

# Reactivity of Diiron Nonacarbonyl in Tetrahydrofuran. I. The Isolation and Characterization of Pyridinetetracarbonyliron and Pyrazinetetracarbonyliron

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**Abstract:** It has been found that when tetrahydrofuran is used as the reaction medium, diiron nonacarbonyl exhibits a pattern of reactivity qualitatively different from that previously known using other reaction media. Among a variety of new products which have been isolated are the simple, amine-substituted derivatives of iron pentacarbonyl, *viz.*,  $\text{LFe}(\text{CO})_4$  with  $\text{L} = \text{pyridine}$  and  $\text{pyrazine}$ . Compounds of this important type have not previously been known, and there has been a general feeling that they might be inaccessible owing to a tendency toward disproportionation. Both of these compounds have been well characterized by spectroscopic and X-ray crystallographic methods. In each case the amine ligand occupies an axial position in an essentially trigonal bipyramidal molecule. The ir spectra show that this structure persists in solution. Interestingly, the rotational orientations of the rings are quite different in the two cases, probably because of intermolecular packing effects. The Fe-N bonds are of identical length, 2.039 (4) Å. The Fe-C bonds are all about 0.03 Å shorter than those in  $\text{Fe}(\text{CO})_5$ , in accordance with the good  $\sigma$ -donor and poor  $\pi$ -acceptor properties of the amine ligands.  $^{13}\text{C}$  nmr spectra show that  $\text{Fe}(\text{CO})_4\text{C}_3\text{H}_5\text{N}$  is fluxional, scrambling axial and equatorial ligands even at  $-90^\circ$ . Principal crystallographic data are: for the pyridine compound, space group  $P2_1/n$ ,  $a = 8.198$  (6) Å;  $b = 10.488$  (5) Å;  $c = 12.080$  (8) Å;  $\beta = 98.74$  (6)°,  $V = 1026.6$  (11) Å<sup>3</sup>,  $Z = 4$ , final  $R_1$  and  $R_2$  values 0.054 and 0.070; for the pyrazine structure, space group  $P2_1/c$ ,  $a = 7.760$  (2) Å,  $b = 10.593$  (3) Å,  $c = 12.801$  (3) Å,  $\beta = 105.69$  (2) Å,  $V = 1013.1$  (4) Å<sup>3</sup>,  $Z = 4$ , final  $R_1$  and  $R_2$  values 0.034 and 0.045.

Each of the three binary iron carbonyls,  $\text{Fe}(\text{CO})_5$ ,  $\text{Fe}_2(\text{CO})_9$ , and  $\text{Fe}_3(\text{CO})_{12}$ , has found employment as a reagent for preparing substituted iron carbonyl species, of which the most numerous and interesting are perhaps those containing olefins and polyolefins as ligands. The use of  $\text{Fe}_2(\text{CO})_9$  has been relatively restricted by its general insolubility, since this property makes it, effectively, sluggish in its reaction. For example, in a series of reactions between  $\text{Fe}_2(\text{CO})_9$  and cyclic polyolefins carried out by Cotton and Deganello<sup>1</sup> using diethyl ether as the reaction medium, the reaction times had to be quite long, *ca.* 100 hr.

It was discovered by us that if tetrahydrofuran (THF) is used the  $\text{Fe}_2(\text{CO})_9$  reacts far more rapidly (*ca.* 30 min) and more extensively. Further study has shown that  $\text{Fe}_2(\text{CO})_9$  dissolves with reaction rather readily in THF alone. When other reagents are added to such solutions or are present in solution from the outset, a variety of new and interesting chemical reactions of  $\text{Fe}_2(\text{CO})_9$  can be observed. In this paper we report (1) two such reactions, leading to substances not previously obtained by any other means, namely,  $\text{Fe}(\text{CO})_4\text{C}_3\text{H}_5\text{N}$  and  $\text{Fe}(\text{CO})_4\text{C}_4\text{H}_4\text{N}_2$ , (2) a full characterization of these new compounds, and (3) a preliminary discussion of the probable cause of the enhanced reactivity of  $\text{Fe}_2(\text{CO})_9$  in the presence of THF. Future reports will describe other reactions of the  $\text{Fe}_2(\text{CO})_9$ -THF system.

## Experimental Section

**Synthesis and Crystal Preparation of  $\text{Fe}(\text{CO})_4\text{C}_3\text{H}_5\text{N}$ .** Pyridine-tetracarbonyliron was prepared by placing 4.0 g (0.011 mol) of diiron nonacarbonyl, purchased from Pressure Chemical Co. and dried *in vacuo*, in a round-bottom flask, and an excess of pyridine (15 g, 0.019 mol) in 100 ml of tetrahydrofuran, which was dried over molecular sieves, was added with stirring under carbon monoxide

flush. The reaction mixture was stirred for 3 hr at  $23^\circ$  under a 1 atm pressure of carbon monoxide. The resulting orange solution was evaporated *in vacuo* to dryness at  $25^\circ$  to give 2.5 g (greater than 45% yield per iron atom) of a brownish orange solid. Large orange crystals of  $\text{Fe}(\text{CO})_4\text{C}_3\text{H}_5\text{N}$  were obtained by recrystallization from pentane at  $0^\circ$ . The ir spectrum recorded in hexane in the carbonyl stretching region has strong bands at 2042, 1970, and  $1943\text{ cm}^{-1}$ .

**Synthesis and Crystal Preparation of  $\text{Fe}(\text{CO})_4\text{C}_4\text{H}_4\text{N}_2$ .** Pyrazine-tetracarbonyliron was prepared in greater than 90% yield (based on pyrazine) by placing 5.0 g (0.0136 mol) of diiron nonacarbonyl dried *in vacuo* in a round-bottom flask and adding under a carbon monoxide flush 1.0 g (0.0125 mol) of pyrazine in 100 ml of tetrahydrofuran which was dried over molecular sieves. The reaction mixture was stirred for 18 hr under a 1 atm pressure of carbon monoxide at  $23^\circ$ . The resulting orange solution was evaporated *in vacuo* to dryness at  $25^\circ$  to give an orange solid. Large crystals of  $\text{Fe}(\text{CO})_4\text{C}_4\text{H}_4\text{N}_2$  were grown from a pentane solution at  $0^\circ$ . The ir spectrum recorded in hexane in the carbonyl stretching region has strong bands at 2043, 1975, and  $1948\text{ cm}^{-1}$ .

