Reaction of 1—3-(η-Acryloyl)tricarbonylferrate with Acyl Halides giving 1 : 1 Adducts, the 2-Acyloxy-1,1-dicarbonyl-1-halogenoferracyclopent-2-en-5-onates [†]

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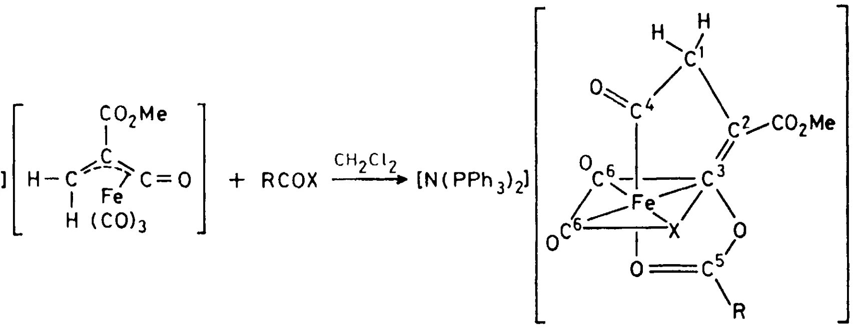
(1—3-η-Acryloyl)tricarbonylferrate (1) reacts with the acyl halides in methylene dichloride at 0 °C to afford unexpected 1 : 1 adducts, which have been deduced to be novel 2-acyloxy-1,1-dicarbonyl-1-halogenoferracyclopent-2-en-5-onates (3a)—(3e). Complex (3a; R = Me, X = Cl) reacts with 2 mol equivalents of $\mathrm{PMe_2Ph}$ to give the bis(dimethylphenylphosphine)ferracyclopentenone (4) by co-ordination of the two dimethylphenylphosphines and dissociation of both the halide ion and the carbonyl group of the enol ester in (3a). The reaction of complex (3a) with $\mathrm{SFO_2(OMe)}$ gives 2-acyloxy-1,1,1-tricarbonylferracyclopentenone (5) by the displacement of the halide ion with CO. A reaction mechanism for formation of (3) *via* (η^3-acyloxyvinylcarbene)tricarbonyliron is proposed.

THE reactions of acylcarbonylmetallate complexes with electrophilic reagents have been studied including the syntheses of the first examples of carbene–Group 6 metal complexes,[1] and the syntheses of aldehydes,[2] acyloins,[3] α-diketones,[3] 1,4-diketones,[4] hemifluorinated ketones,[5] unsymmetrical ketones,[6] and stilbenediol ester.[6] Recently, the first examples of 1—3-η-acryloylferrates (1) were prepared by the reaction of $[\mathrm{FeH(CO)_4}]^-$ with acetylenic compounds [7] or by the reaction of $[\mathrm{Fe(CO)_4}]^{2-}$ with activated halogenovinyl compounds.[8] The reactions of (1) with some electrophiles have been investigated; protonation of (1) gave $[\mathrm{Fe(CO)_4}(\pi\text{-olefin})]$ by an unusual intramolecular decarbonylation,[7] and alkylation of (1) afforded the first η^3-vinylcarbeneiron complexes,[7,8] in which both adjacent olefin and carbene carbon are co-ordinated to the metal.

We now report the reaction of (1) with acyl halides giving unexpected 1 : 1 adducts, which were deduced to be novel dicarbonylhalogenoferracyclopent-2-en-5-onate(1—) complexes having an additional five-membered chelate ring.



(1) (2a)-(2e) (3a)-(3e)

	R	X
(a)	Me	Cl
(b)	Me	Br
(c)	Me	I
(d)	Et	Cl
(e)	$\mathrm{Pr^n}$	Cl

SCHEME 1

RESULTS AND DISCUSSION

Reaction of Tricarbonyl[1—3-η-(2-*methoxycarbonyl*)-*acryloyl*]*ferrate* (1) *with Acyl Halides* (2a)—(2e).—Bis(triphenylphosphine)iminium tricarbonyl[1—3-η-(2-methoxycarbonyl)acryloyl]ferrate (1) reacted readily with acetyl chloride (2a), bromide (2b), iodide (2c), propionyl chloride (2d), or butyryl chloride [‡] (2e) at 0 °C in methylene dichloride to give yellow crystals (3a)—(3e) in yields of 36—85%. Complexes (3a)—(3e) are not the expected (η^3-acyloxyvinylcarbene)tricarbonylirons (6) but 1 : 1 adducts of (1) and (2). On the basis of the following observations, spectral data, reactivities (see below), and the 18-electron rule, (3a)—(3e) have been

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[†] More systematically, (1-acetoxy-2-methoxycarbonyl-4-oxobut-1-ene-1,4-diyl)dicarbonylhalogenoferrates(1—).

