Electron-reservoir complexes and other redox-robust reagents: functions and applications†‡

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The functions and applications of electron-reservoir iron and cobalt sandwich complexes are reviewed with emphasis of the author's work using the 19-electron Fe^I complexes $[(\eta^5\text{-}C_5R_5)Fe(\eta^6\text{-}C_6Me_6)]$, R = H or Me, the most electron-rich neutral molecules known to date and the 17-electron Fe^{III} complex $[(\eta^5\text{-}C_5Me_5)Fe(\eta^6\text{-}C_6Me_6)][SbCl_6]_2$, the strongest known organometallic oxidant. It is shown that the electron-reservoir concept involving steric protection of a central redox site and the resulting redox robustness allows to carry out a variety of functions such as references for the measurement of redox potentials, many useful stoichiometric and catalytic redox reactions, sensing of anions and cations and entry into the area of molecular electronics also including the nanoscale.

1. Introduction

Henry Taube, in addition to being a gentleman, was the pioneer of *molecular electronics* and *molecular engineering* with his work carried out in the 1950s. Having classified the transition-metal ions as substitutionally inert or labile in a seminal review article,[2] he then designed the first inner-sphere electron transfer reactions and showed that the electron transfer using this mechanism was considerably faster than an analogous outer-sphere electron transfer using analogous transition metal ions.[3] He also organized the first electron- or atom-transfer-chain mechanism,[4] a form of electron-transfer-induced *catalysis*, that was (unconsciously) imitated by organic chemist decades later. Finally, among his breakthroughs, he disclosed the first mixed-valent complexes and established the distinction between mixed-valent and average-valent systems,[5] the primitive form of *molecular wires*. Less known is his disclosure of the first electrochemical hysteresis loop[6] that is the ancestor of electron-transfer-triggered *molecular machines*.[7] Taube's molecules and systems had sizes that range around a nanometer, and it is amusing to observe that all these findings are now currently used in *nanosciences* and *nanotechnology*.

Redox chemistry involves physical methods,[8] processes[1–10] (many of which are biological or biomimetic)[9] and reagents.[11] In 1979, we reported the stabilization of Fe^I complexes to form a family of redox-robust 19-electron complexes that are still the most electron-rich neutral molecules known, based on their ionization potentials determined by He^I photoelectron spectroscopy.[12] The prototype of these complexes, $[CpFe(\eta^6\text{-}C_6Me_6)]$, an extremely air-sensitive 19-electron d^7 Fe^I Jahn–Teller active complex, is stable up to 100 °C, and its X-ray crystal structure was recorded.[12] Later, we synthesized the thermally stable (but air sensitive) 17-electron d^5 Fe^{III} complex $[(\eta^5\text{-}C_5Me_5)Fe(\eta^6\text{-}C_6Me_6)][SbCl_6]_2$, the strongest known organometallic oxidant with a potential one volt more positive than its isoelectronic analog ferrocenium (Scheme 1). In this review article, we wish to briefly summarize the functions of these complexes and other redox-robust iron and cobalt sandwiches involving the concept of electron reservoir, *i.e.* the redox robustness of these transition metals when they are embedded in the shell of bulky ligands. A variety of resulting properties and their applications are illustrated in the spirit of Taube's electron transfer principles.

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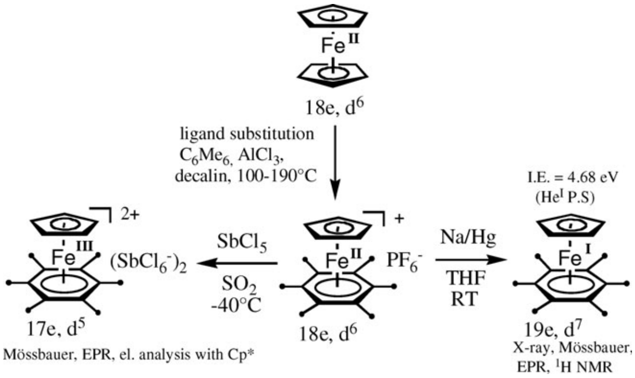
† Dedicated to the Memory of Henry Taube.

‡ Electronic supplementary information (ESI) available: Tables 3 and 4, providing the standard redox potentials E° of the main oxidants and main reductants *vs.* the reference redox systems ferrocenium/ferrocene, decamethylferrocenium/decamethylferrocene, saturated calomel electrode (SCE) and normal hydrogen electrode (NHE). See DOI: 10.1039/b903188j



Scheme 1 Synthesis of the family of electron-reservoir complexes.

2. Permethylated transition-metal sandwiches as references for the determination of redox potentials

The IUPAC recommended to report the standard redox potential of non-aqueous systems $E^{\circ\prime}$ *vs.* the ferrocene/ferrocenium ($FeCp_2{}^{0/+}$) redox couple rather than *vs.* the aqueous saturated calomel electrode[13] which is only modestly stable in non-aqueous solutions.[14] Previously, redox potentials in non-aqueous solutions were reported *vs.* SCE, but subsequently, redox potentials were most often reported *vs.* $FeCp_2{}^{0/+}$. Conversion of values reported *vs.* SCE to values reported *vs.* $FeCp_2{}^{0/+}$ have been made.[21] In spite of the IUPAC recommendation, the absolute redox potential value of the couple $FeCp_2{}^{0/+}$ is dependent on the nature of the solvent and supporting electrolyte, because the iron center which is the subject of redox change is not well protected by the ligand in ferrocenium.[15,16] Indeed, the nucleophiles can interact from the sides with the cationic iron center. The energy of this interaction shifts the redox potential and depends on the nature of the nucleophiles. Therefore, we have selected the permethylated transition-metal sandwiches redox systems shown in Chart 1 (in their 18-electron forms): decamethylferrocene/decamethylferrocenium $[FeCp^*_2]^{0/+}$, decamethylcobaltocene/decamethylcobaltocenium $[CoCp^*_2]^{0/+}$ and $[FeCp(\eta^6\text{-}C_6Me_6)]^{0/+}$ as alternative and complementary reference systems.[16a] In these electron-reservoir complexes, the transition-metal center is really shielded from the external nucleophiles (solvent, counter-anion of the electrolyte), and they do not modify the redox potential value.

Table 1 $E_{1/2}$ values (V) of transition-metal sandwich complexes determined *vs.* SCE[a]

$E_{1/2}$ *vs.* SCE	DMF	CH_3CN	THF	CH_2Cl_2	DMSO	DME
$FeCp_2{}^{0/+}$	0.470	0.382	0.547	0.475	0.435	0.580
$FeCp^*_2{}^{0/+}$	−0.125	−0.125	0.102	−0.070	−0.030	0.140
$CoCp^*_2{}^{0/+}$	−1.402	−1.525	−1.295	−1.497	−1.425	−1.260
$FeCp^*(C_6Me_6)^{0/+}$	−1.762	−1.865	−1.645	—	−1.775	−1.605

[a] $E_{1/2}$ values were determined using the cationic form: $E^\circ \sim E_{1/2} = (E_{pa} + E_{pc})/2$. $n\text{-}Bu_4N^+PF_6{}^-$ (0.1 M); cationic complex: 10^{-3} M; v = 400 mV s^{-1}, T = 20 °C; working and counter electrodes: Pt; reference electrode: SCE; $\Delta E_p = E_{pa} - E_{pc}$ = 40–45 mV (DMF), 45–50 mV (MeCN), 50–55 mV (THF), 50–60 mV (CH_2Cl_2), 50–60 mV (DMSO), 60–70 mV (DME). The shifts *vs.* the theoretical value of 58 mV at 20 °C are due to variations in ohmic compensation. $E_{1/2}$ values were recorded with an accuracy of ±0.005 V except the $E_{1/2}$ value of $[FeCp^*(C_6Me_6)]^{0/+}$ in CH_2Cl_2, which is not accurate because of the interference with the reduction of the solvent. In CH_2Cl_2, $n\text{-}Bu_4N^+$ salts with various counter-anions and concentrations (*vide infra*) were used, but the difference between the $E_{1/2}$ values of $FeCp^*_2{}^{+/0}$ and $CoCp^*_2{}^{+/0}$ remained constant (1.390 V). The difference between the $E_{1/2}$ values of $FeCp_2{}^{+/0}$ and $FeCp^*_2{}^{+/0}$ varied, however, between 0.460 and 0.545 V. The $E_{1/2}$ values *vs.* SCE obtained for $FeCp_2{}^{+/0}$ and $FeCp^*_2{}^{+/0}$ respectively are as follows (V). $n\text{-}Bu_4N^+PF_6{}^-$ (0.1 M: 0.475 and −0.070; 0.4 M: 0.425 and −0.100); $n\text{-}Bu_4N^+BF_4{}^-$ (0.1 M: 0.585 and 0.045; 0.4 M: 0.555 and 0.035); $n\text{-}Bu_4N^+Br^-$ (0.1 M: 0.490 and −0.010; 0.4 M: 0.480 and 0.000); $n\text{-}Bu_4N^+HSO_4{}^-$ (0.1 M: 0.545 and 0.065; 0.4 M: 0.515 and 0.055); $n\text{-}Bu_4N^+Cl^-$ (0.1 M: 0.590 and 0.070; 0.4 M: 0.570 and 0.070).

Table 2 $E_{1/2}$ values (V) of transition-metal sandwich complexes determined *vs.* $FeCp^*_2$[a]

$E_{1/2}$ *vs.* $FeCp^*_2$	DMF	CH_3CN	THF	CH_2Cl_2	DMSO	DME
$FeCp^*_2{}^{0/+}$	0	0	0	0	0	0
$FeCp_2{}^{0/+}$	0.480	0.510	0.440	0.545	0.470	0.440
$CoCp^*_2{}^{0/+}$	1.390	1.390	1.400	1.390	1.395	1.400
$FeCp^*(C_6Me_6)^{0/+}$	1.750	1.745	1.750	—	1.750	1.750

[a] $E_{1/2}$ values were determined using the cationic form: $E^\circ \sim E_{1/2} = (E_{pa} + E_{pc})/2$. $n\text{-}Bu_4N^+PF_6{}^-$ (0.1 M); cationic complex: 10^{-3} M; v = 400 mV s^{-1}, T = 20 °C; working and counter electrodes: Pt; reference electrode: SCE; $\Delta E_p = E_{pa} - E_{pc}$ = 40–45 mV (DMF), 45–50 mV (MeCN), 50–55 mV (THF), 50–60 mV (CH_2Cl_2), 50–60 mV (DMSO), 60–70 mV (DME). The shifts *vs.* the theoretical value of 58 mV at 20 °C are due to variations in ohmic compensation. $E_{1/2}$ values were recorded with an accuracy of ±0.005 V except the $E_{1/2}$ value of $[FeCp^*(C_6Me_6)]^{0/+}$ in CH_2Cl_2, which is not accurate because of the interference with the reduction of the solvent. In CH_2Cl_2, $n\text{-}Bu_4N^+$ salts with various counter-anions and concentrations (*vide infra*) were used, but the difference between the $E_{1/2}$ values of $FeCp^*_2{}^{+/0}$ and $CoCp^*_2{}^{+/0}$ remained constant (1.390 V). The difference between the $E_{1/2}$ values of $FeCp_2{}^{+/0}$ and $FeCp^*_2{}^{+/0}$ varied, however, between 0.460 and 0.545 V. The $E_{1/2}$ values *vs.* SCE obtained for $FeCp_2{}^{+/0}$ and $FeCp^*_2{}^{+/0}$ respectively are as follows (V). $n\text{-}Bu_4N^+PF_6{}^-$ (0.1 M: 0.475 and −0.070; 0.4 M: 0.425 and −0.100); $n\text{-}Bu_4N^+BF_4{}^-$ (0.1 M: 0.585 and 0.045; 0.4 M: 0.555 and 0.035); $n\text{-}Bu_4N^+Br^-$ (0.1 M: 0.490 and −0.010; 0.4 M: 0.480 and 0.000); $n\text{-}Bu_4N^+HSO_4{}^-$ (0.1 M: 0.545 and 0.065; 0.4 M: 0.515 and 0.055); $n\text{-}Bu_4N^+Cl^-$ (0.1 M: 0.590 and 0.070; 0.4 M: 0.570 and 0.070).

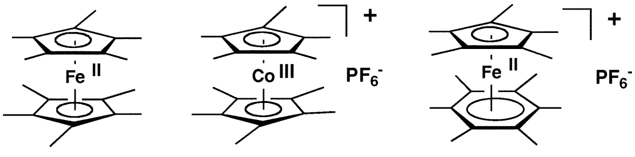


Chart 1

The redox potential values of these redox couples are reported in Table 1 *vs.* SCE in different solvents. The independence of the redox couples of the permethylated redox couples was verified by comparing the values of the redox potentials recorded *vs.* $[FeCp^*_2]^{0/+}$ taken as the reference, which are reported in Table 2 for various solvents. Only the values of the $[FeCp_2]^{0/+}$ couple varies, not those of the permethylated redox couples. This result is consistent with the fact that the redox potentials of the permethylated redox couples are independent of the nature of the solvent and supporting electrolyte. The fact that the $[FeCp_2]^{0/+}$ reference is not quite accurate enough does not mean that the many results that have been reported in the recent literature *vs.* $[FeCp_2]^{0/+}$ have to be re-measured *vs.* the more accurate $[FeCp^*_2]^{0/+}$ reference. Indeed, it is possible to take advantage of all the results obtained *vs.* $[FeCp_2]^{0/+}$ using the conversion of values *vs.* $[FeCp_2]^{0/+}$ to values *vs.* $[FeCp^*_2]^{0/+}$ of Table 2 in various solvents. Likewise, it is possible to use ferrocene continuously as the internal reference, and yet to have a solvent- and electrolyte-independent redox potential by conversion with Table 2. The standard redox potentials of the main reductants and oxidants $E^{\circ\prime}$ *vs.* $[FeCp_2]^{0/+}$, $[FeCp_2]^{0/+}$, SCE and the normal hydrogen electrode (NHE) are given in Table 3 and 4, respectively (ESI‡).[16a]

