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Reactivity of Diiron Nonacarbonyl in Tetrahydrofuran. IV.[1] The Synthesis and Crystal and Molecular Structure of 1,3-Dithianeirontetracarbonyl, (*cyclo*-1,3-$C_4H_8S_2$)Fe$(CO)_4$

F. A. COTTON, J. R. KOLB and B. R. STULTS
Department of Chemistry, Texas A & M University, College Station, Texas 77843, U.S.A.
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Diiron nonacarbonyl and 1,3-dithiacyclohexane (1,3-dithiane) react at room temperature in THF to yield the new compound (cyclo-1,3-$C_4H_8S_2$)Fe$(CO)_4$. The synthesis and corresponding X-ray structural analysis of the mononuclear iron species are presented here. The compound (cyclo-1,3-$C_4H_8S_2$)Fe$(CO)_4$ is the first example of a zerovalent transition metal complex of the synthetically important sulfur heterocycle. X-ray analysis shows a trigonal bipyramidal geometry about the central iron atom. One sulfur atom of the 1,3-dithiane ligand occupies an axial site in the substituted trigonal bipyramid and the ring adopts a chair conformation. The Fe–C axial bond length is 0.02 Å shorter than that in Fe$(CO)_5$ but is longer than those in (pyridine) Fe$(CO)_4$ and (pyrazine)Fe$(CO)_4$ by an equal amount. The mean Fe–C equatorial bond distance of 1.764 Å is significantly shorter (0.04 to 0.07 Å) than any of the distances in the three aforementioned compounds. Crystallographic data are: space group Pn2_1a; a = 13.488(3) Å; b = 9.058(2) Å; c = 9.771(2) Å; Z = 4; V = 1193.8(4) Å^3. The structure was refined anisotropically to $R_1 = 0.056$ and $R_2 = 0.075$. 857 reflections for which $F_0^2 > 3\sigma(F_0^2)$ were collected.

Introduction

The enhanced reactivity of diiron nonacarbonyl in the solvent tetrahydrofuran is by now well-documented.[1–4] Iron carbonyl derivatives, unobtainable by other means, have been synthesized in high yield through utilization of the $Fe_2(CO)_9$–THF system. Although relative intransigence has characterized both the solubility and reactivity of $Fe_2(CO)_9$ in the past,[5] the dinuclear species is now finding a much broader spectrum of synthetic utility. Reaction times have been shortened to a maximum of a few hours and often are as little as a few minutes, and accompanying conditions have been exceptionally mild.

The reaction of 1,3-dithiane, a valuable synthetic reagent in organic chemistry,[6] with $Fe_2(CO)_9$ in THF affords three products, the relative amounts depending primarily upon the gaseous atmosphere prevailing within the reaction vessel. The mononuclear iron carbonyl derivative (*cyclo*-1,3-$C_4H_8S_2$)Fe$(CO)_4$ is the main product when a partial pressure of carbon monoxide is maintained. When a rapid flush of inert gas is maintained during reaction, a dinuclear species, $Fe_2(CO)_7$(*cyclo*-1,3-$C_4H_8S_2$), is obtained and in both reactions a wine-red polynuclear species is also obtained. This report concerns the preparation and single-crystal X-ray crystallographic analysis of the mononuclear iron compound. Reports giving preparative details and structural studies of the remaining products of this reaction as well as dynamic ^{13}C magnetic resonance studies on (*cyclo*-1,3-$C_4H_8S_2$)Fe$(CO)_4$ and (*cyclo*-1,3-$C_4H_8S_2$)$Fe_2(CO)_7$ will appear later.

Experimental

Synthesis and Crystal Preparation

1,3-dithianetetracarbonyliron was prepared by placing 1.50 grams of diiron nonacarbonyl (4.1 mmol) and 0.72 gram of 1,3-dithiane (6.0 mmol) in a 100-ml argon filled flask fitted with a gas inlet and reflux condenser. Both reagents had been previously dried *in vacuo* and the iron carbonyl had been heated to 65° C to remove residual acetic acid. 50 ml of THF which had been distilled immediately prior to use were added by syringe to the reactants and the mixture stirred for three hours under a static argon atmosphere. The red solution was then concentrated and transferred by syringe onto a chromatography column (2.4 × 50 cm) packed with 100–200 mesh florisil. The column was eluted under N_2 with distilled THF. The first amber-colored band down the column following elution of Fe$(CO)_5$ was collected and concentrated to 5 ml. An equal volume of freshly distilled hexane was added to the concentrate and the solution cooled to –15° C. The resulting gold-colored crystals were washed with hexane to yield 0.65 g (27.5% based on $Fe_2(CO)_9$) of 1,3-dithianetetracarbonyliron.

