Cationic Transition-metal Complexes. Part III.[1] Synthesis and Reactions of Tetrakis(isocyanide)rhodium Tetrafluoroborate Complexes

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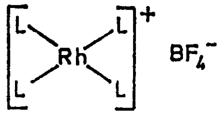
Treatment of $[Rh(1,5\text{-}C_8H_{12})(MeCN)_2]^+BF_4^-$ with Bu^{t}NC, Pr^{i}NC, or *p*-MeOC$_6$H$_4$NC affords $[Rh(RNC)_4]^+BF_4^-$ (R = Bu^t, Pr^i, or *p*-MeOC$_6$H$_4$). Addition of I$_2$, MeI, EtI, Pr^{n}I, Bu^{n}I, PhCH$_2$I, or PhCH$_2$Cl to $[Rh(Bu^tNC)_4]^+BF_4^-$ affords the octahedral Rh^{III} species $[Rh(Bu^tNC)_4XY]^+BF_4^-$. Trimethyloxonium and nitrosyl tetrafluoroborate react with $[Rh(Bu^tNC)_4]^+BF_4^-$ to form respectively compounds containing the dications $[Rh(Bu^tNC)_4Me]^{2+}$ and $[Rh(Bu^tNC)_4NO]^{2+}$. Dimethyl- and diethyl-amine, and the primary amines ethyl-, n-propyl-, isopropyl-, n-butyl-, isobutyl-, and cyclohexyl-amine react rapidly with $[Rh(Bu^tNC)_4]^+BF_4^-$ to form the carbene or amidinium derivatives $[Rh(Bu^tNC)_3C(NHBu^t)NR^1R^2]^+BF_4^-$ ($R^1 = R^2$ = Me or Et; R^1 = H, R^2 = Et, Pr^n, Pr^i, Bu^n, Bu^i, or C$_6$H$_{11}$). The structure of these compounds is discussed together with their isomerisation by C–N rotation. The carbene complexes undergo oxidative-addition reactions with I$_2$, MeI, and PhCH$_2$I to form $[Rh(Bu^tNC)_3\{C(NHBu^t)\text{-}NHR\}XY]^+BF_4^-$.

ALTHOUGH tetrakis(aryl isocyanide) complexes of rhodium(I) and iridium(I), $[M(CNR)_4]^+X^-$ (M = Rh, R = Ph or *p*-MeOC$_6$H$_4$; M = Ir, R = *p*-MeOC$_6$H$_4$; X = ClO$_4$, PF$_6$, Cl, Br, or I) are well known [2-4] little has been reported of their chemistry or that of related compounds. However, during the preparation of this paper two reports described the synthesis of $[Rh(RNC)_4]^+$ cations, which were isolated as Cl$^-$, PF$_6^-$ (ref. 5) or BPh$_4^-$ (ref. 6) salts, and their reactions with halogens, alkyl and acyl halides, and HgCl$_2$. The observation[7] that bis(acetonitrile)(cyclo-octa-1,5-diene)-rhodium or -iridium tetrafluoroborate[8] react with an excess of an isocyanide to give high yields of the complexes $[M(RNC)_4]^+BF_4^-$ (M = Rh or Ir; R = aryl or alkyl) provided an opportunity to study the chemistry of these potentially interesting compounds. In this paper some aspects of the chemistry of $[Rh(CNBu^t)_4]^+BF_4^-$ are reported. The new compounds described were characterised by elemental analysis, i.r. and ^{1}H n.m.r. spectroscopy.

Addition of t-butyl, isopropyl, or *p*-methoxyphenyl isocyanide to $[Rh(1,5\text{-}C_8H_{12})(MeCN)_2]^+BF_4^-$ in methylene chloride led to the displacement of both cyclo-octa-1,5-diene and acetonitrile with formation of (I), (II), or (III) as stable crystalline solids. Lithium chloride in acetone solution reacts with the cationic species (I) to give the dinuclear complex (IV) $[Rh(Bu^tNC)_2Cl]_2$, which showed a single isocyanide stretch in the i.r. spectrum and a singlet ^{1}H n.m.r. resonance. It is probable that (IV) is isostructural with $[Rh(CO)_2Cl]_2$.



(I) L = Bu^{t}NC
(II) L = Pr^{i}NC
(III) L = p-MeOPhNC

$[Rh(Bu^tNC)_2Cl]_2$ (IV)

The cationic complexes (I), (II), and (III) are coordinately unsaturated Rh^I species, and as such might be expected to undergo oxidative-addition reactions. This was confirmed in a detailed study of the reaction of tetrakis-(t-butyl isocyanide)rhodium tetrafluoroborate with iodine, methyl iodide, ethyl iodide, n-propyl iodide, n-butyl iodide, benzyl iodide, and benzyl chloride forming respectively the stable crystalline octahedral Rh^{III} cationic complexes (V)—(XI).

Treatment of (I) with iodine led to an immediate reaction in methylene chloride to give a product which

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[2] L. Malatesta and L. Vallarino, *J. Chem. Soc.*, 1956, 1867.

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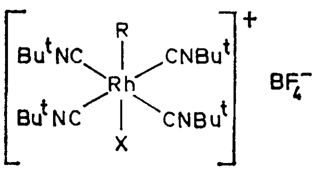
showed only a single isocyanide stretch in the i.r. at higher wavenumber than the parent Rh^I species, indicating an octahedral Rh^{III} complex with the iodine atoms occupying a relative *trans*-configuration.

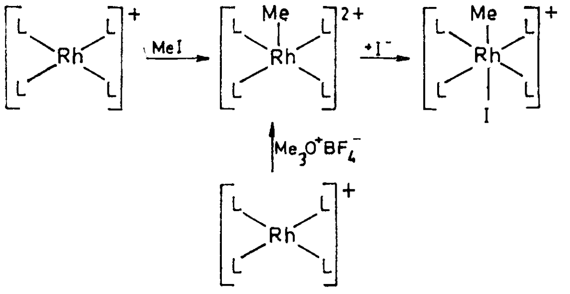


	R	X
(V)	I	I
(VI)	Me	I
(VII)	Et	I
(VIII)	Pr^n	I
(IX)	Bu^n	I
(X)	$PhCH_2$	I
(XI)	$PhCH_2$	Cl

This was confirmed by the presence in the ^1H n.m.r. spectrum of a lone singlet resonance which corresponds to co-ordinated t-butyl isocyanide in only one environment.

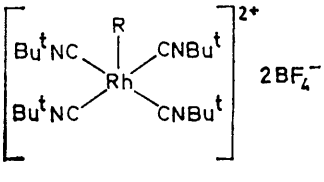
A similar *trans*-addition occurred with MeI, EtI, Pr^nI, Bu^nI, $PhCH_2I$, and $PhCH_2Cl$, as evidenced by the single isocyanide stretch and singlet ^1H n.m.r. resonance for co-ordinated isocyanide. In addition the ^1H n.m.r. spectrum showed resonances corresponding [9] to an alkyl group σ-bonded to rhodium; this being supported by the observation of $^1H-^{103}Rh$ coupling of the order of 2·0 Hz.

