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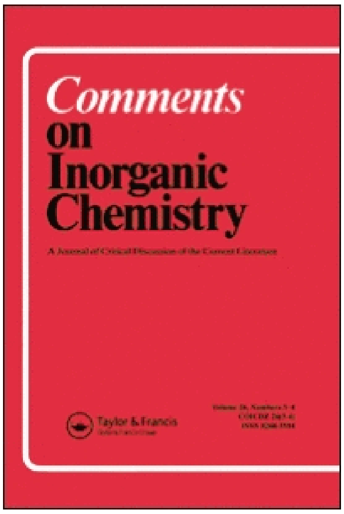

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Let's Not Forget About Electronic Correlation

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Let's Not Forget About Electronic Correlation

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It has been known for over 30 years that electronic correlation has a profound effect on the ground and excited state energies of classical coordination complexes containing more than one unpaired electron. Subdisciplines of inorganic chemistry such as organometallic chemistry and the chemistry of multiply bonded metal clusters have not been too concerned about these effects, since molecules belonging to those classes are typically diamagnetic or, less frequently, paramagnetic for only one unpaired electron. As a result, the description of these systems is often based on the use of more or less quantitative "monoelectronic" arguments, i.e., on the application of valence bond or molecular orbital considerations. This Comment will discuss the limitations of this approach and illustrate the importance of electronic correlation effects (a) in the reaction mechanism of organometallic reactions where the metal has an intermediate formal oxidation state, and (b) in the understanding of ground state properties of certain dinuclear clusters that "fail" to exhibit a high order metal-metal interaction.

Key Words: *electronic correlation, nephelauxetic effects, pairing energy, intermediate oxidation states, kinetics of ligands substitution, electron transfer chain catalysis, multiple metal-metal bonds, edge-sharing bioctahedral Mo(III) complexes, paramagnetic NMR*

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I. ELECTRON CORRELATION EFFECTS IN COORDINATION COMPOUNDS

Classical coordination chemistry has its roots in the fascinating work of Alfred Werner.[1] Two of the most characteristic properties of these substances, i.e., their color and their magnetic properties, were not fully rationalized until the ideas of crystal field theory became widely accepted by the chemical community. In the chemically modified version of the theory, known as *ligand field theory*,[2] not only the "ligand field stabilization energy" and its dependence on the nature of the ligands (*spectrochemical series*), but also electronic correlation effects and their dependence on the nature of the ligands (*nephelauxetic series*), have been of primary importance to rationalize a host of different properties of these molecules, from their optical spectra to their ground state geometry, from their magnetic properties to their EPR spectroscopic properties.

For instance, the fact that CoF_6^{3-} has four unpaired electrons, whereas $Co(NH_3)_6^{3+}$ has none, cannot be explained solely by invoking the octahedral splitting into t_{2g} and e_g orbitals. If it was not for the *pairing energy*, each of these two complexes would be diamagnetic. The energetic separation of t_{2g} and e_g orbitals (ligand field splitting) has to do with the strength of the ligand field, whereas the existence of the pairing energy reflects the existence of electronic correlation and has to do with coulombic and exchange integrals which ultimately depend on the shape and "diffuseness" of the orbits and can also be a function of the ligands as expressed by the nephelauxetic parameter. Whether a complex will have a high spin or a low spin configuration depends on whether the pairing energy is higher or lower than the ligand field splitting. This is illustrated schematically in Fig. 1 for the octahedral d^6 case applicable to the Co^{3+} complexes mentioned above.

Thus, electronic correlation is of vital importance for the rationalization of magnetic and optical properties. It is obvious that there is a thermodynamic factor involved with the *energetic stabilization* of coordination compounds by electron correlation effects. This is illustrated in Fig. 2 for the specific example of an octahedral d^3 complex. We shall refer back to this figure later on in this Comment since a few examples shown later from our work deal with pseudo-octahedral Mo^{3+} complexes. The left-hand side

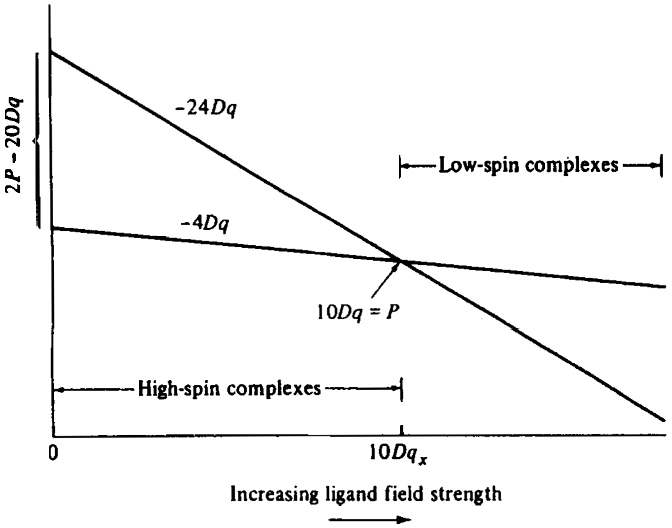


FIGURE 1 Relation of pairing energy of a d^6 octahedral complex to the ligand field stabilization energy. Adapted from J. E. Huheey, *Inorganic Chemistry*, 3rd ed. (Harper & Row, New York, 1983).

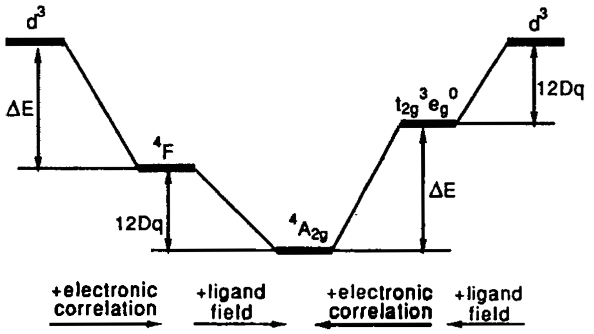


FIGURE 2 Electronic ground state for an octahedral d^3 ion and its relationship to the monoelectronic d^3 configuration, to the ground spectroscopic term (^4F) for an isolated d^3 atom, and for the ground state configuration (t_{2g}^3) for a "monoelectronic" octahedral complex. The possible effect of spin-orbit coupling has not been considered.

of Fig. 2 shows how to obtain the ground state of the octahedral d^3 complex starting from the atomic "monoelectronic" configuration of a gas-phase d^3 ion in a spherically symmetric field having the same strength as the ligand field in the actual complex, by successive application of the electronic correlation and the ligand field as perturbation effects. The effect of the electronic correlation is to energetically split the 120 degenerate microstates of the d^3 configuration to give the ground state or "spectroscopic term" ^4F, which is composed of only 28 microstates. The separation ΔE is a function of the Slater–Condon–Shortley integrals F_0, F_2 and F_4 (or the related Racah parameters B and C).[2] The "rearrangement" of the spherical ligand field into one of octahedral symmetry further splits the ^4F ground state so that only 4 microstates end up in the ground state of type $^4A_{2g}$. The alternative approach of reversing the order of perturbation on the monoelectronic Hamiltonian is shown on the right-hand side of the same figure. The monoelectronic $t_{2g}^3e_g^0$ configuration is what we, as trained coordination chemists, immediately associate with an octahedral complex of a d^3 ion. Doing so, however, we forget that the actual ground state (to this level of approximation[3]) is further energetically stabilized by the amount ΔE which is due to electronic correlation effects. An important point to keep in mind is that, although the energy of the ground state is always lowered by the inclusion of electronic correlation, the energetically stabilizing effect of electronic correlation is going to be comparatively small for closed shell systems and for systems with only one unpaired electron, and will become greater and greater as the number of unpaired electrons increases.

