Reaction of Tetracarbonylferrate with Activated Vinyl Halides to give (1—3-η-Acryloyl)tricarbonylferrates and Alkenyltetracarbonylferrates

By **Take-aki Mitsudo,* Hiroyoshi Watanabe, Yoshihisa Watanabe, Norihiko Nitani,** and **Yoshinobu Takegami,** Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Disodium tetracarbonylferrate reacts with activated vinyl halides in tetrahydrofuran under ambient conditions to give products which depend on the starting halide. The reactions of dimethyl 2-chloroethylene-1,1-dicarboxylate, methyl *Z*-3-chlorocrotonate, *E*-2-chlorovinyl t-butyl ketone, and *E*-2-chlorovinyl phenyl ketone give the corresponding 1—3-η-acryloyltricarbonylferrates and have been isolated as bis(triphenylphosphine)iminium salts (4b)—(4e) in yields of 20—60%. Methyl *E*-3-bromo-2-methylacrylate, 1-chloro-2,2-dicyanoethylene, and *E*-β-bromostyrene give the corresponding alkenyltetracarbonylferrates (5f)—(5h), *E*-3-bromoacrylate a *ca.* 1 : 1 mixture of 1—3-η-acryloyl- (4i) and alkenyl-ferrates (5i), and methyl *E*-3-chlorocrotonate an unusual 1—3-η-acryloyl complex (4j) derived by a 1,3-hydrogen shift. Protonation of (4) and (5) results in tetracarbonyl(η-olefin)iron complexes. The geometry of the starting vinyl compounds is fully retained in the products. Methylation of (4b) with $SFO_2(OMe)$ gives {1—3-η-[2,2-bis(methoxycarbonyl)vinyl]methoxycarbene}tricarbonyliron (9).

ALKENYL-TRANSITION-METAL complexes have been frequently assumed to be key intermediates in various catalytic or non-catalytic organic syntheses by acetylenic or halogenovinyl compounds using transition-metal complexes.[1] Although there have been a number of reports on alkenylmetal complexes,[1,2] less attention has been paid to the characterization of alkenyl-transition-metal complexes in comparison with alkylmetal complexes.[3] Recently, it has been reported that the reaction of $[FeH(CO)_4]^-$ (1) with electron-deficient acetylenic compounds in an aprotic solvent does not give the expected alkenyltetracarbonylferrates but affords novel (η^3-acryloyl)tricarbonylferrates.[4] Furthermore, it has been briefly reported that the reaction of $Na_2[Fe(CO)_4]$ (2) with methyl *Z*-3-bromoacrylate (3a) selectively gave tricarbonyl(1—3-η-*Z*-3-methoxycarbonylacryloyl)ferrate (4a) (Scheme 1).[4] In these reactions, it appears that a carbonyl group is inserted into the alkenyl carbon–iron bond followed by co-ordination of the olefinic group to the vacant site of the iron, showing the unusual reactivity of alkenyl(carbonyl)metal complexes. The present paper deals with the reaction of (2) with various activated halogenovinyl compounds giving a novel series of (1—3-η-acryloyl)tricarbonylferrates (4) and alkenyl tetracarbonylferrates (5).

TABLE 1

Infrared spectral data (cm^{-1}, KBr) [a]

Complex	Carbonyl bands			Other bands
	Metal carbonyl	Acryloyl	Ester, ketone	
(4a) [b]	1 995s, 1 915s, 1 900vs	1 710s	1 675m	1 258s,br [c]
(4b)	2 010s, 1 937sh, 1 918vs	1 730s	1 710m 1 695m	1 260 s,br [c]
(4c)	1 990s, 1 910sh, 1 890vs	1 718s	1 670m	1 260s,br [c]
(4d)	1 985s, 1 905s, 1 887vs	1 722s	1 640s	1 270s,br [c]
(4e)	1 997s, 1 914vs, 1 900(sh)	1 690s	1 618m	1 225s,br [c]
(4i) [d]	1 993s, 1 915s, 1 893vs	1 710m	1 680m	1 260s,br [c]
(4j)	1 977s, 1 905s, 1 875s	1 725s	1 695m	1 255s,br [c]
(5f)	2 015s, 1 935s, 1 908s 1 880s,		1 672s	1 535m, ν(C=C) 1 260s, br [c]
(5g)	2 030s, 1 920vs,br 1 890(sh)			2 220s, ν(C≡N) 1 550m, ν(C=C) 1 380s,br [c]
(5h)	1 998s, 1 905s, 1 880vs,br			1 540m, ν(C=C) 1 260s,br [c]
(5i) [d]	2 008s, 1 920(sh), 1 890vs		1 690s	1 520m, ν(C=C) 1 260s,br [c]
(9)	2 060s, 2 010s, 1 980s		1 722s 1 703s	1 530, ν_{asym} (C⋯C⋯C)
(10)	2 080s, 2 025s, 1 985s,br		1 700s	

[a] s = Strong, m = medium, br = broad. [b] Ref. 4. [c] Bis(triphenylphosphine)iminium salt. [d] Recorded on a liquid film.

