Organoiron Electron-Reservoir Complexes[†]

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The geometry of transition-metal organometallic compounds and the accessibility of multiple oxidation states provide a unique opportunity to design molecular electron reservoirs. This concept is implicit for biological electron carriers and their synthetic models.[1] Molecular electron reservoirs are compounds which store and transfer electrons stoichiometrically or catalytically without decomposition. Organometallic electrochemistry is now well developed;[2] however reversible redox systems for which both the oxidized and reduced forms have been isolated are relatively scarce.

The unusual Fe^I oxidation state can be obtained either by one-electron oxidation of electron-rich Fe^0 complexes[2] or by one-electron reduction of Fe^{II} complexes.[3-6] The latter approach is specially noteworthy because it can lead to the 19-electron structure if no decoordination occurs. Whereas organometallic complexes are commonly known with 8 to 18 electrons in the metal valence shell, violation of the 18-electron rule by an excess of electrons is rare because loss of a ligand usually occurs.

The discovery that 19-electron Fe^I species could be stabilized and isolated (e.g., the $CpFe^I(arene)$ structure) provided the possibility to gain insight into the physics and chemistry of this oxidation state. The 19-electron structure of these neutral complexes and their very negative redox potentials suggested the use of these complexes as molecular electron-reservoirs. Indeed based on their ionization potentials measured by He I photoelectron spectroscopy,[7] the thermally stable $CpFe^I(arene)$ complexes are the most electron-rich molecules known to date. Thus, they can effect a variety of stoichiometric and catalytic electron-transfer (ET) processes.[8] These have implications in organic and organometallic synthesis, molecular activation, biology, and technology of materials.

Several hundred $(CpFe^{II}(arene))^+$ complexes are directly available by ligand exchange of a Cp ring in ferrocene for an arene or by transformation of the arene

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after complexation.[8] One-electron reduction of these cations leads to decomposition of the thermally unstable Fe^I complexes.[9] However, the key starting point to the synthesis and use of electron-reservoir complexes was the discovery that the neutral iron(I) complexes are thermally stable only if the arene ligand is peralkylated or sterically protected.[4-6] Thus, the parent complex of the thermally stable Fe(I) series is $CpFe^IC_6Me_6$, 1, synthesized in 90% yield, from $(CpFe^{II}C_6Me_6)^+PF_6^-$, 2, by Na/Hg reduction.

Functionalization can be effected, for instance to solubilize the Fe^I form in water (vide infra). Indeed, performing the ligand exchange reaction between the Cp ring of ferrocene and C_6Me_6 under CO_2 yields the useful yellow carboxylic acid $(CpCO_2H\ Fe^{II}C_6Me_6)^+$, 3.[10] The latter is reduced to the unstable blue Fe^I acid and further to the thermally stable purple iron(I) carboxylate anion 4. In basic medium, 3 is deprotonated to the zwitterion which is more quickly reduced than 3 to 4.[11]

Other peralkyl complexes $[CpFe^{II}(C_6CH_2R)_6]^+$ (R = Me, 8; $PhCH_2$, 9) are synthesized by reacting 2 with t-BuOK and RX (eq 1; Figure 1). This is a reaction of synthetic potential since, for instance, it gives $C_6(CH_2CH_2Ph)_6$ from C_6Me_6 in 56% overall yield (R =

[†] This article is dedicated to Professor Raymond Calas.

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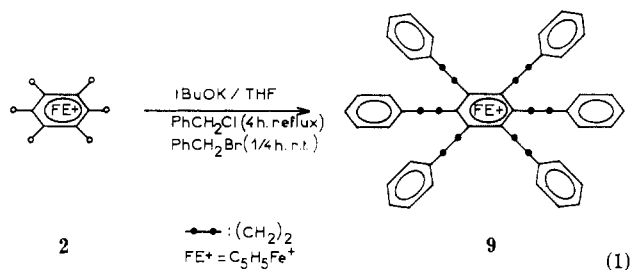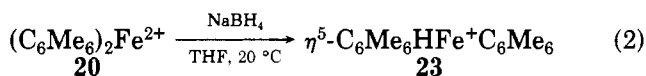
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(1)

Figure 1. X-ray crystal structure of $(CpFe^{II}C_6Et_6)^+PF_6^-$, 8.

293 K

Figure 2. X-ray crystal structure of $CpFe^{I}C_6Me_6$ at 293 K (Fe–Fe distance: 7 Å), from ref 4. The alternating positions of the small Cp and large C_6Me_6 rings are responsible for the presence of two sites (two Mössbauer doublets are observed between 30 and 180 K, see Figure 4).

benzyl, X = Br or Cl).[12]   Similarly, $(CpFe^{II}(1,3,5-C_6H_3-t-Bu_3))^+$, **5**, is available from $(CpFe^{II}(1,3,5-C_6H_3Me_3))^+$.[12]

All these extensive peralkylation reactions proceed by benzylic deprotonation, the acidity being considerably enhanced in the presence of the electron-withdrawing $(CpFe^{II})^+$ group. The deprotonated species is stabilized by its ferrocene like structure. Alkylation of the electrophilic exocyclic methylene by RX regenerates the aromaticity of the original $(CpFe^{II}(arene))^+$ sandwich and the reaction continues.

The fully methylated complex $(C_5Me_5Fe^{II}C_6Me_6)^+$, **6**, cannot be made from substitutionally inert decamethylferrocene, but from $C_5Me_5Fe(CO)_2Br$, as are other $(C_5Me_5Fe^{II}(arene))^+$ complexes.[4,13] On the other hand, $(C_5Me_5Fe^{II}C_6Et_6)^+$ is not accessible. In the presence of C_6Et_6, complexation proceeds with selective cleavage of one Et group even at 70 °C giving the pure pentaethylbenzene complex $(C_5Me_5Fe^{II}C_6Et_5H)^+$, **7**. Na/Hg reductions of the cationic precursors **2**, **5**, **6**, **7**, **8**, and **9** at 20 °C in THF or DME provide the thermally stable green 19-electron complexes **1**, **10**, **11**, **12**, **13**, and **14** in high yields.[4,13] The binuclear fulvalene compounds $[Fe_2(\mu^2,\eta^{10}-C_{10}H_8)(\eta^6-C_6Me_6)(\eta^5-Cp)]^+$, **15**, and $[Fe_2(\mu^2,\eta^{10}-C_{10}H_8)(\eta^6-C_6Me_6)_2]^{2+}$, **16**, are synthesized using similar strategies and give rise to localized respectively delocalized mixed-valence complexes **17** and **18** upon one-electron reduction. The 3 oxidation states $(C_6Me_6)_2Fe^{n+}$, n = 2 (**20**), 1 (**21**), and 0 (**22**), were obtained by Fischer[18] and high-yield syntheses of the reduced complexes (n = 0,1) are now available using Na/Hg reduction at 20 °C.[19] The purple 19-electron complex **21** is also obtained cleanly by protonation of the black 20-electron complex **22** with $H^+PF_6^-$ in ether[20] (compare protonation of Cp_2Ni which gives $Cp_3Ni_2^+$).[21] The reaction of 1 mol of $NaBH_4$ with **20** gives the red complex **21**, isoelectronic with **2** (eq 2). One-electron

