Transition-Metal Radicals: Chameleon Structure and Catalytic Function

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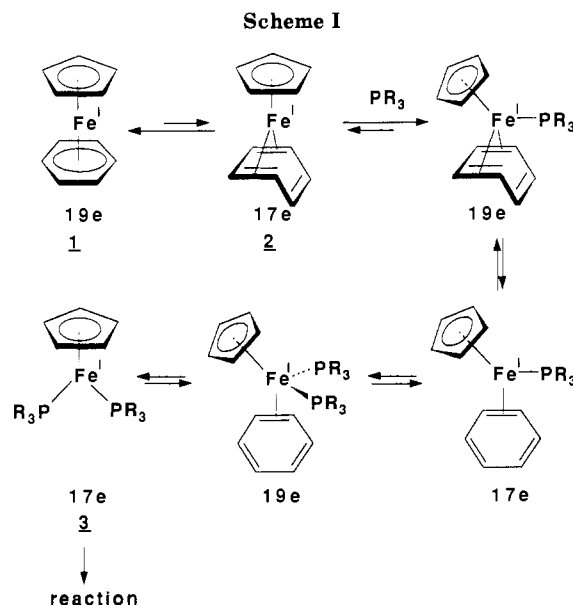
Radicals are of fundamental relevance to areas as varied as organic synthesis, homogeneous catalysis, the chemistry of metabolisms, the degredation of aerobic cells, the generation of tumors, materials science, photoprocesses, and nuclear chemistry. Transition-metal radicals are central to a number of these subjects.[1] I will give here an account of the trends governing their structure, reactivity, and role in electron-transfer (ET) catalysis and finally show that, on these bases, useful functions can be rationally designed with control of reactivity pathways. For this purpose, examples will be taken essentially from new families of piano-stool-shaped organometallic radicals containing several P or S ligands, the coordination of which has been the object of our scrutiny. Considerable attention by pioneers[1,2] in the field of transition-metal radicals has been devoted to metal carbonyls, which behave much as organic radicals in atom-transfer and dimerization reactions. On the other hand, in the carbonyl-free or carbonyl-poor radical chemistry presented here, dimerization is avoided. This feature parallels the relative inhibition of dimerization obtained with steric bulk in organic radicals such as triarylmethyl radicals and brings us more versatility in modulating ET versus radical-type reactions. ET is an essential, more inorganic oriented property of transition-metal radicals that is useful in electrocatalysis and for which the work by Kochi has brought much mechanistic insight during the last decade.[1c] In discussing the behavior of transition-metal radicals, one can compare them to chameleons: their structures have different, interchangeable facets, the modulation of their reactivity is remarkably facile, and their ground state is often not apparent from a given reaction.

Chameleon Structure: What Electron Count?

The classical organometallic electron count formalism, extremely useful for even-electron complexes, may become more tedious with radicals because of their lability. In order to ascertain a count of valence electrons (VE), it is necessary to show experimentally the number and modes of coordination of all the ligands. This can only be achieved with X-ray crystal structures or, occasionally, with the help of infrared, ESR, or Mössbauer spectroscopies. Yet, several structures can have close

Scheme I

energy levels and rapidly interconvert under standard reaction conditions. This property is related to the very low kinetic barriers of these interconversion processes.
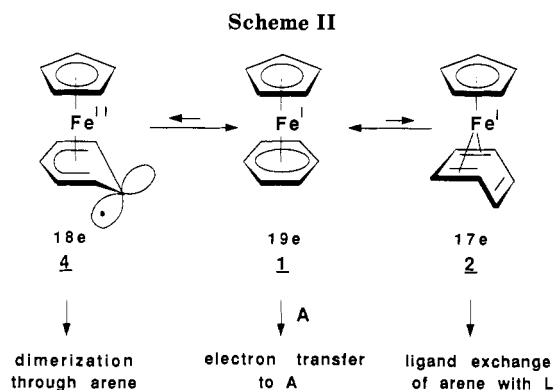
The complexes $Fe^ICp(arene)$ were shown to have 19 VE.[3a-c] However, the accuracy of the spectroscopic techniques does not exclude a small fraction of other species in equilibrium. Indeed, a study of the kinetics of the reactions of this family with phosphines and phosphites,[3d] carried out at low temperature by observing the change of optical density at 710 nm, shows that substitution proceeds by a second-order process with activation parameters $\Delta H^\ddagger = 13.3 \pm 1$ kcal mol^{-1} (1 cal = 4.184 J) and $\Delta S^\ddagger = -22 \pm 3$ cal mol^{-1} K^{-1} for $P(OMe)_3$ and arene = PhMe. The bimolecular reaction, confirmed by the relatively large, negative entropy of activation, indicates that, as known for 17e radicals[4,5]

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Scheme II

Chart I

-o ▫ H or Me
L_1 ▫ L_2 ▫ PMe$_3$ or P(OMe)$_3$
L_1 ▫ dppe, L_2 ▫ CO
stable, 17e radicals

