A small value for the zero-field-splitting parameter, D, is seemingly associated with the very broad NMR resonances observed for the $(TPP)FeO_2^-$ complex. Proton[9b,25] and carbon-13[26,27] NMR studies have served to demonstrate modulation of line widths through zero-field splitting of the otherwise isotropic d^5 ion. Axial coordination by two ligands makes the iron porphyrin pseudooctahedral, and thus the ligand field is more nearly isotropic. In this regard, coordination by peroxo and solvent ligands is expected to induce the small zero-field slitting associated with severe NMR line broadening. The essentially linear Curie law plot is also supportive of small zero-field splitting, as the quadratic temperature dependence for induced dipolar shifts leads to curvature of the Curie plot for other weak-field anionic ligands.[25,28] A value considerably less than the $D = 5.9$ cm^{-1} measured for (TPP)FeCl[29] is expected for $(TPP)FeO_2^-$. Although D is diminished in $(TPP)FeO_2^-$ due to an increased axial ligand field, a sizeable rhombic perturbation (as represented by the zero-field-splitting parameter E) may be invoked to explain the ESR $g = 2$, 4.2, and 8 values.[5] A ratio of $E/D \approx 0.1$ is necessary to produce a rhombic $g = 4$ signal, and the lower D value thus effectively contributes to the rhombicity. Differing pyrrole deuterium linewidths for Me_2SO and acetonitrile solvents may be explained by presence or absence of a coordinated solvent ligand or by specific solvation of the peroxo ligand.

In conclusion, one must ask why the superoxide anion serves as an oxidizing agent for the iron(II) porphyrin but seemingly does not oxidize the manganese(II) analogue. A clear explanation is not found in available redox potential differences. For example, the M(III) → M(II) potentials for chloro complexes of Fe(III) and Mn(III) tetraphenylporphyrins in methylene chloride solvent are −0.29[30] and −0.33 V[31] (vs. SCE), respectively. Potentials are dependent on the nature of the anionic ligand, however, and it would be of interest to measure values for the peroxo and superoxo complexes. The role of solvent coordination at the second axial site may well be important in controlling electron transfer to a coordinated superoxo ligand. In this regard, it should be noted that both manganese(II) and manganese(III) porphyrins show a preference for five-coordination,[31] whereas the iron derivatives will certainly bind appropriate solvent ligands.[22]

Acknowledgment. Support from NIH grant GM 28831-02 and NSF grant CHE 79-10305 is gratefully acknowledged. We wish to thank Mr. Arden Boersma and Mr. Scott Wright for preparation of selected deuterated porphyrins.

Registry No. $(TPP)FeO_2^-$, 83160-26-3; (TPP)FeCl, 16456-81-8; $(TPP)Fe(Me_2SO)_2^+$, 68179-07-7; $(TPP)MnO_2^-$, 83160-27-4; $(TPP)Mn(Me_2SO)^+$, 83160-28-5; $(TPP)Mn(Me_2SO)$, 83160-29-6; (TPP)MnCl, 32195-55-4; KO_2, 12030-88-5; D_2, 7782-39-0.

(25) (a) La Mar, G. N.; Eaton, G. R.; Holm, R. H.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 63-75. (b) Walker, F. A.; La Mar, G. N. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 328-348.
(26) Mispelter, J.; Momenteau, M.; Lhoste, J.-M. *J. Chem. Soc., Dalton Trans.* **1981**, 1729-1734.
(27) Goff, H. M.; Shimomura, E. T.; Phillippi, M. A. *Inorg. Chem.*, in press.
(28) Behere, D. V.; Birdy, R.; Mitra, S. *Inorg. Chem.* **1982**, *21*, 386-390.
(29) (a) Behere, D. V. Marathe, V. R.; Mitra, S. *J. Am. Chem. Soc.* **1977**, *99*, 4149-4150. (b) Behere, D. V.; Birdy, R.; Mitra, S. *Inorg. Chem.* **1981**, *20*, 2786-2789.
(30) Bottomley, L. A.; Kadish, K. M. *Inorg. Chem.* **1981**, *20*, 1348-1357.
(31) Kadish, K. M.; Kelly, S. *Inorg. Chem.* **1979**, *18*, 2968-2971.
(32) Phillippi, M. A.; Shimomura, E. T.; Goff, H. M. *Inorg. Chem.* **1981**, *20*, 1322-1325.
(33) Gans, P.; Marchon, J.-C.; Reed, C. A.; Regnard, J.-R. *Nouv. J. Chim.* **1981**, *5*, 203-204.
(34) La Mar, G. N.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 1782-1790.
(35) Goff, H. M.; La Mar, G. N. *J. Am. Chem. Soc.* **1977**, *99*, 6599-6606.
(36) Wayland, B. B.; Mehne, L. F.; Swartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 2379-2383.

α-Hydride Elimination from Methylene and Neopentylidene Ligands. Preparation and Protonation of Tungsten(IV) Methylidyne and Neopentylidyne Complexes[1]

S. J. Holmes, D. N. Clark, H. W. Turner, and R. R. Schrock*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received December 22, 1981*

Abstract: $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(dmpe)$ (dmpe = $Me_2PCH_2CH_2PMe_2$) reacts with dmpe to give 2,2,5,5-tetramethyl-*trans*-3-hexene and $W(CCMe_3)(dmpe)_2(H)$. Addition of HCl to $W(CCMe_3)(dmpe)_2(H)$ yields $W(CCMe_3)(dmpe)_2Cl$. $W(CCMe_3)(PMe_3)_4Cl$ can be prepared by reducing $W(CCMe_3)(PMe_3)_3Cl_3$ in the presence of PMe_3. The reaction between $WCl_2(PMe_3)_4$ and $AlMe_3$ gives $W(CH)(PMe_3)_4Cl$, which, when treated with dmpe, yields $W(CH)(dmpe)_2Cl$. Protonation of $W(CR)(dmpe)_2Cl$ (R = H or CMe_3) yields cationic, pentagonal bipyramidal methylidyne hydride and neopentylidyne hydride complexes, $[W(CR)(H)(dmpe)_2Cl]^+$. In the case where R = H, the hydride and methylidyne protons exchange intramolecularly at 25 °C on the NMR time scale. Protonation of $W(CR)(PMe_3)_4Cl$ with CF_3SO_3H yields grossly distorted methylene and neopentylidene complexes because (it is believed) four PMe_3 ligands cannot, for steric reasons, form a pentagonal-bipyramidal molecule with four PMe_3 ligands and a hydride in the pentagonal plane. Protonation of $W(CH)(PMe_3)_4Cl$ with HCl yields pentagonal-bipyramidal $W(CH)(H)(PMe_3)_3Cl_2$. An analogous complex, $W(CH)(H)(PMe_3)_3(Cl)(BH_3CN)$, can be prepared by reacting $[W(CH_2)(PMe_3)_4Cl]^+CF_3SO_3^-$ with $NaBH_3CN$. These results suggest that under the right circumstances "α-hydride elimination" from an alkylidene ligand to give an alkylidyne ligand is facile and reversible but that sometimes formation of a distorted alkylidene (including methylene) is as far as the α-elimination reaction can proceed. The driving force for α elimination can be viewed as an oxidation of "tungsten(IV)" to "tungsten(VI)".

The first isolated "tungsten(VI)" alkylidene complex was $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)L_2$ (L = PMe_3 or 0.5dmpe).[2] Now oxo alkylidene complexes[3a] such as $W(O)(CHR)(PMe_3)_2Cl_2$ (R = H, Pr, Ph, CMe_3) and analogous imido alkylidene complexes[3b] have been prepared and characterized. In each type of complex the distortion of the alkylidene ligand (which is characterized by a small M=C—H angle and a low value for J_{CH_α}[4])

(1) Multiple Metal-Carbon Bonds. 26. For part 25, see ref 23.
(2) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774.
(3) (a) Wengrovius, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148. (b) Pedersen, S.; Schrock, R. R., in press.

0002-7863/82/1504-6322$01.25/0

is minimal. But in each case an excellent π-electron donor ligand (neopentylidyne, oxo, or imido) is present, and tungsten is in the 6+ oxidation state (counting the alkylidene ligand as a dianion and the alkylidyne ligand as a trianion). Therefore, we were interested in preparing tungsten alkylidene complexes that did not contain a good π-electron donor and/or in which tungsten was not in the 6+ oxidation state. The discovery of a class of tungsten(IV) neopentylidyne and methylidyne complexes created the opportunity since protonation of these species could in theory yield cationic tungsten(IV) neopentylidene and methylene complexes, respectively. In this paper we report the preparation of four tungsten(IV) alkylidyne complexes of the type $W(CR)L_4Cl$ (R = H or CMe_3, L = PMe_3 or 0.5dmpe) and the results of such protonation reactions.[6]

Results

Preparation of $W(CCMe_3)(dmpe)_2H$. $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)$(dmpe) has been prepared by reacting dmpe with $W(CCMe_3)(CH_2CMe_3)_3$,[2] and it has been structurally characterized.[8] This reaction is one of the few examples of α-hydrogen abstraction in a W(VI) complex.[3b,4] We were interested in the possibility of further reaction with dmpe to yield a tungsten(VI) bis(neopentylidyne) complex by ligand-induced abstraction[9] of the neopentylidene α-hydrogen atom by the neopentyl group. $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)$(dmpe) does react further with dmpe at 140 °C in neat dmpe, but the product is not $W(CCMe_3)_2(dmpe)_2$. One equivalent of exclusively *trans*-$Me_3CCH{=}CHCMe_3$ is formed, and a pentane soluble, monomeric, yellow crystalline compound can be isolated essentially quantitatively by removing the dmpe in vacuo and purified by either recrystallization or sublimation. We propose that this molecule is a *trans*-neopentylidyne hydride complex (eq 1) on the

$$W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(dmpe) \xrightarrow[140\ °C]{dmpe} \textit{trans}\text{-}W(CCMe_3)(dmpe)_2(H) + 2,2,5,5\text{-tetramethyl-}\textit{trans}\text{-3-hexene} \quad (1)$$

basis of the following data. First, its ^1H NMR spectrum shows a 1:4:6:4:1 quintet (J_{HP} = 30 Hz) for the hydride ligand at −6.2 ppm which has ^{183}W satellite peaks (J_{HW} = 30 Hz), which collapses to a singlet on decoupling ^{31}P, and which is absent in the spectrum of the analogous compound prepared from $W(CCMe_3)(CDCMe_3)(CD_2CMe_3)$(dmpe). Second, we see a quintet (J_{CP} = 10 Hz, J_{CW} = 208 Hz) in the ^{13}C NMR spectrum at 280 ppm. The chemical shift and magnitude of the tungsten–carbon coupling are characteristic of a neopentylidyne ligand.[2] Third, the ^{31}P NMR spectrum shows only one signal and is temperature independent down to −80 °C. The only curious aspect of this compound is that we do not see a W–H or W–D stretching mode in the IR spectrum. This phenomenon is by no means unknown however.[10]

$W(CCMe_3)(CHCMe_3)(CH_2CMe_3)$(dmpe) reacts with neat PMe_3 at 150 °C in a sealed tube to give a 50% yield of *trans*-$W(CCMe_3)(dmpe)_2(H)$. We believe the mixed product, $W(CCMe_3)(dmpe)(PMe_3)_2(H)$, disproportionates to give the observed product and $W(CCMe_3)(PMe_3)_4(H)$, which must be thermally unstable at 150 °C.

