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CRYSTAL AND MOLECULAR STRUCTURE OF (η^5-C_5H_5)W[$C_3(CMe_3)_2Me$]-(PMe_3)Cl_2, A SPECIES WITH A TETRAHEDRAL WC_3 CORE FORMED FROM A TUNGSTENACYCLOBUTADIENE COMPLEX VIA ATTACK ON TUNGSTEN BY A PHOSPHORUS-DONOR LIGAND

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Summary

The complex (η^5-C_5H_5)W[$C_3(CMe_3)_2Me$](PMe_3)Cl_2, prepared previously by the reaction of the tungstenacyclobutadiene complex (η^5-C_5H_5)W[C(Ph)C(CMe_3)C-(Ph)]Cl_2 with PMe_3, has been subjected to a single-crystal X-ray diffraction study. This complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; No. 14) with a 10.302(3) Å, b 15.314(3) Å, c 14.130(2) Å, β 98.036(16)°, V 2207.4(8) $Å^3$ and $Z = 4$. Diffraction data (Mo-K_α, 2θ 4.5–50.0°) were collected with a Syntex P2_1 automated four-circle diffractometer and the structure was refined to R 4.7% for all 3919 independent reflections (R 3.4% for those 3290 data with $|F_0| > 3\sigma(|F_0|)$). The molecular geometry approximates that of a "four-legged piano stool" with the tungsten atom surrounded by an η^5-cyclopentadienyl ligand, two chloride ligands (W–Cl(1) 2.538(2) Å, W–Cl(2) 2.504(2) Å) a trimethylphosphine ligand (W–P 2.600(2) Å) and an η^3-[$C_3(CMe_3)_2Me$] ligand. The three carbon atoms of the C_3 ring are tightly bound to tungsten (W–C(1) 2.139(5) Å, W–C(2) 2.150(6) Å W–C(3) 2.200(6) Å) and the WC_3 core of the molecule is closer to a "tungstenatetrahedrane" moiety than to the more familiar η^3-cyclopropenium-tungsten (i.e., $C_3H_3^+$) representation; the C_3 ring is perhaps best termed an η^3-cyclopropenyl system.

Introduction

For some years we have been interested in "high oxidation-state" organometallic complexes of tungsten. We have characterized crystallographically several alkylidyne

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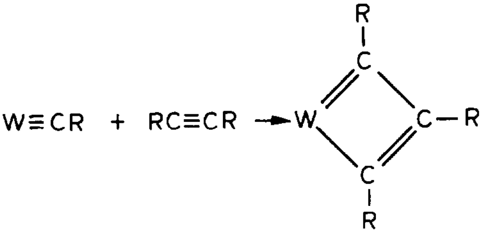
complexes of tungsten [1–7] and a number of tungstenacyclobutadiene complexes formed by addition of internal alkynes to alkylidynetungsten complexes [8–12], see eq. 1.



(1)

It has recently been shown that certain tungstenacyclobutadiene complexes react with donor ligands, rearranging into tetrahedral WC_3 complexes. We have previously characterized the species $W[C_3Me_2(CMe_3)][Me_2N(CH_2)_2NMe_2]Cl_3$ [13,14] and now provide the results of a full crystallographic study on $(\eta^5\text{-}C_5H_5)W[C_3(CMe_3)_2Me]\text{-}(PMe_3)Cl_2$, prepared as in eq. 2. A preliminary account of this work has appeared previously [15].

$$CpW[\eta^2\text{-}1,3\text{-}C_3(CMe_3)_2Me]Cl_2 + PMe_3 \rightarrow CpW[\eta^2\text{-}C_3(CMe_3)_2Me](PMe_3)Cl_2 \quad (2)$$

Experimental

Data collection

Crystals of $(\eta^2\text{-}C_5H_5)W(C_3(CMe_3)_2Me](PMe_3)Cl_2$ were provided by Professor R.R. Schrock and Mr. L.G. McCullough of the Department of Chemistry, Massachusetts Institute of Technology. The crystal selected for the X-ray structural analysis was a reddish-brown parallelepiped of approximate orthogonal dimensions 0.25 × 0.25 × 0.25 mm. It was sealed into a thin-walled glass capillary tube under an inert atmosphere (argon) and was aligned on our Syntex $P2_1$ automated four-circle diffractometer. Set-up operations (i.e., determination of unit cell parameters, Laue group and the orientation matrix) and data collection (via a coupled θ(crystal)–2θ(counter) scan routine) were carried out as described previously [16]; details are listed in Table 1. The systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ are consistent with the standard setting of the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; No. 14) [17].

All data were corrected for absorption and for Lorentz and polarization effects and were converted to unscaled $|F|$ values; any datum with $I(\text{net}) < 0$ was assigned to value of $|F_0| = 0$. Data were placed on an approximate absolute scale by means of a Wilson Plot.

