σ-Bonded Early Transition Metal–Carbon Derivatives. Part III.[1] Complexes of Methyltungsten(VI) Pentahalide, Halide Oxide, and Halide Dioxide

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Methyltungsten(VI) pentachloride has been obtained from WCl_6 with $HgMe_2$, and characterised by n.m.r. and i.r. spectroscopy. Reactions of $WMeCl_5$ with bidentate ligands give $WMeCl_5{\cdot}L$ adducts $\{L = Ph_2P[CH_2]_2PPh_2$ or $O[OP(NMe_2)_2]_2\}$, while unidentate ligands give either extensive reduction [MeCN, $SO(OMe)_2$, $PO(OMe)_3$, or $P(NMe_2)_3O$] or chlorine–oxygen exchange reactions to $WMeCl_3O{\cdot}L$ or $WMeClO_2{\cdot}2L$ compounds [$P(NMe_2)_3O$, PPh_3O, $AsPh_3O$, or SMe_2O]. Alkylation of WCl_4O by $HgMe_2$, $ZnMe_2$, $MgMe_2$, and MgMeI has been investigated and shown to be dependent to a considerable extent on the solvent. The best results are obtained with $MgMe_2$ in pentane containing 7% diethyl ether.

THE only previously isolated σ-bonded alkyl derivatives of tungsten(VI) are the methyl-, ethyl-, and butyltungsten pentachlorides and some of their complexes prepared by Grahlert and Thiele,[2] and hexamethyltungsten prepared by Shortland and Wilkinson.[3] As part of our efforts to develop unequivocal selective routes to alkylated derivatives of early transition-metal halides, and to evaluate how much chemistry can be done on them without breaking the metal–carbon bond,[1,4] we now report an alternative synthesis of methyltungsten(VI) pentachloride and of some new adducts of this compound, as well as the synthesis of a series of methyltungsten(VI) halide oxide derivatives. The latter compounds were obtained either by direct alkylation of tungsten(VI) tetrahalide oxide by dimethyl-magnesium, -zinc, or -mercury, or by a chlorine–oxygen exchange reaction between $WMeCl_5$ and various oxygen ligands in which the metal–carbon bond is preserved.[1,4]

RESULTS AND DISCUSSION

Synthesis and Characterisation of Methyltungsten(VI) *Pentachloride.*—Methyltungsten pentachloride is formed when tungsten hexachloride is treated with half the equivalent of dimethylmercury at −35 °C. However, there is an exchange reaction between $WMeCl_5$ and $HgCl_2$ (as observed for the titanium[5] and niobium[4] analogues) to give the mixed compound HgMeCl and non-alkylated tungsten derivatives. Since this reaction is fast at −20 °C, it is difficult to avoid contamination of

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[1] Part II, C. Santini-Scampucci and J. G. Riess, *J.C.S. Dalton*, 1974, 1433.

[2] W. Grahlert and K. H. Thiele, *Z. anorg. Chem.*, 1971, **383**, 144.

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

[4] (*a*) C. Santini-Scampucci and J. G. Riess, *J.C.S. Dalton*, 1973, 2436; (*b*) *J. Organometallic Chem.*, 1974, **73**, C13; (*c*) J. G. Riess and C. Santini-Scampucci, Communication to the VIIth Internat. Symp. on Organometallic and Inorg. Chem., Sheffield, March 1974.

[5] G. A. Razuvaev and L. M. Bobinova, *Doklady Akad. Nauk, S.S.S.R.*, 1963, **150**, 325; G. W. Parshall and J. J. Mrowca, *Adv. Organometallic Chem.*, 1968, **7**, 157.

the reaction product, even if the mercury dichloride is filtered off quickly, and there is a loss in yield during the purification. To avoid this we used 1 mol. equivalent of $HgMe_2$ at lower temperature according to reaction (1), since no further alkylation occurred even in

$$\mathrm{WCl_6 + HgMe_2 \xrightarrow[-45\ ^\circ C]{CH_2Cl_2} WMeCl_5 + HgMeCl} \qquad (1)$$

the presence of an excess of $HgMe_2$. Methylmercury chloride is easily precipitated on addition of pentane, and $WMeCl_5$ was obtained in 66% yield after evaporation of the solvents. Thus, dimethylmercury is effective as a selective non-reducing monoalkylating agent for early transition-metal halides.[1]

