Preparation and Properties of Hexamethyltungsten †

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The interaction of three equivalents of methyl-lithium with tungsten hexachloride in diethyl ether gives a brown solution from which hexamethyltungsten can be isolated. The chemical and spectroscopic properties of the compound are described. Reaction with nitric oxide gives tetramethylbis(*N*-methyl-*N*-nitrosohydroxylaminato)-tungsten(VI) which is shown by n.m.r. studies to be stereochemically non-rigid at room temperature.

THE preparation of thermally stable binary transition metal alkyls was based on the concept of inhibiting the hydride transfer–alkene elimination reaction,[1-3] which is known to be a common mode of decomposition for metal alkyls. The methyl group is also clearly unable to undergo this elimination reaction and metal methyls are known to be more thermally stable than the corresponding ethyl compounds.[4,5] Apart from the unstable polymeric methyls of copper or manganese the best known binary molecular methyl is the very unstable tetramethyltitanium,[6] which decomposes above about −40°. However, the octahedral adducts with neutral ligands L, of both tetramethyl and trichloro(methyl)-titanium are appreciably more stable than their precursors.[7] This increased stability may be attributed to the blocking by the additional ligands of the co-ordination sites necessary for an inter- or intra-molecular decomposition reaction. The recently reported tetramethylchromium [3,8] is also unstable at room temperature but forms no adducts.

Hence it seemed possible that an octahedral, possibly co-ordinatively saturated binary methyl would be more thermally stable than the tetrahedral methyls of titanium and chromium. Since tungsten forms octahedral compounds when bonded to oxygen and nitrogen in compounds such as $W(OMe)_6$ [9] and $W(NMe_2)_6$,[10] and there is no reason to expect that the tungsten bond to carbon would be weaker than the bond to oxygen or nitrogen, we considered that hexamethyltungsten could be synthesised. The monomethyl, WCl_5Me, has been prepared by the action of dimethylzinc on tungsten hexachloride.[11]

Although the interaction of an excess or a stoicheiometric quantity of methyl-lithium with tungsten hexachloride in diethyl ether does not lead to the formation of hexamethyltungsten, the use of three equivalents of methyl-lithium gives the compound in yields close to 50% based on tungsten. The reaction sequence is obviously complex and has not been studied in detail.

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† No reprints available. Preliminary note: A. Shortland and G. Wilkinson, *Chem. Comm.*, 1972, 318.

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Hexamethyltungsten.—The compound is a red crystalline solid, m.p. *ca.* 30°, and is extremely volatile subliming easily at −30° and 10^{-2} mmHg. It is very air-sensitive and is thermally unstable decomposing slowly on standing at room temperature but it may be stored at −40° under nitrogen or *in vacuo.* The compound is extremely soluble in petroleum, aromatic hydrocarbons, ethers, carbon disulphide, and carbon tetrachloride and is unaffected by them; the solutions may be studied at room temperature in the absence of air.

The mass spectrum shows peaks due to the WMe_5^+ ion with the normal isotope distribution, and to other ions formed by the subsequent loss of further methyl groups $WMe_4^+ \longrightarrow W^+$. No peaks at higher mass number were observed.

The ^1H n.m.r. spectrum in deuteriotoluene shows a single sharp signal at τ 8·38 with satellites due to ^{183}W coupling, $J(^{183}W\text{–}H) = 3{\cdot}0$ Hz; the peak remains sharp on cooling to −90°. The ^{13}C n.m.r. spectrum in deuteriobenzene shows a single peak 1000 Hz upfield from the solvent peaks, with satellites $J(^{183}W\text{–}^{13}C)$ *ca.* 400 Hz. The value of the coupling constant may be compared with the value of 120—140 Hz reported for substituted tungsten carbonyl complexes $W(CO)_5L$.[12]

The i.r. spectrum in solution (Table) shows only the expected peaks due to CH_3 vibrations and a band at 482 cm^{-1} which is assigned as $\nu(W\text{–}C)$. Attempts to obtain a Raman spectrum in solution were unsuccessful due to decomposition in the laser beam even at −78°. The electronic spectra shows rising absorption into the u.v. due to an intense charge-transfer band, the intensity of this band accounts for the deep red colour of the compound.