3. Iron and cobalt sandwich complexes as redox reagents

Organometallic complexes, in particular Fe and Co metallocenes and other sandwich complexes for which at least two redox forms are stable and robust, are very appropriate to carry out clean electron transfer reactions, because side reactions of the substrate are avoided in this way. When very strong reductants are required (alkali metals, aromatic radical anions, benzophenone radical anion), the purity of the reductant is not well established due to air and moisture sensitivity, and it is used in excess in order to insure complete reactions. This type of procedure introduces difficulties to separate products, and in addition over-reduction may proceed. The same can be stated with strong oxidants such as O_2^+ (Bartlett' dioxygenyl salt),[17] C_{60}^+ and C_{76}^+,[18] Ag^+,[19] MX_5 (M = Sb, As; X = F, Cl).[20] Some good single-electron transfer oxidants such as NO^+ are non-innocent, *i.e.* they often participate as ligands in (side) reactions of transition-metal complexes.[21] Thus, it is wise to choose a redox reagent that will provide the exergonic reaction with only a modest exergonicity, and very often organometallic redox reagents, for which both forms are robust, provide the ideal choice. The knowledge of the standard redox potentials of the redox reagents examined in section 1 provides a relatively good guide for the choice of the adequate reagent. It is of course essential to also know the standard reduction or oxidation potential of the substrate that needs be transformed or to measure this potential using cyclic voltammetry (CV). If reduction or oxidation of the substrate is found to be chemically irreversible by CV, then the redox process occurs more easily than indicated by the electrochemical potential, because the redox reaction is driven by the follow-up reaction of the substrate. Comparing with the electrochemical potential, this potential gain is all the larger as the follow-up reaction is faster and can reach several hundred mV. Even if there is no follow-up decomposition of the redox reactants, the exergonicity is not necessarily directly provided by the potential difference between the standard redox potentials of the redox reactants. [22,23] It is only so if there is one unit charge difference between the redox reactants (*vide infra*). Indeed, the ergonicity is provided by the Weller equation that takes into account both the thermodynamic potential of the donor and acceptor substrates and the electrostatic factor (eqn (1) and (2)):[22,23]

$$\begin{aligned}\Delta G^\circ\ (\text{kcal mol}^{-1}) \\ &= 23.06[(E^\circ_D - E^\circ_A) + (Z_A - Z_D - 1)e^2f/ed] &\quad (1)\\ &= 23.06[E^\circ_D - E^\circ_A] + 331.2[(Z_A - Z_D - 1)(f/ed)] &\quad (2)\end{aligned}$$

If, for instance, the monocations are reduced by a neutral organometallic complex, $Z_A - Z_D = 1$, and this electrostatic factor $(Z_A - Z_D - 1)(f/ed)$ is nil. The thermodynamics is then only governed by the redox potentials of the donor and acceptor (simplified Weller equation, eqn (3)).

$$\Delta G^\circ\ (\text{kcal mol}^{-1}) = 23.06[E^\circ_D - E^\circ_A] \qquad (3)$$

If, on the other hand, the reaction is carried out in a solvent of low dielectric constant, or/and if the radii of the donor and acceptor are small, the electrostatic factor can be large, especially if the charges of the donor and acceptor are very different, in particular if the oxidant is an anion (such as in polyoxometallates).[23a,b]

In eqn (3), for instance the redox reaction is 99% achieved if the difference between the redox potential of the oxidant and that of the reductant is 0.12 V for the exchange of one electron at 25 °C.

Certain transition-metal sandwiches including electron-reservoir Fe^I complexes suitably serve as such redox reagents for which both redox forms are stable and can be easily separated after stoichiometric redox reactions. By variation of the number of methyl groups on the rings, a convenient scale of redox reagents is available over a scale of more than 3 volts (Chart 2). Organometallic chemists, in particular the groups of Connelly,[11a,b] Geiger,[11a,c] Hamon and Lapinte,[24] have extensively and successfully used ferrocenium (usually as a BF_4 or PF_6 salt)[25] as a mild monoelectronic oxidant. In fact, the scale is even more widely flexible as shown in Chart 2. Geiger's group has initiated the use of acetylferrocenium,[11]

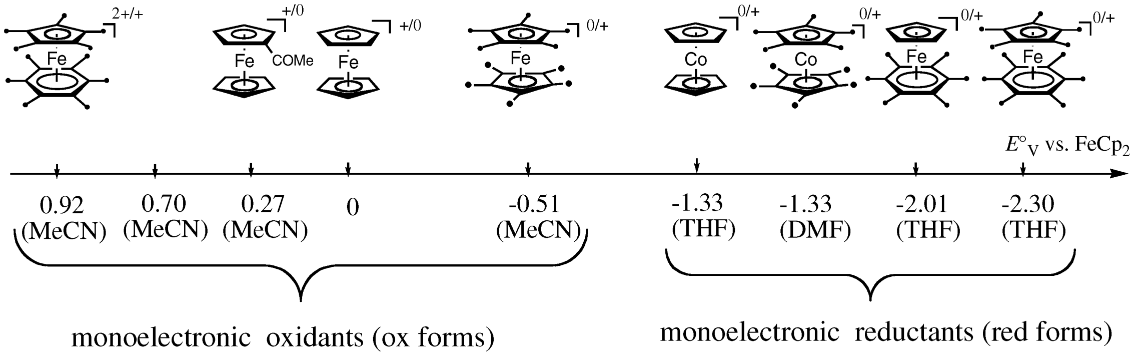


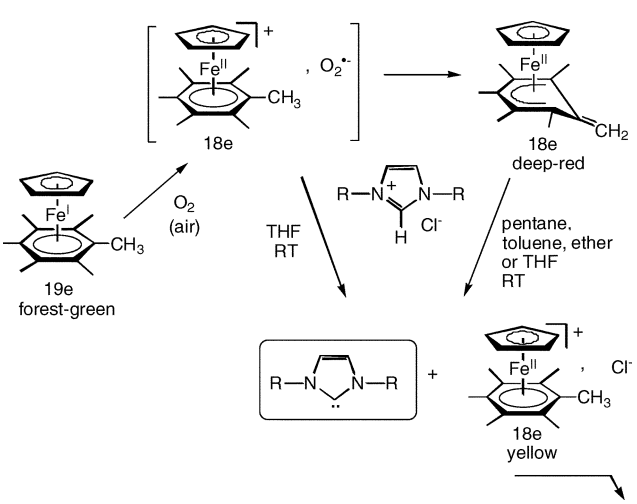
Chart 2

a stronger oxidant than ferrocenium, and some chemists have used cobaltocene[24,26] as a reductant (*vide infra*).[11]

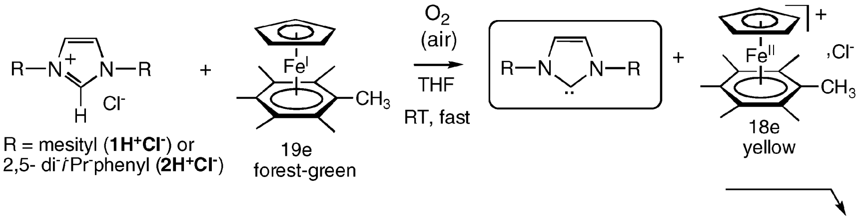
4. Stoichiometric reactions using the genuine 19-electron organo-Fe^I electron-reservoir complex $[CpFe^I(\eta^6\text{-}C_6Me_6)]$ and its functional derivatives

Although the use of cobaltocene, an air sensitive complex yielding a peroxo-bridged dimer upon fast reaction with O_2,[27] has been carried out in several instances,[11,24,26] a general strategy for smooth single-electron reduction using stronger reagents was clearly called for. The air-sensitive complex decamethylcobaltocene[28] has also sometimes been used.[11,29] The antibonding orbital is largely ligand based in these cobalt metallocenes, with only a 40% metal character.[30] Thus, they are not real 19-electron complexes[31] and belong to a large class of complexes resulting from the single-electron reduction of 18-electron precursors for which the extra electron is essentially ligand based. [31,32] On the other hand, a large family of complexes $[(\eta^5\text{-}C_5R_5)Fe^I(\eta^6\text{-arene})]$, R = H or Me,[33] has been synthesized, characterized by a variety of physical techniques and DFT calculations[34,35] and used as very powerful (yet thermally stable) reductants in a variety of processes (*vide infra*). In these complexes, the metal character of the antibonding orbital of e_1* symmetry reaches 80%., *i.e.* the extra electron is protected within the reservoir shell of protecting ligands.[34] For instance, the fully methylated, crystalline complex $[(\eta^5\text{-}C_5Me_5)Fe^I(\eta^6\text{-}C_6Me_6)]$ has a redox potential that is one volt more negative than that of cobaltocene (Scheme 1), and this redox potential is not medium sensitive.[12] The 18-electron cationic precursors $[(\eta^5\text{-}C_5R_5)Fe^I(\eta^6\text{-arene})][PF_6]$ are easily available by reactions of arenes with ferrocene (R = H) or $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2Br]$ (R = Me),[35] or by visible-light photolysis.[36] These complexes can also be functionalized with various Cp substituents ($COCH_3$,[37a] CO_2H,[37b,c] CO_2R,[37d] CONHR,[37d] COSR)[37d] which allows solubilization in water,[37b,c] brings about various colors of the thermally stable 19-electron complexes[37d] and covalent fixation to polymers and dendrimers using the ester and amide linkages.[37d]

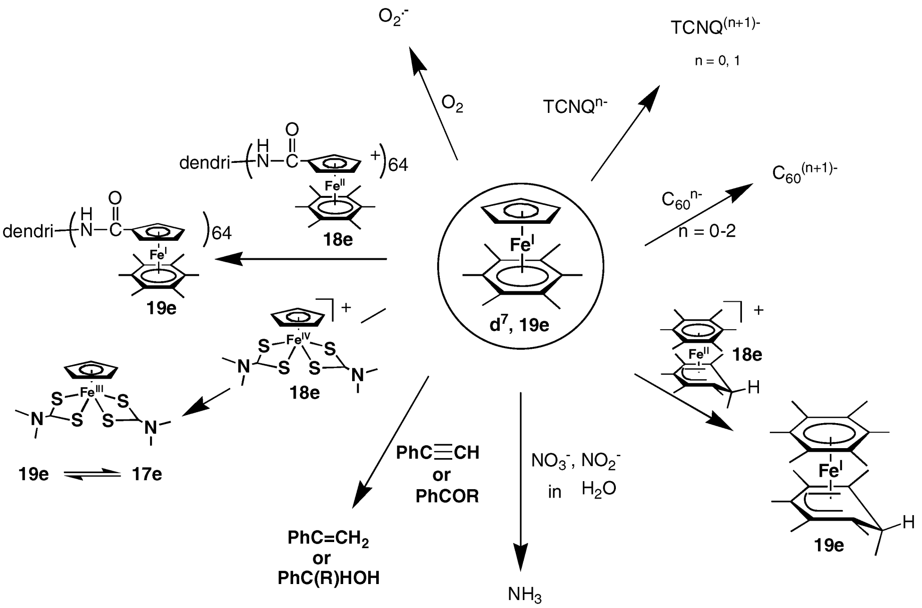
The most straightforward reaction of the prototypal complex $[CpFe^I(\eta^6\text{-}C_6Me_6)]$ is that with air, because there is a one-volt difference between the redox potential of the Fe^{II}/Fe^I system and that of O_2/O_2^- (1 V. *vs.* Cp_2Fe^+/Cp_2Fe in DMF), which makes electron transfer very exergonic.[38] Indeed, the reaction of forest-green $[CpFe^I(\eta^6\text{-}C_6Me_6)]$ with air at –100 °C in frozen THF solution is indicated by a red color appearing at the surface of the frozen green Fe^I solution in an EPR tube. The EPR spectrum recorded is typical of the temperature dependent spectrum of the superoxide radical anion O_2^-,[39] indicating that single electron transfer has occurred. In THF or pentane solution at −78 °C, the reaction is fast, and a blood-red solution appears after addition of 1/4 equiv. O_2 per mol Fe^I has been added. The red complex, virtually quantitatively formed, lacks one H atom compared to the starting 19-electron complex, and its X-ray crystal structure revealed an 18-electron cyclohexadienyl structure,[40a] $[CpFe^{II}(\eta^6\text{-}C_6Me_5{=}CH_2)]$ containing an exocyclic double bond.[40b] Thus, the second step, following the initial electron transfer between Fe^I and O_2, is proton transfer in the caged contact ion pair $[CpFe^{II}(\eta^6\text{-}C_6Me_6), O_2^{\cdot-}]$ from an acidic methyl group of the cationic Fe^{II} intermediate. To support this pathway (in addition to the above EPR experiment), it could be shown that KO_2 deprotonates $[CpFe^I(\eta^6\text{-}C_6Me_6)][PF_6]$ in the presence of 18-crown-6 ether in DMSO. The second step of the reaction of Fe^I to O_2, proton transfer in the caged intermediate ion pair, can be completely inhibited at −80 or 20 °C in THF in the presence of $[Na^+,PF_6^-]$ that is also in the form of a contact ion pair in this solvent.[41] The two contact ion pairs exchange their partners in a very fast process[42] yielding $[CpFe^{II}(\eta^6\text{-}C_6Me_6)][PF_6]$, and also $[Na^+O_2^-]$ whose fast disproportionation to peroxide is an additional driving force for the overall reaction. If there is no methyl group on the arene ligand, then O_2^- adds as a nucleophile onto the arene ligand in the cage cationic intermediate, and the peroxo organo Fe^{II} radical formed coupled with a Fe^I complex to yield a peroxo-bridged cyclohexadienyl dimer, $[CpFe^{II}(\eta^5\text{-}C_6H_6\text{-exo-O–}]_2$, which resembles that formed between cobaltocene and O_2, $[CpCo^{III}(\eta^4\text{-}C_5H_5\text{-exo-O–}]_2$.[27] The salt effect identically operates in this situation. This rather extraordinary salt effect totally inhibiting the reactivity of O_2^- at −80 °C is reminiscent of the superoxide dismutase enzyme although the conditions are very different.[39] This chemistry was further generalized to other 19- and 20-electron complexes[43a,b] and used for Cp and arene functionalization of the electron-reservoir complexes.[43c] Recently, this reaction of $[CpFe^I(\eta^6\text{-}C_6Me_6)]$ with O_2 was applied to the deprotonation of imidazolium salts to *N*-heterocyclic carbenes[44] using air (Scheme 2).[45] The mechanism involves electron transfer from the electron-reservoir complex and O_2 forming superoxide radical anion. The latter either directly deprotonates the imidazolium salt or deprotonation occurs *via* the iron sandwich complex. In principle, this system could also work with other weak acids. Indeed, some functional imidazolium salts cannot be deprotonated using *t*-BuOK that is usually utilized for this deprotonation (Scheme 3).[45] In this case, the new process



Scheme 2 Mechanism of the deprotonation of an imidazolium salt to an *N*-heterocyclic carbene using an electron-reservoir complex and air. Compare the direct pathway and indirect pathway *via* the cyclohexadienylidene intermediate.



Scheme 3 Deprotonation of the weak acid imidazolium using the prototypal electron-reservoir complex $[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ and air under ambient conditions.



