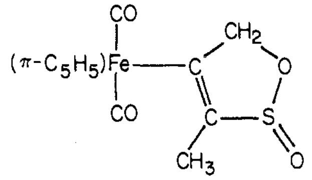

II

Finally, we may note that the present complex readily decomposes in solution forming $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$; an X-ray crystallographic characterization of this new species is currently in progress.[22]

Registry No. $[\pi\text{-}C_5H_5Fe(CO)_2]_2SO_2$, 38999-15-4.

Acknowledgments. This work was made possible by computing time supplied on an IBM 370/155 computer at the Computer Center, University of Illinois at Chicago Circle, and by financial support from the National Science Foundation (Grant No. GP-33018 to M. R. C.). We thank Professor A. Wojcicki for supplying a sample of the material investigated and for his continuing interest in these studies.

[22] M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, 12, 1650 (1973).

Contribution from the Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680

Crystallographic Studies on Sulfur Dioxide Insertion Compounds. V.[1] Elucidation of the Molecular Geometry of *cis*-μ-Carbonyl-μ-(sulfur dioxide)-bis(π-cyclopentadienylcarbonyliron), *cis*-$(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$

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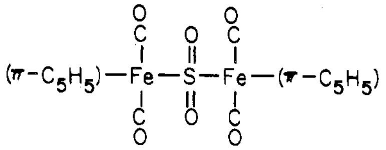
Received January 8, 1973

cis-μ-Carbonyl-μ-(sulfur dioxide)-bis(π-cyclopentadienylcarbonyliron), *cis*-$(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$, crystallizes in the centrosymmetric orthorhombic space group *Pbca* [D_{2h}^{15}; No. 61] with $a = 22.461$ (3), $b = 11.470$ (2), and $c = 21.415$ (3) Å. The measured and calculated densities are respectively 1.865 (10) and 1.878 g cm^{-3} for $Z = 16$. The asymmetric unit contains two $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$ molecules. Single-crystal X-ray diffraction data complete to $2\theta = 46.5°$ (Mo Kα radiation) were collected with a Picker FACS-1 diffractometer, and the structure was solved by means of conventional Patterson and Fourier techniques. Least-squares refinement of atomic positional and thermal parameters, with hydrogen atoms included in calculated positions, converged with $R_F = 5.18\%$ and $R_{wF} = 3.68\%$ for 3975 independent reflections. The two independent molecules have essentially identical conformations, each consisting of two $(\pi\text{-}C_5H_5)Fe(CO)$ units linked by a direct iron–iron bond which is bridged symmetrically by a carbonyl and a sulfur dioxide ligand. The molecule has an overall cis geometry.

Introduction

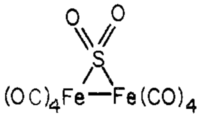
We have recently become interested in molecular species in which sulfur dioxide acts as a bridge between two (or more) metal atoms and we have reported the crystal structure of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(SO_2)$[1,2] in which the two iron atoms are bridged *only* by a sulfur dioxide ligand (as shown in I).



I

A by-product in the synthesis of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(SO_2)$ is $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$;[2] this new molecule also results from the decomposition of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(SO_2)$. The present article concerns the crystallographic characterization of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$.

It may be noted that the results of X-ray diffraction studies have been reported for at least one other species in which sulfur dioxide bridges two metal atoms; the molecular structure of $Fe_2(CO)_8(SO_2)$ (II) has been examined, independently, by two research groups.[3,4]



II

Collection and Reduction of X-Ray Diffraction Data

A sample of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$ was provided by Professor A. Wojcicki of The Ohio State University. Preliminary optical examination showed beautifully formed red octahedra (presumably with well-developed {111} faces). However, these faces had a "matte" appearance, rather than being lustrous. Upon poking with a needle the "crystals" crumbled to powder, indicating that the original material has decomposed at some stage. Careful microexcavation of the rubble formed from some of the larger "crystals" did, however, lead to our obtaining some more-or-less ellipsoidal single crystals, the surfaces of which closely resembled that of a well-dried prune. Discussions with Professor Wojcicki indicated that the method of production of this material had not yet been optimized, that its stability in solution was uncertain, and that recrystallization was not recommended.

A single-crystal X-ray diffraction study was therefore undertaken on a highly nonideal "prune-shaped" crystal of length ~0.3 mm and maximum radius ~0.1 mm.

Preliminary examination of the crystal was carried out using precession and cone-axis photographs, thereby demonstrating the D_{2h} Laue symmetry of the diffraction pattern, obtaining approximate cell dimensions, and revealing the systematic absences $0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, and $hk0$ for $h = 2n + 1$, consistent only with the centrosymmetric orthorhombic space group *Pbca* (D_{2h}^{15}; No. 61).

[1] Part IV: M. R. Churchill, B. G. DeBoer, and K. L. Kalra, *Inorg. Chem.*, 12, 1646 (1973).

[2] M. R. Churchill, B. G. DeBoer, K. L. Kalra, P. Reich-Rohrwig, and A. Wojcicki, *J. Chem. Soc., Chem. Commun.*, 981 (1972).

[3] J. Meunier-Piret, P. Piret, and M. van Meerssche, *Bull. Soc. Chim. Belg.*, 76, 374 (1967).

[4] R. F. Bryan and P. T. Greene, to be submitted for publication.

The crystal was accurately centered on a Picker FACS-1 diffractometer and aligned in an orientation in which the $11,2,\bar{6}$ reflection was coincident with the ϕ axis.[5]

Unit cell parameters and the crystal orientation matrix were determined by automatically optimizing the 2θ, ω, and χ settings of the resolved Mo $K\alpha_1$ component (λ 0.70926 Å) of the diffraction peaks of 12 high-angle reflections ($2\theta = 36$–$57°$), measured under "high-resolution" conditions at 24°. The resulting values are $a = 22.4614$ (31), $b = 11.4702$ (17), and $c = 21.4151$ (27) Å. The unit cell volume is 5517.3 Å^3; the observed density of 1.865 (10) g cm^{-3} is consistent with that calculated for mol wt 389.99 and $Z = 16$ (*i.e.*, $\rho_{\text{calcd}} = 1.878$ g cm^{-3}). The X-ray structural analysis thus requires the location of two crystallographically independent units of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$.

Intensity data were collected[5] using Mo $K\alpha$ radiation [*i.e.*, Mo radiation filtered through a Nb foil, placed between sample and counter, of such thickness that it transmitted ~47% of the incident Mo $K\alpha$ radiation] in conjunction with a coupled θ(crystal)–2θ-(counter) scan of reflections in the horizontal plane. The scan was from 0.8° below the Mo $K\alpha_1$ peak to 0.8° above the Mo $K\alpha_2$ peak, with a scan rate of 2.0°/min. During the θ–2θ scan, a total of C counts was measured in $t(C)$ sec. Stationary-crystal, stationary-counter background counts, each of 20-sec duration, were recorded at the high- and low-2θ extremes of the scan, yielding B_2 and B_1 counts (respectively) for a total background counting time of $t(B) = 40$ sec. Copper foil attenuators, whose transmission factors for Mo $K\alpha$ radiation had accurately been determined previously and which reduced the diffracted beam by successive factors of ~3.0–3.5, were inserted, as necessary, to keep the maximum counting rate below ~8500 counts/sec, thereby avoiding any significant coincidence losses.

