Synthesis of Chloro(trimethylphosphine)tris(trimethylsilylmethyl)-tungsten(IV); Synthesis and Molecular Structure of Di-μ-chloro-bis-[dicarbonyl(trimethylphosphine)(1—2-η-trimethylsilylmethylcarbonyl)-tungsten(II)] †

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The interaction of $[MgCl(CH_2SiMe_3)]$ or $[Mg(CH_2SiMe_3)_2]$ with $[WCl_4(PMe_3)_2]$ yields the five-co-ordinate paramagnetic tungsten(IV) alkyl $[WCl(CH_2SiMe_3)_3(PMe_3)]$ which reacts with carbon monoxide to give an η^2-acyl dimeric complex $[\{WCl(1—2\text{-}\eta\text{-}COCH_2SiMe_3)(CO)_2(PMe_3)\}_2]$. The crystal structure of the latter has been determined from three-dimensional *X*-ray diffraction data collected by counter methods. It crystallizes in the monoclinic space group $P2_1/c$, isomorphous with the molybdenum analogue, with $a = 8.420(3)$, $b = 10.449(3)$, $c = 19.300(4)$ Å, $\beta = 90.59(2)°$, and $Z = 2$. The final *R* value was 0.016 for 1 218 independent observed reflections. The molecule exists as a chloride-bridged dimer with an η^2-acyl linkage. The tungsten–carbon(acyl) bond length is 2.029(7) Å and the tungsten–oxygen(acyl) distance is 2.289(5) Å.

Molybdenum(IV) and tungsten(IV) organometallic complexes containing metal-to-carbon σ bonds other than those with π-cyclopentadienyl groups are relatively uncommon. A five-co-ordinate paramagnetic molybdenum(IV) alkyl, $[MoCl(CH_2SiMe_3)_3(PMe_3)]$, has been prepared and structurally characterized by Wilkinson and co-workers,[1] from the reaction between $[MoCl_4(thf)_2]$ (thf = tetrahydrofuran) and $[Mg(CH_2SiMe_3)_2]$ in the presence of PMe_3. A similar reaction between $[WCl_4(thf)_2]$ and $[Mg(CH_2C_6H_5)_2]$, in the absence of phosphine ligands has been reported [2] to yield diamagnetic $[W(CH_2C_6H_5)_4]$. In contrast, interaction of WCl_6, WCl_5, or WCl_4 with magnesium or lithium reagents derived from Me_3SiCH_2Cl, does not yield W^{IV} derivatives,[3] but instead monomeric and dimeric W^V and W^{VI} carbyne complexes and/or the triply metal–metal bonded W^{III} compound, $[W_2(CH_2SiMe_3)_6]$. We have found that the reaction of $[WCl_4(PMe_3)_2]$ with $[MgCl(CH_2SiMe_3)]$ or $[Mg(CH_2SiMe_3)_2]$ yields the monomeric tungsten(IV) alkyl, $[WCl(CH_2SiMe_3)_3(PMe_3)]$. As with the molybdenum analogue,[1] this complex can be carbonylated at room temperature and pressure to give a tungsten(II) complex of stoicheiometry $[\{WCl(1—2\text{-}\eta\text{-}COCH_2SiMe_3)(CO)_2(PMe_3)\}_2]$. Analytical and spectroscopic data (see Experimental section) are in accord with the structures determined by *X*-ray crystallography.

Results and Discussion

The metathetic reactions of binary or complex chloride derivatives of molybdenum and tungsten with organolithium or organomagnesium reagents have proved to be very complex and are not yet fully understood.[1,3] The interaction between $[WCl_4(PMe_3)_2]$ and $[MgCl(CH_2SiMe_3)]$ or $[Mg(CH_2SiMe_3)_2]$ (2.5 equivalents), described herein, provides an additional example of such complexity. When these reactants are stirred in diethyl ether at room temperature, a blue-violet solution is obtained from which dark blue crystals of $[WCl(CH_2SiMe_3)_3(PMe_3)]$ (1) can be collected in low yield (*ca.* 15%). Although this is the only pure tungsten complex that we have been able to isolate from this system so far, other tungsten-containing compounds, which are still under investigation, are also formed. Complex (1) is thermally stable once isolated as a pure crystalline solid, but is very air and moisture sensitive, both in solution and as a crystalline material. In contrast to $[W(CH_2C_6H_5)_4]$ [2] and $[WCl_3(C_6H_5)]$,[4] which have been reported to be diamagnetic, complex (1) is paramagnetic. Magnetic susceptibility studies, using the Evans' method [5] gave $\mu_{eff.} = 2.37$ B.M. at 35 °C, in the range found for other monomeric chloro(tertiary phosphine)tungsten(IV) derivatives.[6]

Unit-cell data (see Experimental section) for single crystals of (1) were obtained from a least-squares refinement of $(\sin\theta/\lambda)^2$ values for 15 reflections ($\theta > 20°$) accurately centred on an Enraf-Nonius CAD-4 diffractometer. The complex was found to be isostructural with its molybdenum analogue [1] and further data were not collected.