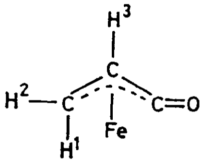
RESULTS AND DISCUSSION

Reaction of $[Fe(CO)_4]^{2-}$ *with Vinyl Halides.*—Vinyl halides having an electron-withdrawing group on the β-carbon readily reacted with a suspension of $Na_2[Fe(CO)_4]$ (2) in tetrahydrofuran (thf) at room temperature. However, the reaction was not simple and there were five groups of reactive vinyl halides: (*i*) those giving $[Fe(\eta^3\text{-acryloyl})(CO)_3]^-$ (4) selectively; (*ii*) those giving $[Fe(alkenyl)(CO)_4]^-$ (5) selectively; (*iii*) those giving a mixture of (4) and (5); (*iv*) those giving (4) accompanied by hydrogen migration; and (*v*) those giving neither (4) nor (5).

Methyl *Z*-3-bromoacrylate (3a),[4] dimethyl 2-chloroethylene-1,1-dicarboxylate (3b), methyl *Z*-3-chlorocrotonate (3c), *E*-2-chlorovinyl t-butyl ketone (3d), and *E*-2-chlorovinyl phenyl ketone (3e) belong to group (*i*), and 1—3-η-acryloyltricarbonylferrates were isolated as their bis(triphenylphosphine)iminium, $[N(PPh_3)_2]^+$, salts (4a)—(4e) in yields of 20—59%. Although the yields of the analytically pure samples were not high, the formation of other products in the reaction solutions or in the raw products was not detected by spectroscopic methods. Analytical, and i.r., ^1H and ^{13}C n.m.r. spectral data of (4a)—(4e) are summarized in Tables 1—4.

TABLE 2

Hydrogen n.m.r. spectral data (δ/p.p.m. relative to $SiMe_4$, *J*/Hz) [a]



Complex	Olefinic proton	CO_2Me (s, 3 H)	Others
(4a) [b]	2.40 (d, H^3, *J* 4.6) 3.57 (d, H^2, *J* 4.6)	3.43	7.3—7.7 (m, 30 H, PPh_3)
(4b) [c]	3.05 (s, H^3)	3.40 3.59	7.3—7.7 (m, 30 H, PPh_3)
(4c) [c]	3.40 (s, H^2)	3.42	1.50 (s, 3 H, Me) 7.5—8.3 (m, 30 H, PPh_3)
(4d) [c]	2.75 (d, H^3, *J* 6.2) 3.54 (d, H^1, *J* 6.2)		2.23 (s, 9 H, Bu^t) 7.3—7.7 (m, 30 H, PPh_3)
(4e) [d]	3.04 (d, H^3, *J* 6.0) 4.07 (d, H^1, *J* 6.0)		7.9—8.2 (m, 5 H, Ph) 7.3—7.7 (m, 30 H, PPh_3)
(4i) [c]	2.77 (d, H^3, *J* 6.0) 3.10 (d, H^1, *J* 6.0)	3.45	7.3—7.7 (m, 30 H, PPh_3)
(4j) [d,e]	2.15 (s, H^1, $J \simeq 0$) 2.51 (s, H^2, $J \simeq 0$)	3.48	$\left.\begin{array}{l}\text{2.29 (1 H, } J \text{ 14.0)}\\ \text{2.92 (1 H, } J \text{ 14.0)}\end{array}\right\}$ AB(q) 7.3—8.0 (m, 30 H, PPh_3)
(5f) [c]	9.45 (s, 1 H)	3.55	2.10 (s, 3 H, Me) 7.3—7.7 (m, 30 H, PPh_3)
(5g) [c]	10.65 (s, 1 H)		7.0—7.9 (m, 30 H, PPh_3)
(5h) [d]	*f*		7.14 (m, 5 H, ph) 7.4—7.7 (m, 30 H, PPh_3)
(5i) [c]	6.34 (d, 1 H, *J* 16.0) 9.67 (d, 1 H, *J* 16.0)		7.3—7.7 (m, 30 H, PPh_3)
(9) [c]	4.33 (s, 1 H)	3.60 3.67	4.60 (s, 3 H,OCMe)
(10) [c]	5.73 (s, 1 H)	3.40	1.50 (s, 3 H, Me) 1.85 (s, 3 H, OCMe)

[a] s = Singlet, d = doublet, m = multiplet. Solvent: CD_2Cl_2. [b] Ref. 4. [c] Recorded at 60 MHz. [d] Recorded at 220 MHz. [e] Recorded at −30 °C. [f] Signals overlapped with those of PPh_3.

The spectral data of these complexes are fully consistent with those of (1—3-η-acryloyl)tricarbonylferrates.[4,*] The characteristic i.r. absorptions due to ν(C=O) of an η^3-acryloyl group are found at *ca.* 1 700 cm^{-1}.[4] Hydrogen-1 and ^{13}C n.m.r. signals of the olefinic groups are found at high fields (Tables 2 and 3) showing that the olefinic groups are co-ordinated to the iron atom,[4] and characteristic ^{13}C n.m.r. absorptions of the acyl carbons of the η^3-acryloyl groups are found at δ 240—249 p.p.m.[4,5] Recently, the *X*-ray molecular structure of bis(triphenylphosphine)iminium [1—3-η-*E*-2,3-bis(methoxycarbonyl)acryloyl]tricarbonylferrate has been determined and it has been shown [6] that the representation (4) is preferable to (4′) (Scheme 1). In these reactions it appears that a carbonyl group is inserted into the alkenyl carbon–iron bond and co-ordination of the olefinic group occurs selectively.

