Å, were $a = 11.392$ (2) Å, $b = 17.291$ (3) Å, $c = 9.340$ (1) Å, $\beta = 103.96$ (1)°, $V = 1778.6$ (1) Å^3, $Z = 2$, $d_{calcd} = 1.458$ g cm^{-3}, and space group $A2/m$.

A total number of 4168 reflections were collected, including redundancies, and were reduced to 2578 unique reflections. Standard moving-crystal, moving-detector techniques were used with the following values: scan speed = 4.0°/min, scan width = 2.0 + dispersion, single background at extremes of scan = 4 s, aperture size = 3.0 × 4.0 mm. The limits of data collection were $5° < 2\theta < 50°$. The number of reflections with $F > 2.33\sigma(F)$ was 2411.

The structure was solved by a combination of direct methods and Fourier techniques. Two molecules of benzene were located in the unit cell. All hydrogen atoms were located and refined isotropically; all other atoms were refined anisotropically, with use of full-matrix techniques. The final residuals are $R(F) = 0.025$ and $R_w(F) = 0.033$. The goodness of fit for the last cycle was 0.904 and the maximum Δ/σ was 0.05. The final difference Fourier map was essentially featureless, with the largest peak being 0.35 e/Å^3.

Acknowledgment. We thank the National Science Foundation for financial support and the Marshal H. Wrubel Computing Center for computing facilities.

Registry No. $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(HNMe_2)_2$, 79681-95-1; $Mo_2(NMe_2)_6$, 51956-20-8; t-BuSH, 75-66-1.

Supplementary Material Available: A table of anisotropic thermal parameters and a listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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[*o*-Phenylenebis(dimethylarsine)]heptacarbonyldiiron. Preparation, Crystal Structure, and Fluxionality in Solution

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Received June 2, 1981

The reaction of $Fe_2(CO)_9$ with *o*-phenylenebis(dimethylarsine), diars, in an atmosphere of CO gives yellow (diars)$Fe_2(CO)_8$ and red (diars)$Fe_2(CO)_7$, separable by chromatography on silica. The red compound crystallizes in space group $P\bar{1}$ with $Z = 2$ and the following unit cell dimensions: $a = 9.706$ (4) Å; $b = 11.876$ (3) Å; $c = 9.576$ (3) Å; $\alpha = 92.41$ (2)°; $\beta = 104.81$ (2)°; $\gamma = 91.25$ (2)°; $V = 1066$ (1) Å^3. The structure consists of dinuclear molecules in which diars is chelated on one iron atom (Fe(1)) to which are also bound two terminal CO groups. Fe(1) also forms a metal-metal bond, 2.566 (1) Å, to Fe(2), which bears three strictly terminal CO groups. Of the remaining two CO groups, one forms a nearly symmetrical bridge while the other is semibridging with its short bond, 1.894 (7) Å, to Fe(2) and its long bond, 2.103 (7) Å, to Fe(1). The ^{13}C NMR spectrum is highly temperature dependent, changing from a five-line spectrum (1:2:2:1:1) at −132 °C to a single-line spectrum at 11 °C. A three-stage process for equivalencing all of the CO's is proposed.

Introduction

It has been found that *o*-phenylenebis(dimethylarsine), diars, reacts with $Fe_2(CO)_9$ to produce a variety of products. The course of the reaction is influenced by concentrations, temperature, and the use of a sweep gas (Ar) to remove CO. We previously described the isolation of (diars)$Fe_3(CO)_{10}$ and reported its crystal structure.[2] In an atmosphere of CO the products are (diars)$Fe_2(CO)_8$ and (diars)$Fe_2(CO)_7$. In this paper we report a structural and dynamical study of the second of these compounds, the stoichiometry of which is analogous to that of (bpy)$Fe_2(CO)_7$, a compound prepared and characterized in one of these laboratories several years earlier.[3] This bpy complex was found to have a complicated structure, the interpretation of which was seminal in the development of the concept of semibridging carbonyl groups.[4]

Initially, our intention in the present study was simply to see how the structure of the title compound compared with that of (bpy)$Fe_2(CO)_7$, for whatever further light this might throw on the role of the semibridging carbonyl groups. However, when we examined the ^{13}C NMR spectrum of (diars)$Fe_2(CO)_7$, we found that the dynamic aspects of this molecule were of unusual interest. In fact, it is the reporting and interpretation of the fluxionality, or carbonyl scrambling, behavior of (diars)$Fe_2(CO)_7$ that will be our chief concern here and we shall defer a detailed discussion of the comparative structural chemistry of (diars)$Fe_2(CO)_7$ and (bpy)$Fe_2(CO)_7$ to a future detailed report on the latter structure.

Experimental Section

Preparation. A mixture of 2.07 g (5.7 mmol) of $Fe_2(CO)_9$, 0.59 g (1.9 mmol) of diars, and 50 mL of freshly distilled THF was stirred for 6 h at 25 °C with a slow stream of carbon monoxide bubbling through the reaction mixture. The solvent was removed under vacuum, leaving a dark red residue, which was redissolved in hexane and transferred to a column of silica in hexane. Elution of the column with a 1:1 hexane:benzene solvent gave first a yellow band and then a red band. The yellow fraction yielded a yellow solid, which was recrystallized from dichloromethane and hexane to give crystalline (diars)$Fe_2(CO)_8$. Anal. Calcd: C, 34.76; H, 2.57. Found: C, 34.8; H, 2.56. IR (cm^{-1}): 2040 (s), 1970 (s), 1930 (s).

Evaporation of the eluate of the red band followed by recrystallization from a mixture of dichloromethane and hexane gave red, crystalline (diars)$Fe_2(CO)_7$. Anal. Calcd: C, 34.30; H, 2.69. Found: C, 34.2; H, 2.69. IR (cm^{-1}): 2050 (s), 1980 (s), 1965 (sh), 1785 (sh), 1765 (m).

