83487-27-8; $Re(N\text{-}t\text{-}Bu)_2Me_3$, 83487-28-9; $Re(N\text{-}t\text{-}Bu)_2(CH_2Ph)_3$, 83487-29-0; $Re(N\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_3$, 83487-30-3; $Re(N\text{-}t\text{-}Bu)_2Cl_3$, 83487-31-4; $Re(N\text{-}t\text{-}Bu)_2Np_3$, 83487-32-5; $Re(N\text{-}t\text{-}Bu)_2(CHSiMe_3)(CH_2SiMe_3)$, 83487-33-6; $Re(N\text{-}t\text{-}Bu)_2(CHPh)(CH_2Ph)$, 83487-34-7; $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(NH_2\text{-}t\text{-}Bu)Cl_2]_2$, 83510-97-8; $Re(C\text{-}t\text{-}Bu)(NH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)Cl_2(Py)$, 83510-98-9; $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(TMEDA)I_2$, 83510-99-0; $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$, 83487-35-8; $Re(CCMe_3(CHCMe_3)Py_2I_2$, 83511-00-6.

Reaction of Tungsten(VI) Alkylidyne Complexes with Acetylenes To Give Tungstenacyclobutadiene and Tungsten Cyclopentadienyl Complexes

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We have reported that $W(C\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_3$ will catalytically metathesize dialkylacetylenes at a high rate, presumably by forming unstable tungstenacyclobutadiene intermediates.[2] On the other hand, while complexes such as $W(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$,[3] $W(C\text{-}t\text{-}Bu)(dme)Cl_3$,[4] and $[NEt_4][W(C\text{-}t\text{-}Bu)Cl_4]$[2] will react with acetylenes, they do not metathesize them catalytically. We report here that $W(C\text{-}t\text{-}Bu)(dme)Cl_3$ reacts with dialkylacetylenes to give a stable tungstenacyclobutadiene complex, that tungstenacyclobutadiene complexes containing certain alkoxide ligands (but not three *tert*-butoxide ligands) are also stable, and that cyclopentadienyl complexes are formed in the presence of excess dialkylacetylene, even (slowly) in the active alkyne metathesis system.

Excess 3-hexyne reacts with $[NEt_4][W(C\text{-}t\text{-}Bu)Cl_4]$ in dichloromethane to give a pentane-soluble paramagnetic red complex with the empirical formula $W(C\text{-}t\text{-}Bu)(CH_3CH_2C{\equiv}CCH_2CH_3)_3Cl_2$ in ~50% yield. 2-Butyne reacts more rapidly with $[NEt_4][W(C\text{-}t\text{-}Bu)Cl_4]$ to give an analogous ether-soluble species. Both can be obtained more straightforwardly by reacting an excess of the alkyne with $W(C\text{-}t\text{-}Bu)(dme)Cl_3$.[4] In this reaction a less soluble, paramagnetic, orange complex with the empirical formula $W(C\text{-}t\text{-}Bu)(alkyne)_2Cl_4$[5] also forms in ~50% yield by weight. A molecular weight study of "$W(C\text{-}t\text{-}Bu)(EtC{\equiv}CEt)_2Cl_4$" in dichloromethane at 0 °C (by differential vapor pressure measurement) showed it to be a dimer.

An X-ray structural study[6] of "$W(C\text{-}t\text{-}Bu)(MeC{\equiv}CMe)_3Cl_2$" shows it to be $W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)(MeC{\equiv}CMe)Cl_2$, a species that is closely related to the diamagnetic Ta(III) derivatives, $Ta(\eta^5\text{-}C_5Me_5)(alkyne)Cl_2$.[7] As in $Ta(\eta^5\text{-}C_5Me_5)(PhC{\equiv}CPh)Cl_2$,[7] the axis of the acetylene ligand in $W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)(MeC{\equiv}CMe)Cl_2$ lies parallel to the plane of the cyclopentadienyl ligand, and the acetylene carbon–carbon bond length is lengthened considerably as a result of its strong bond to the metal. Therefore, we propose that the "$[W(C\text{-}t\text{-}Bu)(alkyne)_2Cl_4]_2$" species are also substituted cyclopentadienyl complexes, $[W(\eta^5\text{-}C_5R_4\text{-}t\text{-}Bu)Cl_4]_2$. Most likely $W(\eta^5\text{-}C_5R_4\text{-}t\text{-}Bu)(RC{\equiv}CR)Cl_2$ and $[W(\eta^5\text{-}C_5R_4\text{-}t\text{-}Bu)Cl_4]_2$ form via disproportionation of some intermediate tungsten(IV) complex, possibly "$W(\eta^5\text{-}C_5R_4\text{-}t\text{-}Bu)Cl_3$" as shown in eq 1 and 2.

