Formation of Cyclopentadienyl Complexes from Tungstenacyclobutadiene Complexes and the X-ray Crystal Structure of an η^3-Cyclopropenyl Complex, W[C(CMe₃)C(Me)C(Me)](Me₂NCH₂CH₂NMe₂)Cl₃

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Trigonal-bipyramidal tungstenacyclobutadiene complexes are formed when 2-butyne or 3-hexyne is added to the neopentylidyne complex W(CCMe₃)(dme)Cl₃ (dme = 1,2-dimethoxyethane). Mono-*tert*-butoxide derivatives W[C(CMe₃)C(R)C(R)](OCMe₃)Cl₂ can be prepared, but attempts to make di-*tert*-butoxide complexes led only to a mixture of alkylidyne complexes W(CR)(OCMe₃)₃ and W(CCMe₃)(OCMe₃)₃. However, pinacolato derivatives W[C(CMe₃)C(Me)C(Me)][OCMe₂CMe₂O]Cl as well as W[C(CMe₃)C-(Me)C(Me)][OCMe₂CMe₂O](OCMe₃) can be prepared and are stable toward loss of an acetylene to give alkylidyne complexes. Addition of pinacol to a mixture of W(CEt)(OCMe₃)₃ and 3-hexyne traps the putative W(C₃Et₃)(OCMe₃)₃ complex to give W(C₃Et₃)(OCMe₂CMe₂O)(OCMe₃). Cyclopentadienyl complexes form when dialkylacetylenes are added to W[C(CMe₃)C(Me)C(Me)]Cl₃, W[C(CMe₃)C(Me)C(Me)]-(OCMe₂CMe₂O)(OCMe₃), or W(C₃Et₃)(OCMe₂CMe₂O)(OCMe₃). When 3-hexyne is added to W[C-(CMe₃)C(Me)C(Me)] complexes, two and only two types of cyclopentadienyl complexes form. One arises by insertion of 3-hexyne into the W–C$_\alpha$ bonds in the W[C(CMe₃)C(Me)C(Me)] ring, while the second appears to arise from the W[C(Me)C(CMe₃)C(Me)] isomer. It is proposed that η^3-cyclopropenyl complexes are also possible reaction intermediates. One can be isolated from the reaction between W[C(CMe₃)C-(Me)C(Me)]Cl₃ and TMEDA. Crystals of W[C₃Me₂(CMe₃)][Me₂N(CH₂)₂NMe₂]Cl₃ belong to the monoclinic space group $P2_1/n$ with a = 10.982 (2) Å, b = 13.257 (4) Å, c = 13.957 (4) Å, β = 105.33 (2)°, and Z = 4. Diffraction data (Mo Kα) were collected with a Syntex P2₁ diffractometer, and the structure was refined to R_F = 3.8% for all 2576 reflections (R_F = 3.0% for those 2285 reflections with $|F_o| > 3.0\sigma(|F_o|)$). The complex is approximately octahedral with a tightly and roughly symmetrically bound η^3-cyclopropenyl ring, a *mer* arrangement of chloride ligands, and one TMEDA nitrogen atom more loosely bound than the other in a position trans to the η^3-C₃ ring.

Introduction

In the preceding two papers[2,3] we discussed acetylene metathesis catalysts that contain 2,6-diisopropylphenoxide or fluoroalkoxide ligands. Trigonal-bipyramidal tungstenacyclobutadiene complexes were observed and two of them structurally characterized. However, the first observed tungstenacyclobutadiene complex, prepared by reacting W(CCMe₃)(dme)Cl₃ (dme = 1,2-dimethoxyethane) with 2-butyne, is clearly *not* a catalyst for metathesizing acetylenes.[4a] In this paper we investigate this and other "failures" in more detail. What we will find is that formation of cyclopentadienyl complexes is the end result. We will also show that the tautomeric form of a tungstenacyclobutadiene complex, an η^3-cyclopropenyl complex, is energetically accessible and a plausible means of "isomerizing" the tungstenacyclobutadiene complex in the process of its reacting with an acetylene. Some of these results have been reported in preliminary communications.[4]

Results

Preparation of Tungstenacyclobutadiene Complexes. Addition of 1 equiv of 2-butyne or 3-hexyne to W(CCMe₃)(dme)Cl₃[5] yields violet, diamagnetic crystals with the composition W(CCMe₃)(RCCR)Cl₃ (R = Me, Et). The ¹³C NMR spectrum of each of these compounds reveals two signals at ca. 265 ppm and a third at ca. 150 ppm (see Table VI), in addition to those ascribable to a *tert*-butyl group and two different R groups. The signals at ~265 (two) and 150 ppm (one) can be assigned to inequivalent α-carbon atoms and a β-carbon atom, respectively, in an α-*tert*-butyl-substituted tungstenacyclobutadiene ring. These complexes are unstable in dichloromethane or chloroform and react immediately with air or water.

An X-ray structural study of "W(CCMe₃)(MeCCMe)Cl₃" confirmed that it is the tungstenacyclobutadiene complex W[C(CMe₃)C(Me)C(Me)]Cl₃.[4a] The molecule is nearly a trigonal bipyramid with axial chloride ligands (∠Cl(1)–W–Cl(2) = 166.12 (9)°) and an essentially planar WC₃ ring lying in the equatorial plane. (See Figure 1 of ref 4a for numbering scheme.) The α-carbon atoms of the substituents and the third chloride ligand also lie in the equatorial plane. The W–C$_\alpha$ bond lengths are *equal* and slightly shorter than the W=C$_\alpha$ double-bond distance of 1.942 (9)

(1) (a) Massachusetts Institute of Technology. (b) State University of New York at Buffalo.

(2) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R., first paper in this issue.

(3) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W., second paper in this issue.

(4) (a) Pedersen, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* 1982, *104*, 6808. (b) Churchill, M. R.; Ziller, J. W.; Pedersen, S. F.; Schrock, R. R. *J. Chem. Soc., Chem. Commun.* 1984, 485.

(5) Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. A.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* 1982, *1*, 1645.
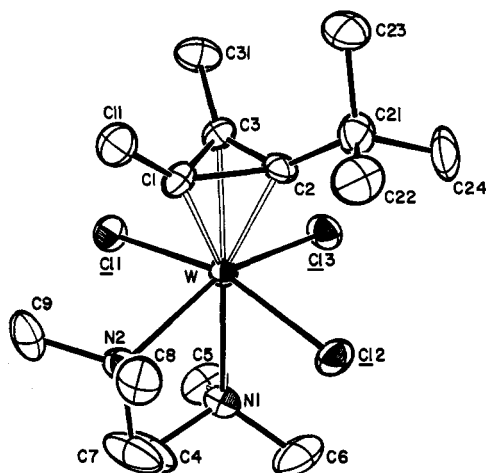
Figure 1. The W[C$_3$Me$_2$(CMe$_3$)][Me$_2$N(CH$_2$)$_2$NMe$_2$]Cl$_3$ molecule, showing the scheme used in labeling non-hydrogen atoms (ORTEP-II diagram; 30% ellipsoids).

Å found in W(CCMe$_3$)(CHCMe$_3$)(CH$_2$CMe$_3$)(dmpe)[6] or 1.882 (14) Å found in W(O)(CHCMe$_3$)(PEt$_3$)Cl$_2$.[7] Carbon–carbon distances within the four-membered ring are intermediate between those expected for purely double and single bonds but are slightly closer to the latter. Three other notable features are the large C$_\alpha$–C$_\beta$–C$_\alpha$ angle (118.9 (8)°), the short W–C$_\beta$ distance (far shorter than the W–C$_\alpha$ single bond length of 2.258 (8) Å in W(CCMe$_3$)-(CHCMe$_3$)(CH$_2$CMe$_3$)(dmpe)[6]), and the large W–C(1)–C(2) and W–C(7)–C(8) angles (149.9 (7)° and 156.6 (7)°, respectively).

W[C(CMe$_3$)C(R)C(R)]Cl$_3$ reacts with *tert*-butyl alcohol in the presence of base as shown in eq 1. The ^{13}C NMR

$$\text{W[C(CMe}_3\text{)C(Me)C(Me)]Cl}_3 + \text{Me}_3\text{COH} \xrightarrow[-\text{NEt}_3\text{HCl}]{+\text{NEt}_3} \quad (1)$$
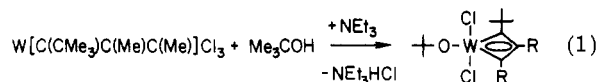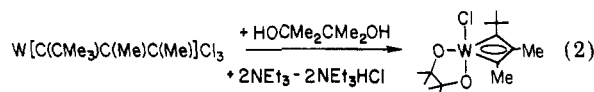
spectra of the mono-*tert*-butoxide complexes are similar to those of the trichloride complexes, except the signal for the β-carbon atom in the ring is found ca. 15 ppm to higher field (see Table VI). Since the ^{1}H NMR spectrum of W[C(CMe$_3$)C(Et)C(Et)](OCMe$_3$)Cl$_2$ exhibits two first-order quartets for the methylene protons of the ethyl groups, the *tert*-butoxide ligand is most likely located in the equatorial position. The W[C(CMe$_3$)C(R)C(R)]-(OCMe$_3$)Cl$_2$ complexes show no sign of decomposing or of rearranging to the β-*tert*-butyl-substituted complexes after being heated in C$_6$D$_6$ to 60 °C for several hours.

Further addition of 1 or 2 equiv of *tert*-butyl alcohol in the presence of NEt$_3$ gives a complex mixture of products, one of which could be identified as W(CHCMe$_3$)-(OCMe$_3$)$_2$Cl$_2$ by its characteristic H$_\alpha$ resonance at 10.67 ppm.[8] Relatively smooth reactions result on addition of 1 or 2 equiv of LiOCMe$_3$ to W[C(CMe$_3$)C(R)C(R)]-(OCMe$_3$)Cl$_2$, but the alkylidyne complexes W(CR)-(OCMe$_3$)$_3$ (R = Me or Et, CMe$_3$) were the only products observed in the NMR spectra of the crude product mixture. We conclude that (most likely) tri-*tert*-butoxy

(6) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454.
(7) Churchill, M. R.; Missert, J. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 3388.
(8) W(CHCMe$_3$)(OCMe$_3$)$_2$Cl$_2$ can be prepared by adding 2 equiv of HCl to W(CCMe$_3$)(OCMe$_3$)$_3$. It is believed to be a trigonal-bipyramidal species containing axial chloride ligands and an alkylidene ligand that lies in the equatorial plane (cf. W(CHCMe$_3$)(OCH$_2$CMe$_3$)$_2$Cl$_2$[9]). It and similar species will be reported in detail elsewhere.
(9) Kress, J.; Wesolek, M.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, *514*.

tungstenacyclobutadiene complexes are relatively unstable with respect to loss of an acetylene.

One of the possible reasons why W[C(CMe$_3$)C(R)C-(R)](OCMe$_3$)$_2$Cl is not observed is because it disproportionates to W[C(CMe$_3$)C(R)C(R)](OCMe$_3$)$_3$ and starting material. Therefore, we attempted to prepare pinacolato derivatives, in the hope that any such disproportionation reaction would be slow. One can be prepared as shown in eq 2. This molecule has the structure shown, according

$$\text{W[C(CMe}_3\text{)C(Me)C(Me)]Cl}_3 \xrightarrow[+2\text{NEt}_3 - 2\text{NEt}_3\text{HCl}]{+\text{HOCMe}_2\text{CMe}_2\text{OH}} \quad (2)$$

to ^{1}H and ^{13}C NMR data. Like the W[C(CMe$_3$)C(R)C-(R)](OCMe$_3$)Cl$_2$ complexes, the pinacolato derivative shows no sign of decomposing or of rearranging to the other possible (β-*tert*-butyl substituted) metallacycle after being heated for several hours at 60 °C in benzene.

