Improved Synthesis and Electronic Structure of the 19- and 20-Electron Complexes $[Fe(\eta^6\text{-}C_6Me_6)_2]^{n+}$, $n = 1,0$[1]

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The 19- and 20-electron complexes $[Fe(\eta^6\text{-}C_6Me_6)_2]^{n+}$($n$ = 1,0) are best synthesized by Na/Hg reduction of $[Fe(\eta^6\text{-}C_6Me_6)_2]^{2+}[PF_6^-]_2$; the extremely negative value of the quadrupole splitting for $[Fe(\eta^6\text{-}C_6Me_6)_2]$, comparison of Mössbauer parameters of $[Fe(\eta^6\text{-}C_6Me_6)_2]^{n+}$ (n = 0,1,2), and the temperature dependence of the quadrupole splitting for $[Fe(\eta^6\text{-}C_6Me_6)_2]^+$ indicate high metal character for the antibonding e_1* orbital and rhombic distortion of the Jahn–Teller-active Fe^I complex.

The investigation of neutral, electron-rich organometallics, especially of metal sandwiches which exhibit several oxidation states, is of interest both in studies of the stoicheiometric[2] and catalytic[3] activation of small molecules by electron transfer and in the search for non-pairwise organometallic mechanisms.[4] Whereas 19-electron complexes are now well characterized,[5,6] the only stable 20-electron complex known is nickelocene[7] (and its methylated derivatives[7c]) and this is not very electron-rich.[7d] Another interesting family is that of the little-studied 19- and 20-electron complexes $[Fe(\eta^6\text{-}C_6Me_6)]^{n+}$, $n = 1,0$,[8] for which three oxidation states are reversibly interrelated $\{n = 2 \rightleftharpoons n = 1$ [$E_{1/2} = -0.5$ V *vs.* saturated calomel electrode (S.C.E.)]; $n = 1 \rightleftharpoons n = 0$ ($E_{1/2} = -1.37$ V *vs.* S.C.E.)$\}$.[8d] However, both complexes are accessible in only a few percent yield by the original Fischer syntheses.[8a] Weber and Brintzinger[8c] have reported ligand exchange reactions and an

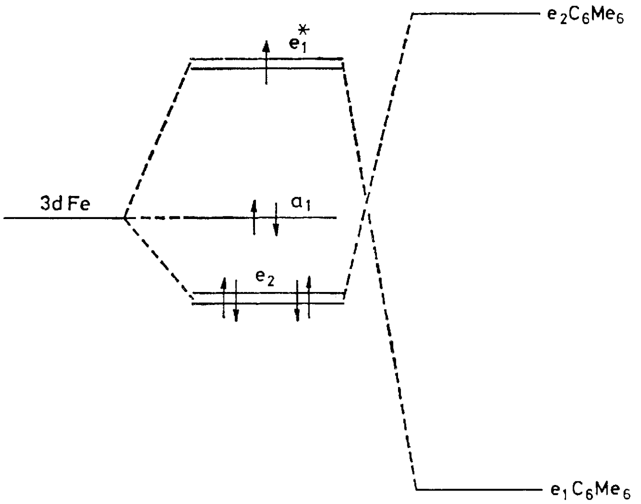

Figure 1. Schematic representation of the d-orbitals in the molecular orbital diagram for $[Fe(C_6Me_6)_2]^+$, $(\mathbf{1})^+$.

$[Fe(\eta^6\text{-}C_6Me_6)]^{n+}$
$(\mathbf{1})\ n = 0$
$(\mathbf{1})^+\ n = 1$

improved synthesis of $[Fe(\eta^6\text{-}C_6Me_6)_2]$, (**1**) using naphthyl sodium, but naphthalene is difficult to remove from this thermally unstable 20-electron complex.

We report here convenient high-yield syntheses of $(\mathbf{1})^+[PF_6^-]$ and (**1**) and Mössbauer data for $(\mathbf{1})^+$ and (**1**) which provide an easy way to determine the structures and purities of these complexes together with an insight into their electronic structures (Figure 1).

