First C_4 Bridged Mixed-valence Iron(II)–Iron(III) Complex delocalized on the Infrared Timescale

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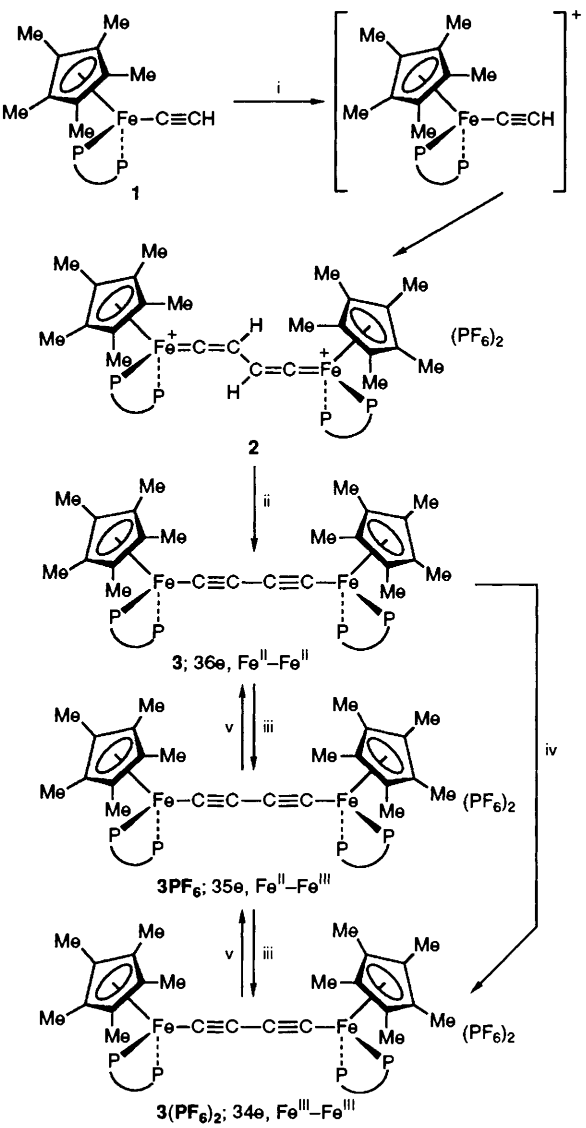
The first 35-electron acetylide bridged diiron complex [{Fe(η^5-C_5Me_5)(dppe)}$_2$(μ-C_4)]PF_6, **3PF₆** [dppe = ethylenebis(diphenylphosphine)] and the 36- and 34-electron bis-iron(II) and bis-iron(III) homologous derivatives are synthesized and it is established that the Fe^{II}–Fe^{III} complex is the first non-trapped mixed-valence compound with two half-sandwich monomeric units joined by a C_4 bridge.

Organometallic complexes whose metal centres are joined by carbon C_x are of interest both in the development of new molecular electronics and material science[1] and in the context of the many new carbon allotropes that have been recently available.[2] Meanwhile considerable literature has appeared on the Fe^{II}–Fe^{III} biferrocene and related sandwich systems,[3] the half-sandwich compounds were not sources of efforts directed towards the synthesis of mixed-valence polymetallic derivatives. The acetylide bridge has been used to join cyclopentadienyl ligands,[3] but the metal–acetylide–metal linkages were not developed to access to a new class of mixed-valence compounds.[4] We report here the first synthesis, characterization and basic physical properties of the 35-electron mixed-valence acetylide bridged diiron complex [{Fe(η^5-C_5Me_5)(dppe)}$_2$(μ-C_4)]PF_6. The 36- and 34-electron bis-iron(II) and bis-iron(III) homologous derivatives are also presented.

The terminal-acetylide complex [Fe(η^5-C_5Me_5)(dppe)(C≡CH)] **1**[5] treated with ferricinium (1 equiv.) in CH_2Cl_2 affords at −80 °C the bis-vinylidene complex [{Fe(η^5-C_5Me_5)(dppe)}$_2$(=C=CH–CH=C=)](PF_6)$_2$, **2** isolated as a brown powder in 90% yield. The ^{13}C NMR spectrum of **2** which shows a triplet at δ 358.5 ($^2J_{PC}$ 34 Hz) and a doublet at δ 108.0 ($^1J_{CH}$ 159 Hz) corresponding respectively to the α-C and β-C carbon atom of the bis-vinylidene bridge is characteristic of the structure.† The formation of **2** comes from the ligand–ligand coupling of the unstable 17-electron [Fe(η^5-C_5Me_5)(dppe)(C≡CH)]PF_6, **1**⁺, formed by the one-electron oxidation of the complex **1**. This reaction is a useful extension to the oxidatively induced coupling of the iron vinylidene [Fe(η^5-C_5H_5)(dppe)(=C=CHMe)]BF_4 reported by Iyer and Selegue,[6] since the secondary bis-vinylidene **2** should be a convenient precursor of bis-acetylide complex. Indeed, deprotonation of the bis-vinylidene compound **2** with KOBu^t (2.4 equiv.) in tetrahydrofuran (THF) at 20 °C gives the corresponding bis-acetylide [{Fe(η^5-C_5Me_5)(dppe)}$_2$(–C≡C–C≡C)] (**3**,† Scheme 1). Compound **3** is isolated as a thermally stable and air-sensitive brown powder in 95% yield. Carbon reso-

