A New Mode of Carbonyl Scrambling. Structure and Dynamics of (1,2-Diazine)heptacarbonyldiiron(*Fe–Fe*)

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Abstract: The title compound has been characterized structurally by x-ray crystallography and dynamically by carbon-13 nuclear magnetic resonance. The structure consists of two roughly trigonal bipyramidal halves, with N atoms in apical positions and one CO shared as a bridging group. There is also an Fe–Fe bond, 2.573 (1) Å, and the molecule has a plane of symmetry containing the bridging CO and bisecting both the Fe–Fe bond and the 1,2-diazine ring. Crystal data: $P\bar{1}$, $Z = 2$; $a = 9.128$ (5) Å, $b = 10.574$ (6) Å, $c = 8.905$ (5) Å, $\alpha = 95.26$ (5)°, $\beta = 119.89$ (4)°, $\gamma = 100.46$ (4)°. The structure was solved and refined to $R_1 = 0.045$ and $R_2 = 0.060$ using 1497 data with $I > 3\sigma(I)$ collected on an automated counter-diffractometer using graphite-monochromated Mo Kα radiation. In solution the ^{13}CO spectrum consists of four lines of relative intensities 1:2:2:2 at −139 °C, with the middle two lines accidently superposed. Shortly above this temperature the first, the last, and one of the middle lines broaden. The latter two coalesce to a single peak at about −120 °C. At about −100 °C a combined resonance of relative intensity 5 appears. This and the remaining line of relative intensity 2 coalesce at about −30 °C. We suggest that the first stages (from −136 to about −60 °C) of broadening and coalescence are due to cycling of the five essentially coplanar "equatorial" CO's over both iron atoms and that the changes observed above about −50 °C are caused by local averaging within each of the equivalent Fe(CO)$_3$ moieties, superimposed on the already rapid cycling process.

Mechanistic study of fluxional and other stereochemically nonrigid molecules[1] has now been underway for about a decade.[2] However, mechanistic study of the scrambling of CO groups and other ligands in polynuclear metal carbonyls goes back only about 5 years,[3] and, despite the appearance of well over 100 papers on the subject, this particular subfield is still in its beginnings.

While binuclear molecules whose bridged forms contain pairs of bridges are rather well understood,[3-5] those having only a single bridge have received much less attention. It has been shown[6,7] that $(\eta^5\text{-}C_5H_5)(CO)Rh(\mu\text{-}CO)Rh(CO)(\eta^5\text{-}C_5H_5)$ and $(\eta^5\text{-}C_5H_5)(CO)Rh(\mu\text{-}CO)Rh[P(OPh)_3](\eta^5\text{-}C_5H_5)$ undergo bridge-terminal exchange with about equal facility. These observations imply that in *both* cases one-for-one interchange of bridge and terminal CO groups occurs, since, for the latter molecule no other pathway seems reasonable.

One other type of binuclear molecule with a single bridge has been investigated,[8] namely, $[(Ph_2PCH_2PPh_2]Fe_2(CO)_7$. The carbon-13 NMR spectrum of this molecule, at all experimentally accessible temperatures, consists of a single 1-3-1 triplet, which implies that all seven CO groups are scrambled over both iron atoms and have time-average equivalence. However, since only the fast-exchange temperature regime is observable, no mechanistic information has been obtained. In the hope of learning more about this type of system we have investigated the structural and dynamical properties of a related molecule $(C_4H_4N_2)Fe_2(CO)_7$, in which the bridging bidentate ligand, $C_4H_4N_2$, is 1,2-diazine, commonly called pyridazine.

Experimental Section

All operations were performed in an atmosphere of dry nitrogen. Solvents were dried over potassium benzophenone and were distilled under nitrogen just prior to use. $(C_4H_4N_2)Fe_2(CO)_7$ was prepared according to the method of Herberhold and Leonhard.[9] Crystals suitable for x-ray crystallographic studies were obtained from THF–hexane at −20 °C.

X-ray Data Collection. A roughly rectangular-prismatic crystal measuring approximately 0.21 × 0.31 × 0.38 mm was sealed in a thin-walled glass capillary. General procedures used for crystal characterization and data collection have been previously described.[10] The crystal was shown to diffract well and had average peak widths at half-heights of 0.2° for several intense reflections.

