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CRYSTAL STRUCTURE OF $(\eta^5\text{-}C_5H_5)\overline{W[C(Ph)C(CMe_3)C}(Ph)]Cl_2$, A MOLECULE POSSESSING A LOCALIZED, NON-PLANAR TUNGSTENACYCLOBUTADIENE RING

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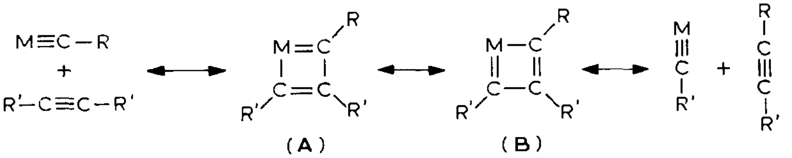
Summary

The complex $(\eta^5\text{-}C_5H_5)\overline{W[C(Ph)C(CMe_3)C}(Ph)]Cl_2$ has been studied by X-ray diffraction techniques. This complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; No. 14) with a 9.8594(38), b 10.8206(17), c 20.580(11) Å, β 92.882(38)°, V 2192.8(15) Å^3 and D(calcd) 1.72 g cm^{-3} for mol. wt. 567.2 and $Z = 4$. Diffraction data were collected with a Syntex P2$_1$ diffractometer and the structure was solved and refined to R_F 3.1% and R_{wF} 2.6% for all 2599 data with 2θ = 4.5–45.0°. The tungsten atom has a coordination environment resembling a "four-legged piano stool". The tungstenacyclobutadiene system is non-planar and localized, individual distances around the WC$_3$ system being (cyclically) W=C(6) 1.943(5), C(6)–C(1) 1.485(7), C(1)=C(13) 1.372(8), and C(13)–W 2.132(5) Å; the W...C(1) distance of 2.339(5) Å is essentially non-bonding.

Introduction

Metallacyclobutadienes are of current interest because they are implicated as intermediates in the metathesis of alkynes [1] see eq. 1. The nature of the intermediate metallacyclobutadiene system is unknown; in principle, it could be a delocalized system or it could exist in two discrete forms (i.e., **A** and **B** of eq. 1).



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A number of metallacyclobutadiene complexes have now been studied by X-ray diffraction techniques. All have planar delocalized MC_3 rings. Those of the Group VIII elements (e.g., $Rh(C_3Ph_3)(PMe_2Ph)_2Cl_2$ [2] and $[Ir(C_3Ph_3)(PMe_3)_2(CO)Cl^+]$ [3]) have an MC_3 system that is elongated along the M...C(β) axis. Those of the earlier transition metal elements (e.g. $W[C(CMe_3)C(Me)C(Me)]Cl_3$ [4,5], $W[C_3Et_3][O\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2]_3$ [6] and $W[C_3Et_3][OCH(CF_3)_2]_3$ [7]) have an MC_3 system that is compressed along the M...C(β) axis; it has been suggested that there is substantial direct M–C(β) bonding in these species [8].

The reaction of disubstituted acetylenes with the species $(\eta^5\text{-}C_5H_5)W(\equiv CCMe_3)Cl_2$ has been shown [9] to give rise to tungstenacyclobutadiene complexes. We now report the detailed molecular structure of the species $(\eta^5\text{-}C_5H_5)W[C(Ph)C(CMe_3)C(Ph)]Cl_2$ made in this manner and we show that it is the first example of a localized non-planar metallacyclobutadiene complex.

Experimental

Data collection. A crystalline sample of the complex was provided by Professor R.R. Schrock (M.I.T.). A dark-red crystal of approximate dimensions 0.10 × 0.17 × 0.35 mm was mounted along its extended direction in a thin-walled glass capillary

TABLE 1

EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY OF $(\eta^5\text{-}C_5H_5)W[C(Ph)C(CMe_3)C(Ph)]Cl_2$

(A) Crystallographic parameters at 23°C (296 K)

crystal system: monoclinic
Space group: $P2_1/c$ (C_{2h}^5; No. 14)
a 9.8594(38) Å
b 10.8206(17) Å
c 20.580(11) Å
β 92.882(38)°

V 2192.8(15) Å^3
formula: $C_{24}H_{24}Cl_2W$
molec. wt 567.2
$Z = 4$
D(calcd) 1.72 g cm^{-3}
μ(Mo-K_α) 58.2 cm^{-1}