Scheme 4 Electron transfer reactions to organic, inorganic and organometallic substrates using the 19-electron Fe^{I} electron-reservoir complex $[CpFe^{I}(\eta^6\text{-}C_6Me_6)]$.

allowing to deprotonate a weak acid with Fe^{I} and air is simple and useful, because *N*-heterocyclic carbenes are superb ligands for catalysis.[46]

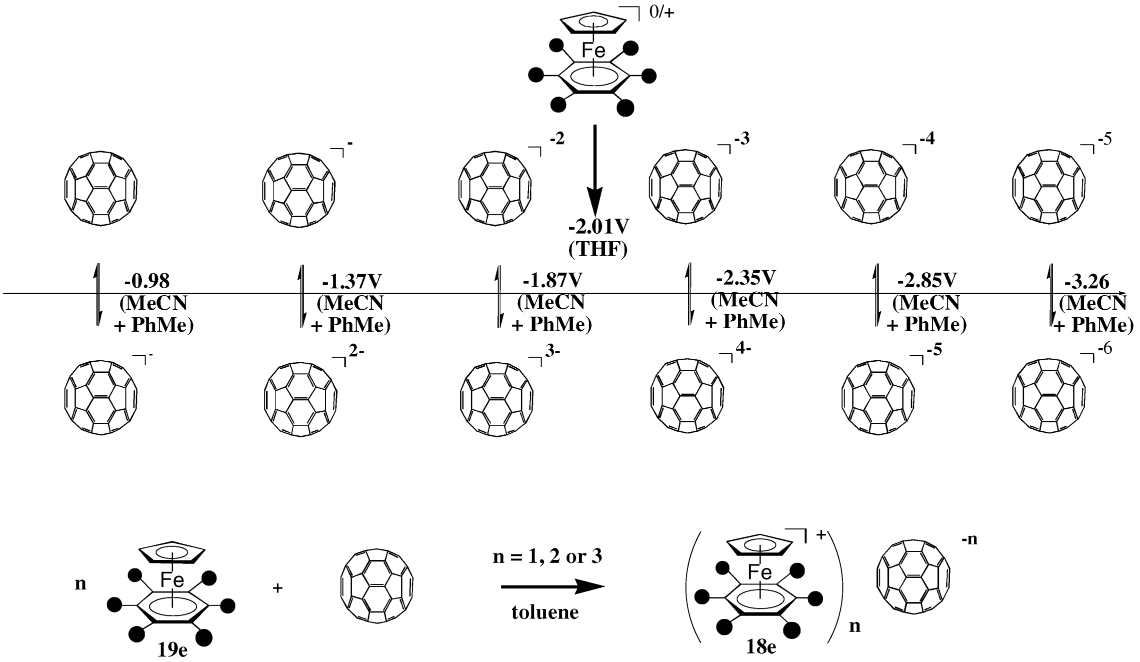
Electron transfer reactions of $[CpFe^{I}(\eta^6\text{-}C_6Me_6)]$ with a variety of organic, inorganic and organometallic substrates is shown in Scheme 4.[47] In some cases (TCNQ, C_{60}), multi-electron reduction of substrates is found, whereas in others (alkynes, ketones, inorganic oxides), reduction proceeds according to electron transfer/proton transfer sequences, and in these cases reductions proceed with large over-potentials, because the redox equilibria are shifted toward products due to fast protonation steps (Scheme 4).

We now focus on fullerenes whose monoelectronic reductions such as that of C_{60} are well known and can be carried out stepwise up to the formation the hexa-anion without breakdown on the electrochemical time scale[48] (although such hexa-charged anions have never been synthesized). Strong chemical reductants such as alkali metals, however, can reduce C_{60} up to the trianion only given the two extreme values of the last reduction potentials. Moreover, the cesium salt of $C_{60}{}^{3-}$ was shown to be a superconductor.[49] Reduction of C_{60} by $[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ gives the mono-, di- or trianion of C_{60} depending on the stoichiometry (Scheme 5).

In the salt of the trianion, the lattice is determined by the large organoiron cation rather than by the anion, however. Thus, its physical properties are only those of a paramagnetic species.[50] Cobaltocene can only reduce C_{60} to its mono-anion and decamethylcobaltocene can reduce it to its dianion. When the Fe^{I} complex is located at the periphery of dendrimers, electron transfer to C_{60} is obtained likewise, for instance to give $C_{60}{}^{\cdot-}$ with the suitable stoichiometry of reactants (Scheme 6).[51]

5. Stoichiometric oxidation reactions using the 17-electron organo-Fe^{III} complex $[(\eta^5\text{-}C_5Me_5)Fe^{III}(\eta^6\text{-}C_6Me_6)][SbCl_6]_2$, the strongest known organometallic oxidant

Oxidation of the yellow 18-electron complex $[Fe^{II}(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)][PF_6]$ by $SbCl_6$ in liquid SO_2 yields the purple 17-electron complex $[Fe^{III}(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)][SbCl_6]_2$, isoelectronic to ferrocenium, that is stable in dry air. The electrochemical oxidation of the monocationic 18-electron complexes $[FeCp(\eta^6\text{-arene})][PF_6]$ in liquid SO_2 shows a reversible monoelectronic wave around +2 V *vs.* SCE, but the 17-electron dicationic complexes are not isolable. The full steric protection of the iron(III) center, with 11 methyl groups, that bears the electron hole in the dication insures stability of the complex. The redox potential of this Fe^{II}/Fe^{III} system is



Scheme 5 Reduction of C_{60} by $[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ to the mono-, di- or trianion depending on the stoichiometry. For the redox potential values of C_{60}, see Echegoyen and co-workers in ref. 48.

1.4 V *vs.* SCE, *i.e.* 1 V more positive than that of ferrocenium. This large difference of redox potential for two isoelectronic redox systems involving the same oxidation state with about the same sandwich structure is only due to the charge difference that is responsible for the difference of electrostatic effect.[52]

It can oxidize $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ to the cation, the monocationic complex $[FeCp(CO)]_4[PF_6]$ to the isostructural dication and $Ru(bpy)_3{}^{2+}$ to the trication (Scheme 7).[52]

6. Electrocatalytic (electron-transfer-chain catalyzed) reactions using the catalyst $[Fe^{I}(\eta^5\text{-}C_5R_5)(\eta^6\text{-}C_6Me_6)]$ (R = H or Me)

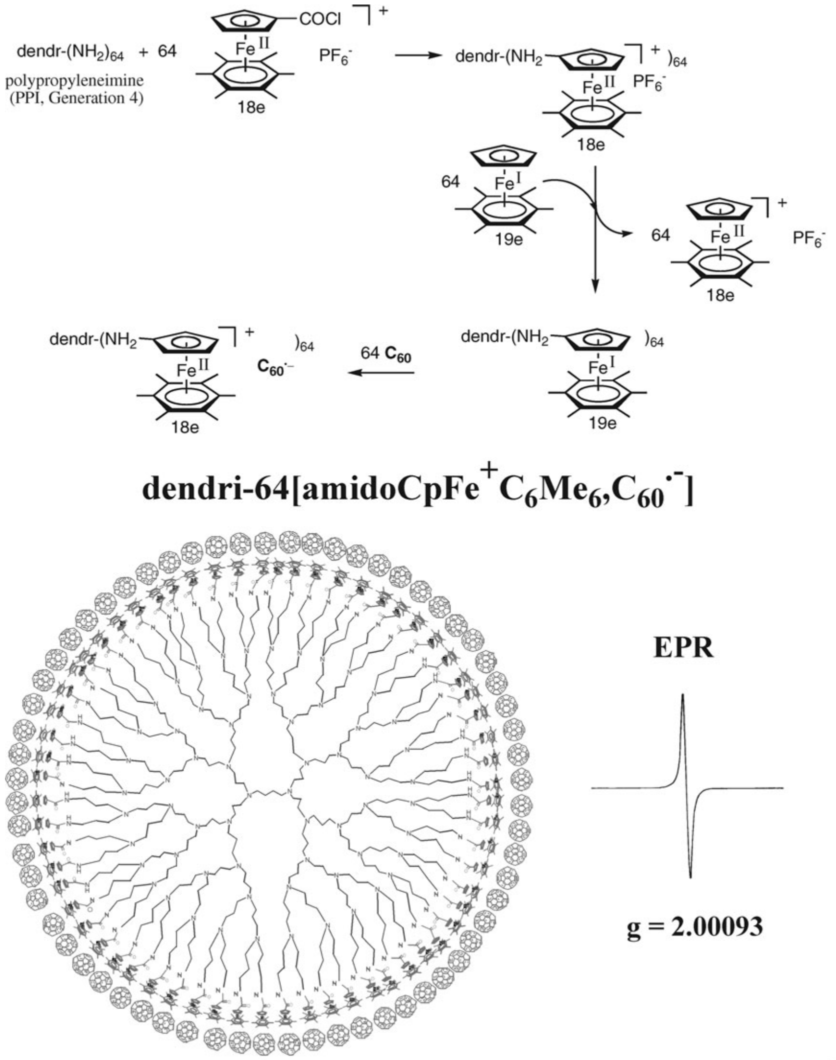
Savéant distinguished *electrocatalysis* that is the catalysis of reactions (that may be non-redox) by electrons or electron holes proceeding according to an electron-transfer-chain mechanism and *redox catalysis* that is the mediation or catalysis of a redox reaction by a redox mediator (outer-sphere) or redox catalyst (inner sphere).[53]

Electron-transfer-chain (or atom-transfer-chain) catalysis, introduced first by Taube with inorganic complexes,[4] has been studied and successfully applied to organotransition-metal synthesis in the early 1980s.[54,55] The electron-reservoir complexes $[Fe^{I}(\eta^5\text{-}C_5R_5)(\eta^6\text{-}C_6Me_6)]$ (R = H or Me) and derivatives are excellent initiators when initiation must be carried out by a reductant, *i.e.* when the product is more electron rich than the starting complex in order to design an exergonic cross electron transfer step in the catalytic chain. For instance, substitution of the toluene ligand in $[Fe^{II}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)][PF_6]$ by three phosphanes can be achieved in a few seconds at room temperature by adding 1% of $[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ in THF.[56]

In fulvalene dimetal carbonyl complexes, *ETC*-induced introduction of PMe_3 leads to the zwitterionic monosubstituted complex in the presence of a catalytic amount of $[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$. Introduction of the second phosphane involving carbonyl substitution does not proceed, however.[57] Substitution of CO by the second PMe_3 ligand can be only achieved using the more powerful reductant $[Fe^{I}(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)]$ as a catalyst (Scheme 8).[58]

In the cluster $[Ru_3(CO)_{12}]$, substitution of carbonyl by phosphane ligands leads to mixtures when it is carried out thermally. Using *ETC* catalysis, CO substitution by phosphanes was shown by Bruce's group to be very selective and clean.[59a] Subsequently, this synthetic strategy was pursued in a dendrimer series. Therefore, dendritic phosphines containing 32 diphenylalkyl phosphine termini were synthesized and showed a single ^{31}P NMR signal signifying the equivalence of the phosphorus atoms around the dendrimer. *ETC* catalysis was initiated by 1% $[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ and carried out using a stoichiometric dendritic phosphine/cluster ratio in order to perform single CO substitution by a dendritic phosphine tether. The resulting product showed a single ^{31}P NMR signal indicating that the 32-phosphine dendrimer has bound 32 $Ru_3(CO)_{11}$ cluster units. A similar procedure was applied to the next generation of dendrimer containing 64 phosphine termini (Scheme 9).[59b,c]

On the oxidation side, a catalytic amount of ferrocenium could serve as electrocatalyst for the fast substitution of two acetonitrile ligands in $[W(CO)_3(MeCN)_3]$ by two terminal alkyne ligands under ambient conditions, provoking metathesis polymerization of terminal alkynes.[60a,b] It was proposed that an alkyne ligand isomerizes to a vinylidene in the tungsten complex, followed by formation of a tungstacyclobutene intermediate that undergoes polymerization *via* the Chauvin–Katz mechanism.[60c–e]



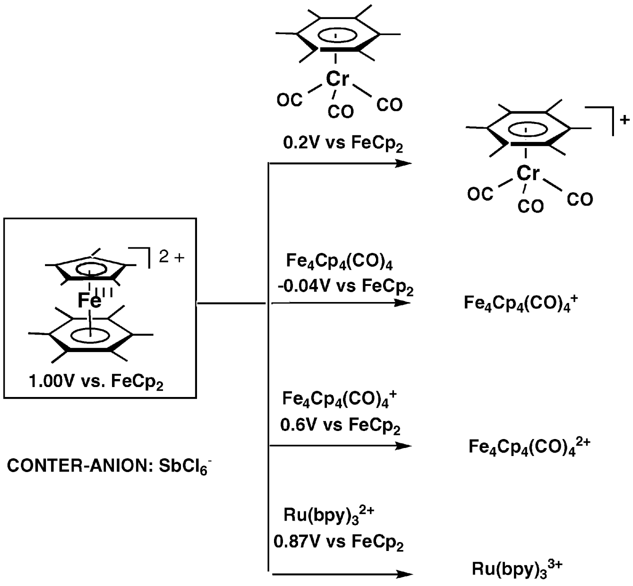
Scheme 6 (Top) Formation of the G_4-PPI dendrimer containing 64 ion pairs $[CpFe^{II}(C_6Me_6)^+, C_{60}^{\bullet -}]$ as termini. (Bottom) 2-D schematic representation and EPR spectrum of $[CpFe^{II}(C_6Me_6)^+C_{60}^{\bullet -}]$.

