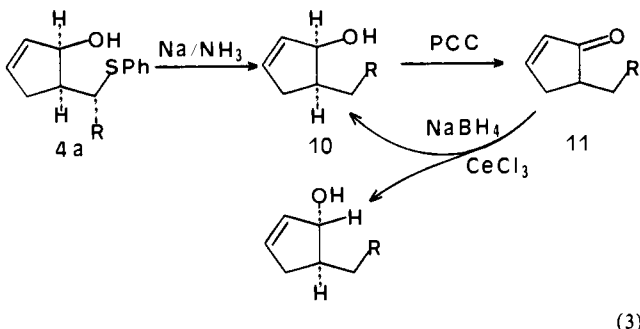


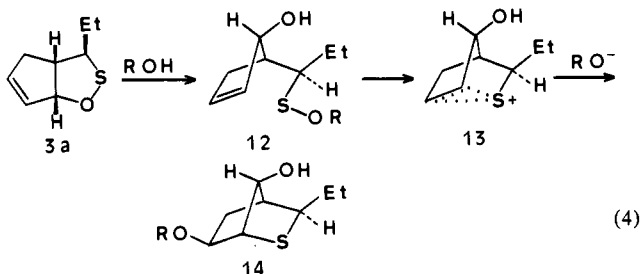
7-ene (**3b**)<sup>4</sup> (bp 55 °C (0.05 mm)), could be prepared by rearrangement of cyclopentadiene-ethanethial *S*-oxide (**1b**) adduct **2b** (67% yield based on **1b** precursor, ethanesulfinyl chloride). Sultene **3a** can be oxidized with MCPBA to a pair of sultines which in turn can be converted to a single sultone.

Sultene **3a** readily reacts with phenyllithium giving alcohol **4a** in quantitative yield. In order to establish the structure of alcohol **4a**, it was desulfurized (Na/NH<sub>3</sub>) giving unsaturated alcohol **10** (eq 3) which was oxidized (PCC)<sup>11</sup> to 5-propyl-2-cyclopentenone



(**11**).<sup>12</sup> Alcohol **10** formed from **4a** is identical with the major product of reduction of **11** with sodium borohydride-cerium chloride.<sup>13</sup> To demonstrate the synthetic utility of alcohol **4a** we have subjected this compound to sequential oxidation at carbon (PCC) and then at sulfur (MCPBA or sodium metaperiodate) at 0 °C followed by flash distillation at 25 °C giving directly (*E*)-5-propylidene-2-cyclopentenone (**6a**, R = Et)<sup>4</sup> by way of unstable sulfoxide **5a** (eq 1), in 42% overall yield from **3a**. In a similar manner (*E*)-5-ethylidene-2-cyclopentenone (**6b**, R = Me)<sup>14a</sup> could be prepared in 38% overall yield from sultene **3b**. Use of substituted cyclopentadienes together with appropriate sulfines should allow synthesis of more complex 5-alkylidene-2-cyclopentenones, of interest as antibiotics.<sup>14b</sup>

Sultene **3a** also reacts rapidly with thiols giving disulfides analogous to **4a** (R'S instead of Ph) and with alcohols giving *exo*-6-alkoxy-*exo*-3-ethyl-*syn*-7-hydroxy-2-thiabicyclo[2.2.1]heptanes (**14**; e.g., R = *t*-Bu<sup>4</sup>), all in quantitative yields. Compounds of type **14** are presumably formed by way of sulfenate esters **12** and episulfonium ions **13** (eq 4). Formation of epi-



sulfonium ions related to **13** from 3-cyclopentenyl derivatives as well as ring opening of these ions to 6,7-disubstituted 2-thiabicyclo[2.2.1]heptanes has been noted previously.<sup>26,15</sup> On standing

(10) Compound **3a** shows UV absorption at 310 nm ( $\epsilon$  60), <sup>13</sup>C NMR peaks at  $\delta$  136.7, 128.1, 95.1, 64.8, 51.0, 39.3, 27.2, and 12.8 ppm, and <sup>1</sup>H NMR peaks at  $\delta$  5.85 (m, 1 H), 5.5 (m, 1 H), 5.2 (m, 1 H), 3.25 (d, 1 H), 2.78 (m, 1 H), 2.4 (m, 2 H), 1.75 (q, 2 H), 0.95 ppm (t, 3 H).

(11) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647-2650. Corey, E. J.; Boger, D. L. *Ibid.* **1978**, 2461-2464.

