Reactions of [Fe(cp)(CO)$_2$Cl] (cp = η-cyclopentadienyl) with 3-Methylbut-2-enoic Acid and its Methyl Ester. *X*-Ray Crystal and Molecular Structure‡ of Bis[dicarbonyl(η-cyclopentadienyl)(3-methylbut-2-enoato)iron(II)]hydrogen Hexafluoroantimonate and μ-Chloro-bis[dicarbonyl(η-cyclopentadienyl)iron(II)] Hexafluoroantimonate

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Reaction of [Fe(cp)(CO)$_2$Cl] (cp = η-C_5H_5) with AgSbF$_6$ in the presence of Me$_2$C=CHCOOH affords red [Fe(cp)(CO)$_2$(Me$_2$C=CHCOOH)][SbF$_6$] with binding through the OH oxygen atom or orange [{Fe(cp)(CO)$_2$(Me$_2$C=CHCOO)}$_2$H][SbF$_6$]. The ester Me$_2$C=CHCOOMe gives [Fe(cp)(CO)$_2$(Me$_2$C=CHCOOMe)][SbF$_6$] for which i.r. studies imply binding through the carbonyl oxygen atom of the ester group. The spectroscopic properties of these compounds are discussed. The *X*-ray structure of [{Fe(cp)(CO)$_2$(Me$_2$C=CHCOO)}$_2$H][SbF$_6$] has been determined. Crystal data: monoclinic, *a* = 29.901(2), *b* = 7.495(2), *c* = 14.006(2) Å, β = 100.65(1)°, space group *C*2/*c*, and *Z* = 4. The cation contains a centre of symmetry and is regarded as being made up of two Fe(cp)(CO)$_2$ units each bound to a carbonyl oxygen atom of a symmetrical (Me$_2$C=CHCOO)$_2$H unit, with the two non-co-ordinated oxygen atoms hydrogen bonded together. The short O(9) ··· O(9′) distance [2.406(9) Å] is indicative of a symmetrical hydrogen bond. The coplanarity of the two acid groups suggests some double bond delocalisation. In CH$_2$Cl$_2$, the compound [Fe(cp)(CO)$_2$(Me$_2$C=CHCOOH)][SbF$_6$] slowly gives [{Fe(cp)(CO)$_2$}$_2$Cl][SbF$_6$] for which the *X*-ray crystal structure shows an angle of 119.4(2)° at the bridging chlorine atom. The crystals of the complex are monoclinic, space group $P2_1/c$, with *a* = 13.805(4), *b* = 12.301(3), *c* = 12.457(3) Å, and β = 111.88(2)°. The structure was solved *via* the heavy-atom method and refined to an *R* value of 0.053 for 4 540 observed diffractometer data.

Although many alkenes readily co-ordinate to transition elements and can thus be activated towards the attack of nucleophiles or the addition of small molecules, the stability constants for alkenes bearing more than two substituents are generally very low. One of the metal fragments that will tolerate geminally disubstituted alkenes is [Fe(cp)(CO)$_2$]$^+$ (cp = η-cyclopentadienyl) for which the 2-methylpropene complex is well known,[1] but readily exchanges 2-methylpropene with other alkenes.[2,3] 1,2-Disubstituted alkene complexes of [Fe(cp)(CO)$_2$]$^+$ are also well known, *e.g.* with acenaphthene,[4] 2,3 dihydrofuran,[5] tetramethylallene,[6] and C_6—C_8 cyclic alkenes.[2,3,7] Alkenes that bear three or more substituents do not appear to co-ordinate to [Fe(cp)(CO)$_2$]$^+$ and their co-ordination is rare for other metal-containing fragments. Isolated examples include [Fe(CO)$_4${MeOOC(H)C=C(COOMe)$_2$}][8] and rhodium complexes of α-amidoacrylic acids for which the alkene co-ordination is stabilised by co-ordination of the amido oxygen atom to form a chelate ring.[9]

During the course of studies aimed at the co-ordination of trisubstituted alkenes to transition elements,[10] we have investigated reactions of [Fe(cp)(CO)$_2$Cl] with 3-methylbut-2-enoic acid and its methyl ester. We now report the results of these investigations.

Results and Discussion

Reaction of [Fe(cp)(CO)$_2$Cl] with AgSbF$_6$ in the presence of Me$_2$C=CHCOOH (molar ratio, 1:1:1) leads to the production of two complexes, one orange and the other red. The orange complex, which is obtained from reactions carried out in methanol–dichloromethane (1:1), has the formula [{Fe(cp)(CO)$_2$(Me$_2$C=CHCOO)}$_2$H][SbF$_6$] and is sufficiently stable for crystallisation, whilst the red complex, which has the stoicheiometry [Fe(cp)(CO)$_2$(Me$_2$C=CHCOOH)][SbF$_6$], is unstable in solution and readily releases the acid in non-polar solvents. In dichloromethane a slow reaction with the solvent occurs to give the known complex[11,12] [{Fe(cp)(CO)$_2$}$_2$Cl][SbF$_6$], for which the *X*-ray crystal structure is described below.

