than the expected van der Waals contact of 3.90 Å using Pauling's radius of 1.95 Å[26] for bromine or the 3.70-Å sum using Bondi's 1.85-Å radius.[27] But in accord with views previously expressed,[10] this is insufficient evidence that the short Br· · ·Br contacts are the result of weak donor-acceptor interactions. Until empirical or theoretical evidence can be developed to support such an interpretation, a more plausible consideration for the short anionic contacts and the angles along the chain is crystal packing forces.

The anionic environment of the tribromide ion is illustrated in Figure 3. As in the MPNA salts, these ions make contact with six surrounding $\mathrm{SbBr_6^-}$ ions, two along the axis at the short distance of 3.607 (3) Å and four approximately perpendicular to the axis at distances ranging from 3.661 (4) to 4.506 (5) Å. The shortest of these involve the terminal bromine atoms of the $\mathrm{Br_3^-}$ ion, in direct contrast with the MPNA salts in which the Sb-Br bonds are directed more toward the centers of the Br-Br bonds.

There is no structural evidence in QNA that the π electrons of the quinolinium ring participate in any donor-acceptor interactions of the type found in crystals of benzene with bromine[28] and *p*-xylene with carbon tetrabromide.[29] Figure 4 illustrates the arrangement of alternating layers of cations and the $\mathrm{SbBr_6^-}$· · ·$\mathrm{Br_3^-}$ chains, a packing sequence duplicated in both 2-MPNA and 4-MPNA. Perpendicular distances between the cation and neighboring bromine atoms of these chains, 3.61 and 3.62 Å, are just slightly shorter than those in 2-MPNA (3.65 and 3.75 Å) and 4-MPNA (3.72 Å). All are equal to or greater than the expected van der Waals sum of 3.62 Å using Bondi's radius of 1.85 Å for bromine and 1.77 Å for aromatic carbon atoms.[27]

In contrast with 2-MPNA and 4-MPNA in which the shortest H· · ·Br distances, involving acidic hydrogen, are only 2.9 Å, a particularly favorable orientation of the quinolinium cation in QNA allows a considerably shorter distance of 2.6 Å to occur, as shown in Figure 5. This distance, as well as an N-H· · ·Br angle of 176°, suggests the presence of an intermolecular N-H· · ·Br hydrogen bond, there being two such interactions per $\mathrm{SbBr_6^-}$ anion. This contact is *ca.* 0.5 Å shorter than the sum of the appropriate van der Waals radii (3.15 Å[26] or 3.05 Å[27]). By comparison, three other pyridinium complexes are also known to exhibit moderately strong $\mathrm{N^+}$-H· · ·Br-(M) hydrogen bonds with H· · ·Br separations ranging from 2.3 to 2.6 Å.[8,30,31] As Figure 5 further illustrates, a pair of C-H· · ·Br contacts at 2.7 Å also occurs with the $\mathrm{SbBr_6^-}$ anion. However, since C-H groups are highly improbable proton donors, crystal packing forces are likely responsible for these particular contacts. Finally, we note in passing that since the short N-H· · ·Br contacts involve only the Br(2) atoms of the $\mathrm{SbBr_6^-}$ ion, it is not surprising to find that the Sb-Br(2) bonds have become the longest of the three independent Sb-Br bonds in the ion.

Registry No. QNA, 39394-71-3.

Supplementary Material Available. A listing of structure factor amplitudes 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, 20× 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 $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2939.

---

(26) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 260.

(27) A. Bondi, *J. Phys. Chem.*, 68, 441 (1964).

(28) O. Hassel and K. O. Stromme, *Acta Chem. Scand.*, 12, 1146 (1958).

(29) F. J. Strieter and D. H. Templeton, *J. Chem. Phys.*, 37, 161 (1962).

(30) M. L. Hackert and R. A. Jacobson, *Acta Crystallogr., Sect. B*, 27, 1658 (1971).

(31) R. E. DeSimone and G. D. Stucky, *Inorg. Chem.*, 10, 1808 (1971).

Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Structure and Spectroscopic Properties of μ-(*o*-Tetrafluorophenylene)-diiron Octacarbonyl, $\mathrm{C_6F_4Fe_2(CO)_8}$

M. J. BENNETT,* W. A. G. GRAHAM, R. P. STEWART, Jr., and R. M. TUGGLE

Received June 22, 1973

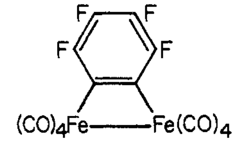
The known compound, μ-(*o*-tetrafluorophenylene)-diiron octacarbonyl, $\mathrm{C_6F_4Fe_2(CO)_8}$, prepared by a rather unusual route, has been identified and characterized by mass, infrared, and ^{19}F nmr spectroscopic techniques. The crystal and molecular structure has been determined from three-dimensional single-crystal X-ray data collected by counter methods. This compound crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 6.739$ (1), $b = 26.966$ (5), and $c = 8.859$ (1) Å, $\beta = 93.78$ (2)°, and $Z = 4$. The structure, solved by heavy-atom techniques, has been refined by full-matrix least-squares methods to a conventional R factor of 0.029 for the 1942 significant, independent intensities measured. Mo Kα radiation was used. Solution of the structure has shown that $\mathrm{C_6F_4Fe_2(CO)_8}$ is, in fact, the *o*-phenylene adduct originally proposed. The Fe-Fe distance is 2.797 (1) Å.

Introduction

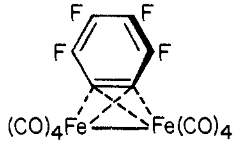
In 1970 Roe and Massey[1] prepared the novel iron complex $\mathrm{C_6F_4Fe_2(CO)_8}$ from the reaction of triiron dodecacarbonyl with tetrafluorobenzyne (generated *in situ*). Based on infrared and mass spectral data the four-membered cyclic structure I was proposed for this compound.[1] An alternative structure that is still consistent with the experimental data is II, in which tetrafluorobenzene is bonded to the two iron atoms in a manner similar to the dicobalt-acetylene linkage in the well-characterized $\mathrm{(C_2H_2)Co_2(CO)_6}$ compounds.[2,3]

---

(1) D. M. Roe and A. G. Massey, *J. Organometal. Chem.*, 23, 547 (1970).



