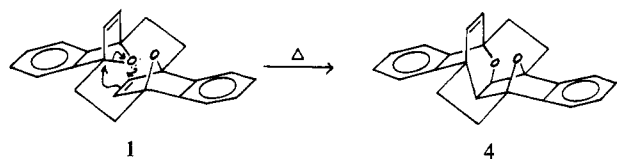


Scheme III



verifying the absence of symmetry. The structure that is most compatible with the above data is **4**.¹⁵

The formation of polycyclic diethers **3** and **4** must take place via two distinct pathways, both of which are probably facilitated by large nonbonded intracavity interactions and both of which give rise to products with reduced intramolecular interactions. Loss of acetylene from **1** by a retro-Diels-Alder reaction would substantially reduce the oxygen-oxygen interaction and give rise to intermediate **5** (see Scheme II). Further loss of acetylene (to give **2**) would compete unfavorably with an intramolecular Diels-Alder reaction in **5** because of the proximity of the dienic and dienophilic moieties and the reactivity of the isobenzofuranoid system toward Diels-Alder reactions. Internal trapping would further reduce the intracavity interaction in **5** and give the relatively unstrained diether **3**. The unusually low temperature at which the loss of acetylene takes place¹⁶ argues for the substantial amount of strain released upon forming **5**, in which one of the oxygen atoms forms part of the planar isobenzofuranoid system.

Attempted trapping of **5** with external dienophiles produces **3** and **4**.¹⁷ Though this result does not initially support the intermediacy of **5** (and perhaps suggests a concerted pathway for **1** → **3**¹⁸), there are at least three reasons why external dienophiles would not compete favorably for the isobenzofuranoid moiety. First, the diene and dienophilic portions in **5** are geometrically disposed to give **3** by a favored intramolecular Diels-Alder reaction.¹⁹ Second, the formation of **3** would be essentially irreversible since there is comparatively little strain associated with it. Third, addition of an external dienophile would be a more difficult process because it would reinstate the original intracavity nonbonded interactions of the oxygen atoms, as in **1**.

Both **3** and **4** are stable under the reaction conditions. Diether **4** is therefore not the precursor of **3**, and its formation must take place via a pathway distinct from **3**. In this instance, the close contact between the oxygen atoms and the proximate olefinic units allows for the release of strain by the migration of one of the

oxygen atoms to an olefinic carbon (see Scheme III), generating the dissymmetry in **4** and reducing the intracavity interactions originally present in **1**. Since **4** is the major product of the thermolysis of **1**, release of strain by this pathway is quite important despite the unusual nature of the reaction between ether and olefin groups.

Whether or not molecular oxygen can be extruded from **1**, or a derivative thereof, is of interest. Further investigations concerning the unusual migration of the oxygen atom in **1**, as well as the chemistry caused by the severity of nonbonded interactions in similar systems, are currently in progress.

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New EXAFS Models for the Iron Sites of the Iron Molybdenum Cofactor of Nitrogenase: The $[(p\text{-CH}_3\text{C}_6\text{H}_4\text{S})_2\text{FeS}_2\text{FeS}_2\text{MoS}_2]^{3-}$ Trianion and the $[(\text{C}_6\text{H}_5\text{O})_2\text{FeS}_2\text{MoS}_2]^{2-}$ Dianion

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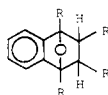
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Received February 1, 1982

The FeMo cofactor¹ from the MoFe protein of the enzyme nitrogenase is known to contain a novel Mo-Fe-S cluster.^{2,3} Two types of related structural unit are now well characterized: those containing the MoFe₃S₄ cubane core,^{4,5} and those containing the "linear" MoS₂Fe core.⁶⁻¹⁰ Several of these synthetic Mo-Fe-S

(15) A crystal structure determination is being carried out on the bromide to confirm this assignment.

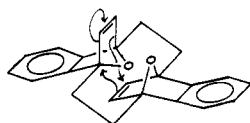
(16) To our knowledge the loss of acetylene to give isobenzofuranoid systems is unknown. Normally, ethylenic units are lost from dihydroprecursors such as **i** to give isobenzofurans but this loss generally takes place at low pressure and at temperatures greater than 600 °C. See: Wiersum, U. E.; Mijs, W. J. *J. Chem. Soc., Chem. Commun.* **1972**, 347-348.



i

(17) Compound **1** was heated with neat dimethylacetylenedicarboxylate or in xylene with a 2-fold excess of the dienophile.