The complex [Fe(cp)(CO)$_2$Cl] also reacts with AgSbF$_6$ in the presence of Me$_2$C=CHCOOMe to give an oily red solid which is difficult to crystallise and is substitution labile in polar solvents. This complex is apparently of formula [Fe(cp)(CO)$_2$(Me$_2$C=CHCOOMe)][SbF$_6$].

These complexes have been characterised by spectroscopic means (see Tables 1 and 2) and the *X*-ray crystal structure of [{Fe(cp)(CO)$_2$(Me$_2$C=CHCOO)}$_2$H][SbF$_6$] has been determined.

Structure of [{Fe(cp)(CO)$_2$(Me$_2$C=CHCOO)}$_2$H][SbF$_6$].—The structure of [{Fe(cp)(CO)$_2$(Me$_2$C=CHCOO)}$_2$H]$^+$ is shown in Figure 1, and selected bond angles are in Table 3. The two Fe(cp)(CO)$_2$(Me$_2$C=CHCOO) units are linked across a centre of symmetry at 0.25, 0.75, 0.5 by a hydrogen-bonded hydrogen atom. This hydrogen atom, which has been identified by a peak in the electron-density map, may be symmetrically bonded to the two oxygen atoms or may be asymmetrically

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‡ *Supplementary data available* (No. SUP 56483, 5 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Infrared data (cm^{-1}) for new iron complexes and their parent alkenes

Compound	ν(O–H)	ν(C≡O)	ν(C=O)	ν(C=C)
Me$_2$C=CHCOOH	3 100vbr	—	1 690s	1 630vs
Me$_2$C=CHCOOMe	—	—	1 720vs, br	1 655vs, br
[Fe(cp)(CO)$_2$(Me$_2$C=CHCOOH)][SbF$_6$]	3 300m, br	2 060vs, 2 015vs	1 665s	1 625s
[{Fe(cp)(CO)$_2$(Me$_2$C=CHCOO)}$_2$H][SbF$_6$]	1 720w, vbr	2 052vs, 2 007vs	1 610m, br	1 645m, br
[Fe(cp)(CO)$_2$(Me$_2$C=CHCOOMe)][SbF$_6$]	—	2 075vs, 2 020vs	1 595s	1 640s, br

Table 2. Proton n.m.r. data for iron complexes and their organic precursors in CD$_2$Cl$_2$ at 25 °C*

Compound	cp	Me$_a$	Me$_b$	H$_c$	OR	J(H$_a$H$_c$)/Hz	J(H$_b$H$_c$)/Hz
Me$_2$C=CHCOOH	—	1.98(d)	2.23(d)	5.78(m)	12.11(br s)	0.8	1.5
Me$_2$C=CHCOOMe	—	1.90(d)	2.17(d)	5.66(m)	3.64(s)	1.0	1.5
[Fe(cp)(CO)$_2$(Me$_2$C=CHCOOH)][SbF$_6$]	5.21(s)	1.95(s)	1.95(s)	5.74(s)	9.76(br s)	0	0
[{Fe(cp)(CO)$_2$(Me$_2$C=CHCOO)}$_2$H][SbF$_6$]	5.16(s)	1.81(s)	1.87(s)	5.56(s)	9.26(br s)	0	0
[Fe(cp)(CO)$_2$(Me$_2$C=CHCOOMe)][SbF$_6$]	5.29(s)	1.99(s)	2.06(s)	5.58(s)	3.82(s)	0	0

* For assignments, see Figures 2 and 3.

Table 3. Selected bond lengths (Å) and angles (°) for [{Fe(cp)(CO)$_2$(Me$_2$C=CHCOO)}$_2$H][SbF$_6$]

Fe(1)–cp(av.)	1.708	C(10)–C(11)	1.463(11)
Fe(1)–C(6)	1.774(10)	C(10)–O(8)	1.238(9)
Fe(1)–C(7)	1.777(11)	C(10)–O(9)	1.283(10)
Fe(1)–O(8)	1.965(6)	C(11)–C(12)	1.318(12)
C(6)–O(6)	1.125(14)	C(12)–C(13)	1.497(15)
C(7)–O(7)	1.123(15)	C(12)–C(14)	1.518(15)
Sb–F(av.)	1.785	O(9) ··· O(9′)	2.406(9)
C(6)–Fe(1)–C(7)	92.9(5)	C(11)–C(10)–O(8)	122.7(7)
C(6)–Fe(1)–O(8)	96.1(4)	C(11)–C(10)–O(9)	117.2(7)
C(7)–Fe(1)–O(8)	97.1(4)	O(8)–C(10)–O(9)	120.0(7)
Fe(1)–C(6)–O(6)	175.7(10)	C(10)–C(11)–C(12)	128.2(8)
Fe(1)–C(7)–O(7)	174.8(10)	C(11)–C(12)–C(13)	125.2(9)
Fe(1)–O(8)–C(10)	126.4(5)	C(11)–C(12)–C(14)	119.2(8)
cp–Fe–C(6)(av.)	123.0	C(13)–C(12)–C(14)	115.6(9)
cp–Fe–C(7)(av.)	122.0	O(9′) ··· O(9)–C(10)	180.0(4)
cp–Fe–O(8)(av.)	120.1		

