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Assembly of Three WS_3Cu_2 Cluster Units by μ_3-S Bridges: Synthesis of $[PPh_4][\{(C_5Me_5)WS_3Cu_2\}_3S_2]$

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Introduction

Construction of aggregated large clusters by linking preformed cluster units remains a challenging subject.[1] Simple sulfur compounds such as S_8,[2] H_2S,[3] HS^-,[4] Li_2S,[5] Na_2S,[6] and Na_2S_2[7] have been used as convenient tools for such a purpose. An important feature of these reagents is that they may remove labile ligands such as Cl^-, Br^-, I^-, CH_3CN, and CO from cluster units and assemble the remaining cluster cores by filling the voids with sulfur atoms. A notable example is the single-sulfur-bridged double cubane $[(Fe_4S_4Cl_3)_2S]^{4-}$, which was obtained from the reaction between $[Fe_4S_4Cl_4]^{2-}$ and Li_2S in CH_3CN.[5a] Two units of the related mixed-metal cubane $[(MoFe_3S_3Cl_4)(C_2O_4)]^{3-}$ were then successfully connected by treating the double cubane with $[Et_4N]CN$ followed by addition of $[Et_4N]SH$, affording the doubly-bridged double-cubane cluster $\{[MoFe_3S_4Cl_2(C_2O_4)](\mu_2\text{-}CN)(\mu_2\text{-}S)]\}^{5-}$.[4b]

Tetrathiometalates are known to serve as precursors of a wide variety of heterometallic sulfide clusters.[8] Our recent synthesis of the half-sandwich trithio complexes $[(C_5Me_5)MS_3Li_2(THF)_2]_2$ (M = Nb, Ta)[9ab] and $[PPh_4][(C_5Me_5)MS_3]$ (M = Mo, W)[9c] expanded the scope of our study, and we examined their cluster forming reactions with appropriate late-transition metal complexes.[10] For instance, $[PPh_4][(C_5Me_5)MS_3]$ was found to react readily with CuNCS and CuBr in CH_3CN, resulting in isolation of $[PPh_4]_2[\{(C_5Me_5)WS_3\}_2Cu_6(NCS)_6]$ and $[PPh_4]_2[\{C_5Me_5)WS_3\}_2Cu_6Br_6]$ (**1**), in which two incomplete cubane WS_3Cu_3 units were weakly connected by NCS and Br bridges, respectively.[10c] The latter cluster **1** carries bromide bound to each copper atom, and we investigated its reaction with Li_2S_2. This communication reports an unprecedented nonanuclear cluster $[PPh_4][\{(C_5Me_5)WS_3Cu_2\}_3S_2]$ (**2**) obtained therefrom, which is an aggregate of three WS_3Cu_2 clusters interconnected by two μ_3-S atoms.

Results and Discussion

A yellow powder of dry Li_2S_2[9b] was added to an acetonitrile solution of $[PPh_4]_2[\{C_5Me_5)WS_3\}_2Cu_6Br_6]$ (**1**) (1:2 molar ratio). The dark red solution immediately darkened, and a black powder gradually precipitated. After the mixture was stirred overnight at ambient temperature, a black powder was filtered off along with LiBr and unreacted Li_2S_2. According to the X-ray fluorescence microanalysis, the black powder does not contain tungsten, and we presume it to be a copper sulfide. The filtrate was concentrated to *ca*. 2 mL *in vacuo*, and diethyl ether was layered on the solution. Dark red prismatic crystals of $[PPh_4][\{(C_5Me_5)WS_3Cu_2\}_3S_2]\cdot 3CH_3CN$ ($\mathbf{2}\cdot 3CH_3CN$) were formed in 3 days in 64% yield. **2** is stable to oxygen and moisture and is soluble in CH_3CN and DMSO. The electronic spectrum of **2** in CH_3CN exhibits absorption band at 399 nm, while the IR spectrum displays $W-S_{br}$ stretching vibrations at 447 (m) and 430 (s) cm^{-1}. The ^1H NMR spectrum of **2** has a single resonance of C_5Me_5 at 1.97 ppm, implying that the three C_5Me_5 groups have the same chemical environment in $(CD_3)_2SO$.

