

reducing the matrix elements yields, for MWRF

$$\frac{\bar{A}_1}{\bar{D}_0} = -\langle e_g(y), \pi^*(\sim Rh_2) | \Lambda^2 | e_g(x), \pi^*(\sim Rh_2) \rangle \quad (6)$$

and for MSSSG the opposite sign.

It is noteworthy that for both the MWRF and MSSSG assignments, evaluation of \bar{A}_1/\bar{D}_0 involves computing identical multicenter integrals, but the signs of \bar{A}_1/\bar{D}_0 ratios are opposite. MO phases were carefully matched with all other computational features. $\langle \ell_z \rangle$ was evaluated in the all-center operator AO matrix mode^{11,14} for $Rh_2(O_2CH)_4$. Bond distances and angles,¹⁵ AO single- ζ 2s and 2p functions for C and O,¹⁶ and $\zeta = 1.2$ for 1s H¹⁷ were from the literature. Rh 5p (double- ζ) and 5s (triple- ζ) functions are our renormalized outermost terms of more complex functions,¹⁸ and the 4d (triple- ζ) function is from the literature.¹⁸ Basis orbital energies from the literature were used (2s, 2p C, O from ref 19; 1s H is -13.6 eV; for Rh 4d, 5s, 5p the VOIPS of Co 3d, 4s, 4p^{19,20} were used with 10 000 cm⁻¹ subtracted from each.²¹ The 100 functions were used to compute the 70 × 70 S and L_z matrices,^{14,22} and subsequently the MO C matrix,²⁰ all on an IBM 3081 (Triangle University Computing Center). We obtain $\bar{A}_1/\bar{D}_0 = +0.985$ for the MWRF assignment, $5e_g \rightarrow 4a_{2u}$, which matches the experimental \bar{A}_1/\bar{D}_0 sign and is in good agreement with the experimental magnitudes for 1-2NCMe and 2-2EtOH and consistent with the $\pi^*(\sim Rh_2) \rightarrow \sigma^*(\sim Rh_2)$ excitation.

The circular dichroism spectra of two $Rh_2(O_2CR)_4L_2$ compounds ($RCO_2 = L$ -mandelate and $L = EtOH$; $RCO_2 = D$ -methoxyphenylacetate and $L = THF$) have been reported and shown to be consistent with the MSSSG assignment,²³ which was at that time generally accepted. However, these data are also consistent with the MWRF assignment.²⁴ The all-center operator matrix treatment of the CD vicinal effect of $Rh_2(D$ -mandelato)₄ will be published elsewhere.¹¹

- (14) Evans, R. S.; Schreiner, A. F.; Hauser, P. J.; Caves, T. C. *Inorg. Chem.* **1975**, *14*, 163.
- (15) Cotton, F. A.; DeBoer, B. G.; LaPrade, M. D.; Pipal, J. R.; Ucko, D. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1971**, *B27*, 1664.
- (16) Clementi, E.; Raimondi, D. L. *J. Chem. Phys.* **1963**, *38*, 2686.
- (17) Palke, W. E.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1966**, *88*, 2384.
- (18) Basch, H.; Gray, H. B. *Theor. Chim. Acta* **1966**, *4*, 367.
- (19) Basch, H.; Viste, A.; Gray, H. B. *Theor. Chim. Acta* **1965**, *3*, 458.
- (20) Ballhausen, C. J.; Gray, H. B. *Molecular Orbital Theory*; W. A. Benjamin: New York, 1965.
- (21) Basch, H.; Gray, H. B. *Inorg. Chem.* **1967**, *6*, 365.
- (22) Evans, R. S.; Schreiner, A. F.; Hauser, P. J. *Inorg. Chem.* **1974**, *13*, 2185.
- (23) Agaskar, P. A.; Cotton, F. A.; Falvello, L. R.; Han, S. *J. Am. Chem. Soc.* **1986**, *108*, 1214.
- (24) Falvello, L. R.; Cotton, F. A., unpublished results.