I.r. spectra in cm^{-1} of hexamethyltungsten and tetramethylbis(*N*-methyl-*N*-nitrosohydroxylaminato)tungsten(VI)

WMe_6 [a]		$WMe_4\{ON(Me)NO\}_2$ [b]		
2980, 2870	C–H str.	1485s	1075w	572s
1395, 1090	C–H def.	1420s	1019w	552s
800	CH_3 rock.	1273s	965s	510m
482	W–C str.	1215w	798m	490m
		1178s	706s	445m
		1160sh	600s	

[a] In CS_2 and CCl_4 solution. [b] In Nujol and hexachlorobutadiene mulls.

The Formation Reaction.—As noted above hexamethyltungsten could only be isolated when a WCl_6 : MeLi ratio of 1 : 3 was used. It is well known that tungsten hexachloride is readily reduced by a variety of organic solvents to give tungsten(V) and tungsten(VI) complexes, well characterised examples are $WCl_4(MeCN)_2$[13] and $WOCl_3(thf)_2$,[14] while the interaction of diethylzinc with WCl_6 in diethyl ether gave $WCl_4(Et_2O)_2$.[11] Similarly, the presence of low valent tungsten complexes has been proposed in the alkene metathesis reactions of WCl_6 with alkylating agents.[15] It seems probable that the first step in the reaction between tungsten hexachloride and methyl-lithium involves a reduction of WCl_6 by diethyl ether, although this reaction may be catalysed by the presence of methyl-lithium. The addition of about two equivalents of methyl-lithium at −20° gave a dark red solution from which an unstable air-sensitive volatile red oil could be obtained. Although no analytical data is available the highest peak in the mass spectra corresponded to WMe_4Cl^+. Whether the highest peak observed corresponds to the molecular ion is uncertain. During the addition of the third equivalent of methyl-lithium there was formed a yellow precipitate which rapidly turned green and redissolved to give a green-brown solution. On warming to room temperature the colour of the solution darkens, and hexamethyltungsten could be isolated from the solution. If only *ca.* 90% of the third equivalent was added the colour of the solution at room temperature remained green-brown and a lower yield of hexamethyltungsten was obtained. The addition of more than three equivalents caused no appreciable colour change, but with more than four equivalents no hexamethyltungsten could be isolated. A reasonable explanation for the reactions with the third equivalent of methyl-lithium is the formation of a relatively stable methyltungsten(V) anion. Polarographic reduction of a *ca.* 10^{-3}M solution of WMe_6 in acetone with tetramethylammonium iodide as supporting electrolyte shows a one electron wave at −1·08 V *vs.* S.C.E., supporting the idea that a tungsten(V) anion plays a part in the reaction pathway. Hexamethyltungsten could then be obtained by disproportionation or oxidation. It may be noted that $W(C_6F_5)_5$ is formed in trace amounts by thermal decomposition of $LiW(C_6F_5)_5$.[16] Attempts to isolate any of the intermediate species were unsuccessful due to the general instability of the compounds, and to a degree of irreproducibility in the final stages of the reaction.

Further study of the reaction, including the interaction of WCl_6 with diethyl ether is clearly necessary. The interaction of methyl-lithium with WCl_6 in tetrahydrofuran or petroleum did not lead to isolatable tungsten methyl species, confirming the importance of diethyl ether in the reaction; however interaction of methyl-lithium with $WCl_4(MeCN)_2$ in diethyl ether did not give WMe_6. Low yields of WMe_6 could be obtained by reaction of $W(OPh)_6$ with methyl-lithium though this reaction probably involves a totally different reaction pathway. Interaction of WF_6 and methyl-lithium under a variety of conditions did not lead to isolatable tungsten-methyl species.

Reactions of Hexamethyltungsten.—(a) *Thermal decomposition.* Thermal decomposition of WMe_6, at room

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temperature in a sealed tube, gave methane with a trace of ethane ($<5\%$). The black residue contained carbon and hydrogen, probably as polymethylene, as well as tungsten, suggesting that the mechanism involves abstraction of a hydrogen from a neighbouring methyl group, to give methane and polymethylene. Approximately three equivalents of methane are produced, so that the approximate stoicheiometry is $WMe_6 \longrightarrow 3CH_4 + (CH_2)_3 + W$.

