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Synthesis and reactivity of $[MCl_2(CNBu^t)_3(PMe_3)_2]$ (M = Mo or W): preparation of $[MCl(CNBu^t)_4(PMe_3)_2]Cl$ and $[M(SnCl_3)(CNBu^t)_3(PMe_3)_3](SnCl_3)$ derivatives. The crystal structure of $[MoCl(CNBu^t)_4(PMe_3)_2]Cl \cdot 2Me_2CO$

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Abstract

The reaction of the sixteen-electron paramagnetic complex $[MCl_2(PMe_3)_4]$ (M = Mo or W) with $CNBu^t$ gives the eighteen-electron diamagnetic seven-coordinate complex $[MoCl_2(CNBu^t)_3(PMe_3)_2]$ (**1**) or $[WCl_2(CNBu^t)_3(PMe_3)_2]$ (**2**). These complexes react with additional $CNBu^t$ to give the complexes $[MCl(CNBu^t)_4(PMe_3)_2]Cl$ (M = Mo (**3**) or W (**4**)). An X-ray diffraction study of **3** shows it to have a capped trigonal prismatic structure in the solid state. The reaction of $[MCl_2(CNBu^t)_3(PMe_3)_2]$ with anhydrous $SnCl_2$ yields the complexes $[M(SnCl_3)(CNBu^t)_3(PMe_3)_3](SnCl_3)$ (M = Mo (**5**) or W (**6**)), which have been studied by ^{119}Sn NMR spectroscopy. A new route to the complex *trans*-$[MoCl_2(PMe_3)_4]$ from $MoCl_5$ has also been developed.

Introduction

One of the most extensively studied groups of seven-coordinate complexes include those of molybdenum(II) and tungsten(II) with isocyanide ligands [1,2]. Although group 6 halocarbonyl-phosphine complexes have been prepared by several procedures [3,4], no stoichiometric analogues with the CO-isoelectronic isocyanide

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ligand have been reported. Since the chemical reactivity of the coordinated isocyanides is of great interest from both synthetic and catalytic viewpoints [5,6], we have prepared seven-coordinate $[MCl_2(CNBu^t)_3(PMe_3)_2]$ (M = Mo or W) as a part of our studies on the reactivity of sixteen-electron six-coordinate molybdenum and tungsten complexes.

The complexes $[MCl_2(CNBu^t)_3(PMe_3)_2]$ exhibit an interesting chemistry, which has allowed us to isolate other seven-coordinate trimethylphosphine compounds, and also new complexes containing the trichlorostannate ligand by insertion of anhydrous $SnCl_2$ into the metal–halide bond. This reaction has a precedent in the chemistry of molybdenum(II) [7], the trichlorostannate ligand having an important influence on the reactivity of the "ML_6" fragment of the complex, as has been reported [8].

Together with the synthesis and characterisation of this range of new seven-coordinate derivatives, we report here relevant spectroscopic properties and a new, more straight-forward, route to the six-coordinate paramagnetic compound *trans*-$[MoCl_2(PMe_3)_4]$.

Results and discussion

It has been reported that the reaction between the sixteen-electron paramagnetic complexes $[MCl_2(PMe_3)_4]$ (M = Mo or W) and CO in boiling THF (tetrahydrofuran) yields the seven-coordinate diagmagnetic derivatives $[MCl_2(CO)_2(PMe_3)_3]$, whose structure has been assigned on the basis of spectroscopic data [3].

The reaction of $[MCl_2(PMe_3)_4]$ with three equivalents of $CNBu^t$ yields the seven-coordinate complexes $[MCl_2(CNBu^t)_3(PMe_3)_2]$ as yellow microcrystalline solids. With other isocyanides CNR (R = benzyl or cyclohexyl), oily isocyanide-containing substances are obtained. The complex $[MoCl_2(CNBu^t)_3(PMe_3)_2]$ (**1**) can be easily prepared at room temperature. However, the preparation of the tungsten analogue **2** requires reflux temperature.

The complexes $[MCl_2(CNBu^t)_3(PMe_3)_2]$ are diagmagnetic, and soluble in THF, acetone and chlorinated solvents. They are quite air stable in the solid state, but are readily oxidised in solution.

The IR spectra of both **1** and **2** are dominated by the strong C≡N stretching band, and also the bands due to the phosphine ligand, together with weak absorptions at 300 cm^{-1} for **1** and 285 cm^{-1} for **2**, assignable to metal–halide vibrations. The visible spectra of these compounds show strong charge-transfer bands near 300 nm, which probably hide *d–d* transitions and are responsible for the intense yellow colour of the complexes.