$W(CCMe_3)(dmpe)_2(H)$ does not react readily with small molecules such as acetonitrile, ethylene, acetone, methyl iodide, isobutylene, or styrene.

Preparation of $W(CR)L_4Cl$ (R = H or CMe_3, L = PMe_3 or 0.5dmpe). $W(CCMe_3)(dmpe)_2(H)$ reacts with 1 equiv of gaseous HCl to give a pentane-soluble, yellow product that closely resembles $W(CCMe_3)(dmpe)_2(H)$ in its physical and spectroscopic properties, except for the fact that no hydride signal is present in its ^1H NMR spectrum. By mass spectroscopy and elemental analysis, it is clear that a chloride has replaced the hydride ligand (eq 2). Presumably hydrogen gas is formed, although we have never confirmed this.

$$W(CCMe_3)(dmpe)_2(H) + HCl \rightarrow W(CCMe_3)(dmpe)_2Cl + H_2 \quad (2)$$

A route to $W(CCMe_3)(PMe_3)_4Cl$ became feasible after the discovery of $W(CCMe_3)(PMe_3)_3Cl_3$.[11] $W(CCMe_3)(PMe_3)_4Cl$ can be prepared in high yield by reducing $W(CCMe_3)(PMe_3)_3Cl_3$ with sodium amalgam in the presence of trimethylphosphine (eq 3). $W(CCMe_3)(PMe_3)_4Cl$ is a pentane-soluble, yellow, crystalline

$$W(CCMe_3)L_3Cl_3 \xrightarrow[L]{2Na/Hg} W(CCMe_3)L_4Cl \qquad (L = PMe_3) \quad (3)$$

species that resembles $W(CCMe_3)(dmpe)_2Cl$ spectroscopically. It does not exchange PMe_3 ligands with free PMe_3 on the NMR time scale at 25 °C. We believe it has a structure analogous to that of the recently prepared $W(CCH_3)(PMe_3)_4(CH_3)$,[12] essentially a trans, octahedral complex in which the PMe_3 ligands are arranged in a puckered fashion alternatively above and below the WP_4 "plane".

A route to the first terminal methylidyne complex, an analogue of $W(CCMe_3)(PMe_3)_4Cl$, is shown in eq 4. The variable amounts

$$WCl_2(PMe_3)_4 \xrightarrow[2.\ 2tmeda]{1.\ 2AlMe_3} W(CH)(PMe_3)_4Cl \quad (60\%) \quad (4)$$

(0.9–1.2 equiv) of a gas that is formed in this reaction consist of 15–30% molecular hydrogen and 70–85% methane. Some chemistry we will see later suggests that a plausible method of forming at least some of the product is that shown in eq 5. The

$$W(CH_3)(Cl)L_4 \xrightarrow{-L} W(CH_2)(H)(Cl)L_3 \xrightarrow[+L]{-H_2} W(CH)L_4Cl \quad (5)$$

methane probably forms by disproportionation or dehydrohalogenation (by $AlMe_3$) of some intermediate methyl or methylene complex. Many other more complex reactions could ultimately yield $W(CH)(PMe_3)_4Cl$ and methane or hydrogen, but since the yield of $W(CH)(PMe_3)_4Cl$ is only moderate, we feel that any further speculation about how it forms is not yet justified. Spectroscopically, $W(CH)(PMe_3)_4Cl$ is similar to the neopentylidyne complexes. Its structure has recently been shown to be a distorted octahedral complex containing trans methylidyne and chloride ligands.[13a]

The fourth member of this set of alkylidyne complexes, $W(CH)(dmpe)_2Cl$, can be obtained as shown in eq 6. ^{31}P NMR spectra suggest that at least one intermediate is formed—a logical one is $W(CH)(PMe_3)_2(dmpe)Cl$—but we have never found conditions that produce high yields of any single intermediate.

$$W(CH)(PMe_3)_4Cl + 2dmpe \xrightarrow[PhCl]{110\ °C} W(CH)(dmpe)_2Cl \quad (6)$$

Protonation of $W(CR)(dmpe)_2Cl$ (R = CMe_3 or H). The addition of 1 equiv of HCl (gaseous or aqueous) to $W(CCMe_3)(dmpe)_2Cl$ yields a white, saltlike product that conducts in acetonitrile or dichloromethane and reacts with bases (including $W(CCMe_3)(dmpe)_2(H)$) to give $W(CCMe_3)(dmpe)_2Cl$ back again in high yield. An analogous reaction using CF_3CO_2H gives a similar product. We propose that each of these products contains

(4) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.
(5) Sharp, P. R.; Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 965.
(6) Part of this work has appeared in preliminary communications.[5,7]
(7) Holmes, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 4599.
(8) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454.
(9) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236.
(10) (a) *Adv. Chem. Ser.* **1978**, *No. 167*. (b) "Transition Metal Hydrides"; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971.
(11) Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3932.
(12) 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.
(13) (a) Churchill, M. R.; Rheingold, A. L.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 3392. (b) Churchill, M. R.; Wasserman, H. J.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 1710.

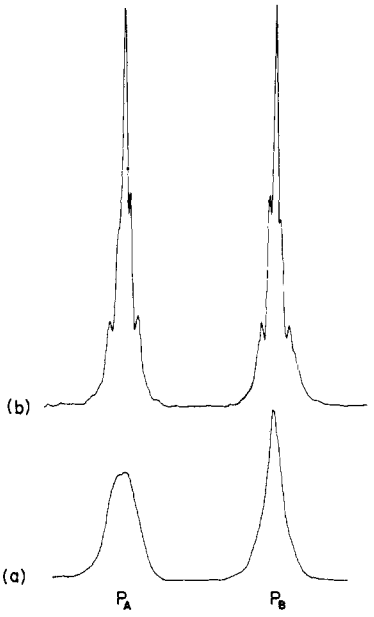
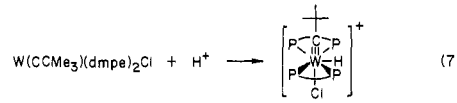


Figure 1. 190 K ^{31}P spectra of $[W(CCMe_3)(dmpe)_2(Cl)(H)]^+$: (a) ^1H coupled, (b) ^1H decoupled.

a cationic neopentylidyne hydride complex that has a pentagonal bipyramidal structure analogous to that of its isoelectronic analogue $Ta(CCMe_3)(H)(dmpe)_2(ClAlMe_3)$[13b] (eq 7). The hydride



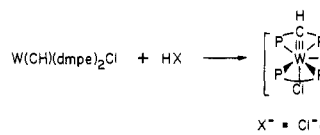
(7)

ligand could not be observed by IR, but we found a signal in the ^1H NMR spectrum at 0.3 ppm (a quintet, $J_{HP} \approx 35$ Hz). Assignment of this signal to the hydride ligand was confirmed by preparing the deuteride complex and observing a signal for the deuteride ligand by ^2H NMR at 0.30 ppm (quintet, $J_{DP} = 6$ Hz). The presence of the hydride can also be inferred from the fact that the ^{31}P NMR spectrum at room temperature, where all phosphorus nuclei are equivalent (see below), consists of a broad doublet with $J_{PH} = 34$ Hz.

The ^{31}P NMR spectrum of $[W(CCMe_3)(dmpe)_2(Cl)(H)]^+Cl^-$ is complicated by the fact that it is temperature dependent. At low temperature the $^{31}P\{^1H\}$ NMR spectrum consists of two multiplets of equal area (Figure 1b), consistent with the structure shown in eq 7. The signal at lower field is broader than that at higher field in the ^1H-coupled spectrum (Figure 1a). In the ^1H-decoupled spectrum at room temperature, the two types of phosphorus nuclei are equivalent. The process that equilibrates the two types of phosphorus nuclei does not consist of deprotonation of $[W(CCMe_3)(dmpe)_2(Cl)(H)]^+$ and reprotonation of $W(CCMe_3)(dmpe)_2Cl$ since coupling between phosphorus and the hydride is preserved (see above). We propose that the hydride comes out of the pentagonal plane into a face-bridging position and moves from face to face in the upper half of the molecule. A more radical description is that the hydride migrates around the W≡C triple bond. This proposal is analogous to that invoked to explain rapid interconversion (on the NMR time scale) of $Ta(CHCMe_3)(dmpe)_2I$ and $Ta(CCMe_3)(H)(dmpe)_2I$ in a 1:1 mixture of the two at 30 °C.[13b]

Low-temperature ^1H and ^{13}C NMR spectra of $[W(CCMe_3)(dmpe)_2(Cl)(H)]^+$ should be consistent with the structure shown in eq 7, but experimental problems prevented our confirming that this is the case.

$W(CH)(dmpe)_2Cl$ reacts with triflic acid or HCl to give white saltlike complexes, which we believe are analogous to $[W(CCMe_3)(dmpe)_2(Cl)(H)]^+$ (eq 8). In the ^1H NMR spectrum of $[W(CH)(H)(dmpe)_2Cl^+]Cl^-$ at 325 K in CD_3CN, a quintet ($J_{HP} = 18$ Hz) that integrates as two protons is found at 3.60 ppm. As the temperature is decreased, this signal broadens and disappears into the base line at 240 K. At 205 K in CD_2Cl_2, a broad singlet is found at 5.16 ppm ($J_{HW} = 79$ Hz) which we assign to a methylidyne proton. The resonance for the proposed hydride ligand is obscured by ligand resonances between 1.5 and 2.2 ppm, but a peak for the hydride ligand can be observed in the IR spectrum ($\nu_{MH} = 1830$ cm^{-1}) and, in the case of the deuterated derivative, in the ^2H NMR spectrum at 1.6 ppm. Thus, the hydride and methylidyne protons exchange at a rate that is rapid on the NMR time scale at 295 K. Persistent coupling of the two protons to the four phosphorus nuclei confirms that the exchange process is intramolecular. A necessary intermediate in this exchange process is a symmetric methylene complex (eq 9), even though a complex containing a distorted methylene ligand (see below) may actually be a lower-energy species.

