# New Synthesis of Hexamethyltungsten(VI). The Octamethyltungstate(VI) Ion †

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The interaction of tungsten hexachloride and trimethylaluminium in a hydrocarbon solvent followed by removal of chlorodimethylaluminium with an amine allows the synthesis of multigram quantities of hexamethyltungsten.

Interaction of $WMe_6$ with an excess of methyl-lithium in diethyl ether produces the anion $[WMe_8]^{2-}$ which has been isolated as the thermally stable dioxan solvate $Li_2[WMe_8]\cdot(C_4H_8O_2)_2$.

THE original preparation [1] of hexamethyltungsten, which involved the interaction of three equivalents of methyl-lithium with tungsten hexachloride in diethyl ether at low temperatures, frequently gave poor, or indeed sometimes zero, yields. Further studies have shown that the more stringent the precautions to exclude air from the solvents and reaction systems, the poorer are the yields. The presence of some oxygen is essential to ensure the formation of the final greenish solution [1] containing tungsten(V) and also in the extraction of the evaporated solution with petroleum to give $WMe_6$.

The reaction is clearly an exceedingly complex one and the role of oxygen is obscure. Attempts to improve the reaction by metering in oxygen were not very successful and attempts to scale up the reaction to provide a gram scale synthesis of $WMe_6$ failed.

The recognition of oxygen requirement did however allow the development of a synthesis of tetramethyloxorhenium,[2] though in this case hydrogen peroxide has been found better than oxygen.

The alkylating agents dimethylzinc and tetramethyltin gave only $MeWCl_5$ [3] from $WCl_6$ but we found [4] that using the more powerful alkylating agent, trimethylaluminium, in a hydrocarbon solvent essentially quantitative yields of $WMe_6$ could be obtained from $WCl_6$.

Although trimethylaluminium has been used to make methyl compounds of transition metals bound also to triphenylphosphine or bipyridyl [*e.g.* $Me_2Fe(PPh_3)_3$ or $Me_2Ni(bipy)_2$ [5]] the only other transition-metal permethyl so obtained is hexamethylrhenium, from $ReOMe_4$.[4]

*Synthesis of Hexamethyltungsten.*—A suspension of tungsten hexachloride in isopentane at −70 °C is treated with six molar equivalents of trimethylaluminium and the mixture allowed to warm to 0 °C. Since only one of the methyl groups of $AlMe_3$ is commonly used in alkylations [6] the problem is to remove the stable $AlMe_2Cl$ formed in the reaction, $WCl_6 + 6AlMe_3 \longrightarrow WMe_6 + 6AlMe_2Cl$, from the unstable $WMe_6$. This can be achieved by cooling the solution to −78 °C and adding cooled liquid trimethylamine; the precipitate of $AlMe_2Cl\cdot NMe_3$ can be removed by filtration at −70 °C. Concentration of the dark orange-red solution in vacuum at *ca.* −10 °C removes the excess of $NMe_3$ and much of the isopentane. Re-cooling to −78 °C and filtration

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† No reprints available.

[1] A. J. Shortland and G. Wilkinson, *J.C.S. Dalton*, 1973, 872.

[2] K. Mertis, D. H. Williamson, and G. Wilkinson, *J.C.S. Dalton*, 1975, 607.

[3] W. Grahlert and K-H. Thiele, *Z. anorg. Chem.*, 1971, **383**, 144; see also C. Santini-Scampucci and J. G. Riess, *J.C.S. Dalton*, 1976, 195 for use of $Me_2Hg$.

[4] Preliminary note: A. L. Galyer, K. Mertis, and G. Wilkinson, *J. Organometallic Chem.*, 1975, **85**, C37; **97**, C65.

[5] Y. Kubo, A. Yamamoto, and S. Ikeda, *J. Organometallic Chem.*, 1972, **46**, C50; T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, 1971, **93**, 3350.