The crystal was found to be triclinic having a unit cell volume consistent with $Z = 2$, indicating the space group to be $P\bar{1}$. This choice was supported at all stages of the subsequent structure solution and refinement. The final lattice constants and orientation matrix used for data collection obtained from the least-squares refinement of the diffraction geometry for 15 high angle reflections, 23.4° < 2θ Mo Kα < 37.4, are: $a = 9.128$ (5) Å, $b = 10.574$ (6) Å, $c = 8.905$ (5) Å, $\alpha = 95.26$ (5)°, $\beta = 119.89$ (4)°, $\gamma = 100.46$ (4)°, $V = 715.9$ (7) Å^3, with $d_{\text{calcd}} = 1.80$ g cm^{-3} for $Z = 2$, and a molecular weight of 387.85.

Data were collected at 22 ± 2 °C using a Syntex $P\bar{1}$ autodiffractometer, equipped with a graphite-crystal monochromator, using Mo Kα radiation and the θ–2θ scan technique. Reflection intensities were recorded using scan rates from 4 to 24° min^{-1} and scan ranges from Mo Kα_1 − 0.9° to Mo Kα_2 + 0.9°. A total of 1740 unique data in the range 0° < Mo Kα < 45.0° were recorded of which 243 reflections having $I < 3\sigma(I)$ were deleted from the data set. Two standard reflections, measured every 250 reflections, showed no significant change during data collection. No absorption correction was applied in view of the small linear absorption coefficient, $\mu = 10.6$ cm^{-1}. The 1497 data that were retained were reduced to a set of relative $|F_o|^2$ after corrections for Lorentz and polarization effects.[11]

Solution and Refinement of the Structure.[11] The coordinates for the two unique iron atoms were derived from a three-dimensional Patterson synthesis. Their positional and isotropic thermal parameters were refined in three cycles of least-squares refinement to discrepancy indices of

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.377$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.468$$

The function minimized during the least-squares refinement is $\Sigma w(|F_o| - |F_c|)^2$, where the weighting factor, w, is equal to $4F_o^2/\sigma(F_o^2)^2$. Atomic scattering factors used in all least-squares refinements were those of Cromer and Waber.[12] Anomalous dispersion effects where included in the calculation of the scattering factors for iron.[13] The remaining 20 non-hydrogen atoms were located using two difference Fourier maps, each following refinement of the atoms located up to that point. The 22 unique non-hydrogen atoms were refined employing first isotropic temperature parameters for all atoms to give $R_1 = 0.079$ and $R_2 = 0.105$ and then anisotropic temperature parameters to give $R_1 = 0.049$ and $R_2 = 0.067$. The four hydrogen atoms were located from a difference Fourier map following the anisotropic refinement. The structure was refined to convergence in three cycles of full-matrix least-squares refinement, employing anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for the four hydrogen atoms, yielding final residuals of $R_1 = 0.045$ and $R_2 = 0.060$. During the final cycle of refinement no parameter shifted by more than 0.02σ, where σ is the estimated standard deviation of an individual parameter. A final difference Fourier map was essentially featureless.

Preparation of Enriched $(C_4H_4N_2)Fe_2(CO)_7$. Attempts to enrich the isotopically normal compound with ^{13}CO by thermally or photo-

Table I. Positional and Thermal Parameters for $(C_4H_4N_2)Fe_2(CO)_7$ and Their Estimated Standard Deviations[a]

Atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	0.4997 (1)	0.28087 (8)	0.21887 (9)	0.0133 (1)	0.00686 (9)	0.0114 (1)	0.0033 (2)	0.0148 (2)	0.0020 (2)
Fe(2)	0.1704 (1)	0.26778 (9)	0.04985 (10)	0.0150 (1)	0.00813 (9)	0.0102 (1)	0.0060 (2)	0.0115 (2)	0.0042 (2)
O(1)	0.2739 (6)	0.0597 (5)	−0.0932 (6)	0.0249 (8)	0.0108 (6)	0.0186 (6)	0.001 (1)	0.021 (1)	−0.009 (1)
O(4)	0.8042 (5)	0.1725 (5)	0.3822 (6)	0.0166 (6)	0.0153 (6)	0.0320 (9)	0.016 (1)	0.026 (1)	0.007 (1)
O(2)	0.6217 (7)	0.5540 (5)	0.4237 (5)	0.0328 (9)	0.0076 (5)	0.0187 (7)	0.002 (1)	0.029 (1)	−0.000 (1)
O(3)	0.5903 (7)	0.3630 (6)	−0.0348 (6)	0.0410 (10)	0.0158 (8)	0.0244 (7)	−0.005 (2)	0.048 (1)	0.005 (1)
O(7)	0.1742 (7)	0.5289 (5)	0.2067 (6)	0.0371 (10)	0.0116 (5)	0.0234 (9)	0.021 (1)	0.025 (1)	0.005 (1)
O(5)	0.1426 (8)	0.3635 (6)	−0.2573 (6)	0.0386 (11)	0.0198 (8)	0.0175 (7)	0.009 (2)	0.032 (1)	0.018 (1)
O(6)	−0.1943 (7)	0.1112 (6)	−0.1642 (7)	0.0191 (10)	0.0136 (7)	0.0227 (9)	0.001 (1)	0.006 (2)	0.006 (1)
N(1)	0.4001 (5)	0.2095 (5)	0.3532 (5)	0.0099 (6)	0.0067 (5)	0.0103 (6)	0.0059 (9)	0.0096 (9)	0.0028 (9)
N(2)	0.2301 (6)	0.2008 (5)	0.2652 (5)	0.0109 (7)	0.0075 (5)	0.0100 (6)	0.0030 (10)	0.0092 (10)	0.0012 (10)
C(1)	0.3008 (8)	0.1510 (7)	0.0119 (7)	0.0213 (10	0.0085 (7)	0.0116 (8)	0.004 (1)	0.018 (1)	0.002 (1)
C(4)	0.6806 (8)	0.2128 (7)	0.3157 (7)	0.0178 (9)	0.0079 (7)	0.0182 (9)	−0.002 (1)	0.024 (1)	−0.002 (1)
C(2)	0.5755 (8)	0.4503 (6)	0.3475 (7)	0.0181 (9)	0.0085 (7)	0.0114 (8)	0.005 (1)	0.017 (1)	0.005 (1)
C(3)	0.5528 (8)	0.3316 (7)	0.0673 (8)	0.0212 (11)	0.0099 (8)	0.0170 (10)	0.001 (2)	0.023 (1)	0.002 (2)
C(7)	0.1762 (9)	0.4294 (7)	0.1521 (8)	0.0208 (11)	0.0100 (7)	0.0135 (9)	0.012 (1)	0.015 (2)	0.010 (1)
C(5)	0.1538 (9)	0.3274 (7)	−0.1362 (8)	0.0180 (11)	0.0115 (8)	0.0138 (10)	0.006 (2)	0.012 (2)	0.004 (2)
C(6)	−0.0543 (8)	0.1713 (7)	−0.0786 (7)	0.0211 (11)	0.0095 (7)	0.0131 (9)	0.009 (2)	0.015 (2)	0.009 (1)
C(8)	0.4774 (8)	0.1754 (6)	0.5133 (7)	0.0152 (9)	0.0070 (6)	0.0126 (8)	0.005 (1)	0.013 (1)	0.004 (1)
C(9)	0.3795 (8)	0.1293 (7)	0.5859 (7)	0.0166 (10)	0.0094 (7)	0.0120 (8)	0.004 (1)	0.014 (1)	0.006 (1)
C(10)	0.2078 (8)	0.1220 (7)	0.4969 (7)	0.0237 (10)	0.0090 (8)	0.0180 (9)	−0.002 (2)	0.031 (1)	0.003 (1)
C(11)	0.1339 (7)	0.1568 (6)	0.3353 (7)	0.0138 (8)	0.0083 (6)	0.0165 (8)	0.007 (1)	0.021 (1)	0.007 (1)
H(1)	0.608 (7)	0.191 (6)	0.568 (7)	4. (1)[c]					
H(2)	0.459 (8)	0.117 (7)	0.695 (8)	6. (2)					
H(3)	0.135 (6)	0.102 (5)	0.525 (6)	2. (1)					
H(4)	0.017 (6)	0.182 (5)	0.274 (5)	2. (1)					

[a] Numbers in parentheses are estimated standard deviations in the last significant digits. [b] The form of the anisotropic thermal parameter is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [c] Isotropic temperature factor.