Qualitative rate measurements demonstrated the reactivity sequence $PhCH_2I > MeI > EtI > Pr^nI > Bu^nI$, which is consistent with a two-electron transfer S_N2 type mechanism of the type which has been established by kinetic studies on both rhodium and iridium systems.[10,11] Recent stereochemical studies [12] on the changes, *i.e.* inversion, in stereochemistry which occur at the substituted carbon atom are consistent with such a mechanism. Thus, it would be expected that reaction of, *e.g.* methyl iodide with $[Rh(Bu^tNC)_4]^+BF_4^-$ would involve an intermediate five-co-ordinate dication.



SCHEME (L = Bu^tNC)

Evidence for the formation and stereochemistry of the postulated dication intermediate was obtained from a study of the reaction of (I) with trimethyloxonium tetrafluoroborate, which afforded white crystals of the five-co-ordinate complex (XII). The observation of a single i.r.-active co-ordinated isocyanide stretching frequency and the presence in the ^1H n.m.r. spectrum of one singlet resonance is compatible with a tetragonal pyramidal geometry for (XII). Reaction of the dication (XII) with iodide anion afforded (VI).



(XII) R = Me
XIII) R = NO

The electrophile NO^+ has been previously shown to react with both low-valent ruthenium [13] and iridium complexes,[14] and therefore, not unexpectedly, nitrosyl tetrafluoroborate in nitromethane was found to react rapidly with (I) to give sea green crystals of the cationic nitrosyl complex (XIII). The i.r. spectrum showed a nitrosyl stretch at 1745 cm^{-1} and a single i.r.-active isocyanide stretching frequency at 2233 cm^{-1}, indicating a tetragonal pyramidal geometry for (XIII) of the kind established for the cations $[IrH(NO)(PPh_3)_3]^+$ and $[IrCl(NO)(CO)(PPh_3)_2]^+$.[15,16] In the case of these monocations, which show ν(NO) in the 1700 cm^{-1} region, a Ir–N–O angle of *ca.* 120° has been established from crystal structure determinations. However, it is difficult because of the dipositive charge to establish with certainty the geometry of the Rh–N–O group present in (XIII). The i.r. band at 1745 cm^{-1} falls in a borderline region between that which would be expected [16] for a linear and a bent nitrosyl. Clearly a crystal structure determination is required.

Isocyanides co-ordinated to certain transition metals have been shown to be susceptible to nucleophilic attack. The first reaction of this type to be reported involved methylisocyanide co-ordinated to platinum: [17] *cis*-$[PtCl_2(MeNC)PEt_3] + EtOH \longrightarrow$ *cis*-$[PtCl_2\{C(OEt)NHMe\}PEt_3]$; the presence of a co-ordinated carbene was confirmed by an *X*-ray single-crystal determination.[17] This synthetic route to carbene complexes has since been extended particularly by the reaction of amines with Fe,[18] Pd,[19-21] Pt,[22,23] and Hg [24] compounds.

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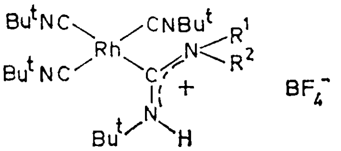
Recently,[25] in a study of the reaction of $[Fe(MeNC)_6]^{2+}$ with methylamine it has been shown that methylamine can add to and link two adjacent co-ordinated isocyanides to form a new chelate ring; a result which is clearly related to the reaction of hydrazine with $[M(MeNC_4]^{2+}$ (M = Pd or Pt) to yield complexes in which hydrazine also adds to and links two isocyanide ligands.[22,23,26] With this background knowledge it was clearly important to examine the reaction of tetrakis-(t-butyl isocyanide)-rhodium tetrafluoroborate with nucleophiles.

Dimethylamine and diethylamine react (at 0—25 °C) with (I), in an excess of the amine as the solvent, to give respectively the yellow crystalline 1 : 1 adducts (XIV) and (XV). The i.r. spectra, which showed N–H stretching frequencies similar to those reported for Pt[17] and Cr[27] amino-carbene complexes, and a band in the 1540 cm^{-1} region assignable to ν(N=C=N), suggested the illustrated structures involving a co-ordinated $C(NMe_2)NHBu^t$ carbene or more correctly a σ-bonded amidinium cation; ^{1}H n.m.r. studies on $[MeC(NHMe)_2]^+$ have shown[28] that there is restricted rotation about the C–N bonds. In agreement with this formulation the ^{1}H n.m.r. spectrum showed three Bu^{t}N resonances, a broad singlet at low field due to N*H*Bu^t and two *Me*N singlet resonances corresponding to methyl groups in 'outside' and 'inside' environments. It is suggested, in agreement with observations[29] on *cis*- and *trans*-$[Cr(CO)_5C(Me)NHMe]$, that the *Me*N chemical shift at higher field be assigned to the MeN *cis* to the rhodium and occupying the 'outside' position of the amidinium cation. Consideration of non-bonding interaction suggest that the t-butyl group in the amidinium system must occupy an 'outside' position, that is *cis* to the rhodium and *trans*-1,3 to a methyl or ethyl group; it being assumed that repulsion between a Bu^t group and the $Rh(Bu^tNC)_3$ group attached to the central carbon of the amidinium system would be minimised due to the relative orientations (see later) of the planes containing $C(NR_2)NHBu^t$ and $Rh(Bu^tNC)_3$. If as seems reasonable this stereochemistry is accepted, then Me_2NH or Et_2NH are undergoing a *cis* addition to co-ordinated isocyanide; of course, on this evidence (see later) it is not possible to say whether there is kinetic or thermodynamic control of the stereochemistry.



	R^1	R^2
(XIV)	Me	Me
(XV)	Et	Et
(XVI)	Et	H
(XVII)	Pr^n	H
(XVIII)	Pr^i	H
(XIX)	Bu^n	H
(XX)	Bu^i	H
(XXI)	C_6H_{11}	H

There remains the question as to the relative orientation of the planes containing the $[C(NR_2)NHBu^t]$ and $Rh(Bu^tNC)_3$ systems. The presence in the ^{1}H n.m.r. spectrum of, for example, (XIV) of *Bu*^{t} resonances of relative intensity 1 : 1 : 2, and only two terminal isocyanide C–N stretching frequencies in the i.r. spectra is clearly consistent with (XIV), where the plane containing the coplanar $[C(NR_2)NHBu^t]$ moiety is perpendicular to the plane containing the rhodium and three isocyanide ligands. Such a stereochemistry has been established in the crystalline state for both *cis*-$[PtCl_2\{C(OEt)NHMe\}PEt_3]$[17] and for *trans*-$[PtCl_2\{C(NPhCH_2)_2\}PEt_3]$,[30] which suggests that π-bonding lies predominantly within the CXY moiety; the Pt–C-(carbene) bond being essentially a single bond. Thus, it is suggested that there is very little backbonding from the rhodium in (XIV)—(XV) to the $C(NR_2)NHBu^t$ group, and that these compounds are best viewed as containing an amidinium cation σ-bonded *via* a central carbon atom to rhodium.

The reaction with amines is not restricted to secondary amines and (I) reacted at room temperature with an excess of ethylamine, n-propylamine, isopropylamine, n-butylamine, isobutylamine, or cyclohexylamine to yield respectively the 1 : 1 adducts (XVI)—(XXI) as yellow crystalline compounds. The i.r. spectra of these monoamine adducts show similar features to those discussed for the dimethyl- and diethyl-amine adducts; a single N–H stretching and two isocyanide stretching frequencies being observed together with a strong band at 1540 cm^{-1} characteristic of the amidinium cation system.

