Two New Preparative Routes to, and ^{57}Fe Mössbauer and Infrared Spectroscopic Measurements on, the Salts of μ-Halogeno-bis[(π-cyclopentadienyl)dicarbonyliron(II)] Cations, $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2X^+$ (Halogeno = Chloro, Bromo, or Iodo)

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The $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2X^+PF_6^-$ salts can be prepared from the corresponding $(\pi\text{-}C_5H_5)Fe(CO)_2X$ complexes (X = Cl, Br, or I) either by reaction with sulphuric acid and subsequent treatment with hexafluorophosphoric acid, or by treatment with silver hexafluorophosphate. The structures of the $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2X^+$ cations are discussed in terms of their ^{57}Fe Mössbauer and i.r. spectra; u.v.–visible spectra are also reported for the complexes.

THE preparation of the μ-halogeno-bis[(π-cyclopentadienyl)dicarbonyliron(II)] cations were first described by Fischer and Moser[1,2] (halogeno = chloro, bromo, or iodo). Subsequently, the μ-iodo-bis[(π-cyclopentadienyl)dicarbonyliron(II)] cation was observed as an intermediate in the formation of (π-cyclopentadienyl)dicarbonyliron(II) iodide by reaction of bis[(π-cyclopentadienyl)dicarbonyliron(I)] with iodine.[3-5] (π-Cyclopentadienyl)dicarbonyliron(II) chloride reacts with boron trichloride to give the corresponding μ-chloro-cation as its tetrachloroborate salt in liquid hydrogen chloride solution.[6] The reaction of (π-cyclopentadienyl)dicarbonyliron(II) chloride with sulphuric acid has previously been reported to evolve hydrogen chloride with the formation of $(\pi\text{-}C_5H_5)Fe(CO)_2O{\cdot}SO_3H$.[7] We report the preparation of the μ-halogeno-bis[(π-cyclopentadienyl)dicarbonyliron(II)] cations by two simple techniques, involving reaction of the (π-cyclopentadienyl)dicarbonyl-

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[1] E. O. Fischer and E. Moser, *J. Organometallic Chem.*, 1965, **3**, 16.

[2] E. O. Fischer and E. Moser, *Z. anorg. Chem.*, 1966, **342**, 156.

[3] D. A. Brown, A. R. Manning, and D. J. Thornhill, *Chem. Comm.*, 1969, 338.

[4] R. J. Haines and A. L. du Preez, *J. Amer. Chem. Soc.*, 1969, **91**, 769.

[5] R. J. Haines and A. L. du Preez, *J. Chem. Soc.* (*A*), 1970, 2341.

[6] D. A. Symon and T. C. Waddington, *J. Chem. Soc.* (*A*), 1971, 953.

[7] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 3653.

iron(II) halides (halide = chloride, bromide, or iodide) with sulphuric acid or with silver hexafluorophosphate. The structure of these cations has not been determined.

TABLE 1

I.r. spectra of the $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2X^+$ cations, X = Cl, Br, or I in the ν(CO) region

Compound	Sample mode	ν(CO)/cm^{-1}
$(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ [a]	H_2SO_4 soln.	2075s, 2055sh, 2029s
$(\pi\text{-}C_5H_5)Fe(CO)_2Br$ [a]	H_2SO_4 soln.	2071s, 2059s, 2023s
$(\pi\text{-}C_5H_5)Fe(CO)_2I$ [a]	H_2SO_4 soln.	2063s, 2049s, 2017s, 2003sh
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2Cl^+PF_6^-$	KBr disc	2058sh, 2050s, 2013s, 2003sh, 2123s,[b] 2073s [b]
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2Cl^+PF_6^-$	CH_2Cl_2 soln.	2071s, 2064sh, 2025s [c]
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2Cl^+PF_6^-$	Nujol mull	2057sh, 2050s, 2013s, 2000sh
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2Br^+PF_6^-$	KBr disc	2057sh, 2043s, 2007sh, 2001s, 2127s,[b] 2074s [b]
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2Br^+PF_6^-$	CH_2Cl_2 soln.	2068, 2058s, 2020 [c]
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2I^+PF_6^-$	KBr disc	2047sh, 2040s, 2013sh, 2007s, 2129s,[b] 2079 [b]
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2I^+PF_6^-$	CH_2Cl_2 soln.	2063s, 2051s, 2017s [c]
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2Cl^+BCl_4^-$ [d]	Nujol	2055sh, 2050s, 2013, 2003

[a] These compounds react with sulphuric acid to give the corresponding $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2X^+$ cation. [b] Bands appeared with time. [c] Bands asymmetric in shape. [d] Measured at 77 K.

