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High Oxidation State Monopentamethylcyclopentadienyl Tungsten Methyl Complexes Including the First d^0 Complex Containing a Highly Distorted Methylene Ligand, $W(\eta^5\text{-}C_5Me_5)(CH_3)_3(CH_2)$

A. H. Liu, R. C. Murray, J. C. Dewan, B. D. Santarsiero,† and R. R. Schrock*

Contribution from the Department of Chemistry, 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. *Received November 14, 1986*

Abstract: $[WCp^*Cl_4]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) can be prepared conveniently on a large scale by adding $WCp^*(CO)_3Me$ to PCl_5. Addition of $[WCp^*Cl_4]_2$ to MeMgCl yields thermally stable tetragonal-pyramidal WCp^*Me_4. Oxidation of WCp^*Me_4 yields $[WCp^*Me_4]^+$, the only documented example of a trigonal-bipyramidal $M(\eta^5\text{-}C_5R_5)L_4$ complex. Crystals of $[WCp^*Me_4][PF_6]$ are orthorhomibc, space group $Cmc2_1$, with $a = 8.880$ (4) Å, $b = 22.364$ (5) Å, $c = 8.970$ (6) Å, $V = 1781.4$ Å^3, and $Z = 4$. The Cp* ring and PF_6^- ion display disorder, but the W and Me groups do not. The W-methyl bond lengths are statistically identical (2.07 (4)-2.16 (2) Å); Me_{eq}-Me_{ax} angles are 76.3 (8)° and 82.8 (14)°. Addition of LiMe to $[WCp^*Me_4]^+$ yields pseudooctahedral, unstable WCp^*Me_5. Both $[WCp^*Me_4]^+$ and WCp^*Me_5 are fluxional on the NMR time scale with $\Delta H^* = 11.1$ (9) kcal mol^{-1} and $\Delta S^* = 13.3$ (15) eu for $[WCp^*Me_4]^+$ and $\Delta H^* = 12.6$ (5) kcal mol^{-1} and $\Delta S^* = -3.8$ (12) eu for WCp^*Me_5. WCp^*Me_5 decomposes in a first-order reaction to give diamagnetic $(WCp^*Me)_2(\mu\text{-}CH)(\mu\text{-}CMe)$ in ~35% yield plus WCp^*Me_4 in ~15% yield after chromatography. The rate-limiting step is believed to be α-hydrogen abstraction to generate $WCp^*Me_3(CH_2)$, which then reacts with WCp^*Me_5. The ethylidyne ligand is proposed to form by transfer of a methyl group to a methylidyne ligand (probably bridging) followed by α-hydrogen abstraction and loss of methane. $WCp^*Me_3(CH_2)$ can be generated in dichloromethane by adding triethylamine to $[WCp^*Me_4]^+$ at −78 °C, characterized spectroscopically, and trapped with pentafluorophenol to give $WCp^*(OC_6F_5)Me_4$. ^1H and ^{13}C NMR spectra suggest that the methylene ligand in $WCp^*Me_3(CH_2)$ is highly distorted (T-shaped). When $WCp^*Me_3(CH_2)$ is allowed to decompose by warming a solution slowly to 25 °C, a 6:1 mixture of $(WCp^*Me)(WCp^*Et)(\mu\text{-}CH)_2$ and $(WCp^*Me)_2(\mu\text{-}CH)(\mu\text{-}CMe)$ forms in a total yield of ~30%. It is proposed that the ethyl ligand in $(WCp^*Me)(WCp^*Et)(\mu\text{-}CH)_2$ forms by migration of a methyl group to the methylene ligand to give WCp^*Me_2Et which then reacts with $WCp^*Me_3(CH_2)$. μ-Methylidyne ligands in all species react with LiMe to give μ-ethylidyne analogues; e.g., $(WCp^*Me)_2(\mu\text{-}CH)(\mu\text{-}CMe)$ reacts with LiMe to give $(WCp^*Me)_2(\mu\text{-}CMe)_2$. Crystals of $(WCp^*Me)_2(\mu\text{-}CMe)_2$ belong to the space group $C2/c$ with $a = 21.295$ (13) Å, $b = 8.860$ (2) Å, $c = 13.856$ (3) Å, $\beta = 106.54$ (3)°, $V = 2506.1$ (10) Å^3, and $Z = 4$. The W_2C_2 ring is slightly bent, with W-C_{bridge} bond lengths of 1.950 (14) and 1.972 (11) Å. The Cp* rings are cisoid. The two WMe groups are eclipsed with the W-Me bond length of 2.199 (14) Å.

Mono-η^5-C_5H_5 complexes are among the most common in organometallic chemistry.[1,2] After pentamethylcyclopentadiene became readily available,[3] many mono-η^5-C_5Me_5 analogues were prepared and their chemistry compared with that of known η^5-C_5H_5 complexes. Soon mono-η^5-C_5Me_5 (Cp*) complexes were discovered that had no η^5-C_5H_5 analogues, e.g., $TaCp^*(olefin)Cl_2$[4] and $IrCp^*H_2(SiMe_3)_2$.[5] Such a circumstance appears to be more common when the metal is in a relatively high oxidation state. One of the likely reasons the Cp* ligand apparently stabilizes high oxidation states is its now well-documented ability to donate electron density to the metal.[6] Another important reason is that decomposition pathways involving η^5-C_5H_5 ring protons are blocked.

Relatively recently we discovered that $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Cl_4]_2$ was a product of the reaction between the tungstacyclobutadiene complex $W[C(t\text{-}Bu)C(Me)C(Me)]Cl_3$ and 2-butyne.[7] We soon developed a practical route to the η^5-C_5Me_5 analogue and found that WCp^*Me_4 could be prepared readily.[8] We were interested in WCp^*Me_4 first as a means of preparing hydride complexes such as $[WCp^*H_3]_4$ and $[WCp^*H_4]_2$,[9] but then we became interested in exploring its chemistry per se. In this paper we report the first collection of results concerning the chemistry of WCp^*Me_4 and related methyl complexes.

Results

Preparation of WCp^*Me_4 and $[WCp^*Me_4]^+$ ($Cp^* = \eta^5\text{-}C_5Me_5$). $[WCp^*Cl_4]_2$ is prepared conveniently on a 20-g scale by adding 2.4-2.5 equiv of $WCp^*(CO)_3Me$ to PCl_5[10] dissolved in dichloromethane. The bright orange product is sparingly soluble in common noncoordinating solvents. It is slightly soluble in dichloromethane. We presume that it is a dimer by analogy with the analogous η^5-C_5Me_4-t-Bu derivative[7] whose molecular weight was measured by differential vapor pressure methods. Crude $[WCp^*Cl_4]_2$ is sufficiently pure for subsequent reactions. $[WCp^*Cl_4]_2$ can be sublimed with difficulty at ~200 °C and <0.1 μm.

$[WCp^*Cl_4]_2$ readily reacts with PMe_3 to form a green, toluene-soluble, crystalline monoadduct. It is a pseudooctahedral species by analogy with structurally characterized $[WCl_4(PMe_3)]_2(\eta^5,\eta^5\text{-}C_5Et_4CH_2CH_2C_5Et_4)$.[11] $[WCp^*Cl_4]_2$ does not react with PPh_3 to give $WCp^*Cl_4(PPh_3)$, probably in part for steric reasons and in part due to the lower basicity of PPh_3 relative to

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† California Institute of Technology.

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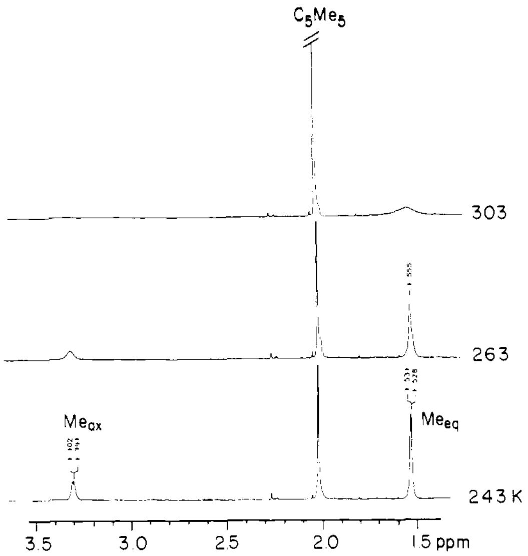

Figure 1. The ^{1}H NMR spectrum of $[WCp^*Me_4][PF_6]$ in CD_2Cl_2 in the range 243–303 K.

PMe_3 in bonding to what must be a quite electrophilic metal site. Other adducts have been observed (e.g. $WCp^*Cl_4(t\text{-BuNC})$), but they have not been fully characterized.[12]

WCp^*Me_4 was prepared initially in ~90% yield by adding 8–10 equiv of $ZnMe_2$ to $WCp^*Cl_4(PMe_3)$ in toluene. (Use of crude $[WCp^*Cl_4]_2$ gave yields of ~40%.) A much more convenient preparation (20-g scale) is to add solid, crude $[WCp^*Cl_4]_2$ to >4 equiv of MeMgCl in THF at 25 °C. A yellow solution forms rapidly, from which yellow to yellow-orange WCp^*Me_4 can be isolated in ~90% yield. We presume that WCp^*Me_4 is a square-pyramidal molecule by analogy with structurally characterized $W(\eta^5\text{-}C_5Et_3Me_2)Me_4$.[7] WCp^*Me_4 is not especially sensitive to air in the solid state, can be chromatographed on dry silica, and sublimes at high vacuum at room temperature. It does not form a stable monoadduct with PMe_3.

Both EPR and NMR signals can be observed for all of the above complexes. $[WCp^*Cl_4]_2$ and $WCp^*Cl_4(PMe_3)$ each show an EPR signal at $g \approx 1.9$ with a half-height width of 50–60 G, while the EPR signal for WCp^*Me_4 is found at $g = 2.01$ with a half-height width of 220 G. The ^{1}H NMR signal for $[WCp^*Cl_4]_2$ (saturated in CD_2Cl_2) is found at 13.48 ppm with $w_{1/2} = 570$ Hz. For $WCp^*Cl_4(PMe_3)$ two signals are observed at –5.75 and –7.42 with $w_{1/2} = 180$ Hz for each. For WCp^*Me_4 a signal is found at 39.70 ppm ($w_{1/2} = 580$ Hz); we assume it can be ascribed to the Cp* methyl groups and that a signal for the methyl groups directly attached to the d^1 metal center cannot be observed.

WCp^*Me_4 can be oxidized cleanly to $[WCp^*Me_4][PF_6]$ with $[FeCp_2][PF_6]$ in dichloromethane. About 2 h are required to oxidize 2–3 g of WCp^*Me_4. $[WCp^*Me_4][PF_6]$ is yellow, crystalline, and soluble in dichloromethane. It can be reduced back to WCp^*Me_4 in >90% yield employing 1 equiv of 0.4% Na amalgam in THF.

The ^{1}H NMR spectrum of $[WCp^*Me_4]^+$ at 303 K shows a sharp Cp* signal and two broad signals in the ratio of 1:3 that sharpen upon cooling the sample to 243 K (Figure 1). The structure observed on each peak at 243 K ($J_{HH} \approx 1.7$ Hz) can be ascribed to long-range coupling of the three protons in the unique methyl group to the nine protons in the other three methyl groups. On the basis of these NMR results we postulate that the lowest energy form of $[WCp^*Me_4]^+$ is a pseudo-trigonal bipyramid in which the methyl groups scramble (most likely) via a square-pyramidal intermediate. Simulation of the methyl group signals in the NMR spectrum shown in Figure 1 over the temperature range 255–313 K yielded values of $\Delta H^{\ddagger} = 11.1$ (9) kcal mol^{-1}, $\Delta S^{\ddagger} = -13.3$ (15) eu, and $\Delta G^{\ddagger}_{296} = 15.0$ (7) kcal mol^{-1} for the process of exchanging axial and equatorial methyl groups (see Experimental Section for details).

