A New Derivative of Triiron Dodecacarbonyl with Borderline Carbonyl Bridges. Octacarbonyldi(tetrahydrothiophene)triiron

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Abstract: The new compound $Fe_3(CO)_8(C_4H_8S)_2$ has been prepared and characterized by X-ray crystallography. The red-black crystals belong to the monoclinic system, space group $C2/c$. The unit cell contains four molecules and has the dimensions $a = 15.251$ (3) Å, $b = 8.402$ (2) Å, $c = 17.445$ (4) Å, $\beta = 104.91$ (2)°, and $V = 2160$ (1) Å^3. The structure was solved by direct methods and refined anisotropically using 1024 reflections with $I > 3\sigma(I)$ to $R_1 = 0.045$ and $R_2 = 0.065$. The molecule lies on a crystallographic twofold axis. The triangular Fe_3 cluster has bridging C_4H_8S molecules on two edges and two extremely unsymmetrical (borderline) CO bridges on the other. The chief interest of the molecule lies in the relationship of these borderline bridges to the more nearly symmetrical bridges found in $Fe_3(CO)_{12}$ and $Fe_3(CO)_{11}PPh_3$ and the essentially symmetrical ones found in $Fe_3(CO)_9(PMe_2Ph)_3$. The series of four compounds provides a basis for discussing one of the the two main classes of grossly unsymmetrical bridging carbonyl groups, namely that class consisting of conjugate (oppositely unsymmetrical) pairs.

We have recently demonstrated that the structure of $Fe_3(CO)_{12}$ can be fairly thoroughly refined[1] even though it is disordered.[2] This refinement showed with certainty that one edge of the Fe_3 triangle is covered by two markedly unsymmetrical bridging carbonyl ligands, with the direction of asymmetry in each bridge opposite to that in the other. The virtual symmetry of the molecule is C_2. There have also been reports of two symmetrically substituted $Fe_3(CO)_{12}$ derivatives. In $Fe_3(CO)_{11}PPh_3$ there is a pair of oppositely unsymmetrical bridges similar to those in $Fe_3(CO)_{12}$ itself.[3] In $Fe_3(CO)_9(PMe_2Ph)_3$, with one substituent on each iron atom, the bridges are symmetrical to within the uncertainties.[4]

In an effort to gain more data bearing upon the structural variability of these bridging arrangements, we have determined the structure of $Fe_3(CO)_8(C_4H_8S)_2$, a new compound. The infrared spectrum of this compound has its lowest CO stretching band at 1903 cm^{-1}, which suggested to us that there would either be no bridging CO groups or that they would be of borderline bridging character. In either case, an interesting addition would be made to the range of structural variations known for such species.

Experimental Section

Synthesis and Crystal Preparation. Diiron nonacarbonyl (5.0 g, 0.0136 mol) was dried under vacuum and placed in a round-bottom flask. Tetrahydrothiophene, C_4H_8S (100 ml), which had been dried over molecular sieves, was added under an argon flush. The reaction mixture was stirred at 23° for 18 hr until all of the $Fe_2(CO)_9$ dissolved. The volume was then reduced under vacuum at 25° to leave about 3 ml of a brown oil. This oil was dissolved in dry pentane and the solution was cooled to about 0°. Over a period of 24 hr, large red-black crystals grew from the solution. The yield was 1.7 g, 30% based on $Fe_2(CO)_9$.

The infrared spectrum measured in methylcyclohexane has CO stretching bands at 2032, 1994, 1982, 1962, and 1903 cm^{-1}.