**Reaction of Diiron Noncarbonyl with THF.** A 3.0 g sample of diiron nonacarbonyl was dried *in vacuo* at  $50^\circ$  to remove traces of acetic acid and was stirred under 1 atm of carbon monoxide gas at  $23^\circ$ , with 100 ml of THF which had been dried over molecular sieves. The reaction proceeded to give a dark green solution containing only triiron dodecacarbonyl and iron pentacarbonyl as identified by the ir spectrum.

A second 3.0 g sample of diiron nonacarbonyl was dried as above and was stirred with 100 ml of dry THF at  $23^\circ$  under a flow of argon gas. This reaction mixture acquired an orange-yellow color immediately and then slowly (over a 1 hr period) changed to a deep red. Ir spectra taken during this reaction sequence were very complex in the carbonyl stretching region ( $2100$ - $1700\text{ cm}^{-1}$ ) and have not been interpreted.

**Crystal Examination and Data Collection.** Large crystals of  $\text{Fe}(\text{CO})_4\text{C}_3\text{H}_5\text{N}$  measuring  $0.40 \times 0.45 \times 0.30\text{ mm}$  and  $\text{Fe}(\text{CO})_4\text{C}_4\text{H}_4\text{N}_2$  measuring  $0.22 \times 0.20 \times 0.40\text{ mm}$  were mounted in thin glass capillaries since the crystals are moderately air-sensitive. Preliminary examination of both crystals and data collection were performed on a Syntex P1 computer-controlled diffractometer equipped with a graphite crystal monochromator. The space group for  $\text{Fe}(\text{CO})_4\text{C}_3\text{H}_5\text{N}$  was found to be  $P2_1/n$  and that for  $\text{Fe}(\text{CO})_4\text{C}_4\text{H}_4\text{N}_2$  was  $P2_1/c$ ; other pertinent crystal data are given in Table I. Unit cell dimensions were determined by the least-squares refinement of the setting angles for 15 strong reflections.

(1) F. A. Cotton and G. Deganello, *J. Organometal. Chem.*, **38**, 147 (1972); *J. Amer. Chem. Soc.*, **95**, 396 (1973).

Table I. Crystal Data

Fe(CO) <sub>4</sub> C <sub>3</sub> H <sub>5</sub> N	Fe(CO) <sub>4</sub> C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>
Formula wt = 247.00	Formula wt = 247.99
<i>a</i> = 8.198 (6) Å	<i>a</i> = 7.760 (2) Å
<i>b</i> = 10.488 (5) Å	<i>b</i> = 10.593 (3) Å
<i>c</i> = 12.080 (8) Å	<i>c</i> = 12.801 (3) Å
$\beta$ = 98.74 (6)°	$\beta$ = 105.69 (2)°
<i>V</i> = 1026.6 (11) Å <sup>3</sup>	<i>V</i> = 1013.1 (4) Å <sup>3</sup>
Monoclinic <i>P</i> 2 <sub>1</sub> / <i>n</i>	Monoclinic <i>P</i> 2 <sub>1</sub> / <i>c</i>
Mo K $\alpha$ radiation	Mo K $\alpha$ radiation
$\mu$ = 15.0 cm <sup>-1</sup>	$\mu$ = 15.3 cm <sup>-1</sup>
<i>d</i> <sub>calcd</sub> = 1.60 g/cm <sup>3</sup>	<i>d</i> <sub>calcd</sub> = 1.63 g/cm <sup>3</sup>

Several reflections from both crystals showed  $\omega$  scan widths at half-height of 0.2°.

Data collection techniques for both crystals were similar to procedures reported previously<sup>2</sup> and only deviations from this procedure will be described here. Collection of data was performed at 23° using Mo K $\alpha$  radiation and the  $\theta$ - $2\theta$  scan technique with a variable scan rate of 4.0–24.0°/min. A symmetric scan range from 1.0° before (Mo K $\alpha$ <sub>1</sub>) to 1.0° after (Mo K $\alpha$ <sub>2</sub>) was used to collect 2689 reflections for Fe(CO)<sub>4</sub>C<sub>3</sub>H<sub>5</sub>N and 2035 reflections for Fe(CO)<sub>4</sub>C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>. Examination of the standard reflections showed no significant variation in intensity, indicating good electronic and crystal stability for both crystals during data collection. A correction for Lorentz and polarization factors was applied to the data sets.<sup>3</sup> No correction for absorption was made in view of the small variation in calculated transmission factors of 52.9 ± 2.0% for Fe(CO)<sub>4</sub>C<sub>3</sub>H<sub>5</sub>N and 68.4 ± 5.2% for Fe(CO)<sub>4</sub>C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>. No evidence for secondary extinction was observed in the data and the parameter *p* = 0.07 was used in the calculation of standard deviations. In the structural refinement only 1410 reflections with  $F_o^2 > 3\sigma(F_o^2)$  were used for the pyridine structure and 1437 reflections with  $F_o^2 > 3\sigma(F_o^2)$  for the pyrazine structure.

**Solution and Refinement of the Structures.** The positions of the iron atoms in both structures were located using three-dimensional Patterson functions.<sup>3</sup> The iron coordinates were refined by two least-squares cycles of refinement; a difference Fourier synthesis then revealed the positions of all the remaining nonhydrogen atoms.

