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Nineteen-Electron Complexes and Their Role in Organometallic Mechanisms

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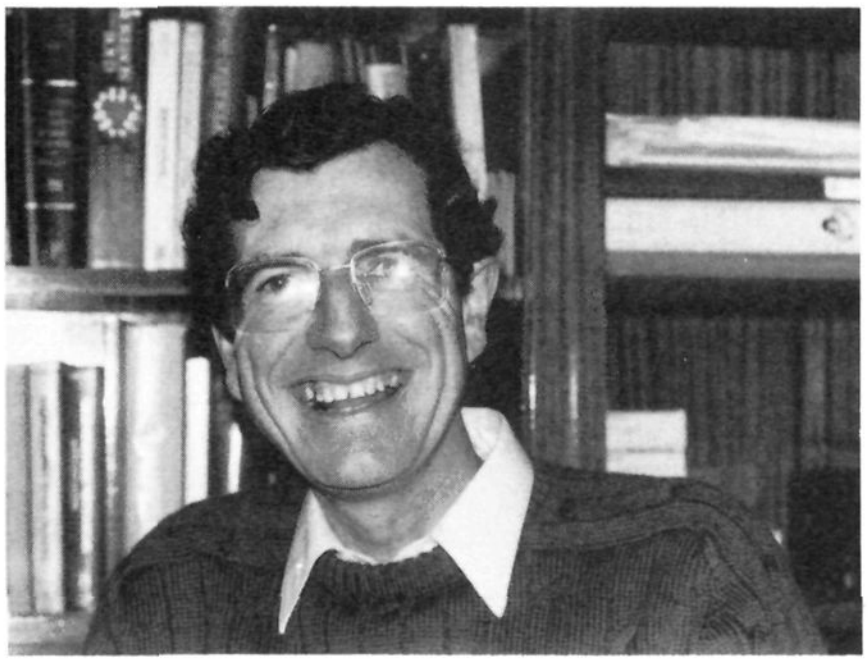
I. Introduction and Scope

Transition-metal organometallic chemistry has been so far dominated by the 16e/18e rule.[1,2] Indeed, in most isolable complexes, the transition metal bears such numbers of electrons in its valence shell, and catalytic mechanisms are depicted by using the 16e/18e interconversion.[3-7] However, as radicals in organic chemistry, transition-metal-centered radicals have long been recognized as playing an important role in redox reactions, chain mechanisms, homolytic cleavage, and catalysis of C–C bond formation.[8,9] They are essential in mediating redox reactions in energy-conversion processes and in biomimetic C–H activation and epoxidation of hydrocarbons.[10] Their intermediacy in industrial processes such as the Wacker reaction[11] is well-known.

Indeed, it is always easy to oxidize or reduce an 18e complex,[12,13] and this simple concept can be extremely fruitful. In terms of electron count, most isolated organometallic radicals have, like ferricinium, 17 valence electrons (VE), and these are reviewed by Baird in this issue.[14] We are concerned here with transition-metal radicals having an electron count in excess with respect to the rare gas (18e) rule, i.e., 19e. Perhaps the first reported 19e complex was cobaltocene,[15,16] found by Wilkinson and Fischer shortly after ferrocene.

The family of 19e radicals is more greatly disputed than the 17e one. For instance, the 19th electron is not really metal based in cobaltocene but is nearly equally shared between cobalt and the Cp ligands.[17] It is the purpose of this review to discuss the existence and role of 19e species in organometallic chemistry. Therefore we shall successively examine their mode of generation, their electronic structure, their reactivity, and their use in stoichiometric and catalytic electron-transfer (ET) reactions.



Didier Astruc was born in Versailles in 1946. After his "3e cycle" Thesis at the University of Rennes (1967–1970), he was appointed at the Technological Institute of Saint-Nazaire as a lecturer (1970) and then as a Master Lecturer (1971). He received his State Doctorate degree from the University of Rennes (1975), and then was a postdoctoral NATO fellow at the Massachusetts Institute of Technology where he worked with Professor R. R. Schrock (1977). In 1978, he was appointed as a CNRS fellow in Rennes where he became a "Maitre de Recherche" in 1980 and developed the chemistry of 19-electron complexes. He was awarded the Prize of the Coordination Chemistry Division of the French Chemical Society in 1981 for his work on "Organometallic Electron Reservoirs". Since 1983, he has been a Professor of Chemistry at the University of Bordeaux I. He was a Visiting Scientist at IBM, San Jose, CA (1979), and a Visiting Professor at the Catholic Universities of Santiago and Valparaiso, Chile (1985), and at the University of Konstanz, FRG (1986). His present research interests include (i) synthetic and mechanistic organometallic chemistry, (ii) applications of transition metals to organic chemistry and material science, (iii) intra- and intermolecular electron-transfer processes, (iv) the coupling of organometallic catalysis with electron-transfer catalysis, and (v) electronic structures and unusual physical properties of molecular transition-metal compounds.

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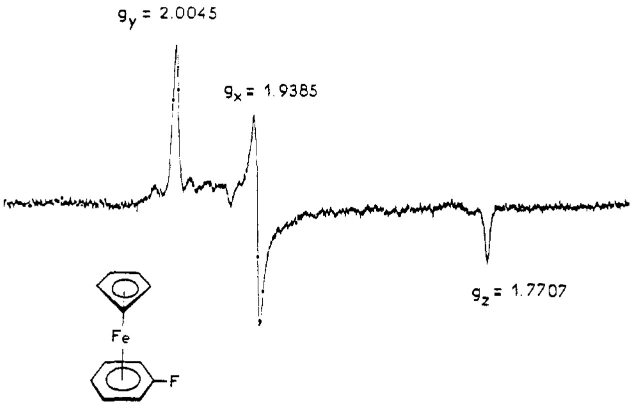


Figure 1. ESR spectrum at 4.2 K of the unstable 19e complex $CpFe^I(C_6H_5F)$ generated by $LiAlH_4$ reduction of the 18e precursor in THF solution at -80 °C.

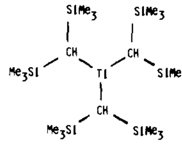
II. Transition-Metal-Centered Radicals: From 7e to 21e

Transition-metal complexes having an odd number of VE are generally paramagnetic. Other types of magnetism may be found, and the search for ferromagnets represents a real challenge at present (cf. the 17e complex $Cp^*Fe_2^+TCNE^-$).[18] Odd-electron paramagnetic organometallic complexes can be called radicals because hydrocarbons bring about a strong ligand field and the metal bears only one unpaired electron (low spin). An exception is the ionic high-spin complex manganocene.[19]

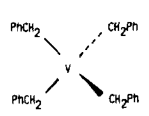
Some paramagnetic early-transition-metal complexes have very few VE because they bear only bulky alkyl ligands: d^1 $Ti[CH(SiMe_3)_2]_3$ has only 7 VE;[20] d^1 VR_4 (R = CH_2Ph, CH_2SiMe_3, 1-norbornyl)[21-24] and d^3 $CrPh_3$[25] have 9 VE; d^3 complexes MnR_4[21,26] have 11 VE; d^5 CoR_4[21,27] complexes have 13 VE; and d^1 Ti(III) radicals of the type Cp_2TiR[20,28,29] (R = CH_2CMe_3, $CH_2CH_2P(Me)Ph$), d^3 vanadocene,[30,31] $Mn(\eta^4\text{-}C_4H_6)_2$,[32] and $Cp^*W(CH_3)_4$[33] bear only 15 VE. The plethora of 17e complexes range from robust (with hydrocarbon and phosphine ligands, but also with methyl and CO) to very transient for binary metal carbonyls $M(CO)_n$ generated by photolytic cleavage of metal-metal-bonded dimers $M_2(CO)_{2n}$ (Mn, Re: n = 5; Co: n = 4).[14,34-38]

The 19e complexes are accessible with the sandwich structure and stabilized by permethylated ligands;[39,40] some other series of delocalized base adducts of 17e complexes are also stable. Transient 19e metal carbonyl and related species play important roles in mechanisms.[36,41] Inorganic chemistry also provides such examples: $Co(NH_3)_6^{2+}$ is labile[42,43] but CoN_6^{2+} is stable with the cage sepulcrate N_6 ligand.[44,45]

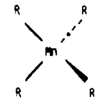
The 21e complexes were sometimes invoked in supersaturated sandwich structures; however, careful investigations show that 21e sandwich species cannot be generated. The complex $Co(C_6Me_6)_2$ turned out to have only 19 VE, the dipole moment (1.78 D) and magnetism (μ_{eff} = 1.86 μ_B) indicating a partial arene decoordination to $\eta^4\text{-}C_6Me_6$.[46] Geiger showed that the cathodic 1e reduction of the 20e complex nickelocene is slow and thus must involve a decoordination in the course of ET,[47] for instance to η^3-Cp, generating a 19e species $[CpNi(\eta^3\text{-}Cp)]^-$. An interesting exception is the dppm adduct of manganocene recently reported by Wilkinson.[48] The X-ray crystal structure shows a tilt of the Cp ligands, which, however, both remain planar.



d^1 . 7 e

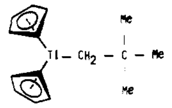


d^1 . 9 e

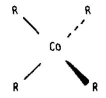


R = Norbornyl

d^3 . 11 e

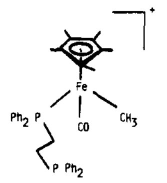


d^1 , 15 e

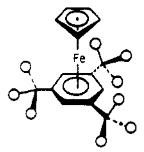


R = Norbornyl

d^5 . 13 e

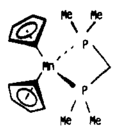


d^5 . 17 e



d^7 , 19 e

—O : CH_3



d^5. 21 e

III. Definition of 19e Radicals

One can define 19e complexes as having 19 VE with a predominant metal character for the HOMO (19th electron). The question of the generation of a 19e species is posed every time an electron is added to an 18e complex either by cathodic reduction or by using a chemical reducing agent. In many instances, the term "19e species" is used to name a monoreduced species without knowledge of the actual electronic structure. Before doing so, it is highly desirable to investigate the spectroscopic properties in order to know whether the HOMO is metal or ligand based.

There are at least three frequently encountered types of cases where the 19e nomenclature is not necessarily justified:

(i) If the 19th electron is in a predominantly ligand orbital, one can speak of a monoreduced ligand but the coordination shell of the metal retains its 18e structure. In this case, the radical center is borne by the ligand, and not by the metal, and the hapticity of the ligand may remain the same. Typical cases are nitrosyl complexes[49] but there are many others.[50]

(ii) If the 19th electron is in an antibonding metal-ligand orbital, decoordination may occur concomitant with or subsequent to ET to the 18e complex. This provides, in the general case of a 2e ligand, a 17e species in which the metal bears the radical center. Decoordination of a single carbon from a polyhapto ligand has also been proposed, but the radical is then ligand based (see i). If decoordination proceeds during ET, a 19e species should not be involved in the process; if it does so subsequent to ET (eq 1 and 2), then a transient 19e species must be considered. The structural consequences of ET in organometallic electrochemistry have been reviewed by Geiger.[51]

$$ML_n^+ \xrightarrow{e^-} ML_n^{\bullet -} \xrightarrow{-L} ML_{n-1}^{\bullet -} \quad (1)$$

$$ML_n \xrightarrow{e^-} ML_{n-1}^{\bullet -} \quad (2)$$

However, if spectroscopic characterization is performed, one should be careful in the attribution of the 19e versus 17e structure of the metal center. If the 19e structure is too labile, and if the 17e one is less so, it may well be that only the 17e species is observed. One problem is that this care or distinction is not always exercised.

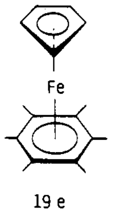
(iii) Monoelectronic reduction of an 18e complex may be accompanied by a second monoelectronic reduction that is less energetic—and thus proceeds faster—than the first one. This is the result of structural rearrangement, e.g., decoordination, and only a 2e reduction to another 18e species is observed without the possibility of characterization of any intermediate paramagnetic species[51-57] (eq 3):

$$\mathrm{Ru}(\eta^6\text{-}C_6Me_6)_2^{2+} \xrightarrow{2e^-} \mathrm{Ru}(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6) \qquad (3)$$

IV. Generation and Characterization of 19e Species

Monoelectronic reduction of 18e complexes to 19e species can be effected by controlled-potential electrolysis (CPE), by alkali-metal reduction (sand, mirrors), or, eventually, by using amalgams or alloys. Depending on the redox potential of the 18e/19e system, various other chemical reagents can be used as monoelectronic reducing agents.[12,13] Dithionite can reduce $Fe(C_6Me_6)_2^{2+}$ to the monocation;[58] alkoxides, hydrazine, or zinc can reduce the dinitronyl complexes $CpW(NO)_2L^+$ (L = P donor).[49] The common main-group hydrides $LiAlH_4$ and $NaBH_4$ can also be used but one must be cautious to avoid hydride transfer. At low temperature (−80 to −60 °C), $LiAlH_4$ transfers an electron to $FeCp(arene)^+$, which is useful for the generation of unstable radicals.[59,60]

CpFe(arene) radicals such as 1 generated (−80 °C) by $LiAlH_4$ reduction of the precursor cations in THF can be characterized by ESR. The rhombic distortion of Fe^I gives rise to three g values close to 2, without hyperfine coupling because of spin–lattice relaxation.



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Labile 19e complexes, also characterized in this way, include the green fluorobenzene and the purple tetramethylthiophene Fe^I complexes (see the ESR spectrum of $CpFe^I(C_6H_5F)$ in Figure 1).[59,61]

In CpFe(polyaromatic), the electronic structure depends on the number of rings in the polyaromatic ligand. The ESR spectrum of Fe^I was obtained for the complexes of benzene, naphthalene, phenanthrene, pyrene, and triphenylene. However, with more than four rings (CpFe complexes of perylene and coronene), it was found that the monoreduced species shows a single line in ESR, indicating a ligand-centered radical. This result can be confirmed by the determination of the ligand character d in the HOMO from the Vlček equation using the $E°$ values obtained in cyclic voltammetry; $E°$'s must be determined for two ligands L_1 and L_2 and for their complexes C_1 and C_2:[62,63]

$$d = \frac{E°_{C_1} - E°_{C_2}}{E°_{L_1} - E°_{L_2}}$$

Vlček's equation assumes that the complex LUMO is a linear combination of two fragment orbitals:

$$\Psi_{ML} = C_M\Phi_M + C_L\Phi_L$$

with a binding energy

$$\epsilon_{ML} = \langle\Psi|\hat{h}|\Psi\rangle + C_M^2H_{MM} + C_L^2H_{LL} + 2C_MC_LH_{ML}$$

where $H_{ij} = \langle\Phi_i|\hat{h}|\Phi_j\rangle$ ($\hat{h}$ is the one-electron effective Hamiltonian of the system). C_M, C_L, and H_{ML} are considered as constant when going from ML_1 to ML_2. It follows

$$\epsilon_{ML_1} - \epsilon_{ML_2} \simeq C_L^2(H_{LL}^1 - H_{LL}^2) \simeq C_L^2(\epsilon_{L_1} - \epsilon_{L_2})$$

where ϵ_L is the one-electron energy or orbital Φ_L in the free ligand L. The quantities C_H, C_L, and H_{ML} are neglected, and the L localization of the molecular orbital Ψ_{ML} is given by

$$C_L^2 = \frac{\epsilon_{ML_1} - \epsilon_{ML_2}}{\epsilon_{L_1} - \epsilon_{L_2}}$$

This leads to Vlček's equation because, for two related compounds, the difference of their LUMO energies is proportional to that of their reduction potential ($\Delta\epsilon \propto \Delta E_{1/2}$). Vlček's equation works well even though it is not the same Φ_L ligand orbital that is involved in the reduction of L and ML (all the π MO levels are shifted by the same order of magnitude in going from one arene ligand to the other). The spin densities, calculated with this equation, increase dramatically with the number of rings in the polyaromatic ligand (Table II) and are remarkly similar to those obtained by Xα calculations.[63]

The 19e, metal-centered radicals are listed in Table I, which also includes the spin densities on the metal and the redox potential of the 18e/19e system. The CpFe(arene) family is listed in Table II, which gives redox potentials of the 18e/19e and 19e/20e redox systems. Ligand-centered radicals are listed in Table III.

In a few particular cases, e.g., nickelocene[64,65] and $Fe(C_6Me_6)_2$, the 19e complex can be generated by monoelectronic oxidation of the 20e complex. In the 20e Fe^0 complex, oxidation can also be performed by protonation with HPF_6, Et_2O[86] (eq 4).

$$Fe(C_6Me_6)_2 \xrightarrow{HPF_6} Fe(C_6Me_6)_2^+PF_6^- + \tfrac{1}{2}H_2 \qquad (4)$$

The Mössbauer parameters of the 18e Fe(II) sandwiches are close to those of ferrocene. In 19e Fe(I) sandwiches, the extra (19th) electron occupies an antibonding, doubly degenerate e_1^* orbital. Thus these systems are Jahn–Teller active and the quadrupole splitting (QS) depends on the temperature (vide infra; section V, Figures 4 and 5). However, at 293 K, QS has reached its high-temperature value, and the large metal character of e_1^* can be estimated from the difference of QS between Fe(II) and Fe(I)[67,68] (Figure 2); calcula-

TABLE I. Thermodynamic Redox Potentials $E°$ and Spin Densities on the Metal for 19e, Metal-Centered Radicals (See Table II for CpFe(arene) Complexes)

19e complex	$E°$ (18e/19e),[a] V	solvent	ref	spin density on the metal, %	technique (spin density)	ref
$Cp*_2VNAr$ (Ar = 2,6-$Me_2C_6H_3$, C_6H_5, 2-PhC_6H_4)	0.67 ± 0.01 vs Ag/$AgClO_4$	CH_2Cl_2	75	100 (V(a_1) orbital nonbonding)	spin-polarized (calcd)	75
$CpMoI(CO)_3^-$ (W)			303		ESR	303
$Cp_2Mn(PMe_3)$						48
$CpFe(C_6Me_6)$	−1.55	DMF	108	75	Mössbauer	94, 117
$Fe(C_6Me_6)_2^+$	−0.48	DMF	305	80	Mössbauer	67, 68
$Fe(C_6Me_6)(C_6Me_6H)$	−1.45	DMF	59	70	Mössbauer	59
$CpFeX(CO)_2^-$ (X = Cl, I)			303			303
$Fe(CO)_2(PPh_3)(\eta^4\text{-}C_6H_8)^-$			304			
Cp_2Co[d]	−0.86	CH_2Cl_2	155, 306, 307	58	ESR	114
$Cp*_2Co$	−1.48	CH_2Cl_2	83		electroch[c] ESR	83 91
$CpCo(C_5H_5BMe)$	−0.46	CH_2Cl_2	86, 308			
$CpCo(C_5H_5BPh)$	−0.44	CH_2Cl_2	86, 308			
$Co(C_5H_5BMe)_2$	−0.02	CH_2Cl_2	86, 308			
$Co(C_5H_5BPh)_2$	+0.05	CH_2Cl_2	86, 308			
$Co(indenyl)_2$	−0.53	CH_2Cl_2	309			
$Co(C_6Me_6)(\eta^4\text{-}C_6Me_6)$						46
$CpCo(CO)_2^-$	$E_p{}^c \sim -2$	MeCN	310	d_{yz} $\sigma*$ 56	IR, ESR Xα (calcd)	77 121
$CpCo(1,3\text{-}COD)^-$	−1.60	MeCN	293	53	EHT (calcd)	294
$CpCo(C_5Ph_4O)^{-b}$	−1.46	THF			ESR	316
$CpCo(1,5\text{-}COD)^-$	−2.45	MeCN	293	51	EHT (calcd)	294
$CpCo(1,4\text{-}R_2N_4)^-$				60	ESR, Xα (calcd)	121
R = Me	−1.53	MeCN	121			
R = Ph	−1.01	MeCN	121			
R = C_6F_5	−0.71	MeCN	121			
R = 2,4 F_2-C_5H_2	−0.97	MeCN	121			
R = 2,6 Me_2-C_6H_3	−1.31	MeCN	121			
Cp_2Ni^+	+0.9	CH_2Cl_2	47			311, 312
$Cp*_2Ni^+$	+0.37	CH_2Cl_2	83			83
CpNi(bpy)					X-ray	314
CpNi(COD)	−0.46	CH_2Cl_2	313			
$(C_5Ph_5)Pd(COD)$	−0.47		315			
$(C_5Ph_5)Pd(bpy)$						
$(C_5Ph_5)Pd(dppe)$						

[a] The electrolyte is 0.1 M $n\text{-}Bu_4N^+X^-$ (BF_4^- or PF_6^-); these ions serve as counterions in ionic complexes. $E°$ values are determined by CV and are reported in volts vs SCE unless specified otherwise. The 18e/19e redox system is reversible unless $E_p{}^c$ is given. [b] C_5Ph_4O = η^4-tetraphenylcyclopentadienone. [c] Spin density determined by electrochemistry using the Vlček equation (see text). For cobalt sandwiches, the $E°$ values are very much influenced by the ligand substituents; this indicates considerable covalency (reduced spin density on Co). [d] For $E°$ values of other substituted cobalticinium salts, see ref 154, 306, and 307.

tions using these Mössbauer parameters confirm that the metal character in e_1* is 75–80%.[124] The isomer shift values are also characteristic of each oxidation state (0–3) in the iron sandwiches.

