Coordination Chemistry Reviews, 76 (1987) 187–235
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE TRANSITION METAL COORDINATION CHEMISTRY OF ANION RADICALS

WOLFGANG KAIM

Institut für Anorganische Chemie, Johann Wolfgang Goethe-Universität, Niederurseler Hang, D-6000 Frankfurt am Main 50 (West Germany)

(Received 4 April 1986)

CONTENTS

ABBREVIATIONS

A	molecule, potential ligand
$A^{\cdot-}$	its anion radical
a.f.c.	antiferromagnetically coupled
bpy	2,2′-bipyridine
bpym	2,2′-bipyrimidine
Cat	catecholate dianion

0010-8545/87/$49.35 ©1987 Elsevier Science Publishers B.V.

Cp	η^5-cyclopentadienyl
diene	bidentate diolefin ligand (norbornadiene etc.)
diphos	bidentate diphosphane ligand
dt	1,2-dithiolene
en	1,2-diaminoethane
EPR	electron paramagnetic resonance
h.s.	high spin
L	ligand
LLCT	ligand-to-ligand charge transfer
LMCT	ligand-to-metal charge transfer
l.s.	low spin
MLCT	metal-to-ligand charge transfer
Q	1,2-quinone
phen	1,10-phenanthroline
pK_{BH^+}	pK_A of acid conjugated to base B
py	pyridine
S.B.	dianionic quadridentate Schiff base ligand
SCE	saturated calomel electrode
SOMO	singly occupied molecular orbital
SQ	1,2-semiquinone (general)
TCNE	tetracyanoethene
THF	tetrahydrofurane
TPP	*meso*-tetraphenylporphine

A. SCOPE AND INTRODUCTION

Most paramagnetic transition metal complexes have unpaired electron(s) localized at the metal center(s) [1] while coordinated ligands are regarded either as even-electron species or as covalently bonded substituents. Transition metal coordination compounds which contain genuine radical ligands, i.e., which have unpaired electron(s) residing mainly in the ligand sphere are less common and may be divided into two categories (**1** and **2**): Complexes with neutral radical ligands $X^{\cdot}$ such as $NO^{\cdot}$ or $R_2NO^{\cdot}$ (**1**) and coordination compounds with anion radical ligands $A^{\cdot -}$ (**2**).

$$(L_nM)(X^{\cdot}) \qquad (L_nM)(A^{\cdot -})$$

1 **2**

This article deals exclusively with the latter kind of paramagnetic complexes and, in most cases, with diamagnetic metal fragments L_nM; compounds which contain both paramagnetic metal centers and odd-electron ligands may exhibit various degrees of spin–spin interaction [2] (cf. Section F).

The study of type **2** complexes pertains to various areas and aspects of coordination chemistry:

(i) It is evident that the negatively charged anion radicals should be suitable ligands for electrophilic metal fragments, forming persistent complexes in which electrostatic stabilization may compensate for the unfavourable open-shell electronic structure. Persistent anion radical complexes usually contain metals in rather low formal oxidation states, often organometallic fragments; otherwise, one would expect rapid intramolecular electron transfer between metal and anion radical ligand, according to the redox potentials of the coordinated fragments (eqn. 1).

$$(L_nM^k)(A^{\bullet-}) \overset{\text{ET}}{\rightarrow} (L_nM^{k-1})(A) \rightarrow \dots \tag{1}$$

(k, $k-1$ are oxidation numbers)

(ii) Anion radicals $A^{\bullet-}$ are derived from neutral molecules A by one-electron reduction and both species may serve as ligands for transition metal fragments.

$$\begin{tikzcd}
A \arrow[r, shift left, "E_0"] \arrow[d, shift left] & A^{\bullet-} \arrow[l, shift left] \arrow[d, shift left, "K'"] \\
(L_nM)(A) \arrow[u, shift left, "K"] \arrow[r, shift left, "E_0'"] & (L_nM)(A^{\bullet-}) \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd} \tag{2}$$

It is attractive to compare the different coordination behaviour of a given metal fragment towards the neutral ligand and towards its reduced form (eqn. 2); in general, $K' > K$ (see section (i) above). Conversely, it has long been known that ligands exhibit very different coordination preferences for different metal oxidation states (cf. the pairs Cu^I/Cu^{II} or Fe^{II}/Fe^{III}). The redox potentials E_0 and E_0' of the free ligand and of its complexes may also differ considerably; as a general rule, metal coordination tends to facilitate the reduction of the ligand ($E_0' > E_0$).

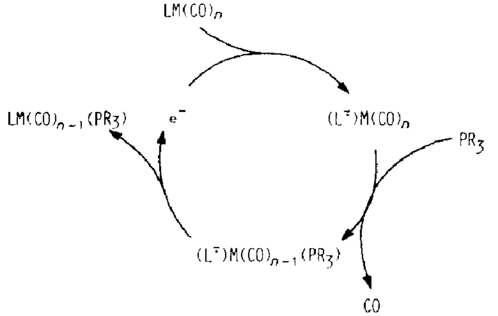
(iii) The distribution of the unpaired electron(s) is often tractable in detail by using spectroscopic techniques, in particular electron paramagnetic resonance (EPR; Section F, i) [1]. Such information may help to eliminate ambiguities concerning the correct assignment of formal oxidation states to the metal(s) and to the "non-innocent" ligand(s) [3] within the following set of rules: (a) a shared electron pair is assigned to the more electronegative of the two atoms sharing it [4a], (b) an unpaired electron is assigned to that moiety, metal or ligand, which exhibits the larger spin population. Oxidation state assignments are often difficult to make for diamagnetic coordination compounds with "non-innocent" ligands [4b], even if they may actually contain anion radical ligands as in the much disputed superoxide complexes [5,6].

(iv) Electron transfer reactivity in the ground state [7] or in electronically excited states [8] of coordination compounds has become an area of extensive research in recent years, and transition metal complexes containing reduced ligands were frequently found as crucial intermediates or as reaction products in metal–metal electron transfer reactions [7,9] and in catalytic processes, including photo- and electro-catalytic cycles [8,10,11]. Two examples will illustrate that important function of species **2**:

Complexes containing electron rich metal fragments and reducible ligands may absorb photons to yield the potentially electron-transfer active metal-to-ligand charge transfer (MLCT) excited states (eqn. 3), which are usually formulated as containing an oxidized metal fragment and anion radical ligand(s) [12,13]. Depending on the lifetimes of the MLCT excited states, these systems can be electron transfer active and catalyze the conversion of light, including solar radiation, into chemical energy, i.e. redox products; one of the most intensively studied yet still poorly understood species of this kind is the complex $[Ru(bpy)_3]^{2+}$ [8,11,14–16].

$$(L_nM^k)(A) \xrightarrow[\text{MLCT}]{h\nu} {}^*[(L_nM^{k+1})(A^{\bar{\bullet}})] \xrightarrow[\text{substrate}]{\text{ET}} \text{products} \qquad (3)$$

Substitution reactions of organometallic compounds may be activated by electron transfer through an electrode (electrocatalysis) [17,18] or through chemical reagents [10], one such example involving anion radical complexes as essential intermediates is the carbonyl/phosphane exchange in heterocyclic carbonylmetal complexes (L = bpy, bpym, etc.; M = Cr, Mo, W; $n = 4$) [19]. This reactivity of anion radical complexes is paralleled by the behaviour of substitutionally labile 17 electron intermediates in the iron [20] or manganese carbonyl series [21].



(4)

$$\boxed{\begin{array}{l} E_{red}(LM(CO)_{n-1}(PR_3)) \\ < E_{red}(LM(CO)_n) \end{array}}$$

Although most of the complexes investigated so far contain only one anion radical ligand, there are a number of complexes of type **3** which contain two or more anion radical ligands and which may have higher

$n = 2,3$
$Y = O, S, NR$

3

multiplicities ($S > 1/2$). In some of these latter cases, it is difficult to arrive at an exact description of the electronic structure because of various intramolecular charge transfer possibilities; detailed structural and spectroscopic studies [22] and quantum mechanical calculations [23] are then required to formulate correctly the ground state of the complex. Obviously, the overall charge of an anion radical complex depends on the number and on the charge of the coordinated metal fragments and may thus be zero or even positive.

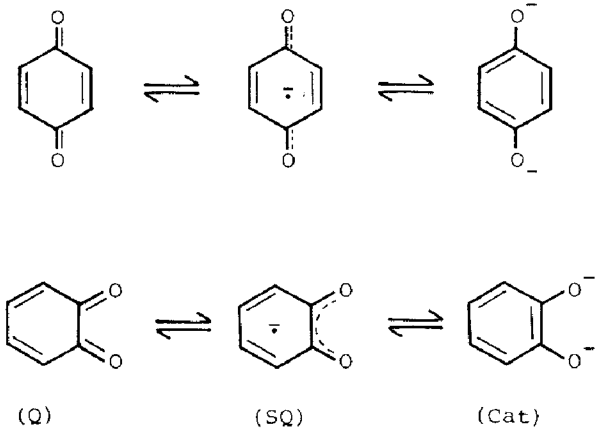
Comprehensive reports on the related subject of organometallic anion radicals appeared in 1976 [24], 1977 [25], and 1978 [10], and there are a number of more recent reviews relevant to the topic of this article. Among these are several reports [22,26–28] and data collections [29] on ketyl and especially 1,2-semiquinone (SQ) complexes, reviews referring to radical complexes with reduced N-heterocyclic ligands such as the bipyridines [30–32], articles on the coordination chemistry of 1,2-dithiolenes and related species [33–35], and reviews on electron-transfer reactions of main group [36] and organotransition metal complexes [37].

B. FORMATION OF ANION RADICALS

Anion radicals are generally formed by one-electron reduction of neutral precursors (eqn. 2), a process which can be accomplished either by chemical reductants such as electropositive metals or by cathodic reduction, i.e. electrochemically. An alternative is the one-electron oxidation of doubly reduced components of two-step reversible redox systems (eqn. 5) [38], well-known substrates for this route are the hydroquinone or catechole dianions which may be converted to the corresponding semiquinones by oxidation [22,26].

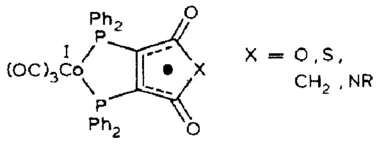
$$(L_nM)(A) \overset{E_0'}{\rightleftharpoons} (L_nM)(A^{\cdot-}) \overset{E_0''}{\rightleftharpoons} (L_nM)(A^{2-}) \qquad (5)$$

The majority of persistent anion radicals owe their stability to an effective delocalization of spin over an extended π system; in addition, nucleophilic solvents such as ethers, amines, amides, or nitriles contribute to the stability of radical anions by solvating the counterion and by removing destructive electrophilic impurities. Many "free" anion radicals are sensitive towards air and protic solvents because O_2 and H^+ are reduced at rather positive

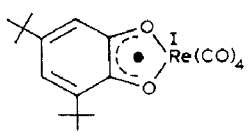


(6)

potentials. This sensitivity leads to considerable difficulties in isolating anion radicals; the crystallization of anion radicals has been accomplished in only a few instances, using large counterions such as complexed alkali metal cations [39]. The countercation problem is absent if positively charged metal fragments coordinate strongly to the anion radical, neutral complexes such as **4** or **5** may then even be purified and isolated by standard preparative techniques [40,41].



4



5

The thermodynamic stability of anion radical compounds towards disproportionation into the dianion and the neutral species within a two-step reversible redox system (5) [38] may be calculated from the redox potentials via eqn. (7).

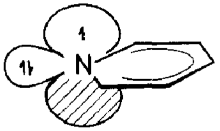
$$K_{\mathrm{com}} = \frac{[(\mathrm{L}_n\mathrm{M})(\mathrm{A}^{\cdot})]^2}{[(\mathrm{L}_n\mathrm{M})(\mathrm{A})][(\mathrm{L}_n\mathrm{M})(\mathrm{A}^{2-})]} = 10^{(E_0' - E_0'')/0.06\,\mathrm{V}} \tag{7}$$

In general, the values K_{com} are quite insensitive towards coordination of different metal fragments unless this coordination causes major changes in the ligand π system; the latter phenomenon has been observed during metal complexation of structurally flexible flavins (cf. **49**) [42].

C. LIGAND PROPERTIES OF ANION RADICALS

Among the properties of a ligand, its σ donor strength is crucial in determining the formation and the stability of the complex. Although the metal coordination site(s) and the localization of the unpaired electron(s) need not be related in anion radical ligands, most examples do involve coordinating centers which are also important parts of the spin-containing π system. Several approaches can be made to estimate this interdependence between coordination equilibria (K and K' in eqn. (2)) and redox equilibria (E_0 and E_0' in eqn. (2).

It was mentioned earlier that the nucleophilicity of a ligand is strongly increased on reduction because of the added negative charge. In a typical situation (eqn. 8), however, the acquired electron resides in a π^* orbital of the ligand while coordination of electrophiles occurs via σ lone pair(s) in the π nodal plane, e.g.



(8)

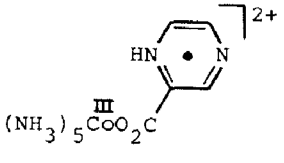
Yet, despite this σ/π orthogonality, the σ coordination of an electrophile to a π center can greatly affect the π levels because it simply increases the electronegativity of the π center (Coulomb term) and thus usually effects a stabilization of π levels.

Conversely, an added electron should raise the σ donor strength ($\sim$ basicity) at the coordinating π center, depending, however, on the MO coefficient at this center [43]. The theoretical background for this dependence was given by Longuet-Higgins [44], eqn. (9) has been discussed in detail and has been successfully applied to estimate physical properties of ligands and complexes as demonstrated recently in studies of a series of N-heterocyclic systems [45].

$$\delta\Delta\left[E_\pi(\text{base}) - E_\pi(\text{acid})\right] = c_{y\mu}^2(h_Y - h_{Y^+})\beta \tag{9}$$

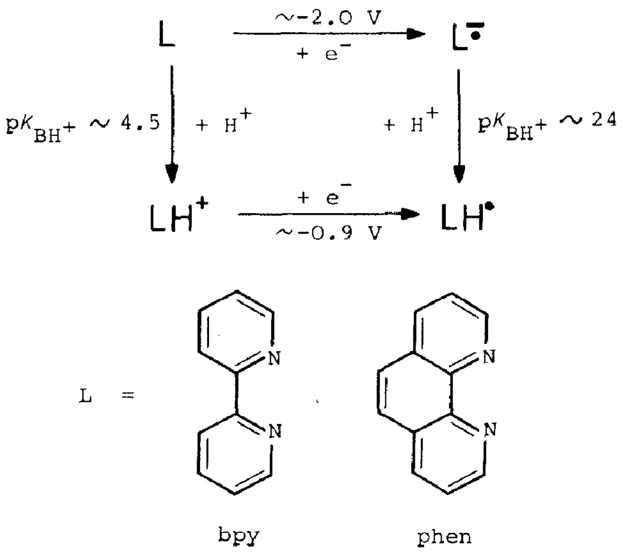
μ = level additionally occupied in the anion radical; c_y = Hückel coefficient at coordination center Y; h_Y, h_{Y^+} = Coulomb integral parameters for base and acid; β = Hückel MO resonance integral.

Direct quantitative determinations of K and K' in eqn. (2) have not been made very often, in fact, most pertinent results involve proton coordination (= acid/base) equilibria. Investigations on mononuclear pyrazine (1,4-diazabenzene) complexes by Taube and coworkers have shown a significant increase in ligand basicity on mere coordination of π back donating metal fragments such as $[M(NH_3)_5]^{2+}$, M = Ru, Os [46]; later pulse-radiolysis studies on pyrazine anion radical-containing systems such as **6** yielded a pK_{BH^+} of about 2.7 whereas the pK_{BH^+} of neutral pyrazine is 0.65 in the first and about -6 in the second protonation step [47]. These results were surprising because they showed an increased basicity for species which



6

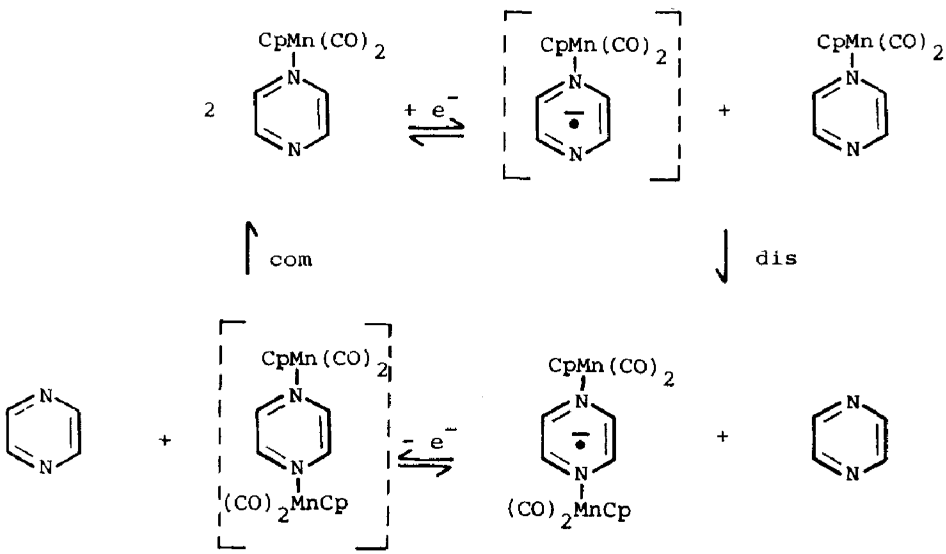
already contain a positively charged metal fragment. Even more striking are the results from pulse-radiolysis studies on α-diimine ligands such as bpy or phen [48]. The chelate effect in such systems helps to raise the pK_{BH^+} of the reduced systems by 20 units above the normal level of about 4–5 in the neutral ligands (eqn. 10)! The basicity of $bpy^{\cdot -}$ thus corresponds to that of the oxide ion, O^{2-}, and it is not surprising, therefore, that a vast number of stable complexes with this anion radical ligand can be obtained [30,32,49], following Herzog's early discoveries [50]. Even very weak oxygen nucleophiles



(10)

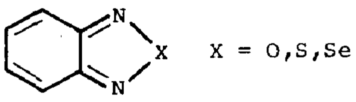
such as O_2 or *p*-benzoquinones become moderately strong bases (pK_{BH^+} ~ 4–5) after reduction to the anion radicals [51]. The consequences of anion radical basicity for proton transfer in organic systems have recently received attention [52,53]; the results of such studies should also bear significance for coordination and transfer of transition metal fragments.

