Isocyanide Complexes of Rhodium and Iridium. Part I. Tetrakisisocyanide Species, Their Oxidative Addition Reactions, and Some Allyl Complexes

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The rhodium(I) and iridium(I) isocyanide complexes $[M(CNR)_4]Z$ (M = Rh, Z = PF_6, R = Me, Pr^i, cyclohexyl, Bu^t, p-$MeOC_6H_4$, p-MeC_6H_4, or p-ClC_6H_4; M = Rh, Z = Cl, R = Bu^t or p-ClC_6H_4; M = Ir, Z = PF_6, R = Bu_t or p-ClC_6H_4) have been prepared. These undergo oxidative addition reactions giving *trans*-$[M(CNR)_4XY]^+$ (various R; X = Cl, Y = Cl, $PhCH_2$, C_3H_5, C_3H_4Me, MeCO, HgCl, or $SnCl_3$; X = Br, Y = Br, CN, $PhCH_2$, or C_3H_5; X = I, Y = I, Me, CF_3, or C_3F_7). Addition of NO^+, p-$MeC_6H_4N_2^+$, or SO_2 afforded $[Rh(NO)(CNR)_4][PF_6]_2$ (R = Pr^i, cyclohexyl, or Bu^t), $[Rh\{N_2(p\text{-}MeC_6H_4)\}(CNBu^t)_4][PF_6]_2$ and $[Rh(SO_2)(CNR)_4][PF_6]$ (R = Pr^i or p-MeC_6H_4), respectively. Treatment of $[Rh(\pi\text{-}C_3H_5)_2Cl]_2$ with one or two moles of RNC (R = p-MeC_6H_4), afforded either $[Rh(\pi\text{-}C_3H_5)_2(CNR)Cl]$ or $[Rh(\pi\text{-}C_3H_5)(\sigma\text{-}C_3H_5)(CNR)_2Cl]$.

THE chemistry of planar rhodium(I) and iridium(I) complexes is characterised by oxidative addition reactions which result in the formation of six-co-ordinate rhodium(III) and iridium(III) compounds.[1] However, despite the observation that $[Rh(CNPh)_4Cl_2]Cl$ had been isolated[2] as an intermediate in the formation of $[Rh(CNPh)_4]^+$ from $RhCl_3$ and PhNC, surprisingly little attention had been paid, until recently, to this aspect of the chemistry of four-co-ordinate isocyanide complexes of rhodium(I) and iridium(I).

When we began our work, the only simple isocyanide complexes of rhodium and iridium known were $[Rh(CNAr)_4]X$ (X = Cl or ClO_4; Ar = Ph, p-$MeOC_6H_4$, p-MeC_6H_4, or p-ClC_6H_4),[3] and $[Ir\{CN(p\text{-}MeC_6H_4)\}_4]X$ (X = Br, I, or ClO_4).[4] We have expanded this series of compounds to include alkyl isocyanide derivatives, and report some of the oxidative addition chemistry of these compounds. A preliminary account of our work has been presented,[5] and, since then, several other workers have reported the reactions of methyl,[6] t-butyl,[7] and aryl isocyanide[8] complexes of rhodium, which extend, and substantiate, our findings.

RESULTS

The Square-planar Complexes, $[M(CNR)_4]^+$.—The rhodium complexes $[Rh(CNR)_4]^+$ (R = Me, Pr^i, cyclohexyl, Bu^t, p-$MeOC_6H_4$, p-MeC_6H_4, or p-ClC_6H_4) were conveniently prepared by the addition of an excess of CNR to $[Rh(CO)_2Cl]_2$ in methanol (*cf.* ref. 3), and, on addition of NH_4PF_6, afforded the hexafluorophosphate salts (analytical and conductivity data, Table 1). Some compounds were obtained directly as the Cl^- salts. The iridium complexes, $[Ir(CNR)_4][PF_6]$ (R = Bu^t or p-ClC_6H_4) were prepared by addition of an excess of RNC to methanolic solutions of $[Ir(CO)(C_8H_{14})Cl]_2$ (C_8H_{14} = cyclo-oct-1-ene), or $[Ir(C_8H_{12})(NCMe)_2][PF_6]$,[10] containing NH_4PF_6.

The reactions between precursors and RNC occurred rapidly at room temperature and deeply coloured solutions (green, red, violet, or blue[3]) were formed. When isolated, all the rhodium complexes, except that containing Bu^tNC, and $[Ir\{CN(p\text{-}ClC_6H_4)\}_4][PF_6]$ were violet or blue (Rh), or green (Ir); $[M(CNBu^t)_4]X$ was yellow.† With the exception of $[Ir(CNBu^t)_4][PF_6]$, all the complexes were stable

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† In the absence of definitive structural data we may speculate that the cations in the deeply coloured species could be stacked in columns in the solid state such that there is a close intermetallic contact which leads to charge transfer bands occurring in the visible region of the electronic spectrum. Such a situation is known to exist in the dichroic (red/green) $Rh(CO)_2(acac)$.[11] That the Bu^tNC-containing complexes exhibit the 'normal' yellow colour is probably a reflection of the steric bulk of the Bu^t substituents which force a separation of the metal atoms, thereby decreasing charge transfer. The occurrence of deep colours in solution may also be accounted for by the continued existence of aggregates, or, of course, by low-energy charge transfer transitions associated with the metal and RNC ligands (the latter situation could also pertain to the solids).

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[4] L. Malatesta and F. Bonati, 'Isocyanide Complexes of Metals,' Wiley–Interscience, 1969, p. 146.

[5] J. W. Dart, M. K. Lloyd, J. A. McCleverty, and R. Mason, *Chem. Comm.*, 1971, 1197.

