TEM micrographs (Figure 3), showed the material to be a mixture of 12.2–26.5-nm spherical particles and single-crystal whiskers, with the latter predominating. TEM–SAD analysis confirmed the whisker phase to be α-ZnS (wurtzite) and the powder to be predominantly β-ZnS (zinc blende). A representative sample whisker, 0.74 μm long with an aspect ratio of 14, is shown in Figure 4. The whiskers typically range from 0.4 to 1.0 μm in length with aspect ratios of 10–18. The reaction temperature and H_2S flow rate are critical parameters in determining whether or not whiskers form. No whiskers were observed in experiments where the furnace temperature was kept below 400 °C or where the H_2S flow rate was greater than 100 mL/min. A flow rate of 70 mL/min was optimum. It must be emphasized that the whiskers form only when the sample is heated in the presence of H_2S, and so the H_2S must play a critical role in the morphological change.

A number of observations indicate that the two factors which are critical to the formation of whiskers are the fibrous morphology of the initial precipitate from eq 2 and the presence of residual organics in the material. As suggested in eq 2, the first step in the reaction of the pentameric precursor with H_2S presumably involves cleavage of the Zn–Et bonds to yield ethane and Zn–SH groups, and such species should readily polymerize to yield a cross-linked, three-dimensional network. When the H_2S flow rate in reaction 2 is low (5 cm³/min), a weakly cross-linked material containing a substantial amount of residual organics precipitates in the fibrous morphology shown in Figure 1. TEM analysis has shown that when this material is heat-treated under H_2S at 500 °C, the fibrous solid progressively changes into a fibrous agglomerate of nanometer-sized ZnS particles that then fuse together to form the whiskers observed in Figures 3 and 4. Other work in our laboratory has shown that higher H_2S flow rates (85 cm³/min) give instead a highly cross-linked precipitate having a particulate morphology, not fibrous, and containing little residual organics. No whiskers form upon 500 °C heat treatment of this latter material.

The process by which the nanometer-sized ZnS particles fuse together to form the whiskers appears to be related to the established high-temperature chemical transport routes to ZnS whiskers. In these methods, a high-purity ZnS source is sublimed at >900 °C, and the vapor is passed into a temperature gradient, where the whiskers grow. Our low-temperature route presumably involves a similar process in which the polymeric precursor reacts with H_2S to form a volatile organometallic product that condenses to fuse the nanometer-sized particles together into a whisker morphology. Consistent with this suggestion is the observation that whiskers are never produced if the H_2S flow rate is high, apparently because the volatile ZnS precursors are swept out of the reaction zone. Furthermore, in some of the TEM analyses on the initially formed white powder produced by eq 1, it was observed that whenever the electron beam was highly focused, the sample vaporized and condensed onto other parts of the TEM grid in a *fibrous morphology*.

In summary, we have shown that micro-sized single-crystal whiskers of ZnS can be reproducibly formed by a novel low-temperature organometallic-based route. These whiskers are precisely the size needed to form composites for IR applications, and experiments are currently in progress to fabricate whisker-reinforced ZnS/ZnS composite materials that should have improved mechanical properties. Those results will be reported in due course.

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Synthesis and X-ray Crystal Structure of Zerovalent Tungsten Aryloxide Dimers

Sir:

The intermediacy of low-valent group 6 transition-metal alkoxide complexes in catalytic processes, e.g., aldehyde/ketone reductions (eq 1)[1] and methanol carbonylation,[2] has been established. Because of the reversible nature of reaction 1 zerovalent,

$$[M]-H^- + R_2CO \rightleftharpoons [M]-OCHR_2^- \qquad (1)$$

mononuclear group 6 metal alkoxides are unstable with respect to formation of the metal hydride and corresponding aldehyde or ketone. Hence, it has proved difficult to isolate and fully characterize these alkoxide species. On the other hand, the aryloxide complexes can be isolated.[3] In this communication we wish to report on the coordination chemistry of μ_2-aryloxide derivatives of tungsten.