Na/Hg reduction of dry, microcrystalline $(\mathbf{1})^{2+}[PF_6^-]_2$ suspended in 1,2-dimethoxyethane (DME) under N_2 proceeds cleanly to (**1**) in 1 h at 20 °C. Removal of the solvent *in vacuo*, followed by extraction with toluene and precipitation by pentane at −90 °C, gives an 82% yield of pure (**1**) which can be recrystallized in toluene–pentane at −21 °C to give large black plates in 76% yield. If the Na/Hg reduction is stopped after 30—40 min, deep-purple microcrystalline $(\mathbf{1})^+[PF_6^-]$ can be isolated in 85% crude yield after removing the solvent *in vacuo*, extraction with acetone, and rapid precipitation with ether [salts of $(\mathbf{1})^+$ are unstable in solution]. The purities of (**1**) and $(\mathbf{1})^+[PF_6^-]$ may be verified by the observation of single Mössbauer quadrupole doublets in the spectra. The Mössbauer spectrum of thermally decomposed (**1**) indicates the formation of iron metal. The Mössbauer parameters of $(\mathbf{1})^+$-$[PF_6^-]$ are typical of an Fe^I sandwich.[6] The quadrupole splitting (Q.S.) value at 293 K (0.4 mm s^{-1}) is 1.6 mm s^{-1} lower than that[9] of $(\mathbf{1})^{2+}[PF_6^-]_2$ (2 mm s^{-1}) indicating high metal character for the singly occupied antibonding e_{1g}^* orbital[10] (*ca.* 80%, Figure 1). If this is also true for (**1**) (note that the ruthenium analogue is an 18-electron complex with one partly decoordinated η^4-arene)[11] it would imply an extremely negative Q.S. value. Unlike $(\mathbf{1})^+$, (**1**) has a temperature-invariant Q.S., consistent with two unpaired electrons on e_1^*. The absolute value of Q.S. is 1.45 mm s^{-1} but its sign must be obtained by examination of either the relative intensities and positions of the lines in the Mössbauer spectra of a single crystal or the splitting into a doublet and triplet of the absorptions in the spectrum of a powder sample in a magnetic field[12] (Figure 2). Both experiments lead to the conclusion that the Q.S. is negative (−1.45 mm s^{-1}), indeed by far the most negative value ever found for a neutral iron complex. Thus the metal character of e_{1g}^* in (**1**) is still higher (*ca.* 90%) than in $(\mathbf{1})^+$. Complex $(\mathbf{1})^+$ is temperature dependent (Figure 3) and the curves Q.S. = $f(T)$ vary dramatically with the nature of the counter-anion which indicates that the molecular electronic structure is extremely dependent on the lattice. The asymmetry of the external potential induces distortions of the Jahn–Teller-active Fe^I sandwiches,[6c] *e.g.* the splitting and population of

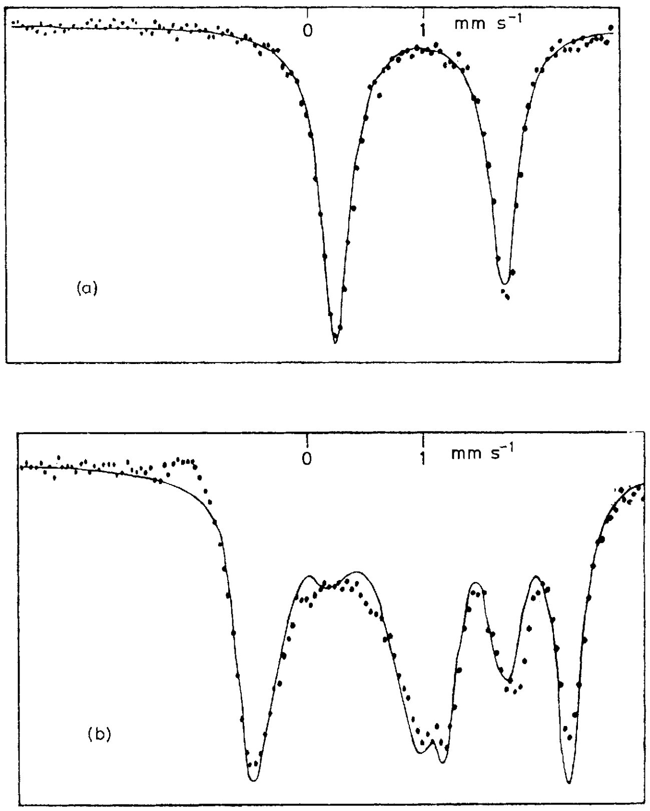

Figure 2. Mössbauer spectra of $[Fe(C_6Me_6)_2]$, (**1**) at 100 K (a) without applied magnetic field, and (b) under a 60 kG magnetic field. Complex (**1**) was diluted in hexane to avoid texture effects occuring in powdered samples. Fitted parameters: I.S. = 1.06 mm s^{-1} *vs.* Fe, Q.S. = −1.45 mm s^{-1}. (a) Splitting into a doublet (left line) and into a triplet (right line) indicating a negative sign for Q.S. (ref. 12), (b) a hyperfine field due to the paramagnetism of (**1**) ($S = 1$) is observed below 100 K.

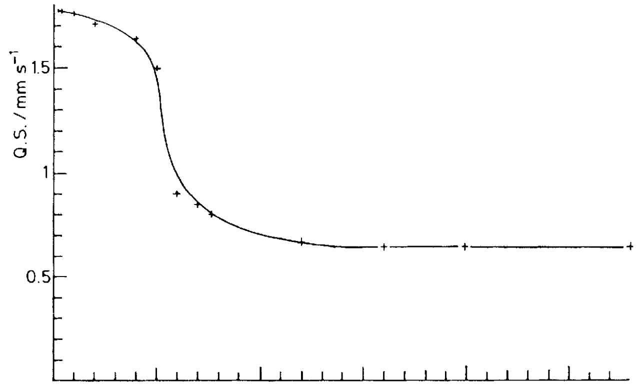

Figure 3. Temperature dependence of the quadrupole splitting for $(\mathbf{1})^+[PF_6^-]$. I.S. = 0.82 mm s^{-1} *vs.* Fe at 300 K. For comparison, the parameters of $(\mathbf{1})^{2+}[PF_6^-]_2$ are I.S. = 0.56 mm s^{-1} and Q.S. = 2 mm s^{-1} at 300 K, close to literature values (ref. 9).

the Kramer's doublet are strongly influenced by the counter-anion lattice. Since these variation of Q.S. do not fit a simple law of thermal population {contrary to $[(C_5R_5)Fe^I(\eta^6\text{-}C_6R_6)]$[6a,b,13] complexes with R = H or Me},[15] the phenomena are complex and probably involve several phases and phase transitions.

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