CRYSTAL STRUCTURE OF $\overline{\text{W[C(CMe}_3\text{)C(Me)}\dot{\text{C}}\text{(Me)]}}\text{Cl}_3$, THE ARCHETYPAL EXAMPLE OF A PLANAR DELOCALIZED TUNGSTENACYCLOBUTADIENE COMPLEX

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(Received February 28th, 1984)

Summary

The complex $\overline{\text{W[C(CMe}_3\text{)C(Me)}\dot{\text{C}}\text{(Me)]}}\text{Cl}_3$ has been subjected to a single-crystal X-ray diffraction study. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (No. 14) with a 10.2710(22), b 10.1132(21), c 12.7205(26) Å, β 96.099(17)°, V 1313.8(5) Å^3 and D(calcd) 2.09 g cm^{-3} for mol. wt. 413.43 and $Z = 4$. Diffractometer data were collected for reflections with $2\theta = 3.7$–$50.0°$ (Mo-K_α) and the structure was solved and refined to R_F 4.6% for 2327 data. The tungsten atom has a distorted trigonal bipyramidal coordination geometry. Two chloride ligands are in axial sites (W–Cl(1) 2.404(2), W–Cl(2) 2.394(2) Å), while the third occupies an equatorial position (W–Cl(3) 2.330(3) Å). The tungstenacyclobutadiene system, W–C(1)–C(6)–C(7), is planar and occupies two equatorial sites. The W–C(α) linkages (W–C(1) 1.861(9), W–C(7) 1.864(8) Å) are equivalent, as are the C(α)–C(β) bond lengths (C(1)–C(6) 1.455(13), C(6)–C(7) 1.478(12) Å).

Introduction

The olefin metathesis reaction (see eq. 1) has been the subject of much investigation during the past few years; much of this work has been summed up in recent review articles [1–4]. It is now fairly convincingly established that the reaction proceeds through alkylidene (carbene) and metallacyclobutane intermediates (see eq. 2), as was originally suggested by Hérisson and Chauvin [5]. Indeed, the various alkylidenemetal species have been observed in situ during the course of a metathesis reaction [6].

$$\text{RCH=CHR} + \text{R'CH=CHR'} \rightleftharpoons 2\text{RCH=CHR'} \tag{1}$$

$$\begin{array}{cccc} \text{M=CHR} & \rightleftharpoons & \text{M–CHR} & \rightleftarrows & \text{M} & + & \text{RCH} \\ + & & | \quad | & & \| & & \| \\ \text{R'CH=CHR'} & & \text{R'HC–CHR'} & & \text{R'CH} & & \text{R'CH} \end{array} \tag{2}$$

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More recently, Schrock and coworkers have reported that the species $W[C(CMe_3)](OCMe_3)_3$ acts as a catalyst to metathesize dialkylacetylenes [7,8]. In strict analogy with the olefin metathesis reaction (vide supra), this acetylene methathesis reaction (or alkyne metathesis reaction) is believed to proceed through a metallacyclobutadiene intermediate [9], see eq. 3.
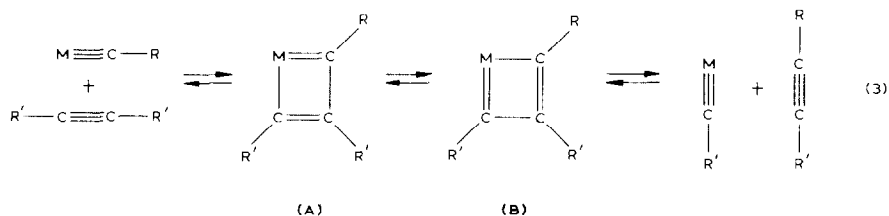
The nature of the intermediate metallacyclobutadiene system is unknown. It could be a delocalized system, or it could exist in two discrete forms (i.e., **A** and **B** of eq. 3).