(B) Collection of X-ray diffraction data

Diffractometer: Syntex $P2_1$
Radiation: Mo-K_α (λ 0.710730 Å)
Monochromator: highly oriented (pyrolytic) graphite, 2θ(m) 12.160° for 002 reflection, equatorial mode, assumed to be 50% perfect/50% ideally mosaic for polarization correction
Reflections measured: $+h$, $+k$, $\pm l$ for 2θ = 4.5–45.0°; 2738 reflections measured and merged to 2599 unique data (filename WPHA, No. 155)
Scan type: coupled θ(crystal)–2θ(counter)
Scan width, deg: $[2\theta(\text{Mo-}K_{\alpha_1})-1.0] \rightarrow [2\theta(\text{Mo-}K_{\alpha_2})+1.0]$
Scan speed (deg/min): 2.50
Background measurement: stationary-crystal and stationary counter at each end of the 2θ scan; each for one-half total scan time
Standards: 3 approximately mutually orthogonal check reflections were remeasured after each batch of 97 reflections; no significant fluctuation nor decay was observed

under an argon atmosphere. The crystal was accurately aligned and centered on our Syntex $P2_1$ automated four-circle diffractometer and X-ray data were collected as has been described previously [10]; details appear in Table 1. Following data collection we collected ψ-scans of four reasonably intense close-to-axial reflections (at well-spaced 2θ values) and used these to provide an empirical absorption correction (interpolating both in 2θ and ϕ) for all diffraction data. All data were then corrected for Lorentz and polarization effects and converted to approximately absolute $|F_0|$ values by means of a Wilson plot. No datum was rejected; any reflection with $I(\text{net}) \leqslant 0$ was assigned a value of $|F_0| = 0$.

The systematic absences $h0l$ for $l = 2n+1$ and $0k0$ for $k = 2n+1$ uniquely define the centrosymmetric monoclinic space group $P2_1/c$.

Solution and refinement of the 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 program package. The analytical form of the scattering factor for the appropriate neutral atoms was used in calculating F_c values; these were corrected both for the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion [11]. The function minimized during least-squares refinement was $\Sigma w(|F_0| - |F_c|)^2$ with $1/w = \{\sigma(|F_0|)\}^2 + \{0.015|F_0|\}^2$.

The structure was solved by direct methods using the program MULTAN [12]. The WCl_2 portion was readily located from an E-map; the remaining non-hydrogen atoms were all located from the first difference-Fourier synthesis. Full-matrix least-squares refinement using anisotropic thermal parameters for all non-hydrogen atoms (244 variables in all) led to convergence with the following discrepancy indices for all 2599 data (none rejected).

$$R_F = 100\left[\frac{\Sigma||F_0| - |F_c||}{\Sigma|F_0|}\right] = 3.1\%$$

$$R_{wF} = 100\left[\frac{\Sigma w(|F_0| - |F_c|)^2}{\Sigma w|F_0|^2}\right]^{1/2} = 2.6\%$$

$$\text{GOF} = \left[\frac{\Sigma w(|F_0| - |F_c|)^2}{(\text{NO} - \text{NV})}\right]^{1/2} = 1.086$$

Here, NO is the number of observations and NV is the number of variables.

The discrepancy indices for those 2319 data with $|F_0| > 3.0\sigma(|F_0|)$ were R_F 2.4% and R_{wF} 2.5%.

Throughout the refinement process, hydrogen atoms were included in calculated positions based upon $d(\text{C–H})$ 0.95 Å [13] and the appropriate trigonal planar (sp^2) or staggered tetrahedral (sp^3) geometry; these positions were not refined, but were continuously up-dated with respect to their attached carbon atoms.

A final difference-Fourier synthesis showed no significant features and tests of the weighting scheme revealed no anomalies. The structure is thus both correct and complete. Final positional and thermal parameters are listed in Tables 2 and 3.

