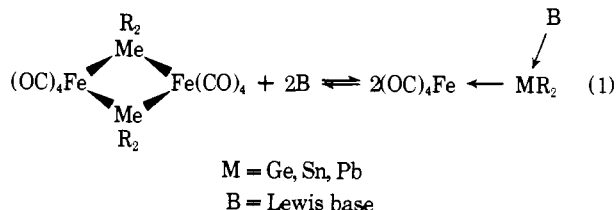# Metal–Metal Bond Cleavage Reactions. The Crystallization and Solid State Structural Characterization of Cadmium Tetracarbonyliron, CdFe(CO)₄

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Abstract: The classical metal–metal bonded oligomer CdFe(CO)₄ (but not the isomorphous HgFe(CO)₄) can be completely cleaved by certain Lewis bases (B) to yield species of the formulation $B_n CdFe(CO)_4$, n = 2 or 3. Reversal of the cleavage allows, for the first time, crystallization of CdFe(CO)₄ and determination of its molecular structure by single-crystal x-ray diffraction. The compound crystallizes from acetone–water in the monoclinic space group C_{2h}^5-$P2_1/n$, with two tetrameric [CdFe(CO)₄]₄ units and four molecules of acetone in a unit cell of dimensions a = 6.292 (4), b = 10.566 (6), c = 26.024 (11) Å, β = 97.80 (3)°. Full-matrix least-squares refinement gave a final value of the conventional R index (on F) of 0.032 for 1602 reflections having $F_o^2 > 3\sigma(F_o^2)$. The molecular structure consists of a nearly planar, centrosymmetric, eight-membered ring of alternating Cd and *cis*-Fe(CO)₄ units. The geometry deviates from D_{4h} square symmetry principally in that two opposite Fe–Cd–Fe angles are 170.25 (5)° and two are 189.85 (5)°. This reflects weak coordination of two cadmium atoms to acetone oxygen atoms (Cd–O = 2.688 (9) Å). The Cd–Fe distances are within experimental error all equal at 2.562 (3) Å. The major distortion from octahedral symmetry about the Fe(CO)₄ groups is a bending of the axial carbonyl ligands toward the ring centroid and away from the vector perpendicular to the plane containing the metal atoms. The result is an average C–Fe–C angle of 154.7 (4)° for these groups. The acetone can be removed from the structure with minimal changes in the metal–metal bonding geometry. The base-induced cleavage reaction for this group 11 system is similar to the previously reported cleavage of [R₂MFe(CO)₄]₂ molecules where M = Ge, Sn, Pb.

The remarkable solid state properties of materials with one-dimensional arrays of interacting metal ions have attracted great interest among chemists as well as physicists.[3] A number of these "chain" compounds exhibit highly anisotropic and sometimes metallic electrical, magnetic, and optical behavior. The ability to control physical characteristics, such as electron transport, by synthesizing "tailor-made" molecules in a rational manner is highly desirable, and represents a crucial challenge to both chemical methodology and solid state theory. Partial oxidation of stacked square-planar complexes[3,4] and the construction of metal-to-metal linked oligomers[5] appear to be two promising ways to maximize the proximity and communication between metal ions in a chain. The second approach is possibly complicated by the nontrivial difficulties of handling and purifying organometallics and coordination compounds with exceedingly high molecular weights. One possible means to circumvent this problem is to employ a variant of the reversible homolytic base cleavage reaction, eq 1, which we reported several years ago.[6] Such an approach

A   B

$$(OC)_4Fe\overset{\underset{Me}{R_2}}{\underset{\underset{R_2}{Me}}{\diamond}}Fe(CO)_4 + 2B \rightleftharpoons 2(OC)_4Fe \longleftarrow MR_2 \quad (1)$$

M = Ge, Sn, Pb
B = Lewis base

might be employed to cleave a crude oligomer, purify the resulting solution, and then to crystallize the pure oligomer by slowly removing the Lewis base.

The compounds CdFe(CO)₄[7a] and HgFe(CO)₄[7b,8] were the first reported examples of metal–metal bonds between main group metals and transition metal carbonyls. It has long been thought (though by no means substantiated) that these relatively intractable materials might have polymeric structures consisting of metal atom chains such as A or B.[9] The cadmium and mercury derivatives were reported to be isostructural by powder diffraction studies.[10] In this paper we report that CdFe(CO)₄ readily undergoes reversible cleavage by certain Lewis bases, and we examine, in detail, the nature of the
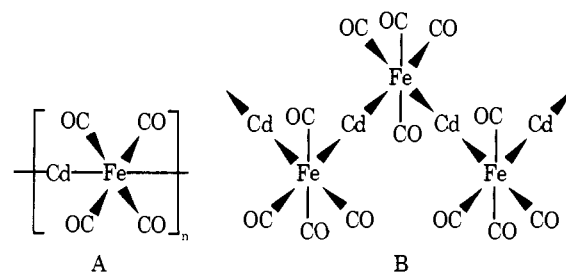
cleaved products in solution. Furthermore, reversing the cleavage allows, for the first time, crystallization of CdFe(CO)₄ and determination of its solid state structure by x-ray diffraction methods. The structure is found to consist of an unusual eight-membered ring. We also report, for comparison in an accompanying article,[11] the solid state molecular structure of the related Lewis base adduct (2,2′-bipyridyl)-cadmium tetracarbonyliron. This molecule exists as a six-membered ring. It is seen that the reversible base cleavage reaction is a viable approach to manipulating certain classes of metal–metal bonded oligomers.

Experimental Section

All operations involving organometallics were carried out under an atmosphere of prepurified nitrogen in Schlenk apparatus or in a glove box. Solvents were thoroughly dried and deoxygenated in a manner appropriate to each, and were distilled under nitrogen immediately prior to use. Elemental analyses were performed by Miss H. Beck, Northwestern University Analytical Services Laboratory, Microtech Laboratory, or Dornis and Kolbe Analytical Laboratory.

Mercury Tetracarbonyliron, HgFe(CO)₄. This was prepared by the procedure of Brauer,[12] and was dried overnight under high vacuum. The infrared spectrum of a Nujol mull was identical with that reported previously.[10]

Diamminecadmium Tetracarbonyliron, (NH₃)₂CdFe(CO)₄. This compound was synthesized by the procedure of Feigl and Krumholz,[7a] and was dried overnight under high vacuum. The infrared spectrum in the C–O stretching region was identical with that reported previously.[13] In addition, bands attributable to coordinated NH₃[14] were observed at 3397 m, 3300 w, 1598 m, 1185 s, and 1160 m cm⁻¹ (Nujol mull).

Bis(pyridine)cadmium Tetracarbonyliron, (py)₂CdFe(CO)₄. Disso-

lution of $(NH_3)_2CdFe(CO)_4$ in an excess of dry pyridine results in the evolution of ammonia and the formation of a yellow solution. Slow evaporation of the pyridine under a stream of nitrogen yields a pale-yellow, microcrystalline solid, which was washed with hexane and dried under high vacuum for 1 h. The yield of $(C_5H_5N)_2CdFe(CO)_4$ was essentially quantitative. The properties are similar to those reported when the compound was prepared via a different route.[13]

Anal. Calcd for $C_{14}H_{10}CdFeN_2O_4$: C, 38.34; H, 2.30; N, 6.39. Found: C, 38.13; H, 2.45; N, 6.42.

Complete IR data (Nujol mull): 1965 s, 1880 vs, br, 1595 m, 1443 m, 1222 m, 1154 w, 1975 m, 1040 m, 1008 m, 755 ms, 700 s cm^{-1}.

