Preparation of the Isocyanide Complexes *trans*-[ReCl(CNR)(dppe)$_2$] (R = Me or Bu^t) and their Reactions with Acid to give Carbyne Complexes. *X*-Ray Crystal Structure of *trans*-[ReCl(CNHMe)(dppe)$_2$][BF$_4$] †

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The complexes *trans*-[ReCl(CNR)(dppe)$_2$] (1, R = Me or Bu^t) have been prepared by replacement of dinitrogen in *trans*-[ReCl(N$_2$)(dppe)$_2$]. The alkyl isocyanide ligands in complexes (1) undergo electrophilic attack at the nitrogen atom by mineral acid (HBF$_4$), forming the carbyne complexes *trans*-[ReCl(CNHR)(dppe)$_2$][BF$_4$] (2, R = Me or Bu^t) and spectroscopic data for these complexes are given.

The *X*-ray structure of *trans*-[ReCl(CNHMe)(dppe)$_2$][BF$_4$] has been determined and shows that the CNMe angle is 123(2)°, the Re–C (carbyne) bond length is 1.80(3) Å, and the C(carbyne)–N bond length is 1.35(3) Å.

In our earlier studies of the reactions of ligating isocyanides [1] we showed that methyl isocyanide ligating the electron-rich metal site ' M(dppe)$_2$ ' (M = Mo or W) in the complexes *trans*-[M(CNMe)$_2$(dppe)$_2$] [2] is susceptible to electrophilic attack at nitrogen by acids (such as HBF$_4$, HCl, H$_2$SO$_4$, and HSFO$_3$) [1] or alkylating agents (MeSFO$_3$, Me$_2$SO$_4$, or [Et$_3$O][BF$_4$]) [3] leading to formation of the carbyne complexes *trans*-[M(CNHMe)(CNMe)(dppe)$_2$]$^+$ and *trans*-[M(CNR'Me)(CNMe)(dppe)$_2$]$^+$ (R' = Me or Et, dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$), respectively.

The instability of these complexes [1-5] precluded their recrystallisation without transformation into different compounds {the hydrides [5] [MH(CNMe)$_2$(dppe)$_2$]$^+$ and the *cis* isomers [3] *cis*-[M(CNR'Me)(CNMe)(dppe)$_2$]$^+$, respectively} and no suitable crystal for *X*-ray analysis was obtained.

Since in the above mentioned carbyne complexes competition of the ligating isocyanide for the electronic π back-donation from the metal may constitute a strong destabilising factor for the strong π-acceptor carbyne ligand, we were interested in preparing related carbyne type complexes having co-ligands without such pronounced electron-accepting properties as isonitriles. We have therefore studied displacement reactions of the isocyanides CNR (R = Me or Bu^t) with the dinitrogen complex *trans*-[ReCl(N$_2$)(dppe)$_2$] and the monoisocyanide species *trans*-[ReCl(CNR)(dppe)$_2$] (1, R = Me or Bu^t) were obtained with the electron-donor chloride co-ligand in the *trans* position relative to the isocyanide. These complexes were then protonated by acid (HBF$_4$) to give the carbyne complexes *trans*-[ReCl(CNHR)(dppe)$_2$]$^+$ (2, R = Me or Bu^t) which have chloride *trans* to carbyne, as it is in the related complexes *trans*-[MX(CNEt$_2$)(CO)$_4$] (where X = halide and M is a Group 6 transition metal).[6]

In contrast to the complexes *trans*-[M(CNHMe)(CNMe)(dppe)$_2$]$^+$ and *trans*-[M(CNR'Me)(CNMe)(dppe)$_2$]$^+$, the chloride species (2) are stable at ambient temperature, either as solids or in solution in solvents such as dichloromethane and tetrahydrofuran (thf) and suitable crystals for *X*-ray structural analysis have been obtained upon recrystallisation of *trans*-[ReCl(CNHMe)(dppe)$_2$][BF$_4$] from dichloromethane–diethyl ether. The work reported here details and extends the preliminary account already published.[7]