Collection of X-Ray Data. A crystal measuring approximately 0.20 × 0.20 × 0.23 mm was selected for data collection and was mounted in a glass capillary to protect it from slow air decomposition. Preliminary examination on the diffractometer of the red-black crystal showed the crystal to be monoclinic. Cell constants at 22° and the orientation matrix for data collection were determined from least-squares refinement of the setting angles for 15 reflections. These dimensions and other crystal data are given in Table I. Several strong reflections showed peaks with a width at

Table I. Crystal Data for $Fe_3(CO)_8(C_4H_8S)_2$

$a = 15.251$ (3) Å	Space group $C2/c$
$b = 8.402$ (2) Å	$V = 2160$ (1) Å^3
$c = 17.445$ (4) Å	$Z = 4$
$\beta = 104.91$ (2)°	

half-height of 0.15° on ω scans. Data were collected at 22° with Mo Kα radiation on a diffractometer equipped with a graphite-crystal incident-beam monochromator. The θ–2θ scan technique with a variable scan rate from 4.0 to 24.0°/min and an asymmetric scan range from 0.7° before Mo Kα_1 to 0.8° after Mo Kα_2 was used to collect 1887 independent data up to a maximum 2θ value of 45°.

The intensities of three reflections were measured every 100 reflections as a check on crystal and electronic stability. These showed no significant variation relative to the standard deviations of the intensities based on counting statistics alone. A correction for Lorentz and polarization factors was applied to the data. See ref 5 for a listing of computer programs used in data reduction and in solving and refining the structure.

No correction for absorption was made in view of the small variation in calculated transmission factors. No evidence for secondary extinction was observed in the data set. In the structural refinement only the 1024 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used. The parameter p used in the calculation of standard deviations was set equal to 0.07.

Solution and Refinement of the Structure. Normalized structure factors were computed using the program FAME. The positions for the three heavy atoms were found by direct methods using the program MULTAN which combines the cyclic application of the tangent formula with multisolution techniques. The starting phase set chosen automatically by the program obtained phases for 265 reflections with E's greater than 1.50. From the 32 phase sets generated one set showed the best figures of merit and was used to generate an E map. The positions of the two iron atoms and the sulfur atom were the top peaks on the E map and their positions

(1) F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, **96**, 4155 (1974).

(2) C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 1351 (1969).

(3) D. J. Dahm and R. A. Jacobson, *J. Amer. Chem. Soc.*, **90**, 5106 (1968).

(4) G. Raper and W. S. McDonald, *J. Chem. Soc. A*, 3430 (1971).

(5) See F. A. Cotton, B. A. Frenz, and A. J. White, *Inorg. Chem.*, **13**, 1407 (1974), for a list of the computer programs used in the present investigation.

were refined by two cycles of full-matrix least squares to give agreement factors of $R_1 = 0.276$ and $R_2 = 0.388$. Scattering factors were taken from the International Tables.[6] Anomalous dispersion effects were included in the calculated structure factors for iron and sulfur atoms, using f' and f'' values given by Cromer and Liberman.[7]

A difference Fourier map then revealed the positions of all the remaining non-hydrogen atoms. The 15 non-hydrogen atoms were first refined isotropically (starting with isotropic temperature factors of 4.0 Å^2) and then by three cycles of full-matrix least-squares anisotropic refinement. The result was a completely converged refinement with no parameter shift exceeding 0.02 times the standard deviation in the parameter, giving final agreement indices of $R_1 = 0.045$ and $R_2 = 0.065$. The esd in an observation of unit weight was 1.40. The hydrogen atoms on the tetrahydrothiophene ring carbon atoms could not be located due apparently to the large anisotropic movement of these atoms.

No systematic trends were found in the data as a function of $\lambda^{-1} \sin \theta$, $|F_o|$, Miller indices, or reflection number. The atomic coordinates and estimated standard deviations are given in Table II. The anisotropic thermal parameters are given in Table III.

Table II. Atomic Positional Parameters for Non-Hydrogen Atoms in $Fe_3(CO)_8(C_4H_8S)_2$

