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 (ν_{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 (Ψ-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.

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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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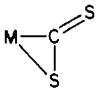
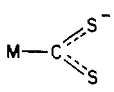
Carbon disulfide has been found to react readily with a number of transition-metal-containing complexes.[1-3] X-ray crystallographic studies[4-6] have shown that a common mode of coordination to a single metal center involves bonding through both carbon and sulfur in an η^2 fashion (I). This type of 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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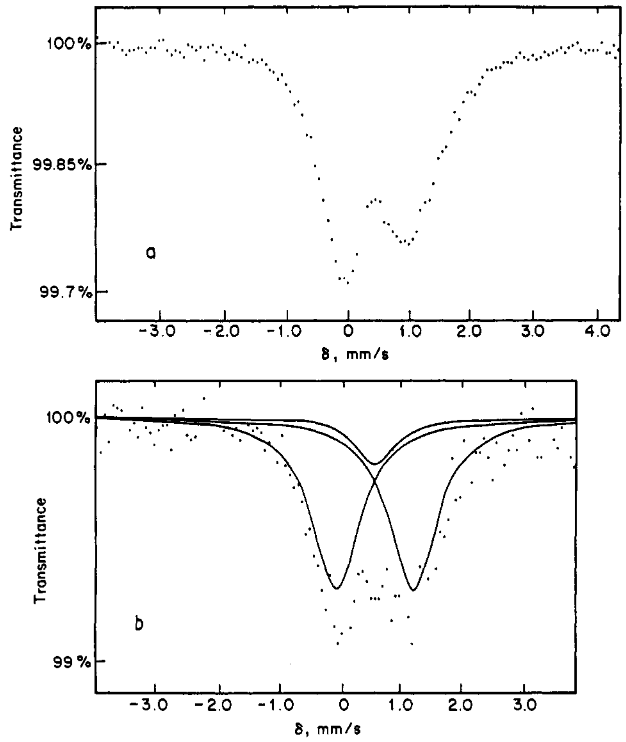

Figure 1. ^{57}Fe Mössbauer spectra of iron atoms cocondensed (a) in a 2% CS_2/Ar matrix at 20 K and (b) in a 100% CS_2 matrix at 20 K, warmed to 80 K, and recooled to 20 K. Solid lines show the individual peaks that make up the best fit for the experimental points.

methods are readily formed and studied. This means that it is possible to examine the nature of the interaction between a single ligand (or single type of ligand) and one metal atom without complications from other ligands or solvent effects. It was our goal, in this study, to determine the type of bonding, as well as the extent of reactivity between CS_2 and iron atoms. Herein, we report the results of several matrix isolation experiments in which either pure CS_2 or CS_2/Ar and CS_2/Kr mixtures were cocondensed with iron atoms and studied by infrared and Mössbauer spectroscopy.

Experimental Section

Detailed descriptions of the Mössbauer and infrared experimental procedures have been previously described.[11] A Perkin-Elmer 683 was used for the infrared experiments. Research grade Kr and ultrahigh-purity Ar, supplied by Linde, were used for both the infrared and Mössbauer experiments without further purification. Enriched ^{57}Fe powder (90+% isotopic purity) supplied by New England Nuclear was used in the Mössbauer experiments, with iron concentrations generally below 0.5% to prevent dimer formation. Carbon disulfide was fractionally distilled twice and underwent three freeze–pump–thaw cycles to remove adventitious air before use in matrix isolation experiments.

Mössbauer spectra were computer-fit with a least-squares routine to a sum of quadrupole doublets with Lorentzian line shapes, after subtraction of the background spectrum. The standard statistical tests, χ^2 and MISFIT, were used as quantitative measures of the quality of the fits. Isomer shifts are reported relative to α-Fe at room temperatures.

Results and Discussion

Mössbauer spectra were obtained for several samples of iron cocondensed with carbon disulfide in pure (100%) CS_2 as well as mixtures of CS_2 with Ar (0.1–20% CS_2) and Kr (0.1–1% CS_2) at 15–20 K. A typical spectrum is shown in Figure 1a. All of the spectra consisted of a single quadrupole doublet at isomer shift $\delta = +0.55 \pm 0.04$ mm/s and quadrupole splitting $\Delta = 1.3 \pm 0.2$ mm/s, indicating the presence of one product of the reaction between Fe and CS_2. In some samples, a moderate-intensity asymmetry in the two lines of the quadrupole doublet was evident. In these cases, the line that was less intense was also somewhat broader, and the areas of both halves of the quadrupole doublets were always equal. This observation supports the identification of the Mössbauer peaks as a quadrupole doublet belonging to a single species rather than as two singlets belonging to two different species with cubic symmetry, which would be a highly unusual situation. Intensity asymmetry of a quadrupole doublet is frequently seen if partial orientation of the Mössbauer absorber occurs with respect to the source of the γ rays.[12] Preferential orientation of the Fe–CS_2 complex as it is forming in the matrix may be causing the asymmetrical doublet.