(b) *With oxygen.* The solid compound is spontaneously flammable in air. However, when a solution in benzene in an n.m.r. tube is treated with dry oxygen the spectrum shows a number of transient species but the final solution is pale yellow. We have isolated the methoxide, $W(OMe)_6$, whose properties are similar to those of an authentic sample.[9] The reaction of $TiMeCl_3$ with oxygen is known to give $Ti(OMe)Cl_3$.[7b]

(c) *With compounds with acidic hydrogens.* WMe_6 reacts rapidly with water and other compounds containing acidic hydrogens to give methane. Reaction with strong acids, *e.g.* CF_3SO_3H, CF_3COOH, and H_2SO_4, gives methane and red oils which did not contain methyl groups. The oils slowly turn blue-green and e.s.r. studies now show the presence of tungsten(v). Attempts to characterise the oils further were unsuccessful.

Interaction with absolute methanol gives the methoxide $W(OMe)_6$ [9] in quantitative yield; similarly the reaction with phenol gave the well characterised phenoxide, $W(OPh)_6$.[17] Although WMe_6 reacts with thiophenol no pure compound could be isolated but toluene-3,4-dithiol ($tdtH_2$) gives initially a red solution which turns blue-green on standing. The electronic spectrum of the latter is similar to that reported for the dithiolate $W(tdt)_3$ isolated by Gray *et al.*[18]

The n.m.r. spectrum of WMe_6 after reaction with dimethylamine shows a number of peaks, the major peak corresponding to $W(NMe_2)_6$; [10] di-isopropylamine gave the corresponding dialkylamide as a single product. Terminal acetylenes gave methane and tungsten-containing red oils which have proved difficult to characterise; there was no reaction with disubstituted acetylenes.

(d) *With halogens.* Treatment with bromine or iodine gave the methyl halide, as the major organic product, and the corresponding metal halide.

(e) *With hydrogen.* In petroleum solution, WMe_6 reacts instantly with hydrogen to give a blue species which is extremely unstable and decomposes rapidly even at $-78°$. The blue species appears to be tungsten(v) from its e.s.r. spectrum. The reaction is inhibited by the addition of tertiary phosphines, alkenes, and pyridine implying an interaction of these ligands with WMe_6 as discussed later.

(f) *With carbon monoxide.* The reaction between CO and WMe_6 in solution is rapid and complex involving several successive reactions. The mixture has not been studied in detail but i.r. spectra show both terminal and acyl stretching frequencies. This reaction also is inhibited by tertiary phosphines and other ligands.

(g) *With tertiary phosphines.* The inhibition of reaction between H_2 and CO and WMe_6 when a tertiary phosphine is present suggests an interaction between WMe_6 and phosphines. Treatment of WMe_6 in petroleum with the liquid tertiary phosphines, $PMePh_2$, PMe_2Ph, $PEtPh_2$, produces no change in colour, but on cooling to $-40°$ red crystals are formed in each case. These melt *ca.* $-10°$. The n.m.r. spectra of the separated crystals after melting or in a solvent show only the peaks due to a mixture of WMe_6 and the phosphine, with a ratio $WMe_6 : R_3P = 1:1$ according to integration of the peak areas. The ratio is quite reproducible from sample to sample with different phosphines. The spectra of the $1:1$ complex with $PMePh_2$ showed significant broadening of both W–Me and P–Me resonances on cooling to $-90°$.

No spectroscopic evidence could be obtained for complexes between WMe_6 and alkenes or pyridine and no complexes could be isolated, although the inhibition of the addition reactions suggests that interaction of the ligands with WMe_6 has occurred.

(h) *With Lewis acids.* The presence of the ion WMe_5^+ in the mass spectrum suggested that the cation might be formed by reaction with Lewis acids, *e.g.*,

$$WMe_6 + AlCl_3 \longrightarrow WMe_5^+ + AlMeCl_3^-.$$

Indeed WMe_6 readily reacts with several Lewis acids including $AlCl_3$, $SbCl_5$, SbF_5, and BF_3 in dichloromethane. N.m.r. evidence suggests the presence of species of this type but the spectra are complicated and no crystalline products have been isolated so far.

