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Preliminary communication

AN EFFICIENT SYNTHESIS OF [1,1] FERROCENOPHANE VIA 1,1'-BIS(6-FULVENYL)FERROCENE

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Summary

[1,1] Ferrocenophane can be prepared by reduction of 1,1'-bis(6-fulvenyl)ferrocene with complex borohydrides to give the dianion of 1,1'-bis(cyclopentadienylmethyl)ferrocene. Reaction of this dianion with ferrous chloride produces the ferrocenophane in good yield.

In [1,1] ferrocenophane 1 (Scheme 1), two ferrocene units are held together in a flexible cisoid conformation by two bridging methylene groups. In connection with the current general interest in the use of chemically modified semiconductor electrodes for the generation of hydrogen from water in solar cells, we were interested in this ferrocenophane, because it has been reported [1] that in acidic aqueous media this material liberated hydrogen, being oxidized itself to the dication. It is believed that the first step in this reaction is protonation on both iron atoms, followed by elimination of molecular hydrogen. The flexibility of the ferrocenophane 1 appears to be of importance in this regard.

The ferrocenophane 1 has been previously obtained by two routes, which unfortunately, are very unsatisfactory. In the first of these [2], 1 was obtained in 1.8% yield by reaction of the dianion of dicyclopentadienylmethane 2 with ferrous chloride. The second preparative method [3] consists of a reduction by $LiAlH_4/AlCl_3$ of the diketone 3, which, however, can only be obtained by two very low yield processes. These difficulties in obtaining the [1,1] ferrocenophane 1 have precluded a thorough investigation of the chemistry of this material, in which two ferrocenes may participate in cooperative redox and catalytic processes.

We here report the efficient preparation of the title compound 1 from

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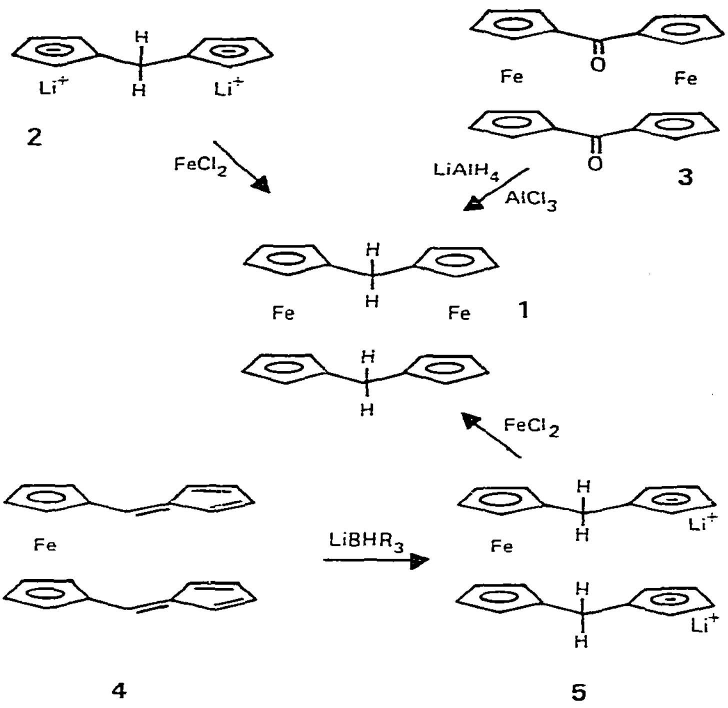

Scheme 1

1,1′-bis(fulvenyl)ferrocene 4, described in the preceding communication.

The principle of this approach to the synthesis of [1,1] ferrocenophane has been previously applied [4] with only limited success in several cases using substituted fulvenylferrocenes. Thus, the bridge-substituted 1,12-dimethyl-[1,1] ferrocenophane has been obtained in "modest" yield by reducing the 6,6′-dimethyl derivative of 4 with $LiAlH_4$ and reaction of the resulting dianion with $FeCl_2$. In our hands, the reduction of the fulvene 4 itself by this method never produced more than 5 to 10% yields of the ferrocenophane 1. One must assume that the cause for the low yield in this reaction lies in the reduction of the ferrous halide by AlH_3, which is left in solution or coordinated to the cyclopentadienide, resulting from the addition of LiH to the fulvene. Precipitation and redissolution of the dianion 5 did not alleviate this problem. It was, therefore, logical to use a reactive hydride, which would produce an inert byproduct. Such hydrides are commercially available in the form of THF solutions of $LiBHEt_3$ or $LiBH(s\text{-}Bu)_3$. With either of these reagents, addition of LiH to the fulvenes in 4 occurs smoothly in refluxing THF. The trialkylboron byproducts do not significantly interfere with the subsequent reaction with $FeCl_2 \cdot 2THF$. In this fashion, we were able to obtain 1 in yields averaging 30 to 45% of pure product, after chromatography on SiO_2 with CCl_4 and recrystallization from heptane. Unfortunately, we were unable to reproduce occasional yields of approximately 50%. The greatest fluctuations in yield occurred with $LiBHEt_3$. We attribute this fact to significant variations in the quality of the commercial reagent. Nevertheless, this synthesis of [1,1]-

ferrocenophane allows us to obtain this material in quantities of several grams at a time. Since in our reaction only even-numbered oligomers of 1 are produced, purification of 1 is much simpler than in ref. 2.

Since in the production of hydrogen from 1 and acid the rotational freedom of the ferrocenophane appears to be important, we have tried to investigate by NMR the exchange of the *exo* and *endo* protons of the bridge methylene groups. In CS_2/CD_2Cl_2 solution at room temperature, all four protons of the methylene bridges in 1 appear as a sharp singlet at 3.44 ppm with a full width at half height of 3 Hz. The ferrocene protons appear as two sharp triplets with $J < 2$ Hz at 4.02 (β-protons) and 4.22 ppm (α-protons). At —70°C, the 3.44 and 4.22 ppm signals begin to broaden, possibly only due to the increased viscosity of the solvent, but even at —100°C, when our sample began to freeze out, no separation of these signals was observable. Hydride abstraction from 1 leads to the *cis*-fixed α-ferrocenylcarbenium ion, in which this rotation is completely frozen out, due to the increased conjugation [5]. It is also possible to prepare a bridge carbanion, for which we are presently investigating the existence of an intramolecular C—H—C hydrogen bond [6]. This anion reacts with $SiCl_4$ to produce the 1-trichlorosilyl-[1,1] ferrocenophane, which we have used in the preparation of modified electrode surfaces. Details about these aspects of our work will be reported separately.

It is evident that the method described above also opens the way to the synthesis of mixed metal metallocenophanes. First examples, such as the mixed $Fe—Co^+$ and the Fe—Ru systems, will be reported elsewhere.

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