Reactions of Metal Carbonyl Derivatives. Part XV.[1] Oxidation Studies of Some η-Cyclopentadienyl Bridging Sulphido- and Phosphino-derivatives of Iron [2]

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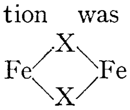
The bridged sulphido- and phosphino-complexes $[Fe(cp)(CO)SR]_2$ (cp = η-C_5H_5; R = Me, Et, Pr^i, Bu^n, Bu^t Bz, or Ph) and $[Fe(cp)(CO)PPh_2]_2$ are readily oxidised by oxygen in aqueous or non-aqueous acidified media, as well as by reagents such as iodine and silver salts, to the paramagnetic species $[Fe(cp)(CO)SR]_2^+$ and $[Fe(cp)(CO)PPh_2]_2^+$ respectively. This oxidation is reversible with reduction being effected by water under basic conditions and by reducing agents such as sodium amalgam, sodium tetrahydroborate, or iodide ions. Further oxidation of the complex $[Fe(cp)(CO)SR]_2^+$ to the dicationic species $[Fe(cp)(CO)SR]_2^{2+}$ can be achieved by treatment with an excess of bromine, silver ions, or nitrosyl hexafluorophosphate. Reduction of this dication is readily effected even by weak reducing agents such as the tetraphenylborate anion. These redox reactions are stereoselective. E.s.r. spectra of the monocationic derivative and Mössbauer spectra of the neutral, monocationic, and dicationic derivatives are reported and discussed in terms of a bonding scheme proposed by Mason and Mingos for bridged binuclear systems of this type. Oxidation affects each iron atom to the same extent and results in a decrease in chemical-isomer shift, consistent with removal of an electron from an MO having predominantly metal *d*-character.

A PREVIOUS study[3] revealed that the complex $[\{Fe(cp)(CO)\}_2Ph_2PR'PPh_2]$ (cp = η-C_5H_5) is rapidly oxidised by various agents such as iodine and silver salts to the paramagnetic species $[\{Fe(cp)(CO)\}_2Ph_2PR'PPh_2]^+$ (R′ = CH_2, C_2H_2, C_2H_4, C_3H_6, or NEt). The stability of the salts of these cations to decomposition was associated with the presence of an  (X = CO) ring, although differences in this, as well as in the stability to further oxidation with iodine, were observed for the different ditertiary phosphines. Room-temperature magnetic susceptibilities of these paramagnetic derivatives correspond to one unpaired electron per two iron atoms but are significantly different from the spin-only value, indicating some orbital contribution. Complexes of the type $[Fe(cp)(CO)_2]_2$ and $[\{Fe(cp)(CO)\}_2Ph_2PR'PPh_2]$ have a formal metal–metal bond order of one.[4] To assist in establishing the nature of the electron involved in the above redox process, the study has now been extended to include complexes which have a similar structural framework but zero metal–metal bond order. Complexes of the type $[Fe(cp)(CO)SR]_2$ were chosen in particular because the phenyl derivative is known to have a near-planar Fe_2X_2 (X = SPh) group and an Fe–Fe distance of *ca.* 340 pm.[5]

Considerable attention has been focussed of late on bridging sulphido-derivatives of iron in view of the possible relevance of the chemistry of these species to that of the non-haeme iron protein systems termed ferredoxins and studies involving the complex $[Fe(cp)(CO)SMe]_2$ have recently been communicated along these lines. Hill and his co-workers have reported that the reaction of this complex with $AgSbF_6$ gives $[Fe(cp)(CO)SMe]_2SbF_6$ and have discussed the e.s.r. and Mössbauer spectra of the oxidised product in terms of those of reduced ferredoxins.[6] Connelly and Dahl have determined the structure of the complex $[FeCp(CO)SMe]_2BF_4$ by *X*-ray crystallography and have shown that oxidation of the parent complex is accompanied by a decrease in the Fe–Fe distance.[7] The metal–metal distance of 292·5(4) pm was interpreted in terms of a one-electron metal–metal bond. The first report of the oxidation of the complex $[Fe(cp)(CO)SMe]_2$ to the corresponding monocationic derivative was however by Dessy *et al.* who showed that it could readily be achieved electrochemically.[8] King and Bisnette subsequently isolated the salt $[Fe(cp)(CO)SMe]_2SbF_6$, employing $AgSbF_6$ as oxidant.[9]

We now report a detailed investigation of the chemical oxidation of complexes of the type $[Fe(cp)(CO)SR]_2$ to $[Fe(cp)(CO)SR]_2^{2+}$ as well as $[Fe(cp)(CO)SR]_2^+$.‡

RESULTS AND DISCUSSION

Treatment of the complexes $[Fe(cp)(CO)SR]_2$ (R = Me, Et, Pr^i, Bu^n, Bu^t, Bz, or Ph) with iodine or silver salts led to the ready formation of the cationic species

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‡ Electrochemical oxidation of the complex $[Fe(cp)(CO)SR]_2$ has recently been investigated elsewhere[10] and thus will not be discussed in any detail in this publication.