Although $WMeCl_5$ had previously been isolated, no physical and spectral characterisations were given. When repeated, Grahlert and Thiele's method using tetramethyltin afforded an identical compound. We characterised it by ^1H n.m.r. spectroscopy [a single peak at δ 3.08 p.p.m. in CH_2Cl_2 and satellites with $J(H-^{183}W)$ 2.9 Hz; no changes were observed between -80 and $+30$ °C]. An absorption band at 465 cm^{-1} in the i.r. spectrum was assigned to the ν(W–C) stretching frequency. The presence of the methyl group is further established by the symmetric and antisymmetric ν(C–H) stretching vibrations at 2 960, 2 920, and 2 850 cm^{-1}, by the symmetric and antisymmetric deformation $\delta(CH_3)$ at 1 450 and 1 405—1 395 cm^{-1}, and by the rocking vibration $\rho(CH_3)$ at 800 cm^{-1} which is characteristic of methyl groups bonded to a metal atom. The vibration at 400 cm^{-1} is attributed to the W–Cl bonds.[6]

Methyltungsten(VI) *Pentachloride Adducts*.—Surprisingly, no simple $WCl_6{\cdot}L$ adducts have so far been firmly established with unidentate ligands.[7] A similar situation exists in the case of $WMeCl_5$: Grahlert and Thiele reported the formation of $WMeCl_5{\cdot}2py$, $WMeCl_5{\cdot}3NHEt_2$, and $[WMeCl_4(py)_3]Cl$ (py = pyridine), but no observation of monoadduct. The unidentate ligands which we have tested did not give simple $WMeCl_5{\cdot}L$ co-ordination compounds. Instead we observed either (*i*) reduction reactions [with MeCN, $SO(OMe)_2$, or $P(NMe_2)_3O$], even at temperatures lower than 0 °C, from which no definite methylated compounds could be isolated, or (*ii*) exchange of two or four chlorine atoms for one or two oxygen atoms [with $P(NMe_2)_3O$, PPh_3O, $AsPh_3O$, and SMe_2O]. Reactions (*ii*) led to isolation of the first monomethylated trichloride oxide and chloride dioxides of tungsten(VI).[4b]

Two $WMeCl_5{\cdot}L$ complexes were isolated with the bidentate ligands octamethylpyrophosphoramide (ompa) and 1,2-bis(diphenylphosphino)ethane (dppe). They are more stable than $WMeCl_5$ (decomp. 65 °C), having decomposition temperatures of 140 and 120 °C respectively. Osmometric molecular-weight determinations in acetonitrile solution showed the ompa complex to be monomeric (Found: 774. Calc.: 662), while the dppe complex is dimeric (Found: 1 454. Calc.: 1 548). The ^1H n.m.r. spectrum of the ompa adduct, recorded at -35 °C in CH_2Cl_2, exhibited a broad pattern at 2.7 p.p.m. in which the Me–W and ligand signals overlapped, and a single broad signal at δ -10.75 p.p.m. in the ^{31}P n.m.r. spectrum. In the i.r. spectrum only one ν(P=O) stretching vibration was observed at 1 175 cm^{-1}, while no vibration which would correspond to an unco-ordinated PO group was found in the region of 1 230 cm^{-1} in Nujol or in CH_2Cl_2. The dppe adduct also showed a symmetric pattern in the ^1H n.m.r. spectrum [$\delta(CH_2-P)$ 3.25; 2.3 p.p.m. in the free ligand]. These data are consistent with the formation of eight-co-ordinate tungsten derivatives.

Methyltungsten(VI) *Trichloride Oxide*.—The direct alkylation of tungsten tetrachloride oxide by various alkylating agents, including $HgMe_2$, $ZnMe_2$, $MgMe_2$, and MgMeI, was investigated, and the reaction was highly solvent dependent. Since methyltungsten trichloride oxide is unstable above -10 °C, the conversion ratios were evaluated either by (*i*) filtration of the yellow crystals at -30 °C, vacuum drying at -45 °C, acid hydrolysis, and subsequent chloride determination by argentimetry, or (*ii*) adduct formation of $WMeCl_3O$ in solution with dppe and weighing the isolated adduct.

Dimethylmercury reacts readily with WCl_4O according to equation (2). The best conversion ratios (80%)

$$\mathrm{HgMe_2 + WOCl_4 \longrightarrow WMeCl_3O + HgMeCl} \qquad (2)$$

were obtained at *ca.* -80 °C in dichloromethane–pentane (2 : 1) with subsequent low-temperature filtration of HgMeCl and unchanged WCl_4O. The reaction was much slower in toluene–pentane and gave a lower conversion ratio (45% at -35 °C for 4 h). In both cases $WMeCl_3O$ was isolated by evaporation of the deep red filtrate at low temperature. The red colouration of the crystals disappears when they are repeatedly washed with pentane at -78 °C and the compound then becomes yellow-orange. When redissolved in pentane it gives an orange solution which turns red on addition of either toluene or CH_2Cl_2. The isolated yellow-orange solid rapidly decomposes at temperatures above -10 °C, or slowly (1 d) even at -45 °C, the main product being WCl_3O (*ca.* 80%). In toluene or pentane solutions the decomposition occurs in a similar fashion above -10 °C, while it is rapid at -50 °C in CH_2Cl_2, which thus appears to react with $WMeCl_3O$.[8] The n.m.r. spectrum of $WMeCl_3O$ in CH_2Cl_2 consisted of a single sharp signal at -80 °C accompanied by satellites due to ^{183}W coupling [δ(Me–W) 3.0 p.p.m., $J(H-^{183}W)$ 3.0 Hz]. Further

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[6] C. Lalau, *Rec. Trav. chim.*, 1965, **84**, 429; H. Heysel, H. Seibert, H. J. Berthold, and G. Groh, *Spectrochim. Acta*, 1970, **A26**, 1595; L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 1966; K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' Wiley, London, 1963.