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TABLE 1

Analytical and conductivity data obtained from rhodium and iridium isonitrile complexes

	Elemental analyses									Infrared data [a]	
	Found				Calc.						
Complex	C	H	N	X [b]	C	H	N	X [b]	Λ [a]	ν(CN)	Other frequencies
$[Rh(CNMe)_4][PF_6]$	25·1	3·2	14·8		25·2	3·2	14·7		83	2222s,br, 2252sh	
$[Rh(CNPr^i)_4][PF_6]$	36·4	5·0	10·5		36·6	5·4	10·7		100	2164s, 2200sh	
$[Rh(CNC_6H_{11})_4][PF_6]$	49·8	6·7	8·4		49·1	6·4	8·2		90	2180s, 2210w	
$[Rh(CNBu^t)_4][PF_6]$	41·5	6·2	9·5		41·3	6·2	9·7		85	2165s	
$[Rh(CNBu^t)_4]Cl$	51·4	7·8	11·8	7·3	51·0	7·7	11·9	7·5	87	2164s	
$[Rh\{CN(p\text{-}MeOC_6H_4\})_4][PF_6]$	43·7	2·3	7·3		43·1	2·1	7·2		82	2150s, 2200w	
$[Rh\{CN(p\text{-}MeC_6H_4)\}_4][PF_6]$	54·0	2·5	7·9		53·6	2·2	7·8		90	2155s, 2192w	
$[Rh\{CN(p\text{-}ClC_6H_4)\}_4]Cl$	47·5	2·4	7·9	26·0	48·8	2·3	8·1	25·8	85	2140s	
$[Ir(CNBu^t)_4][PF_6]$	34·9	4·9	7·2		35·9	5·3	8·4		79	2170s	
$[Ir\{CN(p\text{-}ClC_6H_4)_4\}][PF_6]$	37·8	1·7	6·3	15·7	37·9	1·8	6·3	16·0	80	2165s	
$[Rh(CNMe)_4Cl_2][PF_6]$	19·0	3·1	12·3	15·2	19·8	2·5	11·6	14·7	81	2280s	
$[Rh(CNPr^i)_4Cl_2][PF_6]$	32·6	5·0	9·5	12·1	32·2	4·7	9·4	11·9	*c*	2250s	
$[Rh(CNPr^i)_4Br_2][PF_6]$	28·4	4·3	8·0	23·0	28·1	4·1	8·2	23·4	87	2260s, 2222s	
$[Rh(CNPr^i)_4I_2][PF_6]$	25·4	3·5	7·8	32·1	24·7	3·6	7·2	32·6	92	2210s,	
$[Rh(CNPr^i)_4(CN)Br][PF_6]$	32·6	4·7	11·0	12·7	32·4	4·5	11·0	12·7	93	2265s,br	2240w[ν(CN)]
$[Rh(CNPr^i)_4(Me)I][PF_6]$	30·8	4·6	8·2	20·3	30·9	4·7	8·4	19·6	84	2234s	
$[Rh(CNBu^t)_4Br_4][PF_6]$	31·8	4·8	7·6	21·3	32·4	4·9	7·6	21·6	83	2250s, 2242sh	
$[Rh(CNBu^t)_4I_2][PF_6]$	29·1	4·4	6·8	31·0	28·8	4·3	6·7	30·5	88	2240s	
$[Rh(CNBu^t)_4I_2]Cl$	32·6	4·9	7·9	*d*	33·1	5·0	7·7	*d*	89	2238s	
$[Rh(CNBu^t)_4(COMe)Cl][PF_6]$	40·1	5·9	8·5	5·6	40·1	5·9	8·7	5·4	93	2240s	1722[ν(CO); 226[ν(RhCl)]
$[Rh(CNBu^t)_4(CN)Br][PF_6]$	36·7	5·2	7·7	12·1	36·7	5·2	8·2	11·7	84	2248s,br	2175w[ν(CN)]
$[Rh(CNBu^t)_4(CH_2Ph)Br][PF_6]$	43·1	5·6	7·6		43·1	5·9	7·5		82	2205s	
$[Rh(CNBu^t)_4(Me)I][PF_6]$	34·9	5·4	7·9	17·8	34·9	5·4	7·8	17·6	80	2228s	
$[Rh(CNBu^t)_4(CF_3)I][PF_6]$	33·4	5·1	7·4	16·8	32·5	4·6	7·2	16·3	90	2250s	1085s,br[ν(CF)]
$[Rh(CNBu^t)_4(C_3F_7)I][PF_6]$	31·6	4·1	6·4	15·6	31·5	4·1	6·4	15·1	82	2245s,br	1322s, 1225s,br, 1202s,br, 1168w, 1098s[ν(CF)]
$[Rh\{CN(p\text{-}MeOC_6H_4)\}_4(Me)I][PF_6]$	42·9	3·4	5·7	*c*	42·9	3·4	6·1	*c*	86	2205s	
$[Rh\{CN(p\text{-}MeOC_6H_4)\}_4(HgCl)Cl]Cl$	40·9	3·0	6·7	*c*	40·7	3·0	6·0	*c*	81	2200s	
$[Rh\{CN(p\text{-}MeOC_6H_4)\}_4(SnCl_3)Cl]Cl$	41·2	3·1	5·7	17·0	41·2	3·0	6·0	17·3	78	2160s	
$[Rh\{CN(p\text{-}ClC_6H_4)\}_4(Me)I)Cl$	43·1	2·8	6·8	*c*	42·1	2·3	6·8	*c*	88	2190s	
$[Rh\{CN(p\text{-}ClC_6H_4)\}_2I_2Cl]_2$	25·1	1·2	4·2	*c*	25·1	1·3	4·6	*c*	34	2198,[e] 2218s[e]	
$[Ir(CNBu^t)_4Br_2][PF_6]$	24·4	4·5	7·0	*c*	25·0	4·3	6·8	*c*	81	2220s	
$[Ir(CNBu^t)_4(Me)I][PF_6]$	31·0	4·9	6·6	16·6	31·1	4·8	6·9	15·7	76	2219s	
$[Ir\{CN(p\text{-}ClC_6H_4)\}_4Br_2][PF_6]$	32·4	1·1	5·4	*c*	32·1	1·5	5·4	*c*	85	2198s	
$[Ir\{CN(p\text{-}ClC_6H_4)\}_4(Me)I][PF_6]$	34·0	2·0	5·7	*c*	33·8	1·9	5·4	*c*	78	2188s	
$[Rh(CNPr^i)_4(NO)][PF_6]_2$	26·5	4·2	9·3		27·0	4·0	10·0		156	2240s,br	1770m,br[ν(NO)]
$[Rh(CNC_6H_{11})_4(NO)][PF_6]_2$	39·9	5·5	7·7		39·1	5·1	8·2		*c*	2242s,br	1770m,br[ν(NO)]
$[Rh(CNBu^t)_4(NO)][PF_6]_2$	31·7	4·9	9·1		31·7	4·8	9·3		171	2239s	1765m,br[ν(NO)]
$[Rh(CNBu^t)_4\{N_2(p\text{-}MeC_6H_4)\}][PF_6]_2$	37·4	4·4	9·7		37·7	5·0	9·8		185	2259s, 2280sh 2232sh	1583s[ν(NN)]
$[Rh(CNPr^i)_4(SO_2)][PF_6]$	33·0	5·0	9·4	4·8[f]	32·6	4·8	9·5	5·4[f]	84	2245s,br; 2200sh	1170w, 990s[ν(SO)]
$[Rh\{CN(p\text{-}MeC_6H_4)\}_4(SO)_2)]Cl$	56·8	5·2	8·3	5·4[g]	57·2	4·2	8·3	4·8[g]	85	2190s, 2120s	1310w, 1280w, 1120w[ν(SO)]
$[Rh(CNBu^t)_4(C_3H_5)Cl][PF_6]$	42·4	6·7	8·6	5·6	42·1	6·3	8·5	5·4	80	2240s	1618m[ν(C=C)]
$[Rh\{CN(p\text{-}MeOC_6H_4)\}_4(C_3H_5)Br][PF_6]$	46·1	3·4	6·5	9·3	46·5	3·7	6·2	8·9	92	2190s	1600m[ν(C=C)]
$[Rh\{CN(p\text{-}MeC_6H_4)\}(C_3H_5)_2Cl]$	49·0	5·0	4·6	10·3	49·8	5·0	4·2	10·5	*c*	2180s	513[δ(CCC)]
$[Rh\{CN(p\text{-}MeC_6H_4)\}_2(C_3H_5)_2Cl]$	58·3	5·3	6·3	7·5	58·1	5·3	6·2	7·8	*c*	2200s	513[δ(CCC)
$[Rh\{CN(p\text{-}ClC_6H_4)\}_4(C_3H_5)Cl]Cl$	49·2	3·0	7·6	27·5	48·6	2·7	7·3	27·9	94	2200s	1610m[ν(C=C)]
$[Rh\{CN(p\text{-}ClC_6H_4)\}(C_3H_5)_2Cl]$	43·4	4·0	4·1	20·2	43·5	3·9	3·9	19·8	*c*		511[δ(CCC)]
$[Ir(CNBu^t)_4(C_3H_4Me)][PF_6]$	33·6	5·1	6·5		33·1	4·9	6·4		139	2330s, 2244s	
$[Ir\{CN(p\text{-}ClC_6H_4)\}(C_3H_4Me)Cl][PF_6]$	40·0	2·5	5·4	18·1	39·3	2·4	5·7	18·2	83	*h*	