In several instances, the 19e complex may be directly synthesized from a precursor complex and a suitable ligand. In these cases, the 19e form is the stable one. Examples are the Fischer-type synthesis[69] of $Co(C_6Me_6)_2^{2+}$ and the synthesis of $CpNi(1,4\text{-}Ar_2N_4)$[70] (Ar = 4-MeC_6H_4; N_4 = tetraazabutadiene) from nickelocene.[71]

Addition of a 2e ligand to a 17e complex is a very easy way to generate a 19e species; 19e species generated in this way have sometimes been spectroscopically characterized (the N and P adducts of manganocene[48,72] and Cp_2V[73–75]).

Perhaps the most useful technique for the generation of highly unstable species is ^{60}Co γ irradiation, which can be performed in glasses or matrices at very low temperatures;[76–81] this approach afforded ESR characterization of a number of 19e radicals. For instance, ^{60}Co γ-ray irradiation at 77 K of the families of complexes $M(CO)_5X^-NR_4^+$ (M = Cr, Mo, W) and $Re(CO)_5X$ (X = I or Br) in methyltetrahydrofuran gave electron addition products such as **2**, characterized by large hyperfine coupling to the halogen and metal nuclei.[78] In these cases, the extra electron is located in the metal–halogen σ* antibonding orbital comprising primarily d_{z^2}–p_z.

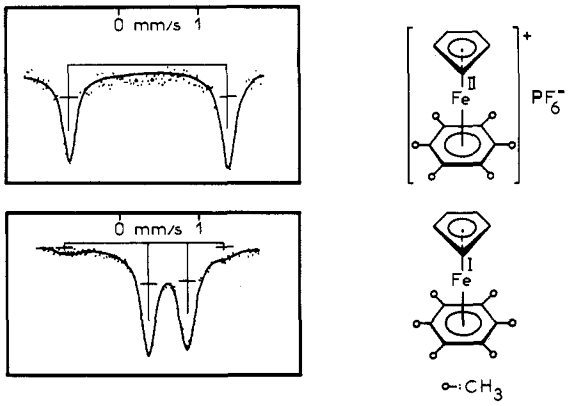
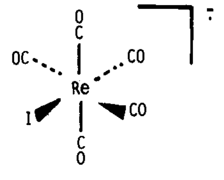


Figure 2. Compared zero-field Mössbauer spectra of the 18e complex $[CpFe^{II}(C_6Me_6)]^+PF_6^-$ (top) and the 19e complex $CpFe^I(C_6Me_6)$ at 293 K. The difference of quadrupole splitting (1.5 mm s^{-1}) gives a good estimation (75%) of the metal character of the HOMO (a pure $d_{xz,yz}$ electron corresponds to 2 mm s^{-1}). See ref 95, 117, and 118.



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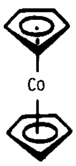
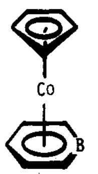
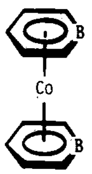
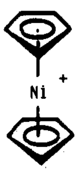
V. Stabilization of 19e Complexes

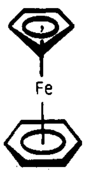
The monoelectronic reduction of the large majority of 18e complexes provides thermally labile species whenever possible but, in some instances, stabilization is possible. For this purpose, one needs to use ligands that can delocalize the 19th electron onto π systems and/or provide steric crowding as for the stabilization of organic radicals.[82] This stereoelectronic requirement is met in cobaltocene[15,16,83] and in some other d^7 late-transition-metal sandwiches:[84-89]



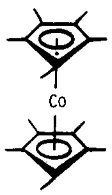


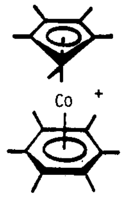


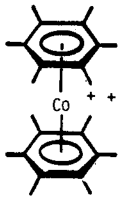


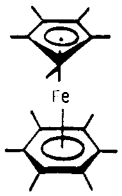


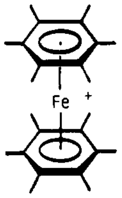
A considerable enhancement of the stabilization is reached by using permethylated C_5 or C_6 rings, which are easily accessible synthetically. Thus, several series of 19e radicals are robust at room temperature in their permethylated form.[39,58,90-92] This 19e family includes sandwich-type complexes that have a cyclohexadienyl ligand.[39]

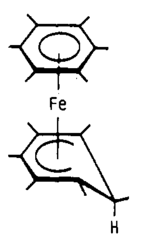












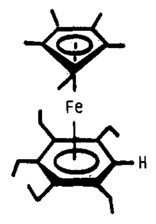
The reaction of eq 5 leads to Cp* complexes:

$$Cp^*Fe(CO)_2Br \xrightarrow[arene^1]{AlCl_3} (Cp^*Fe(arene^2))^+ \qquad (5)$$

$$arene^1 = arene^2 = C_6Me_6$$

$$arene^1 = C_6Et_6,\ arene^2 = C_6Et_5H$$

The Na/Hg reduction of the PF_6^- salt at 20 °C gives the thermally stable 19e complex if the arene ligand bears six Me or five Et groups. Indeed, the reaction of eq 5 with C_6Et_6 gives only the pure C_6Et_5 cationic complex even at 70 °C. However, subsequent reduction to Fe^I shows the thermal stability of the 19e complex 3.[100]



3

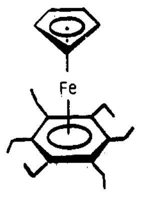
In the CpFe series, peralkylation of the polymethylbenzene ligand of the cationic complex leads to replacement of H's by alkyl groups (eq 6 and 7).[96] Hexafunctionalization is also possible.[101]

$$[CpFe(C_6Me_6)]^+PF_6^- \xrightarrow[t\text{-BuOK}]{RX} CpFe(C_6(CH_2R)_6)^+PF_6^- \qquad (6)$$

$$R = CH_3,\ X = I;\ CH_2Ph,\ X = Br \text{ or } Cl$$

$$CpFe(1,3,5\text{-}Me_3C_6H_3)^+PF_6^- \xrightarrow[t\text{-BuOK}]{CH_3I} CpFe(1,3,5\text{-}t\text{-}Bu_3C_6H_3)^+PF_6^- \qquad (7)$$

Again, Na/Hg reduction readily gives thermally stable 19e complexes 4 and 5.



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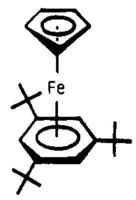


5

Introduction of a functional group on the benzene ligand leads to considerable destabilization. For instance, the pentamethylaniline complex is not stable above 0 °C.[102] However, introduction of a carboxylate function on the Cp ring provides a stable purple anionic 19e radical 6.[103,104] The corresponding blue acid 7 is not stable because of reduction of the Cp side-chain proton by Fe^I.

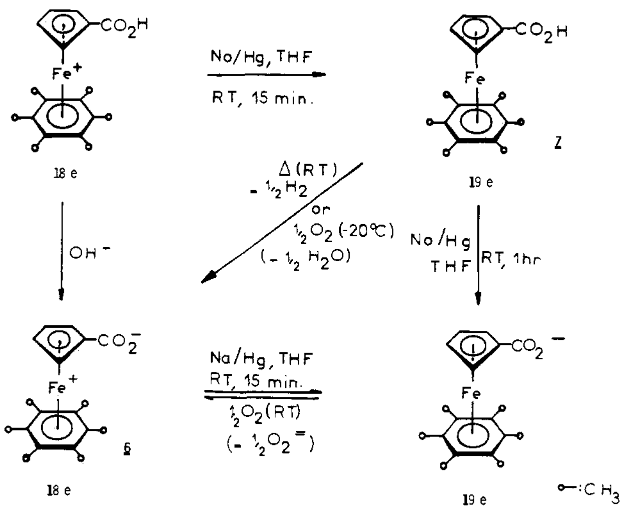


TABLE II[a]

Part a

	cathodic reduction of $[\mathrm{FeCp(arene)}]^+$ on Hg, $-E^\circ$ vs SCE (V)			ligand (arene) character in the SOMO of Fe^{I} complexes (≃spin density)		
					Xα or EH (calcd)[63]	
$[\mathrm{FeCp}(\eta^6\text{-arene})]^+\mathrm{PF_6}^-$ arene	18e/19e	19e/20e	ref	electrochemistry (Vlček's eq)[62]	Xα	EH
C_6H_6	1.36		62[b]	10–15	8	17
	1.41	2.39	56[c]			
	1.30		220[d]			
	1.36		220[c]			
	1.56		159[e]			
	1.62		94[f]			
	1.59		159[e]			
biphenyl	1.27	1.97	62[b]	10–30		
	1.30	2.22	56[c]			
	1.44		159[e]			
naphthalene	1.00		62[b]	15–35	35	
	1.07	1.75	56[c]			
	0.94		220[d]			
	1.04		220[c]			
phenanthrene	1.14	1.68	62[b]	40–60		87
	1.23	1.80	56[c]			
triphenylene	1.14	1.68	62[b]	10–30		91
pyrene	1.10		62[b]	55–75	63	86
perylene	0.80	1.24	62[b]	70–90		91
coronene	1.07		62[b]	80–100		85
fluorene	1.40	2.23	56[c]			
toluene	1.34		220[d]			
	1.41		220[d]			
	1.60		159[e]			
	1.46	2.44	56[c]			
	1.68		94[f]			
ethylbenzene	1.57		159[e]			
1,4-xylene	1.50	2.55	56[c]			
	1.38		220[d]			
	1.47		220[c]			
1,3-xylene	1.62		159[e]			
mesitylene	1.55		56[c]			
	1.62		159[e]			
tert-butylbenzene	1.56		159[e]			
durene	1.45		220[d]			
	1.54		220[c]			
hexamethylbenzene	1.78		94[f]			
	1.55		108[g]			
	1.57	2.34	169[g]			
	1.55		220[d]			
	1.68		220[c]			
hexaethylbenzene	1.66		108[f]			
	1.67		108[f]			
1,3,5-tri-*tert*-butylbenzene	1.37		108[f]			
1,9-dihydroanthracene	1.37	2.15	62[b]			
dihydrophenanthrene	1.31	2.02	62[b]			
chlorobenzene	1.25	2.30	56[c]			
anisole	1.46	2.42	56[c]			
	1.40		220[c]			
	1.47		220[c]			
benzonitrile	1.09	1.87	56[c]			
p-chlorotoluene	1.30	2.10	56[c]			
p-fluorotoluene	1.33	2.36	56[c]			
p-$CH_3C_6H_4SCH_3$	1.39	2.25	56[c]			
p-$CH_3C_6H_4NHCOCH_3$	1.44	1.68	56[c]			
p-methylanisole	1.46	2.55	56[c]			
$PhCO_2Me$	1.05		220[d]			
	1.15		220[c]			
p-$C_6H_4(CO_2Me)_2$	0.83		220[d]			
	0.90		220[c]			
anthraquinone	0.49		220[d]			
	0.55		220[c]			
Ph_2S	1.17		220[d]			
	1.27		200[c]			
$PhNMe_2$	1.49		220[d]			
tetramethylthiophene	1.15	1.95	61[h]			
$[2_2]$(1,4)cyclophane	1.34	2.02	302[d]			
$[2_4]$(1,2,4,5)cyclophane	1.06	1.84	302[d]			
$[2_5]$(1,2,3,4,5)cyclophane	1.08		302[d]			
$[2_6]$(1,2,3,4,5,6)cyclophane	1.34		302[d]			

TABLE II[a] (Continued)

Part b

$[FeCpR(\eta^6\text{-arene})]^+PF_6^-$ CpR	arene	$-E°$, V	ref	ligand (arene) character in the SOMO of Fe^1 complexes (≃spin density)
				electrochemistry (Vlček's eq)[62]
$C_5H_4CH_3$	C_6H_6	1.69	94[f]	
		1.34	220[d]	
		1.43	220[e]	
C_5H_4Et	C_6H_6	1.50	1.59[e]	
		1.48, 2.45	56[c]	
C_5H_4-*n*-Pr	C_6H_6	1.58	159[e]	
C_5H_4-*i*-Pr	C_6H_6	1.58	159[e]	
$C_5H_4CH_2Ph$	C_6H_6	1.57		
$C_5H_4COCH_3$	C_6H_6	1.55, 1.04, 1.28	159[e]	
		1.14, 2.00	56[c]	
C_5H_4COPh	C_6H_6	0.99	220[d]	
		1.08	220[d]	
C_5H_4Cl	C_6H_6	1.25, 2.30	56[c]	
$C_5H_4OCH_3$	C_6H_6	1.46, 2.42	56[c]	
Cp-piperidyl	C_6H_6	1.61	56[c]	
$C_5H_4CO_2CH_3$	C_6H_6	0.99	220[d]	
C_5Me_5	C_6H_6	1.856	94[c]	
		1.58	220[d]	
		1.67	220[c]	
		1.64	62[b]	
C_5Me_5	biphenyl	1.57	62[b]	15–30
C_5Me_5	naphthalene	1.28	62[b]	15–30
C_5Me_5	phenanthrene	1.36, 2.04	62[b]	15–30
C_5Me_5	triphenylene	1.43	62[b]	15–30
C_5Me_5	pyrene	1.32, 1.84	62[b]	15–30
C_5Me_5	C_6Me_6	1.87	94[f]	
		1.75	108[f]	
C_5Me_5	C_6Et_5H	1.80	100[g]	
ferrocenylCp	C_6Me_6	1.58, 2.36	169[g]	

[a] Values of $-E°$ vs SCE for the two reduction waves 18e/19e and 19e/20e determined by polarography (ref 56) or cyclic voltammetry (others). The second wave is not chemically fully reversible in the cases of polyaromatic ligands (see ref 62). [b] DMF, 0.1 M *n*-Bu_4NPF_6. [c] CH_3CN, 0.1 M *n*-Bu_4NBF_4. [d] CH_3COCH_3, *n*-Bu_4NBF_4. [e] H_2O–EtOH, 0.1 M $NaClO_4$. [f] H_2O, 0.1 M LiOH. [g] DMF, *n*-Bu_4NBF_4. [h] DMF, 0.1 M *n*-Bu_4ClO_4.

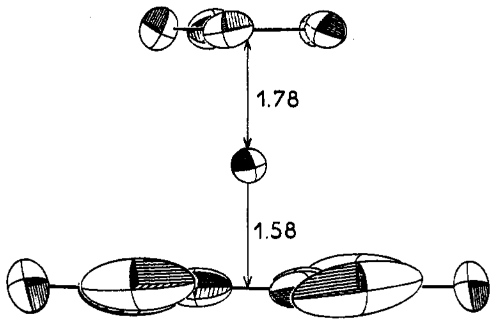


Figure 3. ORTEP of the X-ray crystal structure of the 19e complex $CpFe^I(C_6Me_6)$. Compare the Fe–Cp and Fe–arene distances: only the Fe–Cp bond is significantly longer than in 18e complexes (see ref 93).