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[2] Preliminary communication, J. A. de Beer, R. J. Haines, and R. Greatrex, *J.C.S. Chem. Comm.*, 1972, 1094.

[3] R. J. Haines and A. L. du Preez, *Inorg. Chem.*, 1972, **11**, 330.

[4] O. S. Mills, *Acta Cryst.*, 1958, **11**, 620; R. F. Bryan and P. T. Greene, *J. Chem. Soc.* (*A*), 1970, 3064; R. F. Bryan, P. T. Greene, M. J. Newlands, and D. S. Field, *ibid.*, p. 3068.

[5] G. Ferguson, C. Hannaway, and K. M. S. Islam, *Chem. Comm.*, 1968, 1165.

[6] M. Clare, H. A. O. Hill, C. E. Johnson, and R. Richards, *Chem. Comm.*, 1970, 1376.

[7] N. G. Connelly and L. F. Dahl, *J. Amer. Chem. Soc.*, 1970, **92**, 7472.

[8] R. E. Dessy, F. E. Stary, R. B. King, and M. Waldrop, *J. Amer. Chem. Soc.*, 1966, **88**, 471; R. E. Dessy, R. Kornmann, C. Smith, and R. G. Hayter, *ibid.*, 1968, **90**, 2001.

[9] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1967, **6**, 469.

[10] J. A. McCleverty, personal communication.

$[\mathrm{Fe(cp)(CO)SR}]_2^+$, which could be isolated as the hexafluorophosphate, hexafluoroantimonate, tetrafluoroborate, or tetraphenylborate salts. The oxidation was also effected by oxygen in acidic media and, in particular, passage of air through a suspension of the complex $[\mathrm{Fe(cp)(CO)SMe}]_2$ in dilute hydrochloric or acetic acid in the presence of an excess of $\mathrm{NaBF_4}$ gave the water-soluble derivative $[\mathrm{Fe(cp)(CO)SMe}]_2\mathrm{BF_4}$ according to equation (1). The rate of formation of the

$$4[\mathrm{Fe(cp)(CO)SMe}]_2 + \mathrm{O}_2 + 4\mathrm{H}^+ \rightleftharpoons 4[\mathrm{Fe(cp)(CO)SMe}]_2^+ + 2\mathrm{H_2O} \qquad (1)$$

ionic species was increased by increasing the acidity of the solution, as expected on the basis of the above equation. Significantly the neutral complex was regenerated on treatment of the oxidised product with base, with for instance addition of hydroxide ions to an aqueous solution of the complex $[\mathrm{Fe(cp)(CO)SMe}]_2\mathrm{BF_4}$ leading to separation of $[\mathrm{Fe(cp(CO)SMe}]_2$ from solution. Other bases which were effective in both aqueous and non-aqueous, but not rigorously anhydrous, media include hydrazine, piperidine, and dialkyl- and trialkylamines. Water is essential for the reduction; diethylamine was observed not to effect the reduction under anhydrous conditions, whereas it did so rapidly in the presence of water. It is thus apparent that the base functions as a proton acceptor and not as a reducing agent and that equation (1) is indeed reversible. Addition of a large excess of base in the above reduction resulted in slow precipitation of a yellow carbonyl-free material however. Reduction of the monocationic derivative to the neutral complex was also effected by reducing agents such as sodium amalgam, sodium tetrahydroborate, or iodide ions, although a large excess of the latter was required.

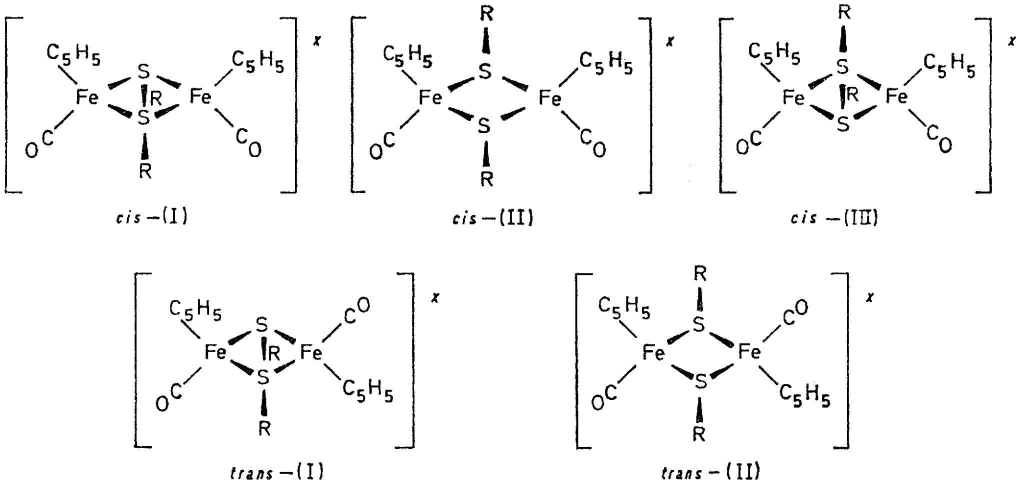
Cyclic voltammograms of complexes of the type $[\mathrm{Fe(cp)(CO)SR}]_2$ exhibited, as well as the wave corresponding to equation (2), a second wave considerably