RESULTS AND DISCUSSION

(*a*) *Reactions of* trans-[ReCl(N$_2$)(dppe)$_2$] *with Isocyanides. Preparation and Characterisation of* trans-[ReCl(CNR)(dppe)$_2$] (1, R = Me *or* Bu^t).—We have found [reaction (1)] that isocyanides will displace dinitrogen from *trans*-[ReCl(N$_2$)(dppe)$_2$], as they will from *trans*-[M(N$_2$)$_2$(dppe)$_2$] (M = Mo or W),[2] but the rhenium complex is the more inert to substitution and more drastic conditions must be used to force quantitative displacement of dinitrogen by isocyanide. Thus, whereas complete displacement of dinitrogen from *trans*-[M(N$_2$)$_2$(dppe)$_2$] by CNMe occurs in about 16 h at 20 °C (M = Mo) or reflux (M = W) in thf, 4—7 d in refluxing thf under argon is necessary for reaction (1) to reach completion. The displacement of N$_2$ is, however, accelerated by irradiation and the reaction goes to completion (with a seven-fold excess of the isocyanide) within 1 d (R = Me) or 2 d (R = Bu^t) in an argon atmosphere under reflux and irradiation from two 100-W tungsten filament bulbs.

$$trans\text{-}[\mathrm{ReCl(N_2)(dppe)_2}] + \mathrm{CNR} \longrightarrow trans\text{-}[\mathrm{ReCl(CNR)(dppe)_2}] + \mathrm{N_2} \quad (1)$$
$$(\mathrm{R = Me\ or\ Bu^t})$$

Complexes (1) are yellow, crystalline solids after recrystallisation from thf–pentane, and they exhibit (Table 1) in the i.r. spectra strong and broad bands assigned to ν(C≡N) at very low values, 1 830 and 1 800 cm^{-1} (for CNMe) and 1 920 cm^{-1} (for CNBu^t), well below the values for the free ligands (2 145 and 2 120 cm^{-1}, in thf, respectively). Similar large lowering of ν(CN) was observed [2] for *trans*-[M(CNR)$_2$(dppe)$_2$] and reflects the strong electron-releasing properties of these dinitrogen-binding sites.

The ^{31}P n.m.r. spectra in CD$_2$Cl$_2$ show singlets, at δ

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† *trans*-Bis[1,2-bis(diphenylphosphino)ethane]chloro(methylaminomethylidyne)rhenium tetrafluoroborate.

TABLE 1

Physical data for the isocyanide complexes *trans*-[ReCl(CNR)(dppe)$_2$] (1, R = Me, Bu^t) and the derived carbyne complexes *trans*-[ReCl(CNHR)(dppe)$_2$][BF$_4$] (2)

			I.r. spectrum [a]				Elemental analysis (%) [b]		
Complex type	R	Colour	ν(NH) [ν(ND)]	ν(C≡N)	ν(C=N)	BF_4^-	C	H	N
(1)	Me [c]	Yellow		1 830 s,br [d] 1 800 s,br [d]			61.5 (61.3)	5.1 (5.0)	1.3 (1.3)
(1)	Bu^t [e]	Yellow		1 920 s,br			62.2 (62.4)	5.5 (5.6)	1.2 (1.2)
(2)	Me	Yellow [f]	3 240 m,br		1 575 s	1 080 vs,br	53.5 (53.6)	4.8 (4.4)	1.0 (1.1) [f]
		Pale yellow [g]	[2 410 m,br]				59.1 (58.8)	4.7 (4.7)	1.1 (1.1) [g]
(2)	Bu^t [f]	Orange	3 280 m,br		1 545 sh 1 530 s	1 060 s	53.8 (53.7)	5.2 (4.5)	1.0 (1.1)

[a] In Nujol mull (cm^{-1}). [b] Calculated values in parentheses. [c] With $\frac{1}{4}$ thf of crystallisation, as evidenced by the ^{1}H n.m.r. spectrum. [d] In variable relative intensities. [e] With thf of crystallisation as evidenced by the ^{1}H n.m.r. spectrum. [f] With CH_2Cl_2 of crystallisation. [g] With C_6H_6 of crystallisation.

108.6 (1, R = Me) and δ 107.7 p.p.m. (1, R = Bu^t) upfield from P(OMe)$_3$, in agreement with a *trans*-geometry for the dppe ligands. In the ^{1}H n.m.r. spectra in CD_2Cl_2 the methyl resonances are the expected singlets at δ 2.42 (for CN*Me*) and δ 0.70 p.p.m. (for CN*Bu^t*) (Table 2).

The solutions of complexes (1) in nitromethane are non-conductors.

