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Preliminary communication

SYNTHESIS AND CHARACTERIZATION OF 1,1'-BIS(6-FULVENYL)-FERROCENE

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Summary

Two efficient syntheses of the previously unknown 1,1'-bis(6-fulvenyl)ferrocene are described. The first involves the preparation of the fulvenylcyclopentadienide ligand anion, which is converted to the fulvenylferrocene by addition of ferrous chloride. The second converts the known dilithioferrocene directly to the bis(fulvenyl)ferrocene by reaction with 6-dimethylaminofulvene. Both syntheses are high yield procedures. Also described are syntheses of the known mono-fulvenylferrocene (ferrocenylfulvene).

Fulvenylferrocenes, particularly the 1,1'-bis(fulvenyl)ferrocenes, are useful synthons in the preparation of homo- and hetero-nuclear metallocenophanes [1,2]. The substituted mono(fulvenyl)ferrocenes 3, 4 and 5 and their parent system 1 as well as the substituted bis(fulvenyl)ferrocenes 6, 7 and 8 are known [3,4,5]. The unsubstituted bis(fulvenyl)ferrocene 2, however, has never been described in the literature. The mono(fulvenyl)ferrocene 1 (6-ferrocenylfulvene) has been obtained and characterized as a product of the Vilsmeier formylation of ferrocene, followed by reaction with sodium cyclopentadienide [6]. In an unsuccessful attempt to prepare the bis(fulvenyl)ferrocene 2, a readily polymerizing red oily product was described [7] as resulting from the reaction of 1,1'-ferrocene dialdehyde with cyclopentadiene.

Since the parent bis(fulvenyl)ferrocene 2 is now known to be a very valuable intermediate in the synthesis of [1,1]ferrocenophane [1] as well as of mixed metal metallocenophanes [2], we are reporting here two efficient syntheses leading to 2 in high yields.

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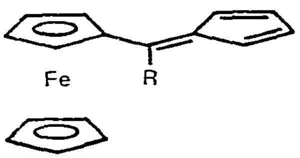
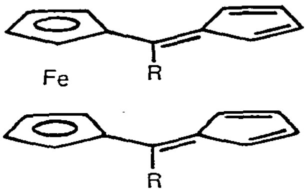


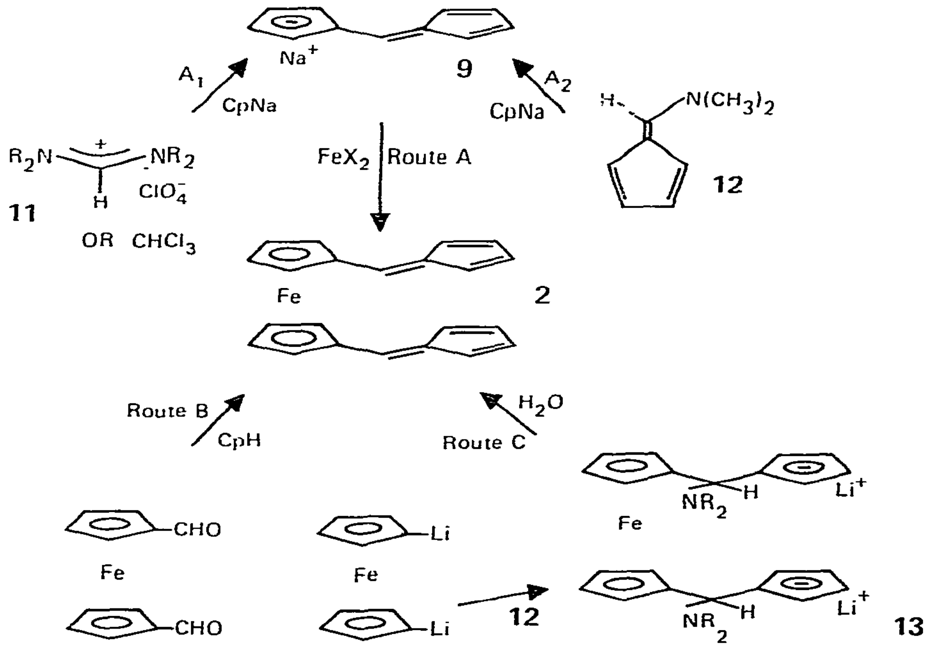


1: $R=H$
3: $R=CH_3$
4: $R=C_6H_5$
5: $R=(CH_3)_2N$

2: $R=H$
6: $R=CH_3$
7: $R=C_6H_5$
8: $R=(CH_3)_2N$

We have considered three preparative routes to **2**, which are outlined in the following. In the first one (route A), the ligand anion is prepared first and then reacted with ferrous halide to form **2**. This route offers generality, so that other fulvenylmetallocenes can be prepared as well [8]. Routes B and C start from a ferrocene derivative and only introduce the fulvene units. Several attempts to use the previously described [7] route B showed that this indeed is not a reasonable pathway. For this reason, and because routes A and C are very successful, we have abstained from trying to improve route B.

