Generation of (chloromethyl)lithium in the presence of triisopropyl borate followed by acidification efficiently yields diisopropyl (chloromethyl)boronate (5).

$$\mathrm{B(O\text{-}\mathit{i}\text{-}Pr)_3 + ICH_2Cl + \mathit{n}\text{-}BuLi \rightarrow \underset{\mathbf{5}}{ClCH_2B(O\text{-}\mathit{i}\text{-}Pr)_2}}$$

In a typical procedure, 5 mmol of boronic ester (1) and 5.4 mmol of iodochloromethane in 20 mL of rigorously dried THF was cooled to −78 °C and stirred under argon during the dropwise addition of 5.3 mmol of 1.6 M *n*-butyllithium in hexane. (If the addition was too rapid, the solution turned yellow.) The mixture was kept overnight at 20–25 °C, concentrated under vacuum, and treated with petroleum ether and concentrated aqueous ammonium chloride. The organic phase was dried over magnesium sulfate and the product **3** distilled bulb to bulb under vacuum. Products were characterized by 90- or 200-MHz ^{1}H NMR, and some were also analyzed by gas chromatography (Table I).[23,24]

To prepare diisopropyl (chloromethyl)boronate (5), 30 mL (48 mmol) of 1.6 M *n*-butyllithium in hexane was added dropwise down the side of the flask to a solution of 3.8 mL (52 mmol) of iodochloromethane and 12 mL (51 mmol) of triisopropyl borate in 60 mL of THF stirred under argon in a −78 °C bath. The mixture was allowed to warm to 10 °C and then acidified with ethereal hydrogen chloride[25] to the end point with methyl orange (added as crystals). Rapid simple distillation under vacuum followed by fractionation through a short Vigreux column yielded 7.2 g (84%) of **5**: bp 65–70 °C (20 torr); NMR same as reported.[10]

Acknowledgment. We thank the National Science Foundation for Grant CHE-8400715 and the Boeing Corp. for a gift to the department of Chemistry in support of purchase of the Nicolet NT-200 NMR instrument.

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(23) Most of these boronic esters have been reported previously: **1b**,[17] **1c**,[16] **1d**,[21] **3b** and **3c**,[5] **1e** and **3d**.[24] A report of **1a** gave no data [Ulmschneider, D.; Goubeau, J. *Chem. Ber.* **1957**, *90*, 2733–2738]; we found the following data: bp 119–121 °C, 90-MHz NMR ($CDCl_3$) δ 0.22 (s), 1.24 (s). Anal. Calcd for $C_7H_{15}BO_2$: C, 59.21; H, 10.65; B, 7.61. Found: C, 59.45; H, 10.35; B, 7.60. Only ^{17}O data have been reported for **3a** [Wrackmeyer, B.; Köster, R. *Chem. Ber.* **1982**, *115*, 2022–2034]; ^{1}H NMR ($CDCl_3$) δ 0.9 (m), 1.25 (s). New compounds include **3e**: 200-MHz NMR δ 4.53 (s, 2, $PhCH_2$), 3.645 (t, 2, OCH_2CH_2B), 1.27 (t, partially obscured, OCH_2CH_2B), other Ph and pinanediol peaks as expected. Anal. Calcd for $C_{19}H_{27}BO_3$: C, 72.62; H, 8.66; B, 3.44. Found: C, 72.72; H, 8.71; B, 3.42. For **1f**: bp 135–137 °C. Anal. Calcd for $C_{19}H_{27}BO_2$: C, 76.52; H, 9.13; B, 3.62. Found: C, 76.54; H, 8.84; B, 4.02.

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Construction of Heterometallic "Thiocubanes" from $M_2S_2(\mu\text{-}S)_2$ Core Complexes: Synthesis of $Co_2M_2S_4(S_2CNEt_2)_2(CH_3CN)_2(CO)_2$ (M = Mo, W) and Structure of the $Co_2Mo_2(\mu_3\text{-}S)_4$ Cluster

Thomas R. Halbert,* Steven A. Cohen, and Edward I. Stiefel*

Exxon Research and Engineering Company
Corporate Research-Science Laboratories
Annandale, New Jersey 08801

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Summary: Molybdenum and tungsten diethyldithiocarbamate complexes containing the $M_2S_2(\mu\text{-}S)_2$ core react with $Co_2(CO)_8$ to form, in high yield, the novel "thiocubane" clusters $M_2Co_2(\mu_3\text{-}S)_4(S_2CNEt_2)_2(CO)_2(CH_3CN)_2$ (M = Mo, W). X-ray crystallography shows these clusters to contain a fully metal–metal bonded tetrahedral core as would be predicted from the 60-electron count.

