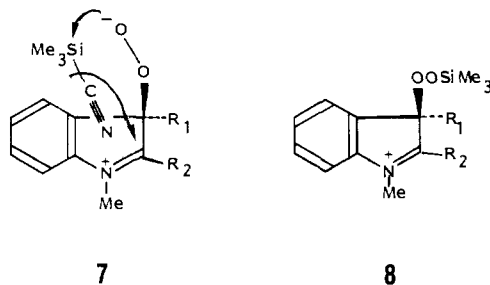


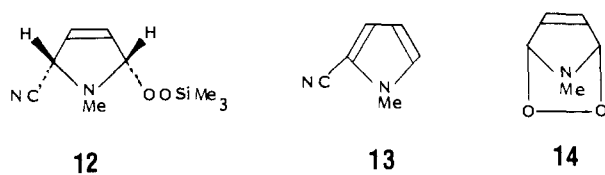
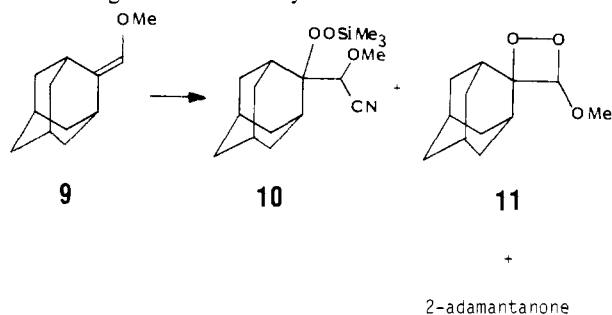
clusive formation of cis adducts was observed at least under the reaction conditions.¹⁹

The formation of cis adducts is significant as it constitutes evidence for the existence of a precursive peroxide intermediate. The results are most easily rationalized by assuming addition of TMSCN to a dipolar peroxide intermediate such as a zwitterion or perepoxide.²⁰ Thus the nucleophilic attack by peroxy anion on the silicon would give a pentacoordinated silicon which deposits directly the cyanide ion at the cationic site of the trapped dipolar species as illustrated as transition state 7 using an example of



zwitterion. However, the observed cis stereoselectivity cannot distinguish between the zwitterion and the alternative perepoxide formation.²¹

TMSCN was found to intercept the precursor of 1,2-dioxetanes formed in photooxygenation of unsymmetrical enol ethers. For example, TPP-sensitized photooxygenation of 2-(methoxymethylene)adamantane (**9**, 50 mM) in the presence of TMSCN (5 equiv) in dichloromethane at $-70\text{ }^{\circ}\text{C}$ produced the adducts **10** (35%), dioxetane **11** (30%), and 2-adamantanone (22%). Without TMSCN **9** gave **11** exclusively.²³ TMSCN did not react with



11 under the conditions of photooxygenation. It was reported that the precursor of **11** was captured by acetaldehyde as solvent at $-78\text{ }^{\circ}\text{C}$.¹² In contrast, photooxygenation of symmetrical enol ethers such as 1,4-dioxene²⁴ and 2,3-diphenyl-1,4-dioxene²⁵ in the presence of a large excess of TMSCN in dichloromethane or acetonitrile produced none of the trapping products but gave only the corresponding dioxetanes and their ring cleavage products.²⁶

(19) However, in the presence of a large excess of TMSCN (more than 10 equiv) at higher temperature, formation of trans adduct was detectable by ^1H NMR in case of **1a**.

(20) TMSCN-assisted ring opening of short-lived indole dioxetanes giving oxiranes by TMSCN is known to provide trans adducts exclusively.²² However, in that case a mixture of cis and trans adducts should be formed.

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Lastly, we demonstrate another example of photooxygenation of heterocycles in the presence of TMSCN. TPP-sensitized photooxygenation of *N*-methylpyrrole in the presence of TMSCN (5 equiv) in dichloromethane at $-70\text{ }^{\circ}\text{C}$ produced **12**²⁸ quantitatively as evidenced by ^1H NMR at $-70\text{ }^{\circ}\text{C}$. On warming to room temperature the adduct **12** was decomposed to afford **13** (90%) with 1,4-elimination of trimethylsilyl hydroperoxide. Addition of excess TMSCN to the solution of endoperoxide **14**,²⁹ prepared by photooxygenation of *N*-methylpyrrole in CDCl_3 at $-60\text{ }^{\circ}\text{C}$, also produced **12** (80%) presumably via trapping of the zwitterionic peroxide that may be in equilibrium with **14**.^{10a,30}

The results of our preliminary investigations demonstrate the potential use of trimethylsilyl cyanide as an excellent trapping agent for dipolar peroxide intermediates in aprotic solvents. The extension of the mechanistic principle and the synthetic applications are in progress.

