volvement of a peroxy intermediate in C-17 side-chain cleavage; however, rearrangement to androgen via the Baeyer-Villiger reaction was not considered an option. We feel that, in light of the above finding, this rearrangement must be considered a viable option. It is consistent with the studies of Akhtar in which ^{18}O was incorporated into acetate and is also consistent with the formation of the Δ^{16} steroids, which are formed by loss of the 17β side chain and the 16α-hydrogen.[9]

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Salt-Induced, Ligand-Controlled, Intra- vs Intermolecular Electron Transfer in a Fulvalene-Bridged Organoiron Diradical

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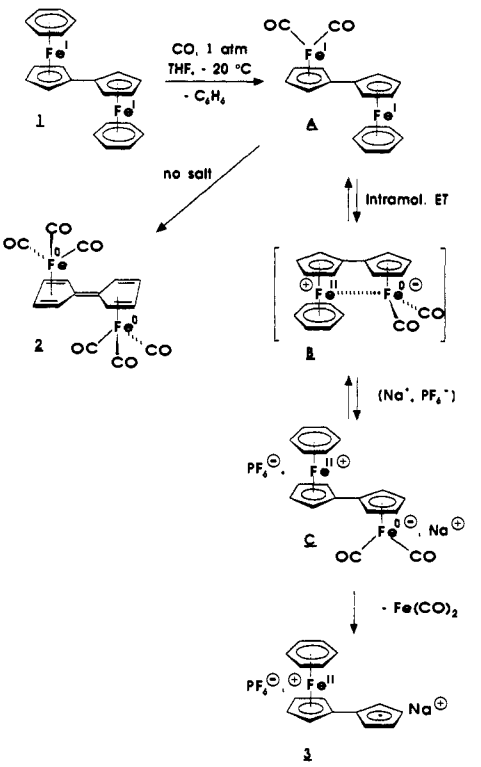
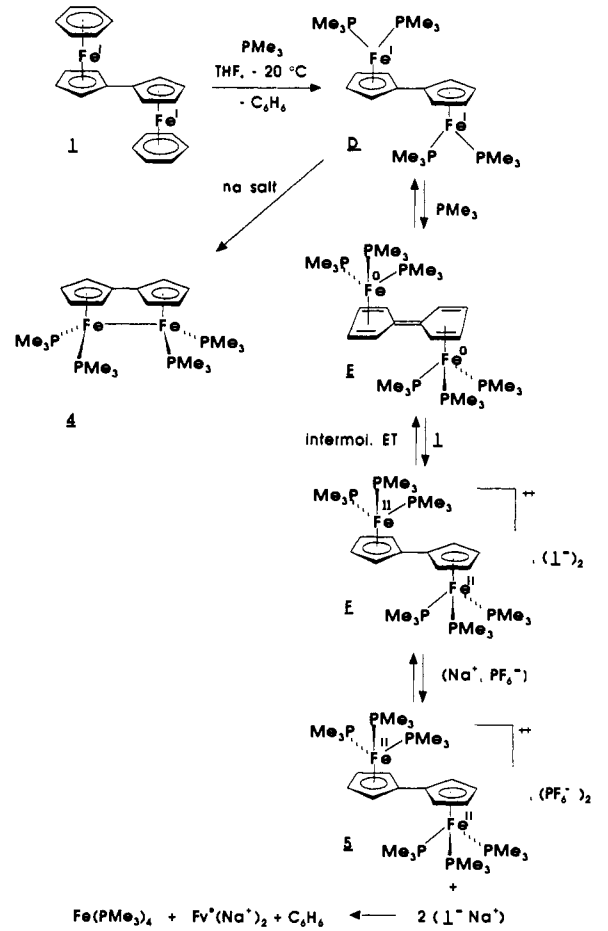
We report that a Na^+ salt induces intramolecular electron transfer (ET) between the two iron redox centers of the fulvalene-bridged diradical **1** upon ligand exchange and that this ET can be switched to intermolecular ET by controlling the donicity of the incoming ligand. This special salt effect[1] is shown here to bear a synthetic potential in transition metal chemistry due to the facility of these elements to change their redox states.[2-4]

The reaction of the bis 19-electron complex $[Fe^I_2(\mu_2,\eta^{10}\text{-Fv})(\eta^6\text{-}C_6H_6)_2]$ (**1**)[5] (Fv = fulvalene)[6] at -20 °C with 1 atm of CO in THF in the absence of $Na^+PF_6^-$ leads as expected to the replacement of both benzene ligands by six CO's, giving the slightly unstable new red diamagnetic complex **2**[7] which indicates elec-