[‡] More bulky acyl halides such as pivaloyl or benzoyl chloride also reacted with (1) but ' neutral ' amorphous compounds were obtained and further investigation was not attempted.

deduced to be bis(triphenylphosphine)iminium 2-acyloxy-1,1-dicarbonyl-1-halogeno-3-methoxycarbonylferracyclopent-2-en-5-onates (Scheme 1). Analytical, i.r., far-i.r., ^1H, and ^{13}C n.m.r. spectral data of (3a)—(3e) are summarized in Tables 1—4.

TABLE 1

Infrared [a] and far-i.r. [b] spectral data (cm^{-1})

	$\nu(C{=}O)$						
Complex	Metal carbonyl region	Ester	C co-ordinated to Fe	O co-ordinated to Fe	$\nu(C{=}C)$	$\nu(Fe{-}X)$	Other bands
(3a)	1 998, 1 930	1 688	1 660	1 636	1 600	270	1 260br [c]
(3b)	1 995, 1 928	1 695	1 657	1 633	1 598	219	1 260br [c]
(3c)	1 998, 1 920	1 660	1 650	1 638	1 590	181	1 275br [c]
(3d)	1 995, 1 930	1 695	1 660	1 638	1 597		1 265br [c]
(3e)	1 995, 1 915	1 690	1 655	1 640	1 595		1 270br [c]
(4)	2 000, 1 950	1 738 1 690	1 630		1 550		
(5)	2 090, 2 075, 2 010	1 710	1 670	1 645	1 615		

[a] KBr discs. [b] Nujol mulls. [c] Bis(triphenylphosphine)iminium cation.

The i.r. spectrum of (3a) showed two bands in the region typical of terminal metal carbonyl groups in negatively charged complexes (1 998vs and 1 930vs cm^{-1}).[9] The spectrum also showed four absorptions in the region of carbonyl and C=C double bonds, ester ν(C=C) at 1 688 cm^{-1},[7-9] ν(C=O) (C co-ordinated to Fe) at 1 660 cm^{-1}, ν(C=O) (O co-ordinated to Fe) at 1 636 cm^{-1},[10] and ν(C=C) at 1 600 cm^{-1}. The fact that the dissociation of the enol ester group caused the shift of the band of (3a) at 1 636 cm^{-1} to 1 738 cm^{-1} supports these assignments [see below, complex (4)]. The far-i.r. spectra of (3a), (3b), and (3c) exhibited an absorption at 270, 219, and 181 cm^{-1} respectively showing the presence of an iron–halide bond.[11] The ^1H n.m.r. spectrum of (3a) exhibited an AB quartet at δ 3.62 (1 H) and 3.20 (1 H) p.p.m. ($|J_{AB}|$ = 19.0 Hz) due to non-equivalent sp^3 methylene protons, in addition to signals for MeCO, MeO, and $[N(PPh_3)_2]^+$. The absence of a symmetry plane including the methylene carbon and the fact that when the halide ion is displaced by a carbonyl group the signals of the sp^3 methylene protons become a singlet in complex (5) (see below) confirmed that the co-ordination geometry of (3a) is as shown in Scheme 1. The ^{13}C n.m.r. spectrum of (3a) showed four signals characteristic of a ferracyclopentenone ring:[12] sp^3 CH_2 at δ 62.4 [t, J(C–H) 128.9 Hz], two olefinic carbons at δ 110.4 and 219.0 (slightly broad), and acyliron group at δ 265.7 p.p.m. [t, J(CCH) 5.9 Hz]. The spectrum also showed a signal at δ 179.1 p.p.m. due to the carbonyl carbon whose oxygen atom is co-ordinated to the iron atom.* Spectral data for (3b)—(3e) were entirely analogous to those for (3a).

