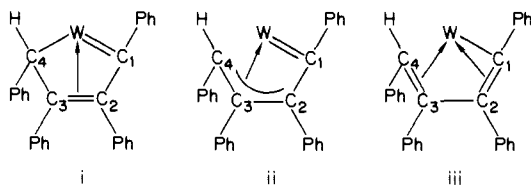


**Table I.** Selected Bond Distances and Angles for  $W(O)(C_4Ph_4H)(S_2CNET_2)$ 

atoms	distance, Å	atoms	angle, deg
W-C1	1.96 (1)	S1-W-C1	138.1 (4)
W-C2	2.52 (1)	S2-W-C4	140.0 (3)
W-C3	2.61 (1)	C2-W-O	141.1 (4)
W-C4	2.25 (1)	C3-W-O	143.6 (4)
W-O	1.66 (1)	C1-W-O	107.7 (5)
W-S1	2.532 (3)	W-C1-C2	94.3 (8)
W-S2	2.417 (3)	C1-C2-C3	116 (1)
C1-C2	1.44 (1)	C2-C3-C4	115 (1)
C2-C3	1.43 (1)	C3-C4-W	86 (1)
C3-C4	1.49 (1)		
C1-C4	2.69 (2)		

The geometry of isomer **a** was determined by single-crystal X-ray diffraction (see Figure 1).<sup>6</sup> Selected distances and angles are listed in Table I. The structure of  $W(O)(C_4Ph_4H)(S_2CNET_2)$  is roughly octahedral with C<sub>2</sub> and C<sub>3</sub> of the metallacycle bound at most only weakly to the metal approximately trans to the oxo ligand (O-W-C2, 141°; O-W-C3, 144°). An alternate description of the coordination geometry as a square pyramid with C<sub>1</sub>, C<sub>4</sub>, S<sub>1</sub>, and S<sub>2</sub> in the basal plane and the tungsten atom displaced toward the oxo ligand in the apical position neglects any bonding of C<sub>2</sub> and C<sub>3</sub> to the metal. A crude structural analogy is provided by high oxidation state early transition metal  $\pi$ -butadiene complexes. In contrast to the nearly equivalent four M-C distances of iron<sup>7</sup> and molybdenum<sup>8</sup>  $\eta^4$ -diene examples, the 2,3-dimethylbutadiene ligand of  $(\pi-C_5H_5)_2Zr(\eta^4-C_6H_{10})^9$  has the two internal carbons 0.3 Å further from the metal than the two terminal carbons. The C<sub>4</sub>-based ligand in  $W(O)(C_4Ph_4H)(S_2CNET_2)$  shows a related asymmetry as it appears to have a metal-carbon double bond to C<sub>1</sub> (1.96 Å cf. 1.94 Å for W=CHCMe<sub>3</sub><sup>10</sup>), a single bond to C<sub>4</sub> (2.25 Å cf. 2.26 Å for W-CH<sub>2</sub>CMe<sub>3</sub><sup>10</sup>) and only weak donation from the C<sub>2</sub> and C<sub>3</sub> to the metal (2.52 and 2.61 Å, respectively). Several resonance structures can be drawn to represent the  $W(\eta^4-C_4Ph_4H)$  fragment. These resonance forms illustrate the similarity of the C(Ph)H terminus to  $\pi$ -allyl and  $\pi$ -butadiene terminal carbons as reflected in the NMR data. In representation iii the W-C<sub>1</sub>-C<sub>2</sub> moiety is reminiscent of  $\eta^2$ -vinyl ligands which have been characterized recently.<sup>11</sup>



The  $\eta^4-C_4Ph_4H$  ligand has been prepared previously by hydride attack on a cationic  $\pi$ -cyclobutadiene ruthenium derivative.<sup>12</sup> The

(6) The crystal selected was monoclinic of space group  $P2_1/c$  with unit cell dimensions of  $a = 16.302(5)$  Å,  $b = 9.450(3)$  Å,  $c = 20.242(7)$  Å, and  $\beta = 108.89(3)^\circ$ , with  $Z = 4$ . Data were collected at ambient temperature on an Enraf-Nonius CAD4 diffractometer using monochromated Mo K $\alpha$  radiation. Of the 6406 reflections monitored, 2487 independent reflections with  $I > 3\sigma(I)$  were used in the structure solution and refinement, which converged to  $R = 7.3\%$  and  $R_w = 6.6\%$  with hydrogens in calculated positions, phenyl carbons refined isotropically, and all other heavy atoms refined anisotropically. An empirical absorption correction was applied based on psi scans with  $\chi$  near  $90^\circ$ .