The ^1H NMR spectra of the complexes are quite simple, consisting of a singlet for the isocyanide protons (27H), and a triplet for the trimethylphosphine protons (18H). The presence of a triplet in the spectrum is due to virtual coupling between the phosphine groups (Table 1), and so the coupling constants are better formulated as $(^2J(PH) + {}^4J(PH))/2$. However, $^{31}P\{^1H\}$ NMR spectra give more structural information. For **1**, an AB pattern is observed, suggesting that the phosphorus atoms are non-equivalent. The value for $^2J(PP)$ also suggests a *trans*- or transoid-arrangement for the phosphine ligands, as for *trans*-molybdenum phosphine complexes [9]. In the $^{13}C\{^1H\}$ NMR spectrum, the presence of two triplets confirms the non-equivalent phosphine configuration, and they are again due to virtual coupling

Table 1

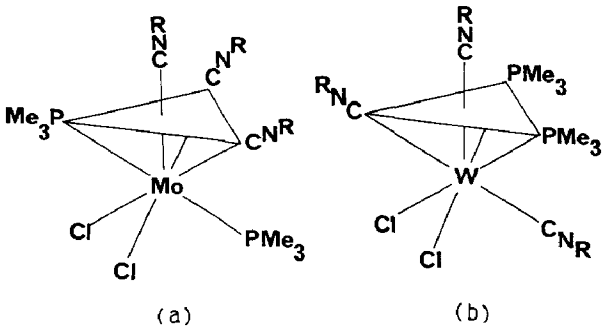
IR and NMR data for the complexes to **1** to **4** [a]

Compound	ν(C≡N) (cm^{-1})	^{31}P{^{1}H} [b]	^{1}H		^{13}C{^{1}H}	
		PMe$_3$	PMe$_3$	CNBu^t	PMe$_3$	CNBu^t
1	2115, 2083, *2002*	−53.50 d −57.43 d ^2J(PP) 105 Hz	1.564 t, 18H J(PH) 4.6 Hz	1.542 s, 27H	14.91 t J(PC) 13 Hz 16.38 t J(PC) 14 Hz	31.06 s 58.22 s 174.23 m
2	2111, 2071, *1989*	−166.8 s ^1J(PW) 172 Hz	1.630 t, 18H J(PH) 4.12 Hz	1.535 s, 27H	15.59 t J(PC) 15.3 Hz	31.23 s 58.20 s
3	*2106*, 2050, 2000	−143.9 s br	1.410 t, 18H J(PH) 4.65 Hz	1.380 s, 36H	15.79 t J(PC) 14 Hz	30.54 s 57.71 s 173.66 m
4	2140, *2110*, 2050	−117.5 s ^1J(PW) 159.7 Hz	1.620 t, 18H J(PH) 4.19 Hz	1.450 s, 36H	15.72 t J(PC) 16.2 Hz	30.66 s 58.90 s 153.60 m

[a] IR in CsI disk or Nujol mull. The values in italics correspond to the strongest ν(C≡N) band. NMR in CDCl$_3$ solution. Abbreviations used: d, doublet; br, broad; t, triplet; s, singlet; m, multiplet. [b] External reference P(OMe)$_3$.

effects between the phosphine groups. Other signals in the spectrum arise from the isocyanide carbon atoms. The isocyanide carbons directly attached to the metal have a very long relaxation time, and appear as a weak broad signal. The spectroscopic data for **1** are consistent with a capped octahedral structure, with the phosphines mutually *trans*-, as found for the analogue carbonyl complex [MoCl$_2$(CO)$_3$(PEt$_3$)$_2$] [10] (Fig. 1a), although stereochemical non-rigidity in solution, common in the chemistry of seven-coordinate derivatives [11], would make the isocyanide groups equivalent. (Only one isocyanide signal is observed in the NMR spectra).

The ^{31}P{^{1}H} NMR spectrum of the tungsten complex **2** exhibits differences, and consists of a singlet with two satellites due to coupling with the ^{183}W nucleus. This suggests the presence of two equivalent phosphine ligands, possibly in a *cis*- or cisoid disposition, if a capped octahedral structure is assumed, as in the molybdenum complex. The ^{13}C{^{1}H} NMR spectrum shows a unique triplet for two virtually



(a) (b)

Fig. 1. Proposed structures for the complexes (a) [MoCl$_2$(CNBu^t)$_3$(PMe$_3$)$_2$] and (b) [WCl$_2$(CNBu^t)$_3$(PMe$_3$)$_2$].

coupled phosphines, together with signals for the isocyanide carbon atoms. In this case, the signal from the isocyanide carbon directly attached to the metal does not appear in the spectrum, because the relaxation time is even longer than that for the molybdenum complex. The structure of this product, as indicated by the spectroscopic data, could be similar to that found for $[WI_2(CO)_3(dmpe)]$ [12], consistent with a capped octahedron with *cis*-phosphines and *cis*-chlorides (Fig. 1b), but there would again be no stereochemical rigidity for the isocyanides in solution.