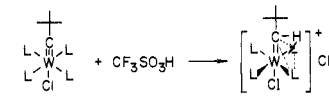


(8)

(9)

At 243 K a broad doublet ($J_{CH} = 125$ Hz) is observed for the methylidyne carbon atom at 263 ppm in the gated ^1H-decoupled ^{13}C NMR spectrum of $[W(CH)(H)(dmpe)_2Cl]^+$. The 125-Hz coupling may be ascribed to that between C_α and the methylidyne proton;[5] coupling between the methylidyne carbon atom and the hydride ligand must be of the order of 5 Hz or less. At 295 K the signal for the methylidyne carbon atom is a triplet ($J_{CH} = 68$ Hz) of quintets ($J_{CP} = 12.5$ Hz) at 263 ppm. The triplet feature is due to the fact that the methylidyne and hydride protons are exchanging rapidly at this temperature. The value for J_{CH}, therefore, is approximately the average of the coupling of the methylidyne carbon atom to the methylidyne proton (125 Hz) and to the hydride ligand (≲5 Hz).

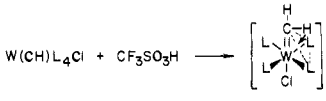
Protonation of $W(CR)(PMe_3)_4Cl$ (R = CMe_3 or H) with CF_3SO_3H. Protonation of $W(CCMe_3)L_4Cl$ (L = PMe_3) with triflic acid yields a red cationic complex that is not a true neopentylidyne hydride complex analogous to that obtained by protonating $W(CCMe_3)(dmpe)_2Cl$. It is better described as a "grossly distorted neopentylidene complex" analogous to its isoelectric tantalum analogue $Ta(CHCMe_3)(PMe_3)_4Cl$,[14] in which the α-hydrogen atom is rapidly migrating around the $C_\alpha L_2$ faces in the upper half of the molecule (eq 10). The main evidence is that



(10)

the signal for the α proton is found at −8.3 ppm as a quintet ($J_{HP} = 8.8$ Hz) and the ^{13}C NMR spectrum shows a doublet resonance at 241.9 ppm with a J_{CH} of only 45 Hz (cf. $Ta(CHCMe_3)L_4Cl$ where δ $H_\alpha = -7.9$ and $J_{CH} = 60$ Hz[14]). Since the ^1H NMR spectrum does not change down to 153 K, the activation energy for the process in which the H_α migrates from face to face must be on the order of ~10 kcal mol^{-1} or less.

Protonation of $W(CH)(PMe_3)_4Cl$ yields a red triflate salt of $[W(CH_2)(PMe_3)_4Cl]^+$ (eq 11). The ^{13}C NMR spectrum of



(11)

$[W(CH_2)L_4Cl]^+$ (gated ^1H decoupled) shows a triplet at 220 ppm with $J_{CH} = 119$ Hz, reasonable values for a methylene complex. The ^1H NMR spectrum at 298 K in CD_2Cl_2 shows a signal for the equivalent methylene protons at −0.16 ppm ($J_{HW} = 51$ Hz),

(14) Fellmann, J. D.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6608.

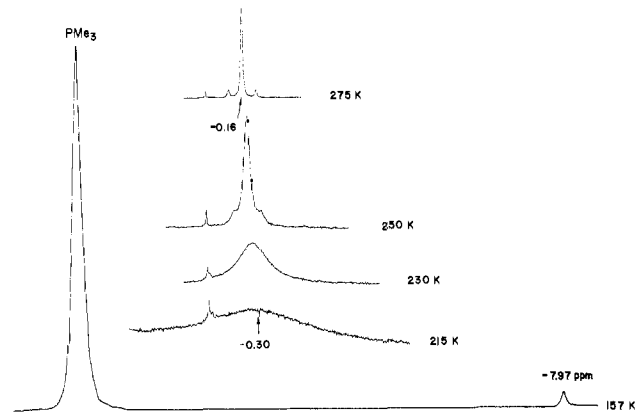


Figure 2. Variable-temperature 250-MHz ^1H NMR spectra of $[W(CH_2)(PMe_3)_4Cl]^+CF_3SO_3^-$ in $CD_2Cl_2/CHFCl_2$ Horizontal scale at 157 K is half that at higher temperatures; peak at ~7.05 ppm at 157 K is obscured by $CHFCl_2$ resonance (see text).

and the $^{31}P\{^1H\}$ NMR spectrum shows a single peak at −31 ppm (J_{PW} = 248 Hz). The couplings to ^{183}W suggest that neither the methylene protons nor the phosphine ligands dissociate at a rate that is rapid on the NMR time scale at 298 K.

NMR spectra of $[W(CH_2)L_4Cl]^+$ (L = PMe_3) are temperature dependent. When an ^1H NMR sample of $[W(CH_2)L_4Cl]^+$ in $CFHCl_2/CD_2Cl_2$ is cooled, the −0.16-ppm peak broadens, shifts upfield to ~−0.30 ppm at ~215 K, and then disappears into the base line at ~190 K (Figure 2). At 165 K a new peak appears at −7.97 ppm with an estimated area of 1 proton. Another peak (presumably also of area 1) can be located at ~7.05 ppm as part of the shoulder on the $CHFCl_2$ peak (not shown in Figure 2). This was confirmed by a magnetization-transfer experiment. Irradiating at 7.05 ppm decreased the intensity of the −7.97-ppm peak due to transfer of the magnetization from one proton (7.05 ppm) to the other (−7.97 ppm).[15,16] Therefore, in the nonfluxional molecule, the "methylene" protons are in two distinct chemical environments, one of which is similar to that of an α-hydrogen atom in a grossly distorted neopentylidene complex (−7.97 ppm) while the other is similar to that of a methylidyne proton[4] (7.05 ppm). Later we attempt to explain why the average of the signals at 7.05 and −7.97 ppm (−0.46 ppm) is further upfield from the observed position for the average peak (−0.30 ppm) before it disappears into the base line (Figure 2).

The ^{31}P NMR spectrum of $[W(CH_2)(PMe_3)_4Cl]^+$ is also temperature dependent. At 300 K the spectrum consists of a singlet at −31 ppm with J_{PW} = 248 Hz. At 143 K two singlets of equal intensity at −22 and −33 ppm are observed, both with J_{PW} = 248 Hz. Therefore, the methylene α-hydrogen atom that interacts with the metal is oriented on a face, rather than along an edge, of the idealized octahedral molecule (as shown in eq 11).

Further evidence in support of distortion of the methylene ligand as shown in eq 11 was obtained from the spectroscopic characterization of the deuterated analogue prepared from $PMe_3D^+CF_3SO_3^-$ and $W(CH)(PMe_3)_4Cl$. The ^1H NMR spectrum of this deuterated methylene complex at 25 °C exhibits two singlets of approximately equal intensity (and a total area of 1) at −0.16 and −1.40 ppm (Figure 3a). The peak at −0.16 ppm is assigned to the methylene protons in $[W(CH_2)L_4Cl]^+$, while the higher field signal, which is slightly broader, is assigned to the methylene proton in $[W(CHD)L_4Cl]^+$. The ^2H NMR spectrum of the deuterated methylene complex at 25 °C also contains two peaks, one being at 0.72 ppm and assigned to the methylene deuterium in the CHD complex, the other at −0.48 ppm and assigned to the deuterium in the CD_2 complex (Figure 3b). All the above assignments were confirmed by recrystallizing the complex in the presence of excess CH_3OD in CH_2Cl_2, thereby enriching it in deuterium. In the ^1H NMR spectrum of the deuterium-enriched sample, the −1.40-ppm peak was more intense than the −0.16-ppm peak, and in the ^2H NMR spectrum, the −0.48-ppm peak was more intense than the 0.72-ppm peak. The enrichment experiment proves that the methylene protons in the methylene complex exchange intermolecularly at a rate that is slow on the NMR time scale, in addition to exchanging intramolecularly at a rate that is on the order of the NMR time scale. A 1:2:1 mixture of CH_2, CHD, and CD_2 complexes results.

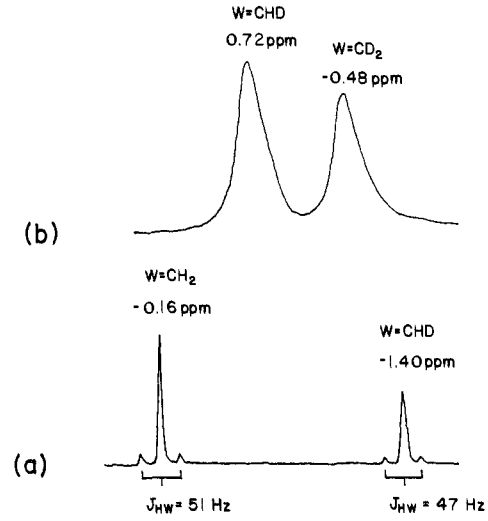


Figure 3. Methylene resonances in the NMR spectra of the approximately 1:2:1 mixture of $[W(CH_2)L_4Cl]^+$, $[W(CHD)L_4Cl]^+$, and $[W(CD_2)L_4Cl]^+$: (a) 250-MHz ^1H, (b) 13.8-MHz ^2H (L = PMe_3).