7. Redox catalysis in water using the catalysts $[Fe^I(\eta^5\text{-}C_5H_4R)(\eta^6\text{-arene})]$ (R = H or CO_2H)

Redox catalysts mediate (outer sphere) or catalyze (inner sphere) reduction or oxidation processes that are thermodynamically favorable (exergonic), but limited by slow kinetics due to extensive structural reorganization. They also facilitate endergonic electron transfers for which the product is reactive enough to shift the redox process. Redox catalysts are important in biological processes for which coupling between several redox catalysts (including mediators and true redox catalysts) are required in complex fundamental processes such as respiration, nitrogen fixation, *etc.*[9] They are also designed for chemical processes (for instance Cu^I/Cu^{II} in the Wacker process),[23b] photochemical processes (water splitting),[23a] and electrochemical processes (fuel cells).[23a,53]

The electron-reservoir complexes $[Fe^I(\eta^5\text{-}C_5H_4R)(\eta^6\text{-}C_6Me_6)]$ (R = H or CO_2H) and derivatives are redox catalysts for nitrate and nitrite cathodic reduction in water using an Hg cathode in alkali aqueous solution. These oxo-anions are not reducible (electroactive) in water at basic pH, and it is water that is reduced to dihydrogen at very negative potentials around −2 V *vs.* SCE. In the presence of the $[Fe^I(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ catalyst, however, these nitrogen oxides are reduced to ammonia. In the absence of a nitrate or nitrite, the redox catalysts slowly catalyze water reduction to dihydrogen. Catalysis of nitrogen oxide reduction to ammonia works whether the reduced form of the catalyst is water-soluble or not (*i.e.* homogeneously or heterogeneously). When a carboxylic group is present on the Cp ring of the catalyst, the catalyst becomes soluble in alkaline water in both the Fe^{II} and Fe^I forms, which gives access to the kinetics of redox catalysis. The rate constant is then directly accessible from the ratio of current intensities for the $Fe^{II/I}$ reduction in the voltammogram measured in the presence and absence of nitrate or nitrite (Scheme 10).[61,62]

The redox system $[FeCp(\eta^6\text{-}C_6Me_6)]^{0/+}$ is not only an electron-reservoir, but also a proton reservoir, the pK_a of the 18-electron cation in DMSO being around 28, *i.e.* 15 pK_a lower than that of the metal-free arene.[63] Thus reactions with excess base (KOH or KO^{t}Bu) and various alkyl- and benzyl halides gives star-shape complexes[64] and their



Scheme 7 The 17-electron Fe^{III} complex $[Fe^{III}(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)][SbCl_6]_2$ as a strong monoelectronic oxidant.

organic stars after removal of the central metal group. It is then possible to covalently attach catalysts at the star branch termini.[62,65] The interest of star- and dendritic catalysts is that they can be removed from the reaction medium unlike monometallic catalysts.[66] It was thus possible to derivatize redox catalysts of the type $[(CpR)Fe(\eta^6\text{-}C_6Me_6)]^+$ onto hexafunctional star-shaped cores in which the R group covalently links the complex to the star tethers (Scheme 11).[43c,62]

The hexairon redox catalysts were found to be about as efficient as mononuclear catalysts (the metal sites do not suffer from steric bulk), whereas introduction of bulk around the iron sandwich by hexasubstitution of the arene ring slowed down the redox catalysis of nitrate and nitrite reduction. This indicates that there is some inner-sphere component in the electron transfer step between the 19-electron complex and nitrate or nitrite. Although the low-oxidation state of Fe^I is not favorable for binding an oxygen atom of these nitrogen oxides, decoordination of an arene double bond to generate a 17-electron Fe^I species that would weakly bind an oxygen atom to facilitate electron transfer is probable given the kinetic data (Scheme 12).[65]

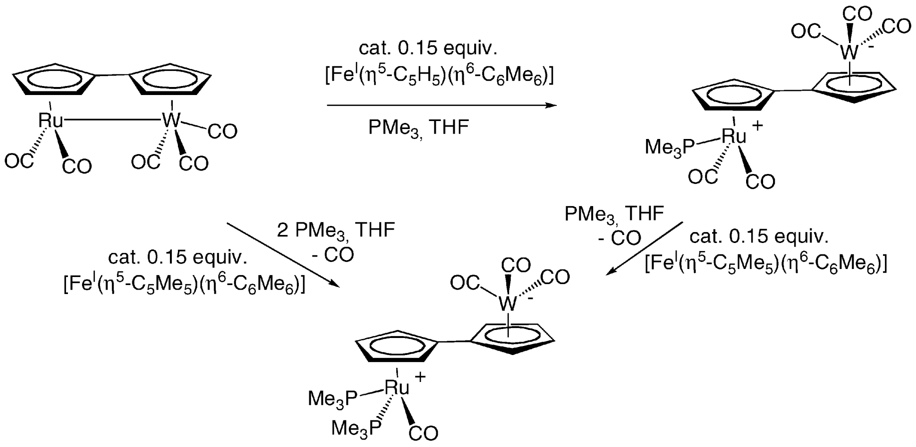
In summary, mono-and star-shaped hexanuclear iron-sandwich electron-reservoir systems bearing the water-solubilizing carboxylate group catalyze cathodic nitrate and nitrite reduction to ammonia on Hg cathode in alkaline water. Kinetic data show that location of the iron catalyst at the termini of the star core is favorable to avoid steric inhibition of the inner-sphere mechanism of redox catalysis.

On the oxidation side, the complex $[Fe^{III}(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)][SbCl_6]_2$ is also a redox catalyst for the oxidation of furfural.[52]

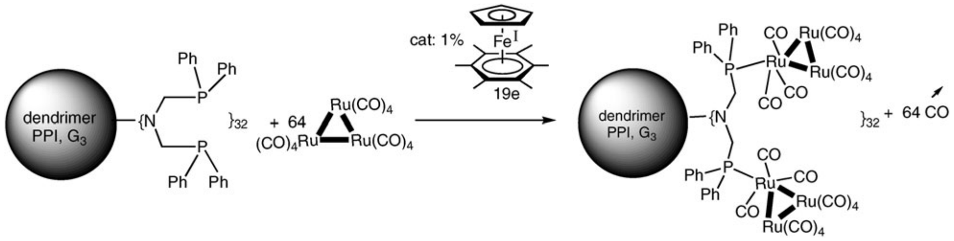
8. Molecular electronics in redox metallocene-containing polymers and dendrimers

Ferrocenyl-containing polymers have been known for a long time from the radical polymerization of vinyl ferrocene,[67] and now represent a very rich family of materials. Bard and Anson first estimated the number of redox units in these polymers in a seminal article using the intensity of the wave observed by cyclic voltammetry,[68a] and coulometry also leads to these numbers.[68b] The inclusion of ferrocene units into polymeric arrays has indeed attracted much attention due to the electronic donating ability, reversible redox chemistry, steric properties and ready functionalization of the redox-stable ferrocenyl group. In particular, Manners' group has reported an impressive family of ferrocenyl polymers synthesized by ferrocenophane-ring opening polymerization, and these polymers show mixed valency resulting in materials electronic properties.[67,69a,b] Such mixed valencies can also be designed by the introduction of two close redox units at the periphery of dendrimers.[69c]

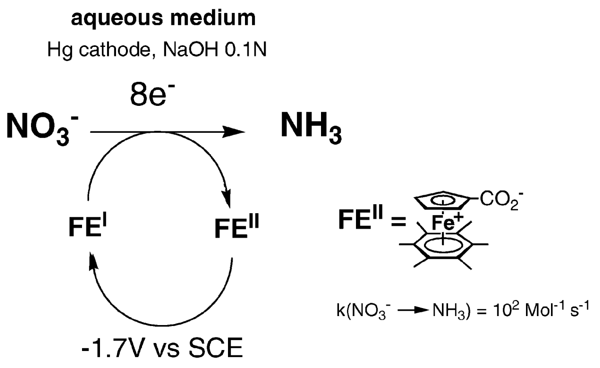
Metallodendrimers[69–75] containing ferrocenyl[72] and other iron-sandwich groups[73a–c] are precise macromolecules whose shapes are better defined than those of polymers and become globular as the generation increases (Chart 3). Dendronized



Scheme 8 Electrocatalytic phosphine addition and electron transfer from Ru to W catalyzed by $[Fe^I(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$. The stronger catalyst $[Fe^I(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)]$ can also catalyze CO substitution by PMe_3 in the zwitterionic complex (top right).



Scheme 9

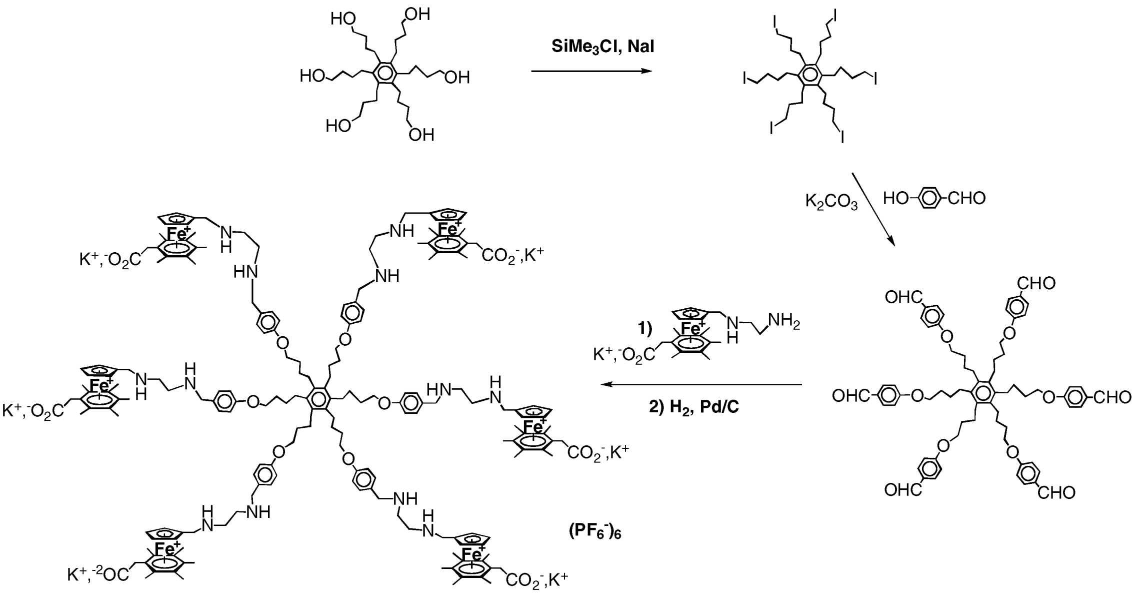


Scheme 10 Redox catalysis of the cathodic reduction of nitrate and nitrite in water on a Hg cathode. These anions are not electroactive in the absence of catalyst in basic aqueous medium (water is then reduced to H_2). The organoiron electron-reservoir redox catalyst is fully stable upon cycling in water.

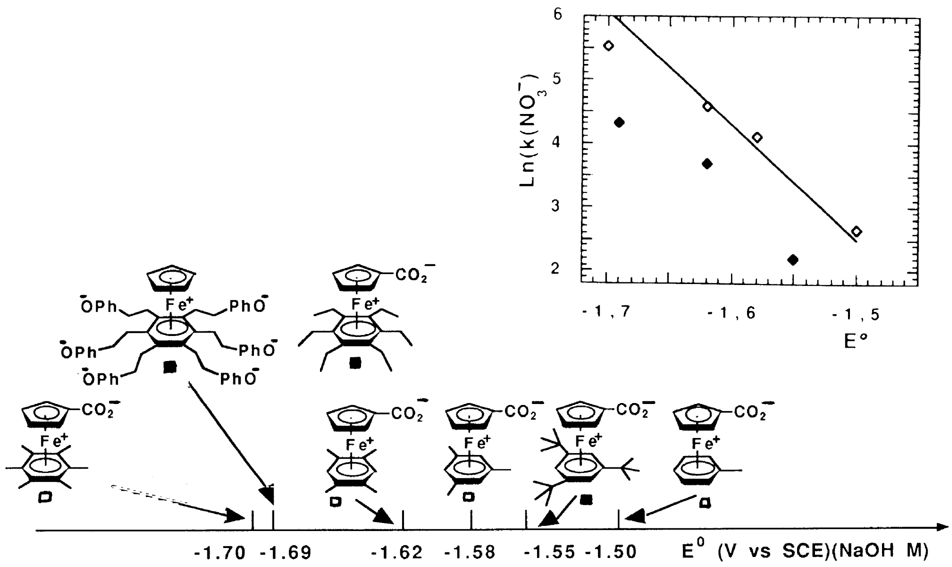
ferrocenyl polymers show intermediate properties between those of ferrocenyl dendrimers and polymers.[73d,e]

Cyclic voltammetry of metal-complex-cored dendrimers indicates that electronic communication is very poor with electrodes due to slow, distant electron transfer problems.[74] On the other hand, the opposite was found with ferrocenyl-terminated dendrimers that always showed electrochemically reversible (fast) electron transfer with electrodes[72] including with dendrimers containing up to 14 000 ferrocenyl termini that have a diameter of 30 nm in dichloromethane solutions.[75]

Even if the intramolecular distance between two redox centers is large (most often more than ten bonds), through-space electron hopping is optimized when the dendritic tethers bring two redox center at the minimum distance between them in a very fast dynamic process. This stepwise electron transfer among the redox centers between the remote ones and the ones that are located near the electrode also brings the electron or electron hole to the electrode faster than the standard electrochemical time scale. A precise analysis of this latter mechanism has been proposed by Amatore *et al.* for dendrimers terminated by $[Ru(terpy)_2]$,$^{2+}$ based on the measured electron hopping rate constant using ultramicroelectrodes and on a Smoluchowski-type model developed to take into account viscosity effects during the displacement of the $Ru^{II}/Ru^{III}(tpy)_2$ redox centers around their equilibrium positions.[76] The same is true, with fast interdendritic electron transfer,[77] so that redox-center-terminated dendrimers in which the redox centers are robust could serve as molecular conductors.



Scheme 11 Synthesis of a star-shaped water-soluble electron-reservoir redox catalyst. No kinetic loss is observed compared to the monoiron complex, and stability upon cycling is retained. The star shape avoids kinetic retardation observed with bulky dendritic cores inhibiting access of the substrate to the metal center.



Scheme 12 Kinetics of the redox catalysis of nitrate cathodic reduction (logarithm of the rate constant, ln k of the mediation step: $Fe^{I} + NO_3^- \rightarrow Fe^{II} + \ldots$) in water as a function of the driving force E° of the redox catalyst. Note the kinetic retardation with the redox catalysts containing a bulky arene ligand that inhibits the approach of nitrate to the iron center. This effect shows the inner-sphere component of the electron transfer mechanism. Non-bulky catalysts are on the straight line. The star-shape catalyst of Scheme 11 nearly falls on this straight line.