The Fe(CO)<sub>4</sub>C<sub>3</sub>H<sub>5</sub>N structure was refined isotropically to the agreement factors

$$R_1 = (\sum |F_o| - |F_c|) / \sum |F_o| = 0.084$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.104$$

The function minimized in least-squares procedure is  $\sum w(|F_o| - |F_c|)^2$  where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure factor amplitudes and *w* is  $4F_o^2/\sigma^2$ , where  $\sigma$  is the esd of  $F_o^2$ . Scattering factors used were taken from Cromer and Waber<sup>4</sup> and anomalous dispersion effects were included for Fe using values of  $\Delta f'$  and  $\Delta f''$  from Cromer and Liberman<sup>5</sup> for both structures. The pyridine structure was subsequently refined anisotropically by two cycles of refinement. A difference Fourier synthesis revealed the positions of the five hydrogen atoms. The entire structure was refined to convergence in three full-matrix least-squares cycles, refining all nonhydrogen atoms anisotropically and hydrogen atom positional parameters, holding their temperature factors constant at 5.0 Å<sup>2</sup>. The final agreement factors were  $R_1 = 0.054$  and  $R_2 = 0.070$ . The error in an observation of unit weight was 1.858.

The refinement of the Fe(CO)<sub>4</sub>C<sub>4</sub>H<sub>4</sub>N<sub>2</sub> structure was achieved by taking the atomic positions of all nonhydrogen atoms from the difference Fourier map based on the iron atom and refining these

parameters anisotropically by three full-matrix least-squares cycles. The preliminary isotropic refinement of nonhydrogen atoms was omitted. The starting isotropic temperature parameters for the oxygen, carbon, and nitrogen atoms were assumed to be 4.0 Å<sup>2</sup> and the iron atom temperature parameter was assumed to be 3.0 Å<sup>2</sup>. The scale factor based on the least-squares refinement of the positional parameters for the iron atom alone was used in the anisotropic refinement. The agreement factors dropped to values to  $R_1 = 0.042$  and  $R_2 = 0.060$ . A difference Fourier synthesis clearly revealed the positions of the four hydrogen atoms. The refinement of the structure converged after three additional full-matrix least-squares cycles refining all nonhydrogen atoms anisotropically and all hydrogen atoms isotropically to give final agreement indices of  $R_1 = 0.034$  and  $R_2 = 0.045$ . The error in an observation of unit weight was 1.050.

No systematic trends were found in the data sets for either structure as a function of  $\lambda^{-1} \sin \theta$ ,  $|F_o|$ , Miller indices, or reflection number. Lists of observed and calculated structure factors and rms amplitudes of thermal vibrations for both compounds are available.<sup>6</sup>

The atomic coordinates and estimated standard deviations for Fe(CO)<sub>4</sub>C<sub>3</sub>H<sub>5</sub>N are given in Table II. Anisotropic thermal parameters for nonhydrogen atoms are given in Table III.

Table II. Atomic Positional Parameters for Fe(CO)<sub>4</sub>C<sub>3</sub>H<sub>5</sub>N

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Fe	0.2082 (1)	0.0461 (1)	0.1746 (1)
O(1)	0.2932 (7)	-0.0328 (5)	-0.0405 (4)
O(2)	0.0993 (7)	0.2921 (5)	0.0723 (4)
O(3)	-0.0145 (7)	-0.1742 (5)	0.1766 (5)
O(4)	0.5585 (6)	0.0143 (6)	0.2693 (5)
N(1)	0.1326 (6)	0.1049 (5)	0.3202 (4)
C(1)	0.2600 (8)	-0.0030 (7)	0.0440 (6)
C(2)	0.1407 (7)	0.1970 (6)	0.1132 (5)
C(3)	0.0723 (9)	-0.0892 (7)	0.1760 (5)
C(4)	0.4222 (8)	0.0281 (7)	0.2364 (5)
C(5)	0.2304 (8)	0.1076 (7)	0.4204 (5)
C(6)	0.1743 (9)	0.1468 (7)	0.5161 (5)
C(7)	0.0164 (9)	0.1859 (7)	0.5131 (6)
C(8)	-0.0856 (9)	0.1837 (8)	0.4115 (6)
C(9)	-0.0246 (8)	0.1404 (8)	0.3189 (6)
H(1)	0.354 (9)	0.076 (6)	0.419 (6)
H(2)	0.239 (9)	0.149 (7)	0.570 (6)
H(3)	-0.031 (8)	0.213 (7)	0.573 (6)
H(4)	0.794 (9)	0.202 (7)	0.400 (6)
H(5)	0.907 (8)	0.140 (7)	0.250 (6)

The atomic coordinates with their estimated standard deviations for Fe(CO)<sub>4</sub>C<sub>4</sub>H<sub>4</sub>N<sub>2</sub> are given in Table IV, and anisotropic thermal parameters for nonhydrogen and isotropic thermal parameters for the four hydrogen atoms are given in Table V.

## Results

The structures and atom numbering for the pyridine and pyrazine compounds are shown in Figures 1 and 2, respectively. Tables VI and VII give bond lengths and bond angles. Least-squares planes and dihedral angles for the two structures are listed in Tables VIII and IX.

Both structures consist of discrete molecules, with no abnormal intermolecular contacts. The structures are very similar and resemble very closely the structure of Fe(CO)<sub>5</sub> with the substitution of one of the axial CO ligands by a pyridine or pyrazine molecule. The coordination of iron in each structure is trigonal bipyramidal with the axial carbonyl trans to the pyridine or pyrazine having a shorter bond distance (av 1.773 Å) than the average equatorial carbonyl bond distance (av 1.807 Å). The iron–nitrogen bond distances are nearly the same, being 2.046 (5) and 2.031 (2) Å for the pyridine and pyrazine structures, respectively.

(2) F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organometal. Chem.*, **50**, 227 (1973).

(3) Computer programs used in reduction of the data and in the solution and refinement of the structure are the following: DATARED by Frenz for data reduction; JIMDAP, a Fourier program by Ibers, based on FORDAP by Zalkin; the least-squares program NUCLS by Doedens and Ibers based on Busing and Levy's ORFLS program; a local modification of Baur's SADIAN program for calculating atomic distances and angles; RSCAN by Doedens for analyzing structure factors; ORTEP by Johnson for illustrations; the function and error program ORFFE by Busing, Martin, and Levy as modified by Brown, Johnson, and Thiessen.