-o ▫ H or Me
unobservable,
too transient 17e radical

since the work by Poë[4a] on Re(CO)$_5$•, the mechanism involves an associative process. The EHT and Xα calculations for [Fe^{I}Cp(C$_6$H$_6$)] (1) by Saillard, Le Beuze, and Rabaâ show that the 19e species 1 and the 17e species [Fe^{I}Cp(η^4-C$_6$H$_6$)] (2) have close energies.[3c,d] Thus, given the too high energy of a hypothetical, sterically demanding 21e species, we proposed that the rate-limiting step in which the P donor attacks the iron center involves 2 and is preceded by a fast preequilibrium 1 (19e) ⇌ 2 (17e). By analogy, it is also reasonable to expect a series of 19e ⇌ 17e interchanges for the various successive steps along the overall arene substitution (Scheme I).

Another reaction, dimerization of the 19e radicals 1 through the arene ligand,[6,7] is not attributable to the 19e form but to the minor 18e structure 4, which bears the radical center on one arene carbon, this ligand being then represented as a η^5-cyclohexadienyl radical (the rate of dimerization is low[3d]). The dominant, most electron rich 19e form is responsible for the many ET reactions with acceptors A,[8] but two other forms are also responsible for the reactivity of 1 (Scheme II).

For the piano-stool radicals Fe^{I}Cp*L$_n$ (n = 2 or 3), isolobal with 1, one may draw even more numerous, rapidly interconverting structures of close energy, given the larger choice of ligands and the possibilities of intermolecular ligand dissociation. Coupling of the C$_5$Me$_5$ ligand of the 18e transient radical [Fe^{II}(η^4-C$_5$Me$_5$)-(CO)$_2$(PPh$_3$)] (5) with the benzyl radical at a Cp* carbon has been observed by Wrighton,[8g,9] but the ground state of 5 may be Fe^I. The 17e radicals [Fe^{I}Cp(PPh$_3$)$_2$] (6) and [Fe^{I}Cp*(η^1-dppe)(CO)] (7) have also been
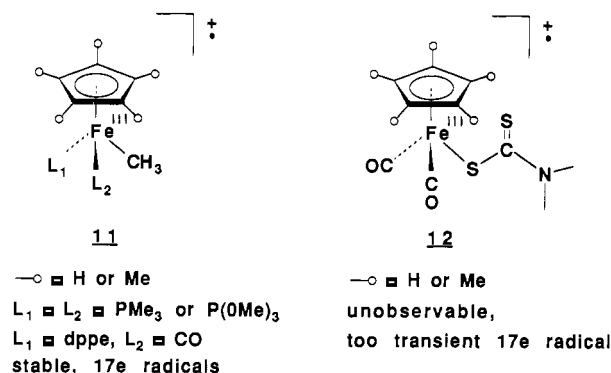
characterized by ESR as iron-centered radicals, and these structures may be responsible for H atom abstraction reactions to give [Fe^{II}Cp(PPh$_3$)$_2$(H)] (8) and [Fe^{II}Cp*(η^1-dppe)(CO)(H)] (9).[3d,10] However, in the second case, this reactivity may also be taken into account by the intermediacy of the 18e ligand-centered radical [Fe^{II}Cp*(η^2-dppe)(C•=O)] (10) in equilibrium with 7. Kochi has demonstrated that 19e metal carbonyl radicals Cr(CO)$_6$•⁻ and Mn(CO)$_4$(PPh$_3$)$_2$• generated electrochemically can abstract a H atom from HSnBu$_3$ to give formyl complexes.[11] This underlines the equilibrium between the metal-centered 19e radical and the 18e carbon-centered isomeric radical, as also observed by Symons[12] for CoCp(CO)$_2$•⁻. Since transition-metal formyl complexes more or less rapidly decompose to metal hydrides,[11] one should not systematically conclude that hydride formation by H atom abstraction from a transition-metal carbonyl radical is a direct reaction of the 17e metal center.

Chameleon Behavior: Influence of Bulk. ET Induced by a Salt

If, on the other hand, the 17e radical is too sterically crowded, the 19e form cannot be obtained by ligand addition as its energy becomes too high. In the piano-stool series, this is the case for the iron–methyl complexes 11[13] (Chart I), but many stable 17e radicals are known in other series,[2b] the pioneering example being ferricinium,[14] a useful one-electron oxidant[15] (vide infra).

