathrm{[Ir(CNBu^t)_3(PPh_3)(Me)I]Cl}$	$\mathrm{(CD_3)_2CO}$	2·35	5	(m) $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_3}$
		8·49	9	(s) $\mathrm{(CH_3)_3CNC}$
		8·94	1	(d) Ir-CH_3; J(PH) 5·0 Hz
$\mathrm{[Ir(CNPr^i)_3(PPh_3)_2(SnPh_3)]Cl_2}$	$\mathrm{(CD_3)_2CO}$	2·40	45	(m) $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_3}$ and $\mathrm{Sn(C_6}\mathit{H}_5\mathrm{)_3}$
		6·50	2	(m) $\mathrm{Me_2C}\mathit{H}\mathrm{NC}$
		8·90	12	(d) $\mathrm{(C}\mathit{H}_3\mathrm{)_3CHNC}$; J(HH) 6·0 Hz
$\mathrm{[Ir(CNBu^t)_2(PPh_3)_2(SnPh_3)Cl]Cl}$	$\mathrm{(CD_3)_2CO}$	2·50	5	(m) $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_3}$ and $\mathrm{Sn(C_6}\mathit{H}_5\mathrm{)_3}$
		2·65	2	(m) $\mathrm{Me_2C}\mathit{H}\mathrm{NC}$
		8·70	3	(s) $\mathrm{(C}\mathit{H}_3\mathrm{)_2CNC}$
$\mathrm{[Ir(CNBu^t)_3(PPh_3)_2(CS_3)]Cl}$	$\mathrm{(CD_3)_2CO}$	2·30	10	(m) $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_3}$
		8·70	9	(s) $\mathrm{(C}\mathit{H}_3\mathrm{)_3CNC}$
$\mathrm{[Ir(CNBu^t)_3(PPh_3)_2(SO_2)]}$	$\mathrm{(CD_3)_2CO}$	2·40	10	(m) $\mathrm{P(C_6}\mathit{H}_5\mathrm{)_3}$
		8·72	9	(s) $\mathrm{(C}\mathit{H}_3\mathrm{)_3CNC}$

analyses, conductivity, and i.r. measurements (Table 2). ^{1}H N.m.r. spectral data obtained from these complexes are collected in Table 3.

Rhodium and Iridium(I) *Complexes.*

Four Co-ordinate Complexes, $[Rh(CNR)_2(PR'_3)_2]^+$ *and* $[Rh(CNR)(PR'_3)_3]^+$.—When we began our work, the only known cationic mixed isocyanide–phosphine complexes were $[Rh(CNR)_2L_2]X$ (R = Ph or *p*-MeOC$_6$H$_4$; L = PPh$_3$, ArPh$_3$, SbPh$_3$, or P(OPh)$_3$; X = Cl, Br, I, or ClO$_4$). These had been obtained by reaction[5] of $[Rh(CO)_2Cl]_2$ with CNR [which gave Rh(CO)(CNR)$_2$Cl] followed by L.

The four-co-ordinate complexes described herein were prepared by addition of CNR to [Rh(CO)(PPh$_3$)$_2$Cl] or its PPh$_2$Me analogue (2 : 1 molar ratio) in methanol or acetone at room temperature. The preparations of [Rh{CN(*p*-MeC$_6$H$_4$)}$_2$(PPh$_2$Me)$_2$][BPh$_4$] and [Rh{CN(*p*-ClC$_6$H$_4$)}$_2$(PPh$_3$)$_2$]X, X = Cl or BPh$_4$, using a literature method,[5] have recently been described.[8] However, with *t*-butyl isocyanide, the five-co-ordinate complex [Rh(CNBu^t)$_3$(PPh$_3$)$_2$]$^+$ was produced, in acetone, methanol, or dichloromethane, regardless of reaction stoicheiometries. However, [Rh(CNBu^t)$_2$ (PPh$_3$)$_2$]Cl has apparently been obtained[10] by reaction of [Rh(PPh$_3$)^{3}Cl] with CNBu^t in benzene. Despite many attempts, we were unable to obtain pure four-co-ordinate mixed isocyanide–phosphine complexes of iridium using [Ir(CO)(PPh$_3$)$_2$Cl] as a precursor. The species most easily obtained (and these were very sensitive towards oxidation) were either pure isocyanide complexes, *e.g.* [Ir(CNR)$_4$]$^+$ (R = Me,[9] Bu^t,[1] or *p*-ClC$_6$H$_4$ [1]) or [Ir(CNR)$_3$(PPh$_3$)$_2$]$^+$ (R = Pr^i, Bu^t, or *p*-ClC$_6$H$_4$).

The i.r. spectra of $[Rh(CNR)_2(PR'_3)_2]^+$ (PR'$_3$ = PPh$_3$ or PPh$_2$Me) exhibited a single CN stretching frequency, consistent with D_{2h} symmetry (B_{3u} mode; *trans*-geometry). The values of ν(CN) were all greater than those of the free ligand suggesting that CNR in these complexes was functioning substantially as a σ-donor. The value of ν(CN) within the series of complexes containing PPh$_3$ decreased in the order CNMe > CNPr^i > CN(*p*-ClC$_6$H$_4$), implying that CNMe is a better σ-donor than CNPr^i * and, more reasonably, that CN(*p*-ClC$_6$H$_4$) is a poorer σ-donor (better π-acceptor) than its alkyl analogues. Similar trends can be seen in the other isocyanide complexes described in this paper, and so it will not be discussed further. The ^{1}H n.m.r. spectra of the complexes containing PPh$_3$ were unexceptional, serving only to confirm their stoicheiometries. The methyl resonances associated with PPh$_2$Me in the spectrum of [Rh{CN(*p*-ClC$_6$H$_4$)}$_2$(PPh$_2$Me)$_2$]$^+$ appeared as an asymmetric triplet. In D_{2h} symmetry, a symmetric triplet would have been expected because of ‘ virtual coupling.’ The occurrence of asymmetry, however, could be accounted for by a bending of the Rh–C–N–R bond angle, leading to an effective removal of symmetry planes within the molecule and hence to an inequivalence of the methyl groups.

