ORGANOMETALLICS

Structural study of W[.eta.5-C5Me4(tert-Bu)](.eta.2-MeC.tplbond.CMe)Cl2, a paramagnetic tungsten(III) species with a four-electron acetylene-metal bond

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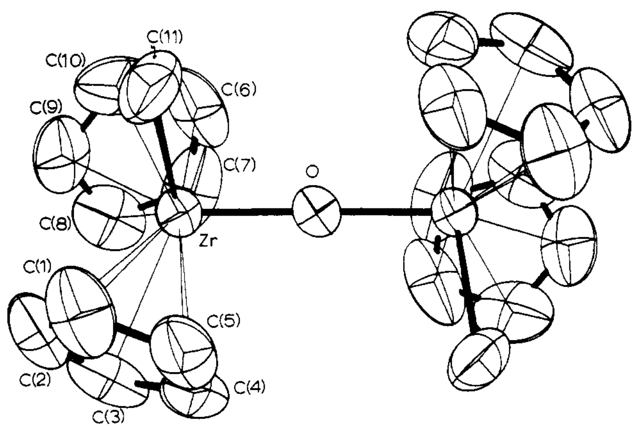

Figure 4. Molecular structure of $[Cp_2Zr(CH_3)]_2O$.

of the two reported Hf–"C(sp^3)" lengths, 2.35 Å.[13]

$[Cp_2Zr(CH_3)]_2O$. The only parameters not mentioned above concern the Zr–O linkage: the length, 1.948 (1) Å, is close to the 1.945 (3) Å value given in $[CpZrCl]_2O$,[28] and 1.966 (5) Å in $[Cp_2Zr(SC_6H_5)]_2O$.[29] The Zr–O–Zr bond angle, 174.1 (3)°, falls within the range for M–O–M (M = group 4b metal), 169–180°.[30] The molecular structure is shown in Figure 4.

Discussion

Two important points concerning the title compounds should be reiterated. First, the published structure of $Cp_2Hf(CH_3)_2$ is probably that of the disordered $Cp_2Hf(Cl)(CH_3)$ or a mixture of $Cp_2Hf(Cl)(CH_3)$ and $Cp_2Hf(CH_3)_2$. This is understandable since (a) the disordered $Cp_2Zr(Cl)(CH_3)$ is isostructural with $Cp_2Zr(CH_3)_2$ and $Cp_2Hf(CH_3)_2$ and (b) it is very difficult to prepare pure $Cp_2M(CH_3)_2$ (M = Zr or Hf) from the reaction of Cp_2MCl_2 with 2 mol of methylating agents.

Second, the present study affords the most accurate value for M–C(sp^3) bond lengths (M = Zr or Hf) in (η^5-ligand)$_2$M[R(sp^3)]$_2$ compounds because (a) the values are internally consistent, (b) for R = CH_3 steric problems are minimized, (c) for (η^5-ligand) = Cp the electronic effects are well-understood, and (d) the values compare well between $Cp_2Zr(CH_3)_2$ and $Cp_2Hf(CH_3)_2$, as well as with M–C(sp^2) bond lengths.[3,4]

Acknowledgment. We are grateful to the National Science Foundation for support of this research.

Registry No. $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$, 12636-72-5; $(\eta^5\text{-}C_5H_5)_2Hf(CH_3)_2$, 37260-88-1; $(\eta^5\text{-}C_5H_5)_2Zr(Cl)(CH_3)$, 1291-45-8; $[(\eta^5\text{-}C_5H_5)_2Zr(CH_3)]_2O$, 79169-19-0.

Supplementary Material Available: A listing of structure factor amplitudes, thermal parameters, and additional bond lengths and angles for all four structures (44 pages). Ordering information is given on any current masthead page.