I



II

In order that the effective atomic number rule be obeyed, the tetrafluorobenzyne group in II could be regarded as a two-electron (rather than four-electron) donor to the diiron unit.[4]

Both structures I and II would be of considerable interest since there is little precedent for either in organometallic chemistry. Dahl and coworkers have recently reported the first example of an *o*-phenylene linkage between two metal atoms in their structural characterization of the $[Pt_4(C_6H_4)_2Cl_{14}]^{2-}$ anion.[10] Although there has been much current interest in the synthesis of benzyne transition-metal complexes,[1,11-13] the first authentic compound of this type, $Os_3(C_6H_4)(PPh_2)_2(CO)_7$, was only recently prepared and verified by X-ray diffraction.[5]

We felt that the novel structural features presented by both I and II warranted a further detailed investigation of $C_6F_4Fe_2(CO)_8$ and we report here the results of our study, which included infrared, mass, and ^{19}F nmr spectral measurements as well as single-crystal X-ray diffraction. We also describe the rather peculiar reaction from which the compound was obtained.

Experimental Section

All operations were carried out under an atmosphere of nitrogen, using Schlenk apparatus. Solvents were dried by appropriate methods and were saturated with nitrogen. Trimethylchlorosilane was distilled under nitrogen immediately before use. All reagents were obtained from commercial sources. Infrared spectra were recorded on Perkin-Elmer Models 421 and 337 spectrophotometers. Band positions in the 2000-cm^{-1} (terminal carbonyl) region are estimated to be accurate to ±1 cm^{-1}. Mass spectra were obtained on AEI MS-2 and MS-12 instruments.

Preparation of $C_6F_4Fe_2(CO)_8$. The salt $Li[(CO)_4FeC(O)C_6F_5]$ was prepared in ether at −78° from pentafluorophenyllithium (31.5 mmol) and iron pentacarbonyl (32.0 mmol), according to the method of Fischer.[14] Solvent and excess iron pentacarbonyl were removed at 0° *in vacuo,* and addition of *n*-pentane (75 ml) to the resulting yellow oil gave a yellow crystalline solid. This slurry was cooled to 0° and trimethylchlorosilane (55 mmol) in *n*-pentane (20 ml) was slowly added to give a blood red solution. After stirring for 15 hr at room temperature, the solution was filtered to remove lithium chloride. Removal of solvent *in vacuo* gave an extremely air-sensitive blood red oil. Repeated attempts at crystallization failed so the oil was chromatographed (*n*-pentane) on Florisil. Three bands were eluted with *n*-pentane, the first and second being $Fe(CO)_5$ and $Fe_3(CO)_{12}$, respectively. Concentration of the third band afforded an orange crystalline product (371 mg, 4.8%). *Anal.* Calcd for $C_{14}F_4O_8Fe_2$: C, 34.76; F, 15.71; Fe, 23.08. Found: C, 34.73; F, 15.72; Fe, 22.83 (Pascher Mikroanalytisches Laboratorium, Bonn, West Germany).

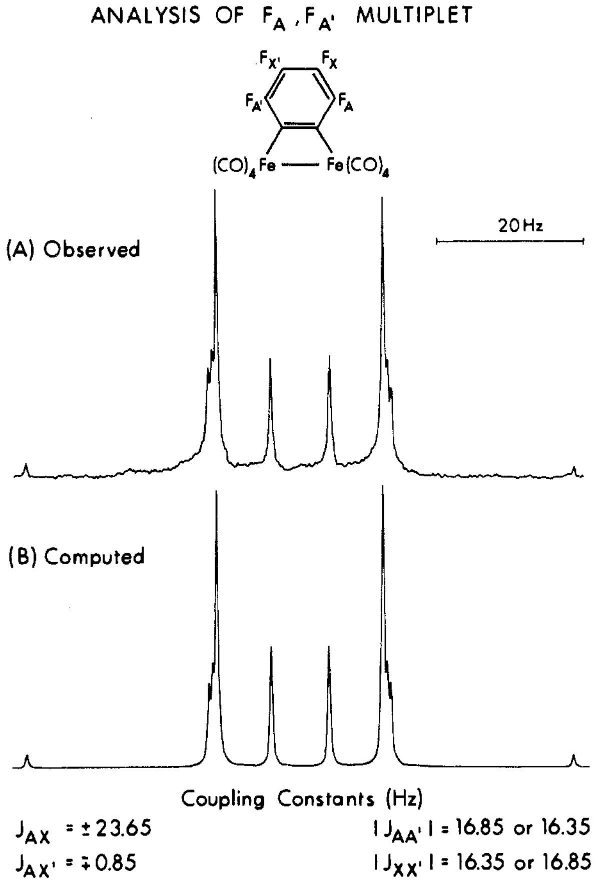


Figure 1. Low-field multiplet (AA') of the ^{19}F Fourier transform spectrum of $C_6F_4Fe_2(CO)_8$ at 84.6 MHz: (A) observed spectrum; (B) computed using coupling constants cited in text.

Infrared Spectra. Spectra obtained in KBr disk and CCl_4 solution showed the following bands: 1623 (m), 1604 (m), 1470, 1467 (s, doublet), 1420 (s), 1351 (w), 1337 (w), 1300 (vw), 1288 (w), 1077 (m), 992 (s), 777 (ms), 756 (s), 692 (s), 636 (ms, shoulder), 611 cm^{-1} (s). An expanded spectrum (cyclohexane solution) gave the following ν(CO) (terminal) (cm^{-1} ± 1): 2117 (m), 2071 (vs), 2052 (m), 2043.5 (s), 2035 (s).

Nmr Spectrum. The ^{19}F nmr spectrum was obtained at 84.6 MHz on a Bruker HFX-10 spectrometer using the Fourier transform method (pulse width 120 μsec). The solvent (CD_2Cl_2) served also as the lock signal, and chemical shifts were measured in hertz from external hexafluorobenzene. The spectrum consists of two symmetrical AA'XX' multiplets at −520.0 and −2637.9 Hz. An expanded scan of the low-field multiplet (AA') is shown in Figure 1A. Analysis of the spectrum by standard procedures[15] gave the following relevant parameters (±0.08 Hz): $K = J_{AA'} + J_{XX'} = 33.20$ Hz, $L = J_{AX} - J_{AX'} = 24.50$ Hz, $M = J_{AA'} - J_{XX'} = 0.50$ Hz, and $N = J_{AX} + J_{AX'} = 22.80$ Hz, where $J_{AX} = \pm 23.65$ Hz, $J_{AX'} = \mp 0.85$ Hz, $|J_{AA'}| = 16.85$ or 16.35 Hz, and $|J_{XX'}| = 16.35$ or 16.85 Hz.