NMR Spectra. These were measured on ^{13}C enriched samples (vide infra) with use of a JEOL PFT 100/Nicolet 1080 Fourier transform spectrometer operating at 25.036 MHz. A sweep width of 7000 Hz and a repetition rate of 1.1 s were employed. The temperatures were measured with a copper–constantan thermocouple inserted into an NMR tube and read on a Leeds and Northrup Model 913 digital thermometer, with an estimated precision of ±1°. The solvent used at all temperatures was 2-methyltetrahydrofuran with 10% toluene-d_8 added for deuterium lock.

A sample of the diiron complex was enriched in ^{13}C carbon monoxide simply by stirring at room-temperature a tetrahydrofuran solution of this material under an atmosphere of 18% enriched ^{13}CO. The labeled derivative was then purified by chromatography and used immediately for the NMR studies.

X-ray Crystallography. A crystal of approximate dimensions 0.1 × 0.1 × 0.1 mm was attached to the end of a glass fiber and mounted

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[1] (a) Texas A&M University. (b) University of Zaragoza.

[2] Bino, A.; Cotton, F. A.; Lahuerta, P.; Puebla, P.; Uson, R. *Inorg. Chem.* **1980**, *19*, 2357.

[3] Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 1233.

[4] Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1.

0020-1669/82/1321-0289$01.25/0

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

atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
As(1)	−0.81298 (6)	−0.74569 (5)	−0.04408 (6)	2.71 (2)	2.71 (2)	1.69 (1)	−0.08 (2)	0.73 (1)	0.27 (1)
As(2)	−0.61439 (6)	−0.69174 (5)	−0.25425 (6)	2.09 (2)	3.49 (2)	2.55 (2)	0.33 (2)	0.92 (1)	0.70 (2)
Fe(1)	−0.85657 (7)	−0.66670 (6)	−0.27278 (8)	2.04 (2)	2.40 (3)	1.78 (2)	0.16 (2)	0.55 (2)	0.36 (2)
Fe(2)	−1.06991 (8)	−0.78012 (7)	−0.43548 (8)	2.46 (3)	2.88 (3)	1.95 (2)	0.07 (3)	0.39 (2)	0.23 (2)
O(1)	−0.8173 (4)	−0.9156 (3)	−0.3310 (4)	3.6 (2)	2.8 (2)	3.0 (1)	0.9 (1)	0.7 (1)	0.1 (1)
O(2)	−1.1326 (4)	−0.6431 (4)	−0.1958 (5)	3.3 (1)	5.0 (2)	3.5 (1)	0.6 (1)	1.6 (1)	−0.5 (1)
O(3)	−0.8813 (5)	−0.5769 (4)	−0.5575 (4)	5.4 (2)	4.4 (2)	2.2 (1)	−0.2 (2)	1.1 (1)	1.1 (1)
O(4)	−0.8309 (6)	−0.4365 (4)	−0.1441 (5)	6.4 (2)	3.1 (2)	4.4 (2)	−0.2 (2)	1.5 (2)	−0.7 (1)
O(5)	−1.3067 (5)	−0.6421 (4)	−0.5877 (6)	4.1 (2)	5.6 (2)	5.0 (2)	1.4 (2)	−0.1 (2)	1.6 (2)
O(6)	−1.0103 (5)	−0.8615 (5)	−0.7068 (5)	5.9 (2)	6.9 (3)	2.4 (1)	0.2 (2)	1.4 (1)	−0.6 (2)
O(7)	−1.2394 (5)	−0.9619 (4)	−0.3550 (6)	4.9 (2)	4.4 (2)	6.2 (2)	−0.9 (2)	2.3 (1)	1.3 (2)
C(1)	−0.8895 (6)	−0.8369 (5)	−0.3461 (6)	2.8 (2)	3.3 (2)	1.5 (1)	−0.1 (2)	0.6 (1)	0.1 (1)
C(2)	−1.0617 (6)	−0.6805 (5)	−0.2675 (6)	2.6 (2)	2.7 (2)	2.4 (2)	0.3 (2)	0.8 (1)	0.3 (2)
C(3)	−0.8799 (6)	−0.6162 (5)	−0.4508 (6)	3.2 (2)	3.2 (2)	2.3 (2)	0.3 (2)	0.8 (1)	0.2 (2)
C(4)	−0.8410 (6)	−0.5264 (5)	−0.1943 (6)	2.9 (2)	3.0 (2)	2.4 (2)	−0.0 (2)	0.6 (1)	0.2 (2)
C(5)	−1.2124 (6)	−0.6919 (5)	−0.5284 (7)	3.0 (2)	3.4 (2)	3.0 (2)	−0.5 (2)	0.4 (2)	0.2 (2)
C(6)	−1.0346 (6)	−0.8302 (5)	−0.6023 (6)	3.0 (2)	4.0 (3)	2.4 (2)	0.2 (2)	0.3 (2)	0.2 (2)
C(7)	−1.1705 (6)	−0.8916 (5)	−0.3865 (7)	2.6 (2)	3.5 (2)	2.8 (2)	0.6 (2)	0.5 (2)	−0.1 (2)
C(8)	−0.5320 (6)	−0.7750 (5)	−0.0829 (7)	2.5 (2)	3.2 (2)	3.0 (2)	0.6 (2)	0.2 (2)	0.5 (2)
C(9)	−0.3916 (7)	−0.8081 (6)	−0.0535 (8)	3.1 (2)	4.7 (3)	4.2 (2)	1.1 (2)	−0.3 (2)	0.3 (2)
C(10)	−0.3400 (8)	−0.8680 (7)	0.0730 (9)	4.4 (3)	5.8 (4)	4.6 (3)	1.5 (3)	−0.9 (3)	0.6 (3)
C(11)	−0.4253 (8)	−0.8915 (7)	0.1633 (8)	5.3 (3)	4.9 (3)	3.5 (2)	1.3 (3)	−1.2 (2)	0.5 (2)
C(12)	−0.5668 (8)	−0.8562 (6)	0.1346 (7)	5.2 (3)	4.4 (3)	2.4 (2)	0.6 (3)	−0.3 (2)	0.2 (2)
C(13)	−0.6192 (6)	−0.7968 (5)	0.0085 (6)	3.1 (2)	3.1 (2)	2.0 (2)	0.3 (2)	0.1 (2)	0.2 (2)
C(14)	−0.9263 (7)	−0.8788 (5)	−0.0219 (7)	4.3 (2)	3.9 (2)	2.8 (2)	−1.4 (2)	1.2 (2)	0.9 (2)
C(15)	−0.8246 (8)	−0.6498 (6)	0.1232 (7)	6.3 (3)	4.2 (3)	2.6 (2)	−0.0 (3)	2.0 (2)	−0.8 (2)
C(16)	−0.5566 (7)	−0.7760 (8)	−0.4092 (7)	5.0 (3)	8.5 (4)	3.5 (2)	2.3 (3)	2.7 (2)	0.5 (2)
C(17)	−0.4876 (7)	−0.5581 (6)	−0.2247 (10)	3.1 (2)	3.9 (3)	7.0 (3)	−0.5 (2)	1.8 (2)	1.4 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$.