Although $W[C(CMe_3)](OCMe_3)_3$ is an efficacious catalyst for metathesizing dialkylacetylenes, certain related species (especially those in which the tungsten atom has a higher coordination number) react stoichiometrically with metal alkylidynes (carbynes) [10]. Thus, addition of one equivalent of 2-butyne to $W[\equiv C(CMe_3)]$-$[Me\overline{O}(CH_2)_2\overline{O}Me]Cl_3$ produces an isolable species of stoichiometry $W[C(CMe_3)]$-$[MeC\equiv CMe]Cl_3$ shown herein to be a tungstenacyclobutadiene complex and hereafter represented as $\overline{W[C(CMe_3)C(Me)\overline{C}(Me)]Cl_3}$.

Interestingly, the reaction of excess 2-butyne [10] with $W[C(CMe_3)]$-$[Me\overline{O}(CH_2)_2\overline{O}Me]Cl_3$ yields an essentially equimolar (in tungsten) mixture of "$W[C(CMe_3)](MeC\equiv CMe)_3Cl_2$" and "$[WC(CMe_3)(MeC\equiv CMe)_2Cl_4]_2$". The former of these has been shown [11] to be an η^5-cyclopentadienyl complex of tungsten(III), $W[\eta^5-C_5Me_4(CMe_3)](\eta^2-MeC\equiv CMe)Cl_2$; the latter is almost certainly a related tungsten(V) species, $[W(\eta^5-C_5Me_4(CMe_3))Cl_4]_2$.

Experimental

Collection of X-ray diffraction data

The complex $W[C(CMe_3)C(Me)\overline{C}(Me)]Cl_3$ characteristically crystallizes as rather thin violet plates. The crystal selected for the single-crystal X-ray diffraction study was of approximate orthogonal dimensions $0.3 \times 0.2 \times 0.1$ mm. It was sealed into a thin-walled glass capillary tube under an argon atmosphere in a KSE re-circulating dry-box which had been specially modified (with a protruding transparent addition mounted between the gloves) so as to allow inspection of crystals through an external binocular polarizing microscope. The capillary was flame-sealed and set (with bees' wax) into an aluminium pin, which was then mounted into a eucentric goniometer and placed on our Syntex $P2_1$ automated four-circle diffractometer. All subsequent set-up operations (i.e., determination of unit cell parameters and the crystal's orientation matrix) and data collection were performed as described previously [12]. Details of the present study are provided in Table 1.

The systematic absences ($h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$) are consistent only with the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; No. 14) [13].

Diffraction data were corrected for absorption, averaged to provide a unique

data-set, corrected for Lorentz and polarization effects and reduced to observed structure factor amplitudes. Any reflection with a net intensity of less than zero was assigned an $|F_0|$ value of zero. All data were retained save for the $11\bar{1}$ reflection which appeared to be slightly "clipped" by the back-stop and also was too intense to be properly corrected for coincidence losses.

Solution and refinement of the crystal structure

All crystallographic calculations were performed on our in-house Syntex XTL system consisting of a Data General NOVA 1200 computer (with parallel floating-point processor), a Diablo disk unit, a Versatec printer/plotter and our locally-modified version of the XTL interactive crystallographic program package.

Data were placed on an approximately absolute scale by means of a Wilson plot. The structure was solved by direct methods using the program MULTAN [14]; an E-map based on the solution with the highest "figure of merit" (with those 248 data having $|E| \geqslant 1.62$) revealed the WCl_3 portion of the molecule. A subsequent difference-Fourier map yielded the positions of all remaining non-hydrogen atoms. Full-matrix least-squares refinement of the scale-factor and positional and anisotropic thermal parameters for the 13 non-hydrogen atoms led to convergence with

TABLE 1

EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY OF $\overline{W[C(C(CMe_3)-}$ $\overline{C(Me)\dot{C}(Me)]Cl_3}$