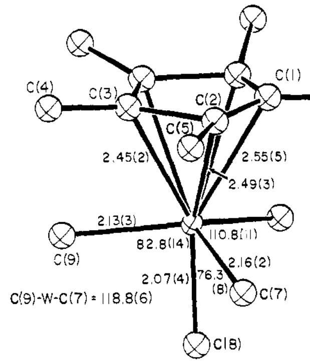

Figure 2. The structure of $[WCp^*Me_4]^+$ with atoms drawn as spheres of arbitrary radius. The mirror plane passes through C(6), C(1), W, C(8), and C(9).

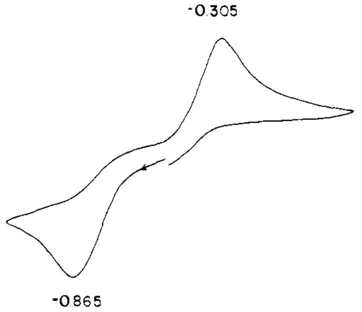

Figure 3. A cyclic voltammogram of $[WCp^*Me_4][PF_6]$ in dichloromethane.

If the above postulate is correct, $[WCp^*Me_4]^+$ would be the only known example of a simple $M(\eta^5\text{-}C_5R_5)L_4$ complex that is not square pyramidal.[2] Therefore, an X-ray structural study was carried out. It confirmed that the overall geometry is trigonal-bipyramidal with a PF_6^- ion widely separated from the metal cation (Figure 2). Both the Cp* ligand and the PF_6^- ion display disorder that could not be resolved (see discussion in Experimental Section), but the W atom and the four methyl groups attached to it refined comparatively well. The mirror plane passes through C(1), C(6), W, C(8), and C(9), so only the unique bond lengths and angles are listed on the figure. There are three features worth noting. First, the equatorial methyl groups are displaced toward the axial methyl group by 10–15° (C(9)–W–C(8) = 82.8 (14)°, C(7)–W–C(8) = 76.3 (8)°), as one would expect in a Cp* complex. Second, the C(9)–W–C(7) bond angle (118.8 (6)°) is somewhat larger than the C(7)–W–C(7)′ bond angle (110.8 (11)°). The difference is statistically valid, and the reasons are not clear. Third, the three independent W–methyl bond lengths are statistically identical.

A potentially interesting phenomenon has been observed in ^{1}H NMR spectra of $[WCp^*Me_4]^+$ in the presence of WCp^*Me_4. The Cp* resonance for $[WCp^*Me_4]^+$ broadens significantly (10–50 Hz) but does not shift, while the already broad methyl resonances (the result of methyl group exchange; Figure 1) do *not* appear to broaden significantly more rapidly than the Cp* resonance. This is not a bulk effect since the signal for ferrocene in the presence of WCp^*Me_4 at the same concentrations as in the above experiment was sharp (1–2 Hz). Studies aimed at explaining these results are underway. The phenomenon is mentioned here only in order to prepare someone who may encounter it.

A CV study of WCp^*Me_4 in dichloromethane shows that it can be oxidized at –0.305 V (E_{p_a}) vs. the ferrocene/ferricenium couple. A cathodic sweep shows a peak at –0.865 V (E_{p_c}) vs. $E_{1/2}$ for the ferrocene/ferricenium couple with an amplitude that is less than that of the oxidation wave, especially at slow sweep rates. A typical CV of $[WCp^*Me_4][PF_6]$ shows complementary behavior (Figure 3), i.e., a cathodic wave at –0.865 V vs. ferrocene/ferricenium and a peak in the anodic return sweep that corresponds to the oxidation of WCp^*Me_4 to $[WCp^*Me_4]^+$. No other peaks

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[12] Okuda, J., unpublished observations.

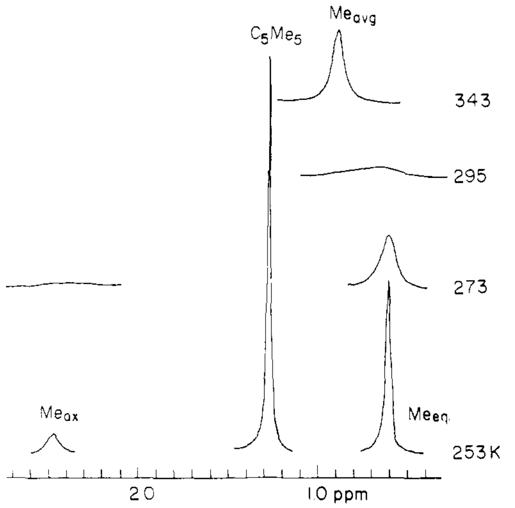


Figure 4. The ^{1}H NMR spectrum of WCp^*Me_5 in toluene-d_8 in the range 253–343 K.

were observed in this range. (The same results were observed at a sweep rate of 200 V s^{-1}.) The fact that WCp^*Me_4 is square-pyramidal (SP) and $[WCp^*Me_4]^+$ is trigonal-bipyramidal (TBP) must be the reason why two widely separated waves are observed. $[WCp^*Me_4]_{SP}$ is oxidized to $[WCp^*Me_4]^+_{SP}$ at −0.305 V. It then rearranges rapidly to $[WCp^*Me_4]^+_{TBP}$, which is then reduced at −0.865 V. Conversely, reduction of $[WCp^*Me_4]^+_{TBP}$ yields $[WCp^*Me_4]_{TBP}$, which rapidly rearranges to $[WCp^*Me_4]_{SP}$. We know from the NMR studies described above that the rate constant for rearrangement of $[WCp^*Me_4]^+_{TBP}$ to $[WCp^*Me_4]^+_{SP}$ (k_1; eq 1) is ~50 s^{-1} at 298 K (assuming that $[WCp^*Me_4]^+_{SP}$

$$[WCp^*Me_4]^+_{TBP} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [WCp^*Me_4]^+_{SP} \qquad (1)$$

is the transition state for scrambling of the methyl groups.) Since $\Delta G^\ddagger$ is 15.0 kcal mol^{-1}, $\Delta G°$ for $[WCp^*Me_4]^+_{SP}$ must be of the order of 10 kcal greater than that for $[WCp^*Me_4]^+_{TBP}$. Therefore, k_{-1} must be very large, and it is unlikely that we could ever devise an experiment that would allow us to observe the reduction of $[WCp^*Me_4]^+_{SP}$ in the cathodic sweep. Although we know nothing about the rates of interconversion of $[WCp^*Me_4]_{SP}$ and $[WCp^*Me_4]_{TBP}$, a rough lower limit for the conversion of $[WCp^*Me_4]_{TBP}$ to $[WCp^*Me_4]_{SP}$ can be estimated on the basis of the CV results at a 200 V s^{-1} sweep rate; $k > 10^3$ s^{-1}.

Preparation and Decomposition of WCp^*Me_5. The addition of 1 equiv of LiMe to $[WCp^*Me_4][PF_6]$ in diethyl ether rapidly gives pentane-soluble, red WCp^*Me_5 in high yield. WCp^*Me_5 can be recrystallized from pentane or ether but decomposes extensively in solution after 2 weeks at −30 to −40 °C. In benzene or toluene its half-life is ~8.5 h at 25 °C. (Details of its decomposition are presented below.) As a solid, however, it can be stored indefinitely at −40 °C. We have shown that WCp^*Me_5 reacts cleanly with HBF_4 to give $[WCp^*Me_4][BF_4]$ and with $[Ph_3C][PF_6]$ to give $[WCp^*Me_4][PF_6]$ and Ph_3CMe in high yield (see Experimental Section). WCp^*Me_5 is too unstable for elemental analysis.

The ^{1}H NMR spectrum of WCp^*Me_5 (Figure 4) is temperature-dependent. At low temperatures methyl resonances are observed in a 4:1 ratio at 0.63 and 2.51 ppm, respectively. These signals coalesce at 295 K and appear as a broad singlet of area 15 at 0.88 ppm at 343 K. These changes do not depend upon concentration and are totally reversible, except that WCp^*Me_5 decomposes with time at the higher temperatures. The ^{13}C NMR spectrum of WCp^*Me_5 shows the resonances for the unique methyl group at 79.15 ppm with J_{CH} = 125 Hz. On the basis of these data we postulate that WCp^*Me_5 is a pseudooctahedral species in which the five methyl groups interconvert readily at ordinary temperatures. Simulation of these spectral changes led to the values $\Delta H^\ddagger$ = 12.6 (5) kcal mol^{-1}, $\Delta S^\ddagger$ = −3.8 (12) eu, and $\Delta G^\ddagger_{296}$ = 13.7 (7) kcal mol^{-1}.

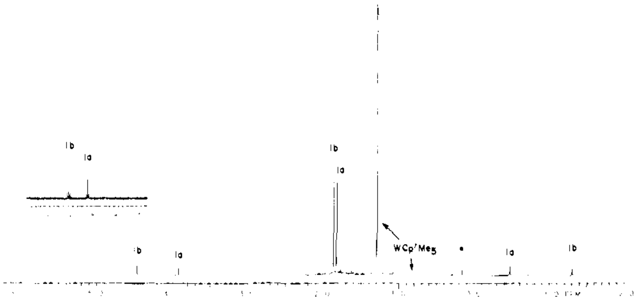


Figure 5. The ^{1}H NMR spectrum of a sample of WCp^*Me_5 in the process of decomposing; **1a** and **1b** are the two diamagnetic products (the asterisk indicates methane).

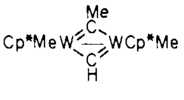
An interesting question is whether a methyl group in WCp^*Me_5 will transfer to $[WCp^*Me_4]^+$. A spectrum of a 1:1 mixture of $[WCp^*(CH_3)_4][PF_6]$ and $WCp^*(CD_3)_5$ in CD_2Cl_2 showed only signals for $[WCp^*(CH_3)_4][PF_6]$ after a period of ~10 min. However, after 10 days at −30 °C (in order to avoid competitive decomposition of $WCp^*(CD_3)_5$) the expected equilibrium mixture of what we presume to be $[WCp^*(CH_3)_x(CD_3)_{4-x}]^+$ and $WCp^*(CH_3)_y(CD_3)_{5-y}$ was observed; we cannot exclude the possibility that CH_zD_{3-z} ligands are present but have *no* reason at this time to suspect that to be the case. Therefore we can say that a methyl group in WCp^*Me_5 transfers relatively slowly to $[WCp^*Me_4]^+$, a species that we know readily accepts a methyl group from methyllithium.

The decomposition of WCp^*Me_5 in C_6D_6 was studied in some detail (see Experimental Section). The decomposition reaction was found to be cleanly first-order over a tenfold concentration range for several half-lives. A temperature study showed $\Delta H^\ddagger$ = 23.2 (1.8) kcal mol^{-1} and $\Delta S^\ddagger$ = −1(6) eu. A similar study employing $WCp^*(CD_3)_5$ showed it to decompose much more slowly. Two values for k_H/k_D are 6 ± 1 (at 25 °C) and 2 ± 1 (at 60 °C). On the basis of these results we propose that the slowest step in the decomposition sequence is an intramolecular α-hydrogen abstraction reaction (eq 2).

$$WCp^*Me_5 \rightarrow WCp^*Me_3(CH_2) + CH_4 \qquad (2)$$

Decomposition of WCp^*Me_5 yields two diamagnetic organometallic products, **1a** and **1b** (Figure 5). The latter appears to be unstable under the reaction conditions and eventually disappears, leaving only **1a**. **1b** does not appear to decompose to **1a**. The total amount of **1a** formed in a typical experiment is 30–35%. The maximum amount of **1b** formed is ~25%. **1a** can be isolated at the end of a reaction in ≳20% yield after chromatography on dry silica (ether eluant).