(4) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, in preparation.

(5) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1971).

(6) See paragraph at end of paper regarding supplementary material.

Table III. Anisotropic Thermal Parameters for Fe(CO)<sub>4</sub>C<sub>5</sub>H<sub>5</sub>N

Atom	$\beta_{11}^a$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Fe	0.0141 (1)	0.0090 (1)	0.0055 (1)	0.0006 (1)	0.0014 (1)	0.0001 (1)
O(1)	0.0315 (12)	0.0166 (7)	0.0080 (4)	0.0054 (8)	0.0055 (6)	-0.0011 (4)
O(2)	0.0286 (11)	0.0117 (6)	0.0082 (4)	0.0038 (7)	0.0041 (5)	0.0021 (4)
O(3)	0.0308 (13)	0.0126 (6)	0.0114 (5)	-0.0066 (8)	0.0009 (6)	-0.0002 (4)
O(4)	0.0157 (8)	0.0228 (9)	0.0111 (5)	0.0042 (7)	0.0004 (5)	0.0012 (5)
N(1)	0.0140 (8)	0.0082 (5)	0.0057 (3)	-0.0007 (5)	0.0011 (4)	0.0001 (3)
C(1)	0.0179 (12)	0.0107 (7)	0.0073 (5)	0.0031 (7)	0.0018 (6)	0.0000 (5)
C(2)	0.0148 (10)	0.0098 (7)	0.0054 (4)	0.0004 (7)	0.0027 (5)	0.0000 (4)
C(3)	0.0195 (12)	0.0109 (8)	0.0068 (5)	-0.0013 (8)	0.0002 (6)	-0.0007 (5)
C(4)	0.0149 (11)	0.0118 (9)	0.0086 (5)	0.0030 (8)	0.0031 (6)	0.0002 (5)
C(5)	0.0181 (12)	0.0110 (7)	0.0064 (5)	0.0007 (8)	0.0003 (6)	0.0002 (5)
C(6)	0.0207 (14)	0.0125 (8)	0.0056 (4)	-0.0004 (8)	0.0000 (6)	-0.0008 (5)
C(7)	0.0219 (14)	0.0119 (8)	0.0073 (5)	0.0004 (9)	0.0044 (7)	-0.0004 (5)
C(8)	0.0169 (12)	0.0161 (10)	0.0081 (6)	0.0034 (9)	0.0036 (7)	-0.0005 (6)
C(9)	0.0138 (11)	0.0164 (10)	0.0065 (5)	0.0016 (8)	0.0018 (6)	0.0002 (6)

<sup>a</sup> Anisotropic temperature parameters are of the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

Table IV. Atomic Positional Parameters for Fe(CO)<sub>4</sub>C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Fe	-0.1678 (1)	0.1871 (1)	0.1424 (1)
O(1)	-0.0413 (5)	-0.0639 (3)	0.1102 (2)
O(2)	0.1594 (4)	0.2928 (3)	0.1014 (3)
O(3)	-0.4953 (4)	0.1399 (3)	-0.0330 (2)
O(4)	-0.1231 (4)	0.1167 (3)	0.3706 (2)
N(1)	-0.2747 (3)	0.3581 (2)	0.1603 (2)
N(2)	-0.4264 (4)	0.5940 (3)	0.1843 (3)
C(1)	-0.0907 (6)	0.0336 (3)	0.1226 (3)
C(2)	0.0306 (5)	0.2552 (4)	0.1155 (3)
C(3)	-0.3675 (5)	0.1582 (3)	0.0339 (3)
C(4)	-0.1439 (4)	0.1473 (3)	0.2829 (3)
C(5)	-0.3834 (5)	0.3746 (3)	0.2245 (3)
C(6)	-0.4561 (6)	0.4901 (4)	0.2360 (3)
C(7)	-0.3227 (5)	0.5758 (3)	0.1187 (3)
C(8)	-0.2482 (5)	0.4611 (3)	0.1064 (3)
H(1)	0.599 (5)	0.301 (3)	0.262 (3)
H(2)	0.472 (5)	0.491 (3)	0.285 (3)
H(3)	0.694 (5)	0.653 (4)	0.084 (3)
H(4)	0.817 (5)	0.451 (3)	0.060 (3)

Table V. Atomic Thermal Parameters for Fe(CO)<sub>4</sub>C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>

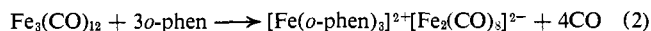
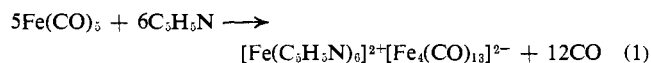
Atom	$\beta_{11}^a$ or $B_{180}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Fe	0.0198 (1)	0.0068 (1)	0.0056 (1)	0.0010 (1)	0.0043 (1)	0.0000 (1)
O(1)	0.0488 (10)	0.0115 (3)	0.0118 (3)	0.0103 (5)	0.0082 (4)	-0.0006 (2)
O(2)	0.0262 (7)	0.0191 (5)	0.0170 (4)	0.0000 (4)	0.0110 (4)	0.0033 (3)
O(3)	0.0381 (8)	0.0110 (3)	0.0103 (3)	0.0000 (4)	-0.0041 (4)	-0.0009 (2)
O(4)	0.0321 (7)	0.0166 (4)	0.0064 (2)	0.0053 (4)	0.0050 (3)	0.0023 (2)
N(1)	0.0167 (5)	0.0071 (2)	0.0056 (2)	-0.0007 (3)	0.0035 (2)	-0.0004 (2)
N(2)	0.0267 (7)	0.0086 (3)	0.0108 (3)	0.0031 (4)	0.0076 (4)	0.0003 (2)
C(1)	0.0294 (9)	0.0089 (4)	0.0071 (2)	0.0032 (5)	0.0055 (4)	-0.0001 (2)
C(2)	0.0240 (8)	0.0103 (4)	0.0095 (3)	0.0016 (5)	0.0068 (4)	0.0013 (3)
C(3)	0.0287 (9)	0.0061 (3)	0.0073 (3)	0.0002 (4)	0.0029 (4)	0.0001 (2)
C(4)	0.0194 (7)	0.0084 (3)	0.0069 (2)	0.0022 (4)	0.0038 (3)	0.0005 (2)
C(5)	0.0260 (8)	0.0088 (3)	0.0094 (3)	0.0031 (4)	0.0091 (4)	0.0017 (3)
C(6)	0.0313 (10)	0.0108 (4)	0.0106 (3)	0.0055 (5)	0.0113 (5)	0.0020 (3)
C(7)	0.0218 (7)	0.0070 (3)	0.0110 (3)	0.0003 (4)	0.0057 (4)	0.0013 (3)
C(8)	0.0209 (7)	0.0088 (3)	0.0075 (2)	-0.0002 (4)	0.0055 (4)	0.0005 (2)
H(1)	5.7 (9)					
H(2)	5.9 (9)					
H(3)	5.4 (8)					
H(4)	4.7 (8)					