$$(C_6Me_6)_2Fe^{2+} \xrightarrow[\text{THF, 20 °C}]{NaBH_4} \eta^5-C_6Me_6HFe^+C_6Me_6 \quad (2)$$
$$\textbf{20} \qquad\qquad\qquad\qquad\qquad \textbf{23}$$

reduction of **23** gives the thermally stable brown complex **24**, isoelectronic with **1** (vide infra).[22,23]

Physical Properties and Electronic Structures

The voltammograms of the cations $(CpFe^{II}(\eta^6-C_6H_{6-n}Me_n))^+$ show that the $18e^-/19e^-$ waves are highly reversible[24] whereas the $19e^-/20e^-$ one is much less so.[25] This is especially marked in coordinating solvents such as CH_3CN. On an electrosynthetic scale, the one-electron reduction on a Hg cathode gives a stable green precipitate of Fe^I complex in aqueous LiOH medium only with the C_6Me_6 ligand.[26]   With other arenes thermally stable orange cyclohexadienyl Fe^{II} dimers are

Table I

Fe^I (q = 0)	1	10	11	12	13	25
Fe^{II} (q = +1)	2	5	6	7	8	18(Fe^IFe^{II})
1st I_E^a	4.68	4.72	4.21		4.34	
E_p^b	-1.55	-1.37	-1.75	-1.78	-1.67	-1.80

^{a} First ionization energy (eV) determined by He I photoelectron spectroscopy for Fe^I complexes.[7] ^{b} First reduction potential E_P vs. SCE(V) determined by cyclic voltammetry (DMF, n-Bu$_4$NBF$_4$ 0.1 M) for Fe^{II} complexes as PF$_6$ salts.

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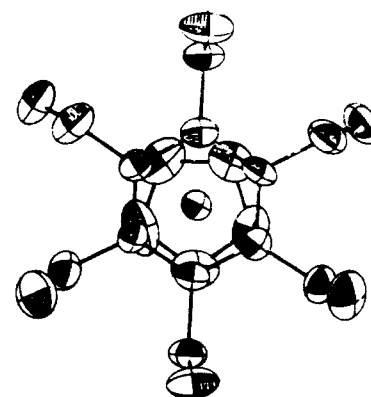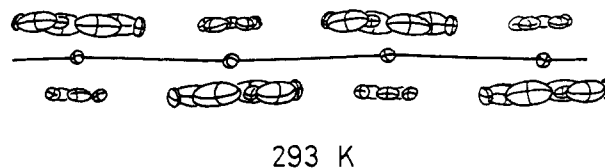
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formed.[26,27] Compound 1 is stable up to 100 °C and can be sublimed at 80 °C (0.2 × 10^{-3} mmHg).[4] The He I photoelectron spectrum could thus be measured by J. C. Green's group for **1, 10, 11,** and **13**. The values of the ionization energies (IE) for these Fe^I complexes are the lowest ever recorded. Although the lowest IE was recorded for **11**, we believe that the neutral complexes **12** and Fe$^I_2$(μ^2,η^{10}-C$_{10}$H$_8$)(η^6-C$_6$Me$_6$)$_2$, **25**, are even more electron-rich given the more negative values of their redox potentials. The IE values correlate with the reduction potentials (Table I).

The X-ray crystal structure of **1** (Figure 2) indicates that both ligands are planar and parallel, in accord with a 19-electron formulation. The Fe–Cp bond (1.78 Å) is longer than in 18-electron complexes whereas the Fe–arene bond (1.58 Å) is not significantly so.[4]

