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FREE RADICAL REACTIONS OF TRANSITION METAL SYSTEMS

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CONTENTS

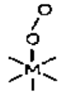
A. INTRODUCTION

The chemical reactivity of transition metal systems has been discussed predominantly in terms of Lewis acid—base interactions involving metal ions and electron pair donor ligands. There is a substantial number of systems in which the transition metal undergoes a free radical type of spin pairing, bonding interaction (as for example in the reaction 2 $NO_2 \rightleftharpoons N_2O_4$). Attempts to force some of the spin-pairing type of interactions into the Lewis acid—base scheme have resulted in mental gymnastics comparable to describing the reaction of a hydrogen atom with a fluorine atom as one in which an electron is transferred to a fluorine atom and the resulting fluoride ion coordinates to a proton. In the process considerable insight into the fundamental nature of the interaction and the factors influencing its magnitude is lost. For example, the important consideration in many of the spin pairing reactions involves the energies and relative energies of the unpaired electrons (one can view copper(II) complexes as stable free radicals because the odd electron occupies a low energy, sterically protected orbital). In this article the interaction will be discussed and the generality of the spin pairing reaction type in transition metal chemistry illustrated. Hopefully, a set of apparently diverse areas of chemistry will be viewed as different manifestations of the same phenomenon. The massive literature in these various areas will not be reviewed extensively.

Spin pairing considerations enable us to unify the discussions of the coordination of dioxygen, spin labels, and nitric oxide as well as antiferromagnetic interactions and metal—metal bonding. The fundamental background needed is qualitative molecular orbital theory. Since in all instances we are interested in the reactivity of molecules with unpaired spin, we shall use these molecules as the starting place for generating new molecular orbitals to describe the adducts formed. Those aspects of the electronic structure of the reactants that do not change significantly upon adduct formation will be omitted from the molecular orbital description of the interaction. This approach is particularly useful for following changes that occur when molecules containing unpaired spins are brought together and these spins pair up, giving rise to a bonding interaction.

B. BINDING OF DIOXYGEN

Our first concern will be with end-on bonded O_2.



Early views [1,2] of the end-on binding of dioxygen to metal ions were formulated as involving nearly complete electron transfer from the metal ion to dioxygen, producing an ionically-bound superoxide ion. In cobalt systems, this conclusion was based upon an analysis of the cobalt hyperfine coupling in the EPR spectrum and a similarity in the O—O stretching frequency of the bound dioxygen to that of superoxide ion. With the publication [3] of the anisotropic hyperfine results from an ^{17}O EPR study, it became clear [4] that one could not conclude that nearly complete electron transfer occurred in the reported complexes. The similarity in the O—O stretching vibration of HO_2 and superoxide ion further indicated [5] that IR spectroscopy is a poor criterion for determining the ionic nature of bound O_2. A spin-pairing model was proposed [5,6] that nicely incorporates all of the known properties of the bound dioxygen complexes. The application of this model to the dioxygen adducts of cobalt(II) is illustrated in Fig. 1. The essential interaction is seen to be the formation of a σ bond arising from the overlap of an oxygen π^* orbital with the d_{z^2} orbital on cobalt. The other π^* orbital of oxygen is orthogonal to d_{z^2} and as ψ_{II} in the complex remains essentially oxygen-atom based. The charge on the dioxygen fragment is defined by the atomic orbital coefficients in ψ_I ($\psi_I = a\psi_{Co} + b\psi_{O-O}$ to a simple first approximation). If $a > b$ the dioxygen would have a positive charge; if $a = b$ dioxygen would be neutral and if $b > a$ dioxygen would be negative. Any factors that would tend to raise the energy of d_{z^2} would increase the oxygen contribution to ψ_I (consider the MO description of HF vs. H_2) and increase the negative charge on the bound O_2. Thus a whole range of O_2 charge can be accommodated by the model. Charges varying from 0.1 e^- transfer into O_2 all the way to 0.8 e^-