$$[\mathrm{Fe(cp)(CO)SR}]_2 - e^- \rightleftharpoons [\mathrm{Fe(cp)(CO)SR}]_2^+ \qquad (2)$$

more anodic in potential which we assign to equilibrium (3). The dicationic species was in fact readily obtained

$$[\mathrm{Fe(cp)(CO)SR}]_2^+ - e^- \rightleftharpoons [\mathrm{Fe(cp)(CO)SR}]_2^{2+} \qquad (3)$$

chemically by treatment of the complex $[\mathrm{Fe(cp)(CO)SR}]_2$ (R = Me, Pr^i, Bz, or Ph) with an excess of bromine, silver salts (*e.g.* $\mathrm{AgSbF_6}$), or nitrosyl hexafluorophosphate, as well as electrochemically by use of controlled-potential electrolysis.* Significantly, the complex $[\mathrm{Fe(cp)(CO)SMe}]_2(\mathrm{BF_4})_2$ was also produced by passage of air through an aqueous solution of $[\mathrm{Fe(cp)(CO)SMe}]_2\mathrm{BF_4}$ and an excess of $\mathrm{NaBF_4}$, provided the pH was adjusted to less than 2. At higher pH values water reduced the dication to the monocationic derivative. Weak reducing agents such as the tetraphenylborate anion are also capable of effecting this reduction.



cis-(I) *cis*-(II) *cis*-(III)

trans-(I) *trans*-(II)

Possible structures for the neutral, monocationic, and dicationic species $[\mathrm{Fe(cp)(CO)SR}]_2^x$ (cp = η-$\mathrm{C_5H_5}$; x = 0, 1+, or 2+). *cis* and *trans* refer to the disposition of the cp groups with respect to each other

It has previously been established that complexes of the type $[\mathrm{Fe(cp)(CO)SR}]_2$ can readily be separated into two isomeric forms which differ in stability and that the 'stable' isomer has a higher C–O stretching frequency than the 'unstable' isomer.[11] Furthermore a single-crystal structure determination[5] has revealed that the cp groups in the 'stable' isomer of $[\mathrm{Fe(cp)(CO)SPh}]_2$ are mutually *cis* with respect to the $\mathrm{Fe_2S_2}$ ring [structures *cis*-(I), *cis*(II), or *cis*-(III) in the Figure]. It is therefore inferred that for all complexes of the type $[\mathrm{Fe(cp)(CO)SR}]_2$ the 'stable' isomer contains cp groups in a *cis*-configuration, whereas in the 'unstable' isomer they are *trans*. It is also relevant that the bridged phosphino-derivative $[\mathrm{Fe(cp)(CO)PMe_2}]_2$ can be isolated in two isomeric forms and that the n.m.r. spectra of the two have been explained in terms of one con-

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* A species, presumed to be either the dication $[\mathrm{Fe(cp)(CO)SMe}]_2^{2+}$ or the monocation $[\mathrm{Fe(cp)(CO)SMe}]^+$, has previously been generated electrochemically but was not isolated.[8]

[11] M. Ahmad, R. Bruce, and G. R. Knox, *J. Organometallic Chem.*, 1966, **6**, 1.

taining *cis*-cp groups and the other containing these groups in *trans*-positions.[12] In the actual conformer of $[Fe(cp)(CO)SPh]_2$ studied by *X*-ray diffraction[5] the phenyl groups were found to be *syn* with respect to each other and *cis* to the carbonyl groups [*cis*-(I)]. We have now found that the material isolated chromatographically as the *cis*-isomer of $[Fe(cp)(CO)SPh]_2$ is in fact a mixture of two conformers [conformer (A) ν(C–O) 1 983, 1 973sh; conformer (B) ν(C–O) 1 973 cm^{-1}, in cyclohexane]. Their structures could not be uniquely assigned to one of the three possible *cis*-conformers of $[Fe(cp)(CO)SPh]_2$ however.