Atom	x	y	z
Fe(1)	0.5086 (1)	0.1706 (1)	0.1765 (1)
Fe(2)	$^1/_2$	0.4385 (2)	$^1/_4$
S	0.4001 (1)	0.3513 (3)	0.1489 (1)
O(1)	0.4021 (5)	0.6662 (9)	0.3242 (6)
O(2)	0.6585 (4)	−0.0122 (8)	0.2733 (4)
O(3)	0.6309 (5)	0.3215 (10)	0.0934 (4)
O(4)	0.4427 (6)	−0.1003 (10)	0.0704 (5)
C(1)	0.4410 (6)	0.5789 (11)	0.2947 (6)
C(2)	0.5958 (6)	0.0646 (10)	0.2423 (5)
C(3)	0.5810 (6)	0.2656 (12)	0.1251 (6)
C(4)	0.4679 (7)	0.0047 (12)	0.1127 (6)
C(5)	0.2795 (6)	0.3303 (12)	0.1499 (6)
C(6)	0.2304 (7)	0.4495 (17)	0.0922 (9)
C(7)	0.2790 (8)	0.5244 (20)	0.0435 (9)
C(8)	0.3769 (6)	0.4690 (12)	0.0542 (5)

Table III. Anisotropic Thermal Parameters for $Fe_3(CO)_8(C_4H_8S)_2$

Atom	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	42 (1)	106 (2)	27 (1)	10 (1)	13 (1)	−1 (1)
Fe(2)	37 (1)	83 (3)	38 (1)	0	14 (1)	0
S	36 (1)	109 (4)	33 (1)	6 (2)	13 (1)	9 (1)
O(1)	73 (5)	185 (14)	100 (5)	26 (7)	42 (4)	−42 (7)
O(2)	63 (4)	186 (12)	45 (3)	52 (7)	9 (3)	−6 (5)
O(3)	77 (5)	266 (17)	68 (4)	15 (7)	50 (4)	25 (7)
O(4)	110 (6)	206 (15)	57 (4)	6 (8)	−4 (4)	−54 (7)
C(1)	37 (5)	135 (17)	56 (5)	1 (8)	14 (4)	−7 (7)
C(2)	51 (5)	121 (14)	24 (3)	9 (8)	8 (3)	−5 (6)
C(3)	44 (5)	185 (19)	45 (4)	26 (9)	24 (4)	6 (7)
C(4)	58 (6)	143 (17)	36 (4)	18 (8)	5 (4)	−4 (7)
C(5)	27 (4)	208 (19)	47 (4)	9 (7)	16 (4)	25 (8)
C(6)	51 (6)	344 (31)	105 (8)	57 (12)	38 (6)	120 (14)
C(7)	63 (7)	453 (37)	91 (8)	85 (14)	36 (6)	120 (15)
C(8)	53 (5)	196 (19)	35 (4)	19 (9)	10 (4)	40 (7)

^{a} The anisotropic temperature parameters are of the form $10^{-4} \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Root-mean-square amplitudes of thermal vibration are given in Table IV. Structure factors for $Fe_3(CO)_8(C_4H_8S)_2$ are given elsewhere.[8]
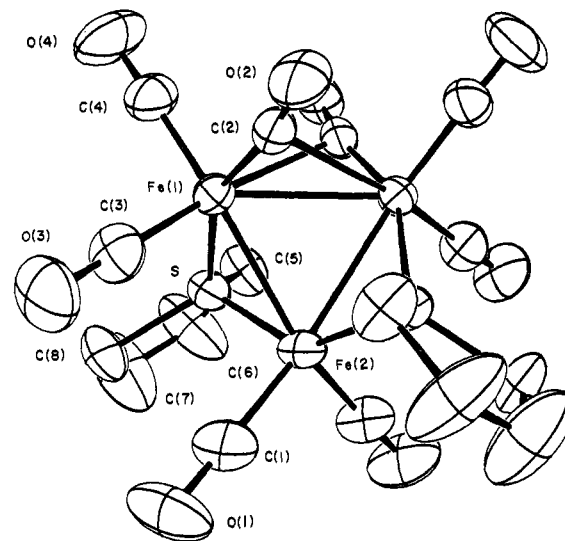
Results

The crystal structure consists of discrete molecules of

(6) D. T. Cromer, "International Tables for X-Ray Crystallography," Vol IV, in preparation.

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

(8) See the paragraph at the end of the paper concerning supplemental material.

