Journal of Organometallic Chemistry, 286 (1985) 27–36
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

X-RAY STRUCTURAL ANALYSIS OF W[C(t-Bu)CHC(t-Bu)][OCH(CF_3)$_2$]$_3$, A MOLECULE CONTAINING A PLANAR TUNGSTENACYCLOBUTADIENE RING WITH NO ALKYL SUBSTITUENT ON THE β-CARBON ATOM

MELVYN ROWEN CHURCHILL * and JOSEPH W. ZILLER

Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14214 (U.S.A.)

(Received September 13th, 1984)

Summary

The tungstenacyclobutadiene complex W[C(t-Bu)CHC(t-Bu)][OCH(CF_3)$_2$]$_3$ crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with a 10.980(1), b 16.530(1), c 16.430(2) Å, β 98.50(1)° and D(calcd) 1.88 g cm^{-3} for mol. wt 836.21 and $Z = 4$. Single-crystal X-ray diffraction data (Mo-K_α) were collected with a Syntex $P2_1$ diffractometer and the structure was refined to R 5.31% for all 3570 unique data with 2θ 4.5–45.0° (R 3.63% for those 2728 data with $|F_0| > 3\sigma(|F_0|)$). The tungsten(VI) atom has a distorted trigonal bipyramidal coordination environment. The planar delocalized WC_3 ring occupies a di-equatorial site with W–C(α) bond lengths of 1.921(10) and 1.889(9) Å; the W $\cdots$ C(β) distance is 2.103(9) Å. Axial and equatorial OCH(CF_3)$_2$ ligands appear to be equally strongly bound to tungsten with W–O distances of 1.954(7)–1.959(7) Å and W–O–C angles of 135.3(6)–138.7(9)°.

Introduction

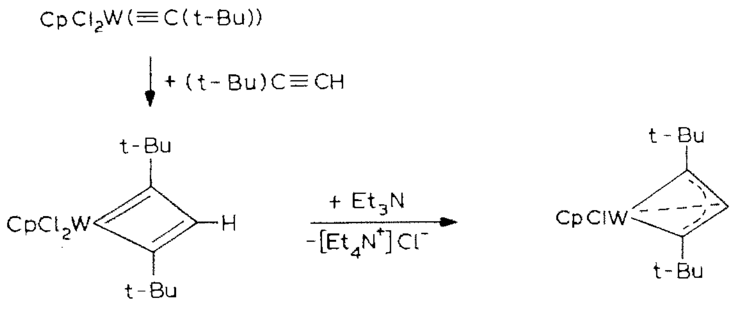
We have recently reported the molecular structures of a variety of trisubstituted tungstenacyclobutadiene complexes. The five-coordinate species W[C(t-Bu)C(Me)C(Me)]Cl_3 [1,2], W[C(Et)C(Et)C(Et)][O-2,6-C_6H_3(i-Pr)$_2$]$_3$ [3] and W[C(Et)C(Et)C(Et)][OCH(CF_3)$_2$]$_3$ [4] each contain a planar delocalized WC_3 in a diequatorial site. However, the species (η^5-C_5H_5)W[C(Ph)C(t-Bu)C(Ph)]Cl_2 [5,6] has a non-planar localized WC_3 system.

Metallacyclobutadiene complexes have been implicated as intermediates in alkyne metathesis [7] in strict analogy with the now-accepted view that metallacyclobutanes are intermediates in olefin metathesis [8]. Schrock and coworkers have found [9,10] that complexes of the type W(≡CR)($OCMe_3$)$_3$ act as catalysts for the metathesis of

* Address correspondence to this author.

0022-328X/85/$03.30

internal alkynes (i.e., RC≡CR′), but not of terminal alkynes (i.e., RC≡CH). A possible explanation for the "non-metathesis" of terminal acetylenes has emerged following the isolation of the species $CpW[C_3(t\text{-}Bu)_2]Cl$ (**1**) from reaction of $CpW(\equiv C(t\text{-}Bu))Cl_2$ and (t-Bu)C≡CH under basic (Et_3N) conditions [11,12]. One can envisage the formation of an intermediate metallacyclobutadiene complex (**2**) with a β-hydrogen followed by dehydrohalogenation of this intermediate (see eq. 1).



(**2**) (**1**)

(1)

Freudenberger and Schrock have recently succeeded in isolating the species $W[C(t\text{-}Bu)CHC(t\text{-}Bu)][OCH(CF_3)_2]_3$ from $W(\equiv C(t\text{-}Bu))[OCH(CF_3)_2]_3$ and (t-Bu)-C≡CH [13]. Since this is, to the best of our knowledge, the first example of a

TABLE 1

EXPERIMENTAL DATA FOR X-RAY DIFFRACTION STUDY OF $W[C(t\text{-}Bu)CHC(t\text{-}Bu)][OCH(CF_3)_2]_3$

(A) Crystal parameters at 21°C (294 K)

Crystal system: monoclinic	V 2949.3(6) Å^3
Space Group: $P2_1/n$	$Z = 4$
a 10.9800(14) Å	formula $C_{20}H_{22}F_{18}O_3W$
b 16.5298(12) Å	mol. wt 836.21
c 16.4303(19) Å	D(calcd) 1.88 g cm^{-3}
β 98.500(10)°	

(B) Collection of X-ray diffraction data

Diffractometer: Syntex $P2_1$

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

Monochromator: highly oriented (pyrolytic) graphite; equatorial mode; 2θ(m) 12.160°; assumed to be 50% perfect for polarization correction.