(26) Recent ab initio MO calculations²⁷ have indicated that the concerted $[2_s + 2_a]$ mechanism is the most favorable for $^1\text{O}_2$ reaction of symmetrical enol ethers, whereas the two-step mechanism involving 1,4-zwitterion is the most probable for unsymmetrical enol ethers. For related recent papers, see ref 5c and 6d.

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36- to 40-Electron Complexes ($\text{C}_6\text{R}_6\text{FeCp}-\text{CpFeC}_6\text{R}_6$)^{n±} (R = H, Me; n = 0-2) and the First Delocalized Mixed Valence Complexes Containing Fe^I

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The electrochemistry and electron-transfer chemistry of binuclear delocalized transition-metal complexes has stimulated the study of mixed-valence systems.² These materials, some of which are biomimetic (e.g., ferredoxin models), have specific physical properties related to electron transfer.² We envisioned that coupling these properties with those of molecular electron reservoirs³ would give a novel class of compounds. For instance, an enhanced potential and efficiency in electron-transfer catalysis (electrocatalysis and redox catalysis)⁴ can be expected with two

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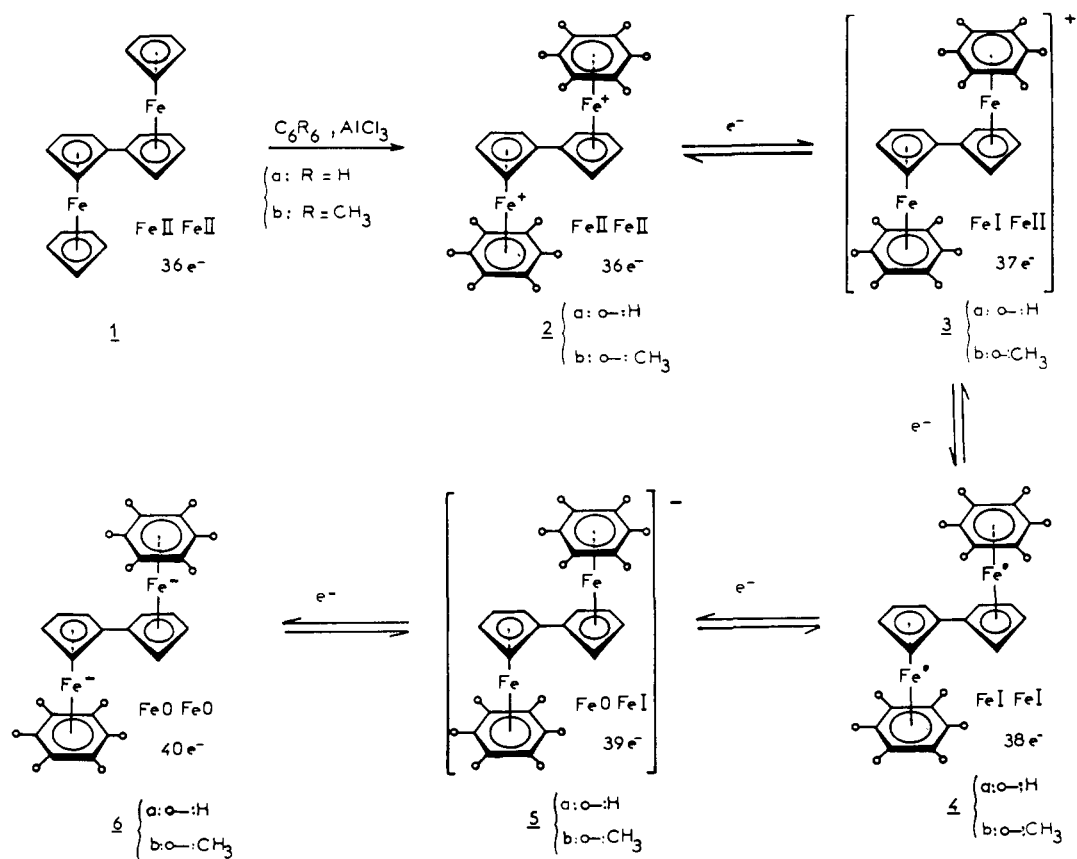
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Scheme I