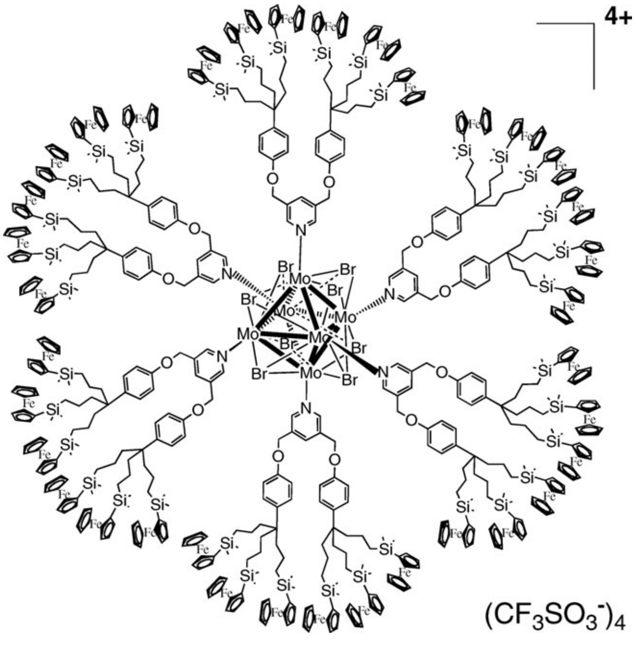


Chart 3

9. Redox-stable metallocene dendrimers as sensors

Redox metallocenes attached to endo-receptors (crowns, calixarenes, polypodal systems, *etc*) are sensors of anions, as nicely shown by Beer's group.[78] The fixation of these redox systems at the termini of dendrimers provide a single wave in cyclic voltammetry that is chemically and electrochemically reversible due to this fast inter-redox-site electron hopping mechanism. This trend allows to use these metallodendrimers as exo-receptors for sensing with several advantages: (i) they are better sensors than monometallic systems, showing positive dendritic effects[79] (*i.e.* sensing improves as the dendrimer generation number increases); (ii) they can be used to modify electrodes all the more easily as they are larger, *i.e.* as the dendrimer generation is higher.[80] These metallodendrimer-derivatized electrodes can be re-used upon washing, because the metallocene dendrimer remains firmly attached to the electrode. The ferrocene-terminated dendrimer have been ;used with various templating cores such as arenes,[81] octahedral inorganic clusters (Chart 3)[82] or gold nanoparticles (Chart 4).[83]

Cobaltocene-terminated dendrimers can be used in the same way, although the multiple charges limit their solubility.[84] The terminal sensor can be an amidoferrocenyl group whereby the amido fragment forms hydrogen bonds with HSO_4^- and (better) $H_2PO_4^-$,[79–81] amino-arene-iron cation specific for bromide and (better) chloride[87] or silylferrocenyl group for oxo-anions and ATP^{2-}[83c] With the amidoferrocenyl termini, the stability of the amidoferrocenium form is questionable, but the robustness was ensured with pentamethylamidoferrocenyl dendrimer termini.[85] The click ferrocenyl dendrimers in which the 1,2,3-triazole groups are directly attached to the ferrocenyl groups present, in addition, the advantage that they can sense both the oxo-anions such as ATP^{2-} and transition-metal cations such as Pd^{II}, Pt^{II}, Cu^{I} and Cu^{II}.[86]

10. Electronic communication through hydrocarbon ligands and metallodendrimers: molecular wires and molecular machines

A molecular wire (MW) consists of a molecule connected between two reservoirs of electrons. The molecular orbitals of the molecule, when the connected electron reservoir groups couple, provide a favorable electron pathway. Such a system was suggested to have the ability to rectify current in the early

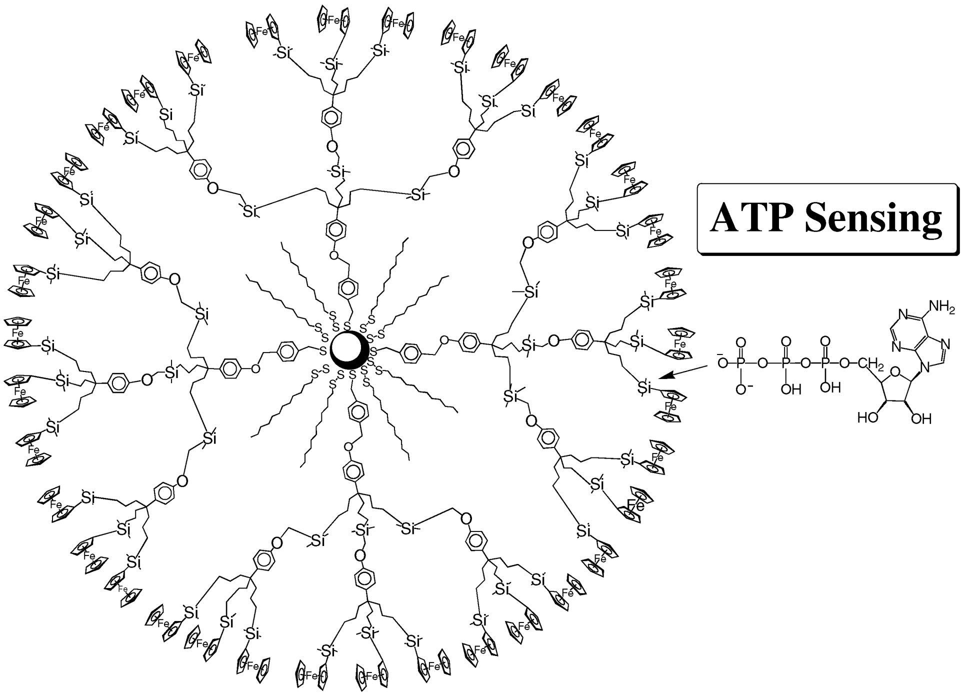


Chart 4

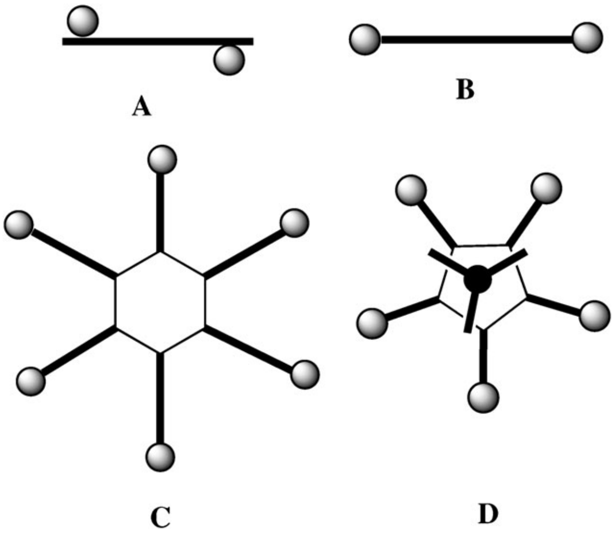


Chart 5

1970s by Aviram and Ratner who are, with Taube, the pioneers of molecular electronics.[88] Research on MWs has attracted considerable attention over the past few years with research on the possibility of rectification and other phenomena, and it now appears as a major area of nanosciences and nanotechnologies.[89] Prominent examples also include polymeric inorganic materials such as Li_2Mo_6Se,[90] but let us concentrate here on conducting organic linkers schematized on Chart 5.

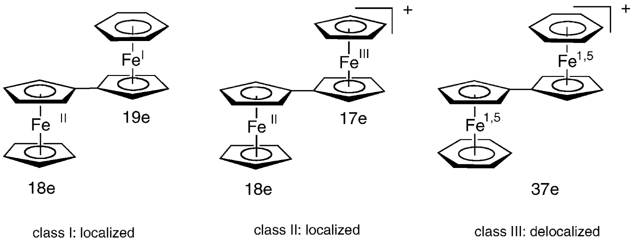


Chart 6

Following Taube's example of electronic communication between two ruthenium centers *via* a pyrazine bridge,[5] other ligand-bridged bimetallic compounds were designed and examined from the point of view of electronic communication between the two metallic redox centers. The question is whether these compounds are delocalized class-III mixed-valence (actually average-valent) or localized class-II mixed-valence with electron transfer between the redox sites.[91] The first well-known example is biferrocene (type **A**, Chart 6) whose monocation $(Fe^{II}Fe^{III})$[92*a*,*b*] is class II (as its permethylated analog[92*c*]), but can become more delocalized with one alkyl substituent per sandwich unit.[92*d*] In other following examples of type **A** from our work with the same fulvalene bridge between two iron centers in sandwich geometry, however, complexes were found to be either localized[93] or delocalized.[94] For instance, they could be perfectly delocalized class III $Fe^{I}Fe^{II}$ compounds[94] even on the infrared time scale (Chart 6).[94*d*] It was found that the non-bridging ancillary ligands play a crucial role, because they intervene in the frontier orbitals. As an example polyaromatic bridges were found to promote a delocalized mixed $Fe^{I}Fe^{II}$ system, and the di-reduced state coupled to distort the diphenyl ligand to a bis-cyclohexadienylidene ligand.[95] The geometry that is involved in these delocalized hydrocarbon-bridged systems is also represented by **A** in Chart 6, and it is found (transiently for the states involving Fe^0) in five oxidation states $Fe^{II}Fe^{II}$, $Fe^{II}Fe^{I}$, $Fe^{I}Fe^{I}$, $Fe^{I}Fe^0$ and Fe^0Fe^0

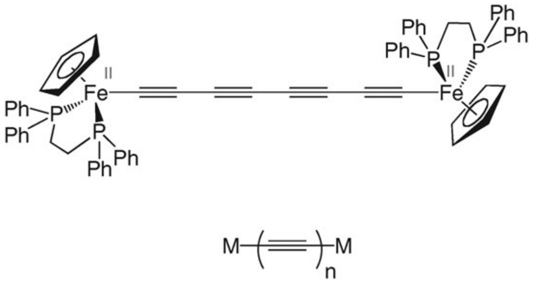


Chart 7

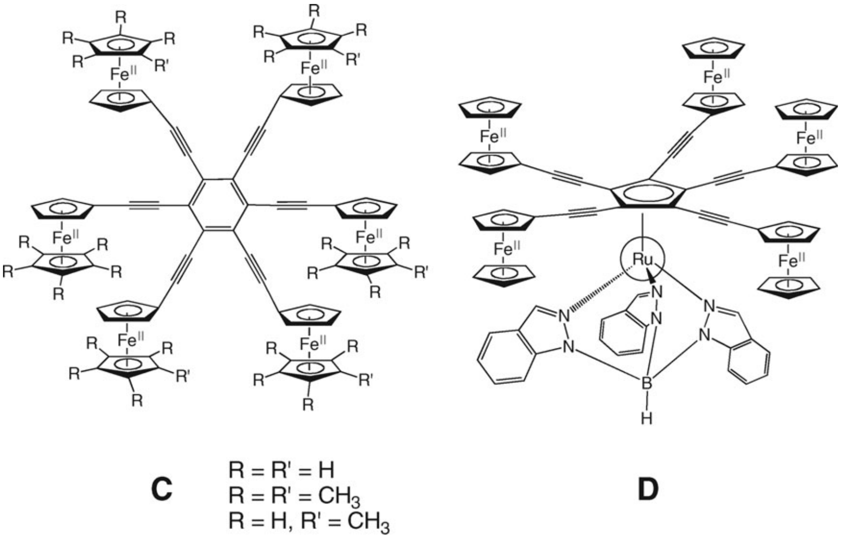
that are represented by cascades of single-electron chemically and electrochemically redox reversible waves in cyclic voltammetry (except the last wave for which the electron transfer is slow meaning structural reorganization, presumably to reduce the hapticity).

The linear geometry **B** was subsequently investigated and synthesized with all-carbon-chain ligands from the mid-1990s by the groups of Lapinte,[96] Bruce,[97] Gladysz[96,98] and Yam.[99] The iron compounds (Chart 7) have a specific interest because of the possibility to easily access to mixed (average) valence $Fe^{II}Fe^{III}$ systems and di-oxidized $Fe^{III}Fe^{III}$ compounds[96] as in the biferrocene derivatives. Moreover, the iron atom is surrounded by the bulky ancillary ligands C_5Me_5 and chelating diphenyldiphosphinoethane so that these complexes behave like electron reservoirs as in permethylated sandwich complexes. This property allowed their stabilization and study in various oxidation states. The groups of Bruce and Gladysz have isolated bimetallic compounds of ruthenium, rhenium and platinum with very long poly-yne chains containing up to 20 carbon atoms, *i.e.* $n = 10$ in Chart 7, and interesting non-linear optical properties have been disclosed.[100]

With a phenylene spacer, diynyl-bridged bimetallic iron complexes are still electronically connected, but much more so in paraphenylene connectors[101] than in meta isomers. Tris(iron-ethynyl)benzene complexes have been isolated and analyzed from the point of view of their mixed valencies, and a certain degree of electronic communication was observed.[102] In contrast, with ferrocenyl termini instead of iron termini, no splitting of the cyclic voltammetry wave of bis(*p*-ferrocenylethynyl)benzene is observed even with perfluorinated tetraarylborate electrolyte salts known to weaken iron pairing.[103] Thus, the absence of electronic communication between the ferrocenyl units in *para* and *meta* positions (due to very weak redox content in the Cp orbital connected to the ethynyl benzene group) allows to isolate the electrostatic factor in mixed valency as observed by cyclic voltammetry. For instance, in hexa(ferrocenylethynyl)benzene (**C**, Chart 8), a single cyclic voltammetry wave is observed using $[n\text{-Bu}_4N][PF_6]$ as the supporting electrolyte, whereas this wave can be split into three two-electron waves or six overlapping single-electron wave by variation of the nature of the supporting electrolyte and/or of the nature and number of methyl groups on the free Cp rings of the six ferrocenyl units.[104]

Such electronic effects are called for in the Toulouse group project of a molecular motor based on **D** (Chart 8) whereby oxidation of selectively only one ferrocenyl center at a nanoelectrode would provoke repulsion of that rotating center from the anode and thus provoke the motor rotation, bringing the oxidized group to the cathode for reduction.[105]

In dendrimers, molecular motions and rearrangements and size variations upon redox change is considerable and connected again to the electrostatic effects of ion pairing. For instance, in a G_5 dendrimer containing 2000 ferrocenyl termini, the dendrimer size increase upon oxidation could be recorded using atomic force microscopy and electron force microscopy in the solid state on a mica surface. The height measured increases from 4.5 ± 0.4 nm in the orange ferrocenyl dendrimer to 6.5 ± 0.6 nm in the dark-blue ferrocenium tetrafluoroborate dendrimer (Scheme 13). The robust nature of both redox forms insures complete reversibility of the process. This means that, upon a simple electric pulse at the right potential, a nanomolecular machinery is at work.[75c]

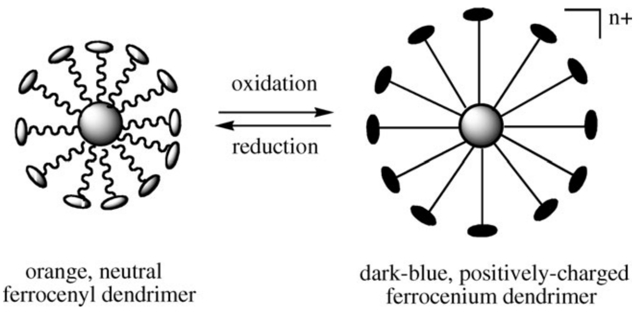


C

$R = R' = H$
$R = R' = CH_3$
$R = H, R' = CH_3$

D

Chart 8



Scheme 13 Representation of the fully reversible redox-induced "breathing" of giant dendrimers terminated with a theoretical number of $3^7 = 2181$ ferrocenyl groups (generation 5, G_5 with 1 → 3 connectivity starting with 3^2 branches for G_0). The actual ferrocenyl branch number for G_5 determined by UV-vis. and coulometry is 2 000 ± 100. Atomic force microscopy (AFM) measurements in the condensed state of the orange Fe^{II} form (left) indicates an average height on the mica surface of 4.5 ± 0.4 nm, whereas the dark blue ferrocenium tetrafluoroborate form with 2000 positive charges (right) exhibits a height of 6.5 ± 0.6 nm measured by electronic force microscopy (EFM).[75c]

11. Conclusion and outlook

In this microreview, we have shown the multiple functions and applications of the concept of electron reservoir molecules, that was introduced 30 years ago.[12] The encapsulation of a redox-active metal center inside a bulky shell of protecting ligands results in the robustness of the complexes throughout a large variety of processes: as references, reagents, electrocatalysts, redox catalysts, robust redox termini for electronic communication, and photochromic polymers and dendrimers also serving as molecular batteries. Very strongly reducing and oxidizing reagents were designed based on this principle, but other redox systems shown here with intermediate potentials in the redox scale are also very useful and will continue to be so in the design of nanodevices. Organometallics, however, are not the only candidates for electron-reservoir systems. Photoelectron transfer with polypyridine ruthenium complexes[106] and other photo-active inorganic and organic compounds[107] are useful for energy conversion, fine chemistry and machinery devices, although the instability of some oxidation states can sometimes be limiting. Metal nanoparticles can accept many quantum-size controlled electron transfers with Coulomb blockades[108] and be used as excellent multi-electron catalysts.[109] Redox-induced switch of spin cross-over for the design of molecular-memory devices is another example of possible future application.[110] It is indeed the synergy between well-designed, versatile molecular components and nanoparticles and surfaces that will the basis of nanoscience and nanotechnology in the 21st century.