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Structural Study of W[η^5-C_5Me_4(*t*-Bu)](η^2-MeC≡CMe)Cl_2, a Paramagnetic Tungsten(III) Species with a Four-Electron Acetylene–Metal Bond

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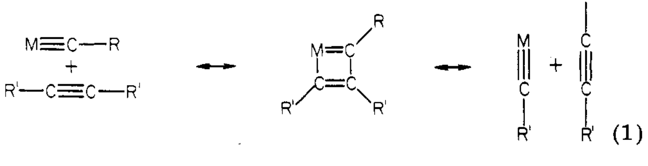
Received November 30, 1982

The complex W[η^5-C_5Me_4(*t*-Bu)](η^2-MeC≡CMe)Cl_2, prepared by Pedersen and Schrock from the reaction of excess 2-butyne with W(≡$CCMe_3$)(dme)Cl_3 (dme = 1,2-dimethoxyethane), crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (No. 14) with a = 8.411 (1) Å, b = 26.639 (5) Å, c = 8.971 (7) Å, and β = 114.32 (1)°. Diffraction data to 2θ = 50° (Mo Kα radiation) were collected with a Syntex $P2_1$ diffractometer, and the structure was refined to R_F = 3.2% and R_{wF} = 3.0% for all 2244 independent data. The paramagnetic complex contains a "strongly bound", four-electron-donating, 2-butyne ligand, with W–C(alkyne) = 2.007 (7) and 2.021 (6) Å and with C–C = 1.312 (10) Å; these parameters are compared with those in various "strongly bound" diamagnetic complexes of tantalum(III) and tungsten(II).

Introduction

The four-coordinate tungsten(VI) complex[1] W(≡$CCMe_3$)($OCMe_3$)$_3$ has recently been shown[2] to be an efficacious catalyst for the metathesis of internal acetylenes. In an extension of the now accepted path for *olefin* metathesis, the acetylene metathesis is believed to proceed through a metallacyclobutadiene intermediate[3] (see eq 1).



(1)

In contrast to the catalytic behavior noted for W(≡$CCMe_3$)($OCMe_3$)$_3$, the related octahedral tungsten(VI) neopentylidyne complex W(≡$CCMe_3$)(dme)Cl_3 (dme = 1,2-dimethoxyethane) is *not* a useful metathesis catalyst.

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[1] We regard the alkylidyne ligand as formally a six-electron-donating trianion and the alkoxide ligand as a monoanion. This approach is consistent with the accepted concept of formal oxidation state, viz., that charge remaining on an atom when all shared (bonding) electrons are formally assigned to the more electronegative of the atoms involved in the bond.

[2] Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981,** *103,* 3932–3934.

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Table I. Experimental Data for the X-ray Diffraction Study of $W[\eta^5\text{-}C_5Me_4(t\text{-}Bu)](\eta^2\text{-}MeC{\equiv}CMe)Cl_2$

(A) Crystal Parameters[a] at 24 °C

cryst system: monoclinic
space group: $P2_1/c$ (No. 14)
$a = 8.411\ (1)$ Å
$b = 26.639\ (5)$ Å
$c = 8.971\ (1)$ Å
$\beta = 114.32\ (1)°$
$V = 1831.6\ (5)$ Å^3
$Z = 4$
mol wt = 522.2
ρ(calcd) = 1.89 g cm^{-3}

(B) Measurement of Data

radiation: Mo Kα ($\bar{\lambda}$ 0.710 730 Å)
monochromator: highly oriented graphite, equatorial
reflctns measd: $h,k,\pm l$
2θ range: 3.7–50.0°
scan type: ω
scan speed: 2.55/min
scan range: 1.0° (0.6° offset from center for bkgd)
reflctns collected: 2437 total, yielding 2244 independent
stds: 3 every 97 reflections; no significant changes in intensity were observed
abs coeff: 69.6 cm^{-1}
weighting scheme: $w = [\{\sigma(|F_o|)\}^2 + \{0.015|F_o|\}^2]^{-1}$
function minimized: $\Sigma w(|F_o| - |F_c|)^2$

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ component of 25 reflections with 2θ = 25–30°.