(12) Agosta, W. C.; Smith, A. B. *J. Am. Chem. Soc.* **1971**, *93*, 5513-5520. Grimaldi, J.; Bertrand, M. *Bull. Soc. Chim. Fr.* **1971**, 957-962. Pohmakotr, M.; Phinyocheep, P. *Tetrahedron Lett.* **1984**, *25*, 2249-2252.

(13) Luche, J.-L. *J. Am. Chem. Soc.* **1978**, *100*, 2226-2227. Luche, J.-L.; Rodriguez-Hahn, L.; Crabbe, P. *J. Chem. Soc., Chem. Commun.* **1978**, 601-602.

(14) (a) Noyori, R.; Ohnishi, Y.; Kato, M. *J. Am. Chem. Soc.* **1972**, *94*, 5105-5106. (b) Methyleneomycin: Siwapinyoyos, T.; Thebtaranonth, Y. *J. Org. Chem.* **1982**, *47*, 598-599. Clavulone: Corey, E. J.; Mehrotra, M. M. *J. Am. Chem. Soc.* **1984**, *106*, 3384.

(15) Ohishi, J.; Tsunooka, K.; Ikegami, S.; Akaboshi, S. *J. Org. Chem.* **1978**, *43*, 4013-4020.

sultene **3a** gradually forms a polymer<sup>4</sup> lacking olefinic protons in the NMR; this polymer may involve a repeating 3-ethyl-6,7-oxy-2-thiabicyclo[2.2.1]heptane system similar to **14**.

**Acknowledgment.** We gratefully acknowledge support for this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, the Soci t  Nationale Elf Aquitaine, the John Simon Guggenheim Memorial Foundation (E.B.), and the National Institutes of Health (J.Z.). Funding for the SUNYA 300-MHz NMR facility was provided by the National Science Foundation (Grant CHE 8313711). We thank Professors Carl Johnson, Frank Davis, and Amos Smith for helpful discussions and Dr. A. A. Bazzi for initial studies on this project.

**Supplementary Material Available:** Tables of spectroscopic and crystal data, atomic coordinates and temperature factors, bond lengths and bond angles, anisotropic temperature factors, hydrogen atom positions, and observed and calculated structure factors and a perspective view of **7a**, R = Et (15 pages). Ordering information is given on any current masthead page.

### Persulfide-Bridged Iron-Molybdenum-Sulfur Clusters of Biological Relevance: Two Synthetic Routes and the Structures of Intermediate and Product Clusters

Julie A. Kovacs, J. K. Bashkin,<sup>1</sup> and R. H. Holm<sup>\*</sup>

Department of Chemistry, Harvard University  
Cambridge, Massachusetts 02138

Received November 29, 1984

Recent research in this laboratory<sup>2-4</sup> has been directed toward attainment of a synthetic representation of the iron-molybdenum cofactor (FeMo-co) of nitrogenase.<sup>5</sup> Among the relevant species are the double- and single-cubane clusters [Mo<sub>2</sub>Fe<sub>6</sub>S<sub>8</sub>( $\mu_2$ -L)<sub>3</sub>(SR)<sub>6</sub>]<sup>3-5</sup> (L = RS<sup>-</sup>, RO<sup>-</sup>)<sup>3,6</sup> and [MoFe<sub>3</sub>S<sub>4</sub>(SR)<sub>3</sub>(cat)L]<sup>2-3,7,4</sup> respectively, which contain the MoFe<sub>3</sub>( $\mu_3$ -S)<sub>4</sub> unit. Single cubanes, in particular, display electronic properties<sup>4c</sup> and a Mo coordination site<sup>4bcf</sup> (XAS criteria) similar to those of FeMo-co.<sup>5,7</sup> We report two synthetic routes to a new class of double cubanes, containing persulfide bridges, and the structures of intermediate and product clusters. Reactions were conducted under anaerobic conditions.

A solution of Li<sub>2</sub>[Fe<sub>2</sub>S<sub>2</sub>(CO)<sub>6</sub>]<sup>8</sup> (5.8 mmol) in 100 mL of THF at -78 °C was treated with equimolar (Et<sub>3</sub>N)<sub>2</sub>[Cl<sub>2</sub>FeMoS<sub>4</sub>]<sup>9</sup> in

(1) NIH Postdoctoral Fellow, 1984-1985.

