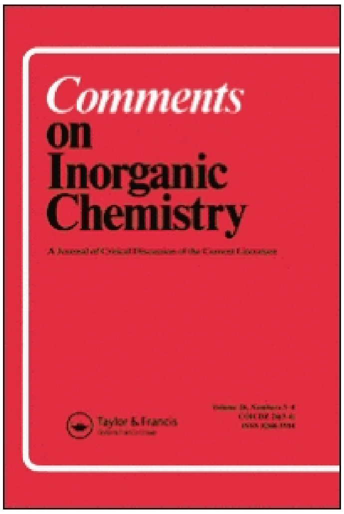

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Application of the *E-C* Approach to Understanding the Bond Energies Thermodynamics of Late-Metal Amido, Aryloxo and Alkoxo Complexes: An Alternative to pπ/dπ Repulsion

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Application of the *E-C* Approach to Understanding the Bond Energies Thermodynamics of Late-Metal Amido, Aryloxo and Alkoxo Complexes: an Alternative to pπ/dπ Repulsion

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The concept of pπ/dπ repulsion in alkoxo and amido complexes of the late transition metals has been critically examined, especially as it relates to recent work by the authors on a series of nickel complexes. The thermodynamic preferences of late-metal M-X bonds ($X = NR_2$, OR) can be explained by an alternative model which uses bond polarity as a starting point and *E-C* theory for quantification. In this model, the greater electrostatic character of the M-X bond (relative to the H-X bond) is sufficient to explain observed thermodynamic trends in ligand exchange reactions, without the inclusion of π-effects. The implications of adopting the polar bonding model have been examined, including discussion of metal alkyl complexes as well as oxo and imido complexes. In general, this polar model appears to lead to greater consistency with observation and deeper understanding, although more data are necessary to clearly determine the best way of describing bonds between late metals and X ligands.

Keywords: *E-C theory, thermodynamics, amido complexes, alkoxo complexes, pπ/dπ repulsion, metal-ligand bonding model*

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MODELS FOR COVALENT BONDS BETWEEN LATE TRANSITION METALS AND N OR O LIGANDS

The study of oxo, imido, amido, alkoxo, and hydroxo complexes of low-valent late transition metals has undergone a period of intense study in the last decade, spurred by two reviews summing up the knowledge at that time.[1,2] Although these species are intermediates or presumed intermediates in biological[3] and industrial[1] oxidation processes, few such compounds had been isolated, compared to numerous compounds for early transition metals. Now, the understanding of such complexes is improving from continued studies.[4,5]

Models have been advanced to rationalize the lack of stability of these compounds as compared to analogous complexes of early transition metals, focusing on thermodynamic properties of the metal-N or metal-O bond. (The same ideas hold for M-F bonds.)[6,7] As a starting point, hard/soft acid-base theory predicts that "soft" late transition metals (as opposed to "hard" early transition metals) should have a relatively low affinity toward "hard" anionic ligands which bind through N or O.[8,9] In a qualitative sense, this approach has been useful; however, hard/soft theory has many exceptions.[10] More recently, a molecular-orbital approach has been advanced which explains the relative weakness of late M-N and M-O covalent bonds in different terms, based on the observation that late transition metals in low oxidation states have nearly or completely filled d-orbitals.[11,12] Since the ligands of interest also contain nonbonding filled orbitals, the thermodynamic instability and high reactivity of M-X complexes were attributed to the unfavorable nonbonding interaction of π symmetry between overlapping filled orbitals (Figure 1), akin to the repulsion which causes weakening of the N-N bond in hydrazine or the F-F bond in difluorine.[11,13]

This pπ/dπ repulsion theory has gained widespread acceptance, in large part because of its close relation to (a) many important studies on the *stabilizing* interaction between filled ligand lone pairs and *empty* metal orbitals in low-coordinate complexes and intermediates,[12] and (b) crystal field theory, which attributes energetic changes to the occupancy of d-orbitals and their repulsion with ligand electrons. In computational studies, crystal-field components to bond energy have also been termed "steric effects," not to be confused with the more common usage of this term for electron repulsion between unbonded atoms.[14] (In one case, a theoretical study was used to evaluate pπ/dπ repulsion.)[15]

