

## Synthesis of Organovanadium Sulfide Cluster Compounds via Bis(methylcyclopentadienyl)divanadium Tetrasulfide

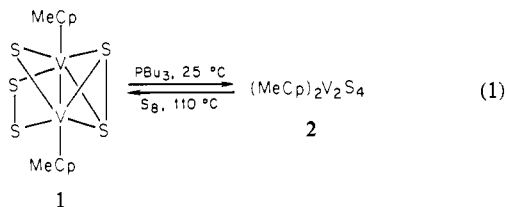
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Recent studies have established the extensive reactivity associated with the chalcogenide ligands in discrete metal sulfido complexes. Such research now promises to provide useful mechanistic and structural models for the role of metal sulfides in catalysis,<sup>1</sup> enzymology,<sup>2</sup> materials science,<sup>3</sup> and mineralogy.<sup>4</sup> Progress toward this goal is, however, coupled to the development of new classes of well-defined and synthetically accessible soluble metal sulfides that are kinetically stable yet reactive at the chalcogenide sites. In this report we describe the synthesis of cyclopentadienylvanadium disulfide dimer and the exploitation of its sulfur-localized reactivity for the assembly of some structurally and electronically unusual cluster compounds. Prior to this work there existed no examples of vanadium sulfide cluster compounds.<sup>5</sup>

Bis(methylcyclopentadienyl)divanadium pentasulfide,  $(\text{MeCp})_2\text{V}_2\text{S}_5$  (**1**), is available in ca. 85% yield via the thermal rearrangement of  $(\text{MeCp})_2\text{VS}_5$ .<sup>6,7</sup> This dimer was found to react cleanly with 1 equiv of *P-n*-Bu<sub>3</sub> to afford the corresponding tetrasulfide,  $(\text{MeCp})_2\text{V}_2\text{S}_4$  (**2**). The desulfurization reaction is conveniently performed in  $\text{CH}_2\text{Cl}_2$  (10 mL/mmol, 25 °C, 10 min); dilution of the resultant red solution with hexane precipitates **2** as analytically pure, slightly air-sensitive purple crystals in 75% yield<sup>8</sup> (eq 1). The reaction is reversible inasmuch as **2** adds sulfur



to reform **1**. <sup>1</sup>H NMR spectroscopy indicates that **2** is diamagnetic and possesses equivalent MeCp ligands; mass spectrometry confirms the dimer formulation. Several structures are conceivable for **2** including those formulated  $(\text{MeCp})_2\text{V}_2(\mu\text{-S})_2(\mu\text{-}\eta^2\text{-S}_2)$ <sup>9</sup> and  $(\text{MeCp})_2\text{V}_2(\mu\text{-}\eta^2\text{-S}_2)$ .<sup>10</sup> The  $\text{V}_2\text{S}_4$  core for  $(\text{MeCp})_2\text{V}_2(\mu\text{-}\eta^2\text{-S}_2)_2$  would be closely related to that found crystallographically in the

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(8) Anal. C, H, S, V. <sup>1</sup>H NMR (90 MHz,  $\text{CDCl}_3$ , sealed tube)  $\delta$  6.64 (m, 2 H), 6.51 (m, 2 H), 2.44 (s, 3 H); 70 eV EI mass spectrum,  $m/e$  388 (100%,  $\text{M}^+$ ), 324 (83%,  $\text{C}_{12}\text{H}_{14}\text{S}_2\text{V}_2^+$ ).

(9) For  $(\text{C}_5\text{Me}_5)_2\text{Mo}_2(\mu\text{-S})_2(\mu\text{-}\eta^2\text{-S}_2)$  see: Brunner, H.; Meier, W.; Wachter, J.; Guggolz, E.; Zahn, T.; Ziegler, M. *Organometallics* **1982**, *1*, 1107.

(10) We thank Dr. A. L. Rheingold (University of Delaware) for his assistance in our attempts to obtain a crystal structure on **2**. A serious disorder problem prevented refinement of the structure.