We were initially surprised to find that the remaining chloride ligand in W[C(CMe$_3$)C(Me)C(Me)]-(OCMe$_2$CMe$_2$O)Cl could be replaced by a *tert*-butoxide ligand to give another thermally stable, *sublimable* tungstenacyclobutadiene complex, W[C(CMe$_3$)C(Me)C-(Me)](OCMe$_2$CMe$_2$O)(OCMe$_3$). Again, there is absolutely no evidence that the WC$_3$ ring rearranges to what one might predict to be the more stable isomer with the *tert*-butyl group in the β-position of the WC$_3$ ring. This molecule is fluxional, as shown by equilibration of the four methyl groups of the pinacolato ligand into two sets of two methyl groups at a rate of the order of the NMR time scale at 25 °C.

The fact that W[C(CMe$_3$)C(Me)C(Me)]-(OCMe$_2$CMe$_2$O)(OCMe$_3$) is so stable prompted us to attempt to trap a putative tri-*tert*-butoxy metallacycle by adding pinacol to a mixture of W(CEt)(OCMe$_3$)$_3$ and 1 equiv of 3-hexyne. The reaction (eq 3) is virtually in-

$$\text{W(CEt)(OCMe}_3\text{)}_3 \xrightarrow[-\text{Me}_3\text{COH}]{+3\text{-hexyne + pinacol}} \quad (3)$$
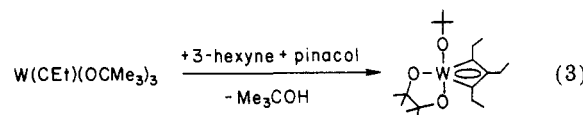
stantaneous. The WC$_3$Et$_3$ complex can be isolated as a distillable, low-melting, red solid whose NMR spectra are closely analogous to the derivatives described above. If one adds pinacol to W(CCMe$_3$)(OCMe$_3$)$_3$ *before* adding 3-hexyne, a neopentylidene complex, W(CHCMe$_3$)-(OCMe$_2$CMe$_2$O)(OCMe$_3$)$_2$, is formed quantitatively, and it does *not* react readily with 3-hexyne. (This neopentylidene complex is related to others we have prepared by protonating neopentylidyne complexes[8] and will not be discussed in detail here.) This result suggests that we are trapping W(C$_3$Et$_3$)(OCMe$_3$)$_3$ rather than "W(CEt)-(OCMe$_2$CMe$_2$O)(OCMe$_3$)" when we add pinacol to a mixture of W(CEt)(OCMe$_3$)$_3$ and 3-hexyne. Incidentally, we have not found it possible to prepare the trimethyl-substituted tungstenacyclobutadiene analogue of the complex shown in eq 3, as 2-butyne is readily polymerized by an as yet unknown mechanism when added to W(CMe)-(OCMe$_3$)$_3$.

The Formation of Cyclopentadienyl Complexes. None of the tungstenacyclobutadiene complexes we have described here will metathesize 3-heptyne. However, some of them do react readily with 2-butyne or 3-hexyne.
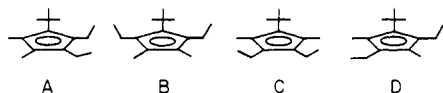
Excess 2-butyne or 3-hexyne reacts immediately with W[C(CMe$_3$)C(R)C(R)]Cl$_3$ (R = Me or Et, respectively) in pentane to give a sparingly soluble, paramagnetic, orange complex with the empirical formula W(CCMe$_3$)(RC≡

Chart I. Possible Cyclopentadienyl Rings Formed by
Adding 3-Hexyne to a W[C(CMe$_3$)C(Me)C(Me)] Complex

A   B   C   D

Scheme I. Formation of Rings A and C

A   C

CR)Cl$_4$ and a soluble, paramagnetic red complex with the empirical formula W(CCMe$_3$)(RC≡CR)$_3$Cl$_2$, each in ~50% yield by weight. IR spectra of the soluble red complex shows a band at ~1670 cm^{-1} characteristic of a tightly bound acetylene ligand. An X-ray structural study[10] of "W(CCMe$_3$)(2-butyne)$_3$Cl$_2$" shows it to be W[η^5-C$_5$Me$_4$-(CMe$_3$)](2-butyne)Cl$_2$, a species that is closely related to the diamagnetic Ta(III) derivatives Ta(η^5-C$_5$Me$_5$)(alkyne)Cl$_2$.[11] As in Ta(η^5-C$_5$Me$_5$)(PhC≡CPh)Cl$_2$,[11] the axis of the acetylene ligand in W[η^5-C$_5$Me$_4$(CMe$_3$)] (MeC≡CMe)Cl$_2$ lies parallel to the plane of the cyclopentadienyl ligand, and the acetylene carbon–carbon bond length is relatively long (1.312 (10) Å). Therefore, we propose that "W(CCMe$_3$)(alkyne)$_2$Cl$_4$" is also a substituted cyclopentadienyl complex, i.e., W[η^5-C$_5$R$_4$(CMe$_3$)]Cl$_4$. This was confirmed by preparing [W(η^5-C$_5$R$_4$(CMe$_3$)]Cl$_4$ in high yield by adding excess chlorine to W[η^5-C$_5$R$_4$(CMe$_3$)]-(alkyne)Cl$_2$ in pentane. A molecular weight study of W[η^5-C$_5$Et$_4$(CMe$_3$)]Cl$_4$ in dichloromethane at 0 °C (by differential vapor pressure measurement) showed it to be a dimer, presumably with two chlorides as bridging ligands.

It seems reasonable to propose that the cyclopentadienyl complexes arise by disproportionation of some intermediate tungsten(IV) species, possibly "W[η^5-C$_5$R$_4$(CMe$_3$)]-Cl$_3$", as shown in eq 4 and 5. Unfortunately, we could not

W(CCMe$_3$)(dme)Cl$_3$ + 2RC≡CR →

               "W[η^5-C$_5$R$_4$(CMe$_3$)]Cl$_3$" (4)

"W[η^5-C$_5$R$_4$(CMe$_3$)]Cl$_3$" $\xrightarrow{0.5RC≡CR}$

0.5W[η^5-C$_5$R$_4$(CMe$_3$)](RC≡CR)Cl$_2$ +

            0.25{W[η^5-C$_5$R$_4$(CMe$_3$)]Cl$_4$}$_2$ (5)
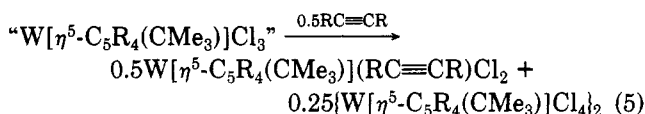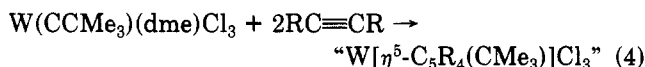
observe "W(η^5-C$_5$R$_4$(CMe$_3$)]Cl$_3$", and an attempt to synthesize it by reducing {W[η^5-C$_5$R$_4$(CMe$_3$)]Cl$_4$}$_2$ with sodium amalgam so far has yielded only an as yet unidentified green two-electron reduction product that does not react readily with 2-butyne or 3-hexyne. At present we have no substantiated proposals for the formation of the "disproportionation" products. However, it is likely on the basis of the work we will describe shortly that formation of the cyclopentadienyl ring is wholly independent of any such "disproportionation reaction".

Neither W[C(CMe$_3$)C(R)C(R)](OCMe$_3$)Cl$_2$ nor W[C-(CMe$_3$)C(Me)C(Me)](OCMe$_2$CMe$_2$O)Cl reacts with 2-butyne or 3-hexyne at 25 °C in 2 h in pentane or ether. The latter complex in one instance was heated to 60 °C in C$_6$D$_6$ in the presence of several equivalents of 3-hexyne without any evidence of reaction. In contrast, W[C(CMe$_3$)C-(Me)C(Me)](OCMe$_2$CMe$_2$O)(OCMe$_3$) reacts readily with 2-butyne as shown in eq 6. We propose that the dioxo


                            (6)

R = Me
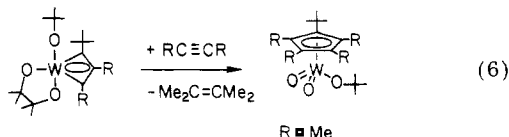
complex is formed when an intermediate W(IV) pinacolato complex decomposes to give tetramethylethylene (detected
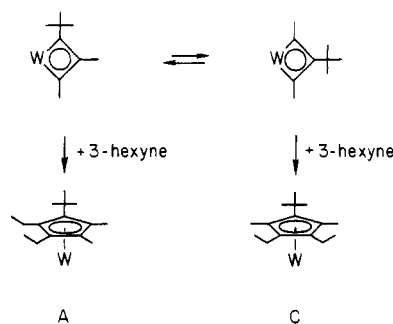
in virtually quantitative yield by GLC). An analogous reaction between W(C$_3$Et$_3$)(OCMe$_2$CMe$_2$O)(OCMe$_3$) and 3-hexyne gives W(η^5-C$_5$Et$_5$)(OCMe$_3$)O$_2$ in good yield. We do not understand at this time why the mono-*tert*-butoxy dichloride and pinacolato monochloride complexes do not react readily with 2-butyne or 3-hexyne.

The simplest mechanism for forming a cyclopentadienyl ring consists of coordination of the alkyne followed by insertion of it into either W–C$_\alpha$ bond to give a "tungstenabenzene" intermediate that then collapses to a cyclopentadienyl complex. If this were the case, then we should be able to form one type of cyclopentadienyl ring that contains more than two substituents (e.g., eq 7). The


                            (7)
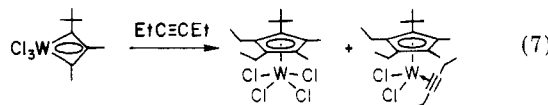
first experiment of this type was complicated by the fact that both products are paramagnetic. Fortunately, the insoluble W(V) tetrachloride complex can be converted into a W(VI) neopentylidyne complex by treatment with dineopentylzinc (eq 8). (The possible mechanisms will

{W[η^5-C(CMe$_3$)Me$_2$Et$_2$]Cl$_4$}$_2$ + 2Zn(CH$_2$CMe$_3$)$_2$ →

        2W[η^5-C(CMe$_3$)Me$_2$Et$_2$](CCMe$_3$)Cl$_2$ (8)
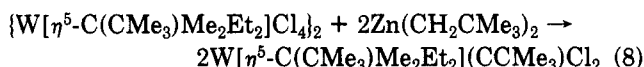
not concern us here.) NMR spectra then revealed that *two* types (and only two types) of cyclopentadienyl rings had formed, one symmetric and one unsymmetric, in a ratio of 4:6, respectively. Four are possible (two unsymmetric, two symmetric; Chart I) if we do *not* insist that the ethyl groups remain on adjacent carbon atoms in the ring. However, the most likely possibility is that the ethyl groups *are* on adjacent carbon atoms; i.e., the rings are A and C, on the basis of some results mentioned below. It is important to note that although excess 3-hexyne was used, we see no evidence for acetylene exchange (i.e., metathesis) to yield a new metallacycle (e.g., W[C(CMe$_3$)C(Et)C(Et)] or W[C(Me)C(Et)C(Et)]) followed by formation of compounds containing other cyclopentadienyl rings (e.g., η^5-CEt$_4$Me).

An important question is whether formation of rings A and C is restricted to the trichloride system. The answer is no, since the reaction between W[C(CMe$_3$)C(Me)C-(Me)](OCMe$_2$CMe$_2$O)(OCMe$_3$) and 3-hexyne produces dioxo complexes that contain what we assume are the same two rings (eq 9), in a ratio of 6:4 instead of 4:6 (see above).