The other extreme is the 17e radical 12, although not so structurally different from 10, for which the 19e structure is very easily accessible due to the entropy factor of the hanging dithiocarbamate (dtc) ligand.[16] Despite very fast scan cyclic voltammetry (5000 V s^{-1}), it was not possible to observe any reversibility in the anodic oxidation of the 18e precursor 10;[16b,c] oxidation

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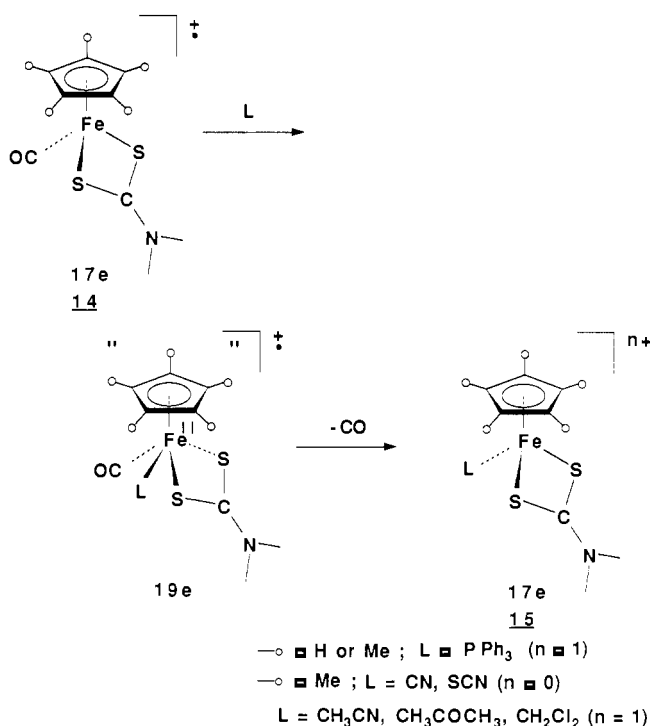(12) Symons, M. C. R.; Bratt, S. W. J. Chem. Soc., Dalton Trans. 1979, 1739.

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Scheme III

—o ◻ H or Me ; L ◻ P Ph₃ (n ◻ 1)

—o ◻ Me ; L = CN, SCN (n ◻ 0)

L = CH₃CN, CH₃COCH₃, CH₂Cl₂ (n = 1)

Scheme IV^a

L = CO : **14** or
L = PPh₃ : **15**

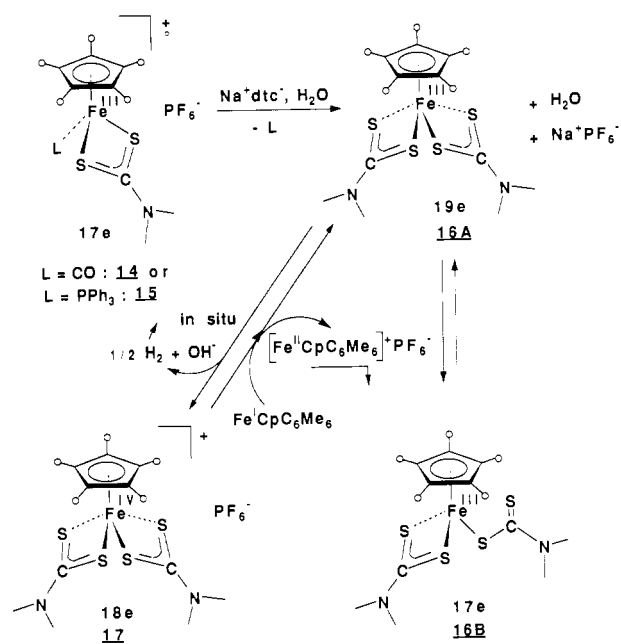^{a} The 17e (**16B**) and 19e (**16A**) forms equilibrate very fast in solution so that the more electron rich 19e form **16A** must be responsible for the reduction of H₂O.

of **13** using ferricinium cleanly gives the 17e, stable complex **14** in which the dtc ligand is chelated[17] (eq 1).

—o ◻ H or Me

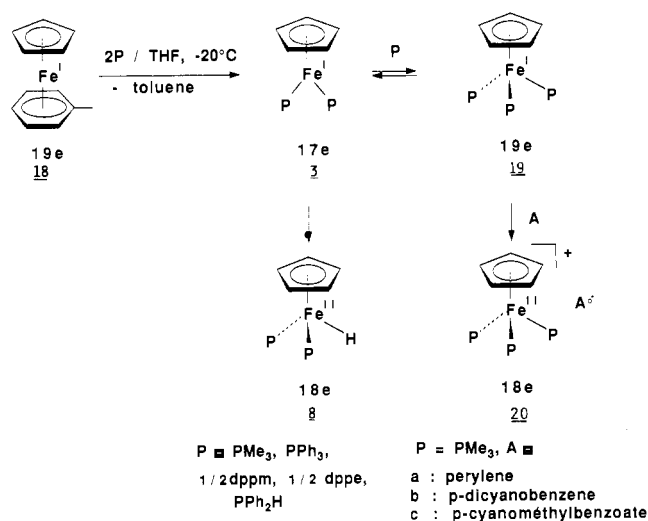**13**   **14**   eq. 1
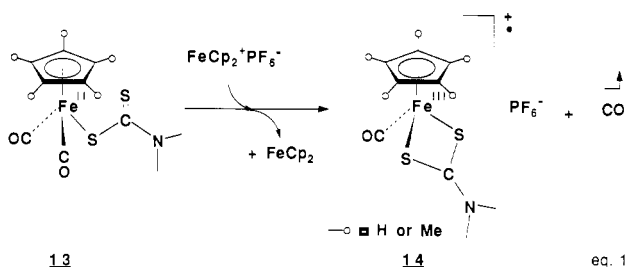
In **14**, CO exchange for a variety of ligands proceeds at low temperature, giving a whole new family of 17e complexes **15**, by an associative process. The latter involves, as known in other cases,[1,2] 19e intermediates or transition states, the bimolecular mechanism being shown by kinetic studies using visible spectroscopy (isosbestic point at 600 nm). Even very weak ligands such as CH₂Cl₂ can replace CO in **14** at low temperature,[17,18] and anionic ligands (CN⁻, SCN⁻) produce neutral 17e complexes that do not dimerize[18] (Scheme III).

