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CRYSTAL STRUCTURE OF A DEPROTONATED TUNGSTENACYCLOBUTADIENE COMPLEX, $(\eta^5\text{-}C_5H_5)W[C_3(CMe_3)_2]Cl$; CHARACTERIZATION OF AN η^3-RCCCR LIGAND

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Summary

The complex $(\eta^5\text{-}C_5H_5)W[C_3(CMe_3)_2]Cl$ has been subjected to an X-ray diffraction study. This complex crystallizes in the non-centrosymmetric orthorhombic space group $Pna2_1$ [C_{2v}^9; No. 33] with a 12.6810(14), b 15.3730(26), c 8.7771(13) Å, V 1711.0(4) Å^3 and $Z = 4$. Diffraction data for $2\theta = 4.5\text{–}50.0°$ (Mo-K_α radiation) were collected on a Syntex $P2_1$ automated four-circle diffractometer and the structure was solved and refined to $R_F = 4.2\%$ and $R_{wF} = 3.1\%$ for all 3021 point-group independent reflections ($R_F = 3.1\%$, $R_{wF} = 2.9\%$ for those 2638 data with $|F_0| > 3\sigma(|F_0|)$). The molecule may be considered as derived by dehydrohalogenation of the tungstenacyclobutadiene complex $(\eta^5\text{-}C_5H_5)W[C(CMe_3)C(H)C(CMe_3)]Cl_2$. The resulting molecule contains a $W[C_3(CMe_3)_2]$ moiety in which the WC_3 core is approximately planar [C(1)–W–C(3)/C(1)–C(2)–C(3) 4.17°] with W–C(1) 1.929(6), W–C(2) 2.049(8) and W–C(3) 1.919(8) Å.

Introduction

We have recently been involved in determining the molecular structures of some tungstenacyclobutadiene complexes, which are of interest because of their implication as intermediates in acetylene metathesis [1]. The five-coordinate "twelve-electron" complexes $W[C(CMe_3)C(Me)C(Me)]Cl_3$ [2,3], $W[C(Et)C(Et)C(Et)][O\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2]_3$ [4], and $W[C(Et)C(Et)C(Et)][OCH(CF_3)_2]_3$ [5] each have a planar delocalized WC_3 ring; in contrast to this, the "sixteen-electron" complex $(\eta^5\text{-}C_5H_5)W[C(Ph)C(CMe_3)C(Ph)]Cl_2$ [6,7] has a non-planar, localized WC_3 ring.

Schrock and coworkers have found that alkylidyne complexes of the type $W(\equiv CR)(OCMe_3)_3$ act as catalysts for the metathesis of disubstituted acetylenes (internal alkynes), but that they do not metathesize terminal acetylenes [8,9].

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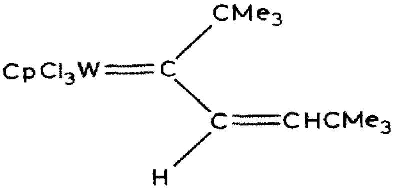
However, it has been shown [10] that $(\eta^5\text{-}C_5H_5)W(\equiv CCMe_3)Cl_2$ (a molecule that will not metathesize alkynes) reacts with $Me_3CC\equiv CH$ in ether to provide two complexes in approximately equal yields: $(\eta^5\text{-}C_5H_5)W[C_3(CMe_3)_2]Cl$ (the complex that is the target of the present structural investigation) and $(\eta^5\text{-}C_5H_5)W[C_3H_2(CMe_3)_2]Cl_3$ (which is believed to have structure **1** [10] on the basis of ^1H and ^{13}C NMR and IR spectroscopy).



(1)

The reaction of $(\eta^5\text{-}C_5H_5)W(\equiv CCMe_3)Cl_2$ with $Me_3CC\equiv CH$ in the presence of Et_3N proceeds as shown in eq. 1, yielding only the species $(\eta^5\text{-}C_5H_5)\text{-}W[C_3(CMe_3)_2]Cl$.

$$(\eta^5\text{-}C_5H_5)W(\equiv CCMe_3)Cl_2 + Me_3CC\equiv CH + Et_3N \rightarrow (\eta^5\text{-}C_5H_5)W[C_3(CMe_3)_2]Cl + [Et_3NH^+][Cl^-] \quad (1)$$

We now report details of the crystal structure of this unusual dehydrogenated tungstenacyclobutadiene complex; the structure was briefly described previously in a communication [10].