Cadmium Tetracarbonyliron, CdFe(CO)$_4$. This was most conveniently prepared by heating solid $(NH_3)_2CdFe(CO)_4$ under high vacuum at 60 °C until bands from coordinated NH_3 were no longer visible in the infrared spectrum (12–24 h). The infrared spectrum of the resulting product was identical with that reported for $CdFe(CO)_4$ prepared by a far less convenient route.[10]

Bis(tetrahydrofuran)cadmium Tetracarbonyliron, (THF)$_2$CdFe(CO)$_4$. This compound was prepared by dissolving $CdFe(CO)_4$ in a moderate excess of THF, and adding two volumes of mesitylene. By very slowly passing nitrogen over the resulting solution, a batch of small crystals was obtained. By further evaporating the supernatant in a stream of nitrogen, a batch of much larger crystals was obtained (up to 5 mm on an edge). The supernatant was next removed by syringe, and the crystals were dried by passing nitrogen over them to remove most of the excess THF, followed by drying overnight in vacuo. Coordination by THF is indicated by the shift of the carbonyl stretching modes to lower frequency.

Anal. Calcd for $C_{12}H_{16}CdFeO_6$: C, 33.95; H, 3.80. Found: C, 33.86; H, 3.53.

Complete IR data (Nujol mull): 2008 ms, 1993 s, 1962 ms, 1950 m. sh, 1939 m, sh, 1916 s, br, 1872 s, 1340 w, 1069 w, 1030 m, 914 w, 872 m cm^{-1}.

(2,2'-Bipyridyl)cadmium Tetracarbonyliron, (bpy)CdFe(CO)$_4$. This was easily prepared either by reaction of a stoichiometric amount of 2,2'-bipyridyl with $(NH_3)_2CdFe(CO)_4$ in benzene or with $CdFe(CO)_4$ in acetone. The microcrystalline orange product was collected by filtration and was dried under high vacuum. A purer product can be obtained by subsequent Soxhlet extraction with benzene. The infrared spectrum of this compound in the C–O stretching region as a Nujol mull was identical with that reported previously.[13]

Anal. Calcd for $C_{14}H_8CdFeN_2O_4$: C, 38.52; H, 1.86; N, 6.42. Found: C, 38.25; H, 1.82; N, 6.53.

Complete IR data (Nujol mull): 1978 s, 1870 vs, br, 1597 w, 1442 w, 1320 w, 1161 w, 1017 w, 762 ms, 741 m cm^{-1}.

(1,10-Phenanthroline)cadmium Tetracarbonyliron, (phen)CdFe(CO)$_4$. The procedure described above was carried out with a stoichiometric quantity of 1,10-phenanthroline to yield, after Soxhlet extraction with benzene, a red-orange microcrystalline solid. The infrared spectrum (Nujol mull) in the C–O stretching region was identical with that reported when the compound was prepared by a different route.[13]

Complete IR data (Nujol mull): 1982 s, 1875 vs, br, 1518 w, 1430 w, 1347 w, 1220 w, 1097 w, 859 w, 838 m, 763 w, 726 w, 610 m cm^{-1}.

Spectroscopic Studies. Infrared spectra were recorded with Beckman IR-5, IR-9, and Perkin-Elmer 267 spectrophotometers. Mulls were prepared in a glove box with dry, degassed Nujol. Solution spectra were recorded in the matched NaCl cells described previously.[15] Solutions were prepared in Schlenk apparatus and were transferred to the cells by syringe. All spectra were calibrated with polystyrene.

Molecular Weight Studies. The apparatus outlined elsewhere[6a,16] was employed for cryoscopic studies in benzene and pyridine. The air stability of (bpy)CdFe(CO)$_4$ allowed confirmatory studies by osmometry.

X-Ray Diffraction Study of CdFe(CO)$_4$. CdFe(CO)$_4$, prepared as described above, was dissolved in an excess of acetone in a three-necked flask under nitrogen. Deionized, degassed water was added to this solution until the first appearance of cloudiness. Nitrogen was then slowly passed over this solution until drops of oil began to form on the bottom of the flask. The nitrogen flow was then decreased to approximately one-tenth the previous rate. When it appeared that no more oil was forming, the nitrogen flow was continued for only a few minutes a day, until crystallization of the oil commenced. Occasionally crystallization would occur too rapidly, producing a solid mass. In this case, more acetone was added to redissolve the compound, and the

process was repeated. Single crystals are best grown by daily increasing the tilt of the flask so that the oil flows away from the crystals already formed. When crystallization was complete, the aqueous phase was removed by syringe, and the crystals were dried by a nitrogen flow. The last traces of solvent were removed under high vacuum. Several of the slightly air-sensitive yellow needles were mounted along the needle axis in capillaries under nitrogen.

All of the crystals exhibited monoclinic symmetry, as determined by Weissenberg and precession photographs. However, each displayed very high mosaicity around the needle axis, ca. 8–10°. More crystals (20) were mounted, and only the twentieth displayed a pattern consisting primarily of spots, although many streaked areas were also present. The mosaicity was ca. 1°. This crystal, of approximate dimensions $0.1 \times 0.2 \times 1.0$ mm, was selected for data collection. (Attempts to cleave the crystals perpendicularly to the needle axis resulted only in shattering of the crystals.) Systematic absences were observed for reflections of the type $0k0$ with k odd. Reflections of the type $h0l$ were normally extinct for $h + l$ odd, with a number of exceptions. High background prohibited unambiguous determination of the space group at this time. However, later analysis of the data indicated that all the film-observed reflections of the $h0l$, $h + l$ odd type actually occurred in regions of equally intense background, and were therefore not observed after background correction. On this basis the correct space group is C_{2h}^5-$P2_1/n$. The cell constants and their standard deviations were obtained from a least-squares refinement of 18 hand-centered reflections, using the Mo $K\alpha_1$ peak at 0.709 300 Å. The unit cell parameters are $a = 6.292$ (4), $b = 10.566$ (6), $c = 26.024$ (11) Å, $\beta = 97.80$ (3)°, $V = 1714$ Å^3.

Owing to the long c axis and high mosaicity of the crystal, data collection necessarily involved the ω scan method. Data were collected in the range $3 \leq 2\theta \leq 45°$ on a Picker FACS-1 computer-controlled four circle x-ray diffractometer equipped with pulse height analyzer and a scintillation counter. Mo $K\alpha_1$ radiation was monochromatized using the 002 face of mosaic graphite. A takeoff angle of 2.7° was used, with fully opened apertures, and the counter placed 31 cm from the crystal. The scan range was from -1 to $1°$ in ω from the peak center at a rate of $1°$/min, with background counts of 20 s at each end of the scan. The intensities of seven standard reflections were monitored every 100 reflections and showed on the average only a 1% decrease in intensity during data collection; no correction for decomposition was deemed necessary. The minimum backgrounds were approximately 10% of the total peak intensity and the average was about 40%. All data were possessed as described previously;[17] a value of 0.04 was used for p in the estimation of $\sigma(F_o^2)$. A total of 2664 reflections was processed, with 1602 unique data having $F_o^2 > 3\sigma(F_o^2)$ used in initial refinements on F_o; 2254 unique data were used in the final refinements on F_o^2.

In refinements on F_o, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively, and w, the weight, is $4F_o^2/\sigma^2(F_o^2)$. The agreement indices are $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$. In refinements on F_o^2, the function minimized was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. The agreement indices in this case are $R = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2$ and $R_w = [\Sigma w|F_o^2 - F_c^2|^2/\Sigma w F_o^4]^{1/2}$. Atomic scattering factors and anomalous dispersion terms were taken from the new tabulation.[18]

After correction for absorption (range of transmission coefficients 0.375–0.650), we located the positions of the two independent cadmium atoms on an origin-removed sharpened Patterson map. Ensuing difference Fourier syntheses clearly revealed the positions of all remaining nonhydrogen atoms, including an acetone of solvation. Isotropic refinement of this model converged to values of R and R_w (on F) of 0.068 and 0.080. A cycle of anisotropic refinement led to values of 0.035 and 0.040. A difference Fourier map, based on inner data, led to the locations of all six hydrogen atoms on the acetone molecule. These positions were then idealized. Two further cycles were now carried out on F_o^2. Final agreement indices on F_o^2 are $R = 0.056$ and $R_w = 0.088$. The error in an observation of unit weight was 1.23 e^2. The corresponding R indices on F_o for those reflections having $F_o^2 > 3\sigma(F_o^2)$ are 0.032 and 0.037, respectively. A final difference Fourier map revealed no peaks greater than 0.75 (17) e/Å^3. The positional and thermal parameters obtained from the last cycle of least-squares refinement are given in Table 1, along with their standard deviations as estimated from the inverse matrix. The standard deviation of a single observation as estimated from agreement among presumed chemically equivalent bond distances agrees well with that estimated