(*b*) *Reactions of the Isocyanide Complexes* trans-[ReCl(CNR)(dppe)$_2$] (1, R = Me *or* Bu^t) *with Acid* (HBF$_4$). *Formation of the Carbyne Complexes* trans-[ReCl(CNHR)(dppe)$_2$][BF$_4$] (2).—Treatment of complexes (1) with

TABLE 2

^{1}H, ^{31}P, and ^{13}C n.m.r. data for the isocyanide complexes *trans*-[ReCl(CNR)(dppe)$_2$] (1, R = Me, Bu^t) and the derived carbyne complexes *trans*-[ReCl(CNHR) (dppe)$_2$][BF$_4$] (2)

(*a*) ^{1}H n.m.r. data

Complex type	R	Temp./°C	δ [a]/p.p.m.	Integration	Assignment	^3J(HNCH)/ Hz ± 0.2 Hz
(1)	Me [b]	27	7.7–6.9 m	40 (40)	$\mathrm{C_6}H_5$ (dppe)	
			3.68 m	1	$\mathrm{C}H_2$ (thf) [c]	
			3.0–2.3 m	8 (8)	$\mathrm{C}H_2$ (dppe)	
			2.42 s	3 (3)	$\mathrm{CNC}H_3$	
			1.87 m	1	$\mathrm{C}H_2$ (thf) [c]	
(1)	Bu^t [b]	27	7.9—6.7 m	40 (40)	$\mathrm{C_6}H_5$ (dppe)	
			3.67 m	4	$\mathrm{C}H_2$ (thf) [c]	
			3.0—2.0 m	8 (8)	$\mathrm{C}H_2$ (dppe)	
			1.84 m	4	$\mathrm{C}H_2$ (thf) [c]	
			0.70 s	8.4 (9)	$\mathrm{C(C}H_3\mathrm{)_3}$	
(2)	Me [b]	27	7.5–7.0 m	40 (40)	$\mathrm{C_6}H_5$ (dppe)	
			4.2—3.9 br	1 (1)	$\mathrm{CN}H\mathrm{CH_3}$	
			3.2—2.5 m,br	8 (8)	$\mathrm{C}H_2$ (dppe)	
			1.50 d	3 (3)	$\mathrm{CNHC}H_3$	5.1
		−12	7.5—6.9 m	40 (40)	$\mathrm{C_6}H_5$ (dppe)	
			4.4—4.0 br	1 (1)	$\mathrm{CN}H\mathrm{CH_3}$	
			3.2—2.5 m,br	8 (8)	$\mathrm{C}H_2$ (dppe)	
			1.30 d	3 (3)	$\mathrm{CNHC}H_3$	5.1
		−68	7.5—6.6 m	40 (40)	$\mathrm{C_6}H_5$(dppe)	
			4.6—4.2 br	0.7 (1)	$\mathrm{CN}H\mathrm{CH_3}$	
			3.2—2.4 m,br	7 (8)	$\mathrm{C}H_2$ (dppe)	
			0.87 br	2.4 (3)	$\mathrm{CNHC}H_3$	
(2)	Bu^t [d]	30	7.4—6.8 m	40 (40)	$\mathrm{C_6}H_5$ (dppe)	
			5.24	2 (2)	$\mathrm{C}H_2\mathrm{Cl_2}$ [c]	
			3.3—3.1 m,br	1 (1)	$\mathrm{CN}H\mathrm{C(CH_3)_3}$	
			3.0—2.4 m,br	8 (8)	$\mathrm{C}H_2$ (dppe)	
			0.26 s	8 (9)	$\mathrm{CNHC(C}H_3\mathrm{)_3}$	

(*b*) ^{31}P-{^{1}H} n.m.r. data

Complex type	R	Temp./°C	δ [e]/p.p.m.	Assignment
(1)	Me [b]	25	108.6 s	*trans* P (dppe)
(1)	Bu^t [b]	25	107.7 s	*trans* P (dppe)
(2)	Me [b]	−60	117.5 s	*trans* P (dppe)

(*c*) ^{13}C-{^{1}H} n.m.r. data

Complex type	R	Temp./°C	δ [a]/p.p.m.	Assignment
(2)	Me [b]	27	223.5—221.9 m,br	$C\mathrm{NHCH_3}$
			136.3—128.1 m,br	$C\mathrm{_6H_5}$ (dppe)
			31.9—31.1 m	$C\mathrm{H_2}$ (dppe)
			26.6 s	$\mathrm{CNH}C\mathrm{H_3}$

[a] Values relative to internal SiMe$_4$. [b] In CD_2Cl_2. [c] Solvent of crystallisation. [d] In $CDCl_3$. [e] Values upfield from external P(OMe)$_3$.