Homometallic "thiocubane" clusters containing an $M_4(\mu_3\text{-}S)_4$ core have been known for some time.[1] Current interest in the Fe–Mo cofactor of nitrogenase,[2] and in the active site structure of group 8–10[18] "promoted", MoS_2-based hydrotreating catalysts,[3] has led to preparation of several heterometallic thiocubanes.[1,2,4–8] In the earlier studies,[2] the synthetic approach was "spontaneous assembly". However, advances in homometallic transition-metal sulfide chemistry have led to smaller clusters which are fragments of the thiocubane unit. These fragments are potential building blocks for heteronuclear thiocubane clusters, and recently this potential appears to have been realized in the use of $Cp_2M_2S_4$ and related compounds to form clusters with $M_2M_2'(\mu_3\text{-}S)_4$ cores.[5–7] In this communication we report the use of $M_2S_4(S_2CNEt_2)_2$ to form a thiocubane of the type $M_2Co_2(\mu_3\text{-}S)_4(S_2CNEt_2)_2(CO)_2L_2$, where L is a solvent or other Lewis base molecule and M = Mo or W. A virtue of this approach is the ready availability of a wide variety of $M_2S_4^{2+}$ core compounds having sulfur or nitrogen ligands replacing the dithiocarbamate ligands.[9] This flexibility provides structural and electronic variation which is not present in the cyclopentadienyl-based systems.

When a solution of $Co_2(CO)_8$ in THF is mixed with an equimolar amount of $Mo_2S_4(S_2CNEt_2)_2$ under an inert atmosphere, rapid evolution of CO is observed, $Mo_2S_4(S_2CNEt_2)_2$ dissolves, and the solution turns a dark green-black color. Addition of hexane leads to precipitation of a dark green-black complex, **1**. Characteristic infrared bands due to Mo=S (545 cm^{-1}) and $Mo_2(\mu\text{-}S)_2$ (465 cm^{-1}) vibrations are replaced by a broad, medium strength band at 515 cm^{-1} and several slightly weaker bands at 393, 365, and 334 cm^{-1}. A strong, broad terminal CO band is apparent at 1980 cm^{-1}, and a number of characteristic Et_2NCS_2 bands are retained. When **1** is dissolved under N_2 in a minimum of acetonitrile, filtered, and allowed to stand, large black crystals of $Mo_2Co_2(\mu_3\text{-}S)_4(S_2CNEt_2)_2(CO)_2(CH_3CN)_2$, **2**, are formed.[10] The cluster **2** can also be prepared in microcrystalline form by direct reaction of $Co_2(CO)_8$ with $Mo_2S_4(S_2CNEt_2)_2$ in CH_3CN. The analo-

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(10) IR spectra of **2** (KBr pellet): 1983 (s), 1960 (s), 1505 (s), 1465 (m), 1442 (m), 1385 (w), 1368 (m), 1310 (w), 1280 (s), 1220 (m), 1152 (m), 1103 (w), 1083 (m), 1008 (w), 976 (w), 922 (w), 851 (w), 790 (w), 578 (w), 521 (m), 498 (w), 436 (vw), 401 (w), 371 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{26}N_4O_2S_8Co_2Mo_2$: C, 22.02; H, 3.00; N, 6.42; Mo, 21.99; Co, 13.51. Found: C, 18.59; H, 2.83, N, 5.11; Mo, 21.10; Co, 14.22.[11]