                            (9)

         60%   40%
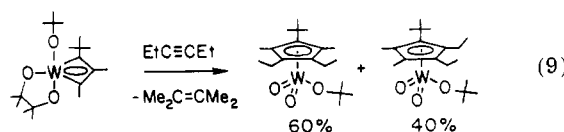
It is in this system that we have proven that the substituents on the added acetylene end up on adjacent carbon

(10) Churchill, M. R.; Wasserman, H. J. *Organometallics* **1983**, *2*, 755.
(11) Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 387.

Table I. Interatomic Distances (A) with Esd's for
W[C₃Me₂(CMe₃)][Me₂N(CH₂)₂NMe₂]Cl₃

(A) Distances from Tungsten Atom			
W–Cl(1)	2.425 (2)	W–C(1)	2.040 (7)
W–Cl(2)	2.399 (2)	W–C(2)	2.115 (7)
W–Cl(3)	2.433 (2)	W–C(3)	2.133 (7)
W–N(1)	2.492 (6)	W–centroid	1.920
W–N(2)	2.325 (6)		

(B) Distances within C₃Me₂(CMe₃) Ligand			
C(1)–C(2)	1.547 (10)	C(21)–C(22)	1.517 (14)
C(1)–C(3)	1.432 (10)	C(21)–C(23)	1.532 (13)
C(2)–C(3)	1.383 (9)	C(21)–C(24)	1.531 (12)
C(1)–C(11)	1.490 (11)	C(3)–C(31)	1.493 (10)
C(2)–C(21)	1.503 (10)		

(C) Distances within Me₂N(CH₂)₂NMe₂ Ligand			
N(1)–C(4)	1.478 (12)	N(2)–C(7)	1.470 (12)
N(1)–C(5)	1.484 (11)	N(2)–C(8)	1.500 (11)
N(1)–C(6)	1.463 (11)	N(2)–C(9)	1.497 (10)
C(4)–C(7)	1.395 (14)		

atoms in the cyclopentadienyl ring. W(C₃Et₃)-(OCMe₂CMe₂O)(OCMe₃) reacts with 2-butyne to give one W(η^5-C₅Et₃Me₂)(OCMe₃)O₂ complex. W(η^5-C₅Et₃Me₂)-(OCMe₃)O₂ was converted into W(η^5-C₅Et₃Me₂)Me₄ in several steps, and W(η^5-C₅Et₃Me₂)Me₄ was shown by an X-ray study to contain an η^5-C₅Et₃Me₂ ring in which the methyl groups are on adjacent carbon atoms.[12a]

The above results do not augur well for preparing multisubstituted cyclopentadienyl ring systems specifically, but they do raise some interesting questions concerning the mechanism of forming cyclopentadienyl rings. Formation of rings A and C can be explained nicely by proposing that 3-hexyne inserts into one of the W–C$_\alpha$ bonds in an α-tert-butyl-substituted WC₃ ring (to give A) or into one of the W–C$_\alpha$ bonds in the β-tert-butyl-substituted ring (to give C; Scheme I). Of course the problem with this proposal is that we have never seen an α-tert-butyl-substituted ring rearrange to a β-tert-butyl-substituted ring. Therefore we must postulate that the rings can rearrange only in the presence of an acetylene, possibly in an intermediate acetylene adduct of the tungstenacyclobutadiene complex. About the time this idea arose we began to observe some relatively strange "adducts" of W[C(CMe₃)C(Me)C(Me)]Cl₃ with nitrogen donors such as TMEDA or pyridine. We examined these species with the idea that they might be related to an acetylene adduct of W[C(CMe₃)C(Me)C(Me)]Cl₃ and therefore would give us a clue as to how the WC₃ ring rearranges in the process of reacting with that acetylene.

Adducts of Tungstenacyclobutadiene Complexes. The addition of 2 equiv of pyridine to W[C(CMe₃)C-(Me)C(Me)Cl₃ *or* the addition of 2-butyne to W-(CCMe₃)(py)₂Cl₃ produces *a mixture of two bis(pyridine) complexes* (by ¹H and ¹³C NMR). One of them contains equivalent pyridine ligands, the other inequivalent pyridine ligands. In the latter, one of the pyridine ligands is labile at 25 °C as evidenced by a broadened NMR signal for it; the spectrum is sharp at –20 °C. The most peculiar feature

(12) (a) W(η^5-C₅Et₃Me₂)(OCMe₃)O₂ was treated with excess HCl in the presence of Me₃SiCl in ether to give yellow W(η^5-C₅Et₃Me₂)(O)Cl₃. Addition of PCl₅ to W(η^5-C₅Et₃Me₂)(O)Cl₃ in dichloromethane followed by PMe₃ yielded green W(η^5-C₅Et₃Me₂)Cl₄(PMe₃). Addition of more than 8 equiv of ZnMe₂ to W(η^5-C₅Et₃Me₂)Cl₄(PMe₃) in toluene gave orange W(η^5-C₅Et₃Me₂)Me₄, which was recrystallized from pentane. Crystals of W(η^5-C₅Et₃Me₂)Me₄ decomposed in the X-ray beam but enough data were collected to establish the connectivity beyond any doubt. See supplementary material for complete details. (b) Covalent radii (0.99 Å for Cl, 0.77 Å for C(sp³)) are taken from: Pauling, L. "Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, New York, 1960; Table 7-2, p 224.
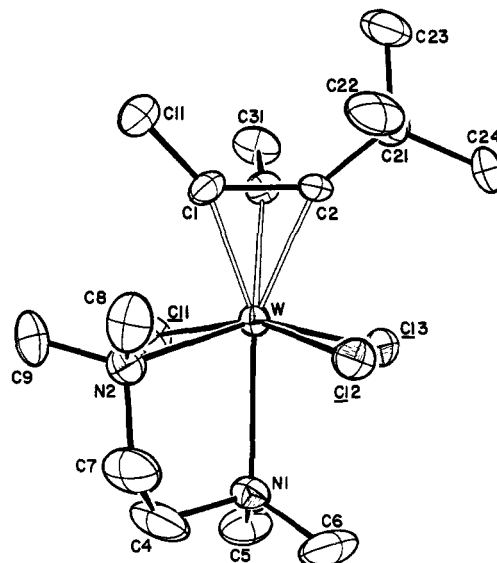

Figure 2. The W[C₃Me₂(CMe₃)][Me₂N(CH₂)₂NMe₂]Cl₃ molecule, showing the displacement of equatorial ligands away from the η^3-CMe₂(CMe₃) ligand and the displacement of substituents from the triatomic carbocyclic ring (ORTEP-II diagram; 30% ellipsoids).

of the ¹³C NMR spectrum at 25 °C is the chemical shifts for what were the WC₃ ring carbon atoms at 171.8, 144.6, 143.1, and 126.2 ppm (both isomers); i.e., only *two* signals per isomer are observed at 25 °C in a range well upfield of where the ring's α-carbon signals are observed in the parent tungstenacycle [at 265.6 (C$_\alpha$) and 259.1 ppm (C$_\alpha'$)].

A TMEDA complex can be prepared similarly in high yield. At 25 °C two TMEDA methyl groups are observed. Again the ¹³C NMR spectrum of the complex at 25 °C reveals only two "ring" carbon signals at 162.4 and 127.6 (br) ppm. This molecule was chosen for the X-ray study.

The crystal of W[C₃Me₂(CMe₃)][Me₂N(CH₂)₂NMe₂]Cl₃ consists of discrete monomeric units separated by normal van der Waals' distances. There are no abnormally short intermolecular contacts. Two views of the molecule along with the labeling of atoms are illustrated in Figures 1 and 2. Interatomic distances and angles are collected in Tables I and II.

The molecule is essentially an octahedral complex containing a symmetrically bound η^3-cyclopropenyl ligand (counting the η^3-C₃ ligand as taking up one coordination site). The η^3-C₃Me₂(CMe₃) ligand and atom N(1) occupy apical positions, while the three chloride ligands take up a meridional configuration in the equatorial plane that is completed by atom N(2). The three tungsten–chlorine distances are similar (W–Cl(1) = 2.425 (2) Å, W–Cl(2) = 2.399 (2) Å, W–Cl(3) = 2.433 (2) Å). The axial W–N(1) bond length of 2.492 (6) Å is 0.167 (8) Å longer than the equatorial W–N(2) bond length of 2.325 (6) Å, a fact that suggests that η^3-C₃Me₂(CMe₃) system exerts a strong trans-lengthening influence. All of the equatorial ligands are displaced below the true equatorial plane by 5–20° (Figure 2) as shown by the angles centroid–W–Cl(1) = 95.6°, centroid–W–Cl(2) = 103.0°, centroid–W–Cl(3) = 95.5°, and centroid–W–N(2) = 109.5°. ("Centroid" is the centroid of the triangle defined by atoms C(1), C(2), and C(3).) Correspondingly, all of the N(1)–W–(equatorial ligand) angles are acute—N(1)–W–Cl(1) = 80.5 (1)Å, N-(1)–W–Cl(2) = 81.2 (1)°, N(1)–W–Cl(3) = 79.1 (1)°, and N(1)–W–N(2) = 75.8 (2)°. The centroid–W–N(1) angle is 173.4°.

The average tungsten–chlorine distance of ~2.42 Å in the present molecule suggests a covalent radius of ~1.43 Å for tungsten (2.42 – 0.99) Å[12] and leads, in turn, to a

Table II. Interatomic Angles (deg) for W[C₃Me₂(CMe₃)][Me₂N(CH₂)₂NMe₂]Cl₃

(A) Selected Angles about the Tungsten Atom

Cl(1)-W-Cl(2)	161.4 (1)	Cl(2)-W-Cl(3)	91.4 (1)	Cl(3)-W-N(2)	154.9 (2)
Cl(1)-W-Cl(3)	88.7 (1)	Cl(2)-W-N(1)	81.2 (1)	Cl(3)-W···centroid	95.5 (-)
Cl(1)-W-N(1)	80.5 (1)	Cl(2)-W-N(2)	85.2 (2)	N(1)-W-N(2)	75.8 (2)
Cl(1)-W-N(2)	86.9 (2)	Cl(2)-W···centroid	103.0 (-)	N(1)-W···centroid	173.4 (-)
Cl(1)-W···centroid	95.6 (-)	Cl(3)-W-N(1)	79.1 (1)	N(2)-W···centroid	109.5

(B) Internal Angles of WC₃ Tetrahedron

C(3)-C(1)-C(2)	55.2 (5)	W-C(2)-C(1)	65.6 (4)	C(1)-W-C(3)	40.1 (3)
C(1)-C(2)-C(3)	58.2 (5)	W-C(2)-C(3)	71.7 (4)	C(2)-W-C(3)	40.0 (3)
C(2)-C(3)-C(1)	66.6 (5)	W-C(3)-C(1)	66.5 (4)	W-C(1)-C(11)	153.8 (6)
W-C(1)-C(2)	70.8 (4)	W-C(3)-C(2)	70.3 (4)	W-C(2)-C(21)	148.5 (5)
W-C(1)-C(3)	73.5 (4)	C(1)-W-C(2)	43.7 (3)	W-C(3)-C(31)	140.7 (5)

(C) External Angles of C₃Me₂(CMe₃) System

C(2)-C(1)-C(11)	130.4 (6)	C(2)-C(3)-C(31)	142.5 (7)	C(2)-C(21)-C(23)	108.7 (7)
C(3)-C(1)-C(11)	129.5 (6)	centroid-C(1)-C(11)	136.5 (-)	C(2)-C(21)-C(24)	109.5 (7)
C(1)-C(2)-C(21)	133.7 (6)	centroid-C(2)-C(21)	144.7 (-)	C(22)-C(21)-C(23)	109.2 (7)
C(3)-C(2)-C(21)	137.7 (7)	centroid-C(3)-C(31)	154.4 (-)	C(22)-C(21)-C(24)	109.7 (7)
C(1)-C(3)-C(31)	135.7 (6)	C(2)-C(21)-C(22)	110.8 (7)	C(23)-C(21)-C(24)	109.0 (7)