[a] Conductivity measurements in $MeNO_2(10^{-4}M)$ in Ω^{-1} cm^2 mol^{-1}, 1 : 1 electrolytes *ca.* 80, 1 : 2 electrolytes *ca.* 150 Ω^{-1} cm^2 mol^{-1}. I.r. data in cm^{-1}, ν(CN) determined in KBr discs, other frequencies in CH_2Cl_2 solution. [b] Halogen analysis. [c] Not measured. [d] Hydrogen analysis: found I, 29·8; Cl 4·8; calc. 30·4, 4·3%. [e] In CH_2Cl_2 solution. [f] S Analysis. [g] S Analysis: found 5·1, calc. 5·3%. [h] ν(CN) for $[Ir\{CN(p\text{-}ClC_6H_4)\}_4C_3H_5Cl][PF_6]$: 2194s, 2220sh cm^{-1}.

towards air. In air, the iridium compound rapidly turned white affording, on the basis of elemental analyses, the oxygen adduct $[Ir(CNBu^t)_4(O_2)][PF_6]$.

The i.r. spectra of these four-co-ordinate species were entirely consistent with their expected D_{4h} symmetry [singlet ν(CN), E_u mode]. However, in a few cases, a weaker band, perhaps the ' inactive ' A_{1g} or B_{1g} mode, was observed at higher frequencies. The CN stretching frequencies occurred in the range 2140—2250 cm^{-1} and ν(NC) for the complexed isocyanide was significantly higher than that in the free ligand; the increase in ν(NC) was greater for the alkyl isocyanides than for their aryl analogues. These data indicate that there is probably little, if any, donation of electron density from the metal to RNC ($d \longrightarrow \pi^*$), and that the increase in ν(CN) on co-ordination can be attributed to the donation of the (weakly anti-bonding) σ-lone pair on the C atom from RNC to the metal. This effect would lead to a strengthening of the CN bond and hence an increase in the stretching force constant, and thus ν(CN).

TABLE 2

Oxidative addition products obtained from rhodium and iridium isocyanide complexes: $[M(CNR)_4]^+ + XY \longrightarrow [M(CNR)_4XY]^+$

		Rh							Ir	
X	Y	Me	Pr^i	Bu^t	p-Me	p-MeO	p-Cl	Ph	Bu^t	p-Cl
Cl	Cl	*a*	*a*				*a*	*b*		
$PhCH_2$	Cl			*c*						
C_3H_5	Cl			*a*						
C_3H_4Me	Cl						*a*			
CH_3CO	Cl			*a*						
ClHg	Cl					*d*				
Cl_3Sn	Cl					*d*				
Br	Br		*a*	*a*	*e*	*e*				
NC	Br		*a*	*a*						
$PhCH_2$	Br			*a*						
C_3H_5	Br					*a*				
I	I	*f*	*a*	*d, c*	*e*	*e*				
Me	I	*f*	*a*	*a, c*		*a*	*a*		*a*	*a*
Et	I			*c*						
Pr^n	I			*c*						
Bu^n	I			*c*						
$PhCH_2$	I			*c*						
CF_3	I			*a*						
C_3F_7	I			*a*						

[a] As PF_6^- salts, this work. [b] Ref. 3. [c] Ref. 8. [d] As chloride salts, this work. [e] Ref. 7. [f] Ref. 6.

Oxidative Addition Reactions and $[M(CNR)_4XY]^+$.—Reaction of $[Rh(CNR)_4]^+$ with the substrate XY (see Table 2 for the compounds formed) in ethanol or dichloromethane readily afforded the six-co-ordinate $[Rh(CNR)_4XY]^+$; the majority of the complexes were isolated as their PF_6^- salts (Table 1). The addition reactions occurred at room temperature, although chlorination of $[Rh(CNMe)_4]^+$ was achieved most effectively by refluxing CCl_4.

Addition of I_2 to $[Rh(CNBu^t)_4]Cl$ afforded a 1 : 1 electrolyte of empirical formula $[Rh(CNBu^t)_4I_2Cl]$, whereas similar treatment of $[Rh\{CN(p\text{-}ClC_6H_4)\}_4]Cl$ gave the binuclear $[Rh\{CN(p\text{-}ClC_6H_4)\}_2I_2Cl]_2$. However, the respective hexafluorophosphate salts both gave $[Rh(CNR)_4I_2][PF_6]$ on treatment with iodine, indicating that, when R = p-ClC_6H_4, the counteranion plays an important role in these oxidative addition reactions.