Solution and refinement of the structure

All subsequent calculations were performed using our locally modified version of the Syntex XTL interactive crystallographic program set [18]. The calculated structure factors were based upon the analytical form of the neutral atoms' scattering factors and were corrected for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dipsersion [19]. The function minimized in the least-squares refinement process was $\Sigma w(|F_0| - |F_c|)^2$ where $1/w = [\{\sigma(|F_0|)\}^2 + \{0.01|F_0|\}^2]$.

TABLE 1

CRYSTALLOGRAPHIC DATA FOR $(\eta^5\text{-}C_5H_5)W[C_3(CMe_3)_2Me](PMe_3)Cl_2$

(A) Unit cell parameters at 24°C (297 K)

Crystal system: monoclinic	Formula: $C_{20}H_{35}Cl_2PW$
Space group: $P2_1/c$ (No. 14)	Molec. wt.: 561.28
a 10.302(3) Å	$Z = 4$
b 15.314(3) Å	D(calcd) 1.69 g cm^{-3}
c 14.130(2) Å	μ(Mo-K_α) 58.5 cm^{-1}
β 98.036(16)°	
V 2207.4(8) Å^3	

(B) Collection of X-Ray Diffraction Data

Diffractometer: Syntex $P2_1$

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

Monochromator: highly oriented (pyrolytic) graphite, 2θ(max) 12.160° for 002 reflection; equatorial mode; assumed 50% perfect/50%/ideally mosaic for polarization correction

Reflections measured: $+h$, $+k$, $\pm l$ for 2θ 4.5–50.0°; 4135 reflections merged to 3913 unique data

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

Scan-speed: 2.50 deg/min

Scan width: $[2\theta(K_{\alpha_1})-1.0]-[2\theta(K_{\alpha_2})+1.0]$ deg

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

Standards: 3 remeasured after each batch of 97 reflections; no significant fluctuations observed

The position of the tungsten atom was determined from a Patterson synthesis. All remaining non-hydrogen atoms were located from difference-Fourier syntheses. Hydrogen atoms were included in idealized positions based upon d(C–H) 0.95 Å [20] and the appropriate trigonal-planar or staggered-tetrahedral geometry. Full matrix least-squares refinement converged with R_F 4.7% and R_{wF} 3.4% for 217 parameters refined against all 3919 unique data and R_F 3.4% and R_{wF} 3.2% for those 3290 data with $|F_0| > 3\sigma(|F_0|)$.

A final difference-Fourier map showed no significant features; the structure is both correct and complete. Positional parameters are collected in Table 2, while thermal parameters are listed in Table 3.

Description of the molecular structure

The crystal consists of an ordered array of discrete molecular units of $(\eta^5\text{-}C_5H_5)W[C_3(CMe_3)_2Me](PMe_3)Cl_2$, which are separated by normal Van der Waals' distances; there are no abnormally short intermolecular contacts. The overall molecular geometry and the atomic labelling scheme are illustrated in Fig. 1. A stereoscopic view of the structure appears as Fig. 2. Interatomic distances and angles are collected in Tables 4 and 5, while interatomic planes are given in Table 6.

The central tungsten atom is linked to an η^5-cyclopentadienyl ring, two chloride ligands, one PMe_3 ligand and the C_3 ring (defined by atoms C(1), C(2) and C(3)). The overall stereochemistry about tungsten approximates to the "four-legged piano stool" arrangement found for such molecules as $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$ [21], see Fig. 3; in this description we regard the C_3 ring as taking up a single coordination site more-or-less *trans* to the PMe_3 ligand. The $(\eta^5\text{-}C_5H_5)W[C_3](P)Cl_2$ core of the molecule has approximate, but not precise C_s symmetry (cf., Fig. 3). The two chloride ligands are close to equivalent, with W–Cl(1) 2.538(2) Å, W–Cl(2) 2.504(2)