It is proper to point out that the "monoelectronic" description of ground state electronic structures has become so widespread, possibly due to the proliferation of semiempirical MO methodologies that are so simple to use even for an experimental chemist like myself, that the existence of electronic correlation and the fact that, indeed, for multielectron systems the "orbitals" are nothing else than a useful construction of our mind, are often forgotten. There are two research areas in which the application of "monoelectronic" tools is highly successful, i.e., organometallic chemistry and the chemistry of metal–metal multiply bonded clusters. This is because the compounds that belong to these classes are most often diamagnetic, or less frequently they contain only one unpaired electron. The purpose of this Comment is to show situations in which the existence of electronic correlation can or must be taken into account to rationalize experimental observations.

II. MORE THAN ONE UNPAIRED ELECTRON IN ORGANOMETALLIC COMPOUNDS

Organometallic chemistry is dominated by low oxidation states and the 18-electron rule. This is because most organometallic ligands are π acidic. All bonding orbitals are highly stabilized and all antibonding orbitals are highly destabilized and thus electronically saturated systems with high HOMO-LUMO gaps are typically achieved. Stable 17-electron radicals (e.g., $V(CO)_6$, $Fe(CO)_3(PPh_3)_2^+$, etc.) owe their existence to steric impediments to dimerization with the formation of metal – metal bonds, and are quite reactive systems especially with respect to reducing agents (their SOMO is low in energy) which transform them into saturated compounds.

Low valent 16-electron complexes are typically short-lived systems (e.g., intermediates or transition states for dissociative ligand substitution or reductive elimination/oxidative addition reactions). The 16 valence electrons occupy 8 out of the 9 available metal orbitals and the last, empty metal-based orbital will not lie too high in energy above the HOMO, resulting in a low HOMO-LUMO gap and a high reactivity toward Lewis bases. Rare examples of isolable, diamagnetic 16-electron complexes can be found (e.g., $WBr_2(CO)_2$(norbornadiene).[4] In those cases the presence of weakly π-donating ligands may raise the energy of the LUMO to give the complexes a higher thermodynamic stability. The reason for these systems to prefer the diamagnetic configuration (Fig. 3a) over the possible alternative paramagnetic configuration (Fig. 3b) has to do with the diffuseness of the metal orbitals in these low-valent systems, resulting in low pairing energies. High spin configurations could be observed only if the two orbitals are very close in energy or accidentally degenerate. Upon increase of the effective positive charge on the metal, the orbitals should contract, and the pairing energies should increase. It is then possible to predict that, in higher oxidation states, the tendency should exist to stabilize

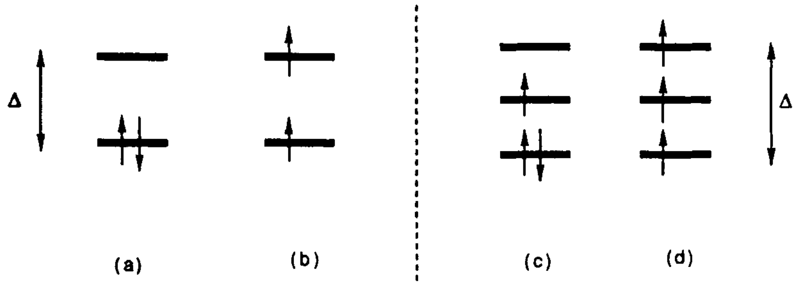


FIGURE 3 Possible electronic configurations for 16-electron (a/b) and 15-electron (c/d) organometallic complexes. In the low spin configurations (a and c), the pairing energy (P) is smaller than Δ. In the high spin configurations (b and d), $P > \Delta$.

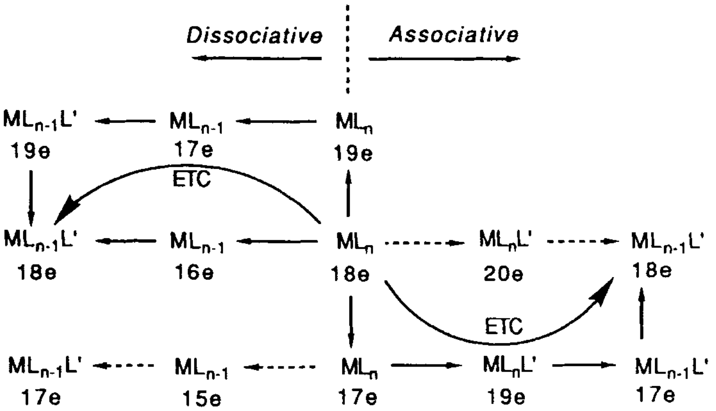


FIGURE 4 Schematic view of the mechanisms of ligand substitution reactions for organometallic compounds.

paramagnetic ($S = 1$) 16-electron configurations and this is indeed observed (for instance, see Section III). Neutral organometallic ligands do not bind strongly enough to higher oxidation state systems due to the reduced π back-bonding, but radical-like ligands [e.g., alkyls, allyls, and cyclopentadienyls] do. Examples are $W(CH_3)_6$,[5] $Mo(\eta^3\text{-}C_3H_5)_4$,[6] and $CpReO_3$.[7]

The same considerations can be applied to more unsaturated systems. Low-valent 15-electron systems having low pairing energies are predicted to be low spin ($S = \frac{1}{2}$, see Fig. 3c) and very reactive, whereas higher-valent systems may have $S = \frac{3}{2}$ configuration (Fig. 3d). There are no examples, to the best of our knowledge, of the former situation whereas the latter one is typical of $CpCr^{III}$ chemistry.[8] Pairing energy has also been invoked to explain the difference in spin state between the isostructural 14-electron $TiX_2(dmpe)$ complexes ($X = Me$, $S = 0$; $X = Cl$, $S = 1$).[9]

If we accept that *intermediate oxidation state* organometallic compounds can display variable spin properties[10] as a result of electronic correlation, we must then accept the idea that electronic correlation may play an important role in the energetic stabilization of the ground state of isolable compounds and reaction intermediates.

III. MECHANISM OF LIGAND SUBSTITUTION IN INTERMEDIATE OXIDATION STATE ORGANOMETALLIC COMPOUNDS

The mechanism of ligand substitution in organometallic compounds has been the subject of detailed investigations. A pictorial summary of the results is shown in Fig. 4. For the saturated systems, the exchange typically occurs through a dissociative mechanism and it is usually slow because a bond must be broken in the slow step and a high energy, highly reactive (presumably low spin) 16-electron intermediate is formed. For *low-valent* 17-electron systems, on the other hand, the exchange typically takes place through an associative mechanism, and it is rather fast as a result of the lack of a large electronic barrier since the incoming ligand can establish a positive interaction with the half-occupied HOMO, which is low in energy as discussed above. Exchange in the 17-electron systems is so much faster than in the corresponding 18-electron complexes that the exchange in the saturated compounds can often be catalytically accelerated by oxidation. The oxidized 17-electron molecules undergo fast exchange, which is followed (if thermodynamics are right) by fast cross-electron transfer with an additional molecule of starting material to generate the substituted 18-electron product and to reform the unsubstituted 17-electron complex which will continue the catalytic cycle. This mechanism has been termed Electron Transfer Chain (ETC) catalyzed substitution.[11] A similar situation exists upon catalytic reduction. In each case the exchange through 17/19-electron systems is more rapid than the exchange through 18/16-electron ones.