TABLE 2

Hydrogen-1 n.m.r. data (δ/p.p.m., J/Hz) [a]

Complex	sp^3–CH_2($|J_{AB}|$/Hz)	CO_2Me (s, 3 H)	Other resonances
(3a) [b,c]	3.62 (ABq, 1 H, J 19.0) 3.20 (ABq, 1 H, J 19.0)	3.60	7.59—7.23 (m, 30 H, PPh_3) 2.25 (s, 3 H, MeCO)
(3b) [b,d]	3.73 (ABq, 1 H, J 19.3) 3.26 (ABq, 1 H, J 19.3)	3.67	7.53—7.41 (m, 30 H, PPh_3) 2.28 (s, 3 H, MeCO)
(3c) [b,c]	3.77 (ABq, 1 H, J 19.5) 3.23 (ABq, 1 H, J 19.5)	3.66	7.70—7.23 (m, 30 H, PPh_3) 2.25 (s, 3 H, MeCO)
(3d) [b,c]	3.61 (ABq, 1 H, J 19.6) 3.21 (ABq, 1 H, J 19.6)	3.59	7.66—7.13 (m, 30 H, PPh_3) 2.56 (q, 2 H, J 8.0, $MeCH_2CO$, italic H_2) 1.14 (t, 3 H, J 8.0, $MeCH_2CO$)
(3e) [b,d]	3.69 (ABq, 1 H, J 19.3) 3.25 (ABq, 1 H, J 19.3)	3.65	7.70—7.30 (m, 30 H, PPh_3) 2.56 (t, 2 H, J 7.2, $MeCH_2CH_2CO$) 1.70 (m, 2 H, $MeCH_2CH_2CO$) 0.94 (t, 3 H, J 7.6, $MeCH_2CH_2CO$)
(4) [e]	3.51 (ABq, 1 H, J 21.0) 2.71 (ABq, 1 H, J 21.0)	3.63	7.58—7.23 (m, 10 H, Ph) 2.30 (s, 3 H, MeCO) 1.67—1.21 (m, 12 H, PMe)
(5) [e]	3.65 (s, 2 H)	3.82	2.45 (s, 3 H, MeCO)

[a] $SiMe_4$ as internal reference. [b] In CD_2Cl_2 solution. [c] Recorded at 220 MHz. [d] Recorded at 100 MHz. [e] In $CDCl_3$ solution, recorded at 60 MHz.

The formation of (3) by the reaction of (1) with (2) may be rationalized as follows. The (η^3-acyloxyvinylcarbene)iron complex (6) is first formed by acylation on the acyl oxygen atom of the acryloyl group. Co-ordination of the carbonyl group of the enol ester may then cause migratory insertion of a carbonyl group into the methylene carbon–iron bond. An analogous migratory insertion was observed in the reaction of tricarbonyl[1—3-η-(1-methoxycarbonylvinyl)methoxycarbene]iron with 2 mol equivalents of PMe_2Ph giving a

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* The chemical shift of carbonyl carbon appears at δ 168.5 p.p.m. when the carbonyl group of the enol ester dissociates in complex (4).

TABLE 3

Carbon-13 n.m.r. spectral data [δ/p.p.m., SiMe$_4$ as internal reference, *J*(^{13}C–H)/Hz] [a]