(18) Because of the geometry of **1**, a concerted loss of acetylene with concomitant cyclization to form **3** can be envisioned (see **ii**).



ii

(19) For similar intramolecular Diels-Alder reactions, where the diene and dienophile are in comparable orientations, see: (a) Cram, D. J.; Montgomery, C. S.; Knox, G. R. *J. Am. Chem. Soc.* **1966**, *88*, 515-525. (b) Wasserman, H. H.; Keehn, P. M. *Ibid.* **1966**, *88*, 4522. (c) Wasserman, H. H.; Keehn, P. M. *Tetrahedron Lett.* **1969**, 3227.

(1) V. K. Shah and W. J. Brill, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 3249 (1977).

(2) (a) J. Rawlings, V. K. Shah, J. R. Chisnell, W. J. Brill, R. Zimmerman, E. Münck, and W. H. Orme-Johnson, *J. Biol. Chem.*, **253**, 1001 (1978); (b) B. H. Huynh, E. Münck, and W. H. Orme-Johnson, *Biochim. Biophys. Acta*, **527**, 192 (1979); (c) B. K. Burgess, E. I. Stiefel, and W. E. Newton, *J. Biol. Chem.*, **255**, 353 (1981); (d) V. K. Shah and W. J. Brill, *Proc. Natl. Acad. Sci. U.S.A.*, **78**, 3438 (1981).

(3) (a) S. P. Cramer, K. O. Hodgson, W. O. Gillum, and L. E. Mortenson, *J. Am. Chem. Soc.*, **100**, 3398 (1978); (b) S. P. Cramer, W. O. Gillum, K. O. Hodgson, L. E. Mortenson, E. I. Stiefel, J. R. Chisnell, W. J. Brill, and V. K. Shah, *ibid.* **100**, 3814 (1978).

(4) (a) T. E. Wolff, J. M. Berg, C. Warrick, K. O. Hodgson, R. H. Holm, and R. B. Frankel, *J. Am. Chem. Soc.*, **100**, 4630 (1978); (b) T. E. Wolff, J. M. Berg, K. O. Hodgson, R. B. Frankel, and R. H. Holm, *ibid.*, **101**, 4140 (1979); (c) T. E. Wolff, J. M. Berg, P. P. Power, K. O. Hodgson, R. H. Holm, and R. B. Frankel, *ibid.*, **101**, 5454 (1979); (d) T. E. Wolff, P. P. Power, R. B. Frankel, and R. H. Holm, *ibid.*, **102**, 4694 (1980); (e) T. E. Wolff, J. M. Berg, P. P. Power, K. O. Hodgson, and R. H. Holm, *Inorg. Chem.*, **19**, 430 (1980); (f) W. H. Armstrong and R. H. Holm, *J. Am. Chem. Soc.*, **103**, 6246 (1981); (g) T. E. Wolff, J. M. Berg, and R. H. Holm, *Inorg. Chem.*, **20**, 174 (1981); (h) W. H. Armstrong, P. K. Mascharak, and R. H. Holm, *ibid.*, **21**, 1699 (1982).

(5) (a) G. Christou, C. D. Garner, F. E. Mabbs, and T. J. King, *J. Chem. Soc., Chem. Commun.*, 740 (1978); (b) S. R. Acott, G. Christou, C. D. Garner, T. J. King, F. E. Mabbs, and R. M. Miller, *Inorg. Chim. Acta*, **35**, L337 (1979); (c) G. Christou, C. D. Garner, R. M. Miller, C. E. Johnson, and J. D. Rush, *J. Chem. Soc., Dalton Trans.*, 2363 (1980); (d) G. Christou and C. D. Garner, *ibid.*, 2354 (1980); (e) G. Christou, D. Collison, C. D. Garner, F. E. Mabbs, and V. Petrouleas, *Inorg. Nucl. Chem. Lett.*, **17**, 137 (1981).

(6) (a) R. H. Tieckelmann, H. C. Silvis, T. A. Kent, B. H. Huynh, J. V. Waszczak, B. K. Teo, and B. A. Averill, *J. Am. Chem. Soc.*, **102**, 5550 (1980); (b) H. C. Silvis and B. A. Averill, *Inorg. Chim. Acta*, **54**, L57 (1981); (c) R. H. Tieckelmann and B. A. Averill, *Inorg. Chim. Acta*, **46**, L35 (1980).