TABLE 2

FINAL ATOMIC POSITIONS (with esd's) FOR $(\eta^5\text{-}C_5H_5)\overline{W[C(Ph)C(CMe_3)C}(Ph)]Cl_2$

Atom	x	y	z	B (Å^2)
W	0.11511(2)	0.07686(2)	0.15126(1)	
Cl(1)	0.17819(15)	0.18409(14)	0.05377(8)	
Cl(2)	0.19528(16)	0.27010(13)	0.20101(8)	
C(1)	0.3186(5)	−0.0294(5)	0.17385(28)	
C(2)	0.4665(5)	−0.0182(6)	0.15351(30)	
C(3)	0.5521(7)	−0.1263(9)	0.1763(5)	
C(4)	0.4673(7)	−0.0140(11)	0.0809(4)	
C(5)	0.5277(8)	0.0964(9)	0.1825(6)	
C(6)	0.2029(5)	−0.0791(5)	0.13291(26)	
C(7)	0.1897(5)	−0.2087(5)	0.11505(27)	
C(8)	0.1143(6)	−0.2428(6)	0.05883(30)	
C(9)	0.1037(7)	−0.3669(6)	0.0409(4)	
C(10)	0.1641(7)	−0.4569(5)	0.0805(4)	
C(11)	0.2379(6)	−0.4234(6)	0.13592(34)	
C(12)	0.2516(6)	−0.3015(5)	0.15361(30)	
C(13)	0.2524(5)	0.0114(4)	0.22686(28)	
C(14)	0.2869(5)	0.0193(6)	0.29586(29)	
C(15)	0.2189(7)	0.0975(7)	0.33615(34)	
C(16)	0.2504(9)	0.1002(8)	0.4026(4)	
C(17)	0.3438(9)	0.0238(11)	0.4303(4)	
C(18)	0.4091(9)	−0.0585(10)	0.3916(4)	
C(19)	0.3808(7)	−0.0600(7)	0.32504(34)	
Cp(1)	−0.0888(6)	0.0074(7)	0.10378(34)	
Cp(2)	−0.0645(6)	−0.0522(6)	0.1651(4)	
Cp(3)	−0.0661(6)	0.0358(7)	0.21388(33)	
Cp(4)	−0.0962(6)	0.1509(7)	0.1854(4)	
Cp(5)	−0.1075(6)	0.1355(7)	0.1179(4)	
H(31)	0.6421	−0.1158	0.1627	6.0
H(32)	0.5533	−0.1311	0.2223	6.0
H(33)	0.5149	−0.2003	0.1580	6.0
H(41)	0.5581	−0.0070	0.0680	6.0
H(42)	0.4278	−0.0875	0.0633	6.0
H(43)	0.4163	0.0554	0.0653	6.0
H(51)	0.6188	0.1039	0.1701	6.0
H(52)	0.4769	0.1661	0.1671	6.0
H(53)	0.5261	0.0922	0.2285	6.0
H(8)	0.0699	−0.1812	0.0325	6.0
H(9)	0.0551	−0.3896	0.0017	6.0
H(10)	0.1543	−0.5416	0.0692	6.0
H(11)	0.2802	−0.4854	0.1625	6.0
H(12)	0.3032	−0.2800	0.1921	6.0
H(15)	0.1497	0.1501	0.3181	6.0
H(16)	0.2049	0.1573	0.4290	6.0
H(17)	0.3644	0.0265	0.4758	6.0
H(18)	0.4737	−0.1145	0.4106	6.0
H(19)	0.4271	−0.1169	0.2989	6.0
HCp(1)	−0.0920	−0.0302	0.0620	6.0
HCp(2)	−0.0496	−0.1382	0.1713	6.0
HCp(3)	−0.0496	0.0206	0.2590	6.0
HCp(4)	−0.1070	0.2264	0.2081	6.0
HCp(5)	−0.1246	0.1991	0.0867	6.0

Description of the molecular structure of $(\eta^5\text{-}C_5H_5)\overline{W[C(Ph)C(CMe_3)C}(Ph)]Cl_2$

The crystal contains an ordered arrangement of discrete monomeric molecular units which are well separated; there are no unusually short intermolecular contacts. The overall molecular geometry and atomic labelling scheme are illustrated in Fig. 1. A stereoscopic view of the molecule is provided in Fig. 2. Interatomic distances and angles are collected in Tables 4 and 5 while intramolecular planes (and dihedral angles) are presented in Table 6.

