Reactions of Tetracarbonylhydridoferrate(0) with Acetylenes in Aprotic Solvents: (1—3-η-Acryloyl)tricarbonylferrates and Tricarbonyl(1—3-η-prop-2-en-1-ylidene)iron Complexes

By **Take-aki Mitsudo,* Yoshihisa Watanabe, Hiroshi Nakanishi, Isao Morishima, Toshiro Inubushi,** and **Yoshinobu Takegami,** Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

The ion $[FeH(CO)_4]^-$ reacts with acetylenes, HC≡CCOR (R = OMe, Me, or H) or $MeO_2CC{\equiv}CCO_2Me$, to give $[Fe(\eta^3\text{-}HR^1C{=}CR^2CO)(CO)_3]^-$ (3) by *trans* addition of the hydride to the acetylenic bond. Protonation of (3) gives $[Fe(\eta\text{-}HR^1C{=}CR^2H)(CO)_4]$ (5) by an intramolecular decarbonylation reaction. Methylation of (3a; R^1 = H, R^2 = CO_2Me) and (3b; R^1 = R^2 = CO_2Me) with $SFO_2(OMe)$ or $[OMe_3][BF_4]$ gives $[Fe\{\eta^3\text{-}C(OMe)C(CO_2Me){=}CH_2\}(CO)_3]$ (6a) and $[Fe\{\eta^3\text{-}trans\text{-}C(OMe)C(CO_2Me){=}C(CO_2Me)H\}(CO)_3]$ (6b). Oxidation of (6a) and (6b) with pyridine *N*-oxide gives $[Fe\{\eta\text{-}H_2C{=}C(CO_2Me)_2\}(CO)_3(py)]$ (7a) and $[Fe\{\eta\text{-}H(MeCO_2)C{=}C(CO_2Me)_2\}(CO)_3(py)]$ (7b), respectively.

TETRACARBONYLHYDRIDOFERRATE(0) (1)[1] has been shown to be a useful reagent for the reductive dimerization of acrylonitrile,[2] for hydrogenation of activated olefins such as isoprene,[3] enamines,[4] and α,β-unsaturated carbonyl compounds,[5] for carbonylation of olefins,[6] acetylenes,[7] and alkyl halides,[8] for reduction of active alkyl halides,[9] acyl halides,[10] and nitro-compounds,[11] for reductive alkylation of amines[12] and activated methylene compounds,[13] and for desulphurization,[14] hydroacylation,[15] and reductive deacylation of Knoevenagel condensates.[16] The hydride (1) has been proposed as the catalytically active species in Reppe's hydroxymethylation of olefins.[17] Almost all these reactions, however, have been carried out in protic solvents such as water and/or alcohols and there have been only a few studies on the reaction intermediates having carbon–iron bonds because of their instability in the reaction solution. Recently we reported the hydroacylation of acrylic esters using (1) in aprotic solvents, and isolated and characterized the reaction intermediate.[15]

On the other hand, the insertion of acetylenic compounds into a transition-metal–hydrogen bond has been investigated and several alkenylmetal complexes have been isolated.[18] These reactions prompted an investigation of the reaction of (1) with acetylenes in aprotic solvents, the results[19] of which are very different from those usually expected.

RESULTS AND DISCUSSION

Reaction of Tetracarbonylhydridoferrate(0) (1) *with Acetylenes.*—Methyl propiolate (2a) reacted readily with $[N(PPh_3)_2][FeH(CO)_4]$[20] (1) at 25 °C in methylene dichloride to give yellow crystals of the 1 : 1 adduct (3a), in 92% yield. Complex (3a) is diamagnetic and stable in air for several hours in the solid state. Spectral data for this complex are very different from those of alkenyltetracarbonylferrates(0) (4) which are expected to be formed by the usual insertion of the acetylene into the Fe–H bond of (1). On the basis of the spectral data and reactivities (see below), the structure of (3a) has been tentatively assigned to tricarbonyl(1—3-η-2-methoxycarbonylacryloyl)ferrate(0) † (Scheme) which may be derived by the insertion of a carbonyl group into the Fe–C bond of (4a) and co-ordination of the olefinic group to the vacant site of the iron atom. The i.r. spectrum

---

† Recently, the inferred structure was verified by *X*-ray analysis.[21]

[1] F. Feigl and P. Krumholz, *Monatsh.*, 1932, **59**, 314; P. Krumholz and H. M. A. Stettiner, *J. Amer. Chem. Soc.*, 1949, **71**, 3035.

[2] M. Misono, Y. Uchida, K. Tamai, and M. Hidai, *Bull. Chem. Soc. Japan*, 1967, **40**, 931.

[3] Y. Takegami, Y. Watanabe, I. Kanaya, T. Mitsudo, T. Okajima, Y. Morishita, and H. Masada, *Bull. Chem. Soc. Japan*, 1968, **41**, 2990.

[4] T. Mitsudo, Y. Watanabe, M. Tanaka, and Y. Takegami, *Bull. Chem. Soc. Japan*, 1975, **48**, 1506.

[5] R. Noyori, I. Umeda, and T. Ishigami, *J. Org. Chem.*, 1972, **37**, 1542.

[6] H. Masada, M. Mizuno, S. Suga, Y. Watanabe, and Y. Takegami, *Bull. Chem. Soc. Japan*, 1970, **43**, 3824; H. W. Sternberg, R. Markby, and I. Wender, *J. Amer. Chem. Soc.*, 1957, **79**, 6116.

[7] I. Wender, R. A. Friedel, R. Markby, and H. W. Sternberg, *J. Amer. Chem. Soc.*, 1955, **77**, 4946; 1956, **78**, 3621; R. Clarkson, E. R. H. Jones, C. P. Wailes, and M. C. Whiting, *ibid.*, 1956, **78**, 6206; H. D. Kaesz, R. B. King, T. A. Manuel, L. P. Nicols, and F. G. A. Stone, *ibid.*, 1960, **82**, 4749.

[8] Y. Takegami, Y. Watanabe, T. Mitsudo, I. Kanaya, and H. Masada, *Bull. Chem. Soc. Japan*, 1968, **41**, 185; Y. Takegami, Y. Watanabe, T. Mitsudo, and T. Okajima, *ibid.*, 1969, **42**, 1992.

