Functional Organometallic Electron Reservoirs:[1] the 19-Electron Complexes $(\eta^5\text{-}C_5H_4CO_2H)(\eta^6\text{-}C_6Me_6)Fe^I$ and $(\eta^5\text{-}C_5H_4CO_2^-)(\eta^6\text{-}C_6Me_6)Fe^I$

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Na–Hg reduction of $[(\eta^5\text{-}C_5H_4CO_2H)(\eta^6\text{-}C_6Me_6)Fe^{II}]^+PF_6^-$, (**1**), rapidly gives the blue, thermally labile, air-sensitive acid $(\eta^5\text{-}C_5H_4CO_2H)(\eta^6\text{-}C_6Me_6)Fe^I$, (**3**), and (more slowly) the purple, thermally stable, extremely reactive, radical anion $(\eta^5\text{-}C_5H_4CO_2^-)(\eta^6\text{-}C_6Me_6)Fe^I$, (**4**), which is also obtained directly by Na–Hg reduction of the zwitterion $(\eta^5\text{-}C_5H_4CO_2^-)(\eta^6\text{-}C_6Me_6)Fe^+PF_6^-$, (**2**); spontaneous oxido-reduction of (**3**) and reaction of (**3**) or (**4**) with O_2 gives (**2**).

Stable Fe^I sandwich complexes have been designed to serve as molecular electron reservoirs, *inter alia* to effect stoicheiometric and catalytic activation of small molecules mediated by electron-transfer.[2] The functionalization of these redox catalysts is a highly desirable goal that we have pursued for some time. In general, functionalization of organometallic complexes is of interest to provide biological probes, modified electrodes, polymeric species, and more soluble catalysts. A large number of robust $[(\eta^5\text{-}C_5H_5)(\eta^6\text{-arene})Fe^{II}]^+$ complexes can be obtained with functional[3] arenes but, in all cases, the Fe^I forms decompose rapidly at or below room temperature. This communication describes the synthesis and characterization of both forms of the functional, quasi-reversible, redox system (**2**)⇌(**4**), and of the related unstable Fe^I acid $(\eta^5\text{-}C_5H_4CO_2H)(\eta^6\text{-}C_6Me_6)Fe$, (**3**).

$$\underset{(\mathbf{2})}{(\eta^5\text{-}C_5H_4CO_2^-)(\eta^6\text{-}C_6Me_6)Fe^+} \rightleftharpoons \underset{(\mathbf{4})}{(\eta^5\text{-}C_5H_4CO_2^-)(\eta^6\text{-}C_6Me_6)Fe}$$

The carboxylate group permits the solubilization of both (**1**) and (**4**) in water[4,5] and was introduced by the reaction of ferrocene with C_6Me_6 in the presence of CO_2 and $AlCl_3$,[5] which gives the precursor $[(\eta^5\text{-}C_5H_4CO_2H)(\eta^6\text{-}C_6Me_6)\text{-}Fe]^+PF_6^-$, (**1**).[4,5] Treatment of (**1**) with 1 equiv. of NaOH, followed by addition of excess of acetone and filtration at −20 °C to remove the soluble $NaPF_6$, gives the pure crystalline yellow zwitterion $(\mathbf{2})\cdot 3H_2O$† after recrystallization from ethanol–acetone. Its Mössbauer parameters (293 K, Q.S. = 1.86 mm s^{-1}, I.S. = 0.54 mm s^{-1} *vs.* Fe) are consistent with a d^6 Fe^{II} structure;[5] the slight decrease of the Q.S. {*vs.*

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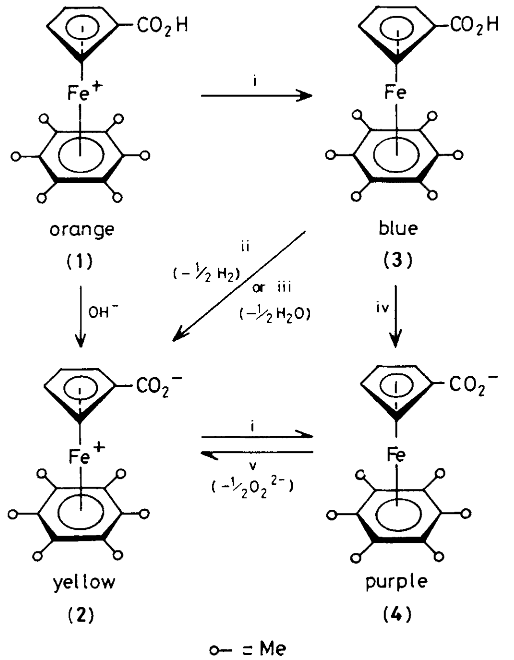
† *Selected analytical data:* (**2**) ^1H n.m.r. (CD_3CN; Me_4Si) δ: 4.66 (t, 2H, C_5H_4), 4.39 (t, 2H, C_5H_4), and 2.39 (s, 18H, C_6Me_6); ^{13}C n.m.r. (D_2O; external DSS, $Me_3SiCH_2CH_2SO_3Na$) δ: 173.1 (CO_2^-), 101.3 (C_6Me_6), 88.7 (substituted C_{Cp}, 82.2 (CH_{Cp}), 80.2 (CH_{Cp}), and 18.4 (C_6Me_6); i.r. (Nujol): 1650br. cm^{-1} (ν_{CO}); (**4**) i.r. (Nujol): 1625br. cm^{-1} (ν_{CO}). Satisfactory elemental analyses were obtained for (**2**) and (**4**).



