Interaction of t-Butyl Isocyanide with Methyl Compounds of Tungsten, Rhenium, Zirconium, Titanium, and Tantalum. The *X*-Ray Crystal Structures of W–N(Bu^t)CMe$_2$(Me)(NBu^t)[N(Bu^t)CMe=CMe$_2$] † and its Hydrogen Chloride Adduct. t-Butyl Isocyanide Complexes of Molybdenum(0), Ruthenium(II), and Rhodium(I)

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The interaction of t-butyl isocyanide with the following methyl compounds leads to the formation of insertion products in which methyl groups are transferred to the isocyanide ligand: hexamethyltungsten, hexamethylrhenium, tetraneopentylzirconium, bis(η-cyclopentadienyl)dimethyltitanium, and dichlorotrimethyltantalum. For WMe$_6$, a unique transfer of five methyl groups occurs to give the complex W–N(Bu^t)CMe$_2$(Me)(NBu^t)[N(Bu^t)CMe=CMe$_2$] (1) whose structure has been determined by *X*-ray crystallography. Crystals of (1) are triclinic, space group $P\bar{1}$, with a = 8.829(2), b = 10.265(1), c = 14.324(5) Å, α = 90.87(2), β = 101.47(2), γ = 82.44(2)°, and Z = 2. The structure was solved by the heavy-atom method and refined to R = 0.057 for 4 069 observed [$I > 1.5\sigma(I)$] diffractometer data. The W–N and W–C bond lengths in the azatungstacyclopropane unit are 1.91(1) and 2.20(1) Å, the W–C(Me) distance is 2.10(1) Å, and the remaining W–N distances are 1.76(1) Å to the t-butylamide, and 1.94(1) Å to the alkylalkeneamide. All W–N bonds are presumed to be strengthened by π-bonding. The complex (1) reacts with three mol of hydrogen chloride to give the salt (2) whose structure has also been determined by *X*-ray methods and shown to be [Me$_2$C=C(Me)NH$_2$Bu^t][W–NH(Bu^t)CMe$_2$(Me)(NBu^t)Cl$_3$]. Crystals of (2) are also triclinic, space group $P\bar{1}$, with a = 11.178(2), b = 12.730(2), c = 12.155(2) Å, α = 84.21(2), β = 111.31(2), γ = 97.59(2)°, and Z = 2. The structure was solved by the heavy-atom method and refined to R = 0.077 for 4 559 observed data. The identification of the components of the structure was complicated by disorder. The main points of interest in the structure are the protonation of the N atom of the azatungstacyclopropane ring leading to an increase in the W–N bond length in the ligand and the shortening of the Bu^{t}N(1)→W bond relative to that in compound (1). The t-butyl isocyanide complexes Mo(CNBu^t)$_6$, RuH$_2$(PMe$_3$)$_2$(CNBu^t)$_2$, and RhMe(CNBu^t)$_4$ were also synthesised. Infrared and ^{1}H, ^{13}C, and ^{31}P n.m.r. spectra of the compounds are reported.

THE transfer of alkyl groups from transition metals to co-ordinated carbon monoxide [1] and nitric oxide [2] is well documented. Less intensively studied are similar alkyl transfers to co-ordinated isocyanides, but reactions to give acylimidoyl complexes with M–C(R)=NR′ groups are known; [3,4] coupling of the ligands *via* C–C bond formation has also been observed.[5] There are no reports of the cleavage of C–N bonds in isocyanides to give M=NR groups, however.[6]

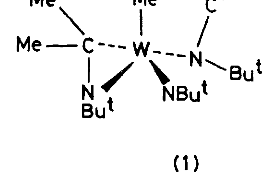
The present work arose through studies on the interaction of t-butyl isocyanide with hexamethyltungsten in which not only was the C–N bond of the isocyanide cleaved to give an organoimido-group, W=NBu^t, with concomitant C–C bond formation between carbon atoms of the CNR groups but the final product was one in which five methyl groups had been transferred from tungsten to the ligands.[7] Only a few cases of double methyl transfers to co-ordinated carbon monoxide are known in which acetone,[8] free or co-ordinated in an oxotantalacyclopropane group,[9] or enediolato-complexes [10] are formed. We now give details of the interaction of CNBu^t with WMe$_6$, extensions to other alkyl compounds, and some other reactions involving isocyanide complexes.

It may be noted that insertion products of various types, *e.g.* η^1- or η^2-dialkyliminoacyls, may also be obtained by the action of alkyl and other halides on neutral or anionic isocyanide complexes such as Fe(CNBu^t)$_5$ or [Mo(η-C$_5$H$_5$)(CO)(CNMe)$_2$]$^-$.[11]

Spectroscopic data for new compounds are collected in Table 1.

RESULTS AND DISCUSSION

A. *Interaction of Metal Methyl Compounds and t-Butyl Isocyanides.*—1. *Hexamethyltungsten.* The interaction of WMe$_6$[12] in isopentane–diethyl ether at −78 °C with excess CNBu^t yields yellow, petroleum-soluble air-stable crystals. The molecular structure determined by *X*-ray diffraction (Figure 1) shows the product to be W–N(Bu^t)CMe$_2$(Me)(NBu^t)[N(Bu^t)CMe=CMe$_2$] (1) and



(1)

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† (*N*-1-Isopropylidene-ethyl-t-butylamido)methyl(t-butylimido)(1,1,3,3-tetramethyl-2-azabutane-1,2-diyl)tungsten(VI).

only with this result to hand could the very complex spectroscopic data be interpreted. The compound contains the following groups bound to tungsten: CH_3, NBu^t, η^2-$N(Bu^t)CMe_2$, and an unusual dialkylamido-group, $N(Bu^t)CMe{=}CMe_2$.