For instance, several recent studies have shown different metal fragment coordination modes in the neutral and reduced states of potentially binucleating ligands. Employing the pyrazine example once more, it turned out to be quite difficult to obtain persistent binuclear complexes of the fragments $(\eta^5\text{-}C_5R_5)(CO)_2Mn$ with that weak base while mononuclear complexes proved to be much more stable [54]. After reduction, i.e., now employing the pyrazine anion radical as ligand, the binuclear species is by far the most preferred coordination compound in that system. EPR and electrochemical studies have shown the formation of the binuclear anionic species from neutral mononuclear complexes via an ECE mechanism (11) [54] (cf. Section F(ii)).

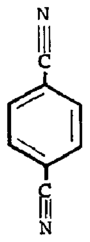


(11)

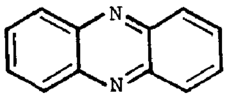
Several other examples involving weakly basic and potentially binucleating ligands such as the 2,1,3-benzochalcogenadiazoles **7** [55] or terephthalonitrile **8** [3] have exhibited similar behaviour. Persistent binuclear metal carbonyl anion radical complexes were obtained in cases when neutral counterparts could not be isolated at all [55,56]. Even more impressive is the observation that phenazine **9** and 2-methyl-1,2,3-benzotriazole **10** form binuclear anion radical complexes with pentacarbonyl-molybdenum and -tungsten fragments [56,57] while the neutral ligands do not show any evidence for coordination with these metal species, presumably because of steric hindrance [56]; all these examples illustrate the vast increase in σ donor strength on one-electron reduction, i.e. anion radical formation.



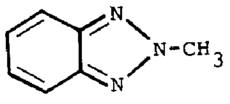
7



8



9



10

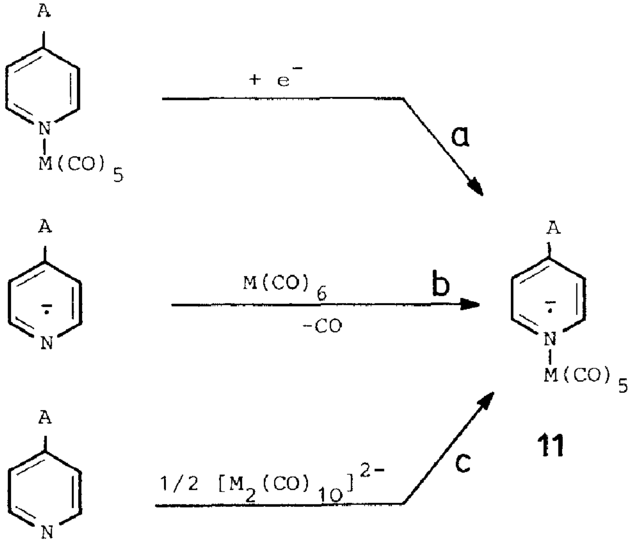
The additional nucleophilicity of reduced π acceptor ligands must also be considered as one of the essential factors for the lack of photodissociation in MLCT excited states (3) [11–13], complexes of this kind could not function as effective electron transfer photocatalysts [11] without such superior coordinative stability.

D. FORMATION OF ANION RADICAL COMPLEXES

Although transition metal complexes of anion radicals may be formed similarly as the paramagnetic free ligands, there are a number of additional interesting mechanisms available to obtain the coordinated species; the "electron transfer" reactions which can lead to the formation of anion radical complexes have received increasing attention in recent years [10,36].

(i) Redox reactions of complexes

Anion radical complexes may be obtained from even-electron precursors by redox processes at an electrode or involving chemical reagents. Reduction, for example, may be accomplished by using a cathode or electropositive metals (12, route a) [58]:



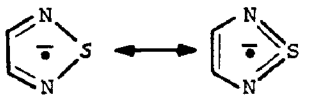
11

(12)

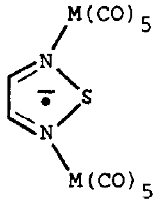
M = Cr, Mo, W

A = π acceptor group

In some instances, less potent chemical reductands such as cobaltocene ($E_{ox} = -0.8$ V vs. S.C.E.) may suffice; this reagent has gained popularity [59] because the resulting cobaltocinium ion represents a large, stable and diamagnetic counterion. A mild reductand such as Cp_2Co can often be employed since many anion radical complexes are formed at much more positive reduction potentials than their free ligand counterparts (Section D, ii); in some cases such as in the 2,1,3-thiadiazole (td) compound series, a binuclear anion radical complex **13** is persistent at room temperature while the ligand radical anion **12** is not [60]!



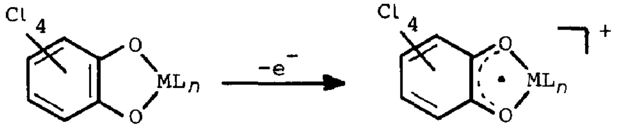
12



13, M = W

(13)

Oxidative processes to yield anion radical complexes have often involved the electron rich catecholate complexes. Some of the earliest examples were reported by Balch [61]:



14

M = Ru^{II}, Rh^{III}, Ir^{III}, Pd^{II}, Pt^{II}

L = CO, PR_3, Cl

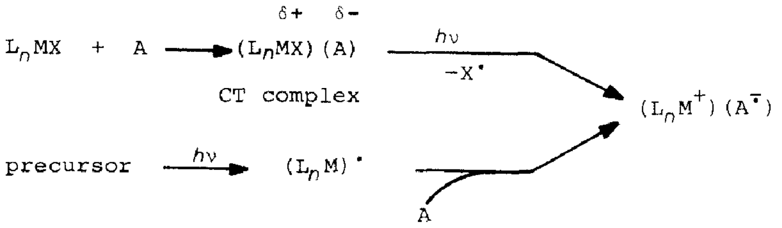
(14)

(ii) Coordination of "free" anion radicals

In contrast to route (i), this reaction sequence implies a reversal of coordination and redox processes, i.e., a preformed anion radical undergoes coordination as any other ligand. Such a reaction sequence is not only convenient in those cases where the anion radical is stable as a salt such as $K^+O_2^{\bar{\cdot}}$, this route may also work well in situ because anion radicals are strong nucleophiles and may even activate substitutionally stable metal species by electron transfer (4) [19,57] as shown in (12, route b) [58].

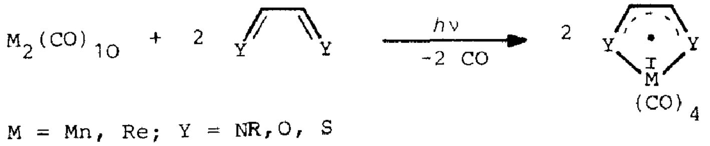
(iii) Photochemical generation

Intramolecular electron transfer within a preformed charge transfer (MLCT) complex [10] or intermolecular electron transfer between photogenerated metal radicals and the even electron ligand [27] are the two main routes by which irradation can produce anion radicals and their coordination compounds (eqns. 15, 16).



(15)

The latter mechanism, often referred to as "spin-trapping" forming "spin adducts", has been proposed for a large number of radical complex-forming reactions even though the intermediates $L_nM^\cdot$ have rarely been observed directly [27,62–64]. Attention is directed to the first alternative which, nevertheless, may require the dissociation of a radical $X^\cdot$ during an "escape" process [36] for balance of spin. Whereas most main group organometallics used in such reactions contain electron-rich metal–carbon or metal–hydrogen bonds [36], the electron-rich transition metal compounds necessary usually contain carbonyl ligands, and, quite often, metal–metal bonds [62–64]. For instance, the discussion on the mechanism of photolysis of $M_2(CO)_{10}$, M = Mn, Re [65], has triggered quite a number of studies on neutral anion radical complexes **15** as products of "spin-trapping" [62–64,113,114,208,209].



15

(16)

(iv) Thermal electron transfer between closed-shell species

Electron transfer between electron rich metal fragments and electron poor ligands may be brought about not only photochemically but also thermally, if the reactands are sufficiently reactive in their ground states. Since most radical complexes are not very persistent at higher temperatures, "thermally" usually refers to ambient temperatures or even below, in the absence of any other activation. Most such reactions described have involved main group organometallics [36]. However, low-valent transition metal compounds such as the carbonyl dimers of group 6 metals (eqn. 12, route c) [58] or of group 7 and 9 metals can also be used with sufficiently π electron deficient ligands [40]. These reactions may be alternatively described as single-electron oxidative additions, other representative examples are the formation of the 1,2-semiquinone complex **16** [66a] or the addition of an electron-rich [21] metal carbonyl fragment to tetracyanoethylene, TCNEI (17) which leads to an antiferromagnetically coupled $\mathrm{TCNE}^{\cdot-}$/l.s. $\mathrm{Mn^{II}}$ complex via a rarely observed single one-electron oxidative addition [66b].

$$(\mathrm{bpy})\mathrm{Cr^{0}(CO)_4} + 2\,\mathrm{Q'} \longrightarrow \underset{\mathbf{16}}{(\mathrm{bpy})\mathrm{Cr^{III}(SQ')(Cat')}} \qquad \mathrm{SQ'} = \mathbf{63}$$

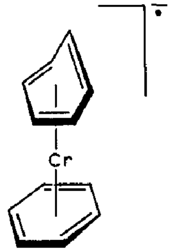
$$\begin{tikzcd} \mathrm{TCNE} + (\mathrm{THF})\mathrm{Mn^{I}Cp(CO)_2} \arrow[r, "-\,\mathrm{THF}"'] & {[(\mathrm{TCNE}^{\cdot-})(^{+}\mathrm{Mn^{II}Cp(CO)_2})]}\ \ \mathrm{a.f.c.} \arrow[dl, "+\,3\ (\mathrm{THF})\mathrm{MnCp(CO)_2}", "-\,3\ \mathrm{THF}"'] \\ {[(\mathrm{MnCp(CO)_2})_3(\mathrm{TCNE}^{\cdot-})(^{+}\mathrm{MnCp(CO)_2})]} & \end{tikzcd} \qquad (17)$$

E. SURVEY OF ANION RADICAL LIGANDS AND OF THEIR COMPLEXES

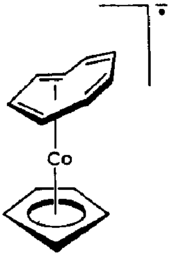
The following section gives a survey of typical anion radical complexes, organized according to the kind of coordinating centers at the radical ligand. Although MLCT excited states of coordination compounds may be formulated as containing anion radical ligands (eqn. 3) and anion radical complexes may often be formed during electrochemical studies, only well-characterized ground state complexes will be presented and discussed here.

(i) Carbon ligands

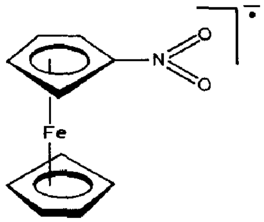
Carbon ligands may coordinate to transition metal fragments in π or σ fashion, regardless of their spin state. As concerns anion radical complexes, polyhapto coordination may occur in sandwich and "half-sandwich" compounds [67–78] such as **17**–**21**,



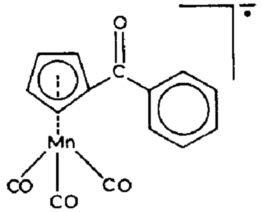
17



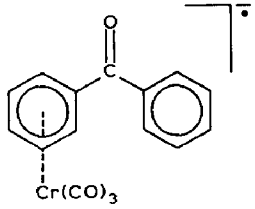
18



19



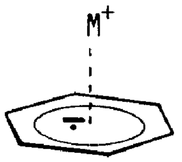
20



21

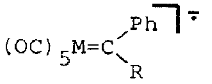
in which the cyclic sandwich "buns" are sufficiently π electron deficient, either by themselves (**17**,**18**) or by π acceptor substitution (**19**–**21**) in order to allow a ligand centered reduction. Nevertheless, **17** and **18** still show substantial metal character of the singly occupied MO as evident from EPR [67,70]. Simple olefins are apparently less suitable to serve as genuine anion radical ligands; olefin iron carbonyl "anion radicals" as reported by Krusic and San Filippo, Jr. and others must be regarded as metal centered paramagnetic species [20] (see, however, eqn. 17).

In this context, it should be called to mind that alkali metal "ion pairs" are observed with benzene (**22**) [79] and many other aromatic anion radicals [80,81], species that may also be described as fluxional "half-sandwich" π complexes. Anion radical complexes which are σ coordinated through a carbon center are less frequent, even though such centers should by very basic; prominent examples are the reduced aromatic carbene complexes **23** [82,83]. Aromatic isonitriles form anion radicals [84], are good π acceptor ligands and should, therefore, also belong to this ligand category. The first examples (**24**) of isonitrile radical complexes (though not involving anion radicals) have been described only recently [85]. Related to **24** are the complexes **25** [86] which may be described as acyl radicals coordinated to diamagnetic metal fragments via the acyl carbon atom. These species display a spin distribution very similar to that in corresponding ketyl anion radicals.



$M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+$

22



$[(OC)_5M{=}C(Ph)(R)]^{\cdot -}$

M = Cr, Mo, W

R = Ph, OR

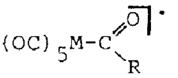
23

$[Mes_2C{-}N{\equiv}C{-}M(CO)_5]^{\cdot}$

M = Cr, W

Mes = mesityl

24



$[(OC)_5M{-}C({=}O)R]^{\cdot}$

M = Cr, W

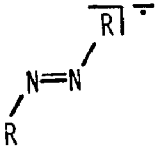
R = alkyl, aryl

25

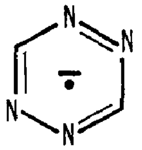
(ii) Nitrogen ligands

The number of anion radical ligands coordinating through nitrogen atoms is quite large, due to the variety of nitrogen ligands available. These ligands generally coordinate via the unshared electron pairs at the nitrogen centers, and the fact that this element occurs predominantly as the isotope ^{14}N with a nuclear spin of $I = 1$ has greatly facilitated the identification of anion radical complexes by EPR.

Most nitrogen containing anion radical ligands contain imine nitrogen centers $X{=}N\diagdown^{\cdot-}$, where X may not only be C (azomethines) but also N (azo compounds) [87] or S(Se) (sulfur-, selenium diimines) [55] such as in **7**$^{\cdot-}$, **26** or **27**.



26

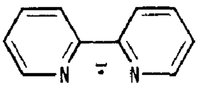


27

Among the azomethine systems, the chelating bidentate α-diimine ligands **28**, Y = NR, take a special position; these ligands may also involve aromatic

28

heterocyclic rings such as in the well-known 2,2′-bipyridine anion radical [30]:

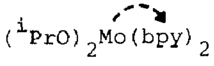


29 (bpy$^{\cdot-}$)

Just as with the related 1,2-dicarbonyl (**28**, Y = O) and 1,2-dithiolene systems (**28**, Y = S), there are numerous transition metal complexes containing one, two or three bpy$^{\cdot-}$ ligands [30,32,49]. Although not always recognized as such in the beginning ("zerovalent metal complexes $M(bpy)_3$" [49,50]), these compounds have become of wide interest in connection with their unusual photo- and electro-chemistry [11,30,32]. As in some other cases described here, the identity of such a ligand as anion radical is not always easy to prove; bpy containing complexes such as **30** [88] or **31** [89] exhibit substantial yet still partial transfer of charge to the ligand in the ground state as is evident from spectroscopic and structural studies.

$$Cp_2Ti^{II}(bpy) \xrightarrow{\sim 700\ cm^{-1}} {}^{::}[Cp_2Ti^{III}(bpy^{\bullet-})]$$

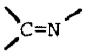
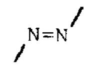
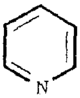
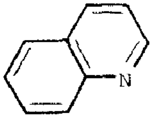
30

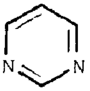
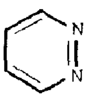
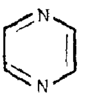


$$({}^iPrO)_2Mo(bpy)_2$$

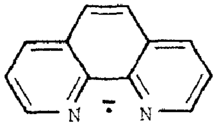
31

Many other α-diimine ligand anion radical systems may be constructed [87,90] by combining $X{=}N\diagdown^-$ building blocks such as

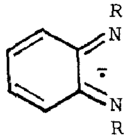
 ,  ,  ,  ,

 ,  ,  , 

Anion radicals of 1,10-phenanthrolines **32** [91,92] and *o*-semiquinonediimines **33** [93–95] derived from *o*-semiquinones (eqn. 6) are also excellent paramagnetic chelate ligands.



