reactive state (presumably $^3$LF) of the Co(III) complex with little or no direct internal conversion to the ground state from the upper excited states in the cobalt complex.

The bimolecular quenching constant (i.e., 680 $M^{-1}$ in Figure 2) represents the product of the lifetime of the donor state of $Fe(bpy)_2(CN)_2$ and the bimolecular rate constant for the sensitization process. Assuming diffusion control as the upper limit for the quenching rate constant, a lower limit of 56 ns can be calculated for the lifetime of the Fe(II) donor state.[13] This lifetime estimate is much longer than the 0.81 and 2.54 ns reported for $Fe(bpy)_3^{2+}$ and $Fe(tpy)_2^{2+}$, respectively.[14] One possible reason for the increase in lifetime is that the LF excited state, which is lowest in energy for $Fe(bpy)_3^{2+}$,[15] may be pushed up by $CN^-$ substitution, and an MLCT excited state becomes lowest in energy for $Fe(bpy)_2(CN)_2$.[16] While this lifetime is still too short to allow the Fe system to be an efficient sensitizer for intermolecular processes, intramolecular processes should be feasible with the proper bridging ligand system.

Energetically, this study shows that 577-nm light will drive the photoelimination reaction of $H_2$ from $Co(bpy)(PEt_2Ph)_2H_2^+$, thus extending into the visible region the frequency of light required for eq 1. The fact that 577-nm light is energetic enough to populate the reactive excited state of $Co(bpy)(PEt_2Ph)_2H_2^+$ suggests that assignment of a LF excited state proposed by Geoffroy and Pierantozzi[10] is correct since a MLCT reactive state would involve too large a Stokes shift for that type of excited state.[17]

**Acknowledgment.** The authors thank the Office of Basic Energy Sciences, Department of Energy (Grant DEAS0980ER10671), for support of this work. K.J.M. acknowledges an R. C. Edwards Graduate Fellowship from Clemson University.

**Registry No.** $Co(bpy)(PEt_2Ph)_2H_2^+$, 47778-79-0; $Fe(bpy)_2(CN)_2$, 14841-10-2; $H_2$, 1333-74-0.

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# Lewis Basicity of Carbonyl Oxygen in the Presence of a Heteroatom: Reaction of $[BiFe_3(CO)_{10}]^-$ with $CH_3SO_3CF_3$

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*Received November 13, 1985*

The basicity of $\mu_2$- and $\mu_3$-carbonyl oxygen atoms has been well established.[2] Alkylation, acylation, protonation, or silylation at such sites has been observed for $[Fe_3(CO)_{11}]^{2-}$,[2] $[HFe_3(CO)_{11}]^-$,[3] $[Fe_4(CO)_{13}]^{2-}$,[4,5] $[HFe_4(CO)_{13}]^-$,[5] $[HRu_3(CO)_{11}]^-$,[6,7] $[HOs_3(CO)_{11}]^-$,[7,8] and $[Co_3(CO)_{10}]^-$.[9] The low-frequency C–O stretching vibration is used as an indication of basicity and the ability to add $R^+$ reagents to the carbonyl oxygen. To date, however, the alkylation of a bridging carbonyl in a cluster that also contains a main-group heteroatom has not been reported. We were, therefore, prompted to attempt alkylation of $[BiFe_3(CO)_{10}]^-$, which we recently synthesized. In this molecule, Bi functions as a 3-electron donor, contributing to a total of 12 skeletal electrons for cluster bonding, consistent with localized edge bonding in a tetrahedron. The Bi atom is thus left with a lone pair, which could possibly be alkylated. On the other hand, the $\mu_3$-CO in this molecule appears to be very basic, as judged by IR analysis ($\nu_{CO}$ = 1650 $cm^{-1}$), and the question raised was, "Which site of attack would be preferred?" To answer this question, we have treated $[BiFe_3(CO)_{10}]^-$ with $CH_3SO_3CF_3$ and have spectroscopically and structurally characterized the product.