Complex	C^1 [b]	C^2	C^3	C^4	C^5	C^6	Other resonances
(3a) [c]	62.4 (t, 128.9)	110.4 [t, *J*(CCH) 5.8]	219.0 [t, *J*(CCCH) 7.8]	265.7 [q, *J*(CCH) 5.9]	179.1 [q, *J*(CCH) 7.9]	206.8 (s) 211.7 (s)	20.4 (q, 131.0, *Me*CO) 50.4 (q, 144.6, CO$_2$*Me*) 162.1 (s, *C*O$_2$Me)
(3b) [c]	63.1 (t, 128.6)	110.5 [t, *J*(CCH) 4.9]	218.7 [t, *J*(CCCH) 6.9]	265.7 (s)	179.2 [q, *J*(CCH) 7.2]	207.3 (s) 212.9 (s)	20.4 (q, 130.2, *Me*CO) 50.5 (q, 145.8, CO$_2$*Me*) 162.3 (s, *C*O$_2$Me)
(3c)	64.8 (t, 131.8)	110.8 (s, br)	218.5 (s, br)	267.7 (s, br)	179.5 (s, br)	208.7 (s) 214.2 (s)	20.4 (q, 130.2, *Me*CO) 30.5 (q, 145.2, CO$_2$*Me*) 169.2 (s, *C*O$_2$Me)
(3d) [c]	62.4 (t, 129.9)	110.3 (s, br)	218.9 (s, br)	265.7 [t, *J*(CCH) 5.9]	182.4 [t, *J*(CCH) 6.8]	206.8 (s) 211.6 (s)	9.0 (q, 128.3, *Me*CH$_2$CO) 27.2 (t, 130.9, Me*C*H$_2$CO) 50.4 (q, 145.5, CO$_2$*Me*) 162.4 (s, *C*O$_2$Me)
(3e) [c]	62.5 (t, 129.9)	110.3 (s, br)	219.1 [t, *J*(CCCH) 6.8]	265.8 [t, *J*(CCH) 5.9]	181.8 [t, *J*(CCH) 5.9]	206.8 (s) 211.8 (s)	13.6 (q, 125.3, *Me*CH$_2$CH$_2$CO) 18.7 (t, 124.0, Me*C*H$_2$CH$_2$CO) 35.6 (t, 127.0, MeCH$_2$*C*H$_2$CO) 50.4 (q, 144.6, CO$_2$*Me*) 161.9 [t, *J*(CCH) 4.0, *C*O$_2$Me]
(4) [d]	60.1 [tdd, 126.8, *J*(CP) 5.9, 18.5]	124.4 [d, *J*(CP) 5.9]	210.2 [dd, *J*(CP) 9.8, 29.3]	274.5 [t, *J*(CP) 24.4]	168.5 (s)	203.5 [dd, *J*(CP) 11.7, 37.1] 207.5 [dd, *J*(CP) 11.7, 41.0]	14.7 15.1 16.4 18.8 [m, *J*(CP) 17—24, *J*(CH) *ca.* 128, P*Me*] 22.7 (q, 129.0, *Me*CO) 50.5 (q, 146.5, CO$_2$*Me*) 161.2 [d, *J*(CP) 3.9, *C*O$_2$Me]
(5) [d]	63.5 (t, 131.9)	114.7 [t, *J*(CCH) 5.9]	194.9 [t, *J*(CCCH) 8.8]	249.6 [t, *J*(CCH) 5.9]	182.6 [q, *J*(CCH) 6.5]	200.6 (s) [e] 201.8 (s)	19.8 (q, 131.5, *Me*CO) 51.2 (q, 147.2, CO$_2$*Me*) 160.3 (s, *C*O$_2$Me)

[a] Computer resolution was 1.9531 Hz. s = Singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, tdd = triplet of double doublets, m = multiplet. [b] See Schemes 1 and 3. [c] In CD$_2$Cl$_2$ solution. [d] In CDCl$_3$ solution. [e] The ratio of the intensities of the peaks at 200.6 and 201.8 p.p.m. is 2 : 1.

TABLE 4

Analytical data

Complex	Yield (%)	Colour	M.p. (θ_c/°C)	Analysis (%) * C	H	N	X
(3a)	85	Yellow	134 (decomp.)	63.5 (63.5)	4.70 (4.40)	1.60 (1.60)	4.30 (4.05)
(3b)	63	Yellow	139	60.5 (60.4)	4.05 (4.20)	1.40 (1.55)	10.25 (8.75)
(3c)	40	Yellow	166	58.5 (57.45)	4.10 (4.00)	1.50 (1.45)	14.75 (13.2)
(3d)	71	Yellow	140	63.6 (63.85)	4.60 (4.55)	1.40 (1.60)	6.40 (4.00)
(3e)	36	Yellow	118	64.15 (64.2)	4.85 (4.70)	1.55 (1.55)	4.15 (3.95)
(4)	27	Pale yellow	142	54.3 (54.55)	5.25 (5.30)		
(5)	17	Yellow	89	40.65 (40.75)	2.50 (2.40)		

* Calculated values are given in parentheses.