active sites having similar redox potentials. We report here the synthesis, electrochemistry, and electronic structure of binuclear Cp-Fe-arene sandwiches **2-6** in which bridging is achieved by the fulvalene ligand. These systems represent the attainment of five oxidation states involving the couples $Fe^{II}Fe^{II}$, $Fe^I Fe^{II}$, $Fe^I Fe^I$, $Fe^0 Fe^I$ and $Fe^0 Fe^0$. In addition, **3** is the first mixed-valence $Fe^I Fe^{II}$ slipped triple decker which is delocalized even at 4.2 K.⁵

These five oxidation states available to the system are clearly discernible in the voltammograms^{6a-c} of the parent $Fe^{II}Fe^{II}$ precursors **2a**^{6d} and $(\eta^{12}, \mu^2-C_{12}H_{10})(\eta^5-CpFe)_2^{2+}(PF_6^-)_2$ (**7**)^{6e} at $-30^\circ C$ on Hg in DMF + Bu_4NBF_4 (0.1 M), showing four quasi-reversible waves⁷ (0.1–0.5 V/s): $36 e^- \rightleftharpoons 37 e^- \rightleftharpoons 38 e^- \rightleftharpoons 39 e^- \rightleftharpoons 40 e^-$ (E° , V: **2a** -1.15, -1.47, -2.10, -2.47; **7** -1.11, -1.25, -2.23, -2.36). The two waves $36 e^- \rightleftharpoons 37 e^-$ and $37 e^- \rightleftharpoons 38 e^-$ are much more separated for **2a** ($\Delta E = 320$ mV) than for **7** ($\Delta E = 140$ mV).⁷ A similar trend⁷ is found for the two other waves $38 e^- \rightleftharpoons 39 e^-$ and $39 e^- \rightleftharpoons 40 e^-$. This finding is consistent with the higher Cp than arene character in the antibonding e^*_1 level

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(7) At $20^\circ C$, however, only the first wave is reversible for **2a** and **7**.

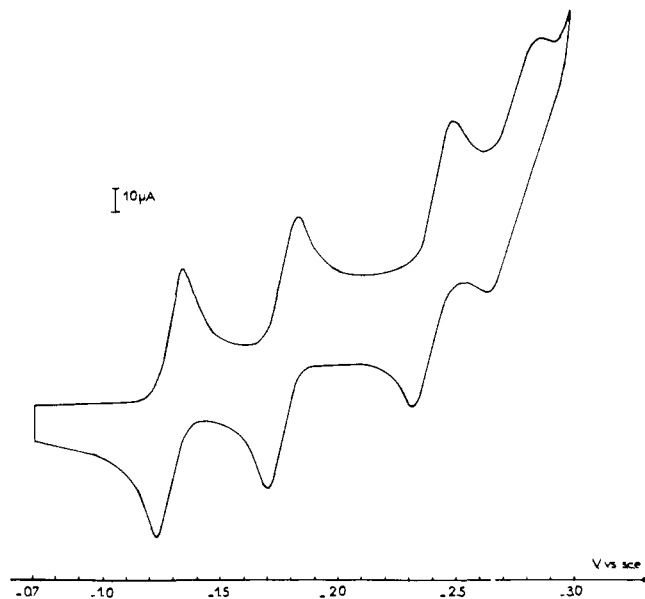


Figure 1. Cyclic voltammogram of a 1.0×10^{-3} M solution of $(\eta^6-C_6Me_6)Fe^{+1/2}(PF_6^-)_2$ (**2b**) in DMF on a hanging Hg cathode/0.1 M Bu_4NBF_4 (scan rate = 0.5 V/s; $-30^\circ C$), E° (V vs sce) -1.28, -1.76, -2.39, -2.73. The reversibility for the couples $Fe^I Fe^I \rightleftharpoons (Fe^0 Fe^I)^-$ $\rightleftharpoons (Fe^0 Fe^0)^{2-}$ is reduced at $20^\circ C$.