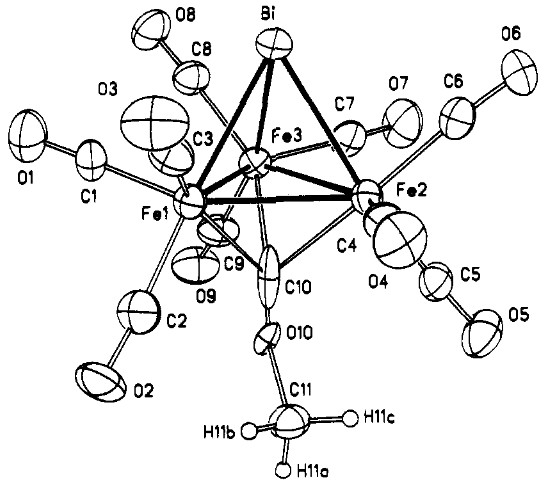

**Figure 1.** Molecular structure and atom labeling scheme for $[Fe_3(CO)_9](\mu_3\text{-}COCH_3)$ drawn with 50% probability ellipsoids.

## Discussion

The structure of the product $BiFe_3(CO)_9(\mu_3\text{-}COCH_3)$ (**1**) as shown in Figure 1 consists of a triangle of iron atoms capped by a $\mu_3$-Bi atom on one side and a $\mu_3$-methoxymethyne ligand on the other and shows conclusively that alkylation has occurred at the oxygen of the $\mu_3$-CO. Selected bond distances and angles are given in Table III. The $^1$H NMR signal for the $CH_3$ group is consistent with values obtained for other methylated carbonyls. The IR spectrum of the terminal carbonyls shows the same pattern as $[BiFe_3(CO)_{10}]^-$, only shifted to higher energy, as expected for a neutral molecule with the same symmetry as the parent, except that the bridging carbonyl band could no longer be located. The Bi–Fe distances are comparable to those found in $Bi_2Fe_3(CO)_9$[10] and $[BiFe_3(CO)_{10}]^-$.[11] The Fe–Fe distances in $[BiFe_3(CO)_{10}]^-$ are not statistically different from those observed for **1**. Unlike trends observed for $[Fe_4(CO)_{13}]^{2-}$,[4] the Fe–$\mu_3$-C distances are virtually unchanged upon alkylation. The unusually short $\mu_3$-C–O distance [1.025 (16) Å] is an artifact created by an unresolvable disorder in the position of the $\mu_3$-C.

The presence of the bismuth atom may have a profound influence on the reactivity of this molecule. We carried out the

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[1] (a) Rice University. (b) University of Delaware.

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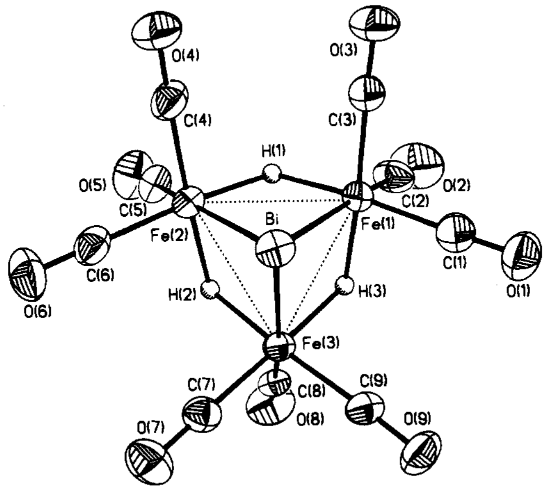

**Figure 2.** Molecular structure and atom labeling scheme for $[Fe_3(CO)_9](\mu\text{-}H)_3(\mu_3\text{-}Bi)$ drawn with 50% probability ellipsoids.