The molecular orbital ordering of metallocenes and bis(arene) metal complexes[28] is e$_2$(d$_{xy}$, d$_{x^2-y^2}$) < a$_1$(d$_{z^2}$) < e$_1$*(d$_{xz}$, d$_{xz}$). The major question concerning the electronic structure of 19-electron Fe^I complexes was whether the 19th electron occupied the e$_1$* metal orbital or the benzene e$_2$ orbital. INDO–SCF calculations indicated these MO levels are close and led to prediction of the instability of Fe^I complexes.[29] Elements of answers to this question were provided. (i) That such Fe^I complexes can be handled up to 100 °C indicates that the extra electron occupies a metal-based molecular orbital rather than being located in a peripheral ligand orbital. (ii) Vlcek's theory[30] gives the ligand "eigenvector" using electrochemical $E_{1/2}$ values:[25a] ($E_{1/2}$ complex A - $E_{1/2}$ complex B)/($E_{1/2}$ ligand A - $E_{1/2}$ ligand B) $\simeq$ 20%. (iii) The long Fe–Cp bond in **1** indicates a larger Cp character for e$_1$* as compared to the arene character. (iv) The ^{1}H NMR spectrum of **1** shows a sharp signal (low spin density) at -2.15 ppm and the Cp protons are found at 35 ppm.[31] In the ^{13}C spectrum, the ring carbons are located at 449 and 584 ppm, CH$_3$ being at -35.9 ppm.[31] Neither of these downfield shifts is large (which is the case for σ and Π delocalization mechanisms).[28a] As in **21**, little spin density is located on the ligands (this is also deduced from the sharpness of the signals). In the ^{1}H NMR spectrum of **11**, the C$_6$Me$_6$ signal is found at 1 ppm whereas the C$_5$Me$_5$ signal is found at -30 ppm. The peak width at the half height of the latter is twice as large as that of the former peak width at the half height indicating the spin density on Cp* is twice that of the arene. The small half-height peak widths confirm the small spin densities on the ligands.[31] (v) The quadrupole splittings (QS) obtained by Mössbauer spectroscopy for the 18- and isostructural 19-electron complexes are, respectively, approximately 2 and 0.5 mm s^{-1}.[32] Since one electron in a d$_{xz}$ orbital corresponds to 2 mm s^{-1},[33] an estimation, confirmed by EHT calculations using Ham's reduction factors,[34] gives
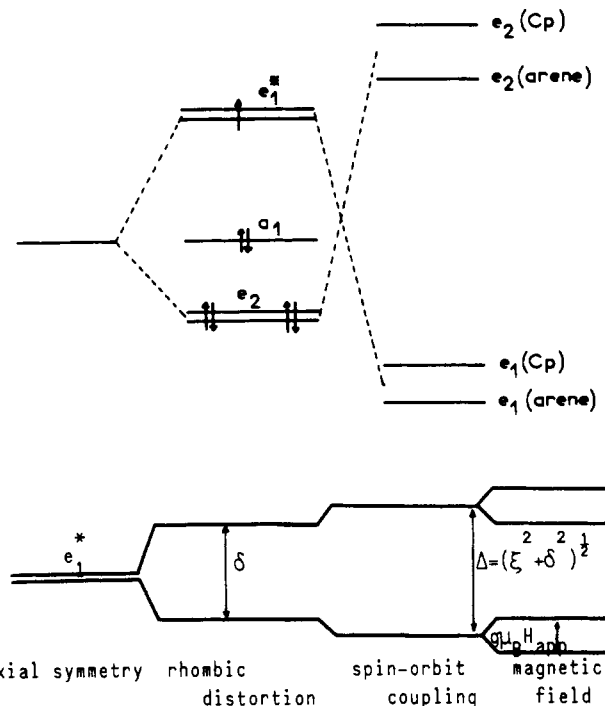

Figure 3. MO diagram for transition-metal sandwiches: d^7 19-e$^-$ CpFe^I(arene) complexes.

a metal character of (2 - 0.5)/2 = 75% for e$_1$* (MO calculations:covalency = 70–83%). (vi) In the EPR spectra, g$_z$ is always less than the free electron, consistent with a d^7($^2\Pi$) ground state.[34]

Another major question is the rhombic distortion connected to the Jahn–Teller activity of the Fe^I sandwiches due to the occupancy of the degenerate e$_1$* level by a single electron. This rhombic distortion (δ) stabilizes the system by lifting the degeneracy; the vibronic coupling term also contributes (see Figure 3). The splitting of e$_1$* in Kramers' doublet is given by Δ = [($p\zeta$)^2 + (2$q\delta$)^2]$^{1/2}$ in the linear coupling approximation where p and q are Ham's reduction factors for the spin-orbit coupling ζ and the rhombic distortion δ respectively and q = 0,5 (1 + p) in the single mode coupling case. The quadrupole splitting varies with temperature according to a th law because of the thermal population of the upper level.[4] Fitting the MO calculation to the QS variation indicates 0.1 < p < 0.3, the important reduction of ζ resulting from the dynamic Jahn–Teller effect at all temperatures.[32] Other manifestations of the dynamic Jahn–Teller effect are the strong host lattice dependence of the g values and the temperature dependence of line width in EPR spectra.[34] Strong cooperativity of the Jahn–Teller effect and rhombic distortion are observed by Mössbauer spectroscopy; the spectra of frozen solutions and those of solid state samples are different for most Fe^I complexes. Thus, specific packings such as that of **1** (Figure 2) have a tremendous influence on the QS values and on their temperature dependence (Figure 4). The consequence of this cooperative distortion finds useful applications in solid state chemistry. For example, oxidation in the bulk or on the surface can be distinguished.[46]

In contrast to Fe^I monomers, the mixed valence complexes **18** do not show temperature variation of the

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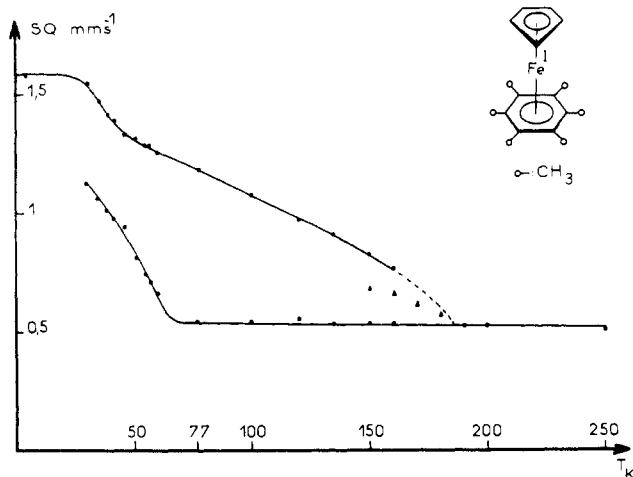
Figure 4. Variation of the Mössbauer quadrupole splitting as a function of temperature for $CpFe^{I}C_6Me_6$, 1. The quadrupole doublet splits into two doublets of equal isomer shifts and intensities between 30 and 180 K. Changes in the X-ray powder spectra are also noted in this range.
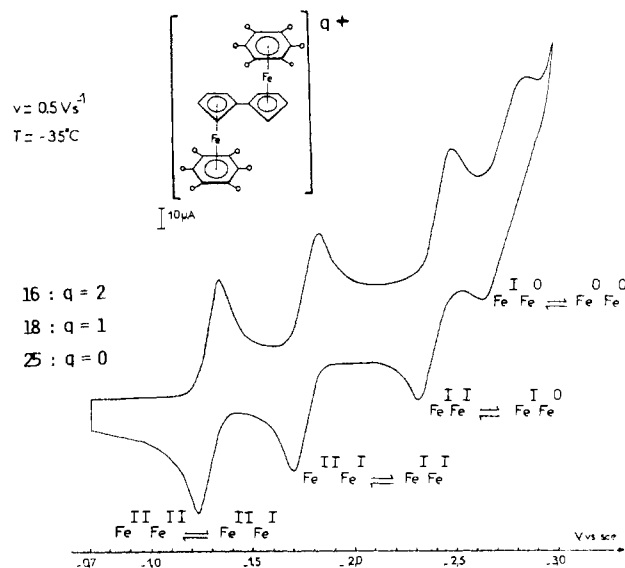

Figure 5. Cyclic voltammogram of 16 ($q = +2$), PF_6^- salt (DMF, n-$Bu_4N^+BF_4^-$ 0.1 M).