Interaction of light petroleum solutions of (1) with carbon monoxide, at room temperature and pressure, produced deposition of a yellow-brown solid, identified as $[\{WCl(COCH_2SiMe_3)(CO)_2(PMe_3)\}_2]$ (2). Although indefinitely stable as a crystalline solid, in the absence of air and moisture, complex (2) decomposes slowly in solution at room temperature, even under N_2. The i.r. spectrum shows two very strong absorptions at 1 920 and 1 825 cm^{-1} that can be assigned to ν(CO) of the terminal carbonyl groups, and a medium intensity band at 1 530 cm^{-1}, which indicates the presence of an η^2-acyl linkage. The ^1H n.m.r. spectrum of (2) (see Experimental section) is in good agreement with the proposed formulation.

The structure and atom numbering scheme for complex (2) are shown in the Figure; it is isostructural with its molybdenum analogue.[1] This complex exists as a chloride-bridged dimer with an η^2-acyl linkage and resides around a crystallographic centre of inversion. The W–P bond distances [2.475(2) Å], W–Cl bridging lengths [2.532(2) and 2.567(2) Å],

† *Supplementary data available* (No. SUP 23525, 10 pp.): structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: B.M. = 0.927×10^{-23} A m^2.

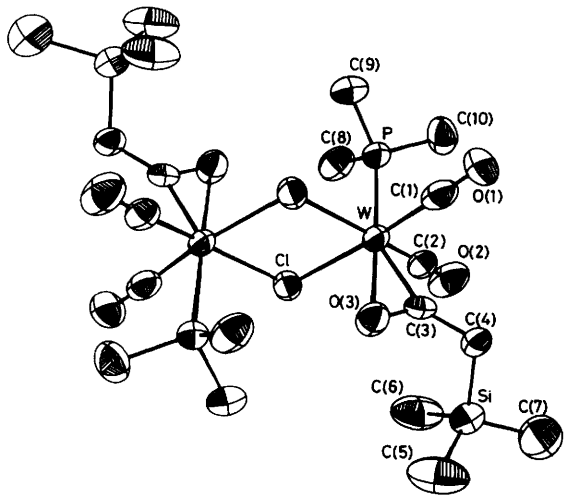

Figure. The molecular structure of di-μ-chloro-bis[dicarbonyl-(trimethylphosphine)(1—2-η-trimethylsilylmethylcarbonyl)-tungsten(II)] (2) with the atoms represented by their 50% probability ellipsoids for thermal motion

Table 1. Interatomic bond distances (Å) and angles (°) for [{WCl(1—2-η-$COCH_2SiMe_3$)$(CO)_2(PMe_3)$}$_2$] (2) with estimated standard deviations in parentheses