The spectral analysis was verified by comparison with the results given by computer analysis.[16] The computed spectrum for the above coupling constants is shown in Figure 1B.

Collection and Reduction of X-Ray Data. Crystals suitable for X-ray studies were obtained by recrystallization from *n*-pentane. Weissenberg and precession photographs established that the crystals belonged to the monoclinic system. The observed systematic

---

(2) W. G. Sly, *J. Amer. Chem. Soc.*, 81, 18 (1959).

(3) N. A. Bailey and R. Mason, *J. Chem. Soc. A*, 1293 (1968).

(4) In view of the unusual multicenter bonding descriptions of the benzyne–triosmium interaction in benzyne–triosmium cluster compounds[5-7] and the acetylene–metal interactions in compounds such as $(EtC_2Et)Co_4(CO)_{10}$[8] and $(PhC_2Ph)Fe_3(CO)_9$,[9] formulation II does not seem entirely unreasonable.

(5) C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland, and R. Mason, *J. Chem. Soc., Chem. Commun.*, 87 (1972).

(6) A. J. Deeming, R. S. Nyholm, and M. Underhill, *J. Chem. Soc., Chem. Commun.*, 224 (1972).

(7) G. J. Gainsford, J. M. Guss, P. R. Ireland, R. Mason, C. W. Bradford, and R. S. Nyholm, *J. Organometal. Chem.*, 40, C70 (1972).

(8) L. F. Dahl and D. L. Smith, *J. Amer. Chem. Soc.*, 84, 2450 (1962).

(9) J. F. Blount, L. F. Dahl, C. Hoogzand, and W. Hubel, *J. Amer. Chem. Soc.*, 88, 292 (1966).

(10) P. M. Cook, L. F. Dahl, and D. W. Dickerhoof, *J. Amer. Chem. Soc.*, 94, 5511 (1972).

(11) E. W. Gowling, S. F. A. Kettle, and G. M. Sharples, *Chem. Commun.*, 21 (1968).

(12) T. L. Gilchrist, F. J. Graveling, and C. W. Rees, *J. Chem. Soc. C*, 977 (1971), and references cited therein.

(13) R. G. Miller and D. P. Kuhlman, *J. Organometal. Chem.*, 26, 401 (1971).

(14) E. O. Fischer, H.-J. Beck, C. G. Kreiter, J. Lynch, J. Muller, and E. Winkler, *Chem. Ber.*, 105, 162 (1972).

(15) E. W. Garbisch, Jr., *J. Chem. Educ.*, 45, 480 (1968).

(16) Program NUMAR: A. R. Quirt, Ph.D. Thesis, University of Alberta, 1972.

absences $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, indicated that the space group was $P2_1/n$, a nonstandard setting of $P2_1/c$ (C_{2h}^5). Least-squares refinement of the unit cell parameters on the 2θ values observed for 12 high-order ($95° < 2\theta < 105°$) reflections accurately centered on a Picker four-circle diffractometer gave the following values: $a = 6.739$ (1), $b = 26.966$ (5), $c = 8.859$ (1) Å, and $\beta = 93.78$ (2)°. Cu Kα_1 radiation (λ 1.54051 Å) and a 2° takeoff angle were used. The density, measured by flotation in an aqueous solution of zinc bromide, 1.999 (1) g cm^{-3}, agrees well with 2.000 g cm^{-3} calculated for four molecules in the unit cell. All measurements were made at 25°. The general positions derived for space group $P2_1/n$ are x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $^1/_2 + x, ^1/_2 - y, ^1/_2 + z$; and $^1/_2 - x, ^1/_2 + y, ^1/_2 - z$. No symmetry need be imposed on the molecule.

For intensity measurements a crystal of approximate dimensions 0.29 × 0.17 × 0.13 mm along *a*, *b*, and *c* was mounted with its *a* axis roughly parallel to the ϕ axis of a Picker FACS-I automatic diffractometer. The crystal faces were identified as the forms $\{010\}$ and $\{011\}$, as well as (120), ($1\bar{2}0$), and ($\bar{1}00$). Intensities were collected by the coupled ω-2θ scan method using graphite monochromated (002 reflection) Mo Kα radiation and a 4° takeoff angle. Symmetric scan ranges with a 2° base width plus allowance for α_1-α_2 dispersion[17] and a scan rate of 1° min^{-1} were used. Stationary background counts (20 sec) were taken at the lower and upper limits of each scan. Intensities were measured with a scintillation counter with the pulse height analyzer set to accept approximately a 95% window when centered on the Mo Kα peak. Crystal and instrumental stability were monitored by a set of three standard reflections measured at regular intervals. These standards remained constant within counting and instrumental error thourghout the entire data collection. The eight reflections whose count rates exceeded the linear response range of the counter were remeasured at reduced current on the X-ray tube. One quadrant of 2829 independent intensities in the range $2\theta \leqslant 50°$ ($(\sin\theta)/\lambda \leqslant 0.60$) was collected. Net intensities were calculated assuming a linear background profile between the scan limits of each reflection. The 1942 reflections for which $I > 3.0\sigma(I)$, where I is based on pure counting statistics, were used in the solution and refinement of the structure.

The data were reduced to values of $|F|$ after correction for Lorentz, polarization, and absorption[18] effects. Standard deviations [$\sigma(F)$] were estimated by the procedure of Doedens and Ibers[19] with a *p* factor of 0.03. The linear absorption coefficient of this compound for Mo Kα radiation is 19.47 cm^{-1}, and the transmission factors ranged from 0.739 to 0.815 for the crystal studied.

Solution and Refinement

The two iron atoms were located in a three-dimensional Patterson map and a subsequent difference Fourier map yielded the positions of the remaining atoms. Full-matrix least-squares refinement for all atoms with isotropic temperature factors converged at $R_1 = 0.069$ and $R_2 = 0.081$. The conventional residual factor $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, and the weighted residual factor $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, where the weights $w = 1/\sigma^2(F_o)$. All least-squares refinements were made on F where the function minimized is $\Sigma w(|F_o| - |F_c|)^2$. The scattering factors of Cromer and Mann[20] were used for all atoms. The scattering factors for iron were corrected for the real and imaginary components of anomalous dispersion of Mo Kα radiation by the factors tabulated by Cromer:[21] $\Delta f' = 0.301$ and $\Delta f'' = 0.845$. Inspection of the intense low-angle data revealed that $|F_o|$ were consistently smaller than $|F_c|$, suggesting an extinction problem. Extinction corrections[22] were applied to the data and refinement was continued, using anisotropic temperature factors for all atoms.