Rather, it reacts stoichiometrically with 1 equiv of alkyne to yield an isolable tungstenacyclobutadiene complex and with an excess of alkyne to yield an approximately 1:1 mixture of two other complexes: a soluble paramagnetic complex of stoichiometry $W(CCMe_3)(alkyne)_3Cl_2$ and a less soluble paramagnetic complex of stoichiometry $W_2(CCMe_3)_2(alkyne)_4Cl_8$.[4]

We have previously reported details of the X-ray determined structure of the metallacyclobutadiene complex $W[C(CMe_3)C(Me)C(Me)]Cl_3$ (derived from the stoichiometric reaction of $W({\equiv}CCMe_3)(dme)Cl_3$ and 2-butyne)[4] and we now report on the structure of the species $W(CCMe_3)(2\text{-butyne})_3Cl_2$ (derived from the reaction of $W({\equiv}CCMe_3)(dme)Cl_3$ and *excess* 2-butyne).

Experimental Section

Crystals were kindly provided by Professor R. R. Schrock of the Massachusetts Institute of Technology. All crystallographic operations (crystal alignment, measurement of unit-cell parameters, and determination of orientation matrix) were carried out in the manner described previously.[5] Details for the present structural study are given in Table I. All data were corrected for Lorentz and polarization factors and for the effects of absorption; they were then converted to $|F_o|$ values. Any datum with a net intensity less than zero was assigned a value of $|F_o| = 0$.

The structure was solved by using Patterson and difference-Fourier techniques and was refined by using full-matrix least squares.[6] All hydrogen atoms were included in calculated positions [d(C–H) = 0.95 Å[7]]. In the final refinement cycle 181 parameters were refined against all 2244 independent reflections (none rejected). The residuals[8] were $R_F = 3.2\%$, $R_{wF} = 3.0\%$, and GOF = 1.36. The discrepancy indices calculated excluding those 244 data having $|F_o| < 3.0(\sigma(F_o))$ were $R_F = 2.5\%$, $R_{wF} = 2.9\%$, and GOF = 1.39. Final positional parameters are listed in Table

Table II. Positional Parameters for Non-Hydrogen Atoms in $W[\eta^5\text{-}C_5Me_4(t\text{-}Bu)](\eta^2\text{-}MeC{\equiv}CMe)Cl_2$

atom	x	y	z
W	0.04204 (3)	0.88060 (1)	0.16713 (3)
Cl(1)	−0.10846 (26)	0.85229 (7)	−0.10509 (20)
Cl(2)	0.28909 (26)	0.89382 (8)	0.10625 (26)
C(1)	−0.09491 (74)	0.82054 (21)	0.26316 (70)
C(2)	−0.01710 (76)	0.85703 (22)	0.39026 (70)
C(3)	0.16619 (73)	0.85686 (21)	0.44049 (67)
C(4)	0.20468 (78)	0.81581 (21)	0.35403 (74)
C(5)	0.04544 (79)	0.79422 (20)	0.24836 (72)
C(6)	−0.28194 (92)	0.80624 (28)	0.17917 (91)
C(7)	−0.1325 (12)	0.88803 (27)	0.4476 (10)
C(8)	0.30593 (87)	0.88501 (23)	0.58608 (81)
C(9)	0.37727 (95)	0.79534 (28)	0.3742 (10)
C(10)	0.0237 (10)	0.75008 (26)	0.13765 (92)
C(11)	0.2340 (12)	0.92897 (29)	0.6447 (10)
C(12)	0.3805 (11)	0.84774 (29)	0.72942 (91)
C(13)	0.4523 (10)	0.90653 (30)	0.5438 (10)
C(14)	−0.12406 (84)	0.93738 (22)	0.14182 (74)
C(15)	0.03522 (85)	0.95542 (22)	0.20087 (75)
C(16)	−0.3086 (10)	0.95464 (27)	0.0778 (11)
C(17)	0.1277 (11)	1.00405 (26)	0.2403 (10)

Table IV. Interatomic Distances (Å) with Esd's for $W[\eta^5\text{-}C_5Me_4(t\text{-}Bu)](\eta^2\text{-}MeC{\equiv}CMe)Cl_2$