By our customary method of electron counting the central tungsten atom is in a formal oxidation state of +6 and is linked to two chloride ions, one $\eta^5\text{-}C_5H_5^-$ anion and (formally) a chelating $[C(Ph)C(CMe_3)C(Ph)]^{3-}$ trianion; the complex has a total of 16 outer valence electrons (i.e., 2 short of the "noble gas configuration"). The coordination geometry about the d^0 W^{VI} center is that of a slightly distorted "four-legged piano stool". Angles from "Cp" (the centroid of the $\eta^5\text{-}C_5H_5$ ligand) to the other ligands are fairly regular, with Cp–W–Cl(1) 113.68°, Cp–W–Cl(2) 111.95°, Cp–W–C(6) 111.23° and Cp–W–C(13) 120.66°. Angles between the "legs" are far less regular, with *cis*-angles (cyclically) being Cl(1)–W–Cl(2) 81.15(5)°, Cl(2)–

TABLE 3

FINAL ANISOTROPIC THERMAL PARAMETERS[a] FOR $(\eta^5\text{-}C_5H_5)\overline{W[C(Ph)C(CMe_3)C}(Ph)]Cl_2$

Atom	$B_{1,1}$	$B_{2,2}$	$B_{3,3}$	$B_{1,2}$	$B_{1,3}$	$B_{2,3}$
W	1.970(10)	1.996(10)	2.471(13)	0.004(8)	−0.146(7)	0.075(9)
Cl(1)	4.13(7)	3.52(7)	3.19(8)	−0.40(6)	−0.20(6)	0.98(6)
Cl(2)	5.28(8)	2.30(6)	4.18(9)	−0.26(6)	−0.27(7)	−0.55(6)
C(1)	2.43(23)	1.96(22)	2.50(32)	0.20(19)	−0.47(22)	0.30(21)
C(2)	2.21(24)	4.53(31)	2.66(32)	0.00(22)	0.12(22)	0.04(25)
C(3)	2.77(31)	9.8(6)	10.7(7)	2.80(35)	1.6(4)	3.9(5)
C(4)	3.32(33)	17.3(9)	3.9(4)	0.5(4)	0.92(29)	1.9(5)
C(5)	4.7(4)	8.7(6)	15.9(9)	−4.0(4)	4.7(5)	−6.0(6)
C(6)	2.11(21)	2.52(23)	2.05(27)	−0.06(19)	−0.31(19)	0.18(21)
C(7)	2.33(22)	2.04(24)	2.78(29)	0.05(19)	−0.16(21)	−0.15(21)
C(8)	4.02(28)	3.42(30)	3.35(33)	0.26(23)	−1.17(25)	−0.42(25)
C(9)	5.5(4)	3.23(32)	5.8(4)	−0.31(28)	−1.65(33)	−1.49(30)
C(10)	5.20(35)	2.01(28)	6.7(5)	−0.57(25)	0.79(34)	−0.88(28)
C(11)	4.57(31)	2.82(29)	4.5(4)	0.48(25)	0.20(28)	0.47(28)
C(12)	3.34(26)	2.37(28)	3.77(34)	0.21(21)	−0.04(24)	0.12(23)
C(13)	2.56(23)	1.09(21)	3.08(34)	−0.45(18)	0.13(23)	−0.19(21)
C(14)	2.88(25)	3.55(27)	2.28(32)	0.11(22)	0.19(24)	−0.32(24)
C(15)	5.00(34)	5.7(4)	3.2(4)	0.53(29)	−0.01(30)	−0.72(30)
C(16)	6.8(4)	7.7(5)	3.2(4)	0.4(4)	0.9(4)	−1.4(4)
C(17)	6.2(5)	12.7(8)	2.9(4)	−1.3(5)	−0.4(4)	−0.5(5)
C(18)	7.8(5)	10.8(7)	2.9(4)	2.1(5)	−0.6(4)	1.5(4)
C(19)	6.3(4)	7.1(5)	2.55(35)	1.81(35)	0.19(32)	0.64(31)
Cp(1)	2.07(26)	5.7(4)	4.8(4)	−0.90(25)	−0.00(26)	−0.82(33)
Cp(2)	2.24(25)	3.82(33)	5.1(4)	−0.93(22)	0.36(25)	0.91(30)
Cp(3)	2.20(25)	6.2(4)	3.7(4)	0.00(25)	1.19(24)	0.31(32)
Cp(4)	2.62(28)	5.2(4)	6.1(5)	0.95(26)	0.84(29)	−0.81(35)
Cp(5)	2.26(27)	5.8(4)	5.9(5)	0.88(26)	0.33(29)	1.0(4)

[a] The anisotropic thermal parameters enter the expression for the calculated structure factor in the form: $\exp[-0.25(h^2a^{\star 2}B_{1,1}+k^2b^{\star 2}B_{2,2}+l^2c^{\star 2}B_{3,3}+2hka^{\star}b^{\star}B_{1,2}+2hla^{\star}c^{\star}B_{1,3}+2klb^{\star}c^{\star}B_{2,3})]$.