The compound is mildly air sensitive in both the solid state and in solution. The infrared spectrum recorded in hexane in the carbonyl stretching region has absorbances at 2063 (vs), 1970 (s) and 1925 (vs) cm^{-1} ($\pm 2\ \mathrm{cm}^{-1}$).

Crystal Examination and Data Collection

The single gold-colored crystals grown from the original THF/hexane solution at –15° C were found to be suitable for X-ray analysis. An irregularly shaped crystal having dimensions 0.38 cm × 0.35 cm × 0.32 cm was glued to the inner wall of a thin glass capillary and the ends of the capillary were sealed.

Preliminary x-ray examination of the crystal and data collection were performed on a computer-controlled Syntex P$\bar{1}$ autodiffractometer equipped with a graphite-crystal monochromator. The operation of the diffractometer and other details of the data collection have been fully described previously[7] and only deviations from these procedural techniques are presented here.

A series of axial rotation photographs showed the crystal to be orthorhombic, with *mmm* Laue symmetry. At this point a small shell of data was collected to obtain high angle reflections for crystal centering and for preliminary space group assignment. The observed systematically absent reflections were consistent with either space group Pnma (centrosymmetric) or $\mathrm{Pna2_1}$ (non-centrosymmetric). The unit cell volume expected for a unit cell containing four molecules would require the molecule to have crystallographic symmetry in space group Pnma. Since the anticipated dinuclear species (the crystalline sample was initially thought to be the dinuclear species) could possess mirror symmetry, data collection proceeded assuming the centrosymmetric space group Pnma (which was later proven incorrect); thus no Freidel pair data were collected. The crystal was shown to be of good quality with average ω-scan peak widths at half height of 0.20° for several strong reflections. The final unit cell dimensions and orientation matrix used for data collection were obtained from the least-squares refinement of the diffraction geometry for 15 high-angle reflections ($20° < 2\Theta_{\mathrm{MoK}\alpha} < 35°$) chosen to give a good sampling of diffractometer settings and reciprocal space. Pertinent crystallographic data is given in Table I.

Diffraction data were collected at 22° ± 1° using MoKα radiation and the Θ–2Θ scan technique employing variable scan rates from 4.0 to 24.0°/min. A total of 1259 unique reflections having $2\Theta_{\mathrm{MoK}\alpha} < 50°$ were collected using symmetric scans from 1.0° before (MoKα_1) to 1.0° after (MoKα_2) with a ratio of scan time to total background time of 1.0. Three standard reflections measured every 100 reflections as a monitor for possible crystal misalignment or decomposition gave no indication of either. In view of the low linear absorption coefficient ($16.187\ \mathrm{cm}^{-1}$), no absorption correction was made and the data were reduced to a set of relative F_{obs}^2 after corrections for Lorentz and polarization effects. A value of p = 0.07 was used for the calculation of the standard deviations in F_{obs}^2. A total of 857 reflections having $F_0^2 > 3\sigma(F_0^2)$ were used for the structure solution and refinement.

Solution and Refinement of the Structure

The positions of a single iron atom and a sulfur bonded to the iron at approximately 2.3 Å were located using three-dimensional Patterson functions. This indicated the compound was not the expected dinuclear one and the correct space group was the accentric counterpart of Pnma. The structure was subsequently solved and refined in the acentric space group, $\mathrm{Pn2_1a}$, a non-standard setting of $\mathrm{Pna2_1}$ (C^9_{2v}, No. 33). The coordinates for the iron and sulfur were refined in two cycles of least-squares to an agreement of $R_1 = 0.356$ using isotropic thermal parameters for both atoms. The phases were sufficiently correct at this point to allow the location of the remaining non-hydrogen atoms from a single difference Fourier synthesis.[8]

The structure was refined using isotropic thermal parameters to agreement factors[9]

$$R_1 = (\Sigma \lvert \lvert F_0 \rvert - \lvert F_c \rvert \rvert / \Sigma \lvert F_0 \rvert = 0.167$$
$$R_2 = [w(\lvert F_0 \rvert - \lvert F_c \rvert)^2 / \Sigma w \lvert F_0 \rvert^2]^{1/2} = 0.188$$