**Table I.** Crystal and Refinement Data for $[Fe_3(CO)_9](\mu_3\text{-}Bi)(\mu_3\text{-}COCH_3)$ (**1**) and $[Fe_3(CO)_9](\mu_3\text{-}Bi)(\mu\text{-}H)_3$ (**2**)

| | **1** | **2** |
|---|---|---|
| space group | $P2_1/n$ (monoclinic) | $P\bar{1}$ (triclinic) |
| $a$, Å | 10.549 (5) | 7.997 (2) |
| $b$, Å | 13.733 (5) | 9.018 (2) |
| $c$, Å | 11.306 (6) | 12.464 (4) |
| $\alpha$, deg | 90 | 78.83 (2) |
| $\beta$, deg | 93.69 (4) | 71.16 (2) |
| $\gamma$, deg | 90 | 68.78 (2) |
| $V$, Å$^3$ | 1634.5 (10) | 790.0 (4) |
| $Z$ | 4 | 2 |
| temp, °C | 23 | 22 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 128.6 | 132.9 |
| $\rho$(calcd), g cm$^{-3}$ | 2.73 | 2.66 |
| cryst color (size, mm) | red black (0.21 × 0.22 × 0.30) | red black (0.13 × 0.22 × 0.30) |
| no. of unique data | 3765 (4117 collected) | 3252 (3408 collected) |
| no. of data for $F_o \geqslant n\sigma(F_o)$ | 2994 ($n$ = 3) | 2677 ($n$ = 5) |
| max/min transm | 0.050/0.037 | 0.271/0.102 |
| $R$(int) | 0.037 | 0.028 |
| data colln range, deg | $4 \leqslant 2\theta \leqslant 52$ | $4 \leqslant 2\theta \leqslant 53$ |
| $R_F$, % | 4.71 | 3.82 |
| $R_{wF}$, % | 4.92 | 3.97 |
| GOF | 1.37 | 1.10 |

reaction of **1** with $H_2$ (1 atm) at 60 °C and observed no reaction after several hours, in contrast to results reported for $HFe_3(CO)_{10}(COCH_3)$, which reacts under those conditions (reversibly) to form $H_3Fe_3(CO)_9(COCH_3)$.[7] Thus **1** appears more stable to CO loss than $HFe_3(CO)_{10}(COCH_3)$. Nor did heating **1** to 110 °C in toluene result in the obvious formation of an analogous new cluster, but the formation of a metallic mirror and loss of **1** were observed.

This lack of reactivity does not appear to be due to the inaccessibility of a stable cluster product, as we have now isolated and structurally characterized $H_3BiFe_3(CO)_9$ (**2**) from the acidification of aqueous methanol solutions of $Bi\{Fe(CO)_4\}_4^{3-}$ which also yielded $Bi_2Fe_3(CO)_9$.[10] This hydride would be the expected cluster product if the methoxy methyne ligand in **1** were completely hydrogenated, but we found no evidence for its formation in that reaction. The identity of **2** was established by its mass spectrum, and the $^1H$ NMR indicated the presence of only one signal typical of bridging hydride ligands. ($\delta = -24.1$). The structure of **2** (Figure 2) was confirmed by X-ray analysis and is very similar to that of **1** with the $\mu_3$-$COCH_3$ ligand being replaced by three $\mu_2$-hydrides. Selected bond distances and angles are given in Table III. The hydrides, located crystallographically, lie slightly below the $Fe_3$ plane away from the Bi atom. We know of no other transition metal/large main group element clusters that possess hydride ligands. The Bi–Fe bonds in **2** are comparable to those in $[BiFe_3(CO)_{10}]^-$ and **1**, while the Fe–Fe distances are considerably longer and are comparable to those in $Bi_2Fe_3(CO)_9$ [2.745 (11) Å average].

