Electrochemical Reduction of a Heterodienetricarbonyliron(0) Complex as a Route to Novel Tricarbonyliron Anions

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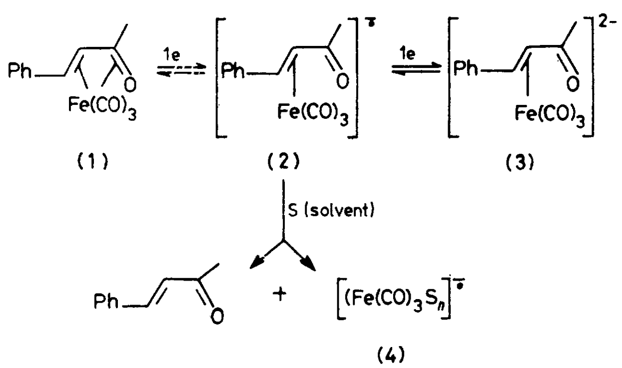
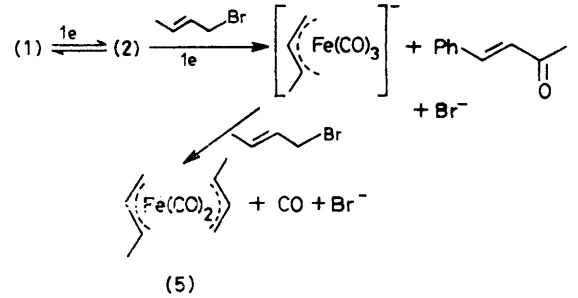
Summary Electrochemical reduction of benzylideneacetonetricarbonyliron(0) (**1**) affords the anionic species (**2**), (**3**), or (**4**); reaction of (**2**) or (**3**) with crotyl halides gives the bisallyliron(II) complex (**5**) and reaction of (**4**) with the tropylium cation gives the polyeneiron(0) complex (**6**).

Electrochemical reduction of polyenetricarbonyliron(0) complexes has been shown to allow the activation of the organic ligand towards electrophilic reagents.[1] By contrast we report here that electrochemical reduction of the heterodienetricarbonyliron(0) complex (**1**) specifically affords the novel anionic units (**2**), (**3**), and (**4**), that we have used as sources of the radical anion $Fe(CO)_3^{\cdot-}$ or of the carbonyl iron dianion for the preparation of allyliron(II) and polyeneiron(0) complexes.

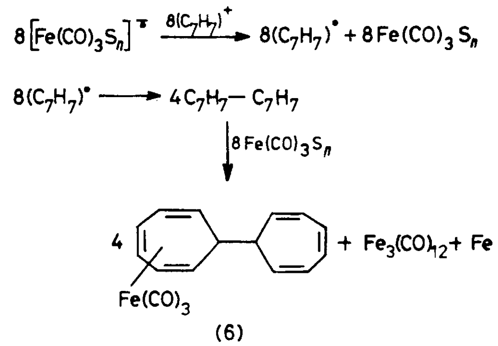


Scheme 1

Benzylideneacetonetricarbonyliron[2] [(bda)Fe(CO)$_3$] (**1**) in tetrahydrofuran (THF) with $Bu_4N^+PF_6^-$ (0·2 M) as the supporting electrolyte was reduced at a mercury electrode. Polarography shows two reduction waves at −0·88 and −1·61 V;† both steps are reversible and one-electron as shown by both cyclic voltammetry, even for scan rate of 20 mV s^{-1}, and coulometry. In contrast, reduction of unco-ordinated bda occurs at −1·68 and −2·76 V. The reduction mechanism is consistent with the reactions in Scheme 1. Electrolysis under an inert atmosphere of a THF solution of (**1**) at −1 and −1·8 V affords solutions of the stable, green radical anion (**2**) and of the unstable, yellow dianion (**3**) respectively. The radical anion (**2**) can be quantitatively oxidized to the precursor (**1**) electrochemically or by addition of suitable cations such as $[Fe(C_5H_5)_2]^+PF_6^-$ ($E_{\frac{1}{2}}$ +0·41 V) or $[C_7H_7]^+PF_6^-$ ($E_{\frac{1}{2}}$ + 0·11 V). The structure of (**2**) was supported by its unco-ordinated ketone carbonyl i.r. absorption at 1675 cm^{-1} and by its e.s.r. spectrum which displays three lines (g 2·0384; a_H 3·8 G) consistent with the hyperfine splitting of two olefinic protons and similar to the signal previously reported for olefintetracarbonyliron radical anions.[3]



Scheme 2



Scheme 3

In the presence of an excess of crotyl bromide [($E_{\frac{1}{2}}$ −1·65 V) the first step of the reduction of (**1**) became irreversible. The corresponding electrolysis at −1·0 V led to the formation of the bis-(η^3-allyl)dicarbonyliron(II) complex (**5**)[4] [i.r. (hexane) ν_{max} 1942 and 1997 cm^{-1}; m/e 222 (M)$^+$, 194 ($M-$CO)$^+$, and 166 ($M-$2CO)$^+$]. A quantitative yield of (**5**) was obtained in a two-electron reduction. Therefore the mechanism shown in Scheme 2 may account for the reduction path.

Nucleophilic substitution of the halide by (**2**) is the critical step in this reaction. When crotyl chloride was used the intermediate (**2**) was not nucleophilic enough for reaction to occur. However, on electrolysis at −2 V, crotyl chloride ($E_{\frac{1}{2}}$ −2·46 V) and (**3**) gave (**5**) in up to 95% yield. It is worth noting that the behaviour of the carbonyliron dianion (**3**) differs significantly from that of Collman's reagent which leads to stable dienetricarbonyliron(0) complex with allyl halides.[5]

The radical anion (**2**) decomposes slowly in THF, but faster in the co-ordinating solvent dimethylformamide, leading to free enone and to a new paramagnetic anion (e.s.r. spectrum: single-line; g 2·0393) whose formation and reactivity support the formulation (**4**) (Scheme 1). Whereas the tropylium cation oxidizes (**2**) giving (**1**) it reacts instantaneously with species (**4**) to afford in 85% yield the tropylideneiron complex‡ (**6**)[6] [ν_{max} (CCl$_4$) 2050, 1988, and 1976 cm^{-1}; m/e 294 ($M-$CO)$^+$, 266 ($M-$2CO)$^+$, and 238 ($M-$3CO)$^+$] besides $Fe_3(CO)_{12}$ and Fe metal. Dimerisation of the tropylium and co-ordination by tricarbonyliron(0) can be rationalized by the mechanism in Scheme 3.

Heterodienetricarbonyliron(0) complexes have been reported to be effective precursors for the transfer of the Fe(CO)$_3$ unit to dienes which cannot be co-ordinated otherwise[2,7] and our preliminary results show that electrochemical reduction of the same type of compound can be used for the transfer of carbonyliron anion species in organometallic synthesis.

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† All potentials refer to the saturated calomel electrode.

‡ The ^{1}H n.m.r. spectrum and elemental analysis also support the formulation (**6**).

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