Methyl *E*-3-bromo-2-methylacrylate (3f), 1-chloro-2,2-dicyanoethylene (3g), and *E*-β-bromostyrene (3h) belong to group (*ii*). Compound (3f) readily reacted with $Na_2[Fe(CO)_4]$ under ambient conditions and treatment of the reaction solution with $[N(PPh_3)_2]Cl$ gave colourless microcrystals (5f) in 42% yield. Spectral data of (5f) were very different from those of (4a)—(4e). The i.r. spectrum showed four strong ν(C=O) absorptions at 1 880—2 015 cm^{-1}, a strong ν(C=O) ester absorption at 1 672 cm^{-1}, and a ν(C=C) band [7] at 1 535 cm^{-1}. The ^1H n.m.r. signal of an olefinic proton at very low field [7] (δ 9.45 p.p.m., s, 1 H) and the ^{13}C n.m.r. signal of an olefinic carbon at δ 174.1 p.p.m.[†] [*J*(C–H) 142 Hz] [8] showed the presence of a σ-alkenyliron group. These spectral data apparently show that (5f) is bis(triphenylphosphine)iminium tetracarbonyl-(*E*-2-methoxycarbonyl-2-methylvinyl)ferrate (see below for the stereochemistry of the olefinic group). Complex (5f) was stable even at its boiling point in thf and the formation of an η^3-acryloyl complex was not observed.

The vinyl halide (3g) readily reacted with $Na_2[Fe(CO)_4]$ and a dark red liquid of the $[N(PPh_3)_2]^+$ salt (5g) was obtained. Although (5g) could not be obtained analytically pure, the spectroscopic data (Tables 1—3) and its reactivity (see below) showed that it is a salt of tetracarbonyl(2,2-dicyanovinyl)ferrate.

E-β-Bromostyrene (3h) was less reactive and a higher temperature (50 °C) and longer reaction time (18h) were needed to complete the reaction. Treatment of the reaction solution with $[N(PPh_3)_2]Cl$ gave pale brown needles of (5h) in 71% yield. Although ^1H and ^{13}C n.m.r. spectra were ambiguous because of overlapping of olefinic signals with those of $[N(PPh_3)_2]^+$, the i.r. spectrum {ν(C=O) at 1 998, 1 905, and 1 880; ν(C=C at 1 540 cm^{-1}; $[N(PPh_3)_2]^+$ at 1 260 cm^{-1}} and the reactivity (see below) showed that (5h) is a salt of tetracarbonyl-(*E*-2-phenylvinyl)ferrate.

Methyl *E*-3-bromoacrylate (3i) belongs to group (*iii*). It readily reacted with $Na_2[Fe(CO)_4]$ and treatment of the reaction mixture with $[N(PPh_3)_2]Cl$ gave a red liquid. The i.r. spectrum (Table 1) and ^1H n.m.r. signals at δ 3.10 and 2.77(*J* 6.0) and at 9.67 and 6.34 p.p.m. (*J* 16.0 Hz) apparently show that the red liquid consists of a mixture of tricarbonyl(1—3-η-*E*-3-methoxycarbonylacryloyl)ferrate (4i) and tetracarbonyl(*E*-2-methoxycarbonylvinyl)ferrate (5i) (51 : 49). When the reaction was carried out in thf–pyrrolidone (1 : 1), the ratio (4i) : (5i) was 57 : 43; however, reaction conditions giving (4i) or (5i) selectively could not be found.

The reaction of methyl *E*-3-chlorocrotonate (3j) with $Na_2[Fe(CO)_4]$ was somewhat different from the previous ones. The substitution reaction readily occurred and

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[*] Formation of several (η^3-acryloyl) metal complexes has been reported (see the refs. cited in ref. 4)

[†] The signal of the other olefinic carbon could not be detected probably because of overlapping with the intense signals of $[N(PPh_3)_2]^+$.

yellow microcrystals of the $[N(PPh_3)_2]^+$ salt of (4j) were isolated in 59% yield. The i.r. spectrum of (4j) exhibited three terminal ν(C=O) (1 977, 1 905, and 1 875 cm^{-1}), a ν(C=O) of an acryloyl group at 1 725 cm^{-1}, and ν(C=O) of the ester at 1 695 cm^{-1} (Table 1) showing that (4j) is also an (η^3-acryloyl)tricarbonylferrate complex.

TABLE 3

Carbon-13 n.m.r. spectral data [δ p.p.m., $SiMe_4$ internal reference, $J(^{13}C-H)$/Hz, in CD_2Cl_2] [a]

Complex	Olefinic carbon	CO_2Me(q)	CO_2Me(s)	Fe–CO(s)	Fe–C=O(s) or Fe=C–OR	Others
(4a)	17.8 (d, 171) 42.4 (d, 153)	50.4	178.4	217.8	246.0	125—133 (PPh_3)
(4b)	24.4 (d, 178) 49.7 (s)	51.0 51.3	173.0 173.0	215.7	241.5	125—133 (PPh_3)
(4c)	32.7 [m, *J*(CCH_{syn}) 5.8] 47.8 [dq, *J*(CH) 153.7, *J*(CCCH) 4.9]	50.3	177.4	217.8	243.9	20.5 [*J*(CH) 127.0, *J*(CCCH) 2.2, Me] 125—134 (PPh_3)
(4d)	19.9 (d, 176) 37.2 (d, 166)			217.8	248.3	28.1 (q, 122.0, CMe_3) 43.1 (CMe_3) 215.7 ($COBu^t$)
(4j)	31.8 (s) 33.4 (dd, 152, 170)	51.3	172.1	219.8	248.9	41.4 (t, 131, CH_2) 125—134 (PPh_3)
(5f)	174.1 (d, 142) [b]	50.7	164.9	219.9		18.9 [qd, *J*(CH) 125, *J*(CCCH) 12, Me] 125—134 (PPh_3)
(5g)	93.9 (s) 228.2 (d, 141)			217.6		117.1 [d, *J*(CCCH) 17.6, CN] 121.3 [d, *J*(CCCH) 7.8, CN] 125—134 (PPh_3)
(9)	41.8 (d, 162) 51.5 (s)	51.6 52.6	166.4 175.9	208.6	270.9	69.3 (q, 150.4, COMe)
(10)	58.4 (s) 81.5 (d, 171)	53.8	175.5	202.5 207.2 208.9		13.3 (q, 129, Me) 21.7 (q, 129, OCMe) 150.5 (s, COMe)