Table I. Structural Parameters (Bond Lengths (Å) and Angles (deg)) for the $[\text{S}_2\text{FeS}_2\text{FeS}_2\text{MoS}_2]^-$ Core of the $[(p\text{-CH}_3\text{C}_6\text{H}_4\text{S})_2\text{FeS}_2\text{FeS}_2\text{MoS}_2]^{3-}$ (1) Anion and for the $[\text{O}_2\text{FeS}_2\text{MoS}_2]^{2-}$ Core of the $[(\text{C}_6\text{H}_5\text{O})_2\text{FeS}_2\text{MoS}_2]^{2-}$ (2) Anion

(a) 1			
Fe1-Mo	2.778 (2)	Fe1-Fe2	2.691 (3)
Fe1-S3	2.235 (4)	Fe2-S1	2.315 (4)
Fe1-S4	2.228 (4)	Fe2-S2	2.325 (4)
Fe1-S5	2.275 (4)	Fe2-S3	2.193 (4)
Fe1-S6	2.280 (4)	Fe2-S4	2.188 (4)
Mo-S5	2.248 (4)	Mo-S7	2.172 (4)
Mo-S6	2.240 (4)	Mo-S8	2.153 (4)
Mo-Fe1-Fe2	176.29 (9)		
Mo-S5-Fe1	75.77 (13)	Fe1-S3-Fe2	74.86 (13)
Mo-S6-Fe1	75.83 (13)	Fe1-S4-Fe2	75.11 (12)
S3-Fe1-S4	103.58 (14)	S1-Fe2-S2	109.21 (15)
S5-Fe1-S6	103.08 (15)	S7-Mo-S8	111.14 (16)
(b) 2			
Fe-Mo	2.797 (4)	Mo-S1	2.279 (6)
Fe-S1	2.273 (7)	Mo-S2	2.266 (7)
Fe-S2	2.308 (8)	Mo-S3	2.144 (11)
Fe-O5	1.861 (19)	Mo-S4	2.107 (12)
Fe-O6	1.932 (19)		
Fe-S1-Mo	75.81 (22)	S3-Mo-S4	113.70 (31)
Fe-S2-Mo	75.38 (22)	O5-Fe-O6	102.43 (70)

clusters have proven to be of particular importance as model systems in the interpretation of both the Fe K-edge EXAFS (extended X-ray absorption fine structure) data of the FeMo cofactor¹¹ and the Mo K-edge EXAFS of the MoFe protein³ of nitrogenase. We report herein single-crystal X-ray diffraction structure determinations and Fe EXAFS spectra of a linear trinuclear cluster anion, $[(p\text{-CH}_3\text{C}_6\text{H}_4\text{S})_2\text{FeS}_2\text{FeS}_2\text{MoS}_2]^{3-}$ (1),^{6c} and a binuclear cluster anion, $[(\text{C}_6\text{H}_5\text{O})_2\text{FeS}_2\text{MoS}_2]^{2-}$ (2).^{6b} We note that **1** is the first structurally characterized Mo-Fe-S cluster to contain iron in *two distinct sites*¹² with localized oxidation states, whereas **2** is the first structurally characterized Mo-Fe-S cluster with terminal oxygen ligation to iron.^{13,14}

The structures of $(\text{Et}_4\text{N})_3[(p\text{-CH}_3\text{C}_6\text{H}_4\text{S})_2\text{FeS}_2\text{FeS}_2\text{MoS}_2]$ (3) and $(\text{Et}_4\text{N})_2[(\text{C}_6\text{H}_5\text{O})_2\text{FeS}_2\text{MoS}_2]$ (4) were solved by conventional Patterson and Fourier techniques. In **3**, two out of three Et_4N^+ cations are disordered. Refinement by full-matrix least-squares methods gave rise to a conventional *R* value of 8.10%, with anisotropic isotropic thermal parameters for the trianion and