Experimental

Data collection

Crystals of the material under investigation were provided by Professor Richard R. Schrock and Mr. Laughlin G. McCullough of the Chemistry Department, Massachusetts Institute of Technology. A number of crystals were inserted into thin-walled glass capillary tubes under an inert atmosphere (Ar) in a KSE recirculating dry-box which had been modified (with a protruding transparent addition mounted between the gloves) so as to allow inspection of crystals through an externally-mounted binocular polarizing microscope. The capillaries were flame-sealed and set (with bees' wax) into aluminum pins and mounted on a eucentric goniometer. The diffraction patterns of the various crystals were investigated photographically on a Syntex $P2_1$ diffractometer. The crystal with the "best" diffraction pattern (a red parallelpiped with approximate orthogonal dimensions $0.2 \times 0.2 \times 0.3$ mm and mounted along its extended direction) was selected for the analysis. Determination of unit cell parameters and data collection were carried out as described previously [11]; details appear in Table 1. (Initially we solved the structure using one octant of data. As a result of some unusual problems, vide infra, we later collected a second octant of data.)

The systematic absences ($0kl$ for $k + l = 2n + 1$ and $h0l$ for $h = 2n + 1$) are compatible with the non-centrosymmetric orthorhombic space group $Pna2_1$ (C_{2v}^9; No. 33) or the centrosymmetric space group $Pnam$ (a non-standard setting of space group $Pnma\text{-}D_{2h}^{16}$; No. 62). Solution of the structure showed the former non-centrosymmetric alternative to be the true space group.

All data were corrected for absorption (μ 72.8 cm^{-1}) by interpolating in 2θ and ϕ between empirical absorption curves mapped out by ψ-scans of four close-to-axial reflections. All data were converted to unscaled $|F_0|$ values following correction for Lorentz and polarization factors and were placed on an approximately absolute scale by means of intensity statistics. Three low angle reflections (011, $01\bar{1}$, 020) were rejected as unreliable, due to possible "clipping" by the backstop.

Solution and refinement of the structure

All calculations were performed using the SUNY-Buffalo modification of the Syntex XTL crystallographic program package. Analytical scattering factors for neutral W, Cl, C and H were used throughout the analysis; these were corrected for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion [12]. The function minimized during least-squares refinement was $\Sigma w(|F_0| - |F_c|)^2$ with $w^{-1} = \sigma^2(|F_0|) + (0.015|F_0|)^2$.

TABLE 1

EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY OF $(\eta^5\text{-}C_5H_5)\text{-}W[C_3(CMe_3)_2]Cl$

(A) Crystallographic parameters at 23°C (296 K) [a]

Crystal system: orthorhombic
Space group: $Pna2_1$ [C_{2v}^9; No. 33]
a 12.6810(14) Å
b 15.3730(26) Å
c 8.7771(13) Å
V 1711.0(4) $Å^3$

Formula: $C_{16}H_{23}ClW$
Molec. wt.: 434.69
$Z = 4$
D(calcd) 1.69 g cm^{-3}
μ(Mo-K_α) 72.8 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 = 4.5–50.0°; 3409 reflections measured and merged to 3021 point-group independent data [filename WCP2 #161]
Scan type: coupled θ(crystal)–2θ(counter)
Scan width (deg): [2θ(Mo-K_{α_1})−0.9] → [2θ(Mo-K_{α_2})+0.9]
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 check reflections (620, 404, 550) were remeasured after each batch of 97 reflections; no significant fluctuation nor decay was observed
Absorption correction: empirical, based upon interpolation (in 2θ and ϕ) between correction curves generated by ψ-scans of four fairly strong close-to-axial reflections: 400 (2θ = 12.85°; max/min = 1.39), 600 (19.32°; 1.39), 801 (26.28°; 1.40), 1000 (32.48°, 1.40)

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[a] Unit cell parameters are based upon a least-squares analysis of the setting angles of the unresolved Mo-K_α components of 25 reflections with 2θ = 21–25°. Reflections used were {552}, {731}, {344} and 353.

The analysis was begun using only one octant of data (+*h*, +*k*, +*l*). The position of the tungsten atom was determined from a Patterson synthesis. A difference-Fourier synthesis phased by this atom (R_F 32%) showed the single chlorine atom to lie at a different *z*-coordinate than the tungsten atom. The non-centrosymmetric space group $Pna2_1$ (rather than *Pnam*, with a mirror plane perpendicular to *z*) is thereby uniquely indicated. The remaining non-hydrogen atoms were located from a difference-Fourier synthesis; refinement converged with