W–Cl	2.567(2)	W–Cl′	2.532(2)
W–P	2.475(2)	W–O(3)	2.289(5)
W–C(1)	1.93(1)	W–C(2)	1.92(1)
W–C(3)	2.029(7)	P–C(8)	1.803(9)
P–C(9)	1.804(9)	P–C(10)	1.795(9)
Si–C(4)	1.906(8)	Si–C(5)	1.84(1)
Si–C(6)	1.83(1)	Si–C(7)	1.83(1)
O(1)–C(1)	1.18(1)	O(2)–C(2)	1.185(9)
O(3)–C(3)	1.233(9)	C(3)–C(4)	1.47(1)
Cl–W–Cl′	79.55(6)	Cl–W–P	96.32(7)
Cl′–W–P	91.76(7)	Cl–W–O(3)	83.9(2)
Cl′–W–O(3)	86.1(1)	P–W–O(3)	177.7(2)
Cl–W–C(1)	173.8(2)	Cl–W–C(1)	94.7(3)
P–W–C(1)	81.5(2)	O(3)–W–C(1)	98.0(3)
Cl–W–C(2)	91.5(3)	Cl′–W–C(2)	166.3(2)
P–W–C(2)	78.8(2)	O(3)–W–C(2)	103.4(3)
C(1)–W–C(2)	93.8(4)	Cl–W–C(3)	103.7(2)
Cl′–W–C(3)	114.7(2)	P–W–C(3)	149.1(2)
O(3)–W–C(3)	32.5(2)	C(1)–W–C(3)	80.7(3)
C(2)–W–C(3)	77.4(3)	W–Cl–W′	100.45(6)
W–P–C(8)	115.8(3)	W–P–C(9)	113.5(3)
C(8)–P–C(9)	102.9(4)	W–P–C(10)	116.7(3)
C(8)–P–C(10)	102.7(4)	C(9)–P–C(10)	103.4(4)
C(4)–Si–C(5)	109.1(4)	C(4)–Si–C(6)	111.2(4)
C(5)–Si–C(6)	108.4(5)	C(4)–Si–C(7)	105.6(5)
C(5)–Si–C(7)	111.8(6)	C(6)–Si–C(7)	110.6(6)
W–O(3)–C(3)	62.1(4)	W–C(1)–O(1)	177.6(8)
W–C(2)–O(2)	179.3(7)	W–C(3)–O(3)	85.4(5)
W–C(3)–C(4)	147.0(6)	O(3)–C(3)–C(4)	127.5(7)
Si–C(4)–C(3)	113.0(5)		

Primed atoms are related to those in Table 2 by a crystallographic centre of inversion at (0, ½, ½).

and the average W–C(carbonyl) bond length [1.92(1) Å] given in Table 1 all agree well with those found for the Mo analogue and other compounds of this type.

The η^2-acyl linkage, as with others we have found, is characterized by a short metal–carbon bond [2.029(7) Å] approaching a normal metal–carbonyl distance, and a metal–oxygen separation [2.289(5) Å] indicative of a single bond. The W–C(acyl) bond length is shorter than the W–O(acyl) distance by 0.26 Å. Corresponding differences in [MoCl(1—2-η-$COCH_2SiMe_3$)$(CO)(PMe_3)_3$],[7] [{MoCl(1—2-η-$COCH_2SiMe_3$)$(CO)_2(PMe_3)$}$_2$],[1] and [WCl(1—2-η-$COCH_2SiMe_3$)$(CO)(PMe_3)_3$][7] of 0.30, 0.27, and 0.23 Å respectively, have been observed.

Experimental

Microanalyses were by Pascher (Bonn) Microanalytical Laboratories and Butterworth Microanalytical Consultancy Ltd., Middlesex. The spectroscopic instruments used were a Perkin-Elmer 457 for i.r. spectra and a Perkin-Elmer R-12A for ^{1}H n.m.r. spectra. Magnetic susceptibilities were determined by the Evans' method.[5] The compound [$Mg(CH_2SiMe_3)_2$] was prepared from [$MgCl(CH_2SiMe_3)$] and 1,4-dioxan, and [$WCl_4(PMe_3)_2$] was prepared[8] from WCl_6 and PMe_3.[9] Solvents were dried using conventional procedures and distilled under N_2 before use. The light petroleum used had b.p. 40—60 °C. All preparations and other operations were carried out under N_2.

Chloro(trimethylphosphine)tris(trimethylsilylmethyl)tungsten(IV) (1).—To a stirred suspension of [$WCl_4(PMe_3)_2$] (0.48 g, *ca.* 1.0 mmol) in diethyl ether (40 cm^3) at −30 °C was added [$MgCl(CH_2SiMe_3)$] or [$Mg(CH_2SiMe_3)_2$] (2.5 equivalents). The resulting mixture was allowed to warm up to −10 °C and stirred at this temperature until almost all the initial [$WCl_4(PMe_3)_2$] had reacted (*ca.* 15 min). The deep blue-violet solution produced was quickly evaporated *in vacuo* at −10 °C and the product dissolved in light petroleum (40 cm^3). The solution was centrifuged to separate insoluble materials and the product crystallized by removing part of the solvent and cooling at −20 °C overnight. Recrystallization from light petroleum gave dark blue crystals of the pure product in *ca.* 15—20% yield (Found: C, 32.0; H, 7.5. $C_{15}H_{42}ClPSi_3W$ requires C, 32.3; H, 7.5%). Infrared (Nujol mull) bands at 1 420, 1 300, 1 280, 1 250, 1 240, 1 135, 940, 870, 835, 750, 720, 700, and 660 cm^{-1}. The complex is paramagnetic as expected for W^{IV}, with $\mu_{eff.}$ = 2.37 B.M., at *ca.* 35 °C (average of two determinations).