TABLE 2

FINAL POSITIONAL PARAMETERS FOR (η^5-C_5H_5)W[$C_3(CMe_3)_2Me$](PMe_3)Cl_2

Atom	*x*	*y*	*z*	*B* (Å^2)
W	0.22110(2)	0.05882(1)	0.21477(2)	
Cl(1)	0.00125(15)	−0.01876(11)	0.18926(12)	
Cl(2)	0.39615(15)	0.12380(10)	0.33498(11)	
P	0.10560(16)	0.12087(11)	0.35263(11)	
C(4)	−0.07120(69)	0.11073(60)	0.34575(57)	
C(5)	0.12505(79)	0.23784(49)	0.36829(54)	
C(6)	0.15877(87)	0.08526(56)	0.47421(48)	
C(1)	0.28705(53)	−0.06437(36)	0.27465(36)	
C(2)	0.26714(56)	−0.07036(38)	0.17008(39)	
C(3)	0.38530(56)	−0.03326(36)	0.21611(40)	
C(11)	0.28479(61)	−0.13085(39)	0.35426(43)	
C(12)	0.36327(72)	−0.10158(50)	0.44869(47)	
C(13)	0.14189(75)	−0.14764(50)	0.36973(50)	
C(14)	0.33924(85)	−0.21868(48)	0.32421(58)	
C(21)	0.21723(67)	−0.13150(46)	0.09201(46)	
C(31)	0.53076(60)	−0.04174(40)	0.20784(46)	
C(32)	0.61261(66)	−0.05360(56)	0.30531(54)	
C(33)	0.58454(69)	0.03791(49)	0.15931(59)	
C(34)	0.54905(71)	−0.12094(53)	0.14570(56)	
C(51)	0.09823(71)	0.16097(58)	0.11762(54)	
C(52)	0.2130(10)	0.20243(45)	0.15421(50)	
C(53)	0.31537(76)	0.16188(61)	0.11905(57)	
C(54)	0.26530(92)	0.09644(55)	0.05992(52)	
C(55)	0.13246(89)	0.09460(52)	0.05671(46)	
H(4A)	−0.0988	0.1362	0.4008	6.0
H(5A)	0.0809	0.2565	0.4194	6.0
H(6A)	0.1076	0.1134	0.5161	6.0
H(12A)	0.3586	−0.1452	0.4958	6.0
H(13A)	0.1401	−0.1891	0.4194	6.0
H(14A)	0.3377	−0.2600	0.3741	6.0
H(21A)	0.2670	−0.1838	0.0986	6.0
H(32A)	0.7025	−0.0586	0.2977	6.0
H(33A)	0.6751	0.0295	0.1558	6.0
H(34A)	0.6392	−0.1272	0.1397	6.0
H(51)	0.0126	0.1745	0.1309	6.0
H(52)	0.2201	0.2508	0.1966	6.0
H(53)	0.4054	0.1769	0.1335	6.0
H(54)	0.3149	0.0581	0.0261	6.0
H(55)	0.0737	0.0556	0.0200	6.0
H(4B)	−0.0948	0.0507	0.3425	6.0
H(4C)	−0.1124	0.1398	0.2902	6.0
H(5B)	0.0888	0.2667	0.3111	6.0
H(5C)	0.2156	0.2515	0.3824	6.0
H(6B)	0.2485	0.0998	0.4919	6.0
H(6C)	0.1480	0.0238	0.4783	6.0
H(12B)	0.3277	−0.0485	0.4687	6.0
H(12C)	0.4521	−0.0926	0.4401	6.0
H(13B)	0.0937	−0.1695	0.3123	6.0
H(13C)	0.1035	−0.0945	0.3868	6.0
H(14B)	0.4268	−0.2109	0.3119	6.0
H(14C)	0.2867	−0.2392	0.2679	6.0
H(21B)	0.2248	−0.1053	0.0320	6.0
H(21C)	0.1277	−0.1444	0.0953	6.0
H(32B)	0.5853	−0.1050	0.3346	6.0
H(32C)	0.6010	−0.0045	0.3444	6.0
H(33B)	0.5732	0.0889	0.1955	6.0
H(33C)	0.5383	0.0443	0.0966	6.0
H(34B)	0.5000	−0.1130	0.0841	6.0
H(34C)	0.5192	−0.1718	0.1744	6.0

TABLE 3

ANISOTROPIC THERMAL PARAMETERS FOR $(\eta^5\text{-}C_5H_5)W[C_3(CMe_3)_2Me](PMe_3)Cl_2$

(These anisotropic thermal parameters are in standard Syntex XTL format and enter the expression for the calculated structure factor in the form: $\exp[-0.25(h^2a^{*2}B_{11} + \ldots 2hka^*b^*_{12} + \ldots)]$)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	2.505(10)	1.9135(94)	2.1353(94)	−0.0400(93)	−0.0049(62)	−0.0289(87)
Cl(1)	2.966(65)	3.846(73)	4.075(72)	−0.573(58)	0.045(55)	−0.756(61)
Cl(2)	3.588(69)	3.136(69)	3.734(68)	−0.436(57)	−0.707(55)	−0.716(56)
P	3.650(74)	2.931(73)	2.901(67)	0.199(60)	0.466(56)	−0.503(56)
C(4)	3.84(34)	7.10(50)	6.22(43)	−0.25(35)	2.04(31)	−1.99(39)
C(5)	6.59(44)	3.73(36)	5.48(40)	0.50(33)	1.13(34)	−1.73(31)
C(6)	8.37(52)	6.34(47)	2.78(30)	2.14(40)	1.57(31)	0.09(29)
C(1)	3.10(24)	2.13(22)	2.36(22)	−0.04(23)	0.05(18)	−0.29(21)
C(2)	3.22(26)	2.60(27)	2.60(24)	0.14(22)	0.38(20)	−0.07(21)
C(3)	2.89(25)	2.20(24)	2.92(25)	0.24(19)	0.15(20)	0.12(19)
C(11)	4.05(31)	2.38(26)	3.49(28)	−0.08(23)	0.12(23)	0.53(22)
C(12)	5.46(38)	4.43(36)	3.44(30)	0.39(31)	−0.32(27)	0.56(27)
C(13)	5.65(39)	4.81(40)	4.22(33)	−1.38(32)	0.98(29)	1.14(29)
C(14)	7.25(47)	3.35(34)	5.83(41)	0.63(33)	1.05(36)	1.13(31)
C(21)	5.04(36)	3.92(33)	3.46(29)	−0.28(29)	0.15(26)	−1.29(26)
C(31)	3.19(27)	3.08(31)	4.21(30)	0.32(23)	0.91(23)	0.27(23)
C(32)	3.18(30)	6.55(46)	5.44(38)	1.13(32)	−0.39(26)	0.15(35)
C(33)	3.67(32)	4.70(41)	6.73(44)	0.03(28)	1.57(30)	0.79(32)
C(34)	4.62(37)	4.99(41)	6.18(42)	1.25(32)	1.66(32)	−0.30(34)
C(51)	3.96(34)	6.69(49)	4.82(37)	2.54(35)	1.09(29)	2.92(36)
C(52)	10.01(62)	2.45(30)	3.45(33)	−0.25(36)	0.18(37)	0.61(25)
C(53)	4.82(39)	6.42(50)	4.89(39)	−1.16(37)	0.25(32)	2.80(37)
C(54)	7.56(52)	4.94(40)	3.44(33)	1.75(39)	2.09(34)	1.53(30)
C(55)	7.63(50)	4.60(37)	2.26(27)	−1.34(36)	−1.12(29)	1.24(26)