(2) (a) Holm, R. H. *Chem. Soc. Rev.* **1981**, *10*, 455. (b) Holm, R. H.; Armstrong, W. H.; Christou, G.; Mascharak, P. K.; Mizobe, Y.; Palermo, R. E.; Yamamura, T. In "Biomimetic Chemistry"; Yoshida, Z.-I., Ise, N., Eds.; Elsevier: New York, 1983; Proceedings of the 2nd International Kyoto Conference on New Aspects of Organic Chemistry, pp 79-99.

(3) (a) Palermo, R. E.; Power, P. P.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 173. (b) Christou, G.; Mascharak, P. K.; Armstrong, W. H.; Papaefthymiou, G. C.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 2820.

(4) (a) Armstrong, W. H.; Mascharak, P. K.; Holm, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 4373. (b) Mascharak, P. K.; Armstrong, W. H.; Mizobe, Y.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 475. (c) Palermo, R. E.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 4310. (d) Mizobe, Y.; Mascharak, P. K.; Palermo, R. E.; Holm, R. H. *Inorg. Chim. Acta* **1983**, *80*, L65. (e) Mascharak, P. K.; Papaefthymiou, G. C.; Armstrong, W. H.; Foner, S.; Frankel, R. B.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 2851. (f) Palermo, R. E.; Singh, R.; Bashkin, J. K.; Holm, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 2600. cat = catechol and substituted derivatives; L' = a variety of ligands.

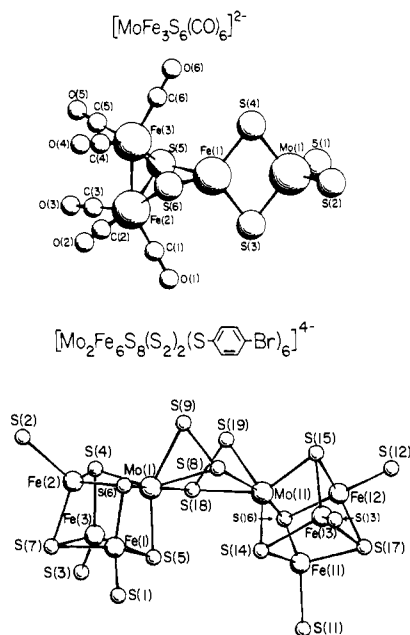
(5) Burgess, B. K.; Newton, W. E. In "Nitrogen Fixation, The Chemical-Biochemical-Genetic Interface"; M ller, A., Newton, W. E., Eds.; Plenum Press: New York, 1983; pp 83-110.

(6) (a) Christou, G.; Garner, C. D. *J. Chem. Soc., Dalton Trans.* **1980**, 2354. (b) Christou, G.; Garner, C. D.; Miller, R. M.; Johnson, C. E.; Rush, J. D. *Ibid.* **1980**, 2363. (c) Christou, G.; Collison, D.; Garner, C. D.; Acott, S. R.; Mabbs, F. E.; Petrouleas, V. *Ibid.* **1982**, 1575.

(7) (a) Conradson, S. D.; Burgess, B. K.; Hodgson, K. O.; Mortenson, L. E.; Newton, W. E., unpublished results. (b) Conradson, S. D., Ph.D. Thesis, Stanford University, CA, 1983.

(8) Seyferth, D.; Henderson, R. S.; Song, L.-C. *J. Organomet. Chem.* **1980**, *192*, C1; *Organometallics* **1982**, *1*, 125.

(9) Tieckelmann, R. H.; Silvis, H. C.; Kent, T. A.; Huynh, B. H.; Waszczak, J. V.; Teo, B.-K.; Averill, B. A. *J. Am. Chem. Soc.* **1980**, *102*, 5550.



**Figure 1.** Structures of intermediate and product clusters.  $[\text{MoFe}_3\text{S}_6(\text{CO})_6]^{2-}$  (1), selected (mean) parameters under  $C_{2v}$  symmetry: Mo-S(1,2), 2.156; Mo-S(3,4), 2.263; Mo-Fe(1), 2.762 (2); Fe(1)-S(3,4), 2.262; Fe(1)-S(5,6), 2.288; S(5)-S(6), 3.107 (6); Fe(2)-Fe(3), 2.491 (4) Å; S(1)-Mo-S(2), 111.9 (2)°; S(3)-Mo-S(4), 104.7 (2)°; S(3)-Fe(1)-S(4), 104.8 (2)°; S(5)-Fe(1)-S(6), 85.6 (2)°; Fe(1)-S(5,6)-Fe(2), 84.4°; Fe(1)-S(5,6)-Fe(3), 85.8°.  $[\text{Mo}_2\text{Fe}_6\text{S}_{12}(\text{S}-p\text{-C}_6\text{H}_4\text{Br})_6]^{4-}$  (5), selected mean values (esd) of distance types from averages over the two independent anions (c = cubane unit): Mo-S<sub>c</sub>, 2.35 (3); Fe-S<sub>c</sub>, 2.25 (3), Mo-Fe, 2.70 (2); Fe-Fe, 2.67 (2); Mo(1)-S(8), 2.47 (4); Mo(1)-S(9), 2.40 (1); Mo(1)-S(18), 2.64 (5); S(8)-S(9), 1.99 (5) Å.