We have established the interconversions illustrated in Scheme I. The aryloxide complexes enclosed in boxes have been isolated as pure compounds and have been fully characterized. The mononuclear aryloxide derivatives $[Et_4N][W(CO)_5OR]$ (R = Ph, $C_6H_4CH_3\text{-}m$)[4] are stable in tetrahydrofuran solution in the presence of 1 atm of carbon monoxide. At ambient temperature in solution these complexes exhibit facile CO ligand exchange as evidenced by the rapid incorporation of ^{13}CO (eq 2). In the

$$W(CO)_5OR^- + {}^{13}CO \rightleftharpoons W(CO)_{5-n}({}^{13}CO)_nOR^- + CO \qquad (2)$$

absence of a carbon monoxide atmosphere these anionic mononuclear complexes afford the tetranuclear derivatives[5,6] $[W_4(CO)_{12}(\mu_3\text{-}OR)_4]^{4-}$, with no spectral evidence for the intermediacy of $[W_2(CO)_8(\mu\text{-}OR)_2]^{2-}$. On the other hand, another dimeric species is isolable that is triply bridged by phenoxide groups, $[W_2(CO)_6(OR)_3]^{3-}$, resulting from reaction of either the monomer or tetramer with excess phenoxide. By way of contrast, thermolysis of $W(CO)_5SPh^-$ causes loss of CO, yielding the double-bridged sulfur dimer $W_2(CO)_8(\mu\text{-}SPh)_2^{2-}$.[7] This dimer exists exclusively as the anti isomer and hence does not undergo further dimerization to the tetranuclear $[W_4(CO)_{12}(\mu\text{-}SPh)_4]^{4-}$ derivative. Evidently, the dimeric phenoxide complex, if formed, is in the syn isomeric form or readily isomerizes to the syn isomer, which leads to the tetranuclear derivative upon loss of carbon monoxide.

The trimethylsilyl oxide complex $W(CO)_5OSiMe_3^-$ (prepared from $W(CO)_5\cdot THF$ and $KOSiMe_3$) is unique in this regard in that in the absence of carbon monoxide it affords the dimer

(1) (a) Gaus, P. L.; Kao, S. C.; Youngdahl, K.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1985**, *107*, 2428. (b) Tooley, P. A.; Ovalles, C.; Kao, S. C.; Darensbourg, D. J.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1986**, *108*, 5465. (c) Marks, L.; Nagy-Magos, Z. *J. Organomet. Chem.* **1985**, *285*, 193.
(2) (a) Darensbourg, D. J.; Gray, R. L.; Ovalles, C.; Pala, M. *J. Mol. Catal.* **1985**, *29*, 285. (b) Darensbourg, D. J.; Gray, R. L.; Ovalles, C. *J. Mol. Catal.* **1987**, *41*, 329.
(3) Darensbourg, D. J.; Sanchez, K. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 290.
(4) The $[Et_4N][W(CO)_5OR]$ complexes were synthesized by the reaction of $W(CO)_5THF$ with the corresponding $[Et_4N][OR]$ salts. X-ray-quality crystals of $[Et_4N][W(CO)_5OPh]$ were grown from concentrated THF solutions saturated with carbon monoxide upon the slow layering of hexane. Anal. Calcd for $[Et_4N][W(CO)_5OPh]$: C, 41.70; H, 4.60; N, 2.56. Found: C, 41.93; H, 4.72; N, 2.47. The complex crystallized in the space group $P\bar{1}$ with two crystallographically independent cations and anions in the unit cell. Unit cell dimensions are $a = 9.416$ Å, $b = 12.665$ Å, $c = 18.371$ Å, $\alpha = 92.383°$, $\beta = 94.505°$, and $\gamma = 95.850°$; $V = 2169.9$ Å³, D(calcd) = 1.675 g cm⁻³, and $R_w = 7.71\%$. An additional complex was synthesized that crystallized with $^1/_2$ mol of water. It was as well characterized crystallographically and shown to have an H_2O molecule bridging phenoxide ligands in adjacent $W(CO)_5OPh^-$ anions. Both structures will be reported in a manuscript to be submitted for publication.
(5) McNeese, T. J.; Cohen, M. B.; Foxman, B. M. *Organometallics* **1984**, *3*, 552.
(6) McNeese, T. J.; Mueller, T. E.; Wierda, D. A.; Darensbourg, D. J.; Delord, T. E. *Inorg. Chem.* **1985**, *24*, 3465.
(7) Darensbourg, D. J.; Sanchez, K. M.; Reibenspies, J. *Inorg. Chem.*, in press.