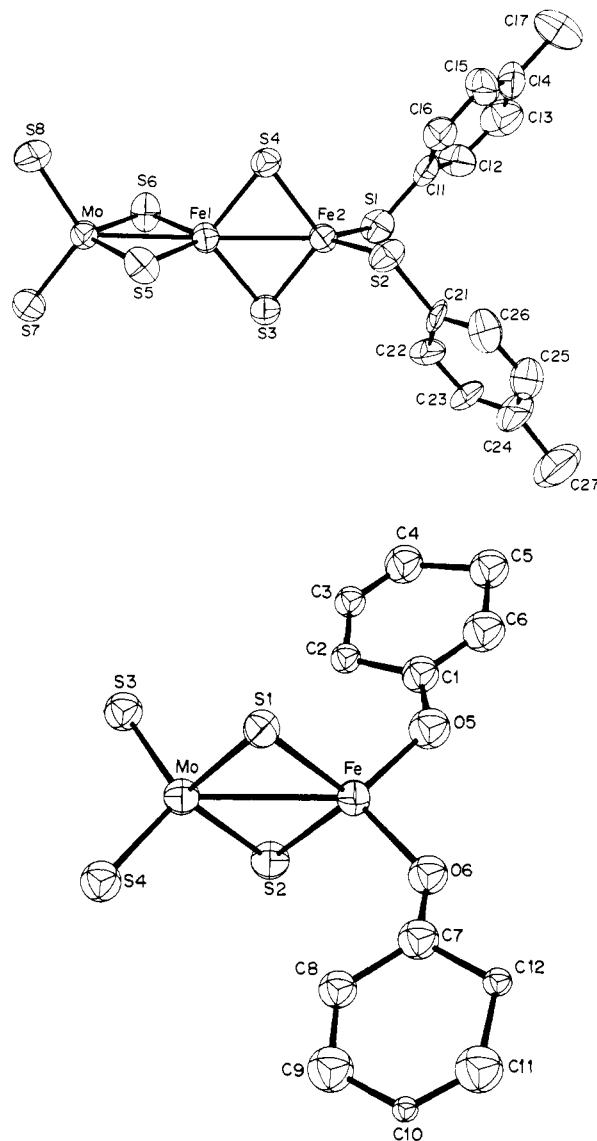


Figure 1. (a, top) Structure of the $[(p\text{-CH}_3\text{C}_6\text{H}_4\text{S})_2\text{FeS}_2\text{FeS}_2\text{MoS}_2]^{3-}$ trianion (**1**) as the Et_4N^+ salt. The atom labeling scheme and 50% probability ellipsoids are shown. (b, bottom) Structure of the $[(\text{C}_6\text{H}_5\text{O})_2\text{FeS}_2\text{MoS}_2]^{2-}$ dianion (**2**) as the Et_4N^+ salt; shown are the 50% probability ellipsoids and the atom labeling scheme.

ordered cation and isotropic thermal parameters for all other atoms.¹⁵ Least-squares refinement of **4** resulted in an *R* value of 14.35%, with anisotropic thermal parameters for Mo, Fe, S1, and S2 and isotropic thermal parameters for all other atoms.¹⁶ The pseudo mirror plane at $y = 1/8$ relating the two halves of the molecule (with Mo, Fe, S1, and S2 residing on the plane) causes severe parameter correlation, thereby preventing further anisotropic refinement. Somewhat specialized refinement procedures must be used to fully refine the structure (in progress).

The structure of **1** is shown in Figure 1a, and relevant structural parameters are given in Table Ia. The trinuclear cluster anion

(7) (a) D. Coucouvanis, E. D. Simhon, D. Swenson, and N. C. Baenziger, *J. Chem. Soc., Chem. Commun.*, 361 (1979); (b) D. Coucouvanis, E. D. Simhon, P. Stremple, and N. C. Baenziger, *Inorg. Chim. Acta.*, **53**, L135 (1981); (c) D. Coucouvanis, N. C. Baenziger, E. D. Simhon, P. Stremple, D. Swenson, A. Kostikas, A. Simopoulos, V. Petrouleas, and V. Papaefthymiou, *J. Am. Chem. Soc.*, **102**, 1730 (1980); (d) D. Coucouvanis, N. C. Baenziger, E. D. Simhon, P. Stremple, D. Swenson, A. Simopoulos, A. Kostikas, V. Petrouleas, and V. Papaefthymiou, *ibid.*, **102**, 1732 (1980); (e) D. Coucouvanis, E. D. Simhon, and N. C. Baenziger, *ibid.*, **102**, 6644 (1980).

(8) (a) A. Müller, M. G. Tülle, and H. Bögge, *Z. Anorg. Allg. Chem.*, **471**, 115 (1980); (b) A. Müller, R. Jostes, M. G. Tülle, A. Trautwein, and E. Bill, *Inorg. Chim. Acta*, **46**, L121 (1980); (c) A. Müller, S. Sarkar, A. M. Domröse, and R. Filgueira, *Z. Naturforsch. Sect. B*, **35B**, 1592 (1980).

(9) J. W. McDonald, G. D. Friesen, and W. E. Newton, *Inorg. Chim. Acta*, **46**, L79 (1980).

(10) P. L. Dahlstrom, S. Kumar, and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 411 (1981).

(11) M. R. Antonio, B. K. Teo, W. H. Orme-Johnson, M. J. Nelson, S. E. Groh, P. A. Lindahl, S. M. Kauzlarich, and B. A. Averill, *J. Am. Chem. Soc.*, **104**, 4703 (1982).

(12) Mössbauer studies^{2b} of the FeMo cofactor also suggest the presence of multiple iron sites.

(13) Recent studies have suggested that oxygen ligands such as methylformamide or citrate may be coordinated to the FeMo cofactor of nitrogenase as isolated; see: (a) B. E. Smith in "Molybdenum Chemistry of Biological Significance", W. E. Newton and S. Otsuka, Eds., Plenum Press, New York, 1980, p 179; (b) W. E. Newton, B. K. Burgess, and E. I. Stiefel, in "Molybdenum Chemistry of Biological Significance", W. E. Newton and S. Otsuka, Eds., Plenum Press, New York, 1980, p 191.