The large magnitude of the chemical shift differences between the $W(CH_2)$, W(CHD), and $W(CD_2)$ signals is significant. Normally, the substitution of ^2H for ^1H on a carbon atom will cause the chemical shift of a geminal proton to shift upfield by ca. 0.02 ppm.[17] In this situation however, the chemical shift difference is 1.2 ppm. This anomaly can be explained on the basis of the proposed interaction of one of the methylene protons with the metal. In any system that involves an exchange of ^2H and ^1H between two sites, ^2H will bind preferentially to the position in which the bond energy is larger.[18] In this example, one would expect that the proton in the methylidyne position would be bound more strongly to the α-carbon atom than the proton in the "bridging" position. For example, in other alkylidene complexes that possess an α proton that is drawn toward the metal, the infrared absorption frequency attributed to this $C-H_\alpha$ bond is 500–700 cm^{-1} less than that of a normal C–H bond.[4] In contrast, monomeric methylidyne complexes have not been found to display an unusual C–H absorption frequency.[5] Thus, in this situation one would anticipate that ^2H would bond preferentially in the "methylidyne" position in the methylene ligand. The effect of incorporating ^2H then will be to shift the weighted average of the ^1H signal to higher field, as observed. For similar reasons, the ^2H NMR resonance for the W(CHD) compound will be shifted to lower field than the average signal in the ^2H NMR spectrum of the $W(CD_2)$ complex by the same amount (1.2 ppm), as is also observed. From the data we can conclude that the form of $[W(CHD)L_4Cl]^+$ in which H is bonded to the $C_\alpha L_2$ face is approximately 0.2 kcal lower in energy than that in which D is bonded to the $C_\alpha L_2$ face.[7]

We can now offer an explanation as to why the CH_2 peak in $[W(CH_2)L_4Cl]^+$ moves upfield as the temperature is lowered. We propose that the degree to which H_α interacts with the metal on the $C_\alpha L_2$ face of the molecule increases slightly as the temperature

(15) (a) Forsen, S.; Hoffmann, R. A. *J. Chem. Phys.* **1963**, *39*, 2892. (b) Forsen, S.; Hoffmann, R. A. *Ibid.* **1964**, *40*, 1189.
(16) (a) Dahlquist, F. W.; Longmuir, K. J.; DuVernet, R. B. *J. Magn. Reson.* **1975**, *17*, 406. (b) Morris, G. A.; Freeman, R. *Ibid.* **1978**, *29*, 433.
(17) Lambert, J. B.; Greifenstein, L. G. *J. Am. Chem. Soc.* **1974**, *96*, 5120 and references therein.
(18) (a) Kreevoy, M. M.; Liang, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 3315 and references therein. (b) Kirchen, R. P.; Okazawa, N.; Ranganayahulu, K.; Rauk, A.; Sorensen, T. S. *J. Am. Chem. Soc.* **1981**, *103*, 587. (c) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726.

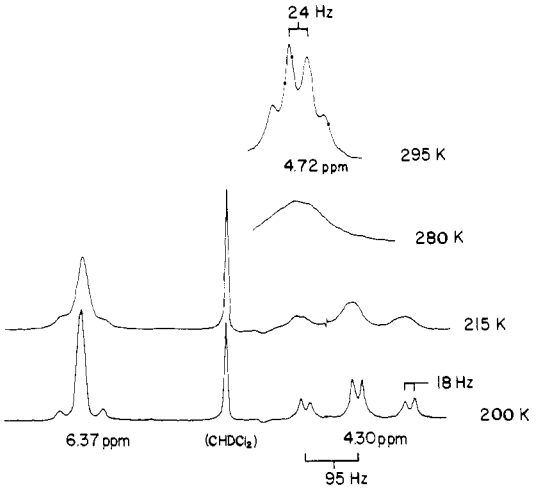


Figure 4. Variable-temperature ^1H NMR spectra of $W(CH)(H)L_3Cl_2$ ($L = PMe_3$) in CD_2Cl_2.

is lowered, perhaps as a result of a slightly more favorable disposition or less thermal motion of PMe_3 ligands in the crowded WL_4 plane at low temperatures.

Other Methylidyne Hydride Complexes. Two neutral methylidyne hydride complexes can be prepared by using Cl^- or BH_3CN^- counterions in place of triflate (eq 12 and 13; $L = PMe_3$).

$$W(CH)L_4Cl + HCl \xrightarrow[-78°]{CH_2Cl_2} \text{(structure)} \quad (12)$$

$$[W(CH_2)L_4Cl]^+CF_3SO_3^- + NaBH_3CN \rightarrow W(CH)(H)L_3(BH_3CN)(Cl) \quad (13)$$

Apparently both Cl^- and BH_3CN^- bind to tungsten more strongly than triflate does and successfully compete with PMe_3 for a coordination position. We believe the cyanoborohydride ligand is coordinated to the metal through the cyanide functionality rather than through the hydrides, since the B–H absorbance occurs at 2340 cm^{-1} in the infrared spectrum, not at ca. 2100 cm^{-1}, as one would expect for a B–H–M mode of bonding. In contrast, ν_{CN} is shifted to 2200 cm^{-1} in the tungsten complex from 2180 cm^{-1} in $NaBH_3CN$. A shift of ν_{CN} 20–30 cm^{-1} to higher energy than ν_{CN} in the free nitrile typically occurs upon coordination to a metal.[19]

Figure 4 shows the temperature-dependent ^1H NMR spectrum of $W(CH)(H)L_3Cl_2$. The hydride resonance can now be observed as a doublet of triplets. At relatively high temperatures, it coalesces with the signal due to the methylidyne proton to give a quartet resonance at 4.72 ppm. The temperature-dependent ^{31}P NMR spectrum is consistent with three types of phosphine ligands, two of which are nearly equivalent and give rise to a multiplet that shows a relatively large J_{PH} of 95 Hz. (See Experimental Section for details.) One important feature of the temperature-dependent spectrum of $W(CH)(H)L_3Cl_2$ that must be explained is the fact that the average of the hydride peak at 4.30 and the methylidyne proton peak at 6.37 ppm is found at ~4.7 ppm, not ~5.3 ppm. There are two explanations we consider most likely. The first is that at 295 K a significant percentage of the complex is in the form of a distorted methylene complex, $W(CH_2)L_3Cl_2$. The second is that the complex is still in the form of a methylidyne hydride complex but that a significant amount of it has a different arrangement of ligands at higher temperatures. In the first case, the weighted-average peak for the two protons would be upfield of 5.3 ppm. In the second case, we could not predict where the weighted-average resonance would be found.

When $W(CH)L_4Cl$ is treated with $Me_3PD^+Cl^-$ (>95% D), we would expect to obtain an approximately 1:1:1:1 mixture of

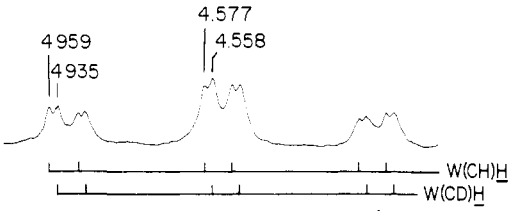


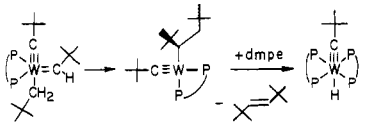
Figure 5. Hydride resonances in the 250-MHz ^1H NMR spectrum of an approximately 1:1:1:1 mixture of $W(CH)(H)L_3Cl_2$, $W(CH)(D)L_3Cl_2$, $W(CD)(H)L_3Cl_2$, and $W(CD)(D)L_3Cl_2$ in $CD_2Cl_2/CHFCl_2$ at 200 K (cf. Figure 4; the slight difference in chemical shift can be traced to the use of $CHFCl_2$ in this experiment).

$W(CH)(H)L_3Cl_2$, $W(CH)(D)L_3Cl_2$, $W(CD)(H)L_3Cl_2$, and $W(CD)(D)L_3cl_2$ ($L = PMe_3$). We can see two separate hydride patterns in the ^1H NMR spectrum of the deuterated compound (Figure 5). The chemical shift difference between these patterns (~0.02 ppm) is what we might expect from the normal effect of deuterium on a vicinal proton.[17] According to this explanation, the peak at 4.577 ppm would be one in the pattern for the hydride resonance in $W(CH)(H)(PMe_3)_3Cl_2$, while the approximately equally intense signal at 4.558 ppm would be part of the pattern for the hydride resonance in $W(CD)(H)(PMe_3)_3Cl_2$. One might also expect to observe two signals for the methylidyne absorbance, one for $W(CH)(H)L_3Cl_2$ and one for $W(CH)(D)L_3Cl_2$. Unfortunately, they apparently cannot be resolved, probably due to the coupling of the methylidyne proton to the phosphine ligands.

The ^1H, ^{13}C, and ^{31}P NMR data that define an interconversion of hydride and methylidyne protons in $W(CH)(H)L_3(Cl)(BH_3CN)$ are similar to those for $W(CH)(H)L_3Cl_2$. The ^{31}P NMR spectrum is strictly first order at low temperature in this case, three doublets of doublets (at 170 K). Of additional interest in the case of $W(CH)(H)L_3(Cl)(BH_3CN)$ is the BH_3CN ligand. The signal for the borohydride protons at 0.66 ppm is a 1:1:1:1 quartet with $J_{HB} = 90$ Hz at 292 K. At 200 K it is a broad singlet at 0.43 ppm. The data that have been collected for $W(CH)(H)(PMe_3)_3(Cl)(BD_3CN)$ demonstrate conclusively that the hydride ligand does not exchange with the BH_3CN protons on the chemical time scale. For example, the W–H absorbance is still present in the IR spectrum of $W(CH)(H)L_3(Cl)(BD_3CN)$, no B–H band can be observed, and several B–D bands can be observed at 1765, 1680, and 1630 cm^{-1}. Also, the ^1H NMR spectrum of $W(CH)(H)L_3(Cl)(BD_3CN)$ at 205 K exhibits no signal for the B–H proton.

Discussion

The most straightforward mechanism for formation of *trans*-$W(CCMe_3)(dmpe)_2(H)$ (eq 1) is shown in eq 14. Migration of



(14)

an alkyl to an alkylidene ligand was first noted in the decomposition of $Cp_2Ta(CHMe)(Me)$ to give $Cp_2Ta(propylene)(H)$ instead of $Cp_2Ta(C_2H_4)(Me)$.[20] It has since been observed in complexes such as $Cp_2Nb(R)[CHOZr(H)(\eta^5\text{-}C_5Me_5)_2]$[21] and intermediate $[Cp_2W(CH_2)(CH_3)]^+$.[22] Preferential formation of *trans*-$Me_3CCH{=}CHCMe_3$ is reasonable since the two *tert*-butyl groups in the alkyl neopentylidyne intermediate should turn away from one another before the metal abstracts one of the two β-hydrogen atoms. We expect that the trans configuration of $W(CCMe_3)(dmpe)_2H$ is thermodynamically preferred over the cis.

The main question we want to try to answer is why alkylidyne hydride complexes are observed in some situations and grossly distorted alkylidene complexes in others. However, it is important

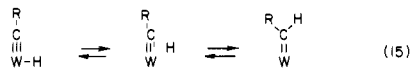
(19) Duckworth, M. W.; Fowles, G. W.; Hoodless, R. A. *J. Chem. Soc.* **1963**, 5665 and references therein.