TABLE 2

FINAL POSITIONAL PARAMETERS (FRACTIONAL COORDINATES) FOR (η^5-C_5H_5)-W[$C_3(CMe_3)_2$]Cl

Atom	*x*	*y*	*z*	*B* (Å^2)
W	0.90221(2)	0.80075(2)	0.25000(0)	
Cl	1.03947(17)	0.85507(16)	0.09854(28)	
C(1)	0.91458(48)	0.67567(40)	0.2520(25)	
C(2)	0.95468(65)	0.70008(55)	0.38291(94)	
C(3)	0.96264(64)	0.78288(49)	0.44794(90)	
C(4)	0.89144(75)	0.58539(56)	0.17666(93)	
C(5)	0.81428(88)	0.53920(64)	0.2869(15)	
C(6)	0.9957(10)	0.53609(67)	0.1706(14)	
C(7)	0.84173(86)	0.59542(68)	0.0225(11)	
C(8)	0.98894(82)	0.80719(60)	0.6092(10)	
C(9)	1.0960(14)	0.7862(16)	0.6430(20)	
C(10)	0.9151(16)	0.7621(14)	0.7148(12)	
C(11)	0.9727(14)	0.90307(88)	0.6315(14)	
C(51)	0.72058(55)	0.80363(57)	0.2487(33)	
C(52)	0.74955(95)	0.82835(92)	0.0925(15)	
C(53)	0.80065(82)	0.90898(80)	0.1059(13)	
C(54)	0.80192(68)	0.93306(56)	0.2657(24)	
C(55)	0.74942(81)	0.86758(86)	0.3438(13)	
H(5)A	0.7968	0.4834	0.2475	6.0
H(5)B	0.8467	0.5328	0.3837	6.0
H(5)C	0.7519	0.5729	0.2969	6.0
H(6)A	0.9848	0.4806	0.1253	6.0
H(6)B	1.0451	0.5681	0.1116	6.0
H(6)C	1.0221	0.5287	0.2710	6.0
H(7)A	0.8287	0.5395	−0.0199	6.0
H(7)B	0.7770	0.6260	0.0322	6.0
H(7)C	0.8879	0.6269	−0.0422	6.0
H(9)A	1.1113	0.8019	0.7452	6.0
H(9)B	1.1066	0.7254	0.6301	6.0
H(9)C	1.1413	0.8171	0.5759	6.0
H(10)A	0.9315	0.7773	0.8168	6.0
H(10)B	0.8447	0.7791	0.6923	6.0
H(10)C	0.9217	0.7009	0.7023	6.0
H(11)A	0.9893	0.9182	0.7336	6.0
H(11)B	1.0172	0.9343	0.5638	6.0
H(11)C	0.9011	0.9173	0.6112	6.0
H(51)	0.6869	0.7509	0.2775	6.0
H(52)	0.7364	0.7965	0.0017	6.0
H(53)	0.8294	0.9420	0.0244	6.0
H(54)	0.8327	0.9838	0.3085	6.0
H(55)	0.7357	0.8680	0.4501	6.0

R_F 4.2, R_{wF} 3.2% and $GOF = 1.24$ for 1618 independent data. (Refinement with crystal chirality reversed, i.e., $x, y, z \rightarrow x, y, -z$, gave higher discrepancy indices.) However, all was not well. Chemically equivalent bond lengths varied widely, e.g. C(8)–Me distances were 1.47, 1.52 and 1.76 Å. We decided that this problem might be due (at least in part) to using only one-half of the point-group independent data. Accordingly, we now collected $+h$, $+k$, $-l$ data and added them to the $+h$, $+k$, $+l$ data. Refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms (and with all hydrogen atoms included in calculated positions, with d(C–H) 0.95 Å [13] and the appropriate staggered tetrahedral or trigonal geometry) led to convergence with R_F 4.2, R_{wF} 3.1% and $GOF = 1.16$ for 162 parameters refined against 3021 point-group independent reflections (R_F 3.1 and R_{wF} 2.9% for those 2638 data with $|F_0| > 3.0\sigma(|F_0|)$). With this increased data set the previously noted problems were greatly diminished. A final difference-Fourier map was "clean".

Final positional parameters are listed in Table 2; anisotropic thermal parameters appear in Table 3.

Description of the molecular geometry of $(\eta^5\text{-}C_5H_5)W[C_3(CMe_3)_2]Cl$

The crystal contains an ordered arrangement of discrete molecular units, separated by normal Van der Waals' distances; there are no abnormally short intermolecular contacts. The overall molecular geometry and atomic labelling scheme is shown in Figs. 1 and 2. Figure 3 provides a stereoscopic view of the molecule.