In solution at room temperature these adducts slowly isomerise; the isomerisation involved rotation about the C–N bond of the amidinium system and was studied in detail for (XX) the isobutylamine adduct. There was little change in the infrared spectrum of (XX) on isomerisation. The ^{1}H n.m.r. spectrum of (XX) which was similar to that observed for the other complexes showed two N*H* resonances, three *Bu*^{t} resonances of relative intensity 1 : 1 : 2 and resonances due to the isobutyl group. The NH·C*H*$_2$·CHMe$_2$ resonance appeared as a double doublet, the coupling with N*H* and C*H* protons being confirmed by decoupling. On isomerisation small changes in some of the chemical shifts occurred, but there was little or no change in the shift of the NH·C*H*$_2$·CHMe$_2$ protons. In the dimethyl- and diethyl-amine adducts shift differences of 0·6—0·7 p.p.m. were observed between the 'inside' and 'outside' N*Me* and NC*H*$_2$ resonances. This suggests that the isomerisation does not involve rotation about the C$\cdots$NHBu^i bond; the shift differences between 'inside' and 'outside' NH*Bu*^{t} resonances would be expected to be small.

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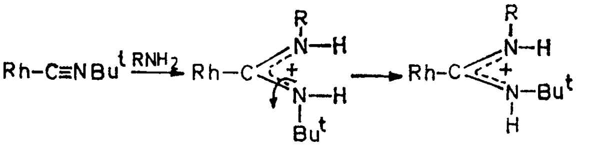
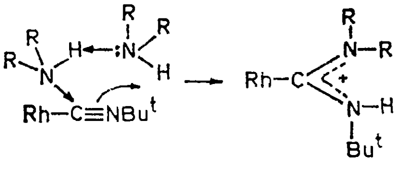
If the reasonable assumption is made that primary amines react in the same way as secondary amines and add *cis* to co-ordinated isocyanide then the thermodynamically controlled product, *i.e.* the isomerised adduct, must have an *amphi*-configuration with one proton and one alkyl group in the ' inside ' position:

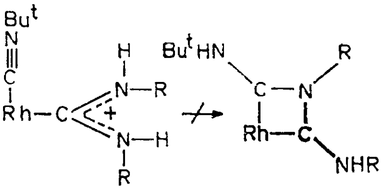


Recent unpublished *X*-ray studies [25] would suggest an *amphi*-configuration is adopted in a number of other complexes. The driving force for the isomerisation can be seen as arising from repulsion in this case between the metal atom and the *cis*-Bu^t group. In the secondary amine adducts this interaction can not be relieved by C–N rotation, and isomerisation does not occur.

It is suggested that the initial *cis*-addition of amine is facilitated by a high amine concentration:



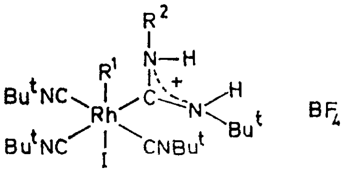
On heating the primary amine adducts there was no evidence for a cyclisation reaction of the kind recently observed [25] with the octahedral complex $[Fe(MeNC)_6]^{2+}$ and $MeNH_2$:



A possible reason for the absence of this kind of reaction is that the plane containing the group $[C(NHR)_2]$ is perpendicular, as suggested for (XIV)—(XV), to that containing the co-ordinated isocyanide. In order to provide a co-ordinated isocyanide in the correct position for reaction the adduct (XVII) was heated in the presence of an excess of Bu^tNC; it was hoped that the species $[Rh(Bu^tNC)_4C(NHBu^t)NHPr^n]^+$ would be formed, thus facilitating a cyclisation reaction. However, tetrakis-(t-butyl isocyanide)rhodium tetrafluoroborate was formed in high yield; a reaction which must involve displacement of $[C(NHBu^t)NHPr^n]$.

An attempt to abstract a proton from the cation (XXI) by treatment with sodium hydroxide led instead to a disproportionation reaction and the formation of $[Rh(Bu^tNC)_4]^+BF_4^-$.

As discussed previously there is probably little π-interaction between the rhodium and the amidinium group present in the complexes (XIV)—(XXI). This suggested that these compounds might also undergo oxidative-addition reactions of the kind observed with $[Rh(Bu^tNC)_4]^+BF_4^-$.

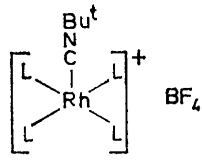


	R^1	R^2
(XXII)	I	Pr^i
(XXIII)	Me	Pr^i
(XXIV)	$PhCH_2$	Pr^i
(XXV)	I	Pr^n
(XXVI)	Me	Pr^n
(XXVII)	PhCH	Pr^n
(XXVIII)	I	C_6H_{11}
(XXIX)	Me	C_6H_{11}
(XXX)	$PhCH_2$	C_6H_{11}

The carbene or amidinium Rh^I complexes (XVII), (XVIII), and (XXI) reacted rapidly with both iodine, and methyl and benzyl iodide to give respectively compounds containing the stable crystalline octahedral Rh^{III} cations (XXV)—(XVII), (XXII)—(XXIV), and (XXVIII)—(XXX). The i.r. spectra all showed two isocyanide stretching frequencies and bands assignable $\nu(N \cdots C \cdots N)$. The ^1H n.m.r. spectrum showed resonances characteristic of the amidinium system, and three *Bu*^{t}N resonances with relative intensity 2 : 1 : 1. These observations are consistent with the illustrated structures, in which the coplanar $[C(NHBu^t)NHR]$ group retains its relative perpendicular orientation to the plane containing $Rh(Bu^tNC)_3$; the oxidative-addition reaction involving a *trans*-addition of the addendum. It is probable that the same reaction path is followed as was discussed for the oxidative reactions of $[Rh(Bu^tNC)_4]^+BF_4^-$. Thus in this type of reaction the carbene ligand remains intact, both Rh^I and Rh^{III} carbene complexes being stable.

It is not possible on the present evidence to establish the stereochemistry of the Rh^{III} amidinium group. Although isomerisation caused by C–N rotation is very slow compared with the oxidative reactions it is clearly possible that the Bu^tN group has an ' inside ' and not an ' outside ' position as illustrated. It is hoped that further work will clarify this question.

Although the $[C(NHBu^t)NHR]$ group remains co-ordinated to rhodium during an oxidative reaction, addition of diphos $(Ph_2P\cdot[CH_2]_2\cdot PPh_2)$ to (XX) led to an immediate colour change and the formation of orange-red crystals of (XXXI), characterised by elemental analysis, the presence of a single isocyanide stretch in the i.r., and by ^1H n.m.r. spectroscopy as the cation $[Rh(diphos)_2(Bu^tNC)]^+BF_4^-$. Clearly this reaction involves displacement of the carbene.



(XXXI) $L_2 = Ph_2P\cdot[CH_2]_2\cdot PPh_2$

EXPERIMENTAL

^{1}H n.m.r. spectra (CDCl$_3$ unless otherwise stated) were recorded on a Varian Associates HA 100 spectrometer at 100 MHz; chemical shifts are relative to tetramethylsilane (τ 10·00). I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer by use of Nujol mulls. All reactions were performed in an atmosphere of oxygen-free nitrogen or *in vacuo*.