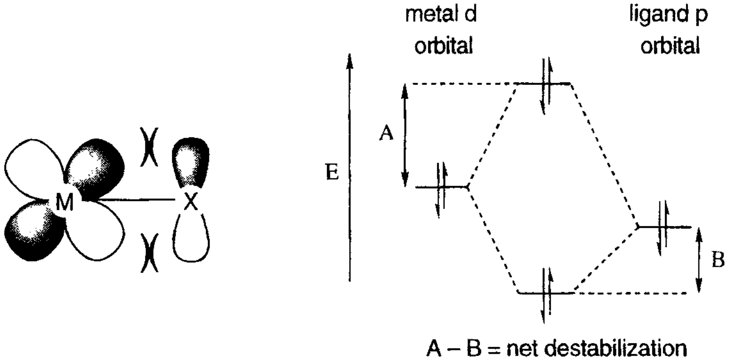


FIGURE 1 According to pπ/dπ repulsion theory, the reactivity of late-metal-NR_2 and -OR bonds is caused by the unfavorable π-symmetry interaction of the filled metal d-orbitals and the filled lone pairs on the ligand

This Comment presents a model which serves as an alternative to pπ/dπ repulsion theory. Interestingly, it can explain the same observations as pπ/dπ repulsion without *any* π-symmetry component, and thus gives a very different view of the late-transition-metal bonding to X (X = amido, alkoxo, aryloxo ligand). This σ-only theory adheres more closely to classical ideas about electronegativity and polarity, and also has the advantage that it can be used quantitatively. After describing the background and content of the work which led to this model, we will discuss some of the implications for viewing bonds between late metals and formally anionic N or O ligands, and finally offer suggestions on how further experiments could distinguish which model better corresponds to chemical reality in general and specific cases.

THERMODYNAMICS FROM LIGAND EXCHANGE REACTIONS

The determination of metal-ligand bond energies is often difficult, especially for X (described as "1-electron" in covalent or "anionic" in ionic electron-counting models)[16] ligands; although some progress has been achieved, our systematic understanding of bonding energetics remains incomplete.[17,18] As most of the known bond energies are for "early" (groups 3–6) transition metals and those in high oxidation states, the problem is especially severe for "late" (groups 8–10) transition metals in low oxidation states, although these metals are equally important in biological and industrial reactions.[19] In many cases, there are no simple methods for the evaluation of *absolute* homolytic bond energies, but fortunately there are easier ways to determine *relative* M-X bond energies which reveal important bonding trends.

Much of the data and discussion in this Comment rely on thermodynamic results from both qualitative and quantitative analysis of reactions of the type shown in equation 1:[20]

$$M - X^1 + H - X^2 \overset{K_{eq}}{\rightleftharpoons} H - X^1 + M - X^2; \quad (1)$$

$$\text{determine } \Delta H(\text{calorimetry}) \text{ or } \Delta G \text{ (from } K_{eq})$$

$$-RT \ln K_{eq} = \Delta G \approx \Delta H = \quad (2)$$
$$D(H - X^2) + D(M - X^1) - D(H - X^1) - D(M - X^2)$$

In these studies, one may assume that $\Delta G \approx \Delta H$, because in reactions in which the number of particles remains constant, no gases are released, and no unusual solvent-substrate or substrate-substrate interactions exist, the entropy changes are very small.[21] Thus, ΔH information is readily available, and a simple rearrangement of equation 2 allows one to derive a more useful relation:

$$D(M - X^2) - D(M - X^1) = D(H - X^2) - D(H - X^1) - \Delta H \quad (3)$$

Usually the H-X bond energies on the right side of equation 3 are known, and one can determine *relative* M-X bond energies. Moreover, by using a large number of X ligands, one can use these data to compare trends in metal-X bond energies to the well-understood trends in H-X bond energies (*e.g.* Hammett correlations)[22] in order to understand the nature of the metal-X bond.[20,23]

EXCHANGE OF ANIONIC LIGANDS AT A NICKEL CENTER; GENERALIZATION TO OTHER LATE METALS

In a recent study on the thermodynamics of nickel-amido, -alkoxo, and -aryloxo complexes using substituent correlations in tandem with these equilibrium techniques, we obtained results which led us to consider explanations for the energies of M-O and M-N bonds other than pπ/dπ repulsion.[24] This work used the exchange of $Cp^*Ni(PEt_3)NHTol$ (Cp^* = pentamethyl-cyclopentadienyl ; Tol = *p*-tolyl) with para-substituted anilines in order to compare the effects of changes in the H-N bond to changes in the M-N bond.

