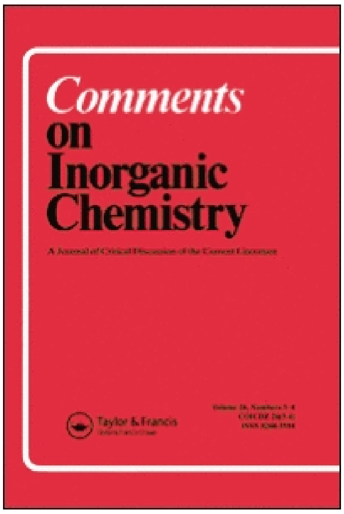

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Evaluating the Role of π-Donor Ligands in Transition Metal Chemistry. Applications of Fenske-Hall Molecular Orbital Calculations and Mulliken Population Analyses

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Evaluating the Role of π-Donor Ligands in Transition Metal Chemistry. Applications of Fenske–Hall Molecular Orbital Calculations and Mulliken Population Analyses

Fenske–Hall molecular orbital calculations are used to probe the electronic structure and bonding of amide and alkoxide ligands bound to a transition metal. A "frozen π-orbital" method is introduced and used to separate σ- and π-bonding effects of these ligands to the metal. Mulliken population analyses are used as a relative measure of π-donor ability of the alkoxide ligand with varying M-O distance, M-O-C(H) angle, and d^n electron count. Population analyses are also used to gauge the effect of π-donor ligands on the π-acceptor role of ancillary ligands such as carbonyl and isocyanide.

INTRODUCTION

Organotransition metal chemistry has developed with soft, π-acceptor ligands such as carbonyl, tertiary phosphines, olefins and cyclopentadienides. These ligands are well suited to low valent, d^n electron-rich metal centers. The complimentary nature of π-donor ligands with early transition elements in thier mid to high oxidation states is an aspect of organotransition metal chemistry of current interest. Work in our laboratory has pointed to several significant consequences of π-donating ligands which include both structural and kinetic effects. Ligand-to-metal π-bonding may perturb d^n electrons, M-M bonding, and the reactivity of other ligands bonded to the same metal center. One would like to quantify these effects, and to this end we describe here how applications of M.O. cal-

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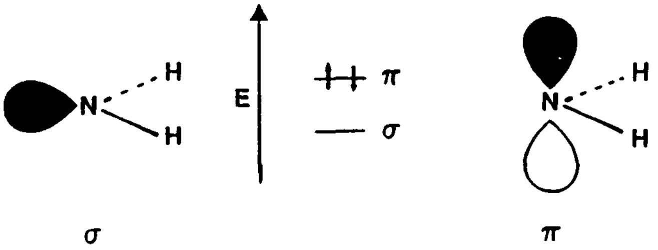
culations employing the Fenske–Hall[1] method and Mulliken population analyses[2] may be used to provide insight into this important point.

METAL–NITROGEN π-BONDING IN TRANSITION METAL DIALKYLAMIDES

The coordination properties of transition metal dialkylamides are largely determined by the steric requirements of the specific dialkylamide ligand and its ability to form both σ and π bonds with a transition metal.[3] Physical evidence suggesting the importance of M-N π-bonding in dialkylamide ligands includes a pronounced tendency for planar M-NC_2 units and short M-N bond lengths as observed in compounds such as $W_2(NMe_2)_6$,[4] $W(NMe_2)_6$,[5] $Nb(NMe_2)_5$,[6] and $Mo(NMe_2)_4$.[7] A striking example of M-N π-bonding is found in $Mo(NMe_2)_4$ which has a molecular structure of D_{2d} symmetry with a nearly tetrahedral MoN_4 core as shown in Fig. 1.[7] A truly tetrahedral d^2 complex would be expected to be paramagnetic with an e^2 orbital configuration. The diamagnetism of this molecule can only be understood by consideration of Mo-N π-bonding.