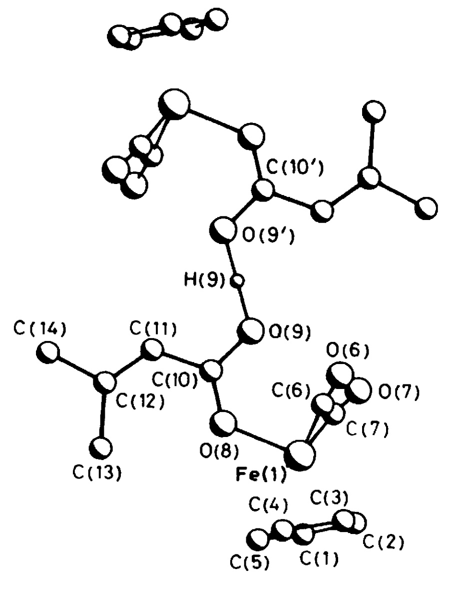

Figure 1. Solid-state structure and numbering scheme for [{Fe(cp)(CO)$_2$(Me$_2$C=CHCOO)}$_2$H]$^+$

Table 4. Selected dihedral angles (°) for [{Fe(cp)(CO)$_2$(Me$_2$C=CHCOO)}$_2$H][SbF$_6$]

O(8)–C(10)–C(11)–C(12)	2.30(14)
O(9)–C(10)–C(11)–C(12)	−179.90(9)
C(11)–C(10)–O(8)–Fe(1)	−178.00(6)
O(9)–C(10)–O(8)–Fe(1)	4.20(10)
C(10)–C(11)–C(12)–C(13)	1.10(15)
C(10)–C(11)–C(12)–C(14)	179.50(9)
C(10)–O(9)–O(9′)–C(10′)	180.00(7)
O(9′)–O(9)–C(10)–O(8)	179.43(6)
O(9′)–O(9)–C(10)–C(11)	1.53(9)

bound. In the latter case, the crystallographic centre of symmetry would arise from disorder of this hydrogen atom throughout the crystal.

Studies on other hydrogen-bonded species[13] have shown that, in general, unsymmetrical hydrogen bonds lead to a distance between the two hydrogen-bonded oxygen atoms of *ca.* 2.6—2.7 Å, whilst a shorter distance (*ca.* 2.5 Å) is observed for symmetrical hydrogen bonds. The O(9) ··· O(9′) distance observed in [{Fe(cp)(CO)$_2$(Me$_2$C=CHCOO)}$_2$H]$^+$ is 2.406(9) Å, consistent with there being a symmetrical hydrogen bond, and the i.r. spectroscopic data are consistent with this suggestion. Such symmetrical hydrogen bonds are not uncommon and examples where carboxylate anions are hydrogen bonded in this way are well known.[13] However, we believe [{Fe(cp)(CO)$_2$(Me$_2$C=CHCOO)}$_2$H]$^+$ to be the first example of a complexed carboxylate ion to be hydrogen bonded in this way. The related [{Fe(cp)(CO)$_2$(PPhBu^{t}O)}$_2$H][BPh$_4$] with an O ··· O distance of 2.403(4) Å has been crystallographically characterised.[14]

The (Me$_2$C=CHCOO)$_2$H unit is essentially planar, with dihedral angles as shown in Table 4. The bond lengths within this unit are comparable with those found for but-2-enoic acid and but-2-enamide (Table 5),[15] both of which crystallise as hydrogen-bonded dimers, consistent with substantial delocalisation of the electrons in the π system. This is reflected by the short C(10)–C(11) bond [1.463(11) Å, *cf.* 1.54 Å for a normal C–C single bond]. The lengths of the C=O bonds in [{Fe(cp)(CO)$_2$(Me$_2$C=CHCOO)}$_2$H]$^+$ [1.238(9) Å] are shorter than in but-2-enoic acid [1.265(9) Å], where the hydrogen bond is asymmetric, but are similar to those found in *e.g.* Na[(MeCOO)$_2$H] (1.243 Å)[16] or potassium chloromaleate(1−) (1.226, 1.240 Å)[17] both of which contain short, probably symmetrical hydrogen bonds. Apparently the effect of co-

Table 5. Bond lengths (Å) for $[\{Fe(cp)(CO)_2(Me_2C=CHCOO)\}_2H][SbF_6]$ (**1**), butenoic acid, and butenamide compared with 'normal' lengths of isolated bonds

	(1)	Butenoic acid	Butenamide	Normal bond length
C(11)–C(12)	1.318(12)	1.293(11)	1.326(7)	1.33
C(10)–C(11)	1.463(11)	1.459(9)	1.502(6)	1.54
C(10)–O(8)	1.238(9)	1.265(9)	1.221(5)	1.21
C(10)–O(9)	1.283(10)	1.287(9)	—	1.30
C(12)–C(14)	1.518(15)	1.502(9)	1.491(7)	1.54