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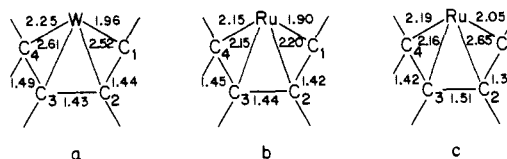
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structure of  $(\pi-C_5H_5)Ru(\eta^4-C_4Ph_4H)$  has all four ligand carbons in one plane as does the tungsten oxo complex reported here. The high trans influence of the oxo ligand and steric congestion around the metal due to the bulky phenyl substituents probably cause the M-C<sub>1</sub>-C<sub>2</sub> angle to open from  $82^\circ$  in the ruthenium case to  $95^\circ$  here with the W-C<sub>2</sub> and W-C<sub>3</sub> distances elongated accordingly. Comparison of the metallacycle ring distances in  $W(O)(C_4Ph_4H)(S_2CNET_2)$  (a),  $(\pi-C_5H_5)Ru(C_4Ph_4H)$  (b),<sup>12</sup> and



$(\pi-C_5H_5)Ru(PPh_3)(C_4(CF_3)_4H)$  (c),<sup>13</sup> where only three rather than five electrons are required from the C<sub>4</sub>R<sub>4</sub>H ligand, underscores the carbenoid character of C<sub>1</sub> for a and b. The formation of a tungsten oxo carbene derivative from a low oxidation state tungsten alkyne complex with acid and aqueous reagents is noteworthy.

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**Supplementary Material Available:** Tables of anisotropic thermal parameters, positional parameters, complete bond distances, calculated hydrogen positions, and  $F_{obsd}$  and  $F_{calcd}$  (24 pages). Ordering information is given on any current masthead page.

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## Synthesis and Characterization of a New Fe/Mo/S Cluster Containing the $[Fe_6Mo_2S_6]^{3+}$ Core. A Precursor to a Possible Structural Analogue for the Fe/Mo Site of Nitrogenase

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Structural and spectroscopic studies on the Fe/Mo center in the Fe/Mo protein of nitrogenase<sup>1</sup> and the nitrogenase cofactor<sup>2</sup> have revealed the presence of a most interesting Fe/Mo/S aggregate.

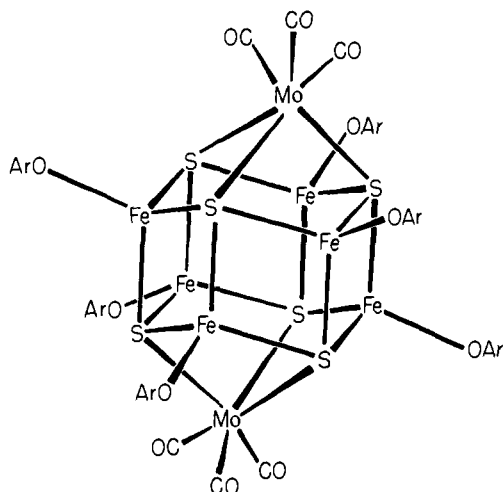
Analyses of the Mo<sup>3</sup> and Fe<sup>4</sup> x-ray absorption fine structures in the Fe/Mo protein of nitrogenase and (for the Mo only) in the nitrogenase cofactor have established (a) the close proximity ( $\sim 2.7$  Å) of the Mo atom or two or three Fe atoms, (b) coordination of three of four S atoms to the Mo atom (at 2.35 Å) and of two or three S atoms to the Fe atom (at 2.25 Å), and (c) the probable

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**Figure 1.** Proposed structure for the  $((\text{Fe}_6\text{S}_6(\text{OPh-}p\text{-CH}_3)_6)(\text{Mo}(\text{CO})_3)_2)^{2-}$  dianion.<sup>16</sup>

coordination of O- or N-containing ligands to the Fe and Mo atoms in the Fe-Mo protein<sup>4</sup> and the cofactor.<sup>3c</sup>

Detailed studies of the <sup>57</sup>Fe Mössbauer spectra of either the Fe/Mo protein or the cofactor<sup>5</sup> and pulsed EPR studies<sup>6</sup> indicate that the metal site consists of a spin-coupled ( $S = 3/2$ )  $\text{Fe}_6\text{Mo}$  aggregate. Furthermore, analyses of the ENDOR spectra of the Fe/Mo protein<sup>7</sup> indicate that the observed six distinct <sup>57</sup>Fe peaks can be grouped into trios having very similar hyperfine parameters.