TABLE 1

Colours and analytical and conductivity data

Complex [a]	Colour	Found (%) C	H	S	Others	Calc. (%) C	H	S	Others	Molar conductivity [b]
$[Fe(cp)(CO)SMe]_2BF_4$	Green	35·4	3·1	13·3	16·0(F)	35·1	3·4	13·4	15·9(F)	138
$[Fe(cp)(CO)SMe]_2PF_6$	Green	31·5	2·9	12·1	6·1(P)	31·3	3·0	11·9	5·8(P)	125
$[Fe(cp)(CO)SMe]_2SbF_6$	Green	26·8	2·8	10·2		26·8	2·6	10·2		140
$[Fe(cp)(CO)SMe]_2BPh_4$	Green	63·9	5·0	9·1		64·2	5·1	9·0		96
$[Fe(cp)(CO)SEt]_2SbF_6$	Green	29·2	3·0	9·5		29·3	3·1	9·8		124
$[Fe(cp)(CO)SEt]_2BPh_4$	Green	65·3	5·4	9·0		65·0	5·5	8·7		90
$[Fe(cp)(CO)SPr^i]_2BPh_4$	Green	66·0	5·9	8·4		65·7	5·8	8·4		90
$[Fe(cp)(CO)SBu^t]_2BF_4$	Green	43·0	4·7	11·2		42·7	5·0	11·4		136
$[Fe(cp)(CO)SBu^t]_2SbF_6$	Green	33·9	4·1	9·2		33·7	4·0	9·0		134
$[Fe(cp)(CO)SBu^t]_2BPh_4$	Green	66·0	6·0	7·7		66·4	6·1	8·1		92
$[Fe(cp)(CO)SBz]_2BF_4$	Green	49·5	4·1	10·2		49·5	3·8	10·2		132
$[Fe(cp)(CO)SBz]_2BPh_4$	Green	69·5	4·8	7·3		69·6	5·1	7·4		84
$[Fe(cp)(CO)SPh]_2BPh_4$	Green	68·5	4·8	7·7		68·1	5·0	7·9		86
$[Fe(cp)(CO)PPh_2]_2BPh_4$	Blue	73·0	5·1		6·1(P)	73·0	5·1		6·3(P)	75
$[Fe(cp(CO)SMe]_2(PF_6)_2$	Yellow	24·9	2·4	9·2	8·9(P)	24·7	2·4	9·4	9·1(P)	191
$[Fe(cp)(CO)SPr^i]_2(PF_6)_2$	Yellow	29·5	3·0	8·9	8·4(P)	29·3	3·3	8·7	8·4(P)	168
$[Fe(cp)(CO)SBu^n]_2(PF_6)_2$	Yellow	31·5	3·6	8·3	8·1(P)	31·4	3·7	8·4	8·1(P)	193
$[Fe(cp)(CO)SBz]_2(PF_6)_2$	Yellow	37·6	3·0	7·9	7·4(P)	37·4	2·9	7·7	7·4(P)	187
$[Fe(cp)(CO)SPh]_2(PF_6)_2$	Yellow	35·8	3·0	7·8	7·5(P)	35·8	2·5	8·0	7·7(P)	191

[a] Bz = $CH_2C_6H_5$ and cp = η-C_5H_5. [b] Λ_M/Ω^{-1} cm^2 mol^{-1}, measured in acetone, 1×10^{-4}—1×10^{-3}M.

TABLE 2

I.r. spectroscopic data

Complex [a]	C–O Stretching wavenumbers [b]
cis-$[Fe(cp)(CO)SMe]_2PF_6$	2 012s, 1 989m [c]
trans-$[Fe(cp)(CO)SMe]_2PF_6$	1 989b [c]
cis-$[Fe(cp)(CO)SEt]_2SbF_6$	2 012s, 1 990m [c]
cis-$[Fe(cp)(CO)SPr^i]_2BPh_4$	2 007s, 1 984m [c]
cis-$[Fe(cp)(CO)SBu^n]_2PF_6$	2 009s, 1 985m [c]
trans-$[Fe(cp)(CO)SBu^n]_2PF_6$	1 996sh, 1 985s [c]
cis-$[Fe(cp)(CO)SBu^t]_2SbF_6$	2 000s, 1 982m [c]
cis-$[Fe(cp)(CO)SBz]_2BPh_4$	2 009s, 1 982m [c]
cis-$[Fe(cp)(CO)SPh]_2PF_6$	2 025s, 1 994m [d]
trans-$[Fe(cp)(CO)SPh]_2ClO_4$	1 983b [c]
cis-$[Fe(cp)(CO)PPh_2]_2BPh_4$	2 010s, 1 975m [c]
cis-$[Fe(cp)(CO)SMe]_2(PF_6)_2$ [e]	2 070 [d]
trans-$[Fe(cp)(CO)SMe]_2(PF_6)_2$	2 049b [f]
cis-$[Fe(cp)(CO)SPr^i]_2(PF_6)_2$	2 066 [d]
cis-$[Fe(cp)(CO)SBu^n]_2(PF_6)_2$ [g]	2 070 [d]
trans-$[Fe(cp)(CO)SBu^n]_2(PF_6)_2$	2 055 [d]
cis-$[Fe(cp)(CO)SBz]_2(PF_6)_2$	2 069 [d]
cis-$[Fe(cp)(CO)SPh]_2(PF_6)_2$	2 079, 2 062sh [d]
trans-$[Fe(cp)(CO)SPh]_2(PF_6)_2$	2 052b [d]

[a] Bz = $CH_2C_6H_5$ and cp = η-C_5H_5. [b] In cm^{-1}: s = strong; ms = medium strong; m = medium; b = broad; sh = shoulder. [c] Measured in CH_2Cl_2. [d] Measured in acetone. [e] N.m.r. data:[h] $\tau(C_5H_5)$ 3·66(b); $\tau(CH_3)$ 7·00(s). [f] Measured on a Nujol mull. [g] N.m.r. data:[h] $\tau(C_5H_5)$ 3·73(b); $\tau(CH_3)$ 8·98(t, J_{HH} 7·5 Hz). [h] Measured in CD_3COCD_3 at 38 °C (Me_4Si reference): s = singlet; t = triplet; b = broad.