We present spectroscopic evidence which strongly supports a symmetrical Fe–X–Fe bond. No explanation of the occurrence of three or four terminal metal carbonyl absorptions in the i.r. spectra of salts of these cations has previously been given.

TABLE 2

^{57}Fe Mössbauer data

Compound	Temp./K	Isomer shift [a] mm s^{-1}	Qudrupole splitting mm s^{-1}	Widths at half height mm s^{-1}	
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2H^+BCl_4^-$	300	0·49	1·87	0·25	b
	4·2	0·60	1·90	0·25	
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2H^+PF_6^-$	300	0·47	1·82	0·25	b
	4·2	0·55	1·83	0·25	
$(\pi\text{-}C_5H_5)Fe(CO)_2Cl$	300	0·51	1·86	0·29	
	78	0·55	1·88		
$(\pi\text{-}C_5H_5)Fe(CO)_2Br$	300	0·52	1·85	0·20	
	78	0·56	1·87		c
$(\pi\text{-}C_5H_5)Fe(CO)_2I$	300	0·49	1·83	0·21	
	78	0·54	1·83		c
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2Cl^+PF_6^-$	300	0·58	1·90	0·24	
	1·3	0·67	1·97	0·29	
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2Br^+PF_6^-$	300	0·55	1·76	0·25	
	1·3	0·63	1·96	0·29	
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2I^+PF_6^-$	300	0·53	1·64	0·27	
	1·3	0·62	1·83	0·30	

[a] Relative to sodium nitroprusside. [b] D. A. Symon and T. C. Waddington, *J. Chem. Soc.* (*A*), 1971, 953. [c] R. H. Herber, R. B. King, and G. K. Wertheim, *Inorg. Chem.*, 1964, **3**, 101.

RESULTS AND DISCUSSION

The (π-cyclopentadienyl)dicarbonyliron(II) halides react with concentrated sulphuric acid to liberate hydrogen halide (0·3—0·7 equivalents), with the formation of bright cherry-red solutions. The i.r. spectra of these solutions (Table 1) over the region 2200—1800 cm^{-1} show absorption bands characteristic of terminal metal carbonyl stretching modes. The absorptions occurred at different frequencies in the three solutions, the frequency decreasing with increasing atomic weight of the parent halide, indicating that a common complex [*e.g.* $(\pi\text{-}C_5H_5)Fe(CO)_2O{\cdot}SO_3H$] was not responsible for the absorptions.

Careful addition of aqueous hexafluorophosphoric acid to these cherry-red solutions led to the isolation of the respective μ-halogeno-bis[(π-cyclopentadienyl)dicarbonyliron(II)] cations as their hexafluorophosphate salts. These cations can have eight basic structures depending on whether the Fe–X–Fe bond is symmetric or asymmetric, linear or bent, and whether the two (π-cyclopentadienyl)dicarbonyliron(II) units are '*cis*' or '*trans*' to each other.

^{57}Fe Mössbauer spectra were recorded in order to detect any non-equivalence in the iron atoms, *i.e.* whether the Fe–X–Fe bond is asymmetric or asymmetric; the results are given in Table 2. ^{57}Fe Mössbauer spectroscopy has been used to study non-equivalence of iron atoms in polynuclear iron complexes.[8-10] Herber *et al.*[8] calculated partial isomer shifts for various ligands and concluded that ligands which donate a lone pair of electrons to the iron atom only make a minor contribution to the isomer shift. Hence substitution of one electron pair donor by another will not alter the resonance of the iron atom. This was very clearly demonstrated when the ^{57}Fe Mössbauer spectrum of $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_3]_2Ph_2PCCPPh_2$ failed to show the presence

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[8] R. H. Herber, R. B. King, and G. K. Wertheim, *Inorg. Chem.*, 1964, **3**, 101.

[9] K. Farmery, M. Milner, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc.* (*A*), 1969, 2339.

[10] R. B. King, L. M. Epstein, and E. W. Gowling, *J. Inorg. Nuclear Chem.*, 1970, **32**, 441.

of two iron atoms in different environments.[11] Bancroft *et al.*,[12] using data collected from a large number of low spin iron(II) complexes, calculated the partial centre shift values (p.c.s.) and partial quadrupole shift values (p.q.s.) for some of the more common ligands. These workers found for chloride, bromide, and iodide p.c.s. values of 0·10, 0·13, and 0·13 mm s^{-1} respectively, and p.q.s. values of −0·30, −0·32, −0·31 mm s^{-1} respectively. In the μ-halogeno-cations if the Fe–X–Fe bond is asymmetric, the observation of two different iron atom resonances would be expected. The observation of a single, quadrupolar split, resonance at a temperature of 1·3 K is consistent with both iron atoms being in similar environments with a non-symmetrical octahedral symmetry about each iron atom.