The function minimized in the least-squares procedure is $\Sigma w(\lvert F_0 \rvert - \lvert F_c \rvert)^2$ where $\lvert F_0 \rvert$ and $\lvert F_c \rvert$ are the observed and calculated structure factor amplitudes and $w = F_0^2/\sigma^2$, where σ is the esd for F_0^2. The scattering factors used were those from Cromer and Waber.[10] Anomalous dispersion correction terms[11] ($\Delta F'$ and $\Delta F''$) for the iron atom were included in the isotropic and all subsequent least-squares refinements. The structural model was refined to convergence in a series of full-matrix least-squares refinements employing anisotropic thermal parameters for the fifteen non-hydrogen atoms of the assymetric unit. The final agreement factors were $R_1 = 0.056$ and $R_2 = 0.075$ with the error in the observation of unit weight being 1.714. Since the Friedel pair data were not available for verification of the absolute configuration, the refined parameters at $R_1 = 0.056$ and $R_2 = 0.075$ were converted to the corresponding positions for the other enantiomorph and refined to convergence resulting in residuals of $R_1 = 0.057$ and $R_2 = 0.076$, support for

TABLE I. Crystal Data for (*Cyclo*-1,3-$C_4H_8S_2$)Fe$(CO)_4$

F.W. 288.13	Monoclinic
a = 13.488(3) Å	Space Group $\mathrm{Pn2_1a}$
b = 9.058(2) Å	F(000) = 584
c = 9.771(2) Å	MoKα radiation
v = 1193.8(4) Å^3	$\mu = 16.187\ \mathrm{cm}^{-1}$
	$d_{calcd.} = 1.603$ g/cc

TABLE II. Atomic Positional Parameters[a] and Refined Anisotropic Thermal Parameters[b].

Atom	X	Y	Z	B(1.1)	B(2.2)	B(3.3)	B(1.2)	B(1.3)	B(2.3)
Fe	0.17201(8)	0.2500(0)	0.08482(9)	0.00647 (6)	0.0110(1)	0.0088(1)	–0.0004(2)	–0.0025(1)	0.0007(3)
S(1)	0.0680(1)	0.1758(3)	–0.0869(2)	0.00542(9)	0.0110(2)	0.0088(2)	–0.0014(3)	0.0004(3)	0.0016(5)
S(2)	–0.1097(2)	0.2726(5)	–0.2419(2)	0.00543(11)	0.0341(6)	0.0159(3)	0.0030(6)	–0.0012(3)	–0.0039(9)
O(1)	0.3087(5)	0.3458(8)	0.3055(5)	0.0139(5)	0.019(1)	0.0127(7)	–0.007(1)	–0.013(1)	–0.004(2)
O(2)	0.1980(7)	0.5409(9)	–0.0430(6)	0.0178(8)	0.014(1)	0.0224(10)	–0.009(2)	–0.004(2)	0.007(2)
O(3)	0.3063(6)	0.0066(9)	0.0340(7)	0.0115(5)	0.018(1)	0.0212(9)	0.008(1)	–0.006(1)	–0.000(2)
O(4)	0.0107(5)	0.2105(11)	0.2755(6)	0.0089(5)	0.044(2)	0.0174(8)	–0.006(2)	–0.001(1)	0.006(2)
C(1)	0.2533(7)	0.310(1)	0.2184(8)	0.0102(7)	0.0098(9)	0.0153(11)	–0.002(2)	0.0013(16)	0.003(2)
C(2)	0.1902(6)	0.428(1)	0.0099(9)	0.0083(5)	0.0124(12)	0.0153(10)	–0.004(2)	–0.0087(14)	–0.002(2)
C(3)	0.2526(7)	0.100(1)	0.0502(8)	0.0075(5)	0.0114(12)	0.0139(11)	0.001(1)	–0.0064(12)	–0.000(2)
C(4)	0.0700(7)	0.235(1)	0.1926(7)	0.0076(5)	0.0392(28)	0.0084(7)	0.007(3)	0.0038(11)	–0.003(3)
C(5)	–0.0302(5)	0.314(1)	–0.1060(6)	0.0046(4)	0.0220(14)	0.0105(9)	0.006(1)	0.0036(10)	–0.004(2)
C(6)	–0.0199(6)	0.288(1)	–0.3884(6)	0.0066(5)	0.0286(26)	0.0117(9)	–0.002(2)	–0.0032(11)	0.002(2)
C(7)	0.0590(5)	0.162(1)	–0.3836(6)	0.0044(4)	0.0203(13)	0.0075(7)	0.000(1)	–0.0010(9)	0.005(2)
C(8)	0.1276(5)	0.204(1)	–0.2435(7)	0.0050(4)	0.0178(13)	0.0092(7)	0.002(1)	0.0005(10)	–0.005(2)