While the exchange in 17-electron complexes does not suffer an electronic barrier, steric factors can dramatically influence the rate of substitution since the coordination number is increased in the transition state. There are in fact examples of sterically crowded molecules where the associative substitution is slowed down so dramatically that the alternative *dissociative* mechanism becomes competitive. This is the case in $(pd)_2V(CO)$(pd = η^5-pentadienyl), where both associative and dissociative substitutions can be observed, whereas exchange in $(2,4\text{-}Me_2pd)V(CO)$ is prevalently dissociative and quite slow.[12]

It has been argued in the literature that, if 16-electron intermediates are high in energy, then 15-electron intermediates should be even higher in energy. We would like to contend that this may be true in low oxidation state substitution reactions for which the intermediates are likely to be low spin, but not necessarily so in intermediate oxidation state chemistry, because high spin electronic configurations may be obtained, with consequent energetic stabilization by the effect of electronic correlation. This is illustrated schematically in Fig. 5. For instance, the 18-electron half-open chromocene carbonyl, Cp(pd)Cr(CO), exchanges CO at about the same rate as (in fact, a little faster than) the corresponding 17-electron vanadium system. Both substitutions are dissociative; thus the intermediates have 16 and 15-electron configurations, respectively.[12,13a] The 16-electron Cp(pd)Cr molecule has two unpaired electrons.[13b] The corresponding 15-electron Cp(pd)V system has not been isolated, but the analogous $Cp(1,5\text{-}C_5H_5(SiMe_3)_2)V$ shows a $S = \frac{1}{2}$ ground state.[13b] Since the two vanadium systems exchange CO with similar rates, the Cp(pd)V intermediate is also likely to have a $S = \frac{1}{2}$ ground state. Thus, it cannot be excluded that the change of spin state in the chromium case on going from starting compound to intermediate contributes to facilitate dissociative exchange with respect to the isostructural vanadium system.

Recently, we have been involved ourselves in the investigation of the mechanism of ligand substitution reactions for intermediate oxidation state organometallic complexes.[14] We have prepared a series of cyclopentadienyl substituted, 17-electron Mo(III) complexes of general formula $CpMoX_2L_2$ (X = halide, L = neutral

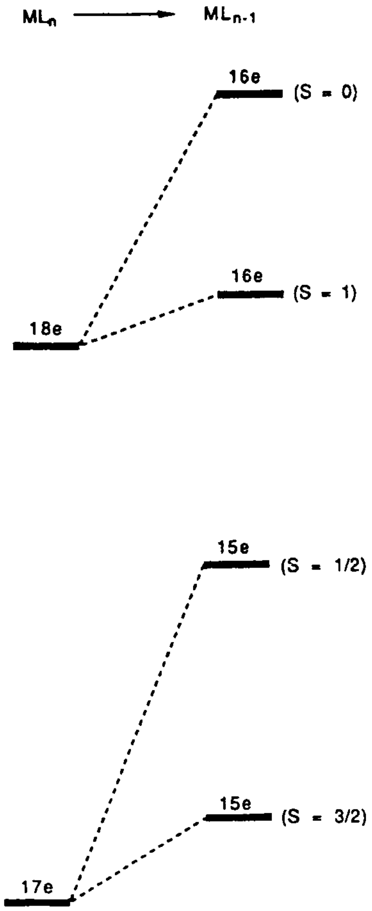


FIGURE 5 Energy/reaction coordinate diagrams for dissociative 18e and 17e ligand substitution reactions.

2e donor),[15] and we decided to investigate the mechanism of ligand exchange in this system. Because of the air sensitivity of the materials and especially the catalytic effect of oxidation on the reaction rates (vide infra), and because the uncatalyzed exchange is quite slow, we could not carry out the kinetic investigations by the traditional UV/visible methodologies: thus we turned to EPR monitoring since the sample tubes can be conveniently flame-sealed before the beginning of each kinetic run. This choice directed our investigations toward the halide exchange rather than the phosphine exchange since the position of the EPR lines is much more sensitive to the nature of the halide than to the nature of the phosphine. In brief, an investigation of the exchange shown in Eq. (1) at four different temperatures gave the values corresponding to both exchange steps. The rate of the second exchange has also been obtained by independent measurements starting from isolated

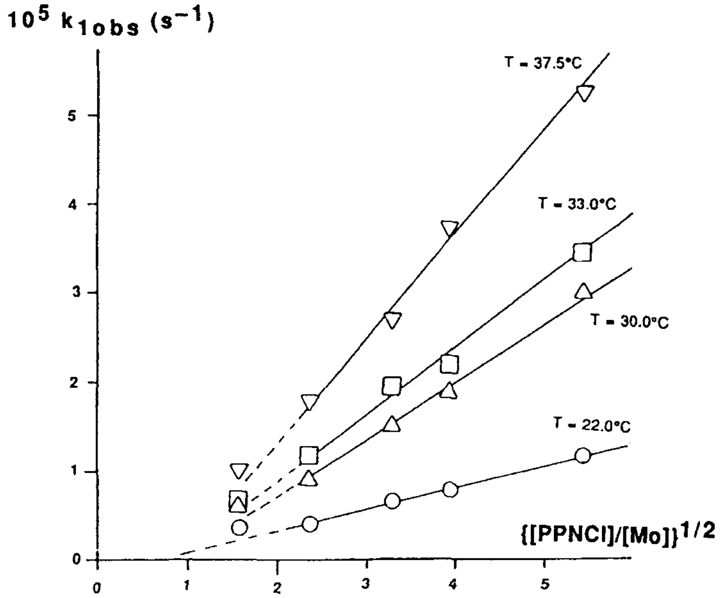


FIGURE 6 Observed pseudo-first-order rate constants for the uncatalyzed exchange of I^- with Cl^- in $CpMoI_2(PMe_3)_2$.

TABLE I

Results of the kinetic analysis according to Eq. (2)

T(°C)	$k_{1i}(M^{-1}s^{-1})$	$k_{1\varphi}(M^{-1}s^{-1})$
22.0	$(1.33 \pm 0.17)\cdot 10^{-3}$	$(0.98 \pm 0.07)\cdot 10^{-4}$
30.0	$(3.90 \pm 0.27)\cdot 10^{-3}$	$(1.33 \pm 0.30)\cdot 10^{-4}$
33.0	$(4.92 \pm 0.43)\cdot 10^{-3}$	$(1.63 \pm 0.50)\cdot 10^{-4}$
37.5	$(8.26 \pm 0.42)\cdot 10^{-3}$	$(1.80 \pm 0.50)\cdot 10^{-4}$

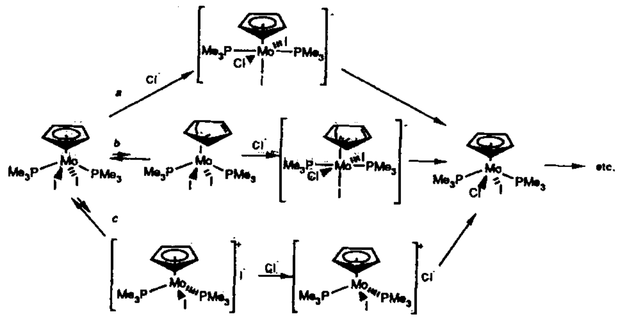
$CpMoICl(PMe_3)_2$. The most accurate results relate to the first substitution step. Pseudo-first-order rate constants are shown in Fig. 6, which fit the two term equation shown in Eq. (2) (PPNCl extensively ion pairs in the solvent of choice, CH_2Cl_2) to give the second order parameters collected in Table I.

$$CpMoI_2(PMe_3)_2 \xrightarrow{Cl^-,\ k_1} CpMoICl(PMe_3)_2 \xrightarrow{Cl^-,\ k_2} CpMoCl_2(PMe_3)_2, \qquad (1)$$

$$k_{1obs} = k_{1i}[Cl^-] + k_{1ip}[PPN^+Cl^-]. \qquad (2)$$

The two independent second order pathways can be easily interpreted as involving, respectively, free chloride and the PPN^+Cl^- ion pair as the nucleophile. An Eyring analysis on the neutral-ion pathway give the activation parameters $\Delta H_{1i} = 13.2 \pm 1.8$ Kcal·mole^{-1} and $\Delta S_{1i} = -26.0 \pm 5.7$ cal·K^{-1}·mol^{-1}. The less important neutral-ion pair pathways did not provide reasonably accurate activation parameters.