$$Cp^*Ni(PEt_3)NHTol \underset{TolNH_2}{\overset{ArNH_2}{\rightleftharpoons}} Cp^*Ni(PEt_3)NHAr \qquad (4)$$

$$K_{eq} \text{ varies from } 0.2\ (Ar = p\text{-}(Me_2N)C_6H_4) \text{ to}$$
$$2000\ (Ar = p\text{-}(MeC(O))C_6H_4)$$

$$Cp^*Ni(PEt_3)NHTol \xrightarrow[TolNH_2]{TolOH} Cp^*Ni(PEt_3)OTol \qquad (5)$$

$$K_{eq} \approx 10^6; \Delta H^\circ = -9.4 \text{ kcal/mol (calorimetry)}$$

Arylamido fragments with electron-donating para-substituents favored bonds to hydrogen and those with electron-withdrawing para-substituents favored bonds to nickel (equation 4). This was expected from pπ/dπ repulsion theory because electron-with drawing groups should cause the electrons of the nitrogen lone pair to be more delocalized into the arene ring. The addition of TolOH to $Cp^*(PEt_3)Ni\text{-}NHTol$ (equation 5) caused complete conversion to $Cp^*(PEt_3)Ni\text{-}OTol$ and $TolNH_2$ ($\Delta H = -9.4$ kcal/mol from calorimetry).[24] Thus, OR ligands were favored over NHR ligands with the *same* R, in metal binding with respect to hydrogen binding. This is also consistent with pπ/dπ repulsion theory because nitrogen is a stronger π-donor than oxygen and thus causes greater repulsion.

Examples of similar preferences can be found for complexes of a range of other late transition metals including Re, Ru, Rh, Ir and Pt; examples are discussed at length elsewhere.[24] The important generalization which applies here is that, for these metals relative to hydrogen, phenolate groups are favored with respect to alkoxide groups, and also with respect to anilide groups (equation 6). Interestingly, *alk*oxide and *aryl*amide groups generally give roughly thermoneutral exchanges:[20,24] thus an aryl appendage makes a nitrogen ligand more like an oxygen ligand. According to pπ/dπ repulsion theory, this reflects the ability of an aryl ring to lower the energy of the high-lying nitrogen p-orbital which is interacting destructively with the metal d-orbital. By analogy, alkylamido complexes should be very unstable relative to their conjugate amines; this is reflected in the scarcity of late-metal alkylamido compounds.[1,2]

$$\text{Bond energy of } M - X \text{ relative to } H - X: \quad \text{OAryl} > \text{OAlkyl} \approx \text{NHAryl} > \text{NHAlkyl} \tag{6}$$

Although these results can be rationalized by pπ/dπ repulsion theory, several observations caused confusion. (1) The bond energies of several alkoxides and amides of the *early* transition metals and lanthanides have been determined; these show that with all other variables held constant, oxygen ligands are favored over nitrogen ligands.[25–27] This trend is *identical* to that observed for late transition metals, despite the fact that pπ/dπ interactions should be *opposite* for electron-rich (π-donor) late metals and electron-poor (π-acceptor) early metals. (2) In the nickel system, there was not a large difference between equilibrium constants for an aniline containing a *para*-dimethylamino group (a resonance π-donor) and one with a *meta*-dimethylamino group (in which the π-donation should be greatly attenuated). Additionally, the substituent correlation did not contain a disproportionately large contribution from the resonance parameter.[22] Both these observations made us doubt that the electron density in the p-orbital of the nitrogen atom in the nickel amides is the dominant factor in deciding the difference between Ni-N and H-N bond energies. (3) No estimates have been made of the magnitude of pπ/dπ-repulsion-induced destabilizing energy in such compounds. The stabilization energy from π-bonding between M and N in early metal alkylamide complexes has been estimated to be less than 10 kcal/mol;[28,29] a nonbonding repulsion force (B – A in Figure 1) would undoubtedly be much weaker than a constructive binding force (B alone). In short, it would be surprising if the energy of pπ/dπ repulsion were more than 1–2 kcal/mol. (4) An explanation based solely on π-effects assumes implicitly that σ-bonding effects are the same in M-X and H-X bonds. Although this point of view has been advanced based on a study of two kinds of M-X bonds,[20] it does not seem intuitively obvious that metal cations, which are generally electropositive and bind through directional hybrid orbitals of substantial d-character, should be well modeled by a proton. These considerations led us to seek a better way to interpret relative M-X bond energies.