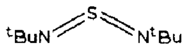
32 (phen$^{\bullet-}$)



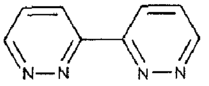
33

Complexes involving a single bpy, phen, or 1,4-diazabutadiene (**28**, Y = NR, R = alkyl, aryl) anion radical ligand were reported with several inorganic [96–98] and main group organometallic ions [91,99,100] and with the following transition metal fragments: $M(CO)_4$, M = Cr, Mo, W [92,101–107]; $Fe(NO)_2$ [108,109]; Co(CO)(NO) [108]; $Mo(CO)_n(PR_3)_{4-n}$, $n = 2$, 3 [110]; $^+M(diene)$, M = Rh, Ir [111,112]; $^+M(CO)_4$, M = Mn, Re [64,113]; $^+Mn(CO)_3Mn(CO)_5$ [114]. More π electron deficient α-diimines may also form localized anion radical complexes with $[Ru(bpy)_2]^{2+}$, this fragment [115–117] as well as the group 6 tetracarbonyls [87,90,118,119] and their phosphane substituted derivatives [19,119,120] have been studied in mono- or bi-nuclear coordination with anion radicals of the following α-diimines: N,N'-di^{t}butylsulfurdiimine **34** [117,118], 3,3′-bipyridazine **35**, 4,4′-bipyrimidine **36**, 2,2′-bipyrazine **37** [90], (μ-)2,2′-bipyrimidine **38** [19],

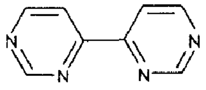
μ-2,5-bis(2-pyridyl)pyrazine **39**, and μ-3,6-bis(2-pyridyl)-1,2,4,5-tetrazine **40** [87,119]; a similar system containing three nitrogen atoms in the chelate arrangement (**28**) is μ-azo-2,2′-bipyridine **41** [87].



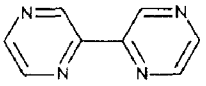
34



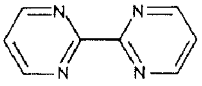
35



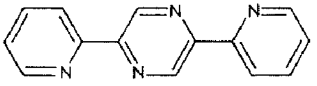
36



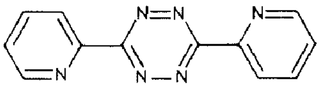
37



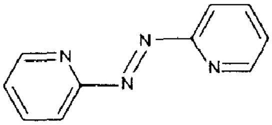
38



39

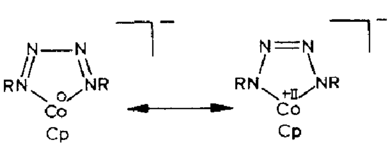


40



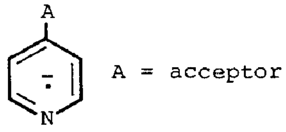
41

The replacement of both carbon centers in the α-diimine configuration (**28**, Y = NR) by nitrogen leads to the very π electron deficient tetraazabutadiene ligands [121,122], however, paramagnetic anionic complexes such as **42** were clearly characterized by EPR as 19 electron metal-centered species [121]. In a localized description, this result strongly suggests a dominating resonance structure B which involves the doubly reduced form of the ligand (cf. structural studies) [122], yet there seems to be a higher degreee of orbital mixing here than in ordinary α-diimine complexes [121].



42 A 42 B

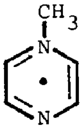
Besides the chelating systems, there are a number of monodentate anion radical ligands known which contain nitrogen coordination sites. These include stabilized pyridine (**43**) [58] or diazoalkane anion radicals **44** [123] and reduced *N*-alkyl pyrazinium species **45** [124], however, most persistent seem to be binuclear transition metal complexes with bridging, doubly monodentate anion radical ligands such as reduced pyrazine **46** [57], quinoxaline **47** [57], phenazine **9**$^{\cdot-}$ [57,125,126], 4,4′-bipyridine **48** [57], μ-4,4′-bipyrimidine **49** [90], 1,2-bis(4-pyridyl)ethene **50** [57], 2,1,3-thiadiazole **12** [60], or 2,1,3-benzochalcogenadiazoles **7**$^{\cdot-}$ [55].



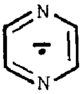
43

$\mathrm{ArHC{=}N{=}N}]^{\cdot -}$

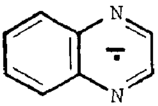
44



45

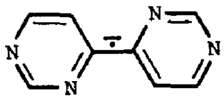


46

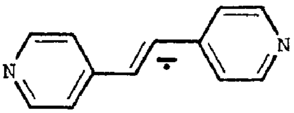


47

48

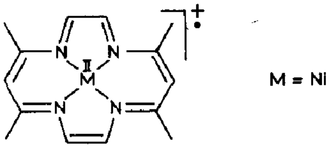


49



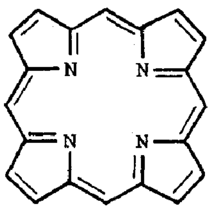
50

Imine nitrogen centers are also present in macrocyclic radical complexes such as **51** [127] or in porphyrin [128] and phthalocyanine radical ions [129].

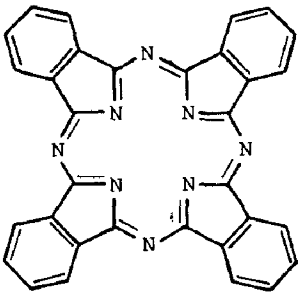


51

It should be noted that phthalocyanine and porphyrin radical cations such as $[(TPP)Zn]^{\cdot+}$ or chlorophyll$^{\cdot+}$ may properly be regarded as complexes between diamagnetic ions and the anion radicals of doubly oxidized and deprotonated (dehydrogenated) species such as **52** and **53** (eqn. 18); the porphyrin π radicals and their biochemically relevant derivatives have been treated in detail elsewhere [128,130] and shall not be further discussed here. In multi-center π systems such as in the phthalocyanines and their complexes, the density of orbitals and excited states becomes quite high and comparative studies have proven useful to assign individual species as anion radical complexes [129].



52

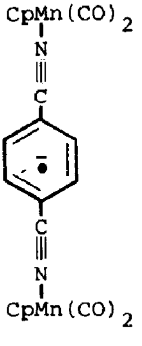


53

$$\mathrm{Pn} \xrightarrow{+\,e^-} \mathrm{Pn}^{\bullet-} \xrightarrow{+\,(\mathrm{L}_n\mathrm{M})^{2+}} [\mathrm{Pn}(\mathrm{ML}_n)]^{\bullet+} \qquad (18)$$

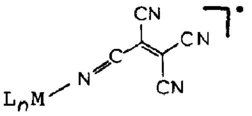
Pn = **52**, **53**

Nitrogen-containing anion radicals can also be obtained from unsaturated nitriles such as terephthalonitrile **8** [3] or tetracyanoethylene, TCNE [131–133]; N-coordinated transition metal complexes such as **54** or **55** have been detected by EPR [3,131] while other systems such as (eqn. 17) [66b] or [(TCNE$^{\bullet-}$)(Cp$_2$XV$^{\mathrm{IV}}$)], X = halogen, [132] represent antiferromagnetically coupled $S = 1/2/S = 1/2$ species (Section F(i)).



54

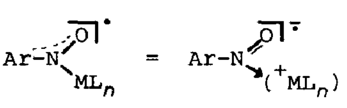
$(\mathrm{L}_n\mathrm{M}^+)(\mathrm{TCNE}^{\bullet-})$ =



55

$\mathrm{L}_n\mathrm{M}$ = Cp(CO)$_3$Cr$^{\mathrm{II}}$
Cp(CO)$_3$Mo$^{\mathrm{II}}$
Cp(CO)$_2$Fe$^{\mathrm{II}}$
(CO)$_5$Mn$^{\mathrm{I}}$

Spin-trapping nitroso aromatics may also undergo facile reduction to anion radicals [134], and the complexes **56** [135] may be described as

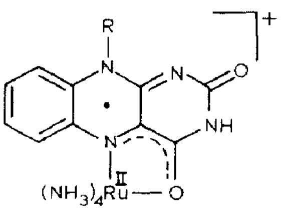


56

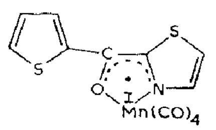
ML_n = $^{\mathrm{II}}$Mo(CO)$_3$Cp
$^{\mathrm{II}}$Fe(CO)$_2$Cp
$^{\mathrm{I}}$Mn(CO)$_5$
$^{\mathrm{I}}$Re(CO)$_5$
$^{\mathrm{I}}$Co(CO)$_3$P(OR)$_3$

nitrosoaromatic anion radicals which coordinate to cationic diamagnetic d^4, d^6, or d^8 metal fragments via the N atom.

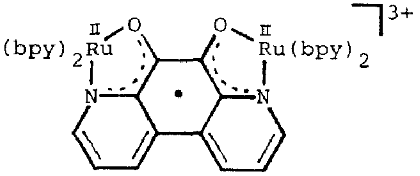
Finally, nitrogen coordination centers in anion radical complexes may also occur in combination with oxygen "supporting" centers; among the few examples are flavin (**57**) [42], 2-thienyl-2-thiazolyl ketone (**58**) [136], and binuclear 4,7-phenanthroline-5,6-dione anion radical complexes (**59**) [137].



57



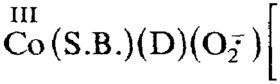
58



59

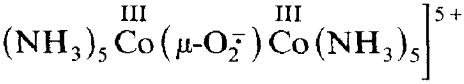
(iii) Oxygen ligands

Of the oxygen-containing anion radicals, the superoxo ligand, $O_2^{\cdot-}$ [6,138], deserves the first mention (transition metal complexes of the related $N_2^{\cdot-}$ ligand have not yet been described although they might be involved as one of the first conceivable intermediates in metal-supported nitrogen fixation! [139]). Superoxide $O_2^{\cdot-}$ ($pK_{BH^+} = 4.5$) forms several mono- and bi-nuclear complexes such as **60** or **61** with electrophilic transition metal fragments [138]. Some of these species are of biochemical relevance in relation to the oxyheme problem ($Fe^{III}/O_2^{\cdot-}$ vs. $Fe^{II}/{}^1O_2 \leftrightarrow Fe^{IV}/O_2^{2-}$ [6,138]) and to the generation and fate of superoxide ion in living systems [140]. The diatomic



$$\overset{III}{Co}(S.B.)(D)(O_2^{\cdot-})$$

60



$$\left[(NH_3)_5\overset{III}{Co}(\mu\text{-}O_2^{\cdot-})\overset{III}{Co}(NH_3)_5\right]^{5+}$$

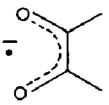
61

S.B. = dianionic quadridentate Schiff base; D = neutral donor

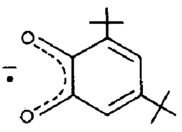
nature of this ligand allows for relatively straightforward assignment of its oxidation state in the complex because of very characteristic "fingerprint" O–O-stretching frequencies and bond lengths [6,138]. Although similar such approaches have been used for SQ [22] and $bpy^{\cdot-}$ [89] complexes (Section F, iv), the significance of such information for the actual charge distribution has been critically discussed [5]. There are, however, some paramagnetic superoxide complexes such as **61** for which EPR results allow a more reliable characterization [141] of the electronic structure [142].

1,2-Semiquinone (SQ) or, more general, 1,2-semidione (α-diketone anion radical) complexes also have some biochemical relevance [143,144] since the catechole moiety is a widely occuring constituent of biological systems; 1,2-semidiones and -quinones have been employed as ligands in alkylated, arylated, halogenated, or benzannelated forms (**62**–**65**, eqn. 6) [22,26–29].

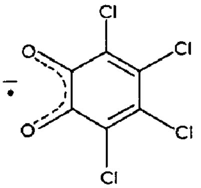
The number of SQ transition metal compounds is very large because of the very facile reduction of *ortho*-quinones ($E_{\mathrm{red}} \approx -0.5$ V vs. SCE), the large comproportionation constants (6,7) of SQ ($K_{\mathrm{com}} \approx 10^{13}$ [145]), and the advantageous five membered ring chelate situation (**28**); many such complexes have been reviewed in recent years [22,26–29].



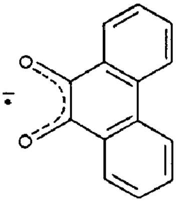
62



63



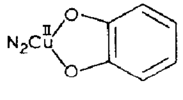
64



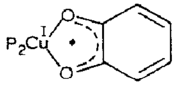
65

In addition to the examples already given (**5**,**14**–**16**), the following rundown gives an impression of the oxidation states of transition metal fragments which can coordinate to single 1,2-semidione and -quinone ligands: solvated inorganic d^0 and d^{10} metal ions such as Sc^{3+}, Y^{3+}, La^{3+}, Zn^{2+}, and Cd^{2+} [143,146]; inorganic and organometallic fragments containing $\mathrm{Ti}^{\mathrm{IV}}$ [147] and $\mathrm{Zr}^{\mathrm{IV}}$ [148], $\mathrm{V}^{\mathrm{III}}$ [149], $\mathrm{Cr}^{\mathrm{III}}$ [66a], Mo^{0} and W^{0} [150], $\mathrm{Mo}^{\mathrm{VI}}$ [229], Mn^{I} and Re^{I} [62–64,136,151–155], $\mathrm{Fe}^{\mathrm{III}}$ [144] and $\mathrm{Ru}^{\mathrm{II}}$ [42,61,156–158], $\mathrm{Co}^{\mathrm{III}}$ [144,148,152,159–163], $\mathrm{Rh}^{\mathrm{III}}$ [61,164,165] and $\mathrm{Ir}^{\mathrm{III}}$ [61], $\mathrm{Ni}^{\mathrm{II}}$ [166], $\mathrm{Pd}^{\mathrm{II}}$ [61,167] and $\mathrm{Pt}^{\mathrm{II}}$ [61,168], Cu^{I} [169,170] and $\mathrm{Cu}^{\mathrm{II}}$ [171,172], Ag^{I} [170], $\mathrm{Hg}^{\mathrm{II}}$ [173] and U^{VI} [174] metal centers. Although most metal fragments in this list are diamagnetic, there are some cases where paramagnetic transition metals coordinate to SQ ligands and strong spin–spin interaction results (Section F(i)) [66,144,149,171,172]. This list is also representative for the kinds of transition metal fragments that may coordinate to anion radical ligands; however, not all of these fragments are sufficiently inert to survive the coordination to more reducing ligands such as most of the α-diimine anion radicals.

Just as the α-diimine anion radicals, the 1,2-semi-diones and -quinones may form complexes which contain two or three such ligands (**3**) in either of the three redox states (eqn. 6), the possibility of electron transfer between the components of such complexes often creates a situation in which the correct assignment of oxidation states is not easy [22,23]. The delicate balance between two electronic structures because of internal electron transfer is nicely illustrated by the copper complexes **66** [171,172,175] and **67** [169,170] where phosphane or other π acid coordination to the copper center in **67** stabilizes the lower valent metal oxidation state and leaves the catecholate ligand to be oxidized to the anion radical form [169,170]. A remarkable, reversible valence isomerization has been reported for the manganese complex **68** which exhibits a temperature dependent equilibrium between two electron transfer related species **68A** and **68B**, the former containing SQ ligands [175]. Although obviously close in energy, the metal and ligand levels retain most of their character in such complexes; much stronger mixing of orbitals occurs in the formally analogous sulfur systems (see below).



66 N_2 = bpy, phen, en

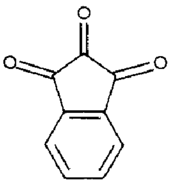


67 P_2 = diphos, $(PPh_3)_2$

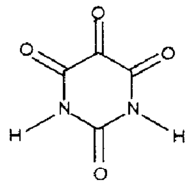
(19)

68A **68B**

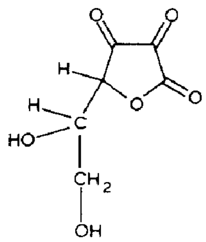
1,2,3-Triketones should be even more π electron deficient than 1,2-diketo compounds. Anion radicals of cyclic species such as ninhydrin **69** [136,176], alloxan **70** [176] or dehydroascorbic acid **71** [177,178] have indeed been used as ligands, mostly for closed shell ions such as Zn^{2+}, Cd^{2+}, or R_2Tl^+ [176,177], but also for manganese carbonyl derivatives [136]. Ligands such as **69** and **70** offer more than one equivalent coordination site and have been designated by von Zelewsky as "alterdentate" [179].



69

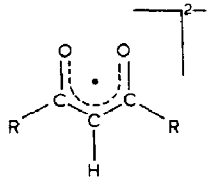


70

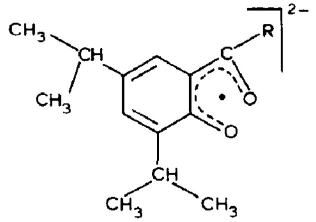


71

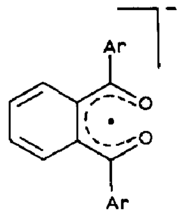
Increase of the chelate ring size from 5 to 6 and 7 leads to paramagnetic ligands such as **72** [180], **73** [181], and **74** [182] which have been observed to form main group metal complexes; note that **72** and **73** are dianion radicals.