<sup>a</sup> The anisotropic temperature parameters are of the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

The infrared spectra of hexane solutions in the CO stretching region indicate that the axially substituted, trigonal bipyramidal structures persist in solution. In each compound three strong CO stretching bands are observed, as expected for Fe(CO)<sub>4</sub> groups with local C<sub>3v</sub> symmetry.

## Discussion

**Synthesis of New Compounds.** The reactions of diiron nonacarbonyl in THF, or other solvents, with nitrogen donor ligands have not been reported previously.<sup>7</sup> There have been many attempts to make simple substitution products of the iron carbonyl molecules with nitrogen donor ligands using Fe(CO)<sub>5</sub> and Fe<sub>3</sub>(CO)<sub>12</sub> as reactants. However, in all cases<sup>7</sup> only redox products containing carbonylate anions were obtained, as in the representative reactions 1 and 2. The

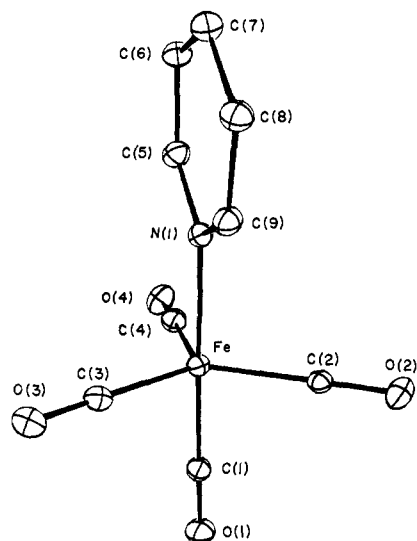


only previously reported compound of the type described here is Fe(CO)<sub>4</sub>NH<sub>3</sub>, prepared by reaction of hydroxylamine-*o*-sulfonate ion with the FeH(CO)<sub>4</sub><sup>-</sup> anion.<sup>8</sup>

We believe that the ready formation, in high yields, of Fe(CO)<sub>4</sub>C<sub>5</sub>H<sub>5</sub>N and Fe(CO)<sub>4</sub>C<sub>4</sub>H<sub>4</sub>N<sub>2</sub> by direct reaction

(7) F. Calderazzo, R. Ercoli, and G. Natta in "Organic Synthesis via Metal Carbonyls," Vol. 1, I. Wender and P. Pino, Ed., Interscience-Wiley, New York, N. Y., 1968, pp 103-108.

(8) W. Hieber and H. Beutner, *Angew. Chem.*, **74**, 154 (1962).

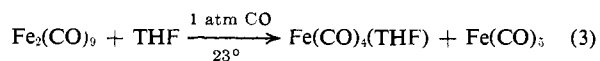


**Figure 1.** The structure of pyridinetetracarbonyliron showing the relationship of the plane of the pyridine to the equatorial carbonyl groups.

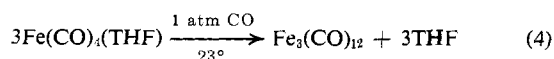
**Table VI.** Bond Lengths and Selected Bond Angles for  $\text{Fe}(\text{CO})_4\text{C}_5\text{H}_5\text{N}$

Bond Lengths (Å)			
Fe-C(1)	1.772 (7)	N(1)-C(5)	1.347 (7)
Fe-C(2)	1.799 (7)	N(1)-C(9)	1.340 (8)
Fe-C(3)	1.806 (8)	C(5)-C(6)	1.370 (9)
Fe-C(4)	1.809 (7)	C(6)-C(7)	1.354 (10)
Fe-N(1)	2.046 (5)	C(7)-C(8)	1.377 (10)
		C(8)-C(9)	1.369 (9)
C(1)-O(1)	1.139 (8)	C(5)-H(1)	1.07 (7)
C(2)-O(2)	1.142 (7)	C(6)-H(2)	0.77 (7)
C(3)-O(3)	1.141 (8)	C(7)-H(3)	0.91 (7)
C(4)-O(4)	1.137 (7)	C(8)-H(4)	1.00 (7)
		C(9)-H(5)	0.93 (7)
Bond Angles (deg)			
C(1)-Fe-C(2)	89.3 (3)	Fe-C(1)-O(1)	179.0 (6)
C(1)-Fe-C(3)	90.7 (3)	Fe-C(2)-O(2)	178.6 (5)
C(1)-Fe-C(4)	89.4 (3)	Fe-C(3)-O(3)	179.5 (6)
C(1)-Fe-N(1)	176.2 (2)	Fe-C(4)-O(4)	176.0 (6)
C(2)-Fe-C(3)	122.9 (3)	Fe-N(1)-C(7)	177.6 (3)
C(2)-Fe-C(4)	118.7 (3)	N(1)-C(5)-C(6)	122.4 (6)
C(3)-Fe-C(4)	118.3 (3)	C(5)-C(6)-C(7)	120.6 (6)
C(2)-Fe-N(1)	88.6 (6)	C(6)-C(7)-C(8)	117.9 (7)
C(3)-Fe-N(1)	87.8 (2)	C(7)-C(8)-C(9)	119.1 (6)
C(4)-Fe-N(1)	91.5 (2)	C(8)-C(9)-N(1)	123.6 (6)
		C(9)-N(1)-C(5)	116.3 (5)

