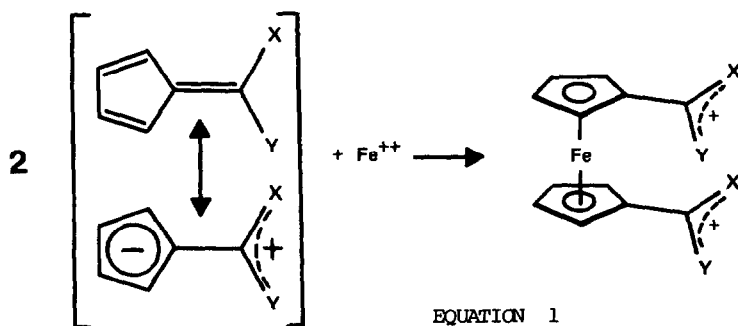


METALLOCENES FROM FULVENES : A NEW SYNTHESIS OF FUNCTIONALLY SUBSTITUTED FERROCENES

Ulrich Mueller-Westerhoff .
IBM Research Laboratory, San Jose, California 95114

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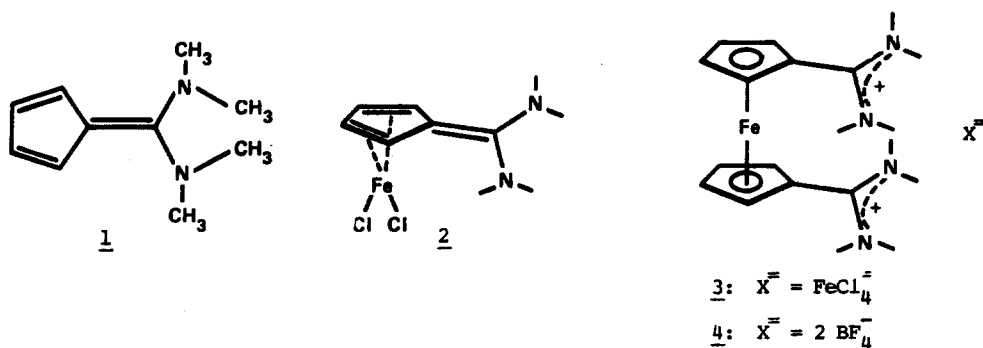
This communication reports the first examples of a direct conversion of fulvenes to ferrocenes. Known syntheses of substituted ferrocenes from fulvenes¹ all involve the reductive addition of metal hydrides or alkyl lithium reagents to fulvenes and the conversion of the resulting substituted cyclopentadienides to the corresponding ferrocenes². The high degree of polarity found in fulvenes should enable them to react directly with transition metal salts to form metallocenes according to eq. 1.



This hypothesis is substantiated by the existence of several fulvene transition metal carbonyl complexes³. The reaction of fulvenes with iron(II) salts leading to functionally 1,1'-disubstituted ferrocenes has now been realized experimentally.

The first choice of the exocyclic fulvene substituents in eq. 1 was X = Y = Me₂N, since the known⁴ 6,6-bis-dimethylaminofulvene 1 not only is thermally stable and highly polar

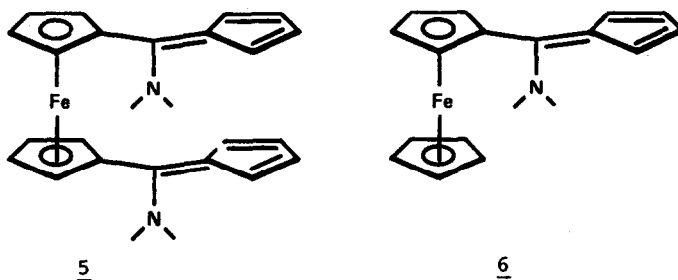
but also can be expected to lead to a ferrocene derivative in which the two positive charges reside predominantly on the carbamidiinium side groups. When 1 was reacted in THF with an excess of ferrous chloride⁵, a dark red non-crystalline compound (possibly the fulvene-FeCl₂ adduct 2) precipitated, which upon heating the reaction mixture to



reflux formed the brick-red crystalline 3 (dec. >145°). Repetition of this reaction with a 2:1 ratio of fulvene to ferrous chloride gave only traces of 3. This indicates that the species responsible for the formation of 3 must be a fulvene-FeCl₂ complex like 2, which is formed in a fast addition, followed by slow⁶ dimerization and rearrangement to 3. When 1 was heated in THF with an equimolar amount of ferrous chloride, 3 was formed in >99% yield.