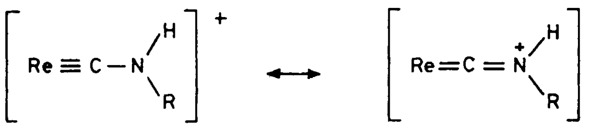
$[Et_2OH][BF_4]$ in benzene or dichloromethane [reaction (2)] leads to the protonation of the isocyanide nitrogen atom and the formation of the carbyne complexes (2) which have been formulated on the basis of microanalytical and i.r., ^1H, ^{31}P, and ^{13}C n.m.r. spectroscopic data (Tables 1 and 2), their formulation being also confirmed by an *X*-ray structure analysis of the complex (2, R = Me).

$$\textit{trans}\text{-}[ReCl(CNR)(dppe)_2] + HBF_4 \longrightarrow \textit{trans}\text{-}[ReCl(CNHR)(dppe)_2][BF_4] \quad (2)$$
$$(2,\ R = Me \text{ or } Bu^t)$$

In the carbyne complexes (2) no further protonation is observed (even in the presence of a 30-fold molar excess of acid), although under the same experimental conditions the related Group 6 metal complexes *trans*-$[M(CNMe)_2(dppe)_2]$ may easily undergo two protonations leading first to the monoprotonated complex *trans*-$[M(CNHMe)(CNMe)(dppe)_2]^+$, which upon further protonic attack forms the hydridocarbyne complex $[MH(CNHMe)(CNMe)(dppe)_2]^{2+}$ or the complex *trans*-$[M(CNHMe)_2(dppe)_2]^{2+}$, depending on the experimental conditions.[4]

Complexes (2) exhibit broad i.r. bands (Table 1) assigned to ν(NH), *e.g.* at 3 240 cm^{-1} in *trans*-$[ReCl(CNHMe)(dppe)_2][BF_4]$ for which a corresponding ν(ND) vibration was observed at 2 410 cm^{-1} in the complex formed upon exchange with D_2O.

The ν(C≡N) bands of the parent isocyanide complexes are not observed and the bands from 1 530 to 1 575 cm^{-1} are assigned to ν(C=N) of the carbyne type ligand CNHR which may thus be represented as shown below with form (b) having a significant weighting. This scheme has also been suggested for the related complexes *trans*-$[M(CNR'Me)(CNMe)(dppe)_2]^+$ (M = Mo or W; R' = H, Me, or Et) [1,3] and $[MX(CNEt_2)(CO)_4]$ (M = Cr, Mo, or W; X = halide).[6]



(a) (b)

The bands expected for the counter ion, BF_4^-, are also observed at 1 060—1 080 cm^{-1}.

In the ^1H n.m.r. spectra of (2) in CD_2Cl_2 or $CDCl_3$ (Table 2) a broad N-*H* resonance appears at δ 4.2—3.9 p.p.m. (2, R = Me) at 27 °C and at δ 3.3—3.1 p.p.m. (2, R = Bu^t) at 30 °C which disappears on addition of D_2O. The CNH*Me* resonance for complex (2, R = Me) has the expected doublet structure which coalesces into a sharp singlet on irradiation at the N*H*CH_3 resonance or upon D_2O addition. The value of the coupling constant [^3J(HNCH) *ca.* 5.1 ± 0.2 Hz] is close to the values for the same CNHMe unit ligating Mo and W.[1]

For the complex (2, R = Bu^t) the Bu^t proton resonance is a singlet at δ 0.26 p.p.m. and the broad CN*H*Bu^t resonance at δ 3.3—3.1 p.p.m. has been assigned on the basis of deuteriation experiments.

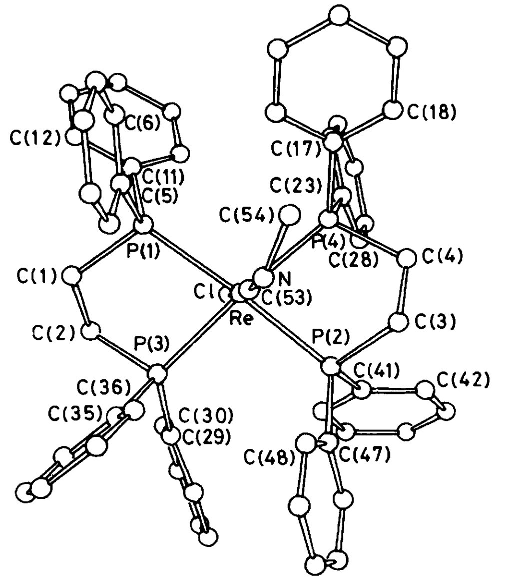
No notable change on cooling has been observed in the ^1H n.m.r. spectrum of complex (2, R = Me) in CD_2Cl_2, apart from a loss in the resolution and a downfield shift of the CN*H*CH_3 resonance with a concomitant shift of the CNHC*H*$_3$ resonance to higher fields (Table 2).