W–C(13) 78.37(14)°, C(13)–W–C(6) 65.18(20)° and C(6)–W–Cl(1) 96.87(15)°, while *trans*-angles are Cl(1)–W–C(13) 125.65(14)° and Cl(2)–W–C(6) 133.44(15)°.

The tungsten–chloride distances (W–Cl(1) 2.426(2) and W–Cl(2) 2.442(2)) Å; average 2.434 Å) suggest a covalent radius of about 1.44 Å (i.e., 2.43–0.99 Å) for the tungsten(VI) atom.

Tungsten–carbon (η^5-C_5H_5) distances range from W–Cp(2) 2.285(6) Å through W–Cp(4) 2.372(6) Å, the average such distance being 2.325 Å. The W–Cp distance is 1.993 Å ("Cp" is the centroid of the η^5-C_5H_5 system). The η^5-C_5H_5 ligand has D_{5h}

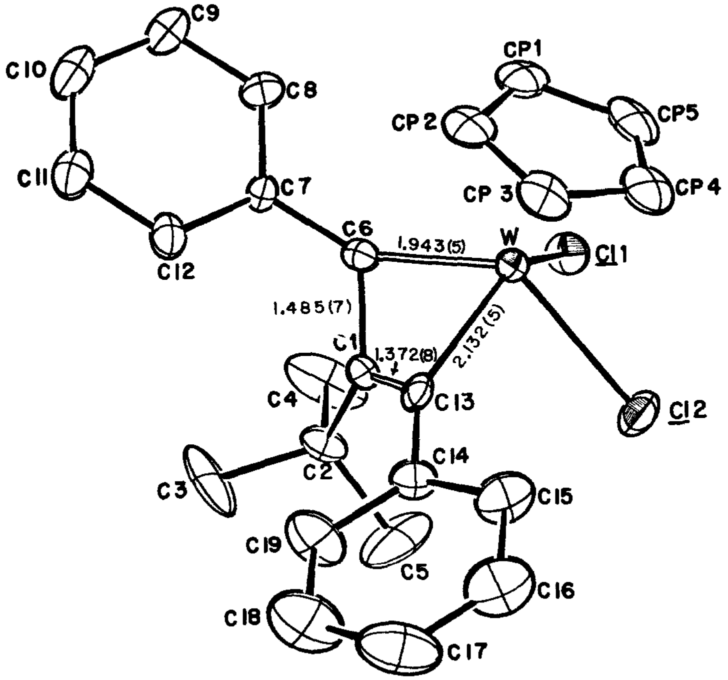


Fig. 1. Labelling of atoms in the (η^5-C_5H_5)$\overline{W[C(Ph)C(CMe_3)C}(Ph)]Cl_2$ molecule [ORTEP-II diagram]. Hydrogen atoms are omitted for clarity.

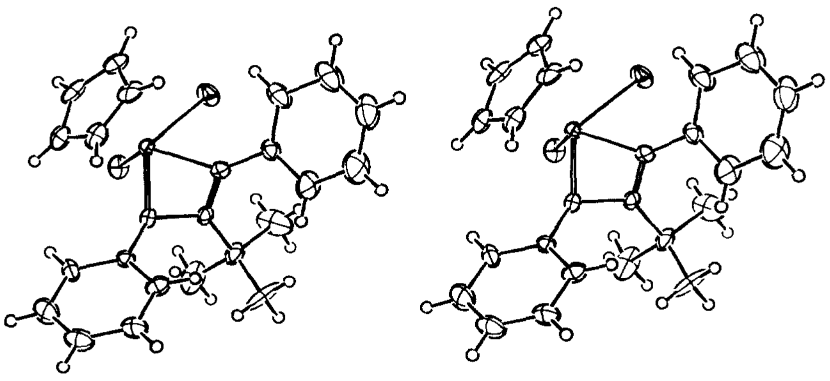


Fig. 2. Stereoscopic view of the (η^5-C_5H_5)$\overline{W[C(Ph)C(CMe_3)C}(Ph)]Cl_2$ molecule with all hydrogen atoms included in idealized positions.