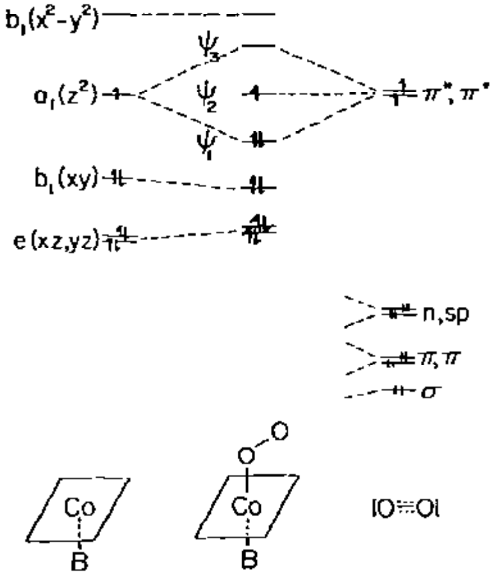


Fig. 1. A molecular orbital description of the binding of dioxygen. With energy plotted on the vertical axis, the essentially *d*-molecular orbitals of a five coordinate cobalt(II) complex are illustrated on the left, the valence molecular orbitals of dioxygen on the right and molecular orbitals of the dioxygen adduct in the center.

transfer have been shown to exist in a series of O_2 adducts. The variation is related to the ligand field strength of the groups attached to cobalt because they influence the d_{z^2} energy.

This spin-pairing model can also be used to explain the influence which axial base variation has on the strength of dioxygen binding. As the axial base coordinated to cobalt is increased in base strength in a series, the d_{z^2} orbital will be driven higher in energy. The higher the d_{z^2} energy, the more energy there is to be gained in forming a Co—O_2 bond when the electron in d_{z^2} drops down to occupy ψ_1 in the adduct. The bond energies for a series of different base adducts to cobalt(II) protoporphyrin(XI) follow this trend [6].

Another advantage of the spin-pairing model as applied to dioxygen binding is its ability to predict the magnetic properties of various metal—dioxygen complexes [5]. As an example, the four metal electrons of high spin Cr(II) complexes and the two oxygen π^* electrons of dioxygen interact to produce an adduct that has two unpaired electrons located in mainly metal based orbitals (see Fig. 2A). As a second example, Mn(II) would [7] form a terminal O_2 adduct by pairing up both oxygen spins, leaving three unpaired electrons on the metal (see Fig. 2B). In both of these instances, the metal—oxygen bond would have a bond order of two, with two separate metal orbital—dioxygen interactions like that described in Fig. 1 for the Co—O

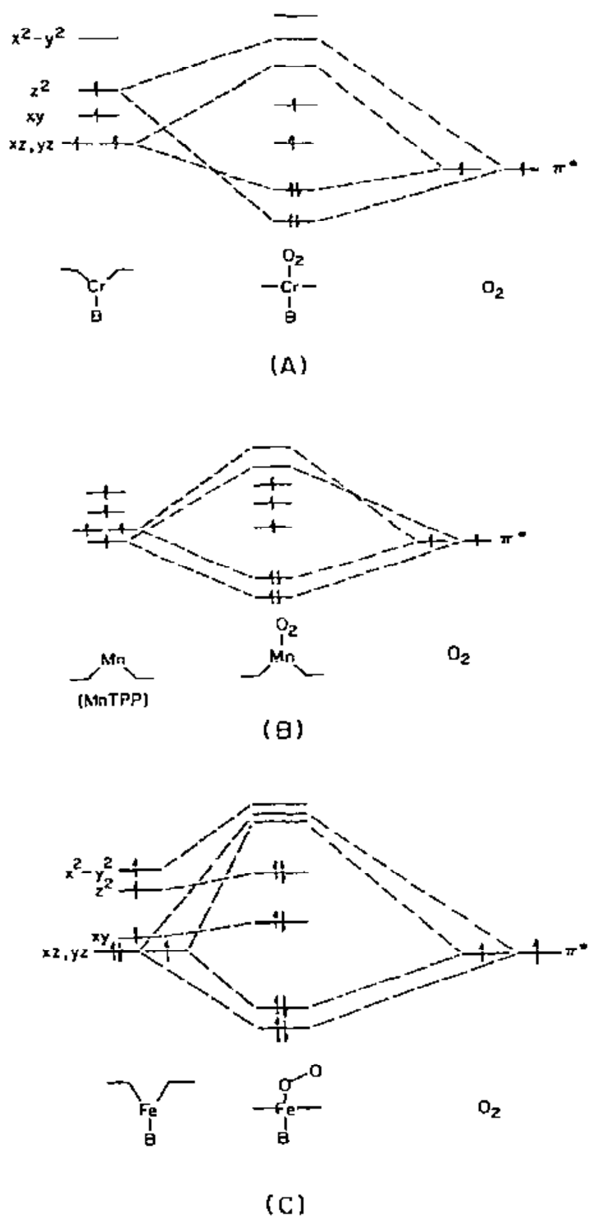
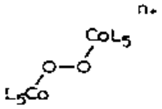