(14) The iron atom in **2** is tetrahedrally coordinated by two O and two S atoms with a distant Mo neighbor. A cluster containing a single MoFe_3S_4 core to which a tris(catecholate)iron(III) complex is attached to the Mo atom via three bridging catecholate oxygens is known.^{4b} This structure shows two distinct iron sites, with three iron atoms having S, Fe, and Mo as nearest neighbors and the fourth iron atom coordinated by six oxygen atoms.

(15) Crystal and refinement data for **3**: $a = 9.072$ (2) Å, $b = 15.364$ (4) Å, $c = 18.591$ (8) Å, $\alpha = 84.90$ (3)°, $\beta = 89.54$ (2)°, $\gamma = 75.43$ (0)°, $V = 2497.7$ Å³; space group *P1*; $Z = 2$; crystal dimensions: $0.35 \times 0.15 \times 0.25$ mm³; $2\theta_{\text{max}} = 45^\circ$ (Mo $K\alpha$ radiation); 6508 unique reflections were collected at the Molecular Structure Corp.; 4568 observed reflections with $F^2 > 3\sigma(F^2)$ were used.

(16) Crystal and refinement data for **4**: $a = 9.587$ (3) Å, $b = 17.182$ (8) Å, $c = 22.937$ (12) Å, $\beta = 94.23$ (3)°; $V = 3768.24$ Å³; space group *P2₁/c*; $Z = 4$; crystal dimensions: $1.0 \times 0.4 \times 0.1$ mm³; $2\theta_{\text{max}} = 50^\circ$ (Mo $K\alpha$ radiation); 6694 unique reflections were collected at Michigan State University; 4064 observed reflections with $F^2 > 3\sigma(F^2)$ were used. The crystal contains one molecule of acetonitrile per formula unit (verified by NMR and IR spectra); the solvent molecule is disordered.

Table II. Best-Fit (Based on Theoretical Functions) Least-Squares Refined Interatomic Distances (in Å) and Debye-Waller Factors (in Å) for the Iron K-Edge Fluorescence EXAFS of $(\text{Et}_4\text{N})_3[(p\text{-CH}_3\text{C}_6\text{H}_4\text{S})_2\text{FeS}_2\text{FeS}_2\text{MoS}_2]$ (**3**) and $(\text{Et}_4\text{N})_2[(\text{C}_6\text{H}_5\text{O})_2\text{FeS}_2\text{MoS}_2]$ (**4**) and Their Comparisons with Crystallographic Results^a

term	3		4	
	best fit	crystallography	best fit	crystallography
Fe-S	<i>r</i> 2.255 (21)	2.256 (11) ^b	2.361 (28)	2.291 (11) ^b
	σ 0.046 (33)		0.025 (33)	
Fe-Fe	<i>r</i> 2.762 (22)	2.691 (3)		
	σ 0.079 (13)			
Fe-Mo	<i>r</i> 2.804 (34)	2.778 (2)	2.803 (50)	2.797 (4)
	σ 0.113 (14)		0.043 (42)	
Fe-O	<i>r</i>		1.847 (47)	1.897 (27) ^b
	σ		0.000 (23)	

^a Estimated standard deviations are in parentheses. ^b Average values.

contains an essentially linear array of three approximately tetrahedral MS_4 units ($\text{M} = \text{Fe}, \text{Fe}, \text{Mo}$) sharing common edges. The observed structural parameters support the mixed-valence description of the cluster originally proposed,^{6c} in which formal oxidation states of 6+, 2+, and 3+ were assigned to Mo, Fe(1), and Fe(2), respectively. The average bridging Fe-S distance for Fe(2) is ca. 0.04 Å shorter than the average Fe(1) distance to the same two sulfur atoms, consistent with a higher formal oxidation state for Fe(2).¹⁷ Moreover, the dimensions of the Fe(2)- S_4 unit are virtually identical with those of the Fe(III)- S_4 units in the $[\text{Fe}_2\text{S}_2(\text{SC}_6\text{H}_4\text{-}p\text{-CH}_3)_4]^{2-}$ ion,¹⁸ while the MoS_2 Fe unit is very similar to that in the $[(\text{C}_6\text{H}_5\text{S})_2\text{FeS}_2\text{MoS}_2]^{2-}$ ion (**5**).^{6a} These results indicate that **1** is the first structurally characterized example of oxidation state localization¹⁹ in a mixed-valence Fe-S complex.