[7] D. L. Keppert, 'The Early Transition Metals,' Academic Press, London, 1972, p. 271.

[8] G. A. Razuvaev and N. Latyaeva, *Russ. Chem. Rev.*, 1965, **34**, 25.

characterisation of the compound was achieved by the preparation of several adducts (see below).

Dimethylmagnesium was more effective for preparing $WMeCl_3O$ provided the reaction was controlled by using appropriate solvent mixtures. Thus the conversion ratio for $WMeCl_3O$ was 63% (isolated as the $WMeCl_3O\cdot dppe$ adduct) in the reaction of 1 equivalent of $MgMe_2$ with WCl_4O in diethyl ether–pentane (7% by volume) according to equation (3). It should be noted

$$WCl_4O + MgMe_2 \xrightarrow{-20\ ^{\circ}C} WMeCl_3O + MgMeCl \quad (3)$$

that the crystalline compound obtained from reaction (3) after evaporation of the solvents at −35 °C is not bound to diethyl ether (no OEt_2 detectable by n.m.r. spectroscopy in its solutions, or among its decomposition products). Extensive reduction occurred in pure OEt_2, even at −78 °C, or in diethyl ether–pentane mixtures containing more than 10% OEt_2 at −35 °C, while no reaction was observed in pure pentane or pure toluene. A similar lack of reactivity was observed by Jacot-Guillarmod *et al.*[9] when dibenzylmagnesium was added to titanium tetrachloride in the absence of OEt_2.

Although the role of OEt_2 is still not understood, it is likely that it plays a part in depolymerising the reactants before reaction. Indeed, WCl_4O is polymeric in the solid,[10] but it is known to form a monomeric adduct with OEt_2.[7] Similarly, dimethylmagnesium is polymeric in the solid state,[11] but in OEt_2 its n.m.r. spectrum suggests the existence of a monomeric adduct $MgMe_2(OEt_2)_2$.[12] When increasing amounts of OEt_2 were added to an equimolar suspension of WCl_4O and $MgMe_2$ in pentane the alkylation reaction became appreciable only when the molar ratio $OEt_2 : (WCl_4O + MgMe_2)$ was equal to or greater than 1 : 1. At the same time the diethyl ether–pentane volume must always remain lower than 7% in order to avoid reduction. When an excess of $MgMe_2$ was used, the yields were lowered, probably because of the formation and subsequent decomposition of polymethylated tungsten derivatives. When methylmagnesium iodide was used as alkylating agent (at −35 °C in 4% diethyl ether–pentane), only extensive reduction to WCl_3O (85% isolated) occurred.

Dimethylzinc reacted with WCl_4O according to equation (4). The reduction to WCl_3O was difficult to

$$WCl_4O + 0.5\,ZnMe_2 \xrightarrow[5\ h]{-25\ ^{\circ}C} WMeCl_3O + 0.5\,ZnCl_2 \quad (4)$$

suppress. Reduction was considerable even at lower temperatures in the presence of OEt_2 or tetrahydrofuran (thf). The best conversion ratio (40% as the dppe adduct) was obtained after *ca.* 5 h in pentane in the presence of small amounts of diethyl ether [*ca.* 0.5 mol of OEt_2 per mol of $(WCl_4O + ZnMe_2)$], the diethyl ether–pentane volume remaining lower than 8%. No alkylation occurred in toluene–pentane (1 : 1). Thus the presence of OEt_2 appears to be necessary in the alkylation by $ZnMe_2$, while it is not with $HgMe_2$.