The complexes $[MCl_2(CNBu^t)_3(PMe_3)_2]$ are reactive in spite of their 18-electron configurations. Although they do not react with CO under pressure, the reaction with additional isocyanide yields the ionic derivatives $[MCl(CNBu^t)_4(PMe_3)_2]Cl$ as yellow microcrystalline solids. Derivatives of composition $[MX(CNR)_6]X$ have been extensively studied by Lippard and co-workers [13], and recently, other workers have also prepared $[MCl(CNR)_4(PMe_3)_2]Cl$ derivatives [14].

The complexes **3** and **4** have IR spectra similar to those for **1** and **2**, although $\nu(C{\equiv}N)$ for the isocyanide ligands is shifted to higher frequencies for the ionic compounds, showing a lower degree of back-donation in the bonding as result of the fall in the electron density on the metal.

Complexes **3** and **4** show similar patterns in their respective ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ spectra (Table 1). For these complexes we assumed a capped trigonal prismatic structure, as described for the complexes $[MX(CNR)_6]X$ [13]. A *cis*-disposition of the phosphine ligands, with four isocyanides in equivalent positions and the chloride in the capping position was proposed for the complexes $[MCl(CNBu^t)_4(PMe_3)_2]Cl$ on the basis of spectroscopic data. However, an X-ray diffraction study of complex **3** (see below) revealed a *trans*-arrangement for the phosphines and two non-equivalent sets of isocyanides, despite the NMR spectrum showing all the isocyanides to be equivalent. This means that **3**, and presumably also **4** are stereochemically non-rigid in solution, as suggested for **1** and **2**.

The complexes $[MCl_2(CNBu^t)_3(PMe_3)_2]$ react with an excess of anhydrous tin(II) chloride in dichloromethane to give the orange $[M(SnCl_3)(CNBu^t)_3(PMe_3)_3](SnCl_3)$ (M = Mo (**5**) or W (**6**)), together with greyish uncharacterised materials. The latter do not contain isocyanide (no $\nu(C{\equiv}N)$ band in the IR spectra), but do contain PMe_3. They also show a band at ca. 1600 cm^{-1} in the IR spectra which has not been assigned.

The IR spectra of the complexes **5** and **6** are essentially the same as those for the starting materials in the range 4000–600 cm^{-1}, with $\nu(C{\equiv}N)$ values of 2079 cm^{-1} for **5** and 2106 cm^{-1} for **6**. However in the far IR region there are bands due to $SnCl_3^-$. Two bands in the same positions for each of **5** and **6** (296 and 255 cm^{-1}) are coincident with those reported for uncoordinated $SnCl_3^-$ [15]. Other medium and strong bands (Table 2) in different positions for **5** and **6** are assigned to coordinated $SnCl_3^-$.

The ^1H NMR spectra for these complexes consist of a singlet for the isocyanide protons and a doublet for trimethylphosphine, in the intensity ratio 1/1 (27H each). $^{31}P\{^1H\}$ NMR spectrum in each case consists of one broad signal, too broad to show coupling with $^{119}Sn/^{117}Sn$ and ^{183}W.

Interest in metal–metal bonding between dissimilar species and the use of tin(II) halides in catalytic olefin activation by platinum metal halide complexes has prompted studies of the tin NMR spectra of transition metal–tin systems [16], and this technique has proved to be very helpful in the study of our complexes.

Table 2

IR and NMR data for the complexes $[M(SnCl_3)(CNBu^t)_3(PMe_3)_3](SnCl_3)$ [a]

Compound	IR and far IR (cm^{-1})			^1H		$^{31}P\{^1H\}$ [b]	^{119}Sn [c]	
	$\nu(C\equiv N)$	$SnCl_3^-$		PMe_3	$CNBu^t$	PMe_3	$SnCl_3^-$	
		coord.	uncoord.				uncoord.	coord.
5	2106	528, 456 348, 319	296, 257	1.795 d, 27H $^2J(PH)$ 8.61 Hz	1.624 s, 27H	−170.27 s br $\Delta\nu_{1/2}$ 208 Hz	−71.8 s	−136.8 q $^2J(SnP)$ 224 Hz
6	2079	529, 511 461, 348	296, 255	1.655 d, 27H $^2J(PH)$ 8.24 Hz	1.590 s, 27H	−137.44 s br $\Delta\nu_{1/2}$ 266 Hz	−65.3 s	83.1 q $^2J(SnP)$ 260 Hz

[a] IR in CsI disk. NMR in $CDCl_3$ solution. Abbreviations used: d, doublet; s, singlet; br, broad; q, quartet; $\Delta\nu_{1/2}$, half-height width. [b] External reference $P(OMe)_3$. [c] External reference $SnMe_4$.

