The Liquid Hydrogen Chloride Solvent System. Part XV.[1] Reactions of the Tetrakis[carbonyl(π-cyclopentadienyl)iron(I)] Complex

By **David A. Symon**, Pure and Applied Chemistry Department, Strathclyde University, Glasgow G1 1XI
Thomas C. Waddington,* Department of Chemistry, University of Durham, Durham DH1 3LE

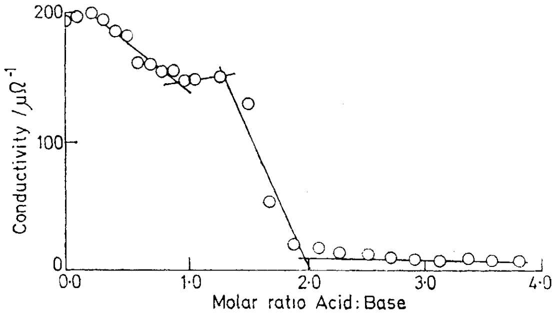
The complex tetrakis[carbonyl(π-cyclopentadienyl)iron(I)], $[(cp)Fe(CO)]_4$, reacts with boron trichloride in liquid hydrogen chloride to give the $\{[(cp)Fe(CO)]_4H_2\}^{2+}$ ion (cp = π-cyclopentadienyl); reaction with phosphorus pentafluoride in hydrogen chloride gives the $[(cp)Fe(CO)]_4{}^+$ ion. An improved procedure for the preparation of the complex $[(cp)Fe(CO)]_4$ is also reported.

SINCE the pioneering work of Wilkinson and Birmingham,[2] a large number of organometallic compounds have been shown to act as bases with protonation occurring at the central metal atom.[1,3-12] It is, however, only recently that diprotonation of an organometallic compound has been observed.[13,14] ^1H N.m.r. studies on a sulphuric acid solution of the complex $[Ir_4(CO)_{12}]$ showed that diprotonation had occurred. All attempts to isolate the diprotonated species failed.[13] We have examined the behaviour of the complex tetrakis[carbonyl(π-cyclopentadienyl)iron(II)] in liquid hydrogen chloride and in other protonic solvents. The complex was first prepared by King[15] in yields of 14%. Yields of the order of 44—56% can readily be achieved using the procedure outlined below. King[15] also reported that powerful oxidising agents [bromine, antimony pentachloride, and tris-(*p*-toluidinium) hexafluorophosphate] gave insoluble black materials. We report the preparation of the $[(cp)Fe(CO)]_4{}^+$ ion (cp = π-cyclopentadienyl) and its isolation as hexafluorophosphate and heptaiodide salts.

RESULTS AND DISCUSSION

The complex $[(cp)Fe(CO)]_4$ is soluble in liquid hydrogen chloride at −95 °C, without loss of carbon monoxide, and can be recovered unchanged at room temperature. A 0·015M solution of the complex in liquid hydrogen chloride has a molar conductance of 20 Ω^{-1} cm^2 mol^{-1}, about half that for a solution of bis[dicarbonyl(π-cyclopentadienyl)iron(I)].[1] Thus $[(cp)Fe(CO)]_4$ is less basic than $[(cp)Fe(CO)_2]_2$, though in both complexes each iron atom is in the I oxidation state and has a π-bonded cyclopentadienyl ligand.

Clearly, a complex with two carbonyl ligands per iron atom can delocalise any positive charge more effectively than a complex with one such ligand. The above argument assumes monoprotonation in the dimeric complex and diprotonation in the tetrameric complex. If monoprotonation of each complex occurs there are four carbonyl ligands which can delocalise the charge, and similar basicities might be expected. In the tetrameric complex the carbonyl ligands must attempt to delocalise a charge of 5+ (four 1+ iron atoms and a proton). In the dimeric complex only a 3+ charge has to be delocalised (two 1+ iron atoms and a proton), suggesting that the dimeric complex is the stronger base even in the case of monoprotonation. In low-spin iron complexes ligands donate electron density to reduce the 1+ charge on the iron atom towards zero. Hence, we must consider the iron atom charge as well as the addition of extra positive charge from protons. The cp ligand has been assumed to play little or no part in the stabilisation of the cations. This is borne out by the fact that very little change in the spectroscopic properties of this ligand occurs in a very wide range of compounds.