(D) Angles within Me₂N(CH₂)₂NMe₂ Ligand

W-N(1)-C(4)	103.4 (5)	C(5)-N(1)-C(6)	105.8 (7)	C(7)-N(2)-C(8)	104.7 (7)
W-N(1)-C(5)	115.5 (5)	N(1)-C(4)-C(7)	115.5 (9)	C(7)-N(2)-C(9)	110.3 (7)
W-N(1)-C(6)	116.7 (5)	W-N(2)-C(7)	107.8 (5)	C(8)-N(2)-C(9)	106.1 (6)
C(4)-N(1)-C(5)	105.3 (7)	W-N(2)-C(8)	112.4 (5)	N(2)-C(7)-C(4)	116.1 (9)
C(4)-N(1)-C(6)	109.5 (7)	W-N(2)-C(9)	115.1 (5)		

Table III. Molecular Planes for
W[C₃Me₂(CMe₃)][Me₂N(CH₂)₂NMe₂]Cl₃

atom	dev, Å	atom	dev, Å
(A) C(1)-C(2)-C(3) Plane			
$-0.9344X + 0.3164Y - 0.1639Z - 1.7696 = 0$			
C(1)*	0.000	W	-1.9106 (3)
C(2)*	0.000	Cl(1)	-2.209 (2)
C(3)*	0.000	Cl(2)	-2.378 (2)
C(11)	1.026 (8)	Cl(3)	-2.377 (2)
C(21)	0.860 (8)	N(1)	-4.401 (6)
C(22)	1.008 (10)	N(2)	-2.473 (6)
C(23)	2.244 (9)	C(4)	-4.727 (10)
C(24)	0.232 (10)	C(7)	-3.915 (10)
C(31)	0.633 (8)		
(B) N(1)-C(4)-C(7) Plane			
$-0.3501X + 0.5435Y - 0.7629Z - 1.2451 = 0$			
N(1)*	0.000	N(2)	1.107 (6)
C(4)*	0.000	W	1.4717 (3)
C(7)*	0.000		
(C) N(2)-C(7)-C(4) Plane			
$0.2009X - 0.2114Y - 0.9565Z - 3.1921 = 0$			
N(2)*	0.000	N(1)	-1.119 (6)
C(7)*	0.000	W	-1.4495 (3)
C(4)*	0.000		

Dihedral Angle (deg)

planes B/C   57.01 (122.99)[a]

[a] Note that the ethylenediamine ring has the usual puckered conformation.

predicted W-C(sp³) bond length of 2.20 Å (1.43 + 0.77) Å.[12b] Each of the tungsten-carbon distances to the η³-C₃Me₂(CMe₃) ligand is substantially *shorter* than 2.20 Å—W-C(1) = 2.040 (7) Å, W-C(2) = 2.115 (7) Å, and W-C(3) = 2.133 (7) Å—resulting in a relatively short W-centroid distance of only 1.920 Å. The ensuing steric interactions could explain why the equatorial ligands are bent out of the equatorial plane and perhaps also to some extent why the ring's substituents are all bent out of the plane of the C₃ ring.

The bending back of the ring substituents can be measured in three ways. First, as shown in Table III, the α-carbon atoms of the substituents are displaced from the

triatomic plane C(1)-C(2)-C(3) in a direction away from the metal atom, such that deviations from the plane are 1.026 (8) Å for C(11), 0.860 (8) Å for C(21), and 0.633 (8) Å for C(31). These deviations correspond to angular displacements[13] of 43.52° for C(11), 34.90° for C(21), and 25.09° for C(31). Second, the sum of the three C-C-C angles about each of the ring atoms is, in each case, substantially different from 360°—315.1° (55.2 + 130.4 + 129.5)° about C(1), 329.6° (58.2 + 133.7 + 137.7)° about C(2), and 344.8° (66.6 + 135.7 + 142.5)° about C(3). Third, the centroid-C(ring)-C(substituent) angles are centroid-C(1)-C(11) = 136.5°, centroid-C(2)-C(21) = 144.7°, and centroid-C(3)-C(31) = 154.4°. The supplements of these angles (43.5°, 35.3°, and 25.6°, respectively) differ from the angles first mentioned above only by there being a component of lateral distortion in the present values. These differences can be related to the variation between the two C′(ring)-C(ring)-C(substituent) angles about a given C(ring) atom and are small for each case.

We come now to a consideration of the bonding between the central tungsten atom and the η³-C₃Me₂(CMe₃) ligand. It is perhaps important to note that the carbon-carbon distances within the triatomic ring vary significantly from one another, with C(1)-C(2) = 1.547 (10) Å, C(1)-C(3) = 1.432 (10) Å, and C(2)-C(3) = 1.383 (9) Å. We are persuaded that these differences are real, rather than a result of some nonrandom systematic errors in our analysis, at least for C(1)-C(2) vs. the other two. Part of the evidence consists of the fact that the ring-to-substituent distances are all similar to one another and within the range expected for carbon-carbon single bonds (cf. C(sp³)-C(sp³) = 1.537 ± 0.005 Å and C(sp²)-C(sp³) = 1.510 ± 0.005 Å)[14] with C(1)-C(11) = 1.490 (11) Å, C(2)-C(21) = 1.503 (10) Å, and C(3)-C(31) = 1.493 (10) Å. We noted above that the W-centroid distance is only 1.920 Å. For comparison, the Mo-centroid distance in the 18-electron octahedral η³-triphenylcyclopropenyl complex Mo(C₃Ph₃)(CO)₂(bpy)Br[15] is 2.06 Å with its Mo-C(ring) distances being 2.193 (18)

(13) Calculated simply as sin⁻¹ [(deviation)/(C ring)-C(substituent) distance)].

(14) *Spec. Publ.—Chem. Soc.* **1965**, *No. 18*, S14s-S15s.

(15) Drew, M. G. B.; Brisdon, B. J.; Day, A. *J. Chem. Soc., Dalton Trans.* **1981**, 1310.

−2.262 (22) Å. Since molybdenum and tungsten have essentially identical covalent radii, it follows that the η^3-$C_3Me_2(CMe_3)$ ring is more strongly bound to tungsten in 16-electron $W[C_3Me_2(CMe_3)][Me_2N(CH_2)_2NMe_2]Cl_3$. We feel most comfortable describing the C_3 ring as an η^3-cyclopropenyl ligand drawn close to the metal as a result of the metal's electron deficiency. However, describing the complex as a tungstenatetrahedrane—W(VI) with a $C_3R_3{}^{3-}$ ligand—is not completely unreasonable. Unfortunately, we cannot at present relate either of these possibilities to the observed C–C distances within the ring (1.547 (10), 1.432 (10), 1.383 (9) Å). In any case, describing the C_3 ring an an aromatic $C_3R_3{}^+$ system seems least satisfactory. We hope to gain some insight into metal–C_3 ring bonding by variable-temperature NMR studies, but as these studies are beyond the scope of this paper they will be presented elsewhere. However, we should at least point out now that in the high-temperature limit spectrum of $W[C_3Me_2(CMe_3)][Me_2N(CH_2)_2NMe_2]Cl_3$ *two* TMEDA methyl groups are found, and free TMEDA does not exchange with coordinated TMEDA on the NMR time scale at the high-temperature limit.

It seems reasonable to propose that the structure of the unsymmetrical isomer of $W[C(CMe_3)C(Me)C(Me)](py)_2Cl_3$ is analogous to that of $W[C(CMe_3)C(Me)C(Me)](TMEDA)Cl_3$, and the labile pyridine ligand is that trans to the η^3-C_3 ring. The pseudooctahedral geometry of the symmetric isomer must be either cis, *fac* or trans, *mer*.

An important question is whether η^3-cyclopropenyl rings can be "degraded" to give alkylidyne complexes. The result shown in eq 10 suggests that they can be. W(CMe)-

$$W[C(CMe_3)C(Me)C(Me)](py)_2Cl_3 + 3LiOCMe_3 \xrightarrow{\text{ether}}$$
$$\text{largely } W(CMe)(OCMe_3)_3(py) \quad (10)$$
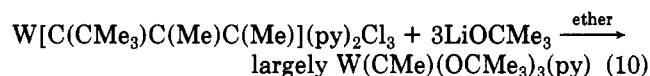
$(OCMe_3)_3(py)$ was identified and quantitated by comparison of its ^{13}C and ^1H NMR spectra with those of an authentic sample prepared by adding pyridine to W-$(CMe)(OCMe_3)_3$.[16] We cannot tell at what point the η^3-cyclopropenyl cage reverts to a tungstenacyclobutadiene ring and finally to an alkylidyne complex, but the fact that it does suggests at least that formation of an η^3-cyclopropenyl complex is not irreversible, in contrast (presumably) to cyclopentadienyl ring formation.

Discussion

We have compared the salient structural features of three tungstenacyclobutadiene complexes in the previous paper;[3] the discussion will not be repeated here. What we have done here is to collect the ^{13}C NMR data for all trigonal-bipyramidal tungstenacyclobutadiene complexes that have appeared in this series of three papers (Table VI).[2,3] All of these molecules are structurally similar, or so we presume from the fact that the three that have been structurally characterized are virtually identical. Therefore it is perhaps not surprising to find that the chemical shifts of the C_α and C_β ring carbon atoms do not vary greatly, the wide variety of ligands notwithstanding. The range for the C_α signals is understandably largest (225–278 ppm); that for the C_β signals is about half as great (129–151 ppm). About the only trend worth pointing out is the somewhat lower field shifts for C_α atoms in molecules containing at least one chloride ligand (241–278 ppm) compared to those not containing chloride ligands (225–250 ppm). But this is the trend one would expect in a wholly organic system;

we do not think it especially significant here. What we think is a relatively significant feature is the relatively large coupling between C_α and the metal in the instances where the effort was made to observe it. Coupling of this magnitude is indicative of significant multiplicity in the W–C_α bond, close to what would be expected for a double bond (cf. $J_{C_\alpha W}$ = 210, 120, and 80 Hz for the W≡C, W=C, and W—C bonds in $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)$-$(PMe_3)_2$[17]).

The stability of the tungstenacyclobutadiene complexes we have prepared in this study toward loss of an acetylene to give alkylidyne complexes can be understood largely on steric grounds. One would think $W[C(CMe_3)C(Me)C$-$(Me)](OCMe_2CMe_2O)(OCMe_3)$ is the most likely complex to lose an acetylene. But the pinacolato ligand is clearly not the steric equivalent of two *tert*-butoxide ligands. It is also not likely to be as good a π-electron donor as two *tert*-butoxide ligands as a result of the constraint imposed by the WO_2C_2 ring. Therefore the metal in a pinacolato complex should be less likely to lose an acetylene than the metal in an analogous di-*tert*-butoxide complex for electronic reasons also. Even the presence of a *tert*-butyl group on the α-carbon atom of the WC_3 ring is of little help in forcing loss of the *tert*-butyl-substituted acetylene. The fact that we could trap, but not observe, analogous tri-*tert*-butoxytungstenacycles strengthens our hypothesis concerning the great importance of steric effects on metallacycle stability.

By comparison with the explanation concerning metallacycle stability, it is significantly more difficult at this stage to explain when a metallacycle will react with additional acetylene to give a cyclopentadienyl ring. The discovery of formation of an η^3-cyclopropenyl ring by adding a simple σ-donor ligand to a tungstenacyclobutadiene complex opens up the possibility that a similar WC_3 cage can form when an acetylene adds to the metal in a $W[C(CMe_3)C(Me)C(Me)]$ complex. Even in the absence of detailed variable-temperature studies we can assume that the η^3-C_3 ring in $W[C_3Me_2(CMe_3)[Me_2N$-$(CH_2)_2NMe_2]Cl_3$ is likely to rotate about the ring–W bond axis at a rate that at least is of the order of or much faster than the chemical time scale. Therefore it seems reasonable to propose that a square-pyramidal η^3-cyclopropenyl complex *could* be formed when an acetylene adds to W-$[C(CMe_3)C(Me)C(Me)]Cl_3$ and that in this manner the regiospecificity of the subsequent acetylene "insertion" step is lost. We would propose that the acetylene inserts into a W–cyclopropenyl single bond and that the resulting β-cyclopropenylvinyl complex rearranges to a cyclopentadienyl complex.