on a Syntex P$\bar{1}$ four-circle diffractometer. Mo Kα (γ = 0.710730 Å) radiation, with a graphite-crystal monochromator in the incident beam, was used.

Rotation photographs and ω scans of several strong reflections indicated that the crystal was of satisfactory quality. Preliminary examinations showed that the crystal belonged to the triclinic system, space group $P\bar{1}$. The unit cell dimensions were obtained by a least-squares fit of 15 strong reflections in the range 25° < 2θ < 35° giving a = 9.706 (4) Å, b = 11.876 (3) Å, c = 9.576 (3) Å, α = 92.41 (2)°, β = 104.81 (2)°, γ = 91.25 (2)°, and V = 1066 (1) Å^3, consistent with Z = 2.

Data were measured by θ–2θ scans. A total of 2283 reflections in the range 3° < 2θ < 45° were collected of which 2261 having $I > 3\sigma(I)$ were used to solve and refine the structure. General procedures for data collection hae been described elsewhere.[5] The data were corrected for Lorentz and polarization effects. The linear absorption coefficient is 46.8 cm^{-1}; no absorption correction was applied because of the uniform shape of the crystal and the fact that ψ scans at χ = 90° for several reflections showed no variation greater than 8%.

The heavy-atom positions were obtained by direct methods using the MULTAN program. Other atoms were found in difference maps.

The structure was refined[6] in space group $P\bar{1}$ to convergence with use of anisotropic thermal parameters for all the nonhydrogen atoms.

The discrepancy indices

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

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

had final values of R_1 = 0.033 and R_2 = 0.049 with an error in an observation of unit weight equal to 1.214. The final difference map showed no peaks of structural significance. A list of the observed and calculated structure factors is available as supplementary material.

Results and Discussion

X-ray Crystallography. The positional and thermal parameters are listed in Table I, and the interatomic distances and angles computed therefrom are given in Table II. A computer-drawn picture of the molecule is presented in Figure 1, and the atomic numbering scheme is defined. We have chosen to display the enantiomorph that most clearly resembles the one previously shown for (bpy)$Fe_2(CO)_7$, and the broad resemblance of the two structures is quite obvious on comparing Figure 1 here with Figure 1 of ref 3. There are many differences in detail, however, which will be discussed elsewhere. One of these is in the Fe–Fe distances: in (diars)$Fe_2(CO)_7$ this is 2.566 (1) Å, whereas in (bpy)$Fe_2(CO)_7$ it is 2.611 (2) Å.

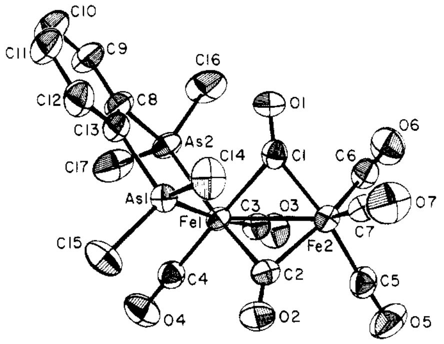

Figure 1. The molecular structure of (diars)$Fe_2(CO)_7$, with the atom numbering scheme shown. Each atom is represented by its ellipsoid of thermal vibration, scaled to enclose 40% of the electron density.

The diars ligand is essentially planar and chelated to Fe(1) with an As–Fe–As angle of 85.71 (3)°. The coordination about Fe(1) is completed by four CO carbon atoms, C(1), C(2), C(3), and C(4), which together with the two arsenic atoms form a distorted octahedron about Fe(1). The Fe(1)–Fe(2) bond is directed approximately along one threefold axis of this distorted octahedron, namely, the one that lies between the Fe(1)–C(1), Fe(1)–C(2), and Fe(1)–C(3) bonds.

The coordination about Fe(2) is less regular, but it too can be described as a distorted octahedron in which C(5), C(6), and C(7) constitute one triangular face and C(1), C(2), and C(3) the one opposite to it. For the first of these the Fe(2)–C distances are all similar, ranging from 1.774 (9) to 1.818 (7)

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(5) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227. Adams, R. D.; Collins, D. M.; Cotton, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 749.

(6) All crystallographic computing was done on a PDP 11/45 computer at the Molecular Structure Corp., College Station, Texas, using the Enraf-Nonius structure determination package.