Refinement converged at the final values $R_1 = 0.029$ and $R_2 = 0.039$. In the last refinement cycle no parameter changed by more than 0.05σ. The extinction factor, C, refined to 1.39×10^{-7}. The final value for the function $[\Sigma w(|F_o| - |F_c|)^2/(n - p)]^{1/2}$ was 1.204. The highest peak in a final difference Fourier map [$\sigma(\Delta\rho)$[24] = 0.08 e/Å^3] was 0.29 e/Å^3, or about 0.05 times the density for a typical carbon atom. This was in the vicinity of Fe(1). Structure factors were calculated for the 887 unobserved reflections and one reflection had $|F_c|$ greater than twice the minimum observable value. The final positional parameters and temperature factors are listed in Table I.[25]

Table I

Final Positional and Thermal Parameters[a]

Atom	x	y	z	B, Å^2 [b]
Fe(1)	0.27771 (7)	0.06974 (2)	0.23602 (5)	2.37
Fe(2)	0.18625 (7)	0.16953 (2)	0.18084 (5)	2.39
F(1)	0.1550 (3)	0.03095 (7)	0.5842 (2)	3.96
F(2)	0.0009 (3)	0.08691 (8)	0.7994 (2)	4.24
F(3)	−0.0765 (4)	0.18382 (8)	0.7502 (2)	4.78
F(4)	−0.0027 (4)	0.22655 (8)	0.4847 (2)	4.40
O(11)	0.3651 (4)	−0.0303 (1)	0.3550 (3)	4.63
O(12)	0.4447 (4)	0.0549 (1)	−0.0607 (3)	4.86
O(13)	0.6521 (4)	0.1030 (1)	0.3935 (3)	4.72
O(14)	−0.1232 (4)	0.0348 (1)	0.1345 (3)	5.02
O(21)	0.0225 (5)	0.2702 (1)	0.1567 (3)	5.74
O(22)	0.3568 (4)	0.1668 (1)	−0.1185 (3)	4.61
O(23)	0.5590 (5)	0.2084 (1)	0.3278 (3)	5.22
O(24)	−0.2176 (4)	0.1397 (1)	0.0728 (3)	4.61
C(1)	0.1162 (5)	0.0794 (1)	0.5528 (4)	2.72
C(2)	0.0366 (5)	0.1077 (1)	0.6643 (3)	2.98
C(3)	−0.0037 (5)	0.1565 (1)	0.6385 (4)	3.14
C(4)	0.0358 (5)	0.1775 (1)	0.5021 (4)	2.84
C(5)	0.1125 (5)	0.1497 (1)	0.3899 (3)	2.34
C(6)	0.1538 (5)	0.1003 (1)	0.4158 (3)	2.29
C(11)	0.3301 (5)	0.0085 (1)	0.3114 (4)	3.10
C(12)	0.3806 (6)	0.0610 (1)	0.0529 (4)	3.25
C(13)	0.5077 (6)	0.0925 (1)	0.3287 (4)	3.05
C(14)	0.0286 (6)	0.0501 (1)	0.1700 (4)	3.21
C(21)	0.0881 (6)	0.2321 (1)	0.1709 (4)	3.51
C(22)	0.2901 (5)	0.1680 (1)	−0.0047 (4)	3.03
C(23)	0.4200 (6)	0.1914 (1)	0.2719 (4)	3.39
C(24)	−0.0585 (6)	0.1481 (1)	0.1132 (4)	3.05

Anisotropic Temperature Factors[c] (×10^3)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	31.2 (3)	32.9 (3)	25.7 (3)	0.8 (2)	3.6 (2)	0.5 (2)
Fe(2)	34.4 (3)	32.4 (3)	24.0 (3)	−2.1 (2)	2.5 (2)	1.2 (2)
F(1)	70 (2)	41 (1)	40 (1)	4 (1)	12 (1)	11 (1)
F(2)	68 (2)	70 (2)	24 (1)	−1 (1)	13 (1)	9 (1)
F(3)	81 (2)	68 (2)	33 (1)	20 (1)	18 (1)	−11 (1)
F(4)	85 (2)	40 (1)	43 (1)	17 (1)	13 (1)	−2 (1)
O(11)	81 (2)	38 (2)	58 (2)	12 (1)	10 (2)	9 (1)
O(12)	76 (2)	70 (2)	40 (2)	10 (2)	27 (2)	−3 (1)
O(13)	39 (2)	74 (2)	65 (2)	−12 (2)	−11 (2)	15 (2)
O(14)	44 (2)	61 (2)	85 (2)	−11 (2)	−16 (2)	0 (2)
O(21)	108 (3)	47 (2)	63 (2)	24 (2)	11 (2)	7 (2)
O(22)	69 (2)	75 (2)	32 (1)	−14 (2)	16 (1)	2 (1)
O(23)	57 (2)	72 (2)	68 (2)	−19 (2)	−17 (2)	−2 (2)
O(24)	38 (2)	80 (2)	56 (2)	−9 (2)	−4 (1)	5 (2)
C(1)	31 (2)	40 (2)	32 (2)	0 (2)	1 (2)	1 (2)
C(2)	39 (2)	53 (2)	21 (2)	4 (2)	6 (2)	3 (2)
C(3)	45 (2)	49 (2)	26 (2)	8 (2)	5 (2)	−9 (2)
C(4)	39 (2)	37 (2)	32 (2)	6 (2)	0 (2)	−1 (2)
C(5)	29 (2)	39 (2)	22 (2)	−2 (2)	1 (1)	−1 (1)
C(6)	28 (2)	35 (2)	23 (2)	−2 (2)	5 (1)	−3 (1)
C(11)	40 (2)	44 (2)	35 (2)	1 (2)	7 (2)	−1 (2)
C(12)	43 (2)	43 (2)	38 (2)	5 (2)	5 (2)	2 (2)
C(13)	38 (2)	42 (2)	37 (2)	4 (2)	6 (2)	9 (2)
C(14)	43 (2)	39 (2)	40 (2)	3 (2)	1 (2)	−4 (2)
C(21)	55 (3)	43 (3)	35 (2)	−2 (2)	5 (2)	0 (2)
C(22)	42 (2)	36 (2)	36 (2)	−9 (2)	−1 (2)	1 (2)
C(23)	44 (3)	48 (2)	36 (2)	−2 (2)	0 (2)	1 (2)
C(24)	41 (2)	47 (2)	28 (2)	−2 (2)	5 (2)	3 (2)

[a] Numbers in parentheses are estimated standard deviations in the last figure quoted. [b] Equivalent isotropic B's. [c] Anisotropic temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Major programs used in the solution and refinement of this structure were SFLS5 by Prewitt for structure factor calculation and least-

---

(17) W. R. Busing, R. D. Ellison, H. A. Levy, S. P. King, and R. T. Roseberry, ORNL Report No. 4143, 1968.