Preparation of Tetrakis(isocyanide)rhodium Tetrafluoroborates.—(a) *Tetrakis-(t-butyl isocyanide)rhodium tetrafluoroborate* (I). A solution of Bu^{t}NC (2·3 ml, 22·0 mmol) in methylene chloride (2 ml) was added dropwise with stirring to bis(acetonitrile)(cyclo-octa-1,5-diene)rhodium tetrafluoroborate (1·0 g, 2·9 mmol) in methylene chloride (5 ml) and the dark yellow-brown solution immediately became pale yellow. Addition of diethyl ether (50 ml) gave a precipitate which was recrystallised from methylene chloride–diethyl ether as bright yellow *crystals* of (I) (1·33 g, 88%), m.p. 170 °C (decomp.) (Found: C, 46·1; H, 6·9; N, 10·8; Rh, 19·8. $C_{20}H_{36}BF_4N_4Rh$ requires C, 46·0; H, 6·9; N, 10·7; Rh, 19·7%); ν(NC): 2168vs cm^{-1}; ^{1}H n.m.r.: τ 8·49 [t, 36H, Bu^{t}N, *J*(HRh) 1·7 Hz].

(b) *Tetrakis(isopropyl isocyanide)rhodium tetrafluoroborate* (II). This was prepared similarly from isopropyl isocyanide (1·0 ml, 12·0 mmol) and bis(acetonitrile)(cyclo-octa-1,5-diene)rhodium tetrafluoroborate (0·10 g, 0·29 mmol) in methylene chloride (5 ml) as sea green *crystals* (0·115 g., 85%), m.p. 134 °C (decomp.) (Found: C, 41·6; H, 6·1; N, 12·0. $C_{16}H_{28}BF_4N_4Rh$ requires C, 41·4; H, 6·0; N, 12·1%); ν(NC): 2171vs cm^{-1}; ^{1}H n.m.r.: τ 5·86 [q of q., 4H, CH, *J*(HH) 6·5 Hz] and 8·53 [d, 24H, C*H*$_3$CH, *J*(HH) 6·5 Hz].

(c) *Tetrakis-(p-methoxyphenyl isocyanide)rhodium tetrafluoroborate* (III). This was prepared similarly from *p*-MeOC$_6$H$_4$NC (0·10 g, 0·75 mmol) and bis(acetonitrile)-(cyclo-octa-1,5-diene)rhodium tetrafluoroborate (0·05 g., 0·145 mmol) in methylene chloride (5 ml) as black *crystals* (0·09 g, 86%), m.p. 151—153 °C (decomp.) (Found: C, 53·2; H, 4·0; N, 7·8; F, 10·4. $C_{32}H_{28}BF_4N_4O_4Rh$ requires C, 53·2; H, 3·9; N, 7·8; F, 10·5%); ν(NC): 2155vs cm^{-1}; ^{1}H n.m.r.: 2·7—3·2 (m, 16H, aromatic) and 6·21 (s, 12H, CH$_3$O).

Reactions of (I).—(a) *Lithium chloride.* A solution of (I) (0·104 g, 0·2 mol) and anhydrous lithium chloride (0·02 g, 0·45 mmol) in dry acetone (10 ml) contained in a Carius tube (50 ml) was heated (60 °C) for 48 h when the bright yellow solution became pale yellow. Solvent was removed *in vacuo* and the methylene chloride soluble material recrystallised (0 °C) from benzene–hexane as pale yellow *crystals* of (IV) (0·051 g, 42%), m.p. 91—93 °C (Found: C, 39·7; H, 6·4; N, 9·2. $C_{20}H_{36}Cl_2N_4Rh_2$ requires C, 39·4; H, 6·0; N, 9·2%), ν(NC): 2230vs cm^{-1}; ^{1}H n.m.r.: τ 8·40 (s, 36H, Bu^{t}N).

(b) *Iodine.* A solution of iodine (0·051 g, 0·21 mmol) in methylene chloride (5 ml) was added dropwise with stirring to a solution of (I) (0·104 g, 0·2 mmol) in methylene chloride (5 ml). An immediate colour change occurred and after 10 min at room temperature diethyl ethyl (30 ml) was added. The precipitated solid was recrystallised from methylene chloride–diethyl ether as orange *crystals* of (V) (0·120 g, 78%), m.p. 131—132 °C (Found: C, 30·9; H, 4·7; N, 7·4. $C_{20}H_{33}BF_4I_2N_4Rh$ requires C, 30·9; H, 4·7; N, 7·2%); ν(NC): 2230vs cm^{-1}; ^{1}H n.m.r.: τ 8·39 (s, 36H, Bu^{t}N).

(c) *Methyl iodide.* A solution of methyl iodide (0·5 ml, 8·2 mmol) and (I) (0·104 g, 0·2 mmol) in methylene chloride (5 ml) was stirred at room temperature for 24 h. Diethyl ether (30 ml) was added and the resultant precipitate recrystallised from methylene chloride–diethyl ether as white *crystals* of (VI) (0·125 g, 93%), m.p. 149 °C (decomp.) (Found: C, 38·1; H, 5·9; N, 8·3; F, 11·4. $C_{21}H_{39}BF_4IN_4Rh$ requires C, 38·1; H, 5·9; N, 8·5; F, 11·5%); ν(NC): 2220vs cm^{-1}; ^{1}H n.m.r.: 8·35 (s, 36H, Bu^{t}N) and 8·69 [d, 3H, CH$_3$Rh, *J*(HRh) 2·0 Hz].

(d) *Ethyl iodide.* A similar reaction (24 h) between ethyl iodide (0·5 ml, 6·2 mmol) and (I) (0·104 g, 0·2 mmol) in methylene chloride (5 ml) gave pale yellow *crystals* of (VII) (0·110 g, 81%), m.p. 151—152 °C (decomp.) (Found: C, 39·1; H, 6·0; I, 18·7; N, 8·2. $C_{22}H_{41}BF_4IN_4Rh$ requires C, 38·9; H, 6·1; I, 18·7; N, 8·3%); ν(NC): 2221vs cm^{-1}; ^{1}H n.m.r.; τ 7·60 [d of q, 2H, CH$_3$C*H*$_2$Rh, *J*(HH) 7·5, *J*(HRh) 2·0 Hz], 8·40 (s, 36H, Bu^{t}N), and 8·67 [t, 3H, C*H*$_3$CH$_2$, *J*(HH) 7·5 Hz].

(e) *n-Propyl iodide.* Similarly, reaction (24 h) of n-propyl iodide (0·5 ml, 5·1 mmol) and (I) (0·104 g, 0·2 mmol) in methylene chloride (5 ml) gave pale yellow *crystals* of (VIII) (0·115 g, 83%), m.p. 139—140 °C (decomp.) (Found: C, 39·9; H, 6·2; I, 18·2; N, 7·9. $C_{23}H_{43}BF_4IN_4Rh$ requires C, 39·9; H, 6·2; I, 18·5; N, 8·1%); ν(NC): 2225vs cm^{-1}; ^{1}H n.m.r.: τ 7·70 [d of t, 2H, C*H*$_2$Rh, *J*(HH) 7·5, *J*(HRh) 2·0 Hz], 8·33 (m, 2H, C*H*$_2$CH$_2$Rh), 8·41 (s, 36H, Bu^{t}N), and 8·97 [t, 3H, C*H*$_3$CH$_2$, *J*(HH) 7·5 Hz].