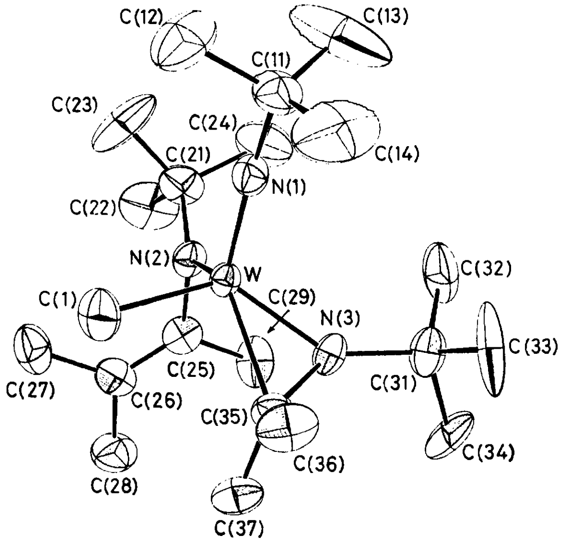


FIGURE 1 Structure of (1) showing the atomic numbering scheme

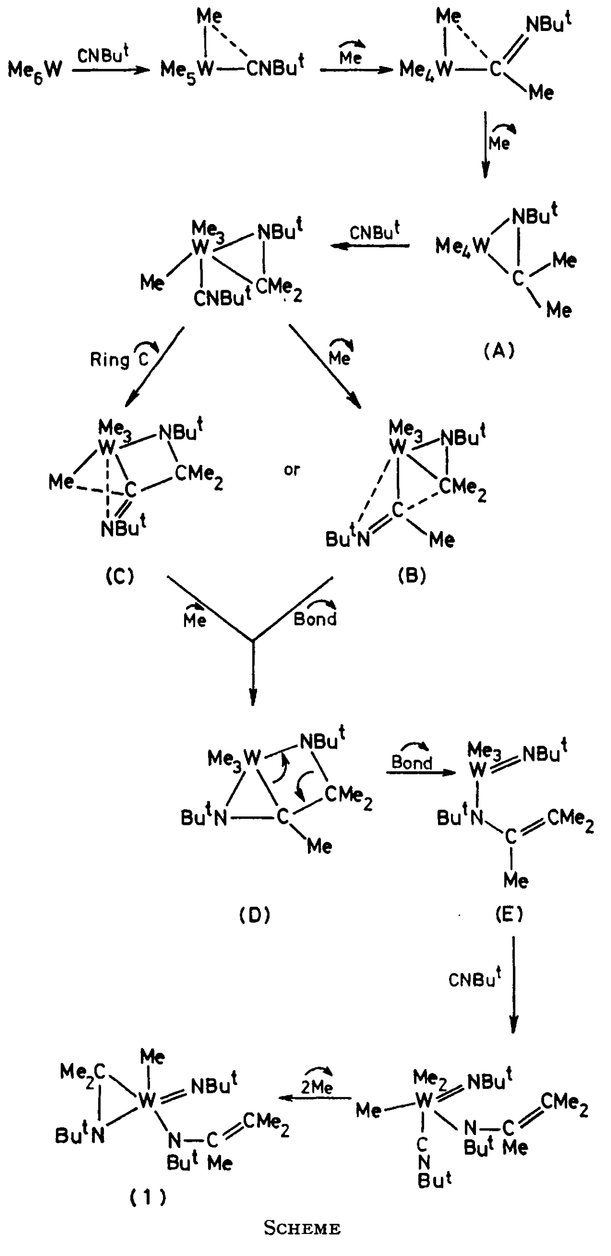
Some of the more important bond lengths and angles are given in Table 2. For the most part, the structure is well defined, but one feature open to question is the representation of the mode of bonding of the $N(Bu^t)CMe_2$ group. Our decision to consider it to be σ-bonded and to form the azatungstacyclopropane unit, rather than act as a π-bonded imine, is based on the geometry at the C and N atoms and the length of the C-N bond, 1.44(2) Å. The complex is thus defined as a five-co-ordinate tungsten(VI) derivative. We might therefore expect the metal atom to be an electron acceptor and the values of the three W-N bonds in the molecule indicate significant $N(p) \rightarrow W(d)$ π-bonding. Interestingly, three π-bonds will give the metal an 18-electron configuration.

The co-ordination geometry of the tungsten atom is difficult to define clearly. The closest approach to one of the regular geometries is square pyramidal with W-N(2) defining the axis and N(1), N(3), C(1), and C(35) forming the base. Even in this representation the W-N(3)-C(35) ring is twisted slightly, relative to the basal plane, and we presume that this is a consequence of the nitrogen atoms N(2) and N(3), which are *trans* to each other seeking to interact with different *d* orbitals in the formation of p_π-d_π bonds.

The n.m.r. data can be interpreted as follows. The ^{13}C-$\{^1H\}$ n.m.r. spectrum has two peaks at δ (p.p.m.) 135.50 and 126.29 that can be assigned to the olefinic carbon atoms of the dialkylamido-group $N(Bu^t)\mathit{C}Me{=}\mathit{C}Me_2$. Four singlets at δ 65.81, 60.93, 60.43, and 56.40 can be assigned to the three different quaternary carbon atoms of the $\mathit{C}Me_3$ groups and to the carbon atom of the heterocycle $\overline{\mathrm{W-N(Bu^t)}\mathit{C}}\mathrm{Me_2}$. All the above resonances remain as singlets in the gated decoupled spectrum. The rest of the spectrum can be assigned to $C\mathit{Me}_3$ groups (δ 34.17, 32.14, 32.02) and to the six different types of methyl carbons (δ 28.94, 28.79, 22.53, 22.20, 21.35, 19.91). All the latter nine singlets are split into quartets in the gated decoupled spectrum confirming their identities as CH_3 groups.

The ^1H n.m.r. spectrum shows singlets for Bu^t groups at δ 1.28, 1.46, and 1.47. Two other singlets at δ 1.87 and 1.92 are assigned to the two non-equivalent methyl groups of the $\overline{\mathrm{W-N(Bu^t)-C}}\mathit{Me}_2$ moiety; in an unisolated tungsten(VI) complex a peak at δ 1.88 was assigned to methyl in $\overline{\mathrm{W-N(Et)-C}}\mathrm{H}\mathit{Me}$.[13]

There is a precedent [3,4] for the initial methyl transfer to co-ordinated isocyanide to give a $W-C(Me){=}NBu^t$



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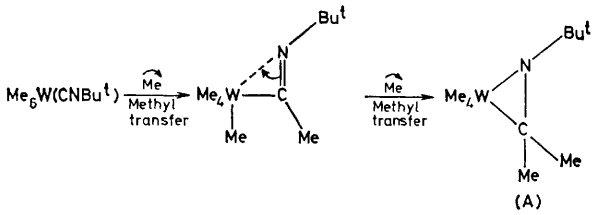
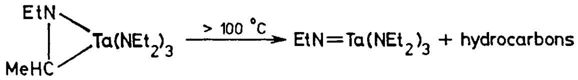
group, while the migration of a second methyl to carbon will generate the η^2-azatungstacyclopropane unit as in species (A) in equation (1).



(1)

An η^2-bonding group of this type, $\overline{\text{W}-\text{N(Et)}-\text{C}}\text{HMe}$, has been detected in the reaction products from the interaction of $LiNEt_2$ and WCl_6.[14] The migration of two methyl groups to co-ordinated CO mentioned earlier,[8,9] to give η^2-$OCMe_2$, is analogous. Co-ordination of a second $CNBu^t$ group to (A) can then occur. There are now two possibilities as outlined in the Scheme, since 'insertion', *i.e.* alkyl migration, can occur either with the methyl group, which will generate another $W-C(Me)=NBu^t$ group as in species (B), or the CMe_2 of the ring can migrate to generate a new heterocyclic ring as in species (C). Bond migration in (B) or a methyl migration in (C) will then lead to the species (D). Since this sytem will be considerably strained, bond migration then allows C–N bond cleavage and generation of the $W-NBu^t$ and $W-N(Bu^t)-C(Me)=CMe_2$ groupings.

A reaction for CO somewhat analogous to the formation of the $W=NBu^t$ group is that leading to Ta=O and $Ta-O-C(Me)=CMe_2$ groups.[9] Although thermolysis of an azatantalacyclopropane complex has been reported to yield an organoimido-group,[14] equation (2), a similar process cannot operate in our case as complex (1) is formed under mild conditions essentially quantitatively with no loss of hydrocarbons.



(2)

Finally, additional co-ordination of a third $CNBu^t$ to species (E) followed by methyl migrations as in equation (1) produces the $\overline{\text{W}-\text{C(Me}_2\text{)N}}\text{Bu}^t$ group found in the final product.

It may be noted that as is usual in insertion reactions there is no change in oxidation state of the metal in any of the intermediate species in the Scheme.

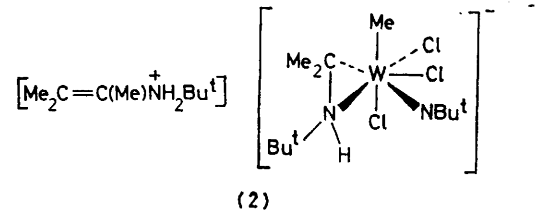
The failure of the sixth methyl group to transfer despite the presence of excess $CNBu^t$ under the reaction conditions employed is doubtless due to the attainment of the 18-electron configuration of the tungsten atom *via* W–N $p_\pi \longrightarrow d_\pi$ bonding so that further co-ordination of isocyanide cannot occur. This situation may be compared with the observation that only two methyl groups of WMe_6 are transferred in the reaction with NO[15] to give $WMe_4[ON(Me)NO]_2$. In this case further reaction is inhibited by co-ordinative saturation of the eight-co-ordinate species produced. In the present case the tungsten(VI) is co-ordinatively unsaturated but electronically saturated.

It may be noted finally that with carbon monoxide (3 atm *), WMe_6 in isopentane reacts to give acetone and $W(CO)_6$ according to the stoicheiometry of equation (3)

$$WMe_6 + 9CO \longrightarrow W(CO)_6 + 3Me_2CO \qquad (3)$$

so that all six methyl groups are transferred. Although intermediates with acetyl groups can be detected spectroscopically using CO (1 atm) none could be isolated in a pure state.

The complex (1) does not react with H_2, NO, SO_2, or alkenes, again suggesting electronic saturation of the metal atom. On refluxing in methanol, $W(OMe)_6$ is formed.



(2)

Reaction with acids. The compound reacts with HBF_4, BF_3, Ph_3CBF_4, and hydrogen halides.

The interaction in petroleum at −20 °C with HCl gives a white precipitate which on recrystallisation from toluene gives crystals of a salt $[Me_2C=C(Me)NH_2Bu^t]^+$-$[\overline{\text{W}-\text{NH(Bu}^t\text{)C}}\text{Me}_2\text{(Me)(NBu}^t\text{)Cl}_3]^-$ (2) which is a 1 : 1 electrolyte in nitromethane.