Table II. Bond Distances and Bond Angles for (diars)$Fe_2(CO)_7$

Bond Distances (Å)

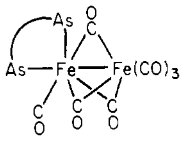
Fe(1)-Fe(2)	2.566 (1)	Fe(2)-C(1)	1.894 (7)
-As(1)	2.361 (1)	-C(2)	1.939 (8)
-As(2)	2.338 (1)	-C(5)	1.818 (7)
-C(1)	2.103 (7)	-C(6)	1.796 (7)
-C(2)	2.007 (7)	-C(7)	1.774 (9)
-C(3)	1.791 (6)	-C(3)	2.686 (8)
-C(4)	1.787 (6)	As(2)-C(8)	1.953 (7)
As(1)-C(13)	1.937 (5)	-C(16)	1.960 (4)
-C(14)	1.955 (5)	-C(17)	1.951 (6)
-C(15)	1.954 (5)		
O(1)-C(1)	1.172 (9)	C(8)-C(9)	1.389 (8)
O(2)-C(2)	1.171 (8)	C(8)-C(13)	1.390 (9)
O(3)-C(3)	1.139 (9)	C(9)-C(10)	1.416 (7)
O(4)-C(4)	1.144 (8)	C(10)-C(11)	1.371 (6)
O(5)-C(5)	1.140 (9)	C(11)-C(12)	1.407 (6)
O(6)-C(6)	1.138 (9)	C(12)-C(13)	1.408 (7)
O(7)-C(7)	1.16 (1)		

Bond Angles (Deg)

Fe(2)-Fe(1)-As(1)	105.95 (3)	Fe(1)-As(1)-C(13)	108.9 (1)
-As(2)	127.69 (4)	-C(14)	118.7 (1)
-C(1)	46.6 (1)	-C(15)	118.9 (1)
-C(2)	48.3 (1)	C(13)-As(1)-C(14)	103.3 (3)
-C(3)	73.7 (1)	-C(15)	103.5 (4)
-C(4)	131.6 (1)	C(14)-As(1)-C(15)	101.5 (5)
As(1)-Fe(1)-As(2)	85.71 (3)	Fe(1)-As(2)-C(8)	109.5 (1)
-C(1)	82.5 (1)	-C(16)	119.5 (1)
-C(2)	83.9 (1)	-C(17)	118.3 (1)
-C(3)	174.8 (1)	C(8)-As(2)-C(16)	103.6 (3)
-C(4)	92.1 (1)	-C(17)	102.0 (4)
As(2)-Fe(1)-C(1)	86.8 (1)	C(16)-As(2)-C(17)	101.7 (3)
-C(2)	166.5 (1)	Fe(1)-C(1)-Fe(2)	79.7 (3)
-C(3)	90.5 (1)	-O(1)	133.9 (6)
-C(4)	97.6 (1)	Fe(2)-C(1)-O(1)	146.3 (6)
C(1)-Fe(1)-C(2)	83.3 (3)	Fe(1)-C(2)-Fe(2)	81.1 (2)
-C(3)	93.8 (3)	-O(2)	136.7 (7)
-C(4)	172.8 (3)	Fe(2)-C(2)-O(2)	142.2 (7)
C(2)-Fe(1)-C(3)	99.4 (3)	Fe(1)-C(3)-O(3)	172.3 (6)
-C(4)	91.4 (3)	Fe(1)-C(4)-O(4)	179.8 (4)
C(3)-Fe(1)-C(4)	91.8 (3)	Fe(2)-C(5)-O(5)	176.1 (7)
Fe(1)-Fe(2)-C(1)	53.7 (1)	Fe(2)-C(6)-O(6)	179.1 (6)
-C(2)	50.6 (1)	Fe(2)-C(7)-O(7)	177.8 (7)
-C(5)	113.2 (1)	As(2)-C(8)-C(9)	120.6 (5)
-C(6)	111.9 (1)	-C(13)	117.0 (4)
-C(7)	127.6 (1)	C(9)-C(8)-C(13)	122.4 (6)
C(1)-Fe(2)-C(2)	91.0 (3)	C(8)-C(9)-C(10)	117.0 (6)
-C(5)	163.8 (3)	C(9)-C(10)-C(11)	121.3 (5)
-C(6)	85.3 (3)	C(10)-C(11)-C(12)	121.4 (4)
-C(7)	95.4 (3)	C(11)-C(12)-C(13)	117.7 (4)
C(2)-Fe(2)-C(5)	85.2 (3)	As(1)-C(13)-C(8)	118.4 (4)
-C(6)	158.3 (3)	-C(12)	121.5 (3)
-C(7)	96.7 (4)	C(8)-C(13)-C(12)	120.1 (5)
C(5)-Fe(2)-C(6)	92.5 (4)		
-C(7)	100.7 (4)		
C(6)-Fe(2)-C(7)	104.8 (3)		

Å and the C–Fe(2)–C angles range from 92.5 (4) to 104.8 (3) Å. Thus, the three ligands on this face are somewhat splayed as compared to the 90° angles of a regular octahedron. The members of the opposite triangular set deviate from regularity mainly in the fact that the Fe(2)–C(3) distance, 2.686 (8) Å, is beyond the normal bonding range, even for a weak bond, and this is best regarded as an intramolecular nonbonded contact. Moreover, Fe(1)–C(3)–O(3) is essentially linear, 172.3 (6)°.