A conductimetric study of the reaction of boron trichloride with the complex $[(cp)Fe(CO)]_4$ in liquid hydrogen chloride showed that addition of boron trichloride reduced the conductance of the solution, with breaks in the curve at 1 : 1 and 2 : 1 molar ratios (acid : base) (Figure). Final conductances were very

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low; the decrease in conductance can be due (i) to adduct formation, (ii) to replacement of a more mobile ion by a less mobile ion or, (iii) to precipitation of conducting material from solution. The conductimetric titration gave no clear indication of the start of precipitation, but at the completion of the titration a green precipitate and an almost colourless solution remained. The increase in mass of the solid product was consistent with the addition of 2 moles of $HBCl_4$ rather than 2 moles of BCl_3, to each mole of $[(cp)Fe(CO)]_4$. The i.r. spectrum of the solid had absorption bands at 698 and 673 cm^{-1}, characteristic of the tetrachloroborate ion, BCl_4^-.[16]

The salt $\{[(cp)Fe(CO)]_4H_2\}^{2+}(BCl_4^-)_2$ was observed to lose hydrogen chloride readily at room temperature to give $[(cp)Fe(CO)]_4,2BCl_3$. The i.r. spectrum of the latter had absorption bands at 806 and 749 cm^{-1}, attributable to co-ordinated boron trichloride. In the i.r. spectra of both the complexes reported above, the carbonyl absorptions were observed at higher frequencies than in the parent complex. The reaction of the complex $[(cp)Fe(CO)]_4$ with triethylaluminium has been observed to give an adduct in which the aluminium atoms are directly co-ordinated to the oxygen atoms of the carbonyl ligands.[17]

A conductimetric titration of the complex $[(cp)Fe(CO)]_4$ using phosphorus pentafluoride as the Lewis acid gave incomplete reaction, but a pure paramagnetic hexafluorophosphate salt could be isolated. This is the first example of a reaction in hydrogen chloride where phosphorus pentafluoride has acted as an oxidising agent [equation (1)]. Ferguson and Meyer [18] have shown that

$$3PF_5 + 2e^- \longrightarrow 2PF_6^- + PF_3 \qquad (1)$$

$[(cp)Fe(CO)]_4$ can be electrochemically oxidised to the mono- and di-cation at potentials of +0·32 and 1·07 V, respectively. Preparation of the hexafluorophosphate salt, $[(cp)Fe(CO)]_4^+PF_6^-$, was carried out by unambiguous routes and shown to be identical with the product isolated from the reaction of the $[(cp)Fe(CO)]_4$ complex with phosphorus pentafluoride in hydrogen chloride.

The oxidation of $[(cp)Fe(CO)]_4$ with chlorine, in liquid hydrogen chloride, could not be followed conductimetrically as individual conductance values varied with time and were not reproducible. Mixtures of products were always obtained. The only carbonyl complex which was formed in any quantity was the monocation, $[(cp)Fe(CO)]_4^+$, although traces of the cation $[(cp)Fe(CO)_3]^+$ were also detected.

I.r. spectra of the complex $[(cp)Fe(CO)]_4$ in a series of acids were recorded over the range 2 200—1 600 cm^{-1} (Table 1). The spectra showed, by movement of carbonyl absorption frequencies to higher wavenumbers, that protonation had occurred. In the more powerful oxidising acids formation of the cation $[(cp)Fe(CO)_3]^+$ occurred. This was shown by the appearance of absorption bands at 2 125 and 2 077 cm^{-1}. In the chlorosulphuric acid mull an absorption band at 2 028 cm^{-1} was also observed. This might be attributable to the formation of the $[(cp)Fe(CO)_2]_2Cl^+$ ion [ν(CO) (in H_2SO_4) 2 075 and 2 029 cm^{-1} (ref. 19)].