Reflections measured: $+h$, $+k$, $\pm l$ for $2\theta = 4.5$–$45.0°$, 4115 total yielding 3570 unique reflections

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

Scan width: symmetrical, $[1.8 + \Delta(\alpha_1 - \alpha_2)]°$

Scan speed: 2.0 deg/min (in 2θ)

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

Standard reflections: three (0,10,1; 3,0,7; 5,$\bar{2}$,$\bar{4}$) collected after each batch of 97 reflections; no sudden fluctuations were observed, but data were corrected for a slight decay from the initial intensity

Absorption coefficient: μ 42.29 cm^{-1}; corrected empirically by interpolation (in 2θ and ϕ) between ψ-scans of close-to-axial reflections.

TABLE 2

FINAL POSITIONAL PARAMETERS FOR $W[\overline{C(t\text{-}Bu)CHC}(t\text{-}Bu)][OCH(CF_3)_2]_3$

Atom	x	y	z	U(iso) (Å^2)
W	0.56848(3)	0.13206(2)	0.75521(2)	
O(1)	0.5649(6)	0.2475(4)	0.7805(5)	
O(2)	0.3908(7)	0.1517(5)	0.7408(6)	
O(3)	0.5101(7)	0.0200(4)	0.7468(4)	
C(1)	0.6790(9)	0.1293(5)	0.6749(6)	
C(2)	0.7576(8)	0.1175(6)	0.7505(6)	
C(3)	0.7125(9)	0.1174(6)	0.8323(6)	
C(1A)	0.7115(11)	0.1319(7)	0.5903(6)	
C(1B)	0.8092(36)	0.0810(25)	0.5774(13)	
C(1C)	0.7588(64)	0.2058(19)	0.5745(19)	
C(1D)	0.6183(29)	0.1129(35)	0.5345(12)	
C(3A)	0.7889(10)	0.1190(7)	0.9144(6)	
C(3B)	0.7124(19)	0.1369(15)	0.9751(10)	
C(3C)	0.8812(32)	0.1792(26)	0.9221(15)	
C(3D)	0.8440(40)	0.0451(20)	0.9347(16)	
C(11)	0.4840(13)	0.3082(8)	0.7703(9)	
C(12)	0.4709(27)	0.3429(11)	0.8548(15)	
C(13)	0.5126(19)	0.3680(9)	0.7094(15)	
C(21)	0.2868(14)	0.1111(9)	0.7185(13)	
C(22)	0.2002(16)	0.1326(12)	0.7774(17)	
C(23)	0.2358(15)	0.1237(14)	0.6295(12)	
C(31)	0.5494(11)	−0.0520(7)	0.7833(7)	
C(32)	0.4734(19)	−0.0773(8)	0.8492(11)	
C(33)	0.5555(17)	−0.1167(8)	0.7201(10)	
F(12A)	0.4457(15)	0.2882(8)	0.9042(7)	
F(12B)	0.5634(21)	0.3782(8)	0.8889(8)	
F(12C)	0.3813(18)	0.4002(9)	0.8440(11)	
F(13A)	0.5289(20)	0.3362(9)	0.6406(8)	
F(13B)	0.6169(12)	0.4065(8)	0.7340(8)	
F(13C)	0.4307(10)	0.4243(7)	0.6910(9)	
F(22A)	0.0858(9)	0.0959(9)	0.7518(8)	
F(22B)	0.2364(13)	0.1083(10)	0.8521(10)	
F(22C)	0.1741(12)	0.2082(7)	0.7805(12)	
F(23A)	0.1422(11)	0.0787(9)	0.6029(8)	
F(23B)	0.1994(13)	0.2009(8)	0.6167(9)	
F(23C)	0.3193(14)	0.1150(10)	0.5812(8)	
F(32A)	0.5151(13)	−0.1378(6)	0.8883(8)	
F(32B)	0.3584(10)	−0.0907(8)	0.8198(7)	
F(32C)	0.4697(11)	−0.0137(6)	0.9009(6)	
F(33A)	0.5957(11)	−0.1842(6)	0.7529(6)	
F(33B)	0.6214(11)	−0.0934(6)	0.6644(6)	
F(33C)	0.4410(12)	−0.1316(6)	0.6794(7)	
H(2)	0.8430	0.1101	0.7488	0.116(45)
H(1B1)	0.7866	0.0255	0.5874	0.08
H(1B2)	0.8810	0.0940	0.6135	0.08
H(1B3)	0.8234	0.0847	0.5219	0.08
H(1C1)	0.8240	0.2195	0.6138	0.08
H(1C2)	0.6926	0.2457	0.5748	0.08
H(1C3)	0.7803	0.2059	0.5207	0.08
H(1D1)	0.5856	0.0633	0.5452	0.08
H(1D2)	0.6425	0.1148	0.4815	0.08
H(1D3)	0.5548	0.1547	0.5356	0.08
H(3B1)	0.6714	0.1866	0.9627	0.08

continued

TABLE 2 (continued)