Addition of only one mole equivalent of CNR to either [Rh(PPh$_2$Me)$_4$]$^+$ or [Rh(CO)(PPh$_2$Me)$_3$]$^+$ in acetone afforded [Rh(CNR)(PPh$_2$Me)$_3$]$^+$. The phosphine ligand methyl proton resonances occurred, in their n.m.r. spectra, as a doublet and a triplet (relative area 2 : 1), consistent with one *trans* and two *cis*-PPh$_2$Me ligands in the planar monoisocyanide complexes.

Five-co-ordinate Complexes, $[M(CNR)_3(PR'_3)_2]^+$, $[Rh(CNR)_2(PR'_3)_3]^+$, and $[Rh(CNR)_4(PR'_3)]^+$.—Reaction of [Rh(CO)(PPh$_3$)$_2$Cl] with CNR (1 : 3 molar ratios) afforded, in most cases, [Rh(CNR)$_3$(PPh$_3$)$_2$]$^+$, and reaction of [Rh(CNPr^i)$_4$]$^+$ with PPh$_3$ (1 : 1 molar ratio) also afforded the appropriate tris-isocyanide bis-phosphine species. As mentioned previously, [Ir(CNR)$_3$(PPh$_3$)$_2$]$^+$ was readily formed from [Ir(CO)(PPh$_3$)$_2$Cl] and CNR, but, because of the reactivity of these iridium complexes, they were isolated as Cl$^-$ rather than PF$_6^-$ salts. The i.r. spectra of the compounds were consistent with D_{3h} symmetry (axial PR'$_3$), the strong doublet (only the complexes containing CNPr^i exhibited a single band) being assigned as the E' mode, being split either because of solid state effects or because of distortions from idealised trigonal bipyramidal geometry, which would also account for the appearance of a third weak band (A_1' mode). Such assignments have been made for ν(CO) in [Ir(CO)$_3$(PR'$_3$)$_2$]$^+$.[5] The methyl proton resonances of the species [Rh(CNMe)$_3$(PR'$_3$)$_2$]$^+$ and [M(CNBu^t)$_3$(PR'$_3$)$_2$]$^+$ occurred as sharp singlets and the signals associated with the methyl group in PPh$_2$Me in [Rh(CNR)$_3$(PPh$_2$Me)$_2$]$^+$ appeared as a broad singlet which was not resolved at −60° (no other spectral changes were observed at this temperature). The ^{1}H n.m.r. spectral data are therefore not inconsistent with D_{3h} symmetry, but the possibility that the complexes are stereochemically non-rigid[4] even at low temperatures cannot be entirely dismissed; attempts to study the behaviour of the ^{1}H n.m.r. spectra over a wide temperature range were hindered by insolubility in unreactive solvents.

Reaction of [Ir(CNPr^i)$_3$(PPh$_3$)$_2$]$^+$ with CO in acetone afforded [Ir(CO)(CNPr^i)$_2$(PPh$_3$)$_2$]$^+$. The CO stretching frequency occurred at 1920 cm^{-1}, and the average value of ν(CN) had increased relative to the value in the tris-isocyanide precursor. These data suggested that in replacing one CNPr^i ligand, the CO had assumed a significant role as π-acceptor, and, indeed, the value of ν(CO) is quite low for a cationic complex of this type.[6,12]

The bis-isocyanide complexes, $[Rh(CNR)_2(PR'_3)_3]^+$,

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* Such data have been obtained from [Rh(CNR)$_4$]$^+$,[1] [Co(CNR)$_3$(PPh$_3$)$_2$]$^+$,[3] and [Cr(NO)(CNR)$_5$]$^+$.[11] Whether the role of CNR is to function primarily as a σ-donor or as a σ-donor/π-acceptor, and what is the relative importance of σ *versus* π-effects in the latter situation, cannot be defined with certainty. However, the relative order of the frequencies in the alkyl systems is the reverse of that reasonably expected.

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[12] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1970, 2705.

were obtained by reaction of either $[\mathrm{Rh(CNR)_4}]^+$ with $\mathrm{PR'_3}$ or of $[\mathrm{Rh(PPh_2Me)_3L}]^+$ ($\mathrm{L = CO}$ or $\mathrm{PPh_2Me}$) with CNR, or by addition of $\mathrm{PPh_3}$ to $[\mathrm{Rh\{CN(}p\mathrm{\text{-}ClC_6H_4)\}_2(PPh_3)_2}]^+$ in acetone. The i.r. spectra of these compounds exhibited are strong and one weak CN stretching frequency, which is not inconsistent with D_{3h} symmetry (axial CNR), provided that the weak band (A_1') arises because of slight distortions (M–CNR bond angle deformations or relative orientations of ligand substituents) from ideal geometry. The methyl resonances in the ^{1}H n.m.r. spectra of $[\mathrm{Rh(CNMe)_3(PR'_3)_2}]^+$ and $[\mathrm{Rh(CNBu^t)_2(PR'_3)_3}]^+$ occurred as sharp singlets whereas those associated with the phosphine ligand in $[\mathrm{Rh(CNR)_2(PPh_2Me)_3}]^+$ were present as broad single lines. These data, too, are not inconsistent with D_{3h} symmetry but cannot, of course, confirm it. Assignment of this geometry to the isocyanide complexes would contrast with the proposed structures for the related $[\mathrm{Ir(CO)_2(PPh_2Me)_3}]^+$.

Reaction of $[\mathrm{Rh(CNPr^i)_4}]^+$ with $\mathrm{PPh_3}$ in refluxing acetone (1 : 1 molar ratio) afforded $[\mathrm{Rh(CNBu^t)_4(PPh_3)}]^+$. Attempts to prepare other related rhodium complexes have so far provided only unsatisfactory results, but the five-co-ordinate iridium species, $[\mathrm{Ir(CNMe)_4L}]^+$ ($\mathrm{L =}$ CNMe or CO) have been recently described.[9]

Mixed Isocyanide Complexes, $[\mathrm{Rh(CNR)(CNR')_2(PPh_3)_2}]^+$.—The ability of $[\mathrm{Rh(CN(}p\mathrm{\text{-}ClC_6H_4)_2(PPh_3)_2}]^+$ to accept a third phosphine ligand, giving $[\mathrm{Rh\{CN(}p\mathrm{\text{-}ClC_6H_4)\}_2(PPh_3)_3}]^+$, suggested that stoicheiometric addition of a different isocyanide would afford a mixed isocyanide complex. Thus, treatment of the p-chlorophenyl isocyanide complex with $\mathrm{CNPr^i}$ afforded $[\mathrm{Rh(CNPr^i)\{CN(}p\mathrm{\text{-}ClC_6H_4)\}_2(PPh_3)_2}]^+$, and addition of $\mathrm{CN(}p\mathrm{\text{-}ClC_6H_4)}$ to $[\mathrm{Rh(CNPr^i)_2(PPh_3)_2}]^+$ gave $[\mathrm{Rh\{CN(}p\mathrm{\text{-}ClC_6H_4)\}(CNPr^i)_2(PPh_3)_2}]^+$. The ^{1}H n.m.r. spectra of these complexes were consistent with their formulations.