Å and angle Cl(1)–W–Cl(2) 145.69(5)°. The tungsten–trimethyphosphine linkage is in the normal range with W–P 2.600(2) Å and the PMe_3 ligand is symmetrically disposed with respect to the chloride ligands, with angle Cl(1)–W–P 77.57(5)° and angle Cl(2)–W–P 73.03(5)°.

Individual W–C distances to the η^5-cyclopentadienyl system range from W–C(51) 2.334(8) Å through W–C(53) 2.373(9) Å and the W $\cdots$ Cp distance (Cp is the centroid of the $\eta^5\text{-}C_5H_5$ ring) is 2.046 Å (cf., values of 2.260(10)–2.376(9) Å and 2.001 Å, respectively, for $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$ [21]). The $\eta^5\text{-}C_5H_5$ system is planar within the limits of experimental error (see Table 6); C–C distances are 1.359(12)–1.408(11) Å and C–C–C angles are 106.7(7)–109.2(8)°.

The three carbon atoms of the C_3 ring are approximately equidistant from the tungsten atom, with W–C(1) 2.139(5) Å, W–C(2) 2.150(6) Å and W–C(3) 2.200(6) Å. The tungsten atom lies +1.991 Å from the plane of the C_3 ring (see Fig. 4). Displacements of the α-carbon atoms of the substituents from the C_3 ring are as follows: −0.908(6) Å for C(11), −0.632(7) Å for C(21) and −0.752(6) Å for C(31). These perpendicular displacements from the C_3 ring translate into angular displacements (calculated as $\sin^{-1}$ (perpendicular displacement)/(C(*ipso*)–C(α) distance)) of 36.7°, 25.2° and 29.6°, respectively. The ring to substituent distances are C(1)–C(11) 1.520(8), C(2)–C(21) 1.483(9) and C(3)–C(31) 1.525(8) Å (average 1.509 ± 0.023 Å). Within the C_3 ring, the carbon–carbon distances are C(1)–C(2)

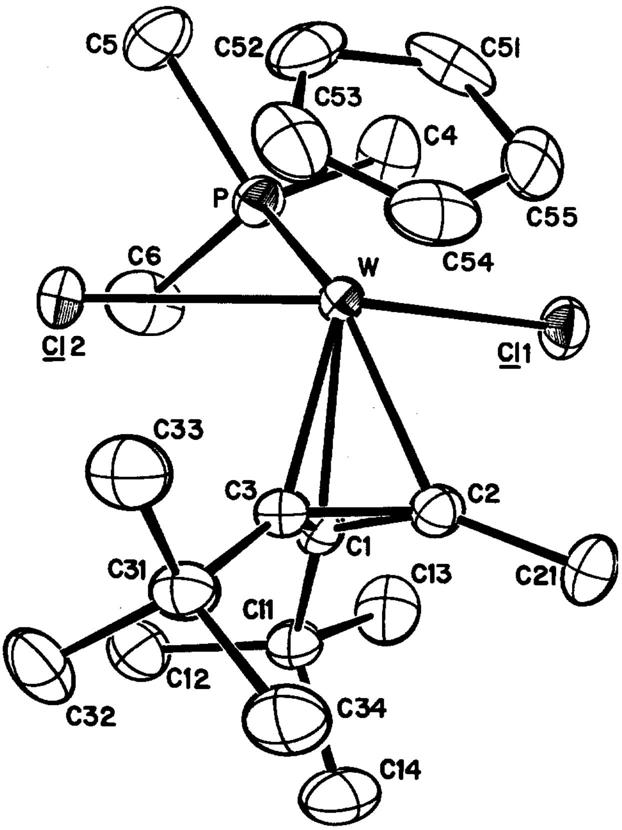


Fig. 1. Labelling of atoms in the (η^5-C_5H_5)W[$C_3(CMe_3)_2Me$](PMe_3)Cl_2 molecule (ORTEP-II diagram).