The X-ray study of **2** showed that an asymmetric unit consists of one $[\{(C_5Me_5)WS_3Cu_2\}_3S_2]^-$ anion, one PPh_4^+ cation, and three CH_3CN solvent molecules. The structure of the anion part of **2** is presented in Figure 1, and important bond lengths and angles are given in Table 1. The structure of $[\{(C_5Me_5)WS_3Cu_2)_3S_2]^-$ can be described as three chemically equivalent $[(C_5Me_5)WS_3Cu_2]^+$ clusters interconnected by two triply bridging S^{2-} ligands. Alternatively, the main frame of the structure may be viewed as a trigonal-face bicapped trigonal prism made of six coppers and two sulfurs, and each of three nonbonded Cu···Cu edges is bound to one $[(C_5Me_5)WS_3]^-$ anion. This core structure resembles that of $[Et_4N]_4[(WSe_4Cu_2)_3Se_2]$, in which three $[WSe_4]^{2-}$ moieties bridge two Cu_3 triangles.[11] One Cu_3 (Cu(1), Cu(4), Cu(5)) triangular plane is nearly parallel (1.4°) to the opposite Cu_3 (Cu(2), Cu(3), Cu(6)) plane. The Cu···Cu distances within the trigonal planes range from 2.91 to 3.06 Å, while those connecting the planes are somewhat longer, being 3.11−3.18 Å. The two sulfur atoms, S(10) and

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(1) (a) Dance, I.; Fisher, K. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; Wiley-Interscience: New York, 1994; Vol. 41, p 637. (b) Müller, A.; Krahn, E. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 1071.

(2) (a) Hagen, K. S.; Watson, A. D.; Holm, R. H. *J. Am. Chem. Soc*. **1983**, *105*, 3905. (b) Pohl, S.; Saak, W. *Z. Naturforsch*. **1988**, *B43*, 457.

(3) (a) Bottomley, G.; Egharevba, G. O.; White, P. S. *J. Am. Chem. Soc*. **1985**, *107*, 4353. (b) Müller, A.; Schladerbeck, N.; Bögge, H. *J. Chem. Soc., Chem. Commun*. **1987**, 35.

(4) (a) Cotton, F. A.; Llusar, R.; Eagle, C. T. *J. Am. Chem. Soc*. **1989**, *111*, 4332. (b) Demadis, K. D.; Cocouvanis, D. *Inorg. Chem*. **1995**, *34*, 436.

(5) (a) Challen, P. R.; Koo, S. M.; Dunham, W. R.; Coucouvanis, D. *J. Am. Chem. Soc*. **1990**, *112*, 2455. (b) Coucouvanis, D.; Challen, P. R.; Koo, S. M.; Davis, W. M.; Butler, W.; Dunham, W. R. *Inorg. Chem*. **1989**, *28*, 4181

(6) Lockemeyer, J. R.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc*. **1989**, *111*, 5733.

(7) Strasdeit, H.; Krebs, B.; Henkel, G. *Inorg. Chem*. **1984**, *23*, 1816.

(8) (a) Christou, G.; Garner, C. D.; Mabbs, F. E.; King, T. J. *J. Chem. Soc., Chem. Commun*. **1978**, 740. (b) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl*. **1981**, *20*, 934. (c) Howard, K. E.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc*. **1986**, *108*, 297. (d) Coucouvanis, D. *Acc. Chem. Res*. **1991**, *24*, 1. (e) Jeannin, Y.; Secheresse, F.; Bernes, S.; Robert, F. *Inorg. Chim. Acta* **1992**, *198−200*, 493. (f) *Molybdenum Enzymes, Cofactors, and Model Systems*; Stiefel, E. I., Coucouvanis, D., Newton, W. E., Eds.; ACS Symposium Series 535; American Chemical Society: Washington, DC, 1993. (g) Holm, R. H. *Pure Appl. Chem*. **1995**, *67*, 2117. (h) Ogo, S.; Suzuki, T.; Ozawa, Y.; Isobe, K. *Inorg. Chem*. **1996**, *35*, 6093.