Scheme I
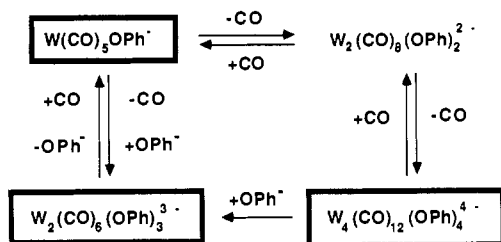
$[W_2(CO)_8(OSiMe_3)_2]^{2-}$, with a subsequent reaction leading to the tetranuclear derivative (eq 3). The dimer $[W_2(CO)_8$-

$$W(CO)_5OSiMe_3^- \xrightarrow{-CO} [W(CO)_4(OSiMe_3)]_2^{2-} \xrightarrow{-CO}$$
$$[W(CO)_3(OSiMe_3)]_4^{4-} \quad (3)$$
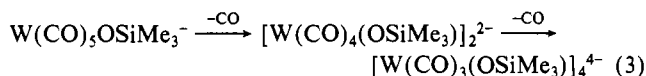
$(OSiMe_3)_2]^{2-}$ was isolated as its K(18-crown-6) salt. This complex is spectroscopically similar to the group 6 metal doubly bridged sulfur dimers $M_2(CO)_8(SR)_2^{2-}$, with $\nu(CO)$ infrared bands at 1967 (w), 1850 (s), 1807 (m), and 1782 (m) cm^{-1} in THF. Interaction of the K(18-crown-6) cation with the bridging silyl oxide ligands might account for the stability of this dimer. An interaction of Na(18-crown-6)$^+$ with the SH ligand of $W(CO)_5SH^-$ has previously been reported.[8] Analogous to the reactions of W_2-$(CO)_8(SR)_2^{2-}$ with phosphines, the $[K(18$-crown-$6)]_2[W_2$-$(CO)_8(OSiMe_3)_2]$ complex reacts with phosphines to afford cis-$W(CO)_4(OSiMe_3)_2(PR_3)^-$ derivatives.

The two most stable aryloxide derivatives contained in Scheme I, $[W_2(CO)_6(OR)_3]^{3-}$ and $[W_4(CO)_{12}(OR)_4]^{4-}$ (R = Ph, $C_6H_4CH_{3-m}$), have infrared spectral features in the $\nu(CO)$ region that are quite similar, both exhibiting C_{3v} localized symmetry about the $W(CO)_3$ moiety. For example, the $[W_2(CO)_6(OPh)_3]^{3-}$ dimer has two strong bands of intensity ratio ~1:2 at 1870 and 1724 cm^{-1}, whereas the $[W_4(CO)_{12}(OPh)_4]^{4-}$ tetramer displays a nearly identical band pattern at 1869 and 1732 cm^{-1}. Because of the spectral similarities of the dimeric and tetrameric species it was of importance to firmly establish their identity by other means.

The dimeric tungsten derivatives $[W_2(CO)_6(OR)_3]^{3-}$ (R = Ph, $C_6H_4CH_{3-m}$) were characterized by X-ray diffraction.[9] Herein, we will describe only the structure of the phenoxide complex.[10] A perspective view of the anion is shown in Figure 1. The tungsten–oxygen distances range from 2.210 (6) to 2.234 (5) Å, with an average value of 2.222 (5) Å. This average bridging tungsten–oxygen distance is quite similar to that observed in the parent $W(CO)_5OPh^-$ species of 2.181 (18) Å.[11] The W–CO
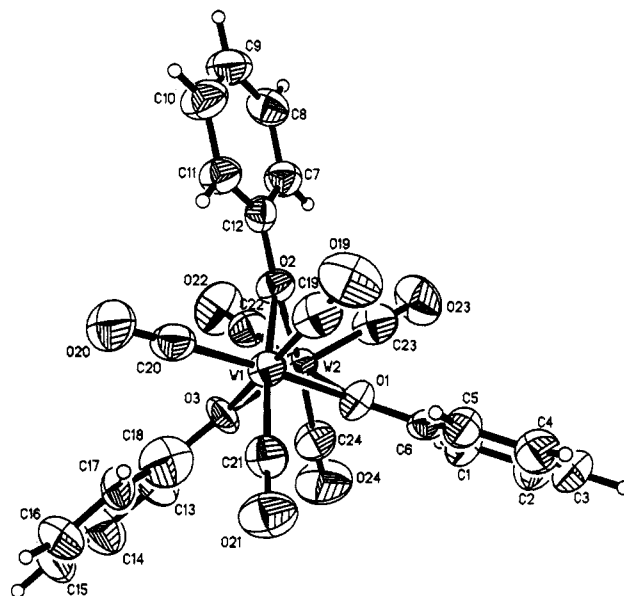