Figure 1. An ORTEP drawing of the structure showing the atom numbering scheme. Atoms are represented by their thermal vibration ellipsoids drawn to enclose 50% of the electron density. The C_4H_8S rings (omitting hydrogen atoms) are seen nearly edge-on.

Table IV. Root-Mean-Square Amplitudes (Å) along Three Principal Axes of Atomic Thermal Ellipsoids

Atom	Min	Intermed	Max
Fe(1)	0.176 (2)	0.197 (2)	0.225 (2)
Fe(2)	0.172 (3)	0.190 (3)	0.237 (2)
S	0.187 (3)	0.188 (3)	0.230 (3)
O(1)	0.18 (1)	0.30 (1)	0.39 (1)
O(2)	0.19 (1)	0.25 (1)	0.32 (1)
O(3)	0.19 (1)	0.30 (1)	0.36 (1)
O(4)	0.19 (1)	0.31 (1)	0.40 (1)
C(1)	0.20 (1)	0.22 (1)	0.29 (1)
C(2)	0.18 (1)	0.21 (1)	0.25 (1)
C(3)	0.17 (1)	0.25 (1)	0.28 (1)
C(4)	0.21 (1)	0.22 (1)	0.28 (1)
C(5)	0.16 (1)	0.23 (1)	0.30 (1)
C(6)	0.20 (2)	0.23 (2)	0.48 (2)
C(7)	0.21 (2)	0.26 (2)	0.49 (2)
C(8)	0.17 (1)	0.24 (1)	0.30 (1)

$Fe_3(CO)_8(C_4H_8S)_2$ with no unusual intermolecular contacts. A crystallographic twofold axis passes through the molecule bisecting the Fe(1)–Fe(1)′ bond and passing through the other iron atom, Fe(2). A view of the molecule which gives the atom numbering scheme is presented in Figure 1. Unnumbered atoms are related by the C_2 axis to numbered atoms and where necessary in the subsequent discussion are identified by the appropriate number and a prime.

The interatomic distances and angles are listed in Tables V and VI, respectively.

Table V. Bond Lengths (Å)^a

Fe(1)–Fe(1)′	2.645 (2)	S–C(5)	1.85 (1)
Fe(1)–Fe(2)	2.611 (2)	S–C(8)	1.85 (1)
Fe(1)–S	2.206 (2)	C(1)–O(1)	1.15 (1)
Fe(2)–S	2.142 (2)	C(2)–O(2)	1.16 (1)
Fe(1)–C(2)	1.76 (1)	C(3)–O(3)	1.15 (1)
Fe(1)–C(2)′	2.55 (1)	C(4)–O(4)	1.15 (1)
Fe(1)–C(3)	1.78 (1)	C(5)–C(6)	1.48 (1)
Fe(1)–C(4)	1.79 (1)	C(6)–C(7)	1.41 (2)
Fe(2)–C(1)	1.78 (1)	C(7)–C(8)	1.52 (1)

^{a} The prime designates an unnumbered atom related by the twofold axis to a numbered one in Figure 1.

Table VI. Selected Bond Angles (deg)[a]