(9) (a) Tatsumi, K.; Inoue, Y.; Nakamura, A.; Cramer, R. E.; VanDoorne, W.; Gilje, J. W. *J. Am. Chem. Soc*. **1989**, *111*, 782. (b) Tatsumi, K.; Inoue, Y.; Kawaguchi, H.; Kohasaka, M.; Nakamura, A.; Cramer, R. E.; VanDoorne, W.; Taogoshi, G. J.; Richmann, P. N.*Organometallics* **1993**, *12*, 352. (c) Kawaguchi, H.; Tatsumi, K. *J. Am. Chem. Soc*. **1995**, *117*, 3885.

(10) (a) Tatsumi, K.; Kawaguchi, H.; Inoue, Y.; Nakamura, A.; Cramer, R. E.; Golen, J. A. *Angew. Chem., Int. Ed. Engl*. **1993**, *32*, 763. (b) Kawaguchi, H.; Tatsumi, K. *Organometallics* **1997**, *16*, 307. (c) Lang, J.-P.; Kawagichi, H.; Ohnishi, S.; Tatsumi, K. *J. Chem. Soc., Chem. Commun*. **1997**, 405.

(11) Christuk, C. C.; Ansari, M. A.; Ibers, J. A. *Angew. Chem., Int. Ed. Engl*. **1992**, *31*, 1477.

S0020-1669(97)00894-X CCC: $15.00

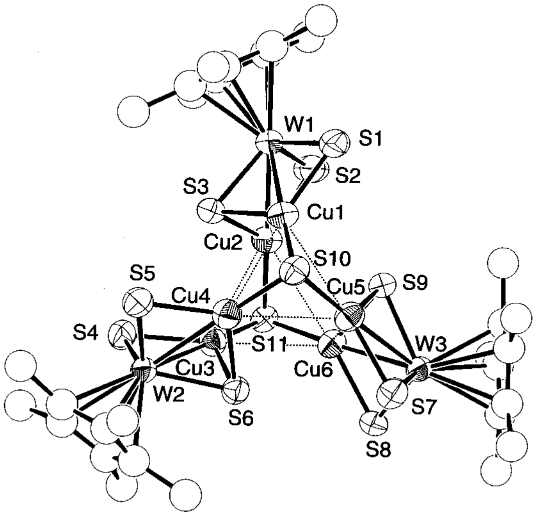

Figure 1. Structure and labeling scheme of the cluster anion of **2**, where only one set of disordered C_5Me_5 groups is shown. The thermal ellipsoids are drawn at the 50% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[PPh_4][\{(C_5Me_5)WS_3Cu_2\}_3S_2]\cdot 3CH_3CN$ (**2**·$3CH_3CN$)

W(1)−Cu(1)	2.675(3)	W(1)−Cu(2)	2.683(3)
W(2)−Cu(3)	2.665(2)	W(2)−Cu(4)	2.682(3)
W(3)−Cu(5)	2.681(3)	W(3)−Cu(6)	2.680(2)
W(1)−S(1)	2.228(5)	W(1)−S(2)	2.236(6)
W(1)−S(3)	2.288(5)	W(2)−S(4)	2.234(5)
W(2)−S(5)	2.233(5)	W(2)−S(6)	2.296(5)
W(3)−S(7)	2.226(5)	W(3)−S(8)	2.236(5)
W(3)−S(9)	2.292(5)	Cu(1)−S(1)	2.221(6)
Cu(1)−S(3)	2.247(5)	Cu(1)−S(10)	2.197(5)
Cu(2)−S(2)	2.218(6)	Cu(2)−S(3)	2.249(5)
Cu(2)−S(11)	2.204(5)	Cu(3)−S(4)	2.209(6)
Cu(3)−S(6)	2.244(5)	Cu(3)−Cu(11)	2.192(5)
Cu(4)−S(5)	2.221(6)	Cu(4)−S(6)	2.257(6)
Cu(4)−S(10)	2.211(6)	Cu(5)−S(7)	2.223(6)
Cu(5)−S(9)	2.221(5)	Cu(5)−S(10)	2.203(6)
Cu(6)−S(8)	2.237(5)	Cu(6)−S(9)	2.237(5)
Cu(6)−S(11)	2.206(5)		