In none of the samples, most notably in those containing low concentrations of CS_2, was there evidence of unreacted iron atoms, readily identified by a single broad peak or doublet at $\delta = -0.75$ mm/s. Nor was there ever any sign of the formation of other species such as unreacted iron dimers, Fe_2, clusters, or other iron-containing products of the reaction with CS_2. Only one species containing iron and CS_2 was formed in these experiments, no matter what the composition of the matrix. The absence of other complexes in dilute matrices indicates that the only product of the reaction between Fe and CS_2 is a compound which contains a single CS_2 ligand and that the reaction stops after one CS_2 is bound. The fact that other matrix isolation experiments in which metal atoms are reacted with ligands to form multicoordinate complexes (for example, CO[11,13] and N_2[14]) show evidence for unsaturated complexes in the dilute matrices further supports this conclusion. Additionally, conditions were such that only monomeric iron complexes were expected to form (i.e. [Fe] < 0.5%). Therefore, it may be concluded that the species formed in these matrices has the chemical formula $Fe(CS_2)$.

In order to determine the stability of $Fe(CS_2)$, a series of annealing experiments were performed. A sample of iron cocondensed in a 100% CS_2 matrix was warmed to 40 K slowly and recooled to 20 K, and a Mössbauer spectrum recorded. The experiment was repeated at 60 and 80 K. Above this temperature, significant evaporation of the matrix takes place. The Mössbauer spectrum remains largely unchanged as long as the sample remained at or below 60 K. The spectrum of the Fe–CS_2 system warmed to 80 K shows the appearance of a new peak (or possibly unresolved doublet) at $\delta = +0.55$ mm/s, which is partially obscured by the original doublet (Figure 1b). A Mössbauer spectrum taken of the sample at room temperature does not show the low-temperature doublet but shows a new one with $\delta = +0.30$ mm/s and $\Delta = 0.71$ mm/s. When the beryllium disk upon which the samples are deposited is cleaned with nitric acid, this doublet is no longer seen, indicating that this signal is not associated with background iron.

These observations may be interpreted to mean that $Fe(CS_2)$ formed in a 100% CS_2 matrix is stable to at least 60 K. Between

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60 and 80 K, the compound begins to decompose to form a new iron-containing species. At room temperature, a very stable, nonvolatile residue remains. The isomer shift of this complex is similar to that found for covalently bound tetragonal FeS ($\delta = +0.35$ mm/s at 300 K).[17,18] Crystalline FeS shows no quadrupole splitting, whereas this complex does. However, this may be explained by the fact that amorphous rather than tetragonal FeS should form under these circumstances. In the former, the Fe is in a less symmetrical environment than in the latter, so that a doublet is expected. The new peak or doublet seen in Figure 1b also has the same isomer shift as FeS at 20 K ($\delta \sim +0.5$ mm/s). The change in δ with temperature is due to the second-order Doppler effect. These observations suggest that $Fe(CS_2)$ dissociates to form FeS upon warming (eq 1).

$$\mathrm{Fe(CS_2)} \xrightarrow{\Delta} \mathrm{FeS} + \mathrm{CS}\ \text{(volatile, decomposes)} \tag{1}$$

Several samples in which iron was cocondensed in dilute carbon disulfide matrices (0.1–10% in Ar) at 20 K were examined by infrared spectroscopy. Matrix-isolated $^{12}CS_2$ in Ar absorbs at 1535 cm^{-1} and natural-abundance $^{13}CS_2$ at 1475 cm^{-1} in the infrared spectrum. A large portion of the CS stretching region (i.e. from 800 to 1500 cm^{-1}) is transparent in the CS_2 matrices. However, no new bands that could be attributed to coordinated CS_2 were ever seen in any of the $Fe/CS_2/Ar$ experiments.