As discussed before for many other similar substitutions, second order kinetics and the large negative activation entropy do not necessarily imply a truly associative mechanism, especially when in the presence of the cyclopentadienyl ligand which may readily slip. At least three mechanisms. (Scheme I) are consistent with the kinetic information. Path *a* (the simple associative mechanism)

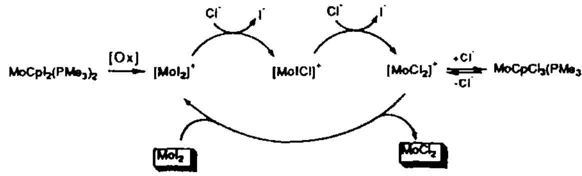


SCHEME I

involves a 19-electron intermediate/transition state, whereas the other two pathways involve 15-electron species and are therefore formally dissociative in character.

A similar kinetic investigation on a slightly modified system where the Cp ring has been replaced with Cp* shows that the rates increase by a factor of approximately 10^5. This rules out 19-electron intermediates, since the Cp* ligand is both bulkier and electronically more releasing than Cp. Thus, we seem to have found another example of a dissociative substitution in a 17-electron organometallic compound. It is certainly possible that the steric bulk of the system is solely responsible for the dissociative nature of this reaction, as proposed for the $(pd)_2V(CO)$ system and derivatives. We note, however, that the HOMO has a relatively high energy in our Mo(III) system (the complex can be easily oxidized, but not as easily reduced),[15a] thus an associative intermediate would not enjoy a great energetic stabilization due to the delocalization of the incoming ligand's lone pair into the half-occupied HOMO. In addition, the metal has a relatively high oxidation state and the expected higher pairing energy might make a 15-electron intermediate prefer a $S = \frac{3}{2}$ ground state, which would involve energetic stabilization as discussed above. Analogous Cp derivatives of Cr(III) with a 15-electron configuration are relatively common and quite stable.[8] One of the future directions of our research will be to synthesize isolable 15-electron Cp- or Cp*-containing Mo(III) compounds and verify whether they have a $S = \frac{1}{2}$ or $S = \frac{3}{2}$ ground state configuration.

Relevant to the argument of electronic correlation and its effect on organometallic reaction mechanisms is also the catalytic effect of oxidation that we have observed on the halide exchange reaction discussed above. We have carried out extensive studies which prove an ETC catalysis, as illustrated schematically in Scheme II (Cp



SCHEME II

and PMe_3 ligands are omitted).[16] The novelty of this mechanism is that, for the first time, ligand exchange in an odd electron system is accelerated by oxidation to an even electron system, rather than the other way around (see Fig. 7).

The oxidation of the diiodide starting material can be conducted stoichiometrically, and the corresponding 16-electron cationic complex has been isolated as PF_6^-, I_3^-, and even I^- salt.[15] These materials are *paramagnetic for two unpaired electrons*. Semiquantitative experiments show that the halide exchange on the 16-electron $[CpMoX_2(PMe_3)_2]^+$ complex is associative in nature and several orders of magnitude faster than the exchange on the corresponding 17-electron neutral species. There is, of course, a coulombic bias to the rate of exchange, since substrate and nucleophile have opposite charge in the Mo(IV) system, although analogous systems show only a mild acceleration of the second order rates of substitution by Cl^- due to the increase in substrate positive charge.[17] However, an important reason for the faster exchange for the Mo(IV) complex is that the 16-electron and 18-electron materials are close in energy. In fact, the diiodide cation

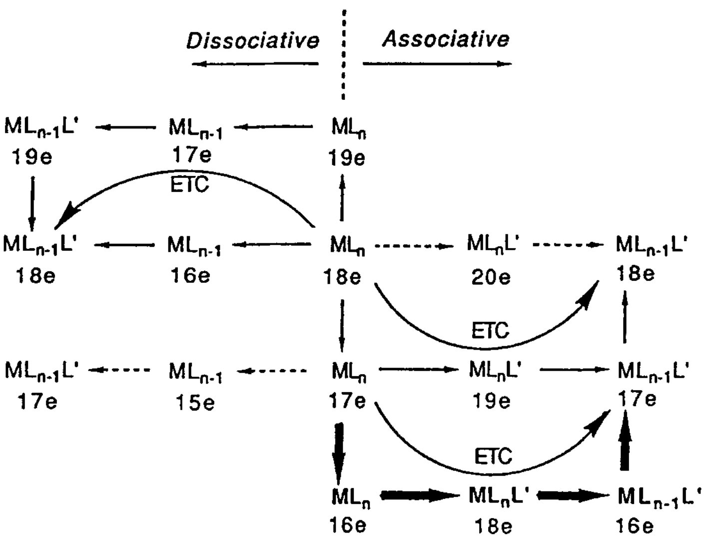


FIGURE 7 Updated schematic view of the mechanisms of ligand substitution reactions for organometallic compounds (cf. Fig. 4).

prefers the 16-electron structure in the salt with the I^- counterion to the alternative neutral 18-electron $CpMoI_3(PMe_3)_2$ (see Fig. 8). On the other hand, the corresponding dichloride cation, $[CpMoCl_2(PMe_3)_2]^+$, reacts with Cl^- to give the 18-electron trichloride system as shown in Scheme II, although this establishes an additional equilibrium with the 16-electron (paramagnetic) $CpMoCl_3(PMe_3)$ by dissociation of one PMe_3 ligand.[16] A proposed reaction coordinate for the ETC halide substitution, as well as for its uncatalyzed version, is illustrated in Fig. 9. Obviously, the steric crowding around the Mo(IV) center may render the 18-electron systems more susceptible to ligand dissociation and energetically stabilize an unsaturated 16-electron structure. However, the fact that these 16-electron systems have a $S = 1$ ground state shows that stabilization by electronic correlation may also play an important role.

In conclusion, caution should be exercised in comparing relative reactivities of different systems when the proposed electronically unsaturated intermediate has the possibility of existing in different spin states.

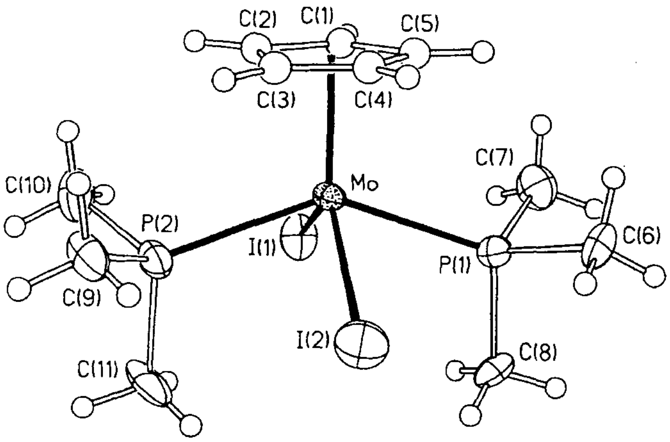


FIGURE 8 ORTEP view of the $[CpMoI_2(PMe_3)_2]^+$ cation in the salt with the I^- counterion. There are no short (< 5.5 Å) contacts between the I^- ion and the Mo center in the cation.