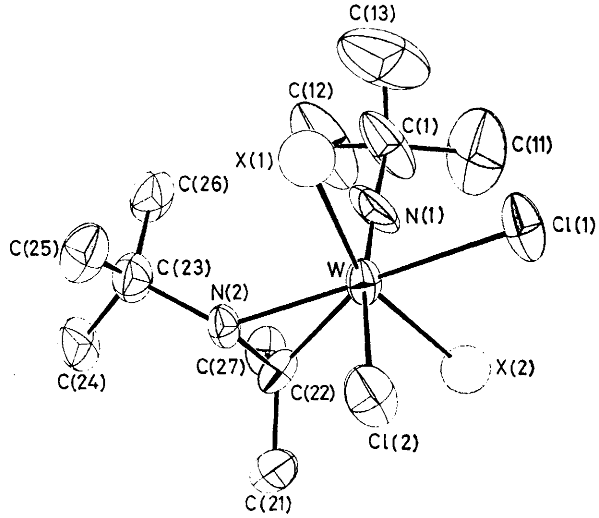


FIGURE 2 Structure of the anion of compound (2), showing atomic numbering

The structure of the anion, which can be formally designated as trichloro(1-methyl-1-t-butylaminoethyl-*C*^{1}-*N*)(t-butylimido)tungstate(1−), is shown in Figure 2; some bond lengths and angles are given in Table 3. For this structure both the anion and cation identification

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* Throughout this paper: 1 atm = 101 325 N m^{-2}; 1 mmHg = (101 325/760) N m^{-2}.

TABLE 1

Hydrogen-1 and carbon-13 n.m.r. data

Compound	$^1\mathrm{H}$ ^{a} δ/p.p.m.		$^{13}\mathrm{C}$ ^{b} δ/p.p.m.	
(1)	1.47s (9) 1.46s (9) 1.28s (9)	$\mathrm{Bu^t}$	135.50s 126.59s	$\mathrm{NBu^t}(\mathit{C}\mathrm{Me}{=}\mathit{C}\mathrm{Me}_2)$
	1.92s (3) 1.87s (3)	$\overline{\mathrm{WNC}}\mathrm{Me}_2$	65.81s 60.93s 60.43s 56.40s	$\mathit{C}\mathrm{Me}_3, \overline{\mathrm{W{-}}\mathit{C}\mathrm{Me}_2\mathrm{N}}\mathrm{Bu^t}$
	1.73s (3) 1.43s (3) 1.25s (6)	Me	34.17s 32.14s 32.02s	$\mathrm{C}\mathit{Me}_3$
			28.94s 28.79s 22.53s 22.20s 21.35s 19.91s	Me
(2)	3.09br,s 2.53br,s	NH	129.27s 125.64s	$\mathit{C}\mathrm{Me}_2{=}\mathit{C}(\mathrm{Me})\mathrm{NH}_2\mathrm{Bu^t}$
	2.89s (3) 2.84s (3) 2.21s (3) 1.89s (3) 1.17s (3) 1.09s (3)	Me	60.61s 60.43s 62.31s	$\mathit{C}\mathrm{Me}_3$
			71.34s	$\overline{\mathrm{W{-}}\mathit{C}\mathrm{Me}_2\mathrm{{-}N}}\mathrm{HBu^t}$
	1.52s (9) 1.43s (9) 1.41s (9)	$\mathrm{C}\mathit{Me}_3$	31.85s 29.42s 29.17s	$\mathrm{C}\mathit{Me}_3$
			18.56s 19.97s 21.35s 29.74s 29.55s 16.17s	Me
(3)	1.25s (18) 1.47s (9) 1.53s (9) 1.54s (9)	$\mathrm{Bu^t}$	195.16s 190.03s	$\mathrm{Re{-}}\mathit{C}{\equiv}\mathrm{NBu^t}$
			182.66s 166.91s	$\mathrm{Re{-}}\mathit{C}{=}\mathrm{N{-}}$
	1.92s (6) 2.19s (6)	$-\mathrm{C}(\mathit{Me}){=}\mathrm{N}-$	58.87s 57.81s 55.46s 55.14s	$\mathit{C}\mathrm{Me}_3$
			31.67s 31.05s 31.47s 32.55s	$\mathrm{C}\mathit{Me}_3$
			32.85s 33.94s	$-\mathrm{C}(\mathit{Me}){=}\mathrm{N}-$
(4)	2.27s (2) 2.20s (4) 2.12s (2)	$\mathrm{C}\mathit{H}_2$	258.9s 255.4s	$\mathrm{ZrC{\equiv}NBu^t},\mathit{C}{\equiv}\mathrm{N}$
	1.22s (18) 1.18s (9) 1.17s (9) 1.30s (9) 1.32s (9)	$\mathrm{C}\mathit{Me}_3$	62.87s 59.80s 59.57s 57.74s	$\mathit{C}\mathrm{Me}_3$
			35.58s 35.42s 35.43s 35.31s	$\mathit{C}\mathrm{H}_2$
			30.81s 30.62s 30.31s 30.15s	$\mathrm{C}\mathit{Me}_3$
(5)	5.12s (10)	$\eta^5\text{-}\mathrm{C}_5\mathrm{H}_5$	106.00s	$\eta^5\text{-}\mathrm{C}_5\mathrm{H}_5$
	2.05s (3)	$-\mathrm{C}(\mathit{Me}){=}\mathrm{N}-$	225.12s	$\mathrm{Ti{-}}\mathit{C}{=}\mathrm{N}$
	0.92s (9)	$\mathrm{C}\mathit{Me}_3$	61.93s	$\mathit{C}\mathrm{Me}_3$
	0.42s (3)	$\mathrm{Ti{-}}\mathit{Me}$	29.79s	$\mathrm{C}\mathit{Me}_3$
			22.30s	$-\mathrm{C}(\mathrm{Me}){=}\mathrm{N}-$
			16.23s	$\mathrm{Ti{-}}\mathit{Me}$

TABLE 1 (*continued*)

Compound	^{1}H [a] δ/p.p.m.		^{13}C [b] δ/p.p.m.	
(6)	2.60s (3)	C(*Me*)=NBu^t	227.27	*C*(Me)=N–
	2.25s (6)		226.10s	
	1.79s (9)	C*Me*$_3$	61.0s	*C*Me$_3$
	1.35s (18)		59.52s	
			32.08s	C*Me*$_3$
			29.84s	
			23.61s	C(*Me*)=NBu^t
			16.88s	
(7)	1.26s	C*Me*$_3$	193.10s	C≡NBu^t
			55.11s	*C*Me$_3$
			33.11s	C*Me*$_3$
(8)	1.58t (18)	P*Me*$_3$ ^2J(P–H) 3 Hz	200.27s	*C*≡NBu^t
	1.16s (18)	C*Me*$_3$	53.12s	*C*Me$_3$
	−8.10t (2)	Ru–H ^2J(P–H) 27 Hz		
			31.79s	C*Me*$_3$, P*Me*$_3$
			31.08s	
(9)	2.99s (3)	Rh–*Me*	203.9s	*C*≡NBu^t
			203.5s	
	2.11s (9)	Bu^t	56.08s	*C*Me$_3$
	1.15s (27)		56.31s	
			30.9s	Rh–*Me*
			30.62s	C*Me*$_3$ (non-equiv.)
			30.31s	C*Me*$_3$ (equiv.)

[a] In [^{2}H$_6$]benzene at 90 MHz, 35 °C; SiMe$_4$ as reference (δ 0.0 p.p.m.). Relative areas in parentheses. [b] In [^{2}H$_6$]benzene at 62.5 MHz, 25 °C; SiMe$_4$ as reference (δ 0.0 p.p.m.).

are complicated by disorder. In the anion, it is necessary to assume that two of the sites which were at first identified as chlorine atoms [X(1) and X(2)] are actually a composite of [$\frac{1}{2}$ Cl + $\frac{1}{2}$ Me]. This was suggested by the W : Cl ratio by analysis of **1 : 3** and the presence of a methyl group bound to tungsten detected in the ^{13}C n.m.r. spectrum. Further, the disorder model explains the high temperature factors and short bonds to the metal originally found for both X(1) and X(2) when refined as Cl atoms.