Fig. 2. The spin pairing interaction of dioxygen in various metal complex adducts. A, chromium(II) systems; B, manganese(II) terminal adducts; C, iron(II) adducts.

adduct. Another favorable advantage of the spin-pairing model is that it readily accommodates and suggests that one attempts to prepare dioxygen adducts of these metals with other spin multiplicities. A different crystalline field in the manganese(II) adduct, for example, could increase the *d*-orbital splittings and cause electrons to pair up, leading to an $S = 1/2$ adduct. Intermediate spin states are also possible.

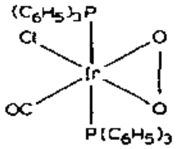
The iron(II) system is particularly interesting because of dioxygen binding to hemoglobin. The high spin iron(II) complex has four unpaired electrons. Spin pairing two electrons to the iron results in a paramagnetic complex with unpaired electrons on the metal. In hemoglobin the ligand field lowers the *d*-orbital symmetries and the metal electrons spin pair, leaving a vacant $d_{x^2-y^2}$ metal orbital, and a diamagnetic adduct results [8] (see Fig. 2C). In all instances where more than one metal-based electron exists in an O_2 adduct, low spin and high spin *d*-orbital configurations can produce O_2 adducts whose spin multiplicity varies with the symmetry and strength of the ligand field.

Bridged peroxo species [9]



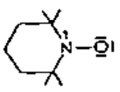
are also readily accounted for with the spin-pairing model. In this system the unpaired electron in ψ_{II} of Fig. 1 is involved in spin-pairing interaction with a *d*-orbital from a second cobalt complex. Once again, a wide variation in the charge of the O_2 fragment in the complex can arise, depending upon the cobalt and oxygen coefficients of the bonding orbitals.

A third bonding mode in dioxygen complexes, pictured below, involves ring formation [10,11]. Bonding of this type adduct can be viewed in terms of the spin-pairing model by using a promotion step to unpair the lone pair d_{z^2} electrons of the d^8 complex by exciting one to $d_{x^2-y^2}$. The two unpaired electrons of this promoted configuration interact with the two electrons of O_2 to produce the diamagnetic adduct.



C. COORDINATION OF SPIN LABELS

The very extensive amount of research on the interaction of transition metal ion complexes with spin labels has been reviewed in an excellent article by S.S. and G.R. Eaton [12]. A typical molecule in this class is illustrated by



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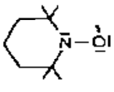