(A) Distances from the Tungsten Atom			
W–Cl(1)	2.364 (2)	W–C(1)	2.334 (6)
W–Cl(2)	2.382 (2)	W–C(2)	2.338 (6)
W–C(14)	2.007 (7)	W–C(3)	2.332 (5)
W–C(15)	2.021 (6)	W–C(4)	2.402 (6)
W–Cp[a]	2.026	W–C(5)	2.410 (5)
W–Ac[b]	1.904		
(B) Distances within the MeC≡CMe Ligand			
C(14)–C(16)	1.489 (11)	C(14)–C(15)	1.312 (10)
C(15)–C(17)	1.477 (10)		
(C) Internal Carbon–Carbon Distances within the $[\eta^5\text{-}C_5Me_4(t\text{-}Bu)]$ Ligand			
C(1)–C(2)	1.435 (8)	C(4)–C(5)	1.406 (9)
C(2)–C(3)	1.417 (9)	C(5)–C(1)	1.426 (9)
C(3)–C(4)	1.452 (8)		
(D) External Distances of the $[\eta^5\text{-}C_5Me_4(t\text{-}Bu)]$ Ligand			
C(1)–C(6)	1.487 (10)	C(5)–C(10)	1.501 (9)
C(2)–C(7)	1.516 (11)	C(8)–C(11)	1.509 (11)
C(3)–C(8)	1.544 (9)	C(8)–C(12)	1.539 (10)
C(4)–C(9)	1.490 (11)	C(8)–C(13)	1.540 (12)

[a] "Cp" represents the centroid of the $C_5Me_4(t\text{-}Bu)$ ring. [b] "Ac" represents the midpoint of the acetylenic C(14)–C(15) bond.

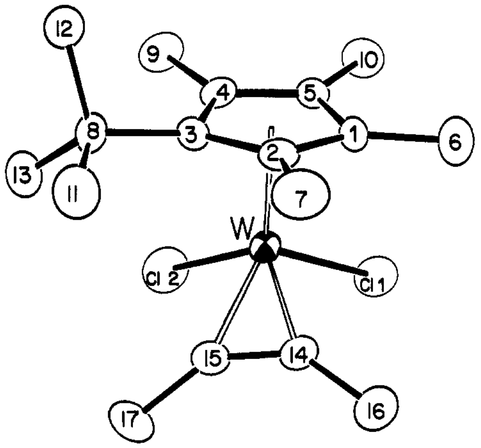

Figure 1. Geometry of the $W[\eta^5\text{-}C_5Me_4(t\text{-}Bu)](\eta^2\text{-}MeC{\equiv}CMe)Cl_2$ molecule. (ORTEP-II diagram; 30% probability ellipsoids; all hydrogen atoms omitted.) Carbon atoms are labeled with numbers only.

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(8) $R_F = [\sum||F_o| - |F_c||/\sum|F_o|] \times 100$; $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} \times 100$; GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$; NO = number of observations; NV = number of variables.

Table V. Interatomic Angles (deg) with Esd's for W[η^5-C_5Me_4(t-Bu)](η^2-MeC≡CMe)Cl_2

(A) Angles around the Tungsten Atom			
C(14)-W-C(15)	38.02 (26)	Cp-W-C(14)	115.5
C(14)-W-Cl(1)	94.12 (19)	Cp-W-C(15)	123.7
C(14)-W-Cl(2)	119.66 (19)	Cp-W-Cl(1)	114.3
C(15)-W-Cl(1)	115.68 (19)	Cp-W-Cl(2)	118.3
C(15)-W-Cl(2)	88.27 (20)	Ac-W-Cl(1)	105.5
Cl(1)-W-Cl(2)	87.53 (7)	Ac-W-Cl(2)	104.2
		Cp-W-Ac	121.4
(B) Angles within the MeC≡CMe Ligand			
W-C(14)-C(15)	71.5 (4)	W-C(15)-C(14)	70.4 (4)
W-C(14)-C(16)	147.4 (5)	W-C(15)-C(17)	148.9 (5)
C(16)-C(14)-C(15)	140.5 (7)	C(17)-C(15)-C(14)	140.1 (7)
(C) Internal C-C-C Angles within the η^5-C_5Me_4(t-Bu) Ligand			
C(5)-C(1)-C(2)	106.4 (5)	C(3)-C(4)-C(5)	107.9 (5)
C(1)-C(2)-C(3)	109.3 (5)	C(4)-C(5)-C(1)	109.3 (5)
C(2)-C(3)-C(4)	106.6 (5)		
(D) Other Angles Involving the η^5-C_5Me_4(t-Bu) Ligand			
C(3)-C(8)-C(11)	113.4 (6)	C(7)-C(2)-C(3)	131.2 (6)
C(3)-C(8)-C(12)	107.4 (6)	C(7)-C(2)-C(1)	119.5 (6)
C(3)-C(8)-C(13)	112.3 (6)	C(8)-C(3)-C(4)	123.9 (5)
C(11)-C(8)-C(12)	107.1 (6)	C(8)-C(3)-C(2)	128.1 (6)
C(11)-C(8)-C(13)	105.8 (6)	C(9)-C(4)-C(5)	122.8 (6)
C(12)-C(8)-C(13)	110.7 (6)	C(9)-C(4)-C(3)	129.1 (6)
C(6)-C(1)-C(2)	128.1 (6)	C(10)-C(5)-C(1)	124.5 (6)
C(6)-C(1)-C(5)	124.8 (6)	C(10)-C(5)-C(4)	126.1 (6)