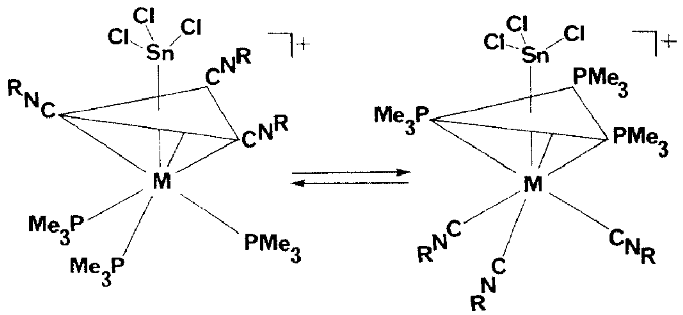


Fig. 2. The two possible isomers for the $[M(SnCl_3)(CNBu^t)_3(PMe_3)_3]^+$ cations (M = Mo or W).

The same pattern is observed for both **5** and **6** in their ^{119}Sn NMR spectra: one quartet and one singlet. The quartet is due to coupling of coordinated $SnCl_3^-$ with three phosphorus atoms, and appears at different chemical shifts for **5** and **6**, as expected, following the general trend previously observed for a series of trimethyltin derivatives $[M(SnMe_3)(\eta^5\text{-}C_5H_5)(CO)_3]$ (M = Cr, Mo or W) [17]. The shielding of the coordinated tin nucleus increases in the sequence (M =) Cr < Mo < W. This effect is dominant with third row transition metals (the "heavy atom effect") [16].

The singlet in the ^{119}Sn NMR spectra of the $[M(SnCl_3)(CNBu^t)_3(PMe_3)_3](SnCl_3)$ derivatives appears at essentially the same chemical shift for **5** and **6**, suggesting that the other $SnCl_3^-$ is free and does not interact with the $[M(SnCl_3)(CNBu^t)_3(PMe_3)_3]^+$ moieties.

These data favour capped octahedral structures for both **5** and **6**, with $SnCl_3^-$ acting as a capping ligand, and with a *fac*-arrangement of isocyanides and phosphines. There are two possible isomers which are not distinguishable from available data, but the broadness of the signals in the $^{31}P\{^1H\}$ NMR spectra suggests that there may be interchange between the two isomers in solution (Fig. 2).

The structure of $[MoCl(CNBu^t)_4(PMe_3)_2]Cl \cdot 2Me_2CO$ *(3)*

The crystal is composed of a lattice of Mo complex cations and chloride anions. There also are large regions which in the freshly recrystallized material contain acetone (solvent) molecules. There are two distinct solvent sites each occupied by an acetone molecule, but the solvent molecules do not appear to have any well-defined positions or orientations. Atomic coordinates are listed in Table 3, and selected bond lengths and angles in Table 4.

The molybdenum complex cation $[MoCl(CNBu^t)_4(PMe_3)_2]^+$ has seven-fold coordination in a capped trigonal prismatic pattern (Fig. 3). The chloro ligand is the capping atom, on the rectangular face formed by two *trans*-isocyanide and two *trans*-phosphine ligands. The opposite edge of the prism has the two remaining isocyanides at its ends. The cation has an almost perfect two-fold symmetry axis along the Mo–Cl bond. As is quite common for related $Mo(CNBu^t)_n$ complexes, there are two possible orientations for each of the t-butyl groups, although for clarity only one is shown in Fig. 3 [13,18].

The Mo–Cl(7) distance of 2.533(5) Å is longer than the Mo–Cl single bond length of 2.45 Å computed from Slater's atomic radii [19], while the Mo–C distances are shorter than the 2.15 Å value predicted by these radii, suggesting that the Mo–C bond orders are greater than 1. These Mo–C distances are in the same range found

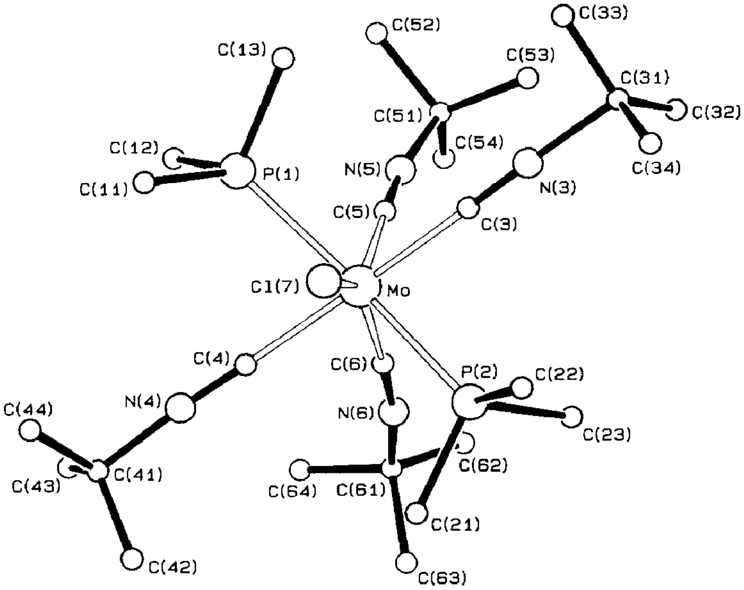


Fig. 3. View of the cation $[MoCl(CNBu^t)_4(PMe_3)_2]^+$, with the atom labelling scheme; the major orientation of each of the disordered t-butyl groups is shown.