The takeoff angle was 3.5° and the scintillation counter (having an aperture of ~6.0 × 6.0 mm) was 330 mm from the crystal.

Prior to collecting intensity data, the intensity of the axial $11,2,\bar{6}$ reflection was measured by a θ–2θ scan at $\chi = 90°$ and at 10° intervals of ϕ from $\phi = 0°$ to $\phi = 350°$. The maximum deviation from the mean intensity was 7%, but this occurred over a fairly narrow range of ϕ [with a minimum intensity at $\phi = 0°$ (and 180°) and a maximum at $\phi = 40°$ (and 220°)]. We decided at this point that no absorption corrections would be possible. A numerical integration method would not be possible due to the numerous "trenches" (*i.e.*, reentrant angles) in our prune-shaped crystal, and a ϕ-scan correction would probably not be reliable. We estimate that neglect of absorption will cause a *maximum* systematic error of 7% in intensity or ~3.5% in $|F_o|$ for those few reflections collected close to $\phi = 0$ and 180° or 40 and 220°. Errors for other data should be significantly smaller.

Data were collected in two "shells." First, all reflections of the type hkl and $hk\bar{l}$ in the angular range $0° < 2\theta < 25°$ were measured. Second, all reflections of the type hkl in the shell defined by $25° \leqslant 2\theta < 46.5°$ were measured. Three strong reflections (0,0,12; 240; 12,0,0) were measured after each batch of 48 reflections in order to monitor crystal decomposition, changes in orientation, etc. Some reduction in intensity (~6%) was noted; a linear decay correction[6] applied to the entire data set reduced root-mean-square deviations in the check reflections to 1.11, 0.80, and 0.82% (respectively).

The integrated intensity, I, and its estimated standard deviation, $\sigma(I)$, were calculated as[5,6]

$$I = q\,[(C + 4.5) - (t(C)/t(B))(B_1 + B_2 + 9.0)]$$

$$\sigma(I) = q\,[(C + 4.5) + (t(C)/t(B))^2(B_1 + B_2 + 9.0) + 24.75 + q^{-2}p^2I^2]^{1/2}$$

The "ignorance factor," p, was given the value 0.04; q represents the combined correction for crystal decay and attenuator used; numerical terms arise from statistics concerning the truncation of the last digit of C, B_1, and B_2 on the punched-tape output from the diffractometer.

Any negative I was reset to zero. All data were retained, none being rejected on the basis of "not being significantly above background."[5]

Structure factor amplitudes (on an arbitrary, rather than absolute, scale) and their estimated standard deviations were derived *via* the expressions $F = (I/Lp)^{1/2}$, $\sigma(F) = [\sigma(I)/Lp]^{1/2}$ for $\sigma(I) \geqslant I$, and $\sigma(F) = [F - \{F^2 - \sigma(I)/Lp\}^{1/2}]$ for $\sigma(I) \leq I$.

Finally, equivalent pairs of hkl and $hk\bar{l}$ reflections were averaged, and their intensity replaced by their σ^{-2}-weighted average, with appropriately adjusted estimated standard deviations.

Elucidation and Refinement of the Structure[7]

Scattering factors for neutral iron, sulfur, oxygen, and carbon[8a] were used; both the real and the imaginary components of anomalous dispersion were included.[8b] For hydrogen contributions, the scattering factors of Mason and Robertson[8c] were used. The function minimized during the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w(hkl) = \sigma^{-2}[|F_o(hkl)|]$.

Discrepancy indices are defined as

$$R_F = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$$

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

The positions of the four crystallographically independent iron atoms were obtained from a three-dimensional Patterson map. A three-dimensional Fourier synthesis, phased by these four iron atoms ($R_F = 36.1\%$, $R_{wF} = 33.6\%$), revealed, unequivocally, the positions of the remaining 38 nonhydrogen atoms in the crystallographic asymmetric unit. Three cycles of full-matrix least-squares refinement of individual positional and isotropic thermal parameters for all 42 nonhydrogen atoms, along with the overall scale factor, converged at $R_F = 9.3\%$, $R_{wF} = 8.9\%$. Anisotropic thermal parameters were assigned to the iron and sulfur atoms and refinement was continued, converging in two cycles to $R_F = 8.3\%$ and $R_{wF} = 7.8\%$. A difference-Fourier synthesis at this stage indicated anisotropy about many of the light-atom positions but did *not* uniquely indicate the positions of the 20 hydrogen atoms. Hydrogen atoms were therefore placed in calculated positions (based on a C–H distance of 0.95 Å[9] and idealized D_{5h} geometry for each π-cyclopentadienyl ligand) and were assigned isotropic thermal parameters equal to $1.2B\,(C_{av})$, where $B\,(C_{av})$ was the average isotropic thermal parameter of carbon atoms in the appropriate five-membered ring. Anisotropic thermal parameters and positional parameters of all nonhydrogen atoms were now refined; two complete cycles[10] led to convergence at $R_F = 5.6\%$ and $R_{wF} = 4.2\%$.

Finally, a survey of intense low-angle reflections showed their $|F_o|$ values to be systematically *greater* than their $|F_c|$ values. A total of 96 reflections with $(\sin\theta)/\lambda < 0.163$ were corrected for this anomaly[11] using the method of "β-filter correction" (or "K-edge correction") which we have described in detail elsewhere.[5] A further two cycles[10] of refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms, and with fixed hydrogen contributions (*vide supra*), led to final convergence, with $(\Delta/\sigma)_{\max} < 0.1$, at $R_F = 5.18\%$ and $R_{wF} = 3.68\%$.

The standard deviation in an observation of unit weight, defined by $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.050; the number of reflections (m) was 3975 and the total number of parameters refined (n) was 379, yielding an m:n ratio of 10.5:1. The function $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ was not appreciably dependent either on θ or on $|F_o|$, thereby indicating a correctly assigned weighting scheme.

The correctness and completeness of the structural analysis were confirmed by a final difference-Fourier synthesis on which the highest features were peaks of 0.47 e Å^{-3} (at 0.45, 0.44, 0.42) and 0.45 e Å^{-3} (at 0.38, 0.34, 0.44 and 0.17, 0.44, 0.35). The highest of these peaks would appear to be related to librational motion of the ring C1–C2–C3–C4–C5 of molecule B.

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(5) Exhaustive details of the experimental procedure have been described previously: M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **12**, 525 (1973).

(6) Data correction and reduction, including the "linear-decay" correction, were performed using the Fortran IV program REDUCE, by B. G. DeBoer.