RELEVANT ASPECTS OF *E-C* THEORY[10]

This theory is based on the assumption that stabilizing interactions have two sources: (a) Coulombic ("electrostatic") contributions from charge separation, and (b) electron-sharing ("covalent") contributions from electron sharing and orbital overlap. According to *E-C* theory, it is possible to separate the bond enthalpy for a covalent bond into two components, E_AE_B (describing the *electrostatic* component of bonding) and C_AC_B (describing the *covalent* component of bonding). Each component is a product of two terms which are specific to the fragments involved. The terms E_A and C_A describe the electrostatic and covalent bonding tendencies of the acceptor or "catimer" (positive end of a polar covalent bond), and E_B and C_B describe the electrostatic and covalent bonding tendencies of the donor or "animer" (negative end of a polar covalent bond). Both E_AE_B and C_AC_B represent properties of the formed molecule, so another term is needed to describe homolytic bond energies: T_AR_B. T_A is the "transference" of the catimer and R_B is the "receptance" of the animer; their product describes the energy of shifting charge in neutral radicals to the polar bond in the molecule.

$$E_AE_B + C_AC_B + T_AR_B = \mathrm{BDE} \tag{7}$$

Values of these six parameters have been derived empirically from fitting to the multitude of known bond energies. Observed deviations are small and invariably can be explained. As expected, ionic compounds have large E_AE_B and T_AR_B terms, C-C bonds have large C_AC_B components, T_A correlates with the ionization energy of the catimer and R_B with the electron affinity of the animer. "Percent ionic character" and "percent covalent character" (as originally defined by Pauling using electronegativity, a one-parameter scale) can be defined as in equation 8.

$$\begin{aligned}\%\ \text{ionic character} &= 100 \times \frac{E_AE_B + T_AR_B}{\Delta H^\circ};\\ \%\ \text{covalent character} &= 100 \times \frac{C_AC_B}{\Delta H^\circ}.\end{aligned} \tag{8}$$

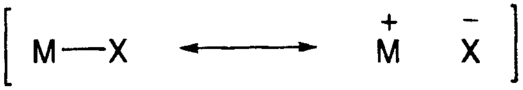
As this multiparameter theory can provide a better way to understand bonding than qualitative electronegativity arguments, it can be used quantitatively to understand substituent effects. In this formalism, the familiar Hammett σ is split into ΔE^X and ΔC^X, which function as electrostatic and covalent substituent constants, and ρ is separated into d^E and d^C, which represent the sensitivity of the equilibrium to electrostatic and covalent effects, respectively. Equation 9 displays the similarity in form of the Hammett equation to the *E-C* equation; X represents the para substituent which is being compared to the unsubstituted analog with H in this position. Although equation 9 shows equilibrium constants, analogous equations can be used for rate constants or for spectroscopic parameters. This two-dimensional analysis may seem more complicated than a Hammett analysis at first glance, but notice that the use of the dual-parameter system eliminates the need for choosing between many different substituent constant scales: Drago has shown that data previously interpreted using σ, $\overset{\circ}{\sigma}$, σ^+,σ^- and σ_I can all be described accurately using ΔE^x and ΔC^x parameters.

$$\textbf{Hammett} : \log K_X - \log K_H = \rho\sigma_X$$
$$\textbf{E}-\textbf{C} : \log K_X - \log K_H = d^E\Delta E^X + d^C\Delta C^X \tag{9}$$

Although other aspects of *E-C* theory are not utilized here, it should be noted that Drago has adapted its use for treating solvation, reaction rates, and spectroscopic results. In a separate study, we have shown the use of Drago's USM (solvation theory) in tandem with *E-C* substituent correlation analyses to understand the mechanisms of metal to organic disulfide electron-transfer reactions.[30]

THE *E-C* MODEL AS IT RELATES TO LATE M-X BONDS [10,31]