In the ^{31}P-{^1H} n.m.r. spectra (Table 2), a singlet is observed for the carbyne complex (2, R = Me) at δ 118 p.p.m. upfield from $P(OMe)_3$, indicating a *trans* configuration for these complexes.

The ^{13}C-{^1H} n.m.r. spectrum of complex (2, R = Me) in CD_2Cl_2 shows a very low field complex multiplet centered at δ 222.7 p.p.m. downfield from $SiMe_4$ which is assigned to the carbyne carbon *C*$NHCH_3$ since this value is in the range observed for related complexes such as *trans*-$[M(CNHMe)(CNMe)(dppe)_2][BF_4]$ (242.4 and 247.8 p.p.m. for M = W and Mo, respectively).[1] A singlet resonance is also observed at δ 26.6 p.p.m. (CNH*C*H_3) and a stronger multiplet resonance at δ 31.9—31.1 p.p.m. (dppe methylene carbons with coupling to the phosphorus atoms).

The structure of the carbyne complexes (2) has been confirmed by the *X*-ray crystal structure of *trans*-$[ReCl(CNHMe)(dppe)_2][BF_4]$.

The molecular structure of the cation is depicted in the Figure; diethyl ether was also detected (half a molecule for each molecule of the complex). Selected bond lengths and angles are listed in Table 4.



Molecular structure of *trans*-$[ReCl(CNHMe)(dppe)_2]^+$ in the complex *trans*-$[ReCl(CNHMe)(dppe)_2][BF_4]\cdot0.5Et_2O$ (2, R = Me). Carbon atoms are labelled sequentially around the phenyl groups

The C(carbyne)–N–CH_3 angle is 123(2)° in agreement with sp^2 hybridisation at N, and the Re–C–N and Cl–Re–C units are linear [175(2) and 176.3(7)°, respectively]. The C(carbyne)–N bond length is 1.35(3) Å which is much longer than the isocyanide CN bond [1.10(1) Å] in *trans*-$[Mo(CNMe)_2(dppe)_2]$ [8] and also longer than the CN bond of the analogous carbyne complex $[CrBr(CNEt_2)$-

$(CO)_4]$[9] [1.294(12) Å]. Nevertheless, the CN distance observed is shorter than the N–CH_3 single bond [1.42(4) Å]. The Re–C bond length of 1.80(3) Å is somewhat longer than the sum of the triple-bond radii of C≡C[10] (0.605 Å) and Re≡Re derived from $[Re_2Cl_4(PEt_3)_4]$[11] (1.116 Å) and $[Re_2Cl_5(MeSCH_2CH_2SMe)_2]$[12] (1.146 Å), *i.e.* the range 1.721—1.751 Å. Some elongation of the Re–C bond is expected in view of the contribution of the canonical form (b) to the bonding.

The mean metal–phosphorus bond length, 2.46(2) Å, is slightly longer than that observed[13] for the dinitrogen complex *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ [2.422(10) Å] but close to that observed for *trans*-$[Mo(CNMe)_2(dppe)_2]$ [2.449(5)].[8]

Conclusions.—This study has shown that our previous conclusions, applied to molybdenum and tungsten, namely that an electron-rich site which binds dinitrogen is capable of activating isocyanide to electrophilic attack, also extends to the $ReCl(dppe)_2$ dinitrogen binding site. This activation is similar to that also observed for dinitrogen itself[14] but clearly isocyanide is intrinsically more susceptible to electrophilic attack than is dinitrogen, because dinitrogen at this rhenium site is not attacked by protons.[15] Other small molecules, such as CS, ligating electron-rich centres also form related carbyne complexes as a result of electrophilic attack.[16]

Presumably a suitable combination of electron-releasing co-ligands is necessary to allow sufficient back-bonding to promote electrophilic attack and not all dinitrogen binding sites will achieve it. We are extending our studies to define the limits of reactivity.