Table I. Positional and Thermal Parameters for the Atoms of $[CdFe(CO)_4]_4 \cdot 2C_3H_6O$

| ATOM	x (Å)	Y	Z	B_{11} OR B, Å^2	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
CO(1)	0.42005(11)	0.552641(61)	0.596848(28)	22.85(21)	5.87(7)	1.42(1)	-2.89(9)	1.13(4)	0.14(2)
CO(2)	0.36459(10)	0.293779(63)	0.506181(24)	19.83(20)	8.19(8)	0.87(1)	0.01(9)	1.50(4)	-0.29(2)
FE(1)	0.26736(17)	0.32806(111	0.597493(44)	12.50(33)	5.75(13)	0.78(2)	-0.74(15)	0.72(6)	0.08(4)
FE(2)	0.46592(18)	0.21908(11)	0.418923(45)	14.32(34)	5.50(12)	0.87(2)	-0.81(15)	0.90(7)	-0.25(4)
C(1)	-0.3169(14)	0.3324(9)	0.09315(36)	18.6(27)	7.9(11)	1.20(17)	-3.5(13)	1.53(52)	-0.51(33)
C(2)	-0.3020(14)	0.1401(9)	0.16025(37)	19.2(28)	10.7(12)	1.06(18)	3.5(13)	0.24(56)	0.32(35)
C(3)	0.0455(14)	0.1983(9)	0.11472(32)	15.8(28)	9.0(10)	0.80(15)	-0.3(13)	0.80(50)	-0.50(32)
C(4)	-0.4619(13)	0.0964(8)	0.06246(32)	15.4(26)	6.6(9)	0.88(15)	-1.0(12)	1.12(52)	0.24(29)
C(5)	0.3866(14)	0.0637(10)	0.43510(36)	16.8(26)	8.6(12)	1.40(18)	0.9(14)	-0.89(54)	-0.59(37)
C(6)	-0.4489(16)	0.1836(9)	0.35839(42)	29.7(34)	8.6(11)	1.50(21)	-0.6(15)	0.60(66)	-0.70(39)
C(7)	-0.2740(13)	0.2150(8)	0.45531(36)	10.2(26)	7.8(10)	1.58(18)	-0.9(12)	1.62(56)	-0.27(34)
C(8)	0.2098(14)	0.2876(8)	0.39661(34)	18.1(29)	7.3(10)	1.13(16)	-0.8(13)	1.08(55)	-0.24(32)
C(9)	0.3177(20)	0.4315(10)	0.28147(47)	47.2(46)	9.4(12)	1.57(23)	0.5(18)	-0.3(8)	-0.91(43)
C(10)	0.1144(25)	0.3591(16)	0.24872(54)	70.0(67)	22.1(23)	2.21(30)	-16.9(31)	1.5(12)	-1.22(65)
C(11)	0.4333(22)	0.4658(15)	0.21737(56)	49.8(53)	24.3(25)	2.53(31)	-8.6(29)	2.9(10)	-1.5(67)
O(1)	-0.3682(11)	0.4374(7)	0.09265(34)	34.9(25)	5.8(7)	3.40(21)	3.1(11)	1.64(56)	-0.09(31)
O(2)	-0.3493(12)	0.1250(9)	0.20109(27)	41.5(28)	22.1(13)	0.96(13)	4.8(14)	2.98(50)	0.91(32)
O(3)	0.2229(11)	0.2214(7)	0.12887(28)	18.3(21)	14.1(9)	2.02(15)	-0.2(11)	0.45(44)	-1.36(30)
O(4)	0.3851(9)	0.0513(6)	0.04169(24)	18.0(19)	10.6(8)	1.36(12)	-5.0(10)	0.32(39)	-0.79(24)
O(5)	0.1530(11)	0.4617(7)	0.05473(31)	38.4(26)	6.4(8)	2.83(19)	4.7(11)	-0.11(54)	-0.60(30)
O(6)	-0.3980(14)	0.1569(8)	0.31903(31)	55.4(34)	19.2(12)	1.46(15)	2.7(16)	4.00(58)	-1.94(35)
O(7)	-0.1044(9)	0.2035(7)	0.47875(26)	13.1(19)	13.9(9)	1.78(14)	-1.5(10)	0.27(41)	-0.36(28)
O(8)	0.0439(10)	0.3281(7)	0.38031(26)	18.3(21)	14.4(9)	1.64(13)	2.8(11)	0.27(42)	0.44(28)
O(9)	0.3853(16)	0.4579(8)	0.30469(33)	77.5(43)	17.1(12)	1.39(15)	-9.1(18)	-2.63(66)	-0.26(36)
H(1)	0.033	0.365	0.277	9.9					
H(2)	0.035	0.393	0.218	9.9					
H(3)	0.147	0.273	0.243	9.9					
H(4)	0.472	0.391	0.200	9.4					
H(5)	0.344	0.517	0.193	9.4					
H(6)	0.560	0.512	0.230	9.4					

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. The quantities given in the table are the thermal coefficients $\times 10^3$.

from the inverse matrix. Root-mean-square amplitudes of vibration are given in Table II.[19] The final values of $10|F_o|$ and $10|F_c|$ in electrons will appear in the microfilm edition.[19] A reflection for which the measured intensity was less than zero is denoted by a negative value of F_o.

X-Ray Powder Diffraction Studies of CdFe(CO)$_4$ and HgFe(CO)$_4$. X-ray powder diffraction patterns were recorded photographically on a Picker 6147 x-ray diffractometer using filtered Cu Kα radiation. Samples were sealed in 0.5-mm glass capillaries under nitrogen and rotated during exposure to ensure average random orientation of the crystallites.

Results

Syntheses. The reaction of mercuric sulfate with iron pentacarbonyl to produce the yellow, insoluble complex HgFe(CO)$_4$ has been known for almost 50 years.[8]

$$Fe(CO)_5 + HgSO_4 + H_2O$$
$$\rightarrow HgFe(CO)_4 + H_2SO_4 + CO_2 \quad (2)$$
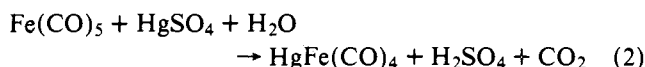
In the presence of Lewis bases such as ammonia and pyridine, cadmium salts and iron pentacarbonyl yield complexes of the stoichiometry B$_2$CdFe(CO)$_4$.[7]

$$Fe(CO)_5 + Cd(OAc)_2 + 2NH_3 + H_2O$$
$$\rightarrow (NH_3)_2CdFe(CO)_4 + CO_2 + 2HOAc \quad (3)$$
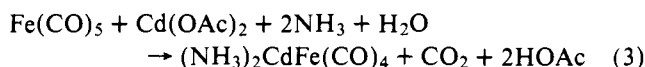
The B = NH$_3$ complex can be prepared on a large scale and is a useful precursor for new as well as known complexes with stronger and/or less volatile bases as in the equation

$$(NH_3)_2CdFe(CO)_4 + 2B \rightarrow B_2CdFe(CO)_4 + 2NH_3 \quad (4)$$
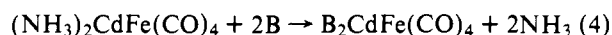
$$B = \text{pyridine, tetrahydrofuran}$$

$$2B = 2,2'\text{-bipyridyl, 1,10-phenanthroline}$$

Removal of the NH$_3$ from (NH$_3$)$_2$CdFe(CO)$_4$ was most conveniently accomplished, in our hands, by heating the solid in vacuo. The product, CdFe(CO)$_4$, is a pale yellow powder, insoluble in noncoordinating solvents. It and the mercury analogue have nearly identical infrared spectral parameters.[9,10] By x-ray powder diffraction techniques we have confirmed the earlier report[10] that CdFe(CO)$_4$ and HgFe(CO)$_4$ are isomorphous.