[6] See T. Mole and E. A. Jeffrey, 'Organoaluminium Compounds,' Elsevier, New York, 1972.

removes more of the $AlMe_2Cl{\cdot}NMe_3$ which is only slightly soluble in isopentane at this temperature.

The resulting concentrated solution of $WMe_6$ can be stored at −25 °C for about a week in the dark but a fine precipitate of metal begins to form after about eight days. By cooling a very concentrated isopentane solution to −100 °C, dark red crystals of $WMe_6$ can be obtained. Pure $WMe_6$ can also be obtained by removal of solvent and sublimation from *ca.* −15 °C to a probe cooled to −70 °C. This procedure is not recommended on a large scale as we have experienced unpredictable and violent detonations during sublimations of several grams of product. Small samples for spectroscopic purposes can be sublimed into n.m.r. tubes or break-seal tubes. The pure $WMe_6$ should be stored below −40 °C and handled with caution. For most purposes petroleum solutions can be used and the concentration of $WMe_6$ determined by tungsten analysis.[7]

*Properties of Hexamethyltungsten.*—The availability of large quantities of material has allowed previous data[1] to be improved or confirmed. The $^1H$ n.m.r. spectra was re-measured in $CCl_3F$ at −20 °C and gives a singlet at $\tau$ 8.2, $J(^{183}W\text{–}H) = 3$ Hz. The proton-decoupled $^{13}C$ n.m.r. at 25.16 MHz in $[^2H_8]$toluene at −50 °C shows a sharp singlet at 83.6 p.p.m. downfield from tetramethylsilane, $J(^{183}W\text{–}^{13}C) = 43.2$ Hz. The proton-decoupled $^{13}C$ n.m.r. spectrum showed a quartet with $J(^{13}C\text{–}^1H) = 124.8$ Hz.

In the mass spectrum (ionisation energy 70 eV, source temperature 24 °C at $4 \times 10^{-8}$ mmHg) $WMe_6$ gave a multiplet about $^{184}WMe_5^+$ ($m/e = 259$) with the correct isotopic ratios. Also present was the multiplet corresponding to $^{184}W^+$ ($m/e = 184$). Between these two peaks was a plethora of lines. On lowering the ionisation energy to 15 eV and increasing the pressure of alkyl to $2 \times 10^{-7}$ mmHg, the multiplet corresponding to the parent ion $^{184}WMe_6^+$ appeared at $m/e = 274$. This parent ion was not observed before[1] and its intensity compared to $WMe_5^+$ peaks is extremely low. Between the $WMe_6^+$ and $WMe_5^+$ multiplets no peaks were observed, but a multiplet not containing tungsten appeared at $m/e$ 281, 282, 283, and 284 with the first being most intense. The species giving rise to this multiplet has not been identified.

Hexamethyltungsten is extremely air-sensitive and will explode if exposed to air. As noted earlier, violent spontaneous detonations *in vacuo* have also been experienced; similar explosive decomposition has recently been reported also for pentamethyltantalum[4] and for tetraisopropylchromium.[8] The alkyl appears little affected by liquid water provided the mixture is heterogeneous and petroleum solutions can be washed with water or even slightly acid solutions. In basic solutions rapid attack occurs.

*Dilithium Octamethyltungstate*(VI).—On the addition of methyl-lithium in diethyl ether to $WMe_6$ in ether the colour changes from red to yellow-orange and bright yellow crystals of a petroleum-soluble ether solvate of $Li_2[WMe_8]$ can be isolated. This salt is stable at 0 °C but decomposes at higher temperatures and is non-volatile. It is very sensitive to water and oxygen especially in solution.

*In vacuo* the salt loses ether to leave a non-volatile yellow powder, $Li_2[WMe_8]$, which is insoluble in non-reacting solvents.

Addition of dioxan to petroleum solutions of the unstable ether solvate gives an orange-red precipitate of the salt $Li_2[WMe_8]{\cdot}(C_4H_8O_2)_2$. This is stable to 25 °C but again is insoluble in non-reacting solvents as well as being sensitive to air and light. It is hydrolysed instantly by water. Reasonably stable salts may also be obtained from 1,2-dimethoxyethane (dme), tetrahydrofuran, *NNN'N'*-tetramethylethylenediamine, 2,2 -bipyridyl, 1,10-phenanthroline, and *NN'*-dimethylpiperidine.