Reaction of Br_2 or MeI with $[Ir(CNR)_4][PF_6]$ afforded the appropriate oxidised addition product. While these reactions were rapid when R = Bu^t, and proceeded at room temperature, formation of the addition products when R = p-ClC_6H_4 would only occur after gentle refluxing in acetonitrile for several minutes. Attempts to add MeCOCl to the iridium complexes clearly resulted in oxidation [ν(CN) increased], but no characterisable products could be obtained.

In all cases, with the possible exception of the dibromides, *trans*-addition products, which exhibited only one CN stretching frequency (Table 1) consistent with C_{4v} (X ≠ Y) or D_{4h} (X = Y) symmetry for $[M(CNR)_4XY]^+$, were formed. The value of ν(CN) increased, relative to that of the appropriate $[M(CNR)_4]^+$, by between 20 and 95 cm^{-1}, on oxidation. Thus ν(CN) can be usefully employed to detect whether oxidation of the parent M^I complex has occurred. This increase reflects, presumably, the reduction of electron density at the metal which, in turn, reduces still further the necessity of RNC to accept ' back donated ' charge, and increases the extent of σ-donation from RNC to the metal. The increase in ν(CN) was greater, on oxidation, in compounds containing alkyl isocyanides than that in the corresponding aryl analogues. This is presumed to be due to the greater σ-donor ability of the alkyl isocyanides. The value of ν(CN) was also effected by the electronegativity of the attached substrate X_2, increasing, in $[Rh(CNPr^i)_4X_2]^+$, in the order X = I < Br < Cl. A comparison of ν(CN) obtained from $[Rh(CNBu^t)_4I_2][PF_6]$ and $[Rh(CNBu^t)_4I_2Cl]$ suggests that the latter also contains the cation $[Rh(CNBu^t)_4I_2]^+$.

The complexes containing BrCN exhibited weak cyanide stretching frequencies at values lower than ν(CN) for the co-ordinated RNC. The acyl complex, $[Rh(CNBu^t)_4(COMe)Cl][PF_6]$ exhibited ν(CO) at 1722 cm^{-1}, and a band at 226 cm^{-1} was assigned to the Rh–Cl stretching mode. The position of frequencies due to Rh–Cl vibrations are dependent on the nature of the *trans*-ligand,[12] and the position of this frequency is consistent with the stretching mode of Cl *trans* to an acyl group.

The solution i.r. spectra of $[Rh\{CN(p\text{-}ClC_6H_4)\}_2I_2Cl]_2$ exhibited two strong ν(NC), which is consistent with the

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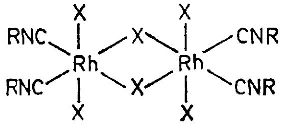
[12] M. Kubota and D. M. Blake, *J. Amer. Chem. Soc.*, 1971, **93**, 1368.

structure (I). It is not known which halogen atoms are bridging, but a structure of this type has also been proposed for $[Rh(CO)_2X_3]_2$.[13]



I: $X_6 = I_4Cl_2$

The presence of singlet resonances due to the Bu^t protons in the ^1H n.m.r. spectra (Table 3) of $[Rh(CNBu^t)_4XY^+$ was consistent with the expected *trans* (XY) geometry. The proton resonances of the methyl group in $[Rh(CNR)_4MeI]^+$ occurred as doublets because of $J(RhH)$ (*ca.* 2·0 Hz) and, of course, this coupling was absent in $[Rh(CNBu^t)_4(COMe)Cl]^+$.

The ^{19}F n.m.r. spectrum of $[Rh(CNBu^t)_4(C_3F_7)I][PF_6]$ exhibited four groups of resonances, associated with the F atoms attached to the α, β, and γ-C atoms, and to the PF_6^- anion.

Species containing NO, *p*-$MeC_6H_4N_2$, *or* SO_2.—The addition of NO^+ or ArN_2^+ (Ar = aryl) to a variety of low-valent ruthenium, rhodium, or iridium complexes has afforded a series of cationic nitrosyl [14] and azo-complexes.[15] Treatment of $[Rh(CNR)_4][PF_6]$ (R = Pr^i, cyclohexyl, or Bu^t) with $NOPF_6$ in methanol afforded the blue or blue-green five-co-ordinate dicationic species $[Rh(NO)(CNR)_4][PF_6]_2$ (the species R = Bu^t, as BF_4^- salt has also been reported [7]). While the species with R = Bu^t was relatively stable towards decomposition in air in the solid or in solution, those where R = Pr^i or cyclohexyl rapidly decomposed giving green, uncharacterisable products. The azo-complex $[Rh(CNBu^t)_4\{N_2(p\text{-}MeC_6H_4)\}][PF_6]_2$ was obtained by addition of the appropriate diazonium salt to

TABLE 3

N.m.r. spectral data obtained from some rhodium and iridium complexes [a]