In the case of the reaction of **14** or **15** with the 3e dtc ligand, the ligand-exchange reaction gives a stable 19e intermediate **16**, which can be isolated or reduce H₂O in situ to OH⁻ and H₂, and **17**, the first Fe^{IV} complex with a Cp-type ligand, is isolated in excellent yields from these reactions.[17,18] The neutral 19e Fe^{III} radical **16** could also be cleanly synthesized by monoelectronic reduction of **17** using 1 equiv of the 19e synthon [Fe^{I}Cp(C₆Me₆)][19] (Scheme IV). This dichotomy of synthetic routes to 19e complexes is noteworthy. The

Scheme V

P ◻ PMe₃, PPh₃,   P = PMe₃, A ◻
1/2dppm, 1/2 dppe,   a : perylene
PPh₂H   b : p-dicyanobenzene
                                   c : p-cyanométhylbenzoate

ability of 19e complexes to behave as reducing agents is well-known.[1c,2h,3,20,21]

Carbonyl-free organoiron radicals with phosphine or phosphite ligands have been generated by mild exchange of the arene ligand in the 19e complex **18**.[3d] This gives rise to a rapid equilibrium between 17e species Fe^{I}Cp(PR₃)₂ (**3**) and 19e species Fe^{I}Cp(PR₃)₃ (**19**) that depends on the size of the P donor. With P = PPh₃, the sterically stabilized 17e radical can be characterized by the triplet found in the ESR spectrum[3d] but the too bulky 19e radical cannot form. On the contrary, with PMe₃, ligand exchange from **18** in the presence of an aromatic acceptor A gives the salts

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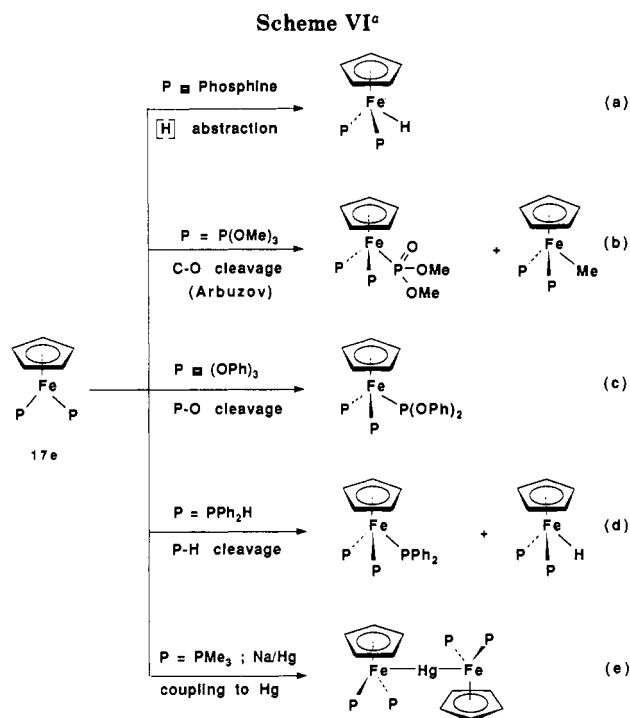
Scheme VI^a

^{a} Radical reactions of the 17e species Fe^{I}CpP$_2$ generated by reaction of Fe^{I}CpC$_6$H$_5$R,R = H or Me (**1, 18**), and P donors in toluene or THF (Scheme V) in the rigorous absence of Na$^+$PF$_6^-$ (these reactions are inhibited by Na$^+$PF$_6^-$). For the coupling to Hg, the radical FeCp(PMe$_3$)$_2$ (**18**) was generated by Na/Hg reduction of [FeCp(PMe$_3$)$_3$]$^+$PF$_6^-$ (**20d**).

[Fe^{II}Cp(PMe$_3$)$_3$]$^+$A$^-$ (**20**) when the thermodynamic potential of A$^{0/-}$ is less negative than that of [FeCp-(PMe$_3$)$_3$]$^{+/0}$ ($E° \simeq -2$ V vs SCE). This results from the formation of the extremely electron rich 19e species **19** subsequently giving monoelectronic reduction of A. In the absence of an acceptor, the radical reactions of the 17e form **3** are observed. In particular with phosphines, a series of carbonyl-free iron hydride complexes **8** have been made easily accessible in this way from **18**. Thus both the 17e and 19e forms are characterized alternatively depending on whether the reaction medium contains an acceptor A (Scheme V).