(7) The following programs were used during the crystallographic analysis: FORDAP (Fourier synthesis, by A. Zalkin), SFIX (derived from SFLS5, by C. T. Prewitt), STAN1 (distances, angles, and their esd's, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson).

(8) (a) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965); (b) D. T. Cromer and D. Lieberman, *J. Chem. Phys.*, **53**, 1891 (1970); (c) R. Mason and G. B. Robertson, *Advan. Struct. Res. Diffr. Methods*, **2**, 57 (1966).

(9) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).

(10) Due to limitations in available computer storage space, not all 379 parameters could be refined at one time. Each "cycle" therefore consisted of two steps: (i) all parameters for nonhydrogen atoms of molecule A were refined, along with parameters for the sulfur and the two iron atoms of molecule B, and the scale factor; (ii) all parameters for nonhydrogen atoms of molecule B were refined, along with parameters for the sulfur and two iron atoms of molecule A, and the scale factor. Hydrogen atom contributions were included, but their parameters were not refined.

(11) This effect results from absorption by the niobium β filter of the short wavelengths which constitute a portion of the initial background for low-angle reflections. The K absorption edge for Nb is 0.65291 Å—see "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, p 61.

Data were inspected for evidence of extinction. No systematic pattern is discernible but it may be noted that disagreement for the "strongest" reflection (212) is quite large, with $|F_o| = 911$ and $|F_c| = 999$ units (1 unit = 0.7289 electron; see ref 12 for the whereabouts of the table of structure factor amplitudes).

Positional and isotropic thermal parameters are listed in Table I; anisotropic thermal parameters are collected in Table II.

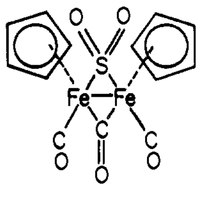
Table I. Final Positional[a] and Isotropic Thermal Parameters[b] for *cis*-$(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$, with Esd's[c]

Atom	*x*	*y*	*z*	*B*, Å^2
		(A) Atoms in Molecule A		
Fe1	0.175658 (22)	0.142810 (44)	0.189852 (25)	2.28
Fe2	0.071169 (23)	0.199102 (44)	0.232079 (24)	2.27
S	0.090105 (40)	0.073268 (85)	0.158226 (47)	2.58
O1	0.07096 (11)	0.10673 (25)	0.09518 (12)	3.94
O2	0.07649 (12)	−0.04859 (21)	0.17314 (15)	4.18
O11	0.16611 (13)	0.36602 (24)	0.25300 (16)	4.94
O12	0.18386 (14)	0.28811 (27)	0.07902 (16)	5.30
O13	0.04071 (14)	0.37909 (25)	0.14250 (16)	4.88
C1	0.24753 (21)	0.14105 (43)	0.25434 (24)	4.80
C2	0.26822 (18)	0.12734 (40)	0.19344 (27)	4.72
C3	0.24360 (21)	0.02739 (41)	0.16742 (22)	4.43
C4	0.20768 (21)	−0.02341 (36)	0.21339 (28)	4.93
C5	0.20951 (21)	0.04661 (47)	0.26639 (23)	5.02
C6	0.07387 (18)	0.18171 (39)	0.33082 (19)	3.72
C7	0.03242 (19)	0.26732 (34)	0.31406 (19)	3.71
C8	−0.01134 (17)	0.21468 (35)	0.27686 (20)	3.59
C9	0.00260 (18)	0.09663 (35)	0.27048 (20)	3.62
C10	0.05593 (19)	0.07508 (33)	0.30305 (20)	3.62
C11	0.14741 (17)	0.27824 (33)	0.23394 (19)	2.98
C12	0.17976 (16)	0.23044 (34)	0.12251 (20)	3.10
C13	0.05172 (17)	0.30656 (34)	0.17701 (19)	3.10
H1	0.2572	0.2022	0.2825	5.6
H2	0.2948	0.1789	0.1727	5.6
H3	0.2502	−0.0019	0.1265	5.6
H4	0.1854	−0.0933	0.2087	5.6
H5	0.1890	0.0330	0.3045	5.6
H6	0.1082	0.1933	0.3561	4.4
H7	0.0338	0.3471	0.3260	4.4
H8	−0.0449	0.2527	0.2591	4.4
H9	−0.0198	0.0406	0.2478	4.4
H10	0.0759	0.0023	0.3062	4.4
		(B) Atoms in Molecule B		
Fe1	0.375578 (24)	0.306568 (49)	0.490708 (25)	2.79
Fe2	0.344602 (22)	0.116986 (43)	0.434239 (25)	2.28
S	0.353588 (45)	0.288948 (82)	0.392529 (44)	2.69
O1	0.29787 (13)	0.34402 (24)	0.37193 (14)	4.21
O2	0.40214 (12)	0.30368 (23)	0.34791 (12)	4.05
O11	0.32680 (13)	0.12357 (25)	0.56899 (14)	4.49
O12	0.26283 (15)	0.41762 (29)	0.51846 (16)	5.56
O13	0.21573 (12)	0.13615 (27)	0.42846 (16)	5.03
C1	0.41982 (22)	0.45280 (46)	0.52352 (29)	5.70
C2	0.45166 (21)	0.40747 (44)	0.47240 (25)	4.92
C3	0.46983 (18)	0.29419 (46)	0.48751 (23)	4.81
C4	0.44976 (21)	0.26925 (50)	0.54925 (27)	5.65
C5	0.41897 (22)	0.36611 (58)	0.57084 (26)	6.29
C6	0.41663 (20)	0.00283 (42)	0.45338 (26)	4.77
C7	0.42469 (17)	0.05504 (35)	0.39518 (22)	3.80
C8	0.37664 (19)	0.02437 (34)	0.35678 (20)	3.62
C9	0.33849 (19)	−0.04711 (36)	0.39337 (26)	4.50
C10	0.36394 (23)	−0.06032 (36)	0.45213 (25)	4.72
C11	0.34115 (16)	0.16083 (35)	0.52070 (20)	2.99
C12	0.30640 (21)	0.37365 (35)	0.50641 (20)	3.61
C13	0.26633 (17)	0.12946 (31)	0.43146 (19)	3.06
H1	0.4022	0.5280	0.5257	6.2
H2	0.4593	0.4467	0.4342	6.2
H3	0.4919	0.2436	0.4612	6.2
H4	0.4559	0.1990	0.5719	6.2
H5	0.4007	0.3726	0.6107	6.2
H6	0.4428	0.0092	0.4881	5.1
H7	0.4572	0.1031	0.3832	5.1
H8	0.3707	0.0476	0.3146	5.1
H9	0.3020	−0.0808	0.3799	5.1
H10	0.3479	−0.1045	0.4857	5.1

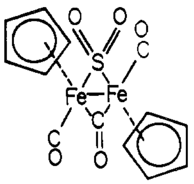
[a] Hydrogen atoms are in calculated positions with C–H = 0.95 Å (*cf.* ref 9). [b] "Equivalent" isotropic thermal parameters, listed for nonhydrogen atoms, correspond to the average of the mean-square displacements along the principal axes of the anisotropic atomic vibration ellipsoid. [c] Estimated standard deviations (esd's), shown in parentheses, are right-adjusted to the least significant digit of the preceding number.