(20) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43.
(21) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650.
(22) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648.

to recognize that there is not as much of a difference between a complex containing a grossly distorted alkylidene ligand and a true alkylidyne hydride complex as might first appear, and the factors that determine whether one or the other is formed are likely to be relatively subtle. Nevertheless, we can at least conclude that the size of the substituent on the alkylidene/alkylidyne ligand (H or CMe_3) is *not* a major determinant. We believe that the W(CR)(dmpe)$_2$Cl complexes (R = H or CMe_3) protonate at the metal because a pentagonal-bipyramidal molecule can form that is structurally analogous to Ta(CCMe$_3$)(H)(dmpe)$_2$(ClAlMe$_3$).[13b] In the analogous PMe_3 complexes, the α-hydrogen atom cannot remain on the metal largely because of the steric problems associated with forming analogous pentagonal-bipyramidal [W(CCMe$_3$)(H)(PMe$_3$)$_4$Cl]$^+$CF$_3$SO$_3^-$. It is clear that even in W(CH)(PMe$_3$)$_4$Cl the PMe_3 ligands cannot be arranged in a plane without puckering.[13a] When only three PMe_3 ligands are present, as in W(CH)(H)L$_3$Cl$_2$ or W(CH)(H)L$_3$Cl(BH$_3$CN), the alkylidyne hydride form is again accessible.

It is interesting to compare the proposed structure for [W(CHCMe$_3$)L$_4$Cl]$^+$ and [W(CH$_2$)L$_4$Cl]$^+$ with the structure of W(CHCMe$_3$)(CO)(PMe$_3$)$_2$Cl$_2$.[23] W(CHCMe$_3$)(CO)(PMe$_3$)$_2$Cl$_2$ is a distorted octahedron in which the α proton of the distorted neopentylidene ligand is bound to a C_αPCl face. The W=C$_\alpha$—H$_\alpha$ angle is only 72.2 (20)° and the W···H$_\alpha$ distance only 1.835 (36) Å. An interesting question in light of the discussion above is why the α-hydrogen atom does not actually transfer to the metal in W(CHCMe$_3$)(CO)(PMe$_3$)$_2$Cl$_2$. From solely a steric point of the view, it should (cf. W(CH)(H)(PMe$_3$)$_3$Cl$_2$). The presence of a CO ligand in place of a PMe_3 ligand must, for electronic reasons, cause the alkylidene tautomer to be favored.

We want to reemphasize that a hydride ligand can migrate to an α-carbon atom and back again with remarkable ease, but only in the case where an intermediate methylene complex formed can we see evidence for this sequence in the form of exchange of the methylidyne and hydride protons. The process is a facile one simply because the first stage of migration of the hydride to C_α of the alkylidyne ligand is what we have called a grossly distorted alkylidene complex in which the hydrogen atom is essentially bridging between tungsten and C_α (eq 15). As a consequence,



(15)

it is not necessarily a simple matter to predict whether the complex will react with incoming ligands as an alkylidyne complex, an alkylidene complex, or in some manner unique to a complex having an α-hydrogen atom bridging between C_α and W.

Three factors that could be viewed as contributing to the driving force for formation of an alkylidyne hydride complex are oxidation of tungsten(IV) to tungsten(VI), an increase in electron count from 16 to 18, and formation of a tungsten–carbon triple bond. The last will perhaps be a more significant factor for tungsten than any other metal, with the possible exception of molybdenum or rhenium. It appears that tungsten will be able to form a triple bond to carbon[11] as readily as it forms a triple bond to nitrogen[24] or to itself.[25]

Experimental Section

All operations, except where otherwise specified, were performed under dinitrogen, either by Schlenk techniques or in a dry box. PMe_3[26] and dmpe[27] were prepared by published methods. W(dmpe)(CH$_2$CMe$_3$)(CHCMe$_3$)(CCMe$_3$) was prepared from W(CCMe$_3$)(CH$_2$CMe$_3$)$_3$ as previously described.[2] WCl$_2$(PMe$_3$)$_4$ was prepared by reducing WCl$_4$(PMe$_3$)$_3$ in THF with sodium amalgam.[28] NEt$_4^+$[W(CCMe$_3$)Cl$_4$]$^-$ was obtained by addition of HCl to W(CCMe$_3$)(CH$_2$CMe$_3$)$_3$ in the presence of NEt$_4^+$Cl$^-$.[11]

Pentane, hexane, and petroleum ether were washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and distilled under dinitrogen from *n*-butyllithium. Reagent grade diethyl ether, tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl under dinitrogen. Reagent grade benzene, methylene chloride, chloroform, and chlorobenzene were dried by refluxing overnight with calcium hydride and distilled.

NMR data are listed in ppm relative to internal Me_4Si for ^1H and ^{13}C and relative to external H_3PO_4 for ^{31}P. They were obtained at relatively high field (250 MHz for ^1H or the equivalent for ^{13}C or ^{31}P) at ca. 30 °C unless otherwise noted. The standard for ^2H NMR spectra was C_6D_6 at 7.15 ppm relative to Si(CD$_3$)$_4$.

Preparation of *trans*-W(CCMe$_3$)(dmpe)$_2$(H). W(dmpe)(CH$_2$CMe$_3$)(CHCMe$_3$)(CCMe$_3$) (1.00 g) was dissolved in 2 mL of dmpe, and the tube was sealed and heated to 120 °C for 15 h. The volatiles were removed in vacuo and shown to contain 1 equiv of *trans*-Me$_3$CCH=CHCMe$_3$ by GLC vs. an internal standard. The green-brown residue was extracted with pentane and treated with activated charcoal. The mixture was filtered and the solvent removed from the yellow filtrate to give a yellow crystalline solid (1.1 g) that could be recrystallized from cyclohexane at −40 °C as yellow needles or sublimed at 120 °C/1 μm).

Anal. Calcd for $WC_{17}H_{42}P_4$: C, 36.83; H, 7.63. Found: C, 36.44; H, 6.83. ^1H NMR (C_6H_6): 1.69 (br m, 12, PMe), 1.50 (br m, 12, PMe′), 1.48 (br m, 8, PCH$_2$), 1.02 (s, 9, CMe$_3$), −6.27 (quintet, 1, J_{HP} = 29 Hz, J_{HW} = 29 Hz, WH). All multiplets sharpen to singlets on decoupling ^{31}P at 24.295 030 MHz. ^{13}C NMR (C_6D_6): 281.6 (quintet, J_{CP} = 10 Hz, J_{CW} = 208 Hz, *C*CMe$_3$), 50.3 (s, *C*Me$_3$), 36.3 (t of quintet, J_{CP} = 11 Hz, J_{CH} = 130 Hz, PCH$_2$), 31.5 (s, C*Me*$_3$), 27.9 (q of quintets, J_{CH} = 125 Hz, J_{CP} = 6 Hz, PMe), 27.2 (q of quintets, J_{CH} = 128 Hz, J_{CP} = 8 Hz, PMe′). The spectrum is the same at 80 °C. $^{13}P\{^1H\}$ NMR (C_6H_6): 24.9 (s, J_{PW} = 278 Hz). No change at −30 °C. A broadened weak (45-Hz half-height width) peak was observed in the proton coupled NMR. M_r (cyclohexane): calcd, 554. Found, 581 ± 30 at 1.1 × 10^{-2} M. Mass spectrum: molecular ion at *m/e* 554 (^{184}W) overlapping with patterns at 555, 553, and 552, each ~15% as intense.

trans-W(CCMe$_3$)(dmpe)$_2$D was prepared analogously.

Preparation of *trans*-W(CCMe$_3$)(dmpe)$_2$Cl. HCl (55 mL, 2.26 mmol) was added at −78 °C to W(CCMe$_3$)(dmpe)$_2$H (1.25 g, 2.26 mmol) dissolved in THF. The mixture was warmed to room temperature, 0.12 g of [W(CCMe$_3$)(dmpe)$_2$(H)Cl]$^+$Cl$^-$ was filtered off (see below), and the yellow mother liquors were evaporated to dryness. The yellow residue was recrystallized from pentane to give yellow plates; yield 1.05 g (79%).

W(CCMe$_3$)(dmpe)$_2$Cl may also be prepared by adding W(CCMe$_3$)(dmpe)$_2$H to [W(CCMe$_3$)(dmpe)$_2$(H)Cl]$^+$Cl$^-$ in chlorobenzene and stirring for 12 h.

Anal. Calcd for $WC_{17}H_{41}P_4Cl$: C, 34.68; H, 6.96. Found: C, 34.83; H, 7.36. ^1H NMR (C_6D_6, 270 MHz): 1.57 (br s, 12, PMe), 1.49 (br s, 12, PMe′), 1.28 (br s, 8, PCH$_2$), 0.81 (s, 9, CMe$_3$). The broad peaks sharpen to sharp singlets on decoupling ^{31}P at 24.295 085 MHz. ^{13}C NMR (C_6D_6): 271.1 (quintet, J_{CP} = 10 Hz, *C*CMe$_3$), 50.54 (s, *C*Me$_3$), 33.97 (quintet, J_{CP} = 10 Hz, PCH$_2$), 32.22 (s, C*Me*$_3$), 24.72 (5-line multiplet 26-Hz wide), 16.73 (5-line multiplet 26-Hz wide). $^{31}P\{^1H\}$ NMR (C_6D_6): 27.7 (s, J_{PW} = 284 Hz). ^{31}P NMR (C_6D_6): 27.4 (half-height width = 35 Hz). $^{31}P\{^1H\}$ NMR (toluene): two resonances at low-*T* limit (200 K, $\Delta\nu$ = 679 Hz, T_c = 225 K). M_r (cyclohexane): calcd, 554. Found, 564 at 3.61 × 10^{-2} M. Mass spectrum *m/e* (relative intensity): calcd; 586 (16.8), 587 (12.4), 588 (26.7), 589 (7.7), 590 (24.9), 591 (4.6), 592 (5.8), 593 (1.1). Found; 586 (13.9), 587 (12.0), 588 (25.9), 589 (8.3), 590 (28.7), 591 (5.6).

Preparation of [W(CCMe$_3$)(dmpe)$_2$(H)Cl]$^+$Cl$^-$. HCl (97 mL, 4.0 mmol) was added at −78 °C to W(CCMe$_3$)(dmpe)$_2$(H) (1.0 g, 1.8 mmol) dissolved in THF (20 mL). The white precipitate that formed was filtered off and recrystallized from dichloromethane by adding ether; yield 0.98 g (92%).