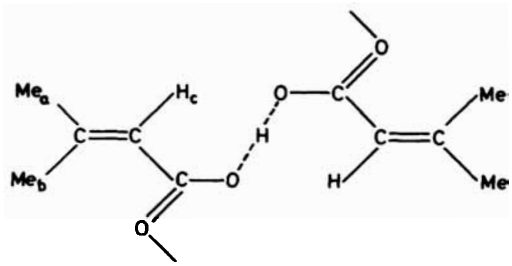

Figure 2. Diagrammatic representation of the bonding in the $[(Me_2C=CHCOO)_2H]^-$ unit of $[\{Fe(cp)(CO)_2(Me_2C=CHCOO)\}_2H]^+$

ordination of the carbonyl group to the iron is little different from the effect of non-bonded interactions with alkali-metal atoms in the other salts containing short hydrogen bonds.[16,17]

Despite this delocalisation the structure is best described as consisting of $[(Me_2C=CHCOO)_2H]^-$ co-ordinated *via* the carbonyl oxygen atoms to two $[Fe(cp)(CO)_2]^+$ units and the delocalisation probably allows some charge neutralisation (Figure 2). The remainder of the structure of the cation is not unusual and the only other feature of note is that each SbF_6^- is surrounded by eight cyclopentadienyl groups which form a spherically symmetrical cavity. The presence of the spherically symmetrical anion in this cavity probably contributes to the rotational disorder observed for this anion.

Spectroscopic Properties of the Complexes.—Important features of the i.r. spectra of $Me_2C=CHCOOR$ (R = Me or H) and of their complexes with $[Fe(cp)(CO)_2]^+$ are listed in Table 1. In all cases, ν(C=O) and ν(C=C) are clearly visible near 1 600 cm^{-1}. It is possible, on the basis of studies carried out using rhodium complexes of the diphenylphosphinous ester, $Ph_2PO_2CCH=CMe_2$,[10] to correlate the position of ν(C=O) and ν(C=C) with the bonding mode of the acrylate group. Thus, for $[\{RhCl(Ph_2PO_2CCH=CMe_2)\}_2]$, which has been shown crystallographically to have binding *via* C=C, ν(C=O) appears to higher frequency than for the free acid (1 690 cm^{-1}) and ν(C=C) is not observed above 1 550 cm^{-1}, whilst, where binding is through the carbonyl oxygen, as in $[Rh(PPh_3)_2(Ph_2PO_2CCH=CMe_2)]^+$, ν(C=C) is at 1 640 cm^{-1} and ν(C=O) is shifted to lower frequency (1 585 cm^{-1}).

The similarity in the values of ν(C=O) and ν(C=C) for $[Fe(cp)(CO)_2(Me_2C=CHCOOH)]^+$ and for the free acid clearly suggest that the π system of the acid is disturbed very little on bonding to the metal and hence that bonding is probably through the OH oxygen atom of the acid, as in Figure 3(*a*). For this complex ν(O–H) is observed as a medium broad band at 3 300 cm^{-1}, suggesting a small amount of hydrogen bonding perhaps to the carbonyl oxygen atom of another bound acid [Figure 3(*a*)].

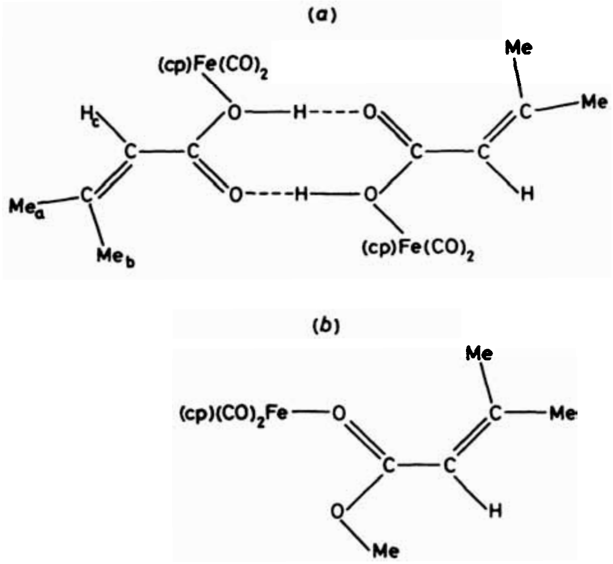

Figure 3. Proposed structure for $[Fe(cp)(CO)_2(Me_2C=CHCOOR)]^+$ where R = H (*a*) or Me (*b*)

The slightly lower values of ν(C=O) and ν(C=C) observed for $[\{Fe(cp)(CO)_2(Me_2C=CHCOO)\}_2H]^+$ are consistent with the observed delocalisation of the π system in the molecule (see above) and with binding through the carbonyl oxygen atom, whilst the failure to observe ν(O–H) near 3 000 cm^{-1} is consistent with there being a symmetrical hydrogen bond. Compounds which contain symmetrical hydrogen bonds generally exhibit variable positions for ν(O–H) and, on the basis of previously observed correlations,[18] an O ••• O distance of 2.41 Å should give ν(O–H) at 1 700—1 800 cm^{-1}. A broad weak feature centred at 1 720 cm^{-1} but overlapping with ν(C=O) is tentatively assigned to ν(O–H) for this complex.

