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Electrochemical Preparation of π-$C_5H_5Fe(CO)_2H$ and Some Other Metal Hydrides by Simultaneous Formation and Protonation of the Parent Anion

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The hydridobiscarbonyl-π-cyclopentadienyl iron, π-$C_5H_5Fe(CO)_2H$, can be prepared by the sodium borohydride reduction of π-$C_5H_5Fe(CO)_2Cl$ in tetrahydrofuran.[1,2]

However, our study of the electrochemical behaviour of π-$C_5H_5Fe(CO)_2I$ and $[\pi$-$C_5H_5Fe(CO)_2]_2$ has shown that the hydride species mentioned above can be easily prepared electrochemically.

The electrosynthesis is based upon the fact that π-$C_5H_5Fe(CO)_2X$ (X = halogen) as well as $[\pi$-$C_5H_5Fe(CO)_2]_2$ are reduced in tetrahydrofuran by two electrons under the formation of the anion, $[\pi$-$C_5H_5Fe(CO)_2]^-$. This anion, countrary to the previous finding,[3] has been found *to react rapidly with proton donors* in tetrahydrofuran under the formation of the corresponding hydride species.[4] The hydride is reduced at more negative potentials than the parent compounds so that the electrolysis of the acidified solutions results in the *formation of the hydride as the final product of the electrode reaction.*

In a typical experiment, a $3\times10^{-3}M$ solution of $[\pi$-$C_5H_5Fe(CO)_2]_2$ in tetrahydrofuran containing $0.1M$ tetrabutylammonium perchlorate and being at the same time $3\times10^{-3}M$ in HCl, was electrolyzed using a mercury pool cathode (about 12 cm^2) and a platinum anode in $0.1M$ aqueous perchlorate separated by a tetrahydrofuran bridge from the cathode compartment. The potential of the mercury pool cathode was kept constant with the use of a potentiostat at -1.7V against the silver-silver perchlorat electrode in $0.1\,M$ tetrabutylammonium perchlorate in tetrahydrofuran. To increase the transport to the electrode the solution was stirred by a magnetic stirrer. The electrolysis was controlled polarographically, using a mercury dropping electrode directly in the electrolyzed solution. The electrolysis was finished within 30 to 40 min. The further steps of the preparation are identical with the previously described procedure.[1,2] The identity of the species obtained electrochemically with that obtained by borohydride reduction was shown by the comparison of the properties of both compounds, which were completely identical.

The described electrosynthesis is especially suitable for the preparation of solutions of the hydride complex which are obtained in a one-step operation without any other reducing agents present in the solution.

By the same electropreparative procedure the hydrido-tri-carbonyl π-cyclopentadienylmolybdenum (electrolyzing at -0.9V), manganese carbonyl hydride (electrolyzing at -1.3V) as well as some other hydride species were obtained. It has to be emphasized that the potentiostatic control of the electrolysis is the vital point of a successful preparation. The potential of the electrolysis has to be chosen in such a way that it is more negative than the reduction potential of the parent compound but more positive than the reduction potential of the hydride itself.

The observed electrochemical behaviour as well as the electro-preparation of the hydride described show unambiguously that even the π-$C_5H_5Fe(CO)_2H$ is formed from the corresponding anion by the reaction with proton donors. A two-step preparation can be made by acidification of the solution of the anion, $[\pi$-$C_5H_5Fe(CO)_2]^-$, obtained by the electrolysis of the solution not containing the hydrochloric acid.

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(1) M. L. H. Green, C. N. Street and G. Wilkinson, *Z. Naturforsch.*, *14b*, 738 (1959).

(2) A. Davison, J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.* 1133 (1963).

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