The proton n.m.r. spectrum of the $[WMe_8]^{2-}$ ion has a singlet at $\tau$ 8.3, close to that of $WMe_6$. The $^{13}C$ resonances of the tetrahydrofuran complex in deuteriotoluene are at 66.27 ($W\text{–}CH_3$), 66.7 ($CH_2O$), and 25.6 ($CH_2$) p.p.m.

Action of two equivalents of acetic acid on $Li_2[WMe_8]{\cdot}(dme)_3$ in petroleum gives two mol equivalents of methane, a quantitative precipitate of lithium acetate and a red solution of $WMe_6$. Four mol equivalents of acetic acid give $CH_4$, lithium acetate, and a red solution. However, on removal of solvent, the red, non-volatile oil is thermally more stable than is $WMe_6$. Its n.m.r. in $CCl_3F$ shows singlets due to $W\text{–}Me$ $\tau$ 8.2 and $CH_3\text{–}C$, $\tau$ 7.94 in the ratio 6 : 2. A petroleum solution of the oil is unaffected by cellulose. Although no evidence for the hydroxyl proton was found in the n.m.r. spectrum it would appear that the species is $WMe_6(CH_3CO_2OH)_2$.

Hexamethyltungsten is also formed by interaction of the $Li_2[WMe_8]$ complexes with trimethyloxonium hexafluorophosphate in dichloromethane at −15 °C.

$$Li_2[WMe_8] + 2[OMe_3][PF_6] \longrightarrow 2Li[PF_6] + WMe_6 + 2MeOMe + 2C_2H_6$$

The unsolvated salt, $Li_2[WMe_8]$, when suspended in isopentane reacts with two mol equivalents of trifluoroacetic acid to give methane and $WMe_6$; this reaction is a convenient method of preparing small amounts of very pure $WMe_6$.

Although attempts to prepare salts $Li_2[WMe_6R_2]$ by use of LiR (R = Et, Ph, Bu$^n$, and $C{\equiv}CPh$) failed, when $R = CH_2SiMe_3$ a mixed alkyl dioxan solvate of stoicheiometry $Li[WMe_6(CH_2SiMe_3)]{\cdot}3C_4H_8O_2$ was obtained.

## DISCUSSION

Although the synthesis of $WMe_6$ from $WCl_6$ and $AlMe_3$ is very successful and we have made as much as 25 g of the compound in a single run, the method does not appear to be generally useful. We have been unable to isolate any permethyl compounds from interaction of $AlMe_3$ with $WF_6$, $WOCl_4$, $UCl_6$, $TaCl_5$, $K_2TaF_7$, $MoOCl_4$,

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[7] F. D. Snell and C. T. Snell, 'Colorimetric Methods of Analysis,' Van Nostrand, Princeton, 1959, vol. 11A, p. 361.

[8] J. Müller and W. Holzinger, *Angew. Chem. Internat. Edn.*, 1975, **14**, 760.

$MoCl_5$, $ReOCl_4$, $ReCl_5$, $OsO_4$, and $Re_2O_7$. In all these cases, reduction to the metal occurred.

The general properties of $WMe_6$, with the exceptions noted earlier, are those given previously.[1] Photoelectron spectroscopy [9] has shown that the $WC_6$ skeleton appears to have $O_h$ symmetry in which the methyl groups are slightly sterically compressed. This steric compression may be partially effective in determining the stability of the permethyl, which is limited by kinetic rather than thermodynamic factors. The hexamethyl is endothermic ($\Delta H_f^0 = +176.5$ kcal mol$^{-1}$) with a fairly high average bond strength ($D = 38.1$ kcal mol$^{-1}$).[10] The formation of methane on thermal decomposition,[1] found also for $TaMe_5$ [11] and $TiMe_4$,[12] must require hydrogen abstraction from one methyl group by another, presumably in the decomposition of the pure substances by a free-radical chain reaction. The decomposition in solution may be sensitive to the presence of impurities and we have found, for example, that $WMe_6$ that had been treated in solution for several hours with triphenylboron in an unsuccessful attempt to exchange methyl groups for phenyl [13] was stable for weeks at −25 °C.