It is possible to reduce substrates A that have a thermodynamic potential more negative than that of **19/20** if the reduction of a is not reversible. This is the case of CO$_2$, rapidly reduced by **19** to CO and CO$_3{}^{2-}$ at -20 °C in THF + Na$^+$PF$_6^-$, whereas **20** and [Fe^{II}Cp-(PMe$_3$)$_2$(CO)]$^+$ (**21**) are formed as PF$_6^-$ salts.^{3d,22a}

The radical reactions of the 17e iron–phosphine species are also varied,^{3d} as shown in Scheme VI. The chameleon behavior of the radicals Fe^{I}CpP$_n$ is illustrated by the complete switch from radical reactions to quantitative ET reactions observed by adding the simple sodium salt Na$^+$PF$_6^-$, even in a catalytic amount.^{3d}

Indeed, in the course of the ligand-exchange reaction between **1** and P donors, ET between the two 19e species 1 and **19** giving the large ion pair **24** (eq 2) is not observed in the absence of salt because the decomposition of the 20e anion [Fe^{0}Cp(toluene)]$^-$ is slowed down by the stabilizing ion pairing with the large cation FeCpP$_3{}^+$; the radical reactions represented in Scheme VI are faster.

eq. 2

This is no longer the case in the presence of the other ion pair [Na$^+$PF$_6^-$] (**23**) in THF because double ion exchange between the two ion pairs **22** and **23** is extremely fast and gives the very unstable ion pair **24** in which the 20e anion rapidly decomposes. In THF, a stoichiometric amount of **23** is needed because **20d** quantitatively precipitates, but in 2:1 THF/CH$_3$CN, the medium is homogeneous and **23** is recycled so that 0.07 equiv of **23** is enough to catalyze the ET reaction of eq 2 and totally inhibits the radical-type reactions (Scheme VII).^{3d}

Similarly, in the absence of a P donor, the ion pair [FeCp(THF)$_3{}^+$,Cp$^-$] collapses to ferrocene so that, in THF, the catalytic Scheme VII applies. The dimerization of **1**, dominant in THF in the absence of a P donor and of **23**, is totally suppressed by the addition of 0.1 equiv of **23**.

This special salt effect^{23} shows again the rapid interconversion between the 17e species Fe^{I}CpP$_2$ and the 19e species Fe^{I}CpP$_3$ (Scheme V, acceptor = **1**) and their reducing power. The ergonicity of the ET (eq 2) depends on the nature of P (in **19**) and of the arene (in **1**). The ET can be endergonic by up to 0.5 V using P = P(OMe)$_3$ and arene = mesitylene and Na$^+$PF$_6^-$ still totally suppresses the radical reaction (Scheme VI) to induce ET.

Catalytic Function of Transition-Metal Radicals: ET Chain

Ligand exchange is the most commonly encountered inorganic chain reaction$^{25-33}$ and can proceed either by H atom transfer chain^{24,25} or by ET chain (ECE),$^{26-33}$ but the latter reaction became most popular in the early 80s and was carefully studied by Kochi in mononuclear^{1c} as well as in cluster chemistry.^{28} Other ET chain inorganic reactions are known: isomerization,^{29} insertion^{30} and extrusion of CO,^{1c} and decomplexation^{31} and

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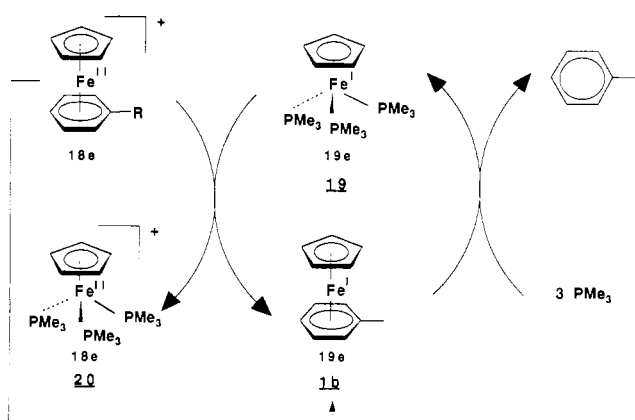
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Scheme VII
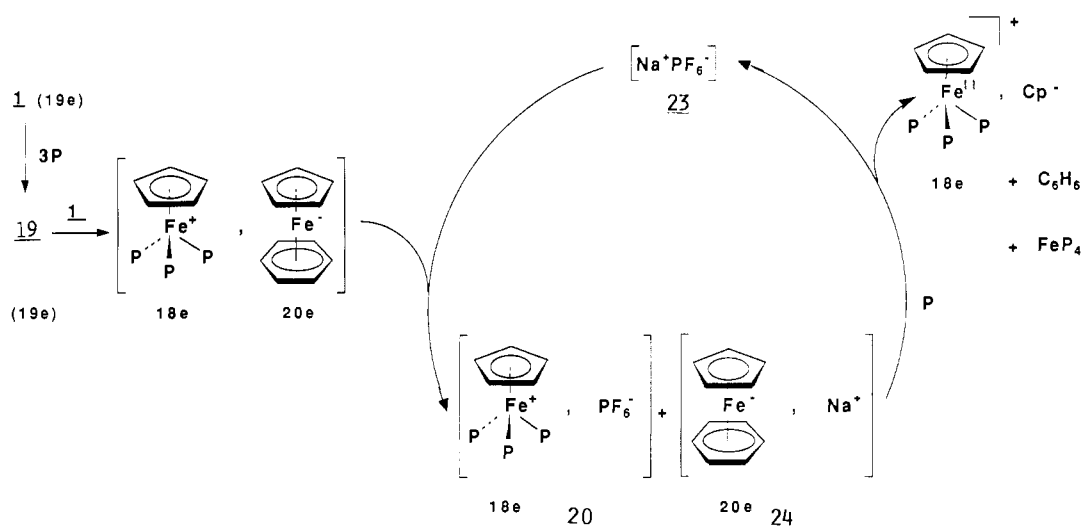
Scheme VIII