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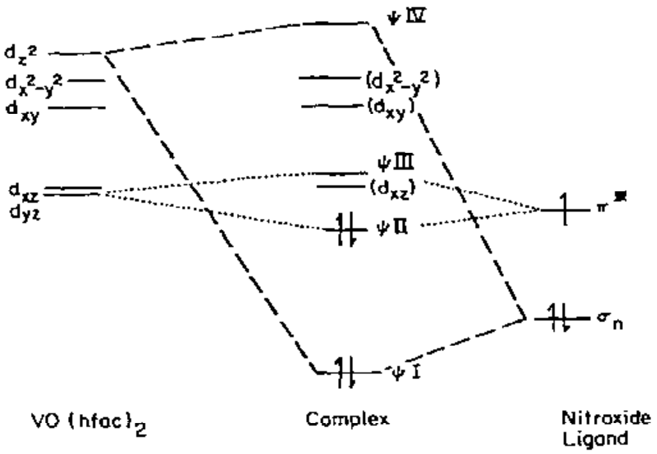


Fig. 3. A simplified molecular orbital diagram for the coordination of a nitroxyl ligand to a d^1 complex.

Molecules containing the N—O functional group are referred to as nitroxyl or nitroxide radicals or ligands. Coordination of diamagnetic Lewis acids to nitroxides occurs to a lone pair on oxygen stabilizing resonance form I above. A resulting increase in the nitrogen hyperfine coupling constant [13] is observed. Coordination of this type of ligand to paramagnetic transition metal complexes in all previously reported instances involves coordination to a lone pair of electrons on oxygen. Cu(hfac)$_2$ (hfac = $CF_3C(O)CHC(O)CCF_3^-$), for example, forms a 1 : 1 adduct with the nitroxide ligand as does VO(hfac)$_2$. In the resulting adduct, the metal unpaired electron and the free radical ligand unpaired electron pair up as shown in the molecular orbital diagram in Fig. 3. The essential Lewis acid—base interaction between the nitroxyl lone pair of electrons and the metal vacant orbital results in the formation of molecular orbital ψ_{I}. The spin-pairing interaction, described as an antiferromagnetic interaction, occurs as a consequence of pairing up electrons in molecular orbital ψ_{II} which is composed of metal and ligand orbitals as illustrated by the dotted lines. The energy difference between the fully electron-paired ground state configuration shown above and the often thermally accessible (at room temperature) paramagnetic state that contains one electron in ψ_{II} and one in ψ_{III} is described by the quantity 2 J.

One interesting feature of the type of interaction leading to ψ_{II} is that in the two adducts that have been studied, no enhanced stabilization of the metal—ligand bond arises from this effect [14]. An explanation for this observation has been offered [15].

D. BINDING OF NITRIC OXIDE AND SULFUR DIOXIDE

The coordination chemistry of NO has led to some fascinating chemistry, an excellent review of which has been prepared by Enemark and Feltham

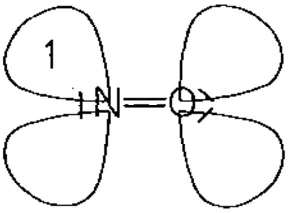


Fig. 4. Electronic structure of NO depicting the charge cloud of the unpaired π electron.

[16]. The nitric oxide molecule is an interesting case to consider in the context of our discussion because in its coordination chemistry it manifests behavior similar to that previously discussed for dioxygen on the one hand and that similar to the spin labels on the other. The electronic structure in Fig. 4 depicts the orbitals of the NO molecule involved in these interactions. When the unpaired π electron of the NO molecule undergoes direct overlap with an unpaired electron on the metal, a spin-pairing, σ bond type interaction (as described for $Co—O_2$), occurs and a bent M—N—O bond results. When, however, the lone pair on nitrogen functions as a Lewis base in its interactions with the transition metal ion, a linear M—NO bond results. In this latter case, the NO is behaving similarly to a nitroxyl ligand with the unpaired π electron of NO pairing up with an unpaired spin on the metal. The interaction in the latter case is described by a molecular orbital diagram comparable to that in Fig. 4. In using the EAN rule, the NO ligand counts as a three electron donor for this type of interaction.