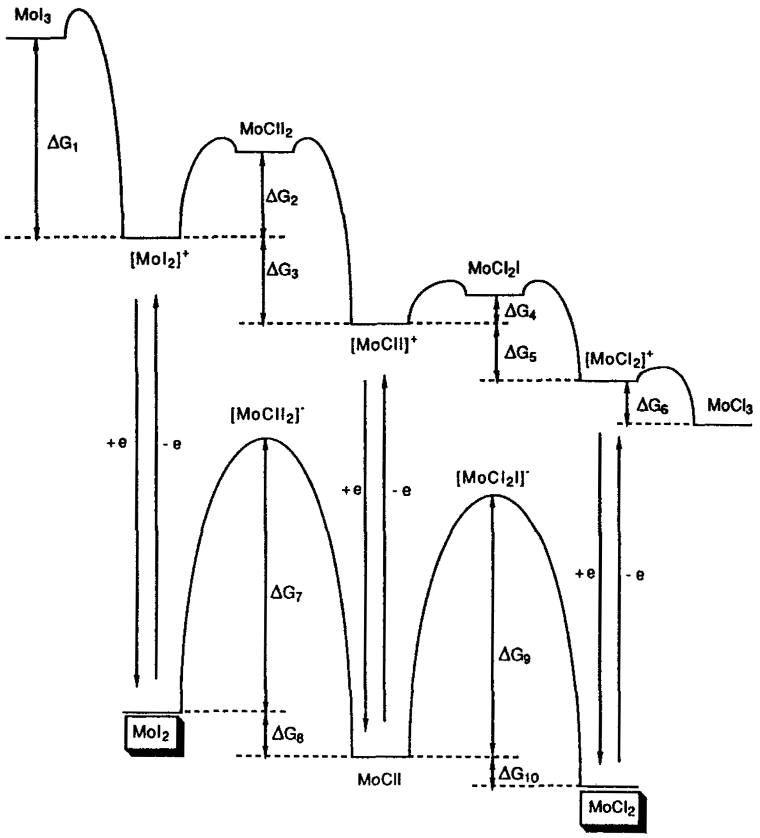


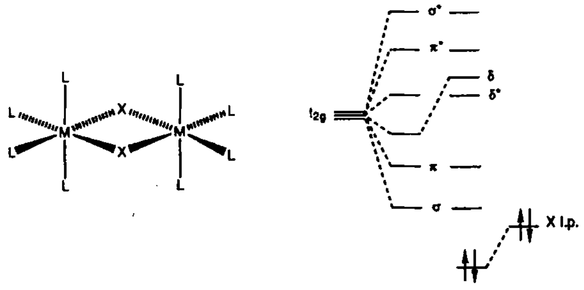
FIGURE 9 Reaction coordinate for the catalyzed and uncatalized halide substitution reaction on $CpMoI_2(PMe_3)_2$ with Cl^-.

IV. MORE THAN ONE UNPAIRED ELECTRON IN MULTIPLY BONDED METAL CLUSTERS

We shall concentrate our attention on dinuclear species, which represent most of the materials under study in higher oxidation state (non-carbonyl) metal atom clusters chemistry.[18] Most of these materials are diamagnetic because the strong metal–metal interactions induce a high separation between bonding and antibonding combinations. This situation is exemplified by the classical quadruply bonded d^4-d^4 dimers, for instance $Re_2Cl_8{}^{2-}$. Although the frontier interaction, of δ type,[18] has a small overlap, the presence of three additional strong bonds (one of σ and two of π symmetry) draws the two metals so close to each other that even the δ bond becomes significantly strong so as, for example, to stabilize the structure in the sterically less favorable eclipsed conformation, and the δ/δ^* separation is never small compared to the pairing energy. For instance, calculations place the ${}^3A_{2u}(\delta\delta^*)$ excited state 0.4 eV above the ground state for D_{4h} $Re_2Cl_8^{2-}$.[19] On the other hand, the diffuseness of the d orbitals (most of these multiply bonded systems are found to be stable for the larger 2nd and 3rd row transition elements) allows the pairing energies to remain low in spite of the relatively high formal oxidation state.

Oxidation and reduction of these diamagnetic molecules can generate paramagnetic species, which contain in most cases only one unpaired electron. More than one unpaired electron is generally present only when symmetry and electron counting give rise to an incompletely filled *degenerate* set as the HOMO. A clear example of this situation is given by the diruthenium(II) tetracarboxylato system, with two unpaired electrons. These materials had long been thought to have a $\sigma^2\pi^4\delta^4\pi^{*3}\delta^{*1}$ or $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*3}$ ground state, but this has in fact recently[20] been shown to be of type $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$. Interestingly, the ordering of δ^* and π^* orbitals is reversed in the diruthenium(II) tetrakis(triazinato) complex, $Ru_2(RNNNR)_4$ (R = *p*-tolyl), which has a diamagnetic $\sigma^2\pi^4\delta^2\pi^{*4}$ configuration.[21] Thus, in neither case is there an orbital splitting smaller than the pairing energy.

Of more specific interest for this Comment are edge-sharing bioctahedral complexes, whose generic structure is illustrated in Scheme III. The bridging ligands are typically halide or isoelectronic groups (alkoxides, sulfido groups, etc.). The electronic structure of this system is well known,[22] and the frontier region of the molecular orbitals is as shown in Scheme III. Given the pseudo-octahedral geometry around each metal center, the metal electrons will be located in two pseudo-t_{2g} sets, which can combine as illustrated to give rise to three metal–metal interactions of σ, π, and δ type. The δ combination is raised in energy by mixing with the proper symmetry linear combination of the bridging groups lone



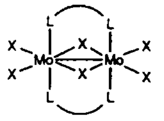
SCHEME III

pairs. Whether the resulting orbital ordering is as shown in Scheme III or whether the δ combination will remain lower than the δ* combination is expected to depend on the nature of the bridging groups. The ordering shown in Scheme III has been calculated for $W_2Cl_4(OH)_2(\mu\text{-}OH)_2(OH_2)_2$,[23] $Mo_2Cl_4(\mu\text{-}SH)_2(SH_2)_4$,[24] and $Mo_2Cl_4(\mu\text{-}Cl)_2(PH_3)_4$,[25] while there is experimental (structural) evidence for such an ordering in the $M_2Cl_4(\mu\text{-}Cl)_2(LL)_2$ (M(III) = d^n metal with $n = 2, 3, 4$, and 5; LL = dmpm or dppm) series of compounds.[26]

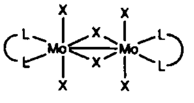
For a d^3-d^3 system, the configuration could either be $\sigma^2\pi^2\delta^2$ or $\sigma^2\pi^2\delta^{*2}$, with an expected small HOMO-LUMO gap. In all systems reported so far, however (with one exception, vide infra), the ground state is found to be diamagnetic and the possible alternative triplet (δδ*) state is only a thermally populated excited state.

V. BOND OR NO BOND BETWEEN MOLYBDENUM ATOMS IN $Mo_2Cl_6(PR_3)_4$ COMPOUNDS?

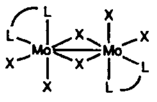
Edge-sharing bioctahedral Mo(III) complexes are relatively common. Before we initiated our own investigations in this area, examples had been reported with structures as illustrated in **I–III**, all containing bidentate ligands, e.g., $Mo_2Cl_6(dppm)_2$ (type **I**),[26] $Mo_2Cl_6(dppe)_2$ (type **II**),[27] and $Mo_2Cl_6(EtSCH_2CH_2SEt)_2$ (type **III**),[28] and all containing a metal–metal bond (2.7–2.8 Å). Derivatives containing only monodentate neutral ligands had not been reported for Mo(III), although at least two were known for W(III), e.g., $W_2Cl_6(py)_4$[29] and $W_2Cl_6(PEt_3)_4$[30] (both also displaying a short metal–metal contact).



I

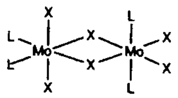


II



III

We set out to synthesize analogous compounds of Mo(III) with monodentate phosphine ligands, and the first one we obtained, i.e., $Mo_2Cl_6(PEt_3)_4$, showed a structure of type **IV** (see Fig. 10) and *no metal–metal bond* (Mo–Mo = 3.730(1) Å).[31]



IV

The failure of this compound to exhibit the expected metal–metal bond of $\sigma^2\pi^2\delta^{*2}$ type was surprising, so we were naturally interested to see whether this is a general phenomenon for dimers with monodentate phosphines and structure **IV**. The second compound we obtained, $Mo_2Cl_6(PMe_2Ph)_4$, has an identical geometry with that of the analogous PEt_3 complex (see Fig. 11), but *this time a metal–metal bond is present* (Mo–Mo = 2.8036(8) Å).[25]

The difference in structure between these two apparently very similar compounds is not merely a solid state effect. ^{1}H-NMR strongly suggests that the solution structures are identical to those found in the solid state. For the metal–metal bonded PMe_2Ph compound, the methyl protons resonate, as expected, as two peaks in a 1:1 ratio. A small paramagnetic shift is observed, which decreases as temperature decreases, consistent with a diamagnetic ground state and thermal population of a paramagnetic excited state, as found for other Mo_2^{6+} edge-sharing bioctahedral structures (see above). For the PEt_3 compound (no metal–metal bond in the solid state), two peaks in a 1:1 ratio are still observed for each type of proton. However, the paramagnetic shifts are much greater than for the PMe_2Ph analogue and they exhibit opposite temperature dependence (as temperature decreases, the shifts increase).