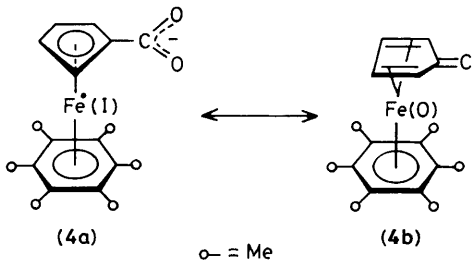
Scheme 1. *Reagents and conditions:* i, Na–Hg, THF, room temperature (r.t.), 15 min; ii, r.t., iii, $\frac{1}{2}O_2$, −20 °C; iv, Na–Hg, THF, r.t. 1 h; v, $\frac{1}{2}O_2$, r.t.

$[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)Fe]^+PF_6^-$: Q.S. = 2 mm s^{-1}} is probably due to the lowering of the sandwich symmetry.

The voltammogramm of (**2**) shows a quasi-reversible $Fe^{II} \rightleftharpoons Fe^{I}$ wave[6] (sweep rate: 0.1 V s^{-1}, *N,N*-dimethylformamide, $Bu^n_4NClO_4$, 0.1 M) at −1.67 V *vs.* standard calomel electrode (s.c.e.), *i.e.* at a potential 0.4 V more negative than the reversible reduction wave of (**1**) (−1.27 V *vs.* s.c.e.), which reflects both the changed electronic effect of the cyclopentadienyl, Cp, substituents and the significant Cp character of the antibonding e_1^* orbital (*ca.* 20%).[6a,7]

The Na–Hg reduction of (**1**) in tetrahydrofuran (THF) proceeds at 20 °C in 15 min, giving the blue Fe^I complex (**3**), soluble in THF and comparable to the known series of thermally stable, pentane-soluble, green complexes $(\eta^5\text{-}C_5R_5)(\eta^6\text{-}C_6R'_6)Fe^I$ (R = H or Me, R′ = Me or Et). Complex (**3**) can also be generated at −90 °C by reaction of (**1**) with $LiAlH_4$ in THF; its e.s.r. spectrum exhibits three *g* values (135 K, $g_x = 2.002$; $g_y = 2.065$; $g_z = 1.929$, as expected for the Fe^I sandwich series).

In the course of the Na–Hg reduction of (**1**), the appearance of (**3**) is only transient because of its spontaneous oxidoreduction to give (**2**) and H_2 at 20 °C. This process is formally, and possibly also in fact, an intramolecular electron transfer from Fe^I to the CO_2H group, to be expected since the irreversible electro-reduction of this group proceeds at a potential only 20 mV more negative than the reduction $Fe^{II} \rightarrow Fe^{I}$. Continuation of this reduction for 1 h gives a purple suspension of (**4**)† [possibly *via* (**3**)]. Complex (**4**) is also obtained more rapidly (15 min) by Na–Hg reduction of (**2**) under analogous conditions, followed by extraction and recrystallization using MeCN (60% yield). The 19-electron Fe^I complexes (**3**) and (**4**) both give the zwitterion (**2**) upon brief contact with O_2 or air (Scheme 1), rather than cyclohexadienyl complexes which would have been provided by H atom abstraction from a methyl substituent on the arene ligand.[8] The e.s.r. spectrum of (**4**) in THF at 133 K also shows the three *g* values ($g_x = 1.999$; $g_y = 2.065$; $g_z = 1.897$) characteristic of Fe^I sandwiches.[7,9] The Mössbauer spectrum of (**4**) at 77 K exhibits parameters specific to the Fe^I series (Q.S. = 1.54 mm s^{-1}, I.S. = 0.82 mm s^{-1}) without splitting of the quadrupole doublet[2a,b,8b] (slight broadening).



Two possible resonance forms of the radical anion (**4**) are (**4a**) and (**4b**). Given the red shifts (colour change from green to purple) obtained upon addition of a carboxylate substituent to the Cp ring of an Fe^I complex, this structural change clearly influences the electronic structure,[2b,7,10] in particular the $e_1^* \rightarrow e_2$ (arene) transition[2b] responsible for the colour. The e.s.r. and Mössbauer data appear to indicate that the contribution of (**4b**), if any, is small.

Radical anion electron reservoir systems, such as (**4**), are desirable because they can activate substrates such as O_2 and NO_3^- *via* electron transfer, and the radical anions thus generated ($O_2^{\cdot -}$ or $NO_3^{\cdot 2-}$) do not react irreversibly in the cage with the oxidized form of the Fe sandwich complex.[11]

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