72

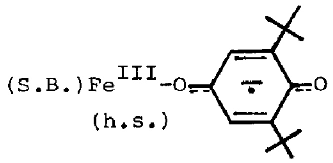


73



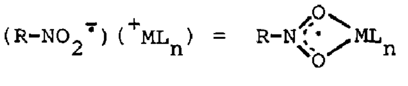
74

Less common than the α-semidione species are complexes of simple ketyls or 1,4-semiquinones (6) [29,178,183,184,187a,c]; in the absence of chelate stabilization, these rather poor nucleophiles ($pK_{BH^+} < 5$) [185,186] do not form stable complexes with moderately electrophilic metal fragments. Strong electrophiles, on the other hand, are often reduced by these anion radicals or form hydroquinone dianion-bridged dimers [187a]. It should be noted at this point that 1,4-seminone coordination compounds may have some biochemical relevance: it is assumed that pheophytin, the primary electron acceptor in bacterial photosynthesis, transfers the electron to a center which contains redox-active *p*-quinones and iron in close proximity [187b]; the use of a sterically hindered 1,4-quinone has recently allowed the first characterization of a mononuclear high-spin iron(III) complex with a 1,4-semiquinone [187a]. Also related to photosynthesis is the hypothesis [187c] that 1,4-semiquinones might serve as bridging ligands between the manganese centers in O_2-releasing enzymes in chloroplasts; a model compound, apparently consisting of two high-spin Mn^{II} centers and four 2-acetyl-1,4-semiquinones, has been related to the water oxidizing enzyme because of qualitatively analogous magnetic behaviour [187c].



S.B. dianionic quadridentate Schiff base

Reduced nitroaromatics, a very important class of anion radicals, are also potential ligands for metal electrophiles; although most known examples involve alkali metal "ion pairs" [81], there have been reports on transition metal complexes as well [188]:



$$(R\text{-}NO_2^{\bullet-})(^+ML_n) = R\text{-}N(O)_2ML_n$$

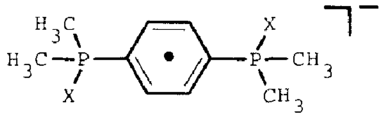
$ML_n = Mn(CO)_{4-n}L_n$

L = group 15 donor

75

(iv) Phosphorus ligands

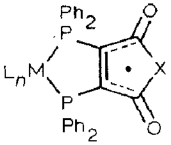
Although there are a number of coordination compounds of reduced aryl phosphanes such as **76** [189], these anion radical ligands are too reducing to accommodate even low-valent transition metal fragments [190]. However,



76

$X = BR_3, AlR_3, R^+,$
NR, O, S, Se

Fenske and coworkers have developed a system (**77**) which contains an ideal combination of π acceptor functionality (keto groups) and five membered ring chelate coordination, offered by two π conjugating phosphorus centers [191].



77

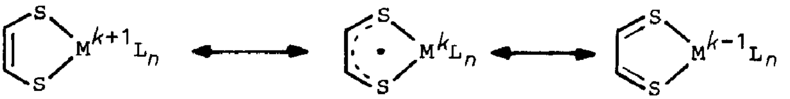
$X = O, S, CH_2$ or NR

$L_nM = (CO)_2CpMo^{II}$
$(CO)_4Mn^{I}$
$(CO)_3Co^{I}$
$(PPh_3)ClPd^{II}$
$(PPh_3)ClPt^{II}$

Synthesis via route D(iv) and structural characterization (**5**) of the paramagnetic complexes **77** clearly showed that they consist of anion radical ligands coordinated to diamagnetic (d^6, d^8, d^{10}) transition metal fragments [40,192–199]. Modification of the group X has turned out to be an effective way to change the properties and the reactivity (Section G) of these unusually stable complexes.

(v) Sulfur ligands

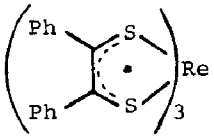
Although elemental sulfur forms a fairly stable anion radical, $S_3^{\cdot-}$, which can coordinate to chloroaluminium compounds [200], no transition metal complexes of this species have yet been described. Main group metal complexes are formed by some aromatic thioketyls [201]. However, the majority of sulfur-containing anion radical complexes involve a chelate situation such as in paramagnetic 1,2-dithiolene (dt) species (**28**, X = S) [33,34]. Unfortunately, the characteristic behavior of sulfur donor centers is to interact very strongly with π systems [218] *and* to act as strong nucleophiles towards transition metals so that extensive mixing of metal and ligand orbitals occurs [202,203]; the often resulting lack of unambiguous spectroscopic information makes it very difficult to establish the anion



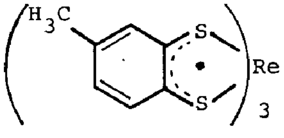
(20)

radical character of a coordinated ligand. Since almost all complexes of this kind contain two or three such ligands [33,34] and there are only a few [204], and less pertinent, free 1,2-dithiosemidiones available for comparison, the localized description implied in the term "anion radical complex" (Section A) can indeed become meaningless.

1,2-Dithiolene and the related dithiocarbamate complexes have been extensively reviewed [33–35,202a]. Two of the few obvious examples of ligand-centered paramagnetic species in this class are the compounds **78** and **79** [205,206] for which the absence of the usually huge [205] ^{185,187}Re coupling in the EPR spectrum strongly suggests the localization of spin somewhere at the ligands. The possibility of long-range interligand interaction between sulfur atoms in such poly(dithiolene) complexes must be considered [205] because of structural evidence [206,207].

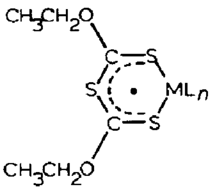


78



79

Better conditions to identify paramagnetic species as anion radical complexes exist in some six membered chelate compounds with sulfur coordination centers; the species **80** which contain the bis(ethoxythiocarbonyl) sulfide anion radical ligand were formed photolytically in a similar fashion to 1,2-semidione analogues (16) [208,209].



$ML_n = {}^{I}Mn(CO)_4$

${}^{I}Mn(CO)_3L$

${}^{II}MoCp(CO)_2$

L = group 15 donor

80

F. SPECTROSCOPY AND STRUCTURE

(i) Magnetic resonance and magnetism

Electronic paramagnetic resonance (EPR) is the predominant spectroscopic method for identification and characterization of paramagnetic species with $S = 1/2$. This spin state is usually a result of coordination of one anion radical ligand to a diamagnetic transition metal fragment; however, it may also be the net result in magnetically coupled systems such as $V(SQ)_3$ where two SQ ligands couple antiferromagnetically with the V^{III} (d^2) ion and leave one uncoupled SQ "free" with $S = 1/2$ [149].

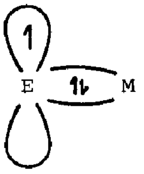
In general, anion radical complexes can be distinguished by EPR from metal-centered paramagnetic species because they should exhibit the typical EPR features of π radical ions [80,210]:

(a) Single lines should be relatively sharp ("natural" linewidth < 0.04 mT) in the absence of special broadening effects such as exchange processes. Remarkable examples of this resolution are the systems $(\mu\text{-L})[M(CO)_5]_2$, M = Mo, W; L = **45–50**, where the linewidths are ~ 0.01 mT (Mo) and ~ 0.02 mT (W); despite the presence of two heavy metal centers with their large spin–orbit coupling constants (see below), the lines are sufficiently sharp to allow detection of metal isotope and even $^{13}C(CO)$ hyperfine splitting in non-enriched material [57]. Of course, the appearance of an EPR spectrum of an anion radical complex may be severely affected by unresolved, overlapping hyperfine structure due to low symmetry or by interacting nuclei in the metal fragment; in unfortunate cases such as for many ruthenium(II) complexes of α-diimines, the net result can be a totally unresolved EPR signal [115–117,211–214].

(b) The hyperfine splitting of the anion radical ligand usually shows only gradual change on metal fragment coordination, unless orbital reversal takes place upon coordination [215]. Those small, yet characteristic changes in the spin distribution may, however, provide some valuable information on the extent of perturbation imposed upon the radical ligand by different metal species. The effect of coordination has been successfully correlated with Hückel MO perturbation calculations in many instances [19,55–58,60,87,90, 91,99,124,216], the HMO calculation procedure still being a superior method for determining π spin populations in planar π radicals [80]. Within this approach, the effect of metal σ coordination to a π system can be described as an increase of effective nuclear charge (or electronegativity) at the coordinating center(s) which, incidentally, also lowers the orbital energies (for reduction!) of the system; strong electrophiles and especially positively charged species cause the largest such perturbations [99].

The spin densities at the coordinating centers as measured by EPR are of more than just special interest because they should correlate with the increase of ligand nucleophilicity in the reduced or MLCT excited state of the parent complexes [45]; a surprisingly large number of experimental properties such as energies, absorbance, band half-widths, and solvatochromic response of MLCT absorption bands as well as lifetimes of MLCT excited states seem to be directly correlated to this increase in ligand σ donor strength and, indirectly, to the spin density at the coordinating centers of the anion radical ligand systems [45,217].

(c) Additional hyperfine interaction of the unpaired electron with nuclei in the coordinated metal fragment(s) can take place via established spin transfer mechanisms such as σ/π spin polarization (eqn. 21) or σ/π hyperconjugation (eqn. 22) [80,120]. Both mechanisms have been shown to operate in metal carbonyl complexes of anion radicals [87] and in substitution products which involve π-accepting [218] organophosphorus and -arsenic groups [19,61,136,155,219]. The magnitude of this additional hyperfine interaction may vary; coupling constants of the directly coordinated metal atoms (α to the π center) usually range between 0.1 and 1% of the isotropic hyperfine coupling constant A_{iso} (unpaired electron exclusively in the *ns* orbital [1]), which corresponds to about 1/10 or less of the usual splitting in metal-centered paramagnetic species (d^n) [210].

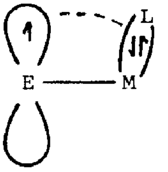


σ/π spin polarization

$$a(\mathrm{M}) = Q \cdot \rho^{\pi}(\mathrm{E}) \tag{21}$$

a : ESR coupling constant

ρ^{π}: π spin population



σ/π hyperconjugation

$$a(\mathrm{L}) = B_0 + B_2 \cdot \rho^{\pi}(\mathrm{E}) \cdot \cos^2(\Theta) \tag{22}$$

Θ : dihedral angle between π orbital at center E and M-L σ bond

B_0, B_2, Q: constants

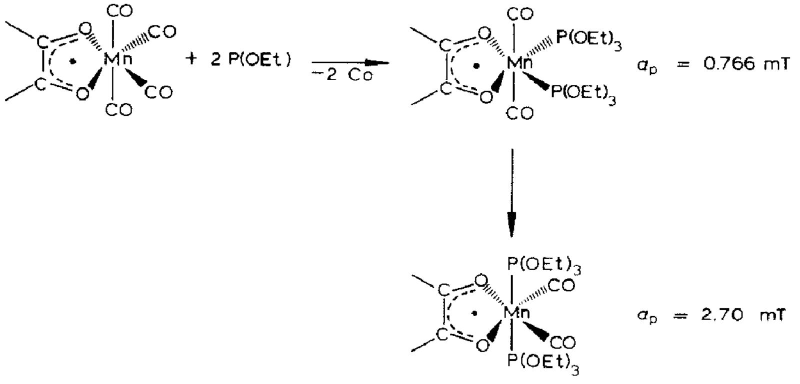
The translation of π spin density ρ^{π} into metal isotope coupling a_{M} is assumed to occur via σ/π spin polarization as in hydrocarbon π radicals [80,210], leading to a McConnell-type [87] equation (21), where Q is a constant.

The small metal coupling in anion radical complexes can be hard to detect experimentally if isotopes with non-zero nuclear spin are present only in low natural abundance. Double coordination of transition metal fragments to centers with high π spin density such as in **40** creates optimal conditions to observe this metal interaction because there are two equivalent metal coordination sites available which cause high satellite line intensities in binuclear complexes for statistical reasons (eqn. 23), because the EPR spectra have comparatively few, widely spaced lines resulting from ^{14}N splitting, and because the spin density at the coordinating nitrogen centers is high due to the localization of spin at only four π centers [87,116].

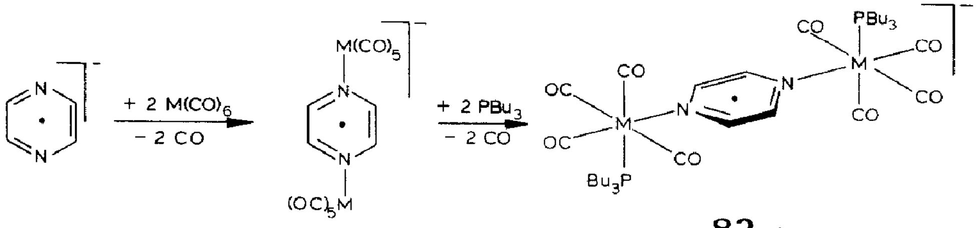
$$W_{m,n} = \prod_{1}^{r} p_r^n (1 - p_r)^{m-n} \binom{m}{n} \tag{23}$$

W = probability of the isotope combination; r = number of the different groups of nuclei; p_r = relative abundance of the isotope; m = total number of equivalent nuclei in one group; n = number of isotopes with the relative abundance p_r.

Coupling constants of hyperconjugatively affected (β) centers can be quite large, as e.g. in anion radical complexes of P-ligand substituted metal carbonyls **81** or **82** [19,61,63,64,110,136,150,153–155,218], where steric effects induce conformations for optimal π/σ_{M-P} hyperconjugation (eqn. (22): $\cos^2(\theta) = 1$).



81



82 M = Mo,W

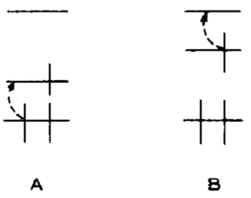
A similar interpretation can be given for the ^{13}C coupling of the *cis*-carbonyls in (μ-L)[M(CO)$_5$]$_2$, M = Mo, W; L = **46**$^{\cdot-}$, **48**$^{\cdot-}$ [57] or **80** [208,209] and for the unresolved ^{14}N splitting which is apparently responsible for the broad lines in anion radical complexes of the [Ru(bpy)$_2$]$^{2+}$ fragment [116,117,211].

(d) The isotropic g values of anion radical complexes, the "chemical shifts", are a very useful source of information concerning the electronic structure of the complex. Deviations of g from the free electron value of

$g_e = 2.0023$ may be attributed to the admixture of higher excited states to the (doublet) radical ground state. According to a first approximation [1,220,221], $g = g_e + \Delta g$ can be expressed as a function of the spin–orbit coupling constants ζ_k of the participating atoms and of the energy differences $E_n - E_0$ between the singly occupied molecular orbital (E_0) and the other completely occupied or unoccupied MOs (E_n: see eqn. (24) and the scheme shown in (25); **L**: angular momentum operator).

$$g = g_e - \tfrac{2}{3}\sum_i \sum_n \sum_{kj} \frac{\langle \psi_o | \zeta_k \mathbf{L}_{ik} \delta_k | \psi_n \rangle \langle \psi_n | \mathbf{L}_{ij} \delta_j | \psi_0 \rangle}{E_n - E_0} = g_e + \Delta g \qquad (24)$$

Since the energy differences are in the denominator of eqn. (24), only the neighbouring levels need be considered as contributing significantly to Δg, however, there are two alternatives regarding its sign:



(25)

For dominating $E_n < E_0$ (case A), g becomes larger than $g_e = 2.0023$, whereas for dominating $E_n > E_0$ (case B), g decreases relative to g_e [220,221].

Although these effects are most conspicuous for paramagnetic transition metal ions [1] such as d^9 systems (case A, $g > g_e$) or d^1 systems (case B, $g < g_e$) where the difference between d levels is much smaller than the gap between d orbitals and the next filled or unfilled s or p levels, this approach may also be employed using eqn. (24) for transition metal complexes of anion radicals with their delocalized π systems [3,19,54,87,90,117].

Anion radical complexes of transition metal fragments usually display rather small deviations of g_{iso} from g_e ($\Delta g \leqslant \pm 0.02$) because the spin is delocalized mainly over light atoms with small spin orbit coupling factors ζ. However, the characteristic changes on going from the ligand anion radical to the complexes can provide valuable information on the electronic structure, i.e. orbital ordering, of those compounds. For instance, most tungsten carbonyl complexes of anion radical ligands have g(W-complex) $> g_e$ because ζ_Wo is rather large (2089 cm^{-1}) and the typical situation in such species is as in (25, A), i.e. a large SOMO/LUMO ($\pi/d\pi^*$) gap [19,87].

There are, however, several cases where the latter relation is reversed because of the presence of a low-lying unoccupied level [19]; two such classes of compounds involve the $(\eta^5\text{-}C_5R_5)(CO)_2Mn^I$ [3,54] and $[(bpy)_2Ru^{II}]^{2+}$ fragments [115–117,211–213] where photochemical and photophysical results are supported by this interpretation [14–16,222]. Vice versa, the low g value of an anion radical complex may then be taken as strong indication for at least one excited state close to the MLCT excited state of the non-reduced precursor complex (25 B): comparative studies on a series of compounds even suggest a relative spacing between the participating levels [117].

(e) The g anisotropy in the EPR spectra of transition metal complexes with anion radical ligands is generally small, even in species which contain heavy metal centers [211–213]; once more, this is a result of the spin delocalization in the ligand π system with little or no contribution from metal d orbitals.