**Table II.** Atom Coordinates ($\times 10^4$) and Temperature Factors (Å$^2$ × $10^3$) for **1** and **2**

| atom | $x$ | $y$ | $z$ | $U_{iso}$[a] |
|---|---|---|---|---|
| Compound **1** | | | | |
| Bi | 392.1 (4) | 1492.4 (3) | 472.5 (3) | 42 (1)* |
| Fe(1) | 156 (1) | 1291 (1) | 2776 (1) | 36 (1)* |
| Fe(2) | −372 (1) | 3037 (1) | 1878 (1) | 38 (1)* |
| Fe(3) | 1773 (1) | 2177 (1) | 1499 (1) | 36 (1)* |
| C(1) | 1170 (10) | 284 (7) | 2571 (10) | 45 (3)* |
| C(2) | 311 (12) | 1199 (9) | 4360 (11) | 58 (4)* |
| C(3) | −1364 (11) | 654 (9) | 2676 (10) | 53 (4)* |
| C(4) | −1970 (10) | 2901 (9) | 2488 (10) | 49 (4)* |
| C(5) | −5 (11) | 4219 (8) | 2463 (11) | 52 (4)* |
| C(6) | −970 (13) | 3591 (9) | 519 (12) | 59 (4)* |
| C(7) | 1936 (11) | 3284 (9) | 554 (10) | 49 (4)* |
| C(8) | 2366 (11) | 1238 (8) | 568 (10) | 49 (4)* |
| C(9) | 3297 (11) | 2344 (9) | 2283 (10) | 54 (4)* |
| C(10) | 1083 (11) | 2611 (9) | 3088 (15) | 62 (5)* |
| C(11) | 904 (11) | 3322 (8) | 4860 (10) | 52 (4)* |
| O(1) | 1805 (10) | −385 (7) | 2475 (9) | 76 (4)* |
| O(2) | 437 (12) | 1083 (8) | 5363 (7) | 83 (4)* |
| O(3) | −2285 (9) | 238 (8) | 2642 (9) | 80 (4)* |
| O(4) | −2840 (9) | 2833 (7) | 2868 (9) | 71 (4)* |
| O(5) | 201 (9) | 4997 (6) | 2821 (9) | 74 (4)* |
| O(6) | −1347 (13) | 4016 (7) | −313 (9) | 95 (5)* |
| O(7) | 2073 (11) | 3842 (7) | 64 (9) | 84 (4)* |
| O(9) | 2837 (9) | 660 (6) | 16 (9) | 66 (3)* |
| O(9) | 4275 (9) | 2422 (8) | 2713 (8) | 72 (3)* |
| O(10) | 1558 (6) | 2934 (4) | 3884 (6) | 26 (2)* |
| Compound **2** | | | | |
| Bi | 1071.2 (5) | 2113.5 (4) | 3995.7 (2) | 40 (1)* |
| Fe(1) | 1145 (2) | 2389 (1) | 1837 (1) | 37 (1)* |
| Fe(2) | 4395 (2) | 1224 (1) | 2518 (1) | 37 (1)* |
| Fe(3) | 2236 (2) | 4414 (1) | 2671 (1) | 34 (1)* |
| O(1) | −2823 (11) | 4229 (9) | 2394 (8) | 82 (4)* |
| O(2) | 1715 (16) | 2957 (12) | −640 (7) | 99 (6)* |
| O(3) | 485 (11) | −663 (8) | 2196 (7) | 72 (4)* |
| O(4) | 4434 (13) | −2087 (8) | 3040 (8) | 83 (4)* |
| O(5) | 7765 (11) | 801 (10) | 581 (6) | 76 (4)* |
| O(6) | 6283 (12) | 1052 (10) | 4225 (6) | 73 (4)* |
| O(7) | 3400 (11) | 4987 (10) | 4505 (6) | 69 (4)* |
| O(8) | 4123 (12) | 6372 (9) | 864 (6) | 73 (4)* |
| O(9) | −1414 (10) | 6858 (8) | 3297 (7) | 67 (3)* |
| C(1) | −1281 (15) | 3518 (12) | 2189 (9) | 55 (4)* |
| C(2) | 1537 (16) | 2716 (11) | 315 (8) | 56 (5)* |
| C(3) | 746 (13) | 511 (10) | 2080 (8) | 48 (4)* |
| C(4) | 4403 (14) | −803 (10) | 2854 (8) | 52 (4)* |
| C(5) | 6445 (13) | 967 (11) | 1309 (8) | 51 (4)* |
| C(6) | 5509 (14) | 1115 (11) | 3585 (8) | 51 (4)* |
| C(7) | 2937 (12) | 4750 (10) | 3784 (7) | 45 (4)* |
| C(8) | 3389 (12) | 5621 (9) | 1546 (7) | 42 (3)* |
| C(9) | −21 (13) | 5866 (10) | 3067 (7) | 43 (3)* |
| H(1) | 3585 (45) | 1556 (101) | 1310 (47) | 53 (25) |
| H(2) | 4469 (86) | 3165 (22) | 2003 (98) | 121 (45) |
| H(3) | 1783 (145) | 4133 (81) | 1447 (54) | 73 (31) |