400 mL of acetonitrile. Addition of ether to the reaction mixture filtrate after 16 h of reaction afforded purple-brown microcrystalline  $(\text{Et}_4\text{N})_2[\text{MoFe}_3\text{S}_6(\text{CO})_6]$  (43%, anion 1;  $\nu_{\text{CO}}$  2042 (m), 2004 (s), 1960 (vs)  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$  ( $\epsilon_{\text{M}}$ ) 331 (23 600), 470 (8960), 549 (5990) nm).<sup>10</sup> The structure of 1<sup>10,11</sup> (Figure 1) reveals the anticipated displacement of chloride from  $[\text{Cl}_2\text{FeMoS}_4]^{2-}$  (2) by  $[\text{Fe}_2\text{S}_2(\text{CO})_6]^{2-}$  (3), whose chelating ability to other metals has been demonstrated.<sup>8,12</sup> Product cluster 1 consists of 3 and the  $\text{FeMoS}_4$  portion of 2, both nearly unperturbed from their appearances in simpler complexes,<sup>13,14</sup> configured so as to approach molecular  $C_{2v}$  symmetry. Accordingly, the Mössbauer spectrum of 1 at 4.2 K consists of two partially resolved quadrupole doublets:  $\delta_1 = -0.08$ ,  $\Delta E_{\text{Q1}} = 0.76$  mm/s;  $\delta_2 = 0.30$ ,  $\Delta E_{\text{Q2}} = 2.02$  mm/s. Doublet 2, ~50% as intense as doublet 1 and with parameters close to those of  $[(\text{PhS})_2\text{FeMoS}_4]^{2-}$ ,<sup>14</sup> arises from tetrahedral Fe(1), which, from the magnetic moment of 1 (4.8  $\mu_{\text{B}}$ ), is high-spin Fe(II). Therefore, the  $[\text{MoFe}_3\text{S}_6]^{2-}$  core of 1 contains formally 2Fe(I) + Fe(II) + Mo(VI) + 6S<sup>2-</sup>.

Cluster 1 (1.1 mmol) in 100 mL of acetonitrile was oxidatively decarbonylated with 2.2 mmol of (*p*-ClC<sub>6</sub>H<sub>4</sub>S)<sub>2</sub> (10 h, 50 °C),

(10) IR, UV-visible, and <sup>1</sup>H NMR spectra, cyclic voltammetry, and magnetic moments were determined in acetonitrile solutions at 297 K. X-ray diffraction data were collected at ambient temperature on a Nicolet P3F four-circle automated diffractometer with graphite-monochromatized Mo K $\alpha$  radiation. Empirical absorption corrections were applied. Structures were solved by a combination of direct methods, and Patterson or Fourier techniques, and were subjected to block cascade least-squares refinements.

(11) Single crystals of  $(\text{Et}_4\text{N})_2[\text{MoFe}_3\text{S}_6(\text{CO})_6]$  were grown by ether diffusion into a propionitrile solution. The compound crystallizes in orthorhombic space group *Pbcn* with *a* = 15.314 (7) Å, *b* = 16.627 (6) Å, *c* = 29.97 (1) Å, and *Z* = 8. With use of 3220 unique data ( $5^\circ \leq 2\theta \leq 45^\circ$ ,  $I \geq 3\sigma(I)$ ) the structure was refined to *R* (*R*<sub>w</sub>) = 8.3 (9.5)%.

(12) Seyferth, D.; Henderson, R. S.; Gallagher, M. K. *J. Organomet. Chem.* **1980**, *193*, C75.

(13) (MeHgS)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>; Mak, T. C. W.; Book, L.; Chieh, C.; Gallagher, M. K.; Song, L.-C.; Seyferth, D. *Inorg. Chim. Acta* **1983**, *73*, 159.