(A) Crystallographic parameters

crystal system: monoclinic	V 1313.8(5) Å^3
space group: $P2_1/c(C_{2h}^5$; No. 14)	formula: $C_9H_{15}Cl_3W$
a 10.2710(22)Å ^{a}	molec. wt.: 413.43
b 10.1132(21)Å ^{a}	$Z = 4$
c 12.7205(26)Å ^{a}	D(calcd) = 2.09 g cm^{-3}
β 96.099(17)° ^{a}	T 297 K (24°C)

(B) Data collection

Diffractometer: Syntex $P2_1$

Radiation: Mo $K_{\bar{\alpha}}(\bar{\lambda}$ 0.710730 Å)

Monochromator: highly oriented (pyrolytic) graphite, equatorial geometry, 2θ(m) 12.2°, assumed 50% perfect

Reflections measd: $+h$, $+k$, $\pm l$ for $2\theta = 3.7$–50.0°: 2472 reflections measured and merged to 2328 independent data. [WCPA file name.]

Scan type: coupled θ(crystal)−2θ(counter)

Scan width: symmetrical, $[2.0 + \Delta(\alpha_1 - \alpha_1)]$°

Scan speed: 2.50 deg/min (in 2θ)

Backgrounds: stationary-crystal, stationary counter at beginning and end of 2θ scan; each for one-half of total scan time

Standards: 3 check reflections (600, 060, 006) measured after each 97 reflections; no significant fluctuation or decay was observed

Absorption: μ 98.6 cm^{-1}; ψ-scans of the close-to-axial reflections $\bar{2}25$ (2θ 19.03°), $\bar{2}36$ (2θ 23.56°), $\bar{1}38$ (2θ 28.58°) and $\bar{2}310$ (2θ 34.98°) were interpolated both in 2θ and in ϕ to provide an empirical correction

^{a} Based upon the automatic centering of the unresolved Mo-$K_{\bar{\alpha}}$ component of 25 reflections with $2\theta = 25$–35°. (Reflections used were {018}, {262}, {15$\bar{7}$}, {611}, {51$\bar{7}$}, {660}, and 44$\bar{5}$.)

TABLE 2

FINAL ATOMIC PARAMETERS FOR $\overline{W[C(CMe_3)C(Me)C(Me)]Cl_3}$

A. Positional parameters

Atom	x	y	z	B
W	0.15890(4)	0.07960(3)	0.11135(3)	
Cl(1)	0.1088(3)	-0.1383(2)	0.0432(2)	
Cl(2)	0.2014(3)	0.3111(2)	0.1349(2)	
Cl(3)	0.2312(3)	0.1182(2)	-0.0534(2)	
C(1)	0.2658(9)	0.0241(9)	0.2305(7)	
C(2)	0.3979(9)	-0.0149(9)	0.2819(7)	
C(3)	0.4476(11)	0.0870(11)	0.3641(9)	
C(4)	0.3966(11)	-0.1530(10)	0.3378(9)	
C(5)	0.4382(10)	-0.0220(11)	0.1946(9)	
C(6)	0.1407(9)	0.0419(8)	0.2727(7)	
C(7)	0.02644(8)	0.0854(8)	0.2006(6)	
C(8)	-0.1028(9)	0.1217(10)	0.2345(8)	
C(9)	0.1199(10)	0.0202(11)	0.3868(7)	
H(3A)	0.5315	0.0613	0.3962	5.5
H(3B)	0.3885	0.0929	0.4164	5.5
H(3C)	0.4539	0.1706	0.3309	5.5
H(4A)	0.4822	-0.1735	0.3692	5.5
H(4B)	0.3684	-0.2187	0.2871	5.5
H(4C)	0.3382	-0.1502	0.3909	5.5
H(5A)	0.5737	-0.0465	0.2239	5.5
H(5B)	0.4915	0.0620	0.1616	5.5
H(5C)	0.4557	-0.0858	0.1436	5.5
H(8A)	-0.1605	0.1464	0.1744	5.5
H(8B)	-0.0923	0.1938	0.2824	5.5
H(8C)	-0.1380	0.0481	0.2681	5.5
H(9A)	0.1996	-0.0074	0.4250	5.5
H(9B)	0.0551	-0.0460	0.3913	5.5
H(9C)	0.0916	0.1003	0.4160	5.5