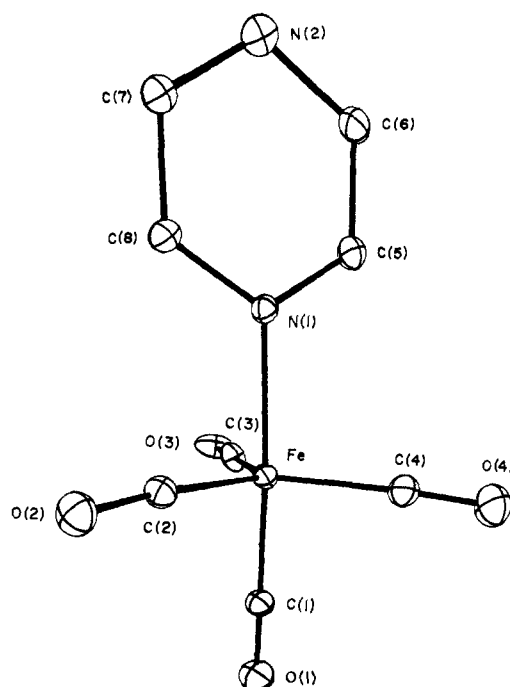
of the ligands with  $\text{Fe}_2(\text{CO})_9$  is a result of the formation of reactive intermediates when  $\text{Fe}_2(\text{CO})_9$  is dissolved in THF. Our provisional view is that  $\text{Fe}_2(\text{CO})_9$  reacts with THF according to eq 3, affording 50% of the iron



as the reactive  $\text{Fe}(\text{CO})_4(\text{THF})$ , from which nitrogen donor ligands can displace the THF. In this way the yield of ca. 45% based on total iron can be readily understood. The eventual formation of  $\text{Fe}_3(\text{CO})_{12}$  when no nitrogen donor ligand is added can be attributed to the reactions in eq 4. We point out, how-



ever, that the reaction system is evidently more com-



**Figure 2.** The structure of pyrazinetetracarbonyliron.

**Table VII.** Bond Lengths and Selected Bond Angles for  $\text{Fe}(\text{CO})_4\text{C}_4\text{H}_4\text{N}_2$

Bond Lengths (Å)			
Fe-C(1)	1.774 (4)	N(1)-C(5)	1.338 (4)
Fe-C(2)	1.816 (4)	N(1)-C(8)	1.336 (4)
Fe-C(3)	1.806 (4)	N(2)-C(6)	1.336 (5)
Fe-C(4)	1.807 (3)	N(2)-C(7)	1.326 (5)
Fe-N(1)	2.031 (2)	C(5)-C(6)	1.371 (5)
		C(7)-C(8)	1.372 (5)
C(1)-O(1)	1.127 (4)	C(5)-H(1)	0.94 (4)
C(2)-O(2)	1.135 (4)	C(6)-H(2)	0.94 (4)
C(3)-O(3)	1.138 (4)	C(7)-H(3)	0.96 (4)
C(4)-O(4)	1.137 (4)	C(8)-H(4)	0.89 (4)
Bond Angles (deg)			
C(1)-Fe-C(2)	90.1 (2)	Fe-C(1)-O(1)	179.8 (4)
C(1)-Fe-C(3)	89.3 (2)	Fe-C(2)-O(2)	176.6 (4)
C(1)-Fe-C(4)	88.9 (1)	Fe-C(3)-O(3)	178.7 (4)
C(1)-Fe-N(1)	175.8 (2)	Fe-C(4)-O(4)	176.2 (3)
C(2)-Fe-C(3)	121.1 (2)	Fe-N(1)-N(2)	179.4 (1)
C(2)-Fe-C(4)	114.7 (2)	N(1)-C(5)-C(6)	121.9 (3)
C(2)-Fe-N(1)	93.4 (1)	C(5)-C(6)-N(2)	123.4 (3)
C(3)-Fe-C(4)	124.2 (2)	C(6)-N(2)-C(7)	114.2 (3)
C(3)-Fe-N(1)	86.9 (1)	N(2)-C(7)-C(8)	123.2 (3)
C(4)-Fe-N(1)	91.8 (1)	C(7)-C(8)-N(1)	122.4 (3)
		C(8)-N(1)-C(5)	114.8 (3)

plicated than implied by eq 3 and 4 when CO pressure is not maintained. Depending on conditions, substitution products of  $\text{Fe}_2(\text{CO})_9$  itself, such as  $\text{Fe}_2(\text{CO})_7$ -dipy<sup>9</sup> and  $\text{Fe}_2(\text{CO})_7[(\text{Ph}_2\text{P})_2\text{CH}_2]$ <sup>10</sup> can be obtained. A more thorough investigation of the nature of  $\text{Fe}_2(\text{CO})_9$ -THF solutions as a function of time, temperature, and CO pressure is required.

It may finally be noted that the CO ligands in the reaction mixture are labile since <sup>13</sup>C-enriched  $\text{Fe}(\text{CO})_4\text{C}_5\text{H}_5\text{N}$  is obtained when the overpressure of CO gas is provided by <sup>13</sup>C-enriched CO.

(9) F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, **96**, 1233 (1974).

(10) F. A. Cotton and J. M. Troup, report in preparation.