As a case study, we will briefly reexamine[7] the electronic structure of D_{2d} $Mo(NH_2)_4$ as a model compound with the aid of Fenske–Hall calculations and Mulliken population analysis.[8] For convenience the results are transformed from an atomic orbital basis set into a molecular orbital basis of the isolated metal and NH_2^- ligand fragments. This fragment and free-ligand representation will facilitate a diret comparison of the ligand populations before and after coordination to the metal.



SCHEME I

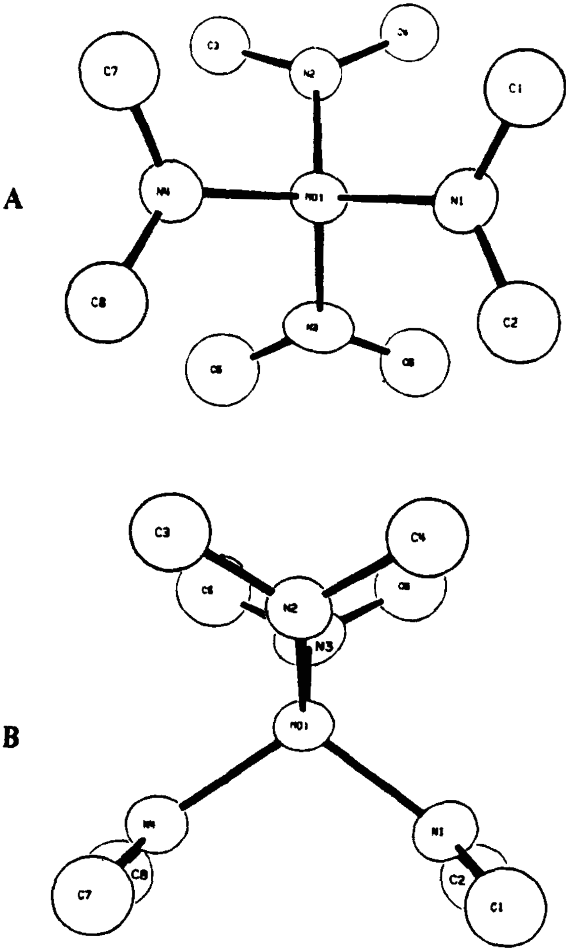


FIGURE 1 Two ORTEP views of the Mo(NMe$_2$)$_4$ molecule from Ref. 8. View B is rotated 90% about the horizontal axis of view A.

The interaction of the amido ligand with the molybdenum atom is most easily visualized in terms of the spatially and energetically inequivalent lone-pair orbitals of the NH$_2^-$ ligand. These lone-pairs can be thought of as derived from a planar, sp^2 hybridized nitrogen atom. There is a relatively low-lying σ lone-pair and a higher-lying π lone-pair, both of which are spatially and energetically inequivalent as depicted qualitatively in Scheme I.

It is possible to isolate and separate the σ and π interactions through what we will call a "frozen π-orbital" method. In this method the ligand π orbitals in the canonical basis are partitioned in the Fock and overlap matrices in a way which is similar to the partitioning of the matrices of a diatomic molecule into core and valence regions as illustrated by Roothaan.[9] The π orbitals are then deleted from variational treatment and we will refer to them as "frozen π orbitals." With this method we can effectively "switch off" π interaction to examine the σ-only interaction in the absence of the π. The π interaction can then be "switched on" and treated as a perturbation.[10]