We may go one step further and suggest that η^3-cyclopropenyl complexes are not *required* intermediates. It is sufficient to postulate only that a nonplanar, fluxional WC_3 ring forms when the acetylene adds to W. (It is interesting to note in this context that a non-planar, fluxional tungstenacyclobutadiene complex has been characterized structurally[18] and that an η^3-cyclopropenyl complex forms[18] when PMe_3 is added to such a species.[19]) Therefore, an attractive explanation as to how a cyclopentadienyl ring forms is that an acetylene reacts with an alkylidene-like W—C bond in a nonplanar tungstenacyclobutadiene complex (eq 11). There is a well-documented example of "insertion" of an acetylene into a M=C bond in a high

(16) Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291.

(17) Clark, D. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774.
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(19) Churchill, M. R.; Fettinger, J. C.; McCullough, L. G.; Schrock, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 3356.

Table IV. Experimental Data for the X-ray Diffraction Study of W[C₃Me₂(CMe₃)][Me₂N(CH₂)₂NMe₂]Cl₃

(A) Crystal Parameters at 23 °C (296 K)

cryst. system: monoclinic $V = 1960$ (1) Å³
space group: $P2_1/n$ formula: $C_{15}H_{31}Cl_3N_2W$
$a = 10.982$ (2) Å mol wt: 529.6
$b = 13.257$ (4) Å $Z = 4$
$c = 13.957$ (4) Å $D(calcd) = 1.80$ g cm⁻³
$\beta = 105.33$ (2)°

(B) Data Collection

diffractometer: Syntex P2₁
radiation: Mo Kα ($\bar{\lambda}$ 0.710 730 Å)
monochromator: pyrolytic graphite, equatorial geometry, $2\theta(m) = 12.2°$, assumed 50% perfect
scan type: coupled θ(crystal)–2θ(counter)
scan speed: 2.0 deg/min (in 2θ)
scan width: symmetrical, $[1.8 + \Delta(\alpha_2 - \alpha_1)]°$
background measurement: stationary-crystal, stationary-counter at beginning and end of 2θ scan; each for one-half of total scan time
standard reflcns: 3 approximately mutually orthogonal check reflections remeasured after each 97 reflections; no significant fluctuations were observed
reflctns measd: $+h,+k,\pm l$ for $2\theta = 4.5-45.0°$; 2732 total reflections were merged to 2576 unique independent data; file name WME2
abs correctn: μ (Mo Kα) = 66.4 cm⁻¹; all data were corrected by interpolation in 2θ and φ between ψ scans of three close-to-axial reflections (204, 305, 406)

oxidation state alkylidene complex[20a] and much evidence that this type of reaction is relatively facile in a variety

(11)

A   B
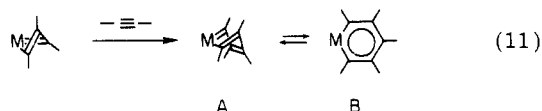
of circumstances.[20b] The product in this case would be a nonplanar "metallacyclohexatriene" complex (A) or a planar "metallabenzene" complex (B). The nonplanar form, if not actually the lower energy species, is probably readily accessible and can react further to give larger and larger, probably exclusively nonplanar M(CR)ₓ ring systems. This is a reasonable, but by no means unique, mechanism for acetylene polymerization. A second possible fate of A (or B) is formation of a C–C bond to give a cyclopentadienyl ring. The third possible fate of A or B may be loss again of an acetylene to give the tungsten-acyclobutadiene complex. Although the higher order metathesis reaction observed in the previous paper need *not* involve an intermediate analogous to that which is a precursor to a cyclopentadienyl complex, the more interesting possibility is that it does, and that whether a C–C bond forms, or not, in general, is a complex function of several factors that collectively can be called "reducibility" of the W(VI) species.

Experimental Section

Refer to earlier papers for general experimental details. W-(CCMe₃)(dme)Cl₃,[5] W(CCMe₃)(OCMe₃)₃,[5] and W(CR)(OCMe₃)₃[16] were prepared by published methods. Pinacol was sublimed prior to use. NEt₃ was distilled from barium oxide. Alkynes were passed through alumina prior to use.

Table V. Final Positional Parameters for W[C₃Me₂(CMe₃)][Me₂N(CH₂)₂NMe₂]Cl₃

atom	x	y	z
W	0.08570 (2)	0.22338 (2)	−0.16006 (2)
Cl(1)	0.12447 (17)	0.29159 (14)	−0.31054 (13)
Cl(2)	0.11088 (18)	0.12907 (15)	−0.00938 (13)
Cl(3)	0.20041 (17)	0.36587 (14)	−0.06912 (14)
N(1)	0.30009 (51)	0.16690 (45)	−0.13671 (43)
N(2)	0.06708 (54)	0.06664 (44)	−0.23727 (46)
C(1)	−0.10420 (60)	0.23268 (56)	−0.22211 (50)
C(2)	−0.07188 (57)	0.28077 (53)	−0.11746 (50)
C(3)	−0.06015 (58)	0.33385 (52)	−0.19981 (48)
C(11)	−0.22697 (70)	0.19602 (63)	−0.28643 (59)
C(21)	−0.14218 (70)	0.29065 (66)	−0.03899 (57)
C(22)	−0.19544 (82)	0.18959 (84)	−0.01888 (70)
C(23)	−0.25082 (78)	0.36554 (77)	−0.07521 (67)
C(24)	−0.05287 (87)	0.33109 (92)	0.05686 (59)
C(31)	−0.08711 (73)	0.43380 (57)	−0.25026 (63)
C(4)	0.29559 (86)	0.07811 (74)	−0.20260 (87)
C(5)	0.39088 (73)	0.23821 (73)	−0.17216 (69)
C(6)	0.37768 (79)	0.13863 (85)	−0.03582 (72)
C(7)	0.19099 (90)	0.01687 (70)	−0.20694 (90)
C(8)	−0.02003 (87)	−0.00259 (60)	−0.20197 (64)
C(9)	0.02017 (85)	0.06904 (64)	−0.34815 (61)
H(4A)	0.3692	0.0380	−0.1799
H(4B)	0.2903	0.1016	−0.2678
H(5A)	0.4027	0.2974	−0.1324
H(5B)	0.3525	0.2555	−0.2394
H(5C)	0.4703	0.2072	−0.1672
H(6A)	0.3859	0.1957	0.0065
H(6B)	0.4594	0.1150	−0.0362
H(6C)	0.3336	0.0867	−0.0122
H(7A)	0.1914	−0.0358	−0.2529
H(7B)	0.2001	−0.0110	−0.1427
H(8A)	−0.1028	0.0249	−0.2191
H(8B)	0.0086	−0.0098	−0.1318
H(8C)	−0.0210	−0.0667	−0.2325
H(9A)	−0.0598	0.1013	−0.3668
H(9B)	0.0123	0.0020	−0.3731
H(9C)	0.0782	0.1052	−0.3748
H(11A)	−0.2148	0.1704	−0.3468
H(11B)	−0.2855	0.2502	−0.3005
H(11C)	−0.2588	0.1440	−0.2529
H(22A)	−0.2394	0.1974	0.0308
H(22B)	−0.1283	0.1428	0.0033
H(22C)	−0.2518	0.1652	−0.0782
H(23A)	−0.2959	0.3724	−0.0261
H(23B)	−0.3061	0.3414	−0.1351
H(23C)	−0.2177	0.4292	−0.0868
H(24A)	−0.0972	0.3373	0.1064
H(24B)	−0.0217	0.3952	0.0444
H(24C)	0.0157	0.2857	0.0790
H(31A)	−0.0592	0.4333	−0.3091
H(31B)	−0.0438	0.4851	−0.2070
H(31C)	−0.1753	0.4464	−0.2667

Collection of X-ray Diffraction Data for W[CMe₂-(CMe₃)][Me₂N(CH₂)₂NMe₂]Cl₃. A crystal of approximate orthogonal dimensions 0.18 × 0.20 × 0.22 mm³ was sealed into a thin-walled capillary in an inert-atmosphere (Ar) KSE drybox that had been modified by adding a protruding transparent section between the gloves. (This enables crystals to be inspected through an externally mounted binoccular microscope.) The capillary was inserted into an aluminum pin (with bees' wax), which was set in an eucentric gongiometer and mounted on the Syntex P2₁ automated four-circle diffractometer at SUNY—Buffalo. Crystal alignment, determination of unit cell parameters and orientation matrix, and data collection were carried out as described previously.[21] Details appear in Table IV. All data were converted to $|F_o|$ values, following correction for absorption and for Lorentz and polarization factors. Any reflection with $I(net) < 0$ was assigned a value of $|F_o| = 0$. No datum was rejected.

All calculations were performed on the SUNY—Buffalo modified version of the Syntex XTL system. The analytical form

(20) (a) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979,** *101,* 3210. (c) Clarke, T. C.; Yannoni, C. S.; Katz, T. J. *Ibid.* **1983,** *105,* 7787.

(21) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977,** *16,* 265.

Table VI. ^{13}C NMR Data for Trigonal-Bipyramidal Tungstenacyclobutadiene Complexes

compound	C_α, ppm	C_β, ppm	$J_{C_\alpha W}$, Hz
W[C(CMe$_3$)C(Me)C(Me)]Cl$_3$	267.5, 263.4	150.7	
W[C(CMe$_3$)C(Et)C(Et)]Cl$_3$	267.6, 266.7	150.3	
W[C(CMe$_3$)C(Me)C(Me)](OCMe$_3$)Cl$_2$	265.6, 259.1	134.2	93, 116
W[C(CMe$_3$)C(Et)C(Et)](OCMe$_3$)Cl$_2$	266.4, 265.7	137.4	93, 110
W[C(CMe$_3$)C(Me)C(Me)][O-2,6-C$_6$H$_3$(i-Pr)$_2$]Cl$_2$	278.5, 270.1	141.3	
W[C(CMe$_3$)C(Me)C(Me)](OCMe$_2$CMe$_2$O)Cl	250.1, 241.3	143.0	
W[C(CMe$_3$)C(Me)C(Me)][O-2,6-C$_6$H$_3$(i-Pr)$_2$]$_2$Cl	258.7, 247.5	132.1	
W[C(CMe$_3$)C(Me)C(Me)](OCMe$_2$CMe$_2$O)(OCMe$_3$)	232.1, 225.2	128.9	122, 134
W(C$_3$Et$_3$)(OCMe$_2$CMe$_2$O)(OCMe$_3$)	226.5	132.9	
W(C$_3$Et$_3$)[O-2,6-C$_6$H$_3$(i-Pr)$_2$]$_3$	244.9	136.6	124
W(C$_3$Pr$_3$)[O-2,6-C$_6$H$_3$(i-Pr)$_2$]$_3$	237.1	134.8	125
W(C$_3$Et$_3$)[OCH(CF$_3$)$_2$]$_3$	242.9	147.3	127
W[C(CMe$_3$)C(Et)C(Et)][OCH(CF$_3$)$_2$]$_3$	250.4, 245.8	147.4	
W(C$_3$Pr$_3$)[OCH(CF$_3$)$_2$]$_3$	241.9	146.3	127
W(C$_3$Me$_3$)[OCMe(CF$_3$)$_2$]$_3$	239.9	133.5	
W(C$_3$Et$_3$)[OCMe(CF$_3$)$_2$]$_3$	256.2	134.4	119

of the appropriate neutral atom scattering factor was corrected for both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion.[22] The function minimized during least-squares refinement processes was $\sum w(|F_o| - |F_c|)^2$, where $w = [(\sigma(|F_o|))^2 + 0.015|F_o|^2]^{-1}$.