[9] H. Alper, *Tetrahedron Letters*, 1975, 2257.

[10] T. E. Cole and R. Pettit, *Tetrahedron Letters*, 1977, 781.

[11] Y. Watanabe, T. Mitsudo, M. Yamashita, and Y. Takegami, *Bull. Chem. Soc. Japan*, 1975, **48**, 1478 and refs. therein.

[12] T. Mitsudo, Y. Watanabe, M. Tanaka, and Y. Takegami, *Bull. Chem. Soc. Japan*, 1971, **44**, 302; T. Mitsudo, Y. Watanabe, M. Tanaka, S. Atsuta, K. Yamamoto, and Y. Takegami, *ibid.*, 1975, **48**, 1506.

[13] G. Cainelli, M. Panunzio, and A. Umani-Ronchi, *J.C.S. Perkin I*, 1975, 1273.

[14] H. Alper, *J. Org. Chem.*, 1976, **38**, 2694.

[15] T. Mitsudo, Y. Watanabe, M. Yamashita, and Y. Takegami, *Chem. Letters*, 1974, 1385.

[16] M. Yamashita, Y. Watanabe, T. Mitsudo, and Y. Takegami, *Tetrahedron Letters*, 1975, 1867.

[17] F. Wada and T. Matsuda, *Chem. Letters*, 1974, 197; *J. Organometallic Chem.*, 1973, **61**, 365.

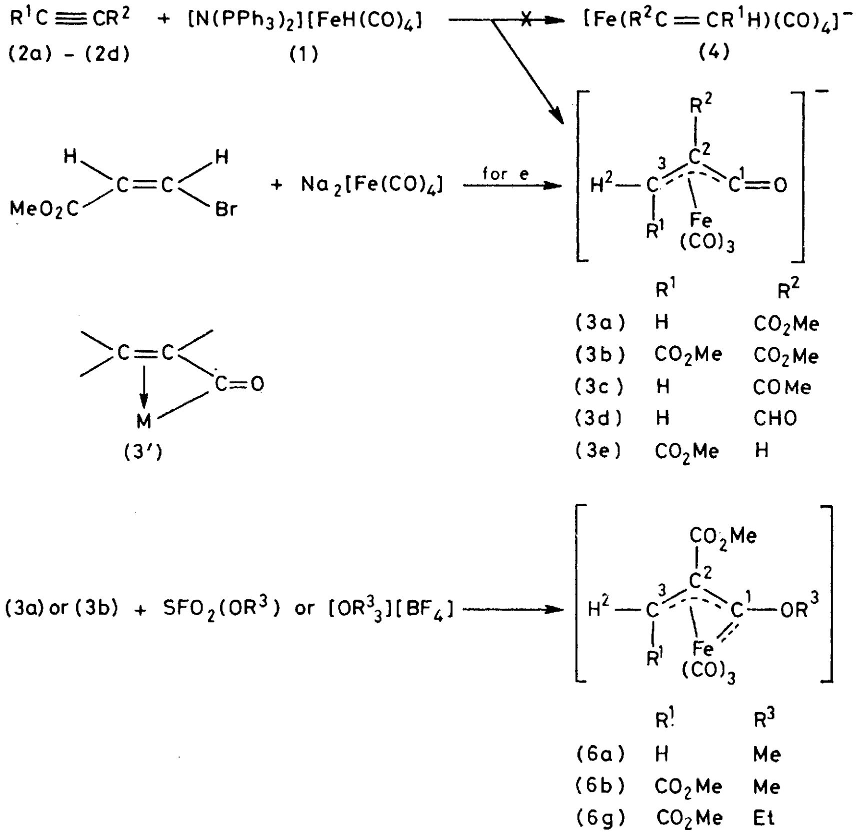
[18] A. Nakamura and S. Otsuka, *J. Mol. Catalysis*, 1975–1976, **1**, 285 and refs. therein.

[19] T. Mitsudo, H. Nakanishi, T. Inubushi, I. Morishima, Y. Watanabe, and Y. Takegami, *J.C.S. Chem. Comm.*, 1976, 416.

[20] M. B. Smith and R. Bau, *J. Amer. Chem. Soc.*, 1973, **95**, 3288.

[21] K. Nakatsu, Y. Inai, T. Mitsudo, H. Nakanishi, Y. Watanabe, and Y. Takegami, presented in part at the VIIIth International Conference on Organometallic Chemistry, Kyoto, September 1977.

of (3a) (Table 1) showed three bands in accordance with a complex having terminal carbonyls and a 1— charge [22] (1 995, 1 910, and 1 900 cm^{-1}). The spectrum also showed medium-strong bands at 1 678 [ν(C=O) of the ester] [15,22] and at 1 720 cm^{-1}, the latter being an unusual band assigned to ν(C=O) of an η^3-acryloyl group. Since ν(C=O) of σ-acryloyltetracarbonylferrate is at 1 560 cm^{-1},[22] the absorption of the acyl group is shifted by 160 cm^{-1} to higher wavenumbers by the intramolecular co-ordination of the olefinic group to the iron atom. This effect corresponds to that reported for the η^3- and σ-acryloylcobalt analogues.[23] The ^{1}H n.m.r. spectrum of (3a) (Table 2) showed two slightly broad (*J ca.* 0 Hz) singlets at high field (δ 2.43 and 1.91 p.p.m.) due to the co-ordinated olefinic group.[24] The ^{13}C n.m.r. spectrum (Table 3) showed two signals for the olefinic carbons co-ordinated to the iron atom at high field [25] {δ 24.6 [dd, $J(^{13}C-H)$ 169 and 153 Hz] and 23.3(s) p.p.m.}. An