[a] Figures in parentheses are estimated standard deviations occuring in the least significant digit.

[b] Anisotropic Thermal Parameters are of the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

TABLE III. Anisotropic B and U Thermal Parameters Derived from β Values[a, b].

No.	Name	U(1.1)	U(2.2)	U(3.3)	U(1.2)	U(1.3)	U(2.3)	B(1.1)	B(2.2)	B(3.3)	B(1.2)	B(1.3)	B(2.3)
1	Fe	0.05959	0.04575	0.04256	–0.00119	–0.00836	0.00162	4.705	3.612	3.360	–0.094	–0.660	0.128
2	S(1)	0.05000	0.04565	0.04233	–0.00435	0.00147	0.00369	3.948	3.605	3.343	–0.344	0.116	0.291
3	S(2)	0.05003	0.14193	0.07669	0.00919	–0.00410	–0.00884	3.950	11.207	6.055	0.725	–0.324	–0.698
4	O(1)	0.12854	0.07742	0.06129	–0.02018	–0.04433	–0.00895	10.149	6.113	4.839	–1.593	–3.500	–0.707
5	O(2)	0.16371	0.05973	0.10830	–0.02897	–0.01472	0.01597	12.926	4.716	8.551	–2.287	–1.162	1.261
6	O(3)	0.10590	0.07382	0.10243	0.02596	–0.02084	–0.00096	8.361	5.828	8.088	2.049	–1.645	–0.075
7	O(4)	0.08176	0.18467	0.08406	–0.01855	–0.00170	0.01395	6.455	14.581	6.637	–1.465	–0.134	1.102
8	C(1)	0.09380	0.04061	0.07384	–0.00477	0.00421	0.00769	7.406	3.206	5.830	–0.377	0.332	0.607
9	C(2)	0.07696	0.05175	0.07377	–0.01123	–0.02903	–0.00370	6.076	4.086	5.825	–0.887	–2.292	–0.292
10	C(3)	0.06869	0.04752	0.06720	0.00464	–0.02121	–0.00081	5.424	3.752	5.306	0.366	–1.674	–0.064
11	C(4)	0.07036	0.16292	0.04085	0.02096	0.01256	–0.00604	5.556	12.863	3.225	1.655	0.992	–0.477
12	C(5)	0.04248	0.09136	0.05061	0.01961	0.01205	–0.00910	3.354	7.214	3.996	1.549	0.951	–0.719
13	C(6)	0.06050	0.11878	0.05648	–0.00615	–0.01060	0.00348	4.777	9.378	4.460	–0.485	–0.837	0.275
14	C(7)	0.04058	0.08435	0.03606	0.00152	–0.00326	0.01083	3.204	6.660	2.847	0.120	–0.257	0.855
15	C(8)	0.04612	0.07394	0.04445	0.00683	0.00180	–0.01055	3.642	5.838	3.509	0.539	0.142	–0.833

[a] B's are of the form $\exp[-1/4(\beta_{11}h^2a^{*2}+\beta_{22}k^2b^{*2}+\beta_{33}l^2c^{*2}+2\beta_{12}hka^*b^*+2\beta_{13}hla^*c^*+2\beta_{23}klb^*c^*)]$.