The structure of **2** is shown in Figure 1b, and relevant structural parameters are given in Table Ib. Replacement of the two terminal mercaptides in **5**^{6a} by two phenoxides in **2** results in an expansion of the MoS_2Fe core, as manifested by increases in the Fe-S (bridging), Fe-Mo, and Mo-S (bridging) distances of ca. 0.03, 0.04, and 0.02 Å. This suggests substantially greater ferrous character for the iron in **2**, consistent with ⁵⁷Fe Mössbauer results,^{6b} and correspondingly less transfer of electron density to molybdenum. The average Fe-O bond distance of 1.897 (27) Å seems unusually short compared with typical Fe(III)-O distances of 1.88–1.92 Å,^{20,21} suggesting a relatively covalent Fe-O bond in **2**, consistent with preliminary NMR and electrochemical studies.^{6b}

In order to assist in the analysis of the Fe EXAFS of the FeMo cofactor, iron K-edge EXAFS (fluorescence) of frozen solutions of **3** and **4** in acetonitrile were obtained at ~160 K at SSRL.²² Fourier transform of the Fe EXAFS of **3** (Figure 2a) shows Fe-S and Fe-Fe/Mo peaks at 1.83 and 2.35 Å (before phase-shift correction), respectively. Similarly, the Fourier transform of the iron EXAFS of **4** (Figure 2b) shows Fe-O, Fe-S, and Fe-Mo peaks at 1.40, 1.88, and 2.55 Å (uncorrected), respectively. The backtransformed filtered $k^3\chi(k)$ data of **3** were resolved into two components, $k^3\chi_S(k)$ for Fe-S bonds and $k^3\chi_M(k)$ for Fe-M ($\text{M} = \text{Fe}, \text{Mo}$) interactions, via a "difference Fourier" technique and fitted with Fe-S (one term) and Fe-(Fe/Mo) (two terms) contributions,²³ respectively (supplementary material, Figure C). The

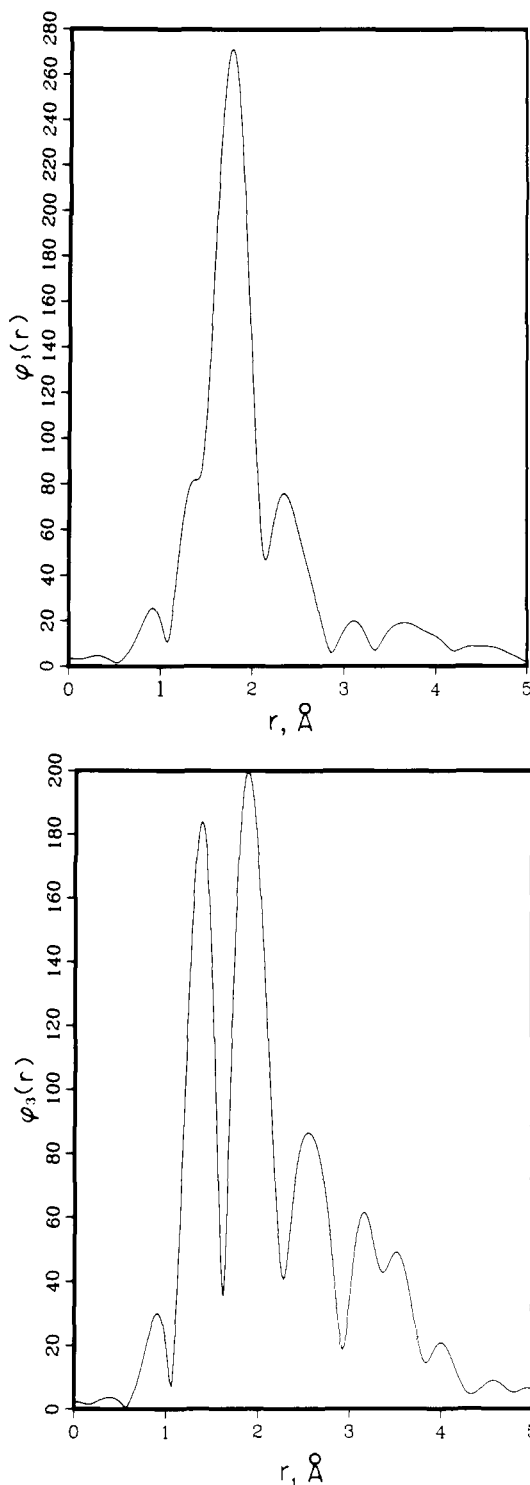


Figure 2. Fourier transforms of the iron K-edge fluorescence EXAFS $k^3\chi(k)$ vs. k for: (a, top) $(\text{Et}_4\text{N})_3[(p\text{-CH}_3\text{C}_6\text{H}_4\text{S})_2\text{FeS}_2\text{FeS}_2\text{MoS}_2]$ (**3**); (b, bottom) $(\text{Et}_4\text{N})_2[(\text{C}_6\text{H}_5\text{O})_2\text{FeS}_2\text{MoS}_2]$ (**4**).

filtered $k^3\chi(k)$ data for **4** were fitted with a three-term model containing Fe-O, Fe-S, and Fe-Mo distances²³ (supplementary material, Figure D). The best-fit results (based on theoretical functions only) are tabulated in Table II. An accuracy of better than 1% and 3% in metal-ligand and metal-metal distances is

(17) (a) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25B**, 925 (1969); (b) R. D. Shannon, *Acta Crystallogr., Sect. A*, **32A**, 751 (1976).

