

**Acknowledgment.** Support from the National Science Foundation is gratefully acknowledged. We thank Seth R. Marder for helpful discussions and Dr. Charles F. Campana (Nicolet Corp.) for help with the X-ray diffraction.

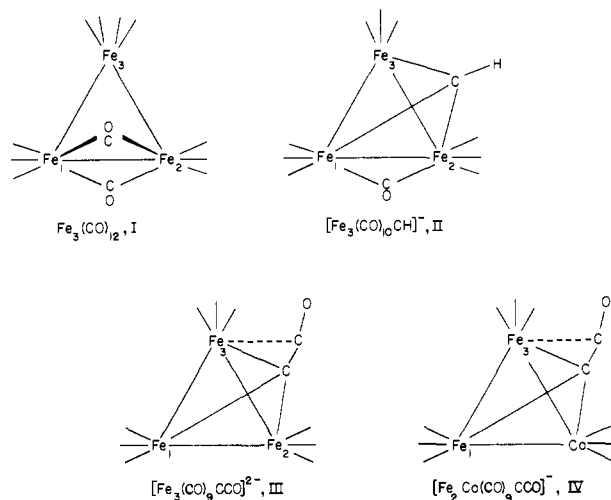
**Supplementary Material Available:** Elemental analysis and spectral characterization of 4, 5, 7, and 9 and tables of crystal structure data for 3 (21 pages). Ordering information is given on any current masthead page.

### Mössbauer Effect Study of $\text{Fe}_3(\text{CO})_{12}$ and the Reduced Carbide Clusters $(\text{PPN})[\text{Fe}_3(\text{CO})_{10}\text{CH}]$ , $(\text{PPN})_2[\text{Fe}_3(\text{CO})_9\text{CCO}]$ , and $(\text{PPN})[\text{Fe}_2\text{Co}(\text{CO})_9\text{CCO}]$

Christopher G. Benson, Gary J. Long,\* J. W. Kolis, and D. F. Shriver

*Departments of Chemistry  
University of Missouri-Rolla  
Rolla, Missouri 65401  
Northwestern University  
Evanston, Illinois 60201  
Received February 4, 1985*

Metal carbide cluster compounds are expected to play a key role in understanding the cleavage of carbon monoxide on a metal surface. With the exception of the isoelectronic four-iron butterfly clusters<sup>1,2</sup>  $\text{Fe}_4(\text{CO})_{13}\text{C}$  and  $[\text{Fe}_4(\text{CO})_{12}\text{C}]^{2-}$  no metal carbide clusters with four or more metal atoms have shown reactivity at the carbide.<sup>3,4</sup> In contrast the three-iron cluster  $[\text{Fe}_3(\text{CO})_9\text{CCO}]^{2-}$  containing the ketenylidene ligand, CCO, has recently been shown to exhibit carbide reactivity and may indicate a role for ketenylidenes in the reduction of carbon monoxide at a surface. The importance of these clusters and the electronic properties at the metal and ligand sites has led us to undertake a detailed Mössbauer effect study of  $\text{Fe}_3(\text{CO})_{12}$  (I) and the closely related reduced carbide clusters  $(\text{PPN})[\text{Fe}_3(\text{CO})_{10}\text{CH}]$  (II),  $(\text{PPN})_2[\text{Fe}_3(\text{CO})_9\text{CCO}]$  (III), and  $(\text{PPN})[\text{Fe}_2\text{Co}(\text{CO})_9\text{CCO}]$  (IV). Mössbauer spectroscopy proved very useful<sup>5</sup> in the structural elucidation of  $\text{Fe}_3(\text{CO})_{12}$ , where it indicates the presence of two distinct iron sites in a two to one ratio,<sup>6,7</sup> and some related heteronuclear trimers.<sup>8-10</sup> Although the X-ray structures of  $\text{Fe}_3(\text{CO})_{12}$  and of both reduced compounds are known,<sup>11,12</sup> few details of the internal



electronic environment are known. The Mössbauer effect isomer shifts have proven useful in elucidating the localization of the electronic density on the iron sites and in understanding the activation of the ketenylidene carbon toward nucleophilic attack.