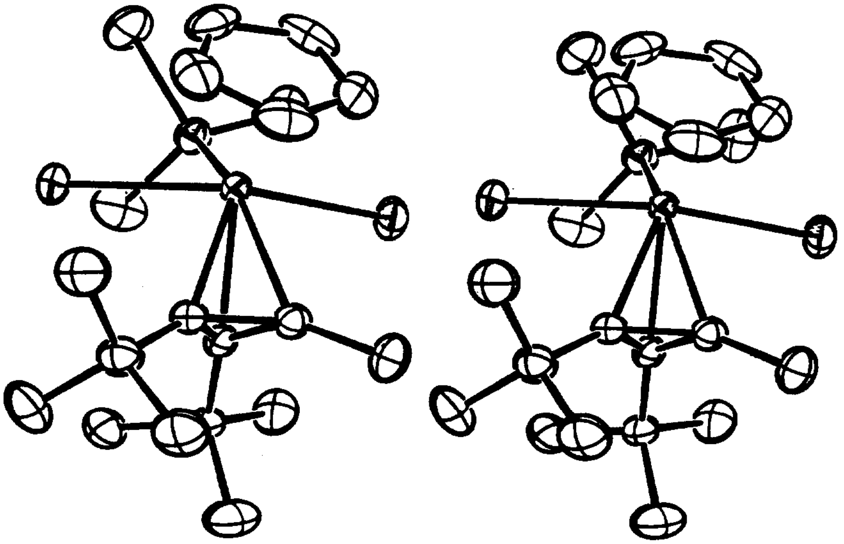


Fig. 2. Stereoscopic view of the (η^5-C_5H_5)W[$C_3(CMe_3)_2Me$](PMe_3)Cl_2 molecule.

TABLE 4

INTERATOMIC DISTANCES (in Å) FOR $(\eta^5\text{-}C_5H_5)W[C_3(CMe_3)_2Me](PMe_3)Cl_2$

Atoms	Dist.	Atoms	Dist.
(A) Distances within WC_3 system			
W–C(1)	2.139(5)	C(1)–C(2)	1.466(7)
W–C(2)	2.150(6)	C(1)–C(3)	1.473(8)
W–C(3)	2.200(6)	C(2)–C(3)	1.416(8)
W···Tr [a]	1.994		
(B) Distances within $(\eta^5\text{-}C_5H_5)W$ moiety			
W–C(51)	2.334(8)	C(51)–C(52)	1.377(12)
W–C(52)	2.357(7)	C(52)–C(53)	1.375(13)
W–C(53)	2.373(9)	C(53)–C(54)	1.359(12)
W–C(54)	2.368(8)	C(54)–C(55)	1.363(13)
W–C(55)	2.356(7)	C(55)–C(51)	1.408(11)
W···Cp [b]	2.046		
(C) Remaining tungsten – ligand and P – C distances			
W–Cl(1)	2.538(2)	P–C(4)	1.817(7)
W–Cl(2)	2.504(2)	P–C(5)	1.813(8)
W–P	2.600(2)	P–C(6)	1.813(7)
(D) Peripheral C – C distances in $C_3(CMe_3)_2Me$ ligand			
C(1)–C(11)	1.520(8)	C(11)–C(12)	1.527(9)
C(2)–C(21)	1.483(9)	C(11)–C(13)	1.540(10)
C(3)–C(31)	1.525(8)	C(11)–C(14)	1.540(10)
C(31)–C(32)	1.522(10)	C(31)–C(34)	1.524(10)
C(31)–C(33)	1.540(10)		

[a] "Tr" is the centroid of the triangle formed by C(1), C(2) and C(3). [b] "Cp" is the centroid of the $\eta^5\text{-}C_5H_5$ ligand as defined by C(51) through C(55).

1.466(7) Å, C(2)–C(3) 1.416(8) Å and C(3)–C(1) 1.473(8) Å; the C(2)–C(3) distance appears to be significantly shorter than the other two intraring distances. This pattern is repeated in the related "tungstenatetrahedrane" species $W[C_3Et_2(CMe_3)](O_2CMe)_3$ (C–C 1.405(11), 1.448(8) and 1.451(10) Å) [22], but not in $W[C_3Me_2(CMe_3)][Me_2N(CH_2)_2NMe_2]Cl_3$ (C–C = 1.383(9), 1.432(10) and 1.547(10) Å [13].

The structure of $[CPh_3^+][ClO_4^-]$ has been reported [23] as have the structures of several transition metal complexes containing the $\eta^3\text{-}C_3Ph_3$ ligand [24–27]. Details on these species have been collected in Table 7, along with information on the three characterized "tungstenatetrahedrane" complexes.