Atom	x	y	z	U(iso) (Å^2)
H(3B2)	0.7608	0.1394	1.0278	0.08
H(3B3)	0.6523	0.0947	0.9752	0.08
H(3C1)	0.8461	0.2301	0.9084	0.08
H(3C2)	0.9387	0.1665	0.8846	0.08
H(3C3)	0.9244	0.1792	0.9763	0.08
H(3D1)	0.7866	0.0037	0.9299	0.08
H(3D2)	0.8892	0.0476	0.9887	0.08
H(3D3)	0.9034	0.0349	0.8970	0.08
H(11)	0.4056	0.2886	0.7456	0.08
H(21)	0.3017	0.0545	0.7220	0.08
H(31)	0.6310	−0.0442	0.8110	0.08

tungstenacyclobutadiene complex with no alkyl substituent (just a hydrogen atom) on the β-carbon atom, we have undertaken a crystallographic analysis of this species.

Experimental

Data collection

Crystals of $\overline{\text{W[C(t-Bu)CHC}}$(t-Bu)][OCH($CF_3$)$_2$]$_3$ were provided by Professor Schrock and Mr. Freudenberger of the Department of Chemistry, Massachusetts Institute of Technology. The crystal selected for the structural analysis was approximately equi-dimensional of diameter ~ 0.1 mm. It was inserted into a thin-walled glass capillary tube under an inert atmosphere (argon) and was aligned on a Syntex P2$_1$ automated four-circle diffractometer. Subsequent set-up operations (i.e., determination of unit cell parameters and the crystal's orientation matrix) and collection of intensity data (via a coupled θ(crystal)–2θ(counter) scan) were carried out according to previously described techniques [14]; details are listed in Table 1. The systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$ are consistent with the centrosymmetric monoclinic space group $P2_1/n$ (a common non-standard setting of $P2_1/c$, C_{2h}^5, No. 14).

All data were corrected for decay, absorption (μ 42.29 cm^{-1}) and Lorentz and polarization effects and were converted to unscaled $|F_0|$ values. Any reflection with a net intensity of less than zero was assigned the value $|F_0| = 0$. Data were placed on an approximate absolute scale by means of a Wilson plot.

Solution and refinement of the structure

The structure was solved and refined using Sheldrick's SHELX76 programs on the CDC Cyber 173 computer at SUNY-Buffalo. The position of the tungsten atom was determined from an "E-map". All remaining non-hydrogen atoms were located from a series of subsequent difference-Fourier syntheses. The structure was refined to convergence using a "block-cascade" least squares refinement procedure. Final discrepancy indices [15] were R_F 5.31% and R_{wF} 6.02% for 380 parameters refined against all 3570 unique data and R_F 3.63% and R_{wF} 4.35% for those 2728 data with $|F_0| > 3\sigma(|F_0|)$. The function minimized was $\Sigma w(|F_0| - |F_c|)^2$ where $1/w = [\sigma(|F_0|)]^2 + [0.004|F_0|]^2$. The calculated structure factors were based upon the analytical form of the neutral atoms' form factors [16a]; both the real ($\Delta f''$) and imaginary ($\Delta f''$) components of anomalous disposition [16b] were included for all non-hydrogen atoms. Hydrogen atoms were included in idealized calculated positions based upon the appropriate planar trigonal or staggered tetrahedral geometry, with d(C–H) 0.95 Å [17].