ferracyclopent-2-en-5-one complex, the structure of which was determined by *X*-ray analysis.[12,*] This migratory insertion affords the unstable unsaturated complex (7) whose vacant site may be occupied by a halide ion to give (3). The possibility that halide ion attacks the iron atom prior to the co-ordination of the enol ester may be excluded because the rate of intramolecular co-ordination of the enol ester to form a five-membered chelate ring would be much faster than that of co-ordination of the halide ion. The fact that co-ordination of a chloride ion to the iron atom was not observed[13] in the reaction of tricarbonyl[1—3-η-(1-methoxycarbonylvinyl)methoxycarbene]iron with chloride supports this assumption.

Reaction of Complex (3a) *with* PMe$_2$Ph.—Complex (3a) reacted with 2 mol equivalents of PMe$_2$Ph at 25 °C to afford pale yellow crystals of 2-acetoxy-1,1-dicarbonyl-

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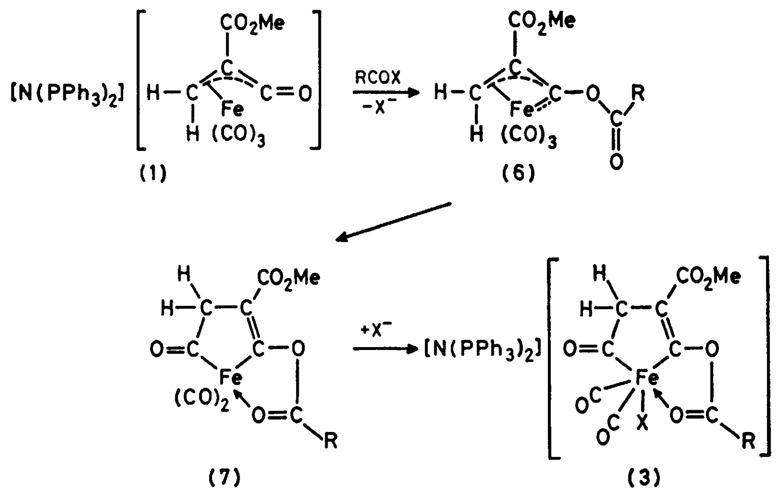
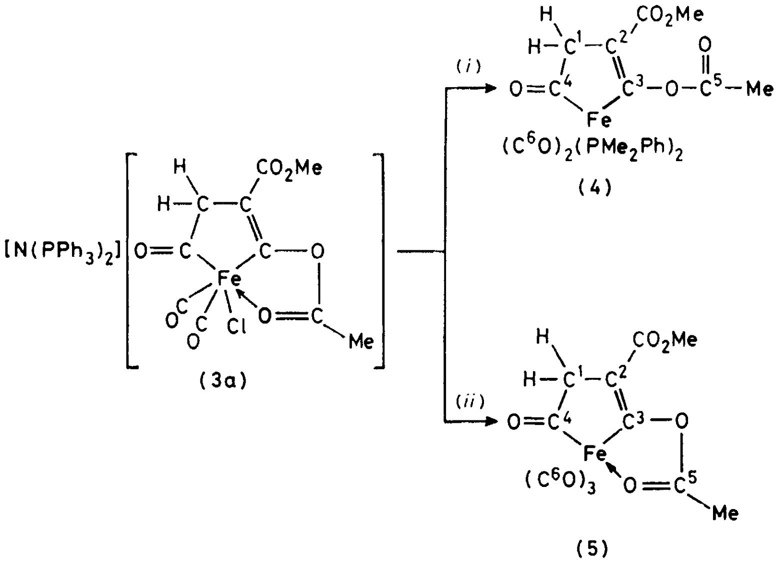
[*] During the reaction shown in Scheme 1 the zerovalent iron complex (1) is oxidized to a divalent iron complex. A similar oxidation was observed in the reaction of an (η^3-vinylcarbene)iron complex with CO or PR$_3$ (T. Mitsudo, T. Sasaki, Y. Watanabe, Y. Takegami, S. Nishigaki, and K. Nakatsu, *J.C.S. Chem. Comm.*, 1978, 252).