Let us first describe the qualitative aspects of an *E-C* model for late metal-X bonds. Since metals are much less electronegative than N and O, M-X bonds are polar, concentrating negative charge on the metal-bound atom. As stated by Pauling, the bond energy in polar bonds is increased by a Coulomb contribution (similar to the higher strength of C-N and C-O bonds compared to C-C bonds: this idea has also been used to explain the anomalously weak F-F bond in difluorine);[13] this stabilization increases with greater electronegativity difference.[32,33] Thus electron-withdrawing groups on X, which favor negative charge on X and increase the bond polarity, should stabilize M-X complexes (Figure 2). This explains why, in metal/proton exchanges of X (Equation 1), oxygen X favor the metal more than nitrogen X, and why X ligands with more electron-withdrawing substituents also favor the metal over the proton. The similar effects of meta- and para-substituents observed in the nickel systems discussed above is more consistent with this model, because the observed substituent effects cannot entirely be explained by resonance interactions with the nitrogen p-orbital. So, it appeared that a model of the Ni-X bonds as very polar (*i.e.* having substantial electrostatic character) was a good way to account for the experimental results on the nickel system and for the general observations on late-metal amides and alkoxides, with no need to invoke π-effects.[24]



$$\left[\mathrm{M{-}X} \longleftrightarrow \overset{+}{\mathrm{M}}\ \ \overset{-}{\mathrm{X}} \right]$$

FIGURE 2 Resonance structures of M-X bonds. As X becomes more electron-withdrawing, the resonance structure on the right becomes more important and the bond energy increases

As shown above, *E-C* theory can be used to describe such models quantitatively. Refinement of the series of equations generated from substitution of known ΔE^x and ΔC^x parameters[34] (see above) and log K_{eq} values for the nickel amido/amine exchanges (equation 4) into equation 9 gave sensitivity factors of $d^E = -18.4$ and $d^C = 1.84$. The signs of these values show that the electrostatic contribution (d^E) acts to strengthen M-X bonds with more electronegative X (relative to H-X), but the covalent contribution acts to weaken M-X bonds with more electronegative X. However, since the ratio $d^C/d^E = -0.1$ is small, the change in binding from H-X to Ni-X is mostly electrostatic in nature, and the electrostatic term dominates the trend in bond energies. These results are displayed graphically in Figure 3, where the electrostatic contribution to log K_{eq} ($d^E \times \Delta E^X$) and the covalent contribution to log K_{eq} ($d^C \times \Delta C^x$) are displayed in different shades; the sum of the two bars (one positive and one negative) is log K_{eq}, as calculated from the *E-C* fit. Two important trends are clear in this system: (1) $d^E \times \Delta E^X$ is always larger than $d^C \times \Delta C^X$; (2) although the two contributions have opposing effects on the Ni-X/H-X bond energy difference, the electrostatic terms are always larger, and they favor electron-withdrawing substituents. These results show quantitatively that the electrostatic component of the bond energy is the main difference between bonding of the $Cp^*Ni(PEt_3)$ fragment and bonding of hydrogen.

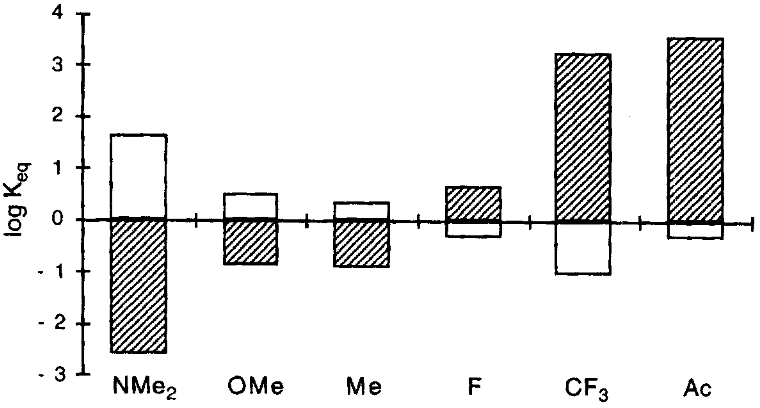


FIGURE 3 Expression of the observed log K_{eq} as a combination of electrostatic (shaded) and covalent (white) parts, for each para substituent used in reference 24. K_{eq} is defined in equation 4

Unfortunately, H-X/Ni-X exchange measurements cannot yet be used to derive E_A and C_A for the Cp*Ni(PEt$_3$) fragment, because (a) the values of E_B and C_B are not known for arylamide ligands, and (b) a much wider range of animers X should be used to derive these values. It is also unfortunate that the *E-C* substituent constant analysis does not use the T_AR_B term; in our refinement it is presumably absorbed into $d^E \times \Delta E^X$, which represents electrostatic bonding.