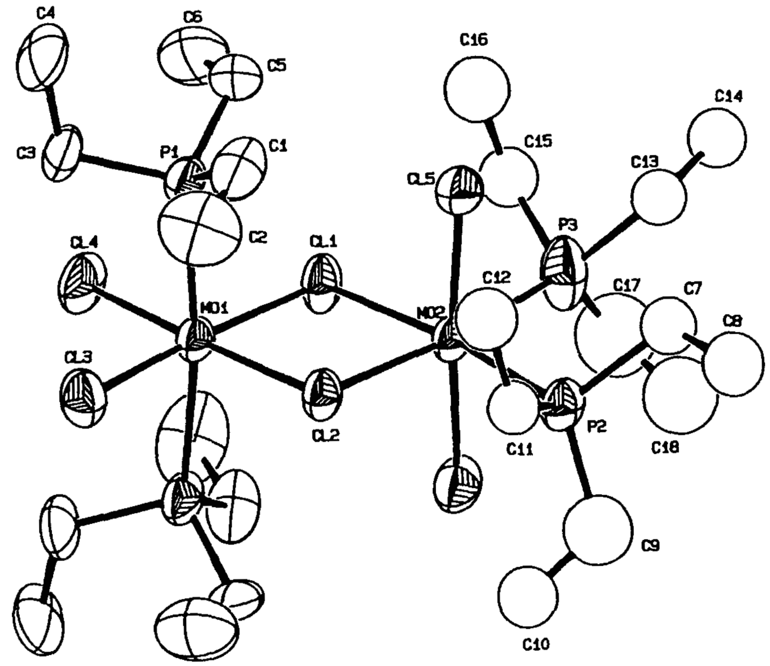


FIGURE 10 An ORTEP view of the $Mo_2Cl_6(PEt_3)_4$ molecule.

The paramagnetic shift varies linearly with inverse temperature (see Fig. 12), indicating a simple Curie paramagnet or an antiferromagnetically coupled system with a small coupling constant and a low critical temperature. In fact, the solid state magnetic susceptibility for the PEt_3 compound is consistent with a small antiferromagnetic coupling (μ_{eff} = 5.05 B. M. per dimer at room temperature vs. the expected value of 6.93 B. M. for 6 unpaired electrons).

Given that two apparently very similar compounds (the only difference being the nature of the substituents on the phosphine ligands) give such a spectacular effect in the extent of metal–metal bonding and magnetic properties, it is in order to at least attempt to provide a rationalization. In our opinion, the explanation resides again in the proper consideration of electronic correlation effects. As shown in Fig. 2, the ground state for an octahedral d^3 ion is

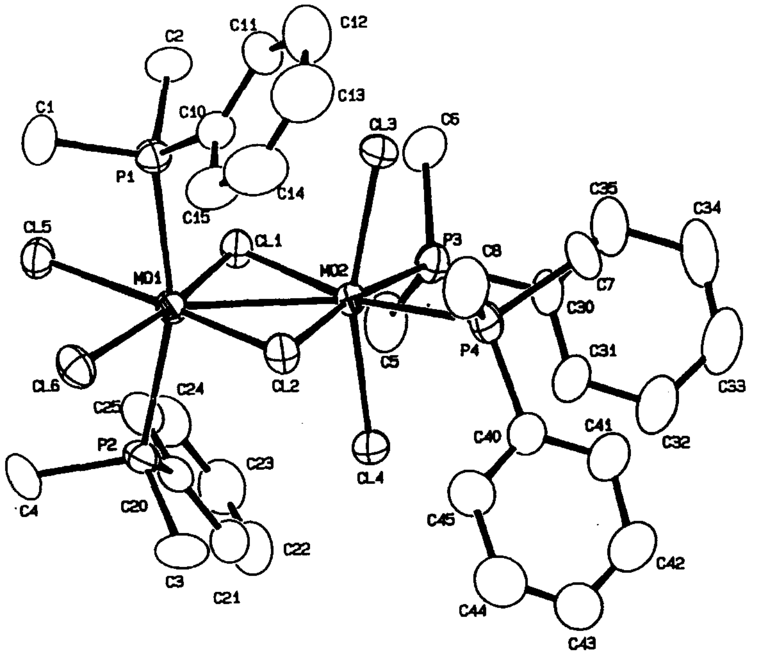


FIGURE 11 An ORTEP view of the $Mo_2Cl_6(PMe_2Ph)_4$ molecule.

energetically stabilized with respect to the ideal "monoelectronic" t_{2g}^3 configuration. Thus, the energetic stabilization achieved by combining two t_{2g}^3 sets to form the metal–metal bond is competing with the natural stabilization of the unpaired electrons because of electronic correlation (see Fig. 13). The energetic balance between the two stabilizations must be very delicate for molybdenum. For the tungsten analogue mentioned above, i.e., $W_2Cl_6(PEt_3)_4$,[30] the presence of a metal–metal interaction (and no paramagnetism: for instance, sharp ^{31}P-NMR resonances can be observed, whereas no ^{31}P-NMR signal is observable for the Mo analogue) may be the result of the combined effect of the higher d-d overlap and lower pairing energies. Conversely, lower d-d overlap and higher pairing energies induce the formation of the nonbonded chromium analogue, $Cr_2Cl_6(PEt_3)_4$.[32]

It is proper at this point to mention other literature examples where similar considerations may apply. For instance, consider the

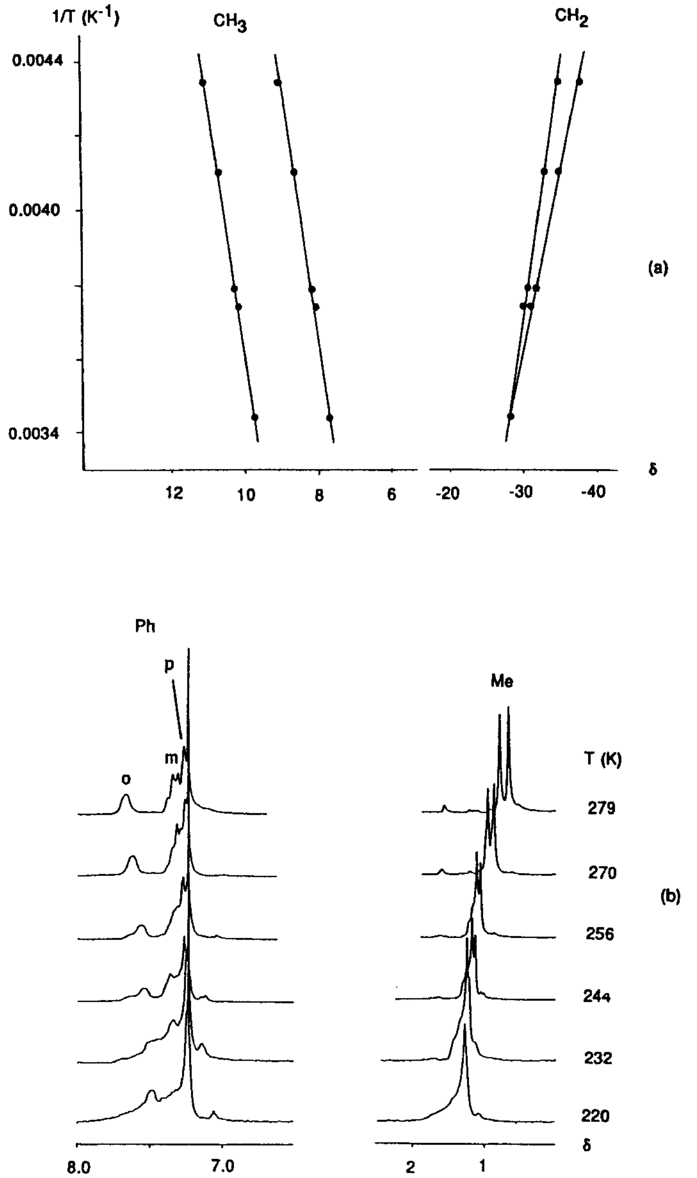


FIGURE 12 Variable-temperature ^{1}H-NMR properties of edge-sharing bioctahedral $Mo_2Cl_6L_4$ compounds. (a) L = PEt_3. (b) L = PMe_2Ph.