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

TABLE 3

ANISOTROPIC THERMAL PARAMETERS FOR $W[C(t\text{-}Bu)CHC(t\text{-}Bu)][OCH(CF_3)_2]_3$ [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W	0.0438(3)	0.0523(3)	0.0486(3)	−0.0014(2)	0.0105(2)	−0.0022(2)
O(1)	0.0772(53)	0.0643(48)	0.0903(53)	−0.0054(40)	0.0226(42)	0.0055(37)
O(2)	0.0421(41)	0.0756(52)	0.1466(86)	−0.0035(48)	0.0240(46)	−0.0032(37)
O(3)	0.0750(49)	0.0538(43)	0.0906(56)	0.0049(36)	0.0124(40)	−0.0015(37)
C(1)	0.0472(54)	0.0637(64)	0.0507(56)	−0.0008(44)	0.0127(44)	−0.0043(44)
C(2)	0.0287(50)	0.0900(79)	0.0576(62)	−0.0081(56)	0.0062(44)	−0.0004(50)
C(3)	0.0573(60)	0.0765(71)	0.0467(56)	−0.0032(49)	0.0106(47)	0.0021(51)
C(1A)	0.0774(74)	0.0843(83)	0.0402(57)	−0.0013(52)	0.0103(54)	0.0018(60)
C(1B)	0.359(45)	0.482(54)	0.090(15)	0.070(23)	0.140(24)	0.197(42)
C(1C)	0.983(115)	0.186(25)	0.194(28)	−0.058(21)	0.353(53)	−0.235(46)
C(1D)	0.184(27)	1.019(113)	0.048(11)	−0.098(27)	0.031(14)	−0.185(43)
C(3A)	0.0617(65)	0.0932(84)	0.0416(56)	0.0001(54)	0.0067(48)	−0.0026(60)
C(3B)	0.113(14)	0.390(37)	0.061(9)	−0.003(14)	0.003(9)	0.026(16)
C(3C)	0.326(38)	0.626(67)	0.123(18)	0.106(29)	−0.115(22)	−0.350(45)
C(3D)	0.500(59)	0.281(32)	0.155(21)	−0.115(22)	−0.221(31)	0.207(38)
C(11)	0.0942(93)	0.0704(80)	0.1019(95)	0.0031(72)	0.0213(78)	−0.0018(70)
C(12)	0.209(24)	0.085(12)	0.141(18)	−0.033(12)	0.097(18)	0.009(14)
C(13)	0.106(13)	0.079(11)	0.173(20)	0.006(11)	0.050(13)	0.014(9)
C(21)	0.086(10)	0.071(9)	0.197(18)	−0.005(11)	0.029(11)	−0.015(8)
C(22)	0.073(11)	0.140(17)	0.203(22)	0.042(15)	0.058(13)	0.017(10)
C(23)	0.057(9)	0.188(21)	0.115(14)	0.040(14)	−0.020(9)	−0.002(11)
C(31)	0.083(8)	0.058(7)	0.073(7)	0.002(6)	0.015(6)	−0.008(6)
C(32)	0.140(15)	0.049(8)	0.132(13)	0.016(8)	0.037(12)	−0.011(8)
C(33)	0.131(14)	0.070(10)	0.089(10)	0.007(7)	0.030(10)	−0.012(8)
F(12A)	0.356(19)	0.168(11)	0.156(10)	0.008(8)	0.168(12)	0.005(12)
F(12B)	0.334(24)	0.163(12)	0.122(9)	−0.060(8)	−0.004(12)	−0.054(12)
F(12C)	0.269(19)	0.178(12)	0.240(16)	−0.025(11)	0.090(15)	0.104(12)
F(13A)	0.385(25)	0.220(14)	0.118(10)	0.059(10)	0.104(13)	0.125(17)
F(13B)	0.154(9)	0.208(12)	0.179(11)	0.096(10)	0.006(8)	−0.063(9)
F(13C)	0.139(9)	0.141(10)	0.246(14)	0.072(10)	0.010(9)	0.027(8)
F(22A)	0.086(7)	0.205(12)	0.270(17)	0.002(10)	0.066(9)	−0.038(7)
F(22B)	0.178(12)	0.286(17)	0.159(11)	0.031(12)	0.067(10)	0.066(12)
F(22C)	0.176(12)	0.112(8)	0.476(26)	−0.014(12)	0.157(14)	0.046(8)
F(23A)	0.134(9)	0.238(15)	0.207(13)	−0.017(10)	−0.025(9)	−0.056(10)
F(23B)	0.198(13)	0.164(11)	0.240(15)	0.076(10)	−0.025(11)	0.025(10)
F(23C)	0.154(11)	0.310(19)	0.149(11)	0.004(10)	0.032(9)	−0.027(11)
F(32A)	0.218(13)	0.153(10)	0.163(10)	0.094(7)	0.085(9)	0.052(8)
F(32B)	0.115(8)	0.189(10)	0.161(9)	0.009(8)	0.040(7)	−0.028(8)
F(32C)	0.236(12)	0.137(8)	0.119(7)	−0.020(6)	0.088(8)	−0.017(8)
F(33A)	0.233(12)	0.075(6)	0.163(10)	−0.007(6)	0.005(9)	0.048(6)
F(33B)	0.193(10)	0.137(8)	0.117(7)	−0.017(6)	0.074(7)	0.022(7)
F(33C)	0.162(11)	0.151(10)	0.109(7)	−0.025(6)	−0.009(7)	−0.030(6)

[a] These anisotropic thermal parameters are consistent with the SHELX 76 format and enter the expression for the calculated structure factor in the form: $\exp[-2\pi^2(h^2a^{\star 2}U_{11} + k^2b^{\star 2}U_{22} + l^2c^{\star 2}U_{33} + klb^{\star}c^{\star}U_{23} + hla^{\star}c^{\star}U_{13} + hka^{\star}b^{\star}U_{12})]$.