The structure was solved by a combination of Patterson, difference Fourier, and full-matrix least-squares refinement techniques. All non-hydrogen atoms were accurately located. Hydrogen atoms were included in calculated positions (either trigonal-planar or staggered tetrahedral geometry) with d(C–H) = 0.95 Å,[23] these positions were not refined but were continuously updated relative to the appropriate new C or N positions. Convergence was reached with $R_F = 3.8\%$, $R_{wF} = 3.2\%$, and GOF = 1.31 for all 2576 reflections[24,25] refined against 190 parameters ($R_F = 3.0\%$ and $R_{wF} = 3.1\%$ for those 2285 reflections with $|F_o| > 3.0\sigma(|F_o|)$; $R_F = 2.6\%$ and $R_{wF} = 2.9\%$ for those 2088 reflections with $|F_o| > 6.0\sigma(|F_o|)$).

A final difference Fourier synthesis showed no significant features. The function $\sum w(|F_o| - |F_c|)^2$ showed no abnormal dependency on $|F_o|$, $(\sin \theta)/\lambda$, sequence number, identity, or parity-class of the crystallographic indices; the weighting scheme is thus satisfactory. Positional parameters are collected in Table V; anisotropic thermal parameters (Table VS) have been deposited.

W[C(CMe$_3$)C(Me)C(Me)]Cl$_3$. An ether solution (50 mL) of W(CCMe$_3$)(dme)Cl$_3$ (1.0 g, 2.2 mmol) was cooled to –20 °C and treated with 2-butyne (174 μL, 2.2 mmol). The reaction was left to stand at –30 °C overnight. Violet crystals were isolated by filtration, washed with pentane, and dried in vacuo (0.72 g, 78%): ^{1}H NMR (C$_6$D$_6$) δ 2.97 (s, 3, C$_\alpha$Me), 2.06 (s, 3, C$_\beta$Me), 1.22 (s, 9, CCMe$_3$); ^{1}H NMR (CD$_2$Cl$_2$) δ 4.15 (s, 3, C$_\alpha$Me), 3.71 (s, 3, C$_\beta$Me), 1.68 (s, 9, CCMe$_3$); ^{13}C NMR (CD$_2$Cl$_2$) δ 267.5 and 263.4 (s, CCMe$_3$ and C$_\alpha$Me), 150.7 (s, C$_\beta$Me), 44.3 (s, CCMe$_3$), 29.5 (q, J_{CH} = 128 Hz, CCMe$_3$), 25.6 and 17.2 (q, J_{CH} = 137 Hz, C$_\alpha$ and C$_\beta$Me).

This complex is relatively unstable in CH$_2$Cl$_2$ and CHCl$_3$. The crystal for the X-ray study was selected from a homogeneous sample; the analogous diethyl complex (below) was fully analyzed.

W[C(CMe$_3$)C(Et)C(Et)]Cl$_3$. The procedure was similar to that used to prepare W[C(CMe$_3$)C(Me)C(Me)]Cl$_3$ (57%): ^{1}H NMR (C$_6$D$_6$) δ 3.53 (q, 2, ^3J_H = 7.4 Hz, $^3J_{HW}$ ≈ 3 Hz, C$_\alpha$CH$_2$CH$_3$), 3.25 (q, 2, ^3J_H = 7.6 Hz, C$_\beta$CH$_2$CH$_3$), 1.39 (t, 3, ^3J_H = 7.4 Hz, C$_\alpha$CH$_2$CH$_3$), 1.29 (s, 9, CCMe$_3$), 0.44 (t, 3, ^3J_H = 7.6 Hz, C$_\beta$CH$_2$CH$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 267.6 and 266.7 (CCMe$_3$ and C$_\alpha$Et, not respectively), 150.3 (C$_\beta$Et), 43.8 (CCMe$_3$), 32.0 (CC-H$_2$CH$_3$), 29.8 (CCMe$_3$), 24.5 (CCH$_2$CH$_3$), 14.3 and 11.9 (CCH$_2$CH$_3$). Anal. Calcd for WC$_{11}$H$_{19}$Cl$_3$: C, 29.93; H, 4.34; Cl, 24.09. Found: C, 30.23; H, 4.50; Cl, 24.39.

W[C(CMe$_3$)C(Me)C(Me)](OCMe$_3$)Cl$_2$. Triethylamine (175 μL, 1.3 mmol) and *tert*-butyl alcohol (119 μL, 1.3 mmol) were

added sequentially to a cold (–30 °C) toluene solution (10 mL) of W[C(CMe$_3$)C(Me)C(Me)]Cl$_3$ (0.52 g, 1.3 mmol). The reaction was stirred for 1 h at room temperature, and the solvent was removed in vacuo. The residue was extracted with ether. The ether extract was filtered, concentrated in vacuo, and cooled to –30 °C to give orange crystals that were isolated by filtration, washed with pentane, and dried in vacuo (two crops, 0.38 g, 67%): ^{1}H NMR (C$_6$D$_6$) δ 3.08 (s, 3, C$_\alpha$Me), 2.16 (s, 3, C$_\beta$Me), 1.75 (s, 9, OCMe$_3$), 1.39 (s, 9, CCMe$_3$); ^{13}C NMR (C$_6$D$_6$) δ 265.6 and 259.1 (s, J_{CW} = 93 Hz and 116 Hz, CCMe$_3$ and C$_\alpha$Me, or vice versa), 134.2 (s, C$_\beta$Me), 87.9 (s, OCMe$_3$), 42.7 (s, CCMe$_3$), 31.1 (q, J_{CH} = 129 Hz, OCMe$_3$ or CCMe$_3$), 29.6 (q, J_{CH} = 128 Hz, OCMe$_3$ or CCMe$_3$), 24.3 (q, J_{CH} = 131 Hz, CMe), 12.4 (q, J_{CH} = 134 Hz, CMe). Anal. Calcd for WC$_{13}$H$_{24}$Cl$_2$O: C, 34.61; H, 5.36. Found: C, 34.56; H, 5.41.

W[C(CMe$_3$)C(Et)C(Et)](OCMe$_3$)Cl$_2$. The procedure was similar to that used to prepare W[C(CMe$_3$)C(Me)C(Me)]-(OCMe$_3$)Cl$_2$ except the product was extracted into pentane (yield 0.13 g, 75%): ^{1}H NMR (C$_6$D$_6$) δ 3.57 (q, 2, ^3J_H = 7.4 Hz, C$_\alpha$CH$_2$CH$_3$), 3.28 (q, 2, ^3J_H = 7.6 Hz, C$_\beta$CH$_2$CH$_3$), 1.73 (s, 9, OCMe$_3$ or CCMe$_3$), 1.57 (t, 3, ^3J_H = 7.4 Hz, C$_\alpha$CH$_2$CH$_3$), 1.43 (s, 9, OCMe$_3$ or CCMe$_3$), 0.68 (t, 3, ^3J_H = 7.6 Hz, C$_\beta$CH$_2$CH$_3$); ^{13}C NMR (C$_6$D$_6$) δ 266.4 and 265.7 (s, J_{CW} ≈ 93 Hz and 110 Hz, CCMe$_3$ and C$_\alpha$Et), 137.4 (s, C$_\beta$Et), 87.9 (s, OCMe$_3$), 43.1 (s, CCMe$_3$), 31.9 (t, J_{CH} = 131 Hz, C$_\alpha$ or C$_\beta$CH$_2$CH$_3$), 31.2 (q, J_{CH} = 127 Hz, OCMe$_3$ or CCMe$_3$), 30.4 (q, J_{CH} = 128 Hz, OCMe$_3$ or CCMe$_3$), 21.5 (t, J_{CH} = 135 Hz, C$_\alpha$ or C$_\beta$CH$_2$CH$_3$), 15.1 and 12.3 (q, J_{CH} ≈ 130 Hz, CCH$_2$CH$_3$).

W[C(CMe$_3$)C(Me)C(Me)](OCMe$_2$CMe$_2$O)Cl. A suspension of W[C(CMe$_3$)C(Me)C(Me)]Cl$_3$ (1.14 g, 2.8 mmol) in ether (40 mL) was cooled to –30 °C, and triethylamine (770 μL, 5.6 mmol) was added. Pinacol (0.33 g, 2.8 mmol) in ether (5 mL) was added dropwise. The product was isolated as before (orange-red crystals, 1.17 g, 92%): ^{1}H NMR (C$_6$D$_6$) δ 3.12 (s, 3, CMe), 2.25 (s, 3, CMe), 1.57 and 1.55 (s, 6, OCMe$_2$CMe$_2$O), 1.36 (s, 9, CCMe$_3$), 1.16 and 1.13 (s, 6, OCMe$_2$CMe$_2$O); ^{1}H NMR (toluene-d_8, 20 °C, ~0.13 M) δ 3.20 (s, 3, CMe), 2.38 (s, 3, CMe), 1.52 and 1.51 (s, 6, OCMe$_2$CMe$_2$O), 1.38 (s, 9, CCMe$_3$), 1.14 and 1.11 (s, 6, OCMe$_2$CMe$_2$O); (57 °C) δ 3.25 (s, 3, CMe), 2.51 (s, 3, CMe), 1.50 and 1.48 (s, 6, OCMe$_2$CMe$_2$O), 1.40 (s, 9, CCMe$_3$), 1.13 and 1.09 (s, 6, OCMe$_2$CMe$_2$O); ^{13}C NMR (C$_6$D$_6$) δ 250.1 and 241.3 (s, CCMe$_3$ and C$_\alpha$Me), 143.0 (s, C$_\beta$Me), 98.5 and 89.7 (s, OCMe$_2$CMe$_2$O), 41.6 (s, CCMe$_3$), 30.8 (q, J_{CH} = 128 Hz, CCMe$_3$), 27.9 and 27.0 (q, J_{CH} ≈ 126 Hz, OCMe$_2$CMe$_2$O), 22.5 (q, J_{CH} = 131 Hz, C$_\alpha$Me or C$_\beta$Me), 13.7 (q, J_{CH} = 134 Hz, C$_\alpha$Me or C$_\beta$Me). Anal. Calcd for WC$_{15}$H$_{27}$O$_2$Cl: C, 39.28; H, 5.93. Found: C, 38.81; H, 5.88.

W[C(CMe$_3$)C(Me)C(Me)](OCMe$_2$CMe$_2$O)(OCMe$_3$). A cold (–30 °C) ether solution (12 mL) of W[C(CMe$_3$)C(Me)C(Me)]-(OCMe$_2$CMe$_2$O)Cl (0.25 g, 0.55 mmol) was treated with LiOCMe$_3$ (44 mg, 0.55 mmol). After 1 h the solvent was removed in vacuo and the residue was extracted with pentane. The extract was filtered through a pad of Celite, concentrated in vacuo, and cooled to –30 °C. Orange crystals (80 mg) were isolated the following day. The solvent was removed from the mother liquors in vacuo, and the resulting solid was sublimed (25 °C, 10^{-3} μm). The extremely soluble product is best isolated by sublimation: ^{1}H

(22) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99–101, 149–150.

(23) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(24) $R_F = 100(\sum||F_o| - |F_c||/\sum|F_o|)\%$, $R_{wF} = 100[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}\%$, and GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO = number of observations and NV = number of refined variables.

(25) Holmes, S. J.; Schrock, R. R. *Organometallics* **1983**, *2*, 1463.