SCHEME

TABLE 1

Infrared spectral data (cm^{-1}) for KBr mulls

	Complex	ν(C=O) metal carbonyl region			acryloyl ν(C=O)	ν(C=O) ester, ketone, or aldehyde	Other bands
(3a)	$[Fe\{\eta^3\text{-}H_2C=C(CO_2Me)CO\}(CO)_3]^-$	1 995	1 910	1 900	1 720	1 678	1 260 [a]
(3b)	$[Fe\{\eta^3\text{-}H(MeCO_2)C=C(CO_2Me)CO\}(CO)_3]^-$	2 015	1 937	1 900	1 742	1 690, 1 678	1 270 [a]
(3c)	$[Fe\{\eta^3\text{-}H_2C=C(COMe)CO\}(CO)_3]^-$	1 995	1 915	1 892	1 710	1 618	1 260 [a]
(3d)	$[Fe\{\eta^3\text{-}H_2C=C(CHO)CO\}(CO)_3]^-$	1 999	1 925	1 900	1 720	1 618	1 260 [a]
(3e)	$[Fe\{\eta^3\text{-}H(MeCO_2)C=CHCO\}(CO)_3]^-$	1 995	1 915	1 900	1 710	1 675	1 258 [a]
(6a)	$[Fe\{\eta^3\text{-}C(OMe)C(CO_2Me)=CH_2\}(CO)_3]$	2 040	1 988	1 970		1 720	1 505 [b]
(6b)	$[Fe\{\eta^3\text{-}\mathit{trans}\text{-}C(OMe)C(CO_2Me)=C(CO_2Me)H\}(CO)_3]$	2 050	2 000	1 980		1 720, 1 698	1 523 [b]
(6g)	$[Fe\{\eta^3\text{-}C(OEt)C(CO_2Me)=C(CO_2Me)H\}(CO)_3]$ [c]	2 050	2 000	1 980		1 710	1 520 [b]
(7a)	$[Fe\{\eta\text{-}H_2C=C(CO_2Me)_2\}(CO)_3(py)]$	2 050	1 990	1 950		1 720, 1 700	1 600 py
(7b)	$[Fe\{\eta\text{-}H(MeCO_2)C=C(CO_2Me)_2\}(CO)_3(py)]$	2 060	1 998	1 977		1 720, 1 698	1 600 py
(7g)	$[Fe\{\eta\text{-}H(MeCO_2)C=C(CO_2Me)(CO_2Et)\}(CO)_3(py)]$	2 060	1 998	1 974		1 718, 1 697	1 600 py

[a] Bis(triphenylphosphine)iminium cation. [b] See text. [c] Recorded on a neat liquid film.

---

[22] W. O. Siegel and J. P. Collman, *J. Amer. Chem. Soc.*, 1972, **94**, 2516.

[23] R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, 1961, **83**, 1097; 1963, **85**, 651.

[24] See, for example; M. Herberhold, 'Metal π-complexes,' Elsevier, Amsterdam, 1974, vol. 2, part 2, p. 32.

[25] J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972, p. 213.

absorption at 242.7 p.p.m. was assigned to the carbonyl carbon of the η^3-acryloyl group.[26]

TABLE 2

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

Complex	Olefinic proton	CO_2Me (s, 3 H)	Other resonances
(3a) [b]	2.43 (s, H^2) [c]	3.40	7.72—7.56 (m, 30 H, PPh_3)
	1.91 (s, H^1)		
(3b) [b]	3.67 (s, H^2)	3.47	7.76—7.60 (m, 30 H, PPh_3)
		3.40	
(3c) [b]	2.50 (s, H^2)		2.13 (s, 3 H, COMe)
	1.93 (s, H^1)		7.67—7.48 (m, 30 H, PPh_3)
(3d) [b]	2.43 (s, H^2)		0.97 (s, 1 H, CHO)
	2.12.(s, H^1)		7.60—7.30 (m, 30 H, $PPh)_3$
(3e) [d]	3.57 (d, 1 H^2, J 4.6)	3.43	7.70—7.30 (m, 30 H, PPh_3)
	2.40 (d, 1 H, J 4.6)		
(6a) [d]	3.22 (s, H^2)	3.67	4.47 (s, 3 H, COMe)
	2.63 (s, H^1)		
(6b) [b]	4.30 (s, H^2)	3.63	4.59 (s, 3 H, COMe)
		3.57	
(6g) [d]	4.30 (s, H^2)	3.63	4.93 (m, 2 H, OCH_2)
		3.57	8.43 (m, 3 H, Me)
(7a) [d]	3.39 (s, 1 H)	3.62	8.43—7.43 (m, 5 H, py)
	2.75 (s, 1 H)	3.07	
(7b) [d]	3.30 (s, 1 H)	3.70	8.43—7.30 (m, 5 H, py)
		3.63	
		3.34	
(7g) [d]	3.23 (s, 1 H)	3.68	4.13 (q, 2 H, OCH_2)
		3.32	1.23 (t, 3 H, Me)
			8.22—7.32 (m, 5 H, py)

[a] In CD_2Cl_2 solution; $SiMe_4$ as internal reference. [b] Recorded at 220 MHz. [c] See Scheme. [d] Recorded at 60 MHz.

TABLE 3

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

Complex	Olefinic carbon	$CO_2\mathit{Me}$	$\mathit{C}O_2Me$	$Fe{-}\mathit{C}{\equiv}O$	$Fe{-}C{=}O$ or $Fe{=}\mathit{C}OR$	Other resonance
(3a)	24.6 (dd, 169, 153)	50.9	174.2	217.2	242.7	135—125 PPh_3
	23.3 (s)					
(3b)	37.1 (d, 159)	51.0	177.4	214.7	235.7	134—135 PPh_3
	25.1 (s)	50.5	172.9			
(3c) *	25.4 (s)			216.9	246.1	134—125 PPh_3
	23.2 (dd)					199.1 *C*OMe
						34.0 CO*Me*
(3d) *	35.9 (s)			216.3	254.4	134—125 PPh_3
	23.5 (dd)					183.2 *C*HO
(3e)	42.4 (d, 153)	50.4	178.4	217.8	246.0	133—125 PPh_3
	17.8 (d, 171)					
(6a)	52.4 (s)	54.1	167.5	210.8	270.0	67.8 CO*Me*
	31.6 (dd, 173, 159)					
(6b)	51.4 (s)	52.6	175.8	208.6	270.9	69.9 CO*Me*
	41.8 (d, 164)	52.2	166.3			
(7b) *	65.2 (s)	53.1	175.6	211.3		155.3 } py
	52.1 (d)	51.6	171.9	209.9		138.4 } py
		49.9	171.2	207.3		126.0 } py

* Off-resonance measurement.