TABLE 3

ANISOTROPIC THERMAL PARAMETERS (Å^2) FOR $(\eta^5\text{-}C_5H_5)W[C_3(CMe_3)_2]Cl$ [a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	2.914(11)	2.639(11)	3.370(11)	0.150(11)	0.053(35)	−0.268(32)
Cl	3.78(10)	4.77(11)	4.96(10)	−0.014(90)	0.518(84)	0.836(91)
C(1)	2.98(26)	2.96(28)	4.47(30)	0.09(23)	0.81(69)	1.28(81)
C(2)	3.64(36)	3.14(36)	4.01(38)	0.13(34)	−0.43(30)	−0.10(33)
C(3)	3.39(36)	3.27(38)	3.56(34)	0.05(31)	−0.37(29)	−0.15(28)
C(4)	5.06(45)	3.33(38)	3.71(31)	−0.73(38)	−0.60(35)	−1.18(30)
C(5)	6.94(56)	5.16(48)	7.8(10)	−3.14(44)	−0.50(52)	0.41(49)
C(6)	5.82(56)	4.35(52)	10.88(82)	0.84(46)	−0.83(51)	−1.66(48)
C(7)	7.46(61)	4.32(48)	5.48(50)	−0.92(48)	−1.85(45)	−1.32(41)
C(8)	5.77(50)	4.48(46)	4.17(40)	0.01(40)	−0.16(38)	−1.09(39)
C(9)	10.1(11)	28.6(26)	9.8(10)	9.5(13)	−5.98(86)	−10.9(13)
C(10)	19.6(17)	17.6(13)	3.52(80)	−10.5(13)	0.65(67)	−1.83(68)
C(11)	15.2(12)	6.58(72)	7.07(69)	−0.73(82)	−2.06(76)	−3.18(61)
C(51)	3.17(29)	4.86(38)	8.33(49)	−0.08(33)	−0.3(11)	1.35(90)
C(52)	4.54(53)	7.87(84)	6.26(64)	2.21(54)	−0.73(51)	−0.69(59)
C(53)	4.12(49)	6.09(63)	6.46(59)	1.26(46)	0.29(47)	2.26(58)
C(54)	4.07(36)	3.92(37)	7.84(75)	1.20(31)	0.04(73)	−2.15(71)
C(55)	2.81(43)	5.49(62)	6.01(58)	1.36(46)	1.22(41)	−0.35(51)

[a] These anisotropic thermal parameters are consistent with the Syntex XTL format and enter the expression for the calculated structure factor in the form: $\exp[-0.25(h^2a^{\star 2}B_{11} + k^2b^{\star 2}B_{22} + l^2c^{\star 2}B_{33} + 2hka^{\star}b^{\star}B_{12} + 2hla^{\star}c^{\star}B_{13} + 2klb^{\star}c^{\star}B_{23})]$.

Interatomic distances and angles are presented in Tables 4 and 5, while intramolecular planes (and dihedral angles) are given in Table 6.

The (η^5-C_5H_5)W[$C_3(CMe_3)_2$]Cl molecule has a tendency toward approximate (but not exact) non-crystallographic C_s (m) symmetry with a pseudo-mirror plane

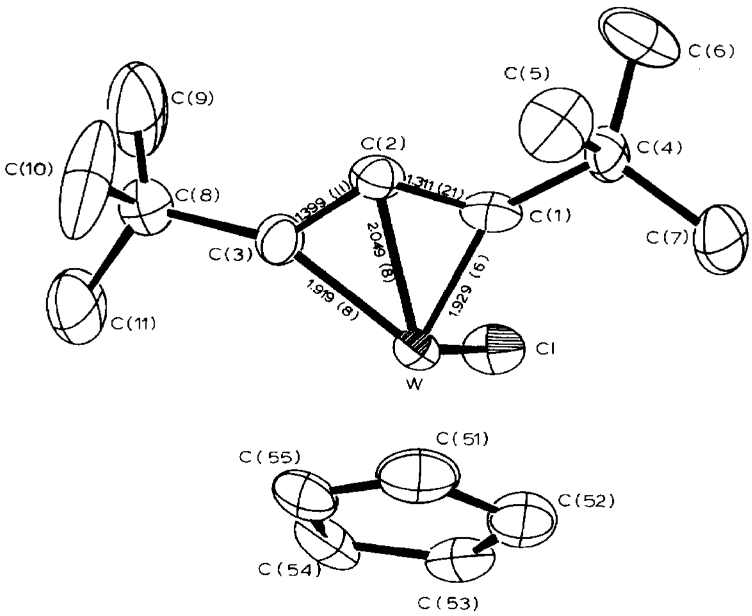


Fig. 1. Important interatomic distances and the atomic labelling scheme for (η^5-C_5H_5)W[$C_3(CMe_3)_2$]Cl. (ORTEP-II diagram).