Because of the large Fe(2)–C(3) distance, we cannot regard the (diars)$Fe_2(CO)_7$ structure as a direct derivative of $Fe_2(CO)_9$ in which two terminal CO groups have been replaced by diars (**1**). If we were to regard both C(1)–O(1) and C(2)–O(2) as symmetrical bridging CO groups, as in **2**, we would have formal electron counts of 19 electrons on Fe(1) and 17 electrons on Fe(2). Since this is not a reasonable allocation, and since one of the bridging CO groups, namely C(1)–O(1), is very unsymmetrical, let us examine a third formulation of the bonding. We begin with the hypothetical singly bridged structure for $Fe_2(CO)_9$, **3**, and replace two terminal CO groups on Fe(1) to get **4**. Since the arsenic atoms have a much greater ratio of donor to acceptor power than CO groups, Fe(1) tends to be more negative than Fe(2) in **4**. If, then, one CO group on Fe(2) leans over, becomes a semibridging CO group, and accepts some electron density from Fe(1), we have an approach to the observed structure, schematically represented by **5**. This form of semibridging CO group is, in principle, the classic one as originally proposed in other cases.[3,4]



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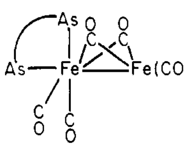

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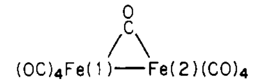

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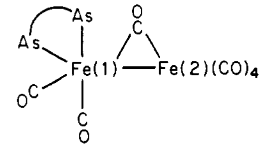

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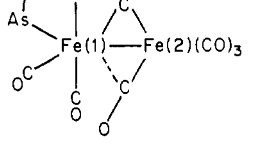


5

This interpretation (**5**) of the (diars)$Fe_2(CO)_7$ structure is not unexceptionable for several reasons. The putative symmetrical bridge, C(2)–O(2), is not fully symmetrical: the Fe–C distances are 1.939 (8) and 2.007 (7) Å, with a significant difference, statistically, of 0.068 (12) Å; the Fe–C–O angles 142.2 (7) and 136.7 (7)° are also significantly different, by 5.5 (1.0)°. On the other hand, the putative semibridging group, C(1)–O(1), deviates considerably from terminal character, with the Fe(2)–C(1)–O(1) angle being 146.3 (6)°, and the Fe(2)–C(1) distance, 1.894 (7) Å, is appreciably longer than the average Fe(2)–C distance for the three fully terminal CO groups, 1.796 (15) Å. Thus, the acceptance of **5** as a schematic description of (diars)$Fe_2(CO)_7$ is not entirely straightforward. However, it is preferable to **1** or **2** and an appreciably better representation is probably not possible in this simple schematic way.

Carbon-13 NMR Spectrum. As can be seen in Figure 2 the spectrum from −132 to +11 °C changes tremendously with temperature. There is one line, at 221.2 ppm, that remains essentially unchanged in width and position throughout, but this is due to a different molecule, the identity of which will be discussed later.

There are then five authentic lines for (diars)$Fe_2(CO)_7$ at −132 °C. Their positions and relative intensities are listed in Table III. This set of lines is clearly inconsistent with the structure of the molecule seen in the crystal, where all seven CO groups are distinct. It is, however, consistent with structure **1**, in which diars has replaced two terminal CO groups of $Fe_2(CO)_9$ in its normal, triply bridged structure. Structure **1** has a plane of symmetry and should have two bridge CO resonances in a 1:2 intensity ratio and three terminal CO resonances in a 2:1:1 ratio.

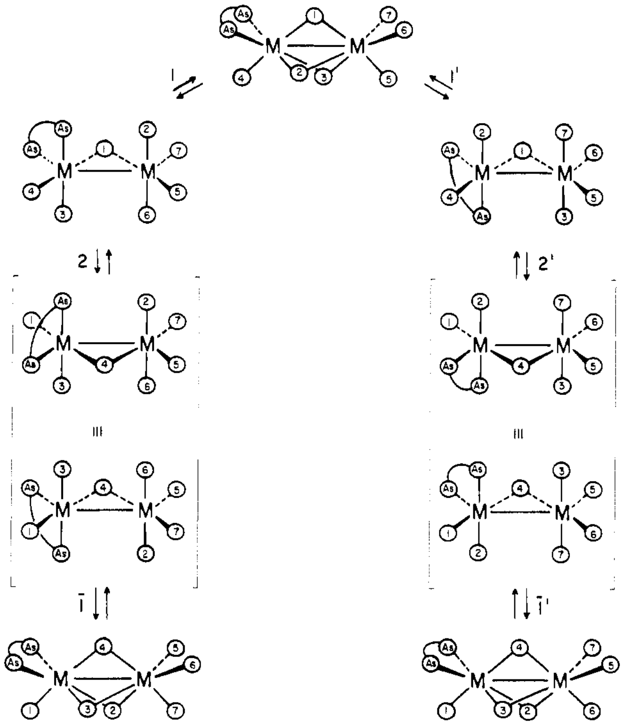
The NMR spectrum is not inconsistent with the possibility that the instantaneous structure in solution is similar to that in the crystal, with equal amounts of the two enantiomers rapidly interconverting by a simple motion in which CO(3) swings into a bridging position as CO(2) swings out, or vice

Table III. Carbon-13 NMR Spectrum of (diars)$Fe_2(CO)_7$ at Various Temperatures^a

temp, °C	obsd and calcd lines
−132 obsd	266.5 (1), 239.2 (2), 214.2 (2), 213.5 (1), 210.5 (1)
−56 obsd	235.3 (2), 223.8 (5)
calcd^b	238.5, 224.1
+11 obsd	226.7
calcd 1^c	228.3
calcd 2^d	227.1

^{a} Line positions in ppm downfield from $Si(CH_3)_4$; numbers in parentheses are relative intensities rounded to the nearest integer. ^{b} Calculated positions using the shifts in the −132 °C spectrum and the pathway explained in the text. ^{c} Weighted average of shifts in the −132 °C spectrum. ^{d} Weighted average of the shifts in the −56 °C spectrum.