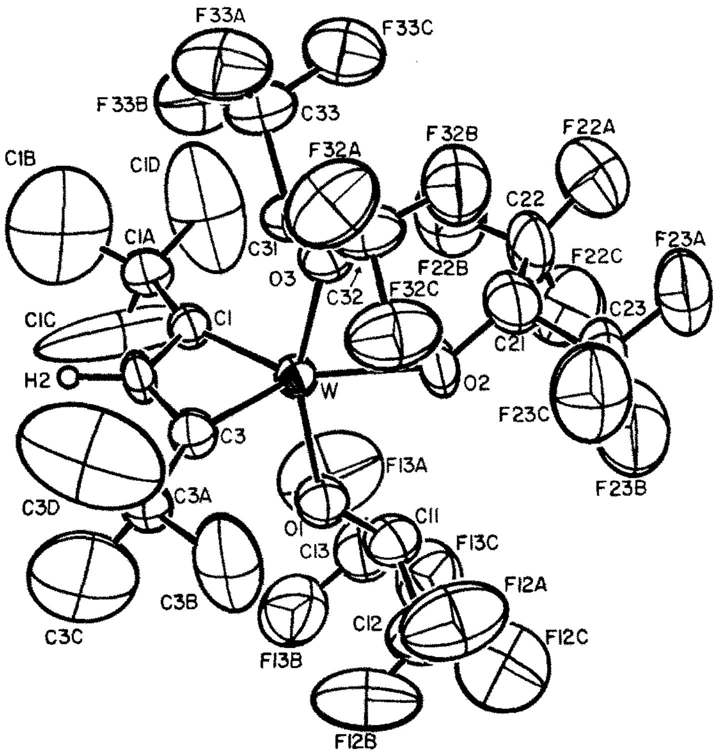


Fig. 1. Molecular geometry and atomic numbering scheme for $\overline{\mathrm{W[C(t\text{-}Bu)CHC(t\text{-}Bu)]}}[\mathrm{OCH(CF_3)_2}]_3$.

Description of the molecular structure

The crystal consists of an ordered assembly of discrete monomeric molecular units which are appropriately separated; there are no unusually short intermolecular contacts. The overall molecular geometry and the atomic labelling scheme is presented in Fig. 1. A stereoscopic view of the structure appears as Fig. 2. Interatomic distances and angles are collected in Tables 4 and 5. It should be noted that the three terminal methyl groups on each t-butyl substituent show huge thermal el-

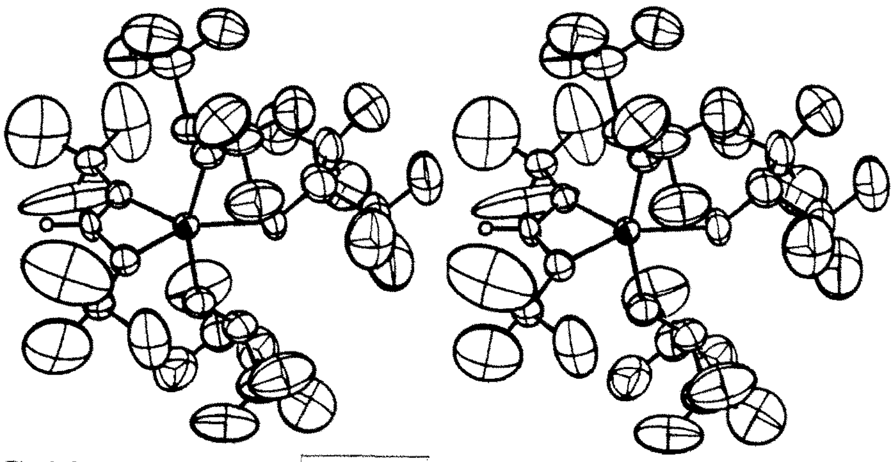


Fig. 2. Stereoscopic view of the $\overline{\mathrm{W[C(t\text{-}Bu)CHC(t\text{-}Bu)]}}[\mathrm{OCH(CF_3)_2}]_3$ molecule.