for capped trigonal prismatic complexes $[MoX(CNBu^t)_6]X$ (X = Br, I) [13,18]. The difference in the Mo–C distances for the isocyanide groups have been previously noted, and are mainly attributable to the coordination pattern and proximity of neighbouring ligands in the crystal; a single resonance is observed in the ^1H NMR spectrum for the isocyanide ligands in solution, suggesting the rapid transposition of these ligands in solution. The dimensions of the isocyanide ligands are normal; the C≡N bond lengths, in the range from 1.14(2) to 1.18(2) Å, agree well with those in the above-mentioned $[MoX(CNBu^t)_6]X$ derivatives, and also in $[Co(CNMe)_5](ClO_4)_2$ (1.15 Å) [20].

The mean distance Mo–P value of 2.513(2) Å is close to those reported for other trimethylphosphinemolybdenum(II) complexes, such as *trans*-$[MoCl_2(PMe_3)_4]$ [23] (2.496(6) Å), although slightly longer because of the change in the coordination number from six to seven.

Experimental

All operations were carried out under dry nitrogen or argon by Schlenk techniques. The solvents were dried over Na/benzophenone, freshly distilled and deoxygenated immediately before use. Microanalyses were by Butterworth Laboratories Ltd., Pascher Mikroanalitisches and Mr. Colin Macdonald at the Nitrogen Fixation Laboratory, University of Sussex. Infrared spectra were recorded on a Perkin–Elmer 883. Visible spectra were recorded on a Perkin–Elmer Lambda-5 UV-vis spectrophotometer. NMR were recorded on a JEOL GSX-270 spectrometer, with $SiMe_4$ (^1H and ^{13}C), $P(OMe)_3$ (^{31}P) or $SnMe_4$ (^{119}Sn) as reference.

The ligands trimethylphosphine [21] and t-butylisocyanide [22] were prepared by published methods. The complexes $[MCl_2(PMe_3)_4]$ (M = Mo or W) were obtained by published methods [23,24], but a new route for the synthesis of *trans*-

Table 3

Final atomic coordinates (fractional $\times 10^4$) for $[MoCl(CNBu^t)_4(PMe_3)_2]Cl \cdot 2Me_2CO$. E.s.d.'s are in parentheses

Atom	*x*	*y*	*z*	S.o.f. [a]
Mo	4966(1)	2500	2369.3(8)	
P(1)	6825(4)	2659(3)	4038(3)	
C(11)	7730(19)	3453(13)	3985(19)	
C(12)	7936(20)	1983(13)	4174(20)	
C(13)	6483(16)	2742(10)	5592(14)	
P(2)	3114(4)	2779(3)	743(3)	
C(21)	3446(18)	3016(13)	−754(17)	
C(22)	2189(20)	3546(13)	991(19)	
C(23)	1987(22)	2077(15)	430(21)	
C(3)	3704(11)	2594(10)	3434(10)	
N(3)	3020(10)	2621(8)	4033(10)	
C(31)	1983(46)	2664(25)	4905(43)	0.6
C(32)	1454(50)	1946(25)	4671(53)	0.6
C(33)	2887(29)	2777(17)	6074(26)	0.6
C(34)	1229(39)	3244(24)	4319(38)	0.6
C(4)	6200(12)	2693(7)	1343(10)	
N(4)	6914(11)	2788(7)	776(11)	
C(41)	7797(24)	2915(14)	−52(27)	0.6
C(42)	7039(27)	3131(20)	−1262(24)	0.6
C(43)	8434(41)	2236(18)	−56(41)	0.6
C(44)	8583(32)	3490(19)	588(31)	0.6
C(5)	5162(15)	1577(10)	3323(14)	
N(5)	5255(15)	1045(10)	3838(14)	
C(51)	5101(20)	442(13)	4578(19)	
C(52)	6151(30)	430(26)	5687(34)	0.6
C(53)	4002(30)	543(27)	5035(41)	0.6
C(54)	5172(48)	−219(23)	3875(42)	0.6
C(6)	4757(16)	1683(10)	1215(15)	
N(6)	4663(14)	1213(10)	497(14)	
C(61)	4760(17)	623(11)	−338(16)	
C(62)	4102(37)	−27(20)	−80(42)	0.6
C(63)	4227(40)	882(25)	−1629(29)	0.6
C(64)	6019(26)	454(28)	−344(44)	0.6
C(31)x	2251(21)	2696(10)	4834(18)	0.4
C(32)x	975(26)	2712(22)	4107(30)	0.4
C(33)x	2546(41)	3366(18)	5603(38)	0.4
C(34)x	2459(51)	2096(22)	5812(44)	0.4
C(41)x	7719(53)	2842(25)	−236(53)	0.4
C(42)x	8901(35)	2817(24)	640(33)	0.4
C(43)x	7508(41)	2228(23)	−1076(39)	0.4
C(44)x	7408(54)	3534(26)	−881(50)	0.4
C(52)x	4032(49)	106(42)	3704(56)	0.4
C(53)x	4625(64)	659(45)	5660(52)	0.4
C(54)x	6133(46)	−50(37)	4860(66)	0.4
C(62)x	5667(33)	790(25)	−1067(36)	0.4
C(63)x	3538(29)	541(34)	−1191(42)	0.4
C(64)x	5089(52)	−20(23)	421(43)	0.4
Cl(7)	4963(4)	3847(2)	2578(4)	
Cl(8)	−49(5)	2889(5)	7330(4)	