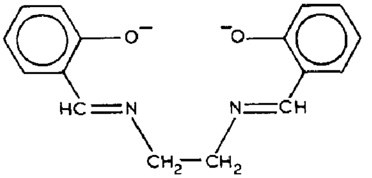
The typical EPR characteristics of anion radical complexes as outlined here should be taken as strongly indicative for that formulation. However, there are also metal-centered paramagnetic species which exhibit, for example, rather sharp lines, superhyperfine coupling of coordinating atoms [223], small isotropic metal hyperfine coupling [224], or $g_{iso} \sim g_e$ [1]. As a caveat, *all* of the above required properties must be displayed by an anion radical complex proper.

EPR line broadening effects may occur in anion radical complexes such as $[Ru(bpy)_3]^+ = [Ru^{II}(bpy^{\cdot-})(bpy)_2]^+$ which offer several equivalent coordination sites for one unpaired electron so that spin migration may occur on the EPR time scale of $10^{-6} - 10^{-8}$ s (see below) [211,212]; more frequently, however, the EPR hyperfine structure of anion radical complexes is insufficiently resolved because of a large number of overlapping lines [116,117]. In those cases, the spin distribution is accessible by more intricate spectroscopic methods such as Electron Nuclear Double Resonance (ENDOR) [202c,225], NMR of paramagnetic molecules [214,226], or high quality X-ray diffraction and subsequent electron deformation density (EDD) determination in the solid state [227,228].

In anion radical complexes with $S > 1/2$, the spin–spin interaction can be studied by triplet EPR spectroscopy [210] (weak interaction) and by measurement of temperature-dependent magnetism. The latter technique has been applied to complexes with more than one anion radical ligand and to species which contain a paramagnetic metal center antiferromagnetically coupled to the anion radical ligand(s) [144,149]. The combination of EPR and magnetic measurements is particularly useful in the study of complexes which contain several paramagnetic components. Hendrickson and coworkers have shown that rather strong metal/SQ interactions are operating in species **83**–**85** [144] whereas the tris-compounds **86** and **87** exhibit a distinct temperature-dependent paramagnetism due to contributions from higher spin states, resulting from relatively weak intramolecular antiferromagnetic interactions [149]. Even the related molybdenum complex **88** displays some remaining paramagnetism (indicating some SQ contribution) [229] although, in general, the heavier transition metals tend to form catecholate complexes on oxidative addition of 1,2-quinones [22].

$\mathrm{Fe(salen)(SQ')}$ $S = 2$ (h.s. $\mathrm{Fe^{III}}$/a.f.c./SQ′)
83
$\mathrm{Mn(salen)(SQ')}$ $S = 3/2$ (h.s. $\mathrm{Mn^{III}}$/a.f.c./SQ′)
84
$\mathrm{Co(salen)(SQ')}$ $S = 1/2$ (l.s. $\mathrm{Co^{III}}$/a.f.c./SQ′)
85

SQ′ = **63**; salen:



$\mathrm{Cr^{III}(SQ'')_3}$ $\mathrm{Fe^{III}(SQ''')_3}$ $\mathrm{Mo^{V}(SQ''')(Cat''')_2}$
86, SQ″ = **64** **87**, SQ‴ = **65** **88**

a.f.c.: antiferromagnetically coupled

As a curiosity and a caveat it may be noted that transition metal complexes of anion radical complexes can exhibit EPR features which clearly indicate the localization of the unpaired electron at the metal center as a result of antiferromagnetic coupling; some examples [230,231] and their correct formulation are given below.

$[\mathrm{Ti(bpy)_3}]^- = \mathrm{Ti^{I}(bpy^{\bullet-})_2(bpy)}$ $S = 1/2$(metal-centered)
89
$[\mathrm{Cr(bpy)_3}]^+ = \mathrm{Cr^{III}(bpy^{\bullet-})_2(bpy)}$ $S = 1/2$(metal-centered)
90
$[\mathrm{Cr(SQ')_3}]^+ = \mathrm{Cr^{III}(SQ')_2(Q')}$ $S = 1/2$(metal-centered)
91
$[\mathrm{Cr(SQ')_3}]^- = \mathrm{Cr^{III}(SQ')_2(Cat')}$ $S = 1/2$(metal-centered)
92 SQ′ = **63**

The delicate balance in the ordering of metal and ligand centered molecular orbitals is illustrated by the isoelectronic species $\mathrm{V^{III}(SQ')_3}$ **93** [149] and "$[\mathrm{Cr(SQ')_3}]^+$" **91** [231] which have their unpaired electrons in different MOs, the former species in a ligand π level and the latter in a metal d orbital [22]. The important role of the anion radical ligand, on the other hand, is demonstrated by observations that the strongest antiferromagnetic coupling with a specific metal center is displayed by the least electrophilic ligands within a series of different SQ ligands [232]. Even more revealing is a comparison between $V(SQ')_3$ **93** [149] and "$V(bpy)_3$" **94** [230], bpy anion radicals are much more basic [48] and stronger reducing than 1,2-semiquinones [51] and thus induce a lower oxidation state of the metal which, in turn, produces a switch of the unpaired electron from the ligand to the metal center! Paradoxically, the *reduction* of the vanadium(III) complex **93** produces an anionic complex with *oxidized* metal, V^V, because of triple intramolecular electron transfer [149b].

$$\begin{array}{lll}
\underset{\mathbf{93}}{V(SQ'')_3} = V^{III}(SQ'')_3 & & S = 1/2(\text{ligand-centered}) \\
\qquad\qquad \searrow +e^- & & \\
\qquad\qquad [V^V(Cat'')_3]^- & & S = 0 \\
 & & \qquad SQ'' = \mathbf{64} \\
\underset{\mathbf{94}}{V(bpy)_3} = V^{II}(bpy^{\bullet-})_2(bpy) & & S = 1/2(\text{metal-centered})
\end{array}$$

In some instances it has even been possible to observe a temperature-dependent intramolecular electron transfer between metal and coordinated ligand in the ground state, as detected by EPR and magnetic measurements; examples involving SQ complexes of manganese (**68**) [175], cobalt (**95**) [234] and iron (**96**) [233] have been reported.

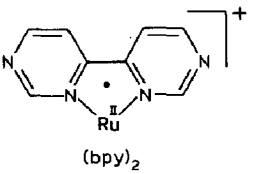
$$Co^{III}(SQ')(Cat')(bpy) \underset{\mathbf{95}}{\rightleftharpoons} Co^{II}(SQ')_2(bpy) \qquad SQ' = \mathbf{63}$$

$$Fe^{III}(SQ'')(Cat'')(bpy) \underset{\mathbf{96}}{\rightleftharpoons} Fe^{II}(SQ'')_2(bpy) \qquad SQ'' = \mathbf{64}$$

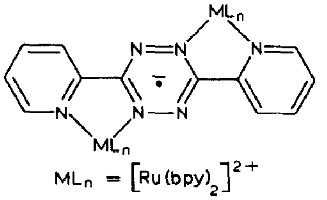
In the bpy series, compound **30** shows a related situation [88]; many intramolecular electron transfer processes have of course been shown to occur via MLCT excitation (3).

The question of localization or delocalization of spin in anion radical complexes, including MLCT excited species, with more than one equivalent "innocent" ligand has received considerable attention in recent years [11,14,16,211–214,235]; this problem is also relevant in those cases where there is more than one coordinated metal fragment present. Whereas the former problem pertains to the question of electron delocalization and electron transfer in organic chemistry, i.e. to electron transfer between metal-coordinated ligands (eqn. 35) [10,31], the latter situation relates to the ligand mediated electron transfer between molecule-bridged metal centers [7–9].

Starting with complexes containing several equivalent or nearly equivalent ligands for reduction to an anion radical, the situation in the reduced forms of $[Ru(bpy)_3]^{2+}$ and related species has been extensively studied and discussed [11,14,16,117,211–214]. The results obtained for these and related, deliberately modified systems [115–117] have illustrated two of the three possible alternatives, viz., full localization, full delocalization, and intermediate behaviour. Localization of spin was observed in singly reduced complexes in which one of the three α-diimine ligands has a distinctly lower π^* level than the other two, such as in **97** [115] or in the binuclear complex **98** [116].

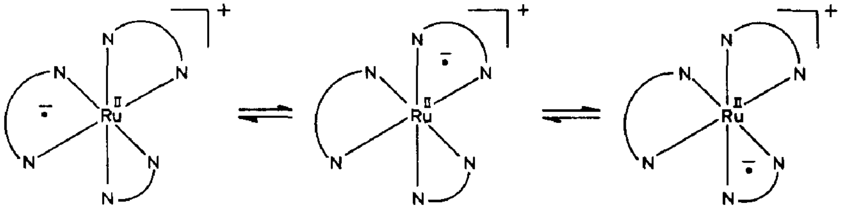


97



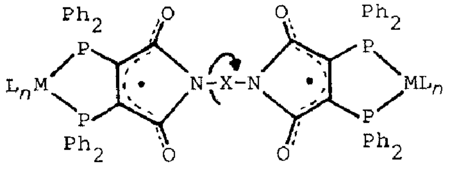
98

Complexes with three completely equivalent ligands, on the other hand, show a broadening of their EPR spectra which cannot be accounted for solely by the poor resolution due to overlapping lines [117]; migration of spin was calculated from temperature dependent line width measurements to occur within the time scale of the EPR experiment ($\sim 10^{-7}$ s) [211,212].



Doubly-reduced species of this kind of complexes contain two ligands with $S = 1/2$ and a singlet (strong interaction) or triplet situation (weak interaction) may be expected; EPR features indicating the latter alternative were observed in complexes such as $\text{Mg(bpy)}_2 = [\text{Mg}^{\text{II}}(\text{bpy})^{\bullet-})_2]$ [236]. However, the complexes $\text{Ru(bpy)}_3 = [\text{Ru}^{\text{II}}(\text{bpy}^{\bullet-})_2(\text{bpy})]$ as well as $[\text{Ru(bpy)}_3]^- = [\text{Ru}^{\text{II}}(\text{bpy}^{\bullet-})_3]^-$ with two or three singly-reduced bpy ligands may be described as containing virtually uncoupled (non-interacting) $S = 1/2$ systems [211,212], the non-coplanar arrangement in the octahedral complexes apparently disfavouring an interaction of the $\text{bpy}^{\bullet-}$ ligands.

Anion radical complexes may contain two or more metal fragments, most binuclear species with equivalent coordination sites such as **13** [55,56], **54** [3], **82** [57,219] or **98** [87,116] have so far shown an even distribution of the small spin density to the two equivalent metal centers. An interesting case is the neutral binuclear species **99** prepared by Fenske and coworkers [199] which again contain non-interacting components, this time individual radical anion complex moieties. As for the $[\text{Ru}(\alpha\text{-diimine})_3]$ systems, the steric situation (orthogonally arranged molecular halves) [199] is intimately connected to the extent of spin–spin interaction.



99

ML_n = $Mn(CO)_4$
$Co(CO)_3$

X = /
$(CH_2)_n$
p-C_6H_4

(26)

The role of paramagnetic bridging ligands in the transmission of ferromagnetic interactions between manganese centers of water oxidizing enzymes in photosynthesis has been discussed in view of a model system involving 2-acetyl-1,4-semiquinones [187c]; there are still few polynuclear transition metal complexes which contain one (17) [66b] or more anion radical ligands such as the clusters $M_4(SQ)_8$, M = Mn, Co, Ni [175].

(ii) Electrochemistry

Among the various electrochemical techniques available to study the formation and reactivity of anion radicals and their complexes, cyclic voltammetry currently enjoys the widest popularity [237]. The electrochemistry of organometallic transition metal compounds in particular has taken a rapid development since the early reports by Dessy and coworkers [101–105] as recent reviews illustrate [37,238,239].

Two kinds of informations from cyclic voltammetry and related experiments must be distinguished:

(a) Redox potentials indicate the threshold necessary for the formation of an anion radical species, the coordination of one or more electrophilic metal fragments generally facilitating the reduction of coordinated ligands (3: $E_0' > E_0$). Besides the first reduction potential of a complex to an anion radical coordination compound, there are often more reversible electron transfer processes occurring which can either involve the formation of dianionic (diamagnetic) ligands [90,117] or the one-electron reduction of other reducible ligands. Complexes with more than one "innocent" ligand can often exhibit multistep redox behavior [30,32,34,93] which apparently involves components containing anion radical ligands; three such examples are **100** [240], **101** [231] and **102** [241].

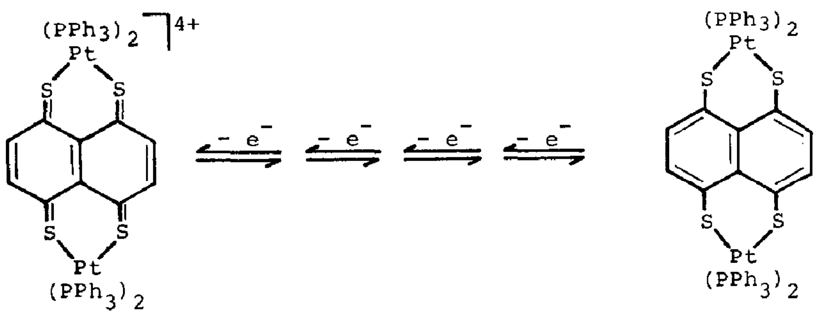
$$[Cr(Q')_3]^{3+} \overset{-e^-}{\rightleftharpoons} \overset{-e^-}{\rightleftharpoons} \overset{-e^-}{\rightleftharpoons} Cr(SQ')_3 \overset{+e^-}{\rightleftharpoons} \overset{+e^-}{\rightleftharpoons} \overset{+e^-}{\rightleftharpoons} [Cr(Cat')_3]^{3-}$$

100, SQ' = **63**

$$[Ru(4,4'\text{-}(CO_2Et)_2bpy)_3]^{2+} \quad \overset{+e^-}{\rightleftharpoons} \overset{+e^-}{\rightleftharpoons} \overset{+e^-}{\rightleftharpoons} \overset{+e^-}{\rightleftharpoons} \overset{+e^-}{\rightleftharpoons} \overset{+e^-}{\rightleftharpoons} \overset{+e^-}{\rightleftharpoons} \overset{+e^-}{\rightleftharpoons} \overset{+e^-}{\rightleftharpoons} \overset{+e^-}{\rightleftharpoons}$$

101

The potential differences $E_0' - E_0''$ are related to the comproportionation



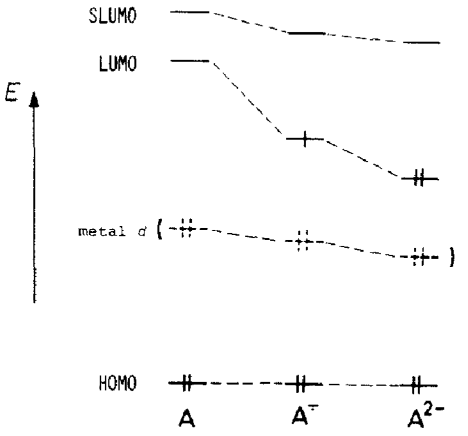
102

constant K_c via eqn. (7). The existence of reversible oxidation and reduction potentials gives a first indication for the possibility of chemically isolating the electrochemically formed species. The criterion "reversible" refers, of course, to the time of the electrochemical experiment; coulometry lasting several minutes generally provides a good measure of the stability of electrogenerated species.

(b) The chemical reactivity of electrogenerated compounds is evident from irreversible behaviour in the cyclovoltammetry experiment [237]; even in the absence of additional reactands (eqn. 4), there are a number of possible reaction paths for anion radical complexes. The anion radical ligand itself can be short-lived and undergo typical anion radical reactions [242] despite the fact that metal coordination has been shown to stabilize less persistent anion radicals such as **12**, **13** [60] or **71**$^{\cdot-}$ [177]. Additional electron uptake by an anion radical complex may be chemically irreversible, thereby providing a sometimes efficient way to reduce stability and preclude isolation of the anion radical species, especially if K_c is small. Simple dissociation, on the other hand, is not common in the formation of anion radical complexes because the reduced ligands are much stronger nucleophiles than their neutral counterparts (Section C). A very typical reaction of anion radical ligands with more than one coordination site is, therefore, the formation of bi- and poly-nuclear complexes even if corresponding species are not formed with the neutral ligands such as with systems **7**–**10** [55–57]. Processes of this kind are analogous to proton exchange reactions of reduced species [52,53] and may be described as ECE(C) mechanisms [237,239] where an initial electrode process is followed by a chemical reaction forming a second electroactive species which, in some instances, may react chemically and revert to the starting system. A four component scheme according to an ECEC mechanism [239] has been presented in equation (11) [54]. Such a formalism also describes the situation in group 6 metal pentacarbonyl complexes of the system **7**/**7**$^{\cdot-}$ [55,56,60] or for the formation of complex **54** where neither a binuclear neutral complex nor a mononuclear anion radical species can be observed [3,243]. Electrochemical techniques have been particularly useful to establish electron transfer catalyzed reactions [17,18] and to determine thermodynamic and kinetic requirements for such processes (4).

(iii) Electronic spectroscopy (UV/VIS/NIR)

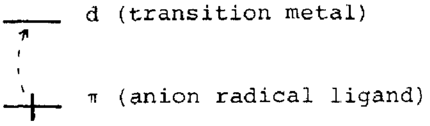
Almost all anion radicals of π systems are colored due to fairly intense transitions in the visible range of the spectrum [244] whereas the further reduced species often exhibit less bathochromically shifted absorptions [158,245]. The reason for this phenomenon lies simply in the fact that the separation of HOMO and LUMO levels in a "normal" molecule is usually much larger than the separation between the LUMO and the Second Lowest Unoccupied Molecular Orbital, SLUMO (27). Despite stabilization of the LUMO upon occupation, there is still a rather small gap between the former LUMO (now Singly Occupied Molecular Orbital, SOMO) and the next unfilled level as illustrated in the one-electron scheme (27); further stabilization through double occupancy in the dianion is then responsible for the hypsochromic shift of the transitions from this orbital relative to the situation in the radical anion.