S(1)−W(1)−S(2)	104.6(2)	S(1)−W(1)−S(3)	105.8(2)
S(2)−W(1)−S(3)	104.7(2)	S(4)−W(2)−S(5)	105.5(2)
S(4)−W(2)−S(6)	105.1(2)	S(5)−W(2)−S(6)	105.4(2)
S(7)−W(3)−S(8)	104.8(2)	S(7)−W(3)−S(9)	104.8(2)
S(8)−W(3)−S(9)	105.6(2)	Cu(1)−W(1)−Cu(2)	71.38(7)
Cu(3)−W(2)−Cu(4)	71.18(7)	Cu(5)−W(3)−Cu(6)	72.83(7)
S(1)−Cu(1)−S(3)	107.5(2)	S(1)−Cu(1)−S(10)	124.2(2)
S(3)−Cu(1)−S(10)	127.6(2)	S(2)−Cu(2)−S(3)	106.7(2)
S(2)−Cu(2)−S(11)	125.0(2)	S(3)−Cu(2)−S(11)	126.9(2)
S(4)−Cu(3)−S(6)	107.7(2)	S(4)−Cu(3)−S(11)	122.7(2)
S(6)−Cu(3)−S(11)	128.3(2)	S(5)−Cu(4)−S(6)	107.1(2)
S(5)−Cu(4)−S(10)	125.9(2)	S(6)−Cu(4)−S(10)	125.6(2)
S(7)−Cu(5)−S(9)	107.4(2)	S(7)−Cu(5)−S(10)	128.3(2)
S(9)−Cu(5)−S(10)	123.6(2)	S(8)−Cu(6)−S(9)	107.4(2)
S(8)−Cu(6)−S(11)	128.2(2)	S(9)−Cu(6)−S(11)	123.1(2)
W(1)−S(1)−Cu(1)	73.9(2)	W(1)−S(2)−Cu(2)	74.1(2)
W(1)−S(3)−Cu(1)	72.3(2)	W(1)−S(3)−Cu(2)	72.5(2)
W(2)−S(4)−Cu(3)	73.7(2)	W(2)−S(5)−Cu(4)	74.1(2)
W(2)−S(6)−Cu(3)	71.9(2)	W(2)−S(6)−Cu(4)	72.2(2)
W(3)−S(7)−Cu(5)	74.1(2)	W(3)−S(8)−Cu(6)	73.6(2)
W(3)−S(9)−Cu(4)	72.9(2)	W(3)−S(9)−Cu(6)	72.5(2)
Cu(1)−S(3)−Cu(2)	88.1(2)	Cu(3)−S(6)−Cu(4)	87.5(2)
Cu(5)−S(9)−Cu(6)	91.1(2)	Cu(1)−S(10)−Cu(4)	82.4(2)
Cu(1)−S(10)−Cu(5)	87.4(2)	Cu(4)−S(10)−Cu(5)	86.2(2)
Cu(2)−S(11)−Cu(3)	84.2(2)	Cu(2)−S(11)−Cu(6)	87.7(2)
Cu(3)−S(11)−Cu(6)	84.1(2)		

S(11), sit 1.37 Å above (or below) the corresponding triangular Cu_3 planes. The dihedral angles between the S_3 planes of three $(C_5Me_5)WS_3$ fragments are all close to 60°, implying that the $[(WS_3Cu_2)_3S_2]$ core possesses an approximate 3-fold symmetry, and the pseudo C_3 axis runs through S(10) and S(11).