Complex	Solvent	τ/δ [b]	R.A. [c]	Assignments
$[Rh(CNPr^i)_4]^+$	$CDCl_3$	5·87	1	(septuplet) Me_2CHNC; $J(HH)$ 6·2 Hz
		8·51	6	(d) $(CH_3)_2CHNC$; $J(HH)$ 615 Hz
$[Ir(CNBu^t)_4]^+$	$(CD_3)_2CO$	8·34	1	(s) $(CH_3)_3CNC$
$[Rh\{CN(p\text{-}MeOC_6H_4)\}_4]^+$	$CDCl_3$	*ca.* 3·0	4	(m) C_6H_4
		6·23	3	(s) CH_3O–
$[Ir\{CN(p\text{-}ClC_6H_4)\}_4]^+$	$(CD_3)_2CO$	2·60		(m) C_6H_4
$[Rh(CNPr^i)_4(Me)I]^+$	$CDCl_3$	5·60	4	(sept) Me_2CHNC; $J(HH)$ 6·7 Hz
		8·46	24	(d) $(CH_3)_3CHNC$; $J(HH)$ 6·5 Hz
		8·76	3	(d) Rh–CH_3; $J(RhH)$ 2·0 Hz
$[Rh(CNBu^t)_4(Me)I]^+$	$CDCl_3$	8·41	12	(s) $(CH_3)_3CNC$
		8·75	1	(d) Rh–CH_3; $J(RhH)$ 2·3 Hz
$[Ir(CNBu^t)_4(Me)I]^+$	$(CD_3)_2CO$	8·05	12	(s) $(CH_3)_3CNC$
				(s) Ir–CH_3
$[Rh\{CN(p\text{-}MeOC_6H_4)\}_4(Me)I]^+$	$CDCl_3$	2·73	16	(dd) AB pair ($J(AB)$ 9·0 Hz; C_6H_4
		6·19	12	(s) CH_3O^-
		8·27	3	(d) Rh–CH_3; $J(RhH)$ 2·3 Hz
$[Ir\{CN(p\text{-}ClC_6H_4\}_4(Me)I]^+$	$(CD_3)_2CO$	2·30	16	(m) C_6H_4
		8·64	3	(s) Ir–CH_3
$[Rh(CNBu^t)_4(CH_2Ph)Br]^+$	$CDCl_3$	2·78	5	(s) C_6H_5
		6·50	2	(d) Rh–CH_2^-; $J(RhH)$ 2·5 Hz
		8·49	36	(s) $(CH_3)_3CNC$
$[Rh(CNBu^t_4(COMe)Cl]^+$	$CDCl_3$	7·32	1	(s) $RhCOCH_3$
		8·35	12	(s) $(CH_3)_3CNC$
$[Ir(CNBu^t)_4Br_2]^+$	$(CD_3)_2CO$	8·20		(s) $(CH_3)_3CNC$
$[Ir\{CN(p\text{-}ClC_6H_4)\}_4Br_2]^+$	$(CD_3)_2CO$	2·30		(dd) AB pair; $J(AB)$ 8·0 Hz; C_6H_4
$[Rh(CNBu^t)_4\{N_2(p\text{-}MeOC_6H_4)\}]^{2+}$	$CDCl_3$	3·00	4	(dd) AB pair; $J(AB)$ 8 Hz; C_6H_4
		6·28	3	(s) CH_3O^-
		8·38	36	(s) $(CH_3)_3CNC$
$[Rh(CNBu^t)_4(C_3H_5)Cl]^+$	$CDCl_3$ [d]	4·00	1	(m) Rh–$CH_2CH{=}CH_2$
		4·85	2	(m) $RhCH_2CH{=}CH_2$
		7·17	2	(d) Rh–CH_2CHCH_2
		8·33	36	(s) $(CH_3)_3CNC$
$[Ir(CNBu^t)_4(2\text{-}MeC_3H_4)]^{2+}$	$(CD_3)_2CO$	8·08	12	(d) $(CH_3)_3CNC$
		8·74	1	(s) 2-$CH_3C_3H_4$
$[Rh\{CN(p\text{-}MeOC_6H_4)\}_4(C_3H_5)Br]^+$	$(CD_3)_2CO$ [d]	*ca.* 3·20	4	(m) br; ($W_{\frac{1}{2}}$ 60 Hz); C_6H_4
		6·28	3	(s) CH_3O^-
$[Ir\{CN(p\text{-}ClC_6H_4)\}_4(2\text{-}MeC_3H_4)Cl]^+$	$(CD_3)_2CO$	2·40	16	(m) C_6H_4
		8·76	3	(s) 2-$CH_3C_3H_4$
$Rh(\pi\text{-}C_3H_5)_2\{CN(p\text{-}MeC_6H_4)\}Cl$	$CDCl_3$ [d]	*ca.* 2·80		(m)br; ($W_{\frac{1}{2}}$ 26 Hz); C_6H_4
		ca. 4·90		(m) allylic protons
		ca. 7·63		(m) overlapping signals due to allylic and CH_3 protons
$[Rh(CNBu^t)_4(C_3F_7)I]^+$	$CDCl_3$	61·50	2	(m) α-CF_2
		73·18	6	(d) PF_6; $J(PF)$ 710 Hz
		79·40	3	(t) γ-CF_3; $J(\alpha\gamma)$ 9·0 Hz
		118·4	2	(s) β-CF_2

[a] As PF_6^- salts, at 100 MHz (^1H) or 90 MHz (^{19}F), at room temperature (20 ± 2 °C). [b] τ Refers to ^1H n.m.r. data, δ in p.p.m. for ^{19}F n.m.r. data, *vs.* $CFCl_2$. [c] Relative area. [d] Recorded at −60 °C.

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$[Rh(CNBu^t)_4][PF_6]$. Attempts to prepare similar iridium nitrosyl and azo-complexes, and to obtain rhodium aryl isocyanides containing NO^+, were unsuccessful. Reactions did occur when the precursors were treated with NO^+, but whether or not the decomposition products contained either NO_2 or NO_3 groups could not be established unequivocally by i.r. spectroscopy.

The i.r. spectra of $[Rh(NO)(CNR)_4]^{2+}$ exhibited one ν(CN), and ν(NO) occurred at *ca.* 1765 cm^{-1}, being little affected by the nature of R. The spectra were consistent with a tetragonal pyramidal structure with apical NO (C_{4v} symmetry) similar to that found in $[Ir(NO)(PPh_3)_3H]^+$ and $[Ir(NO)(CO)(PPh_3)_2Cl]^+$.[15] Attempts to correlate the M–N–O bond angle with ν(NO) have proved to be misleading, and although the iridium cations just mentioned have Ir–N–O bond angles of *ca.* 120°, we can only speculate that similar bending occurs in the isocyanide complexes. The value of ν(NO) in $[Rh(NO)(CNBu^t)_4][PF_6]_2$ was *ca.* 20 cm^{-1} higher than that reported [7] for the corresponding BF_4^- salt. However, it has been noted previously that ν(NO) in a series of isostructural or identical compounds is affected by the counter-anion or -cation.[17]

The i.r. spectrum of $[Rh\{N_2(p\text{-}MeC_6H_4)\}(CNBu^t)_4][PF_6]_2$ also exhibited one ν(CN), and ν(NN) occurred at 1580 cm^{-1}. The structure of this compound is probably similar to that of its isoelectronic nitrosyl analogue, and ν(NN) is low enough to be consistent with the presence of a bent $Rh{-}N{=}N{-}C_6H_4Me$ group.

Reaction of SO_2 with solutions of $[Rh(CNR)_4][PF_6]$ ($R = Pr^i$ or $p\text{-}MeC_6H_4$) afforded the five-co-ordinate adducts $[Rh(SO_2)(CNR)_4][PF_6]$, which appeared to be stable towards aerial oxidation. Their i.r. spectra contained two CN stretching frequencies and bands attributable to co-ordinated SO_2 but not, apparently, SO_4. It has been suggested that SO_2 can act as an acceptor or a donor; [18] in $Ir(CO)(PPh_3)_2(SO_2)Cl$ it is thought to act as an electrophile so that the geometry at the S atom is essentially tetrahedral, whereas in $[Ru(NH_3)_4(SO_2)Cl]^+$ it may function as a nucleophile, the atoms in the $Ru{-}SO_2$ group being coplanar. While the spectral data reported herein do not permit unequivocal structural assignments, it would seem likely that the co-ordinated SO_2 is functioning primarily as an acceptor.