QS, indicating the absence of Kramers doublet and of Jahn–Teller activity. Only one quadrupole doublet is seen at all temperatures down to 4.2 K, indicating that electron exchange between the two iron centers (necessarily through the fulvalene ligand due to the bulk of C_6Me_6) is faster than the Mössbauer frequency (10^{-9} s^{-1} at 4.2 K) and that the thermal barrier is very low.[17] EHMO calculations indicate that a new set of orbitals arises from the coupling of two sandwich units, in which the HOMO is now a single orbital occupied by the 37th electron.[35]
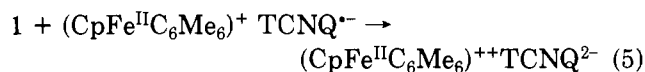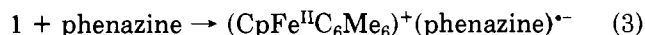
The optical and Mössbauer spectra of the green Fe^IFe^I complex **25** indicate that it resembles Fe^I monomers in terms of electronic structure[17] (except for the dipolar interaction). Thus, free rotation about the Cp–Cp is now no longer restricted by intramolecular ET, which renders both Fe^I sandwiches independent. Altogether, five oxidation states appear in the voltammogram of **16** (Figure 5).

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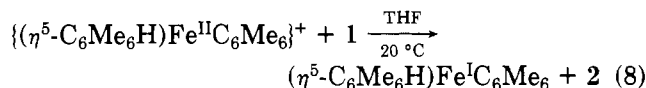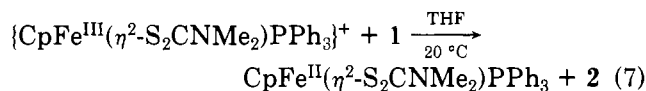
Stoichiometric Electron-Transfers (ET) and Synthetic Applications

$CpFe^{I}C_6Me_6$ is an easily and rapidly accessible, inexpensive electron-reservoir complex which can be synthesized, crystallized, and isolated at 20 °C on a large scale with excellent yield. It is very soluble and stable inter alia in pentane, ether, and THF, which allows ET reactions in these solvents even at reflux. It is also stable in acetone at 20 °C, but reduction of the latter occurs in refluxing THF.

Typically, clean stoichiometric ET reactions are found with delocalized Π systems having reduction potentials lower than the very negative oxidation potential of 1^{36} (-1.55 V vs. SCE in DMF). These reactions are fast at 20 °C in THF.

$$1 + phenazine \rightarrow (CpFe^{II}C_6Me_6)^+(phenazine)^{\cdot-} \quad (3)$$

$$1 + TCNQ \rightarrow (CpFe^{II}C_6Me_6)^+TCNQ^{\cdot-} \quad (4)$$

$$1 + (CpFe^{II}C_6Me_6)^+ \ TCNQ^{\cdot-} \rightarrow$$
$$(CpFe^{II}C_6Me_6)^{++}TCNQ^{2-} \quad (5)$$

$$1 + 2 \ TCNQ \rightarrow (CpFe^{II}C_6Me_6)^+(TCNQ)_2^- \quad (6)$$

Not only the dark blue tetracyanoquinodimethane salt ($TCNQ^-$) but also the purple $TCNQ^{2-}$ salt can be synthesized specifically in good yields depending on the order of addition and stoichiometry. Although neither these salts nor those of intermediate fractional stoichiometry are conducting, those of stoichiometry $(CpFe^{II}C_6Me_6)^+(TCNQ^-)_2$ exhibit the usual range of conductivity[37] already known for TCNQ salts having this stoichiometry[38] with other non TTF-type cations. In fact, the ET reaction provides adequate control of the salt stoichiometry which is not the case otherwise. Although it is useful as a reducing agent, sodium amalgam sometimes leads to decomposition of samples contaminated by mercury; solutions resulting from reduction still contain the Na^+ cation which may be troublesome (vide infra). We found that 1 is an ideal reducing agent for the one-electron reduction of cations. For instance, 17- and 18-electron organometallic cations are conveniently reduced by 1 in THF to neutral complexes having one more valence electron; the salt of **2** precipitates out of solution and is thus easily removed. In the examples below (eq 7 and 8), Na/Hg reduction proved unsuitable whereas high yields were obtained using 1.[39]

$$\{CpFe^{III}(\eta^2\text{-}S_2CNMe_2)PPh_3\}^+ + 1 \xrightarrow[20 \text{ °C}]{THF}$$
$$CpFe^{II}(\eta^2\text{-}S_2CNMe_2)PPh_3 + 2 \quad (7)$$

$$\{(\eta^5\text{-}C_6Me_6H)Fe^{II}C_6Me_6\}^+ + 1 \xrightarrow[20 \text{ °C}]{THF}$$
$$(\eta^5\text{-}C_6Me_6H)Fe^{I}C_6Me_6 + 2 \quad (8)$$

Molecules such as polyaromatics which have a reduction potential more negative than that of **2** and which form kinetically stable radical anions cannot be reduced. However most molecules do not fall in this

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(37) Lequan, R. M.; Lequan, M. Jaouen, G.; Ouahab, L.; Batail, P.; Padiou, J.; Sutherland, R. G. *J. Chem. Soc., Chem. Commun.* **1985**, 116.
(38) Torrance, J. *Acc. Chem. Res.* **1979**, *12*, 79.
(39) Madonik, A. M.; Catheline, D.; Astruc, D., unpublished work.

category because of the great reactivity of the corresponding radical anion. Thus, in many cases, reduction by **1** is driven by this reactivity even if the reduction potential is more negative than that of **2**. A dramatic example is that of CO_2 which is reduced by **1** within a few minutes at 20 °C in THF.[40] The reduction of $^{13}CO_2$ permits analysis of the mixture of $^{13}C_2O_4{}^{2-}$ and $^{13}CO_3{}^-$ by ^{13}C NMR spectroscopy (In eq 9, α and β depend on

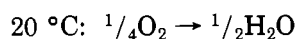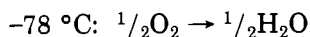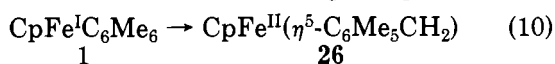$$1 + CO_2 \rightarrow 2 + \alpha C_2O_4{}^{2-} + \beta CO_3{}^{2-} \qquad (9)$$
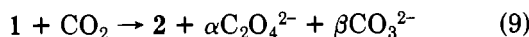
working conditions). Given the known estimated value of the thermodynamic potential for $CO_2/CO_2{}^{\bullet-}$ (2.25 V vs. SCE),[41-43] the overpotential for the reduction by **1** in eq 9 is 0.7 V.