TABLE 4. INTERATOMIC DISTANCES (IN Å) FOR $(\eta^5\text{-}C_5H_5)W[C(Ph)C(CMe_3)C(Ph)]Cl_2$

(A) Distances from the Tungsten Atom			
W–Cl(1)	2.426(2)	W–Cp(1)	2.317(6)
W–Cl(2)	2.442(2)	W–Cp(2)	2.285(6)
W–C(6)	1.943(5)	W–Cp(3)	2.299(6)
W–C(13)	2.132(5)	W–Cp(4)	2.372(6)
W...C(1)	2.339(5)	W–Cp(5)	2.354(6)
		W–Cp[a]	1.993
(B) Distances within the [C(Ph)C(CMe$_3$)C(Ph)] System			
C(1)–C(6)	1.485(7)	C(10)–C(11)	1.370(10)
C(1)–C(13)	1.372(8)	C(11)–C(12)	1.373(8)
C(1)–C(2)	1.543(7)	C(12)–C(7)	1.401(8)
C(2)–C(3)	1.503(11)	C(13)–C(14)	1.446(8)
C(2)–C(4)	1.494(10)	C(14)–C(15)	1.382(9)
C(2)–C(5)	1.490(11)	C(15)–C(16)	1.387(10)
C(6)–C(7)	1.453(7)	C(16)–C(17)	1.344(13)
C(7)–C(8)	1.393(8)	C(17)–C(18)	1.376(14)
C(8)–C(9)	1.396(9)	C(18)–C(19)	1.384(11)
C(9)–C(10)	1.384(10)	C(19)–C(14)	1.378(9)
(C) Distances within the η^5-C_5H_5 Ligand			
Cp(1)–Cp(2)	1.426(10)	Cp(4)–Cp(5)	1.398(12)
Cp(2)–Cp(3)	1.385(10)	Cp(5)–Cp(1)	1.429(11)
Cp(3)–Cp(4)	1.401(10)		

[a] "Cp" is the centroid of the η^5-cyclopentadienyl ring.

TABLE 5. INTERATOMIC ANGLES (in deg.) FOR $(\eta^5\text{-}C_5H_5)W[C(Ph)C(CMe_3)C(Ph)]Cl_2$

(A) Angles around the tungsten atom			
Cl(1)–W–Cl(2)	81.15(5)	Cl(2)–W–C(13)	78.37(14)
Cl(1)–W–C(6)	96.87(15)	Cl(2)–W–Cp[a]	111.95
Cl(1)–W–C(13)	125.65(14)	C(6)–W–C(13)	65.18(20)
Cl(1)–W–Cp[a]	113.68	C(6)–W–Cp[a]	111.23
Cl(2)–W–C(6)	133.44(15)	C(13)–W–Cp[a]	120.66
(B) Angles around the WC$_3$ ring			
W–C(6)–C(7)	148.48(39)	C(13)–C(1)–C(2)	133.19(49)
W–C(6)–C(1)	84.93(31)	W–C(13)–C(1)	80.58(33)
C(7)–C(6)–C(1)	123.32(45)	W–C(13)–C(14)	143.74(40)
C(6)–C(1)–C(13)	100.70(44)	C(1)–C(13)–C(14)	134.63(50)
C(6)–C(1)–C(2)	125.77(46)		
(C) Angles within the C(CMe$_3$) group			
C(1)–C(2)–C(3)	112.22(54)	C(3)–C(2)–C(4)	107.70(62)
C(1)–C(2)–C(4)	109.03(55)	C(3)–C(2)–C(5)	108.28(62)
C(1)–C(2)–C(5)	109.02(56)	C(4)–C(2)–C(5)	110.59(64)
(D) Angles within C(Ph) systems			
C(6)–C(7)–C(8)	120.17(48)	C(13)–C(14)–C(15)	121.91(54)
C(7)–C(8)–C(9)	120.25(56)	C(14)–C(15)–C(16)	120.88(65)
C(8)–C(9)–C(10)	119.84(63)	C(15)–C(16)–C(17)	121.33(79)
C(9)–C(10)–C(11)	119.88(64)	C(16)–C(17)–C(18)	118.93(89)
C(10)–C(11)–C(12)	121.04(60)	C(17)–C(18)–C(19)	120.21(84)
C(11)–C(12)–C(7)	120.30(53)	C(18)–C(19)–C(14)	121.45(70)
C(12)–C(7)–C(8)	118.65(50)	C(19)–C(14)–C(15)	117.10(59)
C(12)–C(7)–C(6)	121.18(47)	C(19)–C(14)–C(13)	120.71(55)
(E) Angles within the η^5-C_5H_5 ring			
Cp(1)–Cp(2)–Cp(3)	108.80(58)	Cp(4)–Cp(5)–Cp(1)	108.25(63)
Cp(2)–Cp(3)–Cp(4)	108.54(60)	Cp(5)–Cp(1)–Cp(2)	106.06(58)
Cp(3)–Cp(4)–Cp(5)	108.28(63)		