The second notable feature is the nature of the azatungstacyclopropane group. We have formulated this to contain a protonated nitrogen atom N(2) for a number of reasons. First, the three bonds to this nitrogen atom are pyramidal, with an angle sum of *ca.* 333° [*cf.* 355° for the equivalent N atom in compound (1)]. Secondly, the W–N(2) bond, at 2.16(2) Å, is much longer than the equivalent bond in compound (1)[1.91(1) Å]. Thirdly, a peak was detected in a difference synthesis for a hydrogen atom in a sensible position (with a N–H distance of 0.9 Å) which completed a tetrahedral geometry for N(2). Finally, there are a number of precedents for this ring structure, notably the molybdenum(II) complex [16] $(\eta^5\text{–C}_5\text{H}_5)(\text{CO})_2\overline{\text{Mo–C(Me)(Ph)N}}\text{H(CHMePh)}$. The anion is thus defined as a seven-co-ordinate tungsten(VI) complex the geometry being best considered as a pentagonal bipyramid, with the Bu^{t}N(1) ⟶ W–Cl(2) unit defining the axis and the remaining atoms, including the N and C atoms of the WNC ring, forming the equatorial girdle. With N→W π-bonding, again the W atom has 18 electrons.

The loss of the π-donating dialkylamido-ligand present in (1) and the π-donor capability of N(2) in the present complex has had a remarkable effect on the multiple Bu^{t}N(1) ⟶ W bond which has shortened by *ca.* 0.1 Å [from 1.76(1) to 1.61(2) Å]. The length of the W–Cl(2)

TABLE 2

Bond distances (Å) and angles (°) for compound (1)

(*a*) Distances

N(1)–W	1.757(12)	C(22)–C(21)	1.488(26)
N(2)–W	1.940(13)	C(23)–C(21)	1.567(28)
N(3)–W	1.907(12)	C(24)–C(21)	1.619(30)
C(1)–W	2.102(16)	C(26)–C(25)	1.368(22)
C(35)–W	2.199(13)	C(29)–C(25)	1.487(22)
C(11)–N(1)	1.468(18)	C(27)–C(26)	1.536(31)
C(21)–N(2)	1.521(19)	C(28)–C(26)	1.495(24)
C(25)–N(2)	1.463(19)	C(32)–C(31)	1.606(26)
C(31)–N(3)	1.487(17)	C(33)–C(31)	1.429(23)
C(35)–N(3)	1.438(16)	C(34)–C(31)	1.397(26)
C(12)–C(11)	1.468(29)	C(36)–C(35)	1.491(20)
C(13)–C(11)	1.467(27)	C(37)–C(35)	1.493(20)
C(14)–C(11)	1.510(31)	C(25)–W	2.781(17)

(*b*) Angles

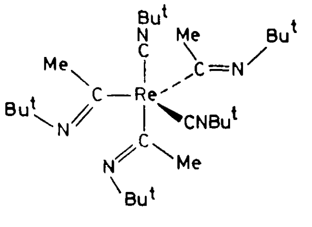
N(2)–W–N(1)	108.9(6)	C(23)–C(21)–N(2)	110.8(15)
N(3)–W–N(1)	110.2(6)	C(23)–C(21)–C(22)	111.7(19)
N(3)–W–N(2)	110.1(5)	C(24)–C(21)–N(2)	103.7(15)
C(1)–W–N(1)	97.9(7)	C(24)–C(21)–C(22)	111.1(21)
C(1)–W–N(2)	105.1(7)	C(24)–C(21)–C(23)	105.5(22)
C(1)–W–N(3)	123.5(7)	C(26)–C(25)–N(2)	119.4(15)
C(35)–W–N(1)	121.6(6)	C(29)–C(25)–W	112.3(11)
C(35)–W–N(2)	127.2(6)	C(29)–C(25)–N(2)	117.4(15)
C(35)–W–N(3)	40.2(4)	C(29)–C(25)–C(26)	123.3(17)
C(35)–W–C(1)	83.3(7)	C(27)–C(26)–C(25)	123.2(17)
C(35)–W–C(25)	97.6(6)	C(28)–C(26)–C(25)	120.8(19)
C(11)–N(1)–W	165.0(11)	C(28)–C(26)–C(27)	115.6(16)
C(21)–N(2)–W	133.2(9)	C(32)–C(31)–N(3)	104.8(13)
C(25)–N(2)–W	108.9(9)	C(33)–C(31)–N(3)	116.5(14)
C(31)–N(3)–W	145.2(10)	C(33)–C(31)–C(32)	110.0(17)
C(35)–N(3)–W	80.9(8)	C(34)–C(31)–N(3)	108.2(16)
C(35)–N(3)–C(31)	128.3(12)	C(34)–C(31)–C(32)	110.1(18)
C(12)–C(11)–N(1)	107.1(15)	C(34)–C(31)–C(33)	107.2(20)
C(13)–C(11)–N(1)	108.8(15)	N(3)–C(35)–W	58.9(7)
C(13)–C(11)–C(12)	116.6(22)	C(36)–C(35)–W	115.5(11)
C(14)–C(11)–N(1)	111.0(16)	C(36)–C(35)–N(3)	120.8(13)
C(14)–C(11)–C(12)	106.7(20)	C(37)–C(35)–W	120.2(10)
C(14)–C(11)–C(13)	106.6(21)	C(37)–C(35)–N(3)	119.2(13)
C(22)–C(21)–N(2)	113.4(16)	C(37)–C(35)–C(36)	112.4(13)

bond *trans* to $Bu^tN(1) \longrightarrow W$ is then explained in terms of a strong *trans* influence.

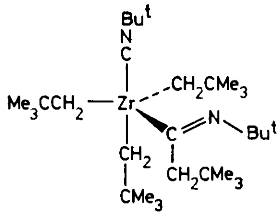
As mentioned earlier, the unequivocal definition of the cation was not possible from the *X*-ray data. Accordingly, its presentation as the quaternary ammonium ion $[Me_2C{=}C(Me){-}NH_2Bu^t]^+$ is based on the quantitative nature of the reaction, the analytical data, and, of course, the idea that it is most likely to have been derived from the alkylamido-group on (1) lost on the formation of (2). The overall reaction thus corresponds to the addition of 3 mol of HCl to (1), leading to the salt (2).

Knowing the structure, the n.m.r. data can be interpreted. The $^{13}C\text{-}\{^1H\}$ spectrum shows two singlets at δ 129.27 and 125.64 for the olefinic atoms of the cation $[Me_2\mathit{C}{=}\mathit{C}(Me)NH_2Bu^t]^+$. Four singlets at δ 71.34, 62.31, 60.43, and 60.61 can be assigned to the three different carbon atoms of the *C*Me groups and to the carbon atom in the $\overline{W{-}NH(Bu^t)\mathit{C}}Me_2$ ring. The rest of the spectrum can be assigned to $C\mathit{Me}_3$ groups (δ 31.85, 29.42, 28.17) and to the six different types of methyl carbons [δ 18.56, 19.97 (W–Me), 21.35, 16.17, 29.55, 29.74]. The ^1H n.m.r. spectrum has singlets for Bu^t groups at δ 1.52, 1.43, 1.41 and two other singlets at δ 2.89, 2.84 for the two non-equivalent methyl groups of the metallocycle.

2. *Hexamethylrhenium.* The paramagnetic alkyl $ReMe_6$[17] in toluene–diethyl ether at −78 °C yields petroleum-soluble orange crystals of a compound of stoicheiometry $Re(CNBu^t)_2[C(Me){=}NBu^t]_3$ (3). The compound is air sensitive, especially in solution. We have been unable to grow crystals suitable for *X*-ray study but comparison of the spectra with that of (1) suggests the structure (3).



(3)



(4)

The i.r. spectrum has bands at 2 105m, 1 980s,br, 1 840s,br, and 1 785m cm^{-1} that can be assigned to CN stretches of isocyanide and $C(Me){=}NBu^t$ groups.

The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum shows two equivalent $C\mathit{Me}_3$ groups at δ 31.67 and three non-equivalent $C\mathit{Me}_3$ groups at δ 31.05, 31.47, and 32.55. Four singlets at δ 195.16, 190.03, 182.66, and 166.91 can be assigned to the carbon atoms of $\mathit{C}NBu^t$ and $\mathit{C}{=}N$. Four singlets at δ 58.87, 57.81, 55.46, and 55.14 are assigned to the four different carbon atoms of $\mathit{C}Me_3$ groups and the inserted carbon atoms of the $C(\mathit{Me}){=}NBu^t$ groups are at δ 32.85 and 33.94 (intensities 2 : 1).