Scheme I

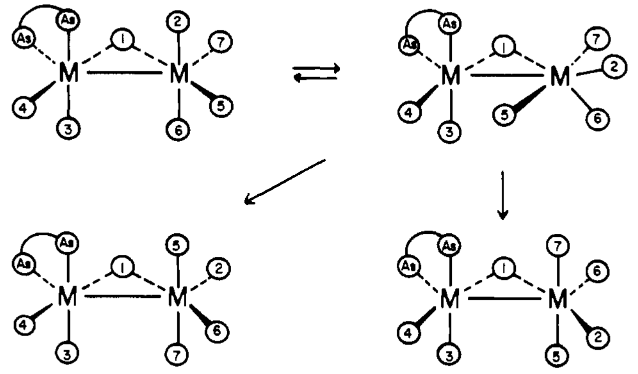


versa. The bridge CO resonance at 266.5 ppm would then be considered to have a normal position, and the line of relative intensity 2 at 239.2 ppm would owe its intermediate chemical shift to the fact that it is caused by one bridge CO and one terminal CO in rapid exchange.

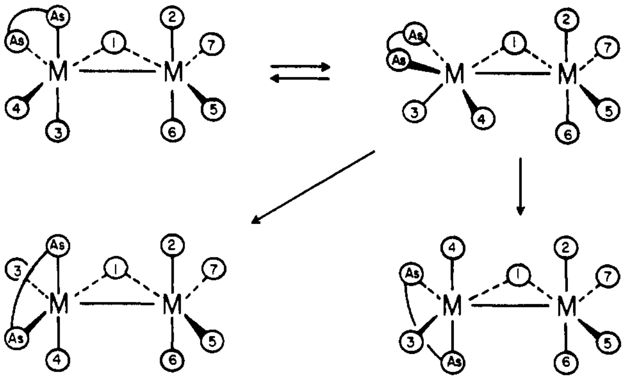
It is impossible to distinguish with certainty between the two possible explanations of the −132 °C spectrum on the evidence at hand. In order to explain the spectra at higher temperatures, it is not necessary to do so. For the sake of simplicity we shall treat the problem as though the instantaneous solution structure is **1** and its slow exchange limit spectrum is that observed at −132 °C.

We now present an explanation of the spectral changes occurring above −132 °C. This explanation has been worked out with the following principles in mind. We have tried to account for the observations by (a) using the least complicated scheme(s) possible, (b) using only structures and structural changes for which there is precedent and prior indication that they have general applicability in the behavior of metal carbonyls, and (c) being as explicit as possible at all stages. We have found that it is possible to explain in detail all the observations without deviating from this methodology. We do not assert that the following explanation is necessarily the only one, but it is the simplest and most logical one we have been able to devise.

Scheme II



Scheme III



Scheme I shows the results of transformation of the triply bridged structure to a singly bridged one (by either of two enantiomeric paths 1 and 1′), followed by reversal of the roles of CO(1) and CO(4) (steps 2 and 2′) and then by restoration of triply bridged structures (steps 1̄ and 1̄′). The net result of rearrangements of this nature is to permute CO(1) and CO(4), to scramble CO(5), CO(6), and CO(7), and to leave CO(2) and CO(3) NMR equivalent as they are to begin with. Scheme I would predict a change of the 1:2:2:1:1 spectrum to a 2:2:3 pattern.

Scheme II shows a representative rearrangement that results when a singly bridged structure traverses a Berry axial/equatorial exchange on the unsubstituted end. When the results of rearrangements of this kind are added to those of scheme I, the overall results is to permute CO(1) and CO(4) and scramble all the five others, CO(3)–CO(7), among themselves. Obviously all that is essential here is the axial/equatorial exchange, and it need not necessarily occur by the Berry arrangement as shown.

Clearly the processes shown in Schemes I and II, operating more or less simultaneously, can account for the changes in the NMR spectrum from −132 to ca. −56 °C. To account for the complete averaging of all signals between −56 and 11 °C, we may assume that a Berry type axial/equatorial exchange process, Scheme III, on the substituted end of the molecule, having a slightly (ca. 2 kcal mol^{-1}) higher activation energy then adds its contribution to those scrambling processes, Schemes I and II, already occurring rapidly.

As shown in Table III the chemical shift values observed at higher temperatures are not exactly equal to those obtained by averaging the values measured at lower temperatures for the lines postulated to be coalescing. Discrepancies of a few ppm are found. This, however, is not unusual, as the following examples will illustrate, and does not therefore detract from the validity of the arguments. In (1,2-diazine)$Fe_2(CO)_7$ the single ^{13}C peak for all CO groups at 26 °C is at 217.0 ppm whereas the weighted average of the four peaks observed at −139 °C is 223.6 ppm.[7] In (1,2-diazine)$Ru_3(CO)_{10}$, the