In the (π-cyclopentadienyl)dicarbonyliron(II) halides (halide = chloride, bromide, or iodide) the *s* electron density at the iron nucleus is less than in the bis[(π-cyclopentadienyl)dicarbonyliron(I)] complex, also the *s* electron density increases as the electronegativity of halide decreases. The μ-halogeno-cations (halogeno = chloro, bromo, or iodo) show a further decrease in *s* electron density and a similar trend with electronegativity of the halogen. The widths at half height of the absorption bands are 0·25 mm s^{-1} at 300 K but on cooling to 1·3 K some broadening occurred. The broadening is most likely to be instrumental as it has a predominately Gaussian line shape rather than the Lorenzian line shape characteristic of genuine resonances.

Examination of the $2p_{\frac{3}{2}}$ levels of the iron atoms of the μ-halogeno-cations by *X*-ray photoelectron spectroscopy also failed to detect any difference in the two iron atoms.[13]

A consideration of local symmetry at the iron atoms would predict two main carbonyl absorption bands in the i.r. due to the carbonyls of a $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2$ unit. Each of these bands should be split by coupling with the carbonyl vibrations on the other $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2$ unit. This splitting may however be small.

In practice the i.r. spectra of the μ-halogeno-bis[(π-cyclopentadienyl)dicarbonyliron(II)] cations depends markedly on the environment but in all cases the high frequency band is split into a doublet. The splitting of the lower frequency band is not well resolved in all cases but the spectra of the hexafluorophosphate salts in KBr discs show this splitting and in those cases where the lower band is not split it is clearly broad and unsymmetric. For example, the i.r. spectra of the bridged compounds in methylene dichloride do not show any splitting of the low frequency carbonyl band. However the band is asymmetric and has a width at half height of *ca.* 24 cm^{-1}, which is in contrast to the two carbonyl absorption bands of the (π-cyclopentadienyl)-dicarbonyliron(II) halides, which when recorded under identical experimental conditions are of approximately equal intensity and with widths at half height of 14—16 cm^{-1}.

The μ-hydrogen-bis[(π-cyclopentadienyl)dicarbonyliron(II)] cation has been observed to decompose readily on warming to form the (π-cyclopentadienyl)tricarbonyliron cation.[6] We have observed that the μ-halogeno-compounds also decompose slowly on gentle heating. The decompositions were followed by monitoring the 2200—1900 cm^{-1} region of their i.r. spectra. The stability of the $[(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2\text{X}^+$ cations (X = H, Cl, Br, or I) were found to increase with increasing atomic weight of X. When X was chlorine or bromine, the only product of decomposition identified was the $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_3{}^+$ ion; when X was iodine $(\pi\text{-C}_5\text{H}_5)\text{-Fe(CO)}_2\text{I}$ was also formed.

TABLE 3

U.v. and visible spectra of the $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{X}$ and $[(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2\text{X}^+\text{PF}_6{}^-$ compounds (X = Cl, Br, or I) over the region 38 000—14 000 cm^{-1}

Compound	Absorption band cm^{-1}	Extinction coefficient (l mol^{-1} cm^{-1})
$(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{Cl}$	21 050	155
	29 850	1 070
	35 590	2 055
$(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{Br}$	21 140	330
	28 740	1 330
	34 130	4 690
$(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{I}$	20 070	570
	29 150	2 330
	38 460	4 740
$[(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2\text{Cl}^+\text{PF}_6{}^-$	19 840	475
	25 550	2 630
	30 000	4 120
	35 340	5 750
$[(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2\text{Br}^+\text{PF}_6{}^-$	19 800	525
	25 640	3 230
	29 240	5 000
	35 840	5 265
$[(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2\text{I}^+\text{PF}_6{}^-$	20 410	740
	25 640	10 200
	28 820	12 800
	37 880	18 365

The u.v.–visible absorption spectra of the (π-cyclopentadienyl)dicarbonyliron(II) halides and of the μ-halogeno-bis[(π-cyclopentadienyl)dicarbonyliron(II)] hexafluorophosphates were recorded in methylene chloride solution (halide = chloride, bromide, or iodide; halogeno = chloro, bromo, or iodo). The results are given in Table 3. The initial analysis of the spectra of the $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{X}$ compounds show them to be composed of a peak at *ca.* 20 000 cm^{-1} which appears as a shoulder on the absorption edge of the higher frequency u.v. band. This higher frequency u.v. band occurs at *ca.* 28 000 cm^{-1} and shows marked distortions, indicating that more than one transition is responsible. A further band at higher frequencies was observed which was distorted by the absorption edge of the solvent (methylene chloride). The intensity of all the absorption bands increased with increasing atomic weight of the halide. The u.v.–visible absorption spectra of the $[(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2\text{X}^+\text{PF}_6{}^-$ salts in methylene chloride

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[11] A. J. Carty, R. W. Ng, W. Carter, G. J. Palenick, and T. Birchall, *Chem. Comm.*, 1969, 1101.