[a] Asterisks indicate equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

## Experimental Section

**Synthesis of $BiFe_3(CO)_9(\mu_3\text{-}COCH_3)$ (1).** Slow alkylation of $[Et_4N][BiFe_3(CO)_{10}]$ (1.00 g) in $CH_2Cl_2$ (60 mL) with $CH_3SO_3CF_3$ (0.30 mL) resulted cleanly in the neutral compound $BiFe_3(CO)_{10}CH_3$ in 65% yield after 2 days. The product was obtained by extraction into hexane after removal of $CH_2Cl_2$ in vacuo. Filtering, concentrating, and cooling produced either a fine powder or single crystals of (**1**), which exhibited a mass spectrum consistent with expected alkylation of $[BiFe_3(CO)_{10}]^-$ showing a parent ion at $m/e$ 672 with regular loss of carbonyls [P − $n$(28)]. IR ($\nu_{CO}$, hexane, cm$^{-1}$): 2077 w, 2022 vs, 1999 s, 1930 sh. $^1H$ NMR (toluene-$d_8$, $Me_4Si$ standard): $\delta$ = 4.00. Anal. Calcd: Fe, 25.00; Bi, 31.20. Found: Fe, 21.70; Bi, 29.74. (The iron analyses were complicated by the loss of an unidentified volatile metal complex upon acid decomposition of the cluster.) As a test for formation of other clusters during the synthesis, the experiment was repeated in

**Table III.** Selected Bond Distances and Angles for **1** and **2**

| **1** | | **2** | |
|---|---|---|---|
| (a) Bond Distances (Å) | | | |
| Bi–Fe(1) | 2.644 (1) | Bi–Fe(1) | 2.638 (1) |
| Bi–Fe(2) | 2.650 (1) | Bi–Fe(2) | 2.639 (1) |
| Bi–Fe(3) | 2.657 (1) | Bi–Fe(3) | 2.641 (1) |
| Fe(1)–Fe(2) | 2.649 (2) | Fe(1)–Fe(2) | 2.772 (2) |
| Fe(2)–Fe(3) | 2.612 (2) | Fe(2)–Fe(3) | 2.774 (1) |
| Fe(1)–Fe(3) | 2.606 (2) | Fe(1)–Fe(3) | 2.776 (2) |
| Fe(1)–C(10) | 2.079 (10) | Fe–H (av) | 1.76 (3) |
| Fe(2)–C(10) | 2.074 (10) | Bi···Bi | 4.690 (1) |
| Fe(3)–C(10) | 2.069 (14) | | |
| C(10)–O(10) | 1.025 (16) | | |
| O(10)–C(11) | 1.514 (14) | | |
| Bi···Bi | 4.325 (1) | | |
| (b) Bond Angles (deg) | | | |
| Fe(1)–C(10)–Fe(2) | 79.3 (5) | Bi–Fe–Fe (av) | 58.3 (0) |
| Fe(1)–C(10)–Fe(3) | 77.9 (5) | Fe–Bi–Fe (av) | 63.3 (0) |
| Fe(2)–C(10)–Fe(3) | 78.2 (6) | Fe–Fe–Fe (av) | 59.9 (1) |
| Fe(1)–C(10)–O(10) | 135.4 (12) | Fe–H–Fe (av) | 104 (2) |
| Fe(2)–C(10)–O(10) | 134.6 (10) | H–Fe–H | 80 (4) |
| Fe(3)–C(10)–O(10) | 128.9 (10) | Bi–Fe–H (av) | 96 (2) |
| angles in $BiFe_3$ tetrahedron | 60 ± 1 | | |