There must be a close analogy between **1a** and **1b**. Both show one Cp* resonance, a 2:1 set of methyl signals, and a resonance of area 1 at low field (18.68 ppm for **1a**, 19.10 ppm for **1b**) with J_{HW} = 16 Hz. The intensity of the tungsten satellites (25–27%) suggests that these protons are coupled to two identical tungsten atoms. ^{13}C NMR spectra (Figure 6) show two low-field resonances for each. One type is at 346.5 ppm for **1a** and 340.3 ppm for **1b**. They are methylidyne-like doublets with J_{CH} = 154 Hz and J_{CW} = 142–144 Hz. A signal for a similar, second type of alkylidyne carbon atom is found at 349.5 for **1a** (Figure 6) and 355.4 for **1b**. Each signal of this type shows long-range coupling to three protons with J_{CH} ≈ 5.4 Hz and J_{CW} ≈ 140 Hz. These data (Table I) suggest that each of these molecules contains a bridging methylidyne and a bridging ethylidyne ligand, viz., one resonance form.



$$\mathrm{Cp^*MeW}\underset{\underset{\mathrm{H}}{\mathrm{C}}}{\overset{\overset{\mathrm{Me}}{\mathrm{C}}}{\rightleftharpoons}}\mathrm{WCp^*Me}$$

A tungsten–tungsten bond is drawn since these species would then be analogous to $W_2(CH_2SiMe_3)_4(\mu\text{-}CSiMe_3)_2$,[13] a structurally

Table I. NMR Data for Bis(alkylidyne)ditungsten Complexes[a]

$(WCp^*Me)_2(\mu\text{-}CH)(\mu\text{-}CMe)$ (**1**)

	^1H		^{13}C	
	1a	**1b**	**1a**	**1b**
C_5Me_5			105.07	107.38
C_5Me_5	1.82	1.86	11.19 (J_{CH} = 127 Hz)	10.77 (J_{CH} = 126 Hz)
WMe	-0.49 (J_{HW} = 7 Hz)	-1.32 (J_{HW} = 7 Hz)	29.73 (J_{CH} = 124 Hz)	23.63 (J_{CH} = 121 Hz)
μ-CMe	3.91	4.46	49.14 (J_{CH} = 122 Hz)	48.30 (J_{CH} = 116 Hz)
μ-CMe			349.52 (J_{CH} = 5 Hz, J_{CW} = 140 Hz)	355.37 (J_{CH} = 7 Hz)
μ-CH	18.68 (J_{HW} = 16 Hz)	19.10 (J_{HW} = 16 Hz)	346.53 (J_{CH} = 154 Hz, J_{CW} = 144 Hz)	340.25 (J_{CH} = 154 Hz, J_{CW} = 142 Hz)
area of tungsten satellites	27%	25%		

$(WCp^*Me)_2(\mu\text{-}CMe)_2$ (**2**)

	^1H		^{13}C	
	2a	**2b**	**2a**	**2b**
C_5Me_5			105.23	107.15
C_5Me_5	1.85	1.82	11.16 (J_{CH} = 126 Hz)	10.77
WMe	-0.62	-1.47	30.31 (J_{CH} = 121 Hz)	23.63
μ-CMe	3.97	4.36	49.61 (J_{CH} = 124 Hz)	47.15
μ-CMe			350.56 (J_{CH} = 6 Hz, J_{CW} = 145 Hz)	353.14

$(WCp^*Me)(WCp^*Et)(\mu\text{-}CH)_2$ (**3**)

	^1H	^{13}C
C_5Me_5		105.81
C_5Me_5	1.82	10.81 (J_{CH} = 127 Hz)
C_5Me_5'		105.54
C_5Me_5'	1.78	10.81 (J_{CH} = 127 Hz)
WMe	-0.25 (J_{HW} = 7 Hz)	30.57 (J_{CH} = 121 Hz)
WCH_2CH_3	0.91 (J_{HH} = 8 Hz)	39.67 (J_{CH} = 120 Hz)
WCH_2CH_3	1.21 (J_{HH} = 8 Hz)	14.04 (J_{CH} = 121 Hz)
μ-CH	18.37 (J_{HW} = 16 Hz)	345.74 (J_{CH} = 152 Hz, J_{CW} = 145 Hz)
	Area of Tungsten Satellites = 26%	

[a] Chemical shifts in ppm.

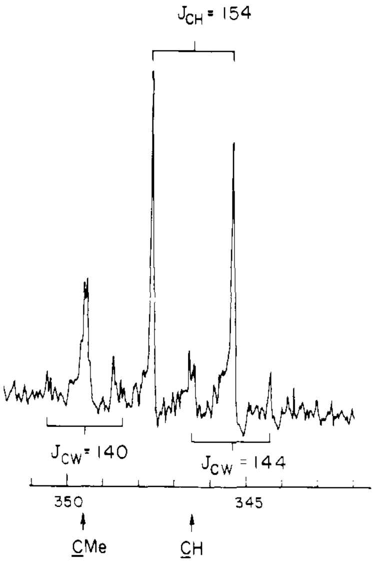


Figure 6. The low-field region of the ^{13}C NMR spectrum of $(WCp^*Me)_2(\mu\text{-}CH)(\mu\text{-}CMe)$ (**1a**).

characterized complex that has been known for several years and more recently prepared complexes such as $W_2(OR)_4(\mu\text{-}CSiMe_3)_2$.[14] We guess that **1a** and **1b** are transoid and cisoid versions (or vice versa).

The only other recognizable product of the decomposition of WCp^*Me_5 is Cp^*WMe_4. It can be isolated in 15–20% yield by chromatography. Therefore, only ~50% of the tungsten can be accounted for. We assume the remainder consists of a mixture of products that do not survive chromatography and which are not diagmagnetic and formed in yield good enough in order to identify them by NMR in the crude reaction mixture.

The yield of **1a** is not especially sensitive to temperature (up to 60 °C). The yield appears to be somewhat lower (~15% by NMR) in more concentrated solutions. If a sample of WCp^*Me_5 in C_6D_6 is irradiated with a medium-pressure mercury lamp, the yield of **1a** drops dramatically (to ~5%). Addition of WCp^*Me_4 to a sample of decomposing WCp^*Me_5 has no dramatic effect upon the yield of **1a**, while decomposition of 10 mg of WCp^*Me_5 in the presence of 200 mg of dihydroanthracene yields only ~10% **1a**. Finally, the decomposition of $WCp^*(CD_3)_5$ gives only about a 10% yield of deuteriated **1a**.

The results so far are consistent with the proposal that **1a** arises by a complex series of reactions, probably bimolecular ones, between the initial decomposition product, $WCp^*Me_3(CH_2)$, and WCp^*Me_5, while WCp^*Me_4 is formed when $WCp^*Me_3(CH_2)$ abstracts $H^\bullet$ from solvent. WCp^*Me_4 also could be formed by loss of a methyl group from WCp^*Me_5. The dramatically lower yield of **1a** under photolytic conditions is consistent with this latter proposal, a greater fraction of homolytic cleavage of a W–Me bond in WCp^*Me_5 giving WCp^*Me_4, instead of α-abstraction giving $WCp^*Me_3(CH_2)$. (It has been established that α-hydrogen abstraction reactions can be assisted by light[15-17] and that in some cases the yields of alkylidene products can decrease dramatically

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(13) (a) Mowat, W.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 1120. (b) Andersen, R. A.; Galyer, A. L.; Wilkinson, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 609. (c) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **1978**, *17*, 696.

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Table II. Selected Bond Distances (Å), Angles (deg), and Dihedral Angles for $(WCp^*Me)_2(\mu\text{-}CMe)_2$

Bond Distances			
W–W	2.606 (1)	W–C(2)	1.950 (14)
W–centroid	2.089	W–C(2′)	1.972 (11)
W–C(1)	2.199 (14)		
Bond Angles			
C(2)–W–C(2′)	93.7 (5)	C(2′)–W–centroid	120.4 (4)
C(2)–W–C(1)	108.5 (6)	W–C(2)–W′	83.3 (5)
C(2′)–W–C(1)	105.9 (5)	W–C(2)–C(3)	138.9 (8)
C(2)–W–centroid	119.1 (3)	W′–C(2)–C(3)	137.7 (9)
C(1)–W–centroid	107.8 (4)		
Dihedral Angle			
Plane 1, W, W′, C(2′); Plane 2, W, W′, C(2)			
Angle between Planes 1 and 2: 25.09°			

in the presence of light.[15]) But before we become preoccupied with possible steps in a complex decomposition reaction after a rate-limiting first step, steps which we are not likely to be able to probe directly, let us present some more facts concerning **1a** and **1b** and their chemistry.

$(WCp^*Me)_2(\mu\text{-}CH)(\mu\text{-}CMe)$ does not react readily with alcohols, water, H_2 (100 atm), or $LiAlH_4$. It does react with HBF_4 or carboxylic acids, but the resulting mixtures could not be characterized. Interestingly, **1a** reacts rapidly and quantitatively with methyllithium to give a bis(ethylidyne) complex, **2a**, instead of the expected lithiocarbyne complex (eq 3). ^1H and ^{13}C NMR

$$(WCp^*Me)_2(\mu\text{-}CH)(\mu\text{-}CMe) + LiMe \rightarrow (WCp^*Me)_2(\mu\text{-}CMe)_2 \quad (3)$$

data of **2a** are very similar to those for **1a** and **1b** (Table I). As expected methyllithium reacts with a mixture of **1a** and **1b** to give a mixture of bis(ethylidyne) complexes **2a** and **2b**. Like **1b**, **2b** decomposes over a period of several hours and cannot be chromatographed. Experiments that probe the mechanism of the reaction shown in eq 3 are presented in a later section.

The X-ray Structure of $(WCp^*Me)_2(\mu\text{-}CMe)_2$ (2a). Crystals of **2a** were selected for an X-ray study in order to eliminate any potential CH/CMe disorder problem. Two views of the structure are shown in Figure 7. Relevant distances and angles are given in Table II.

The structure contains an essentially square, slightly folded W_2C_2 ring core. The relatively short W–W distance is similar to those found in $W_2(CH_2SiMe_3)_4(\mu\text{-}CSiMe_3)_2$[13] and $W_2(OR)_4(\mu\text{-}CSiMe_3)_2$[14] and can be interpreted as indicative of a W–W single bond. The W_2C_2 ring distances (1.950 (14) vs. 1.972 (11) Å) and the WCC angles (138.9 (8) vs. 137.7 (9)°) are virtually identical. (Although the M_2C_2 core in some related compounds[13,14,18] appears at first glance to be unsymmetric, as if one resonance structure containing localized double bonds were dominant, no such distortions can be said to be significant on a statistical basis.) The ethylidyne methyl groups are bent away from the direction in which the W_2C_2 ring is folded, as one would expect.

The coordination geometry about each tungsten atom is of the pseudo-tetrahedral "piano-stool" variety with angles ranging from 107 to 120° between the centroid of the Cp* ligand and the methyl or bridging carbon atoms, and from 94 to 109° between the methyl group and the bridging alkylidyne carbon atoms (Table II). The tungsten–methyl distance is normal, as is the tungsten–ring centroid distance. The dish shape of the Cp* ring is normal. The rather large thermal ellipsoids for at least one of the Cp* methyl groups and ring carbon atom (Figure 7b) could be indicative of some disorder, e.g., slight rotation of the Cp* ring about the Cp*–W bond.