The structure (3) has trigonal-bipyramidal rhenium(III) with a 14-electron configuration. Why the reaction pattern is so different from that of WMe_6 is not clear except that $ReMe_6$ is paramagnetic and, as in the reaction with NO,[2] intermediates from paramagnetic alkyls may differ substantially from those from diamagnetic alkyls. The fate of the three lost methyl groups has not been ascertained but presumably they are transferred to isocyanide and the group(s) reductively eliminated.

The compound $ReOMe_4$[17] also reacts with $CNBu^t$ but the product is an oil. The pentamethyls $NbMe_5$ and $TaMe_5$ also give yellow oils that are distillable at 120 °C, 10^{-4} mmHg, without decomposition but are air sensitive. Their i.r. and n.m.r. spectra are complicated but show features common to those of the W and Re compounds.

TABLE 3

Bond distances (Å) and angles (°) for compound (2)

(*a*) Distances			
Cl(1)–W	2.483(7)	C(11)–C(1)	1.475(49)
Cl(2)–W	2.498(7)	C(12)–C(1)	1.494(37)
Cl(3′)–W	2.458(14)	C(13)–C(1)	1.464(58)
Cl(4′)–W	2.388(19)	C(22)–N(2)	1.432(22)
C(3′)–W	2.240(53)	C(23)–N(2)	1.589(24)
C(4′)–W	2.622(63)	C(22)–C(21)	1.578(30)
N(1)–W	1.609(25)	C(27)–C(22)	1.540(27)
N(2)–W	2.158(14)	C(24)–C(23)	1.549(31)
C(22)–W	2.157(22)	C(25)–C(23)	1.548(32)
C(1)–N(1)	1.566(33)	C(26)–C(23)	1.531(30)
(*b*) Angles			
Cl(2)–W–Cl(1)	83.3(3)	C(22)–W–Cl(3′)	123.3(7)
Cl(3′)–W–Cl(1)	80.8(5)	C(22)–W–Cl(4′)	78.6(7)
Cl(3′)–W–Cl(2)	84.7(5)	C(22)–W–C(3′)	131.0(12)
Cl(4′)–W–Cl(1)	76.5(5)	C(22)–W–C(4′)	73.1(13)
Cl(4′)–W–Cl(2)	89.5(6)	C(22)–W–N(1)	101.6(10)
Cl(4′)–W–Cl(3′)	157.1(5)	C(22)–W–N(2)	38.8(6)
C(3′)–W–Cl(1)	72.8(12)	C(1)–N(1)–W	178.0(19)
C(3′)–W–Cl(2)	83.0(13)	C(22)–N(2)–W	70.6(10)
C(3′)–W–Cl(4′)	14.0(12)	C(23)–N(2)–W	133.9(11)
C(4′)–W–Cl(1)	81.3(13)	N(2)–C(22)–W	70.6(10)
C(4′)–W–Cl(2)	84.2(11)	C(21)–C(22)–W	124.6(14)
C(4′)–W–Cl(3′)	159.9(12)	C(27)–C(22)–W	117.0(15)
C(4′)–W–C(3′)	152.3(16)	C(11)–C(1)–N(1)	101.8(28)
N(1)–W–Cl(1)	86.4(8)	C(12)–C(1)–N(1)	116.7(22)
N(1)–W–Cl(2)	169.4(7)	C(13)–C(1)–N(1)	104.9(30)
N(1)–W–Cl(3′)	91.0(9)	C(12)–C(1)–C(11)	123.6(39)
N(1)–W–Cl(4′)	90.7(10)	C(13)–C(1)–C(11)	101.9(35)
N(1)–W–C(3′)	91.4(15)	C(13)–C(1)–C(12)	105.7(43)
N(1)–W–C(4′)	96.9(13)	C(23)–N(2)–C(22)	126.6(15)
N(2)–W–Cl(1)	159.5(4)	C(21)–C(22)–N(2)	111.4(17)
N(2)–W–Cl(2)	80.9(5)	C(27)–C(22)–N(2)	119.5(16)
N(2)–W–Cl(3′)	84.7(6)	C(24)–C(23)–N(2)	106.3(18)
N(2)–W–Cl(4′)	116.3(6)	C(25)–C(23)–N(2)	103.2(17)
N(2)–W–C(3′)	92.3(13)	C(26)–C(23)–N(2)	110.8(16)
N(2)–W–C(4′)	109.9(13)	C(27)–C(22)–C(21)	109.1(18)
N(2)–W–N(1)	108.4(9)	C(25)–C(23)–C(24)	110.6(20)
C(22)–W–Cl(1)	153.9(5)	C(26)–C(23)–C(24)	114.8(21)
C(22)–W–Cl(2)	88.8(6)	C(26)–C(23)–C(25)	110.4(22)

3. *Tetraneopentylzirconium.* The interaction of CNMe with the tetra-alkenyl $Zr(CPh{=}CMe_2)_4$ gives $Zr[C({=}NMe)(CPh{=}CMe_2)]_4$.[18]

The tetraneopentyl $Zr(\eta\text{-}C_5H_{11})_4$ with $CNBu^t$ in diethyl ether at −20 °C yields white, air-sensitive, petroleum-soluble crystals of $Zr(CH_2CMe_3)_3(CNBu^t)[C(CH_2CMe_3){=}NBu^t]$ (4), whose structure can be assigned on the basis of analytical and spectroscopic data. The i.r. spectrum has CN stretches for both co-ordinated isocyanide and C=N, at 1 994 and 1 642 cm^{-1} respectively.

The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum shows singlets at δ 258.9 ($\mathit{C}{\equiv}N{-}Bu^t$); 255.4 ($-\mathit{C}{=}N$); 62.87, 59.80, 59.57, 57.74 ($\mathit{C}Me_3$); 35.58, 35.42, 35.43, 35.31 ($\mathit{C}H_2CMe_3$), 30.81, 30.62, 30.31, 30.15 ($C\mathit{Me}_3$) p.p.m.

The failure of three of the alkyl groups to transfer to co-ordinated isocyanide presumably is due to steric factors of the bulky ligands since the metal atom is only five-co-ordinate. A carbonyl analogue, $Ti(CH_2Ph)_3(CO)(COCH_2Ph)$, has been proposed as an intermediate (not isolated) in the reaction of $Ti(CH_2Ph)_4$ with CO leading to the diacyl $Ti(CH_2Ph)_2(COCH_2Ph)_2$.[19]

4. *Bis(η-cyclopentadienyl)dimethyltitanium*. Cyclohexyl isocyanide has been shown to react with $Ti(\eta\text{-}C_5H_5)_2Me_2$ [20] and $Ti(\eta\text{-}C_5H_5)_2MePh$ [21] to give only a mono-insertion product, in the latter case containing a $C(Ph)=NC_6H_{11}$ group.

A similar reaction with $CNBu^t$ gives orange $Ti(\eta\text{-}C_5H_5)_2Me[C(Me)=NBu^t]$ (5) which has a peak at 1 704 cm^{-1} in the i.r. for C=N and a $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum with singlets at δ 225.10, 106.0, 61.90, 29.80, 22.3, and 16.2 corresponding respectively to *C*=N, $\eta^5\text{-}C_5H_5$, *C*Me_3, C*Me*$_3$, C–Me, and Ti–*Me*.

5. *Dichlorotrimethyltantalum*(V). The interaction of $CNBu^t$ with $TaMe_5$ has been noted above while the pentahalides of Nb and Ta react with RNC (R = Me or Bu^t) to give $MX_4(CNR)[C(X)=NR]$.[22] For $TaCl_2Me_3$ insertions with NO[23a] and CS_2[23b] as well as RNC (R = *p*-tolyl, cyclohexyl) have been studied; isocyanides [24] give $TaCl_2Me[CMe=NR]_2$. By contrast, however, with $CNBu^t$ air-stable orange crystals of $TaCl_2[C(Me)=NBu^t]_3$ (6) are obtained. The i.r. spectrum shows CN stretches at 1 680 and 1 630 cm^{-1}. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum has singlets at δ 227.27, 226.10 (*C*N); 61.07, 59.52 (*C*Me_3); 22.08, 29.84 (C*Me*$_3$); and 23.61, 16.88 [C(*Me*)=NBu^t]. The structure is evidently trigonal bipyramidal with axial chlorine atoms.