In this study we have isolated both the *cis*- and *trans*-isomers of $[Fe(cp)(CO)SR]_2$ (R = Me, Bu^n, or Ph) and have investigated their redox properties both chemically and electrochemically. The C–O stretching frequencies for the various products are presented in Table 2. The solid-state i.r. spectrum in the C–O stretching region of the monocationic derivative obtained by oxidation of *cis*-$[Fe(cp)(CO)SMe]_2$ corresponds with that reported by Dahl and Connelly for the species which they analysed by *X*-ray crystallography and showed to contain the cp groups in *cis*-positions.[7] Further, in any redox cycle the neutral parent species was found to be regenerated in the isomeric form in which it existed prior to oxidation. Oxidation or reduction of the complexes $[Fe(cp)(CO)SR]_2^x$ ($x = 0$, 1+, or 2+) is thus stereoselective.

Half-wave potentials for one-electron oxidation of the complex $[Fe(cp)(CO)SR]_2$ to $[Fe(cp)(CO)SR]_2^+$ in 1,2-dimethoxyethane are reported in Table 3. The potentials for the process (4) have not been included because the peaks corresponding to this oxidation were found to be rather broad due to coating of the electrode.

TABLE 3

Half-wave potentials for the oxidation step $[Fe(cp)(CO)SR]_2 \longrightarrow [Fe(cp)(CO)SR]_2^+$

Compound [a]	$E_{\frac{1}{2}}$ [b]
cis-$[Fe(cp)(CO)SMe]_2$	−0·40
trans-$[Fe(cp)(CO)SMe]_2$	−0·35
cis-$[Fe(cp)(CO)SEt]_2$	−0·42
cis-$[Fe(cp)(CO)SPr^i]_2$	−0·33
cis-$[Fe(cp)(CO)SBu^n]_2$	−0·44
trans-$[Fe(cp)(CO)SBu^n]_2$	−0·34
cis-$[Fe(cp)(CO)SBu^t]_2$	−0·24
cis-$[Fe(cp)(CO)SBz]_2$	−0·31
cis-$[Fe(cp)(CO)SPh]_2$	−0·25
trans-$[Fe(cp)(CO)SPh]_2$	−0·27

[a] Bz = $CH_2C_6H_5$ and cp = η-C_5H_5. [b] In volts against 10^{-3}M-$AgClO_4$–Ag electrodes using a carbon working electrode. [Complex] = 2×10^{-3}M in 1,2-dimethoxyethane; base electrolyte $Bu^n_4NClO_4$ (0·1M).

$$[Fe(cp)(CO)SR]_2^+ \longrightarrow [Fe(cp)(CO)SR]_2^{2+} \qquad (4)$$

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[12] R. G. Hayter, *J. Amer. Chem. Soc.*, 1963, **85**, 3120.

The half-wave potential for one-electron oxidation of the complex $[\mathrm{Fe(cp)(CO)SPh}]_2$ was more anodic than the corresponding potentials for the alkyl derivatives $[\mathrm{Fe(cp)(CO)SR}]_2$ (R = Me, Et, or $\mathrm{Bu^n}$), as expected on the basis of electronegativity considerations. The half-wave potential was also observed to increase as the group R became bulkier.

TABLE 4

E.s.r. spectroscopic data [a]

Complex [b]	$\langle g \rangle$ [c]	g_1,	g_2,	g_3 [d]
cis-$[\mathrm{Fe(cp)(CO)SMe}]_2\mathrm{BF_4}$	1·998	2·032	2·014	1·941
cis-$[\mathrm{Fe(cp)(CO)SEt}]_2\mathrm{BPh_4}$	1·999	2·037	2·015	1·940
cis-$[\mathrm{Fe(cp)(CO)SPr^i}]_2\mathrm{BPh_4}$	2·000	2·040	2·015	1·935
cis-$[\mathrm{Fe(cp)(CO)SBu^t}]_2\mathrm{BPh_4}$	2·003	2·047	2·014	1·937
cis-$[\mathrm{Fe(cp)(CO)SBz}]_2\mathrm{BPh_4}$	2·001	2·036	2·016	1·938
cis-$[\mathrm{Fe(cp)(CO)SPh}]_2\mathrm{BPh_4}$	2·003	2·043	2·039	1·928
cis-$[\mathrm{Fe(cp)(CO)PPh_2}]_2\mathrm{BPh_4}$	1·989 [e]	2·023 [f]	2·018	1·926

[a] g values ±0·001. [b] Bz = $\mathrm{CH_2C_6H_5}$ and cp = η-$\mathrm{C_5H_5}$. [c] Measured in $\mathrm{CHCl_3}$ at room temperature. [d] Measured in frozen acetone or $\mathrm{CHCl_3}$ at 77 K. [e] $\langle a_\mathrm{p} \rangle$ 4·8 G. [f] a_p = 12·8 G.