^1H NMR (CDCl$_3$, 270 MHz): 2.13 (br s, 8, PCH$_2$), 2.02 (br s, 12, PMe), 1.68 (br s, 12, PMe′), 0.79 (s, 9, CMe$_3$). The broad peaks sharpen to singlets on decoupling ^{31}P at 24.295 060 MHz. ^{13}C NMR (CDCl$_3$): 285.5 (quin, $^2J_{CP}$ = 11 Hz, *C*CMe$_3$), 50.3 (s, *C*CMe$_3$), 30.9 ($^4J_{CP}$ = 129 Hz, CC*Me*$_3$), 28.87 (t of quin, J_{CP} = 12 Hz, J_{CH} = 130 Hz, PCH$_2$), 21.3 (q of quin, J_{CP} = 9 Hz, J_{CH} = 128 Hz, PMe′). At 213 K the signal at 285.5 ppm still shows no evidence of C_αH coupling ($J_{C_\alpha H} \lesssim 5$ Hz). $^{31}P\{^1H\}$ NMR (CDCl$_3$): 29.68 (s, J_{PW} = 168 Hz). ^{31}P NMR (CDCl$_3$): 29.68 (d, J_{PH} = 34 Hz, J_{PW} = 168 Hz). $^{31}P\{^1H\}$ NMR (CDCl$_3$, variable *T*): two resonances at low-*T* limit (220 K, $\Delta\nu$ = 684 Hz, to 242 K); the

(23) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. W. *J. Am. Chem. Soc.* **1982**, *104*, 1739.
(24) Griffith, W. P. *Coord. Chem. Rev.* **1972**, *8*, 369.
(25) Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 356.
(26) (a) Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Met-Org. Chem.* **1974**, *4*, 149. (b) Zingaro, R. A.; McGlothlin, R. F. *J. Chem. Eng. Data* **1963**, *8*, 226.
(27) Parshall, G. W. *J. Inorg. Nucl. Chem.* **1960**, *14*, 291.
(28) Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430.

lower field resonance is broader (half-height width = 250 Hz) than higher field resonance (150 Hz). Conductivity: in MeCN, $\Lambda = 105\ \Omega^{-1}$ cm^{-1} M^{-1} at 4.74×10^{-3} M; in CH_2Cl_2, $\Lambda = 100\ \Omega^{-1}\ cm^{-1}\ M^{-1}$ at 4.74×10^{-3} M.

Preparation of $[W(CCMe_3)(dmpe)_2(D)Cl]^+Cl^-$. The deuteride was prepared in a manner analogous to that used to prepare the hydride above.

^2H NMR ($C_6D_6/CHCl_3$, 13.76 MHz): 0.90 (quin, $^2J_{DP} = 5.9$ Hz).

Preparation of $[W(CCMe_3)(dmpe)_2(H)Cl]^+CF_3CO_2^-$. Trifluoroacetic acid (0.21 g, 1.87 mmol) was added to $W(CCMe_3)(dmpe)_2Cl$ (1.1 g, 1.87 mmol) dissolved in 20 mL of ether. The resulting white powder was filtered off and recrystallized from chloroform by adding ether; yield 1.10 g (84%).

Anal. Calcd for $WC_{19}H_{42}P_4ClO_2F_3$: C, 32.46; H, 5.98. Found: C, 32.31; H, 5.92. Its NMR spectra are nearly identical with those for the chloride salt; O_2CCF_3 is found at 159.2 (q, $^2J_{CF} = 31$ Hz) and O_2CCF_3 at 116.8 (q, $J_{CF} = 299$ Hz).

Preparation of $W(CH)(PMe_3)_4Cl$. A solution of $WCl_2(PMe_3)_4$ (3.36 g, 6 mmol) in 40 mL of toluene was cooled to −10 °C, and $AlMe_3$ (0.87 g, 12 mmol) in 10 mL of toluene was added with stirring. The mixture was allowed to warm to 25 °C. After 24 h, tetramethylethylenediamine (1.39 g, 12 mmol) in 10 mL of toluene was added to the red mixture. All volatiles were removed from the resulting yellow solution. The solid mixture was washed with 3 × 5 mL of cold acetonitrile, and the pale yellow product was dried in vacuo (1.92 g, 64%).

Anal. Calcd for $WC_{13}H_{37}ClP_4$: C, 29.08; H, 6.90. Found: C, 29.17; H, 7.09. ^1H NMR (C_6D_6, 250 MHz): 6.75 (quintet, 1, $J_{HP} = 3.9$ Hz, $J_{HW} = 80.1$ Hz, WCH), 1.54 (t, 36, $J_{HP} = 2.8$ Hz, PMe_3). ^{13}C NMR (C_6D_6, 62.8 MHz): 250 (doublet of quintets, $J_{CH} = 134$ Hz, $J_{CP} = 10.6$ Hz, $J_{CW} = 200$ Hz, WCH), 24 (quartet of quintets, $J_{CH} = 128$ Hz, $J_{CP} = 6.4$ Hz, PMe_3). ^{31}P NMR (C_6D_6, 36.2 MHz): −22.5 (s, $J_{PW} = 284$ Hz).

Preparation of $W(CCMe_3)(PMe_3)_4Cl$. $Et_4N^+[W(CCMe_3)Cl_4]^-$ (3.18 g, 6.0 mmol) was suspended in 20 mL of dichloromethane and 3 equiv of PMe_3 (1.73 mL, 18.0 mmol) was added at 25 °C. After 1 h of stirring, the blue solution had become yellow. The volatiles were removed in vacuo, and the yellow solid was suspended in 20 mL of THF. PMe_3 (1 equiv, 0.58 mL, 6.0 mmol) was added, followed by 2 equiv of sodium amalgam (0.41%, 68 g, 12 mmol). After 2.5 h of stirring at 25 °C, the solvent was removed in vacuo, the residue was extracted with 5 × 20 mL of pentane, and the extract was filtered through Celite. The solvent was removed in vacuo, leaving 3.3 g of yellow solid. The crude product was dissolved in toluene, and the solution was concentrated to 2 mL. Acetonitrile was added (4 mL), and after 1 day at −10 °C, 2.6 g of yellow, crystalline $W(CCMe_3)(PMe_3)_4Cl$ was collected (72%).

^1H NMR (C_6D_6, 250 MHz): 0.99 (s, 9, $CCMe_3$), 1.52 (br s, 36, PMe_3). ^{13}C NMR (C_6D_6, 62.8 MHz): 271 (s, $CCMe_3$), 51.3 (s, $CCMe_3$), 32.4 (q, $J_{CH} = 125$ Hz, $CCMe_3$), 24.6 (q, $J_{CH} = 128$ Hz, PMe_3). ^{31}P NMR (C_6D_6, 36.2 MHz): −23.3 (s, $J_{PW} = 283$ Hz).

Preparation of $W(CH)(dmpe)_2Cl$. $W(CH)(PMe_3)_4Cl$ (3.0 g, 5.6 mmol) was combined with 2.2 equiv of dmpe (1.84 g, 12.3 mmol) in chlorobenzene (10 mL). The mixture was heated in a sealed glass tube at 110 °C for 2 days. The resulting yellow-brown solution was filtered and concentrated to 3 mL. Acetonitrile (10 mL) was added, and after one day at −10 °C, 2.0 g of yellow, crystalline, $W(CH)(dmpe)_2Cl$ was collected. A second crop of 0.30 g was obtained by the same procedure from the mother liquor; total yield 2.3 g (77%).

Anal. Calcd for $WC_{13}H_{33}ClP_4$: C, 29.30; H, 6.20. Found: C, 29.62; H, 6.37. ^1H NMR (C_6D_6, 250 MHz): 5.98 (quintet, 1, $J_{PH} = 2.9$ Hz, $J_{HW} = 83$ Hz, WCH), 1.58 (br s, 12, PMe), 1.52 (br s, 12, PMe), 1.27 (br multiplet, 8, PCH_2). ^{13}C NMR (C_6D_6, 62.8 MHz): 246.2 (doublet of quintets, $J_{CH} = 130$ Hz, $J_{CP} = 11.1$ Hz, $J_{CW} = 205$ Hz, WCH), 33.9 ($J_{CP} = 9.7$ Hz, PCH_2), 25.2 (s, PMe), 15.6 (s, PMe). ^{31}P NMR (C_6H_5Cl, 36.2 MHz): 26.3 (s, $J_{PW} = 283$ Hz).

Preparation of $[W(CH)(H)(dmpe)_2Cl]Cl$. $W(CH)(dmpe)_2Cl$ (1.0 g, 1.9 mmol) was dissolved in 10 mL of dichloromethane, and the solution was cooled to −78 °C. HCl gas (1 equiv) was introduced with a syringe. The yellow solution was allowed to warm to 25 °C and was stirred for 1 h. The solvent was removed in vacuo. The crude, pale yellow product was washed with 2 × 10 mL of toluene and dissolved in dichloromethane. The solution was filtered and concentrated to 2 mL. Toluene (4 mL) was added to the filtrate, and after 1 day at −10 °C, 0.81 g of white, crystalline $[W(CH)(H)(dmpe)_2Cl]Cl$ was collected. A second crop of 0.16 g was obtained similarly from the mother liquor; total yield 0.97 g (90%).

Anal. Calcd for $WC_{13}H_{34}Cl_2P_4$: C, 27.42; H, 5.98. Found: C, 27.50; H, 6.26. IR (Nujol, cm^{-1}): 1830 (br, w, ν_{MH}). ^1H NMR (CD_2Cl_2, 250 MHz, 205 K): 5.16 (br s, 1, $J_{HW} = 79$ Hz, WCH), 2.16 (br m, 4, PCH_2), 2.07 (br s, 4, PCH_2), 1.97 (d, 3, $J_{HP} = 10.7$ Hz, PMe), 1.88 (d, 3, $J_{HP} = 7.7$ Hz, PMe), 1.74 (d, 3, $J_{PH} = 10.3$ Hz, PMe), 1.52 (d, 3, $J_{HP} = 8.5$ Hz, PMe). ^1H NMR (CD_3CN, 250 MHz, 325 K): 3.60 (quintet, 2, $J_{HP} = 18$ Hz, WCH and WH), 2.16 (br m, 8, PCH_2), 2.00 (br s, 12, PMe), 1.71 (br s, 12, PMe). ^{13}C NMR (CD_2Cl_2, 62.8 MHz, 295 K): 263.1 (triplet of quintets, $J_{CH} = 69.4$ Hz, $J_{CP} = 12.5$ Hz, $J_{CW} = 189$ Hz, W(CH)(H)), 28.9 (t, $J_{CH} = 128$ Hz, PCH_2), 21.7 (d q, $J_{CP} = 36.1$ Hz, $J_{CH} = 130$ Hz, PMe), 13.0 (d q, $J_{CP} = 30.5$ Hz, $J_{CH} = 130$ Hz, PMe). ^{13}C NMR (CD_2Cl_2, 62.8 MHz, 243 K): 263.6 (br d, $J_{CH} = 125$ Hz, W(CH)). ^{31}P NMR (CD_2Cl_2, 36.2 MHz, 300 K): 30.4 (br s, $J_{WP} = 166$ Hz). ^{31}P NMR (CD_2Cl_2, 36.2 MHz, 210 K): 40 (m, J_{PH} relatively large but unresolved), 20 (m, J_{PH} relatively small).

