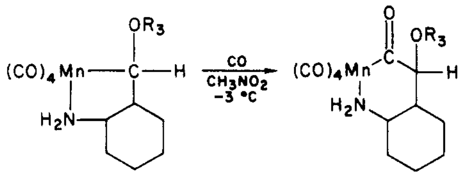


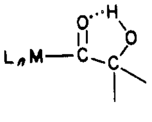
(3)

2c, $R_3 = H$
d, $R_3 = Si(CH_3)_3$

3c
3d

and $(4.0 \pm 0.2) \times 10^{-7}\ s^{-1}$ (**2d**) were measured. Hence, at −3 °C and 250–360 psi of CO in CH_3NO_2, *α-hydroxyalkyl complex 2c carbonylates over 16 times faster than its α-(trimethylsilyl)oxy analogue.*

Previously, we reported that α-((trimethylsilyl)oxy)alkyl complex $(CO)_5MnCH_2OSi(CH_3)_3$ carbonylates ca. 3.5 times *faster* (24 °C, 750–1500 psi) than α-methoxyalkyl complex $(CO)_5MnCH_2OCH_3$.[6b] Hence, there is no evidence that the bulk of the α-(trimethylsilyl)oxy substitute inhibits carbonylation. How then can the more rapid carbonylation of the α-hydroxyalkyl ligand be accounted for? We believe that an important clue is furnished by the IR spectra shown in Figure 1. A comparison of the ν_{OH} region of **3c** and **2c** and the $\nu_{C=O}$ region of **3c** and **3d** clearly indicates the presence of a hydrogen bond in **3c**.[11] This is shown schematically in **4**. Furthermore, the ^{13}C NMR spectra of **3c** (CD_3OD) and **3d** (CD_2Cl_2) are virtually superimposable,[9] except that the acyl resonance of **3c** is 11 ppm downfield of that in **3d**. We suggest that the faster rate of carbonylation of **2c** may be due to *intramolecular hydrogen bond stabilization of the transition state or equilibrium* for the first step of eq 1.[12] As precedent, we note that Shriver found that proton acids can accelerate the carbonylation of $(CO)_5MnCH_3$;[13] he attributed this to *intermolecular* hydrogen bond stabilization of the transition state.



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In summary, we have established the viability of intramolecular hydrogen bonding in metal α-hydroxyacyl complexes. This, when coupled with the above rate data, suggests some possible, previously unrecognized, controlling factors in the conversion of CO/H_2 to ethylene glycol. Further studies of the chemistry of metallacyclic α-hydroxyalkyl complexes are in progress.

Acknowledgment. We thank the Department of Energy for support of this research.

Registry No. 1a, 41742-59-0; **1b**, 41742-60-3; **1c**, 91743-29-2; **2a**, 91743-30-5; **2b**, 91743-31-6; **2c**, 91743-32-7; **2d**, 91743-33-8; **3c**, 91743-34-9; **3d**, 91759-05-6; CO, 630-08-0; ethylene glycol, 107-21-1.

Supplementary Material Available: Tables of IR, ^{13}C NMR, and ^1H NMR spectra and other characterizations of **2a–d** and **3c–d** (4 pages). Ordering information is given on any current masthead page.

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[11] See: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds"; 4th ed.; Wiley: New York, 1981; pp 112–115, 118.

[12] The expected rate equation,[5,6] $-d[\mathbf{2c}]/dt = k_1k_2[CO][\mathbf{2c}]/(k_{-1} + k_2[CO])$, has two limiting cases. When $k_2[CO] >> k_{-1}$, the proposed hydrogen bond induced rate acceleration would reflect stabilization of a transition state (k_1), whereas when $k_{-1} >> k_2[CO]$, the rate acceleration would arise from stabilization of an intermediate (preequilibrium shift). In our experiments, these limiting conditions have apparently not yet been reached. Also, note that in substrates such as **2a–c**, hydrogen bonding would direct the alkyl migration to only *one* of the four inequivalent CO ligands.

[13] Butts, S. B.; Richmond, T. G.; Shriver, D. F. *Inorg. Chem.* **1981**, *20*, 278.