We were unable to obtain any other mixed isocyanide complexes by this route, and could find no evidence for the existence of $[\mathrm{M(CNR)(PR'_3)_4}]^+$, although $[\mathrm{Ir(CNMe)(Ph_2PCH_2CH_2PPh_2)_2}]^+$ has been isolated.[9] While the majority of the complexes reported here contain rhodium, the existence of five-co-ordinate iridium analogues seems to be equally likely, and our efforts to prepare these are continuing.

Oxidative Addition Reactions.—The reactions described here have been largely confined to a selection of complexes, $[\mathrm{M(CNR)_3(PR'_3)_2}]^+$, studies of the behaviour of other complexes are in progress.[13]

All reactions were accompanied by an increase in the CN stretching frequency relative to that in the precursor. This is consistent with the formal oxidation of $\mathrm{M^I}$ to $\mathrm{M^{II}}$ or $\mathrm{M^{III}}$ (i.r. data, Table 2). The complexes were satisfactorily characterised by elemental analyses and by conductivity measurements (Table 2).

Protonation.—Protonation of co-ordinatively saturated five-co-ordinate d^8 transition-metal complexes has not been extensively studied.[14] Addition of $\mathrm{HClO_4}$ to $[\mathrm{Os(CO)_3(PPh_3)_2}]$ afforded[15] $[\mathrm{Os(CO)_3(PPh_3)_2H}][\mathrm{ClO_4}]$, and similar treatment of $[\mathrm{Ru(CO)_2(CNR)(PPh_3)_2}]$ gave[16] $[\mathrm{Ru(CO)_2(CNR)(PPh_3)_2H}]^+$. The species $[\mathrm{Ir(CO)(Me_2PCH_2CH_2PMe_2)_2H}]^{2+}$ was obtained[17] on acidolysis of $[\mathrm{Ir(Me_2PCH_2CH_2PMe_2)_2H(CO_2Me)}]^+$.

Addition of aqueous $\mathrm{HPF_6}$ to $[\mathrm{M(CNR)_3(PPh_3)_2}][\mathrm{PF_6}]$ ($\mathrm{M = Rh}$, $\mathrm{R = Bu^t}$ or p-$\mathrm{ClC_6H_4}$; $\mathrm{M = Ir}$, $\mathrm{R = Bu^t}$, p-$\mathrm{MeC_6H_4}$, or p-$\mathrm{ClC_6H_4}$) in acetone gave colourless solutions from which, in all cases except when $\mathrm{M = Rh}$, $\mathrm{R =}$ p-$\mathrm{ClC_6H_4}$ when only starting material was recovered, the dicationic hydride complexes, $[\mathrm{M(CNR)_3(PPh_3)_2H}][\mathrm{PF_6}]_2$, were isolated as white crystals. No direct evidence for the presence of hydride ligand could be obtained from i.r. spectroscopy, ν(MH) presumably being weak and possibly obscured by ν(CN). However, the ^{1}H n.m.r. spectra of the iridium complexes contained a triplet resonance at high field (τ 17—21) which indicated the presence of a hydride ligand *trans* to CNR and *cis* to two mutually *cis* or *trans* $\mathrm{PPh_3}$ ligands. The hydride resonance was not detected in the ^{1}H n.m.r. spectra of the rhodium complexes, possibly because it was weak and split by coupling with ^{31}P and ^{103}Rh ($I = \frac{1}{2}$). Thus, protonation had occurred at a site *trans* to isocyanide, as in $[\mathrm{Ru(CO)_2(CNR)(PPh_3)_2}]$.[16]

Halogenation.—Halogenation of $\mathrm{Os(CO)_3(PPh_3)_2}$, which eventually gave *cis*-$\mathrm{Os(CO)_2(PPh_3)_2X_2}$, proceeded[18] *via* the intermediate $[\mathrm{Os(CO)_3(PPh_3)_2X}]^+\mathrm{X}^-$. However iodination of $[\mathrm{Rh(CNR)_3(PPh_3)_2}][\mathrm{PF_6}]$ ($\mathrm{R = Bu^t}$ or p-$\mathrm{ClC_6H_4}$) in dichloromethane at room temperature, afforded only $[\mathrm{Rh(CNBu^t)_3(PPh_3)I_2}][\mathrm{PF_6}]$ and $[\mathrm{Rh\{CN(}p\mathrm{\text{-}ClC_6H_4)\}_2(PPh_3)_2I_2}][\mathrm{PF_6}]$, respectively, there being no evidence for $[\mathrm{Rh(CNR)_3(PPh_3)_2I}]^{2+}$. Similar treatment of $[\mathrm{Rh(CNBu^t)_3(PPh_3)_2}]\mathrm{Cl}$, on the contrary, gave exclusively $[\mathrm{Rh(CNBu^t)_3ClI_2}]$; the participation of counteranion in the oxidative addition chemistry of $[\mathrm{Rh\{CN(}p\mathrm{\text{-}ClC_6H_4)\}_4}]^+$ has already been noted.[1] In an attempt to prepare acetyl complexes, we treated $[\mathrm{Rh(CNBu^t)_3(PPh_3)_2}][\mathrm{PF_6}]$ and $[\mathrm{Rh\{CN(}p\mathrm{\text{-}ClC_6H_4)\}_2(PPh_2Me_3)_2}][\mathrm{PF_6}]$ with MeCOCl. The products of these reactions, however, were chloro-species, *viz.* $[\mathrm{Rh(CNBu^t)_3(PPh_3)_2Cl}]^{2+}$ and $[\mathrm{Rh\{CN(}p\mathrm{\text{-}ClC_6H_4)\}_2(PPh_2Me)_2Cl_2}]^+$.*