All indications are that the $\eta^3\text{-}C_3R_3$ ligands in the "tungstenatetrahedrane" complexes are more tightly bound than the $\eta^3\text{-}C_3Ph_3$ ligands in the other complexes. Thus, the C_3 ring in $Ni(\eta^3\text{-}C_3Ph_3)(\eta^5\text{-}C_5H_5)$ [24] is further from the nickel atom than is the C_5 ring by ~ 0.05 Å (perpendicular distances are Ni–C_3 1.779 Å and Ni–C_5 1.726 Å), whereas the C_3 ring in the present $(\eta^5\text{-}C_5H_5)W[C_3(CMe_3)_2Me](PMe_3)Cl_2$ molecule is closer to the tungsten atom than is the C_5 ring by ~ 0.05 Å (1.991 versus 2.046 Å). Furthermore, the phenyl rings of the $\eta^3\text{-}C_3Ph_3$ ligands are bent out of the C_3 plane by only ~ 20° (specifically: 19.2, 19.7 and 20.1° for $Ni(\eta^3\text{-}C_3Ph_3)(\eta^5\text{-}C_5H_5)$ [24] and 16.7, 19.4 and 20.2° for $Ni(\eta^3\text{-}C_3Ph_3)NiCl(py)_2 \cdot py$ [25]) but by more than this for the "tungstenatetrahedrane" complexes, viz., 25.2°,

TABLE 5

INTERATOMIC ANGLES (deg) FOR (η^5-C_5H_5)W[$C_3(CMe_3)_2$Me](PMe_3)Cl_2

Atoms	Angle	atoms	Angle
(A) Angles around the tungsten atom			
Cl(1)-W-Cl(2)	145.69(5)	Cl(2)-W-C(3)	76.64(15)
Cl(1)-W-P	77.57(5)	P-W-C(1)	100.33(15)
Cl(1)-W-C(1)	82.59(15)	P-W-C(2)	134.36(16)
Cl(1)-W-C(2)	75.91(16)	P-W-C(3)	131.26(15)
Cl(1)-W-C(3)	111.77(15)	C(1)-W-C(2)	39.97(21)
Cl(2)-W-P	73.03(5)	C(1)-W-C(3)	39.66(20)
Cl(2)-W-C(1)	85.61(15)	C(2)-W-C(3)	37.98(21)
Cl(2)-W-C(2)	113.41(16)		
(B) Angles around phosphorus			
W-P-C(4)	119.27(27)	C(4)-P-C(5)	100.60(37)
W-P-C(5)	113.47(26)	C(4)-P-C(6)	101.12(27)
W-P-C(6)	119.39(27)	C(5)-P-C(6)	99.67(36)
(C) Angles around C(1), C(2) and C(3)			
W-C(1)-C(11)	147.85(40)	C(2)-C(1)-C(3)	57.62(37)
W-C(1)-C(2)	70.40(31)	C(2)-C(1)-C(11)	133.61(49)
W-C(1)-C(3)	72.41(31)	C(3)-C(1)-C(11)	135.66(49)
W-C(2)-C(21)	137.03(44)	C(1)-C(2)-C(3)	61.44(39)
W-C(2)-C(1)	69.63(30)	C(1)-C(2)-C(21)	140.75(54)
W-C(2)-C(3)	72.94(33)	C(3)-C(2)-C(21)	141.37(55)
W-C(3)-C(1)	67.94(30)	C(1)-C(3)-C(2)	60.94(38)
W-C(3)-C(2)	69.08(32)	C(1)-C(3)-C(31)	140.82(51)
W-C(3)-C(31)	144.74(42)	C(2)-C(3)-C(31)	136.17(52)
(D) Angles within the CMe_3 Groups			
C(1)-C(11)-C(12)	112.89(51)	C(12)-C(11)-C(13)	108.95(54)
C(1)-C(11)-C(13)	109.32(51)	C(12)-C(11)-C(14)	109.18(55)
C(1)-C(11)-C(14)	109.70(52)	C(13)-C(11)-C(14)	106.60(55)
C(3)-C(31)-C(32)	111.53(53)	C(32)-C(31)-C(33)	108.01(56)
C(3)-C(31)-C(33)	112.66(53)	C(32)-C(31)-C(34)	109.20(56)
C(3)-C(31)-C(34)	108.29(53)	C(33)-C(31)-C(34)	107.01(56)
(E) Angles within the η^5-C_5H_5 Ring			
C(55)-C(51)-C(52)	106.7(7)	C(53)-C(54)-C(55)	109.2(8)
C(51)-C(52)-C(53)	108.5(7)	C(54)-C(55)-C(51)	107.5(7)
C(52)-C(53)-C(54)	108.1(8)		