As is apparent in the latter example, it is essential to control the selectivity in ET reactions designed to activate small molecules. A key point in this regard is to understand the ion pair chemistry evolving subsequent ET between molecular electron reservoirs and the substrate. In the case of O_2, the synthetic aim was coupled with the desire to examine the reactivity of the superoxide anion $O_2{}^{\bullet-}$. The conclusion derived thereof will be applicable to the control of ET activation of inter alia ketones, aldehydes, epoxides, and carbon oxides.
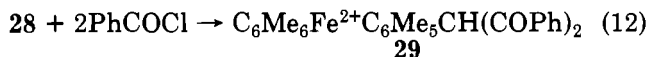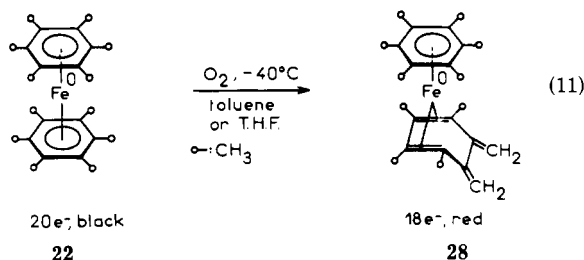
Benzylic Activation Using O_2 and the Versatile Reactivity of $O_2{}^{\bullet-}$ Generated from O_2 and 19-Electron Iron Complexes

Dioxygen reacts under very mild conditions with **1** and other 19-electron $CpFe^I(arene)$ complexes bearing benzylic hydrogens.[44] One benzylic hydrogen atom is formally abstracted, which gives diamagnetic cyclohexadienyl complexes with exocyclic double bonds. For instance with **1**, a 97% yield of **26** is obtained after a 1-min reaction at -78 °C according to eq 10.
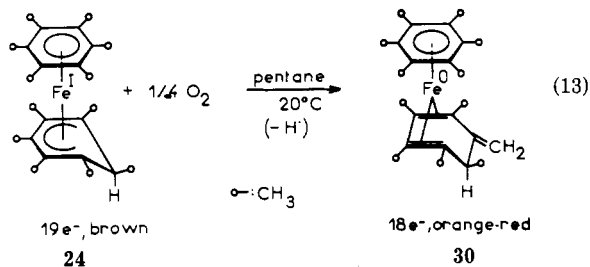
$$CpFe^IC_6Me_6 \rightarrow CpFe^{II}(\eta^5\text{-}C_6Me_5CH_2) \qquad (10)$$
$$\mathbf{1} \qquad\qquad\qquad \mathbf{26}$$

$$-78\ °C:\ {}^1/_2O_2 \rightarrow {}^1/_2H_2O$$

$$20\ °C:\ {}^1/_4O_2 \rightarrow {}^1/_2H_2O$$

The X-ray crystal structure of **26**[45] indicates that the length of the exocyclic bond is 1.376 Å as expected for a double bond. Indeed hydrogenation of **26** to $CpFe^{II}(\eta^5\text{-}C_6Me_6H)$, **27**, on Pd/C in THF proceeds at 20 °C.[45] **26**, a mild nucleophile, is a synthon for the formation of bonds with a variety of elements by reaction with CX_2 (X = O, S), halogens (Cl_2, Br_2, I_2), organic and organometallic halides, metal carbonyls (Fe, Cr, Mo), and unsaturated hydrocarbons (olefins, arenes) activated by complexation to cationic organoiron groups.[45,46]
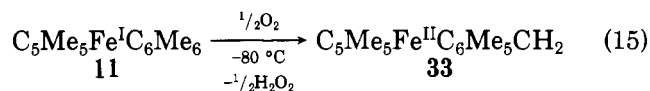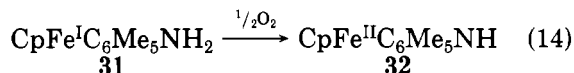
Similarly, **22** reacts with $^1/_2$ mol of O_2 at -40 °C giving the product **28** resulting from double C–H activation (eq 11), an *o*-xylylene complex of the rare intracyclic coordination type[47] which reacts with 2 mol of PhCOCl (eq 12) to give **29**. **24** also reacts with $^1/_2$ mol O_2 to give

$$\mathbf{22} \xrightarrow[\substack{\text{toluene} \\ \text{or T.H.F.} \\ o\text{-:CH}_3}]{O_2,\ -40°C} \mathbf{28} \qquad (11)$$

20 e⁻, black — 22

18 e⁻, red — 28

$$\mathbf{28} + 2PhCOCl \rightarrow C_6Me_6Fe^{2+}C_6Me_5CH(COPh)_2 \qquad (12)$$
$$\mathbf{29}$$

single C–H activation (**30**) like other Fe^I complexes but the H atom is now abstracted from the odd ligand (eq 13). Further, benzoylation of **30** leads to functional polyenes after deprotonation and decomplexation.[48]

$$\mathbf{24} + {}^1/_4\ O_2 \xrightarrow[\substack{20°C \\ (-H^{\bullet})}]{\text{pentane}} \mathbf{30} \qquad (13)$$

19 e⁻, brown — 24

18 e⁻, orange-red — 30

An ET mechanism for the above C–H activation reaction was suspected given the 1-V difference in the redox potentials of the reversible systems **1/2** and $O_2/O_2{}^{\bullet-}$.[46] This was confirmed by monitoring these reactions by EPR, which disclosed the spectrum of $O_2{}^{\bullet-}$. Consistently, *t*-BuOK (in THF) or KO_2 (in THF using 18-crown-6 or in Me_2SO) deprotonates the salts of **2** to give **26**. Also in accord with an ET mechanism followed by deprotonation are the reactions of Fe(I) complexes bearing two kinds of benzylic hydrogens; the more acidic hydrogen is removed by O_2 (eq 14[49] and 15[46]).