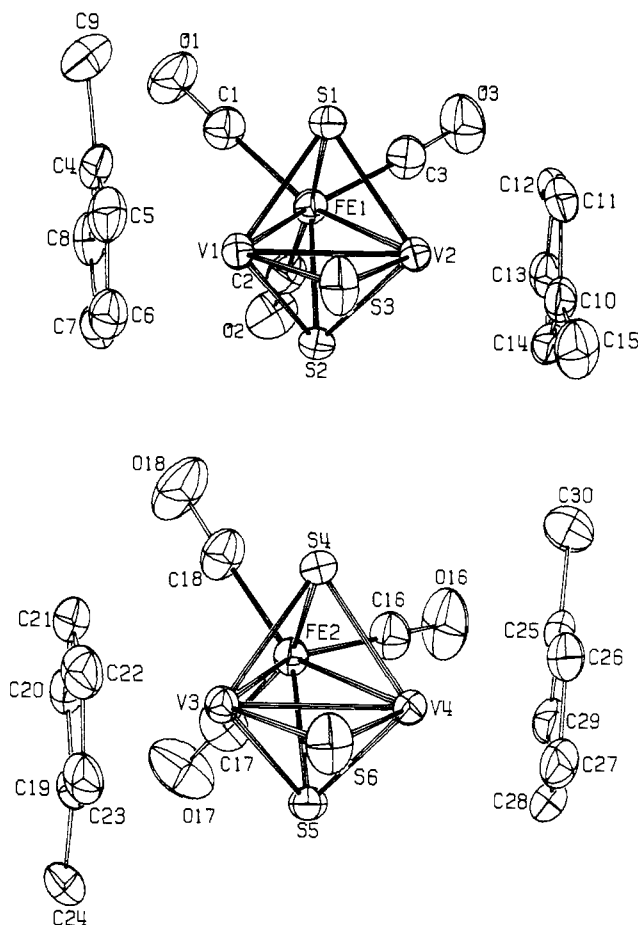
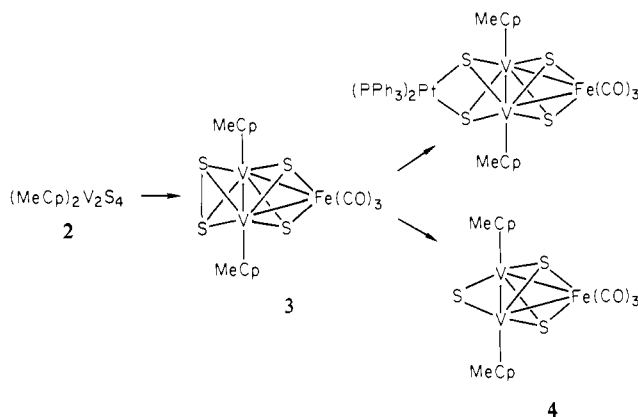


Figure 1. ORTEP plot of the two independent  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{V}_2\text{S}_3\text{Fe}(\text{CO})_3$  molecules with thermal ellipsoids drawn at the 35% probability level.

### Scheme I



mineral patronite  $\text{VS}_4$  ( $[\text{V}(\mu\text{-}\eta^2\text{-S}_2)]_n$ ).<sup>11</sup> Other examples of synthetic metal sulfido clusters are known whose core geometries resemble minerals.<sup>12</sup>

Subsequent to developing a straightforward synthesis of **2**, our attention turned to its utility as a building block for new metal sulfido clusters. **2** reacted readily with  $\text{Fe}(\text{CO})_5$  (5 equiv, 10 mL of  $\text{CH}_2\text{Cl}_2/0.1$  mmol of **2**, 25 °C, 30 min) in the presence of  $\text{Me}_3\text{NO}$  as a decarbonylation agent. Evaporation of the solvent and extraction of the residue with hexanes, followed by recrystallization from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , gave dark green