Cleavage Reactions and Base Adducts of MFe(CO)$_4$. Though it is totally insoluble in noncoordinating solvents such as benzene and hexane, CdFe(CO)$_4$ (but not HgFe(CO)$_4$) dissolves in a variety of coordinating solvents. In cases where the solvent is a sufficiently strong Lewis base, adducts of the stoichiometry B$_2$CdFe(CO)$_4$ can be isolated (vide supra). In cases where B is a weaker and/or more volatile base such as acetone, it is possible to recover the uncomplexed CdFe(CO)$_4$ by pumping under high vacuum. X-ray powder diffraction and infrared spectral studies indicate that the recovered compound is identical with the starting CdFe(CO)$_4$. As will be seen, it is possible to remove the acetone in such a manner as to yield single crystals of sufficient quality for diffraction studies. The exact nature of the species resulting from dissolution of CdFe(CO)$_4$ in coordinating solvents is of great interest in understanding both metal-metal bond cleavage reactions as well as the reverse metal-metal bond formation reactions. The problem was investigated by cryoscopy and infrared spectroscopy.

Table III presents solution molecular weight data for py$_2$CdFe(CO)$_4$ and (bpy)CdFe(CO)$_4$ in benzene, and for CdFe(CO)$_4$ dissolved in pyridine. In each case the complex is found to be predominantly if not exclusively monomeric. A conservative estimate of the error in the derived molecular weights is ±10%. Solution infrared spectra (Figure 1) of the

Table III. Solution Infrared and Molecular Weight Data

Compd[a]	Solvent	C–O stretching frequencies[b]	Concn, m	Mol wt[c]
(bpy)CdFe(CO)$_4$	Benzene	1982 vs, 1922 s, 1894 ms, 1897 sh	0.0057	1243 (436)
			0.0084	1445 (436)
(py)$_2$CdFe(CO)$_4$	Benzene	1991 s, 1918 s, 1912 sh	0.0081	433 (438)
			0.0363	486 (438)
CdFe(CO)$_4$	Pyridine	1976 s, 1908 vs, 1886 sh	0.0118	320 (280)
(THF)$_2$CdFe(CO)$_4$	Benzene	2005 s, 1975 vs		
CdFe(CO)$_4$	THF	1998 s, 1930 vs, 1911 sh		
CdFe(CO)$_4$	Acetone	2007 s, 1938 vs		
[(py)(C$_6$H$_5$)$_2$Sn]Fe(CO)$_4$[d]	Pyridine	2021 s, 1934 sh, 1907 vs		
[(py)(t-C$_4$H$_9$)$_2$Sn]Fe(CO)$_4$[d]	Pyridine	2005 s, 1896 vs		
CdFe(CO)$_4$[e]		2032 s, 2012 m, 1972 ms, 1961 ms		
		1946 m, 1920 s,br, 1840 w,sh		

[a] bpy = 2,2′-bipyridyl; py = pyridine; THF = tetrahydrofuran. [b] In cm^{-1}; m = medium, s = strong, sh = shoulder. [c] Value in parentheses is that calculated for a monomer. [d] From ref 6a. [e] Nujol mull.

various CdFe(CO)$_4$ adducts reveal an appreciable lowering of the ν_{CO} absorptions compared with uncomplexed CdFe(CO)$_4$ in the solid state (Figure 1A). Data are compiled in Table III. The solution band patterns are in excellent accord with the LFe(CO)$_4$ molecules having approximately C_{3v} (trigonal bipyramidal) molecular structures.[20] Indeed, the correspondence to the spectra of the BR$_2$MFe(CO)$_4$ adducts derived from cleavage reaction 1 is very close.[6] The latter compounds were proposed to have structure C,[6,21] and the present results lead us to assign structure D to the CdFe(CO)$_4$

B
OC
\+
R$_2$M—Fe—CO
OC   CO

OC
+
B$_n$Cd—Fe—CO
OC   CO

C   D
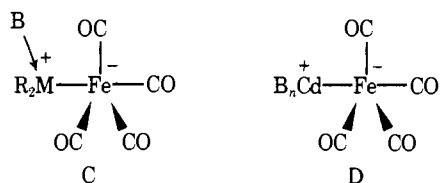
adducts. There is no evidence of Fe(CO)$_4$$^{2-}$ ($\nu_{CO} \approx$ 1780 cm^{-1}),[22] even for very concentrated solutions in high dielectric[6a,23] solvents. Two other details are worth noting. First, the C–O stretching frequencies are somewhat lower in the cadmium system than for the group IV complexes (Table III). This appears to reflect greater negative charge on the –Fe(CO)$_4$ moiety. This phenomenon can also be seen in (C$_6$H$_5$)$_3$SiFe(CO)$_4$$^-$ (ν_{CO} = 2007, 1906, and 1880 cm^{-1} in THF)[24] and in (C$_6$H$_5$)$_3$SnFe(CO)$_4$$^-$ (ν_{CO} = 2001, 1923, 1897, and 1877 cm^{-1} as a Nujol mull).[25] The infrared spectrum of HFe(CO)$_4$$^-$ (C_{3v} symmetry[26]) is similar (2008, 1910, and 1848 cm^{-1} as a Nujol mull[22a]). The second feature of note for the B$_n$CdFe(CO)$_4$ compounds is that the ν_{CO} energies decrease further in coordinating solvents (Table III, e.g., compare py$_2$CdFe(CO)$_4$ in pyridine and in benzene). A reasonable explanation for this observation is that n can be either two or three. The n = 3 compounds are of course isoelectronic with the BR$_2$MFe(CO)$_4$ species.