$$CpFe^IC_6Me_5NH_2 \xrightarrow{{}^1/_2O_2} CpFe^{II}C_6Me_5NH \qquad (14)$$
$$\mathbf{31} \qquad\qquad\qquad \mathbf{32}$$

$$C_5Me_5Fe^IC_6Me_6 \xrightarrow[\substack{-80\ °C \\ -{}^1/_2H_2O_2}]{{}^1/_2O_2} C_5Me_5Fe^{II}C_6Me_5CH_2 \qquad (15)$$
$$\mathbf{11} \qquad\qquad\qquad\qquad \mathbf{33}$$

The reaction of eq 15 is faster than that of eq 10 despite the larger steric bulk, a trend characteristic of a path for which the outer-sphere ET is the rate-limiting step.[50]

Clearly, we had in hand the possibility to generate superoxide $O_2{}^{\bullet-}$ and examine its reactivity. The primary source of information concerning $O_2{}^{\bullet-}$[51] reactivity arises from electrochemical studies in pyridine or DMF and from the chemistry of KO_2 (discovered by Gay Lussac, 1805). However, the poor solubility of KO_2 severely limits its use. (It was demonstrated during the last decade that $O_2{}^{\bullet-}$ is implicated in the toxicity of red cells, membranes, granulocytes, and bacteria[52] and the tox-

(40) Guerchais, V. "3e cycle" Thesis, Rennes, 1984.
(41) Nadjo, L.; Savéant, M. *J. Electroanal. Chem.* **1976**, *73*, 163.
(42) Amatore, C.; Savéant, J.-M. *J. Am. Chem. Soc.* **1981**, *103*, 5021.
(43) Ziessel, R. *Nouv. J. Chim.* **1983**, *7*, 613.
(44) Astruc, D.; Román, E.; Hamon, J.-R.; Batail, P. *J. Am. Chem. Soc.* **1979**, *101*, 2240.
(45) (a) Hamon, J.-R.; Astruc, D.; Román, E.; Batail, P.; Mayerle, J.-J. *J. Am. Chem. Soc.* **1981**, *103*, 2431. (b) Michaud, P.; Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 918. (c) Michaud, P.; Lapinte, C.; Astruc, D. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 97.
(46) Astruc, D.; Hamon, J.-R.; Román, E.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 7502.

(47) Madonik, A. M.; Mandon, D.; Michaud, P.; Lapinte, C.; Astruc, D. *J. Am. Chem. Soc.* **1984**, *106*, 3381.
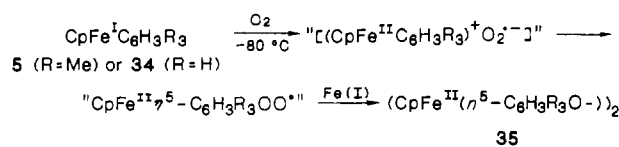(48) Mandon, D.; Astruc, D. *J. Organomet. Chem.* **1986**, *307*, C27.
(49) Michaud, P.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1982**, 416.
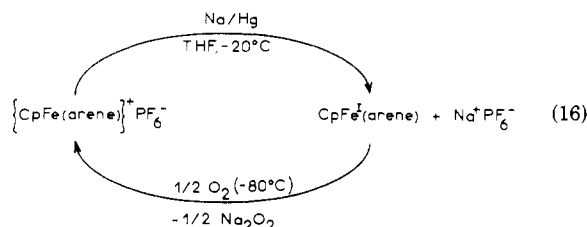(50) Catheline, D.; Astruc, D. *Nouv. J. Chim.* **1984**, *8*, 381.
(51) (a) Lee Ruff, E. *Chem. Soc. Rev.* **1977**, *6*, 195. (b) Fee, J. A.; Valentine, J. S. In *Superoxide and Superoxide Dismutase*; Michelson, A. M., McCord, J. M., Fridovitch, I., Eds.; Academic: New York, 1977; p 19. (c) Sawyer, D. T.; Gibian, M. J. *Tetrahedron* **1979**, *35*, 1471. (d) Sawyer, D. T. *Acc. Chem. Res.* **1979**, *13*, 105. (e) Sawyer, D. T.; Valentine, J. S. *Ibid.* **1981**, *14*, 393. (f) Frimer, A. A. In *Superoxide Dismutase*; Oberley, L. W., Ed.; CRC: Boca Raton, FL; Vol. II, Chapter 5, p 83–125.
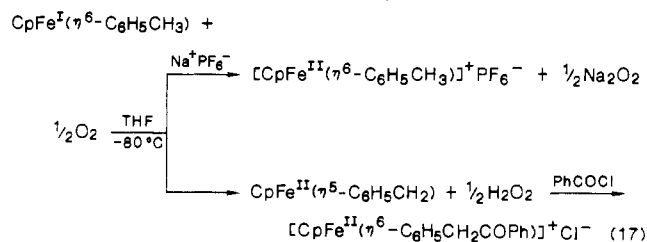
Scheme I

$$CpFe^{I}C_6H_3R_3 \xrightarrow[-80\,°C]{O_2} "[(CpFe^{II}C_6H_3R_3)^{+}O_2^{•-}]" \longrightarrow$$

5 (R=Me) or 34 (R=H)

$$"CpFe^{II}\eta^{5}-C_6H_3R_3OO^{•}" \xrightarrow{Fe(I)} (CpFe^{II}(\eta^{5}-C_6H_3R_3O-))_2$$

35

Scheme II

$$[(CpFe^{II}arene)^{+}, O_2^{-}] + [M^{+}, X^{-}] \rightleftharpoons [(CpFe^{II}arene)^{+}, X^{-}] + [M^{+}, O_2^{-}]$$
large small small large large large small small

deprotonation or nucleophilic attack

precipitation

dismutation

precipitation

icity of $O_2^{•-}$ for microorganisms is well-known since Pasteur's work on *butyric vibrium*. However, the critical role of $O_2^{•-}$ in the aging of aerobic cells still needs to be cleared up.[53])

Attempts to generalize what is formally a H atom abstraction reaction (in fact, the removal of e^-, then of H^+) by O_2 to Fe(I) complexes of other arenes bearing methyl groups first gave disappointing results. Yellow precipitates of $(CpFe^{II}(arene))^+$ PF_6^- salts were quantitatively obtained from oxygenated THF solutions of $CpFe^{I}(arene)$ complexes containing $Na^+PF_6^-$ (eq 16).