II; anisotropic thermal parameters are listed in Table III-S (supplementary material).

Description of the Molecular Structure

Interatomic distances with esd's are collected in Table IV; angles are given in Table V. The molecular geometry and atom-labeling scheme are illustrated in Figure 1.

The molecular contains a central tungsten(III) atom linked to an η^5-C_5Me_4(t-Bu) ligand, a MeC≡CMe ligand, and two chloride ions. The coordination geometry about tungsten may be viewed as pseudotetrahedral. Angles between "Cp" (the centroid of the carbocyclic ring), "Ac" (the midpoint of the acetylenic C(14)–C(15) bond), and the two chloride ligands are Cp–W–Ac = 121.4°, Cp–W–Cl(1) = 114.3°, Cp–W–Cl(2) = 118.3°, Ac–W–Cl(1) = 105.5°, Ac–W–Cl(2) = 104.2°, and Cl(1)–W–Cl(2) = 87.53(7)°.

The η^5-cyclopentadienyl ring is normal, with carbon–carbon distances ranging from 1.406 (9) Å through 1.452 (8) Å [average = 1.427 Å]. The η^5-cyclopentadienyl ring is close to planar (deviations from planarity are 0.029 (6) Å for C(1), −0.035 (6) Å for C(2), 0.026 (6) Å for C(3), −0.008 (6) Å for C(4), and −0.013 (6) Å for C(5)—see Table VI-S). Nevertheless, tungsten–carbon distances are not equivalent; in decreasing order they are W–C(5) = 2.410 (5) Å, W–C(4) = 2.402 (6) Å, W–C(2) = 2.338 (6) Å, W–C(1) = 2.334 (6) Å, and W–C(3) = 2.332 (5) Å. The ring is thus slightly "tipped" so that C(4) and C(5) are the most distant from the tungsten atom; these atoms are the pair trans to the 2-butyne ligand. While this effect could be electronic in nature, it is not clearly apparent in the related complex Ta(η^5-C_5Me_5)(η^2-PhC≡CPh)Cl_2.[9] Steric effects in the two molecules are, however, substantially different. The tungsten–2-butyne complex has a very sterically demanding η^5-C_5Me_4(t-Bu) ligand, whereas the diphenylacetylene ligand is the most bulky ligand in the tantalum complex.

The tungsten atom lies +2.024 Å from the plane of the η^5-cyclopentadienyl ligand. The substituents are not coplanar with the carbocyclic ring; rather, they are displaced in a direction *away from* the tungsten atom. The α-carbon atom of the *tert*-butyl group (C(8)) lies −0.171 (7) Å from the ring plane, while the methyl groups are displaced by lesser amounts; −0.146 (8) Å for C(7), −0.116 (8) Å for C(9), −0.069 (7) Å for C(10), and −0.059 (8) Å for C(6).