**Table VIII.** Least-Square Planes and Dihedral Angles for  $\text{Fe}(\text{CO})_4\text{C}_3\text{H}_5\text{N}$ 

Plane	Atoms defining plane	Equation of mean plane <sup>a</sup>
I	Fe, C(2), C(3), C(4)	$2.995x - 3.178y - 11.180z = -1.475$
II	N(1), C(5), C(6), C(7), C(8), C(9)	$2.411x + 9.845y - 2.691z = 0.485$
III	Fe, C(1), C(4)	$-1.728x - 9.972y + 3.065z = -0.285$

Displacement of Atoms from Mean Plane (Å)					
Plane I		Plane II		Plane III	
Fe	0.000	N(1)	0.006	C(2)	-1.577
C(2)	0.005	C(5)	-0.001	C(3)	1.590
C(3)	0.007	C(6)	-0.008		
C(4)	0.007	C(7)	0.004		
N(1)	-2.041	C(8)	0.010		
C(1)	1.772	C(9)	-0.020		
C(5)	-2.878	C(2)	1.489		
C(9)	-2.611	C(3)	-1.663		
		C(4)	0.173		

Dihedral Angles between Planes (deg)					
I-II	91.1	I-III	89.2	II-III	5.5

<sup>a</sup> Equations have the form  $Ax + By + Cz = D$  where  $x$ ,  $y$ , and  $z$  are fractional monoclinic coordinates.

**Table IX.** Least-Square Planes and Dihedral Angles for  $\text{Fe}(\text{CO})_4\text{C}_4\text{H}_4\text{N}_2$ 

Plane	Atoms defining plane	Equation of mean plane <sup>a</sup>
I	Fe, C(2), C(3), C(4)	$3.006x - 9.644y - 3.128z = -2.754$
II	N(1), C(5), C(6), N(2), C(7), C(8)	$4.786x + 2.361y + 7.169z = 0.672$
III	Fe, C(1), C(3)	$-5.001x - 3.834y + 10.223z = 1.578$

Displacement of Atoms from Mean Plane (Å)					
Plane I		Plane II		Plane III	
Fe	0.000	N(1)	0.008	C(2)	-1.555
C(2)	0.023	C(5)	-0.013	C(4)	1.494
C(3)	0.017	C(6)	-0.006		
C(4)	0.016	N(2)	0.011		
N(1)	-2.027	C(7)	-0.006		
C(1)	1.773	C(8)	-0.009		
C(5)	-2.714	C(2)	0.905		
C(8)	-2.772	C(3)	-1.815		
		C(4)	1.015		

Dihedral Angles between Planes (deg)					
I-II	94.2	I-III	90.8	II-III	89.3

<sup>a</sup> Equations have the form  $Ax + By + Cz = D$  where  $x$ ,  $y$ , and  $z$  are fractional monoclinic coordinates.

**Table X.** A Comparison of Important Bond Distances (Å) for Trigonal Bipyramidal Iron Carbonyl Complexes

Compound	Fe-C <sub>ax</sub> distance	Fe-C <sub>eq</sub> distance av	Fe-ligand distance	C-O distance av	Ref
$\text{Fe}(\text{CO})_5$ X-Ray		1.82 (2)		1.14 (2)	<i>a</i>
$\text{Fe}(\text{CO})_5$ Electron diffraction	$1.806 \pm 0.005$	$1.833 \pm 0.004$		$1.145 \pm 0.003$	<i>b</i>
$\text{Fe}(\text{CO})_4\text{C}_3\text{H}_5\text{N}$	1.772 (7)	1.805 (8)	2.046 (5)	1.140 (8)	<i>c</i>
$\text{Fe}(\text{CO})_4\text{C}_4\text{H}_4\text{N}_2$	1.774 (4)	1.810 (4)	2.031 (2)	1.134 (4)	<i>c</i>
$\text{Fe}(\text{CO})_4\text{P}(\text{HPh})_2$	1.792 (8)	1.793 (9)	2.237 (2)	1.15 (1)	<i>d</i>

<sup>a</sup> A. W. Hanson, *Acta Crystallogr.*, **18**, 502 (1962). <sup>b</sup> B. Beagley, D. W. J. Cruickshank, P. M. Pinder, A. G. Robiette, and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, **25**, 737 (1969). <sup>c</sup> This work. <sup>d</sup> B. T. Kilbourn, K. N. Raeburn, and D. T. Thompson, *J. Chem. Soc. A*, 1906 (1969).

**Description of Structures.** The structures of the two molecules differ by less than four esd's in all important bond distances. Table X compares bond distances in  $\text{Fe}(\text{CO})_4\text{C}_3\text{H}_5\text{N}$  and  $\text{Fe}(\text{CO})_4\text{C}_4\text{H}_4\text{N}_2$  with those in Fe-

$(\text{CO})_5$  and  $\text{Fe}(\text{CO})_4(\text{P}(\text{HPh})_2)$ . The variations in Fe-C distances, both from compound to compound and within each compound, are too small, in comparison with the esd's, to allow any unequivocal conclusion about variations in bond orders. However, the variations, taken at face value, are in general accord with expectations based on accepted ideas about relative  $\sigma$ -donor and  $\pi$ -acceptor capacities of the various ligands and the importance of  $\pi$  bonding in metal carbonyls. Thus, as one axial position is occupied by a ligand which is a progressively stronger  $\sigma$ -donor and weaker  $\pi$ -acceptor (*i.e.*, the series CO, phosphine, amine), the average axial Fe-C distance decreases in the order 1.806, 1.792, 1.773 Å. For the equatorial Fe-C distances there is a drop from  $\text{Fe}(\text{CO})_5$  to the  $\text{Fe}(\text{CO})_4\text{L}$  molecules; the amine and phosphine molecules do not appear to be in the right order, but the difference is less than two esd's and thus of no reliability.

The average Fe-N distance, 2.04 Å, can be used to estimate a single bond radius for iron (by subtracting the radius for an  $\text{sp}^2$  hybridized nitrogen atom of about 0.67 Å) of 1.37 Å. From this, using a single bond radius of 0.70 Å for sp carbon, an Fe-C single bond distance of 2.07 Å is estimated. There is thus a shortening of the order of 0.25–0.30 Å in the Fe-C bonds. For phosphorus, with a tetrahedral single bond radius of 1.10 Å, a single bond distance of 2.47 Å would be calculated. The actual distance, 2.24 Å, would suggest that there is considerable  $\pi$  character in the Fe-P bond.