(f) *n-Butyl iodide.* Similarly (I) (0·104 g, 0·2 mmol) in methylene chloride (5 ml) with n-butyl iodide (0·5 ml, 4·35 mmol) over 48 h gave pale yellow *crystals* of (IX) (0·127 g, 89%), m.p. 129 °C (decomp.) (Found: C, 40·5; H, 6·5; I, 18·5; N, 8·0. $C_{24}H_{45}BF_4IN_4Rh$ requires C, 40·7; H, 6·4; I, 18·0; N, 7·9%; ν(NC): 2217vs cm^{-1}; ^{1}H n.m.r.: τ 7·65 [d of t, 2H, C*H*$_2$Rh, *J*(HH) 7·5, *J*(HRh) 2·0 Hz], 8·37—8·50 (s and m, 36H + 4H, Bu^{t}N + CH$_2$CH$_2$), and 9·04 [t, 3H, C*H*$_3$CH$_2$, *J*(HH) 7·5 Hz].

(g) *Benzyl iodide.* Addition of benzyl iodide (0·045 g., 0·21 mmol) to (I) (0·104 g, 0·2 mmol) in methylene chloride (5 ml) led to an immediate colour change. After 15 min at room temperature addition of diethyl ether (30 ml) followed by recrystallisation from diethyl ether–methylene chloride gave pale yellow *crystals* of (X) (0·103 g., 70%), m.p. 135—136 °C (decomp.) (Found: C, 43·6; H, 5·8; I, 17·4; N, 7·8. $C_{27}H_{43}BF_4IN_4Rh$ requires C, 43·7; H, 5·8; I, 17·2; N, 7·6%); ν(NC): 2217vs cm^{-1}; ^{1}H n.m.r.: τ 2·82 (m, 5H, Ph), 6·42 [d, 2H, PhC*H*$_2$Rh, *J*(HRh) 2·5 Hz], and 8·48 (s, 36H, Bu^{t}N).

(h) *Benzyl chloride.* Benzyl chloride (0·5 ml, 4·3 mmol) reacted slowly (2 weeks) at room temperature with (I) (0·104 g, 0·2 mmol) to give white *crystals* of (XI) (0·110 g, 85%), m.p. 108—109 °C decomp. (Found: C, 50·2; H, 6·6; F, 12·0; N, 8·7. $C_{27}H_{43}BF_4ClN_4Rh$ requires C, 50·0; H, 6·7; F, 11·7; N, 8·7%); ν(NC): 2225vs cm^{-1}; ^{1}H n.m.r. [(CD$_3$)$_2$C=O]: τ 2·91 (m, 5H, Ph), 6·82 [d, 2H, PhC*H*$_2$Rh, *J*(HRh) 2·5 Hz], and 8·57 (s, 36H, Bu^{t}N).

(i) *Trimethyloxonium tetrafluoroborate.* Trimethyloxonium tetrafluoroborate (0·03 g, 0·2 mmol) was added at room temperature to a stirred solution of (I) (0·104 g, 0·2 mmol) in nitromethane (5 ml). After 15 min the solvent was removed *in vacuo* and the residue recrystallised from methylene chloride–diethyl ether to give white *crystals* of (XII) (0·10 g, 81%), m.p. 123—125 °C (decomp.) (Found: C, 40·1; H, 6·1; N, 8·5. $C_{21}H_{39}B_2F_8N_4Rh$ requires C, 40·4; H, 6·3; N, 8·9%); ν(NC): 2221vs cm^{-1}; ^{1}H n.m.r.:

τ 8·37 (s, 36H, Bu^{t}N) and 8·92 [d, 3H, CH_3Rh, J(HRh) 1·7 Hz].

(j) *Nitrosyl tetrafluoroborate.* A solution of $NOBF_4$ (0·025 g, 0·2 mmol) in nitromethane (2 ml) was added to (I) (0·104 g, 0·2 mmol) in nitromethane (5 ml) when the yellow reaction mixture immediately became bright green. Slow evaporation of the solvent in a nitrogen stream gave sea green *crystals* of (XIII) (0·09 g, 70%), m.p. 125—126 °C (decomp.) (Found: C, 36·9; H, 5·8; N, 11·0; F, 23·5. $C_{30}H_{36}B_2F_8N_5ORh$ requires C, 37·5; H, 5·6; N, 11·0; F, 23·8%); ν(NC) 2233vs and 1745s (NO) cm^{-1}; ^{1}H n.m.r. ($MeNO_2$): τ 8·29 (s, 36H, Bu^{t}N).

Reactions of (I) *with Amines.* (a) *Dimethylamine.* A solution of (I) (0·104 g, 0·2 mmol) in excess dimethylamine (10 ml) was stirred at 0 °C for 1 h. Dimethylamine was removed *in vacuo* and the residue recrystallised from diethyl ether to give bright yellow *crystals* of (XIV) (0·08 g, 70%), m.p. 165—166 °C (decomp.) (Found: C, 46·5; H, 7·5; F, 12·7; N, 12·0. $C_{22}H_{43}BF_4N_5Rh$ requires C, 46·5; H, 7·6; F, 13·4; N, 12·3%); ν: 3330m (NH), 2193s (NC), 2133vs (NC), and 1541s (N=C) cm^{-1}; ^{1}H n.m.r.: τ 3·96 [s, 1H, NH(Bu^t)], 6·39 (s, 3H, MeN, inner), 7·10 (s, 3H, MeN, outer), 8·42 (s, 9H, Bu^{t}N), 8·49 (s, 9H, Bu^{t}N), and 8·54 (s, 18H, Bu^{t}N).

(b) *Diethylamine.* Similarly, reaction (24 h) of (I) (0·104 g, 0·2 mmol) with excess of diethylamine (10 ml) at room temperature gave bright yellow *crystals* of (XV) (0·101 g, 85%), m.p. 117—119 °C (decomp.) (Found: C, 48·2; H, 8·0; F, 13·0; N, 11·5. $C_{24}H_{47}BF_4N_5Rh$ requires C, 48·5; H, 7·9; F, 12·8; N, 11·8%); ν: 3342m (NH), 2189s (NC), 2133vs (NC), and 1543s (N=C) cm^{-1}; ^{1}H n.m.r.: τ 4·0 (s, 1H, NHBu^t), 5·73 [q, 2H, CH_3CH_2N, inner, J(HH) 7·0 Hz], 6·63 [q, 2H, CH_3CH_2N, outer, J(HH) 7·0 Hz], 8·43 (s, 9H, Bu^{t}N), 8·50 (s, 9H, Bu^{t}N), 8·55 (s, 18H, Bu^{t}N), 8·81 [t, 3H, CH_3CH_2N, inner, J(HH) 7·0 Hz], and 8·85 [t, 3H, CH_3CH_2N, outer, J(HH) 7·0 Hz].