† Satisfactory C and H analyses were obtained, for **2**, **3**, **3PF₆** and **3(PF₆)₂**. Selected satisfactory spectroscopic data for new compounds: [{Fe(η^5-C_5Me_5)(dppe)}$_2$(=C=CH–CH=C=)](PF_6)$_2$ **2**, IR ν/cm^{-1} (Nujol) C=C 1585; ^1H NMR (20 °C, CD_2Cl_2) δ 4.37 (s, =CH, 2H), 2.89, 2.54 (2m, 8H, PCH_2), 1.52 (s, 30H, C_5Me_5); ^{13}C NMR (20 °C, CD_2Cl_2), δ 358.5 (t, α-C, $^2J_{PC}$ 34 Hz), 108.0 (d, β-C, $^1J_{CH}$ 159 Hz), 100.8 (s, C_5Me$_5$), 10.5 (q, C$_5$*Me*$_5$, $^1J_{CH}$ 128 Hz).

[{Fe(η^5-C_5Me_5)(dppe)}$_2$(–C≡C–C≡C)] **3**, ^1H NMR (20 °C, C_6D_6) δ 2.72, 1.89 (2m, 4H, CH_2), 1.55 (s, 30H, C_5Me_5). ^{13}C NMR (20 °C, C_6D_6), δ 110.2 (s, β-C); 99.7 (t, $^2J_{PC}$ 41 Hz, α-C), 87.8 (s, C_5Me$_5$), 10.5 (s, C$_5$*Me*$_5$).



Scheme 1 *Reagents and conditions*: i, CH_2Cl_2, $[Fe(\eta^5\text{-}C_5H_5)_2]PF_6$ (1 equiv.), −80 °C; ii, THF, Bu^{t}OK (1 equiv.), −80 °C; iii, CH_2Cl_2, $[Fe(\eta^5\text{-}C_5H_5)]PF_6$ (1 equiv.), 20 °C; iv, CH_2Cl_2, $[Fe(\eta^5\text{-}C_5H_5)]PF_6$ (2 equiv.), −80 °C; v, CH_2Cl_2, $[Co(\eta^5\text{-}C_5H_5)_2]$ (1 equiv.), 20 °C

nances of the C_4 bridge are unequivocally assigned on the basis of C–P coupling constant. The β-C carbon atom unusually appears as a singlet at a higher field (δ 110.2) than the α-C carbon (δ 99.7, J_{PC} = 42 Hz).

The initial scan in the cyclic voltammograms (CV) of complex **3** from +0.5 to −1.5 V [*vs.* standard calomel electrode (SCE)] is characterized by two reversible one-electron processes in dichloromethane with the (i_p^a/i_p^c) current ratio of unity. On the Pt anode, the two oxidation waves are observed at E_0 0.045 and −0.675 V *vs.* SCE (*cf.* ferrocene + 0.420 V *vs.* SCE). The anodic and cathodic peak separation ($E_p^a - E_p^c$) is 60 mV with a 100 mVs^{-1} scan rate. The low values of the oxidation potentials show these half-sandwich complexes to be electron-rich compounds. The large wave separation ($|E_1 - E_2|$ = 0.710 V) leads to an important comproportionation constant, [eqn. (1); $K_c = 1 \times 10^{12}$] and establishes that the delocalization of the $Fe^{II} - Fe^{III}$ system is definitely more important than in the biferrocenium series.[7]

$$Fe^{II}\text{–}Fe^{II} + Fe^{III}\text{–}Fe^{III} \rightleftharpoons 2\ Fe^{II}\text{–}Fe^{III} \qquad (1)$$

The addition of a stoichiometric amount of $[Fe(\eta^5\text{-}C_5H_5)_2]PF_6$ to a solution of **3** in CH_2Cl_2, resulted in a rapid colour change from brown-orange to dark-green. After precipitation by pentane, the Fe^{II}–Fe^{III} complex **3PF$_6$** was isolated as dark-green microcrystals in 92% yield. It was a thermally and air-stable compound with identical CV waves to that of its Fe^{II} parent complex. Oxidation of **3PF$_6$** or **3** with 1 or 2 equiv. of ferricinium respectively in CH_2Cl_2 produces a dark-blue solution from which blue microcrystals of **3(PF6)$_2$** are recovered in 95% yield by addition of pentane.

