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o-Phenylenebis(dimethylarsine)decacarbonyltriiron. Preparation and Structure of a Compound with Two Semibridging Carbonyl Ligands

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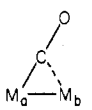
The reaction of $Fe_2(CO)_9$ with *o*-phenylenebis(dimethylarsine) (diars) under a dynamic atmosphere of argon (to sweep out CO) allows the isolation of the title compound, (diars)$Fe_3(CO)_{10}$. The structure of this dark brown crystalline compound has been investigated by X-ray crystallography. The crystals are monoclinic, and a unit cell in space group $P2_1/n$ has dimensions of $a = 9.538$ (2) Å, $b = 11.101$ (2) Å, $c = 21.070$ (3) Å, $\beta = 99.81$ (1)°, $V = 2580$ (1) Å^3, and $Z = 4$. The molecules consist of triangular Fe_3 clusters with the diars chelated to Fe(1). There are no symmetrically bridging CO groups, but one CO group from Fe(2) and one from Fe(3) lean toward Fe(1) and may be described as semibridging CO groups with Fe(1)–C distances of 2.23 ± 0.01 Å. These two semibridging CO groups may be assigned the role of accepting electron density from the electron-rich Fe(1) atom. The two semibridging CO groups are on opposite sides of the Fe_3 plane, and there is a concerted twist of all other ligand atoms so that the only symmetry element retained by the molecule is a twofold axis passing through Fe(1) and bisecting the Fe(2)–Fe(3) bond. The Fe–Fe bonds with the semibridging CO groups are appreciably shorter, 2.602 (1) and 2.597 (1) Å, than the third one, 2.662 (1) Å, between Fe(2) and Fe(3).

Introduction

Very unsymmetrical bridging carbonyl groups of type **1**,



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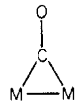

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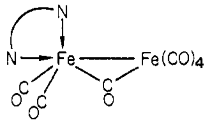
called semibridging carbonyl groups to distinguish them from the truly symmetrical ones, **2**, which may sometimes be slightly distorted, are known to occur under a variety of circumstances.[2] The most common case is where M_b in **1** is (for any of several reasons) appreciably more electron rich than M_a and the semibridging CO group can be considered to accept electron density from M_b as well as from M_a into one of its π^* orbitals. One way in which M_b might be more electron rich than M_a would be by having some ligands that are good donors but relatively poor π acceptors while M_a has only CO groups. This case was first exemplified by $Fe_2(bpy)(CO)_7$ where both bpy nitrogen atoms are coordinated to one metal atom.[3] A hypothetical structure of type **3** distorts to one of type **4**, which is an idealized approximation to the actual structure.[3]



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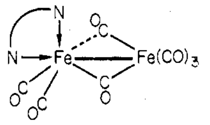

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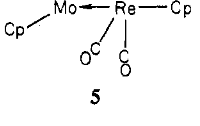
An excellent recent example of semibridging CO groups serving to relieve a metal atom of excessive negative charge is afforded by $(\eta^5\text{-}C_5H_5)_2MoRe(CO)_3(\eta^5\text{-}C_5H_5)$.[4] Structure **5** can be written (where Cp = η^5-C_5H_5) in order to provide each metal atom with an 18-electron configuration. However, this makes the Mo atom formally negative, and two CO groups become semibridging and remove negative charge from the Mo atom to correct this as indicated by **6**, which provides an explanation for the observed structure. This structure is unusual in being relatively symmetrical.



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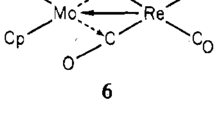

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In the case of $Fe_2(bpy)(CO)_7$ and most other molecules with semibridging CO groups the overall structure is quite unsymmetrical, and detailed analysis is correspondingly difficult. In this paper we report a rather large molecule in which the structure retains considerable symmetry and simplicity and shows the role of semibridging CO groups in relieving charge imbalance very clearly.

The structure reported here is also of interest in relation to previously studied derivatives[2] of $Fe_3(CO)_{12}$ in which one or more CO groups have been replaced by phosphines or similar donors. It is the first case in which there have been two such substitutions on one iron atom but none on the others.