(14)  $[(\text{PhS})_2\text{FeMoS}_4]^{2-}$ : Coucouvanis, D.; Stremple, P.; Simhon, E. D.; Swenson, D.; Baenziger, N. C.; Draganjac, M.; Chan, L. T.; Simopoulos, A.; Papaerthyimou, V.; Kostikas, A.; Petrouleas, V. *Inorg. Chem.* **1983**, *22*, 293. All isomer shifts are quoted vs. Fe metal at 4.2 K.

after which no bound CO was detectable (IR). Isolation of the solid from the addition of THF (50 mL) to the cold reaction mixture filtrate and thorough washing (3:1 v/v acetone/acetonitrile) afforded black microcrystalline  $(\text{Et}_4\text{N})_4[\text{Mo}_2\text{Fe}_6\text{S}_{12}(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_6]$  (37%, anion 4; 348 (sh), 437 (30 600) nm). This procedure effected separation of the more soluble byproduct salts of  $[\text{Fe}_n\text{S}_n(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_4]^{2-}$  (*n* = 2, 4).<sup>15</sup> Cyclic voltammetry ( $E_{1/2} = -0.14$  (oxidation), -1.14, -1.34 V vs. SCE,  $i_{\text{p,c}} \approx i_{\text{p,a}}$ , 100 mV/s<sup>10</sup>) suggested that 4 is a double cubane containing two  $[\text{MoFe}_3\text{S}_4]^{3+}$  cores, whose 0.20-V reduction potential difference implies a Mo···Mo separation of ~3.2–3.8 Å.<sup>3,6b</sup> Suitable single crystals of  $(\text{Et}_4\text{N})_4$ (4) could not be obtained but crystals of  $(\text{Et}_4\text{N})_4[\text{Mo}_2\text{Fe}_6\text{S}_{12}(\text{S}-p\text{-C}_6\text{H}_4\text{Br})_6]$  (anion 5), prepared analogously, were adequate for X-ray structure elucidation but not for precise angle and distance determinations owing to limited data. The asymmetric unit contains eight cations, two structurally equivalent anions 5, and a DMF solvate.<sup>10,16</sup> The structure of 5 (Figure 1) consists of two  $\text{MoFe}_3\text{S}_4$  cubane-type subclusters separated at a Mo(1)···Mo(11) distance of 3.97 (7) Å and unsymmetrically bridged by two  $\mu_2$ - $\eta^3$  persulfide groups. This is a less frequent S<sub>2</sub><sup>2-</sup> bonding mode<sup>17</sup> but is preceded,<sup>18</sup> most directly in  $(\text{Me}_5\text{C}_5)_2\text{Mo}_2\text{S}_{10}$ .<sup>18d</sup> The complete Mo<sub>2</sub>(S<sub>2</sub>)<sub>2</sub> bridge unit has not been encountered previously. Its Mo(1,11)S(8,18) portion deviates from planarity (MoS<sub>2</sub> dihedral angle, 22°), and the nonbridging atoms S(9,19) occur in a syn configuration with their respective MoS<sub>2</sub> fragments roughly parallel (dihedral angle 17°). The overall structure approaches C<sub>2</sub> symmetry, with the pseudoaxis bisecting the S(8)-S(18) and S(9)-S(19) vectors. Unlike all other  $\text{MoFe}_3\text{S}_4$  clusters (effective C<sub>3</sub> or C<sub>3</sub> symmetry), the subclusters of 5 lack local symmetry. Persistence of the solid-state structure in solution follows from the coupled reductions and, incisively, from the three equally intense, isotropically shifted *m*-H resonances (4: 9.32, 13.5, 17.3 ppm downfield of Me<sub>4</sub>Si<sup>10</sup>). The Mössbauer spectrum of solid  $(\text{Et}_4\text{N})_4$ (4) was fit to two doublets ( $\delta_1 = 0.31$ ,  $\Delta E_{\text{Q1}} = 0.96$  mm/s,  $\delta_2 = 0.33$ ,  $\Delta E_{\text{Q2}} = 1.38$  mm/s) whose isomer shifts demonstrate the  $[\text{MoFe}_3\text{S}_4]^{3+}$  oxidation level.<sup>3b,4c</sup> Thus, the formation of 4/5 from 1 is an *oxidatively induced core internal conversion*— $[\text{MoFe}_3(\mu_2\text{-S})_2(\mu_3\text{-S})_2\text{S}_2]^{2-} \rightarrow [\text{MoFe}_3(\mu_3\text{-S})_4(\text{S}_2)]^{1+}$ —in which there is net Fe and S oxidation and Mo reduction and major structural rearrangement. It is likely that S(1,2) of 1 are converted to  $\mu_2$ - $\eta^3$ -S<sub>2</sub><sup>2-</sup> in 4/5. The reaction between  $(\text{Et}_4\text{N})_2[\text{WFe}_3\text{S}_6(\text{CO})_6]$  (from 3 and  $(\text{Et}_4\text{N})_2\text{-}[\text{Cl}_2\text{FeWS}_4]^{19}$ ) and (*p*-ClC<sub>6</sub>H<sub>4</sub>S)<sub>2</sub> does not proceed analogously.  $[(p\text{-ClC}_6\text{H}_4\text{S})_2\text{FeWS}_4]^{2-}$  and  $[\text{Fe}_4\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_4]^{2-}$  are the only identifiable products, suggesting that the usual reducibility order Mo(VI) > W(VI) applies here and promotes core conversion. As a precursor to Fe-Mo-S clusters, 3 has also been employed in other reactions.<sup>20</sup>