TABLE 5

Mössbauer spectroscopic data

Compound [a,b]	Chemical isomer shift [c] δ/mm $\mathrm{s^{-1}}$	Quadrupole splitting Δ/mm $\mathrm{s^{-1}}$	Width at half-height /mm $\mathrm{s^{-1}}$
cis-$[\mathrm{Fe(cp)(CO)SMe}]_2$	0·31 ± 0·01	1·63 ± 0·01	0·30, 0·30
cis-$[\mathrm{Fe(cp)(CO)SEt}]_2$	0·30 ± 0·01	1·69 ± 0·01	0·32, 0·33
cis-$[\mathrm{Fe(cp)(CO)SMe}]_2\mathrm{PF_6}$	0·26 ± 0·01	1·79 ± 0·01	0·31, 0·32
$[\mathrm{Fe(cp)(CO)SMe}]_2\mathrm{SbF_6}$ [d]	0·27	1·79	
cis-$[\mathrm{Fe(cp)(CO)SEt}]_2\mathrm{SbF_6}$	0·29 ± 0·01	1·45 ± 0·01	0·32, 0·31
cis-$[\mathrm{Fe(cp)(CO)SPr^i}]_2\mathrm{PF_6}$	0·28 ± 0·01	1·52 ± 0·01	0·32, 0·33
cis-$[\mathrm{Fe(cp)(CO)SMe}]_2\mathrm{(PF_6)_2}$	0·24 ± 0·01	1·61 ± 0·01	0·31, 0·30
cis-$[\mathrm{Fe(cp)(CO)SPr^i}]_2\mathrm{(PF_6)_2}$	0·25 ± 0·01	1·64 ± 0·01	0·28, 0·28

[a] Measured on powdered samples at 77 K. [b] cp = η-$\mathrm{C_5H_5}$. [c] Relative to metallic iron at 295 K. [d] Data from ref. 6.

E.s.r. spectra of the monocationic derivatives in solution exhibit isotropic g values which are very similar to the spin-only value. These values, as well as the anisotropic g values obtained by taking measurements in frozen acetone or chloroform solutions at 77 K, are reported in Table 4. Magnetic susceptibilities of a number of these complexes were measured at room temperature and found to correspond to one unpaired electron per two iron atoms, the magnetic moment again being very similar to that for the spin-only value. For example, the magnetic moment found for the complex *cis*-$[\mathrm{Fe(cp)(CO)SBz}]_2\mathrm{PF_6}$ at room temperature is 1·69 B.M. These results contrast with those for the complexes of the type $[\{\mathrm{Fe(cp)(CO)}\}_2\mathrm{Ph_2PR'PPh_2}]$-anion.[3] The salts of the dications have magnetic moments of between 0·2 and 0·4 B.M. To shed further light on the distribution of the unpaired electron in the complex $[\mathrm{Fe(cp)(CO)SR}]_2$anion, the corresponding bridging phosphino-derivative $[\mathrm{Fe(cp)(CO)PPh_2}]_2\mathrm{BPh_4}$ was prepared and its e.s.r. spectrum measured in chloroform at room temperature. An incompletely resolved triplet, arising from hyperfine coupling of the unpaired electron with the two phosphorus nuclei of spin $S = \frac{1}{2}$ ($\langle a_\mathrm{p} \rangle$ = 4·8 G), was observed. Coupling was also observed in the frozen solution spectrum but for one of the g values only.

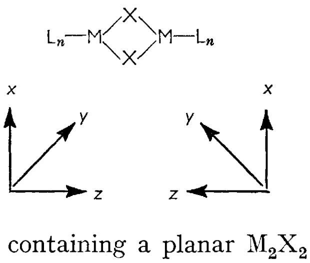
Solution i.r. spectra of the monocations *cis*-$[\mathrm{Fe(cp)(CO)SR}]_2^+$ contained two peaks in the C–O stretching region, whereas spectra of the corresponding neutral parents contained essentially a single peak {$[\mathrm{Fe(cp)(CO)SMe}]_2$: ν(C–O) 1 957s; 1 948sh,w; and 1 926vw $\mathrm{cm^{-1}}$ in cyclohexane}. This suggests that these *cis*-monocationic derivatives occur as a mixture of at least two conformers or isomers in solution. Evidence supporting this view was obtained by studying the oxidation of conformers (A) and (B) of *cis*-$[\mathrm{Fe(cp)(CO)SPh}]_2$. Conformer (A), which in cyclohexane has a strong C–O stretching peak at 1 983 $\mathrm{cm^{-1}}$ and a weak shoulder at 1 973 $\mathrm{cm^{-1}}$ [the latter possibly being due to conformer (B) as an impurity], gave an oxidised product which in dichloromethane exhibited a strong peak at 2 026 $\mathrm{cm^{-1}}$ and a weak peak at 1 998 $\mathrm{cm^{-1}}$, whereas conformer (B) [ν(C–O) 1973 $\mathrm{cm^{-1}}$ in cyclohexane] afforded a monocationic species whose dichloromethane solution exhibited only a single peak at 1 998 $\mathrm{cm^{-1}}$. The spectrum of the latter reverted to one containing peaks at 2 026s and 1 998m $\mathrm{cm^{-1}}$, consistent with an equilibrium between two conformers being established.