EXPERIMENTAL

All air-sensitive materials were handled using standard inert gas flow or high vacuum techniques.

The complex *trans*-$[ReCl(N_2)(dppe)_2]$[15] and the isocyanides (CNMe[17] and $CNBu^t$[18]) were prepared by published methods. Acid and the other reagents were used as supplied. The solvents were purified and dried by standard procedures.

Infrared spectra were determined with a Perkin-Elmer 577 or 457 instrument, and n.m.r. spectra with a JEOL PS 100 (equipped with a 546J digital signal averager), JEOL PFT 100 Fourier-transform, or JEOL FX90Q spectrometers. The solvents used for n.m.r. measurements were scrupulously dried and degassed before use. Conductivities were measured using a Portland Electronics P310 conductivity bridge.

(*a*) *Preparation of the Isocyanide Complexes* (1).—trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*chloro*(*methyl isocyanide*)*rhenium*(I), (1, R = Me). An excess of CNMe (1 cm^3, 21.2 mmol) was added to a suspension of *trans*-$[ReCl(N_2)(dppe)_2]$ (1.23 g, 1.17 mmol) in thf (200 cm^3). The mixture was then heated to reflux under argon and after 1 d all the suspension had gone into solution. The reflux was maintained and 4 d after the beginning of the experiment the greenish yellow clear solution was concentrated and pentane was added always with heating. The solution was then filtered hot and the complex (1, R = Me) precipitated as a yellow crystalline solid upon slow cooling to *ca.* 0 °C. Further crops of this complex could be obtained from the mother-liquor upon concentration and addition of pentane. The solid (total 0.90 g, 73%) was washed with thf–pentane and dried under vacuum.

A lower excess of CNMe could be used but the reflux should be maintained for a longer time in order to allow the reaction to go to completion (*e.g.* refluxing for 7 d was used for an excess of 6 : 1 of the isocyanide).

The reaction may, however, be accelerated upon irradiation from tungsten filament bulbs. Hence, the reaction is complete after refluxing under argon a thf solution (60 cm^3) of the dinitrogen complex (1.01 g, 0.97 mmol) with CNMe (0.3 cm^3, 6.4 mmol), under the irradiation of two 100-W tungsten bulbs.

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*chloro*(*t-butyl isocyanide*)*rhenium*(I), (1, R = Bu^t). An excess of $CNBu^t$ (0.30 cm^3, 2.96 mmol) was added to a suspension of *trans*-$[ReCl(N_2)(dppe)_2]$ (0.349 g, 0.333 mmol) in thf (60 cm^3). The mixture was then heated to reflux under argon (after 1 day all the suspension had gone into solution) and after 5 d the yellow clear solution was concentrated and pentane added, always with heating. The solution was filtered hot and the complex (1, R = Bu^t) separated out as a yellow crystalline solid on slow cooling to *ca.* 0 °C, which was filtered off the solution, washed with thf–pentane, and dried under vacuum. A further crop of this species could be obtained upon concentration and addition of pentane to the mother-liquor (total 0.25 g, 68%).

The reaction is also accelerated by tungsten filament light; *e.g.* it goes to completion within 2 d if a solution of the N_2 complex (0.25 g, 0.24 mmol) in thf (60 cm^3) with $CNBu^t$ (0.15 cm^3, 1.5 mmol) is refluxed under argon with irradiation by two 100-W tungsten bulbs.

(*b*) *Preparation of the Carbyne Complexes* (2).—trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*chloro*(*methylaminocarbyne*)*rhenium tetrafluoroborate*, (2, R = Me). Tetrafluoroboric acid (0.189 mmol, 0.55 cm^3 of an ether solution obtained by 1 : 21 dilution of commercial $[Et_2OH][BF_4]$) was added to a filtered solution of *trans*-$[ReCl(CNMe)(dppe)_2]$ (1, R = Me) (0.200 g, 0.189 mmol) in benzene (50 cm^3). After a few minutes complex (2, R = Me) started to separate out of the solution as a very pale yellow powder. The suspension was stirred overnight at room temperature and the solid was filtered off, washed with benzene, and dried under vacuum. A further crop of this complex could be obtained on concentration of the filtered solution and addition of pentane (total 0.080 g, 37%). A better yield could be obtained by using an excess of acid (*e.g.* 1 : 6), the reaction being carried out either in benzene or in dichloromethane.