[b] U's are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$.

the correct enantiomorph assignment being the model having the lower residuals is given by a Hamilton R-factor ratio test at greater than 99% confidence.[12] The highest peak in a final difference Fourier map following the converged refinement of the correct enantiomorph corresponds to that chemically-anticipated for a ring hydrogen atom. Hydrogen atoms were not, however, included in the structure refinement. A comparison of the final observed and calculated structure factors showed no systematic trends in the data as a function of $\lambda^{-1}\sin\Theta$, $|F_0|$, Miller indices, or reflection number. The data also indicated no secondary effects. A table of structure factors is available elsewhere.[13]

Results

The atomic coordinates and refined anisotropic thermal parameters with errors for the fifteen non-hydrogen atoms are presented in Table II. The B's and U's derived from the anisotropic thermal parameters are given in Table III. A view of the molecular structure of the complex is presented in Figure 1 where the atomic numbering scheme is also defined. Bond lengths are given in Table IV and bond angles in Table V. Table VI gives equations of several least-squares and mean planes within the molecule and the displacement of atoms encompassing the plane from the plane itself. Dihedral angles between planes within the six-membered sulfur-containing heterocycle are also given in Table VI.

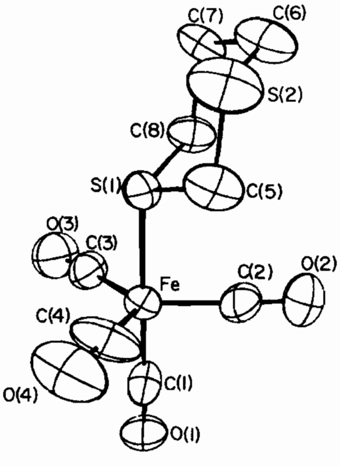

Figure 1. An ORTEP projection of the molecule. Each atom is represented as an ellipsoid encompassing 50% of the electron density. The numbering scheme for the molecule is as indicated.

TABLE IV. Bond Lengths (Å).

Fe–C(1)	1.789(9)
Fe–C(2)	1.786(9)
Fe–C(3)	1.769(9)
Fe–C(4)	1.737(8)
Fe–S(1)	2.288(2)
C(1)–O(1)	1.179(9)
C(2)–O(2)	1.153(11)
C(3)–O(3)	1.128(10)
C(4)–O(4)	1.160(9)
S(1)–C(5)	1.833(8)
C(5)–S(2)	1.747(7)
S(2)–C(6)	1.880(7)
C(6)–C(7)	1.561(13)
C(7)–C(8)	1.695(9)
C(8)–S(1)	1.747(7)

TABLE V. Bond Angles (deg).

C(1)–Fe–C(2)	86.64(35)
C(1)–Fe–C(3)	89.74(39)
C(1)–Fe–C(4)	98.82(40)
C(1)–Fe–S(1)	179.44(28)
O(1)–C(1)–Fe	177.99(80)
O(2)–C(2)–Fe	176.42(78)
O(3)–C(3)–Fe	176.59(76)
O(4)–C(4)–Fe	169.86(93)
C(2)–Fe–C(3)	121.81(40)
C(2)–Fe–C(4)	115.36(54)
C(3)–Fe–C(4)	122.82(53)
S(1)–Fe–C(2)	92.81(24)
S(1)–Fe–C(3)	90.64(26)
S(1)–Fe–C(4)	86.32(31)
Fe–S(1)–C(5)	108.48(26)
Fe–S(1)–C(8)	108.54(23)
S(1)–C(5)–S(2)	111.99(49)
C(5)–S(2)–C(6)	99.68(32)
S(2)–C(6)–C(7)	111.33(62)
C(6)–C(7)–C(8)	103.43(65)
C(7)–C(8)–S(1)	115.08(43)
C(8)–S(1)–C(5)	98.28(33)

The structure of 1,3-dithianetetracarbonyliron is that of a trigonal bipyramid (TBP) with one sulfur atom of the 1,3-dithiane ligand occupying an axial site in the coordination sphere about iron. The structure of this complex closely resembles those for (pyridine)Fe(CO)$_4$ and (pyrazine)Fe(CO)$_4$[2] where each of the heterocycles also occupies an axial position in the TBP. The average of all Fe–C bond distances within the coordination polyhedron is 1.770(9)Å with the axial Fe–C$_1$ distance of 1.789(Å) being greater than any of the three equatorial Fe–C distances (av. 1.764Å).

Persistence of the solid state structure of (*cyclo*-1,3-$C_4H_8S_2$)Fe(CO)$_4$ in solution is indicated by the infrared spectrum in the carbonyl stretching region. Three strong absorbances at 2063, 1970 and 1925 cm^{-1} are observed as expected for a compound in which local C_{3v} symmetry for the Fe(CO)$_4$ unit obtains.

TABLE VI. Weighted Least Squares Planes.