Finally, for $[Fe(cp)(CO)_2(Me_2C=CHCOOMe)]^+$ the two absorptions near 1 600 cm^{-1} are substantially shifted from their positions in the free ester. We assume that this indicates binding through the carbonyl oxygen atom of the ester group [Figure 3(*b*)], and tentatively assign ν(C=O) at 1 595 cm^{-1} and ν(C=C) at 1 640 cm^{-1}.

The intensity of ν(C=C) for the free and bound acid and ester is much greater than is normally observed for unsymmetrical alkenes. This suggests that some intensity borrowing from ν(C=O), probably *via* Fermi resonance, is occurring. In all cases, there is probably substantial mixing of the two vibrations.

The ^1H n.m.r. spectra of the three complexes are unexceptional (Table 2) and the high value of δ for the vinylic proton in each case is consistent with there being no metal–alkene type interaction. For $[Fe(cp)(CO)_2(Me_2C=CHCOOH)]^+$, although the spectrum in CD_2Cl_2 is complicated by the presence of free $Me_2C=CHCOOH$ and presumably $[\{Fe(cp)(CO)_2\}_2Cl]^+$, the methyl resonances of the bound acid appear to give a single resonance, presumably on account of an accidental degeneracy. The lability of $[Fe(cp)(CO)_2(Me_2C=CHCOOMe)]^+$ is confirmed by the observation that ^1H n.m.r. spectra measured in $[^2H_6]$acetone (solv) show only a cyclopentadienyl resonance {presumably from $[Fe(cp)(CO)_2(solv)]^+$} and resonances from free $Me_2C=CHCOOMe$.

The fast atom bombardment mass spectrum of $[\{Fe(cp)(CO)_2(Me_2C=CHCOO)\}_2H][SbF_6]$ in a matrix of 3-nitrobenzyl alcohol shows a signal of medium intensity at *m*/*z* 553 corresponding to the parent ion, $[\{Fe(cp)(CO)_2(Me_2C=CHCOO)\}_2H]^+$, and fragments corresponding to $[Fe(cp)(CO)_2(Me_2C=CHCOOH)]^+$, [Fe(cp)(CO)(Me$_2$C=

Table 6. Selected bond lengths (Å) and angles (°) for $[\{Fe(cp)(CO)_2\}_2Cl][SbF_6]$

Fe(1)–Cl	2.309(4)	Fe(2)–Cl	2.306(3)
Fe(1)–C(6)	1.773(8)	Fe(2)–C(16)	1.810(10)
Fe(1)–C(7)	1.774(8)	Fe(2)–C(17)	1.785(9)
Fe(1)–cp(1)(av.)	1.715	Fe(2)–cp(2)(av.)	1.704
C(6)–O(1)	1.152(10)	C(16)–O(11)	1.110(12)
C(7)–O(2)	1.146(9)	C(17)–O(21)	1.135(10)
Sb(1)–F(av.)	1.841		
cp(1)–Fe(1)–Cl(av.)	123.0	cp(2)–Fe(2)–Cl(av.)	122.9
cp(1)–Fe(1)–C(7)(av.)	122.8	cp(2)–Fe(2)–C(17)(av.)	122.4
cp(1)–Fe(1)–C(6)(av.)	121.8	cp(2)–Fe(2)–C(16)(av.)	124.0
Fe(1)–C(6)–O(1)	179.1(5)	Fe(2)–C(16)–O(11)	177.0(6)
Fe(1)–C(7)–O(2)	178.5(7)	Fe(2)–C(17)–O(21)	177.6(2)
C(7)–Fe(1)–C(6)	93.5(4)	C(17)–Fe(2)–C(16)	93.9(4)
C(6)–Fe(1)–Cl	95.9(3)	C(16)–Fe(2)–Cl	94.7(1)
C(7)–Fe(1)–Cl	92.2(3)	C(17)–Fe(2)–Cl	90.4(3)
Fe(1)–Cl–Fe(2)	119.4(2)		

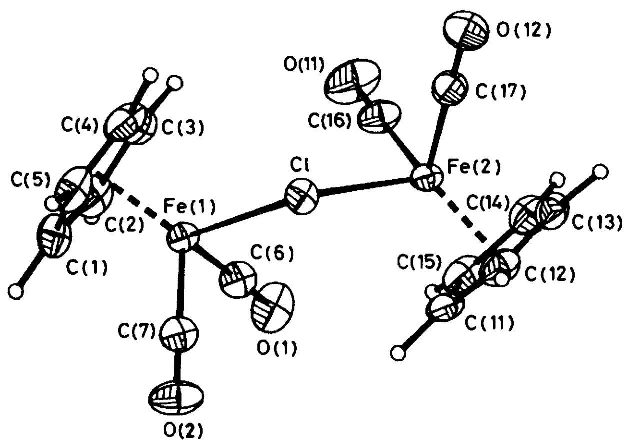

Figure 4. Solid-state structure and numbering scheme for $[\{Fe(cp)(CO)_2\}_2Cl]^+$

CHCOOH)]$^+$, and $[Fe(cp)(Me_2C{=}CHCOOH)]^+$ at *m/z* 277, 249, and 221 respectively. The peaks at *m/z* 277 and 221 were very intense compared with the rest of the spectrum.