The Crystal Structure of CdFe(CO)$_4$. Slow evaporation of solutions of CdFe(CO)$_4$ in acetone–water mixtures yielded pale yellow needles. The bulk samples analyzed for CdFe(CO)$_4$;[27] solid state infrared spectra and x-ray diffraction powder patterns were identical with those of the samples of CdFe(CO)$_4$ prior to crystallization. A large number of crystals (see Experimental Section) was examined before one suitable for data collection was found. The morphology of the data crystal was indistinguishable from that of the other crystals surveyed. The photographic x-ray diffraction patterns (oscillation, Weissenberg, precession) of the crystal selected were identical with those of the 20 other crystals examined, with two minor differences. First, the lattice parameters of the data crystal obtained by centering 16 reflections on the diffracto-
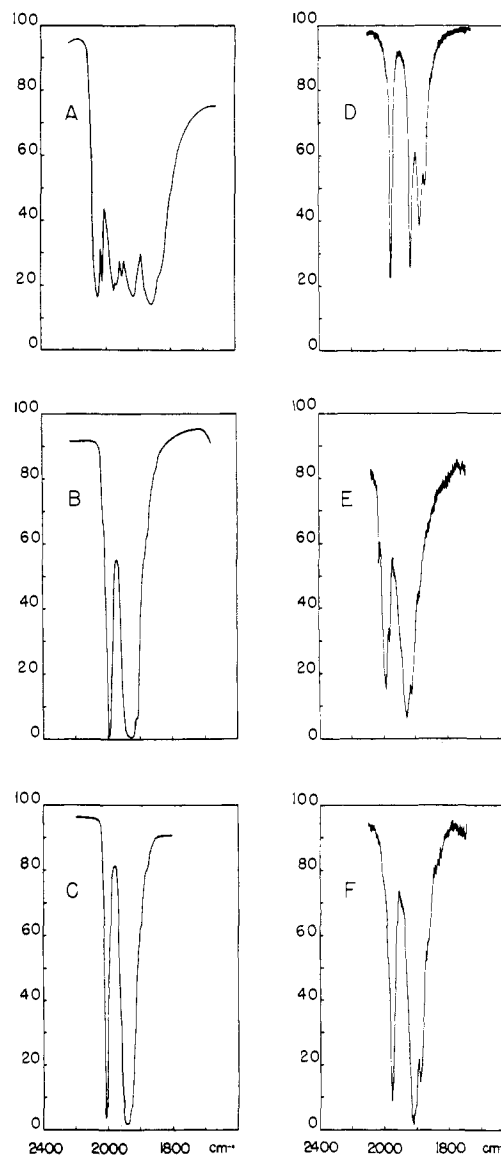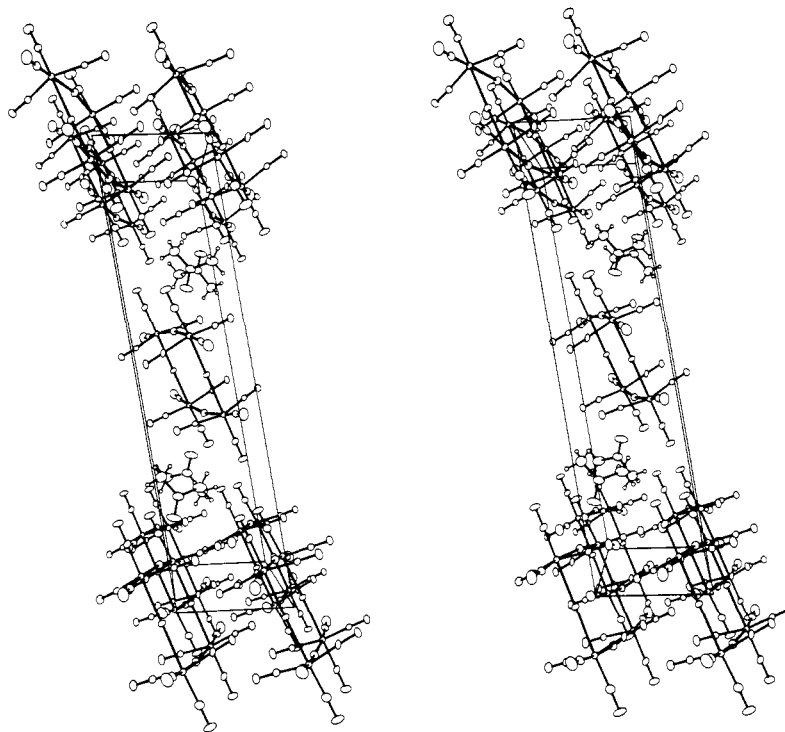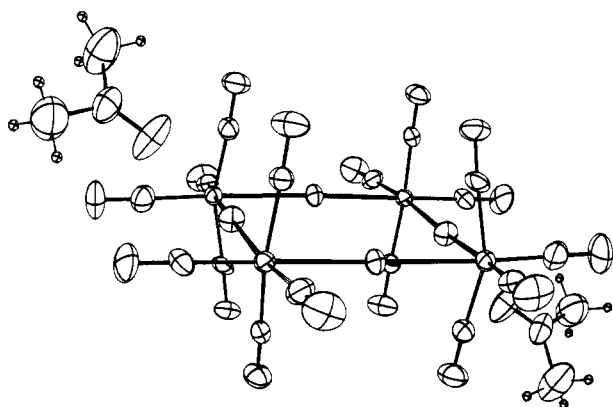

Figure 1. Infrared spectra in the C–O stretching region of (A) CdFe(CO)$_4$ as Nujol mull; (B) CdFe(CO)$_4$ in THF; (C) CdFe(CO)$_4$ in acetone; (D) (bpy)CdFe(CO)$_4$ in benzene; (E) py$_2$CdFe(CO)$_4$ in benzene; (F) py$_2$CdFe(CO)$_4$ in pyridine.

meter were a = 6.292 (4), b = 10.566 (6), c = 26.024 (11) Å, and β = 97.80 (3)°, whereas the axial lengths for the lower quality crystals varied somewhat from crystal to crystal, but

Figure 2. Stereoscopic view of the packing of [CdFe(CO)4]4·2C3H6O in the unit cell. The *x* axis is directed to the left of the page, the *y* axis into the page, and the *z* axis down the page.

Figure 3. Perspective view of [CdFe(CO)4]4·2C3H6O. The 40% probability vibrational ellipsoids are shown.

Table IV. Important Nonbonded Contacts within the [CdFe(CO)4]4 Ring

Contact	Distance, Å	Contact	Distance, Å
Cd(1)–C(3)	2.788 (9)	Cd(2)–C(3)	2.900 (9)
Cd(1)–C(4)	2.910 (8)	Cd(2)–C(4)	2.921 (8)
Cd(1)–C(7)	2.894 (9)	Cd(2)–C(7)	2.904 (8)
Cd(1)–C(8)	2.861 (9)	Cd(2)–C(8)	2.886 (9)

parameters we obtain are not in agreement with those of ref 10, which were derived from powder data.

The solid state structure of CdFe(CO)4 determined from the crystal described above consists of nearly planar, centrosymmetric eight-membered rings. A stereoscopic packing diagram is shown in Figure 2. Intermolecular contacts are normal, the shortest being between acetone oxygen atoms and cadmium atoms (2.688 (9) Å). Other nonbonded contacts are presented in Table IV.

Perspective views of an individual [CdFe(CO)4]4 molecule along with the atom numbering scheme and important metrical data are shown in Figures 3, 4, and 5. Each ring consists of an alternating cycle of iron and cadmium atoms. The iron atoms are coordinated to four carbonyl groups and to two cadmium atoms in a slightly distorted octahedral arrangement. The valence angles about cadmium are only slightly perturbed from linear. Also present in the unit cell of this particular crystal are two acetone molecules per tetramer. The oxygen atoms of the acetone molecules are weakly coordinated to two opposite cadmium atoms of the ring. The positions of the acetone molecules in the unit cell (Figures 2, 3, 4) are such that only nonbonded contacts along the *a* and *c* axes would be appreciably reduced by their removal. This is consistent with the above-noted contraction along these axes. The *y* direction is determined primarily by CO–CO contacts and should be less sensitive to solvent removal.

Selected bond angles and distances are given in Table V. The eight-membered ring is essentially planar, and no metal atom deviates from the best least-squares plane by more than 0.109
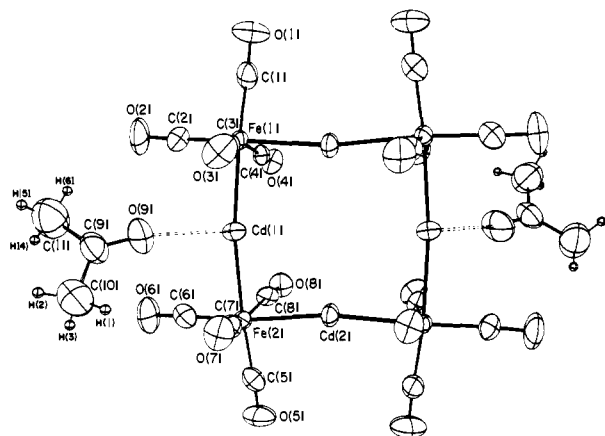
averaged (±0.02 Å) near *a* = 6.19, *b* = 10.58, and *c* = 25.78 Å. As will be seen, the slight expansion of the *a* and *c* axes in the data crystal reflects the presence and positions in the unit cell of two solvent molecules (acetone). The data crystal also displayed considerably less mosaicity than did the other crystals. These displayed lines rather than spots on the Weissenberg photographs, and typically mosaicities of ca. 8–10° were observed about the *a* axis. These results strongly suggest that all samples of CdFe(CO)4 cocrystallize with acetone; when the acetone is partially or completely removed by drying there occurs a slight shrinking of the axes most affected by a change in the filling of the unit cell (*a* and *c*, vide infra) and an increase in the mosaic spread. The analytical data indicate that the bulk of the material had already undergone solvent loss. From these studies it is reasonable to conclude that the structure of the metal–metal bonded framework in the data crystal, which still contains two molecules of acetone in the unit cell, differs only in a minor way (which can be predicted with considerable assurance) from the other crystalline and powder samples of CdFe(CO)4. However, the space group and unit cell

Figure 4. View of [CdFe(CO)₄]₄·2C₃H₆O perpendicular to the molecular plane. The 50% vibrational ellipsoids are shown. The atom numbering scheme applies to the entire centrosymmetric molecule.
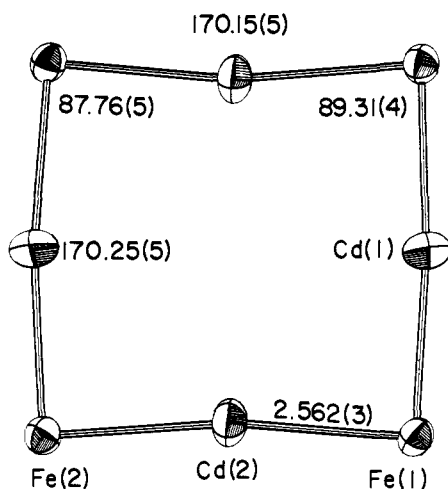

Figure 5. Important bond distances and angles in the eight-membered ring of metals of [CdFe(CO)₄]₄·2C₃H₆O.