In the bent systems, it should again be clear that the charge on the NO fragment can be positive, neutral or negative depending on the metal and nitrogen coefficients in the bonding molecular orbital. In the case of the linear M—N—O systems, the same possibilities exist for the charge on the bound NO fragment. Electron density is donated to the metal in the electron pair donation interaction. Depending, however, upon the nitrogen and metal coefficients in the molecular orbital formed in the spin-pairing interaction, electron density can be moved in or out of the bound NO. The linear structure is not related to the charge on the NO.

Table 1 presents a brief summary of the kinds of nitrosyl complexes that fall into the various classes. Reference 16 should be consulted for a more exhaustive compilation.

A molecular orbital model has been presented that enables one to understand and predict whether or not the M—N—O bond will be linear or bent [16]. In terms of the reactivity considerations presented here, one should dissociate a neutral NO molecule from the complexes presented in Table 1 and then ask the question: will the resulting fragments interact more strongly in a Lewis acid—base fashion (that is, lone pair donation) or will the preference be for spin-pairing, σ bond formation? A highly Lewis acidic metal center will favor the former. $Cr(III)(CN)_5^{3-}$ and $Ir(CO)[(C_6H_5)_3P]_2$, for example, are both recognized as coordinatively unsaturated species that will

TABLE 1

M—N—O geometries for various nitrosyl complexes

Linear	Bent
Six coordinate	
$Cr(CN)_5NO^{3-}$	$Coen_2NOCl^+$
$Mn(CN)_5NO^{3-}$	$Co(NH_3)_5NO^{2+}$
$Fe(CN)_5NO^{2-}$	
Five coordinate	
$MnNO(CO)_4$	$Ir(CO)NOI[(C_6H_5)_3P]_2^+$
$Ru(NO)H[(C_6H_5)_3P]_3$	$Ir(NO)Cl_2[(C_6H_5)_3P]_2$
$IrH(NO)[(C_6H_5)P]_3^+$	CoacacenNO
(all trigonal bipyrimidal structures)	$Co[S_2CN(CH_3)_2]_2NO$
	$NiNON_3P_2$
	(all tetragonal pyrimidal structures)
Four coordinate	
$IrNOCO[(C_6H_5)_3P]_2$	$NiNON_3[(C_6H_5)_3P]_2$
$IrNO[(C_6H_5)_3P]_3$	

be strong Lewis acids. Linear M—N—O bonds result. CoTPP and Coacacen, however, are stable compounds that are weak Lewis acids. Spin-pairing σ bonded formation results for the latter complexes and the M—N—O bonds will be bent. An interesting feature of the interaction of these Co(II) complexes with NO compared to dioxygen is that axial base is not required for spin-pairing, σ bond formation with NO but is required for bonding of O_2. Evidently, NO reacts more readily than O_2 with a low energy metal unpaired electron.

Unfortunately, our ability to predict which bonding mode will be the dominant interaction for a system is hampered by our poor understanding of the Lewis acidity of metal complexes and the factors influencing the energetics of spin-pairing σ bond formation. A large number of structures have been determined on SO_2 complexes that bear on the question of metal acidity and basicity [17]. The SO_2 molecule behaves as a planar ligand when the interaction is essentially electron pair donation from the sulfur lone pair of electrons to a metal Lewis acid. The SO_2 molecule behaves as a pyramidal ligand when the interaction involves electron pair donation from a metal to an acceptor (Lewis acid) orbital of the SO_2. Those systems in which the SO_2 is planar should form linear M—N—O bonds.

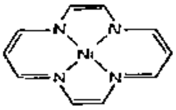
These considerations suggest a set of interesting experiments to try. In the MO model [16] electron count determines whether or not the MNO fragment is linear or bent. Thus it would be of interest to take examples of bent MNO systems in Table 1 and replace some of the ligands with poorer electron pair donating substituents. This will enhance the acidity of the metal center without changing the electron count. Can the NO be made to coordinate in a linear fashion? It is interesting to note in this context that $Co(diars)_2NO^{2+}$ (where diars is a bidentate diarsine ligand) is a linear complex that converts to a bent one when the cobalt acidity is decreased by coordination of a thiocyanate ligand to cobalt, i.e., $Co(diars)_2(SCN)\ NO^+$ is bent [18]. This simplified presentation does not account for all aspects of NO chemistry (for example a complex has been prepared containing a bent and linear NO) but it does simplify much of it.