TABLE 4

INTERATOMIC DISTANCES (in Å) FOR $\overline{W[C(t\text{-}Bu)CHC}(t\text{-}Bu)][OCH(CF_3)_2]_3$

(A) Distances about the tungsten atom			
W–O(1)	1.954(7)	W–C(1)	1.921(10)
W–O(2)	1.957(8)	W–C(2)	2.103(9)
W–O(3)	1.959(7)	W–C(3)	1.889(9)
(B) Distances within $C_3(t\text{-}Bu)_2H$ ligand			
C(1)–C(2)	1.418(13)	C(3)–C(3A)	1.480(13)
C(2)–C(3)	1.499(14)	C(3A)–C(3B)	1.427(23)
C(1)–C(1A)	1.485(15)	C(3A)–C(3C)	1.413(41)
C(1A)–C(1B)	1.404(42)	C(3A)–C(3D)	1.383(36)
C(1A)–C(1C)	1.367(42)		
C(1A)–C(1D)	1.307(30)		
(C) O–C and C–C distance within the $OCH(CF_3)_2$ ligands			
O(1)–C(11)	1.334(15)	C(21)–C(22)	1.496(31)
O(2)–C(21)	1.329(17)	C(21)–C(23)	1.501(27)
O(3)–C(31)	1.373(13)	C(31)–C(32)	1.520(24)
C(11)–C(12)	1.528(28)	C(31)–C(33)	1.498(19)
C(11)–C(13)	1.474(26)		
(D) C–F distances within the $OCH(CF_3)_2$ ligands			
C(12)–F(12A)	1.273(27)	C(23)–F(23A)	1.291(22)
C(12)–F(12B)	1.232(32)	C(23)–F(23B)	1.345(26)
C(12)–F(12C)	1.358(30)	C(23)–F(23C)	1.306(24)
C(13)–F(13A)	1.284(28)	C(32)–F(32A)	1.239(18)
C(13)–F(13B)	1.320(23)	C(32)–F(32B)	1.303(22)
C(13)–F(13C)	1.298(21)	C(32)–F(32C)	1.355(19)
C(22)–F(22A)	1.403(21)	C(33)–F(33A)	1.290(17)
C(22)–F(22B)	1.297(30)	C(33)–F(33B)	1.306(22)
C(22)–F(22C)	1.285(24)	C(33)–F(33C)	1.356(21)

lipsoids; there are clearly large librational motions (possibly even hindered rotation) of the methyl groups about the C(1)–C(1A) axis (for C(1B), C(1C) and C(1D)) and about the C(3)–C(3A) axis (for C(3B), C(3C) and C(3D)). This manifests itself in an artificial contraction and spread in C–Me distances about both C(1A) (C(1A)–Me 1.307(30)–1.404(42) Å) and C(3A) (C(3A)–Me 1.383(36)–1.427(23) Å). The C(ring)–C(t-butyl) distances appear to be normal (viz., C(1)–C(1A) 1.485(15) Å and C(3)–C(3A) 1.480(13) Å) and we do not expect this librational problem to cause any significant systematic errors in other interatomic parameters.

The central tungsten atom is in a formal oxidation state of +6 and is linked to three hexafluoroisopropoxide ligands and (formally) a chelating $C_3H(t\text{-}Bu)_2^{3-}$ ligand. The coordination geometry about the tungsten(VI) center approximates to trigonal bipyramidal, but there are substantial deviations from the idealized angles. Thus, the two axial alkoxide ligands define an O(1)–W–O(3) angle of only 157.2(3)°. The axial-equatorial angles show significant variations with O(1)–W–O(2) 79.2(3)°, O(1)–W–C(1) 101.8(4)°, O(1)–W–C(3) 91.4(4)°, O(3)–W–O(2) 80.7(3)°, O(3)–W–C(1) 99.4(4)° and O(3)–W–C(3) 99.1(4)°. Within the equatorial plane, the C(1)–W–C(3) angle is 84.6(4)°, while the C(α)–W–O angles are inequivalent (O(2)–W–C(1) 129.8(4)° versus O(2)–W–C(3) 145.3(4)°, (see Fig. 3). This same pattern of inequivalence occurs for other trigonal bipyramidal tungstenacyclobutadiene complexes, the L_{equ}–W–C(α) angle being 124.48(28)° and 150.02(26)° in

TABLE 5

INTERATOMIC ANGLES (deg) FOR $W[\overline{C(t\text{-}Bu)CHC}(t\text{-}Bu)][OCH(CF_3)_2]_3$