The similar reaction of dimethyl acetylenedicarboxylate (2b), ethynyl methyl ketone (2c), and propiolaldehyde (2d) with (1) also gave (3b) (yield 95%), (3c) (92%), and (3d) (47%), respectively. An analogous 1-3-η-acryloyltricarbonylferrate was also formed by the reaction of $[Fe(CO)_4]^{2-}$ with methyl (Z)-β-bromoacrylate and isolated as its $[N(PPh_3)_2]^+$ salt (3e) (57%). The spectral data for (3a)—(3e) are summarized in Tables 1—3. The ^1H n.m.r. spectrum of (3e) showed two doublets for the olefinic protons at δ 3.57 and 2.40 p.p.m. whose coupling constant was 4.6 Hz, showing that the *cis* configuration is retained in the product and the reduced $J(H{-}H_{cis})$ value strongly suggests co-ordination of the olefinic group.[27] The ^{13}C n.m.r. spectrum of (3e) exhibits two doublets for the olefinic carbons at δ 17.8 [J(C–H) 171 Hz] and 42.4 p.p.m. [J(C–H) 153 Hz]. The latter is reasonably assigned to the olefinic carbon attached to the methoxycarbonyl group because the absorption of the corresponding carbon in (3a) at δ 24.6 p.p.m. is shifted downfield to 37.1 p.p.m. by the replacement of the hydrogen with a methoxycarbonyl group [see (3b) in Table 3].

The X-ray diffraction study of (3b) [21] showed that the

---

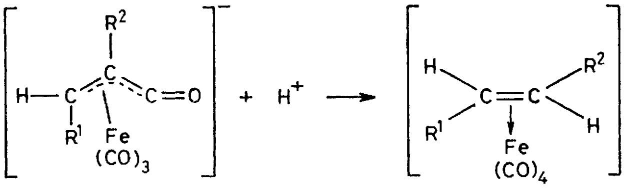
[26] G. C. Levy and G. L. Nelson, 'Carbon-13 NMR for Organic Chemists,' Wiley, New York, 1972, p. 144; J. P. Collman and S. R. Winter, *J. Amer. Chem. Soc.*, 1973, **95**, 4089.

[27] E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv., Chim. Acta*, 1963, **46**, 288; A. N. Nesmeyanov, A. N. K. Ahmed, L. V. Rybin, M. I. Rybinskaya, and Yu. A. Ustynyuk, *J. Organometallic Chem.*, 1967, **10**, 121.

complex is mononuclear and has an η^3-acryloyl structure. The two methoxycarbonyl groups are in a *trans* configuration. The bond lengths C^1–C^2 and C^2–C^3 are almost the same (*ca.* 1.45 Å) and the representation (3a)—(3e) is preferable to (3′) (Scheme). Structures of η^3-acryloylcobalt [28] and -di-iron [29] complexes have been reported, both of which have distorted olefinic groups and are approximately represented as 3′. The formation of η^3-acryloyl complexes was also postulated in the dissociation of a carbonyl group from σ-acryloyltetracarbonylcobalt,[23] and in the reaction of $[WH(C_5H_5)(CO)_2]$ with ynamines[30] on the basis of their spectroscopic data; however, the detailed structures of these complexes have not been established.

The addition reaction of (1) to the acetylenic compounds (2a)—(2d) was not inhibited by a carbon monoxide atmosphere in contrast to the corresponding addition to olefins such as methyl acrylate which was completely hindered by atmospheric carbon monoxide.[15] This fact strongly suggests that the active species in the present reaction is different from that, $[FeH(CO)_3]^-$, proposed in the reaction of olefins.[15] The addition reaction was also not inhibited by radical scavengers such as duroquinone (see below).

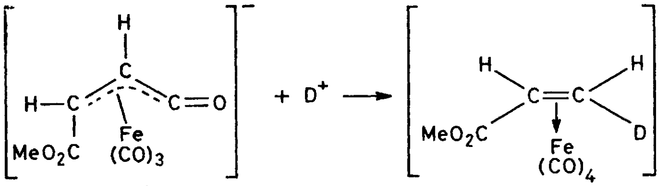
Protonation of the η^3-Acryloyltricarbonylferrates.—The protonation of (3a)—(3e) with trifluoroacetic acid in methylene dichloride gave $[Fe(\eta\text{-}HR^1C{=}CR^2H)(CO)_4]$ (5a)—(5d) quantitatively, confirmed by i.r. and ^1H n.m.r. spectroscopy. The products (5a) [27] and (5c) were isolated in 45 and 80% yield, respectively. This is a novel method for the preparation of $[Fe(\eta\text{-olefin})(CO)_4]$, and (5c) has not been prepared so far by other methods. In this reaction an unusual intramolecular decarbonylation occurs.


(1)

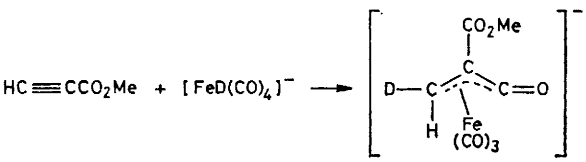
(3a)-(3e) (5a)-(5d)

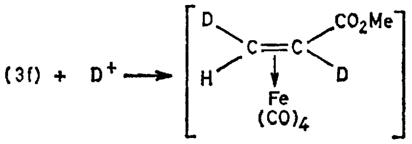
On the basis of the results of deuteriation of complexes (3) the direction of addition of (1) to the acetylenic bonds has been deduced. Deuteriation of (3a) gave $[Fe(H_2C{=}CDCO_2Me)(CO)_4]$,[27] confirming that the acyl carbonyl group is attached to the α-carbon of the ester group. Selective deuteriation of (3e) gave $[Fe(\eta\text{-}cis\text{-}HDC{=}CHCO_2Me)(CO)_4]$ showing that the geometry of the olefinic group is retained during protonation [equation (2)]. Selective deuteriation of $[Fe\{\eta^3\text{-}HDC{=}C(CO_2Me)\text{-}CO\}(CO)_3]^-$ (3f) [δ 1.9 p.p.m. (HDC)], prepared by the reaction of $[FeD(CO)_4]^-$ with methyl propiolate, gave $[Fe(\eta\text{-}trans\text{-}HDC{=}CDCO_2Me)(CO)_4]$ (5f).