B. Anisotropic thermal parameters [a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	3.48(2)	2.92(2)	2.338(15)	0.200(15)	0.670(11)	0.011(13)
Cl(1)	6.63(15)	3.04(9)	3.33(10)	-0.00(9)	0.92(10)	-0.15(8)
Cl(2)	6.8(2)	3.05(10)	4.05(11)	-0.23(9)	0.43(10)	-0.24(8)
Cl(3)	6.35(15)	4.77(12)	3.46(10)	-0.88(10)	2.27(10)	-0.11(9)
C(1)	3.5(4)	3.0(3)	3.3(4)	0.1(3)	0.4(3)	-0.1(3)
C(2)	3.4(4)	3.3(4)	4.1(4)	-0.2(3)	0.0(3)	0.6(4)
C(3)	5.6(6)	5.3(5)	4.8(5)	-0.9(5)	-0.9(4)	-0.2(5)
C(4)	4.5(5)	3.6(5)	7.0(7)	-0.0(4)	-0.6(5)	1.6(5)
C(5)	3.8(5)	5.2(5)	5.6(6)	0.7(4)	1.1(4)	0.6(5)
C(6)	3.7(4)	2.8(4)	2.8(4)	0.1(3)	0.3(3)	-0.3(3)
C(7)	3.4(4)	3.3(3)	2.2(3)	-0.0(3)	0.1(3)	-0.4(3)
C(8)	3.6(5)	4.7(5)	4.3(5)	0.6(4)	1.2(4)	-0.5(4)
C(9)	5.3(6)	5.4(5)	2.5(4)	-0.3(4)	0.8(4)	0.1(4)

[a] In the form: $T = \exp(-0.25 \, (h^2 a^{*2} B_{11} + \ldots 2hka^* b^* B_{12} + \ldots))$.

$R_F = 4.6\%$, $R_{wF} = 4.9\%$ and $\text{GOF} = 2.42$ for 118 variables refined against 2327 independent data ($R_F = 3.9\%$ and $R_{wF} = 4.4\%$ for those 2052 reflections with $|F_0| > 3.0\sigma(|F_0|)$).

Hydrogen atoms were included in calculated positions based upon idealized staggered tetrahedral geometry about carbon and $d(\text{C–H}) = 0.95$ Å [15]; their positions were not refined, but were continuously up-dated with respect to their attached carbon atoms.

A final difference-Fourier synthesis showed no unexpected features and tests of the weighting scheme showed no anomalies. The structure is thus both correct and complete. Final parameters are collected in Table 2.

The analytical form of the scattering factor for the appropriate neutral atoms were used in calculating F_c values; these were corrected for both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion [16].

The function minimized during least squares refinement was $\Sigma w(|F_0| - |F_c|)^2$ with $w = [\{\sigma(|F_0|)\}^2 + (0.02|F_0|^2)]^{-1}$.

Description of the molecular geometry of $\overline{\text{W}[\text{C(CMe}_3)\text{C(Me)}\dot{\text{C}}(\text{Me})]}\text{Cl}_3$

The crystal contains an ordered arrangement of discrete monomeric molecular units which are mutually separated by normal Van der Waals' distances; there are no abnormally short intermolecular contacts. The molecular geometry and atomic labeling scheme is illustrated in Fig. 1. Interatomic distances and angles are collected in Table 3 while intramolecular planes are listed in Table 4.