There is a marked difference between the structures of the pyridine and pyrazine compounds with respect to the rotational orientation of the rings. In the pyridine compound the ring plane closely coincides with one of the equatorial CO ligands and bisects the angle between the other two. The dihedral angle between the plane of the pyridine ring and the plane defined by the axial carbon atom, C(1), the iron atom, and the equatorial carbon atom C(4) is 5.5°. This alignment tilts the pyridine ring away from C(4) to give a C(1)-Fe-N(1) angle of 176.2 (2)°, into the angle between C(2)O(2) and C(3)O(3), and the C(2)-Fe-C(3) angle is opened to 122.9 (3)°, while the C(3)-Fe-C(4) and C(3)-Fe-C(4) angles are contracted to an average of 118.5 (3)°. In the pyrazine compound, the ring plane is rotated

about 33° with respect to the pyridine ring position so that the mean ring plane makes a dihedral angle of 89.3° to the plane defined by the axial carbon atom, C(1), the iron atom, and the equatorial carbon atom

C(3). This is the most staggered conformation obtainable. The apparent implication of this difference in rotational configuration is that the barrier to rotation about the Fe–N bond is not very high, with crystal packing forces having a major influence on the configuration adopted in the crystal.

**Fluxionality of  $\text{Fe}(\text{CO})_4\text{C}_5\text{H}_5\text{N}$ .** It is well known that scrambling of axial and equatorial CO groups occurs rapidly in  $\text{Fe}(\text{CO})_5$ , even at  $-170^\circ$ .<sup>11</sup> It occurred to us that the presence of one ligand distinctly differing from CO in its  $\sigma$ -donor and  $\pi$ -acceptor properties, such as an amine, might introduce a barrier to this process (assumed, generally, to proceed through the Berry pseudorotation pathway) sufficient to allow observation of a slow exchange  $^{13}\text{C}$  spectrum. The reasoning was that the strong  $\sigma$ -donor and virtually nonexistent  $\pi$ -acceptor capacities of pyridine might create such a marked preference for it to occupy an axial site in the trigonal bipyramid, that passage through a trigonal bipyramidal intermediate having pyridine in an equatorial site might be strongly disfavored. Detailed inspection of equatorial–axial exchange of CO groups in an  $\text{Fe}(\text{CO})_4\text{L}$  type molecule by means of the Berry process necessitates such an intermediate. How-

(11) J. P. Jesson and P. Meakin, *J. Amer. Chem. Soc.*, **95**, 1344 (1973).

ever, the  $^{13}\text{C}$  nmr spectrum of 20% enriched  $\text{Fe}(\text{CO})_4\text{C}_5\text{H}_5\text{N}$  is a single sharp line at all temperatures down to *ca.*  $-100^\circ$ . Of course, it is still possible that the slow exchange spectrum—or at least a broadening of the line—might be observed at still lower temperature, but the available cryostat could not be operated at lower temperatures.

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**Supplementary Material Available.** Tables containing the observed and calculated structure amplitudes and the principle axes of the vibrational ellipsoids of both compounds will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$5.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-3438.

## Electronic and Crystallographic Study of Two Cyanide-Bridged Copper(II) Dimers. Magnetic Exchange Interactions through a Linear Cu–CN–Cu Bridge and a Hydrogen-Bonded Cu–CN···H–N–Cu System

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**Abstract:** The single-crystal X-ray structures of  $[\text{Cu}_2([\text{14}]\text{4,11-diene-N}_4)_2\text{CN}](\text{ClO}_4)_3$ , where  $[\text{14}]\text{4,11-diene-N}_4$  is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, and  $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ , where *tren* = 2,2',2''-triaminotriethylamine, have been determined and preliminary results communicated. The copper atom environments are trigonal bipyramidal in both of these Cu(II) dimers; in the former complex there is Cu–CN–Cu bridging while in the latter system bridging is *via* the coordinated cyanide on each copper atom hydrogen bonding through its N atom to a primary amine of the *tren* ligand coordinated to the second Cu atom, Cu–CN···HN–Cu. The electronic structures of the two Cu(II) dimers have been characterized by electronic absorption, ir, esr, and variable-temperature (4.2–283°K) magnetic susceptibility measurements. Low-intensity  $\nu(\text{CN})$  bands are shown to be indicative of CN bridging for these two Cu(II) dimers. Antiferromagnetic exchange is present in both cyanide-bridged dimers, where  $J = -4.8 \text{ cm}^{-1}$  for the Cu–CN–Cu system and  $J = -1.8 \text{ cm}^{-1}$  for the Cu–CN···HN–Cu system. The observed exchange in the hydrogen-bonded *tren* system is of special interest, because it provides a lucid illustration of magnetic exchange through a bridging moiety possessing only  $\sigma$ -electron density. The observed electronic effects are discussed with regard to the coordination geometry and bridge bonding in each molecule, and a comparison is made between the two cyanide-bridged systems and the five-coordinate chloride-bridged compound  $[\text{Cu}_2(\text{tet-b})_2\text{Cl}](\text{ClO}_4)_3$ , where (tet-b) = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. The magnetism ( $J = -144 \text{ cm}^{-1}$ ) for this system is reported in this paper.

The bonding and spectroscopic properties of a considerable number of transition metal complexes with coordinated cyanide have been studied. Although

there are many known and characterized polymeric systems,<sup>3</sup> there is a paucity of reports on metal dimers with cyanide bridging. In the case of Cu(II), this is probably due to the low inherent stability in aqueous

(1) Esso Fellow, 1971–1972; Mobil Fellow, 1972–1973.

(2) Camille and Henry Dreyfus Fellow, 1972–1977.

(3) D. F. Shriver, *Struct. Bonding*, **1**, 32 (1966).