

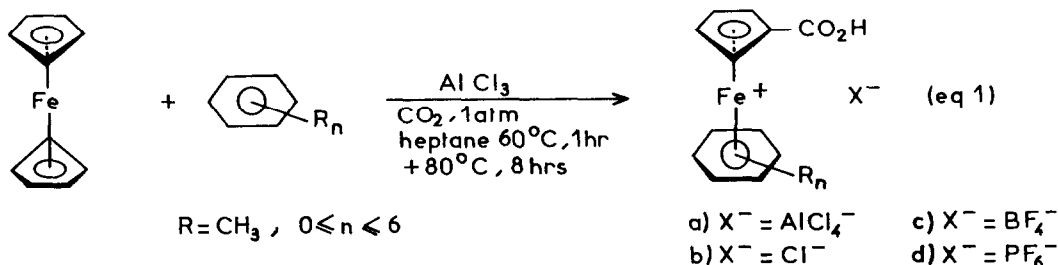
INSERTION OF CO₂ INTO THE $\eta^5\text{-C}_5\text{H}_4\text{-H}$ BOND DURING THE LIGAND EXCHANGE BETWEEN FERROCENE AND ARENES : A ONE-STEP SYNTHESIS OF THE ELECTROCHEMICAL CATALYSTS $\eta^5\text{-C}_5\text{H}_4\text{CO}_2^-\text{Fe}^+\eta^6\text{-ARENE}$.

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The functionalization of organometallic complexes, and specially of sandwich compounds, is of general interest since it provides a means to use them as biological tracers, energy conversion media and soluble catalysts. Yet many series of organometallic complexes suffer from instability, impossible or tedious synthetic routes or prohibitive cost. $\eta^5\text{-C}_5\text{H}_5\text{Fe}\eta^6\text{-C}_6(\text{CH}_3)_6^+$, a d⁶Fe(I) sandwich, is not marred by any of these difficulties and shows activity in the redox catalysis of electroreduction of NO₃⁻ to NH₃ in aq. LiOH 0,1N¹. Since this activity is limited by the insolubility of the reduced form $\eta^5\text{-C}_5\text{H}_5\text{Fe}\eta^6\text{-C}_6(\text{CH}_3)_6$, we have sought to solubilize this d⁷Fe(I) 19 electron complex by introducing a charged functional side chain such as carboxylate.

We report here the one-step synthesis of the acids $(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{HFe}\eta^6\text{-arene})^+$ from ferrocene, AlCl₃, the desired arene and CO₂ at atmospheric pressure (eq. 1).



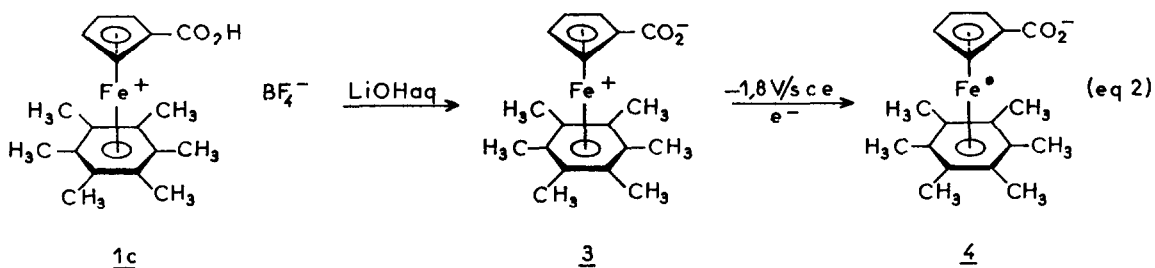
The carboxylation of ferrocene³ and the ligand exchange⁴, both induced by AlCl₃, proceed successively in the same pot. Typically 18.6 g of ferrocene (0.1 mol), 16.2 g of hexamethylbenzene (0.1 mol), 40 g of aluminium chloride (0.3 mol) are stirred for one hour in heptane under CO₂ (1 atm) at 60°C, then 1.8 g H₂O (0.1 mol) is added and the mixture is heated at 80°C for 12 hours. Hydrolysis of the tetrachloroaluminate 1a with water at 0°C provides the chloride 1b. Metathesis with NaBF₄ or aq. HBF₄ gives the tetrafluoroborate 1c.