B. Isocyanide Complexes.—1. *Hexakis(t-butyl isocyanide)molybdenum*(0). Interaction of $Mo_2(CO_2Me)_4$ in the presence of trimethylphosphine under hydrogen (3 atm) with sodium amalgam leads to the hydride $Mo_2H_2(\mu\text{-}H)_2(PMe_3)_6$.[25] A similar reaction but using $CNBu^t$ in place of PMe_3 does not give a hydride but forms $Mo(CNBu^t)_6$ (7) in high yield. The dark red crystalline material is very soluble in petroleum and is air sensitive.

The ^1H n.m.r. spectrum shows only a singlet for the Bu^t groups (δ 1.26) while the $^{13}C\text{-}\{^1H\}$ spectrum has three singlets at δ 193.10, 55.1, and 32.11 assigned to isocyanide, *C*Me_3, and C*Me*$_3$ carbons respectively. The gated decoupled spectrum of the δ 32.11 signal is split into a quartet ($J_{C\text{-}H}$ = 126 Hz). The ^1H n.m.r. spectrum is the same between −80 °C and + 80 °C. The i.r. spectrum both in solution and in the solid state shows intense broad bands at *ca.* 1 970 and 1 885 cm^{-1}; low-energy bands for terminal isocyanides have been attributed to bent M–C–N–R groups.[26]

As far as we are aware the only other neutral octahedral isocyanide is $Mo(CNPh)_6$ obtained in low yield [27] but a number of t-butyl isocyanide complexes of molybdenum(II) are known,[23] and the cation $[Mo(SnCl_3)(CNBu^t)_6]^+$; [29] interaction of $Mo_2(CO_2Me)_4$ with $CNBu^t$ alone gives $Mo^{II}(CNBu^t)_5(CO_2Me)_2$ [28] which may well be an intermediate in the present reaction.

The present complex has been described in a thesis; [30] it should be possible to make other molybdenum(0) isocyanides by this procedure from $Mo_2(CO_2Me)_4$.

As for zerovalent isocyanide complexes of Fe,[31] Ni,[32] and Pd,[33] $Mo(CNBu^t)_6$ reacts oxidatively with methyl iodide to give the red, air-stable seven-co-ordinate complex $[MoMe(CNBu^t)_6]I$.

2. cis-*Dihydrido-bis(t-butyl isocyanide)*-trans-*bis(trimethylphosphine)ruthenium*(II). Interaction of $RuMe_2(PMe_3)_4$ [34] with $CNBu^t$ in tetrahydrofuran (thf) yields white crystals of the petroleum-soluble hydride $RuH_2(PMe_3)_2(CNBu^t)_2$ (8) where the loss of methyl groups and formation of the hydride is presumably due to reaction with thf.[35] The ^1H n.m.r. spectrum has a high-field triplet at δ −8.10 [^2J(P–H) 27 Hz] due to Ru–H, a triplet [δ 1.58, ^2J(P–H) 3 Hz] due to PMe_3, and a singlet (δ 1.16) for the t-butyl groups.

3. *Methyltetrakis(t-butyl isocyanide)rhodium*(I). Interaction of one equivalent of LiMe with $RhCl(CNBu^t)_4$ [36] yields orange, petroleum-soluble crystals of $RhMe(CNBu^t)_4$ (9). The spectroscopic data suggest trigonal-bipyramidal structure. The ^1H n.m.r. spectrum has three singlets δ 2.99, 2.11, and 1.15 (intensities 3 : 9 : 27) corresponding to CH_3, a unique $CNBu^t$, and three equivalent $CNBu^t$ groups respectively. The $^{13}C\text{-}\{^1H\}$ spectrum has singlets at δ 203.9, 203.5, (*C*≡NBu^t); 56.08, 56.31 (*C*Me_3); 30.62, 30.31, (C*Me*$_3$); and 30.9 (Rh-*Me*).

The complex reacts with MeI and $C_2(CN)_4$ but the products have not been characterised.

EXPERIMENTAL

Microanalyses were by Pascher (Bonn) and Imperial College Laboratories. Spectrometers used were Perkin-Elmer R32 (^1H, 90 MHz), Bruker WM 250 (^{31}P n.m.r. at 101.27 MHz and ^{13}C n.m.r. at 62.9 MHz), and Perkin-Elmer 597 (i.r.). Data in p.p.m. referenced to $SiMe_4$ and external 85% H_3PO_4. I.r. spectra are in Nujol unless otherwise stated.

All operations were performed under oxygen-free nitrogen or argon or *in vacuo*. Solvents were dried over sodium and distilled from sodium–benzophenone under nitrogen immediately before use. Light petroleum was b.p. 40—60 °C. Melting points were determined in sealed tubes under nitrogen (uncorrected). Analytical data are collected in Table 4.

1. $\overline{W\text{–}N(Bu^t)C}Me_2(Me)(NBu^t)[N(Bu^t)CMe=CMe_2]$ (1).—Excess t-butyl isocyanide (4 cm^3, 40 mmol) was added to hexamethyltungsten (2.0 g, 7.3 mmol) in isopentane–diethyl ether (1 : 3, 50 cm^3) at −78 °C. The mixture was stirred and allowed to warm slowly to room temperature. After stirring for another 5 h at room temperature, the volatile materials were removed under reduced pressure. The residue was extracted with light petroleum (*ca.* 40 cm^3), filtered and concentrated to *ca.* 20 cm^3, cooled at −20 °C to give pale yellow crystals, m.p. 128—129 °C. Yield, 3.6 g, 95%. I.r.: 1 455s, 1 446m, 1 386m, 1 365s, 1 355s, 1 293s, br, 1 215s, 1 205s, 1 180s, 1 154s, 1 139w, 1 090w, 1 056w, 1 042w, 1 020w, 968w, 950w, 942w, 917s, 805m, 795w cm^{-1}.

2. *Interaction of Compound* (1) *with Hydrogen Chloride: Preparation of* $[Me_2C=C(Me)NH_2Bu^t][\overline{W\text{–}NH(Bu^t)C}Me_2\text{-}$

TABLE 4

Analytical data for the new compounds

Compound	Analyses [a](%) C	H	N	Other	M [b]
(1)	48.3 (48.2)	8.7 (8.6)	8.0 (8.0)		520 (523)
(2)	41.7 (39.9)	7.5 (7.6)	6.4 (6.6)	Cl 16.3 (16.8) W 28.6 (29.1)	320 (632)
(3)	53.5 (52.0)	8.3 (8.3)	10.9 (10.8)		650 (646)
(4)	65.7 (66.5)	11.0 (11.5)	5.8 (5.2)		520 (541)
(5)	69.6 (70.1)	7.9 (8.6)	4.4 (4.8)		280 (291)
(6)	39.3 (39.6)	6.8 (6.6)	7.4 (7.7)	Cl 12.2 (13.0)	530 (546)
(7)	60.7 (60.6)	9.4 (9.1)	13.7 (14.1)		580 (594)
(8)	46.3 (45.6)	9.2 (9.0)	6.6 (6.6)	P 15.0 (14.7)	410 (422)
(9)	55.6 (56.0)	8.9 (8.7)	12.4 (12.4)		440 (450)

[a] Calculated values in parentheses. [b] Cryoscopically in benzene.

(Me)(NBu^t)Cl$_3$] (2).—Dry hydrogen chloride was bubbled slowly through a solution of complex (1) (0.5 g, 0.96 mmol) in light petroleum (50 cm^3) at −20 °C for 5 min. A white precipitate was formed immediately; after warming to room temperature, the precipitate was collected, washed twice with light petroleum (20 cm^3), then recrystallised from toluene, m.p. 102—103 °C. Yield, *ca.* 85%. I.r.: 3 210m, 3 120,m 1 655s [ν(C=C)], 1 600w, 1 545w, 1 490m, 1 480s, 1 395m, 1 282m, 1 265s, 1 243m, 1 216m, 1 192s, 1 168m, 1 096s, 1 040w, 1 020m, 1 006m, 900w, 946w, 890m, 800m, 695w, 650w cm^{-1}. Conductivity (in CH_3NO_2), 25 °C, 10^{-3} mol dm^{-3}: $\Lambda_M = 100\ \Omega^{-1}$ cm^2 mol^{-1}.

