Application of Iron Carbonyls to Organic Synthesis. Mediation of Nucleophilic Addition to Alkenes *via* Tetracarbonyliron Complexes

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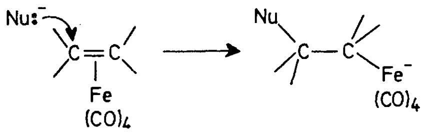
Summary Reaction of the tetracarbonyliron complexes of ethylene and methyl acrylate with malonate ester anions followed by acidic workup affords alkene addition products in good yields.

Tetracarbonyliron complexes of alkenes are well characterized species for which, however, practical applications to organic synthesis have not been developed. We recently began to study the extent to which alkene reactivity is modified in such complexes and report here preliminary results which show that they are new, potentially useful electrophiles for effecting nucleophilic addition to alkenes.



(1)

We believed that the steric accessibility and formation of an alkyltetracarbonylferrate anion might provide driving forces for preferential attack by a nucleophile on the coordinated alkene rather than CO [equation (1)].† Such anions, prepared *via* monoalkylation of $Na_2Fe(CO)_4$, have been characterized as crystalline bis(triphenylphosphine)-imminium salts by Collman and his co-workers,[1] and we expected that the iron carbonyl anion unit, which has stability comparable with that of the acetate anion,[2] would serve as an efficient electron sink. This hypothesis has now been tested with malonate ester anions as nucleophile.

Reaction of π-ethylenetetracarbonyliron (**1a**)[3] with dimethyl sodiomalonate (**2a**) (1 equiv.) at 0 °C in tetrahydrofuran (THF) under argon for 24 h, followed by addition of slightly more than 1 equiv. of trifluoroacetic acid and oxidation of the iron species‡ afforded dimethyl ethylmalonate (**3a**) in 45% yield as determined by v.p.c.§ Use of 2 equiv. of complex (**1a**) increased the yield to 68%, based on (**2a**). Similar treatment of the tetracarbonyliron complex of methyl acrylate (**1b**)[4] with (**2b**) or (**2c**) (2 equiv.) for 5 h at 0 °C led to Michael-type products (**3b**) and (**3c**) in isolated yields of 91 and 88%, respectively. No product which would

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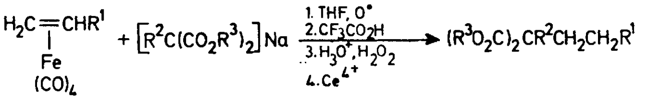
† The effect on alkene reactivity of co-ordination to a tetracarbonyliron unit was first examined by Nesmeyanov and his co-workers, but the reaction of complexes of some $\alpha\beta$-unsaturated ketones with trimethylamine, methoxide, and benzenethiolate ions led to either no reaction, decomposition, or reduction of the olefinic bond. See A. N. Nesmeyanov, L. V. Rybin, N. T. Gubenko, M. I. Rybinskaya, and P. V. Petrovskii, *J. Organometallic Chem.*, 1974, **71**, 271, and refs. cited therein.

‡ The two stage oxidative workup permits efficient separation of organic products and iron species by normal extractive methods without chromatography. Methods for improving this aspect of the reactions are being studied.

§ Products were identified through comparison with authentic samples and by ^1H n.m.r. spectroscopy. Elemental analysis of (**3c**), a new compound, was consistent with the assigned structure.

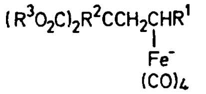
have resulted from α attack of malonate was detected. When conducted at room temperature for 2 h, yields in these latter reactions were essentially unchanged (88%). When these reactions were conducted as described at 0 °C except for replacement of (**1b**) with free methyl acrylate, 30% of (**3b**) was obtained but no (**3c**). In both cases, considerable amounts of higher boiling materials were formed.



$$\underset{\underset{(CO)_4}{Fe}}{H_2C{=}CHR^1} + [R^2C(CO_2R^3)_2]Na \xrightarrow[\substack{3.\,H_3O^+,\,H_2O_2\\4.\,Ce^{4+}}]{\substack{1.\,THF,\,0^{\circ}\\2.\,CF_3CO_2H}} (R^3O_2C)_2CR^2CH_2CH_2R^1$$

(1) (2) (3)

a; $R^1 = R^2 = H$, $R^3 = Me$
b; $R^1 = CO_2Me$, $R^2 = H$, $R^3 = Me$
c; $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = Et$



$$(R^3O_2C)_2R^2CCH_2\underset{\underset{(CO)_4}{Fe^-}}{CHR^1}$$

(4)

The foregoing results comprise the first examples of addition of nucleophiles to alkenes *via* neutral iron carbonyl complexes. The identity of the reaction intermediates is being studied, but if alkyltetracarbonylferrate anions of type (**4**) are involved as expected, protonation of the latter to give a hydridoalkyltetracarbonyliron species followed by reductive elimination[5] would rationalize the formation of the observed products.

Activation of a simple alkene toward attack by a relatively weak nucleophile as exemplified by the formation of (**3a**) from (**1a**) is not unknown,[6] but the relative instability of tetracarbonyliron complexes of simple alkenes is likely to limit practical applications in synthesis. In contrast, complexes of α,β-unsaturated carbonyl systems are considerably more stable, often crystalline materials. Consequently, the regiospecificity and high yields observed and mild conditions employed in the reactions of (**1b**) suggest an alternative approach for effecting Michael addition under aprotic conditions *via* control of the initial addition of nucleophile to the acceptor through formation of a stabilized, masked enolate anion.[6] This point is particularly pertinent to the formation of (**3c**) since under aprotic conditions the ester enolate resulting from addition of (**2c**) to methyl acrylate itself would not have access to exchangeable protons and would be expected either to retrogress to original components or to undergo side reactions.[8] The results of control experiments employing methyl acrylate instead of (**1b**) are consistent with this view.

If alkyltetracarbonylferrate anions of type (**4**) are, in fact, generated in these reactions, coupling of their chemistry[1] with that described herein would present the opportunity for effecting useful synthetic transformations at α and β positions of Michael acceptors.

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[8] H. O. House, 'Modern Synthetic Reactions,' 2nd edn., Benjamin, Menlo Park, California, 1972, pp. 595ff.