E. METAL—METAL BONDING

A ready source of reactive metal radicals can be obtained by homolytic cleavage of direct metal—metal bonds, as in, for example [19], the following

$$Mn_2(CO)_{10} \rightleftharpoons 2\ MnCO_5$$

When $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ are mixed [20], the manganese and rhenium radicals combine to produce a mixture of the starting materials plus diamagnetic $(CO)_5Mn{-}Re(CO)_5$. There have been several reports of systems in which the metal—metal bond is weak enough that detectable amounts of the radical exist in solution equilibrium with the dimer [21]. Estimates of the metal—metal bond energies in these systems have been reported [22]. Free radical reactions of these systems will be covered in the next section. The macrocyclic, d^8 nickel complex pictured below

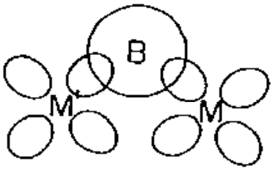


can be oxidized to form a monocation, NiL^+. These radicals couple to form a metal—metal bonded dimer [23].

$$2\ NiL^+ \rightleftharpoons [NiL]_2^{2+}$$

A whole host of metal—metal bonded [24] species exist of the general formula $M_2(RCOO)_4$. Invariably all the electrons on the individual M(II) centers in these dimers are paired up, leading to multiply bonded metal—metal bonds. It is clear that if two metals with unpaired electrons can be held close enough together, the electrons will pair up in a fashion similar to that involved in O_2 binding, leading in the metal—metal case to σ and π-bonds. What this means in terms of metal—metal bond strength and bond order relationship is another matter.

The indirect antiferromagnetic exchange interaction (a Heisenberg interaction) is a more subtle type of a "metal—metal" bonding interaction. Excellent, detailed reviews [25,26] of this topic are also available. This is best understood by viewing a hypothetical example of an interaction between two metal centers joined by a bridging ligand B that consists of a lone pair of



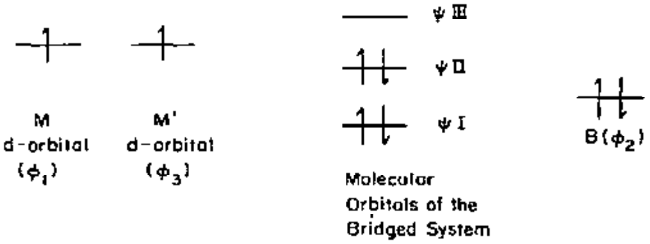


Fig. 5. The orbital overlap involved in the antiferromagnetic interaction of two metal orbitals via the intermediacy of a bridging group B, filled *s* orbital. M and M' are the same element and there is one electron in each *d* orbital.

Fig. 6. The three center molecular orbitals arising from the overlap of the orbitals shown in Fig. 5.

electrons in an *s*-orbital. We shall focus on one electron in a *d*-orbital on each metal center. The overlapping orbitals are shown in Fig. 5. This system is described by a typical 3-center type of molecular orbital interaction (similar to that used to describe HF$_2^-$) leading to the three MOs shown in Fig. 6. In this system, the following wave functions describe the molecular orbitals

$$\psi_{\mathrm{I}} = a\phi_1 + b\phi_2 + c\phi_3$$

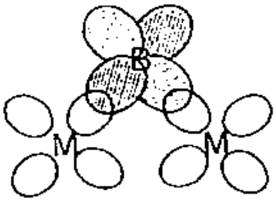
$$\psi_{\mathrm{II}} = a'\phi_1' - c'\phi_3$$

$$\psi_{\mathrm{III}} = a''\phi_1 - b''\phi_2 + c''\phi_3$$

The molecular orbital ψ_{I} is largely B(ϕ_2) and is stabilized relative to the lone pair of electrons of B by coordination to the two metals. This mixes a little M and M' *d*-orbitals into ψ_{I}. Differing contributions of B to ψ_{II} and ψ_{III} and different combinations of M and M' to these orbitals cause them to have different energies in the complex. When the separation of ψ_{II} and ψ_{III} is greater than the pairing energy, a diamagnetic complex results. The energy difference between this ground state and an often thermally accessible excited state that has one electron in ψ_{II} and ψ_{III} is represented as 2 *J*. A negative value for *J* will be used to represent a system in which the ground state is diamagnetic.