The sulfur atoms are classified into three groups, which are μ_2-S (S(1), S(2), S(4), S(5), S(7), S(8)) bridging W and Cu, μ_3-S (S(3), S(6), S(9)) bridging W and two Cu atoms, and μ_3-S′ (S(10) and S(11)) bridging three Cu atoms. Each copper atom adopts a trigonal planar coordination geometry with three sulfurs of different types. The three S−Cu−S angles sum up to 359°. The Cu−S distances of 2.192(5)−2.257(6) Å are normal.[10c] The Cu−(μ_3−S′)−Cu angles of 82.4(2)−87.7(2)° are comparable to those of Cu−(μ_3−S)−Cu angles (87.5(2)−91.1(2)°), but larger than those of Cu−(μ_2−S)−W (73.6(2)−74.1(2)°) and Cu−(μ_3−S)−W (71.9(2)−72.9(2)°). The W−S bond lengths of 2.226(5)−2.296(5) Å are similar to those observed in **1** (2.280(2)−2.284(2) Å) and $[PPh_4]_2[(C_5Me_5)WS_3Cu_3(NCS)_3]_2$ (2.267(3)−2.290(3) Å).[10c] The short W−Cu distances of 2.665(2)−2.683(3) Å suggest a dative interaction between d^{10} Cu^{I} and d^0 W^{VI}. It should be mentioned here that triangular clusters doubly capped by two sulfur atoms from the two sides are known. Examples are $[PPh_4][Et_4N]_3[(WS_4Fe)_3S_2]$,[12a] $[\{(C_5H_5)Ni\}_3S_2]$,[12b] and $[M'_3S_2(dppe)_3][PF_6]_2$ (M′ = Pd, Pt),[13] which are featured by Fe_3S_2, Ni_3S_2, and M'_3S_2 trigonal bipyramid structures.

In the structure of **1**, the two $[(C_5Me_5)WS_3Cu_3Br_3]^-$ are weakly bound, so they may well split in solution and/or in the presence of Li_2S_2. In fact, the ESI−MS study of **1** in CH_3CN showed a set of peaks associated with the isotopic cluster of $[(C_5Me_5)WS_3Cu_3Br_3]^-$ and the parent ion signal was not observed. Thus it is likely that the dissociated species $[(C_5Me_5)WS_3Cu_3Br_3]^-$ degraded into $[(C_5Me_5)WS_3Cu_2]^+$ under the reaction condition, which was then self-assembled into **2** by replacing two Br atoms with $^2/_3$S. The liberated CuBr appears to react further with Li_2S_2, affording a black copper sulfide. In this solution, Li_2S_2 acted as a monosulfide (S^{2-}) transfer reagent, which is not very surprising because lithium sulfides may easily disproportionate in polar solvent.[9c] Our successful isolation of **2** shows that use of Li_2S_2 or related sulfur compounds can be a convenient method to aggregate preformed clusters.

Experimental Section

General Information. All manipulations were carried out under argon using standard Schlenk-line techniques. All solvents were predried over activated molecular sieves and refluxed over the appropriate drying agents under argon and collected by distillation. A ^1H NMR spectrum for **2** was recorded on a Varian UNITYplus-500 spectrometer, and chemical shifts were quoted in δ (ppm) relative to $(CD_3)_2SO$. IR spectrum was recorded on a Perkin-Elmer 2000FT−IR spectrophotometer using KBr pellets. UV−vis spectrum for **2** was measured on a JASCO V-560 spectrophotometer. C, H, and S analyses were performed on a LECO-CHNS microanalyzer.

Preparation of $[PPh_4][\{(C_5Me_5)WS_3Cu_2\}_3S_2]$ (2). To an acetonitrile solution (25 mL) of **1** (0.11 g, 0.046 mmol) was added a yellow powder of dry Li_2S_2[9b] (0.018 g, 0.23 mmol). The dark red solution immediately darkened, and a black powder gradually precipitated. After the mixture was allowed to stir overnight at room temperature, a black powder was removed along with LiBr and unreacted Li_2S_2 by centrifugation. The filtrate was concentrated to *ca.* 2 mL *in vacuo*, and diethyl ether (4 mL) was layered on the solution. Dark red

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(12) (a) Müller, A.; Hellmann, W.; Bögge, H.; Jostes, R.; Römer, M.; Schimanski, U. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 860. (b) Vahrenkamp, H.; Uchtman, V. A.; Dahl, L. F. *J. Am. Chem. Soc.* **1968**, *90*, 3272.

(13) Matsumoto, K.; Saiga, S.; Tanaka, S.; Ooi, S. *J. Chem. Soc., Dalton Trans.* **1991**, 1265.