(27)

In transition metal complexes of anion radicals, the one-electron orbital scheme (27) is further complicated by high-lying occupied metal levels and, in some instances, also by low-lying unoccupied metal centered orbitals [54,116]; such a situation can then allow for further transitions at rather low energies, e.g., in the infrared region of the spectrum.

Ligand-to-metal charge transfer (LMCT) transitions occurring between the generally electron-rich anion radical ligands and coordinated fragments with high metal oxidation states have been established, the process (28,29)



(28)

represents the excited state equivalent of the ground state reaction (1) and is the counterpart of the anion radical complex forming MLCT transition (3).

$$(L_nM^k)(A^{\bullet -}) \xrightarrow[\text{LMCT}]{h\nu} {}^*[(L_nM^{k-1})(A)] \tag{29}$$

The negative solvatochromism of such LMCT bands as observed, e.g. for $(\mathrm{TCNE}^{\bullet -})(^+\mathrm{Mn(CO)_2Cp})$ (17) [66b], results from a decrease of the dipolar character after transfer of charge (29).

Another characteristic yet rarely obvious kind of transition in anion radical complexes is the ligand-to-ligand charge transfer (LLCT) between coordinated ligands of different oxidation state, e.g., between an anion radical, $A^{\bullet -}$, and another reducible ligand, B [158]

$$(B)(L_nM)(A^{\bullet -}) \xrightarrow[\text{LLCT}]{h\nu} {}^*[(B^{\bullet -})(L_nM)(A)] \tag{30}$$

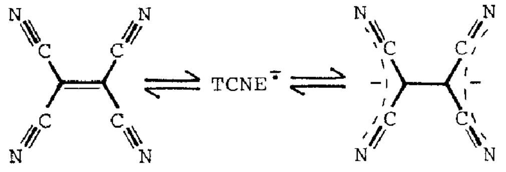
In the case of little interacting identical ligands (30, A = B), the inter-valence transitions of such mixed-valence ligand complexes [66a,233] can be shifted far out into the infrared region of the spectrum as has been observed for $[\mathrm{Ru(bpy)_2(bpy^{\bullet -})}]^+$ [246].

Assignments of transitions in anion radical complexes are not always unambiguous and should preferably be based on a number of related systems such as in the studies on metal phthalocyanine anion radicals [129] or reduced ruthenium(II) complexes with α-diimine [246] and 1,2-quinone-type ligands [158]. Although the number of such investigations is still limited, they may offer quite detailed insight into the electronic structure of coordination compounds.

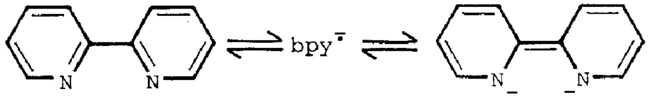
(iv) Structural studies and vibrational spectroscopy

Radical ion formation is usually accompanied by structural changes which can be quite severe [247] and which are often indicative of the oxidation states involved. Typical such changes on anion radical formation of some common reducible ligands are the lengthening of multiple bonds in O_2 [138], TCNE (C=C and C=N) [132], or quinones (C=C, C=O) [22], and the shortening of some single bonds such as the one connecting the two aromatic rings in bpy [39,89,248] upon reduction. These effects illustrate the intermediate position of anion radicals between the neutral oxidized forms and the fully reduced dianionic forms with their different localized valence electron formulae (6,31–33) and can be reproduced by bond order changes as calculated by simple MO methods [43].

$$\mathrm{O{=}O} \rightleftharpoons \mathrm{O_2^{\bullet -}} \rightleftharpoons {}^-\mathrm{O{-}O}^- \tag{31}$$



(32)



(33)

Structural data have been used in many instances to identify ligands as anion radicals when other methods gave less clear-cut answers [22], e.g. for complexes $M_4(SQ)_8$, M = Mn, Co, Ni [175] or **88** [229].

The above considerations may also apply to results obtained from vibrational spectroscopy (IR, Raman), lengthening of multiple bonds being correlated to a reduction in their stretching frequency [22,66b,132,138]. Again, small species such as $O_2^{0/-/2-}$ [138] and $TCNE^{0/-/2-}$ [66b,132,133] but also the larger 1,2-semiquinone [22] and bpy systems [88] have been identified and characterized in different oxidation states as coordinated ligands by vibrational spectroscopy. A very useful experimental extension of this correlation is the Time Resolved Resonance Raman Spectroscopy (TR^3) [249] which has allowed the anion radical ligands formed in MLCT excited states (3) [250] to be characterized.

Infrared spectra and structural data also demonstrate characteristic changes within the coordinated metal fragment and can thus provide valuable clues concerning the changed reactivity of these moieties. For instance, anion radical complexes of metal carbonyls were shown to exhibit a significant reduction of CO stretching frequency [103] due to diminished back bonding. While the σ bonding from anion radicals is greatly enhanced because of the increase in ligand nucleophilicity (Section C), the π back donation is reduced as the ligand π acceptor level is no longer empty but half occupied so that the balance between both synergistic bonding contributions is perturbed [19,56,219]. Accordingly, the destabilized metal carbonyl bond offers the opportunity for enhanced substitutional reactivity which may even take a catalytic path with respect to electron transfer activation (4) [18,19]. Yet, in discussing structural and vibrational data of anion radical complexes, the effect of charge alone must always be considered because charge distribution and spin density are not necessarily closely related [5].

G. REACTIVITY OF ANION RADICAL COMPLEXES

Anion radical complexes of main group or transition metal fragments may show the typical reactivity of anion radical ligands [242], viz., intra- or intermolecular electron transfer in the ground state (1) or in electronically excited states (29), reductive addition of electrophiles to centers of high charge density (cf. the mechanism of the Birch reduction), or substitution reactions. The participation of only the anion radical oxidation state in substitution or addition reactions is often difficult to establish. Neighbouring oxidation states are present to an extent given by the redox equilibrium (7) and may be rate-determining. Electron transfer reactivity can be favoured above addition and substitution reactions by introduction of bulky substituents (steric hindrance) such as in 3,5-di^{t}butyl-1,2-semiquinone **63** and its coordination compounds [22,28,36].

Apart from these well-established reactions patterns and excluding the important role of transition metal/anion radical complexes as transition states or intermediates in inner-sphere electron transfer processes [7,9] and excited state-reactions [8], there are reaction pathways which are available only to coordination compounds of anion radicals and which generally involve the activation of coordinated ligands as brought about by the presence of the anion radical ligand. It is not unexpected, for example, that bound chloride centers become labilized upon reduction of a coordinated co-ligand, as has been demonstrated for a number of ruthenium(II) and osmium(II) chloride complexes which contain the non-innocent ligand bpy [251]:

$$[\mathrm{M(bpy)_2(L)Cl}]^+ \overset{+2e^-}{\rightarrow} [\mathrm{M(bpy^{\cdot-})_2(L)Cl}]^- \underset{-\mathrm{Cl}^-}{\overset{+\mathrm{S}}{\rightarrow}} [\mathrm{M(bpy^{\cdot-})_2(L)S}] \qquad (34)$$

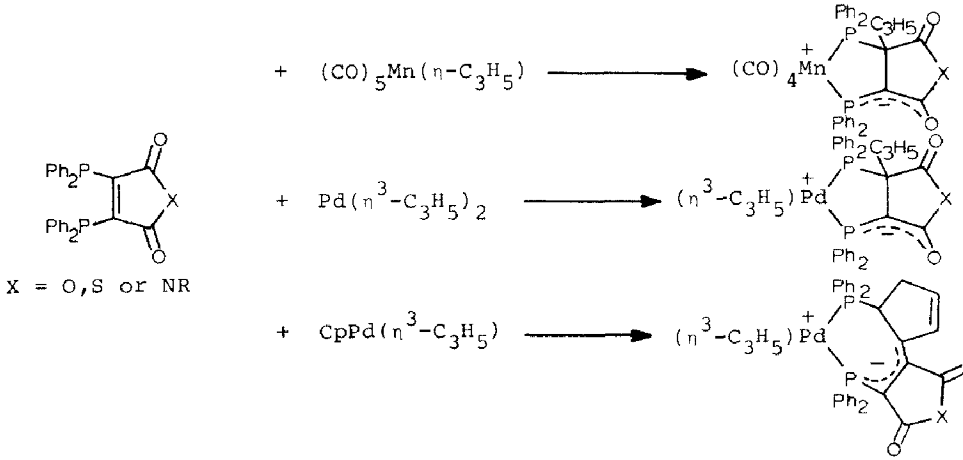
M = Ru, Os; S = substrate

Less obvious is the already discussed substitutional labilization of carbon monoxide in compounds such as **81** or **82** by hyperconjugative spin transfer from the singly reduced ligand to the metal–carbon σ bond (22). Although the rates of substitution are not as high as in corresponding 17-electron metal systems [252], this often catalytic (4) electron transfer activation is a potentially useful alternative in those instances when neither thermal nor photochemical activation can be employed [19]. Group 6 and 7 metal carbonyl complexes of anion radicals have been shown to undergo this substitution [18,136,155,219] although preparative applications are still rare. Most of the $\mathrm{CO/PR_3}$ exchange reactions catalyzed by anion radical formation lead exclusively to products which are singly substituted at each metal center; EPR spectroscopy suggests that after the first substitution, hyperconjugative spin transfer is almost completely directed to the phosphorus ligands [219] (**82**) with their low lying acceptor levels [218] so that little or no activation of further CO ligands remains.

Another attractive possibility within this concept is the reaction between two coordinated ligands at a metal center, one ligand (or both) being activated by reduction to the anion radical state(s). Such an electron transfer variety of the catalytically important "reactions of coordinated ligands" [253] operates in many reductions of electron-poor organic substrates by main group organometallics [36]; it may, however, occur also in the transition metal series, in particular with small, π coordinated unsaturated ligands, which frequently require stepwise coordination and one-electron redox processes for activation.

$$\left(\overset{\delta-}{R}-\overset{\delta+}{L_nM}\right)(A)\xrightarrow{\text{electron transfer}}\left[(R-L_nM)^{\cdot+}(A^{\cdot-})\right]\xrightarrow{\text{escape}}R^{\cdot}+(L_nM^{+})(A^{\cdot-}) \qquad (35)$$

For instance, Fenske and coworkers have repeatedly reported anion radical intermediates of the type **77** in the C–C bond-forming reactions (36) involving allyl [196,197] or cyclopentadienyl transfer [195]:



(36)

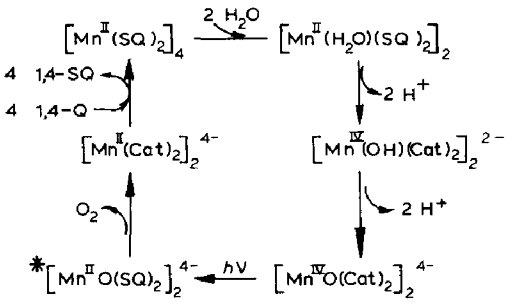
It was further reported that the reduction of O_2, CO or N_2 can be catalyzed by systems which readily form metal/1,2-semiquinone complexes [254,255] and mechanisms for the conversion of O_2 have been presented (37) [254]; a similar model was suggested recently for the reduction of CO_2 using bpy$^{\cdot-}$ containing complexes of ruthenium(II) [251].

$$\begin{tikzcd} 2\,V(SQ)_3 \arrow[r, "O_2", "-2Q"'] & {[VO(SQ)(Cat)]_2} \arrow[r, "1.5O_2", "-4Q"'] & V_2O_5 \arrow[ll, bend left, "-6H_2O", "{12H^+,\ 6Cat.0.5O_2}"'] \end{tikzcd} \qquad (37)$$

As concerns uphill processes, a catalytic scheme involving 1,2-semiquinone complexes of manganese was proposed for the light-driven production of O_2 from water (38) [175].

Examples such as (4), (37) or (38) illustrate how the growing recognition of anion radical complexes in transition metal chemistry does not only stimu-

$$2\,H_2O + 4\ 1{,}4\text{-}Q \xrightarrow{h\nu} O_2 + 4\,H^+ + 4\ 1{,}4\text{-}SQ$$



(38)

late the synthesis of new materials and contribute to the understanding of bonding in coordination compounds of non-innocent partners, it also suggests the use of such species as defined intermediates in electron transfer and photoelectron transfer catalytic [256] processes.

ACKNOWLEDGEMENTS

Our own research in the area of anion radical coordination and electron transfer chemistry has been aided by grants from Deutsche Forschungsgemeinschaft (DFG), Fonds der Chemischen Industrie, Stiftung Volkswagenwerk, Flughafen Frankfurt/Main AG, and from the Hermann Willkomm-Foundation. Generous loans were received from Degussa AG, BASF AG, CIBA-GEIGY AG, and from Wacker Chemie AG.

I am very much indebted to my coworkers, Sylvia Ernst, Renate Gross, Barbara Olbrich-Deussner, Christian Bessenbacher, Stephan Kohlmann, Volker Kasak, and Andreas Schulz, for their intellectual and practical contributions.

A personal fellowship of the Karl Winnacker-Foundation of Hoechst AG is most gratefully acknowledged.

REFERENCES

1 B.A. Goodman and J.B. Raynor, Adv. Inorg. Chem. Radiochem., 13 (1970) 136.

2 S.S. Eaton and G.R. Eaton, Coord. Chem. Rev., 26 (1978) 207. Cf. also L. Fielding, K.M. More, G.R. Eaton and S.S. Eaton, J. Am. Chem. Soc., 108 (1986) 618, and previous papers in that series.

3 For a recent example cf. R. Gross and W. Kaim, Angew. Chem., 97 (1985) 869; Angew. Chem. Int. Ed. Engl., 24 (1985) 856.

4 (a) L. Pauling, General Chemistry, 2nd edn., W.H. Freeman, San Francisco, CA, 1954. (b) C.K. Jørgensen, Oxidation Numbers and Oxidation States, Springer-Verlag, Berlin, 1969, p. 291.

5 A.B.P. Lever, G.A. Ozin and H.B. Gray, Inorg. Chem., 19 (1980) 1823.

6 D.A. Summerville, R.D. Jones, B.M. Hoffman and F. Basolo, J. Chem. Educ., 56 (1979) 157.

7 H. Taube, Electron Transfer Reactions of Complex Ions in Solution, Academic Press, London, 1970.
8 T.J. Meyer, Acc. Chem. Res., 11 (1978) 94; Progr. Inorg. Chem., 30 (1983) 389.
9 E.S. Gould, Acc. Chem. Res., 18 (1985) 22.
10 J.K. Kochi, Organometallic Mechanisms and Catalysis, Academic Press, New York, 1978.
11 K. Kalyanasundaram, Coord. Chem. Rev., 46 (1982) 159.
12 A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd edn., Elsevier, Amsterdam, 1984.
13 G.L. Geoffroy and M.S. Wrighton, Organometallic Photochemistry. Academic Press, New York, 1979.
14 M.K. DeArmond and C.M. Carlin, Coord. Chem. Rev., 36 (1981) 325.
15 H. Yersin and E. Gallhuber, J. Am. Chem. Soc., 106 (1984) 6582.
16 P.S. Braterman, G.A. Heath and L.J. Yellowlees, J. Chem. Soc., Dalton Trans., (1985) 1081.
17 J.M. Saveant, Acc. Chem. Res., 13 (1980) 323.
18 D. Miholova and A.A. Vlček, J. Organomet. Chem., 279 (1985) 317.
19 W. Kaim, Inorg. Chem., 23 (1984) 3365, and unpublished results obtained with R. Gross and B. Olbrich-Deussner.
20 P.J. Krusic and J. San Filippo, Jr., J. Am. Chem. Soc., 104 (1982) 2645.
21 J.W. Hershberger, R.J. Klingler and J.K. Kochi, J. Am. Chem. Soc., 105 (1983) 61; P.M. Zizelman, C. Amatore and J.K. Kochi, Ibid., 106 (1984) 3771; J.K. Kochi, J. Organomet. Chem., 300 (1986) 139.
22 C.G. Pierpoint and R.M. Buchanan, Coord. Chem. Rev., 38 (1981) 45.
23 D.J. Gordon and R.F. Fenske, Inorg. Chem., 21 (1982) 2907.
24 M.F. Lappert and P.W. Lednor, Adv. Organomet. Chem., 14 (1976) 345.
25 P.R. Jones, Adv. Organomet. Chem., 15 (1977) 273.
26 D.H. Chin, S.E. Jones, L.E. Leon, P. Bosserman, M.D. Stallings and D.T. Sawyer, Biological Redox Components, A.C.S. Symp. Ser., 201 (1982) 675. Cf. also M.E. Bodini, G. Copia, R. Robinson and D.T. Sawyer, Inorg. Chem., 22 (1983) 126 and previous papers in that series.
27 K.A.M. Creber, K.S. Chen and J.K.S. Wan, Rev. Chem. Intermed., 5 (1984) 37.
28 M.I. Kabachnik, N.N. Bubnov, S.P. Solodovnikov and A.I. Prokof'ev, Usp. Khim., 53 (1984) 487; Russ. Chem. Rev., 53 (1984) 288.
29 J.A. Pedersen, Handbook of EPR Spectra from Quinones and Quinols, CRC Press, Boca Raton, FL, 1985.
30 C. Creutz, Comments Inorg. Chem., 1 (1982) 293.
31 W. Kaim, Angew. Chem., 95 (1983) 201; Angew. Chem. Int. Ed. Engl., 22 (1983) 171.
32 A.A. Vlček, Coord. Chem. Rev., 43 (1982) 39.
33 J.A. McCleverty, Progr. Inorg. Chem., 10 (1968) 49.
34 R.P. Burns and C.A. McAuliffe, Adv. Inorg. Chem. Radiochem., 22 (1979) 303. Cf. also literature cited in S. Alvarez, R. Vicente and R. Hoffmann, J. Am. Chem. Soc., 107 (1985) 6253.
35 A.M. Bond and R.L. Martin, Coord. Chem. Rev., 54 (1984) 23.
36 W. Kaim, Acc. Chem. Res., 18 (1985) 160.
37 N.G. Connelly and W.E. Geiger, Adv. Organomet. Chem., 23 (1984) 1 and 24 (1985) 87.
28 K. Deuchert and S. Hünig, Angew. Chem., 90 (1978) 927; Angew. Chem. Int. Ed. Engl., 17 (1978) 875. S. Hünig and H. Berneth, Top. Curr. Chem., 92 (1980) 1.
39 J.H. Noordik, J. Schreurs, R.O. Gould, J.J. Mooij and E. de Boer, J. Phys. Chem., 82 (1978) 1105.