chelation.[16b,c,32] We have noted[32] from most reports that the ET chain reactions that work efficiently have an exergonic (thus fast[34]) cross-redox propagation step. There is only one way, oxidation or reduction, to insure the initiation providing this condition.

The rule (based on $E°$ values) works well for the substitution of electron-donating ligands such as MeCN initiated by oxidation in monometallic complexes[1c,28] and for CO substitution initiated by reduction in clusters.[32a,c,35] It is also useful to remove or replace a hydrocarbon ligand by more electron rich ligands in mononuclear complexes.[3d,31,32a,36] For instance, [Fe^{II}Cp(PMe$_3$)$_3$]$^+$PF$_6^-$ and [Fe^{II}Cp(diphos)NCMe]$^+$PF$_6^-$ can be made on a large scale in quantitative yields in a few minutes at 20 °C by introduction of a few milligrams of [Fe^{I}Cp(η^6-toluene)] to a THF suspension or an acetonitrile solution of [Fe^{II}Cp(η^6-toluene)]$^+$PF$_6^-$ containing the appropriate ligand.[3d] With PMe$_3$ (Scheme VIII), the cross-redox step is indeed exergonic by 0.8 V ($\Delta G° = -18.4$ kcal mol^{-1}), which provides a fast ET, avoiding the radical reactions of Scheme VIII. The mechanism of the other propagation step, ligand substitution, is associative (vide supra). The reaction works with all the P donors that fulfill the condition of an exergonic cross-redox step. This is not the case for

P(OPh)$_3$,[3d] and the reaction indeed fails, although [Fe^{II}Cp{P(OPh)$_3$}$_3$]$^+$ is known.[37] The cross-redox step is endergonic by 0.1 V, and the radical reaction of Scheme VI is then observed.

This rule, stating that electrocatalytic reactions do not work when the cross-redox step is expected to be endergonic, ignores the other propagation step: the ligand exchange.[1c] It was thus desirable to try to catalyze the same reaction using either an oxidant or a reductant in the initiation. We have chosen the chelation of the dithiocarbamate ligand, for which the entropy drives the "chemical" propagation step.[38] For the first time, both electrocatalytic cycles were shown to work (Scheme IX), but with limited Coulombic efficiency. In the case of the oxidative initiation,[16b,c] the endergonicity of the cross-redox step slows it down and the isolable 17e chelated cation gives competing side reactions (precipitation in THF or CO exchange with the solvent shown in Scheme IX). With the reductive initiation,[38] the yields are somewhat better but the Coulombic efficiency is now limited by the other propagation step: the loss of the dithiocarbamate ligand competes with its chelation with CO loss. We believe that with suitably designed electron-reservoir ligands this duality of initiation could also be successfully applied.[39]

Coupling Electrocatalysis with Organometallic Catalysis

It is possible, using the same rule, to design the rational synthesis of catalysts by ET chain catalyzed ligand exchange from 18e precatalysts. The oxidatively induced exchange of MeCN ligands by P donors in [W-(CO)$_3$(NCMe)$_3$] (25) was known to proceed with high Coulombic efficiency.[5] Thus, we envisaged replacement of MeCN ligands by alkynes in this W complex to bring at least two alkyne ligands onto the W center. This ligand exchange involves an exergonic cross-redox propagation step. In this way, we meet the conditions of the well-known Chauvin-type[40a] metathesis mecha-