Scheme I



Scheme II



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tronic rearrangement of the fulvalene ligand (Scheme I). Much to our surprise, the same reaction carried out in the presence of 2 equiv of $Na^+PF_6^-$ gave a major product which did not show CO IR bands. The stable red complex **3**[8] obtained in 35% yield has a rare[6f] monometallic fulvalene structure. The elemental analysis shows the presence of the Na^+ and PF_6^- counterions.[8] The cationic Fe^{II} d^6 zwitterionic state is confirmed not only by the NMR and Mössbauer data[8] but also by the cyclic voltammogram, characteristic of the $[Fe^{II}Cp(arene)]^+$ series (a reversible 1-electron wave at -1.32 V vs SCE and a chemically irreversible 1-electron wave at -2.23 V (i_a/i_c = 0 at 20 °C and 0.2 at -50 °C); irreversible oxidation of Cp^- at +0.81 V, 0.4 V s^{-1}, DMF, 0.1 M nBu_4NBF_4, Pt). Thus the $Fe(CO)_2$ fragment was lost from the proposed intermediate A in Scheme I. Compare with the reaction of the mononuclear 19-electron complex $[Fe^ICp(C_6H_6)]$[6c,d] with CO in THF which was reported to give $[FeCp(CO)_2]_2$ whether or not $Na^+PF_6^-$ was present.[9] The change of reaction of **1** in the presence of $Na^+PF_6^-$ is best taken into account by a double ion exchange[5] between the two ion pairs B and $Na^+PF_6^-$ (Scheme I). In B, there is the possibility of stabilization of the zwitterion by intramolecular ion pairing allowed by the free rotation about the Cp-Cp bond (ET is roughly isoergonic[4b,6] and reversible), but this $Fe^+\cdots Fe^-$ interaction must be dislocated by $Na^+PF_6^-$, which drives the formation of **3**.

The reaction of **1** with PMe_3 in THF at -20 °C in the absence of $Na^+PF_6^-$ follows a course similar to that with CO, giving the thermally unstable diamagnetic orange-red complex **4** (Scheme II). The latter was characterized inter alia by the symmetrical fulvalene ^1H and ^{31}P NMR pattern[10] and the mass spectrum, giving a minor peak at $(M = PMe_3)^+$ and major peaks at $(PMe_3)^+$, $(M - 4PMe_3)^+$, and $(FeFv)_n^+$, n = 2 and 3 (biferrocenylene and triferrocenylene, respectively).

The same reaction in the presence of 2 equiv of $Na^+PF_6^-$ gives the stable, orange, new diamagnetic d^6 dication **5** (50%)[11] and the known complex $[Fe(PMe_3)_4]$[9,12] (30%), the formation of which is driven by the decomposition of 1^-Na^+ as in the case of the monoiron chemistry.[9] The formation of **5** (in the maximum disproportionation yield) provides a very efficient entry from sandwich into new piano stool diiron fulvalene chemistry.

Thus from *intramolecular* ET with CO, the $Na^+PF_6^-$-induced ET becomes *intermolecular* with PMe_3. Each time the salt effect is quantitative as in monoiron chemistry[9,13,14] using $Na^+PF_6^-$, a very efficient although common salt. This way to direct and control ET using a simple Na^+ salt brings about a very versatile synthetic tool in molecular chemistry. As an illustration, the electronic communication between two metal centers mediated across a delocalized hydrocarbon ligand was induced and modulated.

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(7) (a) $[Fe_2(\mu_2\text{-Fv})(CO)_6]$ (**2**): ^1H NMR ($CDCl_3$, δ ppm) 5.34, 5.05 (2t, C_5H_4, 2 × 4 H); ^{13}C NMR ($CDCl_3$) 218.63 (*C*O), 88.62, 86.53, 76.03 (C_5H_4); IR (CH_2Cl_2) ν_{CO} 2000, 1940 cm^{-1}; slightly thermally unstable at 20 °C. (b) Butenschön recently reported $[Fe_2(\mu_2\text{-Fv})(CO)_4]$, which differs from **2** inter alia by its stability and NMR and IR: Bister, H. J.; Butenschön, H. *Synlett* **1992**, 22.