N.m.r. spectra of the complexes *cis*-$[\mathrm{Fe(cp)(CO)SR}]_2\mathrm{(PF_6)_2}$ (R = Me or $\mathrm{Bu^n}$) (see Table 2) exhibited single methyl resonances (a triplet in the case of the n-butyl derivative), consistent with these complexes occurring primarily as a conformer with either structure *cis*-(I) or *cis*-(III) in solution. Structure *cis*-(I) would be expected to be the thermodynamically stable form from stereochemical considerations and it is significant that this is the structure of the conformers of $[\mathrm{Fe(cp)(CO)SPh}]_2$ and $[\mathrm{Fe(cp)(CO)SMe}]_2\mathrm{BF_4}$ which were investigated by *X*-ray crystallography.[5,7]

Mössbauer spectra have been obtained for the parent complexes *cis*-$[\mathrm{Fe(cp)(CO)SR}]_2$ (R = Me or Et) as well as the monocationic *cis*-$[\mathrm{Fe(cp)(CO)SR}]_2\mathrm{A}$ (R = Me, A = $\mathrm{PF_6}$; R = Et, A = $\mathrm{SbF_6}$; R = $\mathrm{Pr^i}$, A = $\mathrm{PF_6}$) and dicationic derivatives *cis*-$[\mathrm{Fe(cp)(CO)SR}]_2\mathrm{(PF_6)_2}$ (R = Me or $\mathrm{Pr^i}$). Each spectrum consisted solely of a sharp quadrupole-split doublet, consistent with equivalence of both iron atoms in the cationic derivatives as well as in the neutral parents. The Mössbauer parameters at 77 K are recorded in Table 5. There is a slight dependence of the chemical-isomer shift on the nature of the group R, but this does not obscure an overriding dependence on the total charge of the complex. In each case removal of an electron from the neutral parent reduces the chemical-isomer shift and this trend continues when a second electron is removed. Oxidation is therefore accompanied by an increase in the *s*-electron density at the iron nuclei. The data in Table 5 all refer to measurements at 77 K; some spectra were also obtained at room temperature, but there were no essential differences in the trends observed. It was decided not to extend the measurements down to 4·2 K, mainly because Hill and his co-workers have already reported that the complex $[Fe(cp)(CO)SMe]_2$-SbF_6 gives only a sharp quadrupole doublet at that temperature.[6]

Variations in the quadrupole splitting are much less systematic. The two neutral parents are seen to have values similar to one another and these are similar to values for the two dicationic derivatives. By contrast, the quadrupole splitting for the methyl and ethyl derivatives of the monocations differ considerably from one another. A possible explanation for this is that these monocations adopt different conformations in the solid state. For example, the quadrupole splitting is known to be quite sensitive to the conformation of the R groups in *syn*- and *anti*-$[Fe(CO)_3SMe]_2$ (Δ 0·86 and 1·00 mm s^{-1} respectively).[13] The absence of any regular variation in the magnitude of the quadrupole splitting upon oxidation may simply reflect the fact that the electrons are not highly localised on the metal and make only a small contribution to the electric-field gradient. The result precludes a more precise identification of the particular iron orbitals involved in the highest filled molecular orbital (*vide supra*) and has discouraged us from carrying out applied magnetic-field measurements to determine the signs of the quadrupole-coupling constants for these complexes. Hill and his co-workers did study [6] the effect of an external magnetic field on the spectrum of the complex $[Fe(cp)(CO)SMe]_2SbF_6$ but did not comment on the sign of the quadrupole-coupling constant. Their experiments revealed a low value for the saturation hyperfine field at the iron nuclei, -72 ± 5 kG, which was presumed to be a consequence of the unpaired electron being distributed over both iron atoms.

Mason and Mingos have proposed a bonding scheme for bridged binuclear systems of the type shown below



M = metal
X = bridging ligand
L$_n$ = terminal ligands

and containing a planar M_2X_2 group in which the d_{z^2}, d_{xz}, and d_{yz} orbitals of the metals and *s* and *p* orbitals of the bridging ligands are utilised in bridge bonding.[14] In terms of this scheme the highest filled molecular orbital for complexes of general formula $[Fe(cp)(CO)SR]_2$ is an orbital which is derived essentially from metal d_{yz} orbitals and is thus orthogonal to the M_2X_2 plane and non-bonding with respect to the p_π orbitals (yz^*). It is also antibonding with respect to the metals, so that oxidation of the complex $[Fe(cp)(CO)SR]_2$ to $[Fe(cp)(CO)SR]_2^+$ should only be accompanied by a decrease in the metal–metal distance. In accordance with this prediction the iron–iron distance in the complex $[Fe(cp)(CO)SPh]_2$ is 339 pm, whereas the corresponding distance for $[Fe(cp)(CO)SMe]_2BF_4$ is 292·5 pm, as mentioned above. The Mössbauer chemical-isomer shift data discussed earlier are also consistent with this bonding scheme. An increase in the *s*-electron density at the iron nuclei on oxidation will result from a decrease of the screening of the *s* electrons by the *d* electrons and will thus require that the contribution from the metal *d* orbitals to the filled molecular orbital of highest energy predominates over any contribution from *s* orbitals.