[12] G. M. Bancroft, M. J. Mays, and B. E. Prater, *J. Chem. Soc.* (*A*), 1970, 956.

[13] D. B. Adams, D. T. Clark, D. A. Symon, and T. C. Waddington, unpublished results.

solution follows similar trends, three distinct bands being observed in the u.v. region.

EXPERIMENTAL

All reactions were carried out using degassed solvents and under dry nitrogen atmospheres wherever possible. The hexafluorophosphoric acid solutions were contained in polytetrafluoroethylene apparatus.

Sulphuric acid was AnalaR grade, hexafluorophosphoric acid, silver hexafluorophosphate, and bis[(π-cyclopentadienyl)dicarbonyliron(I)] were obtained commercially. (π-Cyclopentadienyl)dicarbonyliron(II) halides (halide = chloride,[14] bromide,[15] or iodide [16]) were prepared by literature methods.

Analysis and Physical Measurements.—Carbon and hydrogen were determined by microcombustion. Iron was determined by atomic absorptiometry. Chlorine, bromine, and iodine were determined potentiometrically, and phosphorus was estimated spectrophotometrically as the vanadophosphomolybdate complex. I.r. spectra were recorded on a Perkin-Elmer 457 double beam spectrophotometer, over the region 4000—250 cm^{-1}. The instrument was calibrated with deuterium chloride and water vapour; carbonyl absorptions are accurate to ± 1 cm^{-1}. U.v.–visible spectra were recorded on a Unicam SP 800 instrument in 10 mm silica cells.

Preparation of the Compounds.—The μ-halogeno-bis[(π-cyclopentadienyl)dicarbonyliron(II)] hexafluorophosphates, $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2X^+PF_6^-$ (X = Cl, Br, or I) were prepared by either of the two general methods given below.

Method A. Ice-cold sulphuric acid (2 cm^3, sp. gr. 1·84) was added to (π-cyclopentadienyl)dicarbonyliron(II) halide (halide = chloride, bromide, or iodide) (0·005 mol) and homogeneous solution effected. The solution was degassed using a water pump until evolution of hydrogen halide almost ceased. After cooling the solution to 0 °C, ice-cold distilled water (6 cm^3) was added and the solution filtered. Hexafluorophosphoric acid (65% aq. solution) was added dropwise to the filtrate until precipitation ceased. After filtering, the solid product was dissolved in acetone and reprecipitated by the addition of hexane, to give a red crystalline solid.

Method B. A solution of silver hexafluorophosphate (0·0625 g, 0·0025 mol) in toluene (10 cm^3) was added to a solution of (π-cyclopentadienyl)dicarbonyliron(II) halide (halide = chloride, bromide, or iodide) (0·005 mol) in toluene (15 cm^3). After allowing the reaction to proceed for 30 min, the precipitate of silver halide was filtered off. The toluene was removed *in vacuo* to yield a red solid, which after dissolution in acetone and reprecipitation by the addition of hexane gave a red crystalline solid.

μ-Chloro-bis[(π-cyclopentadienyl)dicarbonyliron(II)]hexafluorophosphate was prepared by both the general methods to give a red crystalline solid (Found: C, 31·55. H, 1·9; Cl, 6·4; Fe, 20·6; P, 5·7. $C_{14}H_{10}ClF_6Fe_2O_4P$ requires C, 31·45; H, 1·9; Cl, 6·65; Fe, 20·9; P, 5·8%).

μ-Bromo-bis[(π-cyclopentadienyl)dicarbonyliron(II)]hexafluorophosphate was prepared by both the general methods to give a red crystalline solid (Found: C, 29·05; H, 1·75; Fe, 19·25; P, 5·35. $C_{14}H_{10}BrF_6Fe_2O_4P$ requires C, 29·05; H, 1·75; Fe, 19·3; P, 5·35%).

μ-Iodo-bis[(π-cyclopentadienyl)dicarbonyliron(II)]hexafluorophosphate was prepared by method A to give a red crystalline solid (Found: C, 26·8; H, 1·45; Fe, 17·9; I, 20·3; P, 5·05. $C_{14}H_{10}F_6Fe_2IO_4$ requires C, 26·85; H, 1·6; Fe, 17·85; I, 20·3; P, 4·95%).

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