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

(19) P. K. Mascharak, G. C. Papaefthymiou, R. B. Frankel, and R. H. Holm, *J. Am. Chem. Soc.*, **103**, 6110 (1981).

(20) M. Gerloch and F. E. Mabbs, *J. Chem. Soc. A*, 1598 (1967).

(21) (a) P. Coggon, A. T. McPhail, F. E. Mabbs, and V. N. McLachlan, *J. Chem. Soc. A*, 1014 (1971); (b) M. Gerloch, E. D. McKenzie, and A. D. C. Towl, *ibid.*, 2850 (1969).

(22) Details of the data collection at Stanford Synchrotron Radiation Laboratory are given in the supplementary material, together with the raw X-ray absorption data (Figures A and B) and the filtered and best fit spectra (Figures C and D) for **3** and **4**.

(23) For details of the data analysis, see: (a) B. K. Teo, R. G. Shulman, G. R. Brown, and A. E. Meixner, *J. Am. Chem. Soc.*, **101**, 5624 (1979); (b) B. K. Teo, *Acc. Chem. Res.*, **13**, 412 (1980); (c) B. K. Teo, in "EXAFS Spectroscopy: Techniques and Applications", B. K. Teo and D. C. Joy, Eds., Plenum Press, New York, 1981, pp 13–58; (d) P. A. Lee, P. H. Citrin, P. Eisenberger, and B. M. Kincaid, *Rev. Mod. Phys.*, **53**, 769 (1981); (e) B. K. Teo, M. R. Antonio, B. A. Averill, submitted for publication.

obtained for these multicomponent fits based on theoretical functions alone (i.e., these results are model independent). As reported elsewhere,¹¹ the Fe EXAFS of **3** and **4** together approximate all the major features observed in, and hence are good models for, the Fe EXAFS of the FeMo cofactor.

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Registry No. **1**, 83214-35-1; **2**, 83214-36-2; **3**, 83214-37-3; **4**, 83214-38-4; nitrogenase iron molybdenum cofactor, 72994-52-6.

Supplementary Material Available: Positional and thermal parameters for **3** and **4**, EXAFS data collection and data reduction methodology and Figures A-D showing the raw X-ray absorption data (F/I_0 vs. E , eV) and the Fourier filtered EXAFS, $k^3\chi(k)$ vs. k , spectra with the sum of the fitted waves (10 pages). Ordering information is given on any current masthead page.

Total Synthesis of Gibberellic Acid. A Simple Synthesis of a Key Intermediate

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The total synthesis of gibberellic acid (GA₃, **1**, Scheme I) was first achieved via the key intermediate **2** by a route that was unambiguous with regard to structure and stereochemistry.^{1,2} In addition to the original synthesis of **2** from the Diels-Alder adduct **3**, a second process was developed via the tricyclic ketone **4**.³ Both routes to **2** are fairly lengthy, and although the individual steps are efficient, a simpler and more direct synthesis was clearly desirable. In this note we describe a novel 9-step synthesis of **4** that allows access to **2** in just 16 steps (vs. 25 steps in the original route).

Reaction of lithium cyclopentadienide in ether with 0.83 equiv of 2,3-dibromopropene at 23 °C for 48 h resulted in a mixture of monoalkylated cyclopentadienes, which was equilibrated in situ by stirring with 1,5-diazabicyclo [5.4.0]undec-5-ene (DBU) (0.02 equiv) at 23 °C for 2 h to a mixture of 2- and 1-(2-bromoallyl)cyclopentadienes (ratio ca. 2:1), readily isolated by distillation (bp 26-28 °C (0.08 torr)) in 87% yield.⁴ This mixture was treated with methyl 2-acetylacrylate (1.35 equiv)⁵ and boron trifluoride