Experimental Section

Preparation. A mixture of 4.14 g (11.4 mmol) of $Fe_2(CO)_9$, 1.1 g (3.8 mmol) of diars, and 100 mL of freshly distilled THF was stirred for 3 h at room temperature while argon was bubbled through the reaction mixture. The solvent was removed under reduced pressure, leaving a dark brown solid which was transferred to a silica chromatography column prepared in hexane. Elution of the column with 1:1 benzene:hexane gave first a yellow band (Ia) followed by a brown band (Ib). The yellow band (Ia) was shown to contain (diars)$Fe_2(CO)_8$ according to elemental analysis.

Upon evaporation of the eluate containing the brown band (Ib) a dark solid was obtained. This was recrystallized from a mixture of dichloromethane and hexane to give dark brown crystals of (diars)$Fe_3(CO)_{10}$. Anal. Calcd for $C_{20}H_{16}O_{10}Fe_3As_2$: C, 32.73; H, 2.15. Found: C, 32.3; H, 2.15. Attempts to record the mass spectrum gave only ions of fragments. The ^{1}H NMR spectrum consists of a broad signal at $\delta \sim 7.55$ (relative intensity 1) and a sharp line at $\delta \sim 1.57$ (relative intensity 3). The infrared spectrum in the CO stretching region had bands at 2060 (s), 2010 (s), 1995 (s), 1980 (s), 1960 (sh), and 1760 (m) cm^{-1}. The solid compound appears to be stable in air for at least several months.

X-ray Crystallography. A crystal of approximate dimensions 0.10 × 0.15 × 0.10 mm was attached to the end of a glass fiber and mounted on an Enraf-Nonius CAD-4 four-circle diffractometer. Mo Kα ($\lambda = 0.710730$ Å) radiation, with a graphite-crystal monochromator in the incident beam, was used. All procedures used in preliminary examination, data collection, and solution and refinement of the structure were routine ones that have been described many times previously.[5]