Collectively, the structural and spectroscopic information available for the Fe/Mo/S aggregate in nitrogenase defines the boundaries within which the properties of synthetic analogues must be confined. To date there exist no well-characterized synthetic Fe/Mo/S clusters that adhere to either the stoichiometric or the spectroscopic requirements set forth by the available data on the Fe/Mo/S aggregate in nitrogenase.

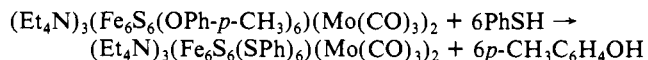
Recently we suggested<sup>8</sup> that a possible synthetic structural analogue for the Fe/Mo/S aggregate in nitrogenase may be obtained by the addition of an appropriate  $\text{MoL}_3$  unit to one of the hexagonal faces of a  $(\text{Fe}_6\text{S}_6\text{L}_6)^{3-}$  "prismane".<sup>8</sup>

In this paper we report on the addition of two  $\text{Mo}(\text{CO})_3$  fragments to the  $(\text{Fe}_6\text{S}_6(\text{OPh-}p\text{-CH}_3)_6)^{3-}$  "prismane" and the formation of what we propose to be a "pentlandite" type of cluster with the  $(\text{Mo}_2\text{Fe}_6\text{S}_6)^{3+}$  core (Figure 1). Structurally related cores such as  $\text{Co}_8\text{S}_6$ ,  $\text{Fe}_4\text{Ni}_4\text{S}_6$ , and  $\text{Fe}_8\text{S}_6$  have been found in  $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$ ,<sup>9</sup> natural pentlandite,<sup>10</sup> and  $[\text{Fe}_8\text{S}_6\text{I}_8]^{2-}$ .<sup>11</sup> The suggestion that a cluster, with a  $\text{Fe}_7\text{Mo}$  core, may be a structural analogue for the Fe/Mo/S aggregate in nitrogenase has been advanced previously.<sup>9</sup>

The reaction of  $(\text{Et}_4\text{N})_3(\text{Fe}_6\text{S}_6(\text{OPh-}p\text{-CH}_3)_6)$  with  $(\text{CH}_3\text{C-N})_3\text{Mo}(\text{CO})_3$ , in  $\text{CH}_3\text{CN}$  in a 1:4 molar ratio, proceeds readily at 75 °C and is complete in ca. 1/2 h. The purple-red crystalline product I,  $(\text{Et}_4\text{N})_3(\text{Fe}_6\text{S}_6(\text{OPh-}p\text{-CH}_3)_6)(\text{Mo}(\text{CO})_3)_2$ , is obtained in 80% yield. Anal. Calcd for  $\text{Mo}_2\text{Fe}_6\text{S}_6\text{O}_{12}\text{N}_3\text{C}_{72}\text{H}_{102}$  (MW = 1920): Mo, 10.00; Fe, 17.5; S, 10.00; N, 2.18; C, 45.0. Found: Mo, 10.16; Fe, 18.03; S, 9.91; N, 2.30; C, 43.9.

The electronic spectrum of I in  $\text{CH}_3\text{CN}$  solution shows a broad band at 468 nm and a shoulder at 260 nm and is appreciably perturbed by comparison to the "parent" prismane that shows<sup>8</sup> absorptions at 427 and 272 nm. The color of I in  $\text{CH}_3\text{CN}$  solution

changes to deep blue purple upon addition of excess PhSH and shows electronic absorptions at 50 and 326 nm. The exchange of the *p*- $\text{CH}_3$ -phenolate ligands in I by  $\text{PhS}^-$  apparently proceeds according to the reaction