Tungsten–chlorine distances are W–Cl(1) = 2.364 (2) Å and W–Cl(2) = 2.382 (2) Å. While there are few, if any, tungsten(III)–chlorine distances available for mononuclear organometallic complexes, we may compare these with tungsten(IV)–chlorine distances of 2.458 (1) and 2.478 (1) Å in W(=$CHCMe_3$)(CO)$(PMe_3)_2Cl_2$,[10] 2.520 (2) Å in W(≡$CHAlMe_{2-x}Cl_{1+x}$)(Cl)$(PMe_3)_3$,[11] and 2.419 (2) and 2.442 (5) Å in W(≡CH)(Cl)$(PMe_3)_4$[11a] and with tungsten(II)–chlorine distances of 2.476 (1) Å in W(η^2-HC≡$COAlCl_3$)(CO)$(PMe_3)_3Cl$[12] and 2.527 (5) and 2.557 (5) Å in [W(CH_2PMe_3)$(CO)_2Cl(PMe_3)_3^+$][$CF_3SO_3^-$].[13a]

The 2-Butyne Ligand. The 2-butyne ligand is in an η^2 mode of coordination to the tungsten(III) atom. The two tungsten–carbon distances are the shortest W–C(acetylene) distances yet observed, with W–C(14) = 2.007 (7) Å and W–C(15) = 2.021 (6) Å (average = 2.014 Å), while the W–Ac distance is 1.904 Å. (For comparison we may note that characteristic tungsten–carbon single- and double-bond lengths are 2.258 (9) and 1.942 (9) Å; these values are taken from an X-ray diffraction study on the tungsten(VI) complex W(≡$CCMe_3$)(=$CHMe_3$)(CH_2CMe_3)(dmpe).[13b])

The carbon atom framework is substantially bent, with ∠C(16)–C(14)–C(15) = 140.5 (7)° and ∠C(17)–C(15)–C(14) = 140.1 (7)°, while the acetylenic C(14)–C(15) linkage is 1.312 (10) Å in length. All of these data are consistent with the acetylene's acting as a four-electron donor, rather than

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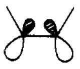
Table VII. Structural and ^{13}C NMR Data on "Strongly Bound" Acetylene Complexes

complex	^{13}C(alkyne), ppm	M–C dist, Å	C–C dist, Å	"electron count"[a]	ref
$Ta(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}C_6H_4)Me_2$	230.5	2.059 (4) 2.091 (4)	1.364 (5)	16e	26
$Ta(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}PhC{\equiv}CPh)Cl_2$	222.3	2.067 (6) 2.075 (6)	1.337 (8)	16e	9
$[TaCl_4(py)(\eta^2\text{-}PhC{\equiv}CPh)^-]$		2.066 (8) 2.069 (8)	1.325 (12)	16e	27
$[TaCl_2(SC_4H_8)(\eta^2\text{-}(t\text{-}Bu)C{\equiv}CMe]_2(\mu\text{-}Cl)_2$		2.029 (13) 2.033 (16)	1.321 (24)	16e	28
$W(CO)(\eta^2\text{-}HC{\equiv}CH)(S_2CNEt_2)_2$		2.015 (9) 2.038 (8)	1.29 (1)	18e	15
$W(\eta^2\text{-}HC{\equiv}COAlCl_3)(CO)(PMe_3)_3Cl$	194.4[b]	2.009 (5) 2.034 (4)	1.316 (6)	18e	12
$W[\eta^5\text{-}C_5Me_4(t\text{-}Bu)](\eta^2\text{-}MeC{\equiv}CMe)Cl_2$		2.007 (7) 2.021 (6)	1.312 (10)	17e	this work

[a] Electrons formally associated with metal atom, counting acetylenic ligand as a four-electron donor. [b] C–H resonance; C-OAlCl$_3$ resonance at either 230.8 or 213.5 ppm.

in its classical two-electron-donating role. This is accomplished by the normal acetylene $\pi(\|)$ donation (1) being accompanied by substantial additional acetylene $\pi(\perp)$ donation (2).[14]