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(1) (a) Texas A&M University. (b) University of Zaragoza.
(2) Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1.
(3) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 1233.
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(5) See, for example: Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
As(1)	0.57572 (7)	0.14048 (6)	0.61045 (3)	3.17 (3)	3.62 (3)	3.43 (3)	0.63 (3)	0.47 (2)	−0.03 (3)
As(2)	0.85231 (7)	−0.02294 (6)	0.63083 (3)	3.29 (3)	3.08 (3)	3.65 (3)	0.51 (3)	0.91 (2)	0.13 (3)
Fe(1)	0.8200 (1)	0.17995 (8)	0.62517 (4)	3.46 (4)	3.11 (4)	3.09 (4)	0.15 (4)	0.20 (3)	0.12 (4)
Fe(2)	1.0381 (1)	0.29758 (9)	0.67631 (4)	4.04 (5)	3.66 (5)	4.04 (4)	0.20 (4)	0.02 (4)	−0.60 (4)
Fe(3)	0.8749 (1)	0.38228 (10)	0.58426 (5)	4.61 (5)	3.81 (5)	4.65 (5)	0.11 (4)	0.46 (4)	0.96 (4)
O(1)	0.9670 (8)	0.6149 (5)	0.6235 (3)	9.3 (4)	4.0 (3)	10.4 (4)	1.0 (3)	0.4 (4)	−1.2 (3)
O(2)	0.6596 (6)	0.4057 (5)	0.6560 (3)	6.1 (3)	5.7 (3)	7.8 (3)	1.4 (2)	2.0 (2)	−0.4 (3)
O(3)	0.7980 (6)	0.1788 (5)	0.7454 (2)	6.5 (3)	7.8 (3)	4.2 (2)	−1.2 (3)	1.7 (2)	−1.1 (2)
O(4)	0.8120 (6)	0.1467 (5)	0.5038 (2)	6.2 (3)	5.8 (3)	3.8 (2)	−0.2 (2)	1.1 (2)	−0.4 (2)
O(5)	1.1184 (5)	0.1239 (4)	0.5986 (4)	3.5 (2)	4.5 (2)	6.2 (2)	0.5 (2)	1.3 (2)	−1.3 (2)
O(6)	1.2710 (6)	0.4421 (5)	0.6490 (3)	5.3 (3)	6.0 (3)	11.7 (4)	−1.2 (3)	2.0 (3)	−0.3 (3)
O(7)	1.2114 (8)	0.1664 (7)	0.7673 (3)	8.7 (4)	10.1 (4)	6.2 (3)	2.4 (3)	−1.0 (3)	1.6 (3)
O(8)	0.9289 (8)	0.4670 (6)	0.7519 (2)	10.0 (4)	7.5 (3)	6.2 (3)	1.1 (3)	2.1 (3)	−2.9 (3)
O(9)	0.6578 (8)	0.4549 (7)	0.4898 (3)	8.9 (4)	8.6 (4)	8.3 (4)	0.3 (4)	−2.4 (3)	2.8 (3)
O(10)	1.0954 (7)	0.3464 (6)	0.5128 (3)	9.7 (3)	6.5 (3)	7.4 (3)	−1.0 (3)	4.3 (2)	0.4 (3)
C(1)	0.9288 (10)	0.5230 (7)	0.6078 (4)	6.5 (4)	4.5 (4)	6.6 (4)	1.7 (4)	0.8 (4)	1.1 (4)
C(2)	0.7458 (9)	0.3659 (8)	0.6305 (4)	4.3 (4)	7.0 (5)	5.8 (4)	0.3 (4)	0.2 (3)	0.3 (4)
C(3)	0.8188 (8)	0.1884 (7)	0.6989 (3)	4.3 (3)	4.6 (4)	3.8 (3)	0.3 (3)	0.6 (3)	−0.6 (3)
C(4)	0.8204 (7)	0.1743 (6)	0.5507 (3)	3.5 (3)	4.1 (3)	3.6 (3)	0.4 (3)	0.4 (2)	0.7 (3)
C(5)	1.0522 (7)	0.1820 (6)	0.6237 (3)	4.3 (3)	3.5 (3)	3.5 (3)	0.4 (3)	0.5 (3)	−0.1 (3)
C(6)	1.1812 (8)	0.3871 (7)	0.6589 (3)	5.0 (4)	4.2 (4)	6.3 (4)	0.7 (3)	1.0 (3)	−0.9 (3)
C(7)	1.1411 (8)	0.2175 (8)	0.7323 (3)	4.9 (4)	5.5 (4)	4.8 (4)	0.6 (3)	−0.1 (3)	−0.2 (4)
C(8)	0.9673 (9)	0.4004 (7)	0.7229 (4)	5.6 (4)	4.7 (4)	5.3 (4)	−0.2 (3)	0.1 (3)	−0.8 (3)
C(9)	0.7441 (10)	0.4244 (7)	0.5254 (4)	6.8 (5)	5.0 (4)	5.8 (4)	−0.0 (4)	−0.0 (4)	1.0 (4)
C(10)	1.0126 (9)	0.3556 (7)	0.5412 (3)	7.1 (4)	3.8 (3)	4.9 (4)	−1.0 (3)	1.2 (3)	1.0 (3)
C(11)	0.6683 (7)	−0.0996 (6)	0.6229 (3)	3.8 (3)	4.3 (3)	2.5 (3)	0.1 (3)	1.3 (2)	0.0 (3)
C(12)	0.6555 (8)	−0.2195 (6)	0.6276 (6)	5.9 (4)	3.2 (3)	3.9 (3)	−0.5 (3)	0.8 (3)	0.1 (3)
C(13)	0.5176 (9)	−0.2687 (7)	0.6214 (3)	6.0 (4)	4.8 (4)	4.9 (4)	−0.8 (4)	0.9 (3)	0.3 (3)
C(14)	0.3986 (9)	−0.1969 (8)	0.6094 (3)	5.1 (4)	5.5 (4)	5.3 (4)	−0.5 (3)	0.7 (3)	0.3 (4)
C(15)	0.4125 (8)	−0.0772 (7)	0.6047 (3)	4.1 (3)	5.3 (4)	3.6 (3)	−1.2 (3)	0.2 (3)	−0.4 (3)
C(16)	0.5464 (7)	−0.0282 (6)	0.6117 (3)	4.0 (3)	3.8 (3)	2.9 (3)	0.1 (3)	0.7 (2)	−0.1 (3)
C(17)	0.4637 (8)	0.1945 (7)	0.6661 (3)	5.0 (3)	5.7 (4)	5.4 (3)	1.2 (3)	2.9 (2)	−1.3 (3)
C(18)	0.4570 (9)	0.1917 (8)	0.5402 (3)	4.9 (4)	7.6 (5)	3.8 (3)	0.4 (4)	−1.0 (3)	1.9 (4)
C(19)	0.9330 (9)	−0.1026 (7)	0.5709 (3)	7.3 (4)	3.8 (3)	7.7 (4)	0.3 (3)	4.5 (3)	−2.1 (3)
C(20)	0.9575 (9)	−0.0899 (7)	0.6992 (4)	5.5 (4)	4.7 (4)	6.0 (4)	1.0 (3)	−1.5 (3)	1.8 (3)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