3. *Tris*(1-t-*butyliminoethyl*)*bis*(t-*butyl isocyanide*)*rhenium*(III), Re(CNBu^t)$_2$[C(Me)=NBu^t]$_3$ (3).—Excess t-butyl isocyanide (2.0 cm^3, 20 mmol) was added to hexamethylrhenium (1.0 g, 3.62 mmol) in toluene–diethyl ether (1 : 1, 50 cm^3) at −78 °C. The mixture was stirred and allowed to warm to room temperature slowly. After stirring for 3 h the volatile materials were removed under reduced pressure and the residue extracted into light petroleum (*ca.* 50 cm^3), the solution was filtered, concentrated to *ca.* 30 cm^3, and cooled at −20 °C to yield orange crystals, m.p. 112—113 °C. Yield, 1.75 g, 75%. I.r.: 2 105m, 1 980s,br, 1 840s,br, 1 785m, 1 615m, 1 550m, 1 232m, 1 210s, 1 040w, 932w, 908w, 890w, 745w cm^{-1}

4. Zr(CH$_2$CMe$_3$)$_3$(CNBu^t)[C(CH$_2$CMe$_3$)=NBu^t] (4).—Excess t-butyl isocyanide (2.5 cm^3, 25 mmol) was added to Zr(CH$_2$CMe$_3$)$_4$ (2.0 g, 5.33 mmol) in diethyl ether (50 cm^3) at −20 °C. After warming slowly to room temperature and stirring for 3 h the solvent was removed and the residue extracted with light petroleum (20 cm^3). After filtering and concentrating to *ca.* 10 cm^3, cooling at −20 °C gave white crystals, m.p. 125—126 °C. Yield, 2.4 g, 85%. I.r.: 1 994s, 1 642s, 1 620s, 1 565s, 1 360s, 1 220s, 1 070w, 1 025w, 962w, 942w, 910w, 895w, 790m, 750s cm^{-1}.

5. Ti(η-C$_5$H$_5$)$_2$(Me)[C(Me)=NBu^t] (5).—Excess t-butyl isocyanide (1.0 cm^3, 10 mmol) was added to Ti(η-C$_5$H$_5$)$_2$Me$_2$ (0.8 g, 3.85 mmol) in diethyl ether (50 cm^3) at −20 °C. After stirring for 3 h at room temperature, the solvent was removed under vacuum and the residue extracted into light petroleum (40 cm^3). The solution was filtered, concentrated to *ca.* 15 cm^3, and cooled at −20 °C to give the orange-brown crystalline product, m.p. 29—30 °C. Yield, 0.84 g, 75%. I.r.: 3 080w, 1 704s, 1 360s, 1 235w, 1 200s, 1 078m, 1 014s, 915w, 825s, 800vs, 755w, 735w cm^{-1}.

6. TaCl$_2$[C(Me)=NBu^t]$_3$(6).—t-Butyl isocyanide (2.0 cm^3, 20 mmol) was added to TaCl$_2$Me$_3$ (1.5 g, 5.0 mmol) in diethyl ether (50 cm^3) at −20 °C. After stirring for 5 h at room temperature, the solvent was removed under reduced pressure and the residue extracted into toluene (30 cm^3). The solution was filtered, concentrated to *ca.* 5 cm^3, and light petroleum diffused slowly onto the toluene solution to give orange crystals, m.p. 131—132 °C. Yield, 2.0 g, 80%. I.r.: 1 680m, 1 630s, 1 405, 1 365s, 1 346m, 1 298m, 1 240s, 1 230s, 1 220s, 1 200vs, 1 140m, 1 040w, 1 030m, 1 022m, 1 003w, 965w, 860m, 805w, 787w, 779w, 650m, 640m, 600w, 575m, 568m, 470s, 458m, 435m, 400w, 380w, 350w, 305vs, 265s, 242s, 230s, 225m, 218w, 209w cm^{-1}.

7. *Hexakis*(t-*butyl isocyanide*)*molybdenum*(0) (7) *and Methylhexakis*(t-*butyl isocyanide*)*molybdenum*(II) *Iodide*.—t-Butyl isocyanide (4.0 cm^3, 40 mmol) was added to a suspension of Mo$_2$(CO$_2$Me)$_4$ (2.0 g, 4.67 mmol) and sodium amalgam (1.0 g Na, in 100 g Hg) in thf (60 cm^3) and the solution stirred (24 h) at room temperature. The red solution was filtered and volatile materials removed under vacuum. The residue was extracted into light petroleum (50 cm^3) which was filtered, reduced to *ca.* 20 cm^3, and cooled at −20 °C to yield red-brown crystals which were collected and dried under vacuum at room temperature. Another batch was obtained from the supernatant on further evaporation and cooling, m.p. 125—126 °C. Yield, 1.3 g, 95%. I.r.: 2 170w, 2 127m, 2 100w, 1 955vs,br, 1 360s, 1 228s, 1 207s,br, 1 032w, 880m, 870m, 735m, 725s cm^{-1}.

The molybdenum(0) complex (0.33 g, 0.55 mmol) in diethyl ether (50 cm^3) was treated with methyl iodide (2.6 cm^3, 0.55 mmol) in diethyl ether (20 cm^3) and the mixture stirred for 2 h at room temperature. The red solid was collected, washed with light petroleum (2 × 20 cm^3) and diethyl ether (2 × 20 cm^3), and recrystallised from thf–diethyl ether (3 : 1) as red-brown *crystals*, m.p. 168—169 °C. Yield, 0.37 g, 90% [Found (calc.): C, 50.4 (50.5), H, 7.7 (7.7), N, 11.3 (11.4), I, 17.1 (17.3)%]. Conductivity (CH$_3$NO$_2$), 25 °C, 10^{-3} mol dm^{-3}: $\Lambda_M = 100\ \Omega^{-1}$ cm^2 mol^{-1}. I.r. (hexane): 2 090w, 1 970s, vbr, 1 885s, vbr cm^{-1}; in Nujol other bands at 1 380 m,1 362m, 1 228s, 1 208s, 1 034w, 900s, 872m, 740w, 725s, 665w cm^{-1}. ^{1}H N.m.r.: δ 1.40 (C*Me*$_3$), 1.59 p.p.m. (Mo-*Me*). ^{13}C-{^{1}H} N.m.r.: δ 163.99 (C≡NBu^t), 57.06 (*C*Me$_3$), 30.04 (C*Me*$_3$), 20.06 p.p.m. (Mo-*Me*).

8. cis-*Dihydrido-bis*(t-*butyl isocyanide*)-trans-*bis*(*trimethylphosphine*)*ruthenium*(II).—Excess t-butyl isocyanide (1.0 cm^3, 10 mmol) was added to RuMe$_2$(PMe$_3$)$_4$ (1.0 g, 2.30 mmol) in thf (50 cm^3) at −20 °C. After stirring for 5 h at room temperature, the solvent was removed under vacuum and the residue extracted into light petroleum (40 cm^3). The solution was filtered, concentrated to *ca.* 15 cm^3, and cooled at −20 °C to give white crystals, m.p. 164—165 °C. Yield, 0.67 g, 68%. I.r.: 2 100s, 1 990vs,br, 1 900m, 1 800m, 1 540m, 1 520s, 1 490s, 1 410m, 1 364s, 1 328m,

1 292w, 1 275m, 1 250w, 1 210s, 1 185m, 1 100w, 1 060w, 940s, 850w, 750w, 665m cm^{-1}. ^{31}P-{^{1}H} N.m.r.: broad singlet at δ −0.4 p.p.m.

9. *Methyltetrakis(t-butyl isocyanide)rhodium*(I).—Methyllithium (1.6 cm^3 of a 1.38 mol dm^{-3} solution in diethyl ether, 2.20 mmol) was added to a suspension of RhCl(CNBu^t)$_4$ (1.0 g, 2.12 mmol) in diethyl ether (50 cm^3) at −20 °C. After stirring 5 h at room temperature, the solvent was removed under vacuum, and the residue was extracted into light petroleum (35 cm^3). The solution was filtered, concentrated to *ca.* 20 cm^3, and cooled at −20 °C to give orange-yellow crystals, m.p. 98—100 °C (decomp.). Yield, 0.76 g, 80%. I.r.: 2 100s,br, 1 575w, 1 420w, 1 350m, 1 330w, 1 210s, 1 080m, 925m, 800w, 865w, 760w, 665w cm^{-1}.