1


2

Within this framework, the d^3 W(III) ion obtains six electrons from the $[\eta^5\text{-}C_5Me_4(t\text{-}Bu)^-]$ anion, four electrons from the two chloride ions and four electrons from the "strongly bound" acetylenic ligand—17 electrons in all. While this phenomenon has only recently been treated by the "frontier orbital" method,[14] it has been recognized for some time that acetylenic ligands tend to be strongly bound to electron-poor transition-metal ions. Thus, a structural study of $W(CO)(\eta^2\text{-}HC{\equiv}CH)(S_2CNEt_2)_2$[15] confirmed spectroscopic indications[16,17] that the η^2-acetylene acted as a four-electron donor in certain molybdenum(II) and tungsten(II) complexes. More recent work has focussed on infrared studies and on ^1H and ^{13}C NMR studies on these species and related oxomolybdenum(IV) and oxotungsten(IV) species.[18–25]

This work has been extended and clarified by a series of X-ray diffraction studies on "strongly bound" acetylene complexes of tantalum(III) and tungsten. Churchill and Youngs have reported results on an η^2-benzyne[26] and η^2-diphenylacetylene[9] complexes of tantalum(III); Cotton and Hall have reported structural studies on η^2-diphenylacetylene[27] and η^2-*tert*-butylmethylacetylene[28] complexes of tantalum(III); Churchill and Wasserman have reported structural studies on an asymmetric η^2-HC≡COAlCl$_3$ complex of tungsten(II).[12] Available geometric and ^{13}C NMR data on these complexes are collected in Table VII. As can clearly be seen, these third-row transition-metal complexes with "strongly bound" (four-electron donor) acetylenic ligands all have the following features.

(1) **Short Metal–Carbon Distances.** Thus, while "normal" acetylenic ligands (i.e., two-electron donor ligands) have metal–carbon distances that are close to the metal–carbon σ-bond length, the "strongly bound" acetylenic ligands have metal–carbon distances that approach a metal–carbon double-bond length.

(2) **Lengthened C–C(alkyne) Distances.** The observed carbon–carbon bond lengths are all substantially longer than the accepted noncoordinated acetylenic C≡C triple-bond distance of $\simeq$ 1.205 Å. The nonconjugated acetylenic ligands (Table VII, last four entries) have carbon–carbon bond lengths in the range 1.29 (1)–1.321 (24) Å; those conjugated to phenyl rings (entries 2 and 3) have carbon–carbon bond lengths of 1.325 (12) and 1.337 (8) Å; and that occurring in a cyclic *benzyne* ligand has a value of 1.364 (5) Å. Most of these values are close to the accepted uncoordinated simple C=C distance of 1.335 ± 0.005 Å.

(3) **^{13}C NMR Shifts Are about δ 225 (Where Available).** The present paramagnetic tungsten(III) species has similar geometric parameters to other molecules in the table; ^{13}C data are not, however, available.

Conclusions

As has been discussed above, the present molecule is a further example of the class of complexes in which an η^2-alkyne ligand is bound to an electron-poor transition metal via a four-electron acetylene-to-metal linkage. There are two particularly interesting features of the present molecule. The first is that a "strongly bound" (four-

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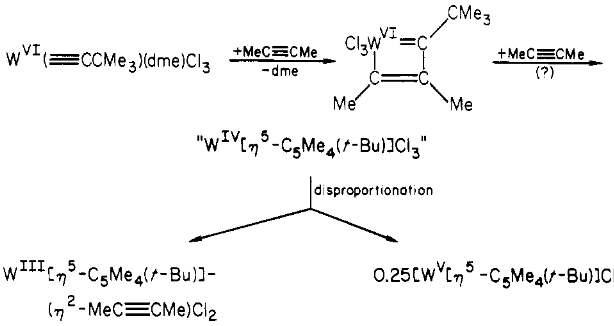
electron-donating) acetylenic ligand is found in a *paramagnetic* tungsten(III) complex. To the best of our knowledge, there is no other example of such a linkage in a paramagnetic species.

