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Molecular batteries: synthesis and characterization of a dendritic 19-electron Fe^{I} complex that reduces C_{60} to its mono-anion†

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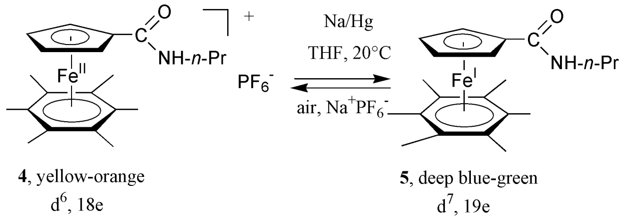
Received (in Cambridge, UK) 20th March 2002, Accepted 9th April 2002

First published as an Advance Article on the web 19th April 2002

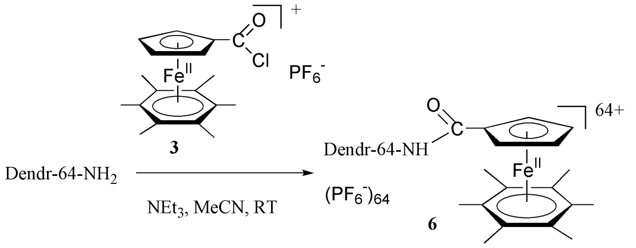
Both redox forms of the dendrimer [dendr-64-NHCOCp-$Fe^{II}(\eta^6$-$C_6Me_6)]^{64+/0}$, 6/7, are synthesized and characterized, and the 19-electron form reduces C_{60} to [dendr-64-NHCOCp$Fe^{II}(\eta^6$-$C_6Me_6)]^{64+}(C_{60}^{-\cdot})_{64}$, 8.

Molecular complexes containing many stable redox systems are excellent molecular batteries that may be major components in molecular-electronic devices.[1] For instance, ferrocenyl dendrimers[2–4] are obvious candidates for such a purpose, because the peripheral sites containing ferrocenyl groups are sufficiently remote from one another. Consequently, they are active at the same redox potential,[5] at least when they are not linked by electron-withdrawing groups that destabilize the ferrocenium form.[3] Ferrocenes are poor reductants, however. The complexes $[Fe(\eta^5$-$C_5R_5)(\eta^6$-$C_6Me_6)]^{2+/+/0}$ are isolobal to ferrocenes in their monocationic state, and are thermally stable, excellent oxidants (R = Me) and reductants (R = H or Me) in their dicationic and neutral forms, respectively. This latter family of electron-reservoir complexes has indeed been shown to be efficient for various stoichiometric and catalytic electron-transfer reactions.[6] Attempts to attach these complexes to dendritic cores *via* the easily functionalizable C_6Me_6 ligand have systematically been marred by insolubility problems. We now find that branching by means of a chlorocarbonyl substituent on the Cp ligand gratifyingly leads, upon reaction with dendritic polyamines, to soluble Fe^{II} metallodendrimers that, in addition, can be reduced to Fe^{I} by the 19-electron complex $[Fe^{I}Cp(\eta^6$-$C_6Me_6)]$, **1**.