Table II. Bond Lengths of $(C_4H_4N_2)Fe_2(CO)_7$ Compared to $\{[(C_6H_5)_2P]_2CH_2\}Fe_2(CO)_7$[a]

	$C_4H_4N_2$	$[(C_6H_5)_2P]_2CH_2$[b]
Fe1-Fe2	2.573 (1)	2.709 (2)
Fe1-C1	1.968 (6)	1.98 (1)
Fe2-C1	1.987 (7)	2.01 (1)
Fe1-C2	1.839 (7)	1.82 (1)
Fe1-C3	1.743 (7)	1.79 (1)
Fe1-C4	1.765 (8)	1.74 (1)
Fe2-C5	1.772 (7)	1.79 (1)
Fe2-C6	1.801 (8)	1.78 (1)
Fe2-C7	1.840 (7)	1.81 (1)
Fe1-N1	1.956 (4)	
Fe2-N2	1.955 (4)	
N1-N2	1.324 (6)	
N1-C8	1.358 (7)	
C8-C9	1.389 (9)	
C9-C10	1.341 (10)	
C10-C11	1.371 (9)	
N2-C11	1.352 (7)	
C8-H1	1.01 (6)	
C9-H2	0.92 (7)	
C10-H3	0.83 (6)	
C11-H4	1.03 (5)	
C1-O1	1.178 (7)	1.19 (1)
C2-O2	1.118 (7)	1.14 (1)
C3-O3	1.174 (7)	1.14 (1)
C4-O4	1.165 (8)	1.16 (1)
C5-O5	1.140 (7)	1.14 (1)
C6-O6	1.124 (7)	1.14 (1)
C7-O7	1.125 (7)	1.16 (1)

[a] Numbers in parentheses are estimated standard deviations in the last significant digits. [b] Taken from ref 8.

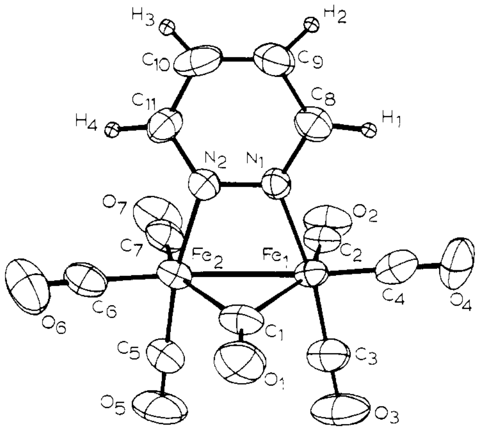


Figure 1. The molecular structure of (1,2-diazine)$Fe_2(CO)_7$. Atoms are represented by their ellipsoids of thermal vibration drawn to enclose 50% of their electron density. The atom numbering scheme is defined.

chemically promoted direct exchange lead to extensive decomposition. Therefore, the following procedure was followed.

Diiron nonacarbonyl (1.50 g; 4.1 mmol) and 100 mL of THF were placed in a 500-mL quartz flask. The flask was immersed in liquid nitrogen and evacuated, and the free volume then filled with CO containing 90% ^{13}C. The closed flask was removed from the liquid nitrogen bath and left overnight to warm to 25 °C. The $Fe_2(CO)_9$ dissolved over a period of 18 h to give a red solution. The flask was again placed in a liquid nitrogen bath, evacuated, and filled with nitrogen. Pyridazine (0.30 mL; 0.33 g; 0.40 mmol) and 100 mL of hexane were introduced and the flask was then irradiated with a UV lamp at ambient temperature for 16 h.

Solvent was then removed under vacuum and the dark solid residue taken up in THF. This solution was chromatographed on Florisil and the blue-green band containing $(C_4H_4N_2)Fe_2(CO)_7$ was isolated and the product recovered by vacuum evaporation. The solid, 0.64 g, 40% yield, was judged by its infrared spectrum to be 20–30% enriched in ^{13}CO.