Preparation of $[W(CH)(H)(dmpe)_2Cl]CF_3SO_3$. $W(CH)(dmpe)_2Cl$ (0.10 g, 0.19 mmol) was dissolved in 5 mL of ether, and 1 equiv of CF_3SO_3H (0.03 g, 0.2 mmol) in 2 mL of ether was added rapidly. The white precipitate that formed immediately was found to be pure $[W(CH)(H)(dmpe)_2Cl]CF_3SO_3$ by ^{31}P NMR.

^{31}P NMR (CH_2Cl_2, 36.2 MHz, 300 K): 30.4 (br s, $J_{PW} = 166$ Hz). IR (Nujol, cm^{-1}): 1830 (br, w, ν_{MH}).

Preparation of $[W(CH)(D)(dmpe)_2Cl]Cl$. $W(CH)(dmpe)_2Cl$ (0.40 g, 0.75 mmol) was dissolved in 5 mL of dichloromethane. $[PMe_3D]Cl$ (1 equiv, 0.085 g, 0.75 mmol) was added rapidly as a solid. After 2 h of stirring, the homogeneous, pale yellow reaction mixture was concentrated to 1 mL and toluene (2 mL) was added. $[W(CH)(D)(dmpe)_2Cl]Cl$ was collected after cooling the solution to −10 °C for 1 day; yield 0.35 g (82%).

^1H NMR (CD_2Cl_2, 250 MHz, 208 K): 5.16 (br s, ca. 0.4, $J_{HW} = 80$ Hz, WCH). All other signals are the same as for $W(CH)(dmpe)_2Cl_2$. ^2H NMR (CH_2Cl_2, 38.4 MHz, 204 K): 5.0 (br s, WCD), 1.6 (br t, $J_{DP} = 10$ Hz, WD). IR (Nujol, cm^{-1}): 1830 (br, weak, ν_{MH}). ν_{WD} was not observed.

Preparation of $[PMe_3D]Cl$. PMe_3 (1.25 mL, 13 mmol) in 5 mL of D_2O was treated with 1 equiv of DCl (290 mL, 13 mmol) by syringe. After 30 min of stirring, the solvent was removed in vacuo. The crude product was dissolved in acetonitrile (50 mL). Concentrating the solution produced 1.4 g of $[PMe_3D]Cl$ (96%).

^{31}P NMR (CH_3CN, 36.2 MHz): −2.8 (1:1:1 triplet, $J_{DP} = 79$ Hz). We estimate that <5% $[PMe_3H]Cl$ was present.

Preparation of $[PMe_3D]CF_3SO_3$. CF_3SO_3H (1.0 g, 6.7 mmol) was dissolved in 5 mL of ether and added to 15 mL of D_2O. After 15 min of stirring, 1.2 equiv of PMe_3 (0.8 mL, 8 mmol) in 5 mL of ether was added. After 30 min, the solvent was removed and the product dried in vacuo. The product contains virtually no $[PMe_3H]CF_3SO_3$ by ^{31}P NMR.

Preparation of $[W(CHCMe_3)(PMe_3)_4Cl]CF_3SO_3$. $W(CCMe_3)(PMe_3)_4Cl$ (0.82 g, 1.38 mmol) was dissolved in 10 mL of ether. CF_3SO_3H (1 equiv) in 3 mL of ether was added rapidly at 25 °C. A tan precipitate formed immediately, leaving a colorless solution. The crude product was recrystallized from minimal dichloromethane by adding toluene and cooling; total yield 0.70 g (68%).

^1H NMR (CD_2Cl_2, 250 MHz, 295 K): −8.4 (quintet, 1, $J_{HP} = 8.8$ Hz, $WCHCMe_3$), 1.14 (s, 9, $WCHCMe_3$), 1.75 (virtual triplet, 36, $J_{HP} = 3.2$ Hz, PMe_3). The signal at −8.3 did not change between 153 and 295 K in 3:1 $CHFCl_2/CD_2Cl_2$. ^{13}C NMR (CD_2Cl_2, 62.8 MHz, 295 K): 241.9 (br d, $J_{CH} = 44$ Hz, $WCHCMe_3$), 121.3 (q, $J_{CF} = 319$ Hz, CF_3SO_3), 31.7 (q, $J_{CH} = 128$ Hz, $CHCMe_3$), 22.5 (quartet of virtual triplets, $J_{CP} = 8$ Hz, $J_{CH} = 130$ Hz, PMe_3), 51.5 (s, $WCHCMe_3$). ^{31}P NMR (CH_2Cl_2, 36.2 MHz, 300 K): −32.0 (s, $J_{PW} = 247$ Hz). IR (Nujol): no band observed between 1500 and 2200 cm^{-1} that could be attributed to a hydride ligand.

Preparation of $[W(CH_2)(PMe_3)_4Cl]CF_3SO_3$. $W(CH)(PMe_3)_4Cl$ (2.0 g, 3.7 mmol) was suspended in 20 mL of ether. CF_3SO_3H (0.56 g, 3.7 mmol) in 3 mL of ether was added over a period of 1 min. A tan precipitate formed immediately, and the yellow solution became colorless. The mixture was filtered, and the product was washed with 2 × 10 mL of toluene followed by 10 mL of pentane; yield 2.45 g (95%). Recrystallization from 1:5 dichloromethane/chlorobenzene yielded a total of 1.75 g (69%).

Anal. Calcd for $WC_{14}H_{38}ClF_3O_3P_4S$: C, 24.48; H, 5.54. Found: C, 24.65; H, 5.72. ^1H NMR (CD_2Cl_2, 250 MHz, 297 K): −0.16 (s, 2, $J_{HW} = 49.8$ Hz, WCH_2), 1.75 (virtual triplet, 36, $J_{HP} = 3.5$ Hz, PMe_3). ^1H NMR (3:1 $CHFCl_2/CD_2Cl_2$, 250 MHz, 157 K): −7.97 (br s, 1, WCH_2), 7.05 (br s, partially obscured by $CHFCl_2$ resonance, WCH_2), 1.8 (br s, PMe_3). ^{13}C NMR (CD_2Cl_2, 62.8 MHz, 295 K): 220.3 (br t, $J_{CH} = 119$ Hz, WCH_2), 121.0 (q, $J_{CF} = 323$ Hz, CF_3SO_3), 21.9 (br q, $J_{CH} = 131$ Hz, PMe_3). ^{31}P NMR (CH_2Cl_2, 36.2 MHz, 300 K): −31.0 (s, $J_{PW} = 248$ Hz). ^{31}P NMR (3:1 $CHFCl_2/CH_2Cl_2$, 36.2 MHz, 143 K): −22.0 (br s, $J_{PW} = 248$ Hz, PMe_3), −32.8 (br s, $J_{PW} = 248$ Hz, PMe_3'); the two signals have approximately equal areas. IR (Nujol): no band between 1500 and 2200 cm^{-1} that could be assigned to a hydride. Conductivity ($C_2H_4Cl_2$): $\Lambda = 29.5\ \Omega^{-1}\ cm^{-1}\ M^{-1}$ at 0.94×10^{-3} M.

Preparation of "$[W(CHD)(PMe_3)_4Cl]CF_3SO_3$". $W(CH)(PMe_3)_4Cl$ (0.7 g, 1.3 mmol) was dissolved in 5 mL of THF, and 1 equiv of $[PMe_3D]CF_3SO_3$ was added rapidly as a solid at −10 °C. The yellow

solution immediately became red and a red precipiate formed. After 1 h of stirring at 25 °C, the solvent was removed in vacuo. The residue was dissolved in dichloromethane, and the solution was filtered and concentrated to 2 mL. Chlorobenzene (10 mL) was added, and after 1 day of cooling at −10 °C, 0.6 g of red crystals were isolated (67%).

^{1}H NMR (CD_2Cl_2, 250 MHz, 292 K): −0.17 (s, 0.5, J_{HW} = 51 Hz, WCH_2), −1.4 (slightly broadened s, 0.5, J_{HW} = 48 Hz, WCHD), 1.75 (br s, 36, PMe_3). ^{2}H NMR (CH_2Cl_2, 13.8 MHz, 300 K): 0.72 (br s, WCHD), −0.48 (br s, WCD_2). ^{31}P NMR (CH_2Cl_2, 36.2 MHz, 300 K): −31.4 (s, J_{PW} = 248 Hz).

A deuterium-enriched sample was prepared by adding 0.6 mL of CH_3OD to a 0.55-g sample in 3 mL of dichloromethane. After 30 min, all volatiles were removed in vacuo and the product was recrystallized as above; yield 0.28 g (56%). The ratio of WCH_2 to WCHD complexes is 1:5. In the ^{2}H NMR spectrum, the broad singlet at −0.48 ppm is much more intense.

Preparation of W(CH)(H)(PMe_3)$_3$Cl$_2$. W(CH)(PMe_3)$_4$Cl (2.28 g, 4.2 mmol) was dissolved in 10 mL of dichloromethane, and the solution was cooled to −78 °C. Gaseous HCl (1 equiv) was added rapidly with a syringe. The yellow solution became red immediately. After several minutes of stirring at −78 °C, the flask was placed in an ice bath at 0 °C and the solvent was removed in vacuo. The residue was recrystallized from minimal chlorobenzene by adding ether and cooling to −10 °C for 1 day; yield 1.35 g (65%).