Fe(1)–Fe(1)′–Fe(2)	59.6 (1)	C(2)′–Fe(1)–C(4)	84.7 (4)
Fe(1)–Fe(2)–Fe(1)′	60.9 (1)	C(3)–Fe(1)–C(4)	101.3 (5)
Fe(1)′–Fe(1)–S	87.4 (1)	Fe(1)–Fe(2)–C(1)	105.8 (3)
Fe(1)–Fe(2)–S	89.7 (1)	Fe(1)–Fe(2)–C(1)′	151.8 (3)
Fe(1)–S–Fe(2)	73.8 (1)	Fe(1)–S–C(5)	128.6 (3)
Fe(2)–Fe(1)–S	52.0 (1)	Fe(1)–S–C(8)	121.6 (3)
Fe(2)–Fe(1)–C(2)	104.0 (3)	Fe(2)–S–C(5)	121.5 (3)
Fe(2)–Fe(1)–C(2)′	84.9 (2)	Fe(2)–S–C(8)	118.2 (3)
Fe(2)–Fe(1)–C(3)	88.7 (3)	Fe(1)–C(2)–O(2)	167.4 (7)
Fe(2)–Fe(1)–C(4)	157.3 (3)	Fe(1)–C′(2)–O′(2)	119.4 (6)
S–Fe(1)–C(2)′	152.9 (3)	Fe(1)–C(3)–O(3)	176.7 (9)
S–Fe(1)–C(2)	79.7 (2)	Fe(1)–C(4)–O(4)	178.3 (10)
S–Fe(1)–C(13)	96.3 (3)	Fe(2)–C(1)–O(1)	178.3 (9)
S–Fe(1)–C(4)	106.2 (3)	C(5)–S–C(8)	95.2 (4)
C(2)–Fe(1)–C(3)	95.4 (4)	S–C(5)–C(6)	105.0 (7)
C(2)′–Fe(1)–C(3)	173.6 (4)	C(5)–C(6)–C(7)	117.3 (9)
C(2)–Fe(1)–C(4)	95.4 (4)	C(6)–C(7)–C(8)	114.9 (10)
		C(7)–C(8)–S	104.7 (7)

[a] The prime designates an unnumbered atom related by the two-fold axis to a numbered one in Figure 1.

The structure can be looked upon as derived from those of $Fe_3(CO)_{12}$ and $Os_3(CO)_{12}$[9] by having two terminal carbonyl groups, each on a different metal atom, replaced by one tetrahydrothiophene molecule which thus serves as a neutral, four-electron bridging ligand. Bridging ligands of this sort would appear to be quite rare, and for C_4H_8S in particular there is evidently only one other example, namely a bridging C_4H_8S group (as well as two which serve as conventional terminal two-electron ligands) in $Nb_2Br_6(C_4H_8S)_3$.[10] The C_4H_8S bridges are somewhat unsymmetrical.

The Fe–Fe distances in this case differ from those in $Fe_3(CO)_{12}$ and its phosphine derivatives. The Fe–Fe bonds which are bridged by the sulfur atoms are about 0.07 Å shorter than the corresponding nonbridged distances in the other compounds. This seems a reasonable consequence of the bridging sulfur atoms. On the other hand the Fe–Fe distance across the other edge of the triangle is roughly 0.09 Å longer here, where the CO bridges are only borderline, than in the other three molecules where CO bridging is much more developed or even, in $Fe_3(CO)_9(PMe_2Ph)_3$, fully developed.

Discussion

The frequent occurrence of highly unsymmetrical bridging carbonyl groups has become clearly recognized in recent years.[11–16] We have been attempting to understand the reasons for their occurrence. In order to do this, we first divide all molecules in which they occur into two broad classes: (I) those in which they occur in compensatory or conjugate pairs, that is, with the direction of asymmetry of one member of the pair opposite to that of the other (ideally, such conjugate pairs are related by a twofold rotation axis)[17] and (II)

those which occur in noncompensatory fashion, there being in some cases[12] only one between a given pair of metal atoms or in other cases[15] two, such that both long bonds are to one metal atom and both short ones to the other.

Those of type II appear to arise when there is a need to equalize what would otherwise be an unequal charge distribution on two adjacent metal atoms. They are fully discussed elsewhere.[16,18] Here we are concerned with class I where the two (or three[17]) metal atoms are equivalent, electronically and structurally. The structure reported here, together with those of $Fe_3(CO)_{12}$,[1,2] $Fe_3(CO)_9(PMe_2Ph)_3$,[4] and the more symmetrical isomer of $Fe_3(CO)_{11}PPh_3$[3] provide the basis for a discussion of class I types of highly unsymmetrical bridges.

Table VII shows the dimensions of the $Fe_2(\mu\text{-}CO)_2$

Table VII. Comparison of the Bridging CO Systems in $Fe_3(CO)_{12}$ and Three Derivatives

Compound	Actual distances	Idealized to C_2 symmetry
$Fe_3(CO)_9(PMe_2Ph)_3$		
$Fe_3(CO)_{11}P(C_6H_5)_3$[a]		
$Fe_3(CO)_{12}$		
$Fe_3(CO)_8(SC_4H_8)_2$		

[a] Isomer with substituent on iron atom not involved in bridging.

portions of each of the four similar molecules. In the middle column the actual, individual bond lengths are

(9) E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962).