The central tungsten atom is in a formal oxidation state of $+6$ and is linked to

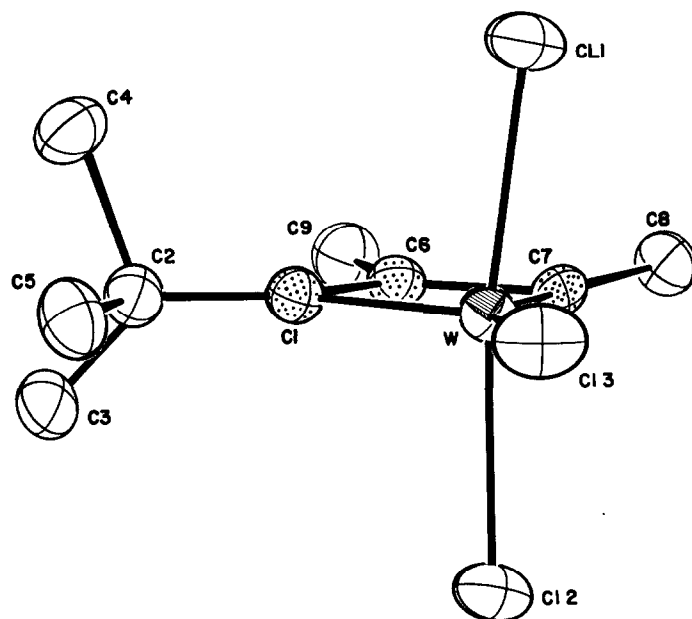Fig. 1. Labeling of atoms in the $\overline{\text{W}[\text{C(CMe}_3)\text{C(Me)}\dot{\text{C}}(\text{Me})]}\text{Cl}_3$ molecule. (ORTEP-II diagram; 30% probability ellipsoids; all hydrogen atoms omitted.)

TABLE 3

INTERATOMIC DISTANCES (Å) AND ANGLES (deg.) FOR $\overline{W[C(CMe_3)C(Me)C(Me)]Cl_3}$

(A) Distances from the tungsten atom			
W–C(1)	1.861(9)	W–Cl(1)	2.404(2)
W $\cdots$ C(6)	2.115(8)	W–Cl(2)	2.394(2)
W–C(7)	1.864(8)	W–Cl(3)	2.330(3)
(B) Distances within the C(CMe₃)C(Me)C(Me) ligand			
C(1)–C(2)	1.495(13)	C(1)–C(6)	1.455(13)
C(2)–C(3)	1.517(14)	C(6)–C(7)	1.478(12)
C(2)–C(4)	1.568(14)	C(6)–C(9)	1.506(12)
C(2)–C(5)	1 523(14)	C(7)–C(8)	1.484(13)
(C) Angles around the tungsten atom			
Cl(1)–W–Cl(2)	166.12(9)	Cl(2)–W–C(7)	91.58(26)
Cl(1)–W–Cl(3)	84.58(9)	Cl(3)–W–C(1)	124 48(28)
Cl(2)–W–Cl(3)	82.98(9)	Cl(3)–W $\cdots$ C(6)	166.55(24)
Cl(1)–W–C(1)	95.88(28)	Cl(3)–W–C(7)	150 02(26)
Cl(1)–W $\cdots$ C(6)	98.44(24)	C(1)–W–C(7)	85.36(37)
Cl(1)–W–C(7)	96.14(26)	C(1)–W $\cdots$ C(6)	42.34(36)
Cl(2)–W–C(1)	96.24(28)	C(7)–W $\cdots$ C(6)	43.03(34)
Cl(2)–W $\cdots$ C(6)	95 09(24)		
(D) W–C–C angles involving the C(CMe₃)C(Me)C(Me) ligand			
W–C(1)–C(2)	149.9(7)	W–C(7)–C(8)	156.6(7)
W–C(1)–C(6)	78.2(5)	W–C(7)–C(6)	77.6(5)
W $\cdots$ C(6)–C(1)	59 5(5)	W $\cdots$ C(6)–C(7)	59.4(4)
W $\cdots$ C(6)–C(9)	176.3(7)		
(E) C–C–C angles within the C(CMe₃)C(Me)C(Me) ligand			
C(2)–C(1)–C(6)	131.8(8)	C(1)–C(6)–C(9)	124 0(8)
C(1)–C(6)–C(7)	118.9(8)	C(7)–C(6)–C(9)	117 2(8)
C(6)–C(7)–C(8)	124.7(8)		
C(1)–C(2)–C(3)	110.2(8)	C(3)–C(2)–C(4)	108 1(8)
C(1)–C(2)–C(4)	112 5(8)	C(3)–C(2)–C(5)	110.4(8)
C(1)–C(2)–C(5)	106.7(8)	C(4)–C(2)–C(5)	108 9(8)