[a] "Cp" is the centroid of the η^5-C_5H_5 ring.

symmetry within the limits of experimental error. Individual carbon–carbon distances range from Cp(2)–Cp(3) 1.385(10) Å through Cp(5)–Cl(1) 1.429(11) Å, (averaging 1.408 ± 0.019 Å), the root-mean-square deviation from planarity for the carbon atoms is only 0.011 Å and the tungsten atom lies 1.9911(2) Å below the η^5-C_5H_5 plane (see plane *E*, Table 6).

We now come to a consideration of the tungstenacyclobutadiene ring. In contradistinction to all other such systems that have been examined crystallographically (i.e., $\overline{W[C(CMe)C(Me)C}(Me)]Cl_3$ [4,5], $W[C_3Et_3][O\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2]_3$ [6] and $W[C_3Et_3][OCH(CF_3)_2]_3$ [7]), the WC_3 ring of the present W[C(Ph)C(CMe$_3$)C(Ph)] system takes up a localized, non-planar configuration. Thus, the W–C(6) distance of 1.943(5) Å is 0.189 ± 0.007 Å shorter than the W–C(13) bond length of 2.132(5) Å; these distances are consistent with their being tungsten–carbon double and single

TABLE 6

SELECTED INTRAMOLECULAR PLANES FOR $(\eta^5\text{-}C_5H_5)\overline{W[C(Ph)C(CMe_3)C}(Ph)]Cl_2$

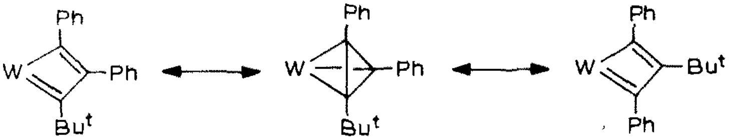
Atom	dev., Å	Atom	dev., Å
(A) The W–C(13)–C(1) plane			
Equation: $0.5054x + 0.8626y - 0\ 0215z - 1.1451 = 0$			
W*	0.000	C(6)	−1.001(5)
C(13)*	0.000	C(14)	0.179(6)
C(1)*	0.000	C(2)	0.861(6)
(B) The W–C(6)–C(1) plane			
Equation: $0.4238x + 0.4032y - 0.8111z + 1.7716 = 0$			
W*	0.000	C(13)	−1.005(6)
C(6)*	0.000	C(7)	−0.314(5)
C(1)*	0.000	C(2)	1.015(6)
(C) The C(6)–W–C(13) plane			
Equation: $0.7690x + 0.4936y - 0.4063z + 0.1003 = 0$			
C(6)*	0.000	C(7)	−0.628(5)
W*	0.000	C(1)	0.768(5)
C(13)*	0.000	C(14)	−0.328(6)
(D) The C(6)–C(1)–C(13) plane			
Equation: $-0.1075x + 0.8953y - 0.4323z + 2.1478 = 0$			
C(6)*	0.000	C(7)	−1.084(5)
C(1)*	0.000	C(2)	0.130(6)
C(13)*	0.000	C(14)	−0.565(6)
		W	1.4434(2)
(E) The η^5-C_5H_5 plane			
Equation: $0.9851x + 0.1596y - 0.0638z + 1.0929 = 0$			
Cp(1)*	0.001(6)	W	1.9911(2)
Cp(2)*	−0.009(6)	Cl(1)	3.0162(15)
Cp(3)*	0.014(6)	Cl(2)	2.9876(16)
Cp(4)*	−0.013(6)	C(6)	2.617(5)
Cp(5)*	0.008(6)	C(13)	3.036(5)
		C(1)	3.731(5)
(F) Dihedral angles (in degrees)			
A/B	54.59	*A/E*	50.44
C/D	57.66	*B/E*	57.75
		C/E	30.43
		D/E	86.30