NMR (C_6D_6) δ 3.30 (s, 3, C_αMe), 2.50 (s, 3, C_βMe), 1.44 and 1.33 (s, 9 each, OCMe$_3$ and CCMe$_3$, not respectively), the pinacol methyl resonances are broad and centered at ~1.30 ppm; ^{1}H NMR (toluene-d_8, -35 °C) δ 3.24 (s, 3, C_αMe), 2.30 (s, 3, C_βMe), 1.61 and 1.53 (s, 3 each, OCMe$_2$CMe$_2$O), 1.48 (s, 9, CCMe$_3$), 1.20 (br s, 6, OCMe$_2$CMe$_2$O); ^{1}H NMR (C_6D_6, 50 °C) δ 3.35 (s, 3, C_αMe), 2.61 (s, 3, C_βMe), 1.43 (s, 9, OCMe$_3$ or CCMe$_3$), 1.28 (s, 6, OCMe$_2$CMe$_2$O), 1.25 (s, 15, OCMe$_3$ or CCMe$_3$ and the other OCMe$_2$CMe$_2$O resonance); ^{13}C{^{1}H} NMR (C_6D_6) δ 232.1 and 225.2 (J_{CW} = 122 Hz and 134 Hz, CCMe$_3$ and C_αMe), 128.9 (C_βMe), 88.3 (OCMe$_2$CMe$_2$O), 75.9 (OCMe$_3$), 40.4 (CCMe$_3$), 31.9, 31.7, and 27.6 (OCMe_3, CCMe_3, and OCMe_2CMe_2O, not assignable), 22.0 and 13.0 (CMe); MS, m/e 496 (^{184}W).

W(C$_3$Et$_3$)(OCMe$_2$CMe$_2$O)(OCMe$_3$). A toluene solution (20 mL) of W(CEt)(OCMe$_3$)$_3$ (1.47 g, 3.3 mmol) was cooled to -20 °C and 3-hexyne was added (376 μL, 3.3 mmol). Pinacol (0.39 g, 3.3 mmol) in toluene (8 mL) was added dropwise to the reaction over a period of 5 min. The reaction was warmed to room temperature, and the solvents were removed in vacuo to give a red oil. The oil was distilled through a short path apparatus at 50 °C and 10^{-3} μm and collected in a flask maintained at -78 °C (1.21 g, 74%): ^{1}H NMR (toluene-d_8) δ 3.87–3.57 (m, 4, C_αCH_2CH$_3$), 3.05 (q, 2, ^3J_H = 7.5 Hz, C_βCH_2CH$_3$), 1.54 (t, 6, ^3J_H = 7.4 Hz, C_αCH$_2$CH_3), 1.33 (s, 9, OCMe$_3$), 0.74 (t, 3, ^3J_H = 7.5 Hz, C_βCH$_2$CH_3); (-40 °C) δ 3.83–3.52 (m, 4, C_αCH_2CH$_3$), 2.88 (q, 2, ^3J_H = 7.6 Hz, C_βCH_2CH$_3$), 1.61 (t, 6, ^3J_H = 7.4 Hz, C_αCH$_2$CH_3), 1.59 (s, 6, OCMe_2CMe$_2$O), 1.42 (s, 9, OCMe$_3$), 1.19 (s, 6, OCMe$_2$CMe_2O), 0.65 (t, 3, ^3J_H = 7.5 Hz, C_βCH$_2$CH_3); (70 °C) δ 3.90–3.65 (m, 4, C_αCH_2CH$_3$), 3.14 (q, 2, C_βCH_2CH$_3$), 1.51 (t, 6, C_αCH$_2$CH_3), 1.29 and 1.27 (s, 21 total, OCMe$_3$ and OCMe$_2$CMe$_2$O), 0.79 (t, 3, C_βCH$_2$CH_3); ^{13}C{^{1}H} NMR (C_6D_6) δ 226.5 (C_αCH$_2$CH$_3$), 132.9 (C_βCH$_2$CH$_3$), 75.6 (OCMe$_3$), 31.8 (OCMe_3), 29.3 (CCH$_2$CH$_3$), 27.6 (OCMe$_2$CMe_2O), 23.2 (CCH_2CH$_3$), 16.0 and 12.9 (CCH$_2$CH_3); MS, m/e 496.

Observation of W(CHCMe$_3$)(OCMe$_2$CMe$_2$O)(OCMe$_3$)$_2$. Pinacol (130 mg, 1.1 mmol) in 2 mL of toluene was added dropwise to a toluene solution (10 mL) of W(CCMe$_3$)(OCMe$_3$)$_3$ (0.53 g, 1.1 mmol). After 5 min the solvent was removed in vacuo, leaving a red/orange oil that could be sublimed at room temperature and 10^{-3} μm; ^{1}H NMR (C_6D_6) δ 6.76 (s, 1, $^2J_{HW}$ = 11.5 Hz, CHCMe$_3$), 1.39 (s, 18, OCMe$_3$), 1.25 and 1.24 (s, total of 21, CHCMe_3 and OCMe$_2$CMe$_2$O, not respectively); ^{13}C NMR (C_6D_6) δ 237.5 (d, J_{CH} = 130 Hz, J_{CW} = 186 Hz, CHCMe$_3$), 92.3 and 80.9 (s, OCMe$_2$CMe$_2$O and OCMe$_3$), 39.5 (s, CHCMe$_3$), 36.1, 30.9, and 26.2 (q, J_{CH} ≈ 125 Hz, OCMe_2CMe_2O, OCMe_3, and CHCMe_3, not respectively).

W[η^5-C$_5$Me$_4$(CMe$_3$)](MeC≡CMe)Cl$_2$ and {W[η^5-C$_5$Me$_4$-(CMe$_3$)]Cl$_4$}$_2$. An ether suspension (50 mL) of W(CCMe$_3$)(dme)Cl$_3$ (4.0 g, 8.9 mmol) was cooled to -30 °C, and 2-butyne (3.5 mL, 44.7 mmol) was added. The mixture was stirred vigorously and allowed to warm to room temperature. After 1.5 h the orange precipitate was filtered off, washed with ether (30 mL) and pentane (30 ml), and dried in vacuo (2.09 g). The ether was removed from the filtrate in vacuo, and 300 mL of pentane was added to the residue. After this solution was stirred for 3 h, the mixture was filtered to give another 0.13 g of W[η^5-C$_5$Me$_4$-(CMe$_3$)]Cl$_4$ (total yield 2.22 g, 99%). The pentane was removed from the filtrate in vacuo, and the red crystals were dissolved in a minimum amount of ether. The solution yielded 1.9 g (88%) of W[η^5-C$_5$Me$_4$(CMe$_3$)](MeC≡CMe)Cl$_2$ after the solution was cooled for several hours at -30 °C: ^{1}H NMR (C_6D_6) δ ~10.9 (br), ~6.0 (br); IR (Nujol) 1676 cm^{-1} ($\nu_{C≡C}$). The crystal for the X-ray study[10] was selected from a homogeneous sample. The analogous ethyl complexes were both analyzed.

W[η^5-C$_5$Et$_4$(CMe$_3$)](EtC≡CEt)Cl$_2$ and {W[η^5-C$_5$Et$_4$-(CMe$_3$)]Cl$_4$}$_2$. W(CCMe$_3$)(dme)Cl$_3$ (1.0 g, 2.2 mmol) in ether (25 mL) was treated with 3-hexyne (1.3 mL, 11.1 mmol). After 2 h the orange precipitate was filtered off. The precipitate was dissolved in dichloromethane, and the solution was filtered through Celite to remove some 3-hexyne polymer. Removing the dichloromethane in vacuo left a bright orange powder that was washed with pentane and dried in vacuo (0.48 g, 77%). This compound may be recrystallized from dichloromethane by addition of ether: ^{1}H NMR (CDCl$_3$) δ 2.85, 2.53, and 2.29 (br); mol wt (differential vapor pressure, CH$_2$Cl$_2$, 0 °C) calcd 1118, found 1141 at 3 × 10^{-2} M. Anal. Calcd for C$_{17}$H$_{29}$Cl$_4$: C, 36.52; H, 5.23;

Cl, 25.37. Found: C, 36.66; H, 5.38; Cl, 26.17.

The ether was removed from the original filtrate in vacuo, and the residue was extracted with pentane (20 mL). The pentane solution was filtered, concentrated in vacuo, and cooled to -30 °C to give 0.52 g of bright red W[η^5-C$_5$Et$_4$(CMe$_3$)](EtC≡CEt)Cl$_2$ (82%): ^{1}H NMR (C_6D_6) δ 4.52, 2.62, 2.02, and 1.14 (br); IR (Nujol) 1665 cm^{-1} ($\nu_{C≡C}$). Anal. Calcd for WC$_{23}$H$_{39}$Cl$_2$: C, 48.44; H, 6.89; Cl, 12.43. Found: C, 48.48; H, 6.91; Cl, 12.37.

W[η^5-C$_5$Me$_4$(CMe$_3$)](OCMe$_3$)O$_2$. 2-Butyne (80 μL, 1.0 mmol) was added to a pentane solution (2 mL) of W[C(CMe$_3$)C(Me)C-(Me)](OCMe$_2$CMe$_2$O)(OCMe$_3$) (0.10 g, 0.20 mmol). After 2 h the pentane and excess 2-butyne were removed in vacuo to give the product as a colorless oil essentially quantitatively: ^{1}H NMR (C_6D_6) δ 2.17 and 1.72 (s, 6 each, η^5-C$_5$Me$_4$CMe$_3$), 1.37 (s, 9, η^5-C$_5$Me$_4$CMe_3), 1.27 (s, 9, OCMe$_3$); ^{13}C{^{1}H} NMR (C_6D_6) δ 124.7, 122.3 and 119.7 (η^5-C$_5$Me$_4$CMe$_3$), 79.7 (OCMe$_3$), 35.4 (η^5-C$_5$Me$_4$CCMe$_3$), 31.9 and 30.3 (η^5-C$_5$Me$_4$CCMe_3 and OCMe_3, not respectively), 14.3 and 10.7 (η^5-C$_5$Me$_4$CMe$_3$).

2,3-Dimethyl-2-butene was identified and quantitated by NMR methods in a small scale reaction. The analogous η^5-C$_5$Et$_5$ complex was analyzed (see below).

W(η^5-C$_5$Et$_5$)(OCMe$_3$)O$_2$. This complex can be prepared by adding 2–3 equiv of 3-hexyne to a concentrated solution of W-(C$_3$Et$_3$)(OCMe$_2$CMe$_2$O)(OCMe$_3$) in pentane. After 24 h at -30 °C the product crystallizes from the reaction mixture in ~75% yield. The product may be recrystallized from pentane: ^{1}H NMR (C_6D_6) δ 2.45 (q, 10, ^3J_H = 7.7 Hz, CH_2CH$_3$), 1.26 (s, 9, OCMe$_3$), 1.03 (t, 15, ^3J_H = 7.7 Hz, CH$_2$CH_3); ^{13}C NMR (C_6D_6) δ 123.6 (η^5-C$_5$Et$_5$), 79.7 (OCMe$_3$), 30.3 (OCMe_3), 19.3 (CH$_2$$CH_3$), 15.7 ($CH_2CH_3$); MS, m/e 494. Anal. Calcd for WC$_{19}$H$_{34}$O$_3$: C, 46.17; H, 6.93. Found: C, 45.78; H, 6.80.

W(η^5-C$_5$Me$_2$Et$_3$)(OCMe$_3$)O$_2$. 2-Butyne (800 μL, 10.2 mmol) was added to a pentane solution 12 mL) of W(C$_3$Et$_3$)-(OCMe$_2$CMe$_2$O)(OCMe$_3$) (1.0 g, 2.0 mmol). After 12 h the pentane and excess 2-butyne were removed in vacuo and the residue was extracted with pentane. The pentane extract was treated with activated charcoal and filtered. The pentane was removed *in vacuo* to give a colorless oily solid: ^{1}H NMR (C_6D_6) δ 2.49 to 2.31 (m, 6, CH_2CH$_3$), 1.89 (s, 6, η^5-C$_5$Me$_2$Et$_3$), 1.22 (s, 9, OCMe$_3$), 1.02 to 0.90 (m, 9, CH$_2$CH_3).