TABLE 4

INTRAMOLECULAR PLANES FOR $\overline{W[C(CMe_3)C(Me)C(Me)]Cl_3}$

| Atom	dev (Å)	Atom	dev. (Å)
(A) The WC₃ plane			
Equation $-0.2098x - 0 9525y - 0 2206z + 1 3864 = 0$			
W*	$-0.002(0)$	C(2)	$-0.035(9)$
C(1)*	0.003(9)	C(3)	$-1.330(11)$
C(6)*	0.004(8)	C(4)	1.158(11)
C(7)*	0.003(8)	C(5)	0.058(11)
Cl(1)	2.376(2)	C(8)	$-0.153(10)$
Cl(2)	$-2.382(2)$	C(9)	$-0.036(11)$
Cl(3)	$-0.116(3)$		
(B) The Cl(1)–W–Cl(2) plane			
Equation: $0.9844x - 0.1610y - 0.0704z - 1.2297 = 0$			
W*	0 000	C(4)	2.279(11)
Cl(1)*	0.000	C(5)	3.311(10)
Cl(2)*	0.000	C(6)	$-0.481(9)$
Cl(3)	1.035(3)	C(7)	$-1.547(9)$
C(1)	0.907(9)	C(8)	$-2.988(10)$
C(2)	2.192(9)	C(9)	$-0.910(11)$
C(3)	2.346(12)		
(C) Dihedral angle			
Plane A/Plane B 92.16 ° (87.84 °)			
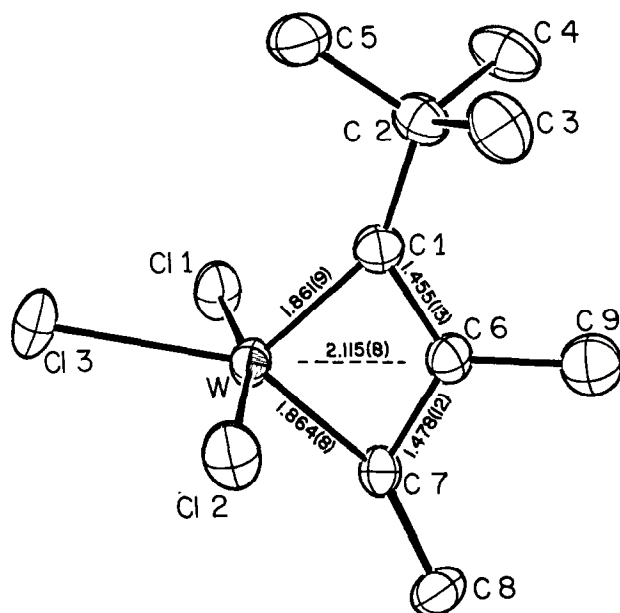
Fig. 2. Geometry of the $\overline{W[C(CMe_3)C(Me)C(Me)]}Cl_3$ molecule, showing dimensions within the WC_3 system.

TABLE 5

SELECTED TUNGSTEN–CARBON BOND LENGTHS (Å)