(A) Angles about tungsten atom			
O(1)–W–O(2)	79.2(3)	O(3)–W–C(1)	99.4(4)
O(1)–W–O(3)	157.2(3)	O(3)–W–C(3)	99.1(4)
O(1)–W–C(1)	101.8(4)	O(3)–W ... C(2)	101.7(3)
O(1)–W–C(3)	91.4(4)	C(1)–W–C(3)	84.6(4)
O(1)–W ... C(2)	99.8(3)	C(1)–W ... C(2)	40.9(4)
O(2)–W–O(3)	80.7(3)	C(3)–W ... C(2)	43.7(4)
O(2)–W–C(3)	145.3(4)	C(1)–W–O(2)	129.8(4)
O(2)–W ... C(2)	170.6(4)		
(B) Angles involving the $C_3(t\text{-}Bu)_2H$ ligand			
C(1)–C(2)–C(3)	123.1(8)	C(2)–C(1)–C(1A)	128.6(9)
W–C(1)–C(2)	76.4(6)	C(2)–C(3)–C(3A)	126.8(9)
W–C(3)–C(2)	75.8(5)		
C(1)–C(1A)–C(1B)	114.8(13)		
C(1)–C(1A)–C(1C)	110.7(17)		
C(1)–C(1A)–C(1D)	112.2(15)		
C(3)–C(3A)–C(3B)	109.1(11)		
C(3)–C(3A)–C(3C)	113.4(14)		
C(3)–C(3A)–C(3D)	112.0(14)		
W–C(1)–C(1A)	154.9(8)		
W–C(3)–C(3A)	156.1(8)		
(C) W–O–C angles			
W–O(1)–C(11)	137.9(7)	W–O(3)-C(31)	135.3(6)
W–O(2)–C(21)	138.7(9)		
(D) O–C–C and C–C–C angles within the $OCH(CF_3)_2$ ligands			
O(1)–C(11)–C(12)	108.6(13)	O(3)–C(31)–C(33)	111.0(10)
O(1)–C(11)–C(13)	112.7(13)	C(12)–C(11)–C(13)	115.0(14)
O(2)–C(21)–C(22)	107.7(15)	C(22)–C(21)–C(23)	114.6(14)
O(2)–C(21)–C(23)	112.4(15)	C(32)–C(31)–C(33)	112.6(11)
O(3)–C(31)–C(32)	112.2(10)		
(E) C–C–F Angles within the $OCH(CF_3)_2$ ligands			
C(11)–C(12)–F(12A)	111.7(15)	C(21)–C(23)–F(23A)	114.5(17)
C(11)–C(12)–F(12B)	114.1(23)	C(21)–C(23)–F(23B)	110.0(16)
C(11)–C(12)–F(12C)	107.9(17)	C(21)–C(23)–F(23C)	112.5(14)
C(11)–C(13)–F(13A)	113.3(14)	C(31)–C(32)–F(32A)	113.0(16)
C(11)–C(13)–F(13B)	112.2(17)	C(31)–C(32)–F(32B)	112.7(14)
C(11)–C(13)–F(13C)	115.4(18)	C(31)–C(32)–F(32C)	107.7(12)
C(21)–C(22)–F(22A)	109.2(18)	C(31)–C(33)–F(33A)	112.1(13)
C(21)–C(22)–F(22B)	113.8(16)	C(31)–C(33)–F(33B)	111.2(12)
C(21)–C(22)–F(22C)	115.0(19)	C(31)–C(33)–F(33C)	109.8(14)
(F) F–C–F angles within the $OCH(CF_3)_2$ ligands			
F(12A)–C(12)–F(12B)	106.8(19)	F(23A)–C(23)–F(23B)	106.9(14)
F(12A)–C(12)–F(12C)	110.9(24)	F(23A)–C(23)–F(23C)	109.0(17)
F(12B)–C(12)–F(12C)	105.2(17)	F(23B)–C(23)–F(23C)	103.2(17)
F(13A)–C(13)–F(13B)	103.8(20)	F(32A)–C(32)–F(32B)	108.6(14)
F(13A)–C(13)–F(13C)	105.7(19)	F(32A)–C(32)–F(32C)	110.2(15)
F(13B)–C(13)–F(13C)	105.4(13)	F(32B)–C(32)–F(32C)	104.3(15)
F(22A)–C(22)–F(22B)	106.6(18)	F(33A)–C(33)–F(33B)	110.9(15)
F(22A)–C(22)–F(22C)	103.7(14)	F(33A)–C(33)–F(33C)	106.5(12)
F(22B)–C(22)–F(22C)	107.7(21)	F(33B)–C(33)–F(33C)	106.1(13)