1,1-bis(dimethylphenylphosphine)-3-methoxycarbonyl-ferracyclopent-2-en-5-one (4) in 27% yield (Scheme 3). The i.r. spectrum of (4) showed two bands in the region of ' neutral ' terminal-carbonyl groups for a complex with a tertiary phosphine ligand[14] (2 000 and 1 950 cm^{-1}), ester ν(C=O) at 1 690, ν(C=O) (C co-ordinated to Fe) at 1 630, and ν(C=C) at 1 550 cm^{-1}. The spectrum also showed a medium-strong band at 1 738 cm^{-1}, which was deduced to be the free carbonyl group of the enol ester which had been co-ordinated to an iron atom in (3a). The ^{1}H n.m.r. spectrum of (4) exhibited an AB quartet at δ 2.71 (1 H) and 3.51 (1 H) p.p.m. ($|J_{AB}|$ 21.0 Hz) due to non-equivalent sp^3 methylene protons. The ^{13}C n.m.r. spectrum of (4) showed four signals characteristic of a ferracyclopentenone ring:[12] sp^3 CH$_2$ at δ 60.1 [tdd, J(C–H) 126.8, J(C–P) 5.9, 18.5 Hz], two olefinic carbons at δ 124.4 [d, J(C–P) 5.9 Hz] and 210.2 [dd, J(C–P) 9.8, 29.3 Hz], and an acyliron group at δ 274.5 p.p.m. [t, J(C–P) 24.4 Hz]. The dissociation of the carbonyl group of the enol ester is confirmed by the ^{13}C n.m.r. spectrum; the chemical shift of the carbonyl carbon of the enol ester in (3a) at δ 179.1 p.p.m. shifts to 168.5 p.p.m. in (4). Co-ordination of the two PMe$_2$Ph groups caused the dissociation of both the halide ion and the enol ester.



SCHEME 2



SCHEME 3 (*i*) 2 PMe$_2$Ph; (*ii*) SFO$_2$(OMe)

Reaction of Complex (3a) *with* SFO$_2$(OMe).—In an attempt to obtain the corresponding carbene complex by methylation of acyl carbonyl oxygen in (3a), the complex was treated with 1 mol equivalent of SFO$_2$(OMe) at 25 °C. However, the yellow crystals obtained were not the expected carbene complex but 2-acetoxy-1,1,1-tricarbonyl-3-methoxycarbonylferracyclopent-2-en-5-one (5) (yield 17%) (Scheme 3). The i.r. spectrum of complex (5) showed three bands in the ' neutral ' terminal-carbonyl region (2 090, 2 075, and 2 010 cm^{-1}), ester ν(C=O) at 1 700 cm^{-1}, ν(C=O) (C co-ordinated to Fe) at 1 670 cm^{-1}, ν(C=O) (O co-ordinated to Fe) at 1 645 cm^{-1}, and ν(C=C) at 1 615 cm^{-1}. The absorption of the carbonyl group at 1 645 cm^{-1} shows that the enol ester is still co-ordinated to the iron atom through the carbonyl oxygen atom. The ^{1}H n.m.r. spectrum of (5) exhibited a singlet at δ 3.65 p.p.m. (2 H) due to equivalent sp^3 methylene protons in addition to signals for MeCO and MeO. The singlet demonstrates the existence of a symmetry plane in this complex. The ^{13}C n.m.r. spectrum also showed four signals characteristic of a ferracyclopentenone ring:[12] sp^3 CH$_2$ at δ 63.5 [t, *J*(C–H) 131.9 Hz], two olefinic carbons at δ 114.7 [t, *J*(CCH) 5.9 Hz] and 194.9 [t, *J*(CCCH) 8.8 Hz], and an acyliron group at δ 249.6 p.p.m. [t, *J*(CCH) 5.9 Hz], as well as the co-ordinated carbonyl carbon of the enol ester at δ 182.6 p.p.m.

The mode of formation of (5) by the reaction of (3a) with SFO$_2$(OMe) is somewhat unclear. When the reaction was carried out in an atmosphere of CO, neither the absorption of CO nor the formation of (5) was observed. No plausible explanation of this effect could be found. The compound SFO$_2$(OMe) may abstract the chloride ion from (3a) to give an unstable unsaturated intermediate which may in turn abstract a CO group from another complex to give (5). The abstraction of chloride ion from (3a) by the treatment of (3a) with Ag[BF$_4$] in an atmosphere of argon or carbon monoxide was investigated. In both cases, although reaction readily occurred and a pale yellow powder was obtained, the spectral data showed that the product consists of a mixture of several complexes including a small amount of (5); none of the complexes could be isolated in pure form.