The side product $\eta^5\text{-C}_5\text{H}_5\text{Fe } \eta^6\text{-C}_6(\text{CH}_3)_6^+\text{BF}_4^-$ 2 is formed by ligand exchange from both ferrocene and ferrocene carboxylic acid ^{2,5}. It is not soluble in water and therefore selectively isolated by precipitation by NaBF_4 in basic aqueous medium (20 % yield). In this medium the desired cationic organometallic acid $\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{HFe } \eta^6\text{-C}_6(\text{CH}_3)_6^+\text{BF}_4^-$ 1c is soluble as the zwitterion $\eta^5\text{-C}_5\text{H}_4\text{FeCO}_2^- \text{Fe } \eta^6\text{-C}_6(\text{CH}_3)_6^+$ 3. The alkaline solution can be used for electrochemical synthesis or catalysis or alternatively the salt 1c can be isolated and stored after precipitation in acidic medium (15 % yield after recrystallization from acetone).

¹H NMR (δ , CD_3COCD_3) : 4.9-5.1 (2 triplets, 4, C_5H_4) ; 2.60 (s, 18, CH_3) ;

¹³C NMR (decoupled, δ ppm, CD_3COCD_3) : 206.6 (CO_2H), 100.6 (C_6), 82.1 and 79.4 (CH_{Cp}), 80.7 (substituted C_{Cp}), 16.9 (CH_3).

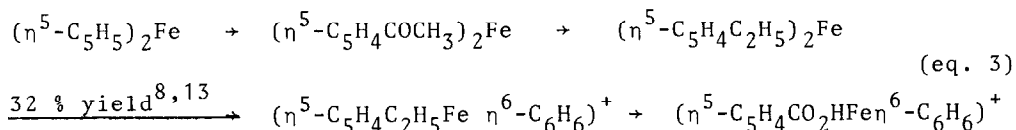
By reduction in aq. NaOH or LiOH 0,1N using a Hg cathode⁶ at -1,8V/s.c.e 3 provides the soluble and stable radical anion $\eta^5\text{-C}_5\text{H}_4\text{CO}_2^- \text{Fe } \eta^6\text{-C}_6(\text{CH}_3)_6$ 4 (eq. 2).



This homogeneous reversible redox system $\text{3} \rightleftharpoons \text{4}$ catalyses the electrochemical reduction of H_2O , NH_2OH and more interestingly of NO_3^- to NH_3 , a reaction which otherwise cannot proceed in aqueous medium ¹.

We have extended the procedure described here for 1 to the synthesis of other complexes of arenes for which the ligand exchange with a ferrocene ring ⁷ is feasible. For example we have prepared under similar conditions $(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{HFe } \eta^6\text{-naphthalene})^+\text{PF}_6^-$ (5, 12 % yield) and $(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{HFe } \eta^6\text{-mesitylene})^+\text{PF}_6^-$ (6, 25 % yield). Elemental analysis, ¹H and ¹³C NMR confirm the proposed structures, as for 1c.

The synthesis of the complex of benzene $(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{HFe } \eta^6\text{-C}_6\text{H}_6)^+\text{PF}_6^-$ (7) has been reported by Nesmeyanov et al by KMnO_4 oxidation of $(\eta^5\text{-C}_5\text{H}_4\text{C}_2\text{H}_5\text{Fe } \eta^6\text{-C}_6\text{H}_6)^+\text{BF}_4^-$ ¹² but this latter synthetic route cannot be extended to other arene complexes unless only CO_2H substituents are desired on the benzene ring¹² as well as on the cyclopentadienyl ring. We have also synthesized 7 by ligand exchange between ferrocene and benzene under CO_2 (34 % yield of 7, pure by ^1H and ^{13}C NMR and analysis), which requires 3 fewer synthetic steps than the reported route¹² (eq. 3). This latter route gave low yields and difficulties in purification of 7 in our hands :



On the contrary, note that the yield of the one-step synthesis with benzene as solvent is better than those obtained with solid arenes for which heptane must be used.

It has been extensively shown that many functional mixed sandwiches of this series are accessible from the acids^{12,14}. The straightforward and easy synthesis of pure acids that we describe will produce these compounds readily.

Since these metallocenic acids are anchored by dimerization in the solid state¹⁵, the crystal structure of 1c should be more readily solved than in the $(\eta^5\text{-C}_5\text{H}_5\text{Fe } \eta^6\text{-arene})^+$ series, for purpose of comparison with the available crystal structure of the 19 electron complex $\eta^5\text{-C}_5\text{H}_5\text{Fe } \eta^6\text{-C}_6(\text{CH}_3)_6$ ¹⁶.

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