0276-7333/85/2304-1689$01.50/0

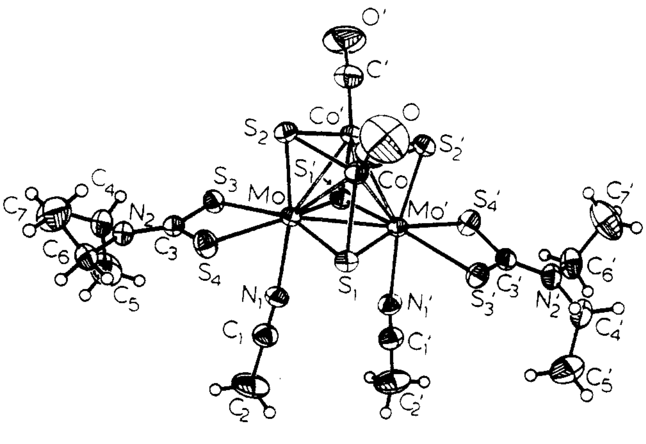

Figure 1. ORTEP drawing of $Co_2Mo_2(\mu_3\text{-}S)_4(S_2CNEt_2)(CO)_2(CH_3CN)_2$, **2**.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) for $Mo_2Co_2S_4(CO)_2(CH_3CN)_2(S_2CNEt_2)_2$

	Bond Lengths		
Mo-Mo'	2.788 (1)	$\mathrm{Co{-}S_1}$	2.184 (1)
Co-Co'	2.533 (1)	$\mathrm{Co{-}S_2}$	2.197 (1)
Mo-Co	2.680 (1)	$\mathrm{Co{-}S_2'}$	2.200 (1)
Mo-Co'	2.671 (1)	$\mathrm{Mo{-}N_1}$	2.238 (2)
$\mathrm{Mo{-}S_1}$	2.359 (1)	Co-C	1.753 (4)
$\mathrm{Mo{-}S_1'}$	2.364 (1)	$\mathrm{Mo{-}S_3}$	2.518 (1)
$\mathrm{Mo{-}S_2}$	2.316 (1)	$\mathrm{Mo{-}S_4}$	2.528 (1)
	Bond Angles		
Mo'MoCo	58.44 (1)	$\mathrm{S_1MoS_1'}$	106.86 (3)
CoMoCo'	56.50 (1)	$\mathrm{S_3MoS_4}$	69.82 (3)
Mo'CoMo	62.81 (1)	$\mathrm{N_1MoS_3}$	78.85 (7)
Co'CoMo	61.58 (1)	$\mathrm{N_1MoS_2}$	167.92 (7)
$\mathrm{S_1CoS_2}$	109.20 (3)	$\mathrm{MoS_1Mo'}$	72.36 (2)
$\mathrm{S_1CoC}$	112.4 (1)	CoCO	176.9 (3)
$\mathrm{S_2CoS_2'}$	105.94 (3)	$\mathrm{MoN_1C_1}$	171.2 (3)

gous tungsten complex **3**[11] is prepared via the latter route starting from $W_2S_4(S_2CNEt_2)_2$.[12]

A single-crystal X-ray diffraction study was carried out on **2**.[13,14] The structure is illustrated in the figure, and selected bond distances and angles are given in the table. The molecule contains a $Co_2Mo_2(\mu_3\text{-}S)_4$ core. The four metal atoms are joined by six metal-metal bonds forming an approximate tetrahedron of C_{2v} symmetry. Each triangular face of the tetrahedron is capped by a sulfur atom to form the overall "thiocubane" core. Each cobalt atom is further bonded to a single terminal CO. The coordination environment about the cobalt atoms (discounting the M-M bonds) is very nearly tetrahedral. Each molybdenum atom is bound to two dithiocarbamate sulfur atoms and to the nitrogen of an acetonitrile molecule, in addition to three capping μ_3-S atoms. The coordination environment about the molybdenum is distorted octahedral. The molecule resides on a crystallographic C_2 axis which bisects the Mo'-Mo' and Co-Co' bonds.