A ferrocenyl substituent (Fc) can also be branched on the Cp ring, which provides a second redox center in the stable 19e complex $(FcC_5H_4)Fe(C_6Me_6)$.[169]

In stable 19e radicals, the molecular and electronic structure is, of course, more easily amenable to study. Several X-ray crystal structures are known. For instance, in $CpFe(C_6Me_6)$, both rings are planar and parallel, which allows discarding the hypothesis of a partial decoordination to a 17e structure.[93] The Cp–Fe distance is 0.1 Å longer than in 18e complexes whereas the arene–Fe bond is not greatly perturbed (Figure 3). The crystal structure of cobaltocene shows a lengthening of 0.05 Å of the metal–carbon distances.[105] The He(I) photoelectron spectroscopy of neutral 19e complexes afforded the observation of low ionization potentials,[106-108] and the lowest values were obtained for the permethylated Fe^I complexes (Table IV). The ionization potential of $Cp^*Fe(C_6Me_6)$ (4.21 eV)[108a] compares with that of potassium metal (4.34 eV).[108b]

Since the largest number of 19e complexes is found in the families of transition-metal sandwiches, let us recall that their well-established electronic structure involves the sequence

$$d_{xz},d_{yz}\ (e_1) > d_{z^2}\ (a_1) \geqslant d_{xy}/d_{x^2-y^2}\ (e_2)$$

holding for metallocenes (Cp_2M), bis(arene)metal, and mixed MCp(arene) complexes[109-112] (Figure 4). The antibonding e_1^* orbital is doubly degenerate. Upon single occupancy (19e), the degeneracy is lifted by a dynamic Jahn–Teller effect, leading to a rhombic distortion[113-115] that is extremely sensitive to the environment.[115] In Fe complexes, the thermal population of the upper Kramer's level can be followed by a variation of the quadrupole splitting observed in Mössbauer spectroscopy (Figure 5).[116-118] With other metals (Co, Ni), ESR and PES are still the best techniques to examine this distortion.[112-114]

A major piece of information that one can obtain from these investigations is the metal and ligand

TABLE III. "19e Species" Characterized by ESR as 18 VE Species with a Ligand-Based Radical Center

complex	radical center	ref
$(CO)_5MC(OMe)Ph^-$	carbene C	318
$(PPh_3)_n(CO)_{4-n}M(bpy)^-$	bpy	319–323
M = Cr, Mo, W; *n* = 0		323
M = Mo, W; *n* = 1		
M = Mo, *n* = 2		
$(CO)_2Mo(bpy)_2^-$	bpy	324
$(DAB)M(CO)_4^-$ (DAB = RN=CR′CR′=NR)	DAB	325–328
$(4\text{-CN-py})M(CO)_5^-$ (M = Cr, Mo, W)	4-CN-py	87
$(CO)_4M(bpym)^-$ (bpym = 2,2′-bipyrimidine)	bpym	329
$(CO)_4M(N_2$ ligand)	N_2 ligand	330
$(CO)_5M(N_2$ ligand) $M(CO)_5$ (M = Cr, Mo, W; N_2 ligand = 3,3′-bipyridazine, 4,4-bipyrimidine, 2,2′-bipyrazine, 2′,2′-bipyrianidine)	N_2 ligand	330
$CpW(NO)_2P(OPh)_3$	NO	49
$CpCrC_7H_7^-$	C_7H_7	331
$Cr(\eta^6\text{-}C_6H_5SiMe_3)_2^-$	arene	332
$Cr(C_6H_6)(\eta^6\text{-}C_6H_5COPh)$	C_6H_5COPh	333
$Cr(C_6H_5COPh)(CO)_3$	C_6H_5COPh	334
Cr(benzoyl,3-Pyrr)$(CO)_3$ (Pyrr = *N*-methylpyrrole)	Ph	335
$(CO)_4MnP_2$ (P_2 = 2,3-bis(diphenylphosphino)maleic anhydride)	P_2	338
$(CO)_4Mn(t\text{-Bu-DAB})$	DAB	216, 217
$(CO)_4Mn(DBuOQ)$	DBuOQ	216, 217
$(CO)_3Mn(DBuOQ)(t\text{-Bu-DAB})$ (DBuOQ = 3,5-di-*tert*-butyl-*o*-benzoquinone)	DBuOQ	216, 217
$(CO)_4Re(DBuOQ)$	DBuOQ	336, 337
$(\eta^5\text{-}PhCOC_5H_4)Mn(CO)_3^-$	$PhCOC_5H_4$	339, 340
$Fe(L\text{–}L)(NO)_2$ (L–L = bpy, *o*-phen, bis(2-pyridyl)ketone)	L–L	341
$Fe(CO)_2(NO)_2^-$	NO	81
$Fe(PPh_3)_2(NO)_2$	NO	342
$Fe(NO)_2LL'_2$ (L = L = THF, MeCN, PPh_3; L = PPh_3, L′ = THF, MeCN)	NO	343
$Fe(NO)_2[Me_2Ga(N_2C_5H_7)(OCH_2CH_2NMe_3)]$	NO	344
$Fe(CO)(NO)_3$	NO	347
$[Ru(bpy)_2(NO)(Cl)]I$	NO	346
$Fe(CO)_2(PPh_3)(\eta^4\text{-COT})^-$	COT	294
CpFe(perylene)	perylene	62, 63, Table II
CpFe(coronene)	coronene	62, 63, Table II
$Co(NO)_2(CO)_2$	NO	155
$CpM(O\text{–}O)(PCy_3)$ (M = Co, Rh; O–O = *o*-chloranil)	O–O	348
$(C_5R_5)Co(\eta^4\text{-COT})^-$ (R = H, Me)	COT	294
$CpRh\ (\eta^4\text{-}C_5R_4O)^-$ (R = Ph, C_6F_5)	C_5R_4O	316
$Co(CO)_3P_2$ (P_2 = 2,3-bis(diphenylphosphino)maleic anhydride)	P_2	338

TABLE IV. First Ionization Energy of Stable 19e Complexes

19e complex	ionization energy,[a] eV	ref
$Cp^*FeC_6Me_6$	4.21	108a[b]
K metal	4.339	108b
$CpFe(C_6Et_6)$	4.34	108a[b]
$CpFe(C_6Me_6)$	4.68	108a[b]
$CpFe(1,3,5\text{-}t\text{-}Bu_3C_6H_3)$	4.72	108a[b]
Cp^*_2Co	4.8	108c[b]
Cp_2Co	5.3	317[c]
$CpCo(C_5H_5BMe)$	6.5	317[c]
$CpCo(C_5H_5BPh)$	6.6	317[c]
$Co(C_5H_5BMe)_2$	7.1	317[c]
$Co(C_5H_5BPh)_2$	7.2	317[c]

[a] This order follows the one found with thermodynamic redox potentials given in Table I. Stable, neutral 19e complexes having an even more negative redox potential than $Cp^*Fe(C_6Me_6)$ are $Cp^*Fe^I(C_6Et_5H)$ and $Fe^I_2(fulvalene)(C_6Me_6)_2$. [b] Determined by He(I) photoelectron spectroscopy; see Green et al.[108] [c] Determined by mass spectrometry; see Herberich et al.[317]

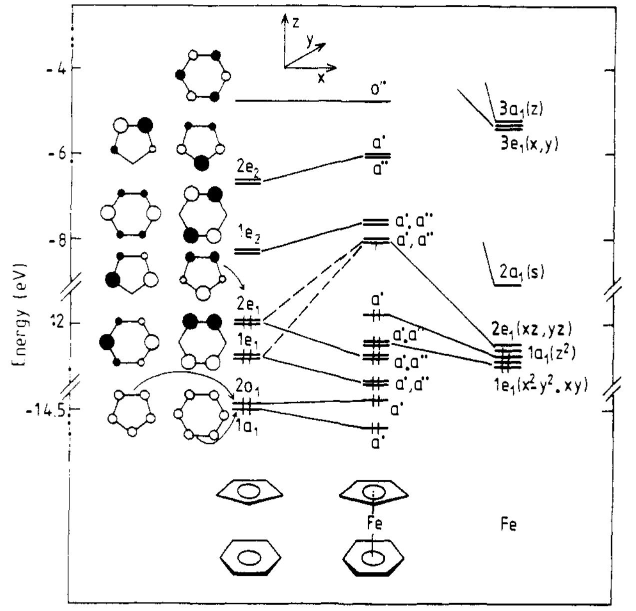


Figure 4. Molecular orbital diagram of the 19e complex $CpFe^I(C_6H_6)$ (from EHT studies; see ref 63).

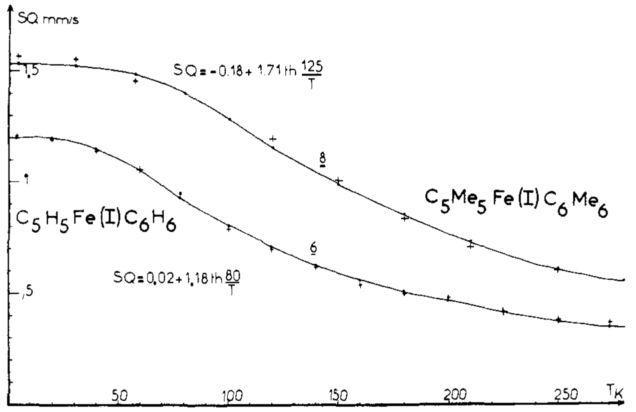
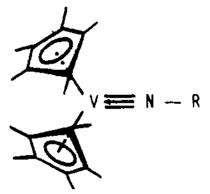
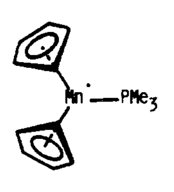


Figure 5. Variation of the quadrupole splitting (SQ) as a function of temperature in the 19e complexes $C_5Me_5Fe^I(C_6Me_6)$ (top curve) and $C_5H_5Fe^I(C_6H_6)$ (bottom curve). The thermal population of the upper Kramer's level was fitted by the indicated *th* laws (rhombic distortion of the Jahn–Teller-active Fe^I sandwiches). In other Fe^I sandwiches with different ring sizes, phase transitions are observable along these curves (see ref 39 and 93).

characters of the e_1^* HOMO. There is, in fact, considerable covalency, which is, however, variable from one metal to another. In the Fe complexes, the ligand character is limited to 20–30% overall, and, thus, one may state that the 19th electron is mainly located on the metal (nature of "electron reservoirs"). This is not so much the case with Co and Ni.[113] The metal character even drops below 50% in Ni sandwiches (from Xα calculations and ESR data), so that their 19e nature is ambiguous.[113-120]

Nonsandwich complexes can also bear 19 VE in some instances but they still have at least one Cp (or preferably Cp*) ligand and either a second Cp (adducts of manganocene) and/or a nitrogen donor ligand. A crystal structure of the remarkable PMe_3 adduct of manganocene 8 has recently been reported, and similar adducts are known with other bases.[48,72] The tetraazabutadiene complexes of $CpCo^-$ (and presumably of CpNi) also have considerable covalency; e.g., the extra electron is approximately "shared" by the metal and the N_4 ligand.[121]





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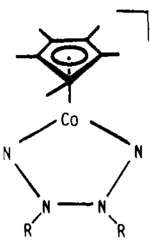
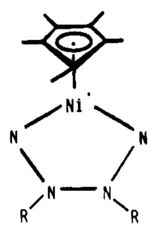




The aryl- and (trimethylsilyl)nitrene adducts of vanadocene obtained by the reaction of eq 8 were first reported by Schubert et al.[73] With decamethyl-

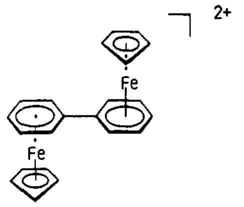
$$ArN_3 + Cp_2{*}V \rightarrow Cp_2{*}V \rightarrow N(Ar)(N{\equiv}N) \rightarrow Cp{*}_2V \equiv N{-}Ar + N_2 \quad (8)$$

vanadocene, they were shown by Gambarotta et al.[74] to be stable enough to provide an X-ray crystal structure of the phenyl derivative. Xα calculations by Trogler[75] showed that these 19e complexes are vanadium-centered radicals. However, they were also shown to be very weak reducing agents as compared to most 19e complexes. Indeed, such a high electron count arises because the nitrene group is regarded as a 4e ligand.

VI. Binuclear 37e and 38e Complexes

When two 18e transition-metal centers are linked by a delocalized ligand, monoelectronic reduction can provide a localized mixed-valence complex with 18 + 19 VE or a delocalized mixed-valence complex with 37 VE. If a second monoelectronic reduction is possible, then different situations are expected depending on the coupling between the two units: (i) "chemical coupling", which gives a diamagnetic complex,[57] (ii) ferromagnetic coupling, which requires orthogonal orbitals (no binuclear organometallic example yet),[122] and (iii) antiferromagnetic coupling, which leaves a 38e biradical.[123,124]

Little information is available from binuclear cobalt sandwiches: the mixed-valence monocation of bis(fulvalene)dicobalt has been briefly mentioned.[125] The isomeric bications 9 and 10 have been made by Hendrickson,[126] and polarographic studies have led to the proposal of intermediacy of mixed-valence monocationic species for each series:[127]



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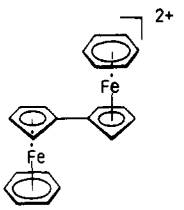
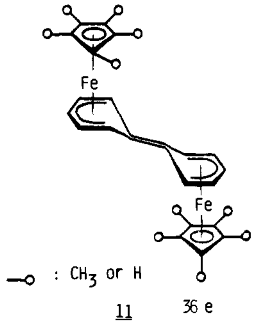


10

However, later CV studies[57] showed that only the fulvalene series can give rise to mixed valency. Reduction of the biphenyl complex proceeds directly by a fast 2e step at −30 °C on a Pt or Hg cathode in DMF. It gives the 36e bicyclohexadienylidene complex resulting from intramolecular coupling within the biphenyl ligand. However, the precursor complex $[Fe_2(\eta^6\text{-biphenyl})Cp{*}_2]^{2+}$ is reduced in two close 1e steps. Reduction of this bication with Na/Hg gives the stable neutral 2e reduction product 11,



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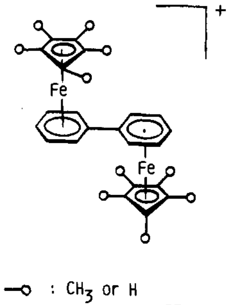
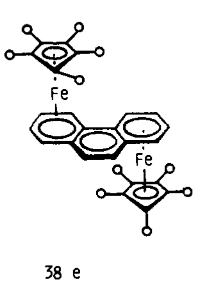


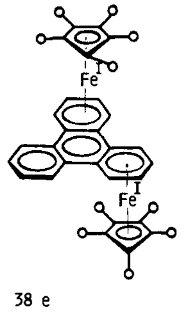
12

for which the bicyclohexadienyl ligand structure was shown by X-ray analysis. Comproportionation between the 36e neutral and dicationic complexes gives the stable 37e mixed-valence monocation 12, which was shown to be delocalized by Mössbauer spectroscopy (a single quadrupole doublet was observed at all temperatures between 4.2 and 298 K). Analogous delocalized mixed-valence complexes are obtained with several polyaromatics as bridging ligands.

The dihydrophenanthrene series also gives rise to chemical coupling upon 2e reduction. On the other hand, the phenanthrene and triphenylene complexes 13 and 14 have a 38e structure, as indicated by Mössbauer, ESR, and NMR data. The Mössbauer parameters also show that much spin density is located on the polyaromatic bridge, indicating that the 38e count is only formal.[128]

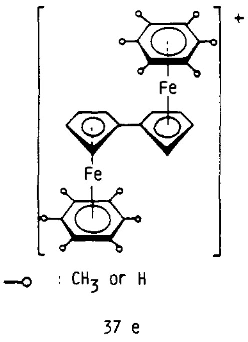


13

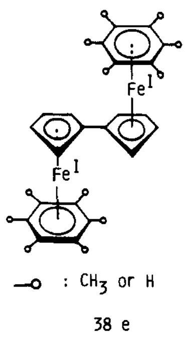


14

The fulvalene series with the C_6Me_6 ancillary ligands provides stable 37e and 38e complexes without chemical coupling in the latter (at 20 °C). The 37e complex 15



15



16

is a metal-centered radical since the induced field (contact, Fermi term) observed in the Mössbauer spectra under 6 T indicates 42% electron on each metal (out of a maximum of 50%).[123] The Mössbauer parameters of **15** are intermediate between those of the 36e and 38e complexes, which indicates that the 38e complex **16** is a true metal-centered biradical.[129] It is subjected to Jahn–Teller activity (as the monomers) above the temperature of the antiferromagnetic transition, unlike **15**, for which the HOMO is not degenerate. The antiferromagnetic transition is observed in **16** at 35 K by magnetic and Mössbauer measurements.[124]

Other biradicals with less than six methyl groups on the arene ligands are also available, and the reactivity of the parent benzene complex is of interest;[130] however, their thermal stability is limited (to -10 °C) as that of the 38e polyaromatic complexes. All these 38e biradicals are conveniently generated by Na/Hg reduction of the dicationic precursors in THF at -15 °C.[123]

VII. Dimerization of 19e Radicals

Since 19e complexes are radicals, they may tend to dimerize. If the radical center is located on the transition metal (e.g., in the heart of the molecular structure) and if the ligands are bulky enough to bring about steric protection of the metal center, then dimerization and other radical type reactions do not occur.

Dimerization through the metal center would add an electron to the metal valence shell. This would make an unlikely total of 20e if no decoordination occurs before or in the course of dimerization. Therefore dimerization of 19e radicals known to occur by metal–metal coupling proceeds via a 17e metal radical intermediate.

Yet the choice of the decoordinated ligand prior to dimerization is not arbitrary although the reports are scarce along this line. The 19e species $CpFe(CO)_2(L)$ and $CpFe(CO)(L)_2$ lose an L ligand before dimerizing.[36] Dimerization is sterically inhibited with some Cp* analogues.[131] Kochi and Amatore showed that the 19e species $Mn(CO)_5(NCMe)$ loses CH_3CN whereas $Mn(CO)_5(PR_3)$ loses either CO or the phosphine, the competition being a direct function of the pK_a value of the phosphine. However, the mechanism of dimerization of these Mn radicals generated by cathodic reduction of the 18e cations does not involve a direct coupling. The 17e species are reduced at the cathode to the 18e anions, which react with the starting cations in a heterolytic pathway[132] (eq 9–12):

$$Mn(CO)_5L^+ + e^- \rightarrow Mn(CO)_5L^\bullet \quad (9)$$

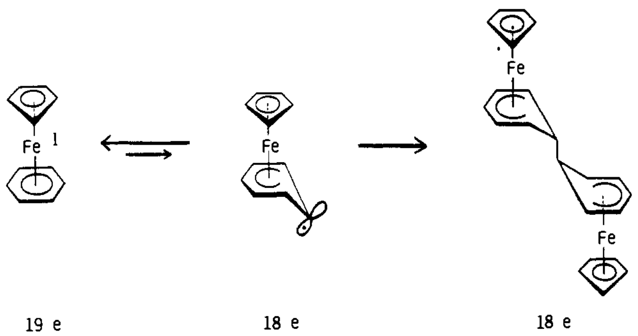
$$Mn(CO)_5L^\bullet \rightarrow Mn(CO)_5^\bullet + L \quad (10)$$

$$Mn(CO)_5^\bullet + e^- \rightarrow Mn(CO)_5^- \quad (11)$$

$$Mn(CO)_5^- + Mn(CO)_5L^+ \rightarrow Mn_2(CO)_{10} + L \quad (12)$$

Another mode of dimerization of 19e radicals is ligand–ligand coupling. This mode does not need to proceed via a 17e intermediate but one may be tempted to believe that so-called 19e radicals that dimerize in such a way are in fact 18e complexes with a ligand-centered radical. This is not necessarily true, at least if one considers the ground-state electronic structure. A typical example is the Fe^I complex $CpFe(C_6H_6)$,[94,133,134] which dimerizes to $[CpFe(\eta^5\text{-}C_6H_6\text{-})]_2$.[94,135,136] This 19e complex has been shown to be a metal-centered radical in which the HOMO has 70% metal character. In addition, the benzene ligand, through which dimerization proceeds, is the part of the molecule having the poorest spin density: only 10% (20% on Cp).[94] A mechanism (Scheme I) may be proposed for dimerization to proceed through a benzene carbon: the 19e complex is in equilibrium with the 18e state (to a small proportion) if this state does not have much higher energy. The radical center therein is thus located on the decoordinated arene carbon through which dimerization subsequently occurs.

SCHEME I



In summary, a ligand-centered *intermediate or transition state is involved in the dimerization of such metal-centered 19e radicals, which should not be confused with the ground-state electronic structure.* However, it is difficult to know whether the transition state is close to reactants or to products since there is a small spin density on the benzene carbons in the ground state (compare the dimerization of $Ph_3C^\bullet$; one of the benzene carbons that couples bears a low spin density).