Reaction of $[\mathrm{Rh(CNBu^t)_3(PPh_3)_2}][\mathrm{PF_6}]$ or $[\mathrm{Rh\{CN(}p\mathrm{\text{-}ClC_6H_4)\}_2(PPh_2Me)_2}][\mathrm{PF_6}]$ with $\mathrm{C_3F_7I}$ and MeI, respectively, at room temperature, afforded the formally $\mathrm{Rh^{II}}$ complexes of empirical formulae $[\mathrm{Rh(CNBu^t)_3(PPh_3)I}]_n[\mathrm{PF_6}]_n$ and $[\mathrm{Rh\{CN(}p\mathrm{\text{-}ClC_6H_4)\}_2(PPh_3)_2I}]_n[\mathrm{PF_6}]_n$. Since these compounds are diamagnetic (^{1}H n.m.r.

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* During the work-up procedure for this complex, a white solid intermediate, which contained isocyanide, phosphine and acyl CO groups, was isolated; this may have been $[\mathrm{Rh\{CN(}p\mathrm{\text{-}ClC_6H_4)\}_2(PPh_2Me)_2(COMe)Cl}]^+$ which decomposed in the presence of chloride ion.

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spectra), they are presumably dimeric ($n = 2$). Binuclear rhodium(II) isocyanide complexes, $[Rh(CNPh)_4I]_2X_2$ ($X = I$ or ClO_4) have been obtained[19] previously.

The ^1H n.m.r. and i.r. spectra of these compounds were not especially informative, although the CN stretching frequencies of $[Rh(CNR)_2(PR'_3)_2X_2]^+$ were consistent with a structure in which the pairs of identical ligands were mutually *trans*.

Alkylation and Allylation.—Addition of alkyl halides to co-ordinatively saturated five-co-ordinate d^8 complexes (excluding those containing π-C_5H_5 ligands, and cobaloximes and their analogues) has been little studied.[14] Reaction of $[Rh(CNBu^t)_3(PPh_3)_2]^+$ with methyl iodide afforded, albeit in low yield, $[Rh(CNBu^t)_4(PPh_3)(Me)]^{2+}$. The yield of this compound could be increased by adding extra $CNBu^t$ and NH_4PF_6 in methanol; PPh_3Me^+ was detected as a byproduct. Attempts to prepare the $CN(p$-$ClC_6H_4)$ analogue resulted only in the formation of an iodo-complex (*vide supra*). The ^1H n.m.r. and i.r. spectra of the methyl complex were consistent with addition of the alkyl group *trans* to PPh_3 (D_{2h}); the methyl resonance appeared as a double doublet [$^2J(RhH)$ and $^3J(PH)$], the t-butyl signals as a singlet, and $\nu(CN)$ was a single band.

Reaction of $[Ir(CNBu^t)_3(PPh_3)_2]Cl$ with methyl iodide gave $[Ir(CNBu^t)_3(PPh_3)(Me)I]Cl$ ($[PPh_3Me]I$ was detected as a by-product) whereas, under identical conditions the analogous Ir^I isopropyl isocyanide compound afforded exclusively $[Ir(CNPr^i)_2(PPh_3)_2(Me)I]Cl$. From a study of molecular models there would appear to be no steric reasons for this specificity and so the electronic properties of the respective ligands would seem to be the important factor in deciding the course of the reaction.

Treatment of $[Rh\{CN(p$-$ClC_6H_4)\}_2(PPh_3)_2][PF_6]$ with C_2F_5I in dichloromethane in a Carius tube at 140° afforded $[Rh\{CN(p$-$ClC_6H_4)\}_2(C_2F_5)I_2]_2$. This compound is presumably similar to $[Rh\{CN(p$-$ClC_6H_4)\}_2I_2Cl]_2$ [1] and $[Rh(CO)_2X_3]_2$ (X = halide)[19] and, like them, exhibited only one acceptor ligand fundamental stretching frequency.

Addition of allyl halides to $[Rh\{P(OR)_3\}_5]^+$ [20] or $[Ir(CO)_x(PPhMe_2)_{5-x}]^+$ ($x = 2$ or 3)[21] afforded a variety of complexes containing σ- or π-bonded allylic groups, with or without concomitant incorporation of halide ion in the complex. With allyl chloride, in the presence of $NaBPh_4$, $[Ir(CNBu^t)_3(PPh_3)_2]Cl$ gave $[Ir(CNBu^t)_3(PPh_3)_2(C_3H_5)][BPh_4]_2$ but if the relative concentration of C_3H_5Cl was increased, and $NaBPh_4$ replaced by NH_4PF_6, the product was $[Ir(CNBu^t)_3(PPh_3)(C_3H_5)Cl][PF_6]$. Both of these complexes would appear to contain σ-bonded allyl groups, but because of solubility difficulties, this could not be confirmed reliably by spectroscopy.

Other Addition Reactions.—Reaction of $[Ir(CNR)_3(PPh_3)_2]Cl$ ($R = Bu^t$ or Pr^i) with $SnPh_3Cl$ afforded $[Ir(CNBu^t)_3(PPh_3)_2(SnPh_3)]Cl_2$ and $[Ir(CNPr^i)_2(PPh_3)_2(SnPh_3)Cl]Cl$, respectively.

Rhodium(I) and iridium(I) complexes containing PPh_3 react readily with CS_2 forming a variety of complexes containing CS and/or CS_2 as ligands.[22] Thus, when $[Ir(CNBu^t)_3(PPh_3)_2]Cl$ was treated with CS_2 *in vacuo* $[Ir(CNBu^t)_3(PPh_3)_2(CS_2)]Cl$ was formed. The value of $\nu(CN)$ had increased, implying that oxidation of Ir^I to Ir^{III} might have occurred, but spectral bands associated with the co-ordinated CS_2 could not be assigned unequivocally because of their coincidence with other ligand modes. Hence, the alternative structures, one containing π-bonded CS_2, as in $[Pt(PPh_3)_2(CS_2)]$,[23] and seven-co-ordinate Ir^{III}, or one containing σ-bonded CS_2, *i.e.* $Ir^I \longleftarrow S{=}C{=}S$, could not be distinguished.