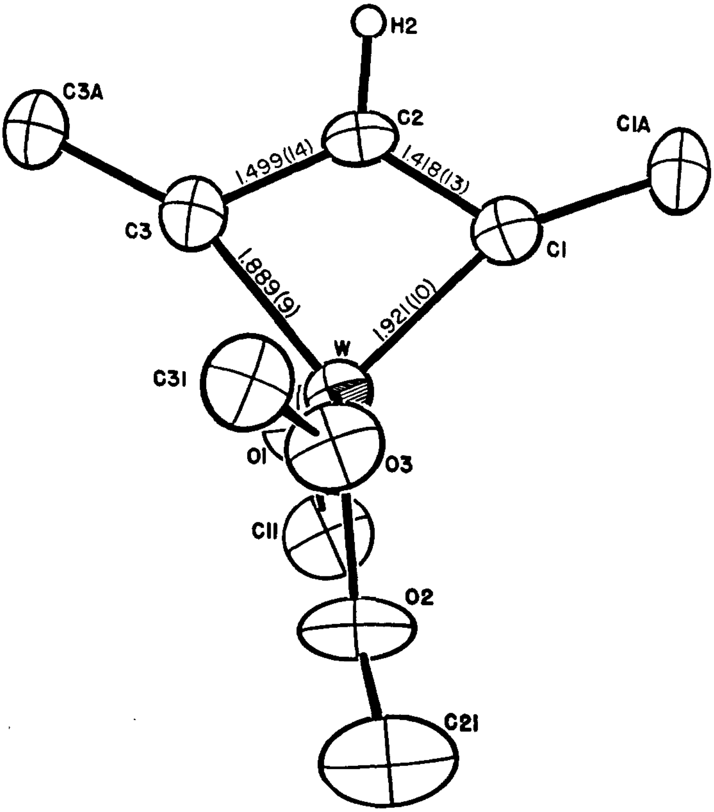


Fig. 3. View of the equatorial coordinations plane (plus the O(1)–C(11) and O(3)–C(31) portions of the axial ligands. Note that the equatorial alkoxide ligand (O(2)–C(21)) is offset from a position bisecting the external C(3)–W–C(1) angle.

W[C(t-Bu)C(Me)C(Me)]Cl_3 [2] and 127.7(3)° and 150.0(4)° in W[C(Et)C(Et)-C(Et)][O-2,6-C_6H_3(i-Pr)$_2$]$_3$ [3]. Professor Albright [18] has recently informed us that theoretical calculations in his research group show that L_{equ}–W–C(α) angles to very "soft", with little energy difference between the observed inequivalent values and the symmetrical bisecting case.

The WC_3 ring (see Fig. 3) is planar within the limits of experimental error, internal angles being C(1)–W–C(3) 84.6(4)°, W–C(3)–C(2) 75.8(5)°, C(1)–C(2)–C(3) 123.1(8)° and W–C(1)–C(2) 76.4(6)° (Σ 359.9°). Dimensions within the WC_3 ring show some apparent variations consistent with minor contributions from bond alternation and with the offset W–O(2) bond (see ref. 3), but a careful analysis indicates that these are not statistically significant differences. Thus, the two W–C(α) distances, W–C(1) 1.921(10) Å and W–C(3) 1.889(9) Å, are within ~ 1.5 σ of the average W–C(α) distance of 1.905 ± 0.014 Å. Similarly, the two C(α)–C(β) distances, C(1)–C(2) 1.418(13) Å and C(3)–C(2) 1.499(14) Å, are each within ~ 2σ of the average C(α)–C(β) distance of 1.458 ± 0.019 Å. These observed distances are in agreement with previous measurements on planar tungstenacyclobutadiene complexes [19a]. The W ··· C(2) distances of 2.103(9) Å are remarkably short, somewhere between the normally accepted W–C single-bond and W=C double-bond distances [19b]. Bursten has suggested that there is direct W–C(β) bonding in planar tungstenacyclobutadiene complexes [20]; more recent calculations by Albright and coworkers [18] are not in accord with this suggestion.

Despite the large size of the t-butyl substituents on C(1) and C(3), the external W–C(α)-substituent angles are very obtuse (i.e., W–C(1)–C(1A) 154.9(8)°) and W–C(3)–C(3A) 156.1(8)°) and in the range normally observed for M=C(α)–C(β) angles in metal alkylidene complexes [21].

The hexafluoroisopropoxide ligands are close to equivalent. The two axial ligands are associated with tungsten–oxygen distances of W–O(1) 1.954(7) Å and W–O(3) 1.959(7) Å and angles of W–O(1)–C(11) 137.9(7)° and W–O(3)–C(31) 135.3(6)°; the single equatorial alkoxide ligand has W–O(2) 1.957(8) Å and W–O(2)–C(21) 138.7(9)°. These results are in accord with our previous structural study of W[C(Et)C(Et)C(Et)][OCH(CF_3)$_2$]$_3$ [4] (W–O(axial) 1.962(12)–1.982(11) Å, W–O(equatorial) 1.932(10)–1.934(10) Å, angle W–O(ax)–C 129.4(9)–133.6(8)°, angle W–O(equ)–C 135.9(11)–138.6(10)°) and show the weak π-donor capabilities of the hexafluoroisopropoxide ligand. Significantly different W–O distances and (particularly) W–O–C angles are observed for axial and equatorial positions for the strongly π-donating 2,6-diisopropylphenoxide ligands in W[C(Et)C(Et)C(Et)][O-2,6-C_6H_3(i-Pr)$_2$]$_3$ [3] (W–O(ax) 1.979(6)–2.008(6) Å, W–O(equ) 1.885(6) Å, angle W–O(ax)–C 131.4(6)–135.1(5)°, angle W–O(equ)–C 151.5(6)°).

Finally, we note that the bonding of the 1,3-disubstituted ligand [C(t-Bu)CHC(t-Bu)] to tungsten is analogous in every way to the bonding of 1,2,3-trisubstituted ligands [C_3R_3] in planar tungstenacyclobutadiene complexes.

Acknowledgments

This work was supported in part, by NSF grant CHE80-23448 (to M.R.C.).

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