Table 3 (continued)

Atom	*x*	*y*	*z*	S.o.f. [a]
Solvent molecules				
C(90)	203(84)	5288(138)	2688(87)	0.5
C(91)	1066(67)	5499(53)	2189(90)	0.5
C(92)	−837(84)	5498(151)	1974(122)	0.5
C(93)	210(140)	5443(121)	3856(83)	0.5
C(90)x	91(187)	5743(60)	2547(129)	0.5
C(91)x	279(100)	5437(51)	1561(78)	0.5
C(92)x	103(77)	6446(56)	2523(69)	0.5
C(93)x	−735(151)	5448(70)	3126(123)	0.5
C(95)	489(83)	5163(83)	7096(181)	0.5
C(96)	−587(76)	4886(57)	6570(93)	0.5
C(97)	1375(63)	4692(43)	7317(67)	0.5
C(98)	331(127)	5660(69)	7948(173)	0.5
C(95)x	−258(75)	5375(56)	7819(81)	0.5
C(96)x	752(98)	5005(130)	7855(190)	0.5
C(97)x	−1245(82)	5044(58)	7368(88)	0.5
C(98)x	−309(84)	5528(61)	8957(74)	0.5

[a] Site occupancy factor, if different from 1.0.

$[MoCl_2(PMe_3)_4]$, analogous to that reported by Richards [25] for the complex $[MoCl_2(PMe_2Ph)_4]$, was developed.

trans-Dichlorotetrakis(trimethylphosphine)molybdenum(II)

Neat PMe_3 (5 cm^3, 50 mmol) was added to $MoCl_5$ (2.7 g, ca. 10 mmol) in THF under argon. Magnesium turnings (5g), activated by being kept at 120 ° C for 48 h, were then added. After 12–18 h stirring under argon residual magnesium was removed by filtration. The dark brown solution was taken to dryness, and the residue extracted with diethyl ether or THF. The extract was filtered, centrifuged, concentrated, and cooled to -20 ° C, to give orange crystals of $[MoCl_2(PMe_3)_4]$ in ca. 60% yield. The product was identified by its IR and ^{1}H NMR spectra.

If the reaction is performed under N_2, a mixture of dinitrogen complexes is obtained as co-product, complicating the separation and purification of the desired complex.

Dichlorotris(t-butylisocyanide)bis(trimethylphosphine)molybdenum(II) (1)

To a solution of 0.48 g (1 mmol) of $[MoCl_2(PMe_3)_4]$ in 30 cm^3 of THF was added $CNBu^t$ (0.34 cm^3, 3 mmol). The reaction mixture was stirred overnight at room temperature and the yellow precipitate then filtered off, washed with THF and Et_2O, and dried in vacuo. The complex can be recrystallised from petroleum ether/dichloromethane, THF/dichloromethane, or acetone. Yield: 65%.

Analysis: Found: C, 43.8; H, 7.95; N, 6.4; P, 10.8. $C_{21}H_{45}Cl_2MoN_3P_2$ calcd.: C, 44.3; H, 7.92; N, 7.3; P 10.9%.