The chlorocarbonyl complex $[Fe^{II}(\eta^5$-$C_5H_4COCl)(\eta^6$-$C_6Me_6)]$ **3** synthesized from the carboxylic acid **2**[6b] and $SOCl_2$ (neat) overnight at reflux, reacts with *n*-propylamine (a model of dendritic amines) in the presence of NEt_3 in MeCN (RT) to give the amide **4**. Reduction of the latter by Na/Hg in THF (RT) gives the deep-blue–green, thermally stable 19-electron complex **5** [eqn. (1)] that shows the classic rhombic distorsion of the Fe^{I} sandwich family, observable by EPR in frozen THF at 77 K (3 *g* values around 2).[6c] Given this stability, we carried out the same reaction of **3** with the commercial DAB-polypropyleneimine dendrimer of generation 5 (64 amino termini) in MeCN–CH_2Cl_2 (2 : 1) in the presence of NEt_3. The polycationic metallodendrimer [dendr-64-NHCOCp$Fe^{II}(\eta^6$-$C_6Me_6)]^{64+}$ **6** was obtained as the PF_6^- salt that is soluble in MeCN and DMF [eqn. (2)]. This dendritic complex **6** was characterized by ^1H and ^{13}C NMR and IR spectroscopies and cyclovoltammetry [a single reversible wave in DMF, at $E_{1/2} = -1.84$ V *vs.* $FeCp_2^{0/+}$; $\Delta E = 60$ mV, see Fig. 1(a)]. The calculated number of redox centers in **6** using the Bard–Anson formula[5b] for polymers that involves the relative wave intensities of the monomer and dendrimer is 63 ± 6. This value is presumably in slight excess because the commercial dendrimer is not perfect.[7] Attempts to reduce **6** with the classic reductants that reduce **4** to **5** such as Na mirror, Na/Hg or $LiAlH_4$ in THF or DME failed due to the insolubility of both **6** and the reductant in the required solvents. The only successful reductant in our hands was the parent 19-electron complex **1**. Titration of **6** in MeCN by color change



(1)



(2)

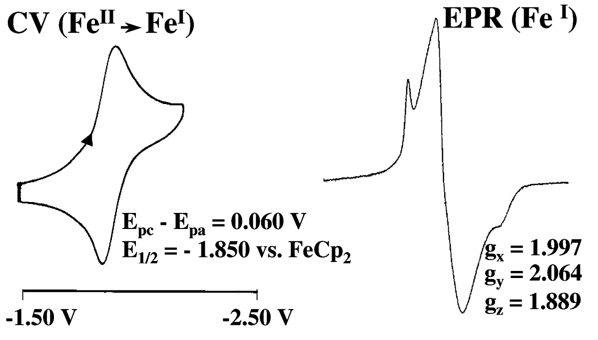


Fig. 1 (a) Cyclovoltammogram of the metallodendrimer **6** in DMF at 293 K, 0.1 M *n*-Bu_4PF_6, Pt, scan rate 0.1 V s^{-1} (left), and (b) EPR of the 19-electron metallodendrimer **7** at 10 K (right).

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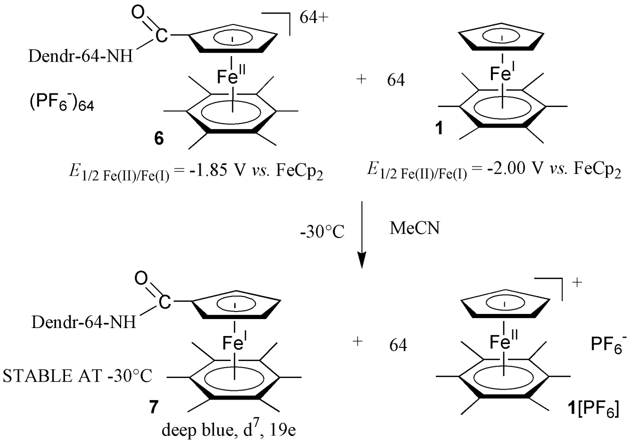
† Electronic supplementary information (ESI) available: experimental procedures and characterization data for the new compounds. See http//www.rsc.org/suppdata/cc/b2/b202684h/

DOI: 10.1039/b202684h

at −30 °C to the neutral, deep-blue–green 19-electron Fe^I dendrimer **7** required 64 mol **1** per mol **6** [eqn. (3)]. The exoergonicity of this electron-transfer reaction, 0.15 eV, is due to the electron-withdrawing amido substituents in the dendrimer **6**. The 19-electron dendrimer **7** decomposes at 0 °C in MeCN. It was characterized by its EPR spectrum at 10 K, confirming, as the deep-blue–green color, the Fe^I-sandwich structure analogous to that of the model **5** [Fig. 1(b)]. Contrary to the case of **1**, however, **7** is EPR-silent above 10 K. This is presumably due to intra-dendritic relaxation among the peripheral Fe^I sandwich units. The intermolecular version of this relaxation effect is known to preclude observation of the spectrum of monomeric Fe^I sandwich complexes in the solid state above 4 K and in solution above 77 K.[6c]