$$W(C\text{-}t\text{-}Bu)(dme)Cl_3 + 2RC{\equiv}CR \rightarrow \text{"}W(\eta^5\text{-}C_5R_4\text{-}t\text{-}Bu)Cl_3\text{"} \quad (1)$$

$$\text{"}W(\eta^5\text{-}C_5R_4\text{-}t\text{-}Bu)Cl_3\text{"} \xrightarrow{0.5RC{\equiv}CR} 0.5W(\eta^5\text{-}C_5R_4\text{-}t\text{-}Bu)(RC{\equiv}CR)Cl_2 + 0.25[W(\eta^5\text{-}C_5R_4\text{-}t\text{-}Bu)Cl_4]_2 \quad (2)$$

Addition of only 1 equiv of 3-hexyne or 2-butyne to $W(C\text{-}t\text{-}Bu)(dme)Cl_3$ yields violet diamagnetic complexes with the formula $W(C\text{-}t\text{-}Bu)(RC{\equiv}CR)Cl_3$.[8] ^{13}C NMR studies suggested that these species are tungstenacyclobutadiene complexes.[9] An X-ray structural study[10] of $W(C\text{-}t\text{-}Bu)(MeC{\equiv}CMe)Cl_3$ confirmed this proposal (Figure 1). The molecule is nearly a trigonal bipyramid with axial chloride ligands ($\angle Cl(1)\text{-}W\text{-}Cl(2)$ = 166.12 (9)°) and

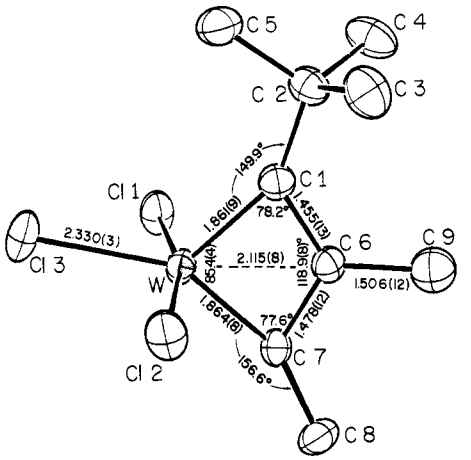
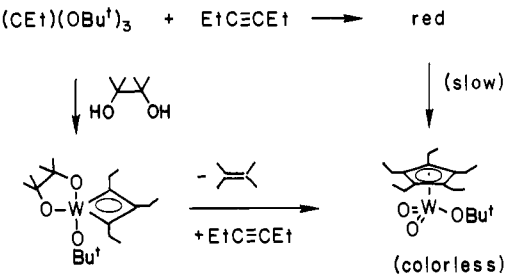


Figure 1. ORTEP-II diagram (30% ellipsoids) of $W[C\text{-}t\text{-}BuCMeCMe]Cl_3$ with hydrogen atoms omitted.

Scheme I



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(3) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774.

(4) Purple $W(C\text{-}t\text{-}Bu)(dme)Cl_3$ is prepared by treating $W(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$ in a mixture of pentane, ether, and 1 equiv of 1,2-dimethoxyethane (dme) with 3 equiv of HCl: Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* **1982**, in press.