Crystal data. $C_{15}H_{42}ClPSi_3W$, M = 557.0, Monoclinic, a = 10.445(4), b = 19.244(6), c = 12.910(5) Å, β = 91.70(3)°, U = 2 593.8 Å^3, Z = 4, D_c = 1.43 g cm^{-3}, space group $P2_1/n$ from the systematic absences in $h0l$, $h + l = 2n + 1$ and in $0k0$, $k = 2n + 1$.

Di-μ-chloro-bis[dicarbonyl(trimethylphosphine)(1—2-η-trimethylsilylmethylcarbonyl)tungsten(II)] (2).—The dark blue solid (0.080 g, *ca.* 0.15 mmol) resulting from cooling the light petroleum solution at −20 °C (see above) was redissolved in light petroleum (10 cm^3) and treated with CO at room temperature and pressure for 2 h. A yellow powder resulted (*ca.* 0.035 g, 40% yield), which was recrystallized from diethyl ether at −20 °C, in the presence of small amounts of PMe_3. Although indefinitely stable at room temperature as a crystalline solid in the absence of air, complex (2) decomposes slowly in solution even when kept under N_2 (Found: C, 27.9; H, 4.5; P, 6.3. $C_{20}H_{40}Cl_2O_6P_2Si_2W_2$ requires C, 25.7; H, 4.2; P, 6.6%). Infrared (Nujol mull) bands at 1 920, 1 825, 1 530, 1 420, 1 310, 1 290, 1 250, 1 180, 1 070, 1 020, 950, 845, 800, 770, 735, 700, and 660 cm^{-1}. ^{1}H N.m.r. (C_6H_6, at *ca.* 35 °C): δ (p.p.m.) 3.25 (s, W–$COCH_2$), 1.85 [d, P–Me, J(P–H) = 10 Hz], 0.30 (s, $SiMe_3$).

X-Ray Data Collection, Structure Determination, and Refinement for [{WCl(1—2-η-$COCH_2SiMe_3$)$(CO)_2(PMe_3)$}$_2$]

Table 2. Final fractional co-ordinates for [{WCl(1—2-η-$COCH_2SiMe_3$)$(CO)_2(PMe_3)$}$_2$] (2) with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
W	0.148 71(4)	0.367 57(3)	0.469 74(2)
Cl	−0.069 1(2)	0.405 0(2)	0.559 58(9)
P	−0.028 2(2)	0.280 1(2)	0.378 1(1)
Si	0.481 0(3)	0.212 7(3)	0.640 3(1)
O(1)	0.395 2(7)	0.341 6(7)	0.351 5(3)
O(2)	0.160 1(8)	0.077 6(6)	0.504 3(4)
O(3)	0.311 5(6)	0.456 2(5)	0.552 4(3)
C(1)	0.302(1)	0.354 4(8)	0.396 5(5)
C(2)	0.155 4(9)	0.188 2(9)	0.490 7(4)
C(3)	0.350 0(9)	0.351 9(8)	0.527 9(4)
C(4)	0.488 2(9)	0.272 9(8)	0.547 2(4)
C(5)	0.556(1)	0.339(1)	0.698 9(5)
C(6)	0.278(1)	0.173(1)	0.665 2(5)
C(7)	0.608(2)	0.070(1)	0.642 8(6)
C(8)	−0.222(1)	0.229 3(9)	0.405 9(5)
C(9)	−0.074(1)	0.393(1)	0.310 2(4)
C(10)	0.043(1)	0.143(1)	0.331 8(5)
H(1) [C(4)]	0.594 8	0.328 4	0.542 5
H(2) [C(4)]	0.490 8	0.183 5	0.508 4
H(3) [C(5)]	0.555 3	0.306 2	0.753 1
H(4) [C(5)]	0.492 9	0.430 4	0.686 4
H(5) [C(5)]	0.677 5	0.359 5	0.691 0
H(6) [C(6)]	0.281 0	0.125 7	0.703 4
H(7) [C(6)]	0.215 1	0.274 2	0.662 3
H(8) [C(6)]	0.207 1	0.111 0	0.634 7
H(9) [C(7)]	0.721 0	0.092 3	0.633 0
H(10) [C(7)]	0.600 0	0.040 9	0.686 1
H(11) [C(7)]	0.570 1	−0.000 2	0.605 2
H(12) [C(8)]	−0.196 5	0.165 1	0.439 6
H(13) [C(8)]	−0.281 4	0.315 7	0.420 0
H(14) [C(8)]	−0.297 6	0.189 4	0.372 9
H(15) [C(9)]	−0.144 0	0.351 5	0.273 2
H(16) [C(9)]	0.022 8	0.406 5	0.286 9
H(17) [C(9)]	−0.130 1	0.457 1	0.328 3
H(18) [C(10)]	0.134 9	0.157 4	0.315 7
H(19) [C(10)]	0.060 2	0.066 6	0.361 9
H(20) [C(10)]	−0.031 7	0.108 9	0.299 3