(i) *With nitric oxide.* The reaction of WMe_6 with nitric oxide gives tetramethylbis(*N*-methyl-*N*-nitrosohydroxylaminato)tungsten(vi) $WMe_4\{ON(Me)NO\}_2$ in quantitative yield. *X*-Ray crystallographic studies [19] show the compound to be eight-co-ordinate with chelating ON(Me)NO groups. This is the only well characterised example of eight-co-ordinate tungsten(vi). Although the insertion of nitric oxide into transition metal to carbon bonds is uncommon, the interaction [20] of nitric oxide with $(\pi\text{-}C_5H_5)_2ZrMe_2$ and related compounds, gives $(\pi\text{-}C_5H_5)_2ZrMe\{ON(Me)NO\}$. No structural evidence is available for this compound although the authors suggest that the ON(Me)NO group is unidentate. It seems most likely that the compound contains a chelate ON(Me)NO group, which would mean that the zirconium would have an effective co-ordination number of nine. The inability to increase the co-ordination number further could then explain the inertness of the second methyl group to reaction with nitric oxide. A similar inertness to further reaction with

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nitric oxide is evident for the tungsten complex since this would lead to ten-co-ordination. The i.r. spectra of the tungsten complex is similar to that reported for $(\pi\text{-}C_5H_5)_2ZrMe\{ON(Me)NO\}$ and for the copper complex $Cu\{ON(Me)NO\}_2$.[20] The observed bands for $WMe_4\{ON(Me)NO\}_2$ are listed in the Table. The n.m.r. spectrum of the complex in dichloromethane at 35° shows two methyl resonance at τ 8·42 and 5·97 in the ratio 4 : 2. The highest peak is clearly due to methyl groups bound to tungsten and shows the appropriate satellites, $J(^{183}W\text{-}H) = 2{\cdot}2$ Hz. The *N*-methyl resonance is very solvent dependent (*cf.* ref. 20) and in other solvents the τ values for N-Me and W-Me respectively are $CHCl_3$, 6·00, 8·32; benzene, 7·18, 7·66; toluene, 7·28, 7·98. There is no change in the N-Me peak on cooling in CH_2Cl_2 or CD_2Cl_2 but the W-Me peak broadens and below −50° is resolved into two peaks of equal intensity, implying two types of methyl groups: no further resolution occurs down to −90°. The crystal structure[19] indicates non-equivalence of the methyl groups on tungsten, but the structure in solution need not be the same as that in the crystal. The molecule is hence stereochemically non-rigid, behaviour for eight-co-ordinate species which has been previously confirmed only for the hydrido-complexes $MH_4(PR_3)_4$, M = W and Mo [21a] and $WH_6(PR_3)_2$.[21b]

The mass spectrum of $WMe_4\{ON(Me)NO\}_2$ has the highest peak corresponding to the loss of one methyl group. The breakdown pattern is consistent with the proposed structure and shows peaks corresponding to species of the type $Me_xWO_y^+$, $x = 0$—3, $y = 0$—2; no corresponding peaks were observed with nitrogen in place of oxygen confirming that the bonding of the ON(Me)NO group is through oxygen rather than through nitrogen.

DISCUSSION

The isolation of WMe_6 may be said to dispose of the view that the highest oxidation states of transition metals are accessible only when the metal atom is bound to electronegative atoms. There now seems no good reason why binary methyls of other transition metals, and even of non-metals such as selenium or tellurium, in their highest oxidation states cannot be isolated provided the key to the synthesis is found. Uranium, for which the hexafluoride and hexachloride are known, should resemble tungsten and preliminary studies indicate that a petroleum soluble methyl compound can be obtained from UCl_6 and MeLi. Although we have failed to obtain a molybdenum analogue, this may be due more to the different mechanism of the reactions with methyllithium which of necessity are with $MoCl_5$ rather than to the instability of the alkyl.

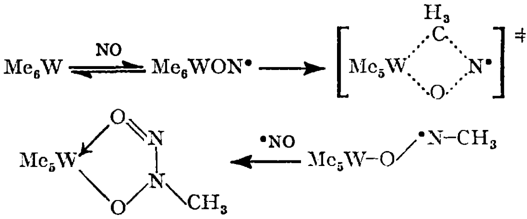
Although no crystallographic study has yet been made the i.r. spectrum is consistent with an octahedral structure, as is the photoelectron spectrum recently published,[22] on the basis of which a simple and obvious molecular orbital scheme has been constructed.