The set of four σ lone-pair NH_2^- orbitals transform as a_1, b_2, and e irreducible representations in the D_{2d} point group. Using our frozen π-orbital approximation, interaction of the set of σ lone-pairs with the molybdenum atom results in a splitting of the Mo 4d atomic orbitals into two sets which can be viewed in terms of "e" and "t_2" orbitals of a tetrahedron. This "σ-only" interaction is shown in the correlation diagram for $Mo(NH_2)_4$ in Fig. 2. It can be seen on the right-hand side of Fig. 2 that our procedure leaves the $(NH_2)_4^{4-}$ π orbitals unperturbed and allows for effective separation of σ and π interactions. Next we can "switch on" the π interaction and rationalize the effects from a simple perturbation theory viewpoint. The set of four π NH_2^- lone-pair orbitals transform as a_1, b_2, and e irreducible representations, which suggests that in principle, four Mo-N π bonds could be formed resulting in an 18-electron valence configuration about molybdenum. A detailed examination of the interactions, however, indicates that only two π bonds are formed. From Fig. 2 it can be seen that the a_1 π interaction is quite large, and this is easily râtionalized in terms of simple perturbation theory. The $4a_1$ "σ-only" orbital (d_{z^2}) is the only metal orbital not destabilized by Mo-N σ-bonding. As a result, it is energetically the closest and has the best overlap with the π lone-pair orbitals, resulting in the formation of a strong a_1 Mo-N π-bond. The b_2 metal orbital ($x^2 - y^2$) also maintains appreciable overlap with the N π lone-pairs, but it is energetically removed as a result of Mo-N σ-bonding, and the resulting Mo-N π-bond is not as strong. The metal e representation is also energetically removed due to σ-bonding, and furthermore has little overlap with the π lone-pairs, resulting in a set of essentially nonbonding lone-pair

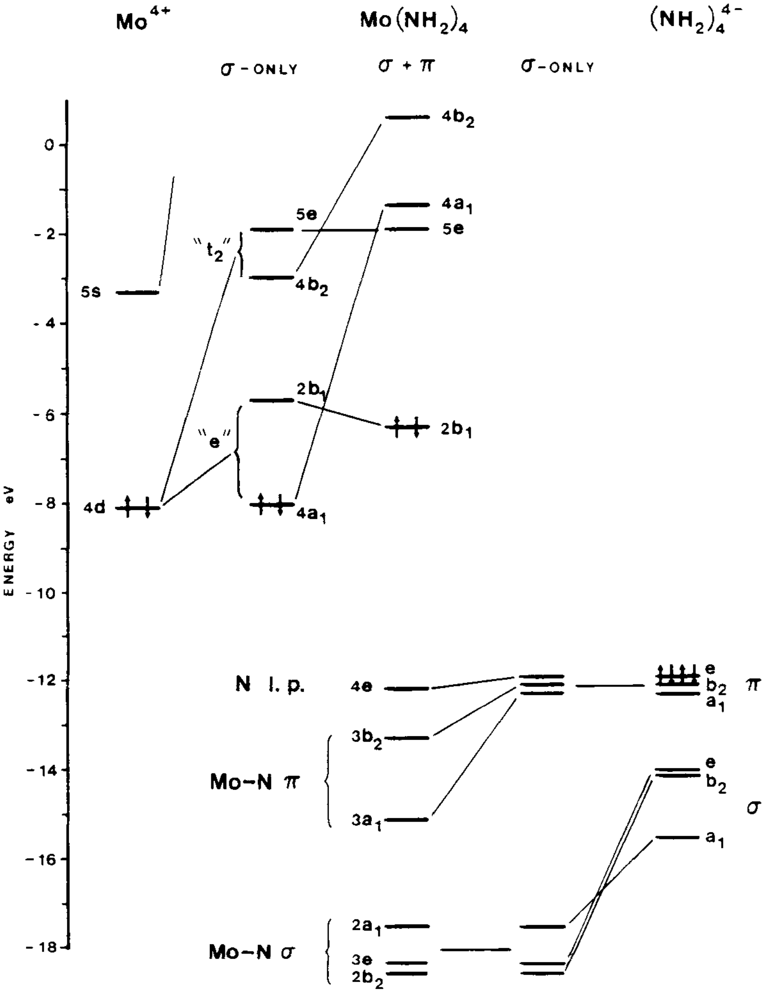


FIGURE 2 Results of Fenske–Hall calculations on $Mo(NH_2)_4$. This diagram shows the effect of ligand σ-bonding in the columns labeled "σ-only." The center column labeled "σ + π" demonstrates the effect of the π lone-pair orbitals as a distinct perturbation to the "σ-only" interaction. The highest occupied orbitals are denoted by arrows.