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An Organometallic Route to Micron-Sized Whiskers of Zinc Sulfide

Sir:

A number of technologies require the development of high-performance optical materials that also meet stringent specifications of optical transparency and thermal, chemical, and mechanical properties.^{1,2} For example, an infrared-transmitting



Figure 1. Transmission electron micrograph of the solid product formed upon reacting $[EtZn(SBu^1)]_2$ with H_2S at a flow rate of 5 cm³/min in CH_2Cl_2 solution at 22 °C.

window material should have low thermal expansion, high melting and decomposition temperatures, chemical inertness to hydrolysis and oxidation, and high fracture toughness. One of the most attractive materials for many IR optical applications is ZnS,³ but this material, as presently fabricated, does not possess the required mechanical properties.

One approach to improving the mechanical properties of a material is to form a self-similar composite,⁴⁻⁶ in this case, ZnS whiskers in a polycrystalline ZnS matrix. To fabricate IR-transmitting ZnS/ZnS composites, it would be necessary to use micron-sized whiskers of ZnS that have length to width ratios (aspect ratios) greater than 10. No present methodology exists for the convenient, large-scale preparation of such whiskers, although larger single crystals and whiskers of ZnS have been made by a variety of high-temperature (>900 °C), generally vapor-phase, routes.⁷⁻¹⁶ We have sought alternative methods for producing ZnS whiskers that would give greater control over the product morphology. Low-temperature organometallic routes are attractive for this purpose, and we report herein a novel route to

- (1) Musikant, S. *Optical Materials*; Dekker: New York, 1985.
- (2) Slack, G. A. "Advanced Materials for Optical Windows"; General Electric Technical Information Series; GE Co.: Schenectady, NY, 1979.
- (3) "Kodak IRTRAN Infrared Optical Materials"; Publication No. U-72; Eastman Kodak Co.: 1971.
- (4) Fitzer, E. "Fiber Reinforced Ceramics and Glasses"; Proceedings of the International Symposium on Factors in Densification and Sintering of Oxide and Non-oxide Ceramics, Hakone, Japan; Gakujutsu Bunken Fukyu-kai: Tokyo, 1978; pp 618-673.
- (5) Fitzer, E.; Schlichting, J. *High Temp. Sci.* **1980**, *13*, 149.
- (6) Yasuda, E.; Schlichting, J. *Z. Werkstofftech.* **1978**, *9*, 310.
- (7) Shichiri, T.; Aikami, T.; Kaninski, J. *J. Cryst. Growth* **1978**, *43*, 320.
- (8) Tempest, P. A.; Ballintyne, W. G. *J. Cryst. Growth* **1974**, *21*, 219.
- (9) Steinberg, I. T.; et al. *J. Cryst. Growth* **1972**, *13/14*, 85.
- (10) Nitsche, R.; Bolsterli, H. U.; Lichtensteiger, M. *Phys. Chem. Solids* **1961**, *21*, 199.
- (11) Fujita, S.; Minoto, H.; Takebe, H.; Noguchi, T. *J. Cryst. Growth* **1979**, *47*, 326.
- (12) Bertoli, M.; Farkas-Jahnke, M.; Lendvay, E.; Nemeth, T. *J. Mater. Sci.* **1969**, *4*, 699.
- (13) Ujii, S.; Kotera, Y. *J. Cryst. Growth* **1971**, *10*, 320.
- (14) Lilley, P.; Jones, P. L.; Litting, C. N. W. *J. Mater. Sci.* **1970**, *5*, 891.
- (15) Vohl, P.; Buchan, W. R.; Genthe, J. E. *J. Electrochem. Soc.* **1969**, *118*, 1842.
- (16) Yim, W. M.; Stofko, E. J. *J. Electrochem. Soc.* **1972**, *121*, 381.