Further evidence of the importance of the presence of an ether was found when we studied the reaction of $ZnMe_2$ with the monomeric $WCl_4O\cdot thf$ adduct in pure pentane.[7] When $ZnMe_2$ was added to a pentane suspension of this yellow adduct at −98 °C there was an immediate displacement of ligand, as shown by (*i*) the precipitation of red needles, probably WCl_4O; and (*ii*) the appearance, above −78 °C, of a singlet at −0.60 p.p.m., and a complex pattern at 3.9 p.p.m., in the n.m.r. spectrum of the reaction mixture. The n.m.r. spectrum is the same as that of $ZnMe_2\cdot 2thf$ in similar conditions. At the same time the singlet of $ZnMe_2$ at −0.42 p.p.m. gradually disappeared. The alkylation reaction occurred when the temperature reached −50 °C and then the reaction proceeded rapidly with side reactions, resulting in a relatively low conversion ratio (*ca.* 20%) for the dppe adduct of the expected compound. The increasing reactivity of $ZnMe_2$ on complex formation has previously been demonstrated by an n.m.r. study of alkyl-group exchange reactions between zinc and cadmium.[13]

To summarise, it appears that the monoalkylation of WCl_4O is most conveniently achieved by using dimethylmagnesium, provided the reaction is controlled with an appropriate solvent mixture. The use of dimethylmercury is not ideal because the best conversions are obtained in CH_2Cl_2, a solvent in which the desired reaction product is not stable. Reduction reactions seem difficult to suppress when dimethylzinc is employed, and quite impossible with methylmagnesium iodide.

Methyltungsten Trichloride Oxide Adducts.—Compounds $WMeCl_3O\cdot tdpo$ and $WMeCl_3O\cdot dppe$ [tdpo = tris(dimethylamino)phosphine oxide] were prepared by addition of the ligands to solutions of the unstable $WMeCl_3O$, isolated, and characterised. The considerable increase in thermal stability on complex formation supports the view that tungsten is probably five-coordinate in $WMeCl_3O$. With dimethyl sulphoxide, the methyltungsten chloride dioxide adduct $WMeClO_2\cdot 2OSMe_2$ was immediately obtained. Such a reaction was not observed with tdpo, even with an excess of ligand; in the latter case the known product $WCl_2O_2\cdot 2tdpo$ [14] forms after several days at −45 °C.

An alternative route to the synthesis of methyltungsten trichloride oxide adducts was provided by the oxygen-abstraction–halogen-exchange reaction between methyltungsten pentachloride and a variety of ligands of the

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[10] M. Adams and R. G. Churchill, *J. Chem. Soc.* (*A*), 1968, 2316.

[11] G. E. Coates, R. Ridley, J. A. Heslop, and M. E. Redwood, *J. Chem. Soc.* (*A*), 1968, 1118.

[12] G. E. Parris and E. C. Ashby, *J. Amer. Chem. Soc.*, 1971, **93**, 1206.

[13] J. Soulati, K. L. Henold, and J. P. Oliver, *J. Amer. Chem. Soc.*, 1971, **93**, 5694.

[14] B. J. Brisdon, *Inorg. Chem.*, 1967, **6**, 1791.

phosphine oxide or arsine oxide type, as previously observed in the case of methylniobium tetrahalides.[1] Thus $WMeCl_5$ reacted with an excess of PPh_3O, $AsPh_3O$, or tdpo, according, for example, to equation (5).

$$WMeCl_5 + 2PPh_3O \longrightarrow WMeCl_3O{\cdot}OPPh_3 + PPh_3Cl_2 \qquad (5)$$

Monitoring of the reactions by n.m.r. spectroscopy showed that $WMeCl_5$ is immediately converted into the 1 : 1 adduct, $WMeCl_3O{\cdot}L$, at −25 °C, even if the L : W ratio is less than 1 : 1. The formation of an intermediate adduct, $WMeCl_5{\cdot}L$, was not detected.[4b,4c]

Methyltungsten(VI) *Chloride Dioxide Adducts.*—No alkylation was observed when $ZnMe_2$, $HgMe_2$, and $MgMe_2$ were treated with tungsten(VI) dichloride dioxide, under a range of conditions: solvents, toluene, diethyl ether, dioxan, and tetrahydrofuran; temperature −80 to 30 °C; and reaction times up to 4 d. When LiMe was added to WCl_2O_2 in ethers, only extensive side reactions, with formation of Li(OMe), were observed. However, we succeeded in preparing $WMeClO_2{\cdot}2OSMe_2$

$$\begin{tikzcd}
WMeCl_5 + SMe_2O \arrow[r, "-25\,^{\circ}C", "CH_2Cl_2"'] & WMeClO_2{\cdot}2OSMe_2 & (6) \\
WMeCl_3O + 3SMe_2O \arrow[ur, "-80\,^{\circ}C", "CH_2Cl_2"'] & & (7)
\end{tikzcd}$$

by the action of SMe_2O on $WMeCl_5$ or $WMeCl_3O$ according to reactions (6) and (7). Both reactions afforded the adduct in 90% yield.