$\text{Fe}_3(\text{CO})_{12}$  was obtained from Alpha Inorganics and recrystallized from 50:50 acetone water. The reduced clusters were the same samples as studied earlier.<sup>12</sup> Mössbauer effect spectra were obtained on a conventional Ranger Scientific constant acceleration spectrometer which utilized a room temperature rhodium matrix cobalt-57 source. The spectra were fit to Lorentzian line shapes by using standard least squares computer minimization techniques<sup>13</sup> and standard error propagation techniques. The resulting Mössbauer spectra which were fit to symmetric doublets of either independent or constrained areas are illustrated in Figure 1. The resulting Mössbauer spectral parameters are listed in Table I where  $\sum\delta$  is the sum of the isomer shifts for the three sites and  $\Delta\delta$  is the change in isomer shift for each iron site upon reduction from  $\text{Fe}_3(\text{CO})_{12}$  to the carbides.

The results obtained for  $\text{Fe}_3(\text{CO})_{12}$  are typical of those found in earlier investigations<sup>6,7</sup> and indicate at 78 K the expected two structurally distinct iron sites<sup>11</sup> in the approximate ratio of two to one where the unique iron site Fe(3) has a virtually symmetric site symmetry and shows little or no quadrupole splitting at 78 K.<sup>14,15</sup> The isomer shift results obtained for  $\text{Fe}_3(\text{CO})_{12}$  are important because they form the basis of our understanding of the spectra obtained upon reduction. The values of  $\sum\delta$  which decrease in going from the neutral to the monocation and dication clusters indicate the expected increase in the s electronic density at the nucleus upon reduction. Perhaps more useful is  $\Delta\delta$  the change in  $\delta$  for each site upon reduction. Upon reduction the value of  $\Delta\delta$  is much larger for the Fe(1,2) sites than for the Fe(3) site. This indicates that upon reduction the added electron or electrons are *predominately* localized on the Fe(1,2) sites, the reduction having a much smaller influence on the electronic density on the Fe(3) site.

The quadrupole interaction values reveal details of the structural changes in the "parent"  $\text{Fe}_3(\text{CO})_{12}$  upon the formation of II. The replacement of a bridging CO group in I by the  $\mu\text{-CH}$  methyne group in II has little influence upon the electronic symmetry at the Fe(1,2) sites, but the displacement of a terminal CO group from Fe(3) causes a dramatic reduction in the symmetry at Fe(3) in II. The further reduction of II to form the ketenylidene containing cluster, III, results in a large decrease in the quadrupole interaction on both the Fe(1,2) and the Fe(3) sites. For the Fe(1,2) site the

\* Address correspondence to this author at the University of Missouri-Rolla.

- (1) Bradley, J. S.; Ansell, G. B.; Hill, E. W. *J. Am. Chem. Soc.* **1979**, *101*, 7417.
- (2) Tachikawa, M.; Muettterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4541.
- (3) Tachikawa, M.; Muettterties, E. L. *Prog. Inorg. Chem.* **1981**, *28*, 203.
- (4) Kolis, J. W.; Basolo, F.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 5626.
- (5) Desiderato, R., Jr.; Dobson, G. R. *J. Chem. Educ.* **1982**, *59*, 752.
- (6) Herber, R. H.; Kingston, W. R.; Wertheim, G. K. *Inorg. Chem.* **1963**, *2*, 153.
- (7) Erickson, N. E.; Fairhall, A. W. *Inorg. Chem.* **1965**, *4*, 1320.
- (8) Farmery, K.; Kilner, M.; Greatrex, R.; Greenwood, N. N. *J. Chem. Soc. A* **1969**, 2339.
- (9) Knight, J.; Mays, M. J. *J. Chem. Soc. A* **1970**, 654.
- (10) Lindauer, M. W.; Spiess, H. W.; Sheline, R. K. *Inorg. Chem.* **1970**, *9*, 1694.
- (11) Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 1351. Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4155.

(12) Kolis, J. W.; Holt, E. M.; Drezdson, M.; Whitmire, K. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 6134.

(13) Longworth, G. In "Mössbauer Spectroscopy Applied to Inorganic Chemistry"; Long, G. J., Ed.; Plenum Publishing Co.: New York, 1984; Vol. 1, p 43.