of the monomeric Fe^I complexes.^{3b} The rather large separation of the two first reduction potentials of **2a** suggests that the mixed-valence monocationic $Fe^I Fe^{II}$ complex **3a** is synthetically more easily accessible than its biphenyl analogue.⁸ Since we know that $Cp(\eta^6-C_6R_6)Fe^I$ complexes are thermally stable for $R = Me$ (**8**)³ and not for $R = H$, we also synthesized the new permethyl

(8) (a) The $LiAlH_4$ reduction of **7** in THF at $-80^\circ C$ leads to a blue $Fe^I Fe^I$ complex.^{8b} (b) Desbois M.-H.; Astruc, D., manuscript in preparation.

precursor **2b** from **1** (Scheme I, 14% yield, orange crystals⁹). The permethylation stabilizes the highly reduced oxidation states as can be seen on the voltammogram of **2b** (Figure 1). Whereas the Na-Hg reduction of **2a** in THF at 20 °C led to decomposition, the analogous reaction with **2b** gave, after 1 h, a deep purple, thermally stable, air-sensitive complex which could be extracted with acetone, precipitated by ether, and recrystallized from acetone at -40 °C (80% yield of **3b**, purple crystals).¹⁰ Contact with air and water, followed by metathesis with H^+PF_6^- , gave back **2b**. The EPR spectra of the samples of **3a,b** in frozen THF solutions at 77 K showed three g values close to 2 (**3a** $g_x = 2.005$, $g_y = 2.072$, $g_z = 1.911$; **3b** $g_x = 2.005$, $g_y = 2.071$, $g_z = 1.906$) corresponding to a rhombic distortion.¹¹ The magnetic susceptibility of **3b** (Gouy method: $m = 1.7 \mu_B$) indicated the presence of a single electron per bis sandwich. This result was confirmed by the Mössbauer spectra under 6 T: the contact (Fermi) term found was 5.5 T, corresponding to 42% electron on each Fe (13 T per electron). Since the HOMO has 83% metal character (vide supra), it means that each sandwich carries only half of an extra electron. The zero field Mössbauer spectra of **3a,b** at 4.2, 77, and 293 K showed a single doublet¹⁰ indicating that only one type of iron is detectable at the Mössbauer frequency (10^9 s^{-1}).

Thus, electron exchange between the two iron centers is faster than 10^9 s^{-1} at 4.2 K, and therefore **3a,b** belong to the class III of the mixed-valence complexes.^{2c} Since the bulky C_6Me_6 ligands prevent the two iron centers from coming close to each other—they must remain on opposite sides of the fulvalene bridge—the electron jump must proceed through it.¹² An outstanding feature of the Mössbauer doublet observed for **3a,b** is that the quadrupole splitting is independent of the temperature, contrasting sharply with temperature dependences observed for all Fe^I monomers.³ This property of the delocalized mixed-valence system **3a,b** suggests a modified electronic structure, e.g., strong electronic coupling between the two sandwiches. We believe that it is due to the fact that, in Fe^I monomers, the $e_1^*(\text{Fe})$ and $e_1(\text{Cp})$ orbitals have close energy levels, a characteristic that was actually the source of the concept leading to the design of such average valence substrates. This coupling is corroborated by preliminary SCC EHT calculations effected with trans Fe units: the thermal population of the upper Kramers' doublet, which causes the variation $\text{QS} = f(T)^2$, is no longer involved since the 37th electron occupies a single orbital of 83% metal character. The purple color of **3** (**3b**: $\lambda = 554 \text{ nm}$, $\epsilon = 7660 \text{ L mol}^{-1} \text{ cm}^{-1}$) is also at variance with the usual dark green found in Fe^I monomers, a color attributed to the $e_1^* \rightarrow e_2$ transition.^{3b} The 38-electron complexes **4** can be generated from **2a-b** and Na-Hg (**4a**) or potassium mirrors (**4b**) in THF.¹³ It is interesting that, as Fe^I monomers, they are also dark green (at -50 °C, $\lambda = 725 \text{ nm}$, $\epsilon = 1400 \text{ L mol}^{-1} \text{ cm}^{-1}$), which suggests an Fe^IFe^I formulation. Another indication along this line is given by EPR spectra, recorded at 77 K in frozen THF, which show the absence of Cp-Cp coupling to diamagnetic Fe^0Fe^0 fulvalene.¹⁴