(5) $W(C\text{-}t\text{-}Bu)(CH_3CH_2C{\equiv}CCH_2CH_3)_2Cl_4$. Anal. Calcd for $WC_{17}H_{29}Cl_4$: C, 36.52; H, 5.23; Cl, 25.37. Found: C, 36.66; H, 5.28; Cl, 26.17. MW (differential vapor pressure, CH_2Cl_2, 0 °C); Calcd: 1118. Found: 1141 at 3×10^{-2} M.

(6) $W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)(MeC{\equiv}CMe)Cl_2$ crystallizes in the monoclinic space group $P2_1/c$ with a = 8.411 (1) Å, b = 26.639 (5) Å, c = 8.971 (1) Å, β = 114.320 (1)°, and ρ(calcd) = 1.89 g cm^{-3} for Z = 4 and M_r 522.2. The final R_F = 3.2% for 181 variables refined against all 2244 absorption corrected data. This structure will be reported in its entirety by M.R.C. and H.J.W.

(7) Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 387.

(8) $W(C\text{-}t\text{-}Bu)(CH_3CH_2C{\equiv}CCH_2CH_3)Cl_3$. 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.

(9) $^{13}C\{^1H\}$ NMR spectrum of $W(C\text{-}t\text{-}Bu)(CH_3C{\equiv}CCH_3)Cl_3$ (CD_2Cl_2) δ 267.5 and 263.4 (C_α), 150.7 (C_β), 44.3 ($CCMe_3$), 29.5 ($CCMe_3$), 25.6 and 17.2 (CMe). $^{13}C\{^1H\}$ NMR spectrum of $W(C\text{-}t\text{-}Bu)(CH_3CH_2C{\equiv}CCH_2CH_3)Cl_3$ (C_6D_6): δ 267.6 and 266.7 (C_α), 150.3 (C_β) 43.8 ($CCMe_3$), 32.0 and 24.5 (CCH_2CH_3), 29.8 ($CCMe_3$), 14.3 and 11.9 (CCH_2CH_3).

(10) $W[C\text{-}t\text{-}BuCMeCMe]Cl_3$ crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with a = 10.271 (2) Å, b = 10.113 (2) Å, c = 12.721 (3) Å, β = 96.10 (2)°, V = 1313.8 (5) Å^3, and ρ(calcd) = 2.09 g cm^{-3} for Z = 4 and M_r 413.4. Diffraction data were collected via a coupled 2θ–θ scan technique[11] using a Syntex $P2_1$ diffractometer and were corrected for absorption. All non-hydrogen atoms were located and refined, the final discrepancy factors being R_F = 4.6% and R_{wF} = 4.4% for all 2327 independent reflections (none rejected) with $4° \le 2\theta \le 50.0°$.

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

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an essentially planar WC_3 ring lying in the equatorial plane. The substituent carbon atoms (C(2), C(8), C(9)) and Cl(3) also lie in the equatorial plane. The W–C_α bond lengths are *equal* and slightly shorter than the W=C_α double bond distance of 1.942 (9) Å found in W(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(dmpe).[12] Carbon–carbon distances within the four-membered ring are intermediate between those expected for pure double and pure single bonds but are slightly closer to the latter. The three most surprising features are the large C_α–C_β–C_α angle (118.9 (8)°), the short W–C_β distance (far shorter than the W–C_α single bond length of 2.258 (8) Å in W(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(dmpe)[12]), and the large W–C(1)–C(2) and W–C(7)–C(8) angles (149.9 (7) and 156.6 (7)°, respectively). These results contrast sharply with those for $Rh(C_3Ph_3)Cl_2(PMe_2Ph)_2$[13] and $[Ir(C_3Ph_3)(CO)(Cl)(PMe_3)_2]^{+}$[14] in which little, if any, multiple metal–carbon bond character is present, and the metallacyclic unit is *compressed* along the C_α–$C_{\alpha'}$ direction. (The C_α–$C_{\alpha'}$ distance in W[C-*t*-BuCMeCMe]Cl_3 is 2.525 (12) Å but in $RhCl_2(PMe_2Ph)_2(C_3Ph_3)$[13] it is only 2.156 (6) Å.)