Structure of $[\{Fe(cp)(CO)_2\}_2Cl][SbF_6]$.—The structure of $[\{Fe(cp)(CO)_2\}_2Cl]^+$ is shown in Figure 4 and selected bond lengths and angles in Table 6. The complex contains two $Fe(cp)(CO)_2$ units bridged by a chlorine atom, the angle at chlorine being 119.4(2)°. The structure of this cation is similar to that of $[\{Fe(cp)(CO)_2\}_2I]^+$, where the angle at iodine is 110.8(1)°.[19] The rather larger angle at chlorine than at iodine is probably caused by steric repulsions between the two $Fe(cp)(CO)_2$ units, which will be higher in the case of the chloro-bridged dimer on account of the smaller covalent radius of chlorine. The $Fe(cp)(CO)_2$ groups have similar parameters to those in $[\{Fe(cp)(CO)_2(Me_2C{=}CHCOO)\}_2H]^+$ and are unexceptional. The fluorine atoms of the SbF_6^- ions are disordered with approximately half occupancy of two isomers related by a 30° rotation about a local C_3 axis of the octahedron.

Experimental

Microanalyses were by Elemental Micro-Analysis Ltd. I.r. spectra were obtained on a Perkin-Elmer 577 grating spectrometer using Nujol mulls between caesium iodide plates, ^1H n.m.r. spectra on Perkin-Elmer R12B (60 MHz) or Bruker WM250 (250 MHz) spectrometers, and mass spectra on a VG 7070E spectrometer. Standard Schlenk-line and catheter-tubing techniques were employed, and all solvents were carefully dried by distillation from CaH_2 (CH_2Cl_2), sodium diphenylketyl [diethyl ether, light petroleum (b.p. 40—60 °C)], or magnesium methoxide (methanol) before use.

3-Methylbut-2-enoic acid (Aldrich) was recrystallised before use and $AgSbF_6$ was stored over phosphorus pentoxide. The complex $[Fe(cp)(CO)_2Cl]$[20] and $Me_2C{=}CHCOOMe$ were prepared by standard methods.

Dicarbonyl(η-cyclopentadienyl)(3-methylbut-2-enoic acid)-iron(II) Hexafluoroantimonate.—Dichloromethane (30 cm^3) was added to a mixture of $[Fe(cp)(CO)_2Cl]$ (0.302 g, 1.42 mmol) and $AgSbF_6$ (0.488 g, 1.42 mmol) and the mixture was stirred for 5 min to give a deep red solution and a white precipitate. The acid $Me_2C{=}CHCOOH$ (0.142 g, 1.42 mmol) in CH_2Cl_2 (20 cm^3) was added and the mixture was stirred for 0.5 h before filtration, concentration to *ca.* 10 cm^3, and cooling to −20 °C. Diethyl ether was added until a red solid began to precipitate and after 0.5 h at −20 °C it was collected, washed with diethyl ether at −20 °C, and dried *in vacuo*. Yield 0.23 g (32%) (Found: C, 28.2; H, 2.45. $C_{12}H_{13}F_6FeO_4Sb$ requires C, 28.1; H, 2.4%).

Bis[dicarbonyl(η-cyclopentadienyl)(3-methylbut-2-enoato)-iron(II)]hydrogen Hexafluoroantimonate.—Dichloromethane (20 cm^3) was added to a mixture of $[Fe(cp)(CO)_2Cl]$ (0.699 g, 3.3 mmol) and $Me_2C{=}CHCOOH$ (0.329 g, 3.3 mmol). After stirring for 1 min, $AgSbF_6$ (1.128 g, 3.3 mmol) in CH_2Cl_2 (30 cm^3) was added and the solution stirred for 0.5 h. The dark orange solution was filtered from the precipitated AgCl and the solvent was evaporated to *ca.* 20 cm^3. Methanol (10 cm^3) was added and the volume of solvent was reduced by evaporation to *ca.* 15 cm^3. On standing a bright orange microcrystalline material precipitated (0.24 g). Cooling of the mother-liquor gave a crop of orange plates (0.134 g). Combined yield 0.37 g (28%) (Found: C, 34.45; H, 3.10. $C_{24}H_{25}F_6Fe_2O_8Sb{\cdot}0.5CH_2Cl_2$ requires C, 35.45; H, 3.20%). The presence of 0.5 mol CH_2Cl_2 per mol of complex cation was confirmed by ^1H n.m.r. spectroscopy.