If we assume that the η^3-acryloyl complexes are formed *via* σ-alkenyl complexes and that the carbonylation reaction occurs with retention of configuration,[31] the addition of (1) to the acetylenic compounds is selective *trans*-α-metallation.[18] Considering the effects of the carbon monoxide atmosphere and the addition of radical scavengers described above, the mechanism of addition of (1) to the acetylenic compounds may be somewhat different from the known mechanisms.[18] A kinetic study to elucidate the reaction mechanism is in progress.


(2)

(3e)


(3f)


(3)

(5f)

On the basis of the observation described above, ^1H n.m.r. signals of the olefinic protons of complexes (3) are fully assigned (Table 2). The disappearance of the signal at δ 2.43 p.p.m. for complex (3f) formed by the *trans* addition of $[FeD(CO)_4]^-$ to (2a) shows that the signal at 2.43 p.p.m. of (3a) is reasonably assigned to H^2 (Scheme). Thus the absorptions at δ 2.50 and 2.43 p.p.m. for (3c) and (3d) are also assigned to the H^2 protons. These results are comparable with the fact that the signal of an *anti* proton is usually found at higher field than that of a *syn* proton in η^3-allylmetal complexes.[32] The signal at δ 3.67 p.p.m. of (3b) is attributed to the H^2 proton, which is shifted 1.24 p.p.m. downfield from the corresponding proton of (3a). This effect may be mainly due to the replacement of H^1 with a methoxycarbonyl group, showing that the absorption at δ 3.57 p.p.m. of (3e) is reasonably assigned to the H^2 proton.

Alkylation of η^3-Acryloyltricarbonylferrates with $SFO_2(OR)$ *or* $[OR_3][BF_4]$.—When (3b) was treated with $SFO_2(OMe)$ or $[OMe_3][BF_4]$ in CH_2Cl_2 at 25 °C the methylated complex (6b) was isolated as yellow crystals in 95% yield. Complex (6b) is stable in air for several hours in the solid

---

[28] M. I. Bruce, B. L. Goodall, A. D. Redhouse, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1972, 1228; M. I. Bruce, B. L. Goodall, and F. G. A. Stone, *J.C.S. Dalton*, 1975, 1652.

[29] F. A. Cotton, J. D. Jamerson, and B. R. Stults, *J. Organometallic Chem.*, 1975, **94**, C53; *Inorg. Chim. Acta*, 1976, **17**, 235.

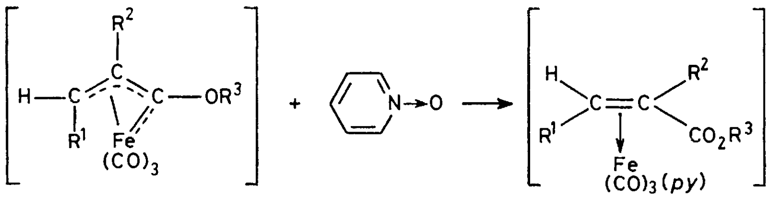
[30] W. Beck, H. Brix, and F. H. Koehler, *J. Organometallic Chem.*, 1976, **121**, 211.

[31] G. M. Whiteside and D. J. Boschetto, *J. Amer. Chem. Soc.*, 1969, **91**, 4313.

[32] M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organometallic Chem.*, 1965, **3**, 71.

state. It is diamagnetic, soluble in organic solvents, and monomeric in benzene (Found: M 322. Required for $C_{11}H_{10}FeO_8$; M 326). The i.r. spectrum of (6b) (Table 1) showed three bands in the 'neutral' terminal-carbonyl region (2 050, 2 000, and 1 980 cm^{-1}), medium-strong bands at 1 720 and 1 698 cm^{-1} [ν(C=O) of esters], and a characteristic band at 1 523 cm^{-1} (see below).

The ^{1}H n.m.r. spectrum of (6b) (Table 2) showed a singlet at δ 4.30 p.p.m. (1 H) for the olefinic proton and also a novel singlet at δ 4.95 p.p.m. for a methoxy-group indicating that methylation has occurred on the oxygen atom of the η^3-acryloyl group in (3b) [33] to form a methoxy(vinyl)carbene iron complex. The ^{13}C n.m.r. spectrum of (6b) showed the olefinic carbons co-ordinated to the iron atom at high field {δ 51.4 (s) and 41.8 p.p.m. [d, J(C–H) 164 Hz]}, and also a signal at very low field (δ 270.9 p.p.m.) which was assigned to a co-ordinated carbene carbon.[34] The absorption of the novel methoxy-group was found at δ 69.6 p.p.m. which is in agreement with those observed for other methoxycarbene metal complexes.[34] The mass spectrum of (6b) showed a parent peak at m/e 326 and peaks at m/e 298, 270, and 242 corresponding to the successive loss of three carbonyl groups. Other peaks at m/e 186 [$L^+ = (MeO_2C)CH{=}C(CO_2Me)C(OMe)^+$], 171 [$L - Me]^+$, and 155 [$L - OMe]^+$ were also observed.



(6a), (6b), or (6g) (4)

	R^1	R^2	R^3
(7a)	H	CO_2Me	Me
(7b)	CO_2Me	CO_2Me	Me
(7g)	CO_2Me	CO_2Me	Et

The spectroscopic and analytical data and the reactivities (see below) are thus consistent with complex (6b) being tricarbonyl[1—3-η-*trans*-1-methoxy-2,3-bis(methoxycarbonyl)prop-2-en-1-ylidene]iron (Scheme). Recently, the X-ray molecular structure of (6b) was determined [35] confirming the postulation described above. Methylation of (3a) with $SFO_2(OMe)$ also gave tricarbonyl(1—3-η-1-methoxy-2-methoxycarbonylprop-2-en-1-ylidene)iron (6a) as yellow crystals melting at *ca.* 20 °C. Ethylation of (3b) with $SFO_2(OEt)$ gave the 1-ethoxy-2,3-bis(methoxycarbonyl)prop-2-en-1-ylidene complex (6g). This complex was a liquid and could not be isolated in pure form; however, its spectral data were in accordance with structure (6). Its ^{1}H n.m.r. spectrum exhibited an ABX_3 pattern for the ethyl protons indicating that the two methylene protons of the ethoxycarbene group are not equivalent, probably because of the sterically hindered rotation of the ethyl group.