TABLE 1

I.r. spectra of the complex tetrakis[carbonyl(π-cyclopentadienyl)iron(I)] in acid mulls in the 2 200—1 600 cm^{-1} region

Acid	Carbonyl absorptions (cm^{-1})
H_2SO_4	1 714s
H_2SO_4/SO_3	2 127w, 2 079m, 1 686s
CH_3SO_3H	1 708s
HSO_3Cl	2 125m, 2 075s, 2 028m, 1 714ms
CF_3CO_2H	1 786,* 1 716m
HPF_6	1 710s
H_2PO_3F	1 716s

* ν(CO) of CF_3CO_2H.

^{1}H N.m.r. studies of the complex $[(cp)Fe(CO)]_4$ over the range τ −20 to +180, in trifluoroacetic and sulphuric acids only showed resonances due to the solvent and a sharp singlet at τ 4·91 [15] attributable to the cp ring protons. The solution in liquid hydrogen chloride was too dilute to observe the cp ring proton resonance. The failure to observe a metal–hydrogen resonance is probably due to rapid exchange with the solvent, so that on the n.m.r. time scale the signal is time-averaged with that of the solvent. Protonation of the cp ligand would not give the sharp singlet observed in the ^{1}H n.m.r. spectrum, and the i.r. studies eliminate protonation of the carbonyl ligand as a possibility.

The i.r. spectrum in the carbonyl stretching region for the complex $[(cp)Fe(CO)]_4$, in solution, gives a single absorption peak. In solid-state studies, however, this region is very complex and several bands are observed. For all the complexes reported the carbonyl stretching region shows a similar pattern. It was not always possible to obtain i.r. solution spectra of the complexes, but for $[(cp)Fe(CO)]_4^+PF_6^-$ in acetonitrile and nitromethane solutions only one carbonyl absorption was observed at 1 715 and 1 716 cm^{-1}, respectively. This indicates that the four carbonyl ligands are equivalent. The fact that all the solid-state spectra are similar suggests that, in all the complexes examined, the four carbonyl ligands are identical. In the case of the $\{[(cp)Fe(CO)]_4H_2\}^{2+}$ ion, the two hydrogen atoms must be situated along two opposite edges of the tetrahedron of iron atoms, which results in the molecule having a D_{2d} symmetry. These facts are supported by ^{57}Fe Mössbauer studies, which are to be published shortly.

EXPERIMENTAL

The apparatus and general techniques have been described previously.[1,20] All hydroscopic materials were handled in

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a glove-box which was flushed with dry nitrogen. Hydrogen chloride, boron trichloride, chlorine, Phosfluorogen A, and the complex $[(cp)Fe(CO)_2]_2$ (cp = π-cyclopentadienyl) were obtained commercially. Phosphorus pentafluoride was prepared by the thermal decomposition of Phosfluorogen A.[21] All volatile materials were purified by trap-to-trap distillation, before use.

Analyses and Physical Measurements.—Weight analyses were carried out as described previously.[20] Conductivities were measured on a Wayne Kerr Bridge type B221. Carbon and hydrogen were determined by microcombustion, iron by atomic absorptiometry. Bromide and iodide were determined potentiometrically, and phosphorus was estimated by visible spectroscopy as the $[PMo_{10}V_2O_{39}]^{3-}$ complex. I.r. spectra were recorded on a Perkin-Elmer 457 double-beam spectrophotometer over the region 4 000—250 cm^{-1}. The instrument was calibrated with deuterium chloride and water vapour; carbonyl absorptions are accurate to ± 1 cm^{-1}. ^1H N.m.r. spectra were recorded on Perkin-Elmer R10 and Varian A56/60D spectrometers.

Preparations.— *Tetrakis[carbonyl(π-cyclopentadienyl)iron*(I)]. The complex bis[dicarbonyl(π-cyclopentadienyl)iron(I)] (56·8 g, 0·16 mol) in xylene (500 cm^3) was heated under reflux in a nitrogen atmosphere in a Pyrex glass apparatus. The refluxing solution was irradiated, using a 500 W mercury discharge lamp placed *ca.* 10—15 cm from the surface of the solution. Aliquot portions were taken from the reaction mixture periodically and, after removal of the solvent *in vacuo*, the residual solid was examined by i.r. spectroscopy. In this way the disappearance of the carbonyl stretching absorptions of the complex $[(cp)Fe(CO)_2]_2$ and the appearance with time of the carbonyl stretching absorption of $[(cp)Fe(CO)]_4$ was monitored. During the course of the reaction, additional carbonyl stretching absorptions appeared and then disappeared. These were thought to be due to the complex $[(cp)(xylene)Fe(CO)_2]$. Isolation of this intermediate was carried out and is described elsewhere. On prolonged irradiation all carbonyl absorptions disappeared and ferrocene could be recovered from the solution in yields of up to *ca.* 10%.