Synthesis and Characterization of Sulfur-Capped Trinuclear Group 6B Metal Clusters

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Summary: The sulfur-capped trinuclear chromium carbonyl cluster $S[Cr(CO)_4]_3^{2-}$ has been synthesized and shown to arise via carbon monoxide loss from the CO-saturated $S[Cr(CO)_5]_3^{2-}$ species. The carbon monoxide ligands display complete stereochemical nonrigidity at ambient temperature. In a low-energy process that occurs below −60 °C the bridging carbon monoxide groups and the set of terminal CO groups that are cis to the capping sulfide moiety undergo fast exchange when compared to their chemical shift differences (1218 Hz at 50.3 MHz). A subsequent, higher energy exchange process of these carbon monoxide ligands with the remaining terminal carbonyl sites (those trans to the sulfide cap) occurs at temperatures greater than −20 °C. Addition of $Cr(^{13}CO)_5THF$ to the $S[Cr(CO)_4]_3^{2-}$ trimer results in formation of $(CO)_5CrS[Cr(CO)_4]_3^{2-}$, where the ^{13}CO ligands are shown to be statistically distributed throughout the tetrameric species.

Our interest in metal carbonyl sulfide and oxide complexes that might serve as useful models for metal carbonyls adsorbed at sulfide or oxide sites on surfaces[1] includes fundamental studies utilizing sulfur and oxygen as good nucleating ligands for group 6B metal carbonyls. A large variety of metal carbonyl derivatives containing oxygen or sulfide donor ligands display facile carbon monoxide exchange; i.e., these ancillary ligands are extremely CO labilizing.[1,2] Indeed this property of group 6B derivatives most readily accounts for the formation of metal species of higher nuclearity. For example, the tetranuclear chromium derivatives $[Cr(CO)_3OR]_4^{4-}$ (R = CH_3, Ph, H), which contain no Cr–Cr bonds, are presumably formed by aggregation of $Cr(CO)_5OR^-$ species.[3,4] Similar synthetic methodology is pivotal in the formation of the tetrameric chromium cluster $[PPN]_2[(\mu\text{-}CO)_3(CO)_9Cr_3(\mu_4\text{-}S)Cr(CO)_5]$,[5] which has recently been reported. This derivative represents the first fully characterized group 6B metal carbonyl cluster, although an early report of $Na_2[Cr_3(CO)_{14}]$ by Behrens may prove to be the first such species prepared.[6,7] We disclose herein further studies aimed at obtaining a better understanding of what promises to be a general route to the elusive group 6B metal carbonyl clusters.

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[1] Darensbourg, D. J.; Rokicki, A.; Kudaroski, R. *Organometallics* **1982**, *1*, 1161.

[2] (a) Darensbourg, D. J.; Rokicki, A. *Organometallics* **1982**, *1*, 1685. (b) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 398. (c) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S.; Kudaroski, R. *Inorg. Chem.* **1982**, *21*, 1656. (d) Darensbourg, D. J.; Walker, N.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1980**, *102*, 1213; *Inorg. Chem.* **1981**, *20*, 1918. (e) Darensbourg, D. J.; Pala, M.; Waller, J. *Organometallics* **1983**, *2*, 1285.

[3] McNeese, T. J.; Cohen, M. B.; Foxman, B. M. *Organometallics* **1984**, *3*, 552.

[4] McNeese, T. J.; Darensbourg, D. J.; Delord, T. *Organometallics*, to be submitted for publication.

[5] Hoefler, M.; Tebbe, K.-F.; Veit, H.; Weiler, N. E. *J. Am. Chem. Soc.* **1983**, *105*, 6338.

[6] Behrens, H.; Haag, W. *Chem. Ber.* **1961**, *94*, 320.

[7] Lin and Ellis have suggested that a solid containing approximately a 4:1 ratio of $Na[HMo_2(CO)_{10}]$ to $Na_4[HMo(CO)_3]_4$ would provide elemental analysis similar to that calculated for Behren's compound, "$Na_2[Mo_3(CO)_{14}]$". Lin, J. T.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 6252.

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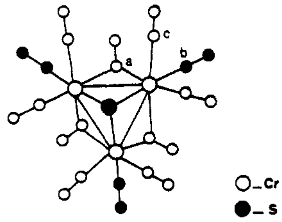
A reaction mixture of 1 equiv of $Cr(CO)_5THF$ (prepared photochemically from $Cr(CO)_6$ in THF) and $[Na][PPN][\{(CO)_5Cr\}_2S]$ (synthesized from $[PPN][\{Cr(CO)_5\}_2SH]$ and NaH)[8] was stirred at 0 °C under nitrogen followed by the addition of [PPN][Cl] in ethanol. The solution was allowed to stir overnight during which time the temperature increased to ambient conditions. The solvent was removed in vacuo and the residue dissolved in acetone. Upon addition of diethyl ether, red crystals of $[PPN]_2[\{(CO)_4Cr\}_3S]\cdot(CH_3)_2CO$ in 53% yield were obtained.[9] During the entire reaction sequence the principal metal carbonyl species present in solution was $\{(CO)_5Cr\}_3S^{2-}$ as evidenced by infrared spectroscopy.[10] When CO was allowed to escape the solution, formation of red crystals of **2** readily takes place, with readmission of a carbon monoxide atmosphere leading to a reformation of **1** (eq 1).

