(η^3-Vinylacyl)tricarbonylferrate and (η^3-Vinylmethoxycarbene)tricarbonyliron Derivatives

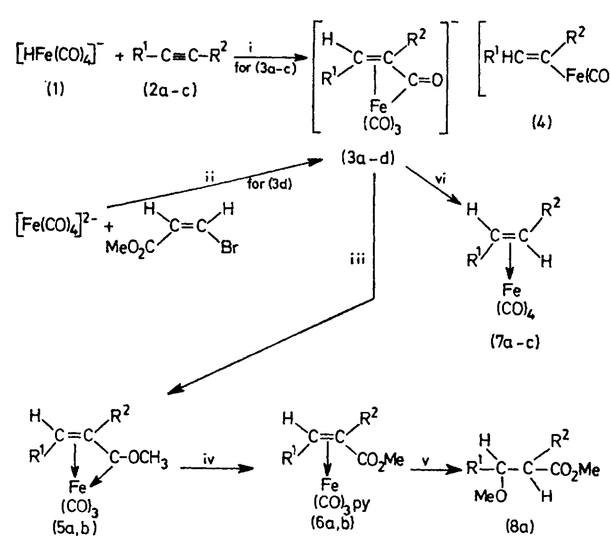
By Take-aki Mitsudo,* Hiroshi Nakanishi, Toshiro Inubushi, Isao Morishima,
Yoshihisa Watanabe, and Yoshinobu Takegami
(*Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto* 606, *Japan*)

Summary The *trans* addition of $[HFe(CO)_4]^-$ to acetylenic compounds gives the first (η^3-vinylacyl)tricarbonylferrates, which are converted into (η^3-vinylalkoxycarbene)-tricarbonyliron derivatives by alkylation with $MeOSO_2F$ or Me_3OBF_4.

Many transition metal–alkoxycarbene complexes have been synthesized by the alkylation of acylmetallate complexes.[1] We now report the preparation of the first (η^3-vinylacyl)-tricarbonylferrates and (η^3-vinylmethoxycarbene)tricarbonyliron derivatives.

$[(Ph_3P)_2N][HFe(CO)_4]$ (**1**) (3 mmol) was treated with the acetylenic compounds (**2a**—**c**) (Scheme) (3 mmol) in CH_2Cl_2 at 25 °C for 30 min. Addition of Et_2O to the reaction mixture gave 1 : 1 adducts, (**3a**—**c**), as yellow crystals in yields of 92—95%.† Analogous adducts were also prepared by the reaction of $Na_2[Fe(CO)_4]$ with β-halogenovinylcarbonyl compounds, such as methyl *cis*-β-bromoacrylate, and isolated as bis[triphenylphosphine]iminium salts, *e.g.* (**3d**).

The methylation of (**3a**) and (**3b**) with $MeOSO_2F$ or Me_3OBF_4 in CH_2Cl_2, and recrystallization of the product from light petroleum (b.p. 37—41 °C), gave yellow crystals of (**5a**) and (**5b**) in yields of 65 and 50% based on (**3**), respectively.‡ On the basis of the following arguments, and the data in the Table, the complexes (**3**) are believed to be the $[(Ph_3P)_2N]^+$ salts of (η^3-vinylacyl)tricarbonylfer-



a; $R^1 = R^2 = CO_2Me$
b; $R^1 = H$, $R^2 = CO_2Me$
c; $R^1 = H$, $R^2 = COMe$
d; $R^1 = CO_2Me$, $R^2 = H$

Scheme. i, CH_2Cl_2; ii, tetrahydrofuran; iii, $MeOSO_2F$ or Me_3OBF_4; iv, C_5H_5NO; v, Ce^{IV} and MeOH; vi, CF_3CO_2H; py = pyridine.

---

† Satisfactory analytical data for all formulated compounds, except the unstable complex (**5b**), have been obtained.

‡ The methylation of (**3c**) and (**3d**) did not give any product that could be isolated.