(c) *Ethylamine.* An excess of ethylamine (*ca.* 5 ml) was condensed (—196 °C) into a Carius tube (50 ml) containing (I) (0·104 g, 0·2 mmol). After 24 h at room temperature the excess of amine was removed *in vacuo* and the residue washed with diethyl ether to give bright yellow *crystals* of (XVI) (0·097 g, 85%), m.p. 127 °C (decomp.) (Found: C, 46·2; H, 7·4; N, 12·3. $C_{22}H_{43}BF_4N_5Rh$ requires C, 46·5; H, 7·6; N, 12·4%); ν: 3320m (NH), 2185s (NC), 2133vs (NC), and 1550s (N=C) cm^{-1}; ^{1}H n.m.r.: τ 3·0 (s, 1H, NHBu^t), 3·13 (m, 1H, NHEt), 6·16 [d of q, 2H, CH_3CH_2NH, J(HH) 7·0, J($NHCH_2$) 6·5 Hz], 8·51 (s, 9H, Bu^{t}N), 8·53 (s, 9H, Bu^{t}N), 8·55 (s, 18H, Bu^{t}N), and 8·85 [t, 3H, CH_3CH_2, J(HH) 7·0 Hz].

(d) *n-Propylamine.* A solution of (I) (0·104 g, 0·2 mmol) in an excess of n-propylamine (5 ml) was stirred at room temperature for 3 h. The excess of amine was removed *in vacuo* and the crystalline residue washed with diethyl ether to give bright yellow *crystals* of (XVII) (0·10 g, 85%), m.p. 122—123 °C (decomp.) (Found: C, 47·6; H, 8·1; N, 12·1. $C_{23}H_{45}BF_4N_5Rh$ requires C, 47·5; H, 7·8; N, 12·1%); ν: 3320m (NH), 2189s (NC), 2138vs (NC), and 1550s (N=C) cm^{-1}; ^{1}H n.m.r.: τ 2·93 (s, 1H, NHBu^t), 3·08 (m, 1H, NHPr^n), 6·25 [d of t, 2H, CH_2NH, J(HH) 6·0, J(NCH_2) 6·0 Hz], 8·39 (m, 2H, CH_2CH_2N, confirmed by double resonance), 8·51 (s, 9H, Bu^{t}N), 8·53 (s, 9H, Bu^{t}N), 8·55 (s, 18H, Bu^{t}N), and 9·07 [t, 3H, CH_3CH_2, J(HH) 7·5 Hz].

(e) *Isopropylamine.* Similarly reaction of (I) (0·104 g, 0·2 mmol) with excess of isopropylamine (5 ml) gave after 3 h at room temperature bright yellow crystals of (XVIII) (0·094 g, 81%), m.p. 98—99 °C (decomp.) (Found: C, 47·7; H, 8·1; F, 12·7; N, 12·0. $C_{23}H_{45}BF_4N_5Rh$ requires C, 47·5; H, 7·8; F, 13·1; N, 12·1%); ν: 3323 m (NH), 2182s (NC), 2130vs (NC), and 1543s (N=C) cm^{-1}; ^{1}H n.m.r.: τ 3·07 (s, 1H, NHBu^t), 3·25 [d, 1H, NHPr^i, J(NCH) 6·0 Hz], 5·73 (m, 1H, CHN), 8·50 (s, 9H, Bu^{t}N), 8·53 (s, 9H, Bu^{t}N), 8·55 (s, 18H, Bu^{t}N), and 8·82 [d, 6H, CH_3CH, J(HH) 6·5 Hz].

(f) *n-Butylamine.* Reaction of (I) (0·104 g, 0·2 mmol) with an excess of n-butylamine (5 ml) gave after 3 h at room temperature bright yellow *crystals* of (XIX) (0·105 g, 89%), m.p. 133 °C (decomp.) (Found: C, 47·8; H, 8·1; N, 11·7. $C_{24}H_{47}BF_4N_5Rh$ requires C, 48·4; H, 7·9; N, 11·8%); ν: 3320m (NH), 2185s (NC), 2137vs (NC), and 1550s (N=C) cm^{-1}; ^{1}H n.m.r.: τ 2·95 (s, 1H, NHBu^t), 3·12 (m, 1H, NHBu^n), 6·20 [d of t, CH_2N, J(HH) 6·5, J($NHCH_2$) 6·0 Hz], 8·45 (m, 2H, CH_2CH_2N, identified by double resonance), 8·51 (s, 9H, Bu^{t}N), 8·53 (s, 9H, Bu^{t}N), 8·55 (s, 18H, Bu^{t}N), 8·65 (m, 2H, $CH_2CH_2CH_2$N, identified by double resonance), and 9·08 [t, 3H, CH_3CH_2, J(HH) 6·5 Hz].

(g) *Isobutylamine.* Similarly (I) (0·104 g, 0·2 mmol with isobutylamine (5 ml) gave after 3 h yellow *crystals* of (XX) (0·105 g, 88%), m.p. 117—118 °C (decomp.) (Found: C, 48·1; H, 8·0; F, 12·8; N, 11·9. $C_{24}H_{47}BF_4N_5Rh$ requires C, 48·4; H, 7·9; F, 12·8; N, 11·8%); ν: 3322m (NH), 2189s (NC), 2137vs (NC), and 1550s (N=C) cm^{-1}; ^{1}H n.m.r.: τ 2·91 (s, 1H, NHBu^t), 3·14 (m, 1H, NHBu^i), 6·38 [d of d, 2H, CH_2NH, J(HH) 6·0, J(NCH_2) 6·0 Hz], 8·12 (m, 1H, CH, identified by double resonance), 8·52 (s, 9H, Bu^{t}N), 8·53 (s, 9H, Bu^{t}N), 8·57 (s, 18H, Bu^{t}N), and 9·06 [d, 6H, CH_3CH, J(HH) 6·5 Hz]. In solution at room temperature (XX) isomerised (6 h) to give a complex with ^{1}H n.m.r. resonances at τ 3·11 (s, 1H, NHBu^t), 3·45 (m, 1H, NHBu^i), 6·40 [d of d, 2H, CH_2NH, J(HH) 6·0, J($NHCH_2$) 6·0 Hz], 7·96 (m, 1H, CH, identified by double resonance), 8·35 (s, 9H, Bu^{t}N), 8·36 (s, 9H, Bu^{t}N), 8·42 (s, 18H, Bu^{t}N), and 8·98 [d, 6H, CH_3CH, J(HH) 6·5 Hz].

(h) *Cyclohexylamine.* An excess of cyclohexylamine (5 ml) and (I) (0·104 g, 0·2 mmol) were stirred together at room temperature for 24 h to give yellow *crystals* of (XXI) 0·107 g, 86%, m.p. 125 °C (decomp.) (Found: C, 50·2; H, 8·0; F, 12·1; N, 11·2. $C_{26}H_{49}BF_4N_5Rh$ requires C, 50·2; H, 7·9; F, 12·2; N, 11·3%); ν: 3320m (NH), 2193s (NC), 2139vs (NC), and 1540s (N=C) cm^{-1}; ^{1}H n.m.r.: τ 3·0 (s, 1H, NHBu^t), 3·20 [d, 1H, NHC_6H_{11}, J(NHCH) 10·0 Hz], and 8·31—8·72 (complex pattern of overlapping resonances, 47H, Bu^{t}N, and C_6H_{11}N).