Allyl Complexes.—The addition of allyl halides to low-valent rhodium and iridium complexes has afforded [18] simple σ-allylic products, derived by straightforward oxidative addition, and π-allylic species. Treatment of $[Rh(CNR)_4][PF_6]$ ($R = Bu^t$, $p\text{-}MeOC_6H_4$ or $p\text{-}ClC_6H_4$) with C_3H_5X (X = Cl or Br) afforded the six-co-ordinate *trans*-$[Rh(CNR)_4(C_3H_5)X][PF_6]$, and $[Ir\{CN(p\text{-}ClC_6H_4)\}_4(2\text{-}MeC_3H_4)Cl][PF_6]$ was obtained similarly. However, reaction of $[Ir(CNBu^t)_4][PF_6]$ with $2\text{-}MeC_3H_4Cl$ in the presence of PF_6^- gave $[Ir(CNBu^t)_4(2\text{-}MeC_3H_4)][PF_6]_2$.

The i.r. spectra of the species $[M(CNR)_4(allyl)X]^+$ exhibited only one ν(NC), and also a band at *ca.* 1600 cm^{-1}, assigned to the (unco-ordinated) C=C groups of the σ-allylic group. Such bands were absent in the spectrum of $[Ir(CNBu^t)_4(2\text{-}MeC_3H_4)]^{2+}$ which probably contains a π-allylic group.

The ^1H n.m.r. spectrum of $[Rh(CNBu^t)_4(C_3H_5)Cl]^+$ did not exhibit resonances at room temperature due to the C_3H_5 group. However, at −60°, a spectrum was obtained which was similar to that observed with $Rh(PPh_3)_2(C_3H_5)Cl_2$,[19] and this confirms that the allyl group is σ-bonded and probably stereochemically non-rigid at room temperature. The spectrum of $[Ir(CNBu^t)_4(2\text{-}MeC_3H_4)][PF_6]_2$ exhibited two distinct resonances, one due to the Bu^t group and the other to the allylic Me substituent. The appearance of the former resonance as a doublet indicates a *cis* arrangement of the two groups of RNC ligands in a molecule probably containing a π-allylic group. The failure to observe resonances due to the allylic protons was due to low solubility of the complex, and perhaps to exchange processes.

In an attempt to obtain more spectral information about allylic isocyanide complexes, we reacted $[Rh(\pi\text{-}C_3H_5)_2Cl]_2$ with one and two molar equivalents of $p\text{-}MeC_6H_4NC$. The products were $[Rh(C_3H_5)_2\{CN(p\text{-}MeC_6H_4)\}Cl$ and $Rh(C_3H_5)_2\{CN(p\text{-}MeC_6H_4)\}_2Cl$, which were non-electrolytes. No definite structural information could be obtained from the i.r. spectra of these compounds, although both exhibited bands due, probably, to the deformation of the C_3 (π-allylic) fragment; [20] the latter complex did not exhibit ν(C=C). At −60°, the ^1H n.m.r. spectra of both compounds consisted of only broad lines, suggesting that relatively fast intramolecular rearrangements were occurring; spectra could not be obtained at lower temperatures because the compounds precipitated from suitable solvents. It seems reasonable, however, that the former complex contains two asymmetric π-allylic groups [*cf.* $Rh(\pi\text{-}C_3H_5)_2(PPh_3)Cl$ [21]] and that the latter has an instantaneous structure $Rh(\pi\text{-}C_3H_5)(\sigma\text{-}C_3H_5)\{CN(p\text{-}MeC_6H_4)\}Cl$.

DISCUSSION

Our results have shown that, as expected, the isocyanide complexes of rhodium(I) and iridium(I) readily undergo oxidative addition reactions. Previous studies of rhodium(I) and iridium(I) phosphine and carbonyl complexes showed [1] that an effective increase of the ' σ-basicity ' and/or a decrease in π-acidity of the ligands led to an increased ability to undergo oxidative addition. However, the complexes containing alkyl isocyanides described herein did not react with H_2 at atmospheric pressures and normal temperatures, and only $[Ir(CNBu^t)_4]^+$ reacted with O_2. We conclude therefore that the isocyanide ligands used in this work do not increase the electron density at the metal atom sufficiently to promote activation of H_2. This contrasts with the behaviour of $[Rh(Me_2PCH_2CH_2PMe_2)_2]^+$ or $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$.[1]

Even with the limited data presently available, we have detected differences between the chemical behaviour of alkyl and aryl isocyanide complexes. Thus reaction of $[Rh(CNBu^t)_4]^+$ with MeCOCl afforded the expected addition product, without decarbonylation,

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whereas such a product was not obtained from $[Rh\{CN(p\text{-}ClC_6H_4)\}_4]^+$ (reactions did occur but the uncharacterisable products contained no acyl or methyl groups, and was not $[Rh\{CN(p\text{-}ClC_6H_4)\}_4Cl_2]^+$). Iodination of $[Rh(CNBu^t)_4]Cl$ gave $[Rh(CNBu^t)_4I_2]Cl$ whereas similar treatment of $[Rh\{CN(p\text{-}ClC_6H_4)_4\}]^+$ afforded $[Rh\{CN(p\text{-}ClC_6H_4)\}_2I_2Cl]_2$.

Addition of an excess of RNC to π-allyl palladium complexes has afforded iminoacyl products,[22] *e.g.* $[Pd\{C(=NR)CH_2CH{:}CH_2\}(CNR)Cl]_2$, but attempts to obtain similar rhodium complexes were unsuccessful.

EXPERIMENTAL

Elemental analyses were determined by the Microanalytical Laboratory of this Department. Conductivities were measured at room temperature (20 ± 2°) using a Phillips conductivity meter. I.r. and n.m.r. spectral data were obtained using Infracord 457, Perkin-Elmer 180, and Varian HA 100 spectrometers, respectively.