$$\underset{\mathbf{1}}{\{(CO)_5Cr\}_3S^{2-}} \rightleftharpoons \underset{\mathbf{2}}{\{(CO)_4Cr\}_3S^{2-}} + 3CO \tag{1}$$

The temperature-dependent ^{13}C NMR spectra (Figure 1) of the $[(CO)_4Cr]_3S^{2-}$ anion suggest a structure analogous to that reported by Hoefler and co-workers[5] with the absence of the appended $Cr(CO)_5$ group.[11] The bridging CO groups (*a*) are assigned the most downfield resonance at 254.0 ppm, with the terminal CO resonances occurring at 229.7 ppm (*c*) and 236.1 ppm (*b*). As anticipated, the resonance for the terminal CO ligands trans to the capping S group occurs downfield from those cis to the μ_3-S donor.[1] The CO ligands display complete stereochemical nonrigidity at ambient temperature with the ^{13}C NMR spectrum exhibiting one resonance at 237.4 ppm, the weighted average of the three different carbonyl signals. The details of this fluxional process are shown in Figure 1 where, in a low-energy pathway, carbon monoxide sites *a* and *c* undergo fast exchange when compared to their chemical shift differences (1218 Hz at 50.3 MHz). Subsequent facile exchange with the *b* carbonyl sites occurs above −20 °C.

Addition of ^{13}C-enriched $Cr(CO)_5THF$ to **2** at ambient temperature results in production of the previously reported $(\mu\text{-}CO)_3(CO)_9Cr_3(\mu_4\text{-}S)Cr(CO)_5^{2-}$ anion in 90% yield with the ^{13}CO label statistically distributed throughout the species.[12] The trinuclear portion of the molecule exhibits a ^{13}C NMR spectrum much like that seen for **2** with resonances corresponding to *a*, *b*, and *c* sites at 252.1, 232.9, and 226.5 ppm, respectively. The $Cr(CO)_5$ portion of the molecule exhibits two carbonyl resonances at 223.7 (CO_{trans}) and 216.4 ppm (CO_{cis}).[13] It was necessary to observe the ^{13}C NMR spectrum of this tetrachromium species at −110 °C, a slightly lower temperature than that needed for derivative **2**, to completely freeze out intramolecular CO exchange. The temperature dependence of the ^{13}C NMR spectrum for the triangular chromium moiety was much the same as that observed for species **2** with the appended $Cr(CO)_5$ unit entering in the exchange process at temperatures greater than 10 °C. Analogous observations were



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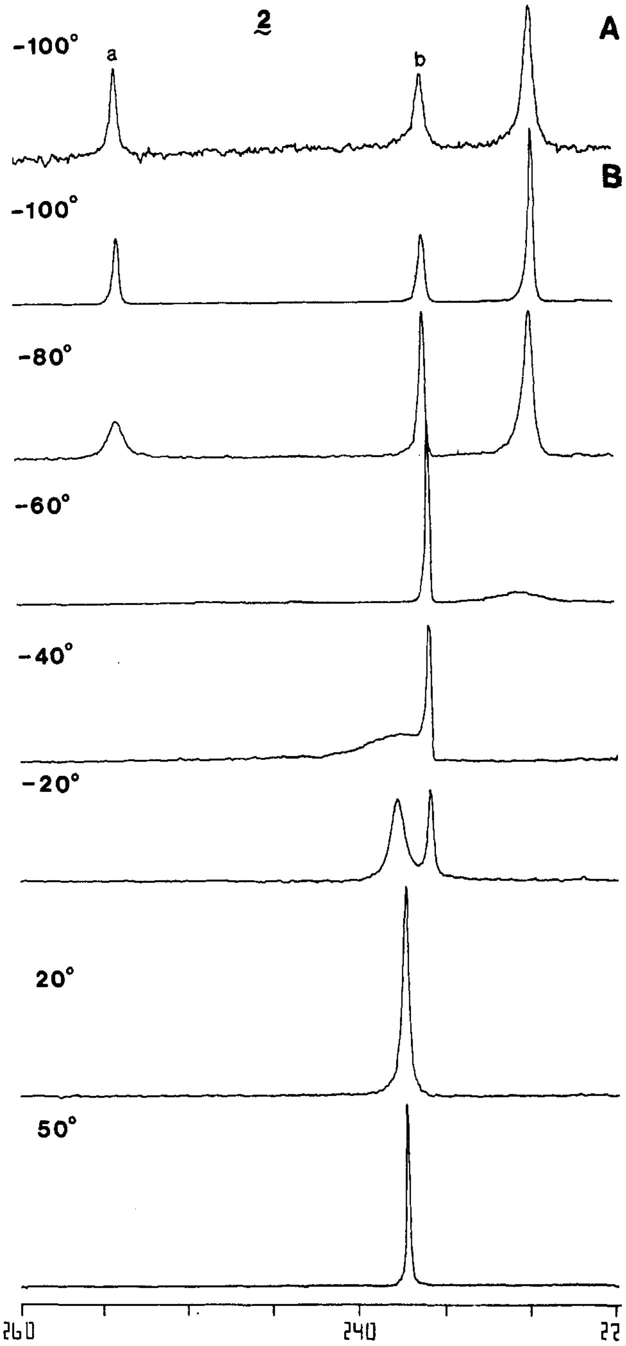