Observation of Isomers of W[η^5-C$_5$Me$_2$Et$_2$(CMe$_3$)]-(OCMe$_3$)O$_2$. A small sample of W[C(CMe$_3$)C(Me)C(Me)]-(OCMe$_2$CMe$_2$CMe$_2$O)(OCMe$_3$) in pentane was treated with excess 3-hexyne. After 24 h the pentane and excess 3-hexyne were removed and the residue was dissolved in C_6D_6. Assume that the cyclopentadienyl isomers are A and C (see text). ^{1}H NMR (C_6D_6) δ 2.92, 2.49 and 2.32 (m, methylene proton of ethyl groups for both isomers), 2.24 (s, 6, η^5-C$_5$Me$_2$Et$_2$(CMe$_3$) of isomer C), 2.14 and 1.75 (s, 3 each, η^5-C$_5$Me$_2$Et$_2$(CMe$_3$) of isomer A), 1.41, 1.36, 1.28(4) and 1.27(7) (s, 9 each, OCMe$_3$ and CCMe$_3$ of both isomers), 1.06 to 0.87 (m, methyl resonances of ethyl groups for both isomers).

Observation of Isomers of W[η^5-C$_5$Me$_2$Et$_2$(CMe$_3$)]-(CCMe$_3$)Cl$_2$. An ether suspension (15 mL) of W[C(CMe$_3$)C-(Me)C(Me)]Cl$_3$ (0.91 g, 2.2 mmol) was cooled to -30 °C, and 3-hexyne (1.0 mL, 16.8 mmol) was added. The reaction was stirred for 3 h at room temperature, and the orange solid was filtered off and washed with ether. The ether and excess 3-hexyne were removed from the filtrate in vacuo and the residue was extracted with pentane. Filtration yielded more orange solid. The combined yield of {W[η^5-C$_5$Me$_2$Et$_2$(CMe$_3$)]Cl$_4$}$_2$ was 0.49 g (84%).

A toluene solution (15 mL) of {W[η^5-C$_5$Me$_2$Et$_2$(CMe$_3$)]Cl$_4$}$_2$ (0.30 g, 0.28 mmol) was cooled to -30 °C, and Zn(CH$_2$CMe$_3$)$_2$ (0.12 g, 0.56 mmol) was added. The solution was warmed to room temperature, and after 4 h the solvent was removed in vacuo. The residue was extracted with pentane. The pentane was removed from the filtrate in vacuo, leaving a purple oil whose ^{1}H NMR spectrum showed it to consist of two isomers, presumably those containing rings of type A and C (see text). (W[η^5-C$_5$Me$_4$-(CMe$_3$)](CCMe$_3$)Cl$_2$ is a crystalline, fully characterized compound.[25] ^{1}H NMR (C_6D_6) δ 3.06 to 2.29 (m, methylene resonances for ethyl groups in both rings), 2.22 (s, 6, η^5-C$_5$Me$_2$Et$_2$(CMe$_3$) of isomer C), 2.15 and 1.93 (s, 3 each, η^5-C$_5$Me$_2$Et$_2$(CMe$_3$) of isomer A), 1.29, 1.23, 1.19, and 1.18 (s, 9 each, W≡CCMe_3 and η^5-C$_5$Me$_2$Et$_2$(CMe_3) of isomers C and A, not respectively), 1.01–0.84 (m, methyl resonances of ethyl groups in both rings).

W[C(CMe$_3$)C(Me)C(Me)](py)$_2$Cl$_3$. W[C(CMe$_3$)C(Me)C-

(Me)]Cl₃ (0.20 g, 0.49 mmol) was dissolved in cold (–30 °C) dichloromethane (8 mL). Pyridine (10 μL, 1.2 mmol) was added, and the reaction was warmed to room temperature. After 20 min the solvent was removed in vacuo and the lime green solid was washed with pentane, dried in vacuo, and recrystallized from dichloromethane by adding ether: ¹H NMR (CD₂Cl₂, –20 °C) δ 9.02 (d, 4, py, sym isomer), 8.62 and 8.52 (d, 2 each, py, asym isomer), 7.80, 7.67, 7.41 and 7.15 (all other py resonances combined), 4.11 (s, 6, CMe, asym isomer), 3.72 (s, 6, CMe, sym isomer), 1.16 (s, 9, CCMe₃, asym isomer), 0.99 (s, 9, CCMe₃, sym isomer); ¹³C{¹H} NMR (CD₂Cl₂) δ 171.8, 144.6, 143.1 and 126.2 (CCMe₃ and CMe), 153.3, 152.6, 151.0, 140.1, 139.3, 138.3, 125.1, 124.3, and 123.4 (py), 398.2 (CCMe₃), 32.3 and 32.1 (CCMe₃), 30.1 (CCMe), 16.5 and 13.6 (CMe). Anal. Calcd for WC₁₉H₂₅N₂Cl₃: C, 39.92; H, 4.41; N, 4.90. Found: C, 40.23; H, 4.51; N, 5.19.

W[C(CMe₃)C(Me)C(Me)](Me₂NCH₂CH₂CH₂NMe₂)Cl₃. A procedure similar to that used to make W[C(CMe₃)C(Me)C(Me)](py)₂Cl₃ is employed in this reaction: ¹H NMR (CD₂Cl₂, 20 °C) δ 4.61 (s, 6, CMe), 2.86 and 2.69 (s with broad resonances underneath, 8 each, Me₂N(CH₂)₂NMe₂), 1.27 (s, 9, CCMe₃); ¹H NMR (CD₂Cl₂, –70 °C) δ 4.53 and 4.36 (br, s, 3 each, CMe), 2.76 and 2.61 (br s, 16 total, Me₂N(CH₂)₂NMe₂), 1.15 (s, 9, CCMe₃); ¹³C NMR (CD₂Cl₂) δ 162.4 (s, CCMe₃), 127.6 (br s, CMe), 63.8 (t, J_{CH} = 141 Hz, NCH₂), 58.5 (t, J_{CH} = 137 Hz, NCH₂), 54.2 (q, J_{CH} = 139 Hz, (CH₃)₂N), 51.4 (q, J_{CH} = 138 Hz, (CH₃)₂N), 39.0 (s, CCMe₃), 32.9 (q, J_{CH} = 127 Hz, CCMe₃), 12.9 (q, J_{CH} = 130 Hz, CMe). Anal. Calcd for WC₁₅H₃₁N₂Cl₃: C, 34.01; H, 5.90; N, 5.29. Found: C, 34.50; H, 5.91; N, 5.27.

Registry No. W[C₃Me₂(CMe₃)][Me₂N(CH₂)₂NMe₂]Cl₃, 91230-63-6; W[C(CMe₃)C(Me)C(Me)]Cl₃, 83487-37-0; W[C-(CMe₃)C(Et)C(Et)]Cl₃, 83487-36-9; W[C(CMe₃)C(Me)C(Me)]-(OCMe₃)Cl₂, 83487-38-1; W[C(CMe₃)C(Et)C(Et)](OCMe₃)Cl₂, 91230-60-3; W[C(CMe₃)C(Me)C(Me)][O-2,6-C₆H₃(*i*-Pr)₂]Cl₂, 91229-81-1; W[C(CMe₃)C(Me)C(Me)](OCMe₂CMe₂O)Cl, 91238-46-9; W[C(CMe₃)C(Me)C(Me)][O-2,6-C₆H₃(*i*-Pr)₂]₂Ch, 91229-82-2; W[C(CMe₃)C(Me)C(Me)](OCMe₂CMe₂O)(OCMe₃), 83487-39-2; W(C₃Et₃)(OCMe₂CMe₂O)(OCMe₃), 83487-40-5; W-(C₃Et₃)[O-2,6-C₆H₃(*i*-Pr)₂]₃, 91229-77-5; W(C₃Pr₃)[O-2,6-C₆H₃(*i*-Pr)₂]₃, 91229-78-6; W(C₃Et₃)[OCH(CF₃)₂]₃, 91202-82-3; W[C(CMe₃)C(Et)C(Et)][OCH(CF₃)₂]₃, 91202-81-2; W(C₃Pr₃)[O-CH(CF₃)₂]₃, 91202-83-4; W(C₃Me₃)[OCMe(CF₃)₂]₃, 91202-84-5; W(C₃Et₃)[OCMe(CF₃)₂]₃, 91208-74-1; W(CHCMe₃)-(OCMe₂CMe₂O)(OCMe₃), 91230-61-4; {W[η^5-C₅Me₄(CMe₃)]Cl₄}₂, 83511-04-0; W[η^5-C₅Me₄(CMe₃)](MeC≡CMe)Cl₂, 83511-02-8; W[η^5-C₅Et₄(CMe₃)](EtC≡CEt)Cl₂, 83511-01-7; {W[η^5-C₅Et₄-(CMe₃)]Cl₄}₂, 83511-03-9; W[η^5-C₅Me₄(CMe₃)](OCMe₃)O₂, 91230-64-7; W(η^5-C₅Et₅)(OCMe₃)O₂, 91230-65-8; W-(η^5-C₅Me₂Et₃)(OCMe₃)O₂, 91230-66-9; W[η^5-C₅Me₂Et₂-(CMe₃)](OCMe₃)O₂ (isomer A), 91230-67-0; W[η^5-C₅Me₂Et₂-(CMe₃)](OCMe₃)O₂ (isomer C), 91230-68-1; {W[η^5-C₅Me₂Et₂-(CMe₃)]Cl₄}₂ (isomer A), 91230-69-2; {W[η^5-C₅Me₂Et₂(CMe₃)]Cl₄}₂ (isomer C), 91230-76-1; W[η^5-C₅Me₂Et₂(CMe₃)](CCMe₃)Cl₂ (isomer A), 91230-70-5; W[η^5-C₅Me₂Et₂(CMe₃)](CCMe₃)Cl₂ (isomer C), 91230-71-6; W[C(CMe₃)C(Me)C(Me)](py)₂Cl₃ (sym isomer), 91230-72-7; W[C(CMe₃)C(Me)C(Me)](py)₂Cl₃ (asym isomer), 91279-92-4; W(CHMe₃)(OCMe₃)₂Cl₂, 91230-62-5; W-(η^5-C₅Et₃Me₂)(O)Cl₃, 91230-73-8; W(η^5-C5Et₃Me₂)Cl₄(PMe₃), 91230-74-9; W(η^5-C₅Et₃Me₂)Me₄, 91230-75-0; W(CCMe₃)(dme)Cl₃, 83416-70-0; W(CEt)(OCMe₃)₃, 82228-88-4; W(CCMe₃)(OCMe₃)₃, 78234-36-3; Zn(CH₂CMe₃)₂, 54773-23-8; ZnMe₂, 544-97-8; 2-butyne, 503-17-3; 3-hexyne, 928-49-4.

Communications

A New Procedure for the Synthesis of α-Silylated Esters and Lactones. Migration of Silicon from Oxygen to Carbon at High Pressure[1]

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Summary: High pressure (10 kbar) induces migration of silicon of O-silylated ketene acetals from oxygen to α-carbon, giving α-silylated esters and lactones in high yields.

α-Silylated esters and lactones are becoming increasingly important as a new class of synthetic intermediates, and several synthetic methods have been developed as witness for example the recent elegant method of Larson.[2] We now wish to report an entirely new approach to this problem: high pressure (ca. 10 kbar) induces the migration of silicon in O-silylated ketene acetals from oxygen to α-carbon (eq 1). The results are summarized in Table I.
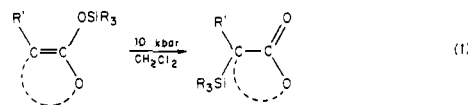
The rearrangement proceeds smoothly at room temperature (entries 1, 4, 6, 8, and 10). Control experiments reveal that such rearrangement does not occur at room temperature in CH₂Cl₂ at atmospheric pressure. The migration occurs even in a ketene acetal disubstituted at

(2) Larson, G. L.; Fuentes, L. M. *J. Am. Chem. Soc.* **1981**, *103*, 2418. All previous approaches are listed in this paper.