Experimental evidence⁷ has confirmed the proposed structure 3, ferrocene-1,1'-bis-N,N',N',N'-tetramethyl-carbamidinium tetrachloroferrate(II). Alkaline hydrolysis of 3 immediately produced ferrocene-1,1'-bis-N,N-dimethylcarboxamide⁷ 7 (92%, mp 133°), identical with a sample prepared from 1,1'-dichlorocarbonyl ferrocene and dimethylamine⁸. Hot aqueous HCl gradually cleaved⁹ 3 to 1 (60% yield). By conversion of 3 to the bis-tetrafluoroborate 4 (red needles⁷, mp 195-96°) and its reaction with sodium cyclopentadienide (CpNa) 1,1'-bis-(6-dimethylamino-6-fulvenyl)-ferrocene⁷ 5 (dark red crystals, mp 147°, electronic spectrum in n-hexane: λ_{max} (log ϵ) 292(4.15), 394(4.29), 500(s) nm) was obtained. Proof for the presence in 3 of the uncommon tetrachloroferrate(II) dianion¹⁰ and for the ferrocenoid structure of 3 is obtained by its reaction with CpNa. In this case, 5 is formed together with an equimolar amount of ferrocene

and <1% of mono-(6-dimethylamino-6-fulvenyl)-ferrocene⁷ 6, which could stem from unreacted 2 occluded in 3. Product separation was achieved conveniently by column chromatography (Al₂O₃ Woelm, basic, activity III, ether/hexane). For comparison, 6 was synthesized from chlorocarbonyl ferrocene via the *N,N*-dimethyl-carboxamide⁷, alkylation of which by triethyl-oxonium tetrafluoroborate gave the oxonium-immonium salt⁷, which reacted with CpNa to give 6 (orange-red needles, mp 124°, electronic spectrum (n-hexane): λ_{max} (log ε) 287(3.97), 383(4.11), 500(s) nm). The NMR spectra of 5 and 6 in CDCl₃ at room temperature (given in τ, internal TMS: compound 5: 6.73(s,12H), 5.43(s,8H), 3.86(broad,4H), 3.19(broad,4H); compound 6: 6.55(s,6H), 5.80(s,5H), 5.52(t,J=2Hz,2H), 5.43(t,J=2Hz,2H), 3.69(m,2H), 3.2(broad,2H)) both show broadening of the fulvene but not of the dimethylamino resonances¹¹.



Other sufficiently polar fulvenes undergo the same reaction (eq. 1). Thus, 6-methyl-6-dimethylamino-fulvene¹² and ferrous chloride reacted in THF to give a salt analogous to 3, hydrolysis of which with aqueous KOH produced 85% (based on starting fulvene) of 1,1'-diacetyl ferrocene, identical with a commercially available authentic sample. Reaction of this salt with CpNa gave ferrocene together with the known¹³ 1,1'-bis-(6-methyl-6-fulvenyl)-ferrocene.

Extensions of this new synthesis and reactions of the synthetically versatile fulvenyl ferrocenes are under investigation.

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4. K.Hafner, G.Schulz and K.Wagner, Liebigs Ann.Chem., 678, 39 (1964); K.Hartke and G.Salamon, Chem. Ber., 103, 133 (1970).
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13. Prepared by base catalyzed condensation of 1,1'-diacetyl ferrocene and cyclopentadiene: M.Furdik, S.Toma and J.Suchy, Chem.Zvesti, 15, 547 (1961).