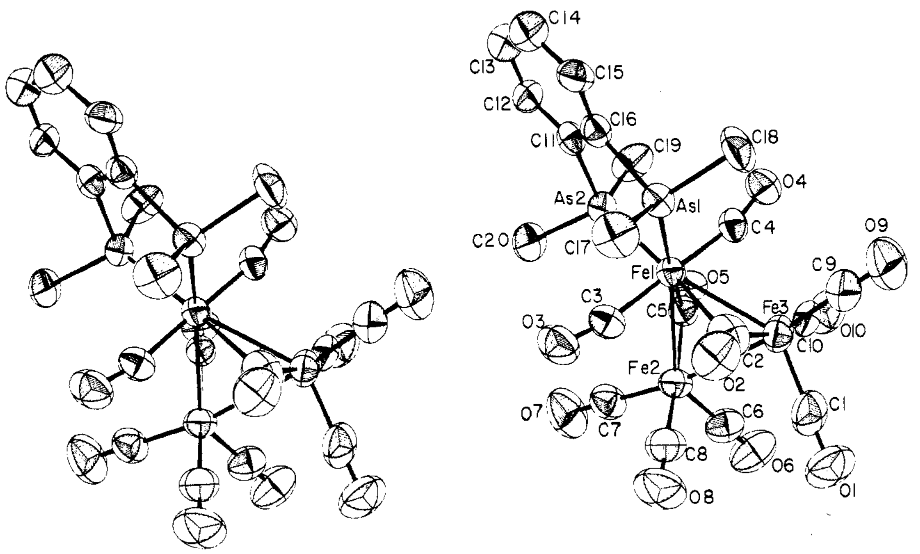


Figure 1. ORTEP stereo drawing of the $Fe_3(CO)_{10}$diars molecule.

The crystal was found to be monoclinic with dimensions a = 9.538 (2) Å, b = 11.101 (2) Å, c = 21.070 (3) Å, β = 99.81 (1)°, and V = 2580 (1) Å^3. With Z = 4, this gives a calculated density of 1.89 g cm^{-3}. Systematic absences indicate unambiguously space group $P2_1/n$. The linear absorption coefficient for Mo Kα radiation is 11.11, and absorption corrections were omitted. The iron and arsenic atoms were located by using the results of a MULTAN direct-method analysis and all remaining nonhydrogen atoms were straightforwardly located in a series of difference maps.

All atoms were refined with anisotropic thermal vibration parameters. Refinement proceeded smoothly to give the results listed in Table I. The largest parameter shift in the last cycle was 0.09 times its esd, and a total of 2516 reflections for which $F_o^2 > \sigma(F_o^2)$ were used to refine 316 variables. The final reliability factors were

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.037$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.056$$

The goodness of fit parameter has a value of 1.27. A listing of F_o and F_c values is available as supplementary material.