Although vinylcarbene metal complexes have been reported,[36] no η^3-vinylcarbene metal complexes were previously known. Complexes (6) are the first examples in which both the adjacent olefin and carbene carbon are co-ordinated to a single metal atom.

The i.r. spectra of complexes (6) exhibited characteristic strong-medium bands at 1 505—1 527 cm^{-1}. These bands were tentatively assigned to ν_{asym}(C–C) of the $C^1\cdots C^2\cdots C^3$ system (Scheme). The X-ray analysis of (6b) [35] showed that the bond lengths of C^1–C^2 and C^2–C^3 were 1.420(4) and 1.428(5) Å, respectively. These bond lengths are comparable to those found in [Fe(η-olefin)$(CO)_4$] [*ca.* 1.40 Å; [37] ν(C–C) at 1 455—1 505 cm^{-1}, weak-medium [38]] or (η-allyl)metal complexes [1.35—1.45 Å; [39] ν_{asym}(C–C) at 1 450—1 480 cm^{-1}, weak-medium [40]]. The increase in intensity of the i.r. absorption in (6) may be due to the presence of the alkoxy-group on C^1 and/or the Fe–C^1 partial double bond [1.819(3) Å] [35] which may increase the dipole moment of the $C^1\cdots C^2\cdots C^3$ system.[41] The ^{13}C n.m.r. spectra of (6) showed a signal for the carbene carbons at *ca.* 270 p.p.m., showing that these carbons are more shielded than those of usual alkoxycarbene metal complexes (300—360 p.p.m.).[34] This effect may be due to the enhanced back donation of electrons from the iron atom to the η^3-vinylcarbene ligand.

Methylation of (3c)—(3e) gave a mixture of thermally unstable liquid complexes and further investigation was not attempted.

Oxidation of Complexes (6) *with Pyridine* N-*Oxide*.—It is well known that the M=C double bonds in alkoxycarbenechromium complexes are selectively converted into a C=O double bond by oxidizing agents to give carboxylic

---

[33] E. O. Fischer and A. Maasboel, *Angew. Chem.*, 1964, **76**, 645; E. O. Fischer and R. Aumann, *Chem. Ber.*, 1969, **102**, 1495.

[34] J. A. Connor, M. Jones, E. W. Randall, and E. Rosenberg, *J.C.S. Dalton*, 1972, 2419; G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhaff, J. Wuller, and L. J. Todd, *Inorg. Chem.*, 1973, **12**, 1071.

[35] K. Nakatsu, T. Mitsudo, H. Nakanishi, Y. Watanabe, and Y. Takegami, *Chem. Letters*, 1977, 1447.

[36] J. A. Connor and E. M. Jones, *J. Chem. Soc. (A)*, 1971, 1974; C. P. Casey and W. R. Brunsvold, *Inorg. Chem.*, 1977, **16**, 391.

[37] C. Pedone and A. Sirigu, *Inorg. Chem.*, 1968, **7**, 2614.

[38] E. K. von Gustorf, M. C. Henry, and C. D. Pietro, *Z. Naturforsch.*, 1966, **B21**, 42.

[39] F. A. Cotton, B. A. Frenz, and J. M. Troup, *J. Organometallic Chem.*, 1973, **61**, 337.

[40] H. P. Fritz, *Ber.*, 1961, **94**, 1217.

[41] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' Wiley-Interscience, New York, 1970, p. 73.

esters.[42] When complex (6b) was treated with pyridine *N*-oxide at room temperature in methylene dichloride air-stable yellow crystals of (7b) were obtained in 45% yield. The i.r. spectrum (Table 1) of (7b) showed three terminal carbonyl bands, the absorptions of a co-ordinated pyridine, and bands of the ester groups. The ^{1}H n.m.r. spectrum (Table 2) showed three singlets of the methoxy groups (δ 3.70, 3.63, and 3.34 p.p.m.), a singlet at 3.30 p.p.m. (1 H) which can be assigned to the proton of the co-ordinated olefin, and multiplets of co-ordinated pyridine at 8.43—7.30 p.p.m. The ^{13}C n.m.r. spectrum of (7b) (Table 3) showed three metal carbonyl bands at *ca.* 200 p.p.m., three carbonyl bands of the esters at *ca.* 170 p.p.m., and two olefinic carbons co-ordinated to the iron atom. The spectral and analytical data and the observed molecular weight (Found: *M* 407. Required for $C_{16}H_{15}FeNO_9$; *M* 421.1) showed that the carbene carbon of (6b) was selectively oxidized with pyridine *N*-oxide to give the corresponding ester group, and the vacant site formed was occupied by the pyridine molecule to afford the new complex (7b). The oxidation of (6a) and (6g) also gave (7a) and (7g) respectively.

The reaction of (7b) with Ce^{4+} in methanol gave 1-methoxy-1,2,2-tris(methoxycarbonyl)ethane (8b) in 34% yield, supporting the structure of (7b). The reaction in ethanol gave the corresponding ethoxy-derivative (8b′).

$$(7b) + Ce^{4+} \xrightarrow{R^4OH} (MeO_2C)(R^4O)CH\text{-}CH(CO_2Me)_2 \quad (5)$$

$$(8b)\ R^4 = Me,\ (8b')\ R^4 = Et$$

EXPERIMENTAL

Infrared spectra were recorded on Hitachi EPI-G2 or 215 grating spectrometers, ^{1}H n.m.r. spectra on JEOL-PMX-60 or Varian HR-220 instruments, and ^{13}C n.m.r. spectra on a JEOL-JNM-PFT-100 system at 25.15 MHz. Mass spectra were obtained on an JMS-01SJ spectrometer. Molecular weights were determined by cryoscopy in benzene. Solvents were dried by published techniques and were distilled in an atmosphere of argon before use. Light petroleum refers to a fraction of b.p. 37—41 °C. Dimethyl acetylenedicarboxylate, methyl propiolate, and ethynyl ketone were commercial samples and purified by distillation before use. Propiolaldehyde,[43] methyl (*Z*)-β-bromoacrylate,[44] bis(triphenylphosphine)iminium chloride,[45] trimethyl-[46] and triethyl-oxonium tetrafluoroborate[47] were prepared as described in the literature. Other reagents were commercial samples and were used without further purification. Except when stated, the reactions were carried out under an argon atmosphere. Analytical data are presented in Table 4, and spectroscopic data for new complexes in Tables 1—3.