orbitals. The perturbations imposed by the π interactions are denoted "$\sigma + \pi$" (Fig. 2) and demonstrate the relative magnitude of destabilization of a_1 and b_2 metal orbitals as a result of Mo-N π-bonding. The diamagnetism in $Mo(NMe_2)_4$ is the result of strong Mo-N π-bonding which destabilizes the metal a_1 orbital, leaving the b_1 orbital as the HOMO for the d^2 system. Of the four π lone-pair orbitals, only two Mo-N π-bonds are formed, and thus a 14 electron configuration at molybdenum is an appropriate description. This contrasts with the simple electron counting of $\sigma^2 + \pi^2$ for each NMe_2 ligand which satisfies the EAN rule.

To amplify the relative magnitude of π-bonding from the a_1, b_2, and e π lone-pairs we turn to the Mulliken populations of the canonical orbitals of the $(NH_2)_4{}^{4-}$ ligand set. Shown in Table I are the Mulliken populations (or orbital occupancies) of the $(NH_2)_4{}^{4-}$ σ and π lone-pair orbitals before and after interaction with the metal. Examination of the "free ligand" σ lone-pair populations (Table I) shows that the a_1 and b_2 orbitals each contain two electrons and the e representation four electrons prior to interaction with the metal. After interaction, the decrease in population seen for the "coordinated ligand" (Table I) is representative of the amount of electron density "donated" to the metal as the result of σ-bonding. Examination of the "free" and "coordinated" π lone-pair populations in Table I clearly establishes the relative magnitude of π-bonding as $a_1 > b_2 > e$. The decrease in the a_1 and b_2 π population represents significant π-bonding, while the minimal decrease in the e π population represents essentially a nonbonding interaction. The a_1 and b_2 π interactions with the metal are depicted qualitatively in Scheme II, and contour plots[8] of these

TABLE I

Selected Mulliken populations of the canonical orbitals of the free and ligated $(NH_2)_4$ ligand set in $Mo(NH_2)_4$

Irreducible Representation	Free Ligand		Coordinated Ligand	
	σ	π	σ	π
a_1	2.000	2.000	1.644	1.341
b_2	2.000	2.000	1.476	1.659
e	4.000	4.000	2.920	3.722

SCHEME II

same orbitals taken as a slice in a plane containing the Mo atom and two N atoms are shown in Fig. 3. Similar analyses of the π-bonding in model compounds of formula $Mo(PH_2)_4$, $Mo(OH)_4$ and $Mo(SH)_4$ have been undertaken, and those results will be presented in detail elsewhere.[8]

METAL–OXYGEN π-BONDING IN TRANSITION METAL ALKOXIDES

The wealth of structural data amassed for metal alkoxides has provided physical evidence for metal–oxygen π-bonding. It has been estimated that a purely σ-bonding Mo(III)-O distance for an Mo_2^{6+} center should be approximately 2.06 Å, and this value is typical of Mo-μ-OR distances, but considerably longer than any seen for terminal Mo-OR groups which fall in the range 1.80–1.96 Å.[11] These short Mo-O distances are strongly suggestive of a considerable amount of double-bond character in such systems. Shorter, terminal M-OR distances are characteristically associated with larger M-O-C angles which may be close to 180°. By contrast, relatively long terminal M-OR distances are associated with small M-O-C angles, typically in the range 120–130°.

Structural comparison of the bonding of alkoxide and aryloxide ligands to the same metal center has shown that M-OAr distances are slightly longer than M-OR distances, however, the M-O-Ar angles are characteristically larger than M-O-R angles even in the