(1) Å (Table VI). Within experimental error the Cd–Fe distances are all equal at 2.562 (3) Å. This value is shorter than distances reported for transition metal–cadmium complexes where additional Lewis bases are also coordinated to cadmium,[8] viz. BCd[Mn(CO)₅]₂, B = 2,2':6'2''-terpyridyl (2.766 (4), 2.799 (5) Å);[28a] B = diglyme (2.714 (2), 2.707 (2) Å);[28b] B = 2,2'-bipyridyl (2.686 (3), 2.680 (3) Å);[28c] B = 1,10-phenanthroline (2.687 (4), 2.675 (4) Å);[28c] and [(bpy)-CdFe(CO)₄]₃, 2.640 (7) Å.[11] The coordination about iron is only slightly distorted from octahedral, with Cd–Fe–Cd bond angles of 87.76 (5) and 89.31 (4)°. These data can be compared with analogous angles of 91.5 (2)° in cis-(Cl₃Ge)₂-Ru(CO)₄,[29] 96.0° in cis-[(C₆H₅)₃Sn]₂Fe(CO)₄,[30a] and of 88.2 (2)° in the five-membered ring [(η⁵-C₅H₅)Co(CO)]₂-(GeCl₂)₂Fe(CO)₄.[31] The angles of course decrease in more constricted four-membered ring systems such as [(CH₃)₂-SnFe(CO)₄]₂[32] (76.3 (4) and 77.4 (3)°) and (CH₃)₄-Sn₃[Fe(CO)₄]₄[33] (76.8 (5)–78.9 (5)°). The same angle increases in systems with less electronegative main group substitutents, as in [(CH₃)₃Si]₂Fe(CO)₄ (111.8 (2)°)[30b] and [(bpy)CdFe(CO)₄]₃ (94.78 (14)–102.04 (16)°).[11] In the molecular plane, the C–Fe–C angles average 97.8 (5)°, and the average cis C–Fe–Cd angles are 88.1 (3) (Fe(1)) and 85.5 (8)° (Fe(2)). The trans C–Fe–Cd angles are also in accord with essentially octahedral coordination, ranging from 173.4 (4) to 177.2 (3)°. The only significant distortion from octahedral geometry at iron involves closing of the trans C–Fe–C

Table V. Selected Distances (Å) and Angles (deg) in [CdFe(CO)₄]₄·2C₃H₆O

Bond Distances

Cd(1)–Fe(1)	2.561 (2)	Fe(1)–C(3)	1.769 (9)	C(1)–O(1)	1.155 (10)	C(7)–O(7)	1.162 (9)
Cd(1)–Fe(2)	2.565 (2)	Fe(1)–C(4)	1.787 (9)	C(2)–O(2)	1.153 (10)	C(8)–O(8)	1.153 (10)
Cd(2)–Fe(1)	2.559 (2)	Fe(2)–C(5)	1.783 (11)	C(3)–O(3)	1.153 (9)	C(9)–C(10)	1.489 (16)
Cd(2)–Fe(2)	2.565 (2)	Fe(2)–C(6)	1.771 (11)	C(4)–O(4)	1.142 (9)	C(9)–C(11)	1.485 (17)
Fe(1)–C(1)	1.776 (10)	Fe(2)–C(7)	1.776 (9)	C(5)–O(5)	1.145 (11)	C(9)–O(9)	1.181 (13)
Fe(1)–C(2)	1.779 (10)	Fe(2)–C(8)	1.791 (9)	C(6)–O(6)	1.149 (11)	Cd(1)–O(9)	2.688 (9)

Bond Angles

Cd(1)–Fe(1)–Cd(2)	89.31 (4)	Cd(1)–Fe(2)–C(5)	175.5 (3)	C(2)–Fe(1)–C(4)	95.9 (4)	Fe(2)–C(5)–O(5)	176.2 (8)
Cd(1)–Fe(2)–Cd(2)	87.76 (5)	Cd(1)–Fe(2)–C(6)	86.1 (3)	C(3)–Fe(1)–C(4)	154.5 (4)	Fe(2)–C(6)–O(6)	177.6 (9)
Fe(1)–Cd(1)–Fe(2)	170.25 (5)	Cd(1)–Fe(2)–C(7)	81.4 (3)	C(5)–Fe(2)–C(6)	98.2 (4)	Fe(2)–C(7)–O(7)	175.3 (8)
Fe(1)–Cd(2)–Fe(2)	170.15 (5)	Cd(1)–Fe(2)–C(8)	80.0 (3)	C(5)–Fe(2)–C(7)	96.8 (4)	Fe(2)–C(8)–O(8)	176.7 (8)
Cd(1)–Fe(1)–C(1)	173.4 (3)	Cd(2)–Fe(2)–C(5)	87.9 (3)	C(5)–Fe(2)–C(8)	100.5 (4)	C(10)–C(9)–C(11)	116.7 (11)
Cd(1)–Fe(1)–C(2)	88.3 (3)	Cd(2)–Fe(2)–C(6)	173.7 (3)	C(6)–Fe(2)–C(7)	95.8 (4)	C(10)–C(9)–O(9)	121.4 (12)
Cd(1)–Fe(1)–C(3)	77.8 (3)	Cd(2)–Fe(2)–C(7)	81.8 (3)	C(6)–Fe(2)–C(8)	99.5 (4)	C(11)–C(9)–O(9)	121.8 (12)
Cd(1)–Fe(1)–C(4)	82.0 (3)	Cd(2)–Fe(2)–C(8)	80.9 (3)	C(7)–Fe(2)–C(8)	154.9 (4)	Cd(1)–O(9)–C(9)	163.1 (8)
Cd(2)–Fe(1)–C(1)	85.0 (3)	C(1)–Fe(1)–C(2)	97.5 (4)	Fe(1)–C(1)–O(1)	176.9 (9)	Fe(1)–Cd(1)–O(9)	94.5 (2)
Cd(2)–Fe(1)–C(2)	177.2 (3)	C(1)–Fe(1)–C(3)	98.2 (4)	Fe(1)–C(2)–O(2)	177.0 (9)	Fe(2)–Cd(1)–O(9)	95.2 (2)
Cd(2)–Fe(1)–C(3)	82.0 (3)	C(1)–Fe(1)–C(4)	100.4 (4)	Fe(1)–C(3)–O(3)	174.8 (8)		
Cd(2)–Fe(1)–C(4)	82.4 (3)	C(2)–Fe(1)–C(3)	98.9 (4)	Fe(1)–C(4)–O(4)	176.4 (7)		