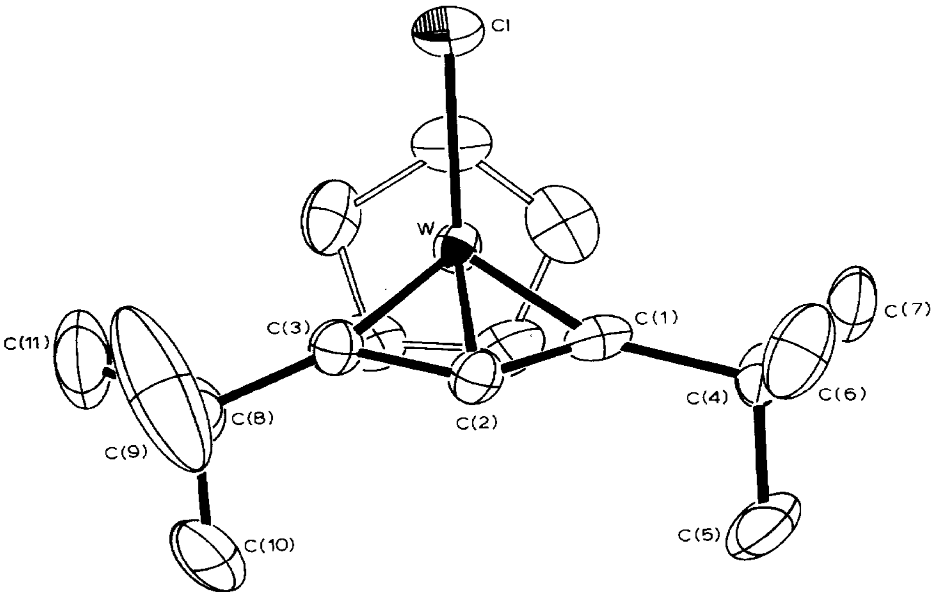


Fig. 2. The (η^5-C_5H_5)W[$C_3(CMe_3)_2$]Cl molecule, projected onto the plane of the η^5-cyclopentadienyl ligand. Note the approximate (non-crystallographic) mirror plane through atoms Cl, W and C(2).

running through atoms Cl, W and C(2) (cf. Fig. 1). Note that this does not coincide with the possibility of mirror plane at $z = 1/4$ (which could convert the space group from $Pna2_1$ to the higher $Pnam$) since the z-coordinates of these atoms are different (z(W) = 0.25, z(Cl) = 0.0985 and z(C(2)) = 0.3829).

The structure determined (even after using both octants of data, $+h$, $+k$, $+l$ and $+h$, $+k$, $-l$) still has certain bond lengths etc. that are not as internally consistent as is usual for a structure at R_F 4.2% with an "overdetermination ratio" (observation to parameter ratio) of 3021/162 (i.e., 18.6/1). We believe that this is probably

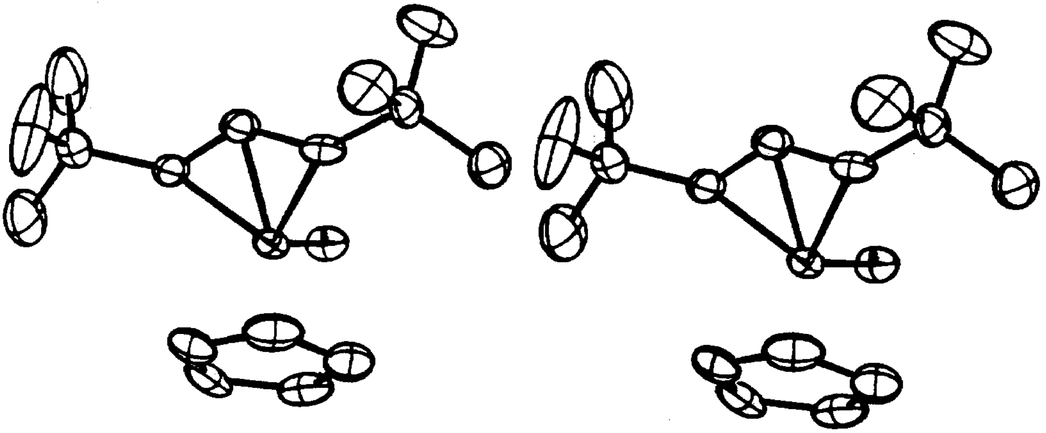


Fig. 3. A stereoscopic view of the (η^5-C_5H_5)W[$C_3(CMe_3)_2$]Cl molecule.