As described above, the formation of complexes (4) and (5) supports the assignment of (3).

Complexes (3), as well as (4) and (5), are to our knowledge the first examples of well characterized ferracyclopent-2-en-5-ones which are the keto-form of the 'ferrole' (ferracyclopenta-2,4-diene-2,4-diol) complexes,[15] derived by the reaction of acetylenes with Na[OH]-Fe(CO)$_5$. These complexes can also be regarded as 'hemienols' of the ferracyclopenta-2,5-dione complexes.[16]

EXPERIMENTAL

Infrared spectra were recorded on a Hitachi EPI-G2 grating spectrometer, far-i.r. spectra on a Hitachi FIS-3, ^{1}H n.m.r. spectra on JEOL-PMX-60, JNM-FX-100, or Varian HR-220 instruments, and ^{13}C n.m.r. spectra on a JNM-FX-100 at 25.05 MHz. Solvents were dried by published techniques and were distilled in an atmosphere of argon before use. Acetyl chloride, bromide, iodide, propionyl chloride, and butyryl chloride were commercial samples purified by distillation before use. Bis(triphenylphosphine)iminium tricarbonyl[1—3-η-(2-methoxycarbonyl)acryloyl]ferrate[7] and dimethylphenylphosphine[17] were prepared as described in the literature. Methyl fluorosulphate was a commercial sample used without further purification. All the reactions were carried out under an argon atmosphere.

Reaction of Tricarbonyl[1—3-η-(2-*methoxycarbonyl*)*acryloyl*]*ferrate* (1) *with Acyl Halides*.—The reaction of acetyl chloride is representative. In a dry two-necked cylindrical flask (50 cm^2), equipped with a gas inlet, rubber septum, and magnetic stirrer, was placed (1) (2.4 g, 3 mmol) and the flask flushed with argon. Methylene dichloride (5 cm^3) and acetyl chloride (0.24 g, 3 mmol) were added by a syringe, and the solution was stirred for 30 min at 0 °C. Addition of diethyl ether (9.5 cm^3) gave a small amount of white precipitate which was filtered off. Further addition of diethyl ether (40 cm^3) to the filtrate afforded a dark red oil, which crystallized in 30 min. The yellow crystals were collected and recrystallized from acetone–diethyl ether. Yield of (3a) (2.2 g, 85%). The reactions of acetyl bromide, acetyl iodide, propionyl chloride, and butyryl chloride were carried out similarly.

Reactions of Complex (3a).—*With* PMe$_2$Ph. A solution of (3a) (1.7 g, 2 mmol) in methylene dichloride (6 cm^3) was treated with dimethylphenylphosphine (0.53 cm^3, 4 mmol) at room temperature. After 30 min the solvent was evaporated off *in vacuo* and the residue was extracted with five 15-cm^3 portions of diethyl ether. Concentration of the solvent to *ca.* 1.5 cm^3 under reduced pressure and cooling on solid CO$_2$ gave yellow crystals which were collected and recrystallized from diethyl ether–n-hexane to give 2-acetoxy-1,1-dicarbonyl-1,1-bis(dimethylphenylphosphine)-3-methoxycarbonylferracyclopent-2-en-5-one (4) (0.30 g, 27%).

With methyl fluorosulphate. To a solution of (3a) (1.7 g, 2 mmol) in methylene dichloride (6 cm^3) was added methyl fluorosulphate (0.16 cm^3, 2 mmol) at room temperature. After 30 min the solvent was evaporated off *in vacuo* and the residue was extracted with four 10-cm^3 portions of diethyl ether. The reaction mixture was concentrated to *ca.* 5 cm^3 under reduced pressure and cooled on solid CO$_2$. The yellow crystals which formed were collected and recrystallized from diethyl ether–n-hexane to give 2-acetoxy-1,1,1-tricarbonyl-3-methoxycarbonylferracyclopent-2-en-5-one (5) (0.11 g, 17%).

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