The Molecular Structure

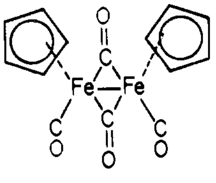
Interatomic distances are shown in Table III, while bond angles are given in Table IV. The labeling of atoms for molecule A is shown in Figure 1 and for molecule B is shown in Figure 2. It can easily be seen that the stereochemistry of the two molecules which define the asymmetric unit is closely similar and varies significantly only in the rotational orientation of the π-cyclopentadienyl rings about their Fe· · ·Cp axes (Cp is defined as the centroid of the π-cyclopentadienyl ligand). This effect is most noticeable for the system C1-C2-C3-C4-C5 in the two molecules. Other features, except the magnitudes and, occasionally, orientation, of the atomic thermal vibration ellipsoids, seem to be constant from one molecule to the other.



III



IV



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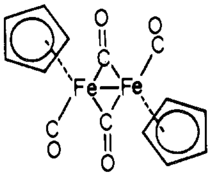

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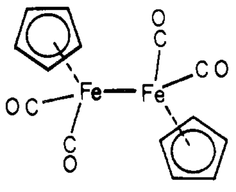
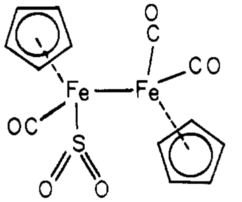


VII



VIII

The molecule is in a cis configuration (*i.e.*, may formally be represented by III, rather than IV). It is possible, however, that the trans isomer (IV) could exist, since the related species $(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$ has been isolated in both cis (V)[13] and trans (VI)[14] forms. The species VII, with no bridging ligands, has been proposed[15] as an intermediate in the equilibration of V and VI, and so, presumably, an isomer of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$ with structure VIII is not impossible. We may note, at this point, that S-bonded sulfur dioxide resembles carbon monoxide in its coordination properties and that species with terminal SO_2 ligands have been synthe-

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(12) A table of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 or \$2.00 for microfiche, referring to code number INORG-73-1650.

(13) R. F. Bryan, P. T. Greene, M. J. Newlands, and D. S. Field, *J. Chem. Soc. A*, 3068 (1970).

(14) R. F. Bryan and P. T. Greene, *J. Chem. Soc. A*, 3064 (1970). The basic molecular geometry of this isomer had been determined many years earlier: O. S. Mills, *Acta Crystallogr.*, 11, 620 (1958).

(15) A. R. Manning, *J. Chem. Soc. A*, 1319 (1968).

Table II. Anisotropic Thermal Parameters[a,b] for Nonhydrogen Atoms in the Two Independent *cis*-$(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$ Molecules

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	⟨*U*⟩[c]
				I. Molecule A			
Fe1	2.08 (2)	2.61 (2)	2.15 (2)	0.05 (2)	−0.04 (2)	−0.16 (2)	(0.18, 0.16, 0.16)
Fe2	2.29 (2)	2.30 (2)	2.22 (2)	0.05 (2)	0.37 (2)	0.13 (2)	(0.18, 0.17, 0.15)
S	2.13 (4)	2.93 (4)	2.66 (4)	−0.22 (3)	0.11 (3)	−0.62 (4)	(0.21, 0.17, 0.16)
O1	3.29 (12)	6.00 (16)	2.54 (13)	0.33 (12)	−0.68 (10)	−0.77 (11)	(0.28, 0.21, 0.16)
O2	4.17 (14)	2.70 (12)	5.66 (19)	−0.98 (11)	0.80 (12)	−0.93 (12)	(0.29, 0.22, 0.16)
O11	4.74 (16)	4.15 (15)	5.93 (18)	−1.79 (13)	1.77 (14)	−2.51 (14)	(0.34, 0.21, 0.17)
O12	5.79 (18)	5.80 (18)	4.30 (17)	−0.22 (14)	0.95 (14)	1.91 (15)	(0.30, 0.27, 0.18)
O13	5.55 (17)	4.24 (15)	4.84 (17)	1.20 (13)	0.09 (14)	1.76 (13)	(0.30, 0.26, 0.18)
C1	3.90 (21)	5.57 (28)	4.92 (24)	1.48 (22)	−1.91 (20)	−1.13 (23)	(0.31, 0.23, 0.17)
C2	2.11 (19)	5.63 (27)	6.43 (32)	0.54 (18)	−0.44 (19)	0.34 (25)	(0.29, 0.27, 0.16)
C3	4.05 (22)	4.77 (24)	4.47 (23)	2.48 (20)	−0.41 (20)	−0.87 (21)	(0.30, 0.23, 0.15)
C4	4.20 (23)	2.75 (20)	7.85 (36)	1.08 (17)	−1.77 (23)	0.95 (22)	(0.33, 0.24, 0.15)
C5	4.16 (23)	6.92 (29)	3.98 (23)	2.29 (23)	−0.01 (19)	2.47 (23)	(0.34, 0.23, 0.15)
C6	3.26 (19)	5.30 (24)	2.60 (19)	−0.68 (18)	0.22 (16)	0.37 (18)	(0.26, 0.20, 0.17)
C7	4.38 (21)	3.76 (20)	2.99 (19)	0.11 (17)	1.69 (17)	−0.25 (17)	(0.26, 0.22, 0.15)
C8	2.68 (18)	4.40 (22)	3.70 (20)	0.62 (16)	1.27 (16)	0.77 (17)	(0.26, 0.21, 0.15)
C9	3.49 (20)	3.83 (20)	3.56 (21)	−1.32 (16)	0.95 (17)	0.34 (17)	(0.25, 0.22, 0.15)
C10	4.80 (23)	2.88 (10)	3.18 (21)	0.40 (17)	1.58 (18)	0.89 (16)	(0.27, 0.19, 0.15)
C11	2.70 (17)	3.23 (19)	3.01 (18)	−0.32 (15)	0.54 (15)	−0.46 (16)	(0.22, 0.19, 0.17)
C12	2.52 (17)	3.45 (19)	3.32 (19)	0.03 (15)	0.28 (15)	−0.24 (17)	(0.21, 0.20, 0.17)
C13	2.75 (18)	3.33 (18)	3.22 (19)	0.24 (15)	0.54 (15)	−0.08 (17)	(0.21, 0.21, 0.17)
				II. Molecule B			
Fe1	2.53 (2)	3.44 (3)	2.41 (2)	−0.51 (2)	−0.11 (2)	−0.53 (2)	(0.22, 0.18, 0.16)
Fe2	1.90 (2)	2.54 (2)	2.39 (2)	−0.03 (2)	−0.05 (2)	0.04 (2)	(0.18, 0.17, 0.15)
S	3.25 (4)	2.71 (4)	2.11 (4)	−0.52 (4)	0.02 (4)	0.27 (3)	(0.21, 0.18, 0.16)
O1	4.51 (14)	4.19 (14)	3.91 (15)	0.97 (12)	−1.15 (12)	0.79 (12)	(0.26, 0.25, 0.17)
O2	4.86 (14)	4.32 (14)	2.95 (13)	−1.49 (12)	1.10 (12)	0.25 (11)	(0.28, 0.22, 0.16)
O11	5.05 (16)	5.55 (17)	2.87 (14)	−0.13 (13)	0.39 (12)	1.28 (13)	(0.28, 0.25, 0.17)
O12	4.86 (17)	6.08 (17)	5.75 (19)	2.54 (15)	1.04 (15)	−0.27 (16)	(0.32, 0.27, 0.18)
O13	2.08 (13)	6.63 (19)	6.37 (19)	0.04 (12)	−0.46 (13)	−0.07 (16)	(0.29, 0.28, 0.16)
C1	4.83 (24)	5.75 (28)	6.50 (33)	−1.97 (20)	0.35 (24)	−3.47 (26)	(0.36, 0.25, 0.16)
C2	3.80 (22)	5.05 (25)	5.91 (30)	−2.19 (20)	0.10 (20)	−1.39 (23)	(0.31, 0.26, 0.16)
C3	2.32 (20)	6.94 (30)	5.18 (27)	−1.44 (19)	−0.59 (18)	−1.47 (24)	(0.31, 0.25, 0.14)
C4	3.55 (22)	7.91 (33)	5.50 (29)	−1.15 (23)	−2.44 (22)	−0.56 (27)	(0.32, 0.30, 0.14)
C5	4.46 (25)	10.34 (42)	4.06 (27)	−2.65 (27)	−0.22 (21)	−3.25 (29)	(0.39, 0.24, 0.16)
C6	3.43 (22)	5.05 (25)	5.83 (29)	2.26 (19)	−0.80 (19)	−0.68 (22)	(0.30, 0.26, 0.15)
C7	2.90 (20)	3.46 (20)	5.03 (26)	0.13 (16)	0.83 (16)	−0.78 (19)	(0.26, 0.20, 0.18)
C8	4.16 (21)	3.28 (19)	3.40 (20)	0.50 (17)	0.70 (18)	−0.62 (16)	(0.24, 0.22, 0.17)
C9	3.28 (21)	2.88 (20)	7.36 (32)	−0.26 (16)	0.29 (21)	−1.97 (21)	(0.32, 0.20, 0.16)
C10	6.14 (28)	2.69 (19)	5.33 (29)	1.26 (19)	1.80 (25)	0.93 (19)	(0.32, 0.22, 0.17)
C11	2.16 (17)	3.95 (19)	2.87 (19)	0.21 (15)	−0.19 (14)	0.42 (16)	(0.23, 0.19, 0.16)
C12	4.53 (22)	3.49 (20)	2.82 (20)	−0.19 (18)	0.18 (17)	−0.31 (16)	(0.24, 0.21, 0.18)
C13	2.64 (18)	3.24 (19)	3.30 (19)	−0.46 (15)	−0.27 (15)	0.05 (16)	(0.21, 0.20, 0.17)