Results

The positional and thermal vibration parameters for $(C_4H_4N_2)Fe_2(CO)_7$ are listed in Table I. The structure of the molecule is shown in Figure 1, where the atom numbering scheme is also defined. Tables II and III give bond lengths and bond angles, respectively, and compare these with the corre-

Table III. Bond Angles of $(C_4H_4N_2)Fe_2(CO)_7$ Compared to $\{[(C_6H_5)_2P]_2CH_2\}Fe_2(CO)_7$[a]

	$C_4H_4N_2$	$[(C_6H_5)_2P]_2CH_2$[b]
Fe2-Fe1-X1[c]	71.2 (1)	92.5 (1)
Fe1-Fe2-X2[d]	71.6 (1)	94.9 (1)
Fe2-Fe1-C1	49.5 (2)	47.6 (3)
Fe1-Fe2-C1	49.1 (2)	46.8 (3)
Fe1-C1-Fe2	81.4 (2)	85.6 (5)
X1-Fe1-C1	85.9 (2)	92.1 (3)
X2-Fe2-C1	85.6 (2)	91.9 (3)
Fe2-Fe1-C2	96.8 (2)	87.3 (4)
Fe2-Fe1-C3	100.2 (2)	96.8 (4)
Fe2-Fe1-C4	153.7 (2)	161.3 (4)
Fe1-Fe2-C5	98.5 (2)	88.3 (4)
Fe1-Fe2-C6	150.0 (2)	147.2 (4)
Fe1-Fe2-C7	100.0 (2)	102.1 (4)
X1-Fe1-C2	93.7 (2)	96.9 (3)
X1-Fe1-C3	170.1 (2)	167.3 (4)
X1-Fe1-C4	94.6 (2)	83.0 (4)
X2-Fe2-C5	169.9 (3)	175.7 (4)
X2-Fe2-C6	96.1 (2)	90.0 (4)
X2-Fe2-C7	92.2 (2)	87.0 (4)
C1-Fe1-C2	144.4 (3)	134.5 (4)
C1-Fe1-C3	84.8 (3)	87.8 (4)
C1-Fe1-C4	109.2 (3)	114.2 (5)
C1-Fe2-C5	86.4 (3)	92.3 (4)
C1-Fe2-C6	104.0 (3)	100.8 (5)
C1-Fe2-C7	148.0 (3)	148.7 (6)
C2-Fe1-C3	92.2 (3)	92.3 (5)
C2-Fe1-C4	106.3 (3)	111.2 (5)
C3-Fe1-C4	91.4 (3)	85.5 (5)
C5-Fe2-C6	91.8 (3)	88.8 (5)
C5-Fe2-C7	91.4 (3)	89.6 (6)
C6-Fe2-C7	108.0 (3)	110.5 (6)
Fe1-C1-O1	139.5 (6)	137.7 (9)
Fe2-C1-O1	138.6 (5)	136.5 (8)
Fe1-C-O(av)	178.3	176
Fe2-C-O(av)	177.7	176
Fe1-N1-N2	108.9 (3)	
Fe2-N2-N1	108.3 (3)	
N2-N1-C8	120.2 (5)	
N1-N2-C11	119.5 (4)	
N1-C8-C9	120.7 (6)	
N2-C11-C10	121.8 (6)	
C8-C9-C10	118.7 (6)	
C9-C10-C11	119.0 (6)	
N1-C8-H1	112 (3)	
C9-C8-H1	128 (3)	
N2-C11-H4	110 (3)	
C10-C11-H4	125 (3)	
C8-C9-H2	105 (5)	
C10-C9-H2	136 (5)	
C9-C10-H3	130 (4)	
C11-C10-H3	111 (4)	

[a] Numbers in parentheses are estimated standard deviations in the last significant digits. [b] Taken from ref 8. [c] X1 refers to N1 in $(C_4H_4N_2)Fe_2(CO)_7$, P1 in $\{[(C_6H_5)_2P]_2CH_2\}Fe_2(CO)_7$. [d] X2 refers to N2 in $(C_4H_4N_2)Fe_2(CO)_7$, P2 in $\{[(C_6H_5)_2P]_2CH_2\}Fe_2(CO)_7$.

sponding dimensions of $(Ph_2PCH_2PPh_2)Fe_2(CO)_7$, which has a very similar structure.

The carbon-13 NMR spectra of various temperatures are shown in Figures 2 and 3.