$$\begin{array}{c}
\text{Na/Hg} \\
\text{THF, -20°C} \\
\{CpFe(arene)\}^{+}PF_6^{-} \quad \rightleftharpoons \quad CpFe^{•}(arene) + Na^+PF_6^{-} \quad (16) \\
1/2\ O_2(-80°C) \\
-1/2\ Na_2O_2
\end{array}$$

The red C–H activation products were quantitatively formed only when $Na^+PF_6^-$ was removed from these solutions (eq 17). This dichotomy, due to the salt effect

$$CpFe^{I}(\eta^{6}-C_6H_5CH_3) +$$

$$\frac{1}{2}O_2 \xrightarrow[-80\,°C]{THF} \begin{cases} \xrightarrow{Na^+PF_6^-} [CpFe^{II}(\eta^{6}-C_6H_5CH_3)]^{+}PF_6^{-} + \frac{1}{2}Na_2O_2 \\ \\ \longrightarrow CpFe^{II}(\eta^{5}-C_6H_5CH_2) + \frac{1}{2}H_2O_2 \xrightarrow{PhCOCl} \end{cases}$$

$$[CpFe^{II}(\eta^{6}-C_6H_5CH_2COPh)]^{+}Cl^{-} \quad (17)$$

of $Na^+PF_6^-$, was confirmed by systematically changing the sizes of the ions. (Mixtures of 1^+X^- and 13 were obtained upon reacting $1 + O_2$ in the presence of these salts, their proportions being consistent with the salt effect.)[54]

When the arenes do not bear benzylic hydrogens, the reaction of Fe^I complexes with O_2 gives dimeric peroxides resulting from nucleophilic attack of the activated arene ligand by $O_2^{•-}$ in the cage (Scheme I).[54,55] In accord with this mechanism, the same salt effect is found to occur "quantitatively" when THF solutions of Fe^I complexes contain $Na^+PF_6^-$ (eq 16), as checked once again by examining the influence of the variation of the ion sizes on the magnitude of the salt effects (e.g. on the ratio 5/35 or 34/35, vide infra).[54] Thus the salt effect is very general whatever the structure of the electron-reservoir complex and the property of $O_2^{•-}$ involved (base or nucleophile). Note that $O_2^{•-}$ dismutates and Na_2O_2 precipitates out of solution when the reactivity of $O_2^{•-}$ in the cage is inhibited by the salt
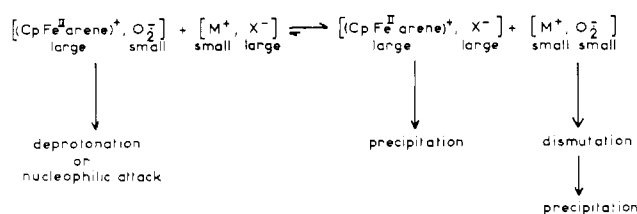
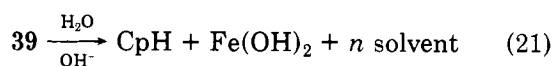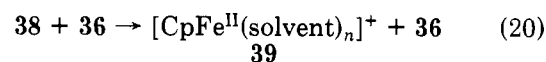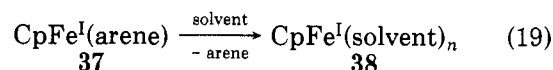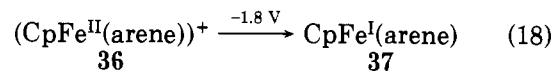effect. That simple Na^+ salts totally inhibit the high reactivity of $O_2^{•-}$ at -80 °C in such a general fashion recalls the efficiency of superoxide dismutase enzymes in biological media.[55] In conclusion, the reactivity of $O_2^{•-}$ generated in cages from Fe^I and O_2 is extreme (-80 °C, rapid reaction) both as a base and as a nucleophile, but can be totally inhibited by Na^+ (Scheme II).

Electrocatalysis and Redox Catalysis

ET-catalyzed reactions are termed electrocatalytic and do not necessarily involve an overall redox change.[56] The ET catalyst can be an electrode or a chemical redox reagent. The decomplexation of $(CpFe^{II}(arene))^+$ complexes in ethanol to cyclopentadiene, Fe^{2+} and arene is an example of an electrocatalytic reaction which we reported several years ago.[26b] The reaction consumes a catalytic amount of cathodic current. Unstable Fe(I) complexes are produced and the arene is replaced by solvent molecules, giving transient $CpFe^{I}(solvent)_n$. The reduction potential of the solvent complex is presumably close to that of the parent complex, the overall reaction being driven by the decomposition of the unstable cation $[CpFe^{II}(solvent)_n]^+$ (eq 18–21).

$$(CpFe^{II}(arene))^+ \xrightarrow{-1.8\ V} CpFe^{I}(arene) \quad (18)$$
$$\quad\quad 36 \quad\quad\quad\quad\quad\quad 37$$

$$CpFe^{I}(arene) \xrightarrow[- \text{arene}]{\text{solvent}} CpFe^{I}(solvent)_n \quad (19)$$
$$\quad\quad 37 \quad\quad\quad\quad\quad\quad 38$$

$$38 + 36 \rightarrow [CpFe^{II}(solvent)_n]^+ + 36 \quad (20)$$
$$\quad\quad\quad\quad\quad\quad 39$$

$$39 \xrightarrow[OH^-]{H_2O} CpH + Fe(OH)_2 + n\ \text{solvent} \quad (21)$$

In the presence of $P(OMe)_3$, the known complex $[CpFe^{II}\{P(OMe)_3\}]^+$ can be obtained.[57a] 1 can be used as the electrocatalyst instead of a cathode.[57b] The electrocatalyst can be either a reducing or an oxidizing agent, depending on the relative electron-releasing abilities of the leaving and incoming ligands. In order to favor equation 20, 38 should be more electron-rich than 37, e.g., the incoming ligand group must be more electron-releasing than the arene.[58] The opposite is true in an electrocatalytic process catalyzed by an oxidant.[59] Ferricinium is a convenient electrocatalyst $(E_{1/2}$ Cp_2Fe/Cp_2Fe^+: $+0.45$ V vs. SCE) because oxidation of a large number of neutral organometallic complexes is accessible. If the leaving and incoming

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(53) Fridovitch, I. In *Free Radicals in Biology*; Pryor, W. A., Ed.; Academic: New York, 1976; p 239. See also ref 2b.