Because all prior double cubanes were prepared by reactions of simple reagents,<sup>3b,6a,21</sup> a similar cluster assembly synthesis was

(15) Mayerle, J. J.; Denmark, S. E.; DePamphilis, B. V.; Ibers, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1975**, *97*, 1032.

(16)  $(\text{Et}_4\text{N})_4$ (5) crystallizes from DMF-ether in the monoclinic noncentrosymmetric space group *Cc* with *a* = 29.58 (7) Å, *b* = 24.21 (3) Å, *c* = 32.39 (4) Å,  $\beta = 113.4$  (1)°, *V* = 17 650 (10) Å<sup>3</sup>, and *Z* = 8. After equivalent observations were merged (*R*<sub>merge</sub> = 7.6%) the structure was refined (heavy atoms anisotropically, phenyl groups and cations treated isotropically as semirigid groups) to *R*(*R*<sub>w</sub>) = 12.1 (14.0)% with use of 4563 independent data ( $5^\circ \leq 2\theta \leq 41^\circ$ ,  $I \geq 2\sigma(I)$ ). Refinement in centrosymmetric *C2/c* was unsuccessful.

(17) Müller, A.; Jaegermann, W.; Enemark, J. H. *Coord. Chem. Rev.* **1982**, *46*, 245.

(18) (a)  $[\text{Mo}_4(\text{NO})_4\text{S}_3]^{4+}$ : Müller, A.; Eltzner, W.; Mohan, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 168. (b)  $[\text{W}_2\text{S}_8\text{OH}_3]^{1-}$ : Sècheresse, F.; Lefebvre, J.; Daran, J. C.; Jeannin, Y. *Inorg. Chim. Acta* **1981**, *54*, L175. (c)  $(\text{MeC}_5\text{H}_4)_2\text{Fe}_2\text{S}_4(\text{CO})$ : Giannotti, C.; Ducourant, A. M.; Chanaud, H.; Chiaroni, A.; Riche, C. *J. Organomet. Chem.* **1977**, *140*, 289. (d) Rakowski DuBois, M.; DuBois, D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064.

(19) Müller, A.; Jostes, R.; Tölle, H. G.; Trautwein, A.; Bill, E. *Inorg. Chim. Acta* **1980**, *46*, L121.

(20) Averill, B. A.; Bose, K. S.; Lamberty, P. E.; Kovacs, J.; Lilley, G. L.; Sinn, E. *Abstr. Pap.—Am. Chem. Soc.* **1984**, *188th*, INOR-8.

(21) (a) Wolff, T. E.; Berg, J. M.; Hodgson, K. O.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1979**, *101*, 4140. (b) Wolff, T. E.; Power, P. P.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4694.

sought for  $[\text{Mo}_2\text{Fe}_6\text{S}_{12}(\text{SR})_6]^{4-}$ . The solid isolated from the dropwise addition (30 min) of 23 mmol of  $\text{FeCl}_3$  in 100 mL of methanol to a mixture of  $\text{NaOMe}$  (69 mmol),  $p\text{-ClC}_6\text{H}_4\text{SH}$  (54 mmol), and  $(\text{NH}_4)_2\text{MoS}_4^{22}$  and  $\text{Na}_2\text{S}_2^{23}$  (both 7.7 mmol) in 300 mL of methanol, followed by 16 h of reaction and addition of  $\text{Et}_4\text{NCl}$  (15 mmol), was extracted with 1 L of acetonitrile. The residue from solvent removal was thoroughly washed with acetone and recrystallized from acetonitrile to afford a black solid identical in all respects with  $(\text{Et}_4\text{N})_4(\mathbf{4})$  prepared via **1**. Although the yield is moderate<sup>24</sup> (15–20%, nonoptimized), the procedure is simple and does not require the isolation of an intermediate.