(18) P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Crystallogr.*, **18**, 1035 (1965).

(19) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).

(20) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(21) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(22) Extinction corrections were applied to $|F_c|$ by the formula of Zachariasen:[23] $|F_c|_{cor} = |F_c|/[1 + \beta(2\theta)CI]$, where C is a parameter varied in the least-squares refinement.

(23) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963).

(24) H. Lipson and W. Cochran, "The Determination of Crystal Structures," G. Bell and Sons, London, 1953, p 308.

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

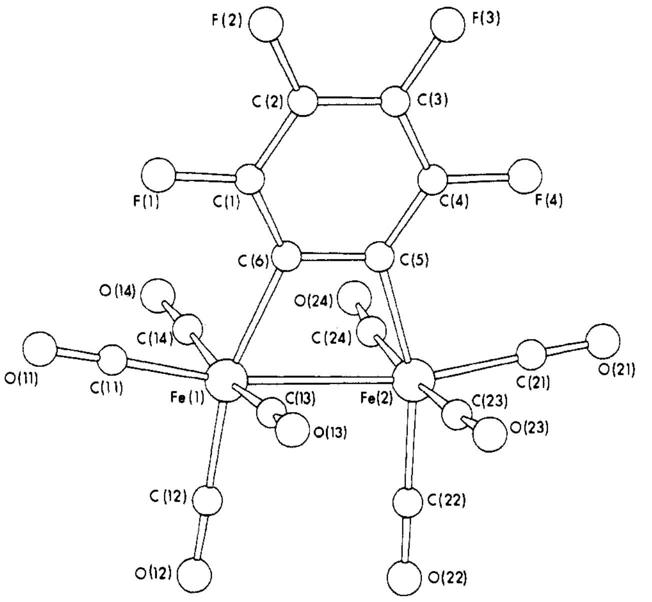


Figure 2. Perspective view of structure of $C_6F_4Fe_2(CO)_8$.

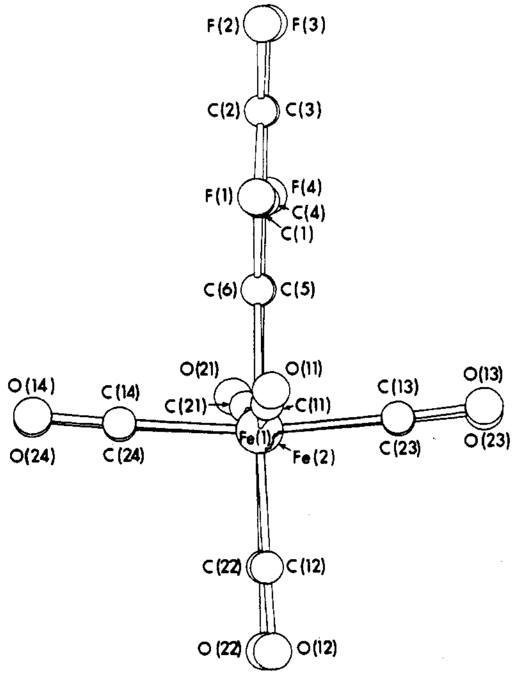


Figure 3. Projection of $C_6F_4Fe_2(CO)_8$ molecule along Fe-Fe bond.

squares refinement and FORDAP by Zalkin for Patterson and Fourier synthesis.

Results and Discussion

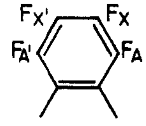
An extremely air-sensitive blood red oil was isolated from the reaction of trimethylchlorosilane with the salt Li[$(CO)_4$-$FeC(O)C_6F_5$][14] in *n*-pentane solution. Attempted purification of this material[26] by chromatography resulted in much decomposition to $Fe(CO)_5$ and $Fe_3(CO)_{12}$. In addition, an orange air-stable crystalline solid was isolated in low yield and was characterized as $C_6F_4Fe_2(CO)_8$ by mass spectrometry and elemental analysis. The fragmentation pattern in the mass spectrum confirmed its identity as the compound first prepared by Roe and Massey[1] by a more direct route.

Table II. Selected Interatomic Distances and Angles[a]