Anal. Calcd for $WC_{10}H_{29}Cl_2P_3$: C, 24.15; H, 5.84. Found: C, 24.55; H, 5.95. ^{1}H NMR (CD_2Cl_2, 250 MHz, 200 K): 6.46 (br s, 1, J_{HW} = 78 Hz, WCH), 4.53 (d t, 1, J_{HP} = 17.7 Hz (d), J_{PH} = 95 Hz (t), WH), 1.80 (d, 18, J_{HP} = 9 Hz, PMe_3), 1.60 (d, 9, J_{HP} = 8.5 Hz, PMe_3'). ^{1}H NMR (CD_2Cl_2, 250 MHz, 292 K): 4.63 (br q, 2, J_{PH} = 24 Hz, W(CH)H), 1.69 (br d, 27, J_{PH} = 8 Hz, PMe_3). ^{13}C NMR (C_6D_5Br, 62.8 MHz, 292 K): 246 (br s, J_{CH} unresolved, W(CH)H), 27.0 (br q, J_{CH} = 131 Hz, PMe_3). ^{31}P NMR (CH_2Cl_2, 36.3 MHz, 300 K): −14.3 (br s, J_{PW} = 200 Hz, J_{PH} unresolved). ^{31}P NMR (CH_2Cl_2, 36.2 MHz, 183 K): −19.2 (d, J_{PP} = 80 Hz, J_{PW} = 200 Hz, J_{PH} small and unresolved, PMe_3), 0.4 (br m, $J_{PH} \simeq$ 86 Hz, PMe_3' and PMe_3''). IR (Nujol, cm^{-1}): 1920 (br m, ν_{WH}). Conductivity ($C_2H_4Cl_2$, 263 K): Λ = 3.6 Ω^{-1} cm^{-1} M^{-1} at 1.11 × 10^{-3} M.

Preparation of W(CH)(D)(PMe_3)$_3$Cl$_2$. W(CH)(PMe_3)$_4$Cl (0.80 g, 1.5 mmol) was dissolved in 5 mL of dichloromethane at 25 °C, and 1 equiv of [PMe_3D]Cl (0.17 g, 1.5 mmol) was added rapidly as a solid. The yellow solution became red immediately. After the solution was stirred for 5 min, the solvent was removed in vacuo and the residue was dissolved in THF. The mixture was filtered, and the filtrate was concentrated to 2 mL. Pentane (3 mL) was added, and after 1 day of cooling at −10 °C, 0.50 g of red, crystalline W(CH)(D)(PMe_3)$_3$Cl$_2$ was collected (66%).

^{1}H NMR (CD_2Cl_2, 250 MHz, 205 K): 6.38 (br s, J_{HW} = 79 Hz, WCH), 4.54 (d t, J_{HP} = 96 Hz (t), J_{HP} = 17.7 Hz (d), W(CH)*H*), 4.52 (d, J_{HP} = 95 Hz (t), J_{HP} = 17.7 Hz (d), W(CD)H), 1.80 (d, J_{HP} = 8.8 Hz, PMe_3), 1.61 (d, J_{HP} = 8.8 Hz, PMe_3). ^{2}H NMR (CH_2Cl_2, 38.4 MHz, 204 K): 6.25 (br s, W(CD)), 4.35 (br s, WD). IR (Nujol, cm^{-1}): 1920 (br m, ν_{MH}). ν_{WD} not observed.

Preparation of W(CH)(H)(PMe_3)$_3$(Cl)(BH_3CN). [$W(CH_2)$(Cl)(PMe_3)$_4$]CF_3SO_3 (3.0 g, 4.4 mmol) was suspended in 20 mL of THF, and $NaBH_3CN$ (0.27 g, 4.4 mmol) was added rapidly as a solid. The mixture was stirred for 3 h, the volatiles were removed in vacuo, and the residue was washed with 3 × 5 mL of toluene. The remaining solid was recrystallized at −10 °C from dichloromethane by adding toluene; yield 1.8 g (82%).

Anal. Calcd for $WC_{11}H_{32}BClNP_3$: C, 26.34; H, 6.39. Found: C, 26.69; H, 6.44. ^{1}H NMR (CD_2Cl_2, 250 MHz, 200 K): 5.99 (br s, 1, J_{HW} = 79 Hz, WCH), 4.33 (m, 1, WH), 1.72 (virt t, 18, J_{HP} = 7.9 Hz, PMe_3), 1.54 (d, 9, J_{HP} = 7.9 Hz, PMe_3'), 0.43 (br s, 3, BH_3CN). ^{1}H NMR (CD_2Cl_2, 250 MHz, 292 K): 3.86 (br q, 2, J_{HP} = 20 Hz, W(CH)H), 1.69 (br s, 27, PMe_3), 0.66 (br 1:1:1:1 q, 3, $J_{HB} \approx$ 90 Hz, BH_3CN). ^{13}C NMR (CD_2Cl_2, 62.8 MHz, 297 K): 248.7 (br s, W(CH)H), 165.4 (br s, BCN), 24.2 (br s, PMe_3), 19.0 (br q, J_{CH} = 127 Hz, PMe_3). ^{31}P NMR (3:1 $CHFCl_2/CD_2Cl_2$, 36.2 MHz, 260 K): −12.4 (br s, PMe_3). ^{31}P NMR (3:1 $CHFCl_2/CD_2Cl_2$, 36.2 MHz, 168 K): −19.1 (dd, J_{PP} = 56 Hz, J_{PP} = 88 Hz, J_{PW} = 185 Hz, PMe_3), 4.2 (dd, J_{PP} = 29 Hz, J_{PP} = 86 Hz, J_{PW} = 166 Hz, PMe_3'), −2.9 (dd, J_{PP} = 29 Hz, J_{PP} = 56 Hz, J_{PW} = 156 Hz, PMe_3''). IR (Nujol, cm^{-1}): 1920 (m, sl br, WH), 2200 (s, sh, CN), 2340 (s, sl br, BH). Conductivity ($C_2H_4Cl_2$): Λ = 1.03 Ω^{-1} cm^{-1} M^{-1} at 1.47 × 10^{-3} M.

Preparation of W(CH)(H)(PMe_3)$_3$(Cl)(BD_3CN). W(CH)(H)(PMe_3)$_3$(Cl)(BD_3CN) was prepared in a manner analogous to that used to prepare W(CH)(H)(PMe_3)$_3$Cl(BH_3CN), except that $NaBD_3CN$ was used in place of $NaBH_3CN$.

^{1}H NMR (CD_2Cl_2, 250 MHz, 205 K): 5.99 (br s, 1, J_{HW} = 79 Hz, WCH), 4.45 (m, 1, WH). All other signals are the same as for W(CH)(H)(PMe_3)$_3$(Cl)(BH_3CN), except that no resonance is observed for the B–H functionality. IR (Nujol, cm^{-1}): 2200 (s, sh, CN), 1920 (m, sl, br, WH), 1765 (s, sl br, BD), 1680 (m, sl br, BD), 1630 (w, sl br, BD), 2340 (vw, BH); a WD band was not observed.

Measurement of the Gases Formed on Preparation of W(CH)(Cl)(PMe_3)$_4$. $WCl_2(PMe_3)_4$ (0.61 g, 1.09 mmol) and $AlMe_3$ (0.16 g, 2.18 mmol) were each dissolved in 3 mL of toluene and placed in separate flasks attached to a vacuum line. Each solution was degassed by three freeze–pump–thaw cycles, and then the $AlMe_3$ was condensed into the flask containing the $WCl_2(PMe_3)_4$ at −196 °C. The mixture was warmed to 25 °C and stirred for 8 h. The gases were transferred to a separate flask of known volume with the use of a Toepler pump. A series of six trials yielded values of 0.93–1.22 equiv of gas, with an average of 1.14.

After isolation of the gases from the reaction mixture, a known quantity of propane (0.114 mmol) was added by means of a Toepler pump. Analysis of the gases on a Spherocarb column led to average values of 70% CH_4 and 85% CH_4 for samples from two different reaction mixtures.

Acknowledgment. We thank the National Science Foundation for support (CHE 79 05307).

Registry No. *trans*-W($CCMe_3$)(dmpe)$_2$(H), 83043-23-6; *trans*-W($CCMe_3$)(dmpe)$_2$(D), 83043-24-7; *trans*-W($CCMe_3$)(dmpe)$_2$Cl, 83043-25-8; [W($CCMe_3$)(dmpe)$_2$(H)Cl]Cl, 83060-48-4; [W($CCMe_3$)(dmpe)$_2$(D)Cl]Cl, 83060-49-5; [W($CCMe_3$)(dmpe)$_2$(H)Cl]CF_3CO_2, 83043-27-0; W(CH)(PMe_3)$_4$Cl, 76642-46-1; W($CCMe_3$)(PMe_3)$_4$Cl, 83043-28-1; W(CH)(dmpe)$_2$Cl, 79217-96-2; [W(CH)(H)(dmpe)$_2$Cl]Cl, 79233-42-4; [W(CH)(H)(dmpe)$_2$Cl]CF_3SO_3, 79254-95-8; [W(CH)(D)(dmpe)$_2$Cl]Cl, 83043-29-2; [PMe_3D]Cl, 83043-38-3; [PMe_3D]CF_3SO_3, 83060-50-8; [W($CHCMe_3$)(PMe_3)$_4$Cl]CF_3SO_3, 83043-31-6; [$W(CH_2)$(PMe_3)$_4$Cl]CF_3SO_3, 79197-71-0; [W(CHD)(PMe_3)$_4$Cl]CF_3SO_3, 83043-33-8; W(CH)(H)(PMe_3)$_3$Cl$_2$, 83043-34-9; W(CH)(D)(PMe_3)$_3$Cl$_2$, 83043-35-0; W(CH)(H)(PMe_3)$_3$(Cl)(BH_3CN), 83043-36-1; W(CH)(H)(PMe_3)$_3$(Cl)(BD_3CN), 83043-37-2; W(dmpe)(CH_2CMe_3)($CHCMe_3$)($CCMe_3$), 68446-90-2; *trans*-Me_3CCH=$CHCMe_3$, 692-48-8; $WCl_2(PMe_3)_4$, 76624-80-1; Et_4N[W($CCMe_3$)Cl_4], 78251-20-4; PMe_3, 594-09-2; DCl, 7698-05-7; CF_3SO_3H, 1493-13-6; D_2O, 7789-20-0; [$W(CH_2)$(Cl)(PMe_3)$_4$]CF_3SO_3, 79197-71-0; $NaBH_3CN$, 25895-60-7; $NaBD_3CN$, 25895-62-9.