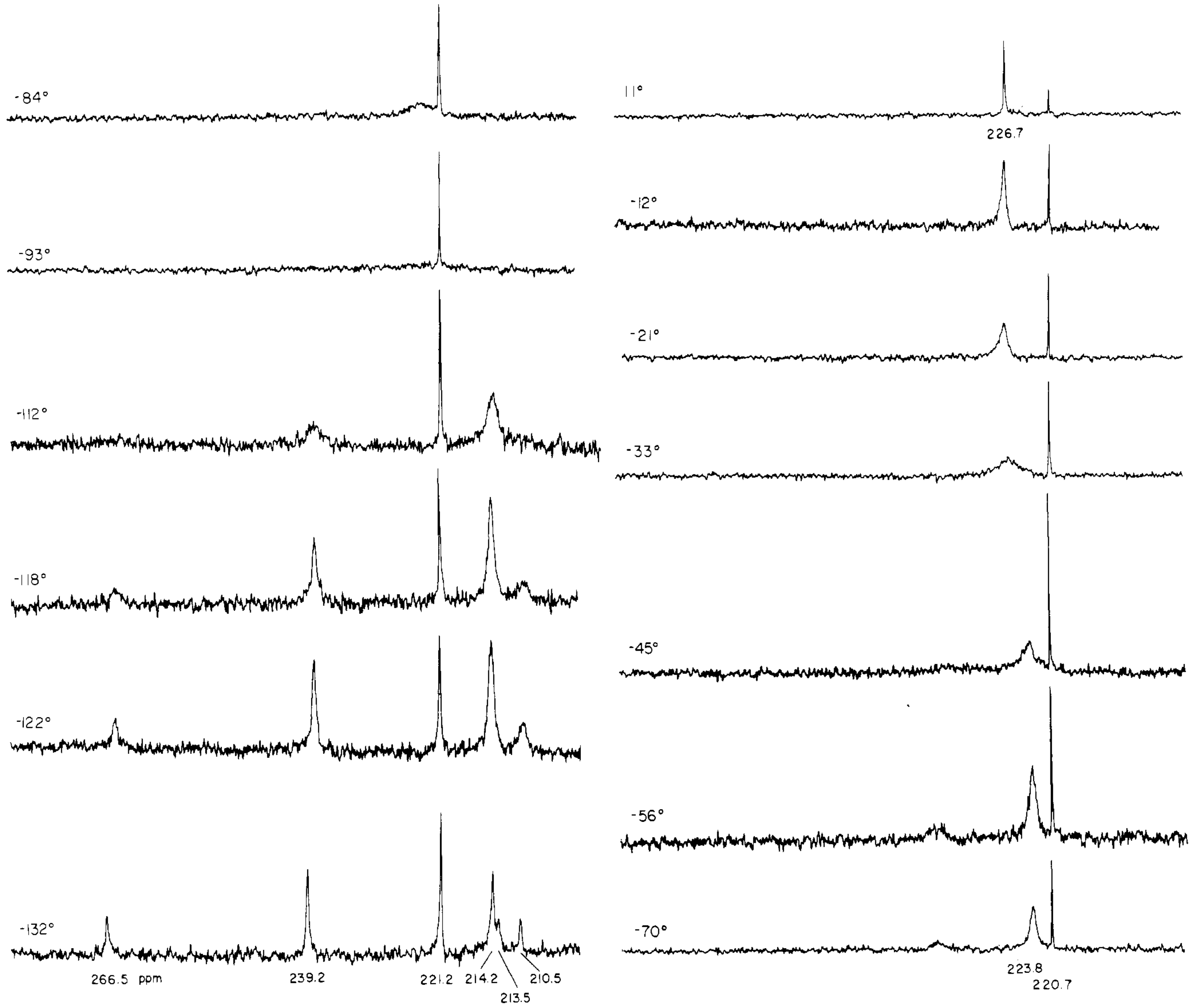


Figure 2. Carbon-13 NMR spectra of (diars)Fe$_2$(CO)$_7$ from −132 to 11 °C. The indicated chemical shifts, in ppm, are downfield from (CH$_3$)$_4$Si.

position of the single line at room temperature is 213.9 ppm while the average of the seven lines in the slow-exchange spectrum at −156 °C is 217.6 ppm.[8] As in the present case the calculated average values are higher than the observed ones.

We have given considerable attention to the question of what is the impurity responsible for the NMR line at ca. 221 ppm, which remains a sharp singlet over the entire temperature range of the measurements. The obvious possibilities are Fe(CO)$_5$ or some simple diars-substituted derivative of it. To test the first of these, we added a small amount of Fe(CO)$_5$ to a solution of the (diars)Fe$_2$(CO)$_7$. The NMR spectrum of the solution then exhibited a third peak, which was attributable to the Fe(CO)$_5$. The next likely impurities were (diars)Fe$_2$(CO)$_8$, a byproduct in the original reaction, and (diars)Fe(CO)$_3$, but spectroscopic analysis quickly ruled out these materials. Also, this impurity was observed to incorporate ^{13}CO very readily into its coordination sphere, certainly much more rapidly than Fe(CO)$_5$, (diars)Fe$_2$(CO)$_8$, or (diars)Fe(CO)$_3$. We also noted that regardless of the nature or extent of prior efforts (e.g., recrystallization or chromatography) to clean up the sample of (diars)Fe$_2$(CO)$_7$, the solutions prepared for NMR study all showed the same amount of "impurity" within the limits (e.g., ±20%) of error.

These observations forced us to consider the possibility that the extraneous resonance is due not to an impurity but to an isomer of (diars)Fe$_2$(CO)$_7$. Support for this idea came from further NMR studies. These experiments showed that the ratio of the intensities of the two resonances at room temperature was greatly dependent on the polarity of the solvent. Hence, in C$_6$D$_6$, the spectrum at 20 °C is similar to that presented in Figure 2 at 11 °C except that the intensities of the two resonances are reversed.

We can only speculate on the identity of this isomer, which must satisfy two main dynamic criteria: (1) It must interconvert with the major isomer on a time scale that is greater than milliseconds even at room temperature but less than minutes, since at room temperature the equilibria between the two is established in about 1 min but the exchange does not affect the NMR spectrum. (2) It must undergo complete internal CO scrambling, which is rapid on the NMR time scale even at −132 °C. It seems impossible to imagine a structure in which all seven CO groups have static equivalence. One structure, which may satisfy both these criteria, is shown schematically as **6**.

It seems reasonable that such a structure could interconvert with that of the major isomer with a half-life of the order of 1 min, but not in a matter of milliseconds. Rapid intramolecular scrambling of the seven CO groups at −132 °C might

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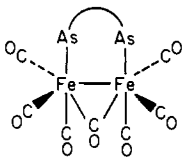
(7) Cotton, F. A.; Hanson, B. E.; Jamerson, J. D.; Stults, B. R. *J. Am. Chem. Soc.* **1977**, *99*, 3293.

(8) Cotton, F. A.; Hanson, B. E.; Jamerson, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 6588.