Reaction of $[Ir(CNBu^t)_3(PPh_3)_2]Cl$ with SO_2 *in vacuo* afforded $[Ir(CNBu^t)_3(PPh_3)_2(SO_2)]Cl$. Again $\nu(CN)$ had increased, but bands characteristic of co-ordinated SO_2 could not be clearly identified. However, it seems likely that the SO_2 functions as an acceptor, as in $[Ir(CO)(PPh_3)_2(SO_2)Cl]$.[24]

In an attempt to prepare $[Ir(CNR)_3(PPh_3)_2][PF_6]$ ($R = Pr^i$, p-MeC_6H_4, or p-ClC_6H_4), using NH_4PF_6 in methanol, we found that oxidation occurred very rapidly, but could only isolate and characterise $[Ir(CNBu^t)_3(PPh_3)_2(OMe)][PF_6]_2$. This compound was insoluble in solvents suitable for ^1H n.m.r. spectral studies. The analogous rhodium complex did not behave similarly. The formation of the methoxide complex contrasts with the behaviour of the analogous $[Ir(CO)_3(PPh_3)_2]^+$ which afforded[25] $[Ir(CO)_2(PPh_3)_2(CO_2Me)]$ on methanolysis, and with the formation of carbene complexes when species such as $[Pt(CNR)(PR'_3)Cl_2]$ were treated[26] with alcohols. It has been noted[27] that $[Ru(CO)(CNR)_2(PPh_3)_2]$ reacted with alcohols giving $[Ru(CO)(CNR)_2(PPh_3)_2(OH)]^+$.

Conclusion.—The oxidative addition reactions described above represent only a preliminary survey of this area of rhodium and iridium isocyanide chemistry. However, at this stage, it would appear that the iridium(I) complexes are, qualitatively, more readily oxidised than their Rh^I analogues. Furthermore, oxidative addition reactions involving $[M(CNR)_3(PPh_3)_2]^+$ resulted most often in the loss of PPh_3 when $R = Bu^t$, and elimination of CNR when $R = Pr^i$, provided that the substrate (XY) was wholly incorporated in the M^{III} complex.

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EXPERIMENTAL

The complexes $[Rh(CO)(PPh_3)_2Cl]$,[28] $[Ir(CO)(PPh_3)_2Cl]$,[29] $[Rh(PPh_2Me)_4][PF_6]$,[30] $[Rh(CO)(PPh_2Me)_3][PF_6]$,[31] and $[Rh(CNR)_4][PF_6]$ (R = Me, Pr^i, Bu^t, or p-ClC_6H_4) [1] were prepared as described in the literature.

Elemental analyses were carried out by the Microanalytical Laboratory of this Department and conductivity measurements were made at room temperature (20 ± 2°) using a Philips Conductivity meter.

I.r. spectra were obtained using Perkin-Elmer 180 and 457 spectrophotometers, and ^1H n.m.r. spectra with a Varian HA 100 spectrometer.

All evaporations, unless otherwise stated, were carried out under reduced pressure, using a water pump. All yields, unless otherwise specified, are based on the rhodium or iridium precursor.

Bis(triphenylphosphine)bis(methyl isocyanide)rhodium Hexafluorophosphate.—*Method A*. When $[Rh(CO)(PPh_3)_2Cl]$ (0·5 g) was dissolved in methanol (15 ml) and treated with CNMe (0·1 g), a gas was evolved and a red solution formed. Addition of NH_4PF_6 (0·1 g) in methanol (15 ml) followed by filtration and evaporation afforded a red oil which was chromatographed on alumina (Spence type A) using acetone as eluant. Several yellow bands separated, and the first was collected, reduced in volume *in vacuo* and treated with n-pentane until the mixture became cloudy. The solution was then cooled at 0 °C and the *complex* formed as yellow crystals (0·15 g, 25%).

Method B. A mixture of $[Rh(CNMe)_4][PF_6]$ (0·1 g) and PPh_3 (0·13 g) (1 : 1 molar ratio) in ether (10 ml) and ethanol (35 ml) was refluxed under N_2 for 4 h. After cooling, the mixture was filtered giving a violet residue (unreacted starting material) and a yellow filtrate. The filtrate was evaporated to low volume, ethanol was added and, on cooling, yellow plates of the *complex* were formed (0·35 g, 65%).

*Bis(triphenylphosphine)bis(isopropyl isocyanide)rhodium, Bis(triphenylphosphine)bis(*p*-chlorophenyl isocyanide)rhodium, Bis(diphenylmethylphosphine)(*p*-chlorophenyl isocyanide)rhodium Hexafluorophosphates.*—These complexes were prepared by method A described for $[Rh(CNMe)_2(PPh_3)_2][PF_6]$ with the following modifications: $[Rh(CNPr^i)_2(PPh_3)_2][PF_6]$, after evaporation, the residue was extracted with dichloromethane and the yellow *complex* crystallised on addition of ethanol (67%); $[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_3)_2][PF_6]$, similarly (91%); $[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_2Me)_2][PF_6]$, after chromatography, the first yellow fraction was collected and partially evaporated, whereupon addition of aliquots of ethanol afforded yellow crystals of the *complex* (72%).

Bis(diphenylmethylphosphine)bis(isopropyl isocyanide)rhodium Hexafluorophosphate.—This complex was obtaind by method B described for $[Rh(CNMe)_2(PPh_3)_2][PF_6]$, and was isolated as yellow crystals (33%).

*Tris(diphenylmethylphosphine)(*p*-chlorophenyl isocyanide)rhodium Hexafluorophosphate.*—*Method A*. $[Rh(CO)(PPh_2Me)_3][PF_6]$ (0·21 g), dissolved in acetone (15 ml), was treated with $CN(p\text{-}ClC_6H_4)$ (0·03 g), and a gas (CO) was evolved. After 20 min the solution was partially evaporated and, on addition of ethanol, afforded the *complex* as beige crystals (0·6 g, 40%).