Interesting trends are observed for methyl-substituted derivatives. The complex $CpFe(C_6Me_5H)$ dimerizes readily[94,136] whereas $CpFe(C_6Me_6)$ and $C_5Me_5Fe(C_6Et_5H)$ do not.[39,100] The presence of up to five methyl substituents on the Cp or benzene ligand accelerates the dimerization. However, this is more marked when the substituents are on the Cp ring. Thus $Cp^*Fe(C_6H_6)$ dimerizes so fast that it is not possible to isolate it in the neat form, contrary to all other Fe^I complexes of monoaromatics.[94] This might seem puzzling at first sight because permethylation increases the energy level of the orbital of the Cp ligand and thus increases the Cp character in the HOMO, which should decrease that on the benzene ligand. In addition, the steric bulk should not favor dimerization. In fact, the e_2 ligand and $e_1{}^*$ metal orbital energies are rather close in $CpFe(C_6H_6)$, and the increase of the $e_1{}^*$ metal level due to permethylation could almost interchange the relative orbital levels, so that the benzene e_2 orbital might become the HOMO of the complex.[63,137] This situation is also generally favorable for partial decoordination,[54] as proposed in Scheme I.

The 18e structure may also be favored when two 19e radicals approach each other; i.e., dimerization is possible because of the change of structure and of spin density distribution along the reaction pathway.

Other 19e sandwich complexes that dimerize very readily are rhodocene[138] and what was proposed to be $Re(C_6Me_6)_2$.[139] Dimerization through methyl-substituted arene carbon probably does not occur. Methyl groups are lost by a retro-Friedel–Crafts mechanism in the course of the Fischer-type synthesis of the cation.[100]

$$\mathrm{ReCl_5} \xrightarrow[\mathrm{C_6Me_6}]{\mathrm{AlCl_3}} \mathrm{Re(C_6Me_{6-n}H_n)_2^+} \xrightarrow{\mathrm{Na/Hg}} [\mathrm{Re}(\eta^5\text{-}\mathrm{C_6Me_{6-n}H_n}\text{-})]_2 \quad (13)$$

Cobaltocene, despite considerable covalency (partial spin density on ligand), does not dimerize. This is possibly due to the fact that, as shown above with the mixed CpFe(arene) complexes, dimerization is more difficult through a Cp than through an arene ligand. Probably, the spin density is largely localized on the Cp ligands in rhodocene since dimerization is fast. This is a general trend for the second- and third-row transition-metal sandwiches, for which partial decoordination tends to occur when the 18e count is overtaken.[56,140,141]

$$2\mathrm{Cp_2M} \rightarrow [\mathrm{CpM}(\eta^4\text{-}\mathrm{C_5H_5}\text{-})]_2 \quad (14)$$

19e: Rh, not Co

Cycloheptatrienyl 19e intermediates or transition states generated by reduction of the precursor cation readily dimerize to bis[(cycloheptatriene)metal tricarbonyl].[142]

$$2[\mathrm{M(CO)_3}(\eta^7\text{-}\mathrm{C_7H_7})]^+ \xrightarrow{e^-} \mathrm{M_2(CO)_6}(\eta^6,\eta^6\text{-}\mathrm{C_{14}H_{14}}) \quad \mathrm{M = Cr, W}$$

$$\xrightarrow{-\mathrm{M(CO)_3}} \mathrm{M(CO)_6}(\eta^6\text{-}\mathrm{C_{14}H_{14}}) \quad (15) \quad \mathrm{M = W}$$

VIII. Other Coupling Reactions and H-Atom Abstraction

The reactions of neutral 19e radicals with organic radicals proceed through a ligand as dimerization and the product adopts an exo stereochemistry:[83,97,143-147]

$$\mathrm{Cp_2Co} \xrightarrow{\mathrm{R^\bullet}} \mathrm{CpCo}(\eta^4\text{-}\mathrm{C_4H_4R}) \quad (16)$$

$\mathrm{R = CCl_3, CH_3, CH{=}CHPh, CH_2C{=}CH, CH_2CO_2R, CCl_2CO_2R}$

$$\mathrm{CpFe(C_6H_6)} \xrightarrow{\mathrm{R^\bullet}} \mathrm{CpFe}(\eta^5\text{-}\mathrm{C_6H_6R}) \quad (17)$$

$\mathrm{R = CCl_3, Ph_3C, PhCH_2, Et, Ph}$

Organic radicals are conveniently generated from the 19e complex and RX to give the 18e cation and halide ion, which consumes half of the 19e complex overall. The reaction of cobaltocene with dihalogenomethane leads to ring extension. Herberich nicely applied this interesting process to dihalogenoboranes, which provided a series of (borabenzene)cobalt complexes.[85-88] The latter are analogues of cobaltocene, with less negative redox potentials. This discovery afforded the development of the chemistry of borabenzene.

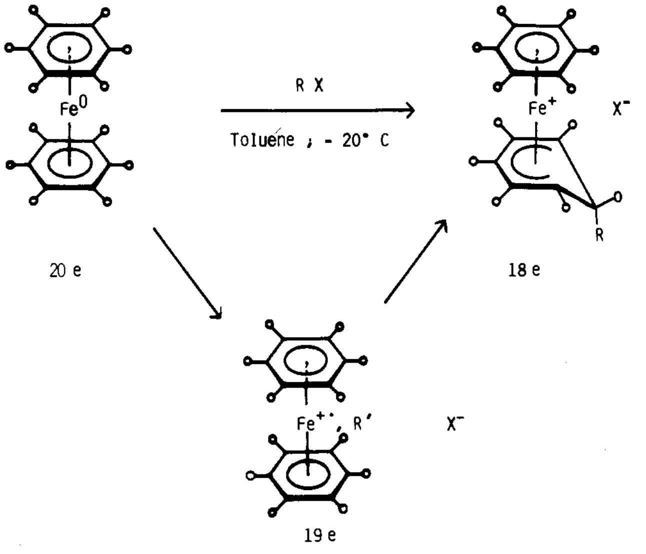
$$\mathrm{Cp_2Co + RBX_2} \rightarrow \mathrm{CpCo}(\eta^6\text{-}\mathrm{C_5H_5BR})^+ \quad (18)$$

$$\mathrm{CpCo}(\eta^6\text{-}\mathrm{C_5H_5BR}) + \mathrm{RBX_2} \rightarrow \mathrm{Co}(\eta^6\text{-}\mathrm{C_5H_5BR})_2^+ \quad (19)$$

Other exo adducts of cobaltocene of the type $(\mathrm{CpCo}(\eta^4\text{-}\mathrm{C_5H_5\text{-}X\text{-}}))_2$ with $\mathrm{X_2 = O_2}$,[148] $\mathrm{C_2F_4}$, and acrylonitrile[149] are known but their mode of formation is not clear.

The reactions of the 20e complex $\mathrm{Fe(C_6Me_6)_2}$ with a variety of functional halides RX lead to 18e cyclohexadienyl complexes[66] resulting from coupling between an arene carbon and $\mathrm{R^\bullet}$ (Scheme II). The reaction is a favorable alternative to the critical addition of organometallics RM to the 18e complexes $\mathrm{Fe(arene)_2^{2+}}$, which invariably gives ET for the $\mathrm{C_6R_6}$ cases (R = H, Me). ET from the 20e complex to RX gives the organic radical $\mathrm{R^\bullet}$ and the 19e radical $[\mathrm{Fe(C_6Me_6)_2}]^+$, which combine to yield the desired functional organometallics. The process is more synthetically productive than that of starting from 19e radicals, a case that leads to the loss of half the starting product used to reduce RX to $\mathrm{R^\bullet}$ (vide supra).

SCHEME II



R = CH$_2$Ph , COPh , CH$_2$CN , CH$_2$CO$_2$Et , CH$_2$CH=CH$_2$. —o : CH$_3$

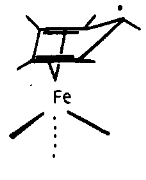
Photolysis of $\mathrm{Cp^*Fe(CO)_2(CH_2Ph)}$ in the presence of L = CO or $\mathrm{PPh_3}$ yields $(\eta^4\text{-}\mathrm{PhCH_2C_5Me_5})\mathrm{Fe(CO)_2L}$, the structure of which was ascertained by X-ray analysis (L = CO).[150] Homolytic cleavage of the iron–benzyl bond and recombination of the benzyl radical with the 19e radical $\mathrm{Cp^*Fe(CO)_2L}$ were demonstrated.

$$\mathrm{Cp^*Fe(CO)_2(CH_2Ph)} \xrightarrow{h\nu} \mathrm{Cp^*Fe(CO)_2^\bullet + PhCH_2^\bullet} \quad (20)$$

$$\underset{17e}{\mathrm{Cp^*Fe(CO)_2^\bullet}} \xrightarrow{\mathrm{L}} \underset{19e}{\mathrm{Cp^*Fe(CO)_2L}} \quad (21)$$

$$\mathrm{Cp^*Fe(CO)_2L + PhCH_2^\bullet} \rightarrow (\eta^4\text{-}\mathrm{PhCH_2\text{-}C_5Me_5})\mathrm{Fe(CO)_2L} \quad (22)$$

The authors conclude that the 19e species $(\mathrm{C_5R_5})\mathrm{Fe(CO)_2L}$ has "considerable radical character in the $\mathrm{C_5R_5}$ system" and suggest the 18e structure **17**:

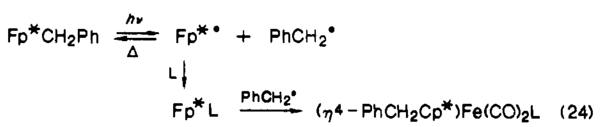


17 (18 e)

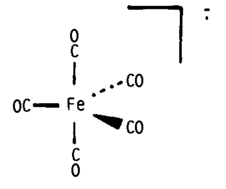
However, one should distinguish the ground-state structure and the intermediate or transition state allowing coupling. We already know that it is not necessary to have a large spin density in the ground state in order to bring about a radical reaction at a given site (cf. section VII on dimerization). It is also more probable that this organoiron radical is a 19e metal-centered radical in the ground state like the isolobal CpFe(arene) complexes.

$$\underset{19e}{\eta^5\text{-}C_5Me_5Fe^\bullet(CO)_2L} \rightleftharpoons \underset{18e}{``\eta^4\text{-}C_5Me_5Fe(CO)_2L"} \quad (23)$$

The benzyl radical combines preferably to the metal center but this reaction is "reversible" whereas coupling to Cp* is not.

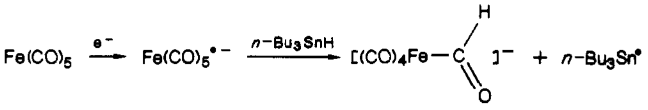


Kochi demonstrated that 19e metal carbonyl species 18, $Cr(CO)_6^{\bullet -}$, and $Mn(CO)_4(PPh_3)_2^\bullet$ generated electrochemically are able to abstract a hydrogen atom from $HSnBu_3$ to give formyl complexes (eq 25).[151,152]



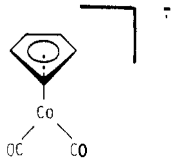
19 e

18



(25)

This idea follows the suggestion by Symons that a 19e anion can be protonated to give a formyl species. During ^{60}Co γ irradiation of $CpCo(CO)_2$, Symons observed the formation the 19e radical anion 19, which further reacts in situ in THF to give CpCo(CO)(CHO).[77]



19 e

19

The H-atom abstraction reactions indicate that there is significant spin density on the C atom of the carbonyl ligand, but again, this spin density need not be "considerable" in the ground state.

These reactions are reminiscent of hydride attack onto diamagnetic metal carbonyl complexes.[153] Indeed, the hydride reduction of several families of complexes, including the carbonyl complex $[Cp^*Fe(\eta^2\text{-dppe})(CO)]^+$, has been shown to proceed by an ET pathway.[131] Thus there is a possibility that, in some instances, hydride reduction of carbonyl complexes to formyl complexes might proceed by an ET pathway involving a 19e species. The hypothesis is also attractive as an alternative Fischer–Tropsch mechanism[60] (eq 26).

$$\underset{18e}{M\text{-}CO^+} \xrightarrow{LiAlH_4} \underset{19e}{M\text{-}CO^\bullet} \xrightarrow{LiAlH_4} \underset{18e}{M\text{-}CHO} \quad (26)$$

IX. Reducing Properties of 19e Complexes

This is perhaps the most obvious property of 19e species since their 1e oxidation should easily provide 18e complexes. However, this is not always true, and the redox potentials of 18e/19e systems span over a wide range. Cationic 19e complexes such as Cp_2Ni^+ and $(arene)_2Fe^+$ have redox potentials close to 0 V vs SCE and can hardly be considered as reducing agents.[47,58,67] The successive replacement of Cp ligands by borabenzenes also leads to lowering the $E°$ values so that bis(borabenzene)cobalt complexes are weaker reducing agents than cobaltocene.[86] The ionization potentials are noted in Table IV.

Another problem to consider if one needs to use a 19e complex as a reducing agent is to avoid radical reactions, e.g., dimerization, coupling with other radicals, and hydrogen- or halogen-atom abstraction. If one wishes to store a 19e radical for further use as a reducing agent, steric protection is necessary in order to inhibit the radical-type reaction. Cobaltocene has been found useful in many instances although its redox potential is not very negative ($E° = -0.9$ V vs SCE).[154,155]

$$Cp_2Co + [(C_5H_5BR)_2Co]^+PF_6^- \rightarrow [Cp_2Co]^+PF_6^- + (C_5H_5BR)_2Co \quad (27)$$

Since CpFe(arene) complexes were found to have much more negative $E°$ values,[156-164] organometallic electron reservoir complexes were designed in this series in order to make more universal reducing agents available.[93]

The C_6Me_6 complex 1, readily synthesized on a large scale from inexpensive reactants such as those of eq 28, was found to be an extremely useful 1e reducing agent, stable up to 100 °C. Detailed synthetic procedures are available.[94,98]

$$Cp_2Fe + C_6Me_6 \xrightarrow[\text{heptane or neat}]{AlCl_3,\ Al} [CpFe(C_6Me_6)]^+ \xrightarrow{Na/Hg} \underset{1}{CpFe(C_6Me_6)} \quad (28)$$

Clean stoichiometric reduction of a variety of organic, organometallic, and inorganic substrates has been achieved.[37,99,165,166]

$$1 + TCNQ \xrightarrow{THF} CpFeC_6Me_6^+,TCNQ^{\bullet -} \quad (29)$$

$$1 + CpFeC_6Me_6^+,TCNQ^{\bullet -} \xrightarrow{THF} [CpFeC_6Me_6^+]_2,TCNQ^{2-} \quad (30)$$

$$1 + 2TCNQ \xrightarrow{THF} CpFeC_6Me_6^+,(TCNQ)_2^- \quad (31)$$

$$1 + \text{phenazine} \xrightarrow{THF} CpFeC_6Me_6^+,\text{phenazine}^{\bullet -} \quad (32)$$

$$1 + \text{bifluorenylidene}^{186} \xrightarrow{THF} CpFeC_6Me_6^+,\text{bifluorenylidene}^{\bullet -} \quad (33)$$

It was found that 1 is a much cleaner reducing agent than Na/Hg and other alkali reducing agents for the 1e reduction of 17e or 18e cationic complexes.[167,168]

$$1 + \underset{17e,\ L\ =\ CO\ \text{or}\ PPh_3}{[Cp^*Fe(\eta^2\text{-}S_2CNMe_2)L]^+PF_6^-} \xrightarrow{THF} 1^+PF_6^- + \underset{18e}{Cp^*Fe(\eta^2\text{-}S_2CNMe_2)L} \quad (34)$$

$$1 + [Cp^*FeL_2CH_3]^+PF_6^- \xrightarrow{THF}$$
17e, L = $^1/_2$dppe or $P(OMe)_3$
$$1^+PF_6^- + \underset{18e}{Cp^*FeL_2CH_3} \quad (35)$$

$$\underset{}{1} + \underset{18e}{[C_6Me_6Fe(\eta^5\text{-}C_6Me_6H)]^+PF_6^-} \xrightarrow{THF} 1^+PF_6^- + \underset{19e}{C_6Me_6Fe(\eta^5\text{-}C_6Me_6H)} \quad (36)$$

Decamethylcobaltocene has also been used occasionally:[56]

$$2Cp^*{}_2Co + [Cp^*MC_6Me_6]^{2+} \rightarrow 2Cp^*{}_2Co^+ + [Cp^*M(\eta^4\text{-}C_6Me_6)]^{2+} \text{ (M = Rh, Ir)} \quad (37)$$

The reduction of substrates having a more negative reduction potential than 1 is exemplified by the reaction of 1 with CO_2, which gives mixtures of carbonate and oxalate.[99,170] Similarly, redox catalysis using 1 or, at best, the water-soluble complex $Cp\text{-}CO_2^-Fe^+C_6Me_6$ allows reduction of NO_3^- to NH_3 ($k = 10^2$ mol^{-1} L s^{-1}) in basic aqueous medium on a Hg cathode at −1.6 V whereas NO_3^- is not reducible in this medium in the absence of the redox catalyst.[171-173] These complexes also serve as redox catalysts for the reduction of protons to H_2

$$2CpFe(C_6Me_6) + 2H_2O \rightarrow 2[CpFe(C_6Me_6)]^+ + H_2 + 2OH^- \quad (38)$$

but it is probable that the mechanism involves an inner-sphere process rather than the thermodynamically unfavorable reduction of H^+ to $H^•$.