Dicarbonyl(η-cyclopentadienyl)(methyl 3-methylbut-2-enoate)iron(II) Hexafluorantimonate.—Dichloromethane (25 cm^3) was added to a mixture of $[Fe(cp)(CO)_2Cl]$ (0.5 g, 2.3 mmol) and $AgSbF_6$ (0.80 g, 2.3 mmol). After stirring for 10 min $Me_2C{=}CHCOOMe$ (0.26 g, 2.3 mmol) in CH_2Cl_2 was added and the solution stirred for 0.5 h. The red solution was filtered from precipitated AgCl and treated with light petroleum (20 cm^3). The red oil was collected, washed with light petroleum (2 × 10 cm^3), and recrystallised from CH_2Cl_2–diethyl ether at −20 °C to give an oily solid. This was collected, washed with diethyl ether, and dried *in vacuo*. Yield 0.4 g (33%) (Found: C, 26.3; H, 2.9; F, 22.7. $C_{13}H_{15}F_6FeO_4Sb$ requires C, 29.6; H, 2.9; F, 21.6%).

Decomposition of $[Fe(cp)(CO)_2(Me_2C{=}CHCOOH)][SbF_6]$ *in Dichloromethane.*—The complex $[Fe(cp)(CO)_2(Me_2C{=}CHCOOH)][SbF_6]$ (0.1 g) was dissolved in CH_2Cl_2 (5 cm^3). After filtration, the solution was stored at −25 °C for several days. The dark red crystals which separated were collected and dried in air. Yield of $[\{Fe(cp)(CO)_2\}_2Cl][SbF_6]$ 0.03 g (49%) (Found: C, 27.4; H, 1.75. $C_{14}H_{10}ClF_6Fe_2O_4Sb$ requires C, 26.9; H, 1.6%).

Crystallography.—$[\{Fe(cp)(CO)_2(Me_2C{=}CHCOO)\}_2H][SbF_6]$. Thin platy crystals were obtained from chlorobenzene–light petroleum at −20 °C.

Table 7. Atom co-ordinates (× 10^4)

Atom	*x*	*y*	*z*
(*a*) $[\{Fe(cp)(CO)_2(Me_2C{=}CHCOO)\}_2H][SbF_6]$			
Sb	0(0)	64(1)	2 500(0)
F(1)	0(0)	2 516(11)	2 500(0)
F(2)	0(0)	−2 369(12)	2 500(0)
F(3)	−74(6)	91(12)	3 720(6)
F(4)	−573(4)	108(17)	2 015(12)
Fe(1)	1 118(0)	6 015(1)	5 006(1)
C(1)	668(3)	5 623(13)	5 952(7)
H(1)	710(3)	6 184(13)	6 674(7)
C(2)	448(3)	6 442(13)	5 102(8)
H(2)	289(3)	7 742(13)	5 052(8)
C(3)	468(3)	5 306(14)	4 335(7)
H(3)	325(3)	5 556(14)	3 580(7)
C(4)	710(3)	3 742(12)	4 715(7)
H(4)	788(3)	2 607(12)	4 300(7)
C(5)	826(3)	3 945(12)	5 715(7)
H(5)	1 006(3)	2 985(12)	6 220(7)
C(6)	1 255(3)	6 410(15)	3 845(7)
O(6)	1 314(3)	6 670(15)	3 087(5)
C(7)	1 245(3)	8 246(13)	5 393(9)
O(7)	1 293(3)	9 688(10)	5 606(9)
C(10)	2 088(2)	5 536(10)	5 508(6)
C(11)	2 511(3)	4 637(11)	5 944(6)
H(11)	2 821(3)	5 290(11)	5 848(6)
C(12)	2 561(3)	3 134(12)	6 441(6)
C(13)	2 180(4)	1 993(16)	6 651(10)
C(14)	3 037(4)	2 437(16)	6 822(8)
O(8)	1 708(2)	4 969(7)	5 589(4)
O(9)	2 123(2)	6 999(8)	5 052(5)
(*b*) $[\{Fe(cp)(CO)_2\}_2Cl][SbF_6]$			
Fe(1)	1 511(1)	1 878(1)	4 030(1)
Fe(2)	4 490(1)	2 370(1)	6 043(1)
Cl	3 252(1)	1 899(1)	4 271(1)
O(1)	1 721(4)	3 320(4)	5 971(5)
O(2)	1 007(5)	3 665(4)	2 369(5)
O(11)	3 640(5)	1 009(5)	7 400(5)
O(12)	5 910(4)	693(4)	5 842(7)
C(1)	34(5)	1 231(6)	3 268(6)
C(2)	430(5)	1 020(5)	4 466(6)
C(3)	1 319(5)	404(6)	4 757(7)
C(4)	1 468(5)	172(5)	3 695(8)
C(5)	686(5)	709(6)	2 790(6)
C(6)	1 646(4)	2 754(5)	5 208(5)
C(7)	1 211(4)	2 956(5)	3 013(5)
C(11)	4 119(5)	4 000(4)	5 641(6)
C(12)	5 106(5)	3 743(5)	5 575(6)
C(13)	5 770(5)	3 395(5)	6 656(7)
C(14)	5 236(6)	3 401(6)	7 404(7)
C(15)	4 198(5)	3 824(5)	6 777(7)
C(16)	3 959(5)	1 505(5)	6 864(6)
C(17)	5 349(4)	1 346(5)	5 895(7)
Sb	7 994(.5)	3 290(.5)	4 639(.5)
F(1)	7 950(5)	2 086(5)	3 746(6)
F(2)	8 147(7)	4 586(6)	5 479(8)
F(3)	8 986(8)	2 510(9)	5 382(9)
F(4)	6 846(8)	3 824(8)	3 489(9)
F(5)	8 822(8)	4 006(9)	4 031(10)
F(6)	7 023(8)	2 509(10)	5 021(10)
F(11)	7 809(9)	4 020(9)	3 364(10)
F(12)	7 873(9)	4 190(10)	5 711(11)
F(13)	9 372(8)	2 966(10)	5 623(12)
F(14)	6 527(7)	3 369(9)	4 098(10)
F(15)	9 360(10)	3 365(10)	4 872(13)
F(16)	7 826(8)	2 536(10)	5 898(10)