Several options exist in preparing the fulvenyl cyclopentadienide anion **9** required for route A (Scheme 1). This anion has been previously observed [9] spectroscopically as a product of the reaction between *N*,*N*′-dimethyl-*N*,*N*′-di-



SCHEME 1

phenylformamidinium perchlorate 11 and sodium cyclopentadienide. We found this reaction to be far from complete, because addition of ferrous chloride to the resulting solution produced a mixture of ferrocene, mono(fulvenyl)ferrocene 1 and bis(fulvenyl)ferrocene 2 in ratios depending upon reaction times, solvent and other less clear variables. The reaction produced, however, sufficient amounts of the anion 9 to allow us to isolate for the first time the bis(fulvenyl)-ferrocene 2 as a crystalline material. Assuming that an aminofulvene would be an intermediate in the above reaction, we have investigated the reaction of the known [10] 6-dimethylaminofulvene 12 with sodium cyclopentadienide in refluxing THF. This reaction is very slow, but it can be accelerated by the addition of [18]crown-6, so that almost complete conversion to 9 can be achieved within 24 h reflux. Addition of $FeCl_2 \cdot 2THF$ to the resulting solution of 9 produces 2 in yields of more than 90%. The anion 9 is also formed in the reaction of sodium cyclopentadienide with $CHCl_3$ in THF. This reaction proceeds in a non-stoichiometric way, with cyclopentadiene and/or its sodium salt always present as by-products, so that the subsequent reaction with ferrous halide again produces a mixture of ferrocene, 1 and 2. Best yields of 2 were around 20%, but a 13% yield of reasonably pure 2 was obtained when a 1/1 ratio of CpNa and $CHCl_3$ was used instead of the 4/1 ratio suggested by the equation $4CpNa + CHCl_3 \rightarrow Na^+9^- + 2CpH + 3NaCl$. In spite of the low yield, this reaction is useful because of its simplicity. The products ferrocene, 1 and 2 can be separated by column chromatography either on Al_2O_3 basic III with hexane or on SiO_2 with a 1/1 mixture of hexane and CCl_4.

By far the most convenient and practical synthesis of 2 is the reaction of the 1,1'-dilithioferrocene-TMEDA complex [11] with two equivalents of 6-dimethylaminofulvene 12. Addition of a THF solution of 12 to a suspension of the dilithioferrocene complex in hexane produces as a double addition product a yellow solution of the dianion 13. Addition of water immediately leads to a deep blood-red solution of the bis(fulvenyl)ferrocene 2 in total yields (based on starting ferrocene) consistently exceeding 80%. A simple recrystallization from hexane, without previous chromatography, leads to the pure product.

The analogous reaction of dilithioferrocene with only one equivalent of the fulvene 12 again leads to a mixture of the three ferrocenes, with the ratio of 1 to 2 approximately 3/2. For the preparation of 1, the original synthesis [6] from ferrocene via formylation and reaction with CpNa still seems to be the most reasonable method. However, as an alternative, we have converted the known [5] dimethylaminofulvenyl ferrocene 5 to 1 by reaction with $LiAlH_4$ in ether, followed by hydrolysis. In the initial step, the ferrocenyldimethylaminomethyl cyclopentadienide is formed. Upon hydrolysis, dimethylamine is instantly eliminated and 1 is formed cleanly. This reaction has its analogy in the known [12] reduction of 12 with $LiAlH_4$ in ether and hydrolysis to give the parent fulvene. If this reaction is carried out in THF, the reduction does not stop after the first hydride addition: amine transfer to the aluminate occurs, followed by further reduction of the resulting fulvene to methyl cyclopentadienide. It is therefore understandable that an attempt to convert the bis(dimethylaminofulvenyl)ferrocene 8 to the dianion 13 failed. Reduction of this bifunctional fulvene only led to a complex mixture of multiply reduced and condensed products.

The monofulvenyl ferrocene 1 forms deep red crystals from hexane with m.p. 60°C (lit. [6] 60°C). Even in the solid, it gradually polymerizes. It was characterized by the following data: elemental analysis: Found: C, 73.02; H, 5.34. $C_{16}H_{14}Fe$ calcd.: C, 73.31; H, 5.38%. UV-VIS spectrum in hexane solution: $\lambda_{max}(\epsilon)$: 485 (2345), 380 (shoulder, 2630), 322 (19075) and 270 (7035) nm; ^1H NMR (δ(ppm) in $CDCl_3$): ferrocene protons at 4.15 (singlet, 5H), 4.48 and 4.61 (multiplets, 2H each), fulvene protons: multiplets at 6.22 (1H), 6.42 (1H), 6.59 (2H) and singlet (1H) at 6.98.

The bis(fulvenyl)ferrocene 2 crystallized from deep red hexane solutions as almost black crystals of m.p. 112°C, which show a considerable tendency to polymerize. Its analytical data are: elemental analysis; Found: C, 78.06; H, 5.40. $C_{22}H_{18}Fe$ calcd.: C, 78,13; H, 5.36%. UV-VIS spectrum in hexane solution: $\lambda_{max}(\epsilon)$ 495 (3120), 412 (shoulder, 4100), 343 (22700) and 303 (23350) nm; ^1H NMR in $CDCl_3$: ferrocene multiplets at 4.43 and 4.60 ppm (4H each), fulvene multiplets at 6.16 (2H), 6.43 (2H) and 6.54 (4H) and singlet at 6.77 ppm (1H).

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