Using the photolysis method it is important to stop the irradiation at the point of maximum intensity of the $[(cp)Fe(CO)]_4$ carbonyl band because over-irradiation was found to decrease the yield of the complex and increase the amount of ferrocene produced. After cooling the reaction mixture was filtered and the moist residue was transferred to the thimble of a Soxhlet apparatus and extracted with methylene chloride, until the washings were colourless or very pale green (this usually occurred after *ca.* 24 h). On cooling, a pure product crystallised out. After reduction of the bulk of the filtrate *in vacuo*, addition of hexane gave a second crop of pure crystals (Found: C, 48·1; H, 3·40; Fe, 37·5. Calc. for $C_{24}H_{20}Fe_4O_4$: C, 48·4; H, 3·40; Fe, 37·5%). The i.r. spectrum of the pure product agreed with that reported by King.[15] The yields of five reactions, using the above procedure, are given in Table 2. The above procedure required *ca.* 7 days and gave yields of the order of 44—56%, compared with the literature preparation which required 19 days and gave a yield of 14%. I.r. absorptions (KBr disc) in this complex were as follows: 3 108sh; 3 096w; 1 673w; 1 656w,sh; 1 644ms; 1 629s; 1 619s; 1 591w,sh; 1 431sh; 1 426m; 1 360w; 1 064w; 1 026w; 1 018w; 1 010w; 933sh; 920w; 870sh; 864m; 836m; 826m; 598m; 574ms; 506w; and 355m cm^{-1}.

Dihydrogen {tetrakis[carbonyl(π-cyclopentadienyl)iron(I)]} *bistetrachloroborate*, $\{[(cp)Fe(CO)]_4H_2\}^{2+}2BCl^{4-}$. The complex $[(cp)Fe(CO)]_4$ (0·3683 g, 0·618 mmol) was degassed *in vacuo* overnight. Hydrogen chloride (10 cm^3, 0·38 mol) was distilled into the ampoule, which was cooled to −196 °C (liquid-nitrogen bath). On warming to −95 °C (toluene slush bath), a homogeneous solution was obtained. The solution was cooled to −196 °C (liquid-nitrogen bath) and boron trichloride (8 mmol) was condensed from the gas phase. The mixture was allowed to react at −84 °C (solid carbon dioxide–acetone slurry) overnight. A dark green solid was precipitated. After removing all volatile compounds *in vacuo* at temperatures below −84 °C, the solid was allowed to warm to room temperature {Found: C, 32·35; H, 2·90; Cl, 28·8; increase in weight over $[(cp)Fe(CO)]_4$ 54·5. Calc. for $C_{24}H_{22}B_2Cl_8Fe_4O_4$: C, 31·85; H, 2·45; Cl, 31·35; increase over $[(cp)Fe(CO)]_4$, 51·9%}. I.r. absorptions in this complex (Nujol mull) were at: 3 115w; 1 726m; 1 706s; 1 700m,sh; 1 684m; 1 060w; 1 016w; 1 006sh; 958w; 950sh; 935sh; 891sh; 870m,sh; 850s; 831s; 738w,sh; 716m,sh; 698s; 673m,sh; 618s; 600s; 584sh; 528s; 516m,sh; 470w; 440w,sh; 368m; and 356m,sh cm^{-1}.

TABLE 2

Yields * on photolysis of the complex $[(cp)Fe(CO)_2]_2$

Expt. no.	Yield/%	Reaction time/days
1	32	$8\frac{1}{2}$
2	44	$7\frac{1}{2}$
3	29	9
4	56	7
5	49	7

* Yield based on the complex $[(cp)Fe(CO)_2]_2$.