Oxidative-addition Reactions of Carbene Complexes.—(a) *Reaction of iodine with* (XVIII). A solution of iodine (0·026 g, 0·1 mmol) in methylene chloride (2 ml) was added dropwise with stirring to (XVIII) (0·058 g, 0·1 mmol) in methylene chloride (3 ml) and the yellow colour became orange. After 10 min at room temperature diethyl ether (30 ml) was added and the precipitate recrystallised from methylene chloride–diethyl ether as orange-brown *crystals* of (XXII) (0·06 g, 72%), m.p. 101—102 °C (Found: C, 33·0; H, 5·6; I, 30·2; N, 8·5. $C_{23}H_{45}BF_4I_2N_5Rh$ requires C, 33·1; H, 5·4; I, 30·5; N, 8·4%); ν: 3340m (NH), 2241s (NC), 2217vs (NC), 1575s (N=C), and 1530m (N=C) cm^{-1}; ^{1}H n.m.r.: τ 3·94 (s and m, overlapping resonances, NHBu^t and NHPr^i), 5·50 (m, 1H, CHCH$_3$), 8·40 (s, 18H, Bu^{t}N), 8·44 (s, 9H, Bu^{t}N), 8·54 (s, 9H, Bu^{t}N), and 8·62 [d, 6H, CH_3CH, J(HH) 6·0 Hz].

(b) *Reactions of methyl iodide with* (XVIII). A solution of (XVIII) (0·058 g, 0·1 mmol) and methyl iodide (0·5 ml, 8·2 mmol) in methylene chloride (5 ml) was stirred at room temperature for 3 h, the colour changing from bright to pale yellow. Addition of diethyl ether (30 ml) and recrystallisation of the precipitate from methylene chloride–diethyl ether gave pale yellow *crystals* of (XXIII) (0·054 g., 75%), m.p. 105° C (decomp.) (Found: C, 39·4; H, 6·7; I, 17·8; N, 9·7. $C_{24}H_{48}BF_4IN_5Rh$ requires C, 39·9; H, 6·7; I, 17·6; N, 9·7%); ν: 3338m (NH), 2229s (NC), 2195vs (NC), 1560s (N=C), and 1532m (N=C) cm^{-1}; ^{1}H n.m.r.: 3·37 (s, 1H, N*H*Bu^t), 3·96 [d, 1H, *NH*Pr^i, *J*(NHCH) 9·0 Hz], 6·00 (m, 1H, *CH*CH$_3$), 8·45 (s, 27H, Bu^{t}N), 8·58 (s, 9H, Bu^{t}N), 8·67 [d, 6H, C*H*$_3$CH, *J*(HH) 6·0 Hz], and 8·97 [d, 3H, C*H*$_3$Rh, *J*(HRh) 2·0 Hz].

(c) *Reaction of benzyl iodide with* (XVIII). Benzyl iodide (0·022 g, 0·1 mmol) reacted immediately at room temperature with (XVIII) (0·058 g, 0·1 mmol) in methylene chloride (5 ml). Addition of diethyl ether (30 ml) and recrystallisation of the precipitate from methylene chloride–diethyl ether gave pale yellow *crystals* of (XXIV) (0·06 g, 75%), m.p. 110—111 °C (decomp.) (Found: C, 44·9; H, 6·7; I, 16·1; N, 8·6. $C_{30}H_{52}BF_4IN_5Rh$ requires C, 45·1; H, 6·5; I, 15·9; N, 8·8%); ν: 3350m (NH), 2233s (NC), 2201vs (NC), 1556s (N=C), and 1527m (N=C) cm^{-1}; ^{1}H n.m.r.: τ 2·80 (m, 5H, Ph), 3·64 (s, 1H, N*H*Bu^t), 3·85 [d, 1H, N*H*Pr^i, *J*(NHCH) 10·0 Hz], 5·82 (m, 1H, *CH*CH$_3$), 6·62 [d, 2H, C$_6$H$_5$C*H*$_2$Rh, *J*(HRh) 3·0 Hz], 8·46 (s, 18H, Bu^{t}NC), 8·52 (s, 9H, Bu^{t}N), 8·59 (s, 9H, Bu^{t}N), and 8·60 [d, 6H, C*H*$_3$CH, *J*(HH) 6·0 Hz].

(d) *Reaction of iodine with* (XVII). A solution of iodine (0·026 g, 0·1 mmol) in methylene chloride (2 ml) was added with stirring at room temperature to a solution of (XVII) (0·058 g, 0·1 mmol) in methylene chloride (3 ml). Reaction occurred immediately. Precipitation with diethyl ether followed by recrystallisation from methylene chloride–diethyl ether gave orange-brown crystals of (XXV) (0·07 g, 84%), m.p. 89—90 °C (decomp.) (Found: C, 33·0; H, 5·3; I, 30·3; N, 8·1. $C_{23}H_{45}BF_4I_2N_5Rh$ requires C, 33·1; H 5·4; I, 30·5; N, 8·4%); ν: 3355m (NH), 2241s (NC), 2209vs (NC), 1565s (N=C), and 1520m (N=C) cm^{-1}; ^{1}H n.m.r.: τ 3·58 (m, 1H, N*H*Pr^n), 3·94 (s, 1H, N*H*Bu^t), 6·26 [d of t, 2H, C*H*$_2$N, *J*(HH) 7·5, *J*(NHCH) 7·5 Hz], 8·42 (s, 18H, Bu^{t}N), 8·43 (s, 9H, Bu^{t}N), 8·40 (m, 2H, C*H*$_2$CH$_2$N, identified by double resonance), 8·55 (s, 9H, Bu^{t}N), and 9·03 [t, 3H, C*H*$_3$CH$_2$, *J*(HH) 7·5 Hz].

(e) *Reaction of methyl iodide with* (XVII). A solution of (XVII) (0·058 g, 0·1 mmol) and methyl iodide (0·5 ml, 8·2 mmol) in methylene chloride was stirred at room temperature for 3 h. Precipitation with diethyl ether followed by recrystallisation from methylene chloride–diethyl ether gave pale yellow *crystals* of (XXVI) (0·05 g, 69%), m.p. 99—100 °C (decomp.) (Found: C, 39·9; H, 7·1; I, 17·4; N, 9·5. $C_{24}H_{48}BF_4IN_5Rh$ requires C, 39·9; H, 6·7; I, 17·6; N, 9·7%); ν: 3356m (NH), 2237s (NC), 2201vs (NC), 1563s (N=C), and 1527m (N=C) cm^{-1}; ^{1}H n.m.r.: 3·37 (s, 1H, N*H*Bu^t), 3·58 (m, 1H, *NH*Pr^n), 6·54 [d of t, 2H, C*H*$_2$N, *J*(HH) 7·5, *J*(NHCH) 7·5 Hz], 8·35 (m, 2H, C*H*$_2$CH$_2$N, identified by double resonance), 8·45 (s, 27H, Bu^{t}N), 8·56 (s, 9H, Bu^{t}N), 8·96 [d, 3H, CH$_3$Rh, *J*(HRh) 2·0 Hz], and 9·02 [t, 3H, C*H*$_2$CH$_2$, *J*(HH) 7·5 Hz].