The most surprising feature of this structure is the fact that it is cisoid. A transoid structure containing a *planar* W_2C_2 ring appears to be a perfectly reasonable alternative from a steric point of view on the basis of figures constructed by using the same WCp^*C_3 arrangement as found in the cisoid structure. This particular cisoid structure seems especially disfavored in view of the eclipsed WMe groups (Me···Me = 3.53 (3) Å) and the eclipsing of each WMe group with a Cp* methyl group (WMe···Me(Cp*) = 3.16 (3) Å). Rotating each Cp* group by 36° would appear to yield a lower energy structure, although by so doing two Cp* methyl groups on the other side of the W_2C_2 ring would then be eclipsed. As noted above the Cp* rings in fact may be disordered slightly so as to relieve the WMe···Me(Cp*) close contact.

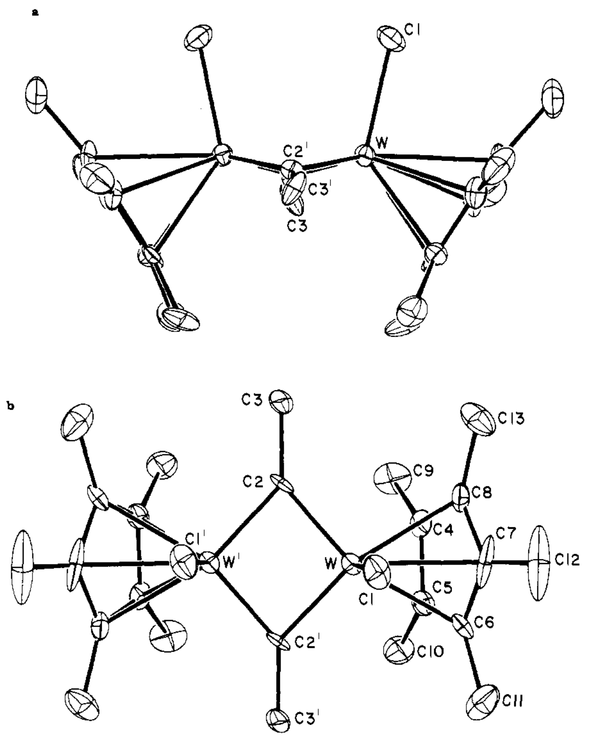

Figure 7. The structure of $(WCp^*Me)_2(\mu\text{-}CMe)_2$ (50% thermal ellipsoids): (a) side view; (b) top view.

We assume that the structure of **1a** is virtually the same as that found for **2a** and that the structure of **1b** is virtually the same as that of **2b**. (Patterns within the NMR data in Table I seem to support this contention.) The most attractive possibility for the structure of **1b**, in view of the overall similarity of the NMR spectra of **1a** and **1b**, is that **1b** is transoid. But if it is, it is unclear why it is so unstable. On the other hand, if it is not transoid, we cannot imagine what the structure might be.

The Observation and Decomposition of $WCp^*Me_3(CH_2)$. Since the reaction between $[TaCp_2Me_2][BF_4]$ and base yields $TaCp_2Me(CH_2)$,[19] we had felt for some time that $[WCp^*Me_4][PF_6]$ should react with some base to yield $WCp^*Me_3(CH_2)$, the suspected initial product of decomposition of WCp^*Me_5. When NEt_3 (1 equiv) is added to $[WCp^*Me_4][PF_6]$ in dichloromethane at <−40 °C, an orange solution is obtained. An ^1H NMR spectrum of this solution suggests that the product of this reaction is in fact $WCp^*Me_3(CH_2)$. In particular, two broad signals of relative area 1 are observed at 4.53 and 9.77 ppm in the −78 °C spectrum. These signals coalesce at approximately −40 °C ($\Delta G^{\ddagger}_{233}$ = 9.7 (2) kcal mol^{-1}) and by −10 °C are replaced by a broad signal of area 2 at the approximate average chemical shift of 7.3 ppm. An upper limit spectrum could not be obtained due to sample decomposition (see below). The ^{13}C NMR spectrum of $WCp^*Me_3(CH_2)$ at 213 and 233 K confirms that a methylene carbon atom is present (δ (C) 255.5) *and* that the two protons in the methylene ligand are *inequivalent* on the NMR time scale at the lower temperature (Figure 8). The observed values for J_{CH} and $J_{CH'}$ are 110 and

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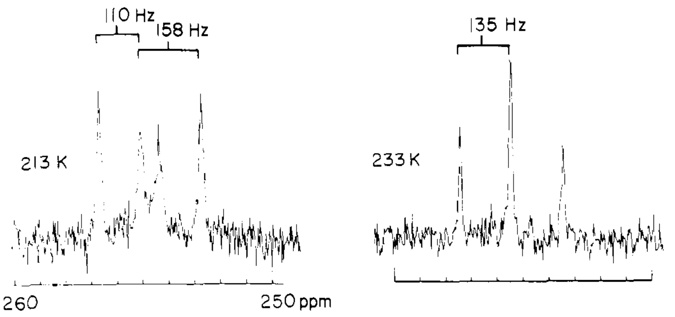
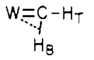
(19) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.



(a) (b)

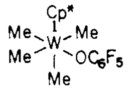
Figure 8. ^{13}C NMR spectrum of $WCp^*Me_3(CH_2)$ at (a) 213 K and (b) 233 K in CD_2Cl_2.

158 Hz. The former is characteristic of coupling between an alkylidene carbon atom and a proton that is more or less bridging between the carbon atom and the metal.[20] The latter is characteristic of J_{CH} in terminal methylidyne complexes.[21] Therefore, we can represent the bonding in the following manner and stipulate that H_B and H_T do not interconvert rapidly on the NMR time scale at −60 °C:



We see only two types of methyl groups under all conditions. Therefore either the methylene ligand lies in a molecular plane that passes through the unique methyl group, or H_B is still sufficiently mobile that this only *appears* to be the case. In any case, H_B and H_T interconvert at higher temperatures to yield a methylene ligand that is symmetric on the NMR time scale in which the observed J_{CH} (135 Hz) is approximately the average of the two values for J_{CH} at 213 K. Some results bearing on the question as to whether $WCp^*Me_3(CH_2)$ is a pseudo-trigonal bipyramid or a square pyramid are presented below.

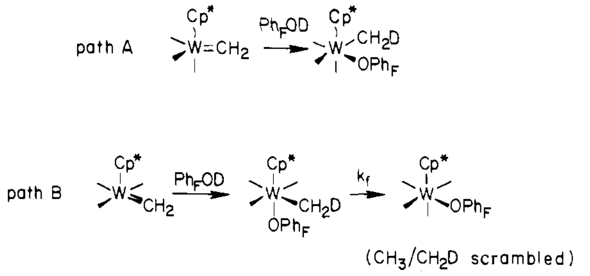
$WCp^*Me_3(CH_2)$ can be trapped with pentafluorophenol ($HOPh_F$). The resulting orange crystalline $WCp^*Me_4(OPh_F)$ can be isolated in >90% yield. Its ^1H and ^{13}C NMR spectra suggest that its structure is pseudooctahedral with a methyl group trans to the Cp* ligand, viz.



The three inequivalent methyl groups do not exchange readily on the NMR time scale. Even when a solution of $WCp^*Me_4(OPh_F)$ in toluene-d_8 is heated to 100 °C, above which the complex begins to decompose to give many products (according to the ^1H NMR spectrum), there is no significant broadening of any of the methyl signals that would suggest that the methyl groups are beginning to exchange at a rate approaching that of the NMR time scale. The formulation of $WCp^*Me_4(OPh_F)$ appears beyond doubt, as it also can be prepared quantitatively by adding $LiOPh_F$ to $[WCp^*Me_4]^+$. These results provide further evidence that $WCp^*Me_3(CH_2)$ is the compound generated upon addition of NEt_3 to $[WCp^*Me_4]^+$ in dichloromethane at low temperature. They also illustrate how easily the methylene ligand can be reprotonated.

We thought it might be possible to determine the most likely structure for $WCp^*Me_3(CH_2)$ by looking at the product obtained by adding C_6F_5OD to it. Both ^1H NMR and ^2H NMR were employed between −70 and 25 °C. Two possible results are shown in Scheme I. At the lowest temperature where a reaction occurred (−30 °C), we could observe only the final product in which deuterium is distributed evenly among all four methyl groups.

Scheme I



According to the NMR spectrum of $WCp^*Me_4(OPh_F)$ at 100 °C we estimate that a maximum rate for interconverting methyl groups to be $\sim 10\ s^{-1}$, which implies that $\Delta G^{\ddagger} \geq 19.8$ kcal mol^{-1}. If we assume that $\Delta S^{\ddagger}$ for methyl groups scrambling in $WCp^*Me_4(OPh_F)$ to be approximately the same as it is in WCp^*Me_5 (−3.8 eu), then at −30 °C $\Delta G^{\ddagger} \geq 19.3$ kcal mol^{-1}, $k \leq 2.3 \times 10^{-5}\ s^{-1}$, and $t_{1/2} \geq 3 \times 10^4$ s. What these estimates suggest is that if path A is correct, we should have been able to observe deuterium in one methyl group before it scrambled with the others. On the other hand path B is more consistent with the labeling result, even though k_f is unrelated to any rate constant we can *directly* measure or estimate. If the more symmetric isomer shown in path B is produced, we cannot observe it, i.e., $k_f \geqslant 0.1\ s^{-1}$, even at −30 °C. There is no reason to believe that such a value for k_f is not possible. A square-pyramidal structure for $WCp^*Me_3(CH_2)$ also is more consistent with the square-pyramidal geometry about the metal found[22a] in the hydrazido(4−) complex $[WCp^*Me_3]_2(\mu\text{-}N_2)$;[22b] i.e., a square-pyramidal geometry might be favored over a pseudo-trigonal-bipyramidal geometry when a strong π-bonding ligand is present. We still do not know exactly how the distorted methylene group is oriented with respect to the other methyl groups, i.e., where the bridging proton (H_B) is located. The proposal we prefer is that H_B is located somewhere beneath the C_4 pseudoplane, but not necessarily directly trans to the Cp* ligand. As we mentioned earlier, H_B could still be jumping rapidly from one side to another and thereby equilibrating what would otherwise be inequivalent Me groups cis to the methylene ligand.[23]

If a sample of $WCp^*Me_3(CH_2)$ in dichloromethane is allowed to decompose by warming a solution slowly from −30 to 25 °C, then the major diamagnetic product (in ~30% yield after chromatography) is $(WCp^*Me)(WCp^*Et)(\mu\text{-}CH)_2$ (**3**); examination of the crude product (before chromatography) showed a 6:1 mixture of $(WCp^*Me)(WCp^*Et)(\mu\text{-}CH)_2$ and $(WCp^*Me)_2(\mu\text{-}CH)(\mu\text{-}CMe)$ to be present. $(WCp^*Me)(WCp^*Et)(\mu\text{-}CH)_2$ has all the NMR characteristics of a molecule of this type (Table I). The important features of the NMR spectra of **3** that distinguish it from **1** and **2** are the presence of two Cp* signals, a single methyl resonance of area 3, and characteristic ethyl resonances at 1.21 (CH_2) and 0.9 ppm (CH_3). We assume that **3** is of the more stable cisoid variety, i.e., isostructural with $(WCp^*Me)_2(\mu\text{-}CMe)_2$ (**2a**). If NEt_3 is added to $[WCp^*Me_4][PF_6]$ in dichloromethane at 25 °C, then the ratio of **3** to **1a** is ~3:1. The solvent is important in this reaction; i.e., $[WCp^*Me_4][PF_6]$ reacts with NEt_3 in *ether* at 25 °C to give **1a** in only ~5% yield (by ^1H NMR). No other diamagnetic product is formed in any significant yield, while WCp^*Me_4 is found in ~15% yield after chromatography.