deuterated methylene chloride with 0.020 g of $[Et_4N][BiFe_3(CO)_{10}]$ and 0.01 mL of $CH_3SO_3CF_3$. An NMR spectrum of the solution after about 1 h showed no trace of any cluster products. After 24 h there was a new peak at the reported chemical shift of **1**, and after 2 days this peak had increased in intensity. The growth of this peak was the only noted change from a range of +10 to −50 ppm in the NMR spectrum of the solution over 3 days. Extraction of the product into hexane left a residue from which no other soluble cluster products could be extracted.

**Synthesis of $H_3BiFe_3(CO)_9$ (2).** The synthesis of $Bi_2Fe_3(CO)_9$, as previously described,[10] was performed, and hexane or petroleum ether extracts were allowed to stand for about 1 month. The precipitated $Bi_2Fe_3(CO)_9$ was removed by filtration, and the solvent and product $Fe(CO)_5$ were removed under vacuum from the filtrate. This residue was redissolved in petroleum ether and chromatographed on Florisil (2.5 × 30 cm) with petroleum ether. Two bands were observed. The first to elute contained $H_3BiFe_3(CO)_9$ as an orange-brown solution, and the second, $Bi_2Fe_3(CO)_9$ as a red-brown solution. The first collection was concentrated and cooled to precipitate **2** in low yield (ca. 0.1 g, <1%). Proton NMR shows a single resonance at $\delta = -24.1$ consistent with the presence of the three equivalent bridging hydride ligands. The mass spectrum showed the parent ion at $m/e$ 632 with regular loss of all CO's. Fragments corresponding to Bi, BiFe, $BiFe_2$, and $BiFe_3$ were all observed. IR ($\nu_{CO}$, hexane, $cm^{-1}$): 2087 w, 2050 s, 2015 m, 2000 w. Anal. Calcd: Fe, 26.52; Bi, 33.08. Found: Fe, 26.81; Bi, 32.28.

**Reaction of $BiFe_3(CO)_9(\mu_3\text{-}COCH_3)$ with $H_2$.** $BiFe_3(CO)_9(\mu_3\text{-}COCH_3)$ (26 mg) was weighed into a Schlenk flask and dissolved in deuterated toluene (2 mL) that had been freeze–thaw-degassed and stored under nitrogen (2 mL). A bubbler was affixed to the flask and hydrogen bubbled through the solution at a moderate rate. The flask was placed into an oil bath that had been heated at 60 °C. The solution was bubbled with hydrogen and heated at this temperature for 4 h. There was no color change noted during this time. The flask was allowed to cool to room temperature under a continued slow purge of hydrogen for about 10 min. A sample of the solution was then transferred via syringe into an NMR tube that had been flushed with nitrogen. The proton NMR spectrum of this solution showed the methyl peak of $BiFe_3(CO)_9(\mu_3\text{-}COCH_3)$ and no evidence of formation of compound **2**. Heating to reflux in toluene produced no new infrared peaks, but the intensities of the CO stretching band for **1** decreased and a metallic mirror was formed.