Similarly, the reaction of Cp_2Co with H^+ gives only Cp_2Co^+ and H_2 via the hydride $[Cp_2CoH]^+$.[173] Protonation of 19e metal hydride radicals is of interest to build a chemical cycle for the conversion of water to H_2.[174,175]

$$M \xrightarrow{H^+} MH^+ \xrightarrow{e^-} MH \xrightarrow{H^+} M^+ + H_2 \quad (39)$$

$M = CpCo(PR_3)_2$

$PR_3 = P(OMe)_3$ or ½dppm

Cobaltocene also reduces MH^+ according to

$$2Cp_2Co + [CpCo(dppe)H]^+ \rightarrow [Cp_2Co]^+ + CpCo(dppe)H \quad (40)$$

$$Cp_2Co + CpCo(dppe)H \rightarrow CpCo(dppe) + CpCo(C_5H_6) \quad (41)$$

Dioxygen is easily reduced by Fe^I complexes as shown by the ESR spectra of the superoxide anion $O_2^{•-}$ obtained from a solution of Fe^I complexes when air is allowed to diffuse in the frozen THF solution of the ESR tube below −100 °C.[95]

$$CpFe(arene) + O_2 \xrightarrow[-100\ °C]{THF} CpFe(arene)^+,O_2^{•-} \quad (42)$$

In fluid solutions at −80 °C, further reactions proceed in the cage ion pair. If the arene bears a benzylic hydrogen, it can be removed under the form of a proton by $O_2^{•-}$, which finally gives H_2O_2 by dismutation of the $HO_2^•$ radical.[176] Otherwise, $O_2^{•-}$ reacts onto the activated benzene ligand to give nucleophilic addition, and the peroxo intermediate couples with the Fe^I complex to give a peroxo dimer.[177,178] With the less electron rich cobaltocene, the analogous reaction might proceed by direct coupling without ET.[148]

$$CpFe(C_6H_5CH_2R) + \tfrac{1}{2}O_2 \xrightarrow[-80\ °C]{THF} CpFe(\eta^5\text{-}C_6H_5{=}CHR) + \tfrac{1}{2}H_2O_2 \quad (43)$$

$$CpFe(C_6H_6) + \tfrac{1}{2}O_2 \xrightarrow[-80\ °C]{THF} CpFe(\eta^5\text{-}C_6H_6\text{-}O\text{-})_2 + \tfrac{1}{2}H_2O_2 \quad (44)$$

That the first ET step proceeds by an outer-sphere process is indicated by the faster reaction of the bulkier, more electron rich complex $Cp^*Fe(C_6Me_6)$. In the latter, a benzylic proton is abstracted rather than a less acidic C_5Me_5 proton. Similarly, $CpFe(C_6Me_5NH_2)$ reduces O_2 to give abstraction of a more acidic NH_2 proton.[102]

$$Cp^*Fe(C_6Me_6) + \tfrac{1}{2}O_2 \xrightarrow[-80\ °C]{THF} Cp^*Fe(\eta^5\text{-}C_6Me_5CH_2) + \tfrac{1}{2}H_2O_2 \quad (45)$$

$$Cp^*Fe(C_6Me_5NH_2) + \tfrac{1}{2}O_2 \xrightarrow[-80\ °C]{THF} Cp^*Fe(\eta^5\text{-}C_6Me_5NH) + \tfrac{1}{2}H_2O_2 \quad (46)$$

Although the reduction potential of acridine is more negative than that of 1, reduction occurs because the radical anion deprotonates 1^+ in the cage, in the same fashion as $O_2^{•-}$

$$1 + \text{acridine} \rightarrow CpFeC_6Me_6^+,\text{acridine}^{•-} \rightarrow CpFe(\eta^5\text{-}C_6Me_5CH_2) + \text{monohydroacridine}^• \quad (47)$$

The monohydroacridine radical is submitted to the same fate as $HO_2^•$, e.g., dismutation to the starting material and the dihydro derivative.[165]

As appears in the following sections, transient 19e species, which cannot be characterized spectroscopically, can also behave as strong reducing agents (associative ligand substitution, disproportionation, ETC catalysis).

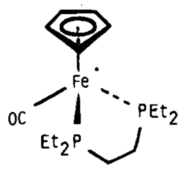
The 19e complexes generated by ligand addition to 17e complexes also behave as reducing agents. A long-known example is $Co(CN)_5^{3-}$, generating the 19e complex $Co(CN)_6^{4-}$ upon addition of $CN^{•-}$.[179]

$$\underset{17e}{Co(CN)_5^{3-}} + CN^- \rightarrow \underset{19e}{Co(CN)_6^{4-}} \quad (48)$$

$$\underset{19e}{Co(CN)_6^{4-}} + \underset{18e}{Co(NH_3)_6^{3+}} \rightarrow \underset{18e}{Co(CN)_6^{3-}} + \underset{19e}{Co(NH_3)_6^{2+}} \quad (49)$$

Analogous reductions of the Co^{III} complexes $Co(NH_3)_5X$ are also feasible for X = PO_4^{3-}, CO_3^{2-}, SO_4^{2-}, and OAc^-.

In the photolytic disproportionation of dimers such as $Cp_2Mo_2(CO)_6$ in the presence of phosphines, Tyler showed[36,180-183] that the intermediate 19e species $CpMo(CO)_2P_2$ reduces the dimers, which propagates a chain mechanism (cf. section XIV). Similarly, the photolytic cleavage of Fp_2 in the presence of depe was shown to generate the 19e species **20**, which can reduce $CpMo(CO)_3Cl$ to $CpMo(CO)_3^-$, $Mo_2(CO)_{10}$ to $Mo(CO)_5^-$, $Cp_2Mo(CO)_6$ to $CpMo(CO)_3^-$, $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$, PQ^{2+} to PQ^+ (paraquat), and Cp_2Co^+ to Cp_2Co.[184,185]



19 e

20

Reduction of water-soluble substrates PQ^{2+} and $Fe(CN)_6^{3-}$ works equally well in micellar solutions when the 19e species $CpFe(CO)_2PBu_3$ is generated by photolysis of Fp_2 in the presence of PBu_3.[186]

$$Cp_2Fe(CO)_4 \xrightarrow{h\nu} 2CpFe(CO)_2^{\bullet} \quad (50)$$

$$\underset{17e}{CpFe(CO)_2^{\bullet}} \xrightarrow[-CO]{dppe} \underset{19e}{CpFeCO(dppe)^{\bullet}} \quad (51a)$$

$$\underset{19e}{CpFeCO(dppe)} + \underset{18e}{[Cp_2Co]^+} \rightarrow \underset{18e}{[CpFeCO(dppe)]^+} + \underset{19e}{Cp_2Co} \quad (51b)$$

The 19e complex $W(CO)_5PPh_3^-$, generated by photolysis of $W_2(CO)_{10}^{2-}$ in the presence of PPh_3, can reduce CO_2 to formate and CO; acetophenone is also reduced.[187]

The ligand can be reduced upon complexation (see also section XII, eq 70–72).

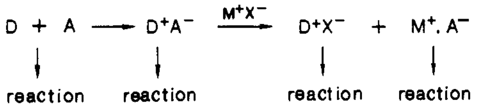
$$W_2(CO)_{10}^{2-} \xrightarrow{h\nu} \underset{17e}{W(CO)_5^{\bullet -}} \xrightarrow{4\text{-}pyCN} \underset{18e}{W(CO)_5(4\text{-}pyCN^{\bullet -})} \quad (52)$$

The reaction of PMe_3 and $P(OMe)_3$ with the 19e complex $CpFe(C_6H_6)$ was shown to produce the 19e intermediate species $CpFeP_3$ (P = PMe_3 or $P(OMe)_3$), which is able to reduce the starting 19e complex to the unstable 20e species $[CpFe(C_6H_6)]^-$ in the presence of $NaPF_6$[130] (cf. section XIII).

As an example of reduction by a 19e species in an electrocatalytic cycle, the species $CpFeL_3$ (L = EtOH, $P(OMe)_3$, PMe_3) reduces $[CpFe(C_6H_6)]^+$ in the cross ET step in the same system as above, but where $CpFe^I(C_6H_6)$ is now introduced only in catalytic amount[188,189] (section XIV).

X. *Special Salt Effects[190] in Reactions of 19e Complexes*

An ET reaction between two neutral species generates an ion pair, and the subsequent reactivity of this ion pair is dramatically dependent on the presence and nature of a salt in the solution.[178,191]



(53)

As can be seen from eq 53, the presence of the salt can lead to ion exchange among the pairs and to follow-up chemistry of the two new ion pairs. The factors that control the overall system are (i) the thermodynamics of the ion pair exchange favoring the association between the ions of comparable sizes, (ii) the thermodynamics of the ET, and (iii) the kinetics of the other reactions.

In the reaction of Fe^I complexes with O_2, the ET reaction is strongly favored by the 1-V difference between the thermodynamic potentials of the two redox systems.[95] Thus, salts have no influence on this ET, but they do strongly influence the follow-up chemistry. We have noted in the above section the reaction of O_2 on Fe^I complexes resulting from the cage reactivity of the ion pair $[CpFe(arene)^+,O_2^{\bullet -}]$. In the presence of $NaPF_6$, this reactivity is totally inhibited because of the thermodynamically favorable ion pair exchange:[177,191]

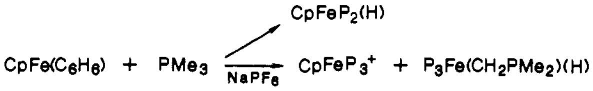
$$[CpFe(arene)^+,O_2^{\bullet -}] + [Na^+,PF_6^-] \rightleftarrows [CpFe(arene)^+,PF_6^-] + [Na^+,O_2^{\bullet -}] \quad (54)$$

Instead of deprotonation or nucleophilic attack, ion pair exchange leads to the formation of $[CpFe(arene)^+]PF_6^-$ and Na_2O_2. The latter results from disproportionation of $O_2^{\bullet -}$, itself induced by Na^+ (vide infra, Fe^I):[178]

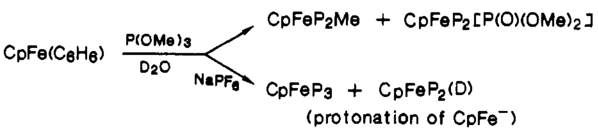
$$\underset{SSIP}{Na^+,THF,O_2^{\bullet -}} \rightarrow \underset{CIP}{Na^+,O_2^{\bullet -}} + THF \quad (55)$$

$$Na^+,THF,O_2^{\bullet -} + Na^+,O_2^{\bullet -} \rightarrow 2Na^+,O_2^{2-} + O_2 + THF \quad (56)$$

Another case is when the ET reaction between A and D is not so exergonic. The presence of the salt can nevertheless lead to the generation of new ion pairs in steady-state amounts that will react rapidly enough to displace the overall system. Then the salt-induced ET is under kinetic control of the follow-up reactions. This type of process is found in the reactions of $CpFe(C_6H_6)$ with P donors.[130] In the absence of salt, radical-type reactions are observed. With 1 equiv of $NaPF_6$, disproportionation of Fe^I to Fe^{II} and Fe^0 is found to proceed quantitatively.



(57)



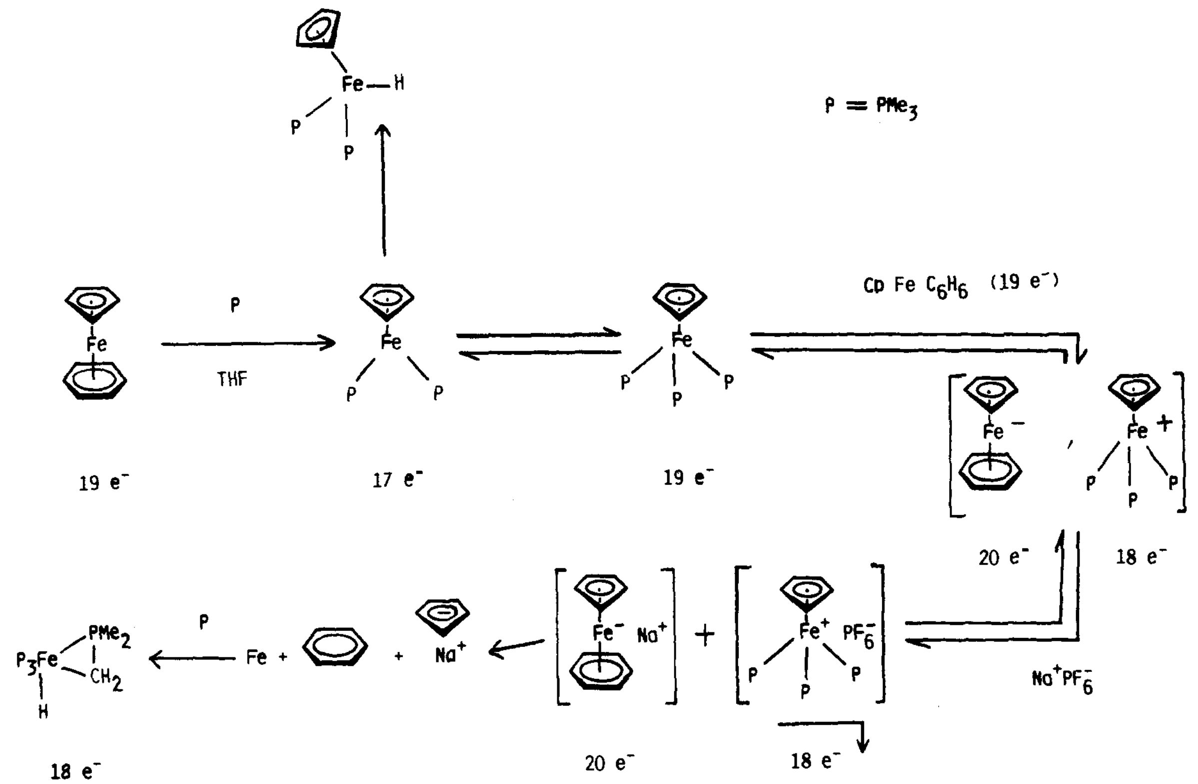
(58)

$$CpFe(C_6H_6) \xrightarrow[\text{(no salt dependence)}]{CO} [CpFe(CO)_2]_2 \quad (59)$$

The key step in the mechanism is the ET from $CpFeP_3$ to $CpFe(C_6H_6)$, giving the large ion pair $[CpFeP_3^+,CpFe(C_6H_6)^-]$. This ET step is favored with good P donors; in the presence of the electron-withdrawing ligand CO, no salt effect is observed. However, the exergonicity of the ET is not a sufficient factor for the disproportionation to proceed because the competing radical reaction is relatively fast. In the absence of salt, the large ion pair is somewhat stabilized despite the lability of the 20e anionic species $CpFeC_6H_6^-$. In the presence of a salt of a small cation such as Na^+, the double exchange among the ion pairs is thermodynamically unfavorable but it generates the extremely reactive ion pair $[CpFe(C_6H_6)^-,Na^+]$. The kinetic control is then in favor of the decomposition of the latter. In the presence of PMe_3, complete decomplexation of the 20e species gives $P_3Fe(PMe_2CH_2)(H)$ whereas in the presence of $P(OMe)_3$, the $CpFe^-$ anion is protonated to generate the hydride $CpFeP_2(H)$ (or $CpFeP_2D$ in the presence of D_2O).

The solvent THF can play the role of the ligand in the absence of an additional ligand. However, displacement of the benzene ligand from $CpFe(C_6H_6)$ is so slow that it hardly competes with the equally slow dimerization (several hours at 20 °C). The presence of 1 equiv of $NaPF_6$ accelerates the disproportionation, and catalytic amounts (7%) were found sufficient to induce complete disproportionation. This indicates that THF ligands may eventually intervene in the ET step of the 19e radical $CpFeL_3$.

SCHEME III



With CpFe[P(OMe)$_3$]$_3$, the 19e species CpFeP$_3$ is a weaker reducing agent than with PMe$_3$ and the ET to CpFe(C$_6$H$_6$) is endergonic. However, the same salt-induced disproportionation occurs because of the kinetic control and because one or two THF molecules could serve as ligands in CpFeP$_{3-n}$S$_n$ (S = THF, P = P(OMe)$_3$).[130]

Another salt effect is found in the reactions of CpFe(C$_6$Me$_6$) with reducible organic substrates such as aldehydes, ketones, and alkynes. It was found that the organic substrates couple with the Cp ligand in the absence of salt whereas they are reduced in the presence of 1 equiv of NaPF$_6$.[192]

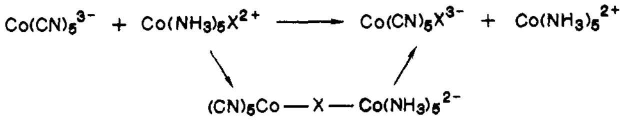
$$\mathrm{CpFeC_6Me_6} + \mathrm{RCOR'} \xrightarrow[\mathrm{NaPF_6}]{\mathrm{MeOH}} [\mathrm{CpFeC_6Me_6}]^+\mathrm{PF_6}^- + \mathrm{RCHOHR'} \quad (60)$$

In summary, simple Na$^+$ salts can be used to inhibit cage reactions, to induce ET, and to orientate synthetic redox processes.

XI. Intermediacy of 19e Species in Inner-Sphere Reactions

(a) Inner-Sphere ET Reactions

This type of reaction was pioneered by Halpern's study of the redox reaction between Co(CN)$_5^{3-}$ and Co(NH$_3$)$_5$X^{2+} (X = Cl$^-$, Br$^-$, I$^-$, N$_3^-$, OH$^-$, NCS$^-$),[193,194] which demonstrated the intermediacy of the bridged species A.



$$\mathrm{Co(CN)_5}^{3-} + \mathrm{Co(NH_3)_5X}^{2+} \longrightarrow \mathrm{Co(CN)_5X}^{3-} + \mathrm{Co(NH_3)_5}^{2+}$$
$$\underset{\mathrm{A}}{\mathrm{(CN)_5Co{-}X{-}Co(NH_3)_5}^{2-}} \quad (61)$$

The base-induced disproportionation of V(CO)$_6$ was also shown to proceed by inner-sphere ET through a bridging isocarbonyl.[195]

$$\mathrm{V(CO)_6} + \mathrm{L} \rightarrow \mathrm{V(CO)_5L} + \mathrm{CO} \quad (62a)$$

$$\mathrm{V(CO)_5L} + \mathrm{V(CO)_6} \rightarrow \underset{\mathrm{B}}{\mathrm{(CO)_5V^+{-}O{-}C{-}V^-(CO)_5}} + \mathrm{L} \quad (62b)$$

$$\mathrm{B} + \mathrm{V(CO)_6} \xrightarrow{\mathrm{L}} \mathrm{(CO)_5V{-}C{-}O{-}VL_4{-}O{-}C{-}V(CO)_5} \quad (63)$$

CpFe(CO)$_2^\bullet$ reacts with [Fe(CN)$_6$]$^{3-}$ to give the CN-bridged complex [Cp(CO)$_2$Fe–NC–Fe(CN)$_5$]$^{3-}$.[36,196]

In these reactions, a 19e species, formed between the 17e radical and the base, is the precursor of the bridged intermediate.

(b) Atom Abstraction Reactions

Halpern[197–199] and Kwiatek[179] extensively studied the reactions of Co(CN)$_5^{3-}$ with organic halides:

$$2\mathrm{Co(CN)_5}^{3-} + \mathrm{RX} \rightarrow \mathrm{Co(CN)_5X}^{3-} + \mathrm{Co(CN)_5R}^{3-} \quad (64a)$$

The mechanism was shown to occur in two steps, the first one being halogen-atom abstraction. The overall reaction follows a second-order rate law

$$-d[\mathrm{Co(CN)_5}^{3-}]/dt = k[\mathrm{Co(CN)_5}^{3-}][\mathrm{RX}]$$

$$\mathrm{Co(CN)_5}^{3-} + \mathrm{RX} \rightarrow \mathrm{Co(CN)_5X}^{3-} + \mathrm{R}^\bullet \quad (64b)$$

$$\mathrm{Co(CN)_5}^{3-} + \mathrm{R}^\bullet \rightarrow \mathrm{Co(CN)_5R}^{3-} \quad (65)$$

The RX adduct C was proposed for the transition state in the first step. A 19e count has been suggested for this adduct.[36]

$[(CN)_5Co\text{-}X\text{-}R]^{3-}$

C

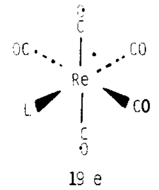
XII. The Fast 17e/19e Interconversion

It was recognized by Poë et al.[200,201] that the 17e radical $Re(CO)_5^{\bullet}$ generated by photolysis of the metal-metal-bonded dimer $Re_2(CO)_{10}$ undergoes ligand substitution via an associative mechanism.[202,203] This means that the reaction proceeds via the 19e intermediate or transition state **21**.

$$\underset{}{Re_2(CO)_{10}} \xrightarrow{h\nu} \underset{17e}{2ReCO_5^{\bullet}} \qquad (66)$$

$$\underset{17e}{Re(CO)_5^{\bullet}} + L \rightarrow \underset{19e}{Re(CO)_5L^{\bullet}}\ (L = PR_3) \qquad (67)$$

$$\underset{19e}{Re(CO)_5L^{\bullet}} \rightarrow \underset{17e}{Re(CO)_4L^{\bullet}} + CO \qquad (68)$$



21

The manganese analogue was shown to follow the same pathway,[202a] and so were the substituted radicals $MnCO_3L_2$ (M = Mn, Re).[202b] The stable 17e complex $V(CO)_6$ was found to undergo facile ligand substitution with phosphines and arsines according to a second-order rate law and activation parameters $\Delta H^{\ddagger} = 10.0 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -27.8 \pm 1.6$ cal mol^{-1} K^{-1} (with PPh_3), consistent with an associative mechanism involving the 19e species **22** as intermediate or transition state.[204,205]

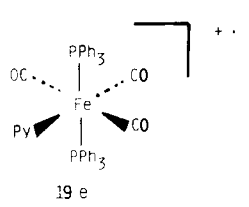
22

19 e

In the presence of pyridine,[206] $[Fe(CO)_3(PPh_3)_2]^+$ undergoes disproportionation according to

$$2[Fe(CO)_3(PPh_3)_2]^+ + 6py \xrightarrow{CH_2Cl_2} Fe(py)_6^{2+} + Fe(CO)_3(PPh_3)_2 + 3CO + 2PPh_3 \qquad (69)$$

Trogler et al. showed that the rate-limiting step of this reaction is associative attack of py on the iron center forming the 19e intermediate or transition state **23**.