The decomposition of $WCp^*Me_3(CH_2)$ at 0 °C was found to be first order by ^1H NMR over a fivefold concentration range in four different experiments. The values obtained are $k \times 10^3\ s^{-1}$ = 1.4, 2.0, 2.6, and 3.0, the samples giving the third and fourth values being five times more concentrated than that giving the

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[20] Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

[21] (a) Holmes, S. J.; Clark, D. J.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6322. (b) Listemann, M. L.; Schrock, R. R. *Organometallics* **1985**, *4*, 74.

[22] (a) Churchill, M. R.; Li, Y.-J. *J. Organometal. Chem.* **1986**, *301*, 49. (b) Murray, R. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 4557.

[23] A similar hopping of H_B from face to face in pseudooctahedral complexes containing similar severely distorted methylene ligands has been observed: Holmes, S. J.; Clark, D. J.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6322.

second value (see Experimental Section). We believe the relatively large range in *k* is observed because the experiment is not easy to do for technical reasons. We feel that the most likely reason for first-order decomposition is rate-limiting migration of a methyl group to the methylene ligand (eq 4). Rapid reaction between

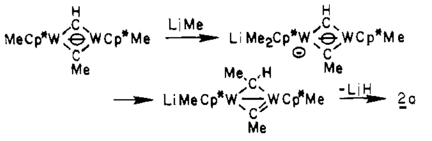
$$WCp^*Me_3(CH_2) \rightarrow WCp^*Me_2(Et) \tag{4}$$

$WCp^*Me_2(Et)$ and $WCp^*Me_3(CH_2)$ could then yield intermediate $(WCp^*Me_2Et)(\mu\text{-}CH_2)(WCp^*Me_3)$ from which both **3** and **1a** could arise, the ratio being determined by whether a methyl ligand or an ethyl ligand is involved in formation of the second bridging alkylidyne ligand (see Discussion).

Reactions Bearing on Formation of Ethylidyne Ligands. In an earlier section we presented the curious reaction of **1** with methyllithium to give **2**. Experiments designed to probe the mechanism of this reaction are presented in this section. As a bonus we are given a hint as to how the ethylidyne ligand in **1** might be formed when WCp^*Me_5 decomposes.

The result shown in eq 5 establishes that methyl groups on tungsten exchange readily while those in ethylidyne ligands do not. Methyl group exchange should be the relatively straightforward result of addition of a methyl group to the metal to give an incipient anionic complex. Therefore we can postulate that addition of a methyl group to the metal is the first step in conversion of **1** to **2** and that subsequent migration of the methyl group to the methylidyne ligand followed by loss of LiH (eq 6) is how the ethylidyne ligand is formed. Migration of a methyl group to an ethylidyne ligand could be slow for steric reasons and methyl exchange in ethylidyne ligands therefore not observed.

$$[WCp^*(CH_3)]_2(\mu\text{-}CCH_3)_2 \xrightarrow[\text{3 h, ether}]{\text{excess LiCD}_3} [WCp^*(CD_3)]_2(\mu\text{-}CCH_3)_2 \tag{5}$$



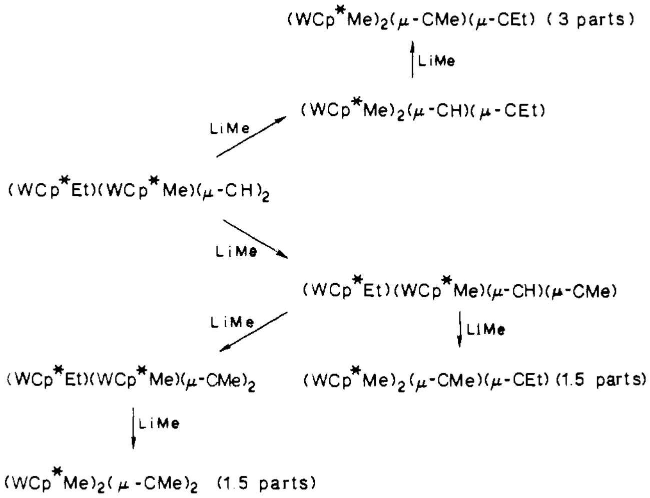
(6)

The results of the experiment shown in eq 7 support the mechanism shown in eq 6. If an ethylidyne-d_3 ligand were to form directly, i.e., *without* CD_3 adding to a metal center first, then the product would contain from 3.00 μ-CCH_3 protons (if $WCH_3/LiCD_3$ scrambling were relatively slow, i.e., the other ethylidyne ligand is pure μ-CCD_3) to 3.30 μ-CCH_3 protons (if $WCH_3/LiCD_3$ scrambling were relatively fast, i.e., the other ethylidyne ligand contains a CH_3 group 2/20 or 10% of the time). In fact the number of μ-CCH_3 protons that are present in the product shown in eq 7 is 3.78. Therefore, we believe that $WCH_3/LiCD_3$ exchange is not complete before some $WC\mathit{H}_3$ group, in competition with a $WC\mathit{D}_3$ group, transfers to the methylidyne carbon atom. Only by converting some WCH_3 groups directly into μ-CCH_3 ligands can the relatively high proton count in the product be explained.

$$(WCp^*Me)_2(\mu\text{-}CH)(\mu\text{-}CMe) + 20LiCD_3 \xrightarrow[\text{ether}]{\text{1.5 h}} (WCp^*Me)_2(\mu\text{-}CMe)_2\text{-}d_x \tag{7}$$

A third experiment provided further evidence that an alkyl group can transfer to a μ-CH ligand. A mixture of 6 parts of $(WCp^*Et)(WCp^*Me)(\mu\text{-}CH)_2$ and 1 part of $(WCp^*Me)_2(\mu\text{-}CH)(\mu\text{-}CMe)$ was treated with excess $LiCH_3$ in ether. The result was a mixture containing 2 parts of $(WCp^*Me)_2(\mu\text{-}CMe)_2$ and 3 parts of a compound whose NMR spectra are totally consistent with it being $(WCp^*Me)_2(\mu\text{-}CMe)(\mu\text{-}CEt)$ (see Experimental Section). Most distinctive is the characteristic low-field chemical shift of the CH_2 protons in the μ-CEt ligand at 4.658 ppm coupled to a methyl group whose protons are found at 0.987 ppm. This result can be explained if the μ-CEt ligand forms by migration of the WEt group to a μ-CH ligand in competition with migration of a WMe group to a μ-CH ligand and if WEt/LiMe exchange is relatively slow. As shown in Scheme II, 6 parts of $(WCp^*Et)(WCp^*Me)(\mu\text{-}CH)_2$ should give rise to a mixture of 4.5 parts of $(WCp^*Me)_2(\mu\text{-}CMe)(\mu\text{-}CEt)$ and 1.5 parts of $(WCp^*Me)_2(\mu\text{-}CMe)_2$, *if* migration of an Et ligand is as likely as migration of a Me ligand. Since 1 part of $(WCp^*Me)_2(\mu\text{-}CH)(\mu\text{-}CMe)$ was present initially, the resulting mixture should contain 4.5/7 or 64% $(WCp^*Me)_2(\mu\text{-}CMe)(\mu\text{-}CEt)$, virtually the observed result (~60%).

Scheme II



On the basis of these experiments we feel confident proposing that a μ-ethylidyne ligand *can* form by methyl group transfer to a μ-methylidyne ligand. We propose that a μ-ethylidyne ligand can form by a related methyl group migration to a methylidyne ligand in a variety of possible intermediates formed upon decomposition of WCp^*Me_5. We realize that all of the above reactions involving LiMe formally must yield LiH (i.e., loss of "H^-" from a μ-CHMe ligand) while loss of methane from a molecule containing a μ-CHMe ligand (to generate a μ-CMe ligand) is potentially quite a different reaction.

Discussion

Alkyl complexes of W(6+) that do not contain some strong π-bonding ligand (e.g., alkylidyne, oxo, imido, alkoxide) are extremely rare. To our knowledge the only example is WMe_6.[24] Therefore, we were surprised to find that $[WCp^*Me_4]^+$ is isolable and that WCp^*Me_5 is as stable as it is given the fact that it must be a relatively crowded, pseudooctahedral species. In retrospect, however, we should not have been surprised, since (i) methyl–carbon bonds of the heavier, earlier metals are not inherently weak toward homolysis,[25] (ii) the predominant form of decomposition, α-hydrogen atom abstraction,[20] appears to be least likely for the smallest of the alkyls, the methyl group, and (iii) intermolecular modes of decomposition (e.g., as in the case of $TaMe_5$[26]) are likely to be considerably slower in relatively crowded or charged species.

The stability of WCp^*Me_4 was also somewhat of a surprise since not so long ago metal–carbon bonds in odd-electron species were thought to be relatively weak toward homolysis to give an even electron metal fragment. There is now abundant evidence that that is not the case,[27] especially for transition metals of the second or third row whose metal–carbon bonds tend to be stronger than those of first row metals.

The key to the chemistry explored here is $WCp^*Me_3(CH_2)$. Its formation by deprotonation of $[WCp^*Me_4]^+$ or by loss of methane from WCp^*Me_5 both have precedent. Deprotonation of $TaCp_2Me_2^+$ to yield $TaCp_2Me(CH_2)$[19] has already been

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[24] Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1981**, 1204.

[25] (a) Lappert, M. F.; Patil, D. S.; Pedley, J. B. *J. Chem. Soc., Chem. Commun.* **1975**, 830. (b) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71. (c) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238. (d) Hartley, F. R., and Patai, S., Eds. The Chemistry of the Metal-Carbon bond; Wiley: 1982; Vol 1, Chapter 2 by G. Pilchner and H. A. Skinner.

[26] Schrock, R. R. *J. Organomet. Chem.* **1976**, *122*, 209.

