Nucleophilic Addition to (Methyl α-chloroacrylate)tetracarbonyliron. Activation of a Vinyl Halide

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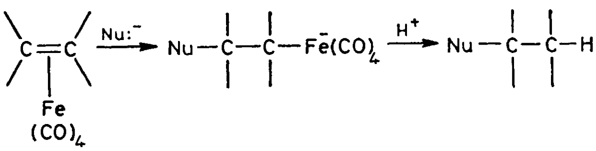
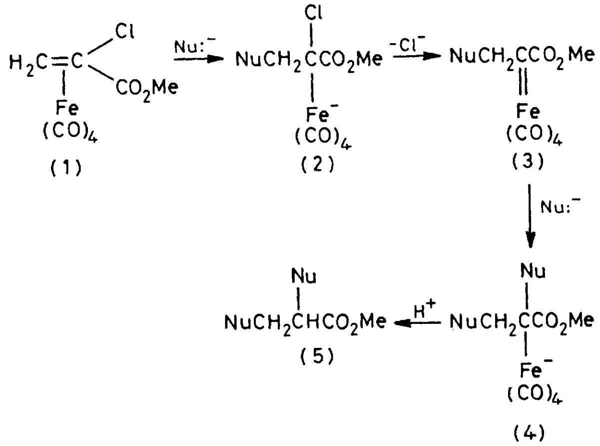
Summary Treatment of the title complex with stabilized anions under aprotic conditions followed by acid affords products corresponding to vicinal incorporation of two equivalents of nucleophile by a process which probably involves an ironcarbene complex.

Recently, we reported that nucleophilic addition to alkenes can be mediated *via* the corresponding tetracarbonyliron complexes,[1] presumably as in equation (1).



$$\underset{\mathrm{Fe(CO)_4}}{\mathrm{C{=}C}} \xrightarrow{\mathrm{Nu:^-}} \mathrm{Nu{-}C{-}C{-}\bar{F}e(CO)_4} \xrightarrow{\mathrm{H^+}} \mathrm{Nu{-}C{-}C{-}H} \quad (1)$$

Whatever the detailed mechanism, the stereochemical fates of the co-ordinated alkene carbons undergoing the trigonal to tetrahedral transition are of considerable interest, and, within the context of equation (1), follow from the stereochemistries of initial nucleophilic attack and subsequent C–H bond formation during protonation. Because the tetracarbonyliron complex of acrylic acid could be resolved by classical techniques[2] and because the correlation of chiralities of appropriate metal complexes and products derived therefrom could in principle answer these questions directly, we have examined the behaviour of the tetracarbonyliron complex (**1**) of methyl α-chloroacrylate in order to establish the stereochemistry of C–H bond formation. We report here, however, that we have been unable to obtain simple Michael addition products from (**1**) and that the results point instead to intervention of an ironcarbene complex.



	Nu
a,	$CH(CO_2Me)_2$
b,	$CH(CO_2Et)_2$
c,	$CMe(CO_2Et)_2$
d,	$CH(COMe)CO_2Et$
e,	$CH(CN)CO_2Et$

Complex (**1**)†‡ reacted with 2 equiv. of dimethyl sodiomalonate at 25 °C in tetrahydrofuran (THF) under argon for 1 h to give, after addition of trifluoroacetic acid, the pentaester (**5a**) (61%, m.p. 85·4—86·1 °C, lit. m.p.[3] 88 °C). N.m.r. (^{1}H and ^{13}C) spectra were fully consistent with the assigned structure, which included five nonequivalent methoxy groups, and hydrolysis–decarboxylation afforded butane-1,2,4-tricarboxylic acid, which was identical (^{1}H n.m.r., i.r., mixed m.p.) with material prepared by ozonolysis of cyclohex-3-ene-1-carboxylic acid. Use of 3 equiv. of nucleophile increased the yield to 68%. Similar reaction with diethyl sodiomalonate afforded the pentaester (**5b**)‡ (63%, b.p. 195—200 °C at 11·5 Torr) which afforded the same triacid on hydrolysis–decarboxylation, and the n.m.r. (^{1}H and ^{13}C) spectra of which were consistent with a homogeneous monomethyltetraethyl ester. Similarly, the sodium salts of diethyl methylmalonate, ethyl acetoacetate, and ethyl cyanoacetate afforded liquid adducts (**5c**)—(**5e**)‡ in 46, 30, and 30% yields, respectively. The diastereoisomeric nature of the latter two products was evident from their n.m.r. spectra. In all cases, the only other products were intractable, higher-boiling materials. All attempts to favour 1 : 1 adduct formation by lowering the temperature, changing solvent and reaction time, and/or using a limited amount of nucleophile were unsuccessful.

The formation of 2 : 1 products (**5**) is most readily accounted for through ironcarbene complex formation. Expulsion of chloride ion from (**2**)[4] and addition of a second equivalent of nucleophile to (**3**)[5] would generate an alkylironcarbonylate anion (**4**) which would be expected to give the observed product on protonation.[6] Since (**3**) can be expected to be a decidedly unstable carbene complex owing to the destabilizing effect of the methoxy carbonyl group,[7] the apparent ease of its formation is noteworthy. A possible explanation is that relief of steric congestion around the incipient carbene carbon in (**2**) provides a significant driving force for elimination.

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† Complex (**1**), m.p. 35·2—35·9 °C, was prepared in 56% yield by a modification of the procedure of Weiss *et al.* (E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, 1963, **46**, 288); δ($CDCl_3$) (Me_4Si) 3·13 (d, 1H, –C*H*=, *J* 3·5 Hz), 3·35 (d, 1H, –CH=, *J* 3·5 Hz), and 3·81 (s, 3H, –OMe); ν(n-heptane) 2075, 1978 cm^{-1} (metal C=O), and 1683 cm^{-1} (ester C=O).

‡ Compositional analyses of all new compounds reported here were consistent with assigned structures.

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[2] G. Paiaro and R. Palumbo, *Gazzetta*, 1967, **97**, 265.

[3] J. W. Baker, *J. Chem. Soc.*, 1935, 188.

[4] An analogous process is probably involved in a number of reactions giving rise to transition metal–carbene complexes: K. Öfele, *Angew. Chem., Internat. Edn.*, 1969, **8**, 916; B. Cetinkaya, M. F. Lappert, and K. Turner, *J.C.S. Chem. Comm.*, 1972, 851; P. J. Fraser, W. R. Roper, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 760; M. Green, F. G. A. Stone, and M. Underhill, *ibid.*, 1975, 939.

[5] Nucleophilic addition to transition metal–carbene complexes is well known. See C. P. Casey in 'Transition Metal Organometallics in Organic Synthesis,' ed. H. Alper, Academic Press, New York, 1976, vol. 1, ch. 3, and references cited therein.

[6] M. P. Cooke, Jr., *J. Amer. Chem. Soc.*, 1970, **92**, 6080.

[7] F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 1972, **16**, 487; D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, **2**, 99.