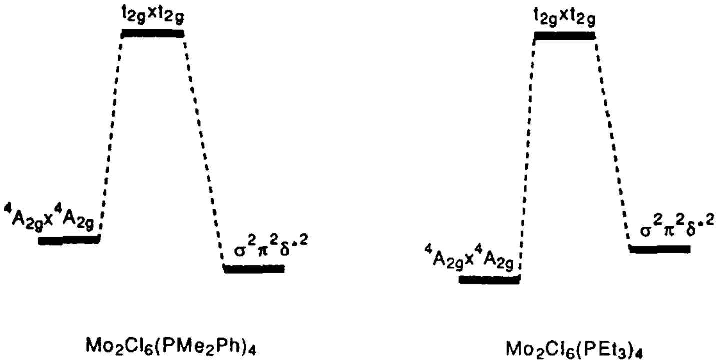
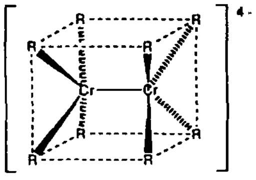


FIGURE 13 Relative energy of the ground states for the metal–metal bonded and nonbonded isomers of structure **IV**.

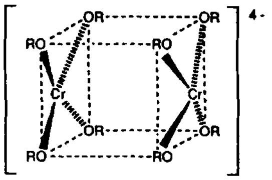
d^4-d^4 edge-sharing bioctahedral dimers $Re_2Cl_6(dppm)_2$ (with a structure of type **I** and a metal–metal bond, Re–Re = 2.616(1) Å)[33] and $Re_2Cl_6(dppe)_2$ (with a structure of type **II** and no metal–metal bond, Re···Re = 3.809(1) Å).[34] A number of hypotheses has been advanced for the explanation of this difference, but none was quite convincing and the case remained known as a *puzzling discrepancy*.[35] The tentative explanation of lone-pair–lone-pair repulsion between the axial chlorine ligands in the dppe compounds does not seem consistent with the observation of metal–metal bonding for d^1-d^1 analogues of Zr_2^{6+} and Hf_2^{6+} with identical structure (e.g., type **II**),[36] given the larger size of the latter ions and the weaker σ^2 metal–metal interaction.

Another interesting comparison is provided by the edge-sharing bioctahedral pairs of complexes M_2Cl_{10} and $M_2(OMe)_{10}$, where M is either d^1 W(V) or d^2 Re(V). For either element, no metal–metal bonding interaction exists in the chloride complexes, whereas a metal–metal bond of σ^2 (W) or $\sigma^2\pi^2$ (Re) type exists in the alkoxide complexes.[37] It has been suggested that replacement of bridging chlorine ligands with bridging oxygen donors may reduce the positive charge on the metal atoms and facilitate d-d overlap. While this argument accounts for the presence of a metal–metal bond in the alkoxide complexes, it does not explain why such interaction is *not* observed for the chloride complexes. Of course, when the formal positive charge on the metals is higher (chloride complexes), the metal orbitals are more contracted and this should cause a higher pairing energy, which will in turn favor a high spin electronic configuration.

Finally, although of a different structural type, the comparison between the quadruply bonded $[Cr_2R_8]^{4-}$ (R = Me or R_2 = butane-1,4-diyl)[38] (type V) and the nonbonded $[Cr_2(OR)_8]^{4-}$ (R = Ph, *i*-Pr)[39] (type VI) deserves brief consideration. In each case, each of the four rectangular faces that span the metal–metal vector is capped by an alkali-metal cation [the $Li(THF)^+$ unit in the alkyl cases, and the $Na(THF)^+$ or $Na(py)^+$ unit in the alkoxide and aryloxide cases].



V



VI

Given the relatively high pairing energies for the small Cr^{2+} ion, it is no surprise that the alkoxide complexes are present as nonbonded dimers. In fact, several mononuclear square planar Cr(II) alkoxide complexes are also known, e.g., $[Na(TMEDA)]_2[Cr(2,6\text{-}Me_2C_6H_3O)_4]$,[39a] and they display magnetic properties similar to those of the dinuclear compounds. The more surprising result is the existence of a bonding interaction for the octaalkyl complexes. Notice also that the corresponding homoleptic aryl materials are mononuclear square-planar, e.g., $[Li(THF)_n]_2[CrAr_4]$ (Ar = mesityl, n = 1; Ar = phenyl, n = 2).[40] A possible explanation that has not been considered so far is that the better electron releasing properties of the alkyl groups expand the metal orbitals to a greater extent and consequently both an increase of d-d overlap and a decrease of pairing energy should result.

Coming back to our edge-sharing Mo(III)-phosphine complexes, a question that naturally arises is: how does the nature of the phosphine substituents influence the metal–metal interaction? By affecting the strength of the metal–metal bond? By affecting the correlation energy? Are steric effects important? Our Fenske–Hall level MO calculations on the model compound $Mo_2Cl_6(PH_3)_4$ suggest[25] that a strong effect on the strength of the metal–metal interaction is not likely to be present (no significant contribution of phosphorus atomic orbitals to the metal–metal bonding orbitals was found). The effect on the correlation energy cannot be predicted at this time because there is practically no information in the literature on the nephelauxetic effect of phosphines. Investigation of nephelauxetic parameters have been carried out on classical coordination compounds typically containing ethers and amines, while phosphines had become fashionable ligands later, at which time they were almost exclusively used in the chemistry of organometallic (diamagnetic) compounds. Thus, fundamental background work in theoretical chemistry and classical coordination chemistry needs to be done (by others) before some of these questions can be answered.

As experimental chemists, we have decided to gather more information by synthesizing more derivatives where the nature of the phosphine substituents is varied in a more controlled fashion. For instance, on going from PEt_3 to PMe_2Ph too many factors change at the same time. Since an examination of the ^1H-NMR spectrum can give us a good qualitative indication of the presence or absence of metal–metal interaction as illustrated in Fig. 12, we have abandoned the tedious search for single crystals in the further development of this chemistry. In fact, it is sometimes impossible to generate the desired edge-sharing bioctahedral Mo(III) compounds selectively in solution as they have a marked tendency to disproportionate to face-sharing bioctahedral and to mononuclear octahedral complexes.[25]

$$3Mo_2Cl_6L_4 \rightarrow 2Mo_2Cl_6L_3 + 2MoCl_3L_3 \qquad (3)$$

The ^1H-NMR of the edge-sharing compounds with $L = PMe_3$ at room temperature shows the expected two peaks in a 1:1 ratio at δ ca. 0 and -1, indicating the presence of a metal–metal bond. Incidentally, this compound has been reported before, but no NMR had been described and it had been assigned an incorrect structure (with all phosphine ligands in axial positions).[41] Thus, the dramatic difference in metal–metal bonding is found between the complexes with PMe_3 and PEt_3, not between those with PMe_3 and PMe_2Ph.

We have thus proceeded to prepare the complexes with the mixed ethyl–methyl phosphines, PMe_2Et and $PMeEt_2$. A summary of the ^1H-NMR properties of these compounds as a function of temperature *vis a vis* the PMe_3 and PEt_3 analogues is shown in Fig.