EXPERIMENTAL

All reactions and manipulations were carried out in an oxygen-free dry argon atmosphere, using Schlenk-tube techniques.[15]

Tungsten hexachloride was freed from contaminating oxides by sublimation at 200 °C (0.01 mmHg); * tungsten tetrachloride oxide,[16] tungsten dichloride dioxide,[16] dimethylmercury,[17] dimethylzinc,[18] and dimethylmagnesium [19] were prepared according to the literature. Dichloromethane, acetonitrile, tris(dimethylamino)phosphine oxide (tdpo) (gift from Pierrefitte Co.), octamethylpyrophosphoramide (ompa) (gift from Murphy Co.), and trimethyl phosphate were dried over P_4O_{10}, distilled, and stored over molecular sieves (4 Å). Dimethyl sulphoxide was dried and distilled over calcium hydride, and dimethyl sulphite over magnesium sulphate. 1,2-Bis(diphenylphosphino)ethane (dppe) (Fluka) was used without further purification.

N.m.r. spectra (chemical shifts in p.p.m. from $SiMe_4$, at −35 °C; *ca.* 10^{-2} mol dm^{-3} solutions) were recorded on a JEOL C-60 HL spectrometer, i.r. spectra as Nujol mulls on a Perkin-Elmer model 557 instrument, and mass spectra on a CEC 21-130 spectrometer. Molecular-weight determinations were made with a Knauer vapour-pressure osmometer. Tungsten was determined gravimetrically as its oxide, chlorine by titration with a silver(I) nitrate solution (Fixanal) in the presence of potassium dichromate.[20] The other elemental analyses were by the Service Central de Microanalyses du CNRS. Melting points were measured in sealed tubes.

Methyltungsten(VI) *Pentachloride.*—Dimethylmercury (1.26 cm^3, 8.2 mmol) was added dropwise at −45 °C to a solution of WCl_6 (3.25 g, 8.25 mmol) in CH_2Cl_2 (40 cm^3) with stirring. After 1 h, cold pentane (120 cm^3) was added to the mixture at −45 °C in order to precipitate methylmercury chloride. After filtration at this temperature, the solvents were evaporated at −20 °C and the green-brown residue was washed with cold pentane (−20 °C; 2 × 10 cm^3). The green-brown powder was slowly recrystallised from dichloromethane–pentane (1 : 5) at −40 °C in *ca.* 1 week, 2.1 g (66%), m.p. 65 °C (decomp.) (Found: C, 3.10; Cl, 47.5. Calc. for CH_3Cl_5W: C, 3.30; Cl, 47.5%). The compound is soluble in toluene and dichloromethane. I.r. spectrum: 2 960m [$\nu_{asym}(CH_3)$]; 2 920m, 2 850m [$\nu_{sym}(CH_3)$]; 1 450m [$\delta_{asym}(CH_3)$]; 1 405—1 395 (sh) [$\delta_{sym}(CH_3)$]; 1 250, 1 090m, 1 040s [ν(C–H)]; 825m, 800s [$\rho(CH_3)$]; 465s [ν(W–C)]; and 400s cm^{-1} [ν(W–Cl)]. N.m.r. spectrum in CH_2Cl_2: δ(Me–W) 3.08 p.p.m., J(H–W) 2.9 Hz.

Methyltungsten(VI) *Trichloride Oxide using Dimethylmagnesium.*—A 0.3 mol dm^{-3} solution (7.0 cm^3) of $MgMe_2$ in diethyl ether was added very slowly to a suspension of WCl_4O (1.5 g) in pentane (150 cm^3) at −20 °C and maintained at this temperature for 4 h with stirring. A brown precipitate appeared, while the solution became yellow-orange. The solution was filtered and the solvents were evaporated at −45 °C, giving yellow-orange needles. This solid can be kept unchanged for several days at liquid-nitrogen temperature; dppe (1.0 g) was added, yield as $WMeCl_3O{\cdot}dppe$, 1.98 g (63%). It decomposes above −10 °C to give WCl_3O (*ca.* 80%). (An elemental analysis on the crude product obtained after evaporation of the solvent at −45 °C gave: Cl, 32.85; W, 57.1. Calc. for CH_3Cl_3OW: Cl, 33.0; W, 57.25%.) N.m.r. spectrum in CH_2Cl_2: δ(Me–W) 3.0 p.p.m., J(H–W) 3.0 Hz.