W[C-*t*-BuCMeCMe]Cl_3 reacts with 1 equiv of *tert*-Butyl alcohol in the presence of NEt_3 to give W[C-*t*-BuCMeCMe](O-*t*-Bu)Cl_2.[15] Addition of a second equivalent of LiO-*t*-Bu to W[C-*t*-BuCMeCMe](O-*t*-Bu)Cl_2 produces only half an equivalent of W(CR)(O-*t*-Bu)$_3$ where R is *t*-Bu or Me. Surprisingly, therefore, W[C-*t*-BuCMeCMe](O-*t*-Bu)($OCMe_2CMe_2O$) can be prepared[16] and is stable toward cleavage of the WC_3 ring or formation of the β-*tert*-butyl-substituted isomer. Furthermore, addition of 1 equiv of pinacol to a mixture of W(CEt)(O-*t*-Bu)$_3$ and 3-hexyne yields an analogous complex, W(C_3Et_3)(O-*t*-Bu)($OCMe_2CMe_2O$)[17] (Scheme I). The pinacolate complexes will not metathesize 3-heptyne. At least one of the reasons is that W(C_3Et_3)(O-*t*-Bu)($OCMe_2CMe_2O$) reacts with an excess of 3-hexyne to give colorless W(η^5-C_5Et_5)(O-*t*-Bu)O_2[18] and tetramethylethylene quantitatively, possibly via intermediate, unstable W(η^5-C_5Et_5)($OCMe_2CMe_2O$)(O-*t*-Bu).[19]

The question that remained was why alkyne metathesis using W(CR)(O-*t*-Bu)$_3$ catalysts eventually ceases? We know that W_2(O-*t*-Bu)$_6$ cannot be formed since it reacts with dialkylacetylenes to give W(CR)(O-*t*-Bu)$_3$.[21] A simpler "active" system consisting of a mixture of W(CEt)(O-*t*-Bu)$_3$ and excess 3-hexyne was allowed to "decompose" to give an as yet unidentified diamagnetic red complex with the empirical composition W(CEt)$_5$(O-*t*-Bu)$_3$ (by ^{1}H and ^{13}C NMR). This red species slowly (days) also decomposed to give colorless W(η^5-C_5Et_5)(O-*t*-Bu)O_2, the only significant diamagnetic product.

We conclude from these results that tungstenacyclobutadiene complexes are the intermediates in the alkyne metathesis reaction and that they can react with additional alkyne to yield cyclopentadienyl complexes. We can also now expect that cleavage of a tungstenacyclobutadiene ring or further reaction to give (ultimately) cyclopentadienyl complexes will likely prove to be very sensitive to the structure of the complex and (especially) the steric and electronic properties of the ligands.

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Registry No. [NEt_4][W(C-*t*-Bu)Cl_4], 78251-20-4; W(C-*t*-Bu)(dme)Cl_3, 83542-12-5; W(η^5-C_5Et_4-*t*-Bu)(EtC≡CEt)Cl_2, 83511-01-7; W(η^5-C_5Me_4-*t*-Bu)(Me≡CMe)Cl_2, 83511-02-8; [W(η^5-C_5Et_4-*t*-Bu)Cl_4]$_2$, 83511-03-9; [W(η^5-C_5Me_4-*t*-Bu)Cl_4]$_2$, 83511-04-0; W(C-*t*-BuCEtCEt)Cl_3, 83487-36-9; W(C-*t*-BuCMeCMe)Cl_3, 83487-37-0; W[C-*t*-BuCMeCMe](O-*t*-Bu)Cl_2, 83487-38-1; W[C-*t*-BuCMeCMe](O-*t*-Bu)($OCMe_2CMe_2O$), 83487-39-2; W(CEt)(O-*t*-Bu)$_3$, 82228-88-4; W(C_3Et_3)(O-*t*-Bu)($OCMe_2CMe_2O$), 83487-40-5; W(η^5-C_5Et_5)(O-*t*-Bu)O_2, 83511-05-1; 3-hexyne, 928-49-4; 2-butyne, 503-17-3; *tert*-butyl alcohol, 75-65-0; pinacol, 76-09-5; tetramethylethylene, 563-79-1.