Plane	Equation of Mean Plane
I C(5)–S(1)–C(8)	$-0.590x-0.687y-0.423z = -1.276$
II C(5)–S(2)–C(7)–C(8)	$0.172x+0.907y-0.384z = 2.894$
III S(2)–C(6)–C(7)	$0.595x-0.578y-5.558z = 0.770$
IV Fe–C(2)–C(3)–C(4)	$-0.5705x-0.265y-0.777z = -2.568$

Displacement of Atoms from Mean Plane, Å

Plane I	C(5)	0.000
	S(1)	0.000
	C(8)	0.000
Plane II	C(5)	0.013
	S(2)	–0.001
	C(7)	0.011
	C(8)	–0.010
Plane III	S(2)	0.000
	C(6)	0.000
	C(7)	0.000
Plane IV	Fe	0.000
	C(2)	0.002
	C(3)	0.002
	C(4)	0.003

Dihedral Angles between Planes, Deg

I–II	55.8
I–III	65.6
II–III	9.9

Discussion

Although crystal structures of complexes containing 1,4-dithiacyclohexane[14] and 1,3,5-trithiacyclohexane,[15] as well as structures of the free thiacyclohexanes themselves[16,17] have been reported, there has been no previous structural characterization of 1,3-dithiacyclohexane or any complex thereof. Table VII gives a comparison of bond lengths and angles for a series of related heterocycles and their complexes. Each compound referred to in Table VII contains a six-membered ring in the chair conformation. Lack of comparable data on 1,3-dithiane systems necessitated comparison with 1,4-dithianes and 1,3,5-trithianes. As can be seen in Table VII, complexation of the ring to an $Fe(CO)_4$ group effects no startling changes in bond distances or angles within the limits of experimental error. The largest deviations from similar compounds in Table VII occur in the C–C (C_7–C_8 in (1,3-dithiane) $Fe(CO)_4$) distance and in the S–C–C angle, both of which are larger by four esd's than any of the other ring distances or angles. This may reflect only the inherent differences in the three similar yet different ring systems. The mean least squares planes given in Table VI indicate that planes II and III, which are defined by opposite ends of the ligand, are very nearly parallel with a dihedral angle of only 9.9°. The ring consists of three individual planes with plane II forming a dihedral angle of 55.8° with plane I, the central plane, and plane III having a dihedral angle of 65.6° with I. It is evident therefore that very little distortion has been introduced into the ring upon complexation of $Fe(CO)_4$ to one sulfur atom.

Variations in the Fe–C distances within this molecule and comparisons with Fe–C distances in other molecules must be discussed with caution since the differences are small and in no case have corrections been made for the effect of thermal motion on the results. For example, in the present case Fe–C(2) and Fe–C(3) do not differ significantly, since the nominal difference is only 0.017Å while each one has an esd of 0.009Å. The value for Fe–C(4) does appear to be significantly shorter (by 0.040Å) than the average of the other two equatorial Fe–C distances, but this may be illusory since C(4) has appreciably greater thermal motion and correction for thermal motion would lengthen Fe–C(4) more than it would lengthen Fe–C(2) and Fe–C(3).

A comparison of Fe–C distances in several $LFe(CO)_4$ molecules is given in Table VIII. The only two trends in these data which seem likely to be real are (1) the Fe–C distances in substituted species are generally shorter than those in $Fe(CO)_5$ itself, and (2) for the amine substituted compounds Fe–C(ax) is perhaps significantly shorter than Fe–C(eq), whereas in the other two substituted compounds, there is no significant difference. The first trend is understandable since replacement of one CO group by a ligand of markedly inferior π-acidity will increase the amount of π-bonding to the remaining four CO groups and thus shorten the Fe–C distances. The second trend, if real, could indicate that there is enough directional character in the metal–ligand π-bonding to mean that the axial CO ligand is more sensitive to the π-acidity of the axial substituent than are the equatorial CO ligands. Thus with the amines, which have the least π-acidity, the axial Fe–C bonds have more π character relative to the equatorial ones, whereas, with the somewhat better π-acid phosphine and sulfide ligands the difference is negligible.

Supplementary Data

A table of calculated and observed structure factors is available from the Editor upon request.

Acknowledgement

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TABLE VII. Comparison of Bond Distances (Å) and Angles (deg) for Similar Six-Membered Sulfur Heterocycles and Their Complexes.