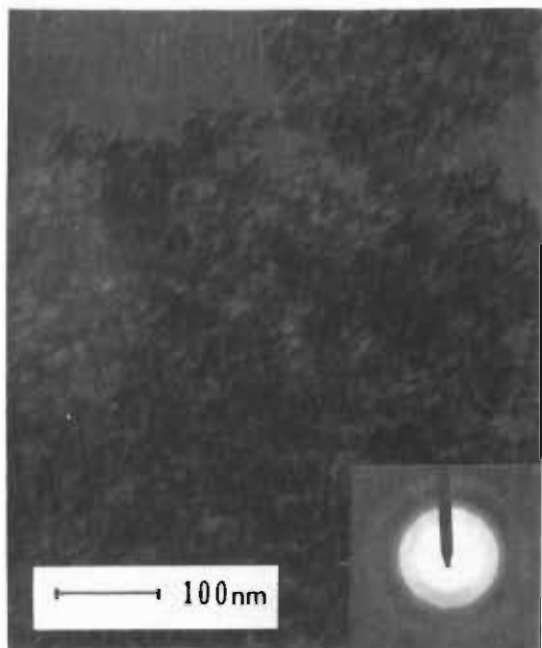
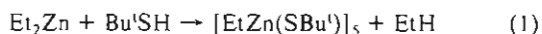


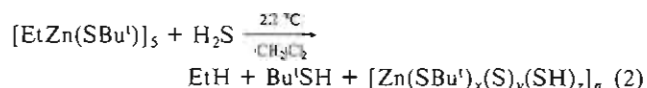
Figure 2. Transmission electron micrograph of the ZnS product formed after heating the sample shown in Figure 1 to 360 °C under an N₂ atmosphere.

micron-sized ZnS whiskers using a combination of organozinc compounds with sulfur delivery agents.

The precursor compound used in this study is the pentameric species [EtZn(SBu¹)]₅, which is highly soluble in organic solvents.¹⁷⁻¹⁹ This known compound can be synthesized in high yields (60–85%) by the low-temperature reaction of Et₂Zn with Bu¹SH, eq 1.¹⁷ When H₂S gas was passed over stirred toluene or CH₂Cl₂



solutions of this species at a flow rate of 5 cm³/min, a white precipitate immediately deposited, and ¹H NMR analysis indicated the formation of Bu¹SH and EtH. IR and Raman analysis showed the presence of significant quantities of residual organics in this precipitate, and an X-ray powder diffraction analysis gave only a very broad band in the region of the most intense ZnS peak (3.12 Å). Transmission electron microscopy showed this material to have a fibrous morphology (Figure 1), and a weak selected-area electron diffraction (SAD) pattern in the TEM analysis indicated the presence of some crystalline ZnS. Elemental analysis showed the presence of Zn, S, C, and H in a 1:1:3.9:8.5 atomic ratio,^{20a} again indicating the presence of significant quantities of residual organics. This product is presumably a mixture of amorphous ZnS and an oligomeric species such as that written in eq 2.



Thermogravimetric analysis of this solid under an N₂ atmosphere gave 11.7% weight loss up to 360 °C, corresponding to partial loss of the residual organics. After the TGA analysis, the X-ray powder diffraction pattern of the remaining solid showed three broad peaks at *d* spacings of 3.11, 1.91, and 1.63 Å, characteristic of ZnS, and the typical ZnS diffraction pattern was seen in a TEM–SAD analysis. Elemental analysis of this heat-treated material showed a Zn:S:C:H atomic ratio of 15.3:15.6:1:4.1,^{20b} indicating significant removal of residual organics upon the heat treatment. Note that the Zn:S ratio is close to the