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(MeCp)<sub>2</sub>V<sub>2</sub>S<sub>4</sub>Fe(CO)<sub>3</sub> (**3**).<sup>13</sup> Compound **3**, typically isolated in ca. 45% yield, was diamagnetic and, unlike **2**, air-stable in solution. <sup>1</sup>H NMR and IR spectroscopy, mass spectrometry, and its derivative chemistry indicated the structure shown in Scheme I.<sup>14</sup> The trigonal bipyramidal M<sub>3</sub>S<sub>2</sub> core is a familiar motif in metal sulfide cluster chemistry; however, the bridging μ-η<sup>2</sup>-S<sub>2</sub> is unusual for organometallic sulfide clusters.<sup>15</sup> The μ-S<sub>2</sub> ligand in **3** is of particular interest because it represents a reactive cluster-bound functional group.<sup>16</sup> Thus treatment of **3** with Pt(C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub> solution, 10 min, 25 °C) gave the tetranuclear cluster (MeCp)<sub>2</sub>V<sub>2</sub>S<sub>4</sub>Fe(CO)<sub>3</sub>Pt(PPh<sub>3</sub>)<sub>2</sub> in quantitative yield (scheme).<sup>17</sup> This preliminary experiment suggests that **2** is a potential precursor to a wide range of heteronuclear sulfide cluster compounds.

Treatment of green CH<sub>2</sub>Cl<sub>2</sub> solutions of **3** with P-*n*-Bu<sub>3</sub> (1 equiv, 5 min, 25 °C) afforded red (MeCp)<sub>2</sub>V<sub>2</sub>S<sub>3</sub>Fe(CO)<sub>3</sub> (**4**) isolated in 75% yield as a crystalline solid after chromatographic workup and crystallization from CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH.<sup>18</sup> The structure of this derivative was elucidated by using single-crystal X-ray diffraction methods (Figure 1).<sup>19</sup> The metals are arrayed as an approximate isosceles triangle, the two Fe-V distances being 2.82 ± 0.01 Å. Two μ<sub>3</sub>-S ligands bridge the three metals while one sulfide lies in the FeV<sub>2</sub> plane and spans the V...V edge. The iron atom is seven-coordinate. The V...V distance of 2.51 Å is 0.15 Å shorter than that in **1** but 0.05 Å longer than the V-V distances in (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>V<sub>2</sub>(CO)<sub>5</sub><sup>20</sup> and (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>V<sub>2</sub>(CO)<sub>4</sub>PPh<sub>3</sub>.<sup>21</sup> The short V...S(**3**) distances of 2.23 (1) Å (cf. 2.45 Å in Cp<sub>2</sub>V(SPh)<sub>2</sub>)<sup>22</sup> suggest partial multiple bonding between these sites as a means of alleviating the electron deficiency of the vanadium atoms.

Compound **4** is formally a 44-e<sup>-</sup> cluster as the desulfurization of **3** converted a 6-e<sup>-</sup> μ-η<sup>2</sup>-S<sub>2</sub> ligand (cf. Fe<sub>2</sub>(μ-S<sub>2</sub>)(CO)<sub>6</sub>)<sup>23</sup> to a 2-e<sup>-</sup> μ-S ligand. The impact of this change appears to be localized at the vanadium centers. Thus the conversion of **3** to **4** is accompanied by a 0.8 ppm downfield shift in the <sup>1</sup>H NMR chemical shift of the cyclopentadienyl ring protons. In contrast, the ν<sub>CO</sub> patterns for **3** and **4** (high-resolution FT IR, cyclohexane solution) are virtually superimposable.

On the basis of our synthetic studies, a rich chemistry of the cyclopentadienylvanadium sulfides appears assured.<sup>24</sup> Furthermore, the predilection of vanadium for electron-deficient configurations suggests that the reactivity of this new generation

of cyclopentadienyl metal sulfides will prove distinctive in comparison with analogous compounds involving the later transition metals.