Next let us consider the case where the bridging ligand B has two pairs of electrons on it in two orthogonal orbitals that are providing the bridging interaction. The orbital overlap is illustrated in Fig. 7. In this system, a three-center bonding description would not apply, but two separate M—B σ bonds would form as shown in Fig. 8. No spin pairing occurs in this case and a paramagnetic complex would result.

With these two extreme examples we have shown how a pathway of overlapping orbitals leads to an antiferromagnetic (spin pairing) interaction. In the real systems studied there is considerable variation in the orbital overlap and an extensive variation in the magnitude of *J*. In the complex below, for



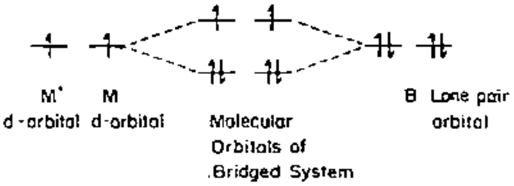
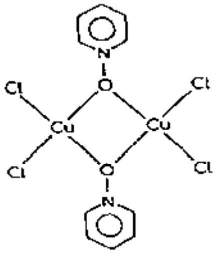


Fig. 7. Bridging two equivalent metal centers, M and M', with a bridging atom that employs two lone pairs of electrons in orthogonal *p*-orbitals. The two *p*-orbitals are shaded differently so they can be distinguished.

Fig. 8. The molecular orbitals resulting from the orbital overlap in Fig. 7.

example,



a value of $J = -545\ \text{cm}^{-1}$ results while in the case of copper(II) and vanadyl(IV) complexes bridged by pyrazine [27]

J values of -19 to ca. $-0.02\ \text{cm}^{-1}$ are observed.

This molecular orbital description is a type of metal—metal bonding interaction. The two metals in the delocalized σ systems described above are bonded in the same way (though much more weakly) that alternate carbons in benzene are bonded by the π-system.

Before concluding this topic we shall describe the situation in which the two metal centers depicted in Fig. 5 are not equivalent. Suppose these two metals are, for example, in the (II) oxidation state prior to complexation. If M is much lower in energy than M', ψ_{II} will consist of M to a larger degree than M', while the opposite conclusion would be reached if M' is lower in energy than M. With this description, systems in which nearly a full of fraction of an electron is transferred to or from M or M' can be described without recourse to fractional oxidation states.

F. MORE COMPLEX METAL FREE RADICAL REACTIONS

The oxidative addition reaction, for example

$$ML_4 + XY \rightarrow ML_4XY$$

in many instances involves nucleophilic attack by the metal (d^8) lone pair on X—Y. Depending on the specific system and set of conditions, free radical kinetics can occur. The significance of the mechanistic details is apparently limited to stereochemical considerations so this topic will not be treated further. In general, the potential surface for a transition metal organometallic reaction is very complex. It contains many low lying pathways for reaction and the lowest energy process can vary with conditions or minor substituent change. Thus it is difficult to deduce generalizations from kinetic measurements on these systems and the mechanistic conclusions are limited to the systems studied. Fortunately, in many instances, the predictions of reactivity are dependent upon thermodynamic considerations and further mechanistic details become intellectual luxuries.