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(59) Ziezelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771, and references therein.
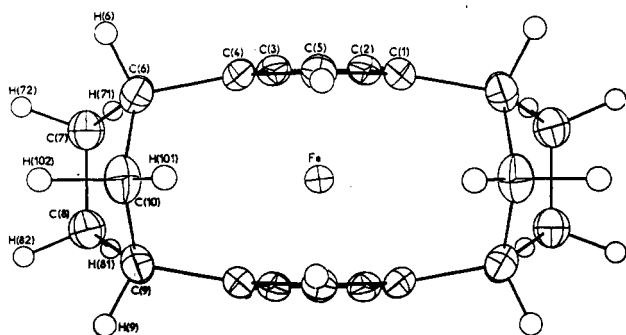
Figure 6. Ortep view of the X-ray crystal structure of the ferrocene cage **39** obtained by cleavage of ferrocene with aluminum chloride:(1,1′,3,3′-bis(cyclopentylene)ferrocene).[62]

ligands have similar electron-releasing properties, electrocatalytic exchange is possible provided it is driven by an irreversible step such as eq 20-21 (see also eq 22). The electrocatalytic chelation of monodentate

$$CpFe^{II}(CO)_2(\eta^1\text{-}SC(S)NMe_2) \xrightarrow[-CO]{Cp_2Fe^+(5\%)}$$
$$CpFe^{II}(CO)(\eta^2\text{-}S_2CNMe_2) \quad (22)$$
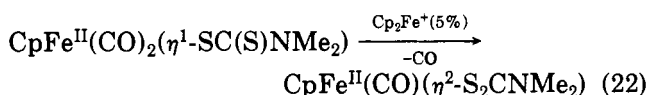
dithiocarbamate is such an example driven by CO loss and chelation of dithiocarbamate.[60]

Stoichiometric oxidation leads to decomposition, except in the presence of PPh₃ which stabilizes [CpFe^III(PPh₃)(η²-S₂CNMe₂)]⁺ (compare eq 7). In order to improve the yields of ferricinium-catalyzed reactions, one must impede the radical-type reactions of ferricinium. Again steric bulk, as in the cage compound **39**, is desirable (Figure 6).

Redox catalysts are reversible redox systems conveying electrons in thermodynamically allowed processes which are kinetically inhibited by overpotential barriers.[56] For instance, nitrate ion cannot be reduced in basic aqueous medium on a mercury cathode. However, in the presence of catalytic amounts of **2**, NH₃ is formed. Under these conditions, **1** and **2** are stable. Although the thermodynamic potential of $NO_3^-/NO_3^{\bullet2-}$, presumably ~2 V/SCE, is more negative than that of $1/1^+$, NO_3^- can be reduced to NH_3 by 1^{61} since the

(60) Catheline, D.; Astruc, D. *Coord. Chem.* 1982, 23, Fr. 41.

overall process is driven by the irreversible reactions of $NO_3^{\bullet2-}$

$$1 + NO_3^- \rightleftharpoons 2 + NO_3^{\bullet2-} \xrightarrow[reduction]{protonation,} NH_3 \quad (23)$$
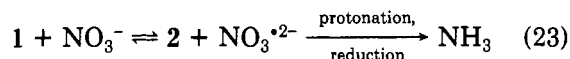
With the soluble redox catalyst **3**,[11] the system is homogeneous and stable ($k \sim 10^2$ mol⁻¹ L s⁻¹).[61] The applied cathodic potential reduces **2** (or **3**) to **1** (or **4**) (~-1.8 V/vs. SCE).

These examples show that electron-rich (19-e⁻) as well as electron-poor (17-e⁻) sandwiches can function as electrocatalysts or redox catalysts.

Conclusion and Outlook

The syntheses of Jahn-Teller active 19-electron Fe(I) compounds, thermally stabilized by peralkylation of an aromatic ligand, provided extremely electron-rich molecules. These compounds activate dioxygen, allowing the examination of the reactivity of superoxide anion and the inhibition of this reactivity by the salt effect. In the near future, this unique possibility of generating cage ion pairs from Fe(I) compounds and various substrates should let us investigate the general influence of salts on the reactivity of such ion pairs. It is likely that the knowledge of these salt effects will provide selectivity in many reductions. The coupling of both ET catalysts **1** and (Cp₂Fe^II)⁺ in the same molecular unit such as **15** provides a bifunctional catalyst. The design of molecular materials with such multiple and stable oxidation states are important in the study of ET processes, electrode modification, and ET catalysis. Finally, stable Fe(I) compounds are excellent candidates as materials for piles and batteries on polymer supports.

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(62) (a) Astruc, D.; Martin, M.; Batail, P. *J. Organomet. Chem.* 1977, *133*, 77. (b) Astruc, D.; Debard, R.; Martin, M.; Batail, P.; Grandjean, D. *Tetrahedron Lett.* 1976, *11*, 829. (c) Batail, P.; Grandjean, D.; Astruc, D.; Dabard, R. *J. Organomet. Chem.* 1976, *110*, 91.

The Chemistry of Activated Bleomycin

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The recognition that DNA serves as a target for small molecules in the initiation of cellular disorders, and in

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the therapy of certain diseases, has served to catalyze increased interest in the interaction of such species with DNA. These include natural[1] and synthetic[2] products

(1) (a) Petrusek, R. L.; Anderson, G. L.; Garner, T. F.; Fannin, Q. L.; Kaplan, D. J.; Zimmer, S. G.; Hurley, L. H. *Biochemistry* 1981, *20*, 1111. (b) Patel, D. J.; Kozlowski, S. A.; Rice, J. A.; Broka, C.; Itakura, K. *Proc. Natl. Acad. Sci. U.S.A.* 1981, *78*, 7281. (c) Van Dyke, M. W.; Hertzberg, R. P.; Dervan, P. B. *Proc. Natl. Acad. Sci. U.S.A.* 1982, *79*, 5470. (d) Kappen, L. S.; Goldberg, I. H. *Biochemistry* 1983, *22*, 4872.