[a] Computer resolution was 1.953 1 Hz except for (4c) (0.549 8 Hz). s = Singlet, d = doublet, t = triplet, dq = doublet of quartets, qd = quartet of doublets, m = multiplet. [b] The signal of the other olefinic carbon could not be detected probably because of overlapping with those of PPh_3.

TABLE 4

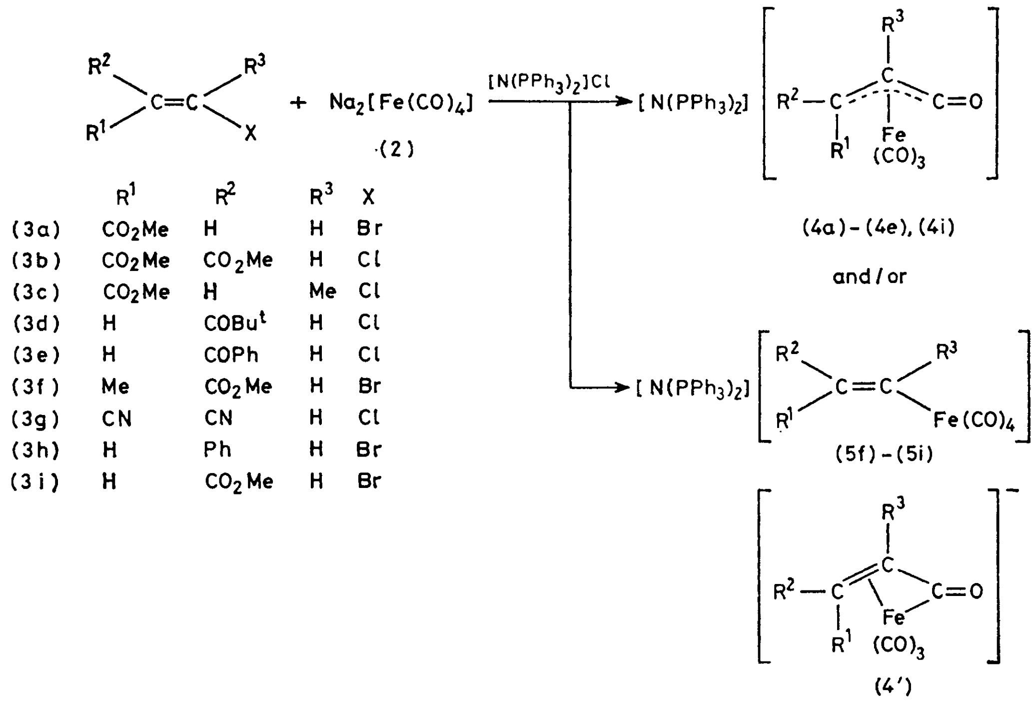
Analytical data

				Analysis (%) *		
Complex	Yield (%)	Colour	M.p. (θ_c/°C)	C	H	N
(4b)	59	Yellow crystals	98 (decomp.)	64.80 (65.05)	4.45 (4.40)	1.35 (1.65)
(4c)	55	Yellow crystals	92 (decomp.)	66.45 (67.10)	4.80 (4.65)	1.40 (1.75)
(4d)	52	Yellow crystals	101 (decomp.)	69.15 (69.05)	5.25 (5.05)	1.85 (1.70)
(4e)	20	Yellow crystals	100 (decomp.)	69.50 (70.25)	4.50 (4.45)	1.80 (1.65)
(4j)	59	Yellow crystals	64 (decomp.)	66.10 (67.10)	4.75 (4.65)	1.55 (1.75)
(5f)	42	Colourless crystals	124 (decomp.)	66.90 (67.10)	4.50 (4.65)	1.90 (1.75)
(5h)	71	Pale brown needles	127 (decomp.)	70.40 (71.20)	4.45 (4.60)	1.75 (1.75)
(9)	29	Yellow crystals	73	40.55 (40.50)	3.05 (3.10)	
(10)	36	Yellow crystals	55	42.55 (42.60)	3.85 (3.55)	

* Calculated values are given in parentheses.

The ^1H n.m.r. spectrum of (4j) was ambiguous at 30 °C because of broadening of the signals. At −30 °C the spectrum showed sharp signals and, to our surprise, the absorption due to the terminal methyl group could not be observed. Instead, two singlets at δ 2.15 (1 H) and 2.51 (1 H) p.p.m. and an AB quartet at 2.29 (1 H) and 2.92 (1 H) p.p.m. (*J* 14.0 Hz) were observed. The ^{13}C n.m.r. spectrum showed an sp^3 methylene carbon at δ 41.4 p.p.m. [*J*(C–H) 131 Hz], two absorptions of a co-ordinated olefinic group [δ 31.8 (s) and 33.4 p.p.m. (dd, 152, 170)], and a singlet at δ 248.9 p.p.m. due to the acyl carbon. These spectral data strongly suggest that a 1,3-hydrogen shift has occurred and a novel tricarbonyl[1—3-η-2-(methoxycarbonylmethyl)acryloyl]ferrate (4j) is formed (Scheme 2). The two singlets and the AB quartet in the ^1H n.m.r. spectrum can be assigned to the co-ordinated vinylidene protons and to the non-equivalent methylene protons of the methoxycarbonylmethyl group, respectively. A plausible route to (4j) is a 1,3-hydrogen shift *via* (η-allene)tricarbonylhydridoferrate (6) (Scheme 2).