The isocyanide ligands used in this work were prepared by standard routes using $POCl_3$, $p\text{-}MeC_6H_4SO_2Cl$, or phosgene.[24] The metal complex precursors $[Rh(CO)_2Cl]_2$,[25] $[Ir(CO)(C_8H_{14})Cl]_2$,[26] and $[Rh(\pi\text{-}C_3H_5)_2Cl]_2$ [27] were obtained by published procedures. The complexes $[Rh(CNR)_4][PF_6]$ (R = $p\text{-}MeOC_6H_4$, $p\text{-}MeC_6H_4$, or $p\text{-}ClC_6H_4$) were prepared by the methods of Malatesta and Vallarino.[3]

Tetrakis(isopropyl isocyanide)rhodium(I) *Hexafluorophosphate*.—When a methanolic solution (10 ml) of $[Rh(CO)_2Cl]_2$ (0·36 g) was treated with Pr^iNC (1·5 g), gas was immediately evolved and the solution turned violet. The complex was precipitated on addition of methanolic $[NH_4][PF_6]$, and recrystallisation was affected from dichloromethane–ethanol. The compound, after washing with water, ethanol, and ether, and being air-dried, was obtained as violet crystals (0·38 g, 80%).

Tetrakis(t-butyl isocyanide)- and Tetrakis(cyclohexyl isocyanide)-rhodium(I) *Hexafluorophosphates*.—These complexes were prepared in the same way as their Pr^iNC analogue, and were isolated as yellow (84%) and dark brown (73%) solids, respectively.

Tetrakis(t-butyl isocyanide)rhodium(I) *Chloride*.—To a solution of $[Rh(CO)_2Cl]_2$ (0·31 g) dissolved in tetrahydrofuran (15 ml) was added Bu^tNC (0·6 g). The solution became yellow rapidly, and a yellow solid was precipitated. This was filtered off, washed with ether, and air dried, giving the complex (0·23 g, 62%).

Tetrakis(methyl isocyanide)rhodium(I) *Hexafluorophosphate*.—When a methanolic solution (15 ml) of $Rh(CO)(PPh_3)_2Cl$ (0·32 g) was treated with MeNC (0·3 g) the solution became deep red and a gas was evolved. After the gas evolution had ceased, the solution was refluxed under N_2 for 1 h and $[NH_4][PF_6]$ (0·1 g) was then added. After cooling the solvent was removed *in vacuo* leaving a brown residue. This was extracted with a small volume of dichloromethane and the solution extract filtered. To the filtrate was added ethanol and the whole was partially evaporated *in vacuo* and cooled. The complex slowly precipitated as a violet solid (0·27 g, 55%).

Tetrakis(isocyanide)iridium(I) *Hexafluorophosphates*, $[Ir(CNR)_4][PF_6]$, R = Bu^t *or* $p\text{-}ClC_6H_4$.—When an excess of RNC was added to an acetone solution of $[Ir(CO)(C_8H_{14})Cl]_2$ or $[Ir(C_8H_{12})(NCMe)_2][PF_6]$ deep purple solutions were formed. Addition of NH_4PF_6, dissolved in acetone, to the reaction mixture containing $[Ir(CO)(C_8H_{14})Cl]_2$, followed by addition of light petroleum (b.p. 40—60°) afforded yellow crystalline precipitates of $[Ir(CNBu^t)_4][PF_6]$ (yellow, 73% yields) or $[Ir\{CN(p\text{-}ClC_6H_4)\}_4][PF_6]$ (green, 85% yields). The former complex turned white in air, forming, probably $[Ir(CNBu^t)_4(O_2)][PF_6]$ or a mixture of the precursor and oxygenated species.

Dichlorotetrakis(methyl isocyanide)rhodium(III) *Hexafluorophosphate*.—A suspension of $[Rh(CNMe)_4][PF_6]$ (0·22 g) in CH_2Cl_2–CCl_4 (1 : 2 *v/v*; 30 ml) was refluxed under N_2 for 5 h. After cooling, the mixture was filtered affording a violet residue (unreacted starting material) and a yellow filtrate. The filtrate was evaporated to dryness, leaving a brown residue which was recrystallised from acetone–light petroleum (b.p. 40—60°). The complex (0·12 g, 48%) was obtained as yellow crystals.

Dichlorotetrakis(isopropyl isocyanide)rhodium(III) *Hexafluorophosphate*.—$[Rh(CNPr^i)_4][PF_6]$ (0·3 g), dissolved in CH_2Cl_2 (15 ml), was treated with HCl gas, and the solution became yellow. Partial evaporation of the solvent *in vacuo* followed by addition of ethanol, afforded the complex as a light yellow powder (0·20 g, 50%).

Dibromotetrakis(t-butyl isocyanide)rhodium(III) *Hexafluorophosphate*.—To $[Rh(CNBu^t)_4][PF_6]$ (0·09 g), dissolved in CH_2Cl_2 (5 ml), was added Br_2 (0·1 ml). To this mixture was added light petroleum (b.p. 40—60 °C) and, after partial evaporation *in vacuo*, the complex was obtained as an orange powder (0·07 g, 72%).

The complexes $[Rh(CNPr^i)_4Br_2][PF_6]$ (pale yellow crystals, 61%), $[Rh(CNBu^t)_4MeI][PF_6]$ (green powder, 81%), $[Rh(CNPr^i)_4MeI][PF_6]$ (orange powder, 75%), $[Rh\{CN(p\text{-}MeOC_6H_4)\}_4MeI][PF_6]$ (grey powder, 52%), $[Rh(CNBu^t)_4(COMe)Cl][PF_6]$ (white powder, 78%), $[Rh(CNBu^t)_4(CN)Br][PF_6]$ (yellow crystals, 76%), $[Rh(CNPr^i)_4(CN)Br][PF_6]$ (yellow crystals, 72%), $[Rh(CNBu^t)_4(CH_2Ph)Br][PF_6]$ (recrystallised from acetone–isopropyl alcohol, light yellow crystals, 57%), $[Rh(CNBu^t)_4(C_3H_5)Br][PF_6]$ (white powder, 64%), $[Rh\{CN(p\text{-}MeOC_6H_4)\}_4(C_3H_5)Br][PF_6]$ recrystallised from acetone–ethanol, light brown crystals, 54%), and $[Rh\{CN(p\text{-}ClC_6H_4)\}_4(C_3H_5)Cl]Cl$ (light brown powder, 41%), were prepared and isolated similarly.

Di-iodotetrakis(t-butyl isocyanide)rhodium(III) *Hexafluorophosphate*.—To $[Rh(CNBu^t)_4][PF_6]$ (0·11 g) dissolved in methanol (12 ml) was added I_2 (0·07 g). On partial evaporation of the solvent a brown powder was precipitated which was filtered off, and recrystallised from CH_2Cl_2–light petroleum (b.p. 40—60°) giving the complex as orange crystals (0·1 g, 66%).