Methyltungsten(VI) *Trichloride Oxide*–1,2-*Bis*(*diphenylphosphino*)*ethane* (1/1).—A solution of dppe (1 g, 2.5 mmol) in CH_2Cl_2 (10 cm^3) was added to a bright yellow solution of $WMeCl_3O$ (2.5 mmol) in pentane (50 cm^3), and cooled to −35 °C. A green-yellow precipitate appeared very rapidly. After filtration of the clear solution at −35 °C, the precipitate was washed with pentane (2 × 10 cm^3), then recrystallised from toluene–pentane (1 : 2) at −45 °C, affording pure $WMeCl_3O{\cdot}dppe$, 1.98 g (63%) (Found: Cl, 14.5; W, 24.5. Calc. for $C_{27}H_{27}Cl_3OP_2W$: Cl, 14.65; W, 24.55%). I.r. spectrum: 1 305, 1 210 [$\rho(CH_2)$]; 1 090m, 1 065m [$\delta(CH_2)$]; 1 020m [ν(C–H)]; 995m [ν(W=O)]; 800m [$\rho(CH_3{-}W)$]; 725s [$\nu_{asym}(PCH_2)$]; 690s [$\nu_{sym}(PCH_2)$]; 530m [ν(W–C)]; 510s [(P–Ph)]; 475m [Ph(C=C)]; 445m; and 420m cm^{-1}. N.m.r. spectrum in CH_2Cl_2: δ(Me) 2.8; δ 7.25; and $\delta(CH_2{-}P)$ 3.4 p.p.m.

Methyltungsten(VI) *Trichloride Oxide.*—*From dimethyl-*

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

[15] D. F. Shriver, 'The Manipulation of Air Sensitive Compounds,' McGraw-Hill, London, 1969.

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[17] G. Brauer, 'Handbook of Preparative Inorganic Chemistry,' Academic Press, London, 1963, vol. 2, p. 1119.

[18] R. R. Renshaw and C. E. Greenlaw, *J. Amer. Chem. Soc.*, 1920, **42**, 1472.

[19] J. Thomas, *Bull. Soc. chim. France*, 1973, 1299.

[20] A. I. Vogel, 'Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1966, pp. 460 and 566.

mercury. Dimethylmercury (0.2 cm³, 2.5 mmol) was added very slowly (1 h) to an orange suspension of WCl_4O (0.8 g, 2.5 mmol) in dichloromethane–pentane (2 : 1) at *ca.* −80 °C. The solution became deep red and was stirred at this temperature for 1 h. Then HgMeCl was filtered off. Evaporation of the solvents, at the same temperature, gave a deep red residue which was agitated with cold pentane (−78 °C; 2 × 10 cm³) in order to remove all CH_2Cl_2. The orange solution yielded (after addition of 0.95 g of dppe) the same compound as above; yield as $WMeCl_3O$·dppe, 0.98 g (55%). The same reaction in toluene at −35 °C in 4 h gave a conversion ratio for $WMeCl_3O$ of only 40%.

From dimethylzinc. Dimethylzinc (0.3 g, 3.2 mmol) was added to a suspension of WCl_4O (2.2 g, 6.4 mmol) in pentane (50 cm³) at −98 °C. After the addition was complete, the mixture was slowly allowed to warm to −25 °C. At this temperature a small amount of OEt_2 (1 cm³, 9.6 mmol) was added. After 5 h of stirring at −25 °C, $ZnCl_2$ and WCl_3O were filtered off at −30 °C. The orange filtrate was cooled at −40 °C; dppe (2.4 g) was added, after purification as above. Yield as the $WMeCl_3O$·dppe adduct, 1.8 g (40%).

From dimethylzinc and tungsten(VI) *tetrachloride oxide–tetrahydrofuran* (1/1). Dimethylzinc (0.06 g, 0.7 mmol) was added to a suspension of WCl_4O·thf (0.6 g, 1.4 mmol) in pentane (30 cm³) at −98 °C. After the addition the mixture was slowly warmed to −50 °C. At this temperature the reaction is spontaneous. Purification was achieved as above yielding $WMeCl_3O$·dppe, 0.2 g (20%).

Methyltungsten Pentachloride–1,2-*Bis*(*diphenylphosphino*)-*ethane* (1/1).—The stoicheiometric amount of dppe (0.6 g, 1.5 mmol) in CH_2Cl_2 (10 cm³) was added to a solution of $WMeCl_5$ (1.5 mmol) in CH_2Cl_2 (10 cm³) at −35 °C. The mixture rapidly became yellow-brown. At the end of the addition the solvent was evaporated at −35 °C. The residue was extracted by cold dichloromethane–pentane (1 : 2) in order to eliminate any excess of bidentate ligand. After filtration the solution was cooled at −45 °C overnight, and gave a brown-green crystalline solid which was isolated by filtration and washed with cold pentane (2 × 5 cm³); yield 0.9 g (80%), m.p. 75 °C; decomposition occurs at *ca.* 110 °C (Found: C, 40.5; H, 3.30; Cl, 23.1. Calc. for $C_{27}H_{27}Cl_5P_2W$: C, 41.85; H, 3.40; Cl, 22.9%), *M* in acetonitrile: 1 454 (Calc.: 774). The complex is soluble in CH_2Cl_2, toluene, and acetonitrile. I.r. spectrum: 1 960w, 1 890w, 1 815w, 1 735w, 1 585w, 1 340m [$\delta_s(CH_3)$]; 1 305m, 1 260m [$\rho(CH_2)$]; 1 189, 1 165m, 1 150s, 1 120m, 1 095s [$\delta(CH_2)$]; 1 065m, 1 025m [α(C–H)]; 995m, 975—955 (sh), 905 (sh), 740s, 725s, 690s [$\nu_{asym}P(CH_2) + \rho(CH_3)$]; 665m, 535s, 510s [ν(W–C) + ν(P–Ph)]; 475m [ϕ(C=C)]; 440w, 400w, 320m, 300s [ν(W–Cl)]; and 280m cm⁻¹. N.m.r. spectrum in acetonitrile: δ(Me–W) 2.5 p.p.m. (br); $\delta(CH_2\text{–}P)$ 3.25; and δ(Ph–P) 7.07 p.p.m.