6

seem unlikely, but it is not by any means out of the question, since it has beeh shown[9] that in (dppm)$Fe_2(CO)_7$, which has an analogous structure, the ^{13}C resonance for all seven CO groups is a sharp 1:2:1 triplet at −103 °C, indicating that all of them are passing rapidly over all positions on both iron atoms. However, let us reiterate that our suggestion of **6** to account for the "impurity" line in the ^{13}C NMR spectra of the title compound is only a plausible speculation and that if it is incorrect our analysis of the line shape changes for the title compound is in no way affected.

Acknowledgment. We are grateful to the Robert A. Welch Foundation for support of the work done at Texas A&M University under Grant No. A-494 and the Comision Asesora de Investigacion Cientifica y Tecnica for a grant. B.W.S.K. was the recipient of a NATO Postdoctoral Fellowship administered by the Natural Sciences and Engineering Research Council of Canada, 1979–1981.

Registry No. (diars)$Fe_2(CO)_8$, 24996-29-0; (diars)$Fe_2(CO)_7$, 79391-63-2; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: A table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(9) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4422.

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Steric Contributions to the Solid-State Structures of Bis(phosphine) Derivatives of Molybdenum Carbonyl. X-ray Structural Studies of *cis*-$Mo(CO)_4[PPh_{3-n}Me_n]_2$ (n = 0, 1, 2)

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Received July 21, 1981

The crystal and molecular structures of three *cis*-$Mo(CO)_4(PR_3)_2$ compounds—$PR_3 = PMe_2Ph$ (**1**), $PR_3 = MePh_2$ (**2**), and $PPh_3 = PR_3$ (**3**)—have been determined to provide data for assessing the influence of steric effects on the stability and reactivity of such molecules. In the order **1**, **2**, **3**, the following changes occur: $\angle$P–Mo–P = 94.78 (5), 92.52 (5), 104.62 (7)°; r(Mo–P) = 2.529 (3), 2.555 (5), 2.577 (2) Å. The irregularity in the angle changes is probably due to the rotational orientations of the ligands in **1** and **2** and may be characteristic of the solid state only. Crystallographic data are as follows. **1**: $P2_12_12_1$ with a = 8.203 (1) Å, b = 9.795 (1) Å, c = 27.604 (4) Å, V = 2217 (1) Å^3, Z = 4. **2**: Pc with a = 9.648 (2) Å, b = 10.670 (3) Å, c = 14.065 (1) Å, β = 98.22 (1)° V = 1433 (1) Å^3, Z = 2. **3**: $P\bar{1}$ with a = 11.522 (1) Å, b = 16.909 (3) Å, c = 9.633 (2) Å, α = 98.05 (2)°, β = 110.29 (1)°, γ = 99.95 (1)°, V = 1693 (1) Å^3, Z = 2. The steric and electronic factors that may affect the molecular structures are discussed, and it is shown that steric factors play a key role (affecting also the chemical reactivity) but not in a quantitatively predictable way.

Introduction

Disubstituted octahedral molybdenum carbonyl derivatives of *cis* stereochemistry, *cis*-$Mo(CO)_4L_2$, where L is a sterically assertive phosphine or phosphite ligand, have been shown to dissociate readily one of the phosphorus donor ligands.[2,3] The reaction described in eq 1 occurs under rather mild conditions

$$cis\text{-}Mo(CO)_4L_2 + CO \rightarrow Mo(CO)_5L + L \qquad (1)$$

by a ligand dissociative process. For example, phosphine or phosphite ligands having large cone angles,[4] Cy_2PhP (162°), PPh_3 (145°), and P(O-*o*-tol)$_3$ (141°), undergo reaction 1 at convenient rates at temperatures ranging from 30 to 75 °C. This steric effect tends to overshadow electronic effects although phosphites are found to dissociate less rapidly than phosphines of comparable size. On the other hand when the phosphorus donor ligand has a small cone angle or is capable of adopting a conformation that minimizes repulsive nonbonding interactions, reaction 1 proceeds slowly or not at all, even at elevated temperatures. On the basis of ^{13}CO-uptake experiments the stereochemistry of the five-coordinate intermediate afforded during reaction 1, [$Mo(CO)_4L$], has been shown to be square pyramidal with the unique ligand (L) occupying a basal coordination site.

For bulky phosphorus donor ligands such as PPh_3 the nonbonding interactions in these *cis*-$Mo(CO)_4L_2$ derivatives can be relieved by isomerization to the trans isomeric form.

Since dissociative loss of the PPh_3 ligand in the *cis*-$Mo(CO)_4(PPh_3)_2$ derivative is more facile than the cis $\rightleftharpoons$ trans isomerization process, the latter process is thought to involve some degree of metal–phosphorus bond breaking in the transition state. On the other hand, for smaller phosphine ligands that are nevertheless somewhat sterically demanding such as the Et_3P and n-Bu_3P ligands (cone angles of 132°), isomerization to an equilibrium mixture favoring the trans isomer occurs via a non-bond-breaking mechanism.[5]

As part of a detailed investigation of possible distortions in the ground-state structures of low-valent transition-metal derivatives containing phosphorus donor ligands, we have determined the solid-state structures of *cis*-$Mo(CO)_4[PPh_{3-n}Me_n]_2$ where n = 0, 1, and 2.

Experimental Section

Compound Preparations. The *cis*-$Mo(CO)_4L_2$ derivatives (L = PMe_2Ph (**1**), $PMePh_2$ (**2**), and PPh_3 (**3**)) were prepared from *cis*-

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(1) Permanent address: Department of Chemistry, Tulane University, New Orleans, LA 70118.

(2) Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680.

(3) Darensbourg, D. J.; Graves, A. H. *Inorg. Chem.* **1979**, *18*, 1257.

(4) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(5) Darensbourg, D. J. *Inorg. Chem.* **1979**, *18*, 14.

0020-1669/82/1321-0294$01.25/0