For systems in which the M_2X_2 group is non-planar, the yz^* orbital will be capable of forming bonding and antibonding combinations with the orbitals of the bridging ligands. The observed hyperfine coupling in the e.s.r. spectrum of the complex $[Fe(cp)(CO)PPh_2]_2BPh_4$ can thus readily be explained in terms of the above bonding scheme by proposing puckering of the Fe_2P_2 ring. Significantly, the Fe_2S_2 group in the complex $[Fe(cp)(CO)SMe]_2BF_4$ in the crystalline state has been established to be non-planar,[7] the angle between the plane defined by the two sulphur atoms and the one iron atom and that defined by the two sulphur atoms and the other iron atom being 153°. Coupling between the unpaired electron and the phosphorus nuclei has also been observed in the e.s.r. spectrum of the complex $[Fe(CO)_3PMe_2]_2^-$ and for this species the Fe_2P_2 group is believed to deviate considerably from planarity.[8,15]

EXPERIMENTAL

I.r., n.m.r., and e.s.r. spectra were recorded on Perkin-Elmer model 621 grating, Varian HA100, and Varian 4502 spectrophotometers respectively. Mössbauer spectra were obtained from powdered samples on a Nuclear Science and Engineering Corporation instrument, model AM-1, coupled with a 400-channel R.I.D.L. analyser, model 34–12B. The radioactive source was a nominal 25 mCi of ^{57}Co diffused into a rhodium matrix, as supplied by the Radiochemical Centre, Amersham. The data were analysed by least-squares curve-fitting programs. Conductivities were measured on a Philips PW9501 conductivity meter. Magnetic susceptibilities were determined by the Gouy method on a Newport Instruments Gouy balance. Cyclic voltammograms were obtained employing a Tacussel PRT 2000 potentiostat and a Tacussel Servovit 2 triangular-wave generator. The half-wave potentials were measured on a Metrohm Polarecord E261 instrument using conventional three-electrode geometry and a Metrohm

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E446 *iR* compensator. Elemental analyses were made by the Alfred Bernhardt Microanalytical Laboratory, Elbach-über-Engelskirchen, West Germany.

The parent complexes $[Fe(cp)(CO)SR]_2$ (R = Me, Et, Pr^i, Bu^n, Bu^t, Bz, or Ph) and $[Fe(cp)(CO)PPh_2]_2$ were synthesised according to literature methods or slight modifications of them.[11,16] The mono- and di-cationic derivatives of $[Fe(cp)(CO)SR]_2$ (R = Me, Et, Pr^i, Bu^n, Bu^t, Bz, or Ph) and $[Fe(cp)(CO)PPh_2]_2$ were synthesised by one of the general methods outlined below. The yields in all reactions were high. Salts of the ion $[Fe(cp)(CO)SPh]_2^{2+}$ could only be isolated pure from the reaction employing $NOPF_6$ as oxidant however.

General Methods of Preparation of the Monocationic Derivatives.—(*a*) A solution of iodine or bromine in methanol or a minimum of dichloromethane was added dropwise to a stirred solution of twice the equimolar amount of the complex $[Fe(cp)(CO)SR]_2$ or $[Fe(cp)(CO)PPh_2]_2$ and an excess of NH_4PF_6, $KSbF_6$, or $NaBPh_4$ in methanol at room temperature. The product which separated from solution was isolated and crystallised from dichloromethane–methanol or acetone–methanol in the case of the $[Fe(cp)(CO)SPh]_2^+$ species.

(*b*) A solution of a silver salt such as $AgSbF_6$, or $NOPF_6$ in methanol or a minimum of dichloromethane, was added dropwise to a stirred solution of an equimolar amount of the complex $[Fe(cp)(CO)SR]_2$ or $[Fe(cp)(CO)PPh_2]_2$ in methanol at room temperature. The material which separated from solution was extracted with dichloromethane, the extract filtered, and the product crystallised as above. Salts of the ion $[Fe(cp)(CO)SPh]_2^+$ could not be isolated pure from the reactions employing silver salts as oxidant however.

(*c*) Air(oxygen) was passed through a solution of the complex $[Fe(cp)(CO)SR]_2$ or $[Fe(cp)(CO)PPh_2]_2$ containing an excess of a large counter-anion such as PF_6^- or BPh_4^- and a small amount of hydrochloric or acetic acid until reaction was complete, as determined by monitoring by means of i.r. The monocationic product was isolated and crystallised as above. A similar procedure was employed to obtain the salt $[Fe(cp)(CO)SMe]_2BF_4$ except that water was used as solvent.

General Methods of Preparation of the Dicationic Derivatives.—(*a*) A solution containing an excess of bromine in dichloromethane was added dropwise to a stirred solution of the complex $[Fe(cp)(CO)SR]_2$ and an excess of NH_4PF_6 (in a minimum amount of methanol) in dichloromethane at room temperature. The product which separated from solution was washed thoroughly with benzene and dichloromethane.

(*b*) A solution containing an excess of $NOPF_6$ in dichloromethane was added dropwise to a stirred solution of the complex $[Fe(cp)(CO)SR]_2$ in dichloromethane. The product which separated from solution was purified as above.

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