Methyltungsten Pentachloride–Octamethylpyrophosphoramide (1/1).—The ligand (0.29 g, 1 mmol) was added to a solution of $WMeCl_5$ (1.1 mmol) in CH_2Cl_2 (30 cm³) at −35 °C. The solution became dark yellow-brown. After partial evaporation of the solvent, the solution (10 cm³) was cooled for 2 d at −45 °C and a dark brown-green solid precipitated. It was filtered off, washed with pentane and dried under reduced pressure for 48 h at room temperature, yield 0.4 g (60%), *M* in acetonitrile: 774 (Calc.: 662), m.p. 140 °C (decomp.) (Found: C, 15.85; H, 3.90; Cl, 27.0. Calc. for $C_9H_{27}Cl_5N_4O_3P_2W$: C, 16.3; H, 4.05; Cl, 26.8%). I.r. spectrum: 1 175s [ν(P=O)]; 1 130m, 1 115m, 1 070m [ν(C–H)]; 1 090—990 (sh),s [ω(P–N)]; 935s [ν_{asym}(P–O–P)]; 790m [$\rho(CH_3)$]; 770—760m [ω(P=O) + ν_{sym}(P–O–P)]; 675m, 545m, 485s, 455m [ν(W–C) + α(P–O) + ν_{sym}(P–O–P)]; and 380s cm⁻¹ [ν(W–Cl) or ν(W–O)]. N.m.r. spectrum in CH_2Cl_2: δ(Me–W) 2.95; δ_L 2.7 (br); and δ_P −10.75 (br) p.p.m. (H_3PO_4).

Methyltungsten Trichloride Oxide–Tris(*dimethylamino*)-*phosphine Oxide* (1/1). *From methyltungsten pentachloride.* Tris(dimethylamino)phosphine oxide (0.59 cm³, 2.4 mmol) was injected through a serum cap into a solution of $WMeCl_5$ (0.08 mmol) in CH_2Cl_2 (10 cm³) at −25 °C. The solution became deep green. After 4 h the solvent was evaporated at this temperature and CH_2Cl_2–toluene–pentane (0.3 : 1 : 0.3) was added to the oily residue. Dark-green plates formed after 2 d at −45 °C, 0.2 g (50%), m.p. 73—74 °C (decomp.) (Found: C, 16.9; H, 4.1; Cl, 21.5; W, 37.6. Calc. for $C_7H_{21}Cl_3N_3O_2PW$: C, 17.15; H, 4.30; Cl, 21.55; W, 37.6%). The complex is very soluble in CH_2Cl_2 and acetonitrile. I.r. spectrum: 1 170s [ν(P=O)]; 1 150m, 1 070m [ν(C–H)]; 1 050—1 010, 1 000 (sh),s [ω(P–N) + ν(W=O)], 800m [$\rho(CH_3)$]; 760—750m [ω(P–N)]; 480m [δ(P=O)]; and 465m cm⁻¹ [ν(W–C)]. N.m.r. spectrum in CH_2Cl_2: δ(Me–W) 3.0 and δ_L 2.67 p.p.m.; *J*(P–H) 12.0 Hz.

From methyltungsten trichloride oxide.—The ligand (0.05 cm³, 0.3 mmol) was added to a deep red solution of $WMeCl_3O$ (0.03 mmol) (from a stock solution titrated by dppe) in CH_2Cl_2 (10 cm³) at *ca.* −80 °C. The solution immediately became deep green. The solvent was evaporated at −35 °C. The complex recrystallised slowly from dichloromethane–toluene–pentane (1 : 1 : 2) at −40 °C, and was identical to $WMeCl_3O$·tdpo.