The solid from which a crystal was selected for the *X*-ray structural analysis was prepared as follows. To a solution of complex (1, R = Me) (0.25 g, 0.24 mmol) in CH_2Cl_2 (15 cm^3) was added $[Et_2OH][BF_4]$ (1.0 cm^3, 7.2 mmol). The solution kept its yellow colour and, after stirring for 6 d, diethyl ether was added slowly until a yellow solid of complex (2, R = Me) started to separate out of the solution. This was then filtered off and the solution was kept at *ca.* 0 °C for 3 weeks. The resulting yellow crystals of the carbyne complex were filtered off, washed with CH_2Cl_2–Et_2O, and dried under vacuum.

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*chloro*(*t-butylaminocarbyne*)*rhenium tetrafluoroborate*, (2, R = Bu^t). To a suspension of *trans*-$[ReCl(CNBu^t)(dppe)_2]$ (1, R = Bu^t) (0.20 g, 0.18 mmol) in C_6H_6 (60 cm^3) was added $[Et_2OH][BF_4]$ (0.15 cm^3, 1.1 mmol) and the mixture was stirred

TABLE 3

Final atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Re	1 720.5(7)	1 246.9(5)	1 734.5(4)
Cl	1 282(5)	2 275(3)	2 283(3)
P(1)	3 388(5)	1 470(3)	2 146(3)
P(2)	78(5)	953(3)	1 389(3)
P(3)	1 608(5)	935(3)	2 967(3)
P(4)	1 568(5)	1 787(3)	605(3)
N	2 366(18)	22(8)	931(10)
C(1)	3 516(21)	1 273(16)	3 081(12)
C(2)	2 562(16)	1 402(13)	3 431(11)
C(3)	152(21)	828(12)	435(13)
C(4)	517(22)	1 449(15)	110(16)
C(53)	2 092(18)	531(13)	1 304(12)
C(54)	2 889(35)	72(17)	309(17)
B	2 725(12)	−1 597(8)	1 011(8)
F(1)	3 299(12)	−1 552(8)	444(8)
F(2)	3 059(12)	−1 190(8)	1 519(8)
F(3)	1 797(12)	−1 437(8)	821(8)
F(4)	2 747(12)	−2 210(8)	1 258(8)
C(5)	4 311(11)	942(7)	1 808(9)
C(6)	5 092(11)	1 183(7)	1 450(9)
C(7)	5 777(11)	768(7)	1 187(9)
C(8)	5 681(11)	112(7)	1 282(9)
C(9)	4 901(11)	−129(7)	1 640(9)
C(10)	4 215(11)	286(7)	1 903(9)
C(11)	3 916(12)	2 262(6)	2 121(9)
C(12)	4 811(12)	2 388(6)	2 440(9)
C(13)	5 210(12)	2 997(6)	2 401(9)
C(14)	4 714(12)	3 480(6)	2 044(9)
C(15)	3 818(12)	3 354(6)	1 726(9)
C(16)	3 419(12)	2 745(6)	1 764(9)
C(17)	2 526(10)	1 754(9)	−23(8)
C(18)	2 335(10)	1 832(9)	−733(8)
C(19)	3 087(10)	1 803(9)	−1 199(8)
C(20)	4 028(10)	1 695(9)	−954(8)
C(21)	4 219(10)	1 616(9)	−244(8)
C(22)	3 467(10)	1 646(9)	222(8)
C(23)	1 312(12)	2 632(6)	585(9)
C(24)	1 990(12)	3 080(6)	377(9)
C(25)	1 783(12)	3 729(6)	417(9)
C(26)	898(12)	3 931(6)	663(9)
C(27)	220(12)	3 484(6)	871(9)
C(28)	428(12)	2 834(6)	832(9)
C(29)	536(10)	1 107(8)	3 447(9)
C(30)	388(10)	1 705(9)	3 740(8)
C(31)	−483(10)	1 842(9)	4 053(8)
C(32)	−1 205(10)	1 380(9)	4 072(8)
C(33)	−1 057(10)	782(9)	3 778(8)
C(34)	−186(10)	645(9)	3 466(8)
C(35)	1 878(13)	121(6)	3 254(9)
C(36)	2 084(13)	−370(6)	2 792(9)
C(37)	2 317(13)	−975(6)	3 045(9)
C(38)	2 346(13)	−1 090(6)	3 759(9)
C(39)	2 140(13)	−598(6)	4 221(9)
C(40)	1 906(13)	7(6)	3 968(9)
C(41)	−928(10)	1 491(7)	1 518(8)
C(42)	−1 603(10)	1 600(7)	931(8)
C(43)	−2 396(10)	1 992(7)	1 091(8)
C(44)	−2 515(10)	2 274(7)	1 740(8)
C(45)	−1 839(10)	2 165(7)	2 277(8)
C(46)	−1 046(10)	1 773(7)	2 166(8)
C(47)	−420(13)	172(7)	1 674(10)
C(48)	137(13)	−378(7)	1 619(10)
C(49)	−210(13)	−959(7)	1 863(10)
C(50)	−1 114(13)	−988(7)	2 161(10)
C(51)	−1 671(13)	−438(7)	2 215(10)
C(52)	−1 324(13)	142(7)	1 972(10)
C(55)	4 863(83)	−1 839(53)	4 806(58)
C(56)	4 205(53)	−1 796(36)	5 436(39)
O(1)	4 346(62)	−1 129(42)	5 816(47)
C(57)	3 714(70)	−1 089(45)	6 332(51)
C(58)	3 734(69)	−327(48)	6 630(50)