Drago has given a more complete analysis of some known M-X bond dissociation energies using an *E-C* model that included T_A and R_B terms (hereafter, "*ECT* model").[31] In this work, the M-X bond energies of complexes of nine transition-metal fragments were fit to an *ECT* model with good results. Important findings included: (a) the percent ionic character did not vary much between early and late transition metals, (b) the E_B trend followed C < N < O, and the C_B trend was C > N > O, and (c) there was no evidence for π-interactions (including backbonding to the cyanide ligand!) in (DPPE)Pt(Me)X or Cp*Ru(PMe$_3$)$_2$X complexes, but there was evidence for ligand-to-metal π-donation in a zirconium alkoxide. The *ECT* fit provided many predictions of unknown M-X bond energies. However, no further work has been done to confirm these predictions, and this still represents only a small number of metal fragments. So, the next step in the application of *E-C* theory to transition-metal complexes should be the collection of thermochemical data with other M, X and ancillary ligands. In analogy to our work, we suggest that exchange reactions are a simple way to do this, using late-metal auxiliaries that are less susceptible to decomposition than nickel amido complexes.

IMPLICATIONS OF AN *E-C* MODEL

In order to further probe the consequences of a σ-only model for late M-X bonds, let us examine several implications of this theory. First, if the pπ/dπ repulsion model is not used, then how can one rationalize the low apparent stability of late-metal-X linkages? The answer becomes clear when one reverses the question: why are early-metal-X linkages anomalously strong? Clearly, early-metal-X bonds (in which the metals typically have empty orbitals of π symmetry) will be strengthened by constructive π-interactions; indeed, "σ-only" M-X bonds in zirconium amides and alkoxides calculated from an *E-C* model are weaker than the experimental values by roughly 20 kcal/mol.[31] In other words, metal-N and metal-O bonds are inherently reactive (as found in group 1 and 2 amides and alkoxides, where π-bonding is not important), but this tendency is lessened in the early transition metals because of stabilizing π-bonding. In this way, well-established models of *constructive* metal-ligand π-interactions can explain the observed stability trends without recourse to repulsive pπ/dπ effects, which we believe are only sufficient to influence conformational choices (probably less than 1 kcal/mol).

It is well-known that late-metal amides and alkoxides are good hydrogen-bond acceptors; a review of pπ/dπ effects attributed this to the high energy of the p-orbital on X.[12] In terms of a polarization model, it is equally simple to rationalize this tendency: in the absence of π-interactions, the substantial negative charge on X renders it a strong hydrogen-bond acceptor.

Also, a qualitative electrostatic model, which attributes polarization to all covalent M-X bonds, rationalizes the affinity of *both* early and late metals for more electronegative ligands in an extremely simple fashion. Examples of this trend include the exceptional stability of perfluorinated alkyl and alkoxide ligands, as well as the disproportionately high strength of bonds to aryl ligands (sp^2 carbon) with respect to alkyl ligands (sp^3 carbon).[19,35–37] Because the metal-bound atom has a high electron density, electron-withdrawing substituents will stabilize the complex without requiring symmetry-allowed π-overlap between the metal and the ligand. In *E-C* terms, the contribution of the electrostatic terms $E_A E_B$ and $T_A R_B$ to the total M-X bond energy is heightened when X is more electron-withdrawing. Note that this is the opposite of the trend for dative ligands such as phosphines, amines, and alkenes, where a preference for ligands with electron-donating groups reflects a large covalent contribution and less electrostatic bonding.[38,39]

A recent review on metal-ligand π-effects stated prominently that pπ/dπ repulsion favors a "reaction which creates a ligand with no lone pairs at the alpha ligand atom."[12] However, alkyl complexes of several different late transition metals are protonated by phenols to produce aryloxo complexes, contradicting this prediction.[40] The polarization model, on the other hand, clearly predicts that all things being equal, metals should thermodynamically favor oxygen ligands over isosteric carbon ligands.