Methyltungsten Trichloride Oxide–Triphenylphosphine Oxide (1/1).—A solution of PPh_3O (1.12 g, 4 mmol) in CH_2Cl_2 (4 cm³) was added to a solution of $WMeCl_5$ (0.8 mmol) in CH_2Cl_2 (10 cm³) at −25 °C. The solution became dark green. After addition the solution was stirred for 4 h at −25 °C. The solvent was evaporated *in vacuo* and the residue was washed with toluene–pentane (2 : 1) in order to dissolve the excess of PPh_3O and the PPh_3Cl_2. The residue when dissolved in CH_2Cl_2 (10 cm³) gave a dark green solution. Dark green plates crystallised at −45 °C after addition of pentane (3 cm³), 0.3 g (60%), m.p. 58 °C, 65—70 °C (decomp.) (Found: C, 37.7; H, 2.90; Cl, 17.4; W, 30.5. Calc. for $C_{19}H_{18}Cl_{13}O_2PW$: C, 38.1; H, 3.00; Cl, 17.55; W, 30.7%). I.r. spectrum: 1 160—1 155s [ν(P=O)]; 1 115m [ν(P–Ph)]; 1 075m [ν(C–H); 1 020s [ν(W=O)]; 800s [$\rho(CH_3)$]; 720s [ν(P–Ph)]; 690m, 610m, 540s [ν(P–Ph)]; 465, 450—445(sh),s [ν(W–C)]; and 410m cm⁻¹ [ν(W–O) or ν(W–Cl)]. N.m.r. spectrum in acetonitrile: δ(Me–W) 2.5 and δ(Ph) 7.6 p.p.m.

Methyltungsten Trichloride Oxide–Triphenylarsine Oxide (1/1).—The reaction of a solution of $AsPh_3O$ (1.6 g, 5 mmol) in CH_2Cl_2 (5 cm³) with $WMeCl_5$ (2.1 mmol) in CH_2Cl_2 (20 cm³), using the same procedure as above, yielded 0.7 g (75%) of a dark green-yellow solid, m.p. 51 °C, 55 °C (decomp.) (Found: C, 35.1; H, 2.6; Cl, 16.3; W, 28.55. Calc. for $C_{19}H_{18}AsCl_3O_2W$: C, 35.5; H, 2.8; Cl, 16.4; W, 28.65%). I.r. spectrum: 1 250m, 1 160m, 1 145m, 1 070s [ν(C–H)]; 1 010s [ν(W=O)]; 960m, 815m, 790s [ν(As=O + $\rho(CH_3)$]; 720s [ν(As–Ph)]; 460m [ν(W–C)]; and 420m cm⁻¹ [ν(W–O) or ν(W–Cl)]. N.m.r. spectrum in acetonitrile: δ(Me–W) 2.6 and δ(Ph) 7.92 p.p.m.

Methyltungsten Chloride Dioxide–Dimethyl Sulphoxide (1/2).—*From methyltungsten pentachloride.* Dimethyl sulphoxide (0.21 cm³, 3 mmol) was added to a brown solution of

$WMeCl_5$ (0.75 mmol) in CH_2Cl_2 (10 cm^3) at −25 °C. The solution became light yellow. The complex $WMeClO_2\cdot 2OSMe_2$ was isolated as white crystals on addition of pentane (5 cm^3) and cooling to −40 °C, 0.25 g (90%), m.p. 110 °C (decomp.) (Found: C, 14.0; H, 3.4; Cl, 8.0; S, 14.8. Calc. for $C_5H_{15}ClO_4S_2W$: C, 14.2; H, 3.55; Cl, 8.5; S, 15.0%). The compound is soluble in acetonitrile. I.r. spectrum: 3 000m, 2 960m [$\nu_{asym} + \nu_{sym}(CH_3)$]; 1 420m [$\delta_{asym}(CH_3{-}W)$]; 1 400m [$\delta_{sym}(CH_3{-}W)$]; 1 320—1 295m [$\delta_{asym} + \delta_{sym}(CH_3{-}S)$]; 1 030s [$\nu(S{=}O)$]; 995s, 985s, 950s [$\nu(W{=}O)$]; 940s, 925vs [$\nu(S{=}O)$]; 890vs [$\nu(W{=}O)$]; 735—720m [$\nu(C{-}S)$]; 455—435 (sh),s [$\nu(W{-}C)$]; 345s,br [$\nu(W{-}Cl)$]; 320m [$\nu(C{-}S{-}O)$]; and 250m cm^{-1} [$\nu(W{-}O)$]. N.m.r. spectrum in acetonitrile: $\delta(Me{-}W)$ 2.85 and $\delta(Me{-}S)$ 2.9 p.p.m.

From methyltungsten trichloride oxide. The ligand (0.41 g, 5.25 mmol) was added to a solution of $WMeCl_3O$ (1.75 mmol) in CH_2Cl_2 (50 cm^3), cooled to −78 °C. The solution became yellow. After the addition was complete the mixture was warmed to −40 °C and pentane (20 cm^3) was added. The adduct precipitated slowly, 0.67 g (90%).

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