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**Registry No.** **1**, 83587-83-1; **2**, 83587-84-2; **3**, 83587-85-3; **4**, 83587-86-4; (MeCp)<sub>2</sub>V<sub>2</sub>S<sub>4</sub>Fe(CO)<sub>3</sub>Pt(PPh<sub>3</sub>)<sub>2</sub>, 83587-87-5; V, 7440-62-2.

**Supplementary Material Available:** Tables of selected bond distances and angles, positional parameters, thermal parameters, and final observed and calculated structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

### Stereochemical Consequences of Photosensitized and Electrode-Catalyzed Oxygenations of Stereoisomeric Di-*tert*-butylbi(bicyclo[3.3.1]non-9-ylidene)

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A number of electron-rich compounds react with singlet oxygen differently than do less electron-rich compounds.<sup>1</sup> In particular, [2 + 2] cycloaddition of singlet oxygen to produce dioxetanes occurs only with electron-rich olefins.<sup>2-5</sup> Recently, Foote,<sup>6</sup> Schaap,<sup>7</sup> Nelsen,<sup>8</sup> and Clennan<sup>9</sup> showed that dioxetanes once thought to be characteristic of singlet oxygen are also produced by electron transfer, e.g., cyanoaromatic-sensitization of several polyaryl olefins and electrode-catalyzed oxygenation of adamantylideneadamantane (**1**).

(13) Anal. C, H, Fe, V. IR (cyclohexane) 2028.5 (s), 1708.5 (s), 1699.5 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 4.95 (m, 2 H), 4.94 (m, 2 H), 1.97 (s, 3 H); field desorption mass spectrum, *m/e* 528 (M<sup>+</sup>).

(14) The structure of **3** has been confirmed by a preliminary X-ray diffraction study. The relationship between **3** and **4** will be covered in a forthcoming full paper.

(15) The cluster Mo<sub>3</sub>S<sub>13</sub><sup>-</sup> contains three μ-η<sup>2</sup>-S<sub>2</sub> ligands; many metal dimers and linear chain compounds (e.g., ref 11) also feature this moiety: Müller, A.; Jostes, R.; Cotton, F. A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 875.

(16) Anal. C, H, Fe, V. IR (toluene) 2013.5 (s), 1954 (br) cm<sup>-1</sup>; <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>) δ 7.32 (m, 15 H), 5.49 (m, 2 H), 5.41 (m, 2 H), 1.90 (s, 3 H); fast-atom bombardment mass spectrum, *m/e* 1163 (C<sub>48</sub>H<sub>44</sub>FeP<sub>2</sub>PtS<sub>4</sub>V<sub>2</sub><sup>+</sup>).

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(18) Anal. C, H, Fe, V. IR (cyclohexane) 2028.5 (s), 1979.0 (s), 1970.0 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 5.98 (s, 2 H), 5.55 (s, 2 H), 2.10 (s, 3 H); field desorption mass spectrum, *m/e* 496 (M<sup>+</sup>).

(19) (C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>V<sub>2</sub>S<sub>3</sub>Fe(CO)<sub>3</sub> (**4**) crystallizes in the monoclinic space group P2<sub>1</sub>/C with *a* = 10.397 (2) Å, *b* = 25.504 (7) Å, *c* = 14.135 (4) Å, β = 102.63(2)°, *V* = 3658 (2) Å<sup>3</sup>, *Z* = 8, μ = 20.93 cm<sup>-1</sup> (Mo Kα, λ 0.71069 Å). A total of 9301 reflections (3° < 2θ < 55°) were collected on a Syntex P2<sub>1</sub> diffractometer of which 8422 were unique. Of these reflections, 5040 with *F*<sub>o</sub> > 3σ(*F*<sub>o</sub>) were used in the subsequent solution and refinement. The final discrepancy factors are 3.8% and 5.1% for *R* and *R*<sub>w</sub>, respectively.

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