	Bond Distances, Å		
Fe(1)-Fe(2)	2.797 (1)	Fe(2)-C(21)	1.813 (4)
Fe(1)-C(11)	1.806 (4)	Fe(2)-C(22)	1.829 (4)
Fe(1)-C(12)	1.821 (4)	Fe(2)-C(23)	1.820 (4)
Fe(1)-C(13)	1.813 (4)	Fe(2)-C(24)	1.812 (4)
Fe(1)-C(14)	1.820 (4)	Fe(2)-C(5)	2.021 (3)
Fe(1)-C(6)	2.022 (3)		
C(1)-C(2)	1.385 (5)	C(5)-C(6)	1.378 (5)
C(1)-C(6)	1.377 (4)	C(3)-C(4)	1.376 (5)
C(1)-F(1)	1.357 (4)	C(4)-C(5)	1.372 (4)
C(2)-F(2)	1.357 (3)	C(4)-F(4)	1.356 (4)
C(2)-C(3)	1.360 (5)	C(3)-F(3)	1.351 (4)
C(11)-O(11)	1.136 (4)	C(21)-O(21)	1.123 (4)
C(12)-O(12)	1.133 (4)	C(22)-O(22)	1.131 (4)
C(13)-O(13)	1.133 (4)	C(23)-O(23)	1.127 (4)
C(14)-O(14)	1.129 (4)	C(24)-O(24)	1.131 (4)
	Angles, Deg		
Fe(2)-Fe(1)-C(6)	69.4 (1)	Fe(1)-Fe(2)-C(5)	69.5 (1)
Fe(2)-Fe(1)-C(11)	168.3 (1)	Fe(1)-Fe(2)-C(21)	168.5 (1)
Fe(2)-Fe(1)-C(12)	93.5 (1)	Fe(1)-Fe(2)-C(22)	92.5 (1)
Fe(2)-Fe(1)-C(13)	85.7 (1)	Fe(1)-Fe(2)-C(23)	93.5 (1)
Fe(2)-Fe(1)-C(14)	92.0 (1)	Fe(1)-Fe(2)-C(24)	86.4 (1)
C(6)-Fe(1)-C(11)	99.3 (1)	C(5)-Fe(2)-C(21)	100.4 (2)
C(6)-Fe(1)-C(12)	162.9 (2)	C(5)-Fe(2)-C(22)	161.7 (1)
C(6)-Fe(1)-C(13)	83.7 (1)	C(5)-Fe(2)-C(23)	86.4 (2)
C(6)-Fe(1)-C(14)	87.2 (1)	C(5)-Fe(2)-C(24)	86.9 (2)
C(11)-Fe(1)-C(12)	97.7 (2)	C(21)-Fe(2)-C(22)	97.9 (2)
C(11)-Fe(1)-C(13)	90.1 (2)	C(21)-Fe(2)-C(23)	91.2 (2)
C(11)-Fe(1)-C(14)	90.4 (2)	C(21)-Fe(2)-C(24)	87.7 (2)
C(12)-Fe(1)-C(13)	94.8 (2)	C(22)-Fe(2)-C(23)	92.0 (2)
C(12)-Fe(1)-C(14)	94.2 (2)	C(22)-Fe(2)-C(24)	95.1 (2)
C(13)-Fe(1)-C(14)	170.8 (2)	C(23)-Fe(2)-C(24)	172.9 (2)
Fe(1)-C(6)-C(5)	110.6 (2)	Fe(2)-C(5)-C(6)	110.4 (2)
Fe(1)-C(6)-C(1)	129.6 (3)	Fe(2)-C(5)-C(4)	130.3 (3)
C(5)-C(6)-C(1)	119.7 (3)	C(6)-C(5)-C(4)	119.3 (3)
C(6)-C(1)-F(1)	122.0 (3)	C(5)-C(4)-F(4)	121.9 (3)
F(1)-C(1)-C(2)	117.6 (3)	F(4)-C(4)-C(3)	117.0 (3)
C(6)-C(1)-C(2)	120.3 (3)	C(5)-C(4)-C(3)	121.1 (3)
C(1)-C(2)-F(2)	120.0 (3)	C(4)-C(3)-F(3)	121.3 (3)
F(2)-C(2)-C(3)	120.2 (3)	F(3)-C(3)-C(2)	118.9 (3)
C(1)-C(2)-C(3)	119.8 (3)	C(4)-C(3)-C(2)	119.8 (3)
Fe(1)-C(11)-O(11)	178.1 (3)	Fe(2)-C(21)-O(21)	176.0 (3)
Fe(1)-C(12)-O(12)	179.0 (3)	Fe(2)-C(22)-O(22)	179.0 (3)
Fe(1)-C(13)-O(13)	174.0 (3)	Fe(2)-C(23)-O(23)	174.9 (4)
Fe(1)-C(14)-O(14)	175.0 (3)	Fe(2)-C(24)-O(24)	172.9 (3)

[a] Numbers in parentheses are estimated standard deviations in the last figure quoted.

The ^{19}F Fourier transform nmr spectrum of $C_6F_4Fe_2(CO)_8$ consists of two AA′XX′ multiplets at −250.0 and −2637.9 Hz from external C_6F_6. This observation suggests the presence of a 1,2-disubstituted tetrafluorobenzene ring (III) and



III

is consistent with either structures I or II. The low-field multiplet is assigned to F_A,$F_{A'}$ by comparison with ^{19}F nmr chemical shifts in various polyfluoroaromatic metal complexes.[28,29] The AA′ multiplet is shown in Figure 1A, together with the spectrum computed using the derived coupling constants $|J_{AA'}| = 16.85$ or 16.35 Hz, $|J_{XX'}| = 16.35$ or 16.85 Hz, $J_{AX} = \pm 23.65$ Hz, and $J_{AX'} = \mp 0.85$ Hz. The

---

[26] Although this highly reactive product could not be characterized, it is possibly the trimethylsiloxy(pentafluorophenyl)-carbene derivative $(CO)_4FeC[OSi(CH_3)_3]C_6F_5$. A similar chromium compound, $(CO)_5CrC[OSi(CH_3)_3]CH_3$, has been prepared by Fischer.[27]

[27] E. Moser and E. O. Fischer, *J. Organometal. Chem.*, 12, P1 (1968).

[28] M. I. Bruce, *J. Chem. Soc. A*, 1459 (1968).

[29] A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, 9, 2578 (1970).

Table III. Weighted[a] Least-Squares Planes of the Form $Ax + By + Cz + D = 0$[b]

Plane no.	Atoms	*A*	*B*	*C*	*D*
1	Fe(1), Fe(2), F(1), F(2), F(3), F(4), O(11), O(12), O(21), O(22), C(1), C(2), C(3), C(4), C(5), C(6), C(11), C(12), C(21), C(22)	0.8912	0.2653	0.3680	−2.8291
2	F(1), F(2), F(3), F(4), C(1), C(2), C(3), C(4), C(5), C(6)	0.9034	0.2328	0.3601	−2.6744
3	Fe(1), Fe(2), O(13), O(23), C(13), C(23)	−0.4966	0.0502	0.8666	−1.0419
4	Fe(1), Fe(2), O(14), O(24), C(14), C(24)	−0.3586	0.0911	0.9291	−1.4882
5[c]	Fe(1), Fe(2)	0.2089	−0.9623	0.1744	

Atoms and Their Distances from Planes, Å

1	Fe(1)	−0.017	Fe(2)	−0.004	F(1)	−0.080
	F(2)	−0.017	F(3)	0.076	F(4)	0.100
	O(11)	0.117	O(12)	0.068	O(21)	−0.332
	O(22)	0.183	C(1)	−0.053	C(2)	−0.023
	C(3)	0.013	C(4)	0.027	C(5)	−0.017
	C(6)	−0.052	C(11)	0.065	C(12)	0.037
	C(21)	−0.173	C(22)	0.102		
2	F(1)	0.015	F(2)	−0.001	F(3)	0.005
	F(4)	0.018	C(1)	−0.001	C(2)	−0.011
	C(3)	−0.019	C(4)	−0.010	C(5)	−0.014
	C(6)	−0.005				
3	Fe(1)	−0.001	Fe(2)	0.002	O(13)	0.044
	O(23)	−0.025	C(13)	−0.003	C(23)	−0.027
4	Fe(1)	0.000	Fe(2)	0.001	O(14)	0.027
	O(24)	−0.006	C(14)	−0.002	C(24)	−0.030