Figure 1. ORTEP drawing of the $W_2(CO)_6(OPh)_3^{3-}$ anion with the atomic labeling scheme.

distances range from 1.889 (10) to 1.923 (9) Å, with an average distance of 1.904 (9) Å. The geometry at each metal center is that of a distorted octahedron, where the O–W–O and O–W-(1)–W(2) angles of the W_2O_3 core are very acute, 70.3° (average) and 41.7° (average), respectively. These angles bring about close contact of the tungsten atoms as well as the oxygen atoms, with the W···W distance being equal to 3.318 (1) Å and the O···O distances averaging 2.56 (1) Å. Similarly, the nonbonding W–W distance in $[K]_3[W_2(CO)_6(OH)_3]$[12] and the Re–Re distance in $[Et_4N][Re_2(CO)_6(OMe)_3]$[13] are short at 3.32 and 3.09 Å, respectively. The narrow O–W–O angle of 70° is compensated for by an expansion of the OC–W–OPh angles, which are greater than 90°.

As depicted in Scheme I, the $W_2(CO)_6(OPh)_3^{3-}$ dimer reacts with 1 atm of carbon monoxide at ambient temperature to re-form the monomer $W(CO)_5OPh^-$ in quantitative yield. However, further reaction of $W(CO)_5OPh^-$ with CO to afford the insertion product $W(CO)_5C(O)OPh^-$ does not occur even at 500 psi of CO. This is in sharp contrast to the rapid insertion reaction of W-$(CO)_5OPh^-$ with carbon dioxide to provide the $W(CO)_5OC$-$(O)OPh^-$ species.[3] Unlike the tungsten phenoxide monomer,[3] the $W_2(CO)_6(OPh)_3^{3-}$ dimer was unreactive toward atmospheric pressure of carbon dioxide.

(8) Cooper, M. K.; Duckworth, P. A.; Henrick, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1981**, 2357.

(9) Crystallographic data for $[Et_4N]_3[W_2(CO)_6(OPh)_3]\cdot 3CH_3CN$: A yellow parallelepiped crystal, 0.41 × 0.41 × 0.60 mm, was mounted in a glass capillary in a random orientation. The crystal system was identified as monoclinic, space group $P2_1/n$. Unit cell dimensions are $a = 11.954$ (2) Å, $b = 19.359$ (4) Å, $c = 26.462$ (5) Å, and $\beta = 102.50$ (2)°; $V = 5979$ (2) Å^3, $Z = 4$, and D(calcd) = 1.471 g cm^{-3}. Data were measured by using Mo Kα radiation ($\lambda = 0.71073$ Å) on a Nicolet R3m/V computer-controlled diffractometer equipped with a highly oriented graphite crystal, incident beam monochromator at ambient temperature ($-14 \le h \le 13$; $-23 \le k \le \phi$; $0 \le l \le 31$; $4 \le 2\theta \le 50°$). A total of 11177 reflections were collected, of which 10574 were unique ($R_{int} = 0.0312$) and 8502 of these had $F \ge 2.5\sigma(F)$. Lorentz and polarization corrections were applied to the data. The structure was solved by direct methods and subsequent difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic temperature factors: $R_F = 5.69\%$ and $R_{wF} = 5.07\%$.

(10) The preparation of this complex from $W(CO)_3(CH_3CN)_3$ and NaOPh has been previously reported in the literature by: Ellis, J. E.; Rochfort, G. L. *Organometallics* **1982**, *1*, 682. We have carried out a similar preparation of this derivative from $W(CO)_3(CH_3CN)_3$ and [Et$_4$N]-[OPh]. Anal. Calcd for $[Et_4N]_3[W_2(CO)_6(OPh)_3]\cdot 3CH_3CN$: C, 48.08; H, 5.71; N, 6.35. Found: C, 47.67; H, 5.62; N, 6.19.

(11) As mentioned in ref 4, there are two independent $W(CO)_5OPh^-$ anions in the unit cell, one with a W–OPh bond distance of 2.181 (18) Å and the other with a corresponding distance of 2.203 (20) Å.

(12) Albano, V. G.; Ciana, G.; Manassero, M. *J. Organomet. Chem.* **1970**, *25*, C55.

(13) Ciani, G.; Sironi, A.; Albinati, A. *Gazz. Chim. Ital.* **1979**, *109*, 615.

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