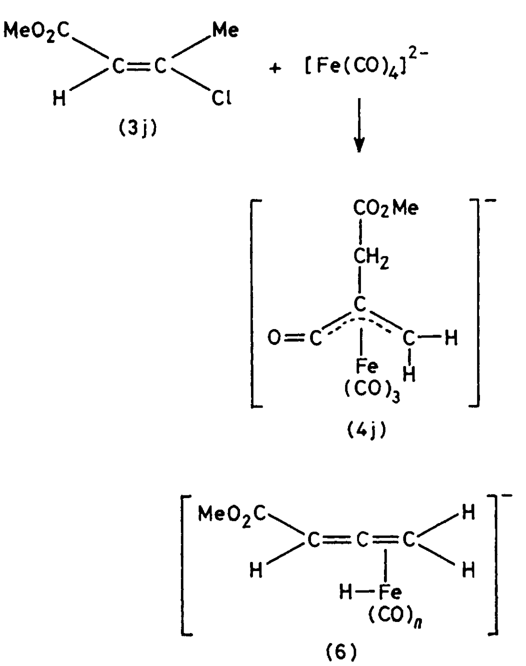
Vinyl halides such as methyl 2-halogenoacrylate, 2-halogenoacrylonitrile, and dimethyl chlorofumarate also reacted with $Na_2[Fe(CO)_4]$ but complexes containing the organic groups were not isolated. Vinyl bromide did not react.



	R^1	R^2	R^3	X
(3a)	CO_2Me	H	H	Br
(3b)	CO_2Me	CO_2Me	H	Cl
(3c)	CO_2Me	H	Me	Cl
(3d)	H	$COBu^t$	H	Cl
(3e)	H	COPh	H	Cl
(3f)	Me	CO_2Me	H	Br
(3g)	CN	CN	H	Cl
(3h)	H	Ph	H	Br
(3i)	H	CO_2Me	H	Br

SCHEME 1

Protonation of (η^3-Acryloyl)tricarbonylferrates or Alkenyltetracarbonylferrates and the Stereochemistry of the Olefinic Group during the Substitution Reaction.—It has been reported that the protonation of (η^3-acryloyl)-tricarbonylferrates gives [Fe(CO)$_4$(η-olefin)] accompanied by unusual intramolecular decarbonylation: deuteriation of (4a) selectively gave [Fe(CO)$_4$(η-*cis*-HDC=CHCO$_2$Me)] showing that the stereochemistry of the olefinic group is retained during the protonation.[4] The protonation and deuteriation of (4d), (4e), and a mixture of (4i) and (5i) also selectively gave the corresponding olefin complexes, the formation of which was observed by ^{1}H n.m.r. spectroscopy [equation (1)]. These facts apparently show that the geometry of the olefinic group in (4d), (4e), and (4i) is *trans* in spite of the reduced coupling constant in the ^{1}H n.m.r. spectra (*J* 6.2, 6.0, and 6.0 Hz, respectively). These reduced coupling constants may be due to the deviation of the olefinic protons from the plane determined by the η^3-acryloyl skeleton,[6] and the coupling constant for the *cis* form is further reduced as is found in (4a) (4.6 Hz). Reduction of coupling constants of olefinic protons caused by co-ordination of the olefinic group to metals has also been observed;[9] however, the smallest coupling constant for the *trans* form was only 8.6 Hz.

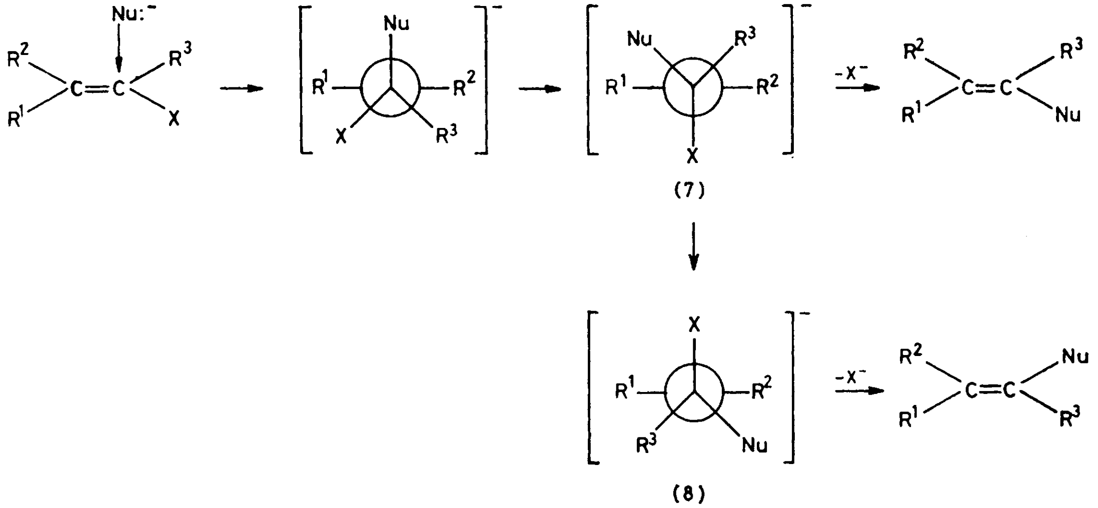


SCHEME 2

Protonation and deuteriation of (5f) and (5h) also gave the corresponding olefin complexes.[10,11] Since the stereochemistry of the olefinic group is retained on carbonylation [4,12] and protonation, the geometry of the parent halogenovinyl compounds is fully retained in the products (4) and (5) (Scheme 1).