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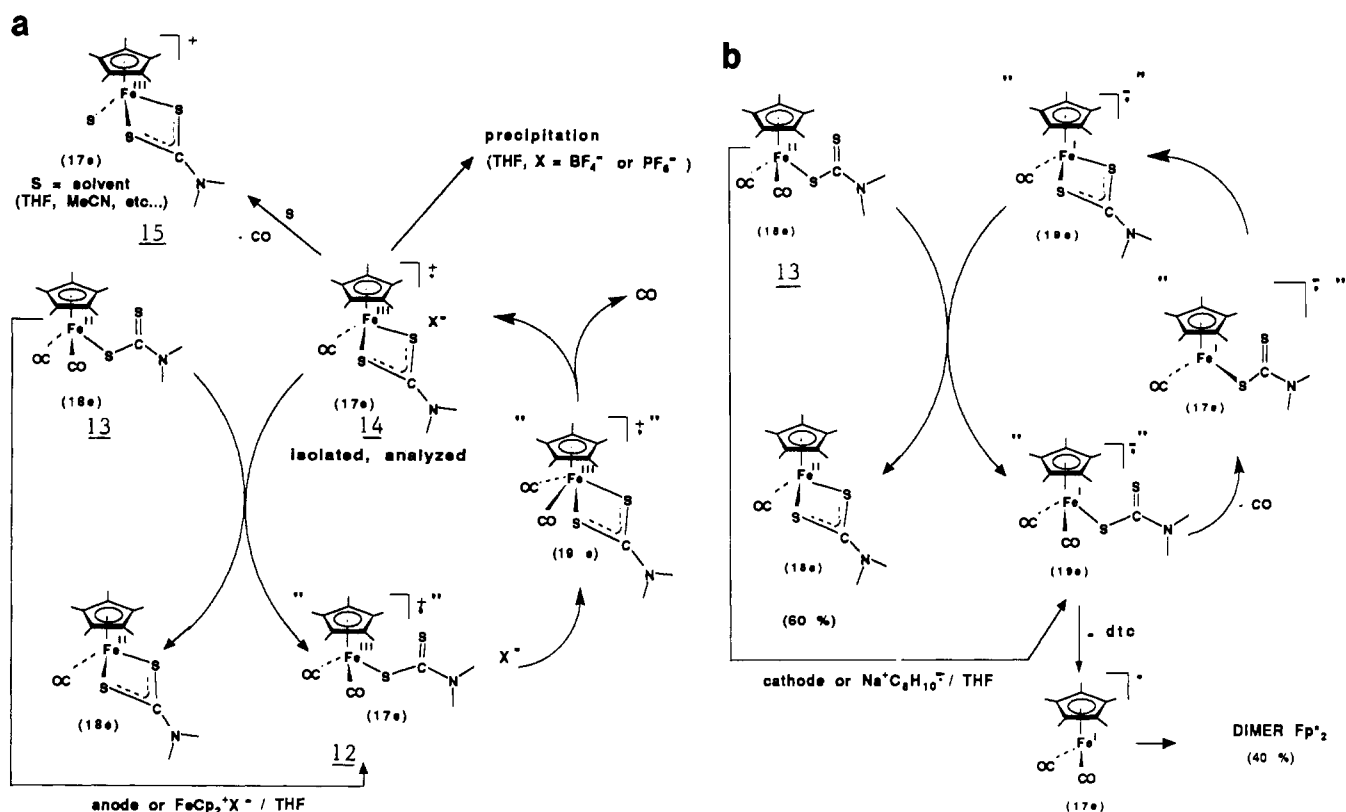(38) Desbois, M.-H.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1990**, 943.

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Scheme IX^a

a

b

^{a} Chelation of the monodentate dtc ligand in [Fe^{II}(C$_5$Me$_5$)(CO)$_2$(η^1-dtc)] (13) catalyzed either by monoelectronic oxidation (left, a) or by monoelectronic reduction (right, b). The cyclic voltammogram of 13 shows both totally irreversible oxidation and reduction.

nism reported by Katz[40b] for alkyne polymerization. That is, of the two alkyne ligands coordinated to the W center, one undergoes a rearrangement to a vinylidene ligand, which then couples with the other to generate the key tungstacyclobutene intermediate. This coupling of the two types of catalysis is represented in Scheme X. The reaction of **25** with terminal alkynes under ambient conditions takes about a week to produce modest yields of polymers. Under the same conditions (2% of the W catalyst **25**) but upon adding a few milligrams of FeCp$_2$$^+PF_6$$^-$ (**26**) (**26:25** ratio = 0.1), the polymerization (MW $\simeq$ 25000) is obtained instantaneously in reasonable yields. In the absence of **26**, no reaction occurs. Evidence that the polymerization is not induced by paramagnetic W^I species, but actually by the W^0 species resulting from electrocatalytic ligand exchange, is provided by the fact that the reaction yield dramatically decreases when the ratio **26:25** reaches 1, an effect also obtained if MeCN, the ligand competitor, is used as the solvent.[15b,33] This coupling process could be useful in various types of catalysis.