Compound	S–C Distance	C–C Distance	C–S–C Angle	S–C–C Angle	S–C–S Angle	Ref.
1,4-dithiane	1.801(13)	1.490(18)	99.0(6)	112.6(9)		a
1,3,5-trithiane	1.811(10)		98.9(6)		114.6(5)	b
1,4-dithiane$[IBr]_2$	1.816(6)	1.523(8)	100.0(3)	111.9(4)		c
1,3,5-trithiane$[HgCl_2]$	1.86(4)		99.(2.1)		113(2.3)	d
1,3-dithiane$[Fe(CO)_4]$	1.833(8)	1.695(9)	98.23(33)	115.08(43)	111.99(49)	e

[a]See reference 16. [b]See reference 17. [c]See reference 14. [d]See reference 15. [e]This work.

TABLE VIII. Comparison of Average Metal–Carbon and Carbon–Oxygen Bond Distances in Similar Five-Coordinate Iron Carbonyl Complexes.

Compound	Fe–C(ax) distance	Ave. Fe–C(eq) distance	Ave. C–O distance	Ref.
$Fe(CO)_5$	1.806(5)	1.833(4)	1.145(3)	a
$Fe(CO)_4C_5H_5N$	1.772(7)	1.805(8)	1.140(8)	b
$Fe(CO)_4C_4H_4N_2$	1.774(4)	1.810(4)	1.134(4)	b
$Fe(CO)_4PHPh_2$	1.792(8)	1.793(9)	1.15(1)	c
$Fe(CO)_4C_4H_8S_2$	1.789(9)	1.764(9)	1.155(10)	d

[a] B. Beagley, D.W.J. Cruikshank, P.M. Pinder, A.G. Robiette and G.M. Sheldrock, *Acta Crystallogr., B25,* 737 (1969). [b] Reference 2. [c] B.T. Kilbourn, K.N. Raeburn and D.T. Thompson, *J. Chem. Soc., A,* 1906 (1969). [d] This work.

References

1 Part III: F.A. Cotton and P. Lahuerta, *Inorg. Chem., 14,* 116 (1975).

2 a) F.A. Cotton and J.M. Troup, *J. Am. Chem. Soc., 96,* 1233 (1974).
b) *ibid., 96,* 3438 (1974). c) *ibid., 96,* 4422 (1974).

3 We wish to take this opportunity to acknowledge that, unbeknownst to us, the observations that $Fe_2(CO)_9$ is considerably more reactive in THF than in other solvents, and that such "solutions" are complex and contain various species, including possibly $Fe(CO)_5$, were reported prior to our own earliest publication[2a] on the subject by Natile and Bor.[4] The observations were given at the end of a paper on a spectroscopic matter and were not subsequently emphasized or exploited, and for these reasons they entirely excaped our notice.

4 G. Natile and G. Bor, *J. Organometal. Chem., 35,* 185 (1972).

5 F.A. Cotton and G. Deganello, *J. Am. Chem. Soc., 95,* 396 (1973).

6 See, for example, D. Seebach, N.R. Jones, and E.J. Corey, *J. Org. Chem., 33,* 300 (1968) and references therein.

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

8 Computer programs used in data reduction and in the solution and partial structure refinement on an IBM 360/65 computer 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 Doeden and Ibers, based on Busing and Levy's ORFLS; a local modification of Baur's SADIAN program for calculating atomic distances and angles.

9 The final structure refinement, bond length and angle calculations with errors, mean-plane calculations and ORTEP drawings were completed using the PDP 11/45 computer and software at the Molecular Structure Corporation, College Station, Texas 77843.

10 D.T. Cromer and J.T. Waber, "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.3.1.

11 D.T. Cromer and D. Liberman, *J. Chem. Phys., 53,* 1819 (1971).

12 W.C. Hamilton, *Acta Crystallogr., 18,* 502 (1965).

13 See paragraph at end of paper concerning supplementary material.

14 C. Knobler, C. Baker, H. Hope and J.D. McCullough, *Inorg. Chem., 10,* 697 (1971).

15 G.W.R. Costello, A.T. McPhail and G.A. Sim, *J. Chem. Soc., A,* 1190 (1966).

16 1,4 dithiane: R.E. Marsh, *Acta Crystallogr., 8,* 91 (1955).

17 G. Valle, V. Busetti, M. Mammi and G. Carazzolo, *Acta Crystallogr., B25,* 1432 (1969).