Dihedral Angles

Planes	Angle, deg	Planes	Angle, deg
2, 5	88.4	2, 4	88.2
2, 3	82.8	3, 4	9.0

[a] Atoms are weighted by the reciprocals of their variances. [b] Coordinates are in an orthogonal system directed along *a*, *b*, and *c**. [c] Fe(1)–Fe(2) vector.

values obtained for $|J_{XX'}|$, J_{AX}, and $J_{AX'}$ are typical when compared with corresponding parameters in ortho-disubstituted organic tetrafluorobenzenes.[28,30,31] The large magnitude of $|J_{AA'}|$ and its similarity to $|J_{XX'}|$ is, however, anomalous and is perhaps peculiar to transition metal containing derivatives.

Solution of the structure has revealed (Figure 2) that $C_6F_4Fe_2(CO)_8$ does indeed form as the *o*-phenylene adduct as proposed[1] by Roe and Massey and not as a benzyne adduct. This study represents the first structural characterization of an *o*-phenylene group bridging two directly bonded metal atoms. Selected interatomic distances and angles are given in Table II. The molecule shows only small, but significant, deviations from C_{2v} symmetry. The C_6F_4 group is twisted by 1.6° with respect to the Fe(1)–Fe(2) vector, and the equatorial carbonyl groups are only slightly displaced from the eclipsed position (Figure 3). This geometry is to be contrasted with that found for an analogous diphenylvinylidene complex[32] in which the equatorial carbonyl groups are staggered by some 33° (*vide infra*). Some pertinent least-squares planes and dihedral angles are given in Table III. It is interesting to note that all carbonyl groups cis to the C_6F_4 group are slightly bent up toward that group: the equatorial carbonyls by about 4.5°, the axial carbonyls by 11.6°. The Fe–Fe distance in this complex, 2.797 (1) Å, is the longest found to date in a ligand-bridged $Fe_2(CO)_8$ complex and one of the longest found in any iron complex. This distance is comparable to 2.780 (5) Å found for the platinum-bridged[33] $(Ph_3PPtCO)Fe_2(CO)_8$ and is substantially longer than 2.635 (3) Å in the diphenylvinylidene-bridged[32] $Ph_2C_2Fe_2(CO)_8$. [The difference in Fe–Fe distances for $Ph_2C_2Fe_2(CO)_8$ and $C_6F_4Fe_2(CO)_8$ probably accounts in part for the observed arrangements (staggered *vs.* eclipsed) of their equatorial carbonyl groups.] A shorter Fe–Fe distance of 2.75 Å is reported[34] for the unbridged[35] $Fe_2(CO)_8{}^{2-}$ anion. The Fe–C distances for the *o*-C_6F_4 group, 2.021 (3) and 2.022 (3) Å, are comparable to other reported Fe–C (sp^2) distances: 1.98 (1) and 1.98 (1) Å in $Ph_2C_2Fe_2(CO)_8$[32] and 1.987 (5)[36] and 2.05 Å[37] in $[C_5H_5Fe(CO)_2C_2H_2]_2$. These distances are shorter than the disputed[38] 2.11 (2) Å found[39] for $C_5H_5Fe(CO)(PPh_3)(C_6H_5)$. All Fe–C (carbonyl) distances are equal to the average distance 1.817 (2) Å to within experimental error. The implication here is that the trans-influencing[40] properties of the *o*-C_6F_4 group and carbonyl group are approximately equal.

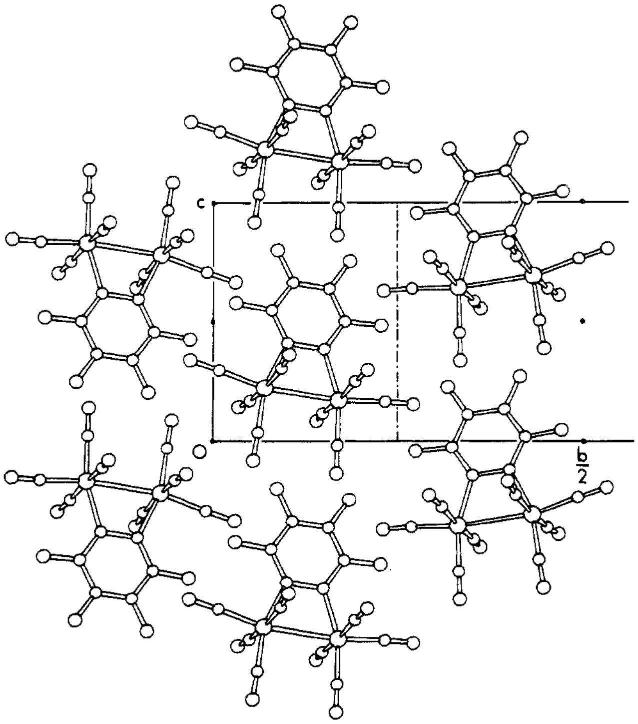


Figure 4. Packing of $C_6F_4Fe_2(CO)_8$ as projected onto the *b*–*c* plane.

---

(30) N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Mol. Phys.*, 8, 133 (1964).

(31) For example, the values of $|J_{XX'}|$, J_{AX}, and $J_{AX'}$ are 19.9, ±20.8, and ∓1.7 Hz in *o*-$C_6F_4Cl_2$. $|J_{AA'}|$ = 7.8 Hz in this compound.[30]

(32) O. S. Mills and A. D. Redhouse, *J. Chem. Soc. A*, 1282 (1968).

(33) R. Mason, J. Zubieta, A. T. T. Hsieh, J. Knight, and M. J. Mays, *J. Chem. Soc., Chem. Commun.*, 200 (1972).

(34) F. S. Stephens and O. S. Mills, private communication to L. F. Dahl, 1970; L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, 92, 7312 (1970).

(35) K. Farmery, M. Kilner, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc. A*, 2339 (1969).

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

(37) R. E. Davis, *Chem. Commun.*, 1218 (1968).