Results and Discussion

Although the structure of (diars)$Fe_3(CO)_{10}$ is basically simple, it is sufficiently large that it is not easily represented

Table II. Selected Interatomic Distances (Å)

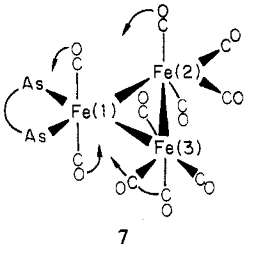
Fe(1)–Fe(2)	2.602 (1)	Fe(2)–C(5)	1.849 (7)
–Fe(3)	2.597 (1)	–C(6)	1.809 (9)
Fe(2)–Fe(3)	2.662 (1)	–C(7)	1.779 (8)
		–C(8)	1.830 (9)
Fe(1)–As(1)	2.339 (1)	Fe(3)–C(1)	1.749 (10)
–As(2)	2.335 (1)	–C(2)	1.804 (9)
–C(3)	1.780 (7)	–C(9)	1.785 (9)
–C(4)	1.795 (7)	–C(10)	1.833 (9)
Fe(1)–C(2)	2.246 (9)	Fe(1)–C(5)	2.221 (7)
C(1)–O(1)	1.15 (1)	C(6)–O(6)	1.12 (1)
C(2)–O(2)	1.20 (1)	C(7)–O(7)	1.14 (1)
C(3)–O(3)	1.17 (1)	C(8)–O(8)	1.13 (1)
C(4)–O(4)	1.16 (1)	C(9)–O(9)	1.14 (1)
C(5)–O(5)	1.15 (1)	C(10)–O(10)	1.13 (1)
As(1)–C(17)	1.948 (6)	As(2)–C(19)	1.968 (7)
–C(18)	1.954 (7)	–C(20)	1.932 (7)
–C(16)	1.949 (7)	–C(11)	1.941 (7)
C(11)–C(12)	1.38 (1)	C(14)–C(15)	1.38 (1)
C(12)–C(13)	1.41 (1)	C(15)–C(16)	1.38 (1)
C(13)–C(14)	1.39 (1)	C(16)–C(11)	1.41 (1)

Table III. Selected Bond Angles (Deg)

Fe(1)–Fe(2)–Fe(3)	59.10 (3)	Fe(1)–C(3)–O(3)	167.5 (7)
Fe(2)–Fe(3)–Fe(1)	59.28 (4)	–C(4)–O(4)	165.7 (6)
Fe(3)–Fe(1)–Fe(2)	61.61 (4)	Fe(2)–C(6)–O(6)	178.9 (8)
C(17)–As(1)–C(18)	101.3 (4)	–C(7)–O(7)	177.5 (8)
–C(16)	101.7 (3)	–C(8)–O(8)	176.9 (8)
–Fe(1)	119.0 (3)	Fe(3)–C(1)–O(1)	178.7 (8)
C(18)–As(1)–C(16)	104.1 (3)	–C(9)–O(9)	176.4 (9)
–Fe(1)	119.3 (3)	–C(10)–O(10)	175.3 (7)
C(16)–As(1)–Fe(1)	109.2 (2)	C(6)–Fe(2)–C(7)	97.1 (4)
C(19)–As(2)–C(20)	103.3 (4)	–C(8)	98.8 (3)
–C(11)	100.4 (3)	C(7)–Fe(2)–C(8)	94.5 (4)
–Fe(1)	118.6 (2)	C(1)–Fe(3)–C(9)	97.9 (4)
C(20)–As(2)–C(11)	103.6 (3)	–C(10)	97.8 (4)
–Fe(1)	119.1 (3)	C(9)–Fe(3)–C(10)	93.9 (4)
C(11)–As(2)–Fe(1)	109.4 (2)	Fe(1)–C(5)–O(5)	129.7 (5)
C(11)–C(12)–C(13)	118.6 (7)	Fe(2)–C(5)–O(5)	151.3 (6)
C(12)–C(13)–C(14)	120.0 (7)	Fe(1)–C(2)–O(2)	129.6 (7)
C(13)–C(14)–C(15)	121.0 (7)	Fe(3)–C(2)–O(2)	151.4 (8)
C(14)–C(15)–C(16)	119.4 (7)	C(3)–Fe(1)–C(4)	178.9 (3)
C(15)–C(16)–C(11)	120.5 (6)	–As(1)	89.2 (2)
C(16)–C(11)–C(12)	120.5 (6)	–As(2)	91.1 (2)
		C(4)–Fe(1)–As(1)	90.8 (2)
		–As(2)	90.0 (2)
		As(1)–Fe(1)–As(2)	86.45 (4)

without the use of a stereo pair. Such a stereoview is presented in Figure 1, and the atom numbering scheme is there defined. The interatomic distances are listed in Table II and the bond angles in Table III.