Preparation of Bis(triphenylphosphine)iminium Tetracarbonylhydridoferrate(0) (1).—Pentacarbonyliron (13.6 cm^3, 0.10 mol) was added to a solution of potassium hydroxide (16.8 g, 0.30 mol) in 99% ethanol (150 cm^3) and the solution was stirred at 30 °C for 1 h. The precipitate of $K_2[CO_3]$ was filtered off and washed with three 20-cm^3 portions of ethanol. To the mixture of the filtrate and the washings was added a solution of bis(triphenylphosphine)iminium chloride (57.6 g, 0.10 mol) in methanol (100 cm^3) and the reaction mixture was stirred for 1 h at room temperature. A white-yellow precipitate was formed and was collected, washed with water (50 cm^3), four 50-cm^3 portions of methanol, and then two 50-cm^3 portions of diethyl ether, and dried under reduced pressure. The precipitate was dissolved in methylene dichloride (50 cm^3) and diethyl ether (150 cm^3) was added slowly. White-yellow crystals were formed and were collected, washed with two 50-cm^3 portions of diethyl ether, and dried at 0.1 mmHg * for 24 h (yield 52.9 g, 75%), m.p. 163—166 °C (decomp.) (Found: C, 67.85; H, 4.60; N, 2.00. $C_{40}H_{31}FeNO_4P_2$ requires C, 67.9; H, 4.40; N, 2.00%). Bis(triphenylphosphine)iminium tetracarbonyldeuterioferrate(0) was prepared by deuteriation of a suspension of disodium tetracarbonylferrate(—II) in tetrahydrofuran (thf) with trifluoroacetic acid followed by the addition of $[N(PPh_3)_2]Cl$.

TABLE 4

Analytical data

Complex	Yield (%)	Colour	M.p. (θ_c/°C)	Analysis (%) * C	H	N
(3a)	92	Yellow	143 (decomp.)	66.65 (66.76)	4.20 (4.45)	1.80 (1.75)
(3b)	95	Yellow	134 (decomp.)	64.5 (65.05)	4.40 (4.40)	1.55 (1.65)
(3c)	92	Yellow	141	68.2 (68.15)	4.80 (4.55)	1.75 (1.80)
(3d)	47	Yellow	129	67.85 (67.80)	4.70 (4.35)	1.85 (1.85)
(3e)	57	Yellow	151	66.50 (66.75)	4.65 (4.45)	1.70 (1.75)
(6a)	50	Yellow	*ca.* 20	39.05 (40.35)	3.40 (3.00)	
(6b)	95	Yellow-orange	74	40.25 (40.55)	3.00 (3.10)	
(7a)	65	Yellow	90	46.45 (46.30)	3.55) (3.60)	3.95 (3.85)
(7b)	45	Yellow	101	45.50 (45.65)	3.65 (3.60)	3.45 (3.35)
(7g)	65	Yellow	105	46.65 (46.9)	3.90 (3.95)	3.40 (3.20)

* Calculated values are given in parentheses.

Reaction of Complex (1) *with Acetylenes*.—The reaction of dimethyl acetylenedicarboxylate is representative. In a dry two-necked cylindrical flask (100 cm^3), equipped with a gas inlet, a rubber stopper, and a magnetic stirrer, was placed (1) (2.1 g, 3.0 mmol) and the flask was flushed with argon. Methylene dichloride (3 cm^3) and dimethyl acetylenedicarboxylate (0.43 g, 3 mmol) were added by a syringe, the solution was stirred for 30 min at 30 °C, and then diethyl ether (80 cm^3) was added. Yellow crystals formed and were collected, washed with methylene dichloride–diethyl ether (1 : 50), and dried at 0.1 mmHg for 24 h. The reactions of methyl propiolate, ethynyl methyl ketone, and propiolaldehyde were carried out similarly. The yields, m.p.s, analytical data, and spectral data of the products are summarized in Tables 1—4.

Reaction of Methyl (*Z*)-β-*Bromoacrylate with* $Na_2[Fe(CO)_4]$. A solution of $[Fe(CO)_5]$ (0.41 cm^3, 3 mmol) in thf (20 cm^3) was added dropwise to 1% sodium amalgam (cm^3) in thf (10 cm^3)

---

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

[42] C. P. Casey, 'Transition Metal Organometallics in Organic Synthesis,' vol. 1, ed. H. Alper, Academic Press, New York, 1976, p. 225.

[43] F. Wille and L. Saffe, *Annalen*, 1950, **568**, 40.

[44] K. Alder, F. Brockhagen, C. Kaiser, and W. Roth, *Annalen*, 1955, **593**, 1.

[45] J. K. Ruff and W. J. Schlieentz, *Inorg. Synth.*, 1974, **15**, 84.

[46] H. Meerwein, *Org. Synth.*, 1973, Coll. vol. **5**, 1096.

[47] H. Meerwein, *Org. Synth.*, 1973, Coll. vol. **5**, 1080.

during 30 min with vigorous stirring. After the removal of the mercury, methyl (Z)-β-bromoacrylate (0.37 cm^3, 3 mmol) was added and the solution was stirred for 1. 5 h at 30 °C followed by the addition of [N(PPh$_3$)$_2$]Cl (1.72 g, 3 mmol) in methylene dichloride (10 cm^3). After the removal of the solvent *in vacuo* the residual solid was extracted with methylene dichloride (5 cm^3) and the extract was filtered. Addition of diethyl ether (25 cm^3) to the filtrate gave yellow crystals of (3e) (1.4 g, 57%).