## EXPERIMENTAL

Microanalyses were carried out by the microanalytical laboratories at Imperial College and A. Bernhardt, Mühlheim. Lithium and tungsten were determined by plasma emission spectrometry by Mr. J. Goulter, Imperial College. N.m.r. spectra were recorded on Perkin-Elmer R12 ($^1H$) and Varian XL-100 (Fourier transform for $^{13}C$) spectrometers. Mass spectra were recorded using AEI-MS9 instruments at Imperial College and at Queen Mary College, London. All operations were performed in an inert atmosphere (nitrogen or argon) using conventional vacuum, Schlenk tube, and glove-box techniques. All solvents were dried and de-oxygenated before use. Trimethylaluminium (Ethyl Corporation) was used as received; tungsten hexachloride was sublimed, *in vacuo* at *ca.* 180 °C before use.

**CAUTION!** Hexamethyltungsten reacts explosively with atmospheric oxygen and may also detonate, under certain circumstances, *in vacuo* or under nitrogen or argon. Great care must be taken especially during sublimations of the solid and when samples are being warmed or cooled *in vacuo* for spectroscopic study or analyses. Safe procedures for the handling of liquid alkylaluminiums have been recently published.[14]

*Hexamethyltungsten.*—To a cooled (−70 °C) suspension of tungsten hexachloride in isopentane (10 cm$^3$ per gram $WCl_6$) was added, *via* a syringe or a dropping funnel, six mol equivalents of trimethylaluminium during 10—15 min. Vigorous stirring was maintained during the addition and was continued as the reaction vessel was allowed to warm slowly to room temperature. After 15 min at *ca.* 20 °C the mixture was slowly recooled to −70 °C and an excess of dry trimethylamine (*ca.* 1.2 cm$^3$ per cm$^3$ $AlMe_3$) was carefully added. The resulting rather heavy slurry was stirred rapidly until the exothermic reaction subsided when the bulky precipitate of $AlMe_2Cl{\cdot}NMe_3$ was filtered off at −70 °C. The deep red-orange filtrate was concentrated *in vacuo* at −10 °C to remove excess of $NMe_3$ and about half the solvent. Recooling to −70 °C and further filtration removed more alkylamine adduct.

Determination of tungsten in the solution at this stage indicated the yield of $WMe_6$ to be 60—70%, the losses being due to entrainment in the bulky precipitate. This precipitate could not be effectively washed because of the relatively high solubility of $AlMe_2Cl{\cdot}NMe_3$ in light petroleum or isopentane. Although other tertiary amines could be used to remove $AlMe_2Cl$, we found the above procedure to be best.

The solution contained traces of aluminium but could be used directly for most purposes. Small samples of pure $WMe_6$ could be obtained by crystallisation of the concentrated solutions at −100 °C or by sublimation *in vacuo* or a stream of argon.

*Dilithium Octamethyltungstate.*—A solution of $WMe_6$ in diethyl ether was treated at −20 °C with an excess of an ethereal solution of methyl-lithium. The yellow-orange solution was evaporated to dryness at −10 °C and the residue extracted with isopentane; the extracts were filtered and the bright yellow filtrate was concentrated, and cooled to −78 °C, to give crystals of the *salt* $Li_2[WMe_8]{\cdot}nEt_2O$. These lost diethyl ether when dried to leave a petroleum-insoluble yellow powder.