The overall shape of the molecule can be most easily understood if we begin with the hypothetical structure 7. In this arrangement the structure is derived from that of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ by replacing two equatorial CO groups on the same metal atom by the arsenic atoms of diars. This structure, like **3** and **5**, is not a stable one, and for the same reason. One atom, in this case Fe(1), has too much negative charge. Fe(1) is a formally zerovalent metal atom to which four ligands are attached, only two of which are capable of back-accepting to a significant extent. Here again, as in the two cases specifically cited above, and a number of others,[2] this excessive charge is allowed to distribute itself more evenly over the whole molecule by a structural change in which semibridging CO groups are formed.



7

A concerted set of twists of the configurations at each metal atom takes place, as indicated by the arrows in **7**. The upper axial CO on Fe(2) and the lower axial CO on Fe(3) swing toward Fe(1) while the set of four ligand atoms on Fe(1) twist so as to make room for these closer approaches of the two CO groups. This results in the observed structure and allows Fe(1) to shift some electron density to each of the CO groups that have moved closer to it.

The semibridging CO groups have dimensions that are quite typical for such entities.[2-4] There is no distinct increase in the shorter Fe–C distances as compared to the average of the Fe–C distances for the other terminal CO groups. For Fe(2)–C(5) and Fe(3)–C(2) the values average 1.80 ± 0.027 Å, and for the other six CO groups attached to Fe(2) and Fe(3) the average Fe–C distance is 1.83 ± 0.022 Å. The two Fe–C–O chains are distinctly bent, however, with angles of 151.3 ± 0.1°, and the carbon atoms approach Fe(1) very closely, with an average distance of 2.23 ± 0.01 Å.

It is interesting to note that in all crowded di- or polynuclear carbonyl molecules there is a tendency for some "nonbonded" contacts to be rather short and for some distortions to occur, with some of these "anomalies" reaching the point where they become similar to, or even indistinguishable[6] from, an electronically caused semibridging CO group. In this compound an incipient effect of this kind is seen for Fe(1)–C(3)–O(3) and Fe(1)–C(4)–O(4), which are more bent, 166.6 ± 1.0°, than are the other six regular terminal CO groups for which the mean angle is 177.3 ± 1.0°; they also make nonbonded contacts, C(3)–Fe(2) and C(4)–Fe(3), which, at an average of 2.55 ± 0.2 Å, are shorter than "normal". Nonetheless, these angles and distances are still considerably different from those mentioned above for the CO groups that we are postulating to be truly "semibridging".

The remaining distances and angles in the molecule all have the expected values. The mean of the Fe–Fe distances, 2.620 Å, is not much different from the corresponding average, 2.639 Å, for $Fe_3(CO)_{12}$ itself.[7] The essential linearity and normal Fe–C distances for those CO groups that are not in a semibridging situation have already been mentioned. The various distances and angles related to the diars ligand are also quite normal.

The infrared spectrum in the CO stretching region is fully consistent with the structure. If we assume that coupling between CO groups on different metal atoms is negligible, we expect three ν_{CO}'s from the $Fe(CO)_3$ groups on Fe(2) and Fe(3), and two ν_{CO}'s from the CO groups on Fe(1), all in the normal range for terminal CO groups. There are, in fact, five bands observed at 2060, 2010, 1995, 1980, and 1960 cm^{-1}. For the semibridging CO groups, coupling with each other should be negligible, and hence one band at a lower frequency would be expected; the observed band at 1760 cm^{-1} can be so assigned.

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Registry No. $(diars)Fe_3(CO)_{10}$, 73770-96-4; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: A table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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