(2).—*Crystal data.* $C_{20}H_{40}Cl_2O_6P_2Si_2W_2$, M = 933.3, Monoclinic, a = 8.420(3), b = 10.449(3), c = 19.300(4) Å, β = 90.59(2)°, U = 1 697.9 Å^3, Z = 2, D_c = 1.83 g cm^{-3}, μ(Mo-K_α) = 75.27 cm^{-1}, F(000) = 896, λ(Mo-K_α) = 0.7107 Å, space group $P2_1/c$. The lattice parameters were determined from a least-squares refinement of the angular settings of 15 reflections (2θ ≥ 30°) accurately centred on an Enraf-Nonius CAD-4 diffractometer.

A crystal of dimensions 0.15 × 0.22 × 0.33 mm was sealed in a thin-walled capillary under an N_2 atmosphere. Data were collected on the diffractometer with graphite-crystal monochromated molybdenum radiation. The diffracted intensities were measured by the ω—2θ scan technique in a manner similar to that described previously.[10] 1 941 Reflections in one independent quadrant out to 2θ ≤ 40° were measured; 1 218 were considered observed [$I \geq 3\sigma(I)$]. The intensities were corrected for Lorentz and polarization effects, and for absorption.

Calculations were carried out with the SHELX system of programs.[11] The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Atomic scattering factors for W, Cl, P, Si, O, and C were taken from Cromer and Waber; [12] those for H were taken from ref. 13. The scattering factor for tungsten was corrected for the real and imaginary components of anomalous dispersion using the values of Cromer and Liberman.[14]

The final fractional co-ordinates for the Mo analogue [1] were used as a starting point in the refinement of this compound. Refinement with isotropic thermal parameters led to a reliability index of R = 0.046. Conversion to anisotropic thermal parameters and further refinement led to R = 0.022. The hydrogen atoms were located on a difference-Fourier map, and their parameters were not refined. Additional cycles of refinement of the non-hydrogen atoms led to final values of R = 0.016 and R' = 0.019. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. A final difference-Fourier map showed no feature greater than 0.2 e Å^{-3}. The standard deviation of an observation of unit weight was 1.80. Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F_c|)$ *vs.* $|F_o|$ or (sin θ)/λ was noted. The final values of the positional parameters are given in Table 2.

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References

1 E. Carmona, G. Wilkinson, J. L. Atwood, R. D. Rogers, W. E. Hunter, and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1978, 465; *J. Chem. Soc., Dalton Trans.*, 1980, 229.
2 K.-H. Thiele, A. Russek, R. Opitz, B. Mohai, and W. Brüser, *Z. Anorg. Allg. Chem.*, 1975, **412**, 11.
3 R. A. Andersen, M. H. Chisholm, J. F. Gibson, W. W. Reichert, I. P. Rothwell, and G. Wilkinson, *Inorg. Chem.*, 1981, **20**, 3934 and refs. 11—13 therein.
4 W. Grahlert, K. Milowski, and U. Langbein, *Z. Chem.*, 1974, **14**, 287, as referenced in R. R. Schrock and G. W. Parshall, *Chem. Rev.*, 1976, **76**, 243.
5 D. F. Evans, *J. Chem. Soc.*, 1959, 2003.
6 See, for example, Z. Dori, *Prog. Inorg. Chem.*, 1981, **28**, 239.
7 R. D. Rogers, J. L. Atwood, E. Carmona, J. M. Marín, M. L. Poveda, and L. Sánchez, manuscript in preparation.
8 E. Carmona, L. Sánchez, M. L. Poveda, R. A. Jones, and J. G. Hefner, *Polyhedron*, in the press.
9 W. Wolfsberger and H. Schmidbaur, *Synth. React. Inorg. Metal-Org. Chem.*, 1974, **4**, 149.
10 J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Dalton Trans.*, 1979, 45.
11 SHELX system of computer programs for *X*-ray structure determination, G. M. Sheldrick, University of Cambridge, 1976.
12 D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 1965, **18**, 104.
13 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, p. 72.
14 D. T. Cromer and D. J. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

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