40 D. Fenske, Chem. Ber., 112 (1979) 363.

41 K.A.M. Creber and J.K.S. Wan, J. Am. Chem. Soc., 103 (1981) 2101.

42 M.J. Clarke and M.G. Dowling, Inorg. Chem., 20 (1981) 3506. F. Müller, L.E.G. Eriksson and A. Ehrenberg, Eur. J. Biochem., 12 (1970) 93.

43 E. Heilbronner and H. Bock, The HMO Model and its Application, Wiley/Verlag Chemie, London/Weinheim, 1976, p. 396.

44 H.C. Longuet-Higgins, J. Chem. Phys., 18 (1950) 275.

45 S. Ernst and W. Kaim, J. Am. Chem. Soc., 108 (1986) 3578.

46 P. Ford, D.F.P. Rudd, R. Gaunder and H. Taube, J. Am. Chem. Soc., 90 (1968) 1187. J. Sen and H. Taube, Acta Chem. Scand. Ser. A, 33 (1979) 125.

47 K. Wieghardt, H. Cohen and D. Meyerstein, Angew. Chem., 90 (1978) 632; Angew. Chem. Int. Ed. Engl., 17 (1978) 608.

48 C.V. Krishnan, C. Creutz, H.A. Schwarz and N. Sutin, J. Am. Chem. Soc., 105 (1983) 5617.

49 W.R. McWhinnie and J.D. Miller, Adv. Inorg. Chem. Radiochem., 12 (1969) 135.

50 S. Herzog, Naturwissenschaften, 43 (1956) 35; S. Herzog, K.C. Renner and N.A. Schön, Z. Naturforsch., Teil B, 12 (1957) 809; S. Herzog and R. Taube, Angew. Chem., 70 (1958) 469.

51 G.E. Adams, Trans. Faraday Soc., 63 (1967) 1175. R.L. Willson, J. Chem. Soc., Chem. Commun., (1971) 1249.

52 S. Cheng and M.D. Hawley, J. Org. Chem., 50 (1985) 3388.

53 C. Amatore, G. Capobianco, G. Farnia, G. Sandona, J.M. Saveant, M.G. Severin and E. Vianello, J. Am. Chem. Soc., 107 (1985) 1815. M.D. Stallings, M.M. Morrison and D.T. Sawyer, Inorg. Chem., 20 (1981) 2655.

54 R. Gross and W. Kaim, Angew. Chem., 96 (1984) 610; Angew. Chem. Int. Ed. Engl., 23 (1984) 614; Inorg. Chem., 25 (1986) 498.

55 W. Kaim, J. Organomet. Chem., 264 (1984) 317; W. Kaim and S. Kohlmann, Inorg. Chim. Acta, 101 (1985) L21.

56 S. Kohlmann, Diploma Thesis, University of Frankfurt, 1985.

57 W. Kaim, Chem. Ber., 115 (1982) 910; Inorg. Chim. Acta, 53 (1981) L151.

58 W. Kaim, Inorg. Chem., 23 (1984) 504; Z. Naturforsch., Teil B, 39 (1984) 801.

59 H.J. Becher, D. Fenske and M. Heymann, Z. Anorg. Allg. Chem., 475 (1981) 27. K.R. Dunbar, R.A. Walton, Inorg. Chem., 24 (1985) 5.

60 W. Kaim and S. Kohlmann, unpublished results.

61 A.L. Balch, J. Am. Chem. Soc., 95 (1973) 2723; M.Y. Girgis, Y.S. Sohn and A.L. Balch, Inorg. Chem., 14 (1975) 2327; J.A. Ladd, M.M. Olmstead and A.L. Balch, ibid., 23 (1984) 2318.

62 A. Hudson, M.F. Lappert, P.W. Lednor and B.K. Nicholson, J. Chem. Soc., Chem. Commun., (1974) 966.

63 A. Alberti and C.M. Camaggi, J. Organomet. Chem., 161 (1978) C63. K. Mochida, J.K. Kochi, K.S. Chen and J.K.S. Wan, J. Am. Chem. Soc., 100 (1978) 2927.

64 K.A.M. Creber, T.I. Ho, M.C. Depew, D. Weir and J.K.S. Wan, Can. J. Chem., 60 (1982) 1504.

65 Cf. I.R. Dunkin, P. Härter and C.J. Shields, J. Am. Chem. Soc., 106 (1984) 7248; A.F. Hepp and M.S. Wrighton, ibid., 105 (1983) 5934, or T. Kobayashi, H. Ohtani, H. Noda, S. Teratani, H. Yamazaki and K. Yasufuku, Organometallics, 5 (1986) 110.

66 (a) R.M. Buchanan, J. Claflin and C.G. Pierpoint, Inorg. Chem., 22 (1983) 2552; A. Vlcek, Jr., ibid., 25 (1986) 522. (b) R. Gross and W. Kaim, submitted.

67 C. Elschenbroich, E. Bilger, J. Koch and J. Weber, J. Am. Chem. Soc., 106 (1984) 4297.

68 C. Elschenbroich and J. Koch, J. Organomet. Chem., 229 (1982) 139.
69 C. Elschenbroich, F. Gerson and F. Stohler, J. Am. Chem. Soc., 95 (1973) 6956.
70 T.A. Albright, W.E. Geiger, Jr., J. Moraczewski and B. Tulyathan, J. Am. Chem. Soc., 103 (1981) 4787.
71 C. Elschenbroich and M. Cais, J. Organomet. Chem., 18 (1969) 135.
72 J. Tirouflet, E. Laviron, R. Dabard and J. Komenda, Bull. Soc. Chim. Fr., 630 (1963) 857 and 1655.
73 W.C. Danen and C.T. West, Tetrahedron Lett., (1970) 219.
74 J.J. McDonnell and D.J. Pochopien, J. Org. Chem., 36 (1971) 2092.
75 N.J. Gogan, C.K. Chu and G.W. Gray, J. Organomet. Chem., 51 (1973) 323.
76 A. Ceccon, A. Romanin and A. Venzo, Transition Met. Chem., 1 (1976) 25.
77 A. Ceccon, C. Corvaja, G. Giacometti and A. Venzo, J. Chem. Soc., Perkin Trans. 2, (1978) 283.
78 N.J. Gogan, I.L. Dickinson, J. Doull and J.R. Patterson, J. Organomet. Chem., 212 (1981) 71.
79 W. Huber, J. Chem. Soc., Chem. Commun., (1985) 1630.
80 F. Gerson, High Resolution E.S.R. Spectroscopy, Wiley/Verlag Chemie, Weinheim, 1970, p. 137.
81 J.H. Sharp and M.C.R. Symons in M. Szwarc (Ed.), Ions and Ion Pairs in Organic Reactions, Vol. 1, Wiley, New York, 1972, p. 177.
82 P.J. Krusic, U. Klabunde, C.P. Casey and T.F. Block, J. Am. Chem. Soc., 98 (1976) 2015.
83 C.P. Casey, L.D. Albin, M.C. Saeman and D.H. Evans, J. Organomet. Chem., 155 (1978) C37.
84 G.F. Longster, J. Myatt and P.F. Todd, J. Chem. Soc. B, (1967) 612.
85 F. Seitz, H. Fischer, J. Reide, T. Schöttle and W. Kaim, Angew. Chem., 98 (1986) 753.
86 R.J. Klingler, J.C. Huffman and J.K. Kochi, Inorg. Chem., 20 (1981) 34.
87 W. Kaim and S. Kohlmann, Inorg. Chem., 25 (1986) 3442.
88 A.M. McPherson, B.F. Fieselmann, D.L. Lichtenberger, G.L. McPherson and G.D. Stucky, J. Am. Chem. Soc., 101 (1979) 3425.
89 M.H. Chisholm, J.C. Huffman, I.P. Rothwell, P.G. Bradley, N. Kress and W.H. Woodruff, J. Am. Chem. Soc., 103 (1981) 4945; M.H. Chisholm, E.M. Kober, D.J. Ironmonger and P. Thornton, Polyhedron, 4 (1985) 1869.
90 W. Kaim and S. Ernst, J. Phys. Chem., 90 (1986) 5010.
91 W. Kaim, J. Am. Chem. Soc., 104 (1982) 3833 and 7385.
92 K.D. Franz, Ph.D. Thesis, J.W. Goethe-Universität, Frankfurt am Main, 1975.
93 A.L. Balch and R.H. Holm, J. Am. Chem. Soc., 88 (1966) 5201. L.F. Warren, Inorg. Chem., 16 (1977) 2814. M. Gross, J.A. Ibers and W.C. Trogler, Organometallics, 1 (1982) 530.
94 M. Zehnder and H. Löliger, Helv. Chim. Acta, 63 (1980) 754. S.M. Peng, C.T. Chen, D.S. Liaw, C.I. Chen and Y. Wang, Inorg. Chim. Acta, 101 (1985) L31.
95 H.B. Stegmann, K.B. Ulmschneider, K. Hieke and K. Scheffler, J. Organomet. Chem., 118 (1976) 259.
96 P. Clopath and A. von Zelewsky, Helv. Chim. Acta, 55 (1972) 52.
97 S. Richter, C. Daul and A. von Zelewsky, Inorg. Chem., 15 (1976) 943.
98 W. Kaim, J. Am. Chem. Soc., 106 (1984) 1712.
99 W. Kaim, Chem. Ber., 114 (1981) 3789.
100 G. van Koten, J.T.B.H. Jastrzebski and K. Vrieze, J. Organomet. Chem., 250 (1983) 49.
101 R.E. Dessy, F.E. Stary, R.B. King and M. Waldrop, J. Am. Chem. Soc., 88 (1966) 471.
102 R.E. Dessy, R.B. King and M. Waldrop, J. Am. Chem. Soc., 88 (1966) 5112.

103 R.E. Dessy and L. Wieczorek, J. Am. Chem. Soc., 91 (1969) 4963.

104 R.E. Dessy, J.C. Charkoudian, T.P. Abeles and A.L. Rheingold, J. Am. Chem. Soc., 92 (1970) 3947.

105 R.E. Dessy and L.A. Bares, Acc. Chem. Res., 5 (1972) 415.

106 Y. Kaizu and H. Kobayashi, Bull. Chem. Soc. Jpn., 45 (1972) 470.

107 K.D. Franz, H. tom Dieck, U. Krynitz and I.W. Renk, J. Organomet. Chem., 64 (1974) 361; K.D. Franz, H. tom Dieck, K.A. Ostoja-Starzewski and F. Hohmann, Tetrahedron, 31 (1975) 1465; H. tom Dieck and E. Kühl, Z. Naturforsch., Teil B, 37 (1982) 324.

108 R.E. Dessy, J.C. Charkoudian and A.L. Rheingold, J. Am. Chem. Soc., 94 (1972) 738.

109 H. Bruder, Ph.D. Thesis, J.W. Goethe-Universität, Frankfurt am Main, 1977.

110 H. tom Dieck, K.D. Franz and F. Hohmann, Chem. Ber., 108 (1975) 163.

111 E. Makrlik, J. Hanzlik, A. Camus, G. Mestroni and G. Zassinovich, J. Organomet. Chem., 142 (1977) 95.

112 W.A. Fordyce and G.A. Crosby, Inorg. Chem., 21 (1982) 1023.

113 A. Alberti and A. Hudson, J. Organomet. Chem., 248 (1983) 199.

114 M.W. Kokkes, D.J. Stufkens and A. Oskam, Inorg. Chem., 24 (1985) 2934.

115 S. Ernst and W. Kaim, Angew. Chem., 97 (1985) 431; Angew. Chem. Int. Ed. Engl., 24 (1985) 430.

116 W. Kaim, S. Ernst, S. Kohlmann and P. Welkerling, Chem. Phys. Lett., 118 (1985) 431.

117 S. Ernst and W. Kaim, submitted for publication.

118 J.A. Hunter, B. King, W.E. Lindsell and M.A. Neish, J. Chem. Soc., Dalton Trans., (1980) 880.

119 W. Kaim, S. Ernst and S. Kohlmann, Polyhedron, 5 (1986) 445.

120 W. Kaim, S. Ernst and S. Kohlmann, unpublished results.

121 M.J. Maroney and W.C. Trogler, J. Am. Chem. Soc., 106 (1984) 4144; M.E. Gross, W.C. Trogler and J.A. Ibers, ibid., 103 (1981) 192.

122 P. Overbosch, G. van Koten, A.L. Spek, G. Roelofsen and A.J.M. Duisenberg, Inorg. Chem., 21 (1982) 3908.

123 Y. Mizobe, R. Ono, Y. Uchida, M. Hidai, M. Tezuka, S. Moue and A. Tsuchiya, J. Organomet. Chem., 204 (1981) 377.

124 D.R. Eaton, J.M. Watkins and R.J. Buist, J. Am. Chem. Soc., 107 (1985) 5604.

125 A.R. Siedle, G. Filipovich, P.E. Toren, F.J. Palensky, E. Cook, R.A. Newmark, W.L. Stebbings, K. Melancon and H.E. Mishmash, J. Organomet. Chem., 246 (1983) 83.

126 A.R. Siedle, K.R. Mann, D.A. Bohling, G. Filipovich, P.E. Toren, F.J. Palensky, R.A. Newmark, R.W. Duerst, W.L. Stebbings, H.E. Mishmash and K. Melancon, Inorg. Chem., 24 (1985) 2216.

127 M. Millar and R.H. Holm, J. Am. Chem. Soc., 97 (1975) 6052.

128 J. Fajer and M.S. Davis in D. Dolphin (Ed.), The Porphyrins, Vol. IV, Academic Press, New York, 1979, p. 197.

129 P.C. Minor, M. Gouterman and A.B.P. Lever, Inorg. Chem., 24 (1985) 1894.

130 J.R. Norris, H. Scheer and J.J. Katz in D. Dolphin (Ed.), The Porphyrins, Vol. IV, Academic Press, New York, 1979, p. 159. F. Lendzian, K. Möbius, M. Plato, U.H. Smith, M.C. Thurnauer and W. Lubitz, Chem. Phys. Lett., 111 (1984) 583, and literature cited.

131 P.J. Krusic, H. Stoklasa, L.E. Manzer and P. Meakin, J. Am. Chem. Soc., 97 (1975) 667.

132 M.F. Rettig and R.M. Wing, Inorg. Chem., 8 (1969) 2685.

133 W. Beck, R. Schlodder and K.H. Lechler, J. Organomet. Chem., 54 (1973) 303; K.L. Amos and N.G. Connelly, ibid., 194 (1980) C57. A.L. Balch, J. Am. Chem. Soc., 98 (1976) 285.