(10) E. T. Maas, Jr., and R. E. McCarley, *Inorg. Chem.*, **12**, 1096 (1973), and personal communications from R. E. McCarley.

(11) R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, **88**, 4847 (1966).

(12) H. B. Chin and R. Bau, *J. Amer. Chem. Soc.*, **95**, 5069 (1973).

(13) M. R. Churchill and M. V. Veidis, *J. Chem. Soc. A*, 2170 (1971).

(14) D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.*, **11**, 838 (1972).

(15) F. A. Cotton, L. Kruczynski, and B. A. Frenz, *J. Amer. Chem. Soc.*, **95**, 951 (1973).

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

(17) Actually, class I can be generalized to include all cases in which the set of metal atoms (which may consist of three or possibly even more) are symmetry equivalent and each one is involved in equal numbers of short and long bonds to bridging CO groups. The general characteristic of class I is that the charge distribution is uniform over all the metal atoms concerned regardless of the degree of asymmetry of the bridges, including all degrees from perfect mirror symmetry at one extreme to essentially complete opening (to give linear, terminal CO ligands) at the other. This implies that, ideally, all bridges in the set have the same degree of asymmetry, whatever degree that may be. An example of the more general situation is provided by the basal triangle of the $Fe_4(CO)_{13}^{2-}$ ion[11] which has idealized C_3 symmetry. The three short distances (1.80, 1.81, and 1.85 all ±0.04 Å), the three long distances (2.24, 2.28, and 2.33 all ±0.04 Å), and the three Fe–C–O angles (151, 155, and 158° all ±3°) form equivalent sets within the errors.

(18) F. A. Cotton, *Progr. Inorg. Chem.*, **18**, 1 (1974).

listed while in the right-hand column are shown averaged distances, where the averaging was done to correspond with C_2 symmetry for each system. Only for $Fe_3(CO)_8(C_4H_8S)_2$ does crystallographic C_2 symmetry actually prevail, but apparent differences from it are all less than two estimated standard deviations. In the case of $Fe_3(CO)_9(PMe_2Ph)_3$, the symmetry does not deviate in a statistically significant way from C_{2v}; that is, the bridging system effectively consists of two equivalent symmetrical bridges.

Over the four compounds described in Table VII, we have degrees of asymmetry in the bridging system which range from that in $Fe_3(CO)_8(C_4H_8S)_2$, where bridging CO groups could be described as only slightly disturbed terminal CO groups ($\angle$ Fe-C-O = 167°), to the situation in $Fe_3(CO)_9(PMe_2Ph)_3$, where essentially symmetrical bridges exist. $Fe_3(CO)_{12}$ and $Fe_3(CO)_{11}$-PPh_3 are intermediate.

We believe that unsymmetrical bridges of class I represent merely intermediate stages in the entire range between the completely nonbridged and the symmetrically bridged extremes, under conditions where the potential energy of the system varies little from one extreme to the other. Thus, these class I systems represent "stopped action" views of the intermediate stages[19] of concerted opening and closing of pairs of CO bridges, a process which plays an essential role in the CO scrambling and isomerization reactions of systems such as $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ and their derivatives.[20-23] In an analogous way the structure observed in the basal plane of the $Fe_4(CO)_{13}^-$ ion[11,17] must closely model an intermediate stage in the interconversion of the C_{3v} and T_d tautomers of Rh_4-$(CO)_{12}$.[24-26]

It is noteworthy (see Table VII) that there is a direct correlation between the length of the Fe-Fe bond and the degree of symmetry of the bridges; the shortest Fe-Fe distance accompanies the most symmetrical bridges and the longest Fe-Fe distance is found in the case where the bridges are borderline. Whether there is a cause and effect relationship or whether both properties are simply effects of some other cause is difficult to deduce at present, but the correlation, whatever its causal basis, may be useful.