Molecule	W–C distance	Reference
(A) Tungsten – carbon triple bonds		
$[W(\equiv CCMe_3)(\eta^5\text{-}C_5Me_4(t\text{-}Bu))I]_2(\mu\text{-}N_2H_2)$	1.769(8)	[17]
$W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$	1.785(8)	[18]
$W(\equiv CH \cdot AlMe_{2-x}Cl_{1+x})(Cl)(PMe_3)_3$	1.807(6)	[19]
$W(\equiv CCMe_3)(PHPh)(PEt_3)_2Cl_2$	1.808(6)	[20]
$W(\equiv C \cdot Al_2Me_4Cl)(PMe_3)_2(CH_3)(\eta^2\text{-}C_2H_4)$	1.813(5)	[21]
$W(\equiv C(p\text{-}tol))(\eta^5\text{-}C_5H_5)(CO)_2$	1.82(2)	[22]
$[\{W(\equiv CPMe_3)(PMe_3)_2Cl_2\}_2{}^{2+}]$	1.833(30)	[23]
(B) Tungsten – carbon double bonds		
$W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$	1.859(4)	[24]
$W(=CHCMe_3)(=O)(PEt_3)Cl_2$	1.882(14)	[25]
$W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$	1.942(9)	[18]
$\overline{W=CPh \cdot C(CMe_3)}=CPh(C_5H_5)Cl_3$	1.943(5)	[26]
$W(=CHCMe_3)(=O)(PMe_3)_2Cl_2$	1.986(21)	[27]
(C) Tungsten – carbon single bonds		
$\overline{W=CPh \cdot C(CMe_3)}=CPh(C_5H_5)Cl_3$	2.132(5)	[26]
$W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$	2.258(9)	[18]
$[W(CH_2PMe_3)(CO)_2Cl(PMe_3)_3]^+$	2 305(7)	[28]

three chloride ions and (formally) a chelating $C_3(CCMe_3)Me_2^{3-}$ ligand. The coordination geometry about the tungsten(VI) center approximates to the trigonal bipyramidal case, but there are substantial deviations of angles from the idealized values of 120° (equatorial–equatorial) and 90° (axial–equatorial), vide infra.

The two chloride ligands are in axial positions with a Cl(1)–W–Cl(2) angle of 166.12(9)° and are associated with longer tungsten–chlorine distances than is the equatorial chloride ligand (i.e., W–Cl(1) 2.404(2) Å and W–Cl(2) 2.394(2) Å vis à vis W–Cl(3) 2.330(3) Å).

The tungstenacyclobutadiene system (see Fig. 2) is planar within the limits of experimental error (the root-mean-square deviation of atoms from the least-squares plane, W–C(1)–C(6)–C(7), is ~ 0.004 Å, see section A, Table 4). The α-carbon atoms of the substituents are displaced slightly from this plane, as is the equatorial chloride ligand, Cl(3). Individual displacements are − 0.035(9) Å for C(2), − 0.036(11) Å for C(9), − 0.153(10) Å for C(8) and − 0.116(3) Å for Cl(3); each atom is displaced in the same sense, i.e., toward Cl(2), rather than Cl(1).

The W–C(α) bond lengths are equivalent (W–C(1) 1.861(9) Å and W–C(7) 1.864(8) Å) and are consistent with there being some multiple bond character in these linkages. In fact, as can be seen from Table 5, the observed W–C(α) distances are in the range normally associated with formal tungsten–carbon double bonds (cf. [17–28]).

The angle subtended at tungsten by the α-carbon atoms of the $C_3(CMe_3)Me_2$ ligand is C(1)–W–C(7) 85.36(37)°. Rather surprisingly, the C(α)–C(β)–C(α′) angle is close to its unperturbed (sp^2) value with angle C(1)–C(6)–C(7) 118.9(8)°. This necessitates, in the planar WC_3 ring, that the two W–C(α)–C(β) angles be acute; observed values are W–C(1)–C(6) 78.2(5)° and W–C(7)–C(6) 77.6(5)°. Other concomitant results are as follows.

(1) Both the W–C(α)-substituent and C(β)–C(α)-substituent angles are greater than the normal sp^2 value of 120°. In fact, the angles W–C(1)–C(2) 149.9(7)° and W–C(7)–C(8) 156.6(7)° have values in the range normally found for the M=C(α)–C(β) systems of tantalum and tungsten alkylidene complexes [29]. The angles C(6)–C(1)–C(2) 131.8(8)° and C(6)–C(7)–C(8) 124.7(8)° are increased from the ideal trigonal planar angle by a lesser amount.