Acknowledgements

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References

1 H. Taube, *Electron Transfer Reactions of Complex Ions in Solution*, Academic Press, New York, 1970; H. Taube, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 329; H. Taube, *Science*, 1984, **226**, 1028; T. J. Meyer and H. Taube, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. Guilard and J. A. McLafferty, Pergamon, Oxford, 1987, vol. 1, ch. 7.2, p. 331; H. Taube, Foreword of D. Astruc, *Electron Transfer and Radical Processes in Transition Metal Chemistry*, VCH, New York, 1995.

2 H. Taube, *Chem. Rev.*, 1951, **50**, 69.

3 H. Taube, H. Myers and R. L. Rich, *J. Am. Chem. Soc.*, 1953, **75**, 4118; H. Taube and H. Myers, *J. Am. Chem. Soc.*, 1954, **76**, 2103.

4 R. L. Rich and H. Taube, *J. Am. Chem. Soc.*, 1954, **76**, 2608.

5 C. Creuz and H. Taube, *J. Am. Chem. Soc.*, 1969, **91**, 3988.

6 M. Sano and H. Taube, *J. Am. Chem. Soc.*, 1991, **113**, 2327; M. Sano and H. Taube, *Inorg. Chem.*, 1994, **33**, 705.

7 J.-P. Collin, C. Dietrich-Buchecker, P. Gavina, M. C. Jimenez-Molero and J.-P. Sauvage, *Acc. Chem. Res.*, 2001, **34**, 477 *Molecular Machines and Motors*, ed. J.-P. Sauvage, Springer, Berlin, 2001; R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi and M. Venturi, *Acc. Chem. Res.*, 2001, **34**, 445; J. F. Stoddart, *Acc. Chem. Res.*, 2001, **34**, 410.

8 *Electron Transfer in Chemistry*, ed. V. Balzani, Wiley, Weinheim, 2001.

9 L. Stryer, *Biochemistry*, Freeman, New York, 2nd edn, 1981; I. Bertini, H. B. Gray, S. J. Lippard and J. S. Valentine, *Bioinorganic Chemistry*, University Science Books, Mill Valley, CA, 1994; *Electron Transfer in Biology and in the Solid State*, ed. M. K. Johnson *et al.*, American Chemical Society, Washington, DC, *Adv. Chem. Ser.*, 1990, No. 226.

10 R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, 1985, **811**, 265; N. S. Hush, *Ann. N. Y. Acad. Sci.*, 2003, **1006**, 1.

11 (*a*) N. G. Connelly and W. E. Geiger, *Adv. Organomet. Chem.*, 1984, **23**, 1; (*b*) W. E. Geiger and N. G. Connelly, *Adv. Organomet. Chem.*, 1985, **24**, 87; (*c*) W. E. Geiger, *J. Organomet. Chem. Libr.*, 1990, **23**, 142; (*d*) N. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877; (*e*) N. G. Connelly, *Chem. Soc. Rev.*, 1989, **18**, 153; (*f*) W. E. Geiger, *Organometallics*, 2007, **26**, 5738 (a historical and perspective account).

12 D. Astruc, J.-R. Hamon, G. Althoff, E. Román, P. Batail, P. Michaud, J.-P. Mariot, F. Varret and D. Cozak, *J. Am. Chem. Soc.*, 1979, **101**, 5445; J.-R. Hamon, D. Astruc and P. Michaud, *J. Am. Chem. Soc.*, 1981, **103**, 758; J. C. Green, M. R. Kelly, M. P. Payne, E. A. Seddon, D. Astruc, J.-R. Hamon and P. Michaud, *Organometallics*, 1983, **2**, 211; D. Astruc, *Acc. Chem. Res.*, 1986, **19**, 377.

13 G. J. Hills, in *Reference Electrodes*, ed. D. Ives and J. G. Janz, Academic Press, New York, 1961, ch. 10.

14 J. F. Coetzee and G. R. Padmanablan, *J. Phys. Chem.*, 1962, **66**, 7708; V. D. Parker, *Adv. Phys. Org. Chem.*, 1983, **19**, 131.

15 J. T. Hupp, *Inorg. Chem.*, 1990, **29**, 5010.

16 (*a*) J. Ruiz and D. Astruc, *C. R. Acad. Sci., Ser. IIc: Chim.*, 1998, **1**, 27; (*b*) I. Noviandry, K. N. Brown, D. S. Fleming, P. T. Gulyas, P. A. Lay, A. F. Masters and L. J. Philips, *J. Phys. Chem. B*, 1999, **103**, 6713; (*c*) J. Ruiz, M.-C. Daniel and D. Astruc, *Can. J. Chem.*, 2006, **84**, 288.

17 Dioxygen has a higher ionization potential (12.08 eV)[17b] than xenon (11.6 eV). It is when he succeeded in making $[O_2][PtF_6]$ that Bartlett had the wonderful idea to make what became the first rare-gas compound, $[Xe][PtF_6]$: (*a*) N. Bartlett and D. H. Lohmann, *J. Chem. Soc.*, 1962, 5253; (*b*) D. W. Turner and D. P. May, *J. Chem. Phys.*, 1966, **45**, 471; (*c*) dioxygenyl salts have been used to oxidize other substrates which are very difficult to oxidize: T. J. Richardson and N. Bartlett, *J. Chem. Soc., Chem. Commun.*, 1974, 427; N. Zücher, T. J. Richardson, O. Glemser and N. Bartlett, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 944; J. P. Dinnocenzo and T. E. Banach, *J. Am. Chem. Soc.*, 1986, **108**, 6063; J. P. Dinnocenzo and T. E. Banach, *J. Am. Chem. Soc.*, 1988, **110**, 971; J. P. Dinnocenzo and T. E. Banach, *J. Am. Chem. Soc.*, 1989, **111**, 8646; (*d*) The $O_2/O_2^{\bullet+}$ oxidation potential has

been estimated to 5.3 V *vs.* SCE. This calculation arises from the value of the ionization potential (12.08 eV),[17b] application of Miller's eqn[17e] and adding 0.34 V to convert the value so obtained to the SCE potential; (*e*) L. L. Miller, G. D. Nordblom and E. A. Mayeda, *J. Org. Chem.*, 1972, **37**, 916.

18 (*a*) R. D. Bolskar, S. Mathur and C. A. Reed, *J. Am. Chem. Soc.*, 1996, **118**, 13093; (*b*) C. A. Reed, *Acc. Chem. Res.*, 1998, **31**, 133; (*c*) R. Dagani, *Chem. Eng. News*, 1998, 49, May 4.

19 D. A. Bohling and K. R. Mann, *Inorg. Chem.*, 1983, **22**, 1561.

20 (*a*) D. J. Liston, Y. J. Lee, W. R. Scheidt and C. A. Reed, *J. Am. Chem. Soc.*, 1989, **111**, 6643; (*b*) K. Shelly, C. A. Reed, Y. J. Lee and W. R. Scheidt, *J. Am. Chem. Soc.*, 1986, **108**, 3117.

21 N. G. Connelly and J. D. Davies, *J. Organomet. Chem.*, 1972, **38**, 385.

22 A. Weller, *Z. Phys. Chem., Neue Folge*, 1982, **133**, 93.

23 (*a*) D. Astruc, *Electron Transfer and Radical Reactions in Transition Metal Chemistry*, VCH, New York, 1995; (*b*) ref. 23*a*, ch. 1, pp. 6–9; (*c*) D. Astruc, *Organometallic Chemistry and Catalysis*, Springer, Heidelberg, 2007, ch. 3, pp. 82–83.

24 C. Roger, P. Hamon, L. Toupet, H. Rabaa, J.-Y. Saillard, J.-R. Hamon and C. Lapinte, *Organometallics*, 1991, **10**, 1045; P. Hamon, L. Toupet, J.-R. Hamon and C. Lapinte, *Organometallics*, 1996, **15**, 10; M. Tilset, I. Fjeldahl, J.-R. Hamon, P. Hamon, L. Toupet, J.-Y. Saillard, K. Costuas and A. Haynes, *J. Am. Chem. Soc.*, 2001, **123**, 9984; J. A. Shaw-Taberlet, S. Sinbandhit, T. Roisnel, J.-R. Hamon and C. Lapinte, *Organometallics*, 2006, **25**, 5311; P. Hamon, F. Justaud, O. Cador, P. Hapiot, S. Rigaut, L. Toupet, L. Ouahab, H. Stueger, J.-R. Hamon and C. Lapinte, *J. Am. Chem. Soc.*, 2008, **130**, 17372; P. Hamon, A. Mari, J.-F. Meunier, L. Toupet, O. Cador, M. Etienne and J.-R. Hamon, *Inorg. Chim. Acta*, 2009, DOI: 10.1016/j.ica.2009.01.017.

25 G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, *J. Am. Chem. Soc.*, 1952, **74**, 2125; T. Kuwana, D. E. Bublitz and G. Hoh, *J. Am. Chem. Soc.*, 1960, **82**, 5811.

26 (*a*) Synthesis of cobaltocenium salts: G. Wilkinson, *J. Am. Chem. Soc.*, 1952, **74**, 6148; (*b*) Synthesis of cobaltocene: G. Wilkinson, P. L. Pauson and F. A. Cotton, *J. Am. Chem. Soc.*, 1954, **76**, 1970; (*c*) R. B. King, *Organometallic Syntheses*, Academic Press, New York, 1965, vol. 1.

27 H. Kojima, S. Takahashi and N. Nagihara, *J. Chem. Soc., Chem. Commun.*, 1973, 230.

28 U. Kölle and F. Khouzami, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 640.

29 D. A. Dixon and J. S. Miller, *J. Am. Chem. Soc.*, 1987, **109**, 3656; D. V. Konarev, S. S. Khasanov, G. Saito, I. I. Vorontsov, A. Otsuka, R. N. Lyubovskaya and Y. M. Antipin, *Inorg. Chem.*, 2003, **42**, 3706; R. Piskorski and B. Jaun, *J. Am. Chem. Soc.*, 2003, **125**, 13120; W. Uhl, L. Cuypers, W. Kaim, B. Schwederski and R. Koch, *Angew. Chem., Int. Ed.*, 2003, **42**, 2422; D. A. Rider, M. A. Winnik and I. Manners, *Chem. Commun.*, 2007, 4483; M. A. Kulandainathan, C. Hall, D. Wolverson, J. S. Ford, S. M. MacDonald and F. Markene, *J. Electroanal. Chem.*, 2007, **606**, 150; C. K. Chan, W. Zhao, S. Barlow, S. Marder and A. Kahn, *Org. Electron.*, 2008, **9**, 575.

30 J. H. Ammeter, *J. Magn. Reson.*, 1978, **30**, 299.

31 D. Fenske, *Chem. Ber.*, 1979, **112**, 363; D. R. Tyler, *Prog. Inorg. Chem.*, 1988, **36**, 125; W. Kaim, *Coord. Chem. Rev.*, 1987, **76**, 187; D. R. Tyler and F. Mao, *Coord. Chem. Rev.*, 1990, **97**, 149; W. Trogler, *J. Organomet. Chem. Libr.*, 1990, **22**, 173; ref. 23*a*, ch. 4, pp. 234–250.

32 D. Astruc, *Chem. Rev.*, 1988, **88**, 1189.

33 C. Moinet, E. Román and D. Astruc, *J. Electroanal. Chem. Interfacial Electrochem.*, 1981, **121**, 241; M. Lacoste and D. Astruc, *J. Chem. Soc., Chem. Commun.*, 1987, 667; M. Lacoste, H. Rabaa, D. Astruc, A. Le Beuze, J.-Y. Saillard, G. Précigoux, C. Courseille, N. Ardoin and W. Bowyer, *Organometallics*, 1989, **8**, 2233; J.-R. Hamon, J.-Y. Saillard, L. Toupet and D. Astruc, *J. Chem. Soc., Chem. Commun.*, 1989, 1662; J.-R. Hamon, P. Hamon, K. Boukheddaden, J. Linarès, F. Varret and D. Astruc, *Inorg. Chim. Acta*, 1995, **240**, 105.

34 J.-P. Mariot, D. Astruc, P. Batail and F. Varret, *J. Phys. C: Solid State Phys.*, 1980, **1**, 319; M. V. Rajasekharan, S. Giezynski, J. H. Ammeter, N. Oswald, J.-R. Hamon, P. Michaud and D. Astruc, *J. Am. Chem. Soc.*, 1982, **104**, 2400; J.-P. Mariot, P. Michaud, S. Lauer, D. Astruc, A. X. Trautwein and F. Varret, *J. Phys.*, 1983, **44**, 1377; F. Varret, J.-P. Mariot, J.-R. Hamon and D. Astruc, *Hyperfine Interact.*, 1988, **39**, 67–81; H. Rabaa, M. Chraibi, D. Astruc, J.-Y. Saillard and A. Le Beuze, *J. Mol. Struct. (THEOCHEM)*, 1991, **251**, 57; F. Ogliaro, D. Astruc, J.-F. Halet and J.-Y. Saillard, *New J. Chem.*, 2000, **24**, 257.

35 D. Astruc, *Tetrahedron*, 1983, **39**, 4027; J.-R. Hamon and D. Astruc, *Organometallics*, 1989, **8**, 2243.

36 D. Catheline and D. Astruc, *Organometallics*, 1984, **3**, 1094; D. Catheline and D. Astruc, *J. Organomet. Chem.*, 1984, **272**, 417; J. Ruiz and D. Astruc, *Inorg. Chim. Acta*, 2008, **361**, 1.