**Reaction of $H_3BiFe_3(CO)_9$ with CO.** A solution of $H_3BiFe_3(CO)_9$ (14 mg) in 20 mL of toluene was purged for approximately 30 min with carbon monoxide and then was allowed to stir ca. 18 h under a slight positive pressure of CO. An infrared spectrum of the solution showed no change. The solution was transferred to a Parr 300-mL minireactor under a flush of nitrogen. The reactor was purged with 500 psi of CO and then pressurized to 900 psi, and the solution was stirred for 48 h at room temperature. Again, the infrared spectrum of the solution showed no change.

**X-ray Structure Determinations.** Crystal and data collection parameters for **1** and **2** are given in Table I. Data were collected by $\theta/2\theta$ methods on a Nicolet R3 diffractometer. The space group for **1** was unambiguously determined from observed systematic absences; the centrosymmetric triclinic space group, $P\bar{1}$, was chosen intially for **2** on the basis of $E$-statistics and confirmed by the chemically reasonable solution and refinement of the structure. Both data sets were corrected for absorption by empirical ($\Psi$-scan) methods. Both structures were solved by using standard heavy-atom methods to locate the Bi atom and difference Fourier syntheses to locate the remaining non-hydrogen atoms. In both structures all non-hydrogen atoms were refined anisotropically. For **1** the methyl group hydrogen atoms were located, but they did not refine smoothly and were ultimately incorporated as idealized, isotropic contributions. In **2** the bridging hydride atoms were located and isotropically refined with the Fe–H distances refined as a single variable. All data reduction and refinement programs are contained in SHELXTL library (Nicolet Corp., Madison, WI).

Table II provides the atomic coordinates for **1** and **2**, and Table III, selected bond distances and angles.

**Acknowledgment.** We wish to acknowledge the Robert A. Welch Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. The high-pressure work was made possible by a grant from the Atlantic Richfield Foundation administered by the Research Corp.

**Registry No.** **1**, 102261-08-5; **2**, 102283-13-6; $[Et_4N][BiFe_3(CO)_{10}]$, 92786-73-7; $CH_3SO_3CF_3$, 333-27-7; Fe, 7439-89-6; Bi, 7440-69-9; CO, 630-08-0.

**Supplementary Material Available:** Listings of complete bond lengths, complete bond angles, and anisotropic thermal temperature factors for $(\mu_3\text{-}Bi)Fe_3(CO)_9(\mu_3\text{-}COCH_3)$ and $(\mu\text{-}H)_3(\mu_3\text{-}Bi)Fe_3(CO)_9$ (6 pages). Ordering information is given on any current masthead page.

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## Reaction of Matrix-Isolated Iron Atoms with Carbon Disulfide

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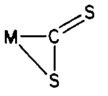
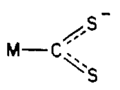
*Received September 5, 1985*

Carbon disulfide has been found to react readily with a number of transition-metal-containing complexes.[1-3] X-ray crystallographic studies[4-6] have shown that a common mode of coordination to a single metal center involves bonding through both carbon and sulfur in an $\eta^2$ fashion (I). This type of complex is readily identified by a characteristic stretching frequency at approximately 950–1250 $cm^{-1}$ in the infrared spectrum.[1] In addition, a number of complexes involving other types of bonding such as coordination through sulfur[7,8] (II) or carbenoid structures[9,10] (III) have been postulated primarily on the basis of spectroscopic evidence.


I


II


III

The $CS_2$-containing complexes that have been reported usually contain other types of ligands and sometimes more than one metal center, factors that might be expected to influence the mode of bonding of the $CS_2$ ligand. Matrix isolation experiments in which metal atoms are cocondensed with the ligand of interest at low (~20 K) temperatures have the advantage that simple binary complexes which may be unobtainable by more conventional

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