(2) The obtuse C(1)–C(6)–C(7) angle of 118.9(8)° causes atom C(6) to be close to the tungsten atom; the W ⋯ C(6) distance of 2.115(8) Å is in the range expected for a tungsten–carbon single bond (cf. Table 5). Looked at from a valence-bond point of view, the geometry about atom C(6) could be regarded as planar four-coordinate, distorted from the idealized square-planar geometry!

These results are in strict contrast to those obtained for the Group VIII metallacycles $Rh[C_3Ph_3](PMe_2Ph)_2Cl_2$ [30] and $[Ir(C_3Ph_3)(PMe_3)_2(CO)Cl^+]$ [31]; in these two species the planar MC_3 system is elongated along the M ⋯ C(β) axis, resulting in the non-bonding M ⋯ C(β) distances Rh ⋯ C(β) 2.582(5) Å and Ir ⋯ C(β) 2.61(2) Å.

These discrepancies have been greatly clarified by a recent theoretical study on the hypothetical d^0 tungsten(VI) species $W(C_3H_3)Cl_3$ [32]. Therewithin it is shown that the π-orbitals of the $C_3H_3^{3-}$ fragment interact with the d_π orbitals of the metal atom to form occupied (bonding) molecular orbitals b_2 and a_2 (HOMO) symmetry. The overlap characteristics of these are shown below in structures C and D. Of particular note is that the b_2 molecular orbital allows for direct overlap between the

(b_2) (a_2)
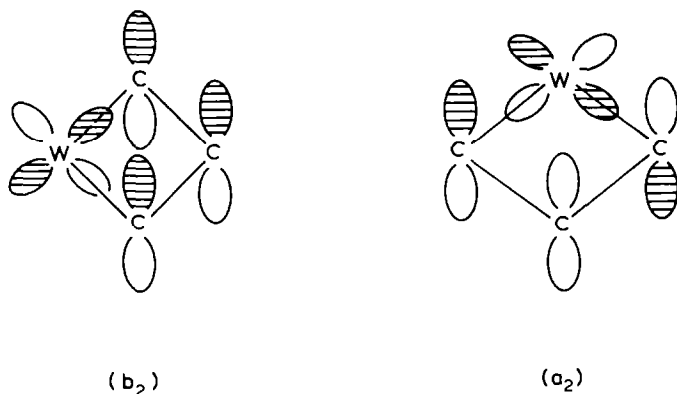
tungsten atom and the β-carbon atom. (This explains the anomalously short W $\cdots$ C(6) distance of 2.115(8) Å in our present complex.)

One point that we do not fully understand concerns the geometry involving atom Cl(3). This atom along with C(1) and C(7) (the α-carbon atoms of the metallacyclobutadiene system) participates in the equatorial coordination plane in the trigonal bipyramidal description of the geometry about tungsten, yet it does not lie precisely trans to the β-carbon atom (in fact, Cl(3)–W–C(6) 166.55(24)°) and the two Cl(3)–W–C(α) angles are inequivalent (Cl(3)–W–C(7) 150.02(26)°, a value some 25.5° greater than Cl(3)–W–C(1) 124.48(28)°).

Finally we note that the closely related metallacyclobutadiene species $\overline{\text{W}[\text{C(Ph)C(CMe}_3\text{)C(Ph)}]}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2$ has a non-planar localized WC_3 ring [26]. Studies are currently underway in an attempt to ascertain whether this is the result of the steric bulk of the η^5-C_5H_5 ligand vis à vis Cl$^-$ or whether it is a change necessary to accomodate the more bulky [C(Ph)C(CMe$_3$)C(Ph)] ligand (as opposed to the present [C(CMe$_3$)C(Me)C(Me)] ligand).

Additional material

A table of observed and calculated structure factor amplitudes is available upon request from M.R.C.

Acknowledgements

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