Method B. $[Rh(PPh_2Me)_4][PF_6]$ (0·14 g) in acetone (15 ml) was treated with $CN(p\text{-}ClC_6H_4)$ (0·02 g), and the solution was allowed to stand at room temperature for 30 min. After partial evaporation and addition of n-hexane, the solution afforded the *complex* as a light brown powder (0·4 g, 40%).

Tris(diphenylmethylphosphine)(isopropyl isocyanide)rhodium Hexafluorophosphate.—A solution of $[Rh(PPh_2Me)_4][PF_6]$ (0·23 g) and $CNPr^i$ (0·02 g) in acetone (20 ml) was refluxed under N_2 for 30 min, cooled and evaporated to dryness. The brown residue was dissolved in warm ethanol (10 ml) and after filtration and cooling, the *complex* precipitated as tan crystals (0·05 g, 40%).

Bis(triphenylphosphine)tris(t-butyl isocyanide)rhodium Hexafluorophosphate.—To $[Rh(CO)(PPh_3)_2Cl]$ (0·2 g) dissolved in dichloromethane (20 ml) was added $CNBu^t$ (0·07 g), and the solution became golden yellow. NH_4PF_6 (0·07 g) was added and the resulting solution was evaporated *in vacuo*. The residue was extracted with dichloromethane and filtered. The yellow filtrate was partially evaporated and, on addition of ethanol followed by cooling, afforded yellow crystals of the *complex* (0·24 g, 81%).

*Bis(triphenylphosphine)tris(*p*-chlorophenyl isocyanide)rhodium Hexafluorophosphate.*—This complex was prepared in the same way as its $CNBu^t$ analogue, and was obtained as lime green crystals (68%).

Bis(triphenylphosphine)tris(isopropyl isocyanide)rhodium Hexafluorophosphate.—A mixture of $[Rh(CNPr^i)_4][PF_6]$ (0·11 g) and PPh_3 (0·05 g) (1 : 1 molar ratio) in acetone–ether (1 : 1 *v/v*; 25 ml) was refluxed under N_2 for 2 h. The solution was then partially evaporated and ethanol was added. On cooling, the *complex* formed as light yellow crystals (0·03 g, 16%).

Bis(triphenylphosphine)tris(t-butyl isocyanide)iridium Chloride.—To a solution of $[Ir(CO)(PPh_3)_2Cl]$ (1·2 g) in toluene (50 ml) under N_2 was added, with stirring, $CNBu^t$ (0·4 g). A gas was evolved, the solution turned deep yellow, and an oily solid formed. The mixture was stirred overnight, ether was added and a yellow powder was produced. This was filtered off and recrystallised from acetone–light petroleum (b.p. 40—60 °C). The *complex* was obtained as yellow crystals (1·1 g, 72%).

*Bis(triphenylphosphine)tris(isopropyl isocyanide)iridium, Bis(triphenylphosphine)tris(*p*-tolyl isocyanide)iridium, and Bis(triphenylphosphine)tris(*p*-chlorophenyl isocyanide)iridium Chlorides.*—These complexes were prepared in the same way as their $CNBu^t$ analogue, and were obtained as pale yellow (62%), dark green (71%), and green (73%) crystals, respectively.

Carbonylbis(triphenylphosphine)bis(isopropyl isocyanide)iridium Chloride.—Carbon monoxide was bubbled through a solution of $[Ir(CNPr^i)_3(PPh_3)_2]Cl$ (0·25 g) in acetone (15 ml) for 10 min. On addition of ether a pale yellow solid was precipitated, which was filtered off and recrystallised from acetone–ether. The *complex* was obtained as pale yellow crystals (0·14 g, 59%).

Tris(triphenylphosphine)bis(methyl isocyanide)rhodium Hexafluorophosphate.—A mixture of $[Rh(CNMe)_4][PF_6]$ (0·2 g) and PPh_3 (0·13 g) in ether (10 ml) and ethanol (35 ml) was refluxed under N_2 for 4 h. The mixture was then

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filtered leaving a violet residue (starting material) and the yellow filtrate was evaporated to low bulk. Ethanol was then added and, after cooling, yellow hexagonal crystals of the *complex* were formed (0·35 g, 65%).

Tris(diphenylmethylphosphine)bis(methyl isocyanide)rhodium and Tris(diphenylmethylphosphine)bis(isopropyl isocyanide)rhodium Hexafluorophosphates.—These complexes were obtained in the same way as $[Rh(CNMe)_2(PPh_3)_3][PF_6]$. The former was recrystallised from acetone–propan-2-ol and isolated as yellow crystals (0·04 g, 33%). The latter was also obtained, without refluxing, as yellow crystals (0·3 g, 56%).

Tris(triphenylphosphine)bis(p-chlorophenyl isocyanide)rhodium Hexafluorophosphate.—To a solution of $[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_3)_2][PF_6]$ (0·15 g) in acetone (10 ml) was added a solution of PPh_3 (0·04 g, 1 : 1 molar ratio) in ether (20 ml), and the mixture was refluxed under N_2 for 4 h. The solution was then cooled, partially evaporated and n-hexane added. The *complex* formed gradually as yellow crystals (0·13 g, 72%).

Tris(diphenylmethylphosphine)bis(t-butyl isocyanide)rhodium Hexafluorophosphate.—To a solution of $[Rh(CNBu^t)_4][PF_6]$ (0·4 g) in acetone (15 ml) was added PPh_2Me (0·3 g; 1 : 3 molar ratio). The mixture was allowed to stand for 30 min at room temperature, and was then partially evaporated. Ethanol was then added and, on cooling, the complex formed as yellow crystals (0·3 g, 56%).

Tris(diphenylmethylphosphine)bis(p-chlorophenyl isocyanide)rhodium Hexafluorophosphate.—To a solution of $[Rh(PPh_2Me)_4][PF_6]$ (0·22 g) in acetone (15 ml) was added $CN(p\text{-}ClC_6H_4)$ (0·07 g; 1 : 2 molar ratio). The solution was then refluxed under N_2 for 4 h, ethanol (7 ml) added, and the mixture cooled. The *complex* precipitated as a yellow powder and was recrystallised from acetone–ethanol (0·07 g, 30%).