Dichlorotris(t-butylisocyanide)bis(trimethylphosphine)tungsten(II) (2)

To a stirred solution of $[WCl_2(PMe_3)_4]$ (0.46 g, 0.83 mmol) in THF was added $CNBu^t$ (0.28 cm^3, 2.47 mmol). The mixture was heated under reflux for 5 h, and then stirred at room temperature for a further 12 h. The yellow solid was isolated as

Table 4

Selected molecular dimensions in the $[\mathrm{MoCl(CNBu^t)_4(PMe_3)_2}]^+$ cation. Bond lengths are in Å, angles in degrees. E.s.d.'s are in parentheses

(a) About the Mo atom			
Mo–P(1)	2.511(4)	Mo–C(5)	2.016(18)
Mo–P(2)	2.516(4)	Mo–C(6)	1.980(18)
Mo–C(3)	2.099(12)	Mo–Cl(7)	2.533(5)
Mo–C(4)	2.065(13)		
P(1)–Mo–P(2)	161.2(2)	P(2)–Mo–C(6)	74.7(5)
P(1)–Mo–C(3)	98.9(3)	C(3)–Mo–C(6)	116.2(7)
P(2)–Mo–C(3)	78.9(3)	C(4)–Mo–C(6)	76.4(6)
P(1)–Mo–C(4)	79.1(3)	C(5)–Mo–C(6)	70.4(7)
P(2)–Mo–C(4)	98.2(3)	P(1)–Mo–Cl(7)	80.4(2)
C(3)–Mo–C(4)	165.1(6)	P(2)–Mo–Cl(7)	80.8(2)
P(1)–Mo–C(5)	74.8(5)	C(3)–Mo–Cl(7)	81.3(5)
P(2)–Mo–C(5)	122.1(5)	C(4)–Mo–Cl(7)	83.9(4)
C(3)–Mo–C(5)	77.1(7)	C(5)–Mo–Cl(7)	143.8(5)
C(4)–Mo–C(5)	116.1(6)	C(6)–Mo–Cl(7)	145.8(5)
P(1)–Mo–C(6)	121.9(5)		
(b) Bond lengths in the ligands			
P(1)–C(11)	1.828(24)	P(2)–C(21)	1.860(20)
P(1)–C(12)	1.785(24)	P(2)–C(22)	1.850(24)
P(1)–C(13)	1.880(16)	P(2)–C(23)	1.825(27)
C(3)–N(3)	1.153(14)	C(4)–N(4)	1.168(16)
N(3)–C(31)	1.72(5)	N(4)–C(41)	1.55(4)
N(3)–C(31)x	1.412(29)	N(4)–C(41)x	1.63(8)
C(5)–N(5)	1.144(21)	C(6)–N(6)	1.180(20)
N(5)–C(51)	1.436(25)	N(6)–C(61)	1.468(23)
(c) Bond angles in the ligands			
Mo–P(1)–C(11)	117.9(7)	Mo–P(2)–C(21)	112.4(7)
Mo–P(1)–C(12)	116.9(8)	Mo–P(2)–C(22)	118.4(7)
C(11)–P(1)–C(12)	100.0(11)	C(21)–P(2)–C(22)	101.5(10)
Mo–P(1)–C(13)	111.6(6)	Mo–P(2)–C(23)	115.9(8)
C(11)–P(1)–C(13)	102.2(9)	C(21)–P(2)–C(23)	106.8(10)
C(12)–P(1)–C(13)	106.5(9)	C(22)–P(2)–C(23)	100.1(11)
Mo–C(3)–N(3)	177.6(16)	Mo–C(4)–N(4)	178.3(12)
C(3)–N(3)–C(31)	179.1(19)	C(4)–N(4)–C(41)	176.3(15)
C(3)–N(3)–C(31)x	175.0(16)	C(4)–N(4)–C(41)x	168.6(19)
Mo–C(5)–N(5)	178.2(16)	Mo–C(6)–N(6)	176.9(15)
C(5)–N(5)–C(51)	165.1(21)	C(6)–N(6)–C(61)	170.5(19)

above and recrystallised by slow evaporation of a THF/dichloromethane solution. Yield: 60%.

Analysis: Found: C, 38.4; H, 7.20; N, 6.3; P, 9.2. $\mathrm{C_{21}H_{45}Cl_2N_3P_2W}$ calcd.: C, 38.4; H, 6.90; N, 6.4; P, 9.4%.

Chlorotetrakis(t-butylisocyanide)bis(trimethylphosphine)molybdenum(II) chloride (3)

A THF slurry of **1** (0.57 g, 1 mmol) was treated with $\mathrm{CNBu^t}$ (0.12 $\mathrm{cm^3}$, ca. 1 mmol). The mixture was stirred overnight at room temperature, the solvent then removed in vacuo, and the yellow residue was washed with THF and Et_2O and dried in vacuo. It was recrystallised as for **1**. Yield: 70%.

Analysis: Found: C, 48.0; H, 8.33; N, 7.5; P, 9.5. $C_{26}H_{54}Cl_2MoN_4P_2$ calcd.: C, 47.9; H, 8.30; N, 8.6; P, 9.5%.