TABLE 4

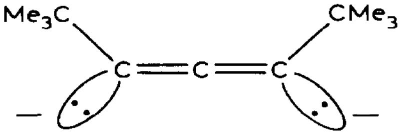
INTERATOMIC DISTANCES (in Å), WITH ESD'S, FOR (η^5-C_5H_5)W[$C_3(CMe_3)_2$]Cl

Distances from tungsten atom			
W–Cl	2.344(2)	W–C(51)	2.304(7)
W–C(1)	1.929(6)	W–C(52)	2.416(13)
W–C(2)	2.049(8)	W–C(53)	2.455(12)
W–C(3)	1.919(8)	W–C(54)	2.403(9)
W ··· Cp [a]	2.061	W–C(55)	2.342(11)
Interior distances of $C_3(CMe_3)_2$ ligand			
C(1)–C(2)	1.311(21)	C(2)–C(3)	1.399(11)
Distances involving CMe_3 groups			
C(1)–C(4)	1.565(14)	C(3)–C(8)	1.501(12)
C(4)–C(5)	1.548(15)	C(8)–C(9)	1.427(20)
C(4)–C(6)	1.525(15)	C(8)–C(10)	1.489(20)
C(4)–C(7)	1.500(13)	C(8)–C(11)	1.501(16)
Distances within (η^5-C_5H_5) ligand			
C(51)–C(52)	1.469(31)	C(54)–C(55)	1.388(18)
C(52)–C(53)	1.403(18)	C(55)–C(51)	1.341(23)
C(53)–C(54)	1.450(23)		

[a] Cp is the midpoint of the η^5-C_5H_5 ligand.

related to the excessive librational motion of one of the CMe_3 groups, specifically, libration of atoms C(9), C(10) and C(11) about the C(3)–C(8) axis. (This can clearly be seen in Figs. 1–3; note, also, that B_{ii} values for atoms C(9), C(10) and C(11) go up to values of 28.6(26), 19.6(17) and 15.2(12) Å^2, respectively (see Table 3).) This causes no major problems, but results in a larger spread in certain chemically equivalent distances than would normally be deemed desirable.

The $C_3(CMe_3)_2$ ligand has the composition and the connectivity of the 1,3-bis(t-butyl)allenediyl dianion (**2**). However, it must be noted that the substituents in the localized structure **2** would occupy planes perpendicular to one another. (A more accurate stereochemical picture is that of **3**.) Clearly, the present structure has a $C_3(CMe_3)_2$ ligand in which a significant reorganization of π-electrons has taken place, (see below under Conclusions).



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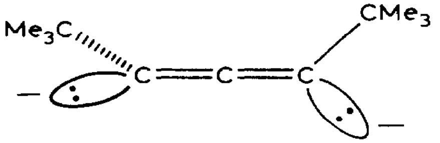

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TABLE 5

INTERATOMIC ANGLES (deg.), WITH ESD'S, FOR (η^5-C_5H_5)$W[C_3(CMe_3)_2]Cl$

Angles about tungsten atom			
Cl–W–C(1)	107.46(42)	C(1)–W–C(3)	79.43(47)
Cl–W–C(2)	110.54(24)	Cp · · · W–Cl	110.91
Cl–W–C(3)	105.54(24)	Cp · · · W–C(1)	124.94
C(1)–W–C(2)	38.33(47)	Cp · · · W–C(2)	138.56
C(2)–W–C(3)	41.12(33)	Cp · · · W–C(3)	124.03
W–C–C and C–C–C angles within WC_3 system			
W–C(1)–C(2)	75.8(7)	C(1)–C(2)–C(3)	130.2(9)
W–C(1)–C(4)	149.8(9)		
W–C(2)–C(1)	65.9(7)	C(4)–C(1)–C(2)	134.2(11)
W–C(2)–C(3)	64.4(5)	C(2)–C(3)–C(8)	128.9(8)
W–C(3)–C(2)	74.5(5)		
W–C(3)–C(8)	155.1(6)		
Angles within CMe_3 groups			
C(1)–C(4)–C(5)	105.1(8)	C(3)–C(8)–C(9)	110.6(11)
C(1)–C(4)–C(6)	107.0(9)	C(3)–C(8)–C(10)	109.3(10)
C(1)–C(4)–C(7)	111.6(8)	C(3)–C(8)–C(11)	109.7(9)
C(5)–C(4)–C(6)	110.0(8)	C(9)–C(8)–C(10)	111.3(12)
C(5)–C(4)–C(7)	110.2(8)	C(9)–C(8)–C(11)	109.0(12)
C(6)–C(4)–C(7)	112.6(8)	C(10)–C(8)–C(11)	106.8(11)
Angles within (η^5-C_5H_5) ligand			
C(55)–C(51)–C(52)	108.8(14)	C(53)–C(54)–C(55)	106.7(11)
C(51)–C(52)–C(53)	105.4(12)	C(54)–C(55)–C(51)	110.8(13)
C(52)–C(53)–C(54)	108.2(11)		