Clusters **4** and **5** are new additions to the general class of  $\text{MoFe}_3\text{S}_4$  double cubanes and are accessible through intermediate **1** and by spontaneous self-assembly. Disulfide decarbonylation and core rearrangement may be a reaction of broader utility, in which case appropriate complexes of **3** would be precursors to new M–S–SR clusters. The conversion  $2\text{Fe}_2\text{S}_2(\text{CO})_6 \rightarrow [\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$  with  $\text{PhSSPh}/\text{PhS}^{-15}$  was the initial example of this type of reaction. Symmetrical  $\text{Mo}(\mu_2\text{-L})_3\text{Mo}$  bridges of double cubanes are not reactive under conditions that maintain subcluster structure.<sup>3a</sup> Disulfide bridges of  $[\text{Mo}_2\text{Fe}_6\text{S}_{12}(\text{SR})_6]^{4-}$  may be reactive, and the conceivable transformations  $\text{Mo}(\text{S}_2)_2\text{Mo} \xrightarrow{\text{L}''} \text{L}''\text{Mo}(\eta^2\text{-S}_2) \xrightarrow{2\text{H}} \text{L}''\text{Mo}(\text{SH})_2$  are under investigation. Addition across a *cis*-dithiol group incorporated in a redox-active cluster offers a potential new method for activation and reduction of unsaturated enzymic substrates.

**Acknowledgment.** This research was supported by NSF Grant CHE 81-06017. X-ray diffraction equipment was obtained by NIH Grant 1 S10 RR 02247. We thank Drs. R. B. Frankel and G. C. Papaefthymiou for the Mössbauer spectral measurements.

**Supplementary Material Available:** Tables of atom coordinates and thermal parameters for  $(\text{Et}_4\text{N})_2[\text{MoFe}_3\text{S}_4(\text{CO})_6]$  and  $(\text{Et}_4\text{N})_4[\text{Mo}_2\text{Fe}_6\text{S}_{12}(\text{S-}p\text{-C}_6\text{H}_4\text{Br})_6]$  (9 pages). Ordering information is given on any current masthead page.

(22) McDonald, J. W.; Friesen, G. D.; Rosenhein, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, 72, 205.

(23) Feher, F.; Berthold, H. J. *Z. Anorg. Allg. Chem.* **1953**, 273, 144.

(24)  $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_4]^{15}$  and another paramagnetic cluster salt (unidentified), both acetone soluble, were observed as byproducts by <sup>1</sup>H NMR.

## Ferro- and Antiferromagnetic Interaction between Two Diphenylcarbene Units Incorporated in the [2.2]Paracyclophane Skeleton

Akira Izuoka, Shigeru Murata, Tadashi Sugawara, and Hiizu Iwamura\*

Division of Applied Molecular Science  
Institute for Molecular Science, Okazaki 444, Japan

Received November 1, 1984

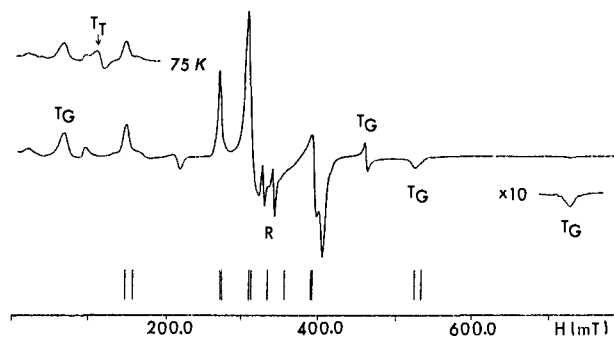
High-spin polycarbenes and polyradicals are considered to be a model for low-dimensional organic ferromagnets.<sup>1</sup> Most of the hitherto known examples, namely, *m*-phenylenebis(phenylmethylene),<sup>2</sup> its higher homologues,<sup>3</sup> 3,6-dimethyleneanthracenediyl-1,8-dioxyl,<sup>4</sup> etc., derive their high-spin multiplicity from the nonbonding molecular orbitals due to the symmetry of

(1) (a) Mataga, N. *Theor. Chim. Acta* **1968**, 10, 372. (b) Ovchinnikov, A. A. *Ibid.* **1978**, 47, 297. (c) Breslow, R. *Pure Appl. Chem.* **1982**, 54, 927. (d) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Ito, K. *J. Am. Chem. Soc.* **1984**, 106, 6449.