37 (*a*) E. Román, R. Dabard, C. Moinet and D. Astruc, *Tetrahedron Lett.*, 1979, **16**, 1433; (*b*) A. Darchen and C. Moinet, *J. Chem. Soc., Chem. Commun.*, 1979, 447; V. Guerchais, E. Román and D. Astruc, *Organometallics*, 1986, **5**, 2505; (*c*) S. Kahlal, C. Ornelas, J. Ruiz, D. Astruc and J.-Y. Saillard, *Organometallics*, 2008, **27**, 3603.

38 (*a*) D. T. Sawyer and J. S. Valentine, *Acc. Chem. Res.*, 1981, **14**, 393; (*b*) D. Astruc, E. Román, J.-R. Hamon and P. Batail, *J. Am. Chem. Soc.*, 1979, **101**, 2240; (*c*) D. Astruc, J.-R. Hamon, E. Román and P. Michaud, *J. Am. Chem. Soc.*, 1981, **103**, 7502; D. Astruc, *Comments Inorg. Chem.*, 1987, **6**, 61.

39 I. Fridovitch, in *Free Radicals in Biology*, ed. W. A. Prioried, Academic Press, New York, 1976, p. 239; Y. A. Ilan, G. Czapski and D. Meisel, *Biochim. Biophys. Acta*, 1976, **430**, 209; A. M. Michelson, J. M. Cord and I. Fridovitch, *Superoxide and Superoxide Dismutase*, Academic Press, New York, 1977.

40 (*a*) R. Hoffmann and P. Hofmann, *J. Am. Chem. Soc.*, 1976, **98**, 598; (*b*) J.-R. Hamon, D. Astruc, E. Román, P. Batail and J. J. Mayerle, *J. Am. Chem. Soc.*, 1981, **103**, 2431.

41 J.-R. Hamon and D. Astruc, *J. Am. Chem. Soc.*, 1983, **105**, 5951; J.-R. Hamon and D. Astruc, *Organometallics*, 1988, **7**, 1036.

42 (*a*) J. D. Simon and K. S. Peters, *Acc. Chem. Res.*, 1984, **17**, 277; (*b*) S. Winstein, L. G. Savedoff and S. Smith, *Tetrahedron Lett.*, 1960, **9**, 24; (*c*) *Ions and Ion Pairs in Organic Reactions*, ed. M. Schwarc, Wiley, New York, 1974; (*d*) A. Loupy, B. Tchoubar and D. Astruc, *Chem. Rev.*, 1992, **92**, 1141.

43 (*a*) A. Madonik and D. Astruc, *J. Am. Chem. Soc.*, 1984, **106**, 2437; (*b*) D. Astruc, D. Mandon, A. M. Madonik, P. Michaud, N. Ardoin and F. Varret, *Organometallics*, 1990, **9**, 2155; (*c*) S. Rigaut, M.-H. Delville and D. Astruc, *J. Am. Chem. Soc.*, 1997, **119**, 11132.

44 D. Bourissou, O. Guerret, F. P. Gabbai and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39.

45 D. Méry, J. Ruiz and D. Astruc, *J. Am. Chem. Soc.*, 2006, **128**, 5602.

46 Y. Chauvin and H. Olivier-Bourbigou, *Chemtech*, 1995, **25**, 9; W. A. Herrmann and C. Köcher, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2163; W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290; M. Scholl, T. M. Trnka, J. P. Morgan and R. H. Grubbs, *Tetrahedron Lett.*, 1999, **40**, 2247; T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18; J. Huang, E. D. Stevens, S. P. Nolan and J. L. Petersen, *J. Am. Chem. Soc.*, 1999, **121**, 2647; L. Jafarpour and S. P. Nolan, *Adv. Organomet. Chem.*, 2001, **46**, 181; L. Ackermann, A. Fürstner, T. Weskamp, F. J. Kohl and W. A. Herrmann, *Tetrahedron Lett.*, 1999, **40**, 4787; ref. 23*c*, ch. 15 and 21.

47 D. Astruc, *New J. Chem.*, 1992, **16**, 305, from special issue *Mechanisms and Processes in Molecular Chemistry*, ed. D. Astruc.

48 Q. S. Xie, E. Perezcordero and E. Echegoyen, *J. Am. Chem. Soc.*, 1992, **114**, 3978.

49 W. H. Hau, A. M. Kini, B. M. Savai, K. D. Carlson, J. M. Williams, M. W. Lathrop, K. R. Lykke, D. H. Parker, P. Wurz, M. J. Pellin, D. M. Gruen, U. Welp, W.-K. Kwok, S. Fleshler, G. W. Crabtree, J. E. Schirber and D. L. Overmyer, *Inorg. Chem.*, 1991, **30**, 2962.

50 C. Bossard, S. Rigaut, D. Astruc, M.-H. Delville, G. Félix, A. Février-Bouvier, J. Amiell, S. Flandrois and P. Delhaès, *J. Chem. Soc., Chem. Commun.*, 1993, 333.

51 J. Ruiz, C. Pradet, D. Varret and D. Astruc, *Chem. Commun.*, 2002, 1108.

52 J. Ruiz, F. Ogliaro, J.-Y. Saillard, J.-F. Halet, F. Varret and D. Astruc, *J. Am. Chem. Soc.*, 1998, **120**, 11693.

53 J.-M. Savéant, *Acc. Chem. Res.*, 1980, **13**, 323; J.-M. Savéant, *Chem. Rev.*, 2008, **108**, 2348.

54 M. Juliard and M. Chanon, *Chem. Rev.*, 1983, **83**, 425; J. K. Kochi, *J. Organomet. Chem.*, 1986, **300**, 139; D. Astruc, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 643, ref. 23*c*, ch. 6.

55 For examples of comprehensive kinetic and mechanistic analysis of organometallic electron-transfer-chain catalysis, see: J. W. Herschberger, C. Amatore and J. K. Kochi, *J. Organomet. Chem.*, 1983, **250**, 445; P. M. Zizelman, C. Amatore and J. K. Kochi, *J. Am. Chem. Soc.*, 1984, **106**, 3771.

56 J. Ruiz, M. Lacoste and D. Astruc, *J. Am. Chem. Soc.*, 1990, **112**, 5471.

57 M.-H. Delville, D. S. Brown, K. P. C. Vollhardt and D. Astruc, *J. Chem. Soc., Chem. Commun.*, 1991, 1355; D. S. Brown, M.-H. Delville, K. P. C. Vollhardt and D. Astruc, *New J. Chem.*, 1992, **16**, 899.

58 D. S. Brown, M.-H. Delville, R. Boese, K. P. C. Vollhardt and D. Astruc, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 661; D. S. Brown, M.-H. Delville, K. P. C. Vollhardt and D. Astruc, *Organometallics*, 1996, **15**, 2360.

59 M. I. Bruce, G. Shaw and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1982, 442; M. I. Bruce, *Coord. Chem. Rev.*, 1997, **76**, 1; E. Alonso, J. Ruiz and D. Astruc, *J. Cluster Sci.*, 1998, **9**, 271; E. Alonso and D. Astruc, *J. Am. Chem. Soc.*, 2000, **122**, 3222.

60 (*a*) M.-H. Desbois and D. Astruc, *J. Chem. Soc., Chem. Commun.*, 1988, 472; (*b*) M.-H. Desbois and D. Astruc, *New J. Chem.*, 1989, **13**, 595; (*c*) Y. Chauvin, *Angew. Chem., Int. Ed.*, 2006, **45**, 3740 (Nobel lecture); (*d*) T. J. Katz and S. J. Lee, *J. Am. Chem. Soc.*, 1980, **102**, 422; (*e*) D. Astruc, *Oil Gas Sci. Technol.*, 2007, **62**, 787.

61 A. Darchen and C. Moinet, *J. Chem. Soc., Chem. Commun.*, 1979, 447; C. Moinet, E. Román and D. Astruc, *J. Electroanal. Chem. Interfacial Electrochem.*, 1981, **121**, 241.

62 S. Rigaut, M.-H. Delville, J. Losada and D. Astruc, *Inorg. Chim. Acta*, 2002, **334**, 225.

63 H. A. Trujillo, J. Ruiz and D. Astruc, *J. Am. Chem. Soc.*, 1999, **121**, 5674.

64 J.-R. Hamon, J.-Y. Saillard, A. Le Beuze, M. McGlinchey and D. Astruc, *J. Am. Chem. Soc.*, 1982, **104**, 7549; F. Moulines and D. Astruc, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1347; F. Moulines and D. Astruc, *J. Chem. Soc., Chem. Commun.*, 1989, 614.

65 D. Astruc, K. Heuze, S. Gatard, D. Méry, S. Nlate and L. Plault, *Adv. Synth. Catal.*, 2005, **347**, 329; J. Lemo, K. Heuze and D. Astruc, *Chem. Commun.*, 2007, 4351.

66 G. E. Oosterom, J. N. H. Reek, P. C. J. Kamer and P. W. van Leeuwen, *Angew. Chem., Int. Ed.*, 2001, **40**, 1828; R. Kreiter, A. W. Kleij, R. J. M. K. Gebbink and G. van Koten, Dendrimers IV: Metal Coordination, Self Assembly, Catalysis, *Top. Curr. Chem.*, 2001, **217**, 163; D. Astruc and F. Chardac, *Chem. Rev.*, 2001, **102**, 2991; R. van Heerbeeck, P. C. J. Kamer, P. W. N. M. van Leeuwen and J. N. H. Reek, *Chem. Rev.*, 2002, **102**, 3717; B. Helms and J. M. J. Fréchet, *Adv. Synth. Catal.*, 2006, **348**, 1125; D. Méry and D. Astruc, *Coord. Chem. Rev.*, 2006, **250**, 1965; R. Andrés, E. de Jesus and J. C. Flores, *New J. Chem.*, 2007, **31**, 1161; E. de Jesús and J. C. Flores, *Ind. Eng. Chem. Res.*, 2008, **47**, 7968.

67 P. Nguyen, P. Gomez-Elipe and I. Manners, *Chem. Rev.*, 1999, **99**, 1515; Richard D. A. Hudson, *J. Organomet. Chem.*, 2001, **637–639**, 47; *Transition-Metal-containing Polymers*, ed. A. S. Abd-El-Aziz and I. Manners, Wiley, New York, 2007.

68 J. B. Flanagan, S. Margel, A. J. Bard and F. C. Anson, *J. Am. Chem. Soc.*, 1978, **100**, 4248; A. J. Bard and R. L. Faulkner, *Electrochemical Methods*, Wiley, New York, 2nd edn, 2001.

69 (*a*) R. Rulkens, A.-J. Lough, I. Manners, S. R. Lovelace, C. Grant and W. E. Geiger, *J. Am. Chem. Soc.*, 1996, **118**, 12683; (*b*) D. A. Foucher, B.-Z. Tang and I. Manners, *J. Am. Chem. Soc.*, 1992, **114**, 6246; (*c*) I. Cuadrado, C. M. Casado, B. Alonso, M. Morán, J. Losada and V. Belsky, *J. Am. Chem. Soc.*, 1997, **119**, 7613.

70 D. Astruc, *Bull. Soc. Chim. Fr.*, 1995, **132**, 875; D. Astruc, *C. R. Seances Acad. Sci., Ser. B*, 1996, **322**, 757; J.-P. Majoral and A.-M. Caminade, *Chem. Rev.*, 1999, **99**, 845; G. R. Newkome, C. N. Moorefield and F. Vögtle, *Dendrimers and Dendrons. Concept, Syntheses, Applications*, Wiley-VCH, Weinheim, 2001; *Dendrimers and Other Dendritic Polymers*, ed. D. Tomalia and J. M. J. Fréchet, Wiley-VCH, New York, 2002; Dendrimers and Nanosciences, *C. R. Chim.*, 2003, **6**, 1117; special issue on dendrimers, *New J. Chem.*, 2007, **31**(7), 1025.

71 G. R. Newkome, E. He and C. N. Moorefield, *Chem. Rev.*, 1999, **99**, 1689; S. H. Hwang, C. D. Shreiner, C. N. Moorefield and G. R. Newkome, *New J. Chem.*, 2007, **31**, 1192.

72 Reviews on ferrocenyl dendrimers: C. M. Casado, I. Cuadrado, M. Morán, B. Alonso, B. Garcia, B. Gonzales and J. Losada, *Coord. Chem. Rev.*, 1999, **185–186**, 53; D. Astruc, C. Ornelas and J. Ruiz, *Acc. Chem. Res.*, 2008, **41**, 841.

73 (*a*) J.-L. Fillaut, R. Boese and D. Astruc, *Synlett*, 1992, 55; (*b*) J.-L. Fillaut and D. Astruc, *J. Chem. Soc., Chem. Commun.*, 1993, 1320; (*c*) J. Guittard, J.-C. Blais, C. Valério, E. Alonso, J. Ruiz, J.-L. Fillaut and D. Astruc, *Pure Appl. Chem.*, 1998, **70**, 809; (*d*) M. Tanabe and I. Manners, *J. Am. Chem. Soc.*, 2004, **126**, 11434; (*e*) E. Boisselier, A. C. K. Shun, J. Ruiz, E. Cloutet, C. Belin and D. Astruc, *New J. Chem.*, 2009, **33**, 246.

74 C. B. Gorman, B. L. Smith, H. Parkhurst, H. Sierputowska-Gracz and C. A. Haney, *J. Am. Chem. Soc.*, 1999, **121**, 9958; C. B. Gorman and J. C. Smith, *Acc. Chem. Res.*, 2001, **34**, 60; S. Nlate, Y. Nieto, J.-C. Blais, J. Ruiz and D. Astruc, *Chem.–Eur. J.*, 2002, **8**, 171; A. E. Kaifer, *Eur. J. Inorg. Chem.*, 2007, 5015.

75 (*a*) J. Ruiz, G. Lafuente, S. Marcen, C. Ornelas, S. Lazare, E. Cloutet, J.-C. Blais and D. Astruc, *J. Am. Chem. Soc.*, 2003, **125**, 7250; (*b*) V. Sartor, L. Djakovitch, J.-L. Fillaut, F. Moulines, F. Neveu, V. Marvaud, J. Guittard, J.-C. Blais and D. Astruc, *J. Am. Chem. Soc.*, 1999, **121**, 2929; (*c*) C. Ornelas, J. Ruiz, C. Belin and D. Astruc, *J. Am. Chem. Soc.*, 2009, **131**, 590.

76 C. Amatore, F. Grun and E. Maisonhaute, *Angew. Chem., Int. Ed.*, 2003, **40**, 4944; C. Amatore, Y. Bouret, E. Maisonhaute, J. I. Goldsmith and H. D. Abruña, *Chem.–Eur. J.*, 2001, **7**, 2206.