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(13) These dark-green THF solutions of Fe^IFe^I complexes **4a,b** were chemically and electrochemically characterized and titrated as follows: addition of $1/2$ mol of I_2 or $1/4$ mol of O_2 at -20 °C gave back (fast) purple precipitates of **3a,b** and 1 mol of NaI or $1/2$ mol of Na_2O_2 , respectively (for salt effects due to NaPF_6 upon formation of $[\text{Fe}^I\text{O}_2^-]$ from $\text{Fe}^I + \text{O}_2$, see: Hamon, J.-R.; Astruc, D. *J. Am. Chem. Soc.* **1983**, *105*, 5951). Further reaction with $1/2$ mol of I_2 or $1/4$ mol of O_2 was slower ($1/2$ h for completion at -20 °C) and gives back the orange solids **2a,b**. Cyclic voltammograms of **4a,b** (THF + DMF, -30 °C, $n\text{-Bu}_4\text{NBF}_4$, Hg) also show the oxidation waves to $\text{Fe}^I\text{Fe}^{II}$ and further to $\text{Fe}^{II}\text{Fe}^{II}$, as in Figure 1.

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The rhombic distortion in **4a** ($g_{\perp} = 1.994$, $g_{\parallel} = 2.076$) and **4b** ($g_{\perp} = 2.019$, $g_{\parallel} = 1.921$) is different from that in **3a-b** or in Fe^I monomers. Despite its thermal instability above -10 °C, **4a** was synthesized by Na-Hg reduction (THF, 4 h, -20 °C) of **2a** followed by filtration at -20 °C; green-black microcrystals were obtained by addition of pentane at -80 °C; they burn explosively upon contact with air. The Mössbauer spectra were recorded under Ar and fitted between 4.2 and 220 K. The values of the parameters (IS = 0.8 mm s^{-1} vs. Fe; QS = 1.43 mm s^{-1} at 4.2 K and 0.6 mm s^{-1} at 220 K) as well as the sharp QS variation (supplementary material, i.e., 0.80 mm s^{-1} at 80 K) are definitive evidence for $d^7 \text{ Fe}^I$ complexes such as $\text{CpFe}^I\text{C}_6\text{R}_6$ (R = H, Me).¹⁵ These data emphasize the specificity of the electronic structure of the average valence complexes containing Fe^I .

Acknowledgment. We thank Drs. J.-J. Girerd (Orsay), B. Nickel, and A. Jeunet (Grenoble) for EPR assistance, Dr. M. Lamotte (Bordeaux) for designing low-temperature UV-vis experiments, and the DGRST for grants to M.H.D. and J.G.

Registry No. **1**, 1287-38-3; **2a**, 53702-58-2; **2b**, 97431-19-1; **3a**, 97431-21-5; **3b**, 97431-20-4; **4a**, 78398-48-8; **4b**, 97431-22-6; **7**, 51539-79-8; C_6Me_6 , 87-85-4.

Supplementary Material Available: Mössbauer spectra of **4a**—variation of the quadrupole splitting with the temperature between 4.2 and 220 K (1 page). Ordering information is given on any current masthead page.

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Intermediacy of the Parent Diazonium Ion (Protonated Dinitrogen, N_2^+H) in the Diazotization of Ammonia and Its Derivatives with $^{15}\text{NO}^+\text{BF}_4^-$ Giving $^{15}\text{N}^{14}\text{N}^{14}$

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Protonated dinitrogen **1**, the parent diazonium ion HN_2^+ , remains elusive in the condensed state. All attempts, including our own,² to effect protonation of dinitrogen even in the strongest superacids (HF-SbF_5) were inconclusive. Direct spectroscopic observation of diazonium ion was not achieved nor was there any effect observed of added nitrogen on the rate of H_2 and D^+ exchange reaction (the change in the exchange rate was used as a probe to detect possible protonation of nitrogen).³ In contrast to the condensed state HN_2^+ , **1** has been observed in the gas phase mass spectrometric and ICR studies.^{4,5} Recently by use of Laser magnetic resonance rotational spectroscopy⁶ the N-H vibration-rotation band of **1** has been detected in ac glow discharge.^{7a} More recently even the N-N stretch has been observed.^{7b} Significantly **1** was also detected in extraterrestrial space indicative of ion-molecular reactions taking place in interstellar cloud chemistry. Theoretical calculation on **1** at STO-3G basis set level

* Dedicated to Professor Rolf Huisgen on occasion of his 65th birthday.

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