Chlorotetrakis(t-butylisocyanide)bis(trimethylphosphine)tungsten(II) chloride (4)

To a stirred suspension of **2** (0.66 g, 1 mmol) in THF was added $CNBu^t$ (0.12 cm^3, ca. 1 mmol). The mixture was heated under reflux for 5 h and then stirred at room temperature for a further 8 h. The solvent was removed in vacuo and the yellow solid washed with several portions of THF and Et_2O, and dried in vacuo. Recrystallisation was carried out as for **2**. Yield: 63%.

Analysis: Found: C, 42.3; H, 7.28; N, 7.5; P, 8.4. $C_{26}H_{54}Cl_2N_4P_2W$ calcd.: C, 42.2; H, 7.31; N, 7.5; P, 8.4%.

Trichlorostannyltris(t-butylisocyanide)tris(trimethylphosphine)molybdenum(II) trichlorostannate (5)

To a stirred solution of **1** (0.57 g, 1 mmol) in 40 cm^3 of dichloromethane was added anhydrous $SnCl_2$ (0.57 g, 3 mmol). The mixture slowly turned dark, and was stirred for 15 h. A greyish solid was removed by filtration. The filtrate was centrifuged and the solvent removed in vacuo to leave a brown-orange residue, which was washed with petroleum ether and dried in vacuo. This product was recrystallised from acetone. Yield: 35%.

Analysis: Found: C, 28.3; H, 5.45; N, 4.1. $C_{24}H_{54}Cl_6MoN_3P_3Sn_2$ calcd.: C, 28.2; H, 5.57; N, 4.1%.

Trichlorostannyltris(t-butylisocyanide)tris(trimethylphosphine)tungsten(II) trichlorostannate (6)

This was obtained and recrystallised as for **5**, starting from 0.66 g, 1 mmol of **2** in 40 cm^3 of dichloromethane, and 0.57 g of anhydrous $SnCl_2$. Yield: 45%.

Analysis: Found: C, 26.0; H, 4.90; N, 3.7. $C_{24}H_{54}Cl_6N_3P_3Sn_2W$ calcd.: C, 25.9; H, 4.86; N, 3.7%.

Crystal structure analysis of $[MoCl(CNBu^t)_4(PMe_3)_2]Cl \cdot 2CH_3CO$

Crystal data: $(C_{26}H_{54}ClMoN_4P_2)^+Cl^- \cdot 2C_3H_6O$, $M = 767.7$. Monoclinic, space group $P2_1$ (No. 4), a 11.563(1), b 18.722(2), c 11.202(2) Å, β 103.67(1)°, V 2356.2 $Å^3$, $Z = 2$, D_c 1.082 g cm^{-3}, $F(000) = 816$, μ(Mo-K_α) 4.8 cm^{-1}, λ(Mo-$K_{\bar{\alpha}}$) 0.71069 Å.

Single crystals suitable for the X-ray structure analysis were obtained as large yellow-orange plates by recrystallisation from acetone at −20 °C. These crystals crumble when they are dried in vacuo, losing the solvent of crystallisation.

The large clear plates were cut to a suitable size and mounted and sealed in capillaries. After photographic examination, one crystal (ca. 0.26 × 0.36 × 0.64 mm) was transferred to the Enraf–Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell parameters (from the centering of 25 reflections, with θ 12–14°, each in four orientations) and measurement of diffraction intensities (to θ_{max} 20°). Corrections were applied for Lorentz-polarisation effects, slight deterioration and absorption (from the crystal shape and size). 2229 unique reflections were used in the SHELX program system [26]. Structure determination was by the heavy atom method; the anion and major features of the cation were readily found, but for each of the t-butyl groups disorder between two orientations was apparent, and in two solvent regions acetone molecules were found to be disordered with no distinct arrangements. In the course of refinement by full-matrix least-squares methods, the t-butyl groups were refined in each orientation with geometrical restraints; similar restraints were applied to two part-molecules of acetone in each region, but the thermal parameters of these atoms indicate that these molecules are poorly resolved.

Anisotropic thermal parameters were allowed only for the Mo, Cl and P atoms; the others were refined isotropically. No hydogen atoms were located or included in the analysis. Refinement was terminated with $R = 0.069$ and $R_w = 0.066$ [26] for 2062 reflections having $I \geqslant 2\sigma(I)$ (and weighted $w = \sigma_F^{-2}$. The major peaks (max. 0.9 eÅ^{-3}) in the final difference map were close to the Mo atom; the next largest peaks (ca. 0.4 eÅ^{-3}) were close to the phosphine methyl groups.

Refinement of the inverted structure (with atomic coordinates $1-x$, $1-y$, $1-z$) showed no significant difference. Scattering factors were taken from reference 27. Computer programs used in this analysis, including SHELX and those listed in Table 4 of reference 28, were run on a MicroVAX II machine at the Nitrogen Fixation Laboratory, University of Sussex.

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