Table VI. Best Weighted Least-Squares Planes

Atom[a]	Distance	Atom	Distance
(a) For [CdFe(CO)$_4$]$_4$, as Defined by the Metal Atoms			
(i) Equation (monoclinic coordinates): $5.462x - 3.075y + 7.306z$			
$= 4.846$			
(ii) Deviations of Atoms from Best Plane, Å			
Cd(1)	0.109 (1)	O(1)	0.011
Cd(2)	−0.060 (1)	O(2)	−0.054
Fe(1)	−0.030 (1)	O(5)	0.420
Fe(2)	0.085 (1)	O(6)	0.290
C(1)	−0.028	C(9)	−2.528
C(2)	−0.048	C(10)	−3.509
C(5)	0.248	C(11)	−2.324
C(6)	0.217	O(11)	−1.924
(b) For the Acetone Molecule, as Defined by the Nonhydrogen Atoms			
(i) Equation (monoclinic coordinates): $3.132x - 9.098y + 0.914z$			
$= -2.684$			
(ii) Deviations of Atoms from Best Plane, Å			
C(9)	−0.008 (2)	H(2)	−0.582
C(10)	0.002 (2)	H(3)	0.885
C(11)	0.002 (2)	H(4)	0.785
O(9)	0.003 (2)	H(5)	−0.766
H(1)	−0.284	H(6)	−0.009
The dihedral angle between the two planes is 43.6°			

[a] The symmetry related atoms have deviations of equal magnitude, but opposite sign, and have been omitted.

angles so that the axial carbonyl groups bend toward the center of the ring (154.4 (4) and 154.9 (4)°). This effect is not uncommon and was observed in [(CH$_3$)$_2$SnFe(CO)$_4$]$_2$[32] (156 (4) and 165 (4)°), [(η^5-C$_5$H$_5$)Co(CO)]$_2$(GeCl$_2$)$_2$Fe(CO)$_4$[31] (172.0 (1)°), and in (CH$_3$)$_4$Sn$_3$[Fe(CO)$_4$]$_4$[33] (158 (2)–165 (2)°). The distortion is far more extreme in, [(bpy)-CdFe(CO)$_4$]$_3$[11] where the analogous angles average 139.5 (25)°. Similarly the angle is 141.2 (2)° in [(CH$_3$)$_3$Si]$_2$ Fe(CO)$_4$;[30b] these latter angles appear to reflect the reduced electronegativity of the main group functionality.[11] Within experimental error, average Fe–C (1.779 (8) Å) and C–O (1.152 (6) Å) distances cis and trans to cadmium atoms are identical. The average Fe–C–O angle is 176.3 (9)°.

The coordination about cadmium is only slightly distorted from linear, with Fe–Cd–Fe angles of 170.25 (5) and 189.85 (5)°. There is less distortion from linearity about the group II metal in the complexes Zn[Co(CO)$_4$]$_2$[34] (177.8 (1)°), Hg[Co(CO)$_4$]$_2$[35] (178.4 (3)°), Hg[Fe(CO)$_2$(NO)P(C$_2$-H$_5$)$_3$]$_2$[36] (180.0 (0)°), and Hg[Co(CO)$_3$(P(n-C$_4$H$_9$)$_3$)]$_2$[37] (180.0 (0)°) where no Lewis base is coordinated to the main group metal. However, the corresponding angles in the above-mentioned BCd[Mn(CO)$_5$]$_2$ derivatives,[28] B = terpyridyl, diglyme, bipyridyl, and phenanthroline, are all in the range 128–136°. In [CdFe(CO)$_4$]$_4$ two opposite cadmium atoms are displaced away from the ring centroid toward the acetone groups and the other two cadmium atoms are displaced toward the ring centroid. The slight displacement toward the acetone molecule suggests that the coordination is weak. Further substantiation is provided by the magnitude of the acetone O–Cd distance (2.688 (9) Å), which is longer than O–Cd distances in urea (2.18–2.34 Å)[38] and peptide (2.407 (5) Å)[39] complexes. The rather obtuse acetone C–O–Cd angle (163.1 (8)°) is also in accord with weak coordination, since values in the range 128–136° are expected in cases of strong interaction.[38] That two cadmium atoms bend away from the ring centroid toward oxygen atoms of the acetone group while the other two cadmium atoms bend inward essentially to the same degree apparently reflects the propensity of the system to maintain the Cd–Fe–Cd angle near 90°. The structure of

the acetone molecule (Table V) is near to that found in free acetone,[40] i.e., C–C, 1.489 (16) vs. 1.517 (3) Å;[40] C–O, 1.153 (10) vs. 1.210 (4) Å;[40] ∠C–C–C, 116.7 (11) vs. 116.0 (2)°; the C–O and one C–H bond of each methyl group are eclipsed.[40]

Discussion

The results of this study provide the first evidence that the base-induced, metal–metal bond homolytic cleavage reaction can be generalized beyond the group IV metal–iron derivatives of eq 1.[6] It is applicable as well to oligomers containing group II metals. The two chemical systems have certain characteristics in common. In the [R$_2$MFe(CO)$_4$]$_2$ series, the propensity for cleavage decreases as the Periodic Table is descended, i.e., M = Ge > Sn ≥ Pb.[6a] Similarly, in the present investigation, CdFe(CO)$_4$ was completely cleaved with relatively weak bases while no reaction was observed with HgFe(CO)$_4$. It has already been established that fragments such as ZnFe(CO)$_4$ are present in aqueous solution,[41] though (NH$_3$)$_3$ZnFe(CO)$_4$ has not yet been freed of base. Thus, the tendency for cleavage Zn ≥ Cd > Hg appears operative. A similar trend has been observed in "ionization" (heterolytic cleavage) reactions of M′–M″–M′ species, M′ = a transition metal functionality and M″ = Zn, Cd, Hg.[8,42] The driving force for the base-induced cleavage probably reflects both the ionic character of the metal–metal bonds as well as the stability of the resulting B$_n$M″Fe(CO)$_4$ species. This stability is also in accord with the tendency of the particular M″ metal to expand its coordination number beyond two. Precedent for these trends is found in the chemical behavior of the corresponding organometallics, R$_2$M″.[43] Here ease of hydrolysis and of Lewis base adduct formation decrease in the order Zn ≥ Cd ≫ Hg. This has been ascribed to the polarity of the R–M bond, which in turn reflects the electronegativity of M″.[43] For the group IV R$_4$M organometallics, this trend is in essentially the opposite direction,[44] which suggests considerations such as nonbonded repulsions,[6a] ring strain,[6a,45] and multiple BR$_2$M = Fe(CO)$_4$ bonding[21a] (E) may also be important in the scission of

E   F

Q = group II or IV metal
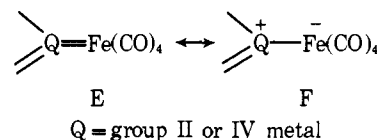
[R$_2$MFe(CO)$_4$]$_2$ compounds. The difference in reactivity with respect to cleavage among the group IV metals[6] is not nearly as great as observed here among the group II metals.
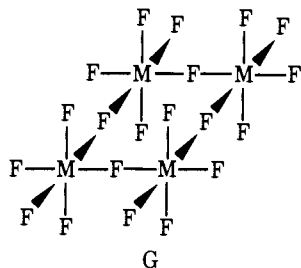
The group IV and group II cleavage products differ somewhat in properties. The lower C–O stretching frequencies recorded for B$_n$CdFe(CO)$_4$ species are indicative of greater negative charge on the tetracarbonyliron fragment, and possibly a greater contribution from the ionic resonance hybrid F. Interestingly, there is no evidence in any of the systems investigated of further cleavage to produce Fe(CO)$_4^{2-}$. However, for B$_n$CdFe(CO)$_4$ there is infrared spectral evidence that, for some Lewis bases, n can be larger than 2 (presumably 3).

The long range goal of the work described in this article is to investigate the utility of the base-induced cleavage reaction and its reverse to crystallize oligomeric metal–metal bonded compounds. This technique allowed crystallization of CdFe(CO)$_4$, and we discovered that the structure, long believed to be polymeric, actually consists of an approximately D_{4h} eight-membered square of alternating Cd and cis-Fe(CO)$_4$ units. Some minor distortion of the square arises from weak coordination of two cadmium atoms by two acetone molecules in the unit cell. It can be shown that the acetone-free derivative has essentially the same configuration, but is probably undistorted. The distortion imparted by the acetone
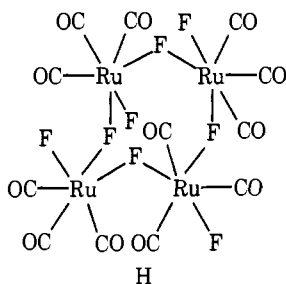
coordination is most likely a reasonably accurate "snapshot" of the reaction coordinate for the initial stage of the cleavage, which ultimately fractures the tetramer into (acetone)$_n$-CdFe(CO)$_4$ units.