The WC_3 system is close to planar; dihedral angles of note are [C(1)–C(2)–C(3)]/[C(1)–W–C(3)] 4.17° and [W–C(1)–C(2)]/[W–C(3)–C(2)] 2.79°.

The W–C(α) distances (W–C(1) 1.929(6) and W–C(3) 1.919(8) Å, average 1.924 ± 0.007 Å) are equivalent and are slightly shorter, by 0.12–0.13 Å, than the W–C(β) distance (W–C(2) 2.049(8) Å). As may be seen in Table 7, the W–C(α)

TABLE 6

IMPORTANT PLANES AND ATOMIC DEVIATIONS (in Å) THEREFROM FOR $(\eta^5\text{-}C_5H_5)W[C_3(CMe_3)_2]Cl$

Atom	Dev.	Atom	Dev.
(A) The C(1)–C(2)–C(3) plane			
Eqn: $0.8915X + 0.1246Y - 0.4355Z - 10.6708 = 0$			
C(1)*	0.000	W	0.1075(2)
C(2)*	0.000	C(4)	-0.146(9)
C(3)*	0.000	C(8)	-0.272(10)
Cl	2.342(2)		
(B) The C(1)–W–C(3) plane			
Eqn: $0.9167X + 0.0711Y - 0.3931Z - 10.5011 = 0$			
W*	0.000	C(2)	0.041(8)
C(1)*	0.000	C(4)	-0.108(9)
C(3)*	0.000	C(8)	-0.224(10)
Cl	2.178(2)		
(C) The W–C(1)–C(2) plane			
Eqn: $0.9035X + 0.0697Y - 0.4228Z - 10.2680 = 0$			
W*	0.000	C(3)	-0.061(8)
C(1)*	0.000	C(4)	-0.082(9)
C(2)*	0.000	C(8)	-0.332(10)
Cl	2.193(2)		
(D) The W–C(3)–C(2) plane			
Eqn: $0.9160X + 0.1014Y - 0.3880Z - 10.8771 = 0$			
W*	0.000	C(1)	-0.058(10)
C(2)*	0.000	C(4)	-0.211(9)
C(3)*	0.000	C(8)	-0.206(10)
Cl	2.195(2)		
(E) The η^5-C_5H_5 ring			
Eqn: $-0.8764X + 0.4655Y - 0.1232Z + 2.5104 = 0$			
C(51)*	-0.016(8)	W	-2.0567(2)
C(52)*	0.008(13)	Cl	-3.030(2)
C(53)*	0.002(11)	C(1)	-3.092(7)
C(54)*	-0.012(9)	C(2)	-3.504(8)
C(55)*	0.018(11)	C(3)	-3.070(8)
Selected dihedral angles (°)			
A/B	4.17	A/E	132.05
C/D	2.79	B/E	136.21
		C/E	135.02
		D/E	135.06

distances are slightly longer and the W–C(β) distance slightly shorter than the values found in planar delocalized tungstenacyclobutadiene complexes. Correspondingly, the C(1)–C(2)–C(3) angle of 130.2(9)° in the present molecule is substantially more obtuse than the C(α)–C(β)–C(α′) angles in the planar tungstenacyclobutadienes.

The C(α)–C(β) distances in the present molecule are C(1)–C(2) 1.311(21) and C(2)–C(3) 1.399(11) Å. The difference of 0.088 Å cannot be regarded as significant for two reasons: (a) the presence of C(2) as a common atom in the two distances C(1)–C(2) and C(2)–C(3) necessarily increases the e.s.d. on the average value from the non-correlated value $[(0.021^2 + 0.011^2)^{1/2} = 0.024$ Å], and (b) we know that there are some systematic errors, due principally to libration, in our model (vide supra).

Other points of interest in the structural results are as follows.