134 P.B. Ayscough, F.P. Sargent and R. Wilson, J. Chem. Soc. B, (1966) 903.
135 A. Hudson, M.F. Lappert and B.K. Nicholson, J. Chem. Soc., Dalton Trans., (1977) 551.
136 A. Alberti and C.M. Camaggi, J. Organomet. Chem., 181 (1979) 355.
137 S. Ernst, V. Kasak, C. Bessenbacher and W. Kaim, Z. Naturforsch., in press.
138 R.D. Jones, D.A. Summerville and F. Basolo, Chem. Rev., 79 (1979) 139.
139 R.A. Henderson, G.J. Leigh and C.J. Pickett, Adv. Inorg. Chem. Radiochem., 27 (1983) 197.
140 Oxygen Radicals in Chemistry and Biology, W. Bors, M. Saran and D. Tait (Eds.), de Gruyter, Berlin, 1984.
141 B.S. Tovrog, D.J. Kitko and R.S. Drago, J. Am. Chem. Soc., 98 (1976) 5144.
142 V.M. Miskowski, J.L. Robbins, I.M. Treitel and H.B. Gray, Inorg. Chem., 14 (1975) 2318.
143 C.C. Felix and R.C. Sealy, J. Am. Chem. Soc., 104 (1982) 1555; C.C. Felix, J.S. Hyde, T. Sarna and R.C. Sealy, ibid., 100 (1978) 3922.
144 S.L. Kessel, R.M. Emberson, P.G. Debrunner and D.N. Hendrickson, Inorg. Chem., 19 (1980) 1170.
145 M.E. Peover, J. Chem. Soc. B, (1962) 4540.
146 D.R. Eaton, Inorg. Chem., 3 (1964) 1268.
147 A. Vlček, Jr., J. Organomet. Chem., 297 (1985) 43.
148 S.G. Kukes, A.I. Prokof'ev, A.S. Masalimov, N.N. Bubnov, S.P. Solodovnikov and M.I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1519.
149 (a) R.M. Buchanan, H.H. Downs, W.B. Shorthill, C.G. Pierpoint, S.L. Kessel and D.N. Hendrickson, J. Am. Chem. Soc., 100 (1978) 4318. See also P.J. Bosserman and D.T. Sawyer, Inorg. Chem., 21 (1982) 1545. (b) M.E. Cuss, N.R. Gordon and C.G. Pierpont, Inorg. Chem., 25 (1986) 3962.
150 D. Weir and J.K.S. Wan, J. Organomet. Chem., 220 (1981) 323.
151 L. Pasimeni, P.L. Zanonato and C. Corvaja, Inorg. Chim. Acta, 37 (1979) 241.
152 G.A. Bowmaker and G.K. Campbell, Aust. J. Chem., 32 (1979) 1897.
153 T. Foster, K.S. Chen and J.K.S. Wan, J. Organomet. Chem., 184 (1980) 113.
154 K.A.M. Creber and J.K.S. Wan, Chem. Phys. Lett., 81 (1981) 453.
155 K.A.M. Creber and J.K.S. Wan, Can. J. Chem., 61 (1983) 1017.
156 N.G. Connelly, I. Manners, J.R.C. Protheroe and M.W. Whiteley, J. Chem. Soc., Dalton Trans., (1984) 2713.
157 V.K. Cherkasov, K.G. Shal'nova, G.A. Abakumov and G.A. Razuvaev, Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 2830.
158 M. Haga, E.S. Dodsworth and A.B.P. Lever, Inorg. Chem., 25 (1986) 447.
159 P.A. Wicklund, L.S. Beckmann and D.G. Brown, Inorg. Chem., 15 (1976) 1996.
160 D.G. Brown and W.D. Hemphill, Inorg. Chem., 18 (1979) 2039.
161 O. Haas and A. von Zelewsky, J. Chem. Res. (S), (1980) 78; J. Chem. Res. (M), (1980) 1228.
162 R.M. Buchanan and C.G. Pierpoint, J. Am. Chem. Soc., 102 (1980) 4951.
163 K. Broadley, N.G. Connelly and W.E. Geiger, J. Chem. Soc., Dalton Trans., (1983) 121.
164 V.I. Nevodchikov, G.A. Abakumov, V.K. Cherkasov and G.A. Razuvaev, J. Organomet. Chem., 214 (1981) 119.
165 N.G. Connelly, M.J. Freeman, I. Manners and A.G. Orpen, J. Chem. Soc., Dalton Trans., (1984) 2703.
166 G.A. Razuvaev, I.A. Teplova, K.G. Shalnova and G.A. Abakumov, J. Organomet. Chem., 157 (1978) 353.
167 I.A. Teplova, K.G. Shal'nova, G.A. Razuvaev and G.A. Abakumov, Dokl. Akad. Nauk SSSR, 235 (1977) 1323.

168 G.A. Abakumov, I.A. Teplova, V.K. Cherkasov and K.G. Shalnova, Inorg. Chim. Acta, 32 (1979) L57.

169 G.A. Razuvaev, V.K. Cherkasov and G.A. Abakumov, J. Organomet. Chem., 160 (1978) 361.

170 W.A. Muraev, W.K. Cherkasov, G.A. Abakumov and G.A. Razuvaev, Dokl. Akad. Nauk SSSR, 236 (1977) 620.

171 S. Harmalker, S.E. Jones and D.T. Sawyer, Inorg. Chem., 22 (1983) 2790.

172 J.S. Thompson and J.C. Calabrese, Inorg. Chem., 24 (1985) 3167.

173 G.A. Abakumov, E.N. Gladyshev, N.S. Vyazankin, G.A. Razuvaev, P.Y. Bayushkin and V.A. Muraev, J. Organomet. Chem., 64 (1974) 327.

174 J.W.M. deBoer, K.S. Chen, Y.C.C. Chung and J.K.S. Wan, J. Am. Chem. Soc., 101 (1979) 5425; D.A. Hutchinson, K.S. Chen, J. Russell and J.K.S. Wan, J. Chem. Phys., 73 (1980) 1862.

175 M.W. Lynch, D.N. Hendrickson, B.J. Fitzgerald and C.G. Pierpoint, J. Am. Chem. Soc., 106 (1984) 2041. See also M.W. Lynch, R.M. Buchanan, C.G. Pierpoint and D.N. Hendrickson, Inorg. Chem., 20 (1981) 1038; S.E. Jones, L.E. Leon and D.T. Sawyer, ibid., 21 (1982) 3692.

176 D. Schaller and A. von Zelewsky, J. Chem. Soc., Chem. Commun., (1979) 948; C. Daul, J.N. Gex, D. Perret, D. Schaller and A. von Zelewsky, J. Am. Chem. Soc., 105 (1983) 7556.

177 H.B. Stegmann, K. Scheffler and P. Schuler, Angew. Chem., 90 (1978) 392; Angew. Chem. Int. Ed. Engl., 17 (1978) 365.

178 M.T. Craw and M.C. Depew, Rev. Chem. Intermed., 6 (1985) 1. C. Creutz, Inorg. Chem., 20 (1981) 4449.

179 A. von Zelewsky, Inorg. Chem., 20 (1981) 4448.

180 C.L. Kwan and J.K. Kochi, J. Am. Chem. Soc., 98 (1976) 4903.

181 A. Staško, A. Tkač, L. Malik and V. Adamčik, J. Organomet. Chem., 92 (1975) 261.

182 M.C.B. Loiá, B.J. Herold and N.M. Atherton, J. Chem. Soc., Perkin Trans. 2, (1980) 1788.

183 K.B. Ulmschneider and H.B. Stegmann in Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, II/9, d1, p 112, Springer-Verlag, Berlin, 1980.

184 M.C. Depew, B.B. Adeleke, A. Rutter and J.K.S. Wan, Can. J. Chem., 63 (1985) 2281.

185 P.S. Rao and E. Hayon, J. Phys. Chem., 77 (1973) 2274.

186 R. Stewart, The Proton: Applications to Organic Chemistry, Academic Press, Orlando, FL, 1985.

187 (a) J.-P.M. Tuchagues and D.N. Hendrickson, Inorg. Chem., 22 (1983) 2545.
(b) W. Lubitz, E.C. Abresch, R.J. Debus, R.A. Isaacson, M.Y. Okamura and G. Feher, Biochim. Biophys. Acta, 808 (1985) 464. J. Deisenhofer, O. Epp, K. Miki, R. Huber and H. Michel, Nature, 318 (1985) 618.
(c) P. Mathur and G.C. Dismukes, J. Am. Chem. Soc., 105 (1983) 7093.

188 A. Alberti and C.M. Camaggi, J. Organomet. Chem., 194 (1980) 343.

189 W. Kaim, Z. Naturforsch., Teil B, 36 (1981) 150; ibid., 40 (1985) 61.

190 R. Gross and W. Kaim, to be published.

191 H.J. Becher, D. Fenske and M. Heymann, Z. Anorg. Allg. Chem., 475 (1981) 27; D. Fenske, H.J. Becher, Chem. Ber., 107 (1974) 117; ibid., 108 (1975) 2115; H.J. Becher, W. Bensmann and D. Fenske, ibid., 110 (1977) 315.

192 D. Fenske, Angew. Chem., 88 (1976) 415; Angew. Chem. Int. Ed. Engl., 15 (1976) 381.

193 W. Bensmann and D. Fenske, Angew. Chem., 91 (1979) 754; Angew. Chem. Int. Ed. Engl., 18 (1979) 677.

194 D. Fenske and A. Christidis, Angew. Chem., 93 (1981) 113; Angew. Chem. Int. Ed. Engl., 20 (1981) 129.
195 D. Fenske and A. Christidis, Z. Naturforsch., Teil B, 36 (1981) 518.
196 D. Fenske, K. Brandt and P. Stock, Z. Naturforsch., Teil B, 36 (1981) 768.
197 D. Fenske and P. Stock, Angew. Chem., 94 (1982) 393; Angew. Chem. Int. Ed. Engl., 21 (1982) 356; Angew. Chem. Suppl., (1982) 862.
198 D. Fenske and W. Bensmann, Z. Naturforsch., Teil B, 39 (1984) 1819; ibid., 40 (1985) 1093.
199 D. Fenske, personal communication.
200 R. Fehrmann, S. von Winbush, G.N. Papatheodorou, R.W. Berg and N.J. Bjerrum, Inorg. Chem., 21 (1982) 3396.
201 A. Alberti, F.P. Colonna, M. Guerra, B.F. Bonini, G. Mazzanti, Z. Dinya and G.F. Pedulli, J. Organomet. Chem., 221 (1981) 47.
202 (a) G.N. Schrauzer, Acc. Chem. Res., 2 (1969) 72.
(b) A. Müller, E. Diemann, R. Jostes and H. Bögge, Angew. Chem., 93 (1981) 957; Angew. Chem. Int. Ed. Engl., 20 (1981) 934.
(c) J. Stach, R. Böttcher and R. Kirmse, Z. Chem., 25 (1985) 1; R. Böttcher, R. Kirmse, J. Stach and C.P. Keijzers, Mol. Phys., 55 (1985) 1431.
203 K.W. Penfield, A.A. Gewirth and E.I. Solomon, J. Am. Chem. Soc., 107 (1985) 4519.
204 G.A. Russell, W.C. Law and M. Zaleta, J. Am. Chem. Soc., 107 (1985) 4175.
205 A.H. Al-Mowali and A.L. Porte, J. Chem. Soc., Dalton Trans., (1975) 250.
206 R. Eisenberg and J.A. Ibers, J. Am. Chem. Soc., 87 (1965) 3776.
207 M. Cowie and M.J. Bennett, Inorg. Chem., 15 (1976) 1595.
208 A. Alberti, M.C. Depew, A. Hudson, W.G. McGimpsey and J.K.S. Wan, J. Organomet. Chem., 280 (1985) C21.
209 W.G. McGimpsey, M.C. Depew and J.K.S. Wan, Organometallics, 3 (1984) 1684.
210 M. Symons, Chemical and Biochemical Aspects of Electron-Spin Resonance Spectroscopy, Van Nostrand-Reinhold, New York, 1978.
211 A.G. Motten, K.W. Hanck and M.K. DeArmond, Chem. Phys. Lett., 79 (1981) 541.
212 D.E. Morris, K.W. Hanck and M.K. DeArmond, J. Am. Chem. Soc., 105 (1983) 3032; J. Electroanal. Chem., 149 (1983) 115.
213 D.E. Morris, K.W. Hanck and M.K. DeArmond, Inorg. Chem., 24 (1985) 977.
214 Y. Ohsawa, M.K. DeArmond, K.W. Hanck and C.G. Moreland, J. Am. Chem. Soc., 107 (1985) 5383.
215 Orbital reversal on protonation: J. Bruhin and F. Gerson, Helv. Chim. Acta, 58 (1975) 2422.
216 W. Kaim, J. Organomet. Chem., 241 (1983) 157.
217 W. Kaim and S. Kohlmann, Inorg. Chem., in press.
218 J.C. Giordan, J.H. Moore, J.A. Tossell and W. Kaim, J. Am. Chem. Soc., 107 (1985) 5600.
219 W. Kaim, J. Organomet. Chem., 262 (1984) 171.
220 A.J. Stone, Mol. Phys., 7 (1964) 311.
221 H. Fischer in J.K. Kochi (Ed.), Free Radicals, Wiley, New York, 1973, Vol. II, p. 452.
222 P.J. Giordano and M.S. Wrighton, Inorg. Chem., 16 (1977) 160.
223 J. Owen and K.W.H. Stevens, Nature, 171 (1953) 836. E.K. Barefield, D.A. Krost, D.S. Edwards, D.G. van Derveer, R.L. Trytko, S.P. O'Rear and A.N. Williamson, J. Am. Chem. Soc., 103 (1981) 6219.
224 J.H. Osborne, A.L. Rheingold and W.C. Trogler, J. Am. Chem. Soc., 107 (1985) 7945.
225 H. Kurreck, B. Kirste and W. Lubitz, Angew. Chem., 96 (1984) 171; Angew. Chem. Int. Ed. Engl., 23 (1984) 173.

226 G.N. LaMar, W. DeW. Horrocks, Jr. and R.H. Holm (Eds.), NMR of Paramagnetic Molecules, Academic Press, New York, 1973.

227 K. Angermund, K.H. Claus, R. Goddard and C. Krüger, Angew. Chem., 97 (1985) 241; Angew. Chem. Int. Ed. Engl., 24 (1985) 237.

228 B. Bogdanovic, N. Janke, C. Krüger, R. Mynott, K. Schlichte and U. Westeppe, Angew. Chem., 97 (1985) 974; Angew. Chem. Int. Ed. Engl., 24 (1985).

229 C.G. Pierpoint and H.H. Downs, J. Am. Chem. Soc., 97 (1975) 2123; C.G. Pierpoint and R.M. Buchanan, ibid., 97 (1975) 4912, 6450.

230 E. König, Z. Naturforsch., 19a (1964) 1139.

231 H.H. Downs, R.M. Buchanan and C.G. Pierpoint, Inorg. Chem., 18 (1979) 1736.

232 R.M. Buchanan, S.C. Kessel, H.H. Downs, C.G. Pierpoint and D.N. Hendrickson, J. Am. Chem. Soc., 100 (1978) 7894.

233 M.W. Lynch, M. Valentine and D.N. Hendrickson, J. Am. Chem. Soc., 104 (1982) 6982.

234 R.M. Buchanan and C.G. Pierpoint, J. Am. Chem. Soc., 102 (1980) 4951.

235 E.M. Kober and T.J. Meyer, Inorg. Chem., 23 (1984) 3877.

236 I.M. Brown and S.I. Weissman, J. Am. Chem. Soc., 85 (1963) 2528. P. Clopath and A. von Zelewsky, Helv. Chim. Acta, 56 (1973) 980.

237 J. Heinze, Angew. Chem., 96 (1984) 823; Angew. Chem. Int. Ed. Engl., 23 (1984) 831.

238 D. De Montauzon, R. Poilblanc, P. Lemoine and M. Gross, Electrochim. Acta, 23 (1978) 1247.

239 W.E. Geiger, Progr. Inorg. Chem., 33 (1985) 275.

240 Y. Ohsawa, M.K. DeArmond, K.W. Hanck, D.E. Morris, D.G. Whitten and P.E. Neveux, Jr., J. Am. Chem. Soc., 105 (1983) 6522.

241 B.K. Teo and P.A. Snyder-Robinson, Inorg. Chem., 18 (1979) 1490.

242 N.L. Holy and J.D. Marcum, Angew. Chem., 83 (1971) 132; Angew. Chem. Int. Ed. Engl., 10 (1971) 115.

243 R. Gross, Thesis, University of Frankfurt, 1986.

244 A.J. Paine and R.O. Loutfy, Rev. Chem. Intermed., 5 (1984) 227.

245 E. König and S. Kremer, Chem. Phys. Lett., 5 (1970) 87; E. König and S. Herzog, J. Inorg. Nucl. Chem., 32 (1970) 585, 601.

246 G.A. Heath, L.J. Yellowlees and P.S. Braterman, J. Chem. Soc., Chem. Commun., (1981) 287; Chem. Phys. Lett., 92 (1982) 646.

247 H. Bock, W. Kaim, H. Nöth and A. Semkov, J. Am. Chem. Soc., 102 (1980) 4421. S.F. Nelsen, W.C. Hollinsed, C.R. Kessel and J.C. Calabrese, ibid., 100 (1978) 7876.

248 M.H. Chisholm, J.A. Connor, J.C. Huffman, E.M. Kober and C. Overton, Inorg. Chem., 23 (1984) 2298.

249 G.H. Atkinson, Adv. Infrared Raman Spectrosc., 9 (1982) 1.

250 P.G. Bradley, N. Kress, B.A. Hornberger, R.F. Dallinger and W.H. Woodruff, J. Am. Chem. Soc., 103 (1981) 7441.

251 B.P. Sullivan, D. Conrad and T.J. Meyer, Inorg. Chem., 24 (1985) 3640.

252 D. Miholova, L. Pospisil and A.A. Vlcek, Contribution THp49-8 at the 23rd International Conference on Coordination Chemistry, Boulder, CO, 1984.

253 Cf. J.P. Collman and L.S. Hegedus, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1980.

254 M.E. Cass, D.L. Greene, R.M. Buchanan and C.G. Pierpoint, J. Am. Chem. Soc., 105 (1983) 2680; M.E. Cass and C.G. Pierpoint, Inorg. Chem., 25 (1986) 123.

255 S.A. Isalva, L.A. Nikonova and A.E. Shilov, Nouv. J. Chim., 5 (1981) 21.

256 M. Chanon and M.L. Tobe, Angew. Chem., 94 (1982) 27; Angew. Chem. Int. Ed. Engl., 21 (1982) 1. M. Julliard and M. Chanon, Chem. Rev., 83 (1983) 425.