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Preliminary communication

ELECTRON TRANSFER PROCESSES INVOLVING FERROCENES. ELECTROGENERATION AND REACTIVITY OF AN UNUSUAL SPECIES, THE MONOCYCLOPENTADIENYLIRON RADICAL

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Summary

The very reactive cyclopentadienyliron species, $(RC_5H_4)Fe$, are relatively easily generated by electrochemical reduction of appropriately substituted and readily available ferrocenes. Thus $(MeCOC_5H_4)Fe$ has been generated by monoelectronic reduction of $(MeCOC_5H_4)_2Fe$; it reacts with CO leading, after further reduction, to the acetyl cyclopentadienyldicarbonyliron anion. Reactions of this anion give ring-substituted cyclopentadienyldicarbonyliron derivatives containing the electron-withdrawing MeCO substituent.

Electrochemical oxidation of ferrocenes has been known since their discovery [1], but it was only recently that we described their electrochemical reduction, which occurs in two monoelectronic steps giving, respectively, the ferrocene radical anions and the dianions [2]. We present here more details on the mechanism of reduction of ferrocene species in which we propose the generation of a very unstable and reactive new iron species, the half-sandwich cyclopentadienyliron. As an example of the reactivity of this coordinatively unsaturated species we outline the nature of its reaction with CO.

Electrolyses of ferrocenes (I), in THF or DMF, at the mercury pool or the platinum electrode, on the level of the second reduction step requires two Faradays and lead to breakdown of the structure into iron and substituted cyclopentadienides which can be used in the synthesis of new functionally substituted cyclopentadienylmetal compounds [2,3]. Electrolyses on the level of the first step (monoelectronic and reversible electrochemically) depend on the experimental conditions. In solution at low temperatures (0°C to −25°C) under an inert atmosphere, electrolyses of I give after a one electron-transfer reaction the stable green radical anions II, which can be oxidized electrochemically to the precursors I, the total yield of the reduction and oxidation processes depends on the temperature and the nature of the solvent, and is nearly quantitative in

THF at −25°C. Electrolyses carried out at about 10°C indicate that two Faradays are consumed and the ferrocene structure is again broken down. In the time scale of electrolyses an ECE (electrochemical—chemical—electrochemical) process then takes place:

$$\begin{tikzcd}
(RC_5H_4)_2Fe \arrow[r, shift left, "1e"] & (RC_5H_4)_2Fe^{-\bullet} \arrow[l, shift left] \arrow[r, "1e"] \arrow[ddl] & (RC_5H_4)_2Fe^{2-} \arrow[r] & 2(RC_5H_4)^- + Fe \\
(I) & (II) & & \\
(RC_5H_4)^- + (RC_5H_4)Fe^{\bullet} \arrow[r, "S(solvent)"] & (RC_5H_4)FeS_2^{\bullet} \arrow[r, "1e"] & (RC_5H_4)FeS_2^- \arrow[ddl] & \\
(III) & (IV) & (V) & \\
& (RC_5H_4)^- + Fe + 2S & &
\end{tikzcd}$$

For the chemical step, we suggest either the generation of the coordinatively unsaturated species III or IV, which might be isoelectronic with the cyclopentadienyldicarbonyliron radical. If III or IV existed it would be very reactive towards coordinating ligands such as CO, and so we performed the reduction of 1,1′-diacetylferrocene at the level of the first step in presence of CO.

Electrolyses under CO pressure confirm the two-electron transfer process. Polarography of THF reduced solution then shows two monoelectronic waves at −0.1 and −0.32 V vs. SCE. The wave at −0.1 V corresponds to the formation of the acetylcyclopentadienide [2] and its maximum indicates the generation of one anion from a starting ferrocene molecule. The anodic wave at −0.32 V at the dropping mercury electrode corresponds to the formation of the acetylcyclopentadienyldicarbonyliron anion VI. The decrease in CO pressure during electrolysis and the infrared spectrum of the reduced solution (ν(CO) 1905 and 1880 cm^{-1}; ν(COMe) 1680 cm^{-1}) are in agreement with the formation of VI. THF solutions of VI are stable under an inert atmosphere and in the absence of moisture.

It proved impossible to isolate VI as a tetrabutylammonium salt because of the difficulty of separating it from a large excess of electrolyte support (Bu_4NPF_6), but VI was subsequently used without further purification. In THF, VI reacts with methyl iodide to give the corresponding methyl complex VII (IR (THF) ν(CO) 2020, 1995 cm^{-1}; ν(COMe) 1680 cm^{-1}; m/e 234 M^+, 206 $(M-CO)^+$, 178 $(M-2CO)^+$ and 163 $(M-2CO-Me)^+$). Electrochemical oxidation of VI at a platinum electrode readily produces the dimer VIII as a mixture of *cis* and *trans* isomers (IR (THF) ν(CO) 1930, 1890, 1860 and 1765 cm^{-1}; ν(COMe) 1680 cm^{-1}; m/e 438 M^+, 382 $(M-2CO)^+$ and 326 $(M-4CO)^+$).

$$(MeCOC_5H_4)_2Fe \xrightarrow[+2e]{+CO} (MeCOC_5H_4)^- + \underset{(VI)}{(MeCOC_5H_4)Fe(CO)_2^-}$$

$$\underset{(VII)}{(MeCOC_5H_4)Fe(CO)_2Me} \xleftarrow{MeI} VI \xrightarrow{\text{Oxidation at Pt}} \underset{(VIII)}{[(MeCOC_5H_4)Fe(CO)_2]_2}$$

Reaction with various ligands of other substituted cyclopentadienyliron compounds obtained by the electrochemical reduction of appropriately substituted and readily available ferrocenes will be described in full later.

References

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