Kinetic studies have been important in demonstrating that metal complexes can undergo free radical reaction types. Extensive research [28] has shown that $Co(CN)_5^{3-}$, bis(dimethylglyoximato) cobalt(II) and cobalt(II)—Schiff base complexes exhibit reactivity patterns toward organic halides that are suggestive of free radical reactions. With $Co(CN)_5^{3-}$, halogen abstraction is the rate determining step in the following reaction sequence

$$Co(CN)_5^{3-} + CH_3I \rightarrow Co(CN)_5I^{3-} + CH_3^{\cdot}$$

$$Co(CN)_5^{3-} + CH_3^{\cdot} \rightarrow Co(CN)_5CH_3^{3-}$$

Typical free radical reactivity patterns are found for alkyl halides: $RCl < RBr < RI$ and $CH_3I < C_2H_5I < (CH_3)_2CHI < (CH_3)_3CI < C_6H_5CH_2I$. Similar free radical halogen abstraction reactions occur between alkyl halides and metals (Na, Mg, Zn, etc.) with the organic product (metal alkyl, alkane, alkene, etc.) being determined by a variety of factors.

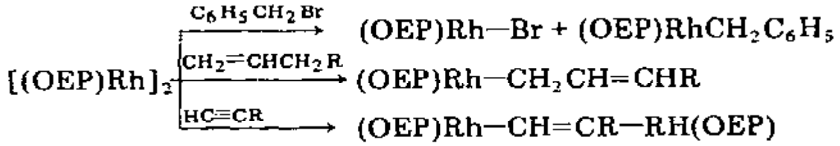
The reaction of $Co(CN)_5^{3-}$ with H_2 is third order, $k[H_2][Co(CN)_5^{3-}]^2$ implying a concerted mechanism [28].

The reactions of low valent rhodium compounds of octaethylporphyrin ($OEPH_2$) undergo some very interesting chemistry some of which is free radical in nature [29].

$$(OEP)Rh(III)Cl + H_2 \xrightarrow{CH_3OH} (OEP)RhH + HCl$$

$$2\ (OEP)Rh{-}H \xrightarrow{benzene} [(OEP)Rh]_2 + H_2$$

The d^7 rhodium porphyrin dimerizes via metal—metal bond formation. The dimer undergoes the following reactions [29]



$$[(OEP)Rh]_2 \begin{cases} \xrightarrow{C_6H_5CH_2Br} (OEP)Rh{-}Br + (OEP)RhCH_2C_6H_5 \\ \xrightarrow{CH_2{=}CHCH_2R} (OEP)Rh{-}CH_2CH{=}CHR \\ \xrightarrow{HC{\equiv}CR} (OEP)Rh{-}CH{=}CR{-}RH(OEP) \end{cases}$$

The dimer will react with dioxygen to form an O_2 adduct [30].

The complex *trans*-$Rh(NH_3)_4(OH_2)H^{2+}$ can be photolyzed [31] to produce the reactive free radical intermediate $Rh(NH_3)_4^{2+}$ (aq). This species coordinates dioxygen and the resulting adduct participates in a radical chain reaction with the starting material to form a hydroperoxo complex

$$Rh(NH_3)_4O_2^{2+} + Rh(NH_3)_4(OH_2)H \rightarrow Rh(NH_3)_4(OH_2)O_2H + Rh(NH_3)_4^{2+}\ (aq)$$

Rupture of metal—metal bonds in polynuclear metal carbonyls has produced a large number of metal carbonyl radicals [32]. The recombination type of reaction, described in the previous section, has been studied in detail [32]. It has been shown [33] that several of these transition metal carbonyl radicals can be employed to initiate free radical polymerization reactions. There is an extensive literature involving free radical pathways and excellent reviews [34,35] can be consulted for more details.

G. SUMMARY

I hope that this brief review has served to show the interrelationships of several different areas. The value of this type of endeavor is manifold. The recognition of the similarities in different systems makes it easier to remember the chemistry. The facts become a new application of phenomena one already knows and understands. The recognition of the similarities also broadens one's view and outlook. Progress often results by transferring information from one system to another and is usually slowed when the same concept has to be rediscovered for each new system. These arguments justify taking this different look at a lot of familiar chemistry.

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