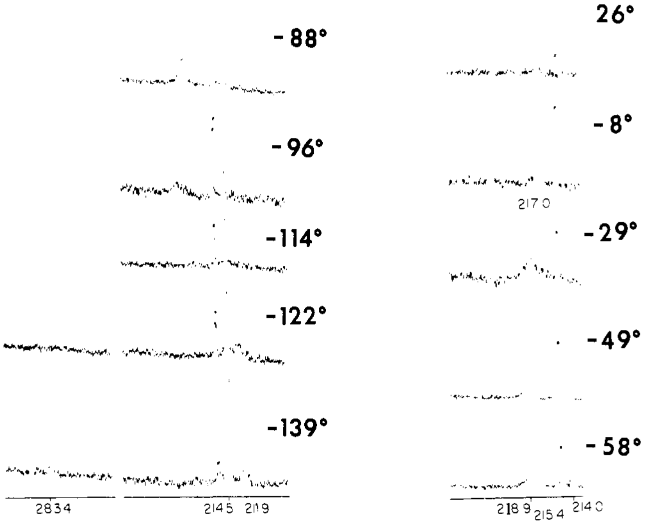


Figure 2. Carbon-13 NMR spectra in the carbonyl region at various temperatures. The peak due to the impurity $(C_4H_4N_2)Fe(CO)_4$ is marked with an asterisk. Chemical shifts are in parts per million downfield from Me_4Si.

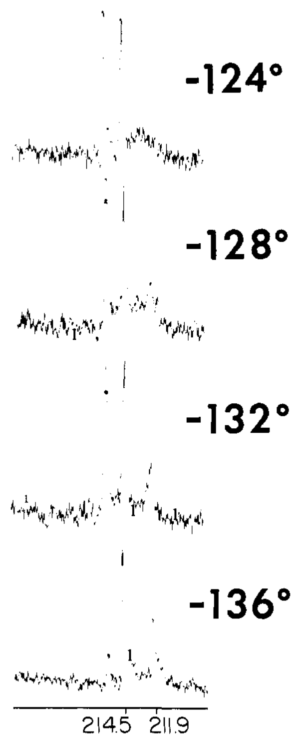


Figure 3. Spectra in the upfield carbonyl region showing details of line collapse.

Discussion

Molecular Structure in the Crystal. The (1,2-diazine)-$Fe_2(CO)_7$ molecule is of the same structural type[14-16] as the previously characterized[8] $(Ph_2PCH_2PPh_2)Fe_2(CO)_7$. It has one bridging CO and three distinct types of terminal CO. The molecule has only one element of symmetry, namely, a plane bisecting the Fe-Fe and the N-N bonds and containing the bridging CO group. It is thus quite different from the stoichiometrically similar $(bpy)Fe_2(CO)_7$ in which the diamine is chelated to one metal atom.[17] The difference is, of course, caused by the geometries of the diamines. bpy is incapable of bridging two metal atoms that are bonded to each other, whereas 1,2-diazine is incapable of forming two bonds to the same metal atom.

While (1,2-diazine)$Fe_2(CO)_7$ and $(Ph_2PCH_2PPh_2)$-$Fe_2(CO)_7$ have qualitatively the same structure there are several quantitative differences. The most striking one is in the Fe-Fe bond lengths, which are 2.573 (1) Å in the present case and 2.709 (2) Å in the $Ph_2PCH_2PPh_2$ compound. This is not particularly surprising since the N-N separation is only 1.324 (6) Å while the P···P separation is 3.00 (4) Å, though part of this effect is offset by the fact that the bond directions from the two N atoms diverge while those of the P atoms are parallel. In any event, the importance of the difference in the Fe-Fe bond lengths, while real and sizeable, should not be overestimated. Fe-Fe single bond distances are known to cover a considerable range, depending on the associated ligands, from as short[18] as 2.372 (2) Å to as long[19] as 2.866 (1) Å.

The difference in Fe-Fe bond lengths is reflected in the different angles at the bridging carbon atoms, 81.4 (2) and 85.6 (5)°. Actually, the effect of the shorter distance in decreasing the angle is somewhat mitigated by the fact that the Fe-C (bridge) distances are also shorter, 1.973 (5) Å, as compared to those in $(Ph_2PCH_2PPh_2)Fe_2(CO)_7$, 2.00 (2) Å.