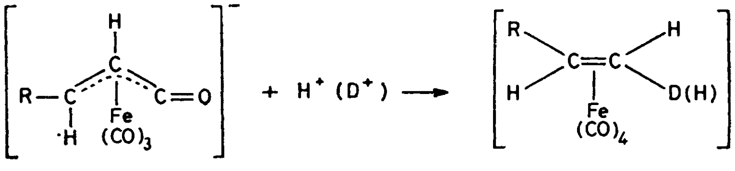
In nucleophilic substitutions of activated halogenovinyl compounds, the geometry of the olefinic group is retained in some cases [13,14] but not in others.[15] A plausible reaction mechanism is of the addition–elimination type controlled by steric effects,[15] where it is assumed that the nucleophile approaches at right angles to the plane of the double bond, and the halide ion leaves along the same path (Scheme 3). The intermediates (7) and (8) give products in which the geometry of the parent olefinic group is retained and not retained, respectively. In the present reactions, the conversion of (7) into (8) would be very difficult because of the bulkiness of the nucleophilic $[Fe(CO)_4]^-$ group, giving products in which the geometry of the starting materials is fully retained.

On the basis of the results described above and a consideration of the substitution effect on the ^1H n.m.r. chemical shifts,[4] the absorptions of olefinic protons in (4b)—(4e) and (4i) can be assigned: the signals at lower field for (4d), (4e), and (4i) may be assigned to ' anti ' protons.



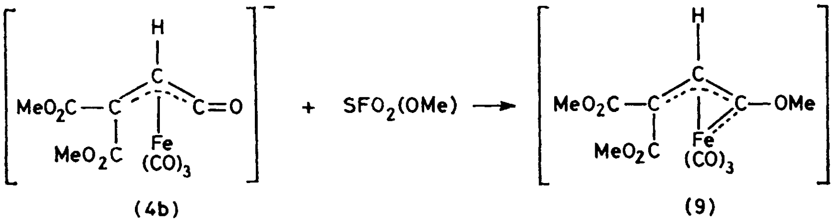
SCHEME 3 (Nu = nucleophile)

Methylation of (η^3-Acryloyl)tricarbonylferrates and Alkenyltetracarbonylferrates.—The methylation of (4b) with $SFO_2(OMe)$ gave a novel η^3-vinylcarbene complex (9) in 29% yield [equation (2)]. The spectroscopic data (Tables 1—3) were fully consistent with those of tricarbonyl(η^3-vinylcarbene)iron complexes * prepared by methylation of (η^3-acryloyl)tricarbonylferrates, obtained by the reaction of acetylenes with (1).[4] The i.r. spectra of the reaction solution of (4c) and (4k) with $SFO_2(OMe)$ exhibited characteristic bands at *ca.* 1 500 cm^{-1} showing the formation of an η^3-vinylcarbene complex, which could not be isolated in a pure form. Complexes (4d) and (4e) reacted with $SFO_2(OMe)$ to give only an amorphous solid and further investigation was not attempted.



(1)

R = Bu^{t}CO, PhCO, or CO_2Me



(2)

The reaction of (5f) with $SFO_2(OMe)$ gave yellow crystals in 36% yield. The i.r. spectra exhibited three terminal ν(C=O) bands and ν(C=O) of the ester group at 1 700 cm^{-1}. The ^{13}C n.m.r. spectrum [(olefinic carbon, δ 81.5 p.p.m. (*J* 171 Hz)] (Table 3) strongly suggests the presence of an olefinic group co-ordinated to the iron. The mass spectrum showed peaks at *m/e* 282 $[Fe(CO)_3L]^+ = M^+$, 254 $[M - CO]^+$, 226 $[M - 2CO]^+$, 198 $[M - 3CO]^+$, and 111 $[L - OMe]^+$. On the basis of these data, the structure of the methylated compound of (5f) was tentatively assigned to (10). However, further investigation is needed to determine the final structure.

EXPERIMENTAL

Infrared spectra were recorded on a Hitachi EPI-G2 grating spectrometer, ^1H n.m.r. spectra on a JEOL-PMX-60

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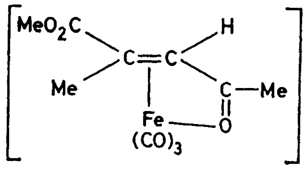
* The *X*-ray molecular structure of {1-3-η-[*E*-1,2-bis(methoxycarbonyl)vinyl]methoxycarbene}tricarbonyliron has been determined.[16]

or a Varian HR-220 instrument, and ^{13}C n.m.r. spectra on a JEOL-JNM-FX-100 at 25.05 MHz. Molecular weights were determined by cryoscopy in benzene. Solvents were dried by published techniques and were distilled in an argon atmosphere before use. Light petroleum refers to that fraction of b.p. 37—41 °C. Dimethyl 2-chloroethylene-1,1-dicarboxylate,[17] methyl *Z*- and *E*-3-chlorocrotonate,[18] t-butyl and phenyl *E*-2-chlorovinyl ketone,[13] methyl *E*-3-bromoacrylate,[15,19] methyl *E*-3-bromo-2-methylacrylate,[20] 1-chloro-2,2-dicyanoethylene,[21] and bis(triphenylphosphine)iminium chloride [22] were prepared by the methods described in the literature. *trans*-β-Bromostyrene and methyl fluorosulphonate were commercial samples purified by distillation before use. Pentacarbonyliron, sodium metal, and other reagents were commercial samples used without further purification. All the reactions were carried out under an argon atmosphere.