Triphenylphosphinetetrakis(t-butyl isocyanide)rhodium Hexafluorophosphate.—To a solution of $[Rh(CNBu^t)_4][PF_6]$ (0·4 g) in acetone (12 ml) was added a solution of PPh_3 (0·18 g; 1 : 1 molar ratio) in ether (10 ml). The solution was refluxed under N_2 for 4 h, cooled, and n-hexane (5 ml) added. The solvent was partially evaporated *in vacuo* and the *complex* formed as yellow crystals (0·3 g, 52%).

Bis(triphenylphosphine)(isopropyl isocyanide)bis(p-chlorophenyl isocyanide)rhodium Hexafluorophosphate.—To $[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_3)_2][PF_6]$ (0·12 g) in methanol (12 ml) was added $CNPr^i$ (0·01 g). The solution was partially evaporated *in vacuo* and cooled, when dark orange needles of the *complex* formed (0·09 g, 71%).

Bis(triphenylphosphine)bis(isopropyl isocyanide)(p-chlorophenyl isocyanide)rhodium Hexafluorophosphate.—To $[Rh(CNPr^i)_2(PPh_3)_2][PF_6]$ (0·2 g) in methanol (15 ml) was added $CN(p\text{-}ClC_6H_4)$ (0·03 g). The solvent was partially evaporated and, after cooling, the *complex* formed gradually as golden yellow platelets (0·17 g, 74%).

Hydridobis(triphenylphosphine)tris(t-butyl isocyanide)rhodium Bis(hexafluorophosphate).—An acetone solution (10 ml) of $[Rh(CNBu^t)_3(PPh_3)_2][PF_6]$ (0·25 g) was treated with HPF_6 (0·05 g, 60% aqueous solution). No appreciable colour change was detected but white crystals gradually formed. These were filtered off, washed with acetone and dried *in vacuo* (0·15 g, 44%).

Hydridobis(triphenylphosphine)tris(t-butyl isocyanide)iridium Bis(tetrafluoroborate).—An acetone solution (10 ml) of $[Ir(CNBu^t)_3(PPh_3)_2]Cl$ (0·17 g) was treated with HBF_4 (2 ml, 40% aqueous solution). The solution became colourless and, on partial evaporation of the solvent, afforded a white precipitate. This was filtered off and recrystallised from acetone–petroleum (b.p. 40—60 °C). The *complex* was isolated as white crystals (0·18 g, 93%).

Hydridobis(triphenylphosphine)tris(p-tolyl isocyanide)iridium and Hydridobis(triphenylphosphine)tris(p-chlorophenyl isocyanide)iridium Bis(hexafluorophosphates).—These complexes were prepared in the same way as their $CNBu^t$ analogue, using HPF_6 (*ca.* 5 ml, 60% aqueous solution). The *complexes*, which were obtained in essentially quantitative yields, were isolated as white crystals.

Di-iodo(triphenylphosphine)tris(t-butyl isocyanide)rhodium Hexafluorophosphate.—Iodine (0·05 g) was added to a solution of $[Rh(CNBu^t)_3(PPh_3)_2][PF_6]$ (0·2 g) in dichloromethane (30 ml), the mixture was filtered and the filtrate partially evaporated. On addition of n-pentane, followed by cooling, the *complex* formed as red-brown crystals (0·15 g, 79%). *Di-iodobis(triphenylphosphine)bis(p-chlorophenylisocyanide)rhodium hexafluorophosphate*, $[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_3)_2I_2][PF_6]$, was prepared similarly, from $[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_3)_2][PF_6]$, and was isolated as brown crystals (75%).

Chlorodi-iodotris(t-butyl isocyanide)rhodium.—To $[Rh(CNBu^t)_3(PPh_3)_2]Cl$, obtained from $[Rh(CO)(PPh_3)_2Cl]$ (0·2 g) and $CNBu^t$ (0·14 g) in dichloromethane (15 ml), was added iodine (0·08 g) in dichloromethane (15 ml). The mixture became deep red, was filtered and partially evaporated. The residue was chromatographed on alumina (Spence type H), using dichloromethane as eluant. The yellow fraction was collected, partially evaporated and, on addition of n-pentane, the *complex* precipitated as orange crystals {0·13 g, 68% based on $[Rh(CO)(PPh_3)_2Cl]$}.

Chlorobis(triphenylphosphine)tris(t-butyl isocyanide)rhodium Bis(hexafluorophosphate).—To a mixture of $[Rh(CO)(PPh_3)_2Cl]$ (0·1 g) and $CNBu^t$ (0·07 g) in dichloromethane (20 ml) was added MeCOCl (1 ml). The solution became colourless, NH_4PF_6 (0·04 g) in ethanol (5 ml) was added, and the solvent removed *in vacuo*. The residue was extracted with dichloromethane, the extract was filtered and treated with ethanol (equal volume). The mixture was then partially evaporated and the *complex* formed as white crystals (0·05 g, 39%).

Dichlorobis(diphenylmethylphosphine)bis(p-chlorophenyl isocyanide)rhodium Hexafluorophosphate.—To a suspension of $[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_2Me)_2][PF_6]$ (0·12 g) in ethanol–ether (1 : 1 *v*/*v*, 20 ml) was added, with stirring, MeCOCl (slight excess). The solution became colourless, and a white solid precipitated which, after 30 min, was filtered off [this compound exhibited ν(CN) and ν(CO)]. The solid was recrystallised from acetone–alcohol, affording the yellow *complex* (0·75 g, 62%).

Bis{iodo(triphenylphosphine)tris(t-butyl isocyanide)rhodium} Bis(hexafluorophosphate).—To $[Rh(CNBu^t)_3(PPh_3)_2][PF_6]$ (0·15 g) dissolved in dichloromethane (10 ml) was added, under N_2, C_3F_7I (a slight excess). The solution became red, NH_4PF_6 (0·04 g) dissolved in methanol (15 ml) was added, and the mixture was then evaporated to dryness. The residue was extracted with dichloromethane (10 ml) and the extract filtered, ethanol being added to the filtrate. The mixture was then slowly evaporated, affording the *complex* as yellow crystals (0·09 g, 52%).