The 1,2-diazine ligand and its bonding to the $Fe_2(CO)_7$ moiety display some interesting features. Formally, each N atom donates an electron pair to an iron atom, as in the $LFe(CO)_4$ molecules[20] where L = pyridine and pyrazine or in $(bpy)Fe_2(CO)_7$.[17] However, in $(C_4H_4N_2)Fe_2(CO)_7$ the iron-nitrogen bond length, 1.955 (4) Å, is considerably shorter than those in these other cases, viz., $(C_5H_5N)Fe(CO)_4$ (2.046 (5) Å),[20] $(C_4H_4N_2)Fe(CO)_4$ (2.031 (2) Å),[20] or $(bpy)Fe_2(CO)_7$ (2.02 (1), 2.04 (1) Å).[17] The iron-nitrogen bond length found here is actually closer to those reported for complexes of the types $N_2Fe_2(CO)_6$ where N_2 represents a diazine ligand which symmetrically bridges both iron atoms (e.g., $(C_5H_8N_2)Fe_2(CO)_6$, 1.915 (7) Å,[21a] and $(C_{12}H_8N_2)$-$Fe_2(CO)_6$, 1.914 (6) Å[21b]). While in the diphenylpyridazine complex,[22] $(\mu\text{-}PhC_4H_2N_2)(\mu\text{-}C_4H_2O_3)Fe(CO)_6$, the Fe-N distances are 2.00 (1) and 2.01 (1) Å. This diversity of Fe-N bond lengths is not easily explained. In the present case there is no significant variation in bond lengths within the $C_4H_4N_2$ ring, suggesting perhaps that the rather short Fe-N bonds are due to electron delocalization over the entire $(C_4H_4N_2)Fe_2$ system in contrast to localization of bonds in other 1,2-diazine derivatives.[23]

The bond lengths observed in the coordinated 1,2-diazine ring here provide an interesting contrast to those observed in 1,2-diazine derivatives in which there is strong evidence for localized bonding.[23] A carbon-nitrogen double bond length of 1.301 (9) Å and a nitrogen-nitrogen single bond length of 1.346 (7) Å in 2*H*-pyridaz-3-thione[24] can be contrasted to the carbon-nitrogen distances, (1.358 17) and 1.352 (7) Å, and nitrogen-nitrogen distances, 1.324 (6) Å, reported here. While the two nitrogen-nitrogen distances differ by an amount that is only on the borderline of significance, the carbon-nitrogen bond lengths of the 1,2-diazine ring are significantly longer than that in 2*H*-pyridaz-3-thione.[24] Furthermore the three other carbon-carbon bond lengths of the coordinated 1,2-diazine ligand (Table III) are comparable to those in other delocalized systems; cf. 1.39 Å in benzene.[25] Hence it is apparent that the coordinated 1,2-diazine ring has a considerable degree of π delocalization.

Structural and Dynamic Properties in Solution. The reported[9] infrared spectrum of $(C_4H_4N_2)Fe_2(CO)_7$ in solution, which we have verified, is entirely consistent with the retention of the solid state structure, at least in a qualitative sense. We shall assume this to be the case in interpreting the NMR spectra.

It has been reported[8] that for the structurally similar molecule $(Ph_2PCH_2PPh_2)Fe_2(CO)_7$ the carbon-13 NMR spectrum at room temperature for the carbonyl carbon atoms contains only one signal, a triplet. This shows that CO groups scramble rapidly over all four kinds of site, almost certainly internuclearly. The limited solubility of $(Ph_2PCH_2PPh_2)$-$Fe_2(CO)_7$ seriously restricts the study of spectra at low temperatures, but we have found that even at −100 °C this triplet shows little if any evidence of broadening. Therefore, it has been impossible to obtain mechanistic information about CO scrambling in this compound.

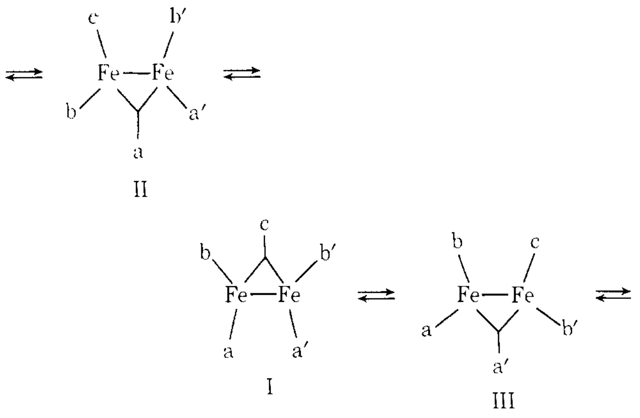
Our study of $(1,2\text{-}C_4H_4N_2)Fe_2(CO)_7$ was undertaken in the hope that this molecule might lend itself of the elucidation of the mechanism in molecules of this structural type. That hope has been fulfilled. As Figure 2 shows, the slow exchange spectrum can be observed, at −139 °C. It consists of four lines of relative intensities 1:2:2:2, with the middle two accidently superposed, in full accord with the molecular structure shown in Figure 1. Even at −139 °C the line at 283.4 ppm due to the bridging CO is somewhat broadened. There is also a broad line, marked with an asterisk, due to an impurity. This line narrows as the temperature rises and need not concern us further at present.[26]