23

Tyler et al. showed that disproportionation of the 17e radicals $MnCO_5^{\bullet}$, $CpMo(CO)_3^{\bullet}$, and $CpFe(CO)_2^{\bullet}$ in the presence of ligands involves a chain mechanism with 19e intermediates such as $MnN_3(CO)_3^{\bullet}$ (N_3 = diethylenetriamine), $CpMo(CO)_2P_2$ (P = phosphine), and $CpFeCO(dppe)^{\bullet}$. Evidence for the chain mechanism is provided by the high quantum yields ($\Phi \gg 1$) measured for the photolysis of the dimeric precursor of the 17e radicals.

In some instances, 17e metal carbonyl radicals can be trapped by reactions with 2e ligands having a delocalized system. In these cases, the complexes obtained are stable because they are 18 VE and the entering ligand is reduced by the metal; the delocalized ligand thus bears the radical center (see Table IV).[187]

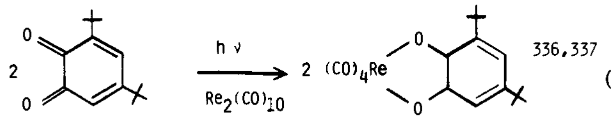
$$M_2(CO)_{2n} + 2P_2 \xrightarrow{h\nu} 2M(CO)_{n-1}P_2 + 2CO^{348} \qquad (70)$$

$Mn_2(CO)_{10}$, $Co_2(CO)_8$;

P_2 = 2,3-bis(diphenylphosphino)maleic anhydride

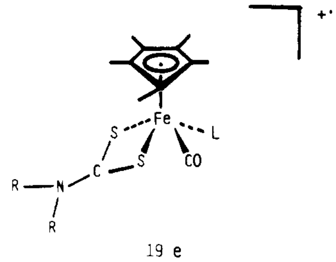
$$Mn_2(CO)_{10} + 2t\text{-Bu-DAB} \xrightarrow{h\nu} 2Mn(CO)_4(t\text{-Bu-DAB})^{216,217} \qquad (71)$$

DAB = 1,4-diaza-1,3-butadiene



(72)

The fast interconversion of 17e and 19e species is now well recognized in several mechanisms. It was shown that ligand substitution proceeds 10^6–10^{10} times faster in 17e radicals than in isostructural 18e species.[205,206] This is due to the fact that the associative pathway is readily available only for the 17e radical. A comparison of substitution rates in 17e radicals shows that the rates decrease as the transition-metal center becomes sterically less accessible. Thus it is likely that 19e species are formed in the presence of a ligand in the mechanisms involving 17e species that are not overcrowded. For instance, coordinating solvents (S) such as THF, acetone, or acetonitrile can serve as entering ligands. The oxidation of 18e complexes in such solvents falls into this category, and some cases of detection of 19e species are given in section XV. As an example, the 17e complex $[Cp^*Fe(dtc)(CO)]^+$ is indefinitely stable in the solid state but rapidly loses CO to provide $[Cp^*Fe(dtc)(S)]^+$ in any of these solvents.[169b,207] If, on the other hand, the coordination sphere is more crowded as in the 17e complex $[CpFe(\eta^2\text{-dppe})CH_3]^+$, no ligand exchange reaction occurs.[168] This behavior is a striking illustration of the necessity of an associative mechanism involving 19e intermediates or transition states such as **24** in ligand exchange reactions of 17e complexes.

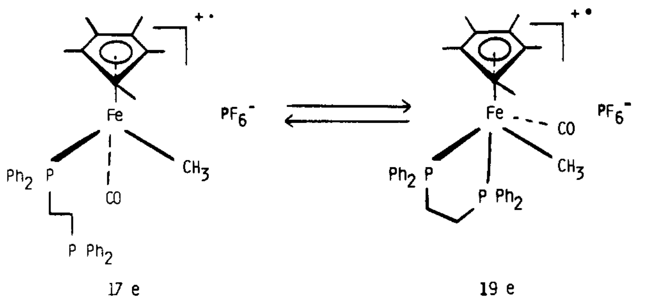


24

\ MeCN, Me$_2$CO, THF

The stability of the 17e complexes $[Cp^*Fe(P)(CO)CH_3]^+$ was found to depend markedly on the nature of P. Even with the bulky phosphine P = PPh_3, the complex was unstable whereas it was found to be per-

SCHEME IV



fectly stable with P = η^1-dppe. It was proposed that this dichotomy could be taken into account by the equilibration of the 17e dppe complex with the 19e chelate form (Scheme IV).

As indicated in section XIV, the 17e/19e interconversion is important for the mechanism of ETC reactions.[41,208]

The 17e species are often easier to characterize than 19e species when they are in fast equilibrium with the latter, which means that they should often be more stable in these many instances. This is the case for the 17e complexes $V(CO)_6$[204] and $Mn(CO)_3P_2$.[203] Monoelectronic reduction of $[Cp^*Fe(\eta^2\text{-dppe})(CO)]^+$ by $LiAlH_4$ at −80 °C yields the hydride $Cp^*Fe(\eta^1\text{-dppe})(CO)(H)$ via the 19e species $Cp^*Fe(\eta^2\text{-dppe})CO$, which rapidly decoordinates to give the 17e species $Cp^*Fe(\eta^1\text{-dppe})(CO)$[131] (see section XV).

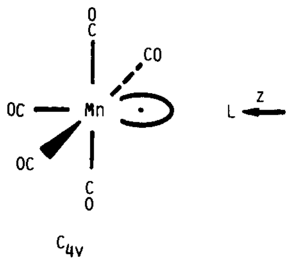
This trend is of course by no means general given the reasonable number of 19e complexes now available. Tyler has proposed evidence indicating that 19e adducts are, in some cases, thermodynamically downhill with respect to 17e precursors and the Lewis base:[209]

$$\underset{17e}{CpMo(CO)_3} + X^- \rightarrow \underset{19e}{CpMo(CO)_3X^-} \qquad (73)$$

The formation of this 19e species is crucial to the mechanism of the photochemical disproportionation of $Cp_2Mo_2(CO)_6$ in the presence of halides or of pseudohalides shown by Tyler (see also section XIV).

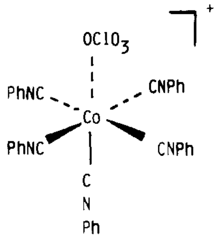
One may question the origin of this extremely fast 17e/19e interchange. The addition of a 2e ligand to a 17e fragment such as $Mn(CO)_5^\bullet$ must take into account the stereochemistry of the latter.

25



The species **25** has a C_{4v} symmetry and an unpaired electron in a d_{z^2} orbital along the z axis.[210] This antibonding orbital provides a formal bond order of $^1/_2$ for the M–CO apical bond. The approach of the 2e ligand L along the z axis results in the formation of a pair of bonding and antibonding orbitals. The bond order of $^1/_2$ is now split in the M–CO and M–L ($^1/_4$ each), which explains the facile substitution process.[36]

As an illustration, the X-ray crystal structure of **26**, recorded by Raymond et al., shows a bond distance between Co and a perchlorate oxygen atom that is intermediate (2.59 Å) between a single bond and a van der Waals interaction (0.1 bond order using the Pauling equation).[211] This complex thus contains a 17e cation with a very loose perchlorate ligand approaching the Co center toward the 19e structure.



26

The ESR data on 19e metal halide carbonyl complexes recorded by Symons[78] showing that the antibonding HOMO is a metal–halogen d_{z^2}–p_z orbital also substantiate this view.

XIII. Ligand Exchange Reactions of 19e Complexes

Most ligand substitution reactions of 19e complexes are due to the fast 17e/19e interconversion (section XII) and therefore follow a dissociative mechanism:[121,212–219]

$$Mn(CO)_3(NCMe)_3 + PPh_3 \rightarrow Mn(CO)_3(NCMe)_2PPh_3 + MeCN \qquad (74)$$

$$Mn(CO)_3(NCMe)_2(PPh_3) + PPh_3 \rightarrow Mn(CO)_3(NCMe)(PPh_3)_2 \qquad (75)$$

$$Mn(CO)_4(bpy)^- + PPh_3 \rightarrow Mn(CO)_3PPh_3(bpy)^- + CO \qquad (76)$$

$$Mn(CO)_4Q + t\text{-Bu-DAB} \rightarrow Mn(CO)_3Q(\eta^1\text{-}t\text{-Bu-DAB}) \qquad (77)$$

Q = 3,5 di-*tert*-butyl-*o*-benzoquinone

DAB = 1,4-diaza-1,3-butadiene

$$CpMo(CO)_2(C\text{-hex-DAB}) + PPh_3 \rightarrow CpMo(CO)PPh_3(C\text{-hex-DAB}) + CO \qquad (78)$$

In the two last examples, one is in fact dealing with ligand substitutions of 18e complexes having a radical-centered ligand.

The exchange of polyhapto ligands is rare. Exchange of benzene for naphthalene was reported to proceed in 6% yield in $CpFe^I$(naphthalene), characterized by oxidation to the 18e cation.[133]

$$CpFe^I(C_6H_6) + \text{naphthalene} \rightarrow CpFe^I(\eta^6\text{-naphthalene}) + C_6H_6 \qquad (79)$$

Ligand exchange of 19e complexes leading to 18e complexes can be performed (i) by exchange of a 6e arene ligand by two 2e ligands, leading to a 17e species that will dimerize, abstract a H atom from the medium, release a H atom to the medium, or initiate a radical version of the Arbuzov rearrangement[130–133,220,221] (It is likely that these ligand exchange reactions start with a rapid preequilibrium $CpFe(\eta^6\text{-}C_6H_6) \rightleftharpoons CpFe(\eta^4\text{-}C_6H_6)$, avoiding associative attacks with 21e intermediates or transition states. This still remains to be demonstrated, however.[130b])

$$CpFe^{I}C_6H_6 + CO \rightarrow [CpFe(CO)_2]_2 \tag{80}$$

$$C_5(CD_3)_5Fe[C_6(CD_3)_6] + CO \rightarrow [C_5(CD_3)_5Fe(CO)_2]_2 \tag{81}$$

$$CpFe(C_6H_6) + PMe_3 \rightarrow CpFe(PMe_3)_2H \tag{82}$$

$$CpFe(C_6H_6) + C_5H_6 \rightarrow Cp_2Fe \tag{83}$$

$$CpFe(C_6H_6) + P(OMe)_3 \rightarrow CpFe[P(OMe)_3]_2[P(O)(OMe)_2] \tag{84}$$

(ii) by exchange of a 5e ligand with two 2e ligands:[145]

$$Cp_2Co + 2L \rightarrow CpCoL_2 \tag{85}$$

$$L = CO, PR_3$$

(iii) by 17e/19e interconversion followed by oxidation in situ of the new 19e species:

(a) disproportionation (see sections IX and XIV); for example[185,222]

$$Fp^{\bullet} + depe \rightarrow CpFe(depe)(CO)^{\bullet} + CO \tag{86}$$

$$CpFe(depe)(CO)^{\bullet} + Fp^{\bullet} \rightarrow CpFe(depe)(CO)^{+},Fp^{-} \tag{87}$$

(b) oxidation by an external reagent (see section IX); for example[184]

$$CpFe(dppe)(CO)^{\bullet} + Fe(CN)_6^{3-} \rightarrow CpFe(dppe)(CO)^{+} + Fe(CN)_6^{4-} \tag{88}$$

(c) ETC catalysis (see section XIV); for example[188–190]

$$CpFe(C_6H_6) + S \rightarrow CpFeS_3 \tag{89}$$

$$CpFeS_3 + [CpFe(C_6H_6)]^{+} \rightarrow [CpFeS_3]^{+} + CpFeC_6H_6 \tag{90}$$

$$S = \text{ethanol}, P(OMe)_3$$

XIV. 19e Intermediates or Transition States in Electrocatalysis

Electrocatalysis or electron transfer chain (ETC) catalysis is the catalysis of reactions by electrons without net current flow (as opposed to redox catalysis, which means catalysis of reduction or oxidation by redox mediators, thus involving a net current flow.[223] Pioneered by Kornblum[224,225] and Russell[226,227] in organic chemistry[228–234] and by Taube[235] in inorganic reactions,[230–236] it was first applied to an organometallic system by Feldberg, who also set up the method of finite differences for the computer simulation of kinetic analysis of the electrochemical data.[237]

This latter technique has been much improved by Savéant and Amatore[239,240] and is currently used by Kochi.[41]

The simplest organometallic reaction, ligand exchange, has been the most studied one.[41,208,233] There are also some examples of migratory CO insertion, isomerization, decomplexation, and chelation reactions.[208] Recently, the coupling of electrocatalysis with organometallic catalysis was shown to be efficient for alkyne polymerization.[241]

The chain induction can be effected by an oxidant (anode, 17e complex such as ferricinium, organic or inorganic oxidant, or excited state whose redox properties with respect to the ground state have been amplified[251]) or by a reducing agent (cathode, 19e complex such as Cp_2Co or $CpFe(C_6R_6)$ (R = H or Me), or organic or inorganic reducing agent). Ligand exchange reactions have been electrocatalyzed for mono- and polynuclear complexes. Note that 19e intermediates or transition states are involved in both types of electrocatalysis induced by an oxidizing or by a reducing agent.

initiation by oxidant

$$\underset{18e}{ML} - e^- \rightarrow \underset{17e}{ML^{\bullet+}} \tag{91}$$

propagation

$$\underset{17e}{ML^{\bullet+}} + L' \rightarrow \underset{17e}{ML'^{\bullet+}} + L \tag{92}$$

$$\underset{17e}{ML'^{\bullet+}} + \underset{18e}{ML} \rightarrow \underset{18e}{ML'} + \underset{17e}{ML^{\bullet+}}$$

initiation by a reducing agent

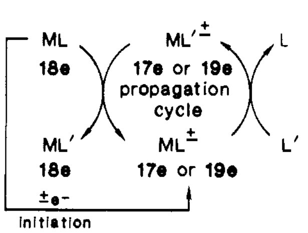
$$\underset{18e}{ML} + e^- \rightarrow \underset{19e}{ML^{\bullet-}} \tag{93}$$

propagation

$$\underset{19e}{ML^{\bullet-}} + L' \rightarrow \underset{19e}{ML'^{\bullet-}} + L \tag{94}$$

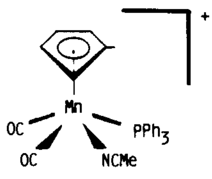
$$\underset{19e}{ML'^{\bullet-}} + \underset{18e}{ML} \rightarrow \underset{18e}{ML'} + \underset{19e}{ML^{\bullet-}} \tag{95}$$

cyclic scheme



Initiation by Oxidation

The role of 19e intermediates or transition states in oxidatively induced electrocatalytic ligand exchange reactions was first demonstated by Kochi[242–244] in his study of the manganese complexe (M = MeCpMn(CO)$_2$). The exchange of the ligands CH_3CN, pyridine, and THF by the less electron-releasing ligands phosphines, phosphites, and isonitriles is possible because the cross ET propagation step is exergonic. Analysis of the kinetics using simulation of the cyclic voltammograms led Kochi to conclude that the ligand exchange between the 17e species in the first propagation step is associative. The examination of the activation parameters (negative entropy of activation) also confirms this mechanism ($\Delta H^{\ddagger} = 4.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -25$ eu for the exchange of MeCN by PPh_3). Thus the 19e species **27** is the intermediate or transition state:

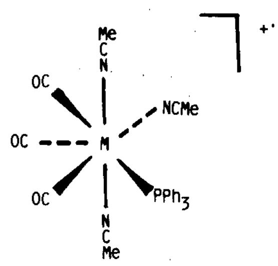


27

$$\underset{17e}{M(MeCN)^{+}} + PPh_3 \rightarrow \underset{19e}{\text{“}M(MeCN)PPh_3{}^{+}\text{”}} \rightarrow \underset{17e}{M(PPh_3)^{+}} + MeCN \tag{96}$$

Moreover, Kochi and Amatore showed that the second-order rate constants for ligand exchange of parasubstituted pyridines with a variety of phosphines was strongly dependent on both the steric and electronic constraints of the entering P ligand.[244]

The complexes $M(CO)_{6-n}(MeCN)_n$ (M = Mo, W; $1 \leqslant n \leqslant 3$) behave in a related way.[245,246] Induction by a small anodic current leads to electrocatalytic ligand exchange with PPh_3 or *t*-BuNC but the associative mechanism could not be proven in this case. It was suggested, however, based on the lack of reaction of the Cr analogues (the 19e intermediate or transition state **28** would be disfavored owing to steric limitation at the Cr center).