(10)

Preparation of Disodium Tetracarbonylferrate [23] *in Tetrahydrofuran* (*thf*).—In a dry three-necked cylindrical flask (200 cm^3) equipped with a gas inlet, magnetic stirrer, dropping funnel, rubber septum inlet, and stopcock on the side wall of the flask near the bottom, 1% sodium amalgam (3 cm^3) was prepared and then dry thf (10 cm^3) was added. To the finely suspended amalgam formed on vigorous stirring was added dropwise a solution of [Fe(CO)$_5$] (0.41 cm^3, 3.0 mmol) in thf (20 cm^3) in the course of 30 min to give a white-yellow suspension of Na$_2$[Fe(CO)$_4$]. The carbon monoxide formed was replaced with argon before the addition of vinyl halides.

Bis(triphenylphosphine)iminium (*η^3-Acryloyl*)*tricarbonylferrates* (4b), (4c), (4d), (4e), *and* (4j).—The preparation of bis(triphenylphosphine)iminium [1—3-η-3,3-bis(methoxycarbonyl)acryloyl]tricarbonylferrate (4b) is representative. To a suspension of Na$_2$[Fe(CO)$_4$] (3 mmol) in thf (30 cm^3) was added dimethyl 2-chloroethylene-1,1-dicarboxylate (3b) (0.40 cm^3, 3.0 mmol) and the solution was stirred for 1.5 h at 24 °C followed by the addition of [N(PPh$_3$)$_2$]Cl (1.7 g, 3.0 mmol) in methylene dichloride (10 cm^3). After stirring for 30 min, the solvent was distilled off *in vacuo* and the residual solid was dissolved in methylene dichloride (5 cm^3). Addition of diethyl ether (12 cm^3) gave a small amount of a brown precipitate which was filtered off. Further addition of diethyl ether (42 cm^3) to the filtrate afforded a dark red oil, which crystallized in 30 min. The yellow crystals formed were collected and recrystallized from methylene dichloride–diethyl ether to give yellow microcrystals of (4b) (1.5 g, 59%).

Bis(*triphenylphosphine*)*iminium Tetracarbonyl*(E-2-*methoxycarbonyl*-2-*methylvinyl*)*ferrate* (5f).—To a suspension of Na$_2$[Fe(CO)$_4$] (3 mmol) in thf (30 cm^3) was added methyl *Z*-3-bromo-2-methylacrylate (0.36 cm^3, 3.0 mmol) and the solution was stirred for 1 h at 25 °C followed by addition of [N(PPh$_3$)$_2$]Cl (1.7 g, 3.0 mmol) in methylene dichloride (10 cm^3). After 30 min, solvent was distilled off *in vacuo* and the residual solid was dissolved in methylene dichloride (5 cm^3). Diethyl ether (8.5 cm^3) was added and the solution was filtered. Further addition of diethyl ether (10.5 cm^3) gave white crystals which were recrystallized from methylene dichloride–diethyl ether to give 1.0 g (42%) of (5f).

Reaction of 1-*Chloro*-2,2-*dicyanoethylene with* Na$_2$[Fe(CO)$_4$].—To a suspension of Na$_2$[Fe(CO)$_4$] (3 mmol) in thf was added 1-chloro-2,2-dicyanoethylene (0.27 cm^3, 3.0 mmol) at 25 °C. After 30 min, [N(PPh$_3$)$_2$]Cl (1.7 g 3.0 mmol) in methylene dichloride (10 cm^3) was added and the solvent was distilled off *in vacuo*. The residual solid was dissolved in methylene dichloride (5 cm^3) and diethyl ether (12 cm^3) was added. The precipitate formed was filtered off and addition of diethyl ether (50 cm^3) to the filtrate gave a dark red oil. The supernatant was removed with a syringe and the dark red oil was washed with diethyl ether and dried under reduced pressure, yield of (5g) 1.5 g (50%).

Reaction of E-β-*Bromostyrene with* Na$_2$[Fe(CO)$_4$].—To a suspension of Na$_2$[Fe(CO)$_4$] (9.0 mmol) in thf (60 cm^3) was added *E*-β-bromostyrene (1.2 cm^3, 9.0 mmol) with stirring for 18 h at 50 °C. After cooling to room temperature, a solution of [N(PPh$_3$)$_2$]Cl (5.2 g, 9.0 mmol) in methylene dichloride (15 cm^3) was added and the solvent was distilled off *in vacuo*. The residual solid was dissolved in methylene dichloride (35 cm^3) and diethyl ether (7 cm^3) was added. The brown precipitate formed was filtered off and addition of diethyl ether (76 cm^3) to the filtrate afforded brown microcrystals. Recrystallization from methylene dichloride–diethyl ether (1 : 4) gave pale brown needles of bis(triphenylphosphine)iminium tetracarbonyl(*E*-2-phenylvinyl)ferrate (5h) (5.2 g, 71%).