Conclusion and Prospects

Seventeen-electron, 18e (ligand centered), and 19e radicals rapidly interconvert. These three forms have close energy levels so that the reactivity of each of them can be observed, depending on the reaction medium and conditions. This chameleon structure–reactivity relationship should thus be subjected to caution regarding its interpretation, a given reactivity being not always due to the most stable (ground) state structure of a radical.

Fast ligand exchange reactions in radicals can generate very powerful reducing agents. These two key

Scheme X
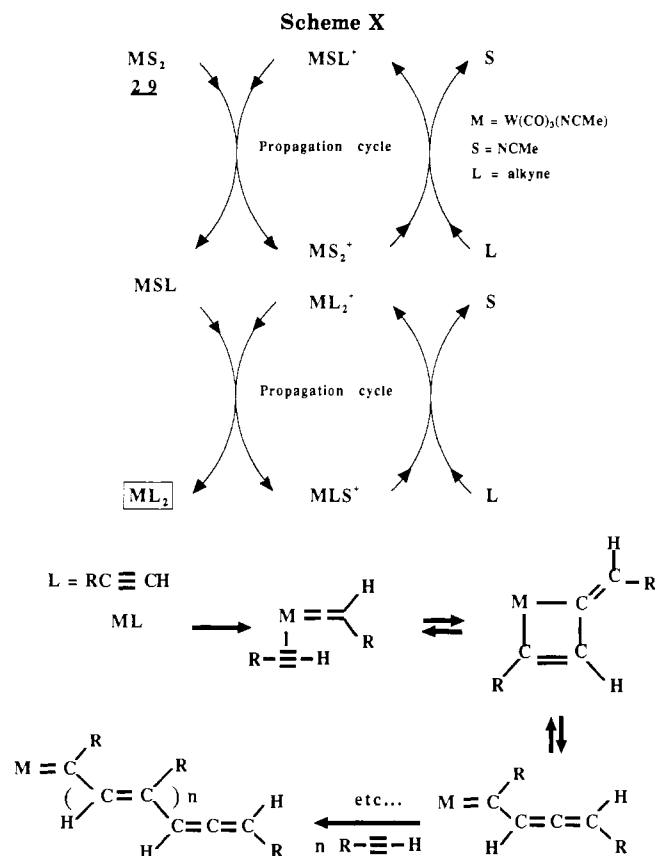
properties lead to ET chain ligand exchange reactions. We have noted that most $\bar{E}C\bar{E}$ reactions only work if the cross ET step is exergonic, which is obtained by the suitable choice, oxidative or reductive, of the initiation.

On the other hand, the first example of an ET chain reaction that can be initiated in either way also illustrates the problem of side reactions. Electron-reservoir ligands should be helpful in switching the mode of initiation of the ET chains.

An application of the suitably initiated electrocatalytic ligand exchange reaction is the coupling between ECE and organometallic catalysis with the aim of improving the reaction conditions, yields, and selectivities of transition-metal catalysis. Exemplified here by the facile induction of the polymerization of terminal alkynes, this principle should find considerable extension in the near future to other types of catalytic reactions. In more general terms, the coupling between several types of catalysis, some of which involve ET, is one of the keys for future achievement and improvement of technological processes.[41]

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Identification of Molecular Adsorbates by LITD/FTMS: A Breakthrough for Surface Chemistry

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Introduction

During the last 20 years, enormous progress has been made in the development of new and more precise probes of the solid–gas interface. Techniques such as low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) provide information about the elemental composition and structure of the surface layer, and X-ray photoelectron spectroscopy (XPS) is a sensitive method for determining the elemental composition and oxidation state of surface adsorbates. These methods are of only limited usefulness to a chemist, however, because they reveal little about the *molecular* composition of the surface species. Electron energy loss spectroscopy (EELS) and infrared spectroscopy can be used to identify simple molecular adsorbates, but identifying complex species, such as are encountered in problems related to catalysis, lubrication, adhesion, corrosion, and microelectronics fabrication, remains a difficult problem. Part of the difficulty results because very high detection sensitivity is required. For example, one monolayer of adsorbed material corresponds to about 3 pmol distributed over a surface area of 1 mm^2. Another difficulty is that small signals from the adsorbate can be overwhelmed by those arising from the bulk substrate.

In this Account we describe an exciting new surface analysis method called LITD/FTMS.[1-4] Laser-induced thermal desorption (LITD) utilizes a pulsed laser beam to rapidly heat the surface and remove intact neutral molecular species. These are then ionized by an electron beam, trapped in a magnetic field, and detected by Fourier transform mass spectrometry (FTMS).[5-8] FTMS has two distinct advantages: high mass resolution and the ability to record all masses simultaneously from a *single* laser shot. LITD/FTMS is a highly sensitive and rapid method for identifying complex molecular species adsorbed on surfaces. Intermediates in catalytic reactions can be observed, and rate constants for surface-catalyzed reactions can be measured.

Principles of LITD/FTMS

The sequence of events for a LITD/FTMS experiment is shown in Figure 1.[9-12] Figure 1a shows a pulsed

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