28

19 e

M = Mo, W

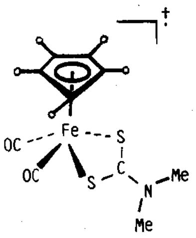
The monodentate dithiocarbamate complexes $(C_5R_5)Fe(CO)_2(\eta^1\text{-dtc})$ (R = H or Me) give the chelate complexes $(C_5R_5)Fe(CO)(\eta^2\text{-dtc})$ upon addition of catalytic amounts of ferricinium[39,246] or of anodic current.[207] The anodic oxidation is completely irreversible even at scan rates reaching 5000 V s^{-1}. Since other 17e Fe^{III} complexes such as $[Cp^*Fe(CO)(\eta^1\text{-dppe})CH_3]^+$ are stable, it is believed that the fast reaction of the cation $[(C_5R_5)Fe(CO)_2(\eta^1\text{-dtc})]^+$ is due to the entropy-favored attack of the free sulfur onto the cationic iron center (i.e., the process is associative and involves a 19e intermediate or transition state).

$$\underset{18e}{Cp(CO)_2Fe(\eta^1\text{-dtc})} \xrightarrow{-e^-} \underset{17e}{Cp(CO)_2Fe(\eta^1\text{-dtc})^{\bullet +}} \quad (97)$$

$$\underset{17e}{Cp(CO)_2Fe(\eta^1\text{-dtc})^{\bullet +}} \rightarrow \underset{19e}{Cp(CO)_2Fe(\eta^2\text{-dtc})^{\bullet +}} \quad (98)$$

$$\underset{19e}{\text{“}Cp(CO)_2Fe(\eta^2\text{-dtc})^{\bullet +}\text{”}} \rightarrow \underset{17e}{Cp(CO)Fe(\eta^2\text{-dtc})^+} \quad (99)$$

$$Cp(CO)Fe(\eta^2\text{-dtc})^+ + Cp(CO)_2Fe(\eta^1\text{-dtc}) \rightarrow Cp(CO)Fe(\eta^2\text{-dtc}) + Cp(CO)_2Fe(\eta^1\text{-dtc})^+ \quad (100)$$



29

—o = H or Me

Initiation by Reduction

The initiation by reducing agents or by a cathodic current gives CO exchange[247-249] by other ligands but this type of process suffers low yields and Coulombic efficiencies because of the side reactions of the 19e or 17e metal carbonyl anions such as dimerization. A typical mechanism could be formulated as follows:

initiation

$$Fe(CO)_5 + e^- \rightarrow \underset{\mathbf{16}}{Fe(CO)_5^{\bullet -}}(19e) \quad (101)$$

propagation

$$Fe(CO)_5^{\bullet -}\ (19e) \rightarrow Fe(CO)_4^{\bullet -}\ (17e) \quad (102)$$

$$Fe(CO)_4^{\bullet -}\ (17e) + P \rightarrow Fe(CO)_4P^{\bullet -}\ (19e) \quad (103)$$

$$Fe(CO)_4P^{\bullet -}\ (19e) + Fe(CO)_5 \rightarrow Fe(CO)_4P + Fe(CO)_5^{\bullet -} \quad (104)$$

termination

$$Fe(CO)_4^{\bullet -} \rightarrow Fe_2(CO)_8^{2-} \quad (105)$$

A 19e species (analogue or **20**) generated by photolysis of Fp_2 with dppe can electrocatalyze CO exchange by dppe in Fe complexes via reductive initiation.

$$Fe(CO)_5 \xrightarrow[\text{dppe}]{e^-} Fe(CO)_4(\eta^1\text{-dppe}) \quad (106)$$

The decomplexation of complexes $[CpFe(arene)]^+$ was shown to be catalyzed by a cathodic current in 95% ethanol when the arene ligand is not peralkylated. The decomplexation reaction proceeds via the 19e radical $CpFe^I(arene)$, which further loses the arene ligand replaced by solvent molecules.[188] The following electrocatalytic mechanism was proposed:

initiation

$$CpFe(arene)^+ \xrightarrow{e^-} CpFe^I(arene) \quad (107)$$

propagation

$$CpFe^I(arene) + nS \rightarrow CpFeS_n + arene \quad (108)$$

$$CpFeS_n + CpFe(arene)^+ \rightarrow CpFeS_n^+ + CpFe(arene) \quad (109)$$

$$CpFeS_n^+ \xrightarrow{H_2O} C_5H_6 + Fe(OH)_2 + nS \quad (110)$$

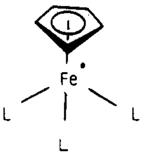
$$S = EtOH;\ arene = C_6H_{6-n}Me_n\ (n < 6)$$

Although the nature of the intermediate is not known, it is probable that it involves an electron-rich 19e species $CpFeS_3$. The latter would be more electron-rich than $CpFeS_2$, and this property is required for the exergonicity of the cross ET step. In the presence of $P(OMe)_3$, the cation $CpFe[P(OMe)_3]_3^+$ is trapped in acetonitrile solution.[189] The electrocatalytic synthesis of $CpFeL_3^+$ is now conveniently available on a large scale in THF suspension using the 19e complex $CpFeC_6H_6$ as the catalyst and is probably the easiest way to the carbonyl-free piano-stool complexes.[190]

$$CpFe(C_6H_6)^+PF_6^- + L \xrightarrow[\text{THF}]{1\%\ CpFeC_6H_6} CpFeL_3^+PF_6^- + C_6H_6 \quad (111)$$

$$L = P(OMe)_3,\ PMe_3$$

Note that in this type of electrocatalytic process, 19e species **30** are involved in both the initiation and the propagation steps.



30 19 e

L = solvent or P donor $L_3 = C_6H_6$

A process parallel to ETC catalysis is H-atom-transfer chain catalysis. In the latter, initiation can be provided either by ET or by H-atom transfer using AIBN homolysis. The decarbonylation of formyl rhenate complexes can be catalyzed by either means.[250a]

initiation

$$\text{(re)CHO} + \text{Me}_2\text{C}^{\bullet}\text{CN} \rightarrow \text{(re)CO}^{\bullet} + \text{Me}_2\text{CHCN} \quad (112)$$

propagation

$$\text{(re)CO}^{\bullet} \rightarrow \text{re}^{\bullet} + \text{CO} \quad (113)$$

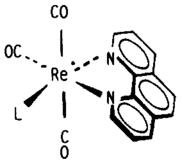
$$\text{re}^{\bullet} + \text{(re)CHO} \rightarrow \text{(re)H} + \text{(re)CO}^{\bullet} \quad (114)$$

$$\text{re} = \text{(CO)}_5\text{ReRe(CO)}_4^-$$

The intermediacy of 19e species ((re)CO$^{\bullet}$) is involved as well in this process. Kochi's group also demonstrated that the cathodic reduction of $(CO)_3Mn(NCMe)_3^+$ in the presence of PPh_2Me gives $(CO)_3Mn(PPh_2Me)_2(H)$ via (i) electrocatalytic exchange of two NCMe ligands by PPh_2Me, (ii) ET, providing the 19e complex $(CO)_3Mn(NCMe)_2(PPh_2Me)_2^+$, (iii) H-atom transfer to a carbonyl carbon, providing the formyl species $(CO)_2Mn(NCMe)(PPh_2Me)_2(CHO)$, and (iv) H-atom-transfer chain catalysis of decomposition of this formyl complex to $(CO)_3Mn(PPh_2Me)_2(H)$ as in eq 113 and 114.[250b]

Photoelectrocatalysis

Possibly the most interesting example of ETC catalysis involving the intermediacy of 19e complexes was reported by Wrighton and uses an excited-state ET in Re complexes.[251] The exchange of the CH_3CN ligand by PPh_3 is propagated at the 19e level 31 after photoionization has produced the 19e initiator. The excited state is a strong oxidant ($E°$ = 1.5 V vs SCE) that is quenched by PPh_3 to provide the 19e species. Thus PPh_3 plays both the role of the quencher and that of the incoming ligand:



31 19 e

L = CH_3CN , PPh_3

initiation

$$\text{[Re]CH}_3\text{CN}^+ \xrightarrow{h\nu} \text{[Re]CH}_3\text{CN}^{+*} \quad (115)$$

$$\underset{18e}{\text{[Re]CH}_3\text{CN}^{+*}} + \text{PPh}_3 \rightarrow \underset{19e}{\text{[Re]CH}_3\text{CN}} + \text{PPh}_3^+ \quad (116)$$

propagation

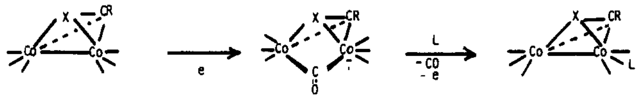
$$\underset{19e}{\text{[Re]CH}_3\text{CN}} + \text{PPh}_3 \rightarrow \underset{19e}{\text{[Re]PPh}_3} + \text{CH}_3\text{CN} \quad (117)$$

$$\underset{19e}{\text{[Re]PPh}_3} + \underset{18e}{\text{[Re]CH}_3\text{CN}^+} \rightarrow \underset{18e}{\text{[Re]PPh}_3^+} + \underset{19e}{\text{[Re]CH}_3\text{CN}} \quad (118)$$

$$\text{[Re]} = \text{Re(CO)}_3\text{(phen)}$$

The reaction can also be more classically induced by a Pt cathode at a controlled potential of −1.1 V vs SCE in CH_3CN/0.1 M n-Bu_4NClO_4.

SCHEME V



X = RC or Co(CO)$_3$

Electrocatalysis in Clusters

Electrocatalysis of ligand substitution is also very useful in cluster chemistry, for which only initiation by reducing agents (or by a cathode) is efficient.[252-267] Rieger, who opened this field,[247] suggested that cluster radical anions generate 17e metal centers by cleavage of metal–metal bonds. Substitution would then proceed at the 17e center by an associative mechanism that thus involves a 19e intermediate or transition state (Scheme V).

Mechanistic studies of the electrocatalytic replacement of CO by $P(OMe)_3$ in the phosphinidene cluster $Fe_3(CO)_9(\mu_3\text{-}PPh)_2$ in acetonitrile led Kochi to show that cleavage of an Fe–P bond in the radical anion occurs before substitution at a 17e center[263-265] (Scheme VI). If one assumes that the ligand exchange then follows an associative pathway at this 17e iron center, it means that a 19e intermediate or transition state is involved along this pathway. Thus it appears that the implication of such species is general for electrocatalytic ligand exchange in clusters as well as in mononuclear complexes.

Migratory CO Insertion

Besides all these ligand exchange reactions, electrocatalysis has been used for isomerization[268-272] and for migratory CO insertion.[273-276] Whereas mechanistic studies have not yet proven the intermediacy of 19e species in the former, there is ample evidence in the latter.

Cathodic reduction was found by Vlček to electrocatalyze the migratory CO insertion in the Fe–CH_3 bond of $CpFe(CO)_2Me$ in THF in the presence of PPh_3.[273] The reaction involves the intermediacy of a 19e species:

initiation

$$\underset{18e}{\text{CpFe(CO)}_2\text{Me}} + e^- \rightarrow \underset{19e}{\text{CpFe(CO)}_2\text{Me}^{\bullet-}} \quad (119)$$

propagation

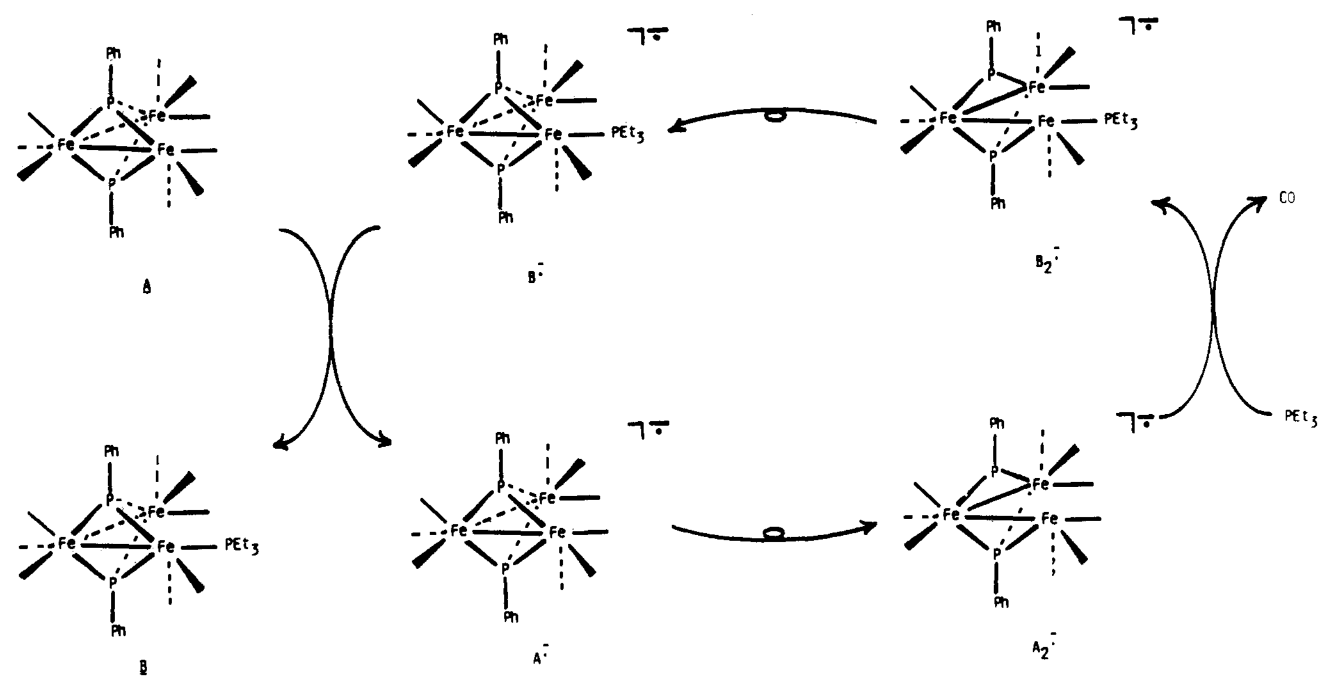
$$\underset{19e}{\text{CpFe(CO)}_2\text{Me}^{\bullet-}} \xrightarrow{\text{PPh}_3} \underset{19e}{\text{CpFeCO(PPh}_3\text{)(COMe)}^{\bullet-}} \quad (120)$$

$$\underset{19e}{\text{CpFeCO(PPh}_3\text{)(COMe)}^{\bullet-}} + \underset{18e}{\text{CpFe(CO)}_2\text{Me}} \rightarrow \underset{18e}{\text{CpFeCO(PPh}_3\text{)(COMe)}} + \underset{19e}{\text{CpFe(CO)}_2\text{Me}^{\bullet-}} \quad (121)$$

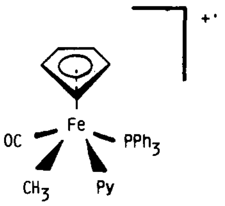
In the absence of phosphine, the cathodic reduction of $CpFe(CO)_3Me$ is partially reversible, and the 19e species can be oxidized to the 18e complex by reaction with dioxygen.

It is worth noting that this electrocatalytic migratory insertion was independently reported by Magnuson and Giering[274] using induction with an anodic current or ferricinium in acetonitrile or pyridine. Further elec-

SCHEME VI



trochemical studies by Grubbs[275] suggested that the reaction also involves a 19e intermediate **32**, which was latter demonstrated by Trogler, also using CV.[276]



32

19 e

initiation

$$\underset{18e}{\mathrm{CpFe(CO)(PPh_3)CH_3}} - e^- \rightarrow \underset{17e}{[\mathrm{CpFe(CO)(PPh_3)CH_3}]^+} \quad (122)$$

$$\underset{17e}{[\mathrm{CpFe(CO)(PPh_3)CH_3}]^+} + \mathrm{CH_3CN} \rightarrow \underset{19e}{[\mathrm{CpFe(CO)(PPh_3)(CH_3CN)CH_3}]^+} \quad (123a)$$

$$\underset{19e}{[\mathrm{CpFe(CO)(PPh_3)(CH_3CN)CH_3}]^+} \rightarrow \underset{17e}{[\mathrm{CpFe(PPh_3)(CH_3CN)COCH_3}]^+} \quad (123b)$$

$$\underset{17e}{[\mathrm{CpFe(PPh_3)(CH_3CN)COCH_3}]^+} + \underset{18e}{\mathrm{CpFe(CO)(PPh_3)CH_3}} \rightarrow \underset{18e}{\mathrm{CpFe(PPh_3)(CH_3CN)COCH_3}} + \underset{17e}{[\mathrm{CpFe(CO)(PPh_3)CH_3}]^+} \quad (124)$$

Thus, interestingly, electrocatalytic carbonyl insertion can take place in these CpFe complexes using either reductive or oxidative initiation because, in both cases, the cross ET propagation step is exergonic (eq 121 and 124). The overall free energy $\Delta G°$ for the propagation cycle must be negative. In fact, this includes both the cross redox step and the chemical reaction of the radicals. In the absence of knowledge of the latter, one has a good chance to make the ET chain reaction work by choosing the initiation mode (oxidation or reduction) such that $\Delta G°_{\mathrm{ET}} < 0$. However, in one case, the chelation of dithiocarbamate complex (vide supra), $\Delta G°_{\mathrm{ET}}$ is positive, and the propagation cycle is thus driven by the irreversible chemical step (chelation with loss of CO).

Finally, it turns out that 19e intermediates or transition states are generally involved in electrocatalysis whatever the mode of induction; this is due to their fast interconversion with 17e species (sections XII and XIII).

Disproportionation

In the 1930s, Hieber pioneered the studies of the disproportionation of metal carbonyl dimers.[183,277] Many of these thermal and photochemical reactions proceed according to

$$\mathrm{M_2(CO)_{2n}} + m\mathrm{L} \rightarrow [\mathrm{M(CO)}_{n-m+1}\mathrm{L}_m]^+,[\mathrm{M(CO)}_n]^- \quad (125)$$

After the first kinetic studies by Heck[278] on $\mathrm{Co(CO)_4SnCl_3}$, it was recognized by Brown[279-281] that the disproportionation of metal carbonyl dimers follows a radical chain pathway strongly influenced by the stereoelectronic properties of the added ligand L. This radical chain pathway resembles ETC-catalyzed reactions. In some cases, these reactions have indeed been directly initiated by added reducing agents. Tyler indicated that the disproportionation mechanism generally involves the intermediacy of 19e complexes:[180-184]

$$\mathrm{Cp_2Mo_2(CO)_6} \xrightarrow{h\nu} 2\mathrm{CpMo(CO)_3}^\bullet \quad (126)$$

$$\rightarrow \mathrm{CpMo(CO)_3}^\bullet + 2\mathrm{P} \rightarrow \mathrm{CpMo(CO)_2P_2}^\bullet + \mathrm{CO} \quad (127)$$

$$\mathrm{CpMo(CO)_2P_2}^\bullet + \mathrm{Cp_2Mo_2(CO)_6} \rightarrow \mathrm{CpMo(CO)_2P_2}^+ + \mathrm{Cp_2Mo_2(CO)_6}^- \quad (128)$$

$$\mathrm{Cp_2Mo_2(CO)_6}^- \rightarrow \mathrm{CpMo(CO)_3}^- + \mathrm{CpMo(CO)_3}^\bullet \quad (129)$$

With $Mn_2(CO)_{10}$, the inefficiency of the disproportionation in the presence of amines N was attributed to the necessity of $Mn_2(CO)_{10}$ to substitute twice and to add a third ligand to form the 19e intermediate $Mn(CO)_3N_3^{\bullet}$. Consistently, the use of a tridentate ligand N_3 is an efficient means of forming this 19e intermediate.[282,283]

$$Mn_2(CO)_{10} \xrightarrow{h\nu} 2Mn(CO)_5^{\bullet} \qquad (130)$$

$$Mn(CO)_5^{\bullet} + N_3 \rightarrow Mn(CO)_3N_3^{\bullet} + 2CO \qquad (131)$$

$$Mn(CO)_3N_3^{\bullet} + Mn_2(CO)_{10} \rightarrow Mn(CO)_3N_3^+ + Mn_2(CO)_{10}^- \qquad (132)$$

$$Mn_2(CO)_{10}^- \rightarrow Mn(CO)_5^- + Mn(CO)_5^{\bullet} \qquad (133)$$

With $Cp_2Fe_2(CO)_4$, the disproportionation also works in this way, but only with (dialkylphosphino)ethane as donor.[222] With other donors, the back ET reaction prevents formation of the disproportionation products. However, the intermediacy of the 19e species $CpFe(CO)P_2$ was shown[185] by trapping experiments as indicated in section IX.

$$Fp_2 \overset{h\nu}{\rightleftarrows} 2Fp^{\bullet} \qquad (134)$$

$$Fp^{\bullet} + depe \rightarrow CpFe(CO)(depe)^{\bullet} + CO \qquad (135)$$

$$CpFe(CO)(depe)^{\bullet} + Fp_2 \rightarrow CpFe(CO)(depe)^+ + Fp_2^{\bullet -} \qquad (136)$$

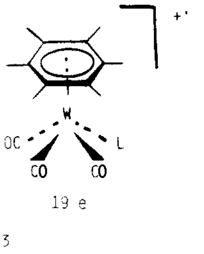
$$Fp_2^{\bullet -} \rightarrow Fp^- + Fp^{\bullet} \qquad (137)$$

In all these reactions, the reducing ability of the 19e species is crucial to the propagation of the chain pathway. Therefore, donor ligands and chelates work better as indicated by the high quantum yields of the photochemical reactions largely exceeding unity.