bonds respectively [14]. Similarly, the C(1)–C(13) distance of 1.372(8) Å is 0.113 ± 0.011 Å shorter than the C(1)–C(6) distance of 1.485(7) Å; these values may be compared to the accepted values of C=C ~ 1.335 Å and C(sp^2)–C(sp^2) (single bond) ~ 1.465 Å [15]. The non-planarity of the WC_3 system is clearly indicated by the dihedral angles [C(6)–W–C(13)]/[C(6)–C(1)–C(13)] 57.66° and [W–C(13)–C(1)]/[W–C(6)–C(1)] 54.59°.

The W...C(1) distance of 2.339(5) Å is formally non-bonding and is substantially longer than the W–C(*β*) distances observed in planar delocalized WC_3 systems (viz., W–C(*β*) 2.115(8) Å in $W[C(CMe_3)C(Me)C(Me)]Cl_3$ [4,5], 2.159(10) Å in $W[C_3Et_3][O\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2]_3$ [6] and 2.093(14) Å and 2.100(15) Å for two independent molecules in $W[C_3Et_3][OCH(CF_3)_2]_3$ [7]).

Angles within the WC_3 system are C(6)–W–C(13) 65.18(20)°, W–C(13)–C(1) 80.58(33)°, W–C(6)–C(1) 84.93(31)° and C(6)–C(1)–C(13) 100.70(44)°; the external angles at the *α*-carbon (i.e., W–C(6)–C(7) 148.48(39)° and W–C(13)–C(14) 143.74(40)°) are unusually large and resemble those found for the M=C(*α*)–C(*β*) angles in metal alkylidenes [16]; however, this feature is common to both planar and non-planar WC_3 systems.

The present complex, $(\eta^5\text{-}C_5H_5)W[C(Ph)C(CMe_3)C(Ph)]Cl_2$, is formed by addition of PhC≡CPh to the alkylidyne complex $(\eta^5\text{-}C_5H_5)W(\equiv CCMe_3)Cl_2$. The reaction requires addition of PhC≡CPh to the $W\equiv CCMe_3$ bond followed by some process that permutes the various CR fragments (since the product no longer has adjacent CPh groups). It it tempting to speculate that this could occur through a "metallatetrahedrane" intermediate (possibly as shown in eq. 2). The case for such an intermediate is greatly strengthened by the recent isolation and structural characterization of the "tungstenatetrahedrane" complexes $W[C(CMe_3)C(Me)C(Me)](Me_2NCH_2CH_2NMe_2)Cl_3$ [17,18] and $(\eta^5\text{-}C_5H_5)W[C_3(CMe_3)_2Me](PMe_3)Cl_2$ [19].



(2)

Finally we must confess to being presently unsure as to why $W[C(CMe_3)C(Me)C(Me)]Cl_3$ has a planar localized WC_3 system, whereas the present closely-related species, $(\eta^5\text{-}C_5H_5)W[C(Ph)C(CMe_3)C(Ph)]Cl_2$, has a non-planar delocalized WC_3 system. The only changes from the first to the second are (i) substitution of a chloride ligand by an $\eta^5\text{-}C_5H_5$ ligand, and (ii) variation in the substituents around the C_3 system (from CMe_3, Me, Me to Ph, CMe_3, Ph). A careful look at the stereoscopic view of the present $(\eta^5\text{-}C_5H_5)W[C(Ph)C(CMe_3)C(Ph)]Cl_2$ molecule shows no obvious hindrance to its attaining a planar configuration to the WC_3 ring. We are thus led to suspect that the change is brought about by electronic, rather than steric, factors; the present localized non-planar WC_3 system is associated with a "16-electron" configuration while all delocalized planar WC_3 systems are associated with the "12-electron" configuration.

Additional material

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

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