Scheme I

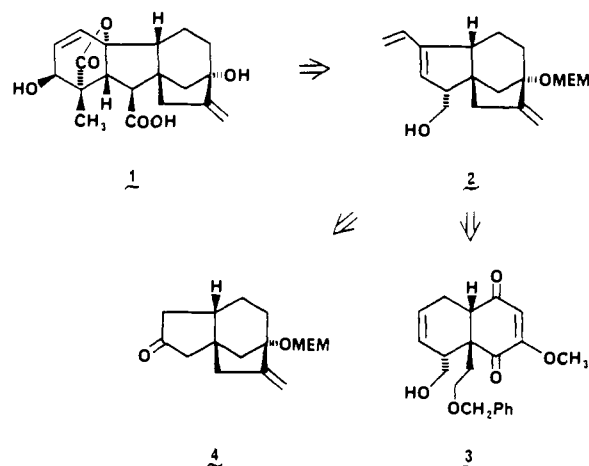
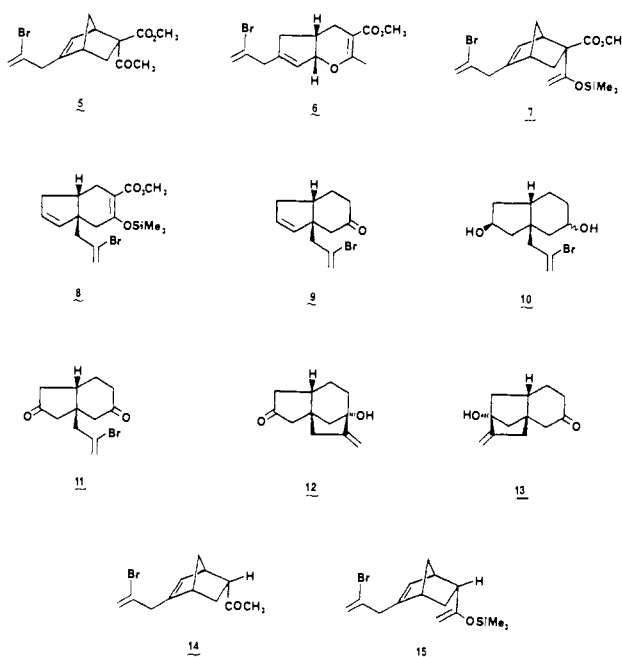


Chart I



etherate (1.1 equiv in methylene chloride at -78 °C for 30 min to afford after chromatography the desired Diels-Alder adduct, *endo*-2-acetyl-*exo*-2-carbomethoxy-5-(2-bromoallyl)-5-norbornene (**5**, Chart I) in 53% yield. ¹H NMR analysis indicated a >30:1 ratio of *endo*/*exo*-acetyl substituents in accord with expectations that Lewis acid catalysis would result not only in high position-selectivity but also in enhancement of the propensity of acetyl to adopt the *endo* orientation.^{6a} The only other compound that could be isolated from the Diels-Alder reaction was the bicyclic dihydropyran **6** (20% yield), the product of an unusual Diels-Alder reaction of 1-(2-bromoallyl)cyclopentadiene as a dienophile component with methyl 2-acetylacrylate as a diene component.^{6b}

Treatment of adduct **5** with trimethylsilyl triflate⁷ (2.0 equiv) and triethylamine (4.0 equiv) in methylene chloride at 23 °C for

(1) Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S.; Siret, P.; Keck, G. E.; Gras J.-L. *J. Am. Chem. Soc.* **1978**, *100*, 8031.

(2) Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S.; Keck, G. E.; Gopalan, B.; Larsen, S. D.; Siret, P.; Gras, J.-L. *J. Am. Chem. Soc.* **1978**, *100*, 8034.

(3) Corey, E. J.; Smith, J. G. *J. Am. Chem. Soc.* **1979**, *101*, 1038.

(4) Supplementary material for this publication contains proton magnetic resonance, infrared, and mass spectral data, as well as detailed experimental procedures. The supplementary material is reproduced from the Ph.D. dissertation of John E. Munroe, Harvard University, 1982. All reactions involving air-sensitive reagents or products were performed under an inert atmosphere (argon).

(5) We found the method of preparation of methyl 2-acetylacrylate reported previously [Masuno, M.; Asahara, T. Japanese Patent 2219 (1953); *Chem. Abstr.* **1955**, *49*, 1780g] to be unsatisfactory. An effective preparation of this reactive dienophile was accomplished by the following sequence: (1) reaction of methyl α -methylacetoacetate with phenylsulfenyl chloride (methylene chloride, 0 °C, 100% yield); (2) oxidation of sulfide to sulfoxide (*m*-chloroperbenzoic acid, methylene chloride, -40 °C, 100% yield); (3) phenylsulfenic acid elimination (distillation in vacuo from sulfolane at 60 °C with collection of methyl 2-acetylacrylate in a receiver at -78 °C, 47% yield).

(6) (a) Harrison, I. T.; Grayshan, R.; Williams, T.; Semenovski, A.; Fried, J. H. *Tetrahedron Lett.* **1972**, 5151. (b) Snider, B. B. *Ibid.* **1980**, *21*, 1133.

(7) Review: Simchen, G.; et al. *Synthesis* **1982**, 1.