XV. Spectroscopic Characterization of 19e Intermediates

The lability of 19e metal carbonyls generally does not allow their spectroscopic observation in organometallic reactions although ^{60}Co γ irradiation in matrices of 18e complexes makes it possible to characterize the monoreduced radicals by ESR.[76-81] There are also a number of spectroscopically observable 19e complexes with stabilizing ligands. These observations follow direct, suitable syntheses, but the detection of intermediates in mechanisms is more difficult.

Anodic oxidation of $(C_6Me_6)W(CO)_3$ yields a 17e radical cation that rapidly complexes MeCN, DMF, or PR_3 to generate a metastable 19e intermediate **33** detectable by electrochemistry.[275]



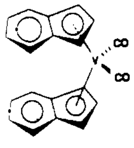
33

19 e

L = MeCN, DMF, PR_3

The 19e species **32** was also directly observed by electrochemistry as an intermediate during the oxidatively induced migratory CO insertion reaction of $CpFe(CH_3)(CO)(PPh_3)$ in the presence of pyridine.[276]

The reversible 1e reduction of $[(\eta^5\text{-indenyl})V(CO)_2][PF_6]$ leads to the 17e radical $(\eta^5\text{-indenyl})(\eta^3\text{-indenyl})V(CO)_2$ with a slipped ring. Low-temperature electrochemical studies suggest that this 17e radical is in equilibrium with the 19e species **34**.[205]



34

19 e

The reactions of nucleophiles with ligands of organometallic cations are an essential way to make new bonds and to functionalize hydrocarbons.[284-286] Rules according to charge control have been published by Davies et al. to predict the site of attack,[284,285] although orbital control turns out to be more important since it dominates when both types of control are in conflict.[287-290] The ET pathway leading to a 19e species is a major alternative to nucleophilic attack on an 18e cation:

$$Nu^- + M^+ (18e) \rightarrow Nu^{\bullet} + M^{\bullet} (19e) \qquad (138)$$

This pathway inhibits the formation of the new bond if the nucleophile is a carbanion. All types of carbanions react with $(C_6R_6)_2Fe^{2+}(PF_6^-)_2$ to give ET reactions[287,288] in which the 19e species $(C_6R_6)_2Fe^+PF_6^-$ can be characterized by ESR (three g values characteristic of rhombic distortion of Fe^I; see section IV).

$$(C_6R_6)_2Fe^{2+} + RM \rightarrow (C_6R_6)_2Fe^+ + R^{\bullet} + M^+ \qquad (139)$$

Fortunately, hydride protection[286-290] can overcome this problem, and arenes can be functionalized in this way by temporary sandwich complexation to Fe^{II}.

The hydride attack, unlike that of the carbanion, leads to the same product by both the "classical" pairwise mechanism and the ET mechanism. Thus, in this case, for which the pairwise mechanism was strongly anchored in popular belief, the ET pathway was much more difficult to prove. Yet $NaBH_4$ or $LiAlH_4$ reduction of a large number of $[CpFe(arene)]^+$ complexes was shown to proceed by the ET pathway since ESR characterization of the 19e intermediate could be achieved. Moreover, when the reactions were performed at a controlled temperature with $LiAlH_4$, the ET step and the H-atom-transfer step could be sufficiently well separated, so that the intermediate could be isolated and characterized by Mössbauer spectroscopy at 77 K.[59] The latter technique is especially useful since it gives a quantitative picture of the iron species in frozen solution:

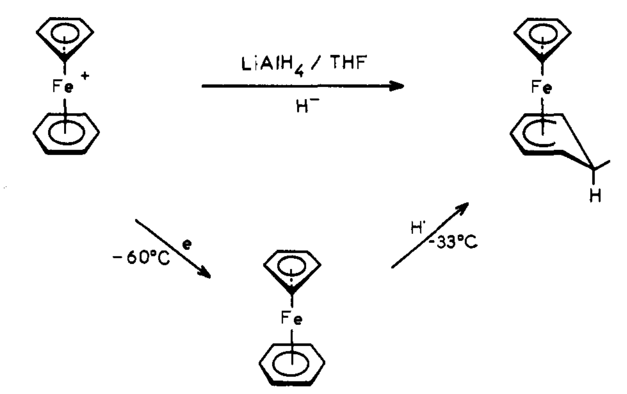
$$CpFe(\eta^6\text{-}C_6R_6)^+ \xrightarrow[\text{THF or DME}]{LiAlH_4} CpFe^I(\eta^6\text{-}C_6R_6) \qquad (140)$$

$$CpFe^I(\eta^6\text{-}C_6R_6) \xrightarrow[\text{THF or DME}]{LiAlH_4} CpFe(\eta^5\text{-}C_6R_6H) \qquad (141)$$

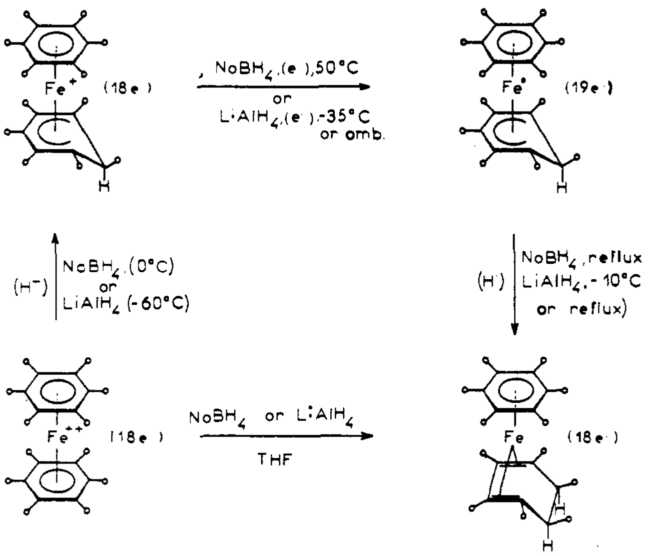
R = H, D, or Me (exo)

The intermediacy of the 19e species could be demonstrated by ESR even in the case of highly unstable 19e intermediates (see section IV). The hydride reduction of $[(C_6Me_6)Fe(\eta^5\text{-}C_6Me_6H)]^+$ also proceeds by

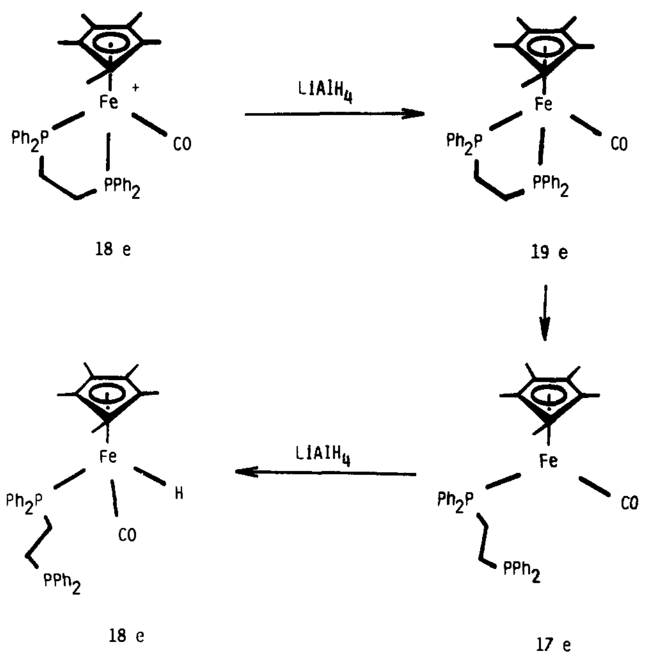
SCHEME VII



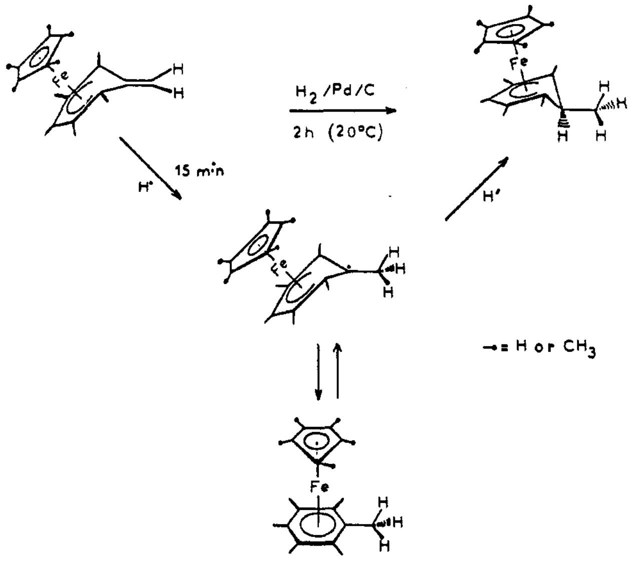
SCHEME VIII



SCHEME IX



SCHEME X



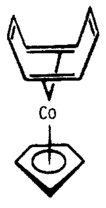
an ET path. The H-atom transfer proceeds onto the ring opposite to that predicted by Davies' rule (Scheme VIII).[59]

Similarly, the $LiAlH_4$ reduction of $[Cp^*Fe(\eta^2\text{-dppe})CO]^+$ in THF was monitored by ESR at a temperature close to the freezing point of the suspension. A paramagnetic species noted by ESR could be either the 19e species or the 17e species $Cp^*Fe(dppe)CO$.[131] Thus, although the ET path is also well established in this case, it is not yet certain whether the 19e species is an intermediate: the P ligand could decoordinate in the course of ET or subsequent to ET (Scheme IX).

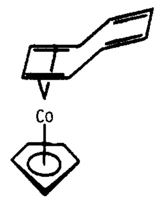
The hydrogenation of the olefins $(C_5R_5)Fe(\eta^5\text{-}C_6Me_5{=}CH_2)$ (R = H or Me) by H_2 on Pd/C gives the reduced complexes $(C_5R_5)Fe(\eta^5\text{-}C_6Me_6H)$ smoothly at 20 °C but the intermediacy of the 19e complexes $(C_5R_5)Fe(\eta^6\text{-}C_6Me_6)$ could be followed by IR and Mössbauer spectroscopies. The 19e complexes correspond to semihydrogenated products formally suspected to be involved in the hydrogenation of simple olefins[291] (Scheme X).

The isomerization of cyclooctatetraene and of cyclooctadiene in $(C_5R_5)Co(1,5\text{-COT})$ (R = H or Me) and $CpCo(1,5\text{-COD})$ was elegantly shown by Geiger[292–294] to be induced by a cathodic current. Thus it was demonstrated that the preferred mode of coordination of COT and of COD depends on the redox state. The 1,5 mode is preferred in 18e complexes $CpCoL_2$, and isomerization to the conjugated 1,3 isomers is adopted at the 19e level. This results of a need for the 19e species to delocalize the extra electron onto a conjugated metal–ligand system. The isomerization process was found to be slower with COD than with COT. This can be taken into account by the necessity of a H shift via metal–hydride intermediates in the COD complexes only. Since the redox potentials (18e/19e) of the 1,3 forms are lower than those of their 1,5 isomers, the isomerization process is not electrocatalytic (section XIV) but stoichiometric in electrons.

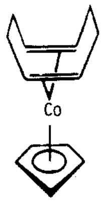
The isomerization at the 18e level was slow enough to allow the characterization of the 1,3 isomers by NMR after oxidation of the 19e 1,5 forms. The monoelectronic reduction of the 1,5 complexes produced the 1,3 19e species, isomerization proceeding subsequent to or concomitant with ET. Although the possible 19e intermediates **35**$^-$ are not detectable, the 19e species **36**$^-$ were fully characterized by ESR, and the extra electron was found to reside on the COT ligand. In the COD series, both the 1,5 and 1,3 19e species **37**$^-$ and **38**$^-$ were characterized by ESR, which showed that the unpaired electron is predominantly metal centered.[294]



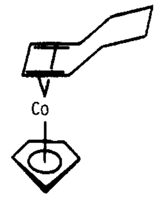
35 (1,5)



36 (1,3)



37 (1,5)



38 (1,3)

$$\begin{tikzcd}
\underset{18\,e}{35} \arrow[r] \arrow[d, shift left] & \underset{19\,e}{35^-} \arrow[d] \\
\underset{18\,e}{36} \arrow[u, shift left] & \underset{19\,e}{36^-} \arrow[l]
\end{tikzcd}
\quad \text{OR} \quad
\begin{tikzcd}
\underset{18\,e}{35} \arrow[d, shift left] \arrow[dr] & \\
\underset{18\,e}{36} \arrow[u, shift left] & \underset{19\,e}{36^-} \arrow[l]
\end{tikzcd}$$

$$\begin{tikzcd}
\underset{18\,e}{37} \arrow[r] \arrow[d, shift left] & \underset{19\,e}{37^-} \arrow[d] \\
\underset{18\,e}{38} \arrow[u, shift left] & \underset{19\,e}{38^-} \arrow[l]
\end{tikzcd}$$

XVI. Conclusion

Whereas the notion of 17e species as well accepted, given the stability of the ferricinium salts, violation of the 18e rule by 19e species took longer to become established. Most monoelectronic reductions of 18e complexes were believed to involve decoordination of a ligand concomitant with ET, which is probably not the case. The first crystal structure of a true 19e complex was that of $CpFe(C_6Me_6)$, a very useful 1e reducing agent, in which the spin density is essentially metal based. Nineteen-electron complexes have currently been stabilized by steric bulk and electronic delocalization. However, when this delocalization onto the ligand is marked, the so-called 19e complexes (nitrosyl, bipyridine, COT) are in fact 18e species that are ligand-based radicals.

The 19e complexes can thus be classified as follows:

(i) metal-centered radicals that have truly 19 VE (the HOMO has a high metal character)

(ii) species with a high degree of covalency at the HOMO level ("18.5e" species such as d^7 Co and Ni sandwiches)

(iii) "37e" average valence bimetallic complexes having close to 18.5 VE

(iv) metal carbonyl species resulting from the 1e reduction of 18e complexes (the 19th electron resides in a σ^* or π^* orbital (for instance, $Fe(CO)_5^{\bullet -}$)

(v) base adducts of 17e complexes where the 19th electron resides in a σ^* orbital such as $[CpFe(CH_3)(CO)(PPh_3)(py)]^+$

(vi) 18e complexes with a monoreduced ligand (the radical center resides on the ligand (such as $Mo(CO)_4(bpy)^-$)

Their two main modes of formation are (i) monoelectronic reduction of 18e precursors and (ii) ligand addition to 17e complexes.

Their reactivity involves readily available pathways such as ET from the metal to a ligand (or to a part of it), or to a substrate, and ligand decoordination.

The intermediacy of 19e species in mechanisms is now also a demonstrated feature of reactions involving metal-centered radicals. It is often a consequence of the fast 17e/19e interconversion, observed for the associative mechanisms of the fast ligand substitution in 17e complexes, including the electrocatalytic (ETC) processes. Nineteen-electron complexes behave as "electron reservoirs" in both stoichiometric (clean one-electron reducing agents) and catalytic reactions such as disproportionation, ligand substitution, and migratory CO insertion. Coupling of electrocatalysis with classical organometallic catalysis is a promising application of the 17e/19e interconversion, complementary to the 16e/18e rule; 19e species are necessarily involved in mechanisms for which 17e species intervene if space is provided in the coordination sphere of the metal for the entering ligand. Thus, they should be intermediates in catalytic processes such as, for instance, the hydroformylation of styrene with cobalt carbonyl.[295-300] In the formation of aryl esters from phenyl bromide, CO, and alkoxides catalyzed by $NaCo(CO)_4$

$$PhBr + CO + NaOR \xrightarrow[NaCo(CO)_4]{h\nu} PhCOOR \qquad (142)$$

$$R = CMe_2CH_2Me$$

Brunet and Caubere[301] proposed the intermediacy of a 19e species:

$$Ph^\bullet + Co(CO)_4Na \rightarrow PhCo(CO)_4Na \qquad (143)$$

It is probable that the recognition of the existence and role of 19e species in mechanisms will lead in the near future to the finding of new processes that may involve multicatalytic components with sophisticated technological devices.

XVII. Abbreviations

A	one-electron acceptor
AIBN	azobis(isobutyronitrile)
Ar	aryl radical
Bu	butyl radical
t-Bu	*tert*-butyl radical
C-hex	cyclohexyl radical
CIP	contact ion pair
COD	cyclooctadiene
COT	cyclooctatetraene
Cp	η^5-C_5H_5 or C_5H_4–
Cp*	η^5-$C_5(CH_3)_5$
CV	cyclic voltammetry
D	one-electron donor
DAB	diazabutadiene
DMF	dimethylformamide
EHT	extended Hückel theory
$E°$	thermodynamic redox potential
ESR	electron spin resonance
ET	electron transfer
ETC	electron transfer chain
Et	ethyl radical
Fc	ferrocenyl radical
Fp	$(\eta^5\text{-}C_5H_5)Fe(CO)_2^\bullet$
Fp*	$[\eta^5\text{-}C_5(CH_3)_5]Fe(CO)_2^\bullet$

HOMO	highest occupied molecular orbital
L	two-electron ligand
N	amine ligand
NR_4^+	tetraalkylammonium
Me	methyl radical
P	phosphine or phosphite ligand
PQ	paraquat
i-Pr	isopropyl radical
n-Pr	*n*-propyl radical
PES	photoelectron spectroscopy
S	solvent as a 2e ligand
SCE	saturated calomel electrode
SSIP	solvent-separated ion pair
SOMO	singly occupied molecular orbital
TCNE	tetracyanoethylene
TCNQ	tetracyanoquinodimethane
THF	tetrahydrofuran
VE	valence electron
bpy	bipyridine
bz	benzene
depe	(diethylphosphino)ethane
dppe	(diphenylphosphino)ethane
dtc	dimethyldithiocarbamate
e	electron
19e	19 electron

XVIII. Acknowledgments

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