(8) $[Fe_2(\eta^5\text{-Fv})(C_6H_6)(NaPF_6)]$ (**3**): ^1H NMR (CD_3COCD_3, δ ppm) 6.10 (s, C_6H_6, 6 H), 5.24, 5.08, 4.70, 4.47 (4t, C_5H_4, 4 × 2 H); ^{13}C NMR (CD_3COCD_3) 89.6 (C_6H_6), 96.31, 78.23, 76.83, 73.61, 72.44, 69.31 ($C_5H_4C_5H_4$); Mössbauer (mm/s vs Fe, 293 K) I.S. 0.52, Q.S. 1.61; CV (DMF, 0.1 M nBu_4NBF_4, Pt, 20 °C, 0.4 V/s) $E°$ (V vs SCE) - 1.32 V (i_a/i_c = 0.8), ΔE_p = 90 mV, E_{pc} = -2.23 V (irrev), E_{pa} = +0.81 V (i_c/i_a = 0), (-50 °C) $E°$ (V vs SCE) -1.35 V (i_a/i_c = 1), 2.19 V (i_a/i_c = 0.2), ΔE_p = 170 mV, +0.84 (irrev). Anal. Calcd for $C_{16}H_{14}FeNaPF_6$: C, 44.68; H, 3.28. Found: C, 44.87; H, 3.30. The modest yield of **3** is due to the instability of the diradical **1** above -10 °C; 10% of the oxidation product $[Fe^+(C_6H_6)(\mu_2\text{-Fv})(CO)_2]_2\text{-}(PF_6^-)_2$ was also found.

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(10) (a) $[Fe_2(\mu_2\text{-Fv})(PMe_3)_4]$, (**4**): ^1H NMR ($C_6D_5CD_3$, δ ppm) 3.652, 3.345 (2t, C_5H_4, 2 × 4 H); 1.458-0.987 (2m, CH_3, 36 H); ^{31}P NMR ($C_6D_5CD_3$, δ vs 85% H_3PO_4) 26.70. (b) Butenschön's complex[7b] is the "carbonyl equivalent" of **4**.

(11) $[Fe_2(\mu_2\text{-Fv})(PMe_3)_6](PF_6^-)_2$ (**5**): ^1H NMR (CD_3CN, δ ppm) 5.04, 4.63 (2m, $C_5H_4C_5H_4$, 8 H), 1.55 (m, Me, 54 H); ^{31}P NMR (CD_3COCD_3) 22.4; ^{13}C NMR (CD_3COCD_3) 88.23, 82.9, 78.35 ($C_5H_4C_5H_4$), 22.23 (m, $P(CH_3)_3$); Mössbauer (mm/s vs Fe, 293 K) I.S. 0.320, Q.S. 1.762; CV (DMF 0.1 M nBu_4NBF_4, Pt, -30 °C, 0.4 V/s) E (V vs SCE) - 1.65 (i_a/i_c = 0), + 0.70 (i_c/i_a = 1), ΔE_p = 70 mV, + 1.08 (i_c/i_a = 0.9; quasi-reversible). Anal. Calcd for $C_{28}H_{62}Fe_2P_8F_{12}$: C, 34.07; H, 6.28. Found: C, 34.50; H, 5.74. (b) The salt-induced ET reaction (Scheme II) is the only route to **6** (for instance, photolysis of $1^{2+}(PF_6^-)_2$ in CH_3CN in the presence of excess PMe_3 could not yield **6**).

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Rapid Photopolymerization of Immunoprotective Gels in Contact with Cells and Tissue

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Microencapsulation and cell transplantation technology hold promise in many areas of medicine and biotechnology, such as the treatment of diabetes[1-4] and the evaluation of candidate antiviral[5] and antitumor[6] drugs. Successful microencapsulation of cells requires that the cells survive encapsulation and retain their normal function, that the membrane be stable under physiological conditions over several years, and that it be permselective with a molecular weight cutoff in the range 50 000-100 000 Da so as to be immunoprotective. It is also important that the microcapsules be biocompatible so as to resist a fibrous reaction by the host, as is seen in some currently investigated microcapsules,[2,7] which can greatly reduce oxygen and nutrient diffusion to the transplanted cells.

The polymerization of materials in intimate contact with cells or tissue without loss of viability is quite difficult. Polymerization of acrylamide monomer upon microspherical scaffolds of agarose-containing cells has been performed successfully,[8] but this can generate excessive local heating and cytotoxicity if attempted directly on tissue.[9] Here we report the synthesis of stable, biocompatible gels with permselectivity appropriate for immunoprotection via rapid photopolymerization of water-soluble poly(ethylene glycol)-based macromers in direct contact with cells and tissue without cytotoxicity. The particular polymerization scheme chosen permitted gelation in the presence of dissolved oxygen, which is generally important in maintaining cell viability.

The use of poly(ethylene glycol) (PEG) to obtain biocompatibility by reducing protein adsorption, cell adhesion, and fibrous encapsulation of materials is well established.[10-13] PEG diacrylates

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