The parent $Mo_2S_4(S_2CNEt_2)_2$ moiety appears as an essentially intact unit in the cluster, with the Mo-Mo' bond length decreased very slightly from 2.817[15] to 2.788 Å. The Mo-S-Mo' bridge angles and bond lengths have changed little. However, the dihedral angle between the MoS_1S_1' and $Mo'S_1S_1'$ planes has opened up from 147.9° to 164.4°, and the initially terminal Mo═S bonds have elongated from 2.09 to 2.312 Å as their role changes to a bridging μ_3 mode, wherein the sulfur atoms are bound to two cobalt atoms as well as to the original Mo center. The binding of two acetonitrile molecules raises the overall cluster electron count to 60 electrons, the predicted number for a stable M_4 tetrahedral cluster with six M-M bonds.[16]

The present complexes provide an interesting model for the promotion effect of cobalt in Co—Mo catalysts. When the Co fragments bind to the terminal Mo═S groups, open sites on the Mo centers are produced; i.e., the parent $Mo_2S_4(S_2CNEt_2)_2$ shows no tendency to bind CH_3CN, but the dicobalt adduct (thiocubane) clearly binds two CH_3CN ligands. Presumably, the weakened Mo-S bonding along the z axis makes the d_{z^2}, d_{xz}, and d_{yz} orbitals of molybdenum more available as acceptor orbitals, leading to binding of acetonitrile at the sixth coordination site. Thus, the sites trans to Mo-S are analogous to vancancies on Mo whose affinity for ligands may be enhanced by the presence of cobalt.

Acknowledgment. We wish to thank Dr. C. S. Day of Crystalytics Co. for carrying out the single-crystal diffraction study and Dr. D. Van Engen of the Analytical Division of Exxon Research and Engineering Co. for completion of the powder diffraction experiments.

Supplementary Material Available: Crystallography details, including tables of atomic coordinates, thermal parameters, bond lengths, bond angles, and structure factors (26 pages). Ordering information is given on any current masthead page.

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[11] IR spectra of **3** (KBr pellet): 1961 (s), 1938 (s), 1505 (s), 1456 (w), 1436 (m), 1358 (w), 1300 (w), 1273 (m), 1209 (m), 1147 (m), 1095 (w), 1075 (m), 915 (w), 847 (w), 783 (w), 521 (m), 394 (w), 368 (w) cm^{-1}. Anal. Calcd for $C_{16}H_{26}N_4O_2S_8Co_2W_2$: C, 18.33; H, 2.50; N, 5.34; S, 24.46; W, 35.07. Found: C, 18.03; H, 2.49; N, 5.27; S, 23.64; W, 35.27. X-ray powder diffraction experiments ($6 \le 2\theta \le 62°$, Cu radiation, manual Phillips diffractometer) indicate **2** and **3** are isomorphous, based on relative intensities and d spacings of diffraction peaks [**2** (powder data), $a = 21.220$ (3) Å, $b = 10.666$ (2) Å, $c = 13.600$ (2) Å, $\beta = 99.52$ (1)°; **3** (powder data), $a = 21.08$ (5) Å, $b = 10.56$ (3) Å, $c = 13.54$ (3) Å, $\beta = 99.53$ (7)°].

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[13] The complete structure determination was carried out by Dr. C. S. Day of Crystalytics Co., P. O. Box 82286, Lincoln, NB 68501.

[14] Crystal data: space group $C2/c—C^6_{2h}$ (No. 15),[17] with $a = 21.248$ (5) Å, $b = 10.682$ (3) Å, $c = 13.617$ (4) Å, $\beta = 99.53$ (2)°, $V = 3048$ (1) $Å^3$, and $Z = 4$. The structure was solved by using direct methods and Fourier difference techniques. $R_F = 0.027$ and $R_{wF} = 0.026$ for 2896 independent reflections with $I > 3.0\sigma(I)$ and $3° < 2\theta < 55°$ (Mo K_α radiation). Anisotropic thermal prameters were utilized for all non-hydrogen atoms.

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[18] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

An α-Lithio Boronic Ester from an α-Trimethylstannyl Boronic Ester

Donald S. Matteson* and John W. Wilson[1]

Department of Chemistry, Washington State University
Pullman, Washington 99164-4690

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Summary: Pinacol (1-chloroethyl)boronate (**1a**) and lithiotrimethylstannane have yielded pinacol [1-(trimethyl-

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[1] On leave from the University of Ulster at Coleraine, Aug-Dec, 1984.