(3)

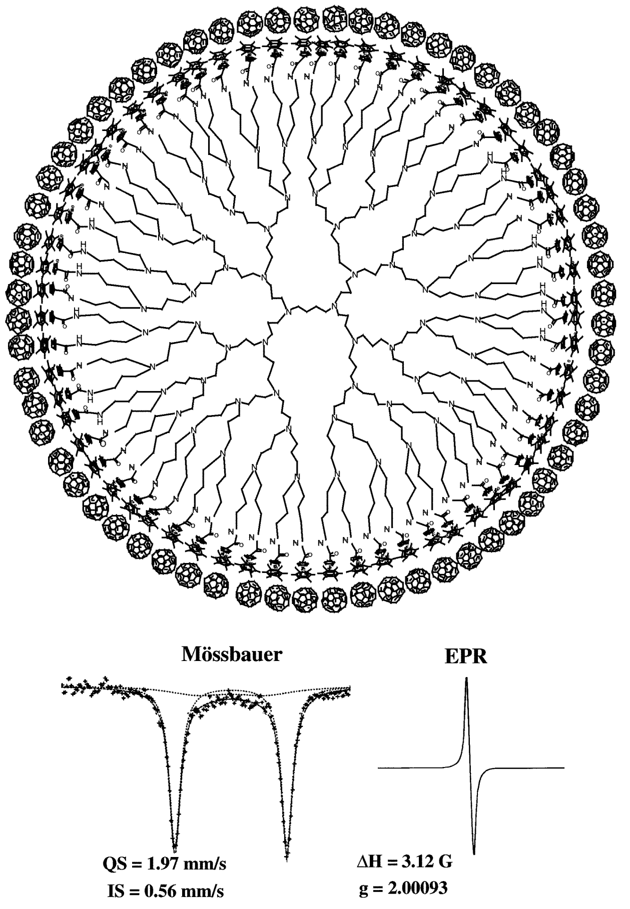
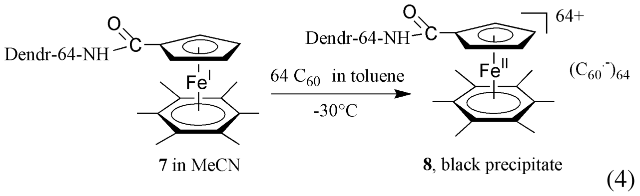


Fig. 2 [Dendr-64-NHCOCpFe(C_6Me_6)]$^{64+}$($C_{60}^{\bullet-}$)$_{64}$, **8**, resulting from the reaction of **7** with C_{60} in MeCN–toluene at −30 °C and (below) Mössbauer (77 K, left) and EPR specta (298 K, right).

This acetonitrile solution of the 64-Fe^I dendrimer **7** was used for the reaction with C_{60}, the stoichiometry found upon titration of **7** by C_{60} being Fe^I:C_{60} = 1:1 (64 C_{60} per dendrimer). Indeed, upon reaction with a toluene solution of C_{60}, the deep-blue–green color of **7** disappeared, leaving a yellow solution that contained **1**[PF$_6$] and a black precipitate of **8** [eqn. (4)].



(4)

Tentative extraction of this precipitate with toluene yielded a colorless solution, which indicated that no C_{60} was present. The Mössbauer spectra of this black solid **8** is a clean quadrupole doublet whose parameters at 77 K (Fig. 2) show the presence of an Fe^{II} sandwich complex of the same family as **1**$^+$.[6a,c] Its EPR spectrum recorded at 298 K shows the same EPR spectrum as that of **1**$^+C_{60}^-$.[6d] It can thus be concluded that C_{60} has been reduced to its monoanion, as designed for a process that is exergonic by 0.9 eV.[8] The [dendr-Fe^{II}]$^+C_{60}^-$ units of **8** being very large, they are most likely located at the dendrimer periphery, presumably with rather tight ion pairs although the number of fullerene layers and overall molecular size are unknown (Fig. 2).

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