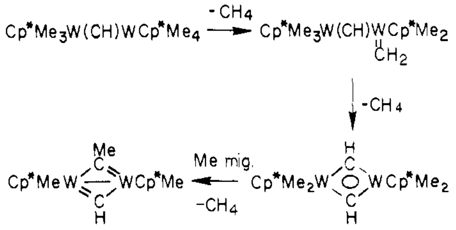
[27] See, for example: Teuben, J. H. *J. Organomet. Chem.* **1974**, *69*, 241.

mentioned. However, formation of a methylene ligand by α-hydrogen abstraction in a methyl ligand has been difficult to document,[19,24] since, as we have found here, subsequent decomposition of the methylene complex is usually fast. The one notable exception is the photochemical generation of a methylene complex from a trimethyltantalum complex.[17] The magnitude of the isotope effect for decomposition of WCp*Me$_5$ (k_H/k_D = 6 ± 1 at 25 °C) is consistent with what is found in the tantalum neopentyl systems TaCp(CH$_2$CMe$_3$)$_2$Cl$_2$ (k_H/k_D = 5.4 at 20 °C) and TaCp(CHDCMe$_3$)$_2$Br$_2$ (k_H/k_D = 6 at 25 °C), where the neopentylidene products are stable and well-characterized.[15]

The finding that WCp*Me$_4$(OC$_6$F$_5$) does not readily decompose to WCp*Me$_2$(OC$_6$F$_5$)(CH$_2$) has little direct precedent in the literature. However, there are some unpublished results from our laboratory from several years ago that are analogous; Ta(CH$_2$CMe$_3$)$_4$Cl decomposes at <−10 °C to give (unstable) Ta(CHCMe$_3$)(CH$_2$CMe$_3$)$_2$Cl, while Ta(CH$_2$CMe$_3$)$_4$(OCMe$_3$) gives Ta(CHCMe$_3$)(CH$_2$CMe$_3$)$_2$(OCMe$_3$) (quantitatively) only upon heating to 70 °C.[28] Other results in the literature suggest that alkoxide ligands dramatically slow down reactions involving β-hydrogen transfer. For example, Cp*Cl$_2\overline{\text{TaCH}_2\text{CH(Me)CH(Me)CH}_2}$ rearranges rapidly to 2,3-dimethyl-1-butene, while isolable Cp*Cl(OMe)$\overline{\text{TaCH}_2\text{CH(Me)CH(Me)CH}_2}$ decomposes at ~1/40 the rate.[29] We also know that replacing chloride ligands by *tert*-butoxide ligands dramatically slows down the rate of rearrangement of tantalacyclobutane rings or (less certainly) alkylidene ligands to olefins.[30] Therefore the trend seems to be that alkoxide ligands slow down a variety of hydrogen abstraction reactions. The greater stability of WCp*Me$_4$(OC$_6$F$_5$) relative to WCp*Me$_5$ is yet another example of this trend. We propose that the π-electron donating ability of an alkoxide ligand (even perfluorophenoxide) relative to an alkyl or halide ligand is what reduces the extent of activation of α-hydrogen atoms (e.g., W(μ-H)(CH$_2$))[31] toward abstraction by a neighboring alkyl group.

The distortion of the methylene ligand in WCp*Me$_3$(CH$_2$) can account for the instability of this complex, since the hydrogen atom bridging between tungsten and carbon should be quite acidic and could be removed readily by a relatively basic methyl group either intramolecularly (to give WCp*Me$_2$(CH)) or intermolecularly (see below). The metal interacts strongly with a C–H electron pair in the methylene ligand in an attempt to create a metal–carbon triple bond. This circumstance appears to arise most often when there is no π-bonding (oxo, imido, alkylidyne) or π-electron-donating ligand (e.g., alkoxide) present. In W(O)(CH$_2$)(PR$_3$)$_2$Cl$_2$ and related complexes, for example, the alkylidene ligands are "normal", i.e., compaiatively symmetrical with relatively high values for J_{CH} (~130 Hz).[32] In complexes of the type W(CHR)(OR)$_2$X$_2$ the relatively "normal" value for J_{CH} in the alkylidene ligand would suggest that they also are relatively undistorted.[33] The presence of a π-bonding ligand is not always sufficient to prevent some distortion of the alkylidene ligand if the overall electron count is low and the metal center is electrophilic, as is the case in W(CHCMe$_3$)(N-2,6-C$_6$H$_3$-*i*-Pr$_2$)[OCMe(CF$_3$)$_2$]$_2$ (J_{CH} = 110 Hz).[34] It seems plausible that some distorted methyl group[31] is present in WCp*Me$_5$ (i.e., W(μ-H)(CH$_2$)) but that the bridging proton is not as activated as it is in WCp*Me$_3$(CH$_2$). Therefore under conditions where WCp*Me$_3$(CH$_2$) is generated from WCp*Me$_5$ by loss of methane, it decomposes rapidly. Although distorted methylene ligands have been observed before in complexes in which the metal is in a formal oxidation state two electrons less than that found here[21a] and in (primarily) d^0 neopentylidene complexes,[20] we believe WCp*Me$_3$(CH$_2$) to be the first example of a distorted methylene ligand in a complex in which the metal is in its highest possile oxidation state.

Scheme III



Since (WCp*Me)$_2$(μ-CH)(μ-CMe) appears to be a thermodynamic sink, it probably can form via several different pathways. We only offer two possibilities here. The alternative we favor is shown in eq 8 and Scheme III. The attractive feature of the

$$\text{WCp*Me}_3\text{(CH}_2\text{)} + \text{WCp*Me}_5 \xrightarrow{-\text{CH}_4} \text{Cp*Me}_3\text{W(}\mu\text{-CH)WCp*Me}_4 \qquad (8)$$

reaction shown in eq 8 is that intermolecular α-hydrogen abstraction appears to dominate in methyl systems that have been explored so far (e.g., TaMe$_5$[26]) in the absence of coordinating ligands. However, it is possible that intramolecular α-hydrogen abstraction (eq 9)[35] *does* compete with intermolecular α-hydrogen abstraction and that an ethylidene ligand is formed as shown in eq 10. Subsequent loss of methane (eq 11) followed by formation of the μ-methylidyne ligand would lead to **1** (eq 12). It should

$$\text{WCp*Me}_3\text{(CH}_2\text{)} \xrightarrow{-\text{CH}_4} \text{WCp*Me}_2\text{(CH)} \qquad (9)$$

$$\text{WCp*Me}_2\text{(CH)} + \text{WCp*Me}_5 \rightarrow \text{Cp*Me}_2\text{W(}\mu\text{-CHMe)WCp*Me}_4 \qquad (10)$$

$$\text{Cp*Me}_2\text{W(}\mu\text{-CHMe)WCp*Me}_4 \xrightarrow{-\text{CH}_4} \text{Cp*Me}_2\text{W(}\mu\text{-CMe)WCp*Me}_3 \qquad (11)$$

$$\text{Cp*Me}_2\text{W(}\mu\text{-CMe)WCp*Me}_3 \xrightarrow{-2\text{CH}_4} \mathbf{1} \qquad (12)$$

be noted that a terminal ethylidyne ligand forms when WMe$_6$ decomposes in the presence of PMe$_3$.[24] It was postulated that a methyl group transferred to a terminal methylidyne ligand to give an incipient ethylidene ligand which then lost an α-hydrogen atom to give methane. Unfortunately there are no more details available about the WMe$_6$ decomposition than there are about the WCp*Me$_5$ decomposition, so all such proposals are unsubstantiated at this point.

The proposition that the ethyl ligand in **3** forms by migration of a methyl group to a methylene ligand is attractive since alkyl migration to an alkylidene ligand has been proposed in a number of systems,[36,37] the best documented being bis(cyclopentadienyl) complexes of tungsten,[37a] tantalum,[37b] and niobium.[37b] Alkyl migration to an alkylidene ligand can be viewed as a reduction of the metal, especially in high oxidation state alkylidene complexes where the alkylidene ligand can be viewed as a dianion. In this case the result of methyl alkylidene ligand can be viewed as a dianion. In this case the result of methyl migration in WCp*Me$_3$(CH$_2$) is intermediate WCp*Me$_2$Et. It is remarkable to us that the ethyl ligand not only then survives intermolecular reactions between WCp*Me$_2$Et and WCp*Me$_3$(CH$_2$) but also perhaps gives rise to the μ-ethylidyne ligand in **1a** by preferentially

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(28) (a) Fellmann, J. D. Ph.D. Thesis, MIT, 1980. (b) See: Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359, for a related, stable alkyl complex.

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(32) Wengrovius, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148.

(33) Aguero, A.; Kress, J.; Osborn, J. *J. Chem. Soc., Chem. Commun.* **1985**, 793.

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(35) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342.

(36) (a) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43. (b) Holmes, S. J.; Clark, D. J.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6322.

(37) (a) Jernakoff, P.; Cooper, N. J. *Organometallics* **1986**, *5*, 747 and references therein. (b) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. (c) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984.

losing two α-hydrogen atoms. If we assume that incipient $\mathrm{WCp^*Me_2Et}$ reacts with the pool of $\mathrm{WCp^*Me_3(CH_2)}$ and that the methylene ligand gives rise to a methylidyne ligand, then the likelihood of forming a second methylidyne ligand is five times greater than forming an ethylidyne ligand (all else being equal), approximately what is observed. Preferential loss of α-hydrogen atoms from an ethyl ligand would not be unprecedented; for several years Cooper has been studying similar phenomena in tungsten bis(byclopentadienyl) complexes.[38] The fact that the reaction shown in eq 13 must occur to only a small extent, if at all, could

$$\mathrm{WCp^*Me_2Et + WCp^*Me_3(CH_2)} \xrightarrow{-\mathrm{C_2H_6}} \mathrm{Cp^*Me_2W(\mu\text{-}CH)WCp^*Me_3} \quad (13)$$

be explained on steric grounds; i.e., methane formation is simply much faster than ethane formation. For this reason the decomposition sequence that gives $\mathrm{(WCp^*Me)(WCp^*Et)(\mu\text{-}CH)_2}$ then falls into the same class as that which yields **1**; each consists of methane formation plus a single methyl migration to give a $\mathrm{C_2}$ ligand that is retained in the final product.

Experimental Section

General experimental procedures can be found elsewhere.[9]

NMR data are listed vs. $\mathrm{Me_4Si}$ at 250–300-MHz ^{1}H. Routine aliphatic coupling constants and obvious multiplicities are not listed.

Cyclic voltammetric measurements were performed with a Princeton Applied Research (PAR) Model 175 Universal programmer, a PAR Model 173 potentiostat, and a Model 179 digital coulometer. A PAR Model RE0089 X-Y recorder was used to record cyclic voltammograms with scan rates up to 1 V s^{-1}. Cyclic voltammograms with scan rates greater than 1 V s^{-1} were recorded with a Tektronix type 549 storage oscilloscope. Measurements were made in the three electrode configuration with a platinum auxiliary electrode, an Ag/Ag$^+$ reference electrode, and either a 0.016-in. platinum wire, or a 25-μm platinum wire (sealed in a soft glass pipette and contacted with mercury) working electrode. A small amount of ferrocene was added at the end of each experiment as a reference.

NMR band shapes were calculated by using the DNMR4 program of Bushweller et al. (Quantum Chemistry Program Exchange No. 466).

Preparation of $\mathrm{[WCp^*Cl_4]_2}$. A solution of $\mathrm{WCp^*(CO)_3Me}$[10] (10.0 g, 23.9 mmol) in 20 mL of dichloromethane was added dropwise over 20 min at 25 °C to a stirred suspension of $\mathrm{PCl_5}$ (12.45 g, 59.8 mmol) in 40 mL of dichloromethane. Carbon monoxide evolved, and the solution turned orange and eventually red. The solution was then refluxed for 6 h. Orange $\mathrm{[WCp^*Cl_4]_2}$ was filtered off, washed with dichloromethane, THF, and ether, and dried to give 9.9 g of product (90% yield). It can be used in later reactions as is or sublimed (with difficulty on a small scale) at 200 °C (<0.005 μm): ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 13.48 (br, $\mathrm{C_5Me_5}$); EPR ($\mathrm{CH_2Cl_2}$) $g = 1.92$, $w_{1/2} = 50$ G. Anal. Calcd for $\mathrm{WC_{10}H_{15}Cl_4}$: C, 26.06; H, 3.28; Cl, 30.77. Found: C, 26.30; H, 3.38; Cl, 29.27.