The second feature of interest concerns the occurrence of a pentasubstituted η^5-cyclopentadienyl ligand in the molecule. It should be noted that the production of highly substituted cyclopentadienyl systems is not straightforward and that much synthetic work in organometallic chemistry has been confined to the easily obtained C_5Me_5 and C_5Me_4Et systems. The present η^5-$C_5Me_4(t\text{-Bu})$ ligand is clearly formed by the *net* coupling of one neopentylidyne ligand and two 2-butyne molecules. There are some indications[4] that this type of reaction can provide a rather general route to highly substituted η^5-cyclopentadienyl systems (see eq 2). Of course, unsymmetrical acetylenes

$$\mathrm{W({\equiv}CR)(dme)Cl_3} \xrightarrow{\text{excess } \mathrm{R'C{\equiv}CR'}} 0.5\mathrm{W(\eta^5\text{-}C_5R'_4R)(\eta^2\text{-}R'C{\equiv}CR')Cl_2} + 0.25[\mathrm{W(\eta^5\text{-}C_5R'_4R)Cl_4}]_2 \quad (2)$$

could be used (e.g., $R'C{\equiv}CR''$); the disadvantage here is that a mixture of isomeric cyclopentadienyl systems would be formed and separation could become a major problem. A further possibility is that functionalized acetylenes could be used, providing an entry into more complex cyclopentadienyl systems.

The pathway of the reaction is not firmly established. A possible sequence for the reaction of $W({\equiv}CCMe_3)(dme)Cl_3$ and 2-butyne is shown in eq 3. The intermediacy of the tungstenacyclobutadiene complex is established, as is the nature (and approximate relative quantities) of the final products.[4] A disproportionation reaction clearly must occur, and an intermediate complex of stoichiometry $W[\eta^5\text{-}C_5Me_4(t\text{-Bu})]Cl_3$ provides perhaps the simplest possible intermediate. The disproportionation of a (presumably diamagnetic) tungsten(IV) complex into *paramagnetic* tungsten(III) and tungsten(V) complexes is, however, unusual in organometallic chemistry. Clearly, however, further work is required before this type of coupling reaction is understood in detail.



(3)

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Registry No. $W[\eta^5\text{-}C_5Me_4(t\text{-Bu})](\eta^2\text{-}MeC{\equiv}CMe)Cl_2$, 83511-02-8.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, calculated positions for hydrogen atoms (Table II-S), anisotropic thermal parameters (Table III-S), and least-squares planes (Table VI-S) (19 pages). Ordering information is given on any current masthead page.

Stereospecific Additions of Dimethylsilylene and Diphenylsilylene to Olefins[1,2]

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Dimethyl- and diphenylsilylene add stereospecifically to *cis*- and *trans*-2-butene to give the corresponding siliranes. Easy additions to cyclopentene and cyclohexene indicate that the cycloadditions are cis. Opening of the siliranes by methanol also occurs in stereospecifically cis fashion.

Introduction

Singlet carbenes add to olefins with retention of stereochemistry; triplets do not. Behind that simple sentence lies a rich, complex matrix of theory and experiment, interwoven with liberal amounts of intuitive conjecture and occasional wishful thinking.[5] Even today, debate over both detailed mechanistic description[5] and, occasionally, the fundamental reaction pathways surfaces.[6] Never-

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[1] We dedicate this paper to the memory of Professor Xu Jigong, Fudan University, Shanghai, People's Republic of China.

[2] A portion of this work has been previously communicated.[3] Other parts are taken from the Ph.D. Thesis of V. J. T., Princeton University, 1981. Presented, in part, by S.-h.W. at: "The Second Chinese-Japanese-United States Symposium on Organometallic and Inorganic Chemistry", Shanghai, June 14–18, 1981. Grateful acknowledgment is made to the National Science Foundation for support through Grants CHE-77-24625 and CHE-81-01212.

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[4] Much of this work was done while Shi-hui Wu was at Princeton University, on leave from Fudan University, Shanghai, People's Republic of China.

[5] For a summary of recent developments see: (a) Moss, R. A.; Jones, M., Jr. In "Reactive Intermediates"; Wiley: New York, 1978; Vol. 1, Chapter 3, p 69. (b) *Ibid.*, 1981; Vol. 2, Chapter 3, p 59. (c) For history see: "Carbenes"; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973, 1975; Vols. I and II. W. Kirmse, "Carbene Chemistry", 2nd ed., Academic Press: New York, 1971.

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