[a] In units of Å² and in the same form as the normal isotropic thermal parameter. These coefficients enter the equation for the calculated structure factor in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] Estimated standard deviations are derived from the inverse of the final least-squares matrices. [c] These are the root-mean-square amplitudes of vibration (in Å) along the three principal axes of the atomic vibrations ellipsoids. For orientations, see Figures 1 and 2.

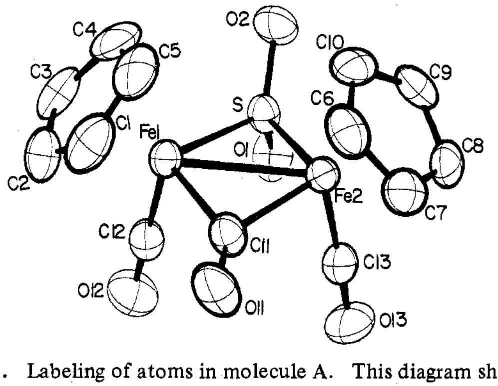
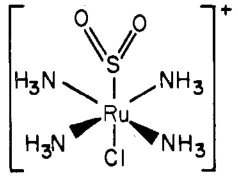
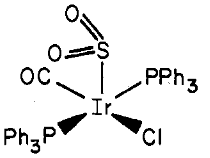


Figure 1. Labeling of atoms in molecule A. This diagram shows the 50% probability envelopes for the vibration ellipsoids of nonhydrogen atoms. Hydrogen atoms are omitted from this diagram for the sake of clarity.

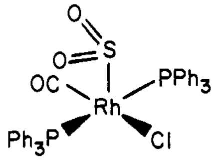
sized and some of them characterized *via* X-ray diffraction techniques, *e.g.*, $[Ru(NH_3)_4(SO_2)Cl^+]$ (IX),[16] $Ir(PPh_3)_2Cl(CO)(SO_2)$ (X),[17] and $Rh(PPh_3)_2Cl(CO)(SO_2)$ (XI).[18]



IX



X



XI

Within the diamagnetic *cis*-$(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$ molecule each iron atom may be formally assigned an oxidation number of +1 (*i.e.*, d^7 outer electronic configuration); the appropriate 18-electron ("noble gas") configuration is

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(16) L. H. Vogt, J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, 4, 1157 (1965).

(17) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 5, 405 (1966).

(18) K. W. Muir and J. A. Ibers, *Inorg. Chem.*, 8, 1921 (1969).

Table III. Interatomic Distances (Å) for *cis*-$(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$, with Estimated Standard Deviations[a]