Tetrakis[carbonyl(π-cyclopentadienyl)iron(I)]*-bis(boron trichloride)*, $[(cp)Fe(CO)]_4,2BCl_3$. This complex was prepared in an identical manner to $\{[(cp)Fe(CO)]_4H_2\}^{2+},2BCl_4^-$, except that the product was pumped at room temperature for *ca.* 30 min further {Found: C, 34·2; H, 2·05; Cl, 25·7; increase in weight over $[(cp)Fe(CO)]_4$, 38·95. Calc. for $C_{24}H_{20}B_2Cl_6Fe_4O_4$: C, 34·75; H, 2·45; Cl, 25·65; increase in weight over $[(cp)Fe(CO)]_4$, 39·3%}. I.r. absorptions in this complex (Nujol mull) were at: 3 109w; 1 706m; 1 667s; 1 065w; 1 015m; 962m; 883m; 848s; 834s; 806s; 749m,sh; 741w,sh; 721w,sh; 629s,sh; 619s; 600s; and 581m,sh cm^{-1}.

Tetrakis[carbonyl(π-cyclopentadienyl)iron(I)] *hexafluorophosphate*, $[(cp)Fe(CO)]_4{}^+PF_6{}^-$, *method* (a). The complex $[(cp)Fe(CO)]_4$ (0·1280 g, 0·215 mmol) was degassed *in vacuo* overnight. Hydrogen chloride (10 cm^3, 0·38 mol) was condensed into the ampoule after cooling to −196 °C (liquid-nitrogen bath). On warming to −95 °C (toluene slush bath), a homogeneous solution was obtained. The solution was cooled to −196 °C (liquid-nitrogen bath) and phosphorus pentafluoride (3 mmol) was condensed in from the gas phase. The mixture was allowed to react at −84 °C (solid carbon dioxide–acetone slurry) overnight before removing all volatile compounds *in vacuo*. After warming to room temperature, the solid product was washed with methylene chloride, leaving an insoluble green solid (Found: C, 38·45; H, 2·80; Fe, 30·2; P, 3·95. Calc. for $C_{24}H_{20}F_6Fe_4O_4P$: C, 38·9; H, 2·70; Fe, 30·15; P, 4·20%).

Method (b). The complex $[(cp)Fe(CO)]_4$ (5·95 g, 0·01 mol) and tetra-n-butylammonium hexafluorophosphate (3·81 g, 0·01 mol) were dissolved in a minimum quantity of

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methylene chloride. After filtering through a sinter, a solution of bromine (0·8 g, 0·01 mol) in methylene chloride (200 cm^3) was added dropwise to the filtrate. After filtration the precipitate was dissolved in acetone and reprecipitated by the careful addition of hexane (Found: C, 39·05; H, 2·70; Fe, 30·2; P, 3·95. Calc. for $C_{24}H_{20}F_6Fe_4O_4P$: C, 38·9; H, 2·70; Fe, 30·15; P, 4·20%).

Method (c). A solution of triphenylmethylium hexafluorophosphate (1·88 g, 0·005 mol), in a minimum quantity of methylene chloride, was added dropwise to the complex $[(cp)Fe(CO)]_4$ (2·98 g, 0·005 mol) in methylene chloride (150 cm^3). Triphenylmethylium hexafluorophosphate was prepared immediately before use, by dissolving triphenyl methanol in propionic anhydride and, after cooling the solution to 10 °C, adding hexafluorophosphoric acid (4·5 cm^3, 65%) slowly, keeping the temperature below 15 °C. After the yellow crystals which formed had settled, the supernatant liquor was decanted, and the solid washed quickly with four portions of cold dry diethyl ether (3 cm^3) and finally dried *in vacuo*. The solution of the iron complex was filtered and the residue dissolved in acetone and reprecipitated by addition of hexane (Found: C, 38·3; H, 2·80; Fe, 30·1. Calc. for $C_{24}H_{20}F_6Fe_4O_4P$: C, 38·9; H, 2·70; Fe, 30·15%). The i.r. spectra of the complexes from these three preparations were identical and consisted of (KBr disc): 3 113w; 1 738w,sh; 1 719m,sh; 1 702s; 1 693s; 1 431w; 1 424m; 1 358vw; 1 120vw; 1 062w; 1 016w; 1 006w; 951w; 856s; 838s; 824s; 556s; 498m; 478m; and 356m cm^{-1}.