Preparation of $\mathrm{WCp^*Cl_4(PMe_3)}$. $\mathrm{[WCp^*Cl_4]^2}$ (2.0 g, 4.3 mmol) was placed in dichloromethane (20 mL) and $\mathrm{PMe_3}$ (883 μL, 8.6 mmol) was added. $\mathrm{[WCp^*Cl_4]_2}$ dissolved to give a green solution. After 2 h the solvent was removed in vacuo to give 2.14 g (92%) of $\mathrm{WCp^*Cl_4(PMe_3)}$. It may be recrystallized from toluene: ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ −5.75 (br, $\mathrm{C_5Me_5}$), −7.42 (br, $\mathrm{PMe_3}$); EPR (toluene) $g = 1.90$, width at half height = 64 G. Anal. Calcd for $\mathrm{WC_{13}H_{24}Cl_4P}$: C, 29.08; H, 4.51; Cl, 26.41. Found: C, 29.42; H, 4.48; Cl, 25.64.

Preparation of $\mathrm{WCp^*Me_4}$. (a) Using $\mathrm{ZnMe_2}$. $\mathrm{[WCp^*Cl_4]_2}$ (7.0 g, 15.2 mmol) was placed in dichloromethane (50 mL), and excess $\mathrm{PMe_3}$ (2 mL, 19.7 mmol) was added. After 1 h the solvent was removed in vacuo. The green solid was placed in toluene (200 mL), and $\mathrm{ZnMe_2}$ (8.4 mL, 122 mmol) was added all at once. In 20 s the solution was yellow. After 2 h, the solution was filtered and the solvent was removed in vacuo. The solid was extracted with pentane, and the combined extracts were filtered. Pentane was removed stepwise in vacuo, giving 5.06 g (88%) of yellow $\mathrm{WCp^*Me_4}$ that is pure enough for subsequent reactions. It may be recrystallized from pentane: ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 39.70 (br, $\mathrm{C_5Me_5}$); EPR (pentane) $g = 2.01$, width at half height = 220 G. Anal. Calcd for $\mathrm{WC_{14}H_{27}}$: C, 44.34; H, 7.18; Cl, 0. Found: C, 44.01; H, 6.66; Cl, <0.5.

(b) Using MeMgCl. A 2.8 M solution of MeMgCl (3.10 mL, 8.68 mmol) was diluted to 30 mL with THF. This solution was stirred as $\mathrm{[WCp^*Cl_4]_2}$ (1.0 g, 2.17 mmol) was added slowly as a solid. After 30 min, the solvent was removed in vacuo and the residue was extracted with pentane. The solution was filtered, and solvent was removed stepwise in vacuo to give 767 mg (93%) of $\mathrm{WCp^*Me_4}$.

$\mathrm{WCp^*(CD_3)_4}$ can be prepared by treating $\mathrm{[WCp^*Cl_4]_2}$ with $\mathrm{CD_3MgI}$ in the manner described above.

Preparation of $\mathrm{[WCp^*Me_4][PF_6]}$. $\mathrm{WCp^*Me_4}$ (2.96 g, 7.8 mmol) was placed in 50 mL of dichloromethane. $\mathrm{[FeCp_2][PF_6]}$[39] (2.48 g, 7.5 mmol) was added as a solid slowly to this stirred solution. After addition was complete (~10 min), the reaction was stirred 2 h or until the blue $\mathrm{[FeCp_2][PF_6]}$ had been consumed. Ether (50 mL) was added to the reaction mixture, and the yellow microcrystalline solid that formed was filtered off, washed with dichloromethane and ether, and dried (yield 3.63 g, 89%). The compound is pure enough for most purposes. It can be recrystallized in small amounts by dissolving it in dichloromethane and placing an open vial of this solution in a larger closed vial containing ether. The ether is allowed to diffuse into the solution at −30 °C: ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 300 MHz) δ 3.35 (broad lump, 1, $\mathrm{WMe_{ax}}$), 2.06 (s, 5, $\mathrm{C_5Me_5}$), 1.58 (broad lump, 3, $\mathrm{WMe_{eq}}$); ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 300 MHz, 213 K) δ 3.26 (m, 1, $J_{HH} = 2$, $\mathrm{WMe_{ax}}$), 1.99 (s, 5, $\mathrm{C_5Me_5}$), 1.50 (q, 3, $J_{HH} = 2$, $\mathrm{WMe_{eq}}$); ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 67.9 MHz) δ 122.52 ($C_5\mathrm{Me_5}$), 80 (br, WMe), 11.17 ($\mathrm{C_5}Me_5$); ^{31}P NMR ($\mathrm{CD_2Cl_2}$, 109 MHz) δ −144.4 (sept, $J_{PF} = 713$ Hz); ^{19}F NMR ($\mathrm{CD_2Cl_2}$, 235.4 MHz, $\mathrm{CFCl_3}$ = 0 ppm) δ 65.97 (d, $J_{FP} = 711$ Hz). Anal. Calcd for $\mathrm{WC_{14}H_{27}PF_6}$: C, 32.08; H, 5.19; P, 5.91. Found: C, 32.56; H, 5.29; P, 5.69.

$\mathrm{[WCp^*(CD_3)_4][PF_6]}$ was synthesized via the oxidation of $\mathrm{WCp^*(CD_3)_4}$.

Reduction of $\mathrm{[WCp^*Me_4][PF_6]}$ with Sodium Amalgam. $\mathrm{[WCp^*Me_4][PF_6]}$ (0.2 g, 0.38 mmol) was placed in THF (5 mL). Sodium amalgam (2.13 g, 0.41%, 0.38 mmol) was added, and the solution was stirred for 4 h. The solution was filtered, and solvent was removed in vacuo. The solid was extracted with pentane, and the solution was filtered. Removal of solvent gave 0.13 g of $\mathrm{WCp^*Me_4}$ (90%) which was identified by comparison of its EPR and IR spectra with those of authentic material.

Preparation of $\mathrm{WCp^*Me_5}$. $\mathrm{[WCp^*Me_4][PF_6]}$ (1.0 g, 1.91 mmol) was placed in 50 mL of ether. A solution of LiMe (1.91 mmol) in ether was added dropwise at room temperature. The solution immediately turned deep red as all the solids entered into solution. The solvent was removed, and the red solid was extracted with pentane. The extract was filtered, and the solvent was removed from the filtrate to give 0.69 g (92%) of $\mathrm{WCp^*Me_5}$. Recrystallization from ether at −40 °C gave small red needles: ^{1}H NMR ($\mathrm{C_6D_6}$, 250 MHz) δ 1.28 (s, 15, $\mathrm{C_5Me_5}$), 0.83 (broad lump, WMe); ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 250 MHz) δ 1.73 (s, 15, $\mathrm{C_5Me_5}$), 0.36 (broad lump, WMe); ^{1}H NMR (toluene-d_8, 250 MHz, 193 K) δ 1.20 (s, 15, $\mathrm{C_5Me_5}$), 0.71 (s, 12, $\mathrm{WMe_{eq}}$), 2.63 (s, 3, $\mathrm{WMe_{ax}}$); ^{1}H NMR (toluene-d_8, 250 MHz, 343 K) δ 1.37 (s, 15, $\mathrm{C_5Me_5}$), 0.87 (s, 15, WMe); ^{13}C{^{1}H} NMR (toluene-d_8, 67.9 MHz, 230 K) δ 9.65 ($\mathrm{C_5}Me_5$), 112.92 ($C_5\mathrm{Me_5}$), 54.9 ($\mathrm{WMe_{eq}}$), 79.15 ($\mathrm{WMe_{ax}}$).

$\mathrm{WCp^*(CD_3)_5}$ was prepared by addition of $\mathrm{LiCD_3}$ to $\mathrm{[WCp^*(CD_3)_4][PF_6]}$.

Reaction of $\mathrm{WCp^*Me_5}$ with $\mathrm{HBF_4}$. $\mathrm{WCp^*Me_5}$ (0.15 g, 0.38 mmol) was placed in 10 mL of ether, and $\mathrm{HBF_4{\cdot}Et_2O}$ (0.13 g in 5 mL of ether) was added dropwise over 2 min. The solution was stirred for 1 h, and 0.07 g (40%) of $\mathrm{[WCp^*Me_4][BF_4]}$ was isolated. It was identified on the basis of comparison of its NMR and IR spectra with those of $\mathrm{[WCp^*Me_4][PF_6]}$.

Reaction of $\mathrm{WCp^*Me_5}$ with $\mathrm{[CPh_3][BF_4]}$. $\mathrm{WCp^*Me_5}$ (20 mg, 0.051 mmol), $\mathrm{[CPh_3][BF_4]}$ (17 mg, 0.051 mmol), and ferrocene (19 mg, 0.102 mmol) were combined in $\mathrm{CD_2Cl_2}$. An ^{1}H NMR spectrum showed $\mathrm{[WCp^*Me_4]^+}$ and $\mathrm{CPh_3Me}$ to be formed in ~93% yield (vs. ferrocene standard).

Kinetic Studies of the Decomposition of $\mathrm{Cp^*WMe_5}$. The disappearance of the Cp* signal in the ^{1}H NMR spectrum of $\mathrm{WCp^*Me_5}$ in $\mathrm{C_6D_6}$ was monitored vs. ferrocene as the internal standard. Probe temperatures were calibrated with methanol and ethylene glycol. The data consisted of three runs at 25 °C, four at 40 °C, and one at 60 °C. R factors were >0.997 in each case over at least 3 half-lives of $\mathrm{WCp^*Me_5}$. The R factor in the Arrhenius plot was 0.999. The decomposition of $\mathrm{WCp^*(CD_3)_5}$ was followed in an analogous fashion at 25 and 60 °C. At 25 °C $k = 3.68 \times 10^{-6}$ s^{-1} ($R = 0.993$) and at 60 °C $k = 6.63 \times 10^{-4}$ s^{-1} ($R = 0.996$) for values of $k_H/k_D = 6 \pm 1$ (at 25 °C) and 2 ± 1 (at 60 °C).

Preparation of $\mathrm{(WCp^*Me)_2(\mu\text{-}CH)(\mu\text{-}CMe)}$ (1a). $\mathrm{[WCp^*Me_4][PF_6]}$ (1 g, 1.91 mmol) was converted into $\mathrm{WCp^*Me_5}$ via the procedure described above. The $\mathrm{WCp^*Me_5}$ was taken up in 50 mL of toluene, and this solution was heated in a Schlenk tube in the dark at 60 °C for 2 h. The solvent was removed in vacuo, and the residue was extracted with

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[38] (a) Hayes, J. C.; Jernakoff, P.; Miller, G. A.; Cooper, N. J. *Pure Appl. Chem.* **1984**, *56*, 25. (b) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570. (c) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648.

[39] Nesmeyanov, A. N.; Materikova, R. B.; Lyatifov, I. R.; Kurbanov, T. K.; Kochetkova, N. S. *J. Organomet. Chem.* **1978**, *145*, 241.

minimal pentane. This sample was loaded onto a silica column (Alfa silica gel, 70 μm, dried in vacuo 24 h). WCp^*Me_4 (0.03 g, 4%)) was recovered by using pentane as the eluant. $(WCp^*Me)_2(\mu\text{-}CH)(\mu\text{-}CMe)$ was recovered by using ether as the eluant and recrystallized from ether (yield 0.26 g, 38%). (See Table I for NMR data.) Mass spectrum, *m/e* 708 with correct isotope pattern (simulated). Anal. Calcd for $W_2C_{25}H_{40}$: C, 42.39; H, 5.69. Found: C, 42.18; H, 5.76.

"*trans*"-$(WCp^*Me)_2(\mu\text{-}CH)(\mu\text{-}CMe)$ was identified only by NMR in situ (see Table I).