Bis{iodobis(diphenylmethylphosphine)bis(p-chlorophenyl isocyanide)rhodium} Bis(hexafluorophosphate).—A solution of $[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_2Me)_2][PF_6]$ (0·3 g) in dichloromethane (15 ml) was treated with MeI (0·05 g) and after

10 min the solvent was partially evaporated. On addition of n-hexane, the complex precipitated as yellow needles (0·12 g, 44%).

Methyl(triphenylphosphine)tetrakis(t-butyl isocyanide)rhodium Bis(hexafluorophosphate).—To a dichloromethane solution (25 ml) of $[Rh(CNBu^t)_3(PPh_3)_2]Cl$, prepared from $[Rh(CO)(PPh_3)_2Cl]$ (0·2 g) and $CNBu^t$ (0·09 g) was added MeI (0·05 g), and the mixture was allowed to stand for 30 min, during which time it became colourless. A solution of NH_4PF_6 (0·05 g) in methanol (15 ml) was added to the mixture and the resulting solution was evaporated to dryness. The light yellow residue was extracted with dichloromethane (10 ml), and the extract was filtered. After addition of ethanol (5 ml), the solution was partially evaporated. On cooling, a solid formed which was filtered off, washed with ethanol and dried *in vacuo*. The *complex* was obtained as white crystals (0·21 g, 72% based on $[Rh(CO)(PPh_3)_2Cl]$ and a slight excess of $CNBu^t$). The phosphonium salt, $[PPh_3Me]I$, was obtained by evaporating the mother liquor to dryness.

Iodomethyl(triphenylphosphine)tris(t-butyl isocyanide)iridium Chloride.—An acetone solution (15 ml) of $[Ir(CNBu^t)_3(PPh_3)_2]Cl$ (0·17 g) was treated with MeI (0·2 ml) and the yellow mixture rapidly became colourless. On addition of petroleum (b.p. 40—60 °C), a solid was precipitated which was filtered off and recrystallised from acetone–petroleum, affording the *complex* as white crystals (0·13 g, 87%).

Iodomethylbis(triphenylphosphine)bis(isopropyl isocyanide)iridium Chloride, $[Ir(CNPr^i)_2(PPh_3)_2(Me)I]Cl$, was obtained similarly, as white crystals (0·11 g, 60%).

*Bis(di-iodopentafluoroethyl)bis(*p*-chlorophenyl isocyanide)rhodium.*—A mixture of $[Rh\{CN(p\text{-}ClC_6H_4)\}_2(PPh_3)_2][PF_6]$ (0·15 g) and C_2F_5I (a slight excess) in dichloromethane (10 ml) was allowed to react in a sealed evacuated tube at 140 °C for 2 h. The tube was then cooled and opened, the solution was filtered and partially evaporated *in vacuo*. On addition of n-hexane, violet crystals of the *complex* formed (0·02 g, 54%).

The mass spectrum (A.E.I. MS 9; 200°, 7·5 keV) of the compound did not exhibit a molecular ion, the highest peak observed (*m/e* 613) corresponding to $[Rh\}CN(p\text{-}ClC_6H_4)\}(C_2F_5)I_2]^+$.

Allylbis(triphenylphosphine)tris(t-butyl isocyanide)iridium Bis(tetraphenylborate).—To an acetone solution (10 ml) of $[Ir(CNBu^t)_3(PPh_3)_2]Cl$ (0·20 g) was added C_3H_5Cl (0·5 ml), and the mixture became colourless. A solid was precipitated on addition of petroleum (b.p. 40—60 °C), and was filtered off. This solid was dissolved in methanol to which was added a slight excess of $NaBPh_4$. The white solid which precipitated was filtered off and recrystallised from acetone–ether affording the *complex* as white crystals (0·15 g, 46%).

Chloro(allyl)(triphenylphosphine)tris(t-butyl isocyanide)iridium Hexafluorophosphate.—An acetone solution (10 ml) of $[Ir(CNBu^t)_3(PPh_3)_2]Cl$ (0·19 g) was treated with C_3H_5Cl (0·8 ml), and the colourless solution was allowed to stand for 10 min. A white solid was precipitated from this on addition of petroleum (b.p. 40—60 °C). This was filtered off, redissolved in methanol, treated with NH_4PF_6, whereupon white crystals of the *complex* were formed. These were filtered off and recrystallised from acetone–petroleum (b.p. 40—60 °C) (0·13 g, 74%).

Chloro(triphenylstannyl)bis(triphenylphosphine)bis(isopropyl isocyanide)iridium Chloride.—To an acetone solution (10 ml) of $[Ir(CNPr^i)_3(PPh_3)_2]Cl$ (0·14 g) was added $SnPh_3Cl$ (0·2 g, recrystallised from ether). After *ca.* 15 min ether was added and the *complex* precipitated as white crystals. These were filtered off, washed with ether and dried *in vacuo* (0·18 g, 97%).

(Triphenylstannyl)bis(triphenylphosphine)tris(t-butyl isocyanide)iridium Dichloride.—This compound was obtained in the same way as that above, being precipitated by petroleum (b.p. 40—60 °C), and was isolated as off-white crystals (0·20 g, 80%).

(Carbon disulphide)bis(triphenylphosphine)tris(t-butyl isocyanide)iridium Chloride and (Sulphur dioxide)bis(triphenylphosphine)tris(t-butyl isocyanide)iridium Chloride.—Reaction between $[Ir(CNBu^t)_3(PPh_3)_2]Cl$, dissolved in acetone (10 ml) and either CS_2 or SO_2 (slight excesses), occurred in sealed evacuated tubes at room temperature. After 2 h, the tubes were opened, the solutions were evaporated to dryness *in vacuo*, and the residue recrystallised from acetone–petroleum (b.p. 40—60 °C). The *complexes*, which decomposed slowly in air, were obtained as pale yellow crystals (71 and 89% respectively).

Methoxobis(triphenylphosphine)tris(t-butyl isocyanide)iridium Bis(hexafluorophosphate).—When $[Ir(CNBu^t)_3(PPh_3)_2]Cl$ (0·21 g) was dissolved in methanol (10 ml), the initially yellow solution became colourless. On addition of an excess of NH_4PF_6, a white solid precipitated, which was filtered off, washed with methanol and ether, and air dried. The *complex* was obtained as white crystals (0·20 g, 74%).

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