In the accompanying paper[11] we discuss in more detail those factors which influence the shapes of oligomeric metal–metal bonded molecules. We note here that there is considerable precedent outside of the chemistry of metal–metal bonds for the square eight-membered ring observed in [CdFe(CO)$_4$]$_4$. A number of pentavalent metal fluorides possess the NbF$_5$ structure (MF$_5$, M = Nb, Ta, Mo, W), G;[46] several metal

$$
\begin{array}{c}
\text{F} \quad \text{F} \qquad \text{F} \quad \text{F} \\
\text{F—M—F—M—F} \\
\text{F} \quad \text{F} \quad \text{F} \quad \text{F} \\
\text{F—M—F—M—F} \\
\text{F} \quad \text{F} \qquad \text{F} \quad \text{F}
\end{array}
$$

G

chlorofluorides (e.g., NbCl$_4$F)[46] and oxyfluorides (e.g., WOF$_4$)[46] have similar configurations. The metal carbonyl

$$
\begin{array}{c}
\text{OC} \quad \text{CO} \quad \text{F} \quad \text{CO} \\
\text{OC—Ru} \qquad \text{Ru—CO} \\
\text{F} \quad \text{F} \quad \text{OC} \quad \text{F} \quad \text{CO} \\
\text{OC—Ru} \qquad \text{Ru—CO} \\
\text{OC} \quad \text{CO} \quad \text{OC} \quad \text{F}
\end{array}
$$

H

fluoride RuF$_2$(CO)$_3$ has idealized structure H[47] with bridging Ru–F–Ru angles of 145°. The presence of an atom which forms linear or nearly linear bridges (F) and of a "corner" species which can attain a cis-octahedral configuration are obvious prerequisites for the square, eight-membered ring.[48]

Supplementary Material Available: a listing of root-mean-square amplitudes of vibration (Table II) and the structure amplitude table (17 pages). Ordering information is given on any current masthead page.

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(1) NSF Predoctoral Fellow, 1973–present.
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Metal–Metal Bond Cleavage Reactions. The Crystal and Molecular Structure of (2,2'-Bipyridyl)cadmium Tetracarbonyliron, (bpy)CdFe(CO)₄

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Abstract: The complex (bpy)CdFe(CO)₄ crystallizes from hot 1,2,4-trichlorobenzene as a trimer with the stoichiometry [(bpy)-CdFe(CO)₄]₃·¾C₆H₃Cl₃. The crystals belong to the tetragonal space group S_4^1-$P\bar{4}$ with eight six-membered metal–metal bonded rings and six solvent molecules in a unit cell of dimensions $a = b = 29.049$ (10), $c = 13.241$ (5) Å, $V = 11\,170$ Å³. Full-matrix least-squares refinement yielded a final value of the conventional R index (on F) of 0.066 for 5643 reflections having $F_o^2 > 3\sigma(F_o^2)$. The molecular structure consists of nearly planar rings of alternating cis-Fe(CO)₄ and (bpy)Cd units. The ring is distorted from ideal D_{3h} to approximate C_2 symmetry by compression along a C_2 axis in the plane of the ring. All Fe–Cd distances are equal within experimental error [2.640 (7) Å]. The Cd–Fe–Cd angles vary from 138.81 (15) to 148.40 (15)°, and the Fe–Cd–Fe angles from 94.78 (14) to 102.04 (16)°. The iron coordination geometry is significantly distorted from an octahedral one toward a tetrahedral one in which cadmium atoms cap two of the faces. There is evidence for a weak semibridging interaction between carbonyl carbon and cadmium atoms. The Cd–Fe bonding in [(bpy)CdFe(CO)₄]₃ appears to be more ionic than in [CdFe(CO)₄]₄. The trimeric compound dissociates in benzene solution.

In an accompanying article[3] we discussed means to purify and to crystallize certain classes of oligomeric metal–metal bonded materials by employing reversible base-induced cleavage reactions. This allowed the crystallization of CdFe(CO)₄[4]

$$[CdFe(CO)_4]_4 + 4nB \rightleftharpoons 4B_nCd^+{-}^-Fe(CO)_4 \quad (1)$$
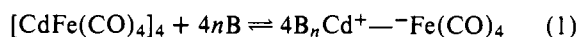
$$B = \text{acetone, THF, NH}_3$$

and unambiguous definition of the molecular structure by x-ray diffraction.[3] The molecule was found to possess an unusual tetrameric structure consisting of nearly square-planar centrosymmetric eight-membered ring of alternating Cd and cis-Fe(CO)₄ units (A). The nature of the base-induced

A   B

C
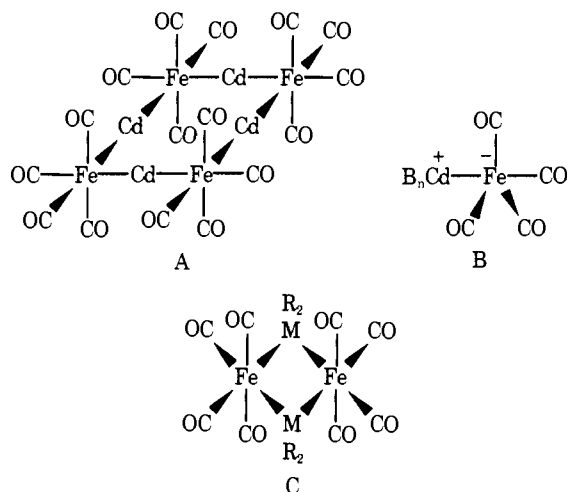
cleavage products in solution was proposed on the basis of cryoscopic molecular weight and infrared spectral studies to

be B. These measurements, of course, provided no quantitative structural details and no information on the solid state geometry. They also yielded little information on what features of B might provide a driving force for the metal–metal bond breaking process. For $n = 2$ it was not clear why a dimeric structure could not exist, as found in the isoelectronic, structurally well-characterized group IV metal–iron dimers [R₂MFe(CO)₄]₂[5] (C), M = Si, Ge, Sn, Pb. These show little tendency to undergo unassisted dissociation.[6] The $n = 3$ species are isoelectronic with the group IV cleavage products, B·R₂MFe(CO)₄,[7] the structural details of which have not been obtained and can only be inferred from spectral studies[7] and by comparison with the B·R₂MCr(CO)₅ derivatives.[7b,8] For these reasons we have undertaken an x-ray diffraction study of the B$_n$CdFe(CO)₄ adduct where B$_n$ = 2,2'-bipyridyl.[9] In this compound the base is sufficiently strong and nonvolatile so that stable crystals can be grown. Mössbauer data[9] suggested that the coordination about iron was probably cis octahedral, but provided no further structural information. Dimeric and polymeric states of (bpy)CdFe(CO)₄ aggregation were recognized as possibilities.[9] We discuss here our results on the rather complex crystal structure of this molecule. Our data reveal the presence of unusual six-membered metal–metal bonded rings and somewhat different Cd–Fe interactions than were found in the base-free eight-membered ring of [CdFe(CO)₄]₄.

Experimental Section

X-Ray Diffraction Study of (bpy)CdFe(CO)₄. The compound was synthesized as described previously.[3] Attempts at crystallization (by slow cooling) from a number of solvents (benzene, toluene, CH₂Cl₂/hexane) yielded well-formed single crystals which became opaque and crumbled on isolation owing to loss of occluded solvent. However, stable crystals could be obtained from less volatile solvents, such as 1,2,4-trichlorobenzene, by very slow cooling of hot saturated