Supplementary Material Available: Listings of positional parameters and observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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(15) The *tert*-butoxide ligand is believed to be in the equatorial position in W[C-*t*-BuCMeCMe](O-*t*-Bu)Cl_2. Anal. Calcd for $WC_{13}H_{24}Cl_2O$: C, 34.61; H, 5.36. Found, C, 34.56; H, 5.41. ^{1}H NMR (C_6D_6) δ 3.08 (s, 3, CMe), 2.16 (s, 3, CMe), 1.75 (s, 9, O-*t*-Bu), 1.39 (s, 9, C-*t*-Bu); ^{13}C{^{1}H} NMR (C_6D_6) δ 265.6 and 259.1 (J_{CW} = 93, 116 Hz, C_α), 134.2 (C_β), 87.9 ($OCMe_3$), 42.7 ($CCMe_3$), 31.1 and 29.6 ($OCMe_3$ and $CCMe_3$), 24.3 and 12.4 (CMe).
(16) ^{13}C{^{1}H} NMR (C_6D_6) δ 232.1 and 225.2 (J_{CW} = 122, 134 Hz, C_α), 128.9 (C_β), 88.3 ($O_2C_2Me_4$), 75.9 ($OCMe_3$), 40.4 ($CCMe_3$), 31.9, 31.7 and 27.6 ($OCMe_3$, $CCMe_3$ and $O_2C_2Me_4$, not assignable), 22.0 and 13.0 (CMe). Molecular ion found at 496 in mass spectrum.
(17) ^{13}C{^{1}H} NMR (C_6D_6) δ 226.5 ($C_\alpha CH_2CH_3$), 132.9 ($C_\beta CH_2CH_3$), 75.6 ($OCMe_3$), 31.8 ($OCMe_3$), 29.3 (CCH_2CH_3), 27.6 ($O_2C_2Me_4$), 23.2 (CCH_2CH_3), 16.0 and 12.9 (CCH_2CH_3). Molecular ion found at 496 in mass spectrum.
(18) W(η^5-C_5Et_5)(O-*t*-Bu)O_2. Anal. Calcd for $WC_{19}H_{34}O_3$: C, 46.17; H, 6.93. Found: C, 45.78; H, 6.80. Mass spectrum molecular ion at 494. ^{13}C{^{1}H} NMR (C_6D_6) δ 123.6 (η^5-C_5Et_5), 79.7 ($OCMe_3$), 30.3 ($OCMe_3$), 19.3 (CH_2CH_3), 15.7 (CH_2CH_3).
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Protiodesilylation Reactions of Simple β-Hydroxysilanes (and α-Hydroxysilanes). Homo-Brook Rearrangements[1]

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β-Hydroxysilanes have been of considerable interest as precursors to geometrically defined olefins and heteroatom-substituted olefins because of their stereospecific olefin-forming β-elimination reactions, and therefore a number of methods to prepare diastereomerically pure β-hydroxysilanes have been developed.[2] We have recently become interested in the possibility that the R_3Si group in a β-hydroxysilane could be replaced by H (protiodesilylation) or by another substituent, thus enabling β-hydroxysilanes to serve as precursors to saturated organic systems. Here we report that simple unactivated β-hydroxysilanes can undergo protiodesilylation when treated with base in aqueous dimethyl sulfoxide (Me_2SO), that unactivated α-hydroxysilanes also undergo protiodesilylation (essentially a Brook rearrangement followed by hydrolysis) under these conditions, and that both reactions take place with complete retention of stereochemistry at carbon.

Cleavage of unactivated carbon–silicon bonds is ordinarily quite difficult. Our earlier work with α,β-dihydroxysilanes[3] suggested to us that base-induced protiodesilylation reactions should be facilitated by the presence of a β hydroxyl as shown in the mechanistic rationale in Scheme I. Simple (unactivated) β-hydroxysilanes normally undergo facile β-elimination reactions when treated with base under aprotic conditions (e.g., KH/THF). (The reaction is considerably accelerated by the presence of anion-

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