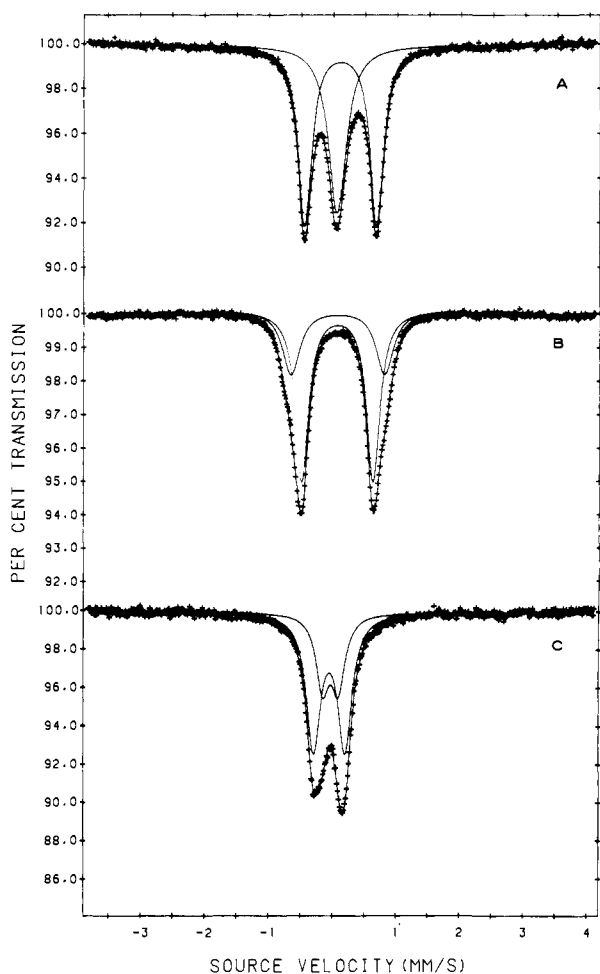
(14) The temperature dependence of the Mössbauer spectrum of  $\text{Fe}_3(\text{CO})_{12}$  is currently under investigation<sup>15</sup> and shows an increasing quadrupole interaction for this site with increasing temperature.

(15) Long, G. J.; Benson, C. G., unpublished results.

**Table I.** Mössbauer Effect Spectral Parameters<sup>a</sup>

compd	site	$\delta_{\text{Fe}}$	$\Delta E_{\text{Q}}$	$\Gamma$	<i>A</i> , %	$\chi^2$	$\Delta\delta$	$\Sigma\delta$	Fe-CO <sup>b</sup>	Fe- $\mu$ -CO	$n_e^c$
Fe <sub>3</sub> (CO) <sub>12</sub>	Fe(1,2)	0.115 (4)	1.119 (6)	0.259 (2)	61.4	1.29	0	0.287 (7)	3	2	0
	Fe(3)	0.057 (4)	0 <sup>d</sup>	0.316 (3)	38.6		0		4	0	0
[PPN][Fe <sub>3</sub> (CO) <sub>10</sub> CH]	Fe(1,2)	0.002 (3)	1.145 (5)	0.251 (2)	66.7 <sup>d</sup>	1.27	0.113 (5)	0.005 (6)	3	1	1/2
	Fe(3)	0.001 (4)	1.540 (7)	0.334 (4)	33.3 <sup>d</sup>		0.056 (6)		3	0	0
[PPN][Fe <sub>2</sub> Co(CO) <sub>9</sub> CCO]	Fe(1)	-0.019 (4)	0.905 (4)	0.236 (3)	50.0 <sup>d</sup>	0.64	0.134 (6)	-0.017 (6)	3	1	1/2
	Fe(3)	0.002 (5)	0.746 (5)	0.276 (6)	50.0 <sup>d</sup>		0.055 (6)		3	0	0
[PPN] <sub>2</sub> [Fe <sub>3</sub> (CO) <sub>9</sub> CCO]	Fe(1,2)	-0.041 (4)	0.494 (2)	0.267 (4)	66.7 <sup>d</sup>	0.85	0.156 (6)	-0.101 (7)	3	1	1
	Fe(3)	-0.019 (4)	0.224 (2)	0.253 (6)	33.3 <sup>d</sup>		0.076 (6)		3	0	0

<sup>a</sup>All data in mm/s obtained at 78 K relative to natural abundance  $\alpha$ -iron foil. <sup>b</sup>The number of indicated bonds at each iron site. <sup>c</sup>The approximate localization of the electron added to the cluster upon reduction. <sup>d</sup>Component variable constrained to the given value.