(38) M. R. Churchill, *Perspect. Struct. Chem.*, 3, 91 (1970).

(39) V. A. Semion and Yu. T. Struchkov, *J. Struct. Chem.*, 10, 80 (1969).

(40) R. McWeeny, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, 47, 20 (1969).

The crystalline packing of $C_6F_4Fe_2(CO)_8$, as shown in Figure 4, has no intermolecular contacts significantly below those predicted from sums of van der Waals radii.

Acknowledgment. We thank the National Research Council (Canada) for generous support of this work.

Registry No. $(CH_3)_3SiCl$, 75-77-4; $Li[(CO)_4FeC(O)C_6H_5]$, 41765-66-6; $C_6F_4Fe_2(CO)_8$, 29160-38-1.

Supplementary Material Available. A listing of structure factor amplitudes 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, 20× 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 \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2944.

Contribution from the Department of Chemistry, Brown University, Providence, Rhode Island 02912

Binuclear Nitrosyl Complexes. Synthesis and Structure Determination of Dinitrosylbis(μ-diphenylphosphido)-bis(tertiary phosphine)diruthenium, $[Ru(\mu\text{-}PPh_2)(NO)L]_2$ ($L = PMePh_2, PPh_3$)

JOSEPH REED, ARTHUR J. SCHULTZ, CORTLANDT G. PIERPONT, and RICHARD EISENBERG*

Received April 20, 1973

The binuclear complexes $[Ru(\mu\text{-}PPh_2)(NO)L]_2$ ($L = PMePh_2$, PPh_3) have been synthesized and the structure of the methyldiphenylphosphine complex has been determined by single-crystal X-ray methods using intensity data collected by the θ-2θ scan technique. $[Ru(\mu\text{-}PPh_2)(NO)(PMePh_2)]_2$ crystallizes in space group $P2_1/c$ of the monoclinic system in a cell of dimensions $a = 13.12$ (1), $b = 12.95$ (1), $c = 15.94$ (2) Å, $\beta = 120.2$ (1)°, and $V = 2341$ Å^3. The experimental and calculated densities of 1.46 (2) and 1.47 g/cm^3 agree for two dimer units per unit cell. The structure was solved by standard Patterson and Fourier methods and has been refined by a least-squares procedure to a final R factor of 0.054 for 1659 reflections having $F_o^2 > 3\sigma(F_o^2)$. The dimeric complex is crystallographically required to be centrosymmetric with the ruthenium atoms bridged by diphenylphosphido groups. The coordination geometry about each Ru atom (excluding the Ru-Ru bond) is a distorted tetrahedron. The nitrosyl is terminally coordinated in a linear manner with an Ru-N distance of 1.697 (12) Å and an Ru-N-O bond angle of 174.1 (10)°. The Ru-Ru distance of 2.629 (2) Å is relatively short compared with corresponding values in ruthenium cluster compounds and is consistent with the formulation of the Ru-Ru bond in these systems as a metal-metal double bond. The Ru-P distances in the structure are 2.315 (4) Å for the terminal phosphine ligand and 2.304 (4) Å for the bridging phosphide ligands. The syntheses of the binuclear complexes were devised after the structure determination of the methyldiphenylphosphine system was completed. It involves the *in situ* generation of $LiPPh_2$ as the way for introducing the bridging ligands.

Introduction

Nitric oxide has been postulated to activate metal ions in catalytically active complexes by virtue of its dual coordinating ability.[1] This ability, which has been described as amphoteric behavior,[1,2] manifests itself structurally in the linear and bent modes of nitrosyl coordination corresponding, at least formally, to NO^+ and NO^-, respectively.[2-6] Interconversion between these two bonding modes was proposed in 1969 by Collman, *et al.*,[1] who viewed the nitrosyl ligand acting as an electron pair sink and pump in catalytically active complexes. This interconversion of bonding modes was considered in terms of an intramolecular redox reaction[1,7] during which a stereochemical change occurs at the metal center concomitantly with the bending and straightening of the M-N-O unit. Collman's proposal meant that nitrosyls could achieve coordinative unsaturation in a unique way *via* a bending of the nitrosyl group. In addition, the reverse process could be viewed as providing a driving force for the dissociation of the complexed substrate from the catalyst center at the end of the reaction sequence.[8]

To date, there have been reports of a number of nitrosyl complexes acting as catalysts for diverse reactions. These include $Rh(NO)(PPh_3)_3$ for hydrogenation,[1] $Fe(CO)_2(NO)_2$ for diene dimerization,[9] $MoCl_2(NO)_2(PPh_3)_2$ with aluminum alkyls for olefin metathesis,[10] and $MH(NO)L_3$ (M = Ru, Os; L = tertiary phosphine) for hydrogenation and isomerization.[11] The last series of complexes was synthesized by Wilson and Osborn, who also observed that for certain of the tertiary phosphines, the complexes exhibit fluxional behavior.[11] This stereochemical nonrigidity, when coupled with recent discussions of the bonding in nitrosyl complexes,[4,8,12] appears to lend support to Collman's hypothesis regarding the interconversion of nitrosyl bonding modes in catalytically active systems.

Recently there has been an upsurge of interest in polynuclear complexes as homogeneous catalysts because of their potential utility in multicenter catalyzed reactions and because of the view that such multicenter systems better

---

(1) J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.*, 91, 5659 (1969).

(2) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 9, 1105 (1970).

(3) The recent papers of ref 4-6 contain most references to earlier structural work in the area of nitrosyl complexes.

(4) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 12, 199 (1973).

(5) C. P. Brock and J. A. Ibers, *Inorg. Chem.*, 11, 2812 (1972).

(6) J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, 11, 1420 (1972).

(7) J. P. Collman, P. Farnham, and G. Dolcetti, *J. Amer. Chem. Soc.*, 93, 1788 (1971).

(8) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 11, 1094 (1972).

(9) J. P. Candlin and W. H. Janes, *J. Chem. Soc. C*, 1856 (1968).

(10) E. A. Zuech, W. B. Hughes, D. H. Kubicek, and E. T. Kittleman, *J. Amer. Chem. Soc.*, 92, 528 (1970).

(11) S. T. Wilson and J. A. Osborn, *J. Amer. Chem. Soc.*, 93, 3068 (1971).

(12) C. G. Pierpont and R. Eisenberg, *J. Amer. Chem. Soc.*, 93, 4905 (1971).