TABLE 5

Atom co-ordinates ($\times 10^4$) for compound (1)

Atom	*x*	*y*	*z*
W	1 674(1)	1 975(0)	2 175(0)
N(1)	2 659(13)	2 717(11)	1 418(7)
N(2)	2 689(12)	195(10)	2 469(8)
N(3)	1 693(12)	2 957(9)	3 318(7)
C(1)	−369(17)	1 770(18)	1 173(12)
C(11)	3 160(20)	3 625(17)	793(12)
C(12)	2 648(32)	3 204(22)	−190(16)
C(13)	4 836(23)	3 674(30)	1 113(25)
C(14)	2 359(36)	5 006(20)	865(23)
C(21)	4 082(18)	−618(15)	2 174(14)
C(22)	4 312(28)	−2 015(19)	2 496(22)
C(23)	3 984(35)	−498(23)	1 074(13)
C(24)	5 542(22)	126(32)	2 665(26)
C(25)	2 016(18)	−354(15)	3 207(10)
C(26)	702(18)	−952(14)	2 947(15)
C(27)	50(25)	−1 316(19)	1 915(18)
C(28)	−88(21)	−1 429(19)	3 683(13)
C(29)	2 817(24)	−225(16)	4 214(13)
C(31)	2 608(19)	3 769(15)	4 030(9)
C(32)	4 391(20)	3 138(21)	4 098(14)
C(33)	2 436(27)	5 144(17)	3 825(17)
C(34)	2 146(31)	3 631(27)	4 902(15)
C(35)	44(14)	3 142(12)	2 938(9)
C(36)	−741(20)	4 408(16)	2 469(13)
C(37)	−1 008(18)	2 480(17)	3 418(12)

Crystallographic Studies.—Crystal data. Compound (1). $C_{21}H_{45}N_3W$, $M = 523.46$, Triclinic, $a = 8.829(2)$, $b = 10.265(1)$, $c = 14.324(5)$ Å, $\alpha = 90.87(2)$, $\beta = 101.47(2)$, $\gamma = 82.44(2)°$, $U = 1\,261.0$ Å^3, $Z = 2$, $D_c = 1.38$ g cm^{-3}, $F(000) = 532$, μ(Mo-K_α) = 43.84 cm^{-1}, space group $P\bar{1}$.

Compound (2). $C_{21}H_{48}Cl_3N_3W$, $M = 632.84$, Triclinic, $a = 11.178(2)$, $b = 12.730(2)$, $c = 12.155(2)$ Å, $\alpha = 84.21(2)$, $\beta = 111.31(2)$, $\gamma = 97.59(2)°$, $U = 1\,594.7$ Å^3, $Z = 2$, $D_c = 1.32$ g cm^{-3}, $F(000) = 600$, μ(Mo-K_α) = 36.27 cm^{-1}, space group $P\bar{1}$.

Data collection. The data were collected [37] using a CAD4 diffractometer and Mo-K_α radiation ($\lambda = 0.710\,69$ Å, graphite monochromator), θ—2θ scan mode.

Compound (1). $1.5 \leqslant \theta \leqslant 25°$, 4 525 data measured, 4 069 observed [$I > 1.5\sigma(I)$]. Absorption corrected.

Compound (2). $1.5 \leqslant \theta \leqslant 25°$, 5 769 data measured (at 269 K), 4 559 observed [$I > 1.5\sigma(I)$]. Crystal decay *ca.* 15%, corrected; not corrected for absorption. Crystal quality poor, with variable and generally large ω peak widths.

Structure solution and refinement. The heavy-atom method was used for both compounds and all non-hydrogen atoms were refined anisotropically. For compound (1) some of the methyl hydrogen atoms were located in difference syntheses but the remainder could not be found. Accordingly, all were included in the calculation of F_c with idealised positions defined by the SHELX [38] AFIX facility. Refinement for compound (2) was problematical. The non-hydrogen atoms of the complex anion were refined with anisotropic thermal parameters although some of the U_{ii} values adopted very large values (up to 0.38 Å^2). Two monoatomic ligands on the metal which had overall large thermal parameters were eventually treated as disordered [$\frac{1}{2}$ Cl + $\frac{1}{2}$ Me]. This resulted in the anion formulation $[\overline{\text{W–NH(Bu}^t\text{)CMe}_2}\text{(Me)(NBu}^t\text{)Cl}_3]^-$ and somewhat improved thermal parameters for the atoms in question.

TABLE 6

Atom co-ordinates ($\times 10^4$) for compound (2)

Atom	*x*	*y*	*z*
W	3 335(1)	1 923(1)	2 783(1)
Cl(1)	1 592(5)	1 150(4)	1 041(5)
Cl(2)	3 392(6)	37(4)	3 585(5)
Cl(3′)	4 662(12)	1 433(12)	1 724(14)
Cl(4′)	1 420(18)	2 008(16)	3 197(15)
C(3′)	4 285(40)	1 368(37)	1 642(43)
C(4′)	1 391(59)	1 893(39)	3 510(42)
N(1)	3 146(19)	3 046(21)	2 036(14)
C(1)	2 915(38)	4 121(19)	1 279(25)
C(11)	1 499(38)	4 009(32)	690(46)
C(12)	3 670(45)	5 098(20)	1 864(34)
C(13)	3 349(61)	4 014(36)	298(39)
N(2)	5 133(12)	2 087(10)	4 263(12)
C(21)	3 964(21)	1 737(18)	5 678(21)
C(22)	4 129(16)	2 420(15)	4 574(18)
C(23)	6 510(19)	2 717(17)	4 439(20)
C(24)	7 094(21)	3 006(18)	5 750(20)
C(25)	7 265(21)	1 883(20)	4 205(23)
C(26)	6 395(21)	3 665(19)	3 539(24)
C(27)	4 132(19)	3 602(15)	4 747(20)
C(10S)	7 649(*)	−177(81)	1 546(91)
C(11S)	361(46)	1 342(38)	−2 479(41)
N(10S)	8 290(32)	774(27)	896(31)
C(20S)	7 953(30)	1 702(25)	187(28)
C(21S)	8 095(39)	1 901(32)	−868(36)
C(22S)	8 032(32)	2 565(26)	932(30)
C(23S)	3 610(45)	−1 290(37)	552(41)
C(100)	1 370(29)	−179(24)	−1 596(27)
C(200)	931(46)	671(39)	−2 348(43)
C(300)	778(53)	370(44)	−3 563(49)
C(1A)	445(28)	4 269(23)	4 943(27)
C(2A)	369(40)	4 851(33)	6 303(36)

* Primed atoms correspond to the disordered Cl, Me groups, Cl(3′) + C(3′) ≡ X(1), Cl(4′) + C(4′) ≡ X(2). Atoms from C(10S) onwards correspond to peaks thought to belong to the disordered cation and possible solvent molecules.

The atoms assumed to form the cation could only be refined with isotropic thermal parameters and even then it was not possible to identify the nature of this fragment unequivocally. In addition, some solvent may be present since a third fragment was found in difference syntheses. These problems are almost certainly associated with disorder and/or the crystal decomposition which occurred during data collection, and which probably explain also the poor crystal quality. The cation and solvent fragments were thus represented by partial, isotropic atoms, where the occupancy factors were assigned on the basis of peak heights in the difference syntheses.

The final $R(= \Sigma|F_o - F_c|/\Sigma|F_o|)$ and R' [$= \Sigma(|F_o - F_c|w^2)/\Sigma(F_o \cdot w^2)$] values were 0.057, 0.059 and 0.077, 0.077 for compounds (1) and (2) respectively. All computations were carried out on the ICL 2980 at Queen Mary College using programs listed in ref. 38, which also gives the source of the scattering-factor data used. The final non-hydrogen atom co-ordinates are given in Tables 5 and 6. Anisotropic thermal parameters, complete lists of bond lengths and angles, and Tables of observed and calculated structure factors have been deposited as Supplementary Publication No. SUP 23116 (40 pp.).*

We thank the S.R.C. for support of this work.

[1/292 *Received, 20th February*, 1981]

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

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