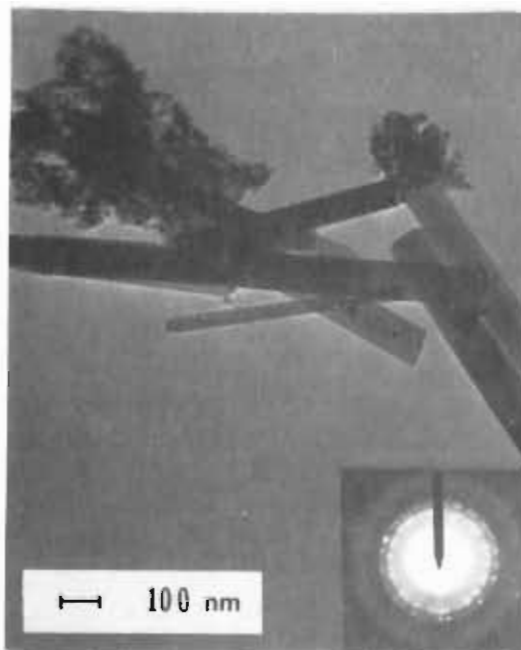


Figure 3. Transmission electron micrograph of the ZnS product formed upon heating the sample shown in Figure 1 at 500 °C for 2 h under a flowing H₂S atmosphere.

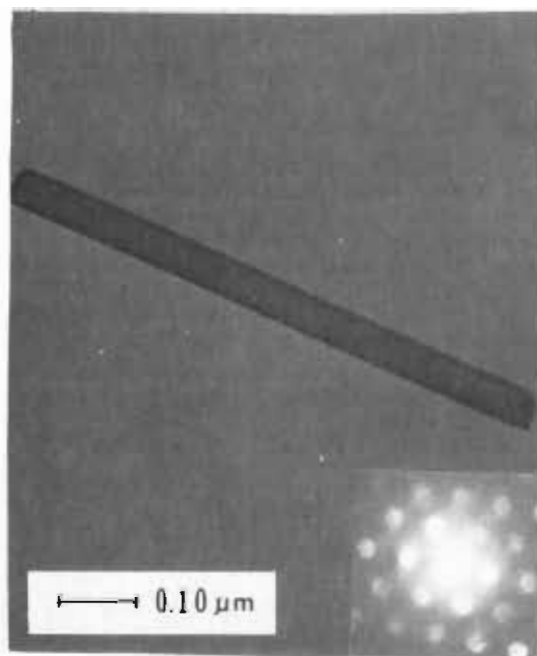


Figure 4. Transmission electron micrograph of a ZnS single-crystal wurtzite whisker (0.74-μm length, 0.05-μm width) selected from the sample shown in Figure 3.

1:1 ratio of ZnS. After this heat treatment under N₂, electron microscopy showed the product to be highly agglomerated and composed of 5.9–9.6-nm spherical particles (Figure 2).

A significant morphological transformation occurred when the solid product of eq 2 was heated under flowing H₂S at 500 °C for 2 h.²¹ An X-ray diffraction pattern of the gray powder obtained after this treatment indicated the presence of ZnS, and

(21) The thermolysis was conducted by placing the sample in a Pyrex boat in a tube furnace under a flowing H₂S atmosphere (20–75 cm³/min). The temperature was ramped from 22 to 350 °C over a 45-min time period, and this temperature was held for 2 h. The temperature was quickly increased to 200 °C and held for 2 h and then to 250 °C and held for 1 h. Finally, the sample was heated to 500 °C over a 1-h period and then held at 500 °C for 2 h. The whiskers formed in the same region of the boat as the initial powder sample.

(17) Coates, G. E.; Ridley, D. J. *J. Chem. Soc.* **1965**, 1870.
 (18) Coates, G. E.; Ridley, D. J. *J. Chem. Soc. A* **1966**, 1064.
 (19) Adamson, G. W.; Shearer, H. M. M.; Spencer, C. B. *Acta Crystallogr.* **1966**, *S21*, A135.
 (20) (a) Anal. Zn, 39.26; S, 17.18; C, 26.01; H, 4.75. (b) Anal. Zn, 65.17; S, 32.53; C, 0.78; H, 0.27.

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 cm^3/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 cm^3/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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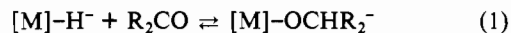
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Synthesis and X-ray Crystal Structure of Zerovalent Tungsten Aryloxy Dimers

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,



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 aryloxy complexes can be isolated.³ In this communication we wish to report on the coordination chemistry of μ_2 -aryloxy derivatives of tungsten.