A further correlation of interest has to do with the infrared absorption frequencies of unsymmetrically bridging CO groups. We have previously noted among certain class II molecules that there were CO bands in the 1800–1900-cm^{-1} range,[27] i.e., higher than usual for symmetrical bridges in neutral molecules and lower than usual for terminal groups in neutral molecules.[28] It thus seemed that the appearance of bands in this intermediate region could be an indication though not, of course, a proof of the presence of unsymmetrical bridges. It might further be supposed that the frequencies of the bands due to unsymmetrical bridges might increase with increasing asymmetry. The present series of compounds offers an excellent opportunity to test that supposition.

For $Fe_3(CO)_9(PMe_2Ph)_3$[29] the only bands below 1947 cm^{-1} are two at 1745 and 1792 cm^{-1}; i.e., in the region for symmetrical bridges; this is in accord with the structure. For $Fe_3(CO)_8(C_4H_8S)_2$, where the degree of asymmetry is very great and the bridges border on being terminal CO groups, the CO stretching band of lowest frequency is at 1903 cm^{-1}. For the intermediate case, $Fe_3(CO)_{12}$, the solid compound is reported[30] to have bands between 1830 and 1875 cm^{-1}. Thus, at least for these compounds, the correlation between frequency and degree of asymmetry seems satisfactory.

Finally, we observe that the structure of $Fe_3(CO)_8$-$(C_4H_8S)_2$ and the relationships discussed here in detail are all in harmony with our earlier[1] proposals that in $Fe_3(CO)_{12}$ itself (1) the energy of the molecule varies little on passing from a symmetrically bridged structure (C_{2v}) via unsymmetrically bridged intermediates (C_2), such as that immobilized in the crystal, to a completely unbridged one (D_{3h}) like that in $Os_3(CO)_{12}$, (2) such a rearrangement process, proceeding reversibly on each of the three edges, can account for complete scrambling of the CO ligands (which ^{13}C nmr shows to be the case), and (3) that the activation energy for this process is probably very low, rendering it unlikely that a slow exchange limit nmr spectrum can be reached within the limits of experimental constraints.

(19) It was earlier suggested[15] that the unsymmetrical bridges in $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$ might be considered as models of the transition state for carbonyl scrambling processes. While it is true that the geometry of each individual semibridging CO group in that structure must resemble the structure of any single CO group which is in course of changing from a terminal to a bridging position (or vice versa), we now emphasize that it is class I systems which truly portray the entire pattern which should exist in a system, such as $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$, at an intermediate stage of concerted, pairwise bridge-terminal interchange.[20-23]

(20) R. D. Adams and F. A. Cotton, J. Amer. Chem. Soc., 95, 6589 (1973).

(21) R. D. Adams, M. Brice, and F. A. Cotton, J. Amer. Chem. Soc., 95, 6594 (1973).

(22) F. A. Cotton, Bull. Chim. Soc. Fr., 2588 (1973).

(23) F. A. Cotton, L. Kruczynski, and A. J. White, Inorg. Chem., 13, 1402 (1974).

(24) F. A. Cotton, Inorg. Chem., 5, 1083 (1966).

(25) F. A. Cotton, L. Kruczynski, B. L. Shapiro, and L. F. Johnson, J. Amer. Chem. Soc., 94, 6191 (1972).

(26) J. Evans, B. F. G. Johnson, J. Lewis, J. R. Norton, and F. A. Cotton, J. Chem. Soc., Chem. Commun., 807 (1973).

(27) For example in $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$, which has three terminal CO groups and two semibridging CO groups[15] and molecular symmetry such that there should be five infrared bands, there are three bands above 1900 cm^{-1} which can be assigned to the terminal CO groups and bands at 1833 and 1871 cm^{-1} which must be due to the semibridging CO groups. Similar observations have been made in other cases and will be reported and commented upon elsewhere.

(28) Cf. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley-Interscience, New York, N. Y., 1972, pp 693–695.

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