**Figure 1.** Mössbauer effect spectra obtained at 78 K for (A) Fe<sub>3</sub>(CO)<sub>12</sub> (I), (B) [PPN][Fe<sub>3</sub>(CO)<sub>10</sub>CH] (II), and (C) [PPN]<sub>2</sub>[Fe<sub>3</sub>(CO)<sub>9</sub>CCO] (III).

increase in site electronic symmetry is largely expected as the loss of the  $\mu$ -CO group yields a site with roughly 6-fold octahedral coordination. The even larger reduction of  $\Delta E_{\text{Q}}$  for the Fe(3) site in III and its resultant high electronic symmetry is no doubt a result of the interaction<sup>16</sup> between the Fe(3) atom and the ketylidene group as indicated by the broken bond in the schematic of III. A similar increase in the electronic symmetry at Fe(3) in IV is observed if one compares the decreased quadrupole interaction at Fe(3) with that found in II. In fact, this interaction to increase the electronic symmetry at the Fe(3) in III and IV may be the driving force behind the tilting of the CCO toward the metal plane as expected in III and observed<sup>16</sup> in IV. No similar interaction would be needed in H<sub>2</sub>Os<sub>3</sub>(CO)<sub>9</sub>(CCO), which is observed<sup>17</sup> to have the CCO group normal to the Os<sub>3</sub> metal plane.

(16) Kolis, J. W.; Holt, E. M.; Hriljac, J. A.; Shriver, D. F. *Organometallics* 1984, 3, 496.

(17) Shapley, J. R.; Strickland, D. S.; St. George, G. M.; Churchill, M. R.; Bueno, C. *Organometallics* 1983, 2, 185.

Our results help to explain the nucleophilic reactivity of III toward methylating agents and acids.<sup>16</sup> The selective partial localization of the added electrons on the Fe(1,2) sites in the reduced clusters yields a stronger nucleophilic potential at the bridging carbon. The smaller added electronic density at Fe(3) upon reduction permits a significant interaction between Fe(3) and the ketylidene group facilitating the breaking of the carbon-carbon bond and the formation of the resulting  $\mu$ -CO group from the ketylidene ligand.

**Acknowledgment.** We thank the donors of the Petroleum Research Foundation administered by the American Chemical Society, for their support of this research.

**Registry No.** I, 17685-52-8; II-PPN, 83220-20-6; III-(PPN)<sub>2</sub>, 88690-38-4; IV-PPN, 97633-81-3.

### Isolation and Structure of Tunichrome B-1, a Reducing Blood Pigment from the Tunicate *Ascidia nigra* L.

Reimar C. Bruening,<sup>†</sup> Eugene M. Oltz, Jun Furukawa, and Koji Nakanishi\*

Department of Chemistry, Columbia University  
New York, New York 10027

Kenneth Kustin

Department of Chemistry, Brandeis University  
Waltham, Massachusetts 02254

Received March 22, 1985

The hematology of tunicates, a class of common marine organisms that selectively accumulate metals such as V, Fe, Mo, Nb, has puzzled scientists for over 70 years.<sup>1</sup> The black tunicate *Ascidia nigra* (Linnaeus) sequesters vanadium as the pentavalent vanadate, concentrates it by 10<sup>6</sup>-fold,<sup>2</sup> and stores the metal in its reduced V(III) or V(IV) states<sup>3,4</sup> at physiological pH (ca. 7.2),<sup>5</sup> possibly as a hexaquo or other complex.<sup>6</sup> The apparent contradiction that V(III) is unstable in aqueous media at pH above 2.5 can be overcome by assuming the presence of a strong reductant that also serves as a good complexing agent. We believe that this role is fulfilled by the tunichromes,<sup>7</sup> the bright yellow

<sup>†</sup> Current address: Department of Chemistry, University of Hawaii.

(1) (a) Henze, M. *Hoppe-Seyler's Z. Physiol. Chem.* 1911, 72, 494. (b) Edean, R. *Nature (London)* 1953, 172, 123. (c) Levine, E. P. *Science (Washington, D.C)* 1961, 133, 1352. (d) Kokubu, N.; Hidaka, T. *Nature (London)* 1965, 205, 1028.

(2) Dingley, A. L.; Kustin, K.; Macara, I. G.; McLeod, G. C. *Biochim. Biophys. Acta* 1981, 649, 493 and references therein.

(3) Rezaeva, L. T. *Fed. Proc. Transl.* 1964, Suppl. 24, 836.

(4) Swinehart, J. H.; Biggs, W. R.; Halko, D. J.; Schroeder, N. C. *Biol. Bull.* 1974, 146, 302.

(5) Dingley, A. L.; Kustin, K.; Macara, I. G.; McLeod, G. C.; Roberts, M. F. *Biochem. Biophys. Acta* 1982, 720, 384.

(6) (a) Carlson, R. M. K. *Proc. Natl. Acad. Sci. U.S.A.* 1975, 72, 2216.

(b) Tullius, T. D.; Gillum, W. O.; Carlson, R. M. K.; Hodgson, K. O. *J. Am. Chem. Soc.* 1980, 102, 5670.