Figure 1. Temperature-dependent ^{13}C NMR spectra of $S[Cr(CO)_4]_3^{2-}$ in tetrahydrofuran. A: natural abundance spectrum at −100 °C, chemical shift values are *a* = 254.0 ppm, *b* = 236.1 ppm, and *c* = 229.7 pm. B: spectrum of ^{13}C-enriched sample used in temperature-dependent studies at −100 °C.

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(9) Anal. Calcd: C, 62.97; H, 4.01; N, 1.69; P, 7.47; S, 1.93. Found: C, 63.10; H, 4.18; N, 1.50; P, 7.55; S, 2.03. The infrared spectrum in the ν_{CO} region in tetrahydrofuran: 2008 (vw), 1946 (s), 1898 (s), 1847 (m), 1787 (w), and 1715 (w) cm^{-1} (acetone). The dark red crystals crystallized in a monoclinic space group, with unit cell constants *a* = 25.792 (2) Å, *b* = 14.29 (1) Å, *c* = 26.69 (1) Å, *β* = 96.21 (4)°, and *V* = 9779.4 $Å^3$. A complete X-ray structural analysis of this species is underway.

(10) Obtained as a yellow powder. The infrared spectrum in the ν_{CO} region in tetrahydrofuran is typical of $M(CO)_5$ species: 2044 (m), 1937 (s), 1873 (m) cm^{-1}. The ^{13}C NMR spectrum displays two peaks at 218.9 and 223.9 ppm of relative intensity 4:1. On a highly ^{13}C-enriched sample the peak at 218.9 ppm is split into a doublet with the peak at 223.9 ppm being split into a quintet ($J_{^{13}C-^{13}C}$ = 5.8 Hz).

(11) ^{13}C NMR spectra were detd. on a Varian XL-200 spectrometer in THF-d_8 on both natural abundance and ^{13}C-enriched samples.

(12) The derivative prepared from non-^{13}CO-enriched $Cr(CO)_5THF$ provided an infrared spectrum essentially the same as that reported in ref 5.

(13) These are the expected chemical shift values for a S–$Cr(CO)_5$ unit, unlike those values provided in ref 5. The values are quite similar to those noted for species 1, with analogous ^{13}C–^{13}C coupling constants being observed.

noted when ^{13}C-enriched W(CO)$_5$THF was added to the S[Cr$_3$(CO)$_{12}$]$^{2-}$ anion.

Acknowledgment. The financial support of the Robert A. Welch Foundation is greatly appreciated.

Registry No. 1, 91670-43-8; 2^{2-} [PPN$^+$]$_2$·(CH$_3$)$_2$CO, 91670-45-0; [Na][PPN][{(CO)$_5$Cr}$_2$S], 87039-34-7; (μ-CO)$_3$(CO)$_9$Cr$_3$(μ_4-S)Cr(CO)$_5$$^{2-}$, 87050-03-1; Cr(CO)$_5$THF, 15038-41-2; W(CO)$_5$THF, 36477-75-5.