Since the formation of adducts with tertiary phosphines clearly shows that WMe_6 has the capability of expanding its co-ordination sphere to form seven-co-ordinate species, the initial reaction of any ligand, L, is presumably one of addition, *i.e.*, $WMe_6 + L \rightleftharpoons WMe_6L$. With the less sterically hindered ligands eight-co-ordinate species may be formed. Since there are no appreciable changes in either the electronic or n.m.r. spectra on addition of pyridine, alkenes, or tertiary phosphines the determination of formation constants will present some difficulty. The reaction of CO and NO also presumably proceed by way of the seven-co-ordinate adduct followed by transfer of methyl to the co-ordinated ligand as in other well known 'insertion' reactions; again we have so far been unable to obtain spectroscopic evidence for such species. The thermal decomposition of WMe_6 may also proceed through intermediates or transition states in which the co-ordination number is increased through formation of bridged methyl groups.

For nitric oxide it has been established that in transition metal nitrosyls, the bonding is through nitrogen. However, since methyl transfer to nitrogen occurs, it is possible in this case that the initial adduct involves oxygen bonding:

$$Me_6W + NO \rightleftharpoons Me_6WON\cdot$$

Methyl transfer to this radical species would also generate a radical and further reaction with NO can then readily occur to generate the {ON(Me)NO} group. The latter reaction is likely to be much faster than the methyl transfer reaction. Thus it seems reasonable to suggest that the reaction proceeds by the steps shown in the Scheme. From the *X*-ray structure determination[19] the two chelate rings have the methyl groups on nitrogen in the *cis*-positions. This, presumably, is a consequence of the mechanism of the formation of the second chelate ring by attack of NO on the seven-co-ordinate intermediate with one chelate ring. We have been able to show by following the reaction of NO with WMe_6 in solution using n.m.r. that the chelate rings are indeed formed successively. The single methyl resonance of WMe_6 is replaced first by two peaks in the ratio 5 : 1 at τ 8·36 and 5·82 corresponding to $WMe_5\{ON(Me)NO\}$.



SCHEME

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These are then replaced by the two peaks in the ratio 4 : 2 for the final product. We have not attempted to isolate the intermediate.

It may be noted finally that the *X*-ray structure shows that the chelate rings are essentially planar and the N–N distance is *ca.* 1·23 Å; delocalisation of electron density to give a quasi-aromatic ring, as *e.g.*, in acetylacetonates, may be involved.

EXPERIMENTAL

Microanalysis by the microanalytical laboratories of Imperial College, Bernhardt, and Beller. Tungsten analysis by atomic absorption on a Perkin-Elmer 303 spectrometer. N.m.r. spectra were recorded on Perkin-Elmer R14 and R12B, Varian HA100, and Bruker HFX-90 spectrometers. I.r. spectra were obtained using Perkin-Elmer 325 and 475 spectrometers. Mass spectra were recorded on an A.E.I. MS9 spectrometer. All preparations and operations were carried out under oxygen-free nitrogen or *in vacuo*. All solvents were dried and degassed before use, petroleum used had b.p. 30—40°. Methyl-lithium was prepared as a *ca.* 1M solution in diethyl-ether from methylbromide and lithium. Tungsten hexachloride was sublimed under chlorine before use.

Hexamethyltungsten.—Methyl-lithium (90 mmol) in diethyl ether was added over a period of 30 min to a suspension of tungsten hexachloride (12 g, 30 mmol) in diethyl ether at −20°. The final colour of the solution at −20° was green-brown; on warming to room temperature the colour was dark brown. The ether was removed at 0° *in vacuo*, to give a black residue which was extracted with petroleum to give a deep-red solution which was filtered. After removal of the petroleum at *ca.* −20° *in vacuo*, the residue was sublimed at room temperature to a probe at *ca.* −10° to give red *crystals* of the compound. In view of the volatility this procedure was used only when pure crystalline compound was required. For most purposes, after removal of petroleum, the compound can be sublimed to a probe cooled to −78° to give a red oil, due to the presence of trace amounts of solvent. The yields may be as high as 40% based on WCl_6 (Found: W, 67·0. $C_6H_{18}W$ requires W, 68·6%).

Tetramethylbis(N-*methyl*-N-*nitrosohydroxylaminato*)-*tungsten*(VI).—When nitric oxide was bubbled through a solution of hexamethyltungsten (*ca.* 2·5 g) in toluene (20 ml), the colour changed from dark red to orange-red. On concentration to *ca.* 5 ml and cooling to −20° red *crystals* were obtained in essentially quantitative yield. Recrystallised from toluene, m.p. 135° decomp. (Found: C, 17·8; H, 4·3; N, 14·0. $C_6H_{18}N_4O_4W$ requires C, 18·2; H, 4·5; N, 14·2%).

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