Reaction of Methyl E-3-*Bromoacrylate with* Na$_2$[Fe(CO)$_4$].—To a suspension of Na$_2$[Fe(CO)$_4$] (3.0 mmol) in thf (30 cm^3) was added methyl *E*-3-bromoacrylate (0.37 cm^3, 3.0 mmol) at room temperature. After 30 min, a solution of [N(PPh$_3$)$_2$]Cl (1.7 g, 3.0 mmol) in methylene dichloride was added. The solvent was distilled off and the residual solid was dissolved in methylene dichloride (5 cm^3). Diethyl ether (10 cm^3) was added, the solution was filtered, and the addition of diethyl ether (50 cm^3) to the filtrate gave a dark red oily complex. The supernatant was removed and the liquid was washed with diethyl ether and dried *in vacuo*. The yield of the mixture of (4i) and (5i) was 1.2 g (51%).

Protonation of (1—3-η-E-3-*Pivaloylacryloyl*)- (4d) *and* (1—3-η-E-3-*Benzoylacryloyl*)-*tricarbonylferrate* (4e).—Protonation of (4d) and (4e) was carried out in an n.m.r. sample tube. To a solution of (4d) (100 mg) in CD$_2$Cl$_2$ (0.4 cm^3) was added trifluoroacetic acid (14 μl): δ(220 MHz) 1.30 (s, 9 H), 2.66 (d, 1 H, *J* 7.5), 2.96 (d, 1 H, *J* 11.3), and 3.75 p.p.m. (q, 1 H, *J* 7.5 and 11.3 Hz). Complex (4d) was also treated with CF$_3$CO$_2$D in a similar manner: δ 2.96 (d, 1 H, *J* 11.3) and 3.75 p.p.m. (d, 1 H, *J* 11.3 Hz).

Complex (4e) was treated with CF$_3$CO$_2$H exactly as above: δ(220 MHz) 2.73 (d, 1 H, *J* 7.0), 3.14 (d, 1 H, *J* 12.0), and 4.27 p.p.m. (q, 1 H, *J* 7.0 and 12.0 Hz). It was also treated with CF$_3$CO$_2$D: δ 3.14 (d, 1 H, *J* 12.0) and 4.27 p.p.m. (d, 1 H, *J* 12.0 Hz).

Protonation of (5f).—A solution of (5f) (3.0 mmol) in methylene dichloride (10 cm^3) was treated with CF$_3$CO$_2$H (0.23 cm^3, 3.0 mmol) at room temperature. The solvent was evaporated *in vacuo*, and the residue was extracted with two 10-cm^3 portions of benzene. Evaporation of the solvent *in vacuo* gave a brown liquid, the distillation of which at 3×10^{-3} Torr * at 50 °C gave a yellow liquid complex

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* 1 Torr = (101 325/760) Pa.

(0.21 g, 29%). The i.r. and ^1H n.m.r. spectra of the liquid complex were identical with those reported for tetracarbonyl(η-methyl methacrylate)iron.[10] When (5f) was treated with CF_3CO_2D, the n.m.r. signal of the above complex at δ 2.84 p.p.m. was not present.

Protonation of (5h).—A solution of (5h) (2.4 g, 3 mmol) in methylene dichloride (5 cm^3) was treated with CF_3CO_2H of (0.23 cm^3, 3 mmol) at room temperature. After 10 min, the solvent was distilled off and the residual solid was extracted with three 5-cm^3 portions of light petroleum. Evaporation of the solvent from the extracts gave 0.51 g (63%) of a red solid, whose i.r., mass, and ^1H n.m.r. spectra were identical with those of tetracarbonyl(η-styrene)iron.[11] Deuteriation of (5f) with CF_3CO_2D was carried out in an n.m.r. sample tube. The signal of the styrene complex at δ 2.77 p.p.m. was not present and only a couple of doublets at 3.27 (J 14.0) and 4.66 p.p.m. (J 14.0 Hz) were observed.

Methylation of (4b).—A solution of (4b) (2.6 g, 3.0 mmol) in methylene dichloride (3 cm^3) was treated with SFO_2-(OMe) (0.24 cm^3, 3.0 mmol) at 0 °C. After 30 min the solvent was distilled off *in vacuo* and the residual solid was extracted with eight 10-cm^3 portions of light petroleum. The extract was concentrated to *ca.* 5 cm^3 and cooled at -78 °C for 12 h. Yellow crystals were collected and washed with cold light petroleum (5 cm^3) to give (9) (0.28 g, 29%), M 309 (Calc. for $C_{11}H_{10}FeO_8$: 326).

Methylation of (5f).—A solution of (5f) (1.6 g, 2.0 mmol) in methylene dichoride (10 cm^3) was treated with SFO_2-(OMe) (0.16 cm^3, 2.0 mmol). The solvent was evaporated and the residual solid was extracted with two 15-cm^3 portions of light petroleum. The extract was concentrated to 5 cm^3 and was gradually cooled to -78 °C to afford a bright yellow precipitate, recrystallization of which from light petroleum gave 0.20 g (36%) of (10), M 265 (Calc. for $C_{10}H_{10}FeO_6$: 282); m/e 282, 254, 226, 198, 170, and 111.

We thank Dr. S. Uemura for his very helpful advice and support. This study was partly supported by a grant from the Ministry of Education.

[8/1022 *Received*, 1*st June*, 1978]

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