Methathesis of Molybdenum–Molybdenum Triple Bonds with Acetylenes To Give Alkylidyne Complexes[1]

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Summary: Mo$_2$(OCMe$_3$)$_6$ reacts with phenylacetylene in pentane to produce Mo(CPh)(OCMe$_3$)$_3$ in ~60% yield (by ^{1}H NMR) in ~2 h. It can be isolated by sublimation in ~30% yield. In the presence of quinuclidine (quin) Mo$_2$(OCMe$_3$)$_6$ reacts with phenylacetylene to yield an inseparable 1:1 mixture of Mo(CPh)(OCMe$_3$)$_3$(quin) and Mo(CH)(OCMe$_3$)$_3$(quin) in a combined yield of ~60%. Analogous reactions between Mo$_2$(OCMe$_3$)$_6$ and 1-pentyne in the presence of quinuclidine yield oily 1-pentyne oligomers containing a mixture of Mo(CPr)(OCMe$_3$)$_3$(quin) and Mo(CH)(OCMe$_3$)$_3$(quin) in ~50% yield (by ^{1}H NMR). In the absence of quinuclidine only Mo(CPr)(OCMe$_3$)$_3$ is observed by NMR in the oily product mixture. Addition of acetylene to Mo$_2$(OCMe$_3$)$_6$ yields what we propose to be Mo$_2$(OCMe$_3$)$_6$(μ-C$_2$H$_2$), which upon attempted recrystallization loses acetylene to reform Mo$_2$(OCMe$_3$)$_6$.

Two years ago we reported that W$_2$(OCMe$_3$)$_6$ reacts with disubstituted acetylenes to give alkylidyne complexes of the type W(CR)(OCMe$_3$)$_3$ and with nitriles to give a mixture of W(CR)(OCMe$_3$)$_3$ and [W(N)(OCMe$_3$)$_3$]$_x$.[2] The reaction appeared to be highly specific in that other W$_2$X$_6$ complexes (e.g., X = NMe$_2$, OCH$_2$CMe$_3$, CH$_2$SiMe$_3$) either did not react with acetylenes or nitriles or did not give alkylidyne complexes. We thought it peculiar that Mo$_2$(OCMe$_3$)$_6$ also did not react with disubstituted acetylenes or with nitriles, especially since reactions between both W$_2$(OR)$_6$ and Mo$_2$(OR)$_6$ (R = *i*-Pr, *t*-Bu, CH$_2$-*t*-Bu) and acetylenes have produced a number of interesting, closely related, dimeric compounds containing one or more acetylenes.[3] Here we report that the Mo$\equiv$Mo bond in Mo$_2$(OCMe$_3$)$_6$ *can* be cleaved under mild conditions, but only by terminal acetylenes.

Mo$_2$(OCMe$_3$)$_6$[4] in pentane (~50 mg in ~3 mL) reacts immediately with 15 equiv of phenylacetylene to give a brown solution and over a period of 2 h a brown precipitate. The solvent was removed from the filtrate to give a brown residue that by ^{13}C NMR was shown to contain Mo(CPh)(OCMe$_3$)$_3$ in a yield of 50–60% (^{1}H NMR vs. an internal standard).[5] Mo(CPh)(OCMe$_3$)$_3$ can be sublimed from the crude mixture at 65 °C (0.001 μm) in ~30% yield (vs. Mo$_2$(OCMe$_3$)$_6$.[7] Lowering the temperature (6 h at 0 °C, 12 h at 25 °C) did not improve the yield (~40% crude). Use of fewer equivalents of phenylacetylene leads to incomplete consumption of Mo$_2$(OCMe$_3$)$_6$. The yield also was not improved by adding a dilute solution of the acetylene to a solution of Mo$_2$(OCMe$_3$)$_6$ (concentrated or dilute) over a period of 1 h. On the basis of these results we can only conclude that the Mo$\equiv$Mo bond is split by PhC$\equiv$CH; we do not know the fate of "Mo(CH)(OCMe$_3$)$_3$".