77 F. Hauquier, J. Ghilane, B. Fabre and P. Hapiot, *J. Am. Chem. Soc.*, 2008, **130**, 2748; A. Wang, C. Ornelas, D. Astruc and P. Hapiot, *J. Am. Chem. Soc.*, 2009, **131**, in press.

78 P. D. Beer, *Adv. Inorg. Chem.*, 1992, **39**, 79; P. D. Beer, *Chem. Commun.*, 1996, 689; P. D. Beer, *Acc. Chem. Res.*, 1998, **31**, 71; P. D. Beer, P. Gale and Z. Chen, *Adv. Phys. Org. Chem.*, 1998, **31**, 1; P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486.

79 C. Valério, J.-L. Fillaut, J. Ruiz, J. Guittard, J.-C. Blais and D. Astruc, *J. Am. Chem. Soc.*, 1997, **119**, 2588; J. Guittard, J.-C. Blais, C. Valério, E. Alonso, J. Ruiz, J.-L. Fillaut and D. Astruc, *Pure Appl. Chem.*, 1998, **70**, 809; B. Alonso, C.-M. Casado, I. Cuadrado, M. Morán and A. E. Kaifer, *Chem. Commun.*, 2002, 1778; M. P. G. Armada, J. Losada, M. Zamora, B. Alonso, I. Cuadrado and C. M. Casado, *Bioelectrochemistry*, 2006, **69**, 65.

80 J. Ruiz, M.-J. Ruiz-Medel, M.-C. Daniel, J.-C. Blais and D. Astruc, *Chem. Commun.*, 2003, 464; M.-C. Daniel, J. Ruiz, J.-C. Blais, N. Daro and D. Astruc, *Chem.–Eur. J.*, 2003, **9**, 4371; D. Astruc, M.-C. Daniel and J. Ruiz, *Chem. Commun.*, 2004, 2637; M.- C. Daniel, J. Ruiz, S. Nlate and D. Astruc, *J. Inorg. Organomet. Polym. Mater.*, 2005, **15**, 107.

81 M.-C. Daniel, J. Ruiz, S. Nlate, J. Palumbo, J.-C. Blais and D. Astruc, *Chem. Commun.*, 2001, 2000; B. Alonso, D. Astruc, J.-C. Blais, S. Nlate, S. Rigaut, J. Ruiz, V. Sartor and C. Valério, *C. R. Acad. Sci., Ser. IIc: Chim.*, 2001, **4**, 173; D. Astruc, J.-C. Blais, M.-C. Daniel, S. Gatard, S. Nlate and J. Ruiz, *C. R. Chim.*, 2003, **6**, 111.

82 D. Méry, L. Plault, S. Nlate, D. Astruc, S. Cordier, K. Kirackci and C. Perrin, *Z. Anorg. Allg. Chem.*, 2005, **631**, 2746; D. Méry, L. Plault, C. Ornelas, J. Ruiz, S. Nlate, D. Astruc, J.-C. Blais, J. Rodrigues, S. Cordier, K. Kiracki and C. Perrin, *Inorg. Chem.*, 2006, **45**, 1156.

83 (*a*) A. Labande and D. Astruc, *Chem. Commun.*, 2000, 1007; (*b*) A. Labande, J. Ruiz and D. Astruc, *J. Am. Chem. Soc.*, 2002, **124**, 1782; D. Astruc, *Pure Appl. Chem.*, 2003, **75**, 461; (*c*) M.-C. Daniel, J. Ruiz and D. Astruc, *J. Am. Chem. Soc.*, 2003, **125**, 1150.

84 E. Alonso, C. Valério, J. Ruiz and D. Astruc, *New J. Chem.*, 1997, **21**, 1139; B. Gonzales, C. M. Casado, B. Alonso, I. Cuadrado, M. Morán, Y. Wang and A. E. Kaifer, *Chem. Commun.*, 1998, 2569; C. Valério, J. Ruiz, J.-L. Fillaut and D. Astruc, *C. R. Acad. Sci., Ser. IIc: Chim.*, 1999, **2**, 79; C. M. Casado, B. Gonzales and

I. Cuadrado, *Angew. Chem., Int. Ed.*, 2000, **39**, 2135; B. Gonzales, I. Cuadrado, C. M. Casado and C. J. Pastor, *Organometallics*, 2000, **19**, 5518; K. Takada, D. J. Diaz, H. D. Abruña, I. Cuadrado, B. Gonzales, C. M. Casdo, B. Alonso and J. Losada, *Chem.–Eur. J.*, 2001, **7**, 1109; C. Ornelas, J. Ruiz and D. Astruc, *Organometallics*, 2009, **28**, DOI: 10.1021/om900079y.

85 M.-C. Daniel, F. Ba, J. Ruiz and D. Astruc, *Inorg. Chem.*, 2004, **43**, 8649; D. Astruc, M.-C. Daniel and J. Ruiz, *Top. Organomet. Chem.*, 2006, **20**, 121.

86 C. Ornelas, J. Ruiz, E. Cloutet, S. Alves and D. Astruc, *Angew. Chem., Int. Ed.*, 2007, **46**, 872; C. Ornelas, L. Salmon, J. Ruiz and D. Astruc, *Chem.–Eur. J.*, 2008, **14**, 50; J. Camponovo, J. Ruiz, E. Cloutet and D. Astruc, *Chem.–Eur. J.*, 2009, **15**, 2990.

87 C. Valério, E. Alonso, J. Ruiz, J.-C. Blais and D. Astruc, *Angew. Chem., Int. Ed.*, 1999, **38**, 1747; B. Alonso, P. García Armada, J. Losada, I. Cuadrado, B. González and C. M. Casado, *Biosens. Bioelectron.*, 2004, **19**, 1617.

88 A. Aviram and M. A. Ratner, *Chem. Phys. Lett.*, 1974, **29**, 257.

89 L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar, T. P. Burgin, L. Jones II, D. L. Allara, J. M. Tour and P. S. Weiss, *Science*, 1996, **271**, 1705; R. P. Andres, J. D. Bielefeld, J. I. Henderson, D. B. Janes, V. R. Kolagunta, C. P. Kubiak, W. J. Mahoney and R. G. Osifchin, *Science*, 1996, **273**, 1690; C. A. Mirkin, R. L. Letsinger, R. C. Mucic and J. J. Storhoff, *Nature*, 1996, **382**, 607; M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin and J. M. Tour, *Science*, 1997, **278**, 252; S. Frank, P. Poncharal, Z. L. Wang and W. A. de Heer, *Science*, 1998, **280**, 1744.

90 J. M. Tarascon, G. W. Hull and F. J. Di Salvo, *Mater. Res. Bull.*, 1984, **19**, 915.

91 (*a*) M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247; (*b*) G. C. Allen and N. S. Hush, *Prog. Inorg. Chem.*, 1967, **8**, 367; (*c*) J. P. Launay, *Chem. Soc. Rev.*, 2001, **30**, 386; (*d*) Ref. 23*a*, ch. 1.

92 (*a*) D. O. Cowan, G. A. Candela and F. Kaufman, *J. Am. Chem. Soc.*, 1971, **93**, 3889; (*b*) U. T. Mueller-Westerhoff, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 702; (*c*) M.-H. Delville, F. Robert, P. Gouzher, J. Linares, K. Boukhedadden, F. Varret and D. Astruc, *J. Organomet. Chem.*, 1993, **451**, C10; (*d*) D. N. Hendrickson, S. M. Oh, T. Y. Dong, T. Kambara, M. J. Cohn and M. F. Moore, *Comments Inorg. Chem.*, 1985, **4**, 329.

93 M.-H. Desbois, J. Guillin, J.-P. Mariot, F. Varret and D. Astruc, *J. Chem. Soc., Chem. Commun.*, 1985, 447; M.-H. Desbois, D. Astruc, J. Guillin and F. Varret, *Organometallics*, 1989, **8**, 1848; M.-H. Desbois and D. Astruc, *Organometallics*, 1989, **8**, 1841; M.-H. Delville-Desbois, M. Lacoste and D. Astruc, *J. Am. Chem. Soc.*, 1992, **114**, 8310.

94 (*a*) M.-H. Desbois, D. Astruc, J. Guillin, J.-P. Mariot and F. Varret, *J. Am. Chem. Soc.*, 1985, **107**, 52; (*b*) J. Guillin, M.-H. Desbois, J.-P. Mariot, S. Lauer, A. X. Trautwein, F. Varret and D. Astruc, *Hyperfine Interact.*, 1986, **28**, 761; (*c*) M.-H. Desbois, D. Astruc, J. Guillin, F. Varret, A. X. Trautwein and G. Villeneuve, *J. Am. Chem. Soc.*, 1989, **111**, 5800; (*d*) M.-H. Delville, S. Rittinger and D. Astruc, *J. Chem. Soc., Chem. Commun.*, 1992, 519.

95 M. Lacoste, F. Varret, L. Toupet and D. Astruc, *J. Am. Chem. Soc.*, 1987, **109**, 6504; F. Varret, M. Lacoste and D. Astruc, *Hyperfine Interact.*, 1988, **39**, 147; J. Guillin, F. Varret, M.-H. Desbois, M. Lacoste and D. Astruc, *J. Phys.*, 1988, **C8**, 837; D. Astruc, M. Lacoste and L. Toupet, *J. Chem. Soc., Chem. Commun.*, 1990, 558; M. Lacoste, H. Rabaa, D. Astruc, N. Ardoin, F. Varret, J.-Y. Saillard and A. Le Beuze, *J. Am. Chem. Soc.*, 1990, **112**, 9548.

96 N. Le Narvor, L. Toupet and C. Lapinte, *J. Am. Chem. Soc.*, 1995, **117**, 7129; F. Coat and C. Lapinte, *Organometallics*, 1996, **15**, 477; F. Paul and C. Lapinte, *Coord. Chem. Rev.*, 1998, **178**, 431; F. Paul, W. E. Meyer, L. Toupet, J. A. Gladysz, C. Lapinte and H. J. Jiao, *J. Am. Chem. Soc.*, 2000, **122**, 9405; R. Packheiser, L. M. Lohan, B. Brauer, F. Justaud F C. Lapinte and H. Lang, *J. Organomet. Chem.*, 2008, **693**, 2898; R. Packheiser, L. M. Lohan, B. Brauer, F. Justaud F. C. Lapinte and H. Lang, *Organometallics*, 2008, **27**, 344.

97 M. Bruce, *Coord. Chem. Rev.*, 1997, **166**, 91; M. I. Bruce, *Chem. Rev.*, 1998, **98**, 2797; M. I. Bruce, B. C. Hall, B. D. Kelly, P. J. Low, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1999, 3719; M. I. Bruce and P. J. Low, *Adv. Organomet. Chem.*, 2001, **48**, 3184; Bruce and P. J. Low, *Adv. Organomet. Chem.*, 2004, **50**, 179.

98 T. Bartik, B. Bartik, M. Brady, R. Dembinski and J. A. Gladysz, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 414; R. Dembinski, T. Bartik, B. Bartik and J. A. Gladysz, *J. Am. Chem. Soc.*, 2000, **122**, 810; S. Szafert and J. A. Gladysz, *Chem. Rev.*, 2002, **103**, 4175.

99 V. W. W. Yam, V. C. Y. Lau and K. K. Cheung, *Organometallics*, 1996, **15**, 1740; V. W. W. Yam, K. M. C. Wong and N. Y. Zhu, *Angew. Chem., Int. Ed.*, 2003, **42**, 1400.

100 M. Samoc, G. D. Dalton and J. A. Gladysz, *Inorg. Chem.*, 2008, **47**, 21.

101 N. Le Narvor and C. Lapinte, *Organometallics*, 1995, **14**, 634.

102 T. Weyland, C. Lapinte, G. Frapper and C. Lapinte, *Organometallics*, 1997, **16**, 2024; T. Weyland, K. Costuas, A. Mari, J.-F. Halet and C. Lapinte, *Organometallics*, 1998, **17**, 5569; T. Weyland, I. Ledoux, S. Brasselet and C. Lapinte, *Organometallics*, 2000, **19**, 5325; T. Weyland, K. Kostuas, L. Toupet, J.-F. Halet and C. Lapinte, *Organometallics*, 2000, **19**, 4228.

103 F. Barrière, N. Camine and W. E. Geiger, *J. Am. Chem. Soc.*, 2002, **124**, 7262; F. Barrière and W. E. Geiger, *J. Am. Chem. Soc.*, 2006, **128**, 3980.

104 A. K. Diallo, J.-C. Daran, F. Varret, J. Ruiz and D. Astruc, *Angew. Chem., Int. Ed.*, 2009, **48**, 3141.

105 J.-P. Launay and C. Coudret, in *Electron Transfer in Chemistry*, ed. V. Balzani, Wiley-VCH, Weinheim, 2001, vol. 5, ch. 1, p. 3; G. Rapenne, J.-P. Launay and C. Joachim, *J. Phys.: Condens. Matter*, 2006, **18**, S1797; A. Carella, C. Coudret, G. Guirado, G. Rapenne, G. Vive and J.-P. Launay, *Dalton Trans.*, 2007, 177; G. Vives, A. Carella, J.-P. Launay and G. Rapenne, *Coord. Chem. Rev.*, 2008, **252**, 1451.

106 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewski, *Coord. Chem. Rev.*, 1988, **84**, 85; J.-P. Sauvage, J.-P. Colin, J.-C. Chambon, V. Balzani, F. Barigelleti, L. De Cola and L. Flamigni, *Chem. Rev.*, 1994, **94**, 993; V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni and M. Venturi, *Acc. Chem. Res.*, 1998, **31**, 26; V. Balzani, *Pure Appl. Chem.*, 2008, **80**, 1631.

107 M. A. Fox, in *Electron Transfer in Chemistry*, ed. V. Balzani, Wiley-VCH, Weinheim, 2001, vol. 3, ch. 8, p. 271.

108 B. M. Quinn, P. Lilgeroth, V. Ruiz, T. Laaksonen and K. Konturi, *J. Am. Chem. Soc.*, 2003, **125**, 6644; M. C. Daniel and D. Astruc, *Chem. Rev.*, 2004, **104**, 293.

109 M. Kirch, J.-P. Sauvage and J.-M. Lehn, *Helv. Chim. Acta*, 1979, **62**, 1345; D. Astruc, F. Lu and J. Ruiz, *Angew. Chem., Int. Ed.*, 2005, **44**, 7852.

110 J. A. Real, E. Andres, M. C. Munoz, M. Julve, T. Granier, A. Bousseksou and F. Varret, *Science*, 1995, **268**, 265; S. Bonhommeau, G. Molnar, A. Galet, A. Zwick, J. A. Real and J. J. McGarvey, *Angew. Chem., Int. Ed.*, 2005, **44**, 4069.