Atoms	Molecule A	Molecule B
(A) Distances from Iron Atoms		
Fe1-Fe2	2.597 (1)	2.584 (1)
Fe1-S	2.187 (1)	2.169 (1)
Fe2-S	2.181 (1)	2.175 (1)
Fe1-C11	1.925 (4)	1.951 (4)
Fe2-C11	1.939 (4)	1.920 (4)
Fe1· · ·Cp1[b]	1.734 (1)	1.728 (1)
Fe2· · ·Cp2[b]	1.737 (1)	1.735 (1)
Fe1-C1	2.125 (4)	2.072 (4)
Fe1-C2	2.088 (4)	2.101 (4)
Fe1-C3	2.077 (4)	2.123 (4)
Fe1-C4	2.099 (4)	2.129 (5)
Fe1-C5	2.117 (4)	2.088 (5)
Fe2-C6	2.125 (4)	2.121 (4)
Fe2-C7	2.110 (4)	2.107 (4)
Fe2-C8	2.094 (4)	2.097 (4)
Fe2-C9	2.105 (4)	2.080 (4)
Fe2-C10	2.110 (4)	2.115 (4)
Fe1-C12	1.760 (4)	1.766 (5)
Fe2-C13	1.761 (4)	1.765 (4)
(B) Distances from Sulfur Atoms		
S-O1	1.470 (3)	1.470 (3)
S-O2	1.466 (3)	1.460 (3)
(C) Distances within Carbonyl Ligands		
C11-O11	1.165 (4)	1.165 (5)
C12-O12	1.146 (5)	1.131 (5)
C13-O13	1.140 (5)	1.141 (4)
(D) Distances within π-Cyclopentadienyl Rings		
C1-C2	1.394 (7)	1.407 (7)
C2-C3	1.390 (6)	1.400 (7)
C3-C4	1.400 (6)	1.426 (7)
C4-C5	1.391 (7)	1.388 (8)
C5-C1	1.403 (7)	1.420 (8)
C6-C7	1.400 (6)	1.395 (6)
C7-C8	1.402 (6)	1.402 (6)
C8-C9	1.397 (5)	1.422 (6)
C9-C10	1.408 (6)	1.390 (7)
C10-C6	1.419 (6)	1.388 (6)

[a] Distances are not corrected for thermal motion. Esd's include errors in the unit cell parameters and the effect of all positional correlation factors of magnitude >0.10. [b] Cp1 is the centroid of the ring C1-C2-C3-C4-C5, and Cp2 is the centroid of the ring C6-C7-C8-C9-C10.

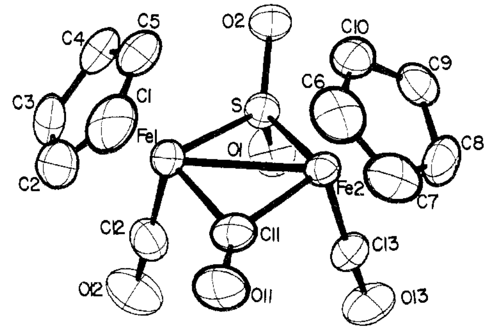

Figure 2. Labeling of atoms in molecule B, showing 50% probability envelopes for the vibration ellipsoids of nonhydrogen atoms.

then achieved by the donation of six electrons from a π-cyclopentadienyl anion, two electrons from a terminal carbonyl group, and one electron each from a bridging carbonyl ligand, a bridging sulfur dioxide ligand, and the other iron atom.

The Fe-C(π-cyclopentadienyl) distances range from 2.077 (4) to 2.125 (4) and 2.094 (4) to 2.125 (4) Å for the two rings in molecule A and from 2.072 (4) to 2.129 (5) and 2.080 (4)-2.121 (4) Å for the rings in molecule B. The mean value for the 20 distances is 2.104 Å, as compared to such values as 2.104 Å in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(SO_2)$,[1,2] 2.106 Å in *trans*-$(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$,[14] 2.109 Å in *cis*-$(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$,[13] 2.094 Å in $(\pi\text{-}C_5H_5)Fe(CO)_2C_4H_5SO_2$,[19] and 2.089 Å in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(C_4H_4)$.[20] The four in-

Table IV. Interatomic Angles (deg) for *cis*-$(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$

Atomic	Molecule A	Molecule B
(A) Angles Involving Iron Atoms		
Fe2-Fe1-S	53.43 (3)	53.60 (3)
Fe1-Fe2-S	53.64 (3)	53.41 (3)
Fe2-Fe1-C11	47.99 (10)	47.63 (10)
Fe1-Fe2-C11	47.56 (10)	48.63 (10)
S-Fe1-C11	98.98 (12)	98.57 (13)
S-Fe2-C11	98.77 (12)	99.34 (12)
Fe2-Fe1-C12	100.99 (10)	102.64 (10)
Fe1-Fe2-C13	99.50 (10)	102.46 (10)
S-Fe1-C12	90.08 (13)	91.42 (14)
S-Fe2-C13	91.53 (14)	90.29 (12)
C11-Fe1-C12	87.61 (18)	87.82 (17)
C11-Fe2-C13	84.56 (17)	88.34 (17)
Cp1-Fe1-Fe2[a]	134.67 (3)	133.92 (3)
Cp2-Fe2-Fe1[a]	135.06 (3)	132.87 (3)
Cp1-Fe1-S[a]	126.82 (4)	126.06 (4)
Cp2-Fe2-S[a]	124.05 (4)	124.20 (4)
Cp1-Fe1-C11[a]	119.99 (12)	120.81 (12)
Cp2-Fe2-C11[a]	122.97 (12)	121.22 (12)
Cp1-Fe1-C12[a]	123.57 (12)	122.70 (14)
Cp2-Fe2-C13[a]	124.82 (13)	124.36 (12)
C1-Fe1-C2	38.62 (20)	39.41 (19)
C2-Fe1-C3	38.98 (17)	38.71 (18)
C3-Fe1-C4	39.17 (18)	39.19 (19)
C4-Fe1-C5	38.52 (18)	38.42 (24)
C5-Fe1-C1	38.64 (19)	39.91 (20)
C6-Fe2-C7	38.61 (16)	38.51 (17)
C7-Fe2-C8	38.95 (16)	38.95 (16)
C8-Fe2-C9	38.85 (14)	39.79 (17)
C9-Fe2-C10	39.03 (17)	38.70 (19)
C10-Fe2-C6	39.14 (16)	38.25 (18)
(B) Angles Involving Bridging Ligands		
Fe1-S-Fe2	72.93 (04)	72.99 (04)
O1-S-O2	112.78 (17)	112.95 (18)
Fe1-S-O1	116.47 (12)	116.41 (13)
Fe2-S-O1	115.86 (12)	115.73 (12)
Fe1-S-O2	117.66 (12)	116.97 (12)
Fe2-S-O2	115.70 (13)	116.31 (12)
Fe1-C11-Fe2	84.45 (15)	83.74 (16)
Fe1-C11-O11	138.62 (32)	135.78 (34)
Fe2-C11-O11	136.96 (32)	140.47 (34)
(C) Angles Involving Terminal Carbonyl Groups		
Fe1-C12-O12	178.32 (42)	177.61 (43)
Fe2-C13-O13	177.24 (40)	178.49 (43)
(D) Angles within π-Cyclopentadienyl Systems		
C5-C1-C2	106.73 (26)	107.66 (47)
C1-C2-C3	109.61 (43)	108.13 (48)
C2-C3-C4	106.90 (43)	107.97 (45)
C3-C4-C5	108.45 (40)	107.81 (52)
C4-C5-C1	108.29 (37)	108.43 (49)
C10-C6-C7	107.96 (37)	108.52 (43)
C6-C7-C8	108.06 (35)	108.46 (37)
C7-C8-C9	108.42 (35)	106.59 (38)
C8-C9-C10	108.21 (36)	108.29 (38)
C9-C10-C6	107.34 (34)	108.13 (43)

[a] See footnote *b* to Table III.