29.6° and 36.7° for the substituents in the present (η^5-C_5H_5)W[$C_3(CMe_3)_2$-Me](PMe_3)Cl_2 molecule; 25.09, 34.90 and 43.52° for W[$C_3Me_2(CMe_3)$][Me_2-$N(CH_2)_2NMe_2$]Cl_3 [13]; 21.54, 26.50 and 30.25° for W[$C_3Et_2(CMe_3)$](O_2CMe)$_3$ [22]. The structural evidence suggests that the η^3-C_3R_3 ligands in these tungsten complexes are tightly bound and are not simply two-electron donating η^3-cyclopropenium (η^3-$C_3R_3^+$) ligands. A survey of Table 7 shows that the perpendicular Mo–(C_3 ring) distance in Mo(η^3–C_3Ph_3)$(CO)_2$(bipy)Br [27] is 2.06 Å and that the individual Mo–C distances range from 2.193(18) Å through 2.262(22) Å (average 2.220 Å). Since Mo and W have almost identical covalent radii (as a result of the lanthanide contraction), it follows that similar W–(C_3 ring) and W–C distances are to be expected. This is not the case. Thus, in the present (η^5-C_5H_5)W[$C_3(CMe_3)_2$Me](PMe_3)Cl_2 molecule we have W–(C_3 ring) 1.991 Å and

TABLE 6

INTRAMOLECULAR PLANES AND ATOMIC DEVIATIONS THEREFROM

Atom	Dev. (Å)	Atom	Dev. (Å)
(A) C(1)–C(2)–C(3) plane			
$-0.4235x + 0.9041y - 0.0571z + 2.1333 = 0$			
C(1)*	0.000	C(11)	−0.908(6)
C(2)*	0.000	C(21)	−0.632(7)
C(3)*	0.000	C(31)	−0.752(6)
W	1.9913(2)		
(B) C(51) → C(55) plane			
$0.0054x + 0.6356y - 0.7720z - 0.3085 = 0$			
C(51)*	−0.008(8)	Cl(1)	−2.537(2)
C(52)*	0.006(7)	Cl(2)	−2.703(2)
C(53)*	−0.002(9)	P	−2.939(2)
C(54)*	−0.003(8)	C(1)	−3.889(5)
C(55)*	0.007(7)	C(2)	−2.817(6)
W	−2.0457(2)	C(3)	−2.947(6)
Dihedral angle(°) plane A/plane B 51.94° (128.06)°.			

W–C (aver) 2.163 Å. For W[$C_3Me_2(CMe_3)$][$Me_2N(CH_2)_2NMe_2$]Cl_3 [13], W–(C_3 ring) 1.911 Å and W–C (aver) 2.096 Å; for W[$C_3Et_2(CMe_3)$](O_2CMe)$_3$ [22], W–(C_3 ring) 1.942 Å and W–C (aver) 2.112 Å. Although the pattern of C(ring)–C(ring)

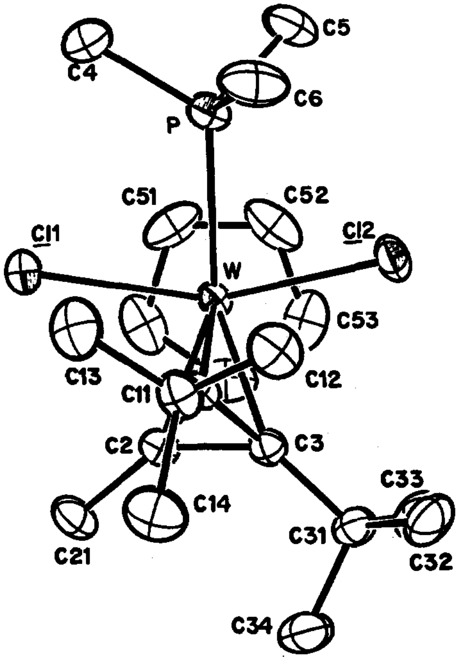


Fig. 3. The (η^5-C_5H_5)W[$C_3(CMe_3)_2Me$](PMe_3)Cl_2 molecule, projected onto the plane of the (η^5-C_5H_5) ligand.

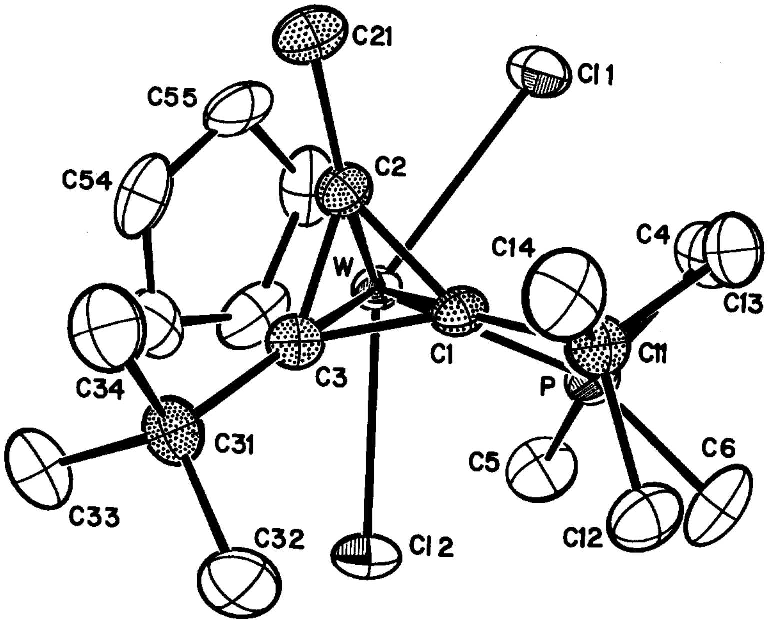


Fig. 4. The (η^5-C_5H_5)$W[C_3(CMe_3)_2Me](PMe_3)Cl_2$ molecule, viewed in the plane of the η^3-C_3 ligand.