On addition of a slight excess of 1,4-dioxan to a solution of the ether solvate in light petroleum (b.p. 30—40 °C), the bisdioxan solvate was immediately precipitated as an orange-red *powder* [Found: $CH_4$ (by hydrolysis and collection in gas burette) 7.8 mol equiv; O, 12.3; Li, 2.9; W, 38.3. $C_{16}H_{40}Li_2O_4W$ requires $CH_4$, 8 mol equiv.; O, 12.9; Li, 2.8; W, 37.2%].

Similarly 1,2-dimethoxyethane precipitated the salt $Li_2[W(CH_3)_8]{\cdot}(C_4H_{10}O_2)_3$ as a red *powder* (Found: C, 41.1; H, 8.6; W, 29.2. $C_{20}H_{54}Li_2O_6W$ requires C, 40.8; H, 9.2; W, 31.2%).

*Reaction of Trimethylsilylmethyl-lithium and Hexamethyltungsten.*—A light petroleum (b.p. 30—40 °C) solution of $WMe_6$ containing a slight excess of 1,2-dimethoxyethane was diluted with an equal volume of diethyl ether and then treated at −10 °C with an excess of $Me_3SiCH_2Li$ (0.9M-solution in hexane). Immediately a precipitate of the bright orange *salt* formed and this was filtered off, washed with isopentane (2 × 25 cm$^3$), and pumped dry at 0 °C [Found: Li, 1.03 ± 0.02; W, 26.9 ± 0.9%; Li/W = 1.01; $LiWMe_6(CH_2SiMe_3){\cdot}(C_4H_{10}O_2)_3$ requires Li, 1.09; W, 28.8%; Li/W = 1.00]. N.m.r.: $\tau$ 8.3 Me(W) and $\tau$ 8.5 Me(Si), ratio 2 : 1.

*Reaction of Dilithium Octamethyltungstate with Acetic Acid.*—(a) To a suspension of $Li_2[WMe_8]{\cdot}(C_4H_{10}O_2)_3$ (1.5 g, 2.4 mmol) in isopentane (25 cm$^3$) at 20 °C was added dry acetic acid (0.28 cm$^3$, 4.8 mmol). Methane was vigorously evolved and the solid dissolved to give a red solution and a fine pale precipitate ($MeCO_2Li$). After being stirred at 0 °C for 1 h the mixture was filtered and the solvent removed to leave a volatile red oil. Sublimation onto a probe at −10 °C and n.m.r. analysis identified the oil as being $WMe_6$ ($\tau$ 8.3) contaminated with 1,2-dimethoxyethane ($\tau$ 6.60, 6.75).

(b) A suspension of $Li_2[WMe_8]{\cdot}(C_4H_{10}O_2)_3$ was treated

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[9] A. L. Galyer, G. Wilkinson, and D. R. Lloyd, *J.C.S. Chem. Comm.*, 1975, 497.

[10] F. A. Adedeji, J. A. Connor, H. A. Skinner, A. L. Galyer, and G. Wilkinson, *J.C.S. Chem. Comm.*, 1976, 159.

[11] R. R. Schrock and P. Meakin, *J. Amer. Chem. Soc.*, 1974, **96**, 5288.

[12] H. J. Berthold and G. Groh, *Z. anorg. Chem.*, 1963, **319**, 230.

[13] *Cf.* P. Zdunneck and K-H. Thiele, *J. Organometallic Chem.*, 1970, **22**, 659.

[14] D. W. Harvey, A. Meistess, and T. Mole, *Austral. J. Chem.*, 1974, **27**, 1639.

similarly except that four mol equivalents of acetic acid were used. After the gas evolution had ceased the mixture was filtered; the filtrate was evaporated to a small volume and dry cellulose powder (2 g) was added to it. After being stirred for 15 min at 0 °C the mixture was filtered and evaporated to leave a red oil which failed to crystallize at $-150$ °C. The n.m.r. in $CCl_3F$ at 0 °C showed only a trace of 1,2-dimethoxyethane, a singlet at $\tau$ 7.94 ($MeCO_2H$) and a singlet at $\tau$ 8.2 ($WMe_6$) in the ratio 1 : 3.

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