The complexes $[Rh(CNBu^t)_4I_2]Cl$ (from $[Rh(CNBu^t)_4]Cl$), $[Rh\{CN(p\text{-}ClC_6H_4)_4I_2][PF_6]$, and $[Rh\{CN(p\text{-}ClC_6H_4)\}_2I_2Cl]_2$ were similarly obtained as orange crystals (40, 54, and 52%, respectively).

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Iodo(trifluoromethyl)tetrakis(t-butyl isocyanide)rhodium(III) *Hexafluorophosphate*.—A mixture of $[Rh(CNBu^t)_4][PF_6]$ (0·11 g) and CF_3I (an excess) in CH_2Cl_2 (5 ml) was allowed to react at room temperature in a sealed evacuated tube for 30 min. The tube was then opened, the mixture filtered and n-hexane added to the filtrate. The solution was then partially evaporated in a stream of N_2, affording the complex as yellow crystals. These were filtered off and dried in air (0·07 g, 55%).

The complex $[Rh(CNBu^t)_4(C_3F_7)I][PF_6]$ was obtained similarly as yellow crystals (62%).

Nitrosyltetrakis(t-butyl isocyanide)rhodium Hexafluorophosphate.—To an acetone solution (20 ml) of $[Rh(CNBu^t)_4][PF_6]$ (0·25 g) was added $NOPF_6$ (0·1 g). The solution became green, and green-blue crystals precipitated. These were filtered off, washed with ethanol, and dried *in vacuo* (0·2 g, 62%).

The complexes $[Rh(NO)(CNPr^i)_4][PF_6]_2$ (turquoise, 45%) and $[Rh(NO)(\text{cyclohexyl isocyanide})_4][PF_6]_2$ (green crystals, 41%), which were unstable in air, were prepared similarly.

(Sulphur dioxide)tetrakis(isopropyl isocyanide)rhodium Hexafluorophosphate.—A mixture of $[Rh(CNPr^i)_4][PF_6]$ (0·17 g) and SO_2 (an excess) in CH_2Cl_2 (10 ml) was allowed to stand at room temperature in a sealed evacuated tube for 15 min. The tube was then opened and light petroleum (b.p. 40—60 °C) added to the solution. The solvent was then evaporated *in vacuo* at low temperature (solid CO_2–acetone) affording the complex which was precipitated and filtered off as dark green crystals (0·11 g, 59%).

The complex $[Rh(SO_2)\{CN(p\text{-}MeC_6H_4)\}_4][PF_6]$ was obtained similarly as a light brown powder (62%).

Chloro(chloromercurio)tetrakis(p-*methoxyphenylisocyanide*)-*rhodium*(III) *Chloride*.—To $[Rh\{CN(p\text{-}MeOC_6H_4)\}_4]Cl$ (0·28 g) dissolved in $CHCl_3$ (10 ml) was added a soluton of $HgCl_2$ (0·11 g) in ethanol (15 ml). The solution was evaporated *in vacuo* to low bulk and the product precipitated. The complex was recrystallised from acetone–isopropyl alcohol and was obtained as yellow-green crystals (0·18 g, 46%).

Chloro(trichlorostannyl)tetrakis(p-*methoxyphenyl isocyanide*)*rhodium*(III) *Chloride*.—To $[Rh(CO)_2Cl]_2$ (0·15 g) dissolved in methanol (15 ml) was added $p\text{-}MeOC_6H_4NC$ (0·5 g) and $SnCl_4,5H_2O$ (0·2 g) in ethanol (5 ml). The solution was then evaporated *in vacuo* to low bulk and the product precipitated as a brown powder. The complex, which was recrystallised from acetone–ethanol and was filtered off, washed with water and ethanol, and air dried, was obtained as light brown crystals (0·13 g, 38% based on $[Rh(CO)_2Cl]_2$).

Chloro (p-*tolyl isocyanide*)*bis*(π-*allyl*)*rhodium*(III).—To a CH_2Cl_2 solution (15 ml) of $[Rh(\pi\text{-}C_3H_5)_2Cl]_2$ (0·21 g) was added a solution of $p\text{-}MeC_6H_4NC$ (0·12 g) in CH_2Cl_2 (10 ml). The mixture was allowed to stand at room temperature for 30 min, and light petroleum (b.p. 40—60 °C) was added. The solution was then reduced *in vacuo* and a brown powder precipitated. This was filtered off and recrystallised from CH_2Cl_2–petroleum (b.p. 40—60°) giving brown crystals (0·22 g, 69%).

The complex $Rh(\pi\text{-}C_3H_5)_2\{CN(p\text{-}ClC_6H_4)\}Cl$ was obtained similarly as a brown powder (54%).

Chlorobis(p-*tolyl isocyanide*)*bis*(*allyl*)*rhodium*(III).—This complex was obtained in the same way as that described above, using $[Rh(\pi\text{-}C_3H_5)_2Cl]_2$ (0·19 g) and $p\text{-}MeC_6H_4NC$ (0·21 g). The complex was obtained as brown crystals (0·27 g, 34%).

(Iodomethyl)tetrakis(t-butyl isocyanide)iridium(III) *Hexafluorophosphate*.—To a solution of $[Ir(CNBu^t)_4][PF_6]$ (0·25 g) in acetone (20 ml) under nitrogen was added MeI (0·5 ml). The solution changed from yellow to colourless, and when petroleum (b.p. 40—60°) was added the white crystals of the complex precipitated (0·20 g, 82%).

The complexes $[Ir(CNBu^t)_4Br_2][PF_6]$ and $[Ir(CNBu^t)_4(2\text{-}MeC_3H_4)][PF_6]_2$ (excess of PF_6^- was present) were obtained similarly as white crystals (45 and 51% respectively).

(Iodomethyl)tetrakis(p-*chlorophenyl isocyanide*)*iridium*(III) *Hexafluorophosphate*.—A mixture of $[Ir\{CN(p\text{-}ClC_6H_4)\}_4][PF_6]$ (0·2 g) and MeI (0·2 ml) in acetonitrile was gently refluxed for 5 min during which time it changed in colour from green to dark red. The solvent was then removed *in vacuo* and the residue was recrystallised from acetone–petroleum (b.p. 40—60°) affording the complex as dark red crystals (0·18 g, 74%).

The complexes $[Ir\{CN(p\text{-}ClC_6H_4)\}_4Br_2][PF_6]$ and $[Ir\{CN(p\text{-}ClC_6H_4)\}_4(2\text{-}MeC_3H_4)Cl][PF_6]$ were obtained similarly as dark red crystals (63 and 80% respectively).

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