One possible explanation is that the CS stretching bands are too weak to be resolved by the infrared spectrophotometer used in the experiments. To test this hypothesis, an experiment in which nickel was cocondensed in a 1% CS_2/Kr matrix at 20 K was repeated using the same conditions that were used for the iron experiments. The reaction of nickel in low-temperature CS_2/Ar and CS_2/Kr matrices has been reported by Ozin et al.[17] New bands in the CS stretching region of the infrared spectrum were detected, which were assigned to several $Ni–CS_2$ compounds in which CS_2 is bound through both carbon and sulfur as in I. Under the conditions employed in this study, the spectra published by Ozin were reproduced, indicating that the CS stretching bands in the nickel complexes are easily detected. This suggests, but does not prove conclusively, that such peaks should be seen in the IR spectrum if $Fe(CS_2)$ has bonding similar to that seen in the nickel complexes.

Another possibility for the apparent lack of CS stretching bands in the infrared spectra of iron cocondensed with CS_2 in a CS_2/Ar matrix is that these bands coincide with the strong free-CS_2 stretch at about 1535 cm^{-1}. If CS_2 is bound to iron in a linear fashion through sulfur, as in II, the expected frequency of the CS stretching band is about 1520 cm^{-1}.[1] Such a peak would indeed be obscured by the broad band of matrix-isolated free CS_2.

Although Mössbauer results do not usually give any direct information about bonding or structure of compounds, the spectra obtained for this study do provide some clues, particularly when compared to results obtained on other matrix-isolated systems. These comparisons yield the following relevant information. First, there is evidence for only one iron–CS_2 compound, $Fe(CS_2)$, in all of the matrices, whereas, for nickel,[17] up to three CS_2 ligands can coordinate to give $Ni(CS_2)_x$ (x = 1–3). Second, the isomer shift for $Fe(CS_2)$ of +0.55 mm/s is similar to that found for $Fe(C_2H_4)$[18] (+0.55 mm/s) and $Fe(NH_3)$[19] (+0.60 mm/s) complexes in which σ-bonding predominates. Third, matrix isolation experiments in which iron is cocondensed with reactive gases show that multicoordinate complexes are formed when the ligands are π-acids as in CO,[11] N_2,[14] and NO.[20] If the ligands are poor π-acceptors, such as NH_3, only monocoordinate complexes are formed.[19] Interestingly, nickel will coordinate up to three ethylene ligands in a π-bound fashion[21] whereas iron coordinates only one,[18] and the bonding is primarily via σ-donation. The final piece of evidence is that $Fe(CS_2)$ decomposes upon heating to form FeS.

It is apparent, then, that $Fe(CS_2)$ is probably σ-bonded, as would be found in linearly coordinated CS_2 (II), in contrast to the case of the nickel compounds. This difference in behavior between iron and nickel with CS_2 is analogous to that seen with ethylene.

Finally, an important feature of the Fe/CS_2 experiments was the total absence of unreacted iron atoms even in matrices containing as little as 0.1% CS_2 in Kr. It is usual to find unreacted iron atoms in matrices such as pure CO.[11] This has been explained by the fact that energy needs to be supplied to iron atoms in the ground state, $(3d)^6(4s)^2$, in order to promote them to the $(3d)^7(4s)^1$ state. Apparently, the CS_2 reaction differs in that little or no activation energy is required, implying that the interaction may occur with atoms in the ground state. Whatever the explanation, this system is distinguished by the fact that it has been found to be the most reactive one involving matrix-isolated iron atoms to date. This is even more remarkable in light of the fact that there is no evidence for reaction products when iron is cocondensed with CO_2.[22]

Summary

It has been shown that the cocondensation of iron with CS_2 in low-temperature matrices leads to the formation of one complex with stoichiometry $Fe(CS_2)$. The evidence at hand strongly suggests that CS_2 is σ-bonded to Fe, probably through S in a linear geometry. The unusually high reactivity and the very different behaviors of Fe and Ni toward CS_2 are striking features of this system.

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Registry No. $Fe(CS_2)$, 102505-25-9; FeS, 1317-37-9; Fe, 7439-89-6; CS_2, 75-15-0.

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Laser Photolysis Studies of Nickel(II) Tetraphenylporphyrin in a Mixed Solvent of Pyridine and Toluene in the Temperature Range 180–300 K

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Since chemical and physical properties of metalloporphyrins are markedly dependent on the nature of axial ligands, the studies on the binding of ligands by metalloporphyrins have been extensively carried out by optical absorption, ESR, and NMR measurements.[1-3] For nickel(II) porphyrins, it is confirmed that five- and six-coordinate complexes are produced in the presence of pyridine or piperidine.[4-6] The absorption spectra of the

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