Table 2. Crystallographic Data for $[PPh_4][\{(C_5Me_5)WS_3Cu_2\}_3S_2]\cdot 3CH_3CN$ (**2**·3CH$_3$CN)

formula	$C_{60}H_{74}Cu_6N_3PS_{11}W_3$
fw	2153.72
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
a, Å	15.477(4)
b, Å	21.652(5)
c, Å	21.623(2)
α, deg	
β, deg	91.35(1)
γ, deg	
V, Å^3	7244(2)
Z	4
D_{calcd}, g·cm^{-3}	1.975
μ, cm^{-1}	68.49
λ(Mo Kα), Å	0.710 69
R^a	0.049
$R_w{}^b$	0.055
GOF^c	1.63

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$. [c] GOF $= \{\sum w(|F_o| - |F_c|)^2/(M - N)\}^{1/2}$, where M is the number of reflections and N is the number of parameters.

prismatic crystals of **2**·3CH$_3$CN were formed in 3 days and were collected by filtration, washed with CH$_3$CN/Et$_2$O (1:5 v/v), and dried *in vacuo*. Yield: 0.04 g (64%). Anal. Calcd for $C_{54}H_{65}Cu_6PS_{11}W_3$: C, 31.94; H, 3.23; S, 17.23. Found: C, 32.12; H, 3.19; S, 17.48. ^{1}H NMR (DMSO-d_6, 500 MHz, 25 °C): δ 7.72−7.97 (PPh$_4{}^+$, m, 20H); 1.97 (C$_5$Me$_5$, s, 45H). IR (KBr pellets): 1482 (m), 1435 (m), 1187 (w), 1164 (m), 1107 (s), 1024 (m), 995 (m), 804 (m), 756 (m), 722(s), 690 (s), 527 (s), 447 (m), 430(s) cm^{-1}. UV−vis (CH$_3$CN) λ_{max}/nm (ϵ_{max}/M^{-1} cm^{-1}): 399 (21 300).

X-ray Structure Determination. X-ray-quality crystals of **2**·3CH$_3$CN were obtained directly from the preparation as described above. Diffraction data were collected on a Rigaku AFC7R diffractometer at ambient temperature by using graphite-monochromated Mo Kα radiation (0.710 79 Å). A dark red single crystal of **2**·3CH$_3$CN with dimensions 0.40 × 0.25 × 0.30 mm was sealed in a capillary under argon. Cell constants and an orientation matrix for data collection were obtained from least-squares refinements using the setting angles of 25 carefully centered reflections in the range $22.6 < 2\theta < 24.7°$ for **2**·3CH$_3$CN. The intensities of three representative reflections monitored every 150 reflections showed no sign of significant decay. An empirical absorption correction using the ψ scan technique was applied, which resulted in transmission factors ranging from 0.91 to 1.00 for **2**·3CH$_3$CN. Of the 10 197 reflections that were collected, 9753 were unique. The data were corrected for Lorentz and polarization effects.

The structure of **2**·3CH$_3$CN was solved by direct methods[14] and expanded using Fourier techniques.[15] The three C$_5$Me$_5$ groups were found to be disordered over two positions and they were refined as rigid groups with occupancy factors of 0.60:0.40 for C(1)−C(10) and 0.50:0.50 for C(11)−C(30). W, Cu, P, S, and C from the [PPh$_4$]$^+$ cation were refined anisotropically, while the isotropic temperature factors were applied to the C and N atoms from three CH$_3$CN solvent molecules and disordered C atoms of C$_5$Me$_5$ groups. All the hydrogen atoms except those on the disordered C$_5$Me$_5$ groups were placed at calculated positions without refinement. The final R and R_w factors were 0.049 and 0.055, respectively, for 5563 unique reflections with $I > 3.00\sigma(I)$. The maximum and minimum residual peaks on the final difference Fourier map are 1.37 and −1.27 e/Å^3, respectively. Neutral atom scattering factors were taken from the Cromer and Waber.[16] Crystallographic calculations were carried out with a teXsan crystallographic software package from Molecular Structure Corp. (1985, 1992). Crystallographic data for **2**•3CH$_3$CN are summarized in Table 2.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure determination of $[PPh_4][\{(C_5Me_5)WS_3Cu_2\}_3S_2]\cdot 3CH_3CN$ is available on the Internet only. Ordering information is given on any current masthead page.

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(14) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, England, 1985; p 175.

(15) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *DIRDIF94*: *The DIRDIF-94 Program System.* Technical Report of the Crystallography Laboratory, University of Nijmegen: The Netherlands, 1992.

(16) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.