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(19) M. R. Churchill and J. Wormald, *J. Amer. Chem. Soc.*, **93**, 354 (1971).

(20) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **8**, 1936 (1969).

dependent Fe· · ·Cp[21] distances are in good agreement with one another, individual values being Fe1· · ·Cp1 = 1.734 (1), Fe2· · ·Cp2 = 1.737 (1) Å [for molecule A] and Fe1· · ·Cp1 = 1.728 (1), Fe2· · ·Cp2 = 1.735 (1) Å [for molecule B].

The remaining ligands are fairly regularly distributed about the iron atoms; thus the four independent angles of the type Cp-Fe-S[21] range from 124.05 (4) to 126.82 (4)°, the angles Cp-Fe-C11 range from 119.99 (12) to 122.97 (12)°, and the angles Cp-Fe-CO(terminal) range from 122.70 (14) to 124.82 (13)°.

Between the three simple ligands the range of angles is S-Fe-C11 = 98.57 (13)-99.34 (12)°, S-Fe-CO(terminal) = 90.08 (13)-91.53 (14)°, and C11-Fe-CO(terminal) = 84.56 (17)-88.34 (17)°. These variations in a given type of angle *are* statistically significant but presumably result from such effects as intramolecular and intermolecular contacts and are of little chemical importance.

Each of the π-cyclopentadienyl rings has D_{5h} symmetry within the limits of experimental error. Carbon-carbon distances within the four rings have the ranges 1.390 (6)-1.403 (7) and 1.397 (5)-1.419 (6) Å [for molecule A] and 1.388 (8)-1.426 (7) and 1.388 (6)-1.422 (6) Å [for molecule B]. Mean C-C distances within the carbocyclic rings are 1.396, 1.405, 1.408, and 1.399 Å (respectively).

It is clear that these observed distances are systematically reduced from their true values by libration of the five-membered carbocyclic rings about their Fe· · ·Cp[21] axes. The true value for the length of a C-C(π-cyclopentadienyl) linkage is ~1.43 Å; this value comes from an electron diffraction study of $(\pi\text{-}C_5H_5)_2Fe$ (1.431 Å)[22] and from a number of X-ray diffraction studies of materials in which the π-cyclopentadienyl ring has bulky substituents or is locked by exterior bonds into a fixed rotational orientation. [Mean C-C values thus obtained include 1.427 Å in (azulene)$Fe_2(CO)_5$,[23] 1.430 Å in (azulene)$_2$Fe,[24] 1.423 Å in (azulene)$_2Fe_4(CO)_{10}$,[25] 1.436 Å in (fulvalene)$_2$Fe$_2$,[26] 1.431 Å in (acenaphthylene)$Fe_2(CO)_5$,[27] 1.431 Å in $(\pi\text{-}C_5Me_5)Fe(CO)_2SO_2CH_2CH{=}CHPh$,[28] 1.424 Å in $(\pi\text{-}C_5H_4CO_2H)_2Fe$,[29] and 1.426 Å in $(\pi\text{-}C_5H_4COMe)_2Fe$.[30]]

Wheatley's (now rather out-of-date) survey[31] of π-cyclopentadienyl distances indicated a mean C-C distance of Recent and more precise [not, necessarily, more *accurate*!] values from X-ray diffraction studies of complexes containing unsubstituted π-cyclopentadienyl ligands include mean values of 1.396 Å in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SO_2$,[1] 1.375 Å in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(C_4H_4)$,[20] and 1.411 Å in $[(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3H_4\text{-})]_2$.[32] It is clear, however, that the contraction of the C-C(π-cyclopentadienyl) linkage from its true value of ~1.43 Å is a quantitative function of the degree of librational motion of the ring. Insufficient precise data are presently available to enable this relationship to be determined from *experimental data* (rather than from theoretical calculation).

Bond distances within the terminal carbonyl groups are normal and internally consistent, with Fe-CO ranging from 1.760 (4) to 1.766 (5) Å [average 1.763 Å] and C-O from 1.131 (5) to 1.146 (5) Å [average 1.140 Å]; these values may be compared with corresponding distances of 1.768 and 1.140 Å in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(SO_2)$[1] and 1.766 and 1.145 Å in $(\pi\text{-}C_5Me_5)Fe(CO)_2SO_2CH_2CH{=}CHPh$.[28] Within the present molecule Fe-C-O(terminal) angles are all close to linear, ranging from 177.24 (40) to 178.49 (43)°.

Distances and angles associated with the bridging carbonyl group [Fe-C11 = 1.920 (4)-1.951 (4) Å; Fe1-C11-Fe2 = 83.74 (16)-84.45 (15)°; Fe-C11-O11 = 135.78 (34)-140.47 (34)°] are more-or-less symmetrical and are in agreement with values from other studies, *e.g.*, Fe-C = 1.910 (5)-1.918 (5) Å, Fe-C-Fe = 82.9 (2)°, Fe-C-O = 138.4 (4)-138.8 (4)° in *trans*-$(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$;[14] Fe-C = 1.917 (7)-1.918 (7) Å, Fe-C-Fe = 82.4 (3)-82.8 (3)°, Fe-C-O = 137.8 (6)-139.4 (6)° in *cis*-$(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$.[13]

The bridging C-O distances of 1.165 (4) and 1.165 (5) Å in the present molecule are slightly, but significantly, longer than the C-O(terminal) distances [*vide supra*].

The Fe1-Fe2 distances in the present molecule are 2.597 (1) Å [molecule A] and 2.584 (1) Å [molecule B]; the difference of 0.013 Å is small but represents ~9σ [$\sigma_{\text{Diff}} = (\sigma_1^2 + \sigma_2^2)^{1/2}$]. We have no explanation for this observation. It is unlikely that it results from our lack of an absorption correction, and all distances in the two molecules, other than those involving the $Fe(CO)(SO_2)Fe$ bridge, are identical within the limits of experimental error [see Table III].

Iron-iron distances in simple binuclear species having carbonyl groups as their only bridging ligands appear to be shorter than the present mean distance of 2.591 Å—*cf.* values of 2.534 (2) Å in *trans*-$(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$,[14] 2.531 (2) Å in *cis*-$(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$,[13] 2.508 (3) Å in (azulene)$_2Fe_4(CO)_{10}$,[25] and 2.510 (2) Å in $[\pi\text{-}C_5H_4CH(NMe_2)]_2Fe_2(CO)_4$.[33]

Iron-sulfur distances in the two $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$ molecules again seem to differ with Fe1-S = 2.187 (1) and Fe2-S = 2.181 (1) Å [average 2.184 Å] for molecule A and Fe1-S = 2.169 (1) and Fe2-S = 2.175 (1) Å [average 2.172 Å] for molecule B. Possibly this is an artifact caused by the different orientations of the thermal vibration ellipsoids of the sulfur atoms in the two molecules (compare Figures 1 and 2).