Studies in the related tungsten system[6] have shown that W$_2$(OCMe$_3$)$_6$ reacts with PhC$\equiv$CH in the presence of quinuclidine (1-azabicyclo[2.2.2]octane) to produce a 1:1 mixture of W(CPh)(OCMe$_3$)$_3$(quin) and W(CH)(OCMe$_3$)$_3$(quin) in high yield. The reaction between Mo$_2$(OCMe$_3$)$_6$ and PhC$\equiv$CH (3 equiv/dimer) in the presence of quinuclidine (8 equiv) proceeds analogously (eq 1) in ~60% yield (by ^{1}H NMR vs. CH$_2$Cl$_2$ as an internal standard) in 2 h in pentane. The methylidyne proton in Mo(CH)(OCMe$_3$)$_3$(quin) is observed at 3.98 ppm (in C$_6$D$_6$) and the methylidyne carbon atom at 267.2 ppm (in C$_6$D$_6$; J_{CH} = 146 Hz) in the crude reaction mixture (cf. W(CH)(OCMe$_3$)$_3$(quin)[10]). Slow, partial sublimation of the crude reaction mixture at 25 °C and 0.001 μm yields a virtually identical mixture of Mo(CPh)(OCMe$_3$)$_3$(quin) and Mo(CH)(OCMe$_3$)$_3$(quin). So far we have not found a way to separate these two compounds. We propose that Mo(CH)(OCMe$_3$)$_3$(quin) is produced when the primary product Mo(CH)(OCMe$_3$)$_3$ is trapped by quinuclidine. In the absence of quinuclidine some of the methylidyne complex is *probably* converted into Mo(CPh)(OCMe$_3$)$_3$, judging from the 50 ± 5% yield quoted above, although whether that conversion consists of a metathesis reaction between Mo(CH)(OCMe$_3$)$_3$ and PhC$\equiv$CH is unknown.[11]

$$\mathrm{Mo_2(OCMe_3)_6 \xrightarrow[quin]{PhC\equiv CH} Mo(CPh)(OCMe_3)_3(quin) + Mo(CH)(OCMe_3)_3(quin)} \tag{1}$$

A reaction similar to that shown in eq 1 in the presence of pyridine (4 equiv) yields only Mo(CPh)(OCMe$_3$)$_3$(py) in ~50% yield by ^{1}H NMR (vs. CH$_2$Cl$_2$). Attempted sublimation of Mo(CPh)(OCMe$_3$)$_3$(py) from the crude reaction mixture yielded only Mo(CPh)(OCMe$_3$)$_3$.

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(1) Multiple Metal-Carbon Bonds. 36. For part 35 see ref 6.

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(4) Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *Inorg. Chem.* **1977**, *16*, 1801.

(5) δ(CPh) 276.7 in Mo(CPh)(OCMe$_3$)$_3$ in C$_6$D$_6$; cf. δ(CPh) 257.0 in W(CPh)(OCMe$_3$)$_3$ in C$_6$D$_6$.[6]

(6) Listemann, M. L.; Schrock, R. R. *Organometallics*, in press.

(7) (a) Anal. Calcd for MoC$_{19}$H$_{32}$O$_3$: C, 56.43; H, 7.97. Found: C, 55.73; H, 7.86. (b) We have recently discovered[8] that Mo(CCMe$_3$)(OCMe$_3$)$_3$ can be prepared from MoO$_2$Cl$_2$ via (Mo(CCMe$_3$)(CH$_2$CMe$_3$)$_3$.[9] Although Mo(CCMe$_3$)(OCMe$_3$)$_3$ does *not* react with disubstituted acetylenes, it *will* react with terminal acetylenes to give Mo(CR)(OCMe$_3$)$_3$ and Me$_3$CC$\equiv$CH quantitatively McCullough, L., unpublished results). Both Mo(CPh)(OCMe$_3$)$_3$ and Mo(CPr)(OCMe$_3$)$_3$ (inter alia) have been prepared by this method. Addition of quinuclidine to Mo(CPr)(OCMe$_3$)$_3$ gives Mo(CPr)(OCMe$_3$)$_3$(quin) quantitatively, while addition of pyridine to Mo(CPh)(OCMe$_3$)$_3$ gives Mo(CPh)(OCMe$_3$)$_3$(py).

(8) McCullough, L. G.; Schrock, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 4067.

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

(10) In W(CH)(OCMe$_3$)$_3$(quin) the methylidyne proton is observed at 5.15 ppm and the carbon atom at 247.1 ppm (J_{CW} = 287 Hz, J_{CH} = 147 Hz) in C$_6$D$_6$.[6]

(11) Chisholm has obtained strong evidence that W$_2$(μ-C$_2$H$_2$)(py)(OCMe$_3$)$_5$(μ-OCMe$_3$) is in equilibrium with "W(CH)(OCMe$_3$)$_3$" in the presence of pyridine (probably as an unstable pyridine adduct, W(CH)(OCMe$_3$)$_3$(py)).[3b] Conceivably, therefore, Mo(CH)(OCMe$_3$)$_3$ could decompose bimolecularly to reform Mo$_2$(OCMe$_3$)$_6$, which could then react with more PhC$\equiv$CH.

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