(1) The two chemically equivalent C–CMe_3 linkages, C(1)–C(4) 1.565(14) and C(3)–C(8) 1.501(12) Å, have an average value of 1.533 ± 0.045 Å. Distances within the CMe_3 group based on atom C(4) are normal (C(4)–C(5) 1.548(15), C(4)–C(6) 1.525(15), C(4)–C(7) 1.500(13) Å; average = 1.524 ± 0.024 Å), while those based on C(8) are in less good agreement and show some evidence of artificial librational contraction (viz., C(8)–C(9) 1.427(20), C(8)–C(10) 1.489(20), C(8)–C(11) 1.501(16) Å; average = 1.472 ± 0.040 Å).

(2) Individual W–C(η^5-C_5H_5) distances range from W–C(51) 2.304(7) through W–C(53) 2.455(12) Å, the average value being 2.384 Å; the W ··· Cp distance is 2.061 Å. The C–C distances range from 1.341(23) through 1.469(31), averaging 1.410 ± 0.051 Å. These results are in essential agreement with studies on such simple species as (η^5-C_5H_5)W(CO)$_3$Cl [14], although the W ··· Cp distance there is rather shorter (2.001 Å).

TABLE 7

TUNGSTEN–CARBON DISTANCES (Å) AND ANGLES (°) IN TUNGSTENACYCLOBUTADIENE COMPLEXES

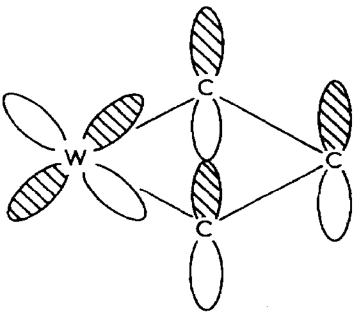
Complex	W–C(α)	W–C(β)	∠C(α)–C(β)–C(α′)	Ref.
Delocalized, planar WC_3R_3 systems				
W[C(CMe_3)C(Me)C(Me)]Cl_3	1.861(9) 1.864(8)	2.115(8)	118.9(8)	3
W[C(Et)C(Et)C(Et)](OR)$_3$ (R = 2,6-C_6H_3(i-Pr)$_2$)	1.949(9) 1.883(10)	2.159(10)	120.8(9)	4
W[C(Et)C(Et)C(Et)](OR)$_3$ (R = CH(CF_3)$_2$)	1.864(14) 1.902(16)	2.093(14)	122.4(13)	5
– (2nd molecule)	1.860(17) 1.885(15)	2.100(15)	121.4(14)	
Localized, non-planar WC_3R_3 system				
CpW[C(Ph)C(CMe_3)C(Ph)]Cl_2	1.943(5) 2.132(5)	2.339(5)	100.7(4)	7
Dehydrogenated (WC_3R_2) system				
CpW[C_3(CMe_3)$_2$]Cl	1.919(8) 1.929(6)	2.049(8)	130.2(9)	This work

(3) The W–Cl distance of 2.344(2) Å in the present molecule is reduced from those of 2.426(2) and 2.442(2) Å in the related W^{VI} species $(\eta^5\text{-}C_5H_5)W[C(Ph)C(CMe_3)C(Ph)]_2Cl_2$ [6,7].

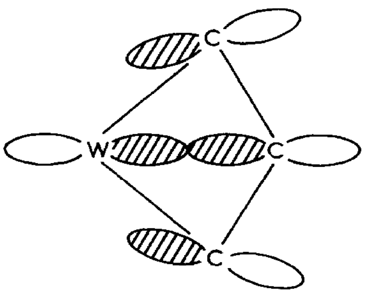
Conclusions

One of the major surprises of this analysis is that the $W[C_3R_2]$ system so closely resembles a planar delocalized WC_3R_3 system. Equivalent W–C distances differ by only ~ 0.05–0.1 Å. The only evidence that the C(β) atom in the $W[C_3(CMe_3)_2]$ ligand is substantially different from that in a WC_3R_3 system comes from ^{13}C NMR spectroscopy [10]. Atom C(β) in the $W[C_3(CMe_3)_2]$ system is directly coupled to tungsten (δ 197.1, J(CW) 26 Hz) as are the C(α) atoms (δ 220.4, J(CW) 127 Hz); no such coupling is observed in the closely-related tungstenacyclobutadiene complexes.

The bonding of the $C_3(CMe_3)_2$ ligand to tungsten also presents some difficulties. Perhaps the best description is that the WC_3 unit contains two orthogonal delocalized π-systems. The first, a π-system perpendicular to the WC_3 ring, forms a delocalized system such as found in a delocalized metallacyclobutadiene system (see **4**); the second π-system is coplanar with the WC_3 ring (see **5**). We are most grateful to the unknown "referee C" of this manuscript for his comments on the bonding in this complex.



(4)



(5)

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

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