Protonation of Bis(triphenylphosphine)iminium [1—3-η-trans-2,3-*Bis(methoxycarbonyl)acryloyl*]*tricarbonylferrate*(0) (3b).—A solution of (3b) (1.4 g, 1.7 mmol) in acetone (18 cm^3) was treated with trifluoroacetic acid (0.18 cm^3, 1.7 mmol) at 30 °C for 30 min. The reaction mixture was concentrated to *ca.* 10 cm^3 under reduced pressure and cooled in an ice-bath. Yellow crystals were formed and collected, and recrystallization from acetone gave tetracarbonyl(η-dimethyl fumarate)iron (0.24 g, 45%), m.p. 135—137 °C (decomp.) [lit.,[27] 137 °C (decomp.)] (Found: C, 38.5; H, 2.90. $C_{10}H_8FeO_8$ requires C, 38.5; H, 2.60%). Its i.r. and ^{1}H n.m.r. spectra were identical with those reported.[27]

Protonation of Bis(triphenylphosphine)iminium (1—3-η-2-*Acetylacryloyl*)*tricarbonylferrate*(0) (3c).—A solution of (3c) (0.39 g, 0.50 mmol) in methylene dichloride (1.0 cm^3) was treated with trifluoroacetic acid (0.05 cm^3) at room temperature for 30 min. After evaporation of the solvent, the residual orange solid was sublimed at 25 °C (0.025 mmHg) to give yellow tetracarbonyl(η-methyl vinyl ketone)iron (0.095 g, 80%), m.p. 16—17 °C [Found: C, 39.8; H, 2.85%; *M* 238 (mass spectrum). $C_8H_6FeO_5$ requires C, 40.75; H, 2.55%; *M* 237.97]. Infrared spectrum (liquid film): 2 098s, 2 040s, 2 020s, 1 980s, and 1 666s cm^{-1}. Hydrogen-1 n.m.r. spectrum (220 MHz, in CD_2Cl_2): 2.27 (3 H, s), 2.56 (1 H, d, J 7.0), 2.87 (1 H, d, J 11.5), and 3.58 p.p.m. (1 H, dd, J 7.0 Hz, 11.5).

Alkylation of Complexes (3). Methylation of (3b) is representative. To a solution of (3b) (17.0 g, 20 mmol) in methylene dichloride (30 cm^3) was added methyl fluorosulphate (1.3 cm^3, 20 mmol) at room temperature. After 5 min the solvent was evaporated off *in vacuo* and the residue was extracted with five 20-cm^3 portions of diethyl ether. Removal of the solvent and recrystallization of the residual solid from diethyl ether–light petroleum (10 : 1) at −10 °C gave orange-yellow crystals of tricarbonyl[1—3-η-*trans*-1-methoxy-2,3-bis(methoxycarbonyl)prop-2-en-1-ylidene]-iron (6b) (6.2 g, 95%). Methylation with [OMe$_3$][BF$_4$] gave a similar result. Ethylation of (3b) with SFO$_2$(OEt) or [OEt$_3$][BF$_4$] was carried out in a similar manner. However, a dark red-brown liquid was obtained and the complex could not be isolated in pure form; the liquid was submitted to further reactions. Complex (3a) was also methylated in a similar way.

Oxidation of Complexes (6) *with Pyridine* N-*Oxide*.—The reaction of (6b) is representative. To a solution of (6b) (3.3 g, 10 mmol) in methylene dichloride (10 cm^3) was added a solution of pyridine N-oxide (0.95 g, 10 mmol) in methylene dichloride (10 cm^3) and the reaction mixture was agitated for 1 h at room temperature. The solvent was evaporated off and recrystallization of the residual solid from methanol gave yellow crystals of tricarbonylpyridine[η-1,1,2-tris(methoxycarbonyl)ethylene]iron (7b) (1.9 g, 45%), *M* 407 ($C_{16}H_{15}FeNO_9$ requires *M* 421.1). The oxidation of (6a) and (6g) was carried out similarly.

Reaction of Complex (7b) *with* Ce^{4+} *in Alcohols*.—To a solution of (7b) (0.88 g, 3 mmol) in methanol (10 cm^3) was added a solution of Ce[NH$_4$][NO$_3$]$_5$ (18.8 g) in methanol (50 cm^3) and the solution was stirred at room temperature overnight. After the evaporation of the solvent, the residual solid was extracted with three 20-cm^3 portions of methylene dichloride and the extracts were dried over disodium sulphate. After removal of the solvent, the residual liquid was subjected to preparative layer chromatography on silica gel. Elution with diethyl ether followed by distillation gave 1-methoxy-1,2,2-tris(methoxycarbonyl)ethane (8b), b.p. 91—101 °C (0.5 mmHg), 0.24 g (34%) [Found: C, 46.15; H, 6.30%; *M* 234 (mass spectrum). $C_9H_{14}O_7$ requires C, 46.15; H, 6.05%; *M* 234.2]. Infrared spectrum (liquid film): ν(C=O) of ester at 1 740 cm^{-1}. Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 3.74 (6 H, s, 2 CO$_2$Me), 3.70 (3 H, s, CO$_2$Me), 3.65 (3 H, s, OMe), and 4.12 p.p.m. (AB q, J 8.0 Hz, CH–CH). The similar reaction in ethanol gave 1-ethoxy-1,2,2-tris(methoxycarbonyl)ethane, b.p. 110 °C (0.5 mmHg), 55%) [Found: C, 48.3; H, 6.30; *M* 248 (mass spectrum). $C_{10}H_{16}O_7$ requires C, 48.4; H, 6.50%; *M* 248.2], ν(C=O) of ester at 1 740 cm^{-1}. Hydrogen-1 n.m.r. spectrum in $CDCl_4$: δ 3.72 (6 H, s, 2 CO$_2$Me), 3.68 (3 H, s, CO$_2$Me), 3.70 (2 H, q, J 7.5 Hz, CH$_2$), 2.53 (3 H, t, J 7.5 Hz, CH$_3$), and 4.13 p.p.m. (AB q, J 8.3 Hz, CH–CH).

We thank Dr. S. Inagaki for helpful discussions, the Ministry of Education for support, and Professor J. K. Ruff for a preprint of ref. 45.

[7/2107 *Received*, 21*th December*, 1977]