rates, and not the expected alkenylferrate salts (**4**), and complexes (**5**) are believed to be (η^3-vinylmethoxycarbene)-tricarbonyliron derivatives. (i) Complexes (**3**) and (**5**) are diamagnetic and (**5a**) is monomeric in benzene solution, *M* (Rast) 322 (calc. for $C_{11}H_{10}O_8Fe$: 326). (ii) The ^1H n.m.r. spectra of (**3**) and (**5**) in CD_2Cl_2 exhibit, in addition to the signals of the cation and the ester or the ketone, olefinic protons [two slightly broad singlets for (**3b**) and (**3c**) at high fields, δ 1·9—4·3], which strongly suggests the co-ordination of the olefinic groups to the iron.[2] (iii) The ^{13}C n.m.r. spectra of (**3**) and (**5**) exhibit two peaks at abnormally high fields (δ 18—54 p.p.m.), confirming the above suggestions.[3] The *J* (^{13}C–H) values (153—173 Hz) show that these carbons are of sp^2 type. Further, the signals at very low fields, *ca.* 240 p.p.m. in (**3**) and *ca.* 270 p.p.m. in (**5**), can reasonably be assigned to the acyl carbon[4] and the carbene carbon,[5] respectively, co-ordinated to iron. (iv) The i.r. spectra of (**3a—d**) exhibit, in addition to the ferrate terminal carbonyl and ester or ketone carbonyl bands, a broad and strong absorption around 1740–1710 cm^{-1}. This band is assigned to CO of the η^3-vinylacyliron group. The observed value of $\Delta\nu_{C=O}$ ($= \nu_{C=O}\,\eta^3 - \nu_{C=O}\,\eta^1$)[6] of the vinylacylferrate is *ca.* 160 cm^{-1}, which corresponds to that reported for the η^3- and η^1-vinylacylcobalt analogues.[7] This characteristic band disappeared when (**3**) was either methylated or protonated. The chemical properties of the complexes are also in agreement with the structures assigned. In addition to the methylation of (**3a**) and (**3b**) giving (**5a**) and (**5b**), respectively, the oxidation of (**5a**) and (**5b**) with pyridine *N*-oxide gave (1,1,2-trimethoxycarbonylethylene)- (**6a**), and (1,1-dimethoxycarbonylethylene)-tricarbonylpyridineiron, (**6b**), respectively.§ The co-ordinated carbene carbon is selectively oxidized to the ester group[8] and the pyridine molecule occupies the vacant site. The oxidation of (**6a**) by Ce^{IV} in methanol gave 1,1,2-trimethoxycarbonyl-2-methoxyethane, (**8a**).

TABLE. (η^3-Vinylacyl)tricarbonylferrates and (η^3-vinylcarbene)-tricarbonyliron derivatives.

Complex	^1H n.m.r. δ (CD_2Cl_2, olefinic H) (*J*/Hz)	^{13}C n.m.r. δ (CD_2Cl_2, Fe–CO⁻) p.p.m.	ν (FeC≡O) cm^{-1}
(**3a**)	3·67 (s)	235·7	2015, 1937 1918
(**3b**)	2·43 (s) 1·91 (s)	242·7	1995, 1910
(**3c**)	2·50 (s) 1·93 (s)	246·1	1995, 1915 1892
(**3d**)	3·57 (d, 4·6) 2·40 (d, 4·6)	246·0	1995, 1915 1900
(**5a**)	4·30 (s)	270·9	2050, 2000
(**5b**)	3·22 (s) 2·63 (s)	270·0	2040, 1988

The direction of the addition and the *trans* addition of (**1**) to (**2**) can be deduced, based on the following facts. (i) The protonation of (**3a—d**) with trifluoroacetic acid gave (π-olefin)tetracarbonyliron complexes (**7a—c**) by a route involving decarbonylation of the vinylacyl group. From (**3b**), (π-methyl acrylate)tetracarbonyliron[9] was obtained quantitatively. The deuteriation of (**3b**) gave [(π-$MeO_2CDC{=}CH_2$)$Fe(CO)_4$] indicating that the acyl carbon is attached to the α-carbon of the ester group. The direction of addition in (**1**) is the opposite to that in the reaction of [$HMn(CO)_5$] and acetylenes.[10] (ii) The deuteriation of [η^3-*cis*-$MeO_2CCH{=}CHCOFe(CO)_3$]⁻ (**3d**), derived from methyl *cis*-β-bromoacrylate and $[Fe(CO)_4]^{2-}$, gave selectively [(π-*cis*-$MeO_2CCH{=}CHD$)$Fe(CO)_4$] indicating that the stereochemistry of the olefinic group is completely retained during the protonation of (**3**). (iii) The protonation of (**3a**) selectively gave (π-dimethyl fumarate)tetracarbonyliron (**7a**).[9] (iv) The deuteriation of [η^3-$HDC{=}C(CO_2Me)COFe(CO)_3$]⁻, derived from (**2b**) with $[DFe(CO)_4]^-$, gave selectively (π-*trans*-$MeO_2CCD{=}CHD$)$Fe(CO)_4$].

(*Received*, 12*th March*, 1976; *Com.* 254.)

---

§ Complexes (**3a—d**) were too unstable to enable the conductance to be measured in polar solvents such as nitromethane.

[1] *E.g.*, D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545.
[2] *E.g.*, M. Herberhold, 'Metal π-Complexes,' Elsevier, Amsterdam, 1974, vol. 2, part 2, p. 32.
[3] J. B. Stothers, 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York, 1972, p. 213.
[4] J. P. Collman and S. R. Winter, *J. Amer. Chem. Soc.*, 1973, **95**, 4089; G. C. Levy and G. L. Nelson, 'Carbon-13 N.M.R. for Organic Chemists,' Wiley, New York, 1972, p. 144.
[5] M. H. Chisholm, H. C. Clark, J. E. H. Ward, and K. Yasufuku, *Inorg. Chem.*, 1975, **14**, 893.
[6] W. O. Siegle and J. P. Collman, *J. Amer. Chem. Soc.*, 1972, **94**, 2516.
[7] R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, 1961, **83**, 1097; 1963, **85**, 651.
[8] C. P. Casey, T. J. Burkhardt, *J. Amer. Chem. Soc.*, 1972, **94**, 6453.
[9] E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, 1963, **46**, 288.
[10] B. L. Booth and R. G. Hargreaves, *J. Chem. Soc.* (*A*), 1969, 2766.