The sulfur atoms each have a distorted tetrahedral stereochemical environment. Angles have the following ranges (*cf.* Table IV): Fe1-S-Fe1 = 72.93 (4)-72.99 (4)°, Fe-S-O = 115.70 (13)-117.66 (12)°, O1-S-O2 = 112.78 (17)-112.95 (18)°. [Analogous values in $Fe_2(CO)_8(SO_2)$ are reported, respectively, as 75.78 (5), 114.1 (2)-115.9 (1), and 114.6 (2)°;[4] previously determined values were[3] 75.6 (2), 114.5 (5)-116.6 (5), and 113.9 (7)°.]

Sulfur-oxygen distances in the present structure range from 1.460 (3) to 1.470 (3) Å, the mean value being 1.467 Å. [The corresponding distances in $Fe_2(CO)_8(SO_2)$ are 1.461 (3) and 1.462 (4) Å (see ref 4), previously reported values[3] being 1.436 (14) and 1.464 (12) Å.]

The sulfur-oxygen distances found in the present structure do appear to be slightly shorter than those found in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(SO_2)$[1] (*i.e.*, 1.4797 (15) and 1.4764 (14) Å).

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(21) Cp represents the centroid of the π-cyclopentadienyl ring—see footnote *b* to Table III.

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Finally we may note that the dihedral angle between the bridging systems Fe1-S-Fe2 and Fe1-C11-Fe2 is 158.3° in molecule A and 157.4° in molecule B. This may be compared with an angle of 154.7° between the two Fe-(CO)-Fe bridges in (azulene)$_2$Fe$_4$(CO)$_{10}$.[25]

Registry No. *cis*-(π-C$_5$H$_5$)$_2$Fe$_2$(CO)$_3$(SO$_2$), 39797-02-9.

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Crystal Structures of Transition Metal Aryls. VI.[1-6] Molecular Geometry of *trans*-Bromobis(methyldiphenylphosphine)(σ-pentafluorophenyl)nickel(II), Including the Location and Refinement of Hydrogen Atoms

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The complex *trans*-bromobis(methyldiphenylphosphine)(σ-pentafluorophenyl)nickel(II), *trans*-(PPh$_2$Me)$_2$Ni(σ-C$_6$F$_5$)Br, crystallizes in the centrosymmetric monoclinic space group $C2/c$ ($C_{2h}{}^6$; No. 15) with a = 27.434 (4), b = 11.543 (2), c = 21.433 (3) Å; and β = 114.13 (1)°. The observed density (1.49 (2) g cm^{-3}) is consistent with that calculated for M = 706.21, V = 6194.3 Å^3, and Z = 8 (ρ_{calcd} = 1.514 g cm^{-3}). X-Ray diffraction data were collected with a Picker FACS-1 automated diffractometer and the structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. All atoms, including hydrogens, have been located, the final discrepancy indices being R_F = 6.16% and R_{wF} = 4.28% for the 3459 independent reflections representing data complete to 2θ = 42.5° (Mo Kα radiation). The central nickel(II) atom is in (slightly distorted) square-planar coordination with Ni–PPh$_2$Me = 2.215 (1) and 2.216 (1) Å, Ni–Br = 2.325 (1) Å, and Ni–σ-C$_6$F$_5$ = 1.880 (4) Å. This last value is compared with Ni–σ-C$_6$F$_5$ distances of 1.939 (3) Å in *trans*-(PPh$_2$Me)$_2$Ni(σ-C$_6$F$_5$)$_2$ and 1.978 (10) Å in *trans*-(PPh$_2$Me)$_2$Ni(σ-C$_6$F$_5$)(σ-C$_6$Cl$_5$).

Introduction

For some years we have been interested in the structural characterization of the transition metal-carbon σ bond and have demonstrated conclusively that a metal-perfluoroalkyl σ bond is shorter than the analogous metal-alkyl bond,[7] that a metal-σ-vinyl linkage is shorter than the corresponding metal-alkyl bond,[8] and that a metal-σ-acyl bond is contracted relative to a metal-alkyl bond.[9]

Structural characterization of the metal-σ-aryl linkage has proved rather more difficult. Thus, studies on the species (π-C$_5$H$_5$)Ni(PPh$_3$)(σ-C$_6$H$_5$)[5] and (π-C$_5$H$_5$)Ni(PPh$_3$)(σ-C$_6$F$_5$)[6] revealed the distances Ni-σ-C$_6$H$_5$ = 1.904 (7) Å and Ni-σ-C$_6$F$_5$ = 1.914 (14) Å, but these results are inconclusive insofar as no analogous nickel-alkyl distance has been measured. The molybdenum complex, (π-C$_7$H$_7$)Mo(CO)$_2$(σ-C$_6$F$_5$)[4] was found to have a Mo-σ-C$_6$F$_5$ distance of 2.244 (9) Å as compared to molybdenum-alkyl distances of 2.397 (19) Å in (π-C$_5$H$_5$)Mo(CO)$_3$C$_2$H$_5$,[10] 2.36 (2) Å in (π-C$_5$H$_5$)Mo(CO)$_3$CH$_2$CO$_2$H,[11] and 2.383 (10) Å in [(azulene)Mo(CO)$_3$CH$_3$]$_2$.[12] There are thus some indications that a metal-σ-aryl distance is typically ~0.1 Å shorter than the analogous metal-alkyl distance (see also ref 13).

[It may be noted here that Parshall and Mrowca state[14] (in our opinion, erroneously) that "for σ-alkyl *and aryl* [our italics] compounds, C–M bond lengths are almost exactly those predicted by addition of the covalent radii for carbon and for the transition metal in the appropriate valence state."]

We have recently begun a series of systematic studies on *trans*-(PPh$_2$Me)$_2$Ni(σ-C$_6$F$_5$)(X) species with a view toward ascertaining how changes in the nature of X affect the trans Ni-σ-C$_6$F$_5$ bond. Previous parts of this series have involved accurate structural reports of *trans*-(PPh$_2$Me)$_2$Ni(σ-C$_6$F$_5$)(σ-C$_6$Cl$_5$)[3] and *trans*-(PPh$_2$Me)$_2$Ni(σ-C$_6$F$_5$)$_2$;[2] herewithin we describe the results of an X-ray diffraction study of *trans*-(PPh$_2$Me)$_2$Ni(σ-C$_6$F$_5$)Br.

Collection and Correction of the X-Ray Diffraction Data

Yellow crystals of the complex were supplied by Professor M. D. Rausch.[15] Preliminary $h(0\text{-}3)l$ Weissenberg photographs, a b-axis rotation photograph, $(0\text{-}3)kl$ and $hk(0\text{-}3)$ precession photographs, and a and c cone-axis photographs yielded approximate cell dimensions, demonstrated the C_{2h} $(2/m)$ Laue symmetry of the diffraction

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[1] For previous parts in the series, see ref 2–6.

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[6] Part I: M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 2970 (1968).

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