We have established the interconversions illustrated in Scheme I. The aryloxy complexes enclosed in boxes have been isolated as pure compounds and have been fully characterized. The mononuclear aryloxy derivatives $[\text{Et}_4\text{N}][\text{W}(\text{CO})_5\text{OR}]$ (R = Ph, $\text{C}_6\text{H}_4\text{CH}_3$ -*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 ¹³CO (eq 2). In the



absence of a carbon monoxide atmosphere these anionic mononuclear complexes afford the tetranuclear derivatives^{5,6} $[\text{W}_4(\text{CO})_{12}(\mu_3\text{-OR})_4]^{4-}$, with no spectral evidence for the intermediacy of $[\text{W}_2(\text{CO})_8(\mu\text{-OR})_2]^{2-}$. On the other hand, another dimeric species is isolable that is triply bridged by phenoxide groups, $[\text{W}_2(\text{CO})_6(\text{OR})_3]^{3-}$, resulting from reaction of either the monomer or tetramer with excess phenoxide. By way of contrast, thermolysis of $\text{W}(\text{CO})_5\text{SPh}^-$ causes loss of CO, yielding the double-bridged sulfur dimer $\text{W}_2(\text{CO})_8(\mu\text{-SPh})_2^{2-}$.⁷ This dimer exists exclusively as the anti isomer and hence does not undergo further dimerization to the tetranuclear $[\text{W}_4(\text{CO})_{12}(\mu\text{-SPh})_4]^{4-}$ 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 $\text{W}(\text{CO})_5\text{OSiMe}_3^-$ (prepared from $\text{W}(\text{CO})_5\text{THF}$ 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.; Darenbourg, M. Y. *J. Am. Chem. Soc.* **1985**, *107*, 2428. (b) Tooley, P. A.; Ovalles, C.; Kao, S. C.; Darenbourg, D. J.; Darenbourg, M. Y. *J. Am. Chem. Soc.* **1986**, *108*, 5465. (c) Marks, L.; Nagy-Magos, Z. *J. Organomet. Chem.* **1985**, *285*, 193.
- (2) (a) Darenbourg, D. J.; Gray, R. L.; Ovalles, C.; Pala, M. *J. Mol. Catal.* **1985**, *29*, 285. (b) Darenbourg, D. J.; Gray, R. L.; Ovalles, C. *J. Mol. Catal.* **1987**, *41*, 329.
- (3) Darenbourg, D. J.; Sanchez, K. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 290.
- (4) The $[\text{Et}_4\text{N}][\text{W}(\text{CO})_5\text{OR}]$ complexes were synthesized by the reaction of $\text{W}(\text{CO})_5\text{THF}$ with the corresponding $[\text{Et}_4\text{N}][\text{OR}]$ salts. X-ray-quality crystals of $[\text{Et}_4\text{N}][\text{W}(\text{CO})_5\text{OPh}]$ were grown from concentrated THF solutions saturated with carbon monoxide upon the slow layering of hexane. Anal. Calcd for $[\text{Et}_4\text{N}][\text{W}(\text{CO})_5\text{OPh}]$: 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 $a = 9.416 \text{ \AA}$, $b = 12.665 \text{ \AA}$, $c = 18.371 \text{ \AA}$, $\alpha = 92.383^\circ$, $\beta = 94.505^\circ$, and $\gamma = 95.850^\circ$; $V = 2169.9 \text{ \AA}^3$, $D(\text{calcd}) = 1.675 \text{ g cm}^{-3}$, 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 $\text{W}(\text{CO})_5\text{OPh}^-$ 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.; Darenbourg, D. J.; Delord, T. E. *Inorg. Chem.* **1985**, *24*, 3465.
- (7) Darenbourg, D. J.; Sanchez, K. M.; Reibenspies, J. *Inorg. Chem.*, in press.