(f) *Reaction of benzyl iodide with* (XVII). A solution of (XVII) (0·058 g, 0·1 mmol) in methylene chloride (5 ml) reacted immediately at room temperature with benzyl iodide (0·022 g, 0·1 mmol). After 10 min the volume of the solution was reduced (1 ml) *in vacuo* and diethyl ether (30 ml) added. The precipitate was recrystallised from methylene chloride–diethyl ether as yellow *crystals* of (XXVII) (0·057 g, 71%), m.p. 40 °C (decomp.) (Found: C, 44·8; H, 6·7; I, 15·8; N, 9·1. $C_{30}H_{52}BF_4N_5IRh$ requires C, 45·1; H, 6·5; I, 15·9; N, 8·8%); ν: 3365m (NH), 2229s (NC), 2197vs (NC), 1563s (N=C), and 1520m (N=C) cm^{-1}; ^{1}H n.m.r.: τ 2·80 (m, 5H, Ph), 3·55 (m, 1H, N*H*Pr^n), 3·72 (s, 1H, N*H*Bu^t), 6·36 [d of t, 2H, C*H*$_2$N, *J*(HH) 7·0, *J*(NHCH) 7·0 Hz], 6·65 [d, 2H, C$_6$H$_5$C*H*$_2$, *J*(HRh) 3·0 Hz], 8·40 (m, 2H, C*H*$_2$CH$_2$N, identified by double resonance), 8·49 (s, 18H, Bu^{t}N), 8·53 (s, 9H, Bu^{t}N), 8·60 (s, 9H, Bu^{t}N), and 9·0 [t, 3H, C*H*$_3$CH$_2$, *J*(HH) 7·0 Hz].

(g) *Reaction of iodine with* (XXI). Addition of iodine (0·026 g, 0·1 mmol) in methylene chloride (2 ml) to a solution of (XXI) (0·062 g, 0·1 mmol) in methylene chloride (3 ml) led to an immediate reaction. Diethyl ether (30 ml) was added and the precipitate recrystallised from methylene chloride–diethyl ether as orange-brown *crystals* of (XXVIII) (0·06 g, 69%), m.p. 101 °C (decomp.) (Found: C, 35·8; H, 5·9; N, 8·1. $C_{26}H_{49}BF_4I_2N_5Rh$ requires C, 35·7; H, 5·6; N, 8·0%); ν: 3350m (NH), 2241s (NC), 2213vs (NC), 1565s (N=C), and 1520m (N=C) cm^{-1}; ^{1}H n.m.r.: τ 3·84 (s, 1H, N*H*Bu^t), 3·91 [d, 1H, N*H*·C$_6$H$_{11}$, *J*(NHCH) 10·0 Hz], 8·10—8·74 (complex pattern, 11H, C$_6$H$_{11}$), 8·40 (s, 18H, Bu^{t}N), 8·43 (s, 9H, Bu^{t}N), and 8·55 (s, 9H, Bu^{t}N).

(h) *Reaction of methyl iodide with* (XXI). Methyl iodide (0·5 ml, 8·2 mmol) was added to a stirred solution of (XXI) (0·062 g, 0·1 mmol) in methylene chloride (5 ml). After 1 h at room temperature the volume of the solvent was reduced (1 ml) *in vacuo* and diethyl ether (30 ml) added. The resultant precipitate was recrystallised from diethyl ether–methylene chloride as pale yellow *crystals* of (XXIX) (0·05 g, 65%), m.p. 79—80 °C (decomp.) (Found: C, 42·5; H, 7·1; N, 9·2. $C_{27}H_{52}BF_4IN_5Rh$ requires C, 42·5; H, 6·8; N, 9·2%); ν: 3347m (NH), 2233s (NC), 2197vs (NC), 1556s (N=C), and 1525m (N=C) cm^{-1}; ^{1}H n.m.r.: τ 3·38 (s, 1H, N*H*Bu^t), 3·91 [d, 1H, N*H*C$_6$H$_{11}$, *J*(NHCH) 10·0 Hz], 8·14—8·81 (complex pattern, 11H, C$_6$H$_{11}$), 8·43 (s, 27H, Bu^{t}N), 8·56 (s, 9H, Bu^{t}N), and 8·95 [d, 3H, C*H*$_3$Rh, *J*(HRh) 2·2 Hz].

(i) *Reaction of benzyl iodide with* (XXI). Addition of benzyl iodide (0·022 g, 0·1 mmol) to (XXI) (0·062 g, 0·1 mmol) in methylene chloride (2 ml) led to an immediate reaction. Addition of diethyl ether followed by recrystallisation gave orange-yellow *crystals* of (XXX) (0·055 g, 66%), m.p. 90—91 °C (decomp.) (Found: C, 46·8; H, 7·0; N, 8·9. $C_{33}H_{56}BF_4IN_5Rh$ requires C, 47·1; H, 6·7; N, 8·4%); ν: 3348m (NH), 2233s (NC), 2197vs (NC), 1556s (N=C), and 1525m (N=C) cm^{-1}; ^{1}H n.m.r.: τ 2·79 (m, 5H, Ph), 3·56 (s, 1H, N*H*Bu^t), 3·81 [d, 1H, N*H*C$_6$H$_{11}$, *J*(NHCH) 10·0 Hz], 6·60 [d, 2H, PhC*H*$_2$Rh, *J*(HRh) 3·0 Hz], 8·18—8·93 (complex pattern, 11H, C$_6$H$_{11}$), 8·48 (s, 18H, Bu^{t}N), 8·52 (s, 9H, Bu^{t}N), and 8·59 (s, 9H, Bu^{t}N).

Reaction of t-Butyl Isocyanide with (XVII).—A solution of (XVII) (0·10 g, 0·172 mmol) and Bu^{t}NC (0·5 ml, 4·8 mmol) in methylene chloride (10 ml) contained in a sealed Carius tube (50 ml) was heated (60 °C) for 12 h. Solvent was removed *in vacuo* and the residue recrystallised from methylene chloride–diethyl ether to give bright yellow crystals of (I) (0·08 g, 89%) identical (i.r., n.m.r. spectroscopy) with that prepared directly.

Reaction of Sodium Hydroxide with (XXI).—A solution of aqueous sodium hydroxide (2 ml, 0·2M-solution) was added to (XXI) (0·150 g, 0·24 mmol) in acetonitrile (10 ml).

After 48 h at room temperature the volume was reduced *in vacuo*, diethyl ether added and the precipitate recrystallised from methylene chloride–diethyl ether to give yellow crystals of (I) (0·07 g, 56%).

Reaction of Bis-1,2-(*diphenylphosphino*)*ethane with* (XX).—Addition at room temperature of bis-1,2-(diphenylphosphino)ethane (0·20 g, 0·5 mmol) to a solution of (XX) (0·120 g, 0·2 mmol) in methylene chloride (5 ml) led to an immediate colour change from yellow to orange-red. After 30 min at room temperature the volume was reduced *in vacuo*, and the precipitate obtained on addition of hexane, recrystallised from methylene chloride–hexane to give orange-red *crystals* of (XXXI) (0·149 g, 70%), m.p. 137—139 °C (Found: C, 63·5; H, 5·4; N, 1·4; P, 11·3. $C_{57}H_{57}BF_4NP_4Rh$ requires C, 64·0; H, 5·4; N, 1·3; P, 11·6%); ν: 2125s (NC) cm^{-1}; ^{1}H n.m.r.: τ 2·81 (m, 40H, Ph), 7·76 (m, 8H, CH_2P), and 9·11 (s, 9H, Bu^{t}N).

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