Preparation of $[(WCp^*Me)(\mu\text{-}CMe)]_2$ (2). $(WCp^*Me)_2(\mu\text{-}CMe)(\mu\text{-}CH)$ (0.20 g, 0.20 mmol) was dissolved in 20 mL of diethyl ether. While this solution was stirred, 5.65 mmol of LiMe in ether was added. After 2 h, the solvent was removed and the residue was extracted with pentane. The solution was filtered, and solvent was removed to yield 0.186 g (91%) of $[(WCp^*Me)(\mu\text{-}CMe)]_2$. (See Table I for NMR data.) Anal. Calcd for $WC_{13}H_{18}$: C, 43.23; H, 5.97. Found: C, 42.44, 44.41; H, 5.87, 6.12.

Preparation of $(WCp^*Me)(WCp^*Et)(\mu\text{-}CH)_2$ (3). $[WCp^*Me_4][PF_6]$ (0.6 g, 0.95 mmol) was added to 10 mL of dichloromethane, and the slurry was cooled to −78 °C. NEt_3 (0.24 g, 133 μL, 0.95 mmol) in 5 mL of dichloromethane was added dropwise while the slurry was stirred. All the $[WCp^*Me_4][PF_6]$ dissolved to give a pale translucent orange solution. Upon warming to room temperature, the solution turned green. The solvent was removed, and the residue was extracted with pentane. Examination of this crude product by ^1H NMR showed it to consist of a 1:6 mixture of $(WCp^*Me)_2(\mu\text{-}CH)(\mu\text{-}CMe)$ and $(WCp^*Me)(WCp^*Et)(\mu\text{-}CH)_2$. The crude sample was loaded onto a silica column. Cp^*WMe_4 (0.069 g, 19%) was recovered by using pentane as the eluant. $(WCp^*Me)(WCp^*Et)(\mu\text{-}CH)_2$ (0.101 g, 30%) was recovered by using ether as the eluant. At room temperature a similar reaction yielded a 1:3 mixture of $(WCp^*Me)_2(\mu\text{-}CH)(\mu\text{-}CMe)$ and $(WCp^*Me)(WCp^*Et)(\mu\text{-}CH)_2$ (by NMR of the crude product in C_6D_6). (See Table I for NMR data.)

Generation of $WCp^*Me_3(CH_2)$. $[WCp^*WMe_4][PF_6]$ (0.2 g, 0.38 mmol for ^{13}C NMR; 0.05 g, 0.095 mmol for ^1H NMR) was added to an NMR tube that had been attached to a ground-glass joint. On a high vacuum line, NEt_3 (0.038 g, 53 μL, 0.38 mmol for ^{13}C NMR; 0.0024 g, 13 μL, 0.095 mmol for ^1H NMR) was transferred into the NMR tube. The NMR tube was then sealed and introduced into a precooled probe: ^1H NMR (CD_2Cl_2, 195 K, 300 MHz) δ 1.79 (s, 15, C_5Me_5), 0.61 (s, 6, WMe_{cis}), 0.68 (s, 3, WMe_{trans}), 4.53 (br, $W{=}CH_AH_B$), 9.77 (br, $W{=}CH_AH_B$); ^1H NMR (CD_2Cl_2, 265 K, 300 MHz) δ 1.84 (s, 15, C_5Me_5), 0.72 (s, 6, WMe_{cis}), 0.79 (s, 3, WMe_{trans}), 7.3 (v br, $W{=}CH_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 67.9 MHz, 213 K) δ 105.27 (C_5Me_5), 10.26 (C_5Me_5), 31.26 (J_{CH} = 125 Hz, J_{CW} = 54 Hz, WMe_{cis}), 36.90 (J_{CH} = 121 Hz, WMe_{trans}), 254.22 (dd, J_{CH} = 110 158 Hz, $W{=}CH_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 67.9 MHz, 233 K) δ 105.74 (C_5Me_5), 10.64 (C_5Me_5), 32.01 (WMe_{cis}), 57.69 (WMe_{trans}), 255.95 (t, J_{CH} = 135 Hz $W{=}CH_2$).

Kinetic Studies of the Decomposition of $WCp^*Me_3(CH_2)$. $WCp^*Me_3(CH_2)$ was generated in an NMR tube at −78 °C as described above. The NMR tube was sealed and introduced into a precooled probe. The temperature of the probe was raised to 0 °C, and the disappearance of the methylene signal in the ^1H NMR spectrum of $WCp^*Me_3(CH_2)$ in CD_2Cl_2 was monitored vs. mesitylene ring protons as the internal standard.

Reaction of $WCp^*Me_3(CH_2)$ with C_6F_5OH. An orange solution of $WCp^*Me_3(CH_2)$ (0.95 mmol) was generated at −78 °C as described in the preparation of $(WCp^*Me)(WCp^*Et)(\mu\text{-}CH)_2$ (**3**). C_6F_5OH (0.18 g, 0.98 mmol) in 5 mL of dichloromethane was added dropwise. Upon warming to room temperature, the solution remained orange. The solvent was removed, and the residue was extracted with pentane. Crystallization from a mixture of pentane and ether yielded 0.51 g of $WCp^*Me_4(OC_6F_5)$ (95%): ^1H NMR (C_6D_6, 300 MHz) δ 1.50 (s, 3, WMe_{ax}), 1.39 (s, 15, C_5Me_5), 1.25 (s, 6, WMe_{cis}), 0.02 (s, 3, WMe_{trans}); ^1H NMR (CD_2Cl_2, 300 MHz) δ 1.84 (s, 15, C_5Me_5), 1.00 (s, 9, MWe_{cis} and WMe_{ax}), −0.31 (s, 3, WMe_{trans}); $^{13}C\{^1H\}$ NMR (C_6D_6, 67.9 MHz) δ 9.76 (C_5Me_5), 118.36 (C_5Me_5), 75.32 (J_{CW} = 71 Hz, WMe_{ax}), 49.30 (J_{CW} = 53 Hz, WMe_{cis}), 38.71 (J_{CW} = 48 Hz, WMe_{trans}), 136, 140, 132.8 (m, OC_6F_5); ^{19}F NMR (C_6D_6, 282 MHz) δ −159.41 (d, 2, J_{FF} = 49 Hz, F_{ortho}), −165.94 (d, 2, J_{FF} = 46 Hz, F_{meta}), −170.66 (t, 1, J_{FF} = 24 Hz, F_{para}). Anal. Calcd for $WC_{20}H_{27}OF_5$: C, 42.72; H, 4.84. Found: C, 42.90; H, 5.00.

$WCp^*Me_4(OC_6F_5)$ also can be prepared in virtually quantitative yield by treating $[WCp^*Me_4][PF_6]$ (0.050 g, 0.095 mmol) with KOC_6F_5 (0.020 g, 0.095 mmol) in diethyl ether.

The reaction between $WCp^*Me_3(CH_2)$ and C_6F_5OD was monitored by both ^1H and ^2H NMR. $WCp^*Me_3(CH_2)$ (0.095 mmol) was generated at −78 °C in CD_2Cl_2 for proton and CH_2Cl_2 for deuterium NMR. C_6F_5OD (0.018 g, 0.098 mmol) in 0.2 mL of dichloromethane was introduced via syringe. Each NMR tube was sealed and introduced into a precooled probe. The probe temperature was raised slowly, and ^1H and ^2H spectra were recorded periodically. The reaction proceeded at a convenient rate at ∼−30 °C.

Reaction of $(WCp^*Me)(WCp^*Et)(\mu\text{-}CH)_2$ (3) with Methyllithium. $(WCp^*Me)(WCp^*Et)(\mu\text{-}CH)_2$ (0.20 g, 0.28 mmol) was dissolved in 20 mL of diethyl ether. While this solution was stirred, 5.65 mmol of LiMe in ether was added. After 7 h the solvent was removed and the residue was extracted with pentane. The solution was filtered, and solvent was removed to yield *cis*-$[(WCp^*Me)(\mu\text{-}CMe)]_2$ (**2a**) and $(WCp^*Me)_2(\mu\text{-}CMe)(\mu\text{-}CEt)$. ^1H NMR of latter in C_6D_6: δ 1.88 (s, 15, C_5Me_5), −0.70 (s, 6, WMe), 4.02 (s, 3, μ-CMe), 4.66 (q, 2, $\mu\text{-}CCH_2CH_3$), 0.99 (t, 3, $\mu\text{-}CCH_2CH_3$).

X-ray Structure of $[WCp^*Me_4][PF_6]$. X-ray data were collected at −65° on an Enraf-Nonius CAD4F-11 diffractometer equipped with a liquid-nitrogen low-temperature device and using Mo Kα radiation. Data collection, reduction, and refinement procedures have been described elsewhere.[40] An absorption correction was applied by use of the program ORABS. A total of 1158 reflections ($+h,+k,+l$) were collected in the range $3° \le 2\theta \le 55°$ with the 1035 having $I_o > 2\sigma(I_o)$ being used in the structure refinement which was by full-matrix least-squares techniques (60 variables) using SHELX-76. Final R_1 = 0.059 and R_2 = 0.058. Hydrogen atoms were ignored, and only the W and P atoms were refined anisotropically. The final difference-Fourier map showed no chemically significant features. The Cp* ligand and the PF_6^- ion appear to be disordered. Data were collected on three separate occasions on three different crystals, but the refinement of the structure was never completely satisfactory. The choices of space group are *Cmcm*, *Cmc*2$_1$, and *C*2*cm*. The centrosymmetric *Cmcm* would require the W atom to sit on a special position having *mm* or 2/*m* symmetry which is impossible for the molecule under study. The P atom, which is large enough to appear unambiguously no matter which space group is assumed, has the same *x* coordinate as the W atom, but a different *z* coordinate. Therefore it cannot lie on a mirror plane perpendicular to *C*, and *C*2*cm* thereby can be ruled out. The structure is reported in space group *Cmc*2$_1$. Crystal data: a = 8.880 (4) Å, b = 22.364 (5) Å, c = 8.970 (6) Å, V = 1781.4 Å^3, Z = 4, mol wt = 532.3 g, ρ(calcd) = 1.985 g cm^{-3}, μ = 63.0 cm^{-1}.

X-ray Structure of $(WCp^*Me)_2(\mu\text{-}CMe)_2$ (2a). X-ray data were collected at 25 °C on an Enraf-Nonius CAD4F-11 diffractometer using Mo Kα radiation. Details of the data collection, reduction, and refinement procedures were similar to those described elsewhere.[40] A total of 3985 reflections ($\pm h,+k,+l$) were collected in the range $3° < 2\theta < 40°$, yielding 1175 reflections averaged over 2/*m* symmetry, with the 1036 having $I_o > 2\sigma(I_o)$ being used in the structure refinement which was by full-matrix least-squares techniques (148 variables) using SHELX-76. A linear correction for the decrease in intensity was made (maximum decay ≈ 5%). Final R_1 = 0.036 and R_2 = 0.043. Hydrogen atoms were placed in calculated positions (C–H = 0.95 Å), and all remaining atoms were refined anisotropically. The largest peak on the final difference Fourier map was 0.76 e Å^{-3}. Crystal data: a = 21.295 (13) Å, b = 8.860 (2) Å, c = 13.856 (3) Å, β = 106.54 (3)°, V = 2506.1 Å^3, space group *C*2/*c*, Z = 4, mol wt = 2889.5 g, ρ(calcd) = 1.914 g cm^{-3}, μ = 87.5 cm^{-1}. No absorption correction was applied.

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Supplementary Material Available: A table of final coordinates for $[WCp^*Me_4][PF_6]$ and a table of final coordinates and thermal parameters for $(WCp^*Me)_2(\mu\text{-}CMe)_2$ (2 pages); listings of observed and calculated structure factors for $(WCp^*Me)_2(\mu\text{-}CMe)_2$ and $[WCp^*Me_4][PF_6]$ (10 pages). Ordering information is given on any current masthead page.

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[40] Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379.