during *ca.* 60 h. The solution was taken to dryness and the solid was crystallised from CH_2Cl_2–Et_2O yielding complex (2, R = Bu^t) as an orange crystalline solid (0.090 g, 42%).

Crystal Structure Determination.—Crystal data. $C_{54}H_{52}ClNP_4Re\cdot BF_4\cdot 0.5C_4H_{10}O$, $M = 1\,184.6$, Monoclinic, $a = 13.875(3)$, $b = 20.978(4)$, $c = 19.250(3)$ Å, $\beta = 91.62(1)°$, $U = 5\,600.8$ Å^3, $D_c = 1.41$, $F(000) = 2\,388$, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 25.1$ cm^{-1}. Space group $P2_1/c$ from systematic absences of $0k0$ for k odd and $h0l$ for l odd.

The data crystal was obtained by addition of Et_2O to a CH_2Cl_2 solution of (2, R = Me) and cooling at 0 °C. It was roughly spherical of diameter *ca.* 0.2 mm and was sealed in a capillary tube. Accurate cell parameters were derived from the setting angles for 12 reflections on a Hilger and Watts 7290 diffractometer. Intensities for $hk \pm l$ reflections with $2 < \theta < 20°$ were measured by an ω—2θ step scan using Mo-K_α radiation with a graphite crystal monochromator. Three standard reflections were remeasured after every 100 reflections and showed no significant variation during the data collection. After corrections for Lorentz and polarisation effects but not for absorption, any equivalent data were averaged and 3 450 unique reflections with $I > 2\sigma(I)$ were used in the structure analysis.

The positions of all the non-hydrogen atoms of the cation and anion were found by routine heavy-atom methods and refined by full-matrix least squares. The BF_4^- group was refined as an idealised rigid body (B–F 1.37 Å) with the B atom isotropic. The phenyl groups were refined as idealised rigid bodies with H atoms attached and C atoms isotropic, and with a common $U_{iso.}$ for the H atoms which refined to 0.14 Å^2. The remaining atoms were anisotropic. A difference map revealed the atoms of a diethyl ether molecule of solvent which was included at an occupancy of 0.5. The refinement converged at $R = 0.086$, $R' = 0.121$, where $w = 0.68/[\sigma^2(F) + 0.017\ F^2]$ with a maximum shift/error of 0.1. It proved impossible to locate the remaining H atoms on a difference map.

The structure analysis was done with the SHELX program system of G. M. Sheldrick. Scattering factors and dispersion corrections were taken from ref. 19. Final atomic co-ordinates are listed in Table 3, and selected bond lengths and angles in Table 4. Intramolecular distances and angles, listings of temperature factors, H atom positions, and structure factors have been deposited as Supplementary Publication No. SUP 23026 (20 pp.).*

TABLE 4

Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances			
Re–Cl	2.484(6)	Re–P(4)	2.455(6)
Re–P(1)	2.469(7)	Re–C(53)	1.798(30)
Re–P(2)	2.435(7)	N–C(53)	1.347(32)
Re–P(3)	2.470(6)	N–C(54)	1.422(36)
(*b*) Angles			
C(53)–Re–Cl	176.3(7)	C(53)–Re–P(4)	89.8(7)
C(53)–Re–P(1)	91.6(8)	C(54)–N–C(53)	123.3(22)
C(53)–Re–P(2)	86.6(8)	N–C(53)–Re	175.2(18)
C(53)–Re–P(3)	104.3(7)		

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

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