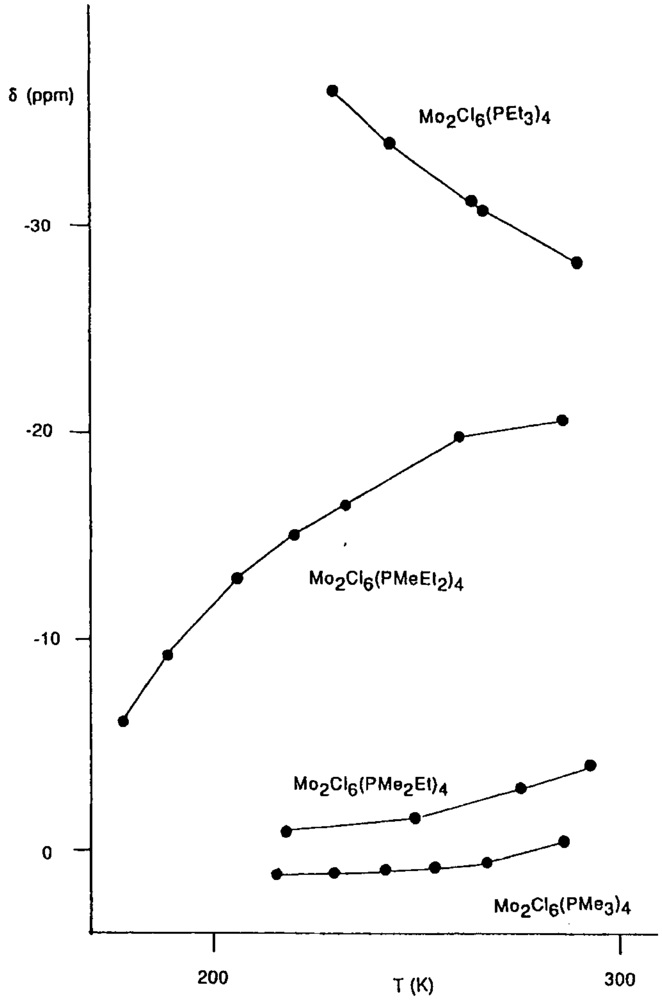


FIGURE 14 Average chemical shift as a function of temperature for the phosphine α-protons in compounds $Mo_2Cl_6(PMe_xEt_{3-x})_4$ (x = 0, 1, 2, 3).

14. As can be seen, the variation of magnetic properties is monotonic from PMe_3 to PEt_3. The PMe_2Et derivative is slightly more paramagnetic than the PMe_3 derivative, but it shows a diamagnetic ground state. The $PMeEt_2$ derivative is much more paramagnetic at room temperature, in fact closer to the PEt_3 derivative than to the PMe_3 one (judging from the position of the paramagnetic shift, which should be regarded only as a qualitative measure of the magnetic properties given the different chemical environment in the different compounds). However, the magnetism drops dramatically as temperature decreases, indicating again a diamagnetic ground state.

There is an additional interesting consideration to be made. By simple group theoretical considerations, it is possible to predict that the two ground states for bonded ($\sigma^2\pi^2\delta^{*2}$) and nonbonded (${}^4A_{2g} \times {}^4A_{2g}$) dimers have different symmetry and thus do not correlate with each other along the ideal "reaction coordinate" which transforms one isomer into the other (see Fig. 15). This argument allows the prediction of an activation barrier for the interconversion of the isomers and an interesting question arises as to whether a derivative having the two ground states at comparable energy would show isomers in solution at the same time. The data shown in Fig. 14 for the $PMeEt_2$ complex show intermediate magnetic properties between those of bonded and nonbonded isomers, but there is no indication (down to ca. 200 K) for the freezing out of an equilibrium between two different isomers. A very low or non-existent barrier to the interconversion of the isomers may be caused by mixing of the various states due to spin-orbit coupling effects, which are known to be quite large for molybdenum.

The data shown in Fig. 14 for the $PMeEt_2$ complex seems to be consistent with a temperature independent, intermediate metal–metal separation resulting in an intermediate antiferromagnetic coupling, but a temperature-dependent metal–metal interaction (stronger bond at low temperature) or a mixture of two isomers in very fast equilibrium cannot be excluded. A way to gain more insight into this problem would be to see whether the solid state magnetic susceptibility would fit the Heisenberg magnetic exchange model with a constant value of J.[42] Unfortunately, we could not isolate this compound in the pure state because of the dispro-

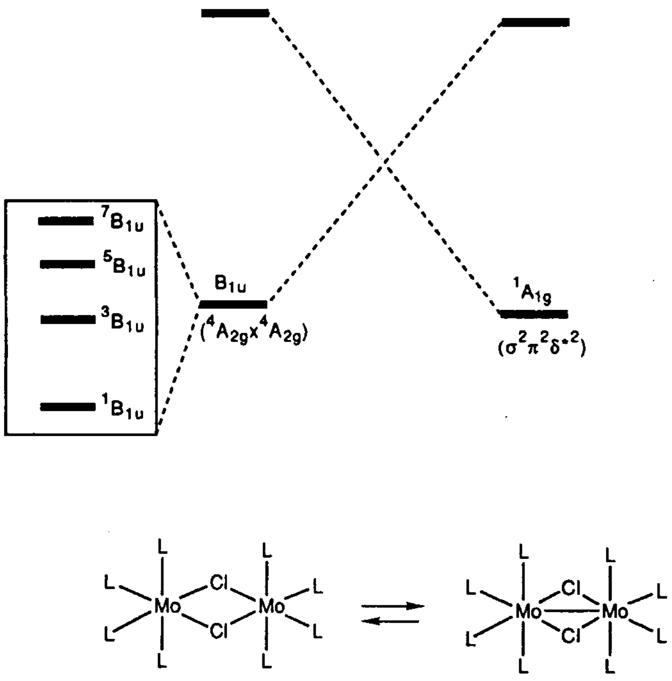


FIGURE 15 Reaction coordinate for the interconversion of metal–metal bonded and nonbonded $Mo_2Cl_6L_4$ isomers (symmetry labels refer to the ideal D_{2h} symmetry).

portionation reaction illustrated in Eq. (3), and a mixture of edge-sharing bioctahedral, face-sharing bioctahedral, and mononuclear octahedral complexes is directly obtained during the synthetic procedure. We were fortunate that the characterization in solution is rendered possible by the α-proton chemical shifts being in a different region with respect to the corresponding protons of the face-sharing dimer (only slight paramagnetic shifts) and monomer (larger paramagnetic shifts with Curie-type temperature dependence). It is worth observing that a similar situation is apparently present for the d^5-d^5 "pseudo-edge-sharing bioctahedral" compound $[Cp^*RuCl(\mu\text{-}Cl)]_2$, for which the temperature dependent ^{1}H-NMR shift has a similar trend as shown in Fig. 14 for the $Mo_2Cl_6(PMeEt_2)_4$ compound. For the ruthenium complex, bonded and nonbonded isomeric forms coexist in the solid state.[43]

To conclude, the effect of electronic correlation makes certain dinuclear compounds exist as metal–metal nonbonded isomers when other similar compounds show a metal–metal interaction. An interesting case of a system with intermediate magnetic properties between metal–metal bonded and nonbonded, i.e., $Mo_2Cl_6(PMeEt_2)_4$, has been generated and characterized in solution by variable temperature ^{1}H-NMR, and other compounds with similar characteristics could presumably be synthesized in the future. It will be a synthetic challenge to obtain one such compound as a pure crystalline solid so that the nature of the magnetic interaction can be investigated by variable temperature solid state magnetic susceptibility.

VI. CONCLUSIONS

This Comment has hopefully shown that it is important to keep in mind energetic effects due to electronic correlation when the proper conditions are met (electronically unsaturated compounds and high pairing energies). As a provocative conclusion, I would like to observe that inorganic chemists have long been aware of electronic correlation effects from the interpretation of the magnetic properties and optical spectra of coordination compounds, whereas organic chemists do not typically deal with situations where these effects are important (but there are exceptions: see singlet and triplet carbenes . . .). Let us not forget that a coordination compound, whether with or without metal–carbon bonds, is a coordination compound.

Acknowledgments

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