TABLE 7

DISTANCES (in Å) WITHIN C_3R_3 COMPLEXES

Complex	$M-C_3(\perp)$	M–C	C–C(ring)	C(ring)–C(subst)	Ref.
$[C_3Ph_3^+][ClO_4^-]$	–	–	1.373(5)	1.436(5)	23
$Ni(C_3Ph_3)(C_5H_5)$	1.779	1.953(66)	1.421(8)	1.439(8)	24
		1.961(6)	1.427(8)	1.451(8)	
		1.968(6)	1.437(8)	1.466(8)	
$Ni(C_3Ph_3)Cl(py)_2py$	1.759	1.896(8)	1.414(11)	1.456(11)	25
		1.958(8)	1.422(11)	1.459(12)	
		1.968(8)	1.429(11)	1.461(12)	
$Co(C_3Ph_3)(CO)_3$	–	1.995(3)	1.410(5)	1.456(4)	26
		2.008(3)	1.421(5)	1.460(5)	
		2.024(3)	1.428(5)	1.462(2)	
$Mo(C_3Ph_3)(CO)_2(bipy)Br$	2.06	2.193(18)	1.413(30)	1.436(23)	27
		2.204(26)	1.454(26)	1.456(20)	
		2.262(22)	1.455(26)	1.495(21)	
$CpW[C_3(CMe_3)_2Me](PMe_3)Cl_2$	1.991	2.139(5)	1.416(8)	1.483(9)	present work
		2.150(6)	1.466(7)	1.520(8)	
		2.200(6)	1.473(8)	1.525(8)	
$W[C_3Me_2(CMe_3)](tmeda)Cl_3$	1.911	2.040(7)	1.383(9)	1.490(11)	13
		2.115(7)	1.432(10)	1.493(10)	
		2.133(7)	1.547(10)	1.503(10)	
$W[C_3Et_2(CMe_3)](O_2CMe)_3$	1.942	2.089(5)	1.405(11)	1.483(9)	22
		2.114(7)	1.448(8)	1.491(11)	
		2.134(6)	1.451(10)	1.500(15)	

distances is not presently understood, Table 7 does reveal a systematic pattern of C(ring)–C(substituent) distances. These are short in an uncoordinated $C_3Ph_3^+$ ion (1.436(5) Å in $[C_3Ph_3^+][ClO_4^-]$ [21]), increase slightly in the coordinated η^3-cyclopropenium complexes (1.452 Å (aver) in $Ni(\eta^3\text{-}C_3Ph_3)(\eta^5\text{-}C_5H_5)$ [24], 1.459 Å (aver) in $Ni(\eta^3\text{-}C_3Ph_3)Cl(py)_2 \cdot py$ [25], 1.459 Å (aver) in $Co(\eta^3\text{-}C_3Ph_3)(CO)_3$ [26] and 1.462 Å (aver) in $Mo(\eta^3\text{-}C_3Ph_3)(CO)_2(bipy)Br$ [27]) and are increased further in the tungsten complexes (1.509 Å (aver) in $(\eta^5\text{-}C_5H_5)W[C_3(CMe_3)_2Me](PMe_3)Cl_2$, 1.497 Å (aver) in $W[C_3Me_2(CMe_3)][Me_2N(CH_2)_2NMe_2]Cl_3$ [13] and 1.491 Å (aver) in $W[C_3Et_2(CMe_3)](O_2CMe)_3)$ [22].

In keeping with these structural data, it is found that the η^3-C_3R_3 rings do not rotate readily in the "tungstenatetrahedrane" complexes [14,15], whereas the estimated barrier to ring rotation in the hypothetical $Fe(\eta^3\text{-}C_3H_3)(CO)_3$ is 6–7 kcal/mol [28] and ring rotation is observed in other η^3-C_3R_3 complexes [29].

All these data indicate that the complex is not best regarded as a W^{II}–$(C_3R_3^+)$ complex; preferable alternatives are the formulations W^{IV}–$(C_3R_3^-)$ or, perhaps, even W^{VI}–$(C_3R_3^{3-})$. Note that all of these alternatives involve the same molecular orbitals. The only point of ambiguity is the degree to which metal → ligand electron donation takes place.

With these ambiguities in mind, the nomenclature of such species tends to become an exercise in semantics. It would seem preferable to follow both Hoffmann [28] and Schrock [13] in referring to these species as η^3-cyclopropenyl complexes.

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

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