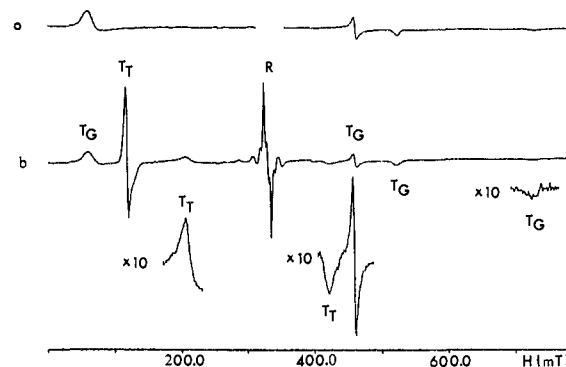
(2) (a) Itoh, K. *Chem. Phys. Lett.* **1967**, 1, 235. (b) *Pure Appl. Chem.* **1978**, 50, 1251. (c) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, 89, 5076.

(3) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1983**, 105, 3722.

(4) (a) Seeger, D. E.; Berson, J. A. *J. Am. Chem. Soc.* **1983**, 105, 5144. (b) *Ibid.* **1983**, 105, 5146.



**Figure 1.** ESR spectrum obtained after irradiation of **1a** in 2-methyltetrahydrofuran at 11 K. Lines indicate the calculated transition of the quintet state based on the third-order perturbation method.  $T_G$  is assigned to a monocarbene which presumably was formed by failure in removal of the second diazo group or by further reaction with solvent molecules at one of the carbenic centers (for  $T_T$ ; see text).

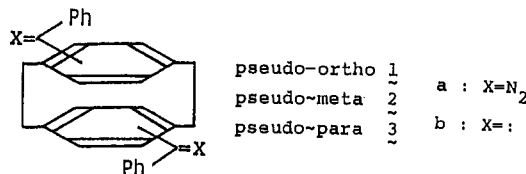


**Figure 2.** ESR spectra obtained (a) in the dark after generation of **2b** by irradiation of **2a** at 11 K and (b) when (a) was warmed to 60 K.  $T_G$  is assigned to a monocarbene as explained in Figure 1. R is a triplet biradical species formed adventitiously (for  $T_T$ ; see text).

the alternant hydrocarbon skeleton. We wish to report here a novel system in which spin multiplicity of dicarbenes is controlled by the overlapping modes of spin-distributed benzene rings incorporated in the rigid [2.2]paracyclophane framework.

According to McConnell's theory on intermolecular magnetic interaction,<sup>5</sup> exchange interaction between two aromatic radicals can be ferromagnetic when the product of spin densities at two interacting sites on different molecules is negative in sign, since the exchange integral is negative between organic radicals at a distance of the van der Waals contact. The spin distribution of diphenylcarbene is given by the ENDOR experiment.<sup>6</sup>

Among the three isomers of bis(phenylmethylene)[2.2]paracyclophanes (**1b–3b**) with different orientation of the two phe-



nylmethylene substituents, we note that only the pseudoortho and pseudopara isomers satisfy McConnell's condition. The sign of the spin density product at each interacting site between the two benzene rings is all negative in pseudoortho and pseudopara isomers and all positive in the pseudometa one.<sup>7</sup> Thus the different spin distribution is expected to result in the quintet ground state for **1b** and **3b** and in the singlet ground state for **2b**.

(5) McConnell, H. M. *J. Chem. Phys.* **1963**, 39, 1910.

(6) Hutchison, C. A., Jr.; Kohler, B. E. *J. Chem. Phys.* **1969**, 51, 3327.

(7) The spin distribution may be also caused by the through-bond mechanism via the strained ethano bridges. The direction of spin distribution, however, is the same as the through-space  $p_z$ - $p_z$  interaction. Therefore this mechanism is not explicitly mentioned in the above argument.