Complex **3** shows one characteristic doublet (77 K, *IS* = 0.27 mm s^{-1} *vs.* Fe, *QS* = 2.01 mm s^{-1}) by ^{57}Fe Mössbauer spectroscopy as for other half-sandwich Fe^{II} complexes.[8] The Mössbauer spectrum of the bication **[3(PF6)$_2$]** displays a doublet [77 K, *IS* = 0.18 mm s^{-1} (*vs.* Fe), *QS* = 1.05 mm s^{-1}] with two lines of unequal intensity owing to the magnetic relaxation phenomenon at the iron(III) centre, whereas the spectrum of the monocation **3PF$_6$** exhibits also a single doublet with parameters intermediate between those measured for **3** and **3(PF$_6$)$_2$** [77 K, *IS* = 0.21 mm s^{-1} (*vs.* Fe), *QS* = 1.32 mm s^{-1}]. A Mössbauer spectrum was also run at 4.2 K for **3PF$_6$** and its features are identical to those of the spectrum recorded at 77 K. The mixed-valance monocation **3PF$_6$** appears to be delocalized on the Mössbauer timescale. It is clear that the electron-transfer rate is more than *ca.* 10^7 s^{-1} even at 4.2 K.

Molecular vibrations occur on a shorter timescale of *ca.* 10^{-11} s, and consequently, it is possible to observe whether the electron-transfer rate is greater than 10^{12}–10^{13} s^{-1}. The spectrum of the neutral Fe^{II}–Fe^{II} complex **3** exhibits two absorptions in the region of the C≡C bond stretching at 1880 and 1955 cm^{-1} whereas those of the bis-Fe^{III}–Fe^{III} compound are located at 1950 and 2160 cm^{-1}. The IR spectrum of the mixed-valence species also displays two absorptions at 1880 and 1973 cm^{-1}, positions intermediate between those of the parent dioxidized and direduced complexes. One might expect a fully delocalized valence to show bands at the averaged position between those of the corresponding neutral molecule and dication, whereas the observed spectrum of **3PF$_6$** is not very different from that of **3**. Indeed, one stretching band has shifted by only 18 cm^{-1} from **3** and the other is unchanged. The spectrum of **3PF$_6$** is not the overlying of the spectra of **3** and **(3PF$_6$)$_2$**, and as a consequence the compound appears to be a delocalized mixed-valence complex on the IR timescale and there is probably no barrier to thermal electron transfer.[9] The one-odd electron binuclear complex **3PF$_6$** can be regarded, in terms of Robin and Day classification,[10c] as a delocalized class III mixed-valence compound.

The intervalence transfer (IT) band is a particularly characteristic feature generally present in the near-IR region of the electronic absorption spectrum for a mixed-valence complex.[10] The IT band appears in the near-IR spectra of **3PF$_6$** at 1326 nm (ε = 11 700 dm^3 mol^{-1} cm^{-1}, CH_2Cl_2). This absorption is absent from the spectra of both the **3** and **3(PF$_6$)$_2$** species. In this respect, the IT band observed for the mixed-valence Fe^{II}–Fe^{III} sandwich species [bis(fulvalene)-diiron]$^+$ (λ = 1550 nm, ε = 2100 dm^3 mol^{-1} cm^{-1})[7b] and {[2.2]ferrocenophane-1,13-diyne}$^+$ (1 = 1760 nm ε = 3100 dm^3 mol^{-1} cm^{-1})[7c] are weaker in intensity. According to the PKS theory, electronic coupling between the two metal centres in centrosymmetric binuclear complex is gauged by the parameter ε which is the main parameter to reflect a change in the bridge.[11] The metal–metal C_4 bridge in a half-sandwich series appears to be much more efficient for the electronic coupling of the Fe^{II} and Fe^{III} centres that two C_2 bridges between two ferrocene units. Moreover, the C_4 bridge appears to be also very attractive for the electronic coupling of the Fe^{III}–Fe^{III} centres since the dication **3(PF$_6$)$_2$** is ESR silent as expected for a spin-paired compound.

Finally, we have demonstrated that besides the biferrocene series which needs two bridged fulvalene ligands to exhibit a delocalized behaviour on the IR timescale, we have synthesized the first nontrapped mixed-valence Fe^{II}–Fe^{III} complex with one C_4 bridge between the two half-sandwich monomeric units.

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