$$[\mathrm{M}]-\mathrm{CH_2R'} + \mathrm{ROH} \rightarrow [\mathrm{M}]-\mathrm{OR} + \mathrm{R'CH_3} \qquad (10)$$

Although speculative, it is interesting to consider the new outlook from an *ECT* view of M-N and M-O *multiple* bonds. The pπ/dπ repulsion model predicts that late-metal oxo and imido complexes should behave as nucleophiles because their lone pairs are localized on the ligand. However, in metallobiochemistry, late-metal oxo species have electrophilic character, as evidenced by their reactivity: model d^4 iron[41] and ruthenium[42] oxo complexes (as well as postulated copper oxo complexes)[3,43] epoxidize unsubstituted styrenes and hydroxylate hydrocarbons. Similarly, the original statement of pπ/dπ theory predicted that the first oxo complex of the Co triad would be cationic to reduce the metal's electron density,[11] but the first iridium oxo complex to be synthesized ($\mathrm{Mes_3Ir{=}O}$) is neutral and contains poorly-polarizing alkyl auxiliary ligands![44] An *E-C* model can accommodate these data because the late metal-oxygen or metal-nitrogen *double* bond has a large covalent component $C_A C_B$ and a small transfer component $T_A R_B$, allowing the electronegative oxygen or nitrogen atom to maintain its electron-attracting capacity. This contrasts with imido and oxo complexes of early and high-valent transition metals, in which the metal-ligand bonding has greater electrostatic character according to calculation.[45] Hopefully, quantitative thermochemical analyses of these reactive and interesting systems will eventually be possible using *E-C* theory.

TESTING THE APPLICABILITY OF *E-C* MODELS TO M-X BONDS

The main obstacle to determining the broad applicability of this polarization model to late metal-X bonds is the lack of a large set of systematic bond energy data. In contrast to the measurement of absolute bond energies, the easier exchange methods described above enable the researcher to obtain useful relative bond energy information which can be used to evaluate the competing theories. Hopefully, enough data can be collected with these methods to examine the merits of each model and to create a firm database for making continued experimental forays into the details of metal-ligand bonding. We suggest that such studies utilize (a) stable auxiliary ligands, so a wide range of X ligands can be examined and so ΔH values can be derived from the temperature dependence of K_{eq}, (b) easily varied ligand sets, so the effect of "ancillary" ligands can be evaluated,[46] and (c) a relatively spacious ligand pocket for X, so steric effects are not a complicating factor.

E-C models and pπ/dπ repulsion are not mutually exclusive. As Drago has stated, π-effects are manifested as a deviation from an *E-C* fit, as long as the database has representatives with widely varying π-donor and π-acceptor capacities.[31,39] If pπ/dπ destabilization is occurring, then one would expect M-X bond energies for late metals bound to extremely good π-donors (*e.g.* alkylamides) to be smaller than predicted from the *E-C* fit. Although the data so far collected do not support such a deviation,[31] continued studies (especially with electron-rich metal fragments) would show if the lack of π-effects is a general phenomenon or whether additional π_A and π_B parameters allow one to more accurately model the data.

SUMMARY

This Comment has outlined a qualitative polarization model for viewing the thermochemistry of M-X bonds; M-L bonds (L = neutral, "dative" ligand)[16] can also be treated using similar arguments, except that M-L bonds conversely have a larger covalent than electrostatic component.[24,38,39] *E-C* theory can be used to test the validity of models in a quantitative way. Additionally, this approach has shown that the prevailing pπ/dπ view of complexes between late transition metals and N, O, and F ligands can be replaced with a σ-only theory without harm, and it has already begun to improve our understanding of bonding energetics.

However, neither the pπ/dπ model nor the polarization model presented here is adequately supported by thermochemical data which allow one to unequivocally choose one of these theories over the other: only more data will solve this problem. A large, systematically collected database will allow the detailed evaluation of E_A, C_A, and T_A parameters for many metal-containing fragments with respect to (a) periodic trends, (b) the effect of oxidation state, and (c) the effect of ancillary ligands. Also, *E-C* studies on complexes in actual catalytic systems will elucidate the important features of the metals and co-ligands that contribute to unique catalyst properties. The quantification of these effects will eventually provide a high level of predictability in the chemistry of transition metal compounds.

Acknowledgments

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