Tetrakis[carbonyl(π-cyclopentadienyl)iron(I)*] heptaiodide*, $[(cp)Fe(CO)]_4{}^+I_7{}^-$. To the complex $[(cp)Fe(CO)]_4$ (5·95 g, 0·01 mol) in methylene chloride (250 cm^3), iodine (8·9 g, 0·07 mol) dissolved in a minimum quantity of methylene chloride was added dropwise. After the solution had been stirred overnight filtration gave a pale green solid (Found: C, 19·4; H, 1·35; Fe, 15·6; I, 60·1. Calc. for $C_{24}H_{20}Fe_4I_7O_4$: C, 19·4; H, 1·35; Fe, 15·05; I, 59·85%). The i.r. spectrum of the complex (KCl disc) contained the following bands: 3 108w; 1 734m; 1 704s,sh; 1 694s; 1 664w,sh; 1 426w; 1 356vw; 1 120vw; 1 061w; 1 006w; 938w; 874m; 846m; 495m,sh; 476m; and 356m cm^{-1}.

Reaction of Tetrakis[carbonyl(π-cyclopentadienyl)iron(I)*] with Chlorine in Liquid Hydrogen Chloride.*—The complex $[(cp)Fe(CO)]_4$ (0·077 g, 0·130 mmol) was degassed overnight. Hydrogen chloride (7 cm^3, 0·25 mol) was condensed onto the solid, cooled to −196 °C (liquid-nitrogen bath). Warming to −95 °C (toluene slush bath), gave a homogeneous solution. After cooling to −196 °C (liquid-nitrogen bath), chlorine (0·17 mmol) was condensed from the gas phase and the mixture was allowed to react at −95 °C for *ca.* 4 h. On cooling to −196 °C (liquid-nitrogen bath), some non-condensable gas was detected (*ca.* 6 mm in 65 cm^3, 0·03 mol). Removal of all volatile compounds, at low temperature, resulted in a green solid being isolated at room temperature. The i.r. spectrum showed carbonyl absorptions at 2 122w, 2 074w, 2 048m, 2 002m, 1 692s, and 1 623m cm^{-1}. Attempts to separate the components were not successful. The products smelt of chlorocarbons, suggesting that chlorination of the cp ring had taken place.

Conductimetric Studies of Tetrakis[carbonyl(π-cyclopentadienyl)iron(I)*] Solutions in Hydrogen Chloride.*—(a) *With boron trichloride.* The complex $[(cp)Fe(CO)]_4$ (0·0533 g, 0·0896 mmol) was degassed overnight in a conductivity cell. After cooling to −196 °C (liquid-nitrogen bath), hydrogen chloride (7 cm^3, 0·25 mol) was condensed from the gas phase. Aliquot portions of boron trichloride were added from the gas phase and the reaction followed conductimetrically. Breaks in the titration curve were observed at 1 : 1 and 2 : 1 mole ratios (acid : base) (Figure).

(b) *With chlorine.* The complex (0·0777 g, 0·130 mmol) was degassed overnight. After cooling to −196 °C (liquid-nitrogen bath), hydrogen chloride (7 cm^3, 0·25 mol) was condensed in from the gas phase. Aliquot portions of chlorine were added from the gas phase and the reaction followed conductimetrically. A general increase in conductivity was observed, but the individual conductivities were very variable.

I.r. Spectra of Tetrakis[carbonyl(π-cyclopentadienyl)iron(I)*] in Some Strong Anhydrous Acids.*—The complex was degassed overnight, as were the acids used in this study. Solutions of the complex were prepared under an atmosphere of nitrogen, smeared between Polythene sheets, and examined in the 2 200—1 600 cm^{-1} region by i.r. spectroscopy. Carbonyl absorption bands are given in Table 1.

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