Between −139 and −122 °C the bridging CO resonance broadens so much as to virtually disappear and two of the three resonances of relative intensity 2 also broaden greatly, while the third one remains sharp. At −96 °C a broad signal at ~227 ppm, of relative intensity 5, can be seen. This sharpens between −96 and −58 °C but at about that temperature it again begins to broaden as the previously unchanged signal at 214.5 ppm does also. Between −29 and +26 °C a signal at 217 ppm forms and sharpens.

It is clear that the total averaging of all the signals into one occurs in two distinct stages. In stage I five CO groups, including the bridging CO are being equivalenced by some dynamic process. This stage is observed up to about −60 °C. After this stage is well advanced, stage II, in which the remaining two CO's are equivalenced with the five, commences.

There are three reasonable ways to choose the five CO's being equivalenced in stage I, and no rigorous way to decide between them. These are, in terms of the numbering scheme shown in Figure 1 [(a) $C_1O_1 + (C_2O_2, C_7O_7) + (C_4O_4, C_6O_6)$; (b) $C_1O_1 + (C_2O_2, C_7O_7) + (C_3O_3, C_5O_5)$; (c) $C_1O_1 + (C_4O_4, C_6O_6) + (C_3O_3, C_5O_5)$] where pairs that are equivalent under the idealized mirror symmetry are included in parentheses.

Intuitively, we prefer set (a), since this corresponds to a cycling of five essentially coplanar CO groups which remain always in or near their original common plane. The molecular structure can be thought of as a combination of two trigonal-bipyramidally pentacoordinated iron atoms, sharing the bridging CO group and also united by an Fe-Fe bond. Equivalencing within set (a), by means of the following scheme



results from omnidirectional circulation of the CO groups in the common equatorial plane.

A closer examination of the proposed mechanism shows that in each step one of the nuclei labeled b and b′ in I remains in the same type environment, while a, a′, and c all change. Thus, the resonance due to nuclei in the environment of b and b′ in I should broaden, initially, only half as fast as the other resonance of relative intensity 2 due to the nuclei in the environment of a and a′. Computer simulations were carried out to display the differential rates of collapse in detail. The experimental spectra have exactly the expected behavior, within experimental error, as can be seen in Figure 3, where the changes in the high field carbonyl signals between −139 and −122 °C are shown in detail. If, as we propose it is set (a) within which the cycling of five carbonyl groups occurs, then carbonyls of type b, b′ have a chemical shift of 211.9 ppm.

One thing which is rigorously certain from the observation that the two signals of relative intensity 2 that collapse in stage I collapse at unequal rates is that the scrambling process is, indeed, one of the cyclic ones and not a random one, for the latter would result in uniform collapse of both lines.

For stage II we postulate the kind of local scrambling within each $Fe(CO)_3$ moiety that has been observed in many other cases.[27-34] Thus, stage II involves scrambling within each of the sets (C_2O_2, C_3O_3, C_4O_4) and (C_5O_5, C_6O_6, C_7O_7). These processes, superimposed upon the cycling of the five CO groups in any one of the three sets (a), (b), or (c), above, will lead to a single-line spectrum.

It is significant that the type of process we are proposing for stage I involves, in effect, one-for-one exchange of a bridging and a terminal CO group rather than pairwise opening and closing of bridges.[35] In this case, of course, the one-for-one exchange is not of the simple type that evidently occurs in $Cp_2Rh_2(CO)_2P(OPh)_3$,[7] but is instead part of a more complex pattern in which three other CO groups are also required to move in unison.

Acknowledgment. We are grateful to The Robert A. Welch Foundation for support, under Grant No. A494, and to the National Science Foundation for funds used to purchase the JEOL-PFT 100 spectrometer.

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