Crystal data. $C_{24}H_{25}F_6Fe_2O_8Sb$, M = 789, monoclinic, a = 29.901(2), b = 7.495(2), c = 14.006(2) Å, β = 100.65(1)°, U = 3 084.62 Å^3, $F(000)$ = 1 560, space group $C2/c$, D_m = 1.667 g cm^{-3}, Z = 4, D_c = 1.699 g cm^{-3}, Mo-K_α radiation, λ = 0.710 7 Å, μ = 18.73 cm^{-1}.

Intensity data were recorded on a CAD4 diffractometer by measuring in four octants of reciprocal space to $\theta_{max.}$ = 25°. These were merged to give 2 713 unique reflections and corrected for absorption empirically. The structure was solved by Patterson and Fourier methods. The positions and anisotropic vibrational parameters of all non-hydrogen atoms were refined. Hydrogen atoms in the cyclopentadienyl group and on C(11) were included in the structure-factor calculation (one isotropic vibrational parameter employed for all hydrogen atoms). The final R factor was 0.049 for 1 972 reflections with $F > 2.5\sigma(F)$. The largest peaks in the final difference map were 0.5—1 e Å^{-3} in the vicinity of the SbF_6^- and Fe atom. A peak of 0.3 e Å^{-3} appeared at the centre of symmetry between O(9) and O(9′), 2.41 Å apart. In Figure 1, this has been included as a hydrogen atom, H(9).

The SbF_6^- group lies on a two-fold axis and the Sb–F and F–F distances were constrained to correspond to octahedral geometry; some of the anisotropic vibrational parameters derived by least-squares refinement are unrealistically large and must imply some orientational disorder of the anion. However, the final difference map shows that these vibrational parameters provide an adequate model for the electron density in this region. Some other atoms, notably the carbonyl oxygen atoms, C(13), and O(9) also have very anisotropic vibrational parameters suggesting that there may also be some disorder in these regions. The fractional co-ordinates are in Table 7.

Computations were made using the program SHELX 76[21] on an IBM 4341 computer.

$[\{Fe(cp)(CO)_2\}_2Cl][SbF_6]$. *Crystal data.* $C_{14}H_{10}ClF_6Fe_2O_4Sb$, M = 625, monoclinic, a = 13.805(4), b = 12.301(3), c = 12.457(3) Å, β = 111.88(2)°, U = 1 963.1 Å^3, Z = 4, D_c = 2.11 g cm^{-3}, $F(000)$ = 1 200, space group $P2_1/c$, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 30.2 cm^{-1}.

A total of 6 412 intensity data were measured with 5 707 unique and 4 540 with $I > 1.5\sigma(I)$. Final R values were R = 0.053 and $R' = [\Sigma(w\Delta)^2/\Delta wF_o^2]^{\frac{1}{2}}$ = 0.065.[22]

Preliminary cell dimensions were obtained from photographs and refined using the setting angles for 25 reflections automatically determined on an Enraf–Nonius CAD4 diffractometer. Intensities were collected with nickel-filtered Mo-K_α radiation in the ω—2θ scan mode. The structure was solved *via* the heavy-atom method and refined by full-matrix least squares. All non-hydrogen atoms were located in a difference map and assigned anisotropic thermal parameters. Twelve sites were located for fluorine atoms around the antimony atom which after refinement were fixed at half occupancy. Hydrogen atoms were located experimentally and refined with isotropic thermal parameters. The fractional co-ordinates are in Table 7.

Computations were made using the program SHELX 76[21] on a DEC VAX 11/750 computer. An absorption correction was performed using the program DIFABS.[22]

Acknowledgements

We thank the S.E.R.C. for a Studentship (to D. C. C.), the purchase of the high-field n.m.r. machine, and other support of the *X*-ray work. D. J. C-H. is Sir Edward Frankland Fellow of the Royal Society of Chemistry, 1984—1985.

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Received 29th July 1985; *Paper* 5/1301