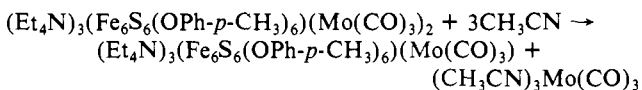


and has a precedent in the chemistry of the  $(\text{Fe}_6\text{S}_6(\text{OPh-}p\text{-CH}_3)_6)^{3-}$  cluster.<sup>8</sup> The infrared spectrum of I shows two strong C-O stretching vibrations (KBr) at 1915 and 1860  $\text{cm}^{-1}$ . The sharp doublet clearly indicates that the local symmetry around the  $\text{Mo}(\text{CO})_3$  fragment is  $C_{3v}$  and is quite similar to the doublet observed in the IR spectrum of the tricarbonyl(1,4,7-trithiacyclononane)molybdenum complex.<sup>12</sup> The latter contains a tridentate cyclic trithioether ligand and shows the C-O stretching vibrations (KBr) at 1915 and 1783  $\text{cm}^{-1}$ . The <sup>57</sup>Fe Mössbauer spectrum of I at 125 K shows a sharp quadrupole doublet with an isomer shift (IS) of 0.532 (2) mm/s (vs. Fe) and a quadrupole splitting ( $\Delta E_Q$ ) of 0.845 mm/s. These values are similar to those we reported<sup>8</sup> for the "parent" prismane at 0.476 mm/s and 1.016 mm/s for  $\Delta E_Q$  and IS, respectively.

The electrochemistry of I was studied<sup>13</sup> by cyclic voltammetry in  $\text{CH}_2\text{Cl}_2$ . A wide scan from 1.0 to -1.50 V shows waves at 0.69, 0.24, -0.39, -0.93, and -1.38 V. The waves at -0.39 and -0.93 V correspond to the 3-/4- and 4-/5- couples, respectively, and by all criteria indicate reversible processes. The analogous reversible waves for the  $(\text{Et}_4\text{N})_3(\text{Fe}_6\text{S}_6)(\text{SPh})_6(\text{Mo}(\text{CO})_3)_2$  complex are found at -0.34 and -0.78 V. The latter was obtained in situ by the addition of a slight excess of PhSH to  $\text{CH}_2\text{Cl}_2$ /electrolyte solutions of I.

Addition of the  $\text{Mo}(\text{CO})_3$  fragments to the paramagnetic ( $S = 1/2$ )  $(\text{Fe}_6\text{S}_6(\text{OPh-}p\text{-CH}_3)_6)^{3-}$  prismane<sup>8,14</sup> does not change its magnetic ground state and the EPR spectra of I at 10 K show a typical  $S = 1/2$  signal.<sup>15</sup>

The <sup>1</sup>H NMR spectra of I display isotropically shifted resonances associated with the *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{O}^-$  ligands. In  $\text{CH}_3\text{CN-}d_3$  solution these resonances appear as a predominant set at 14.47 (meta H), 11.88 (para  $\text{CH}_3$ ), and -3.00 ppm (ortho H). a minor set of resonances also is present at 13.19 and 12.84, 9.93 and 9.62, and -0.50 and -0.70 ppm. The relative intensity of this set of doublets increases upon the addition of  $(\text{Et}_4\text{N})_3(\text{Fe}_6\text{S}_6(\text{OPh-}p\text{-CH}_3)_6)$  and decreases when  $(\text{CH}_3\text{CN})_3\text{Mo}(\text{CO})_3$  is added to the NMR solutions of I. On the basis of these observations we conclude that, in solution, I coexists with the 1:1  $\text{Mo}(\text{CO})_3$  adduct according to the equilibrium



On the basis of stoichiometric, spectroscopic, and magnetic ground-state criteria, I cannot be considered as a satisfactory analogue for the Fe/Mo/S center in nitrogenase. The  $[(\text{Fe}_6\text{S}_6(\text{OR})_6)(\text{Mo}(\text{CO})_3)]^{2-}$  derivative of I, however, has a stoichiometry more closely resembling that of the Fe/Mo/S aggregate in nitrogenase. The reactions of I and the isolation and characterization of the 1:1 adduct currently are investigated in our laboratory.

**Acknowledgment.** This research was supported by a grant from the National Institutes of Health (GM-26671). We are indebted to Dr. W. R. Dunham for the preliminary Mössbauer and EPR measurements.

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(16) Recently we finished the crystal structure of the  $(\text{Et}_4\text{N})_4\text{Fe}_6\text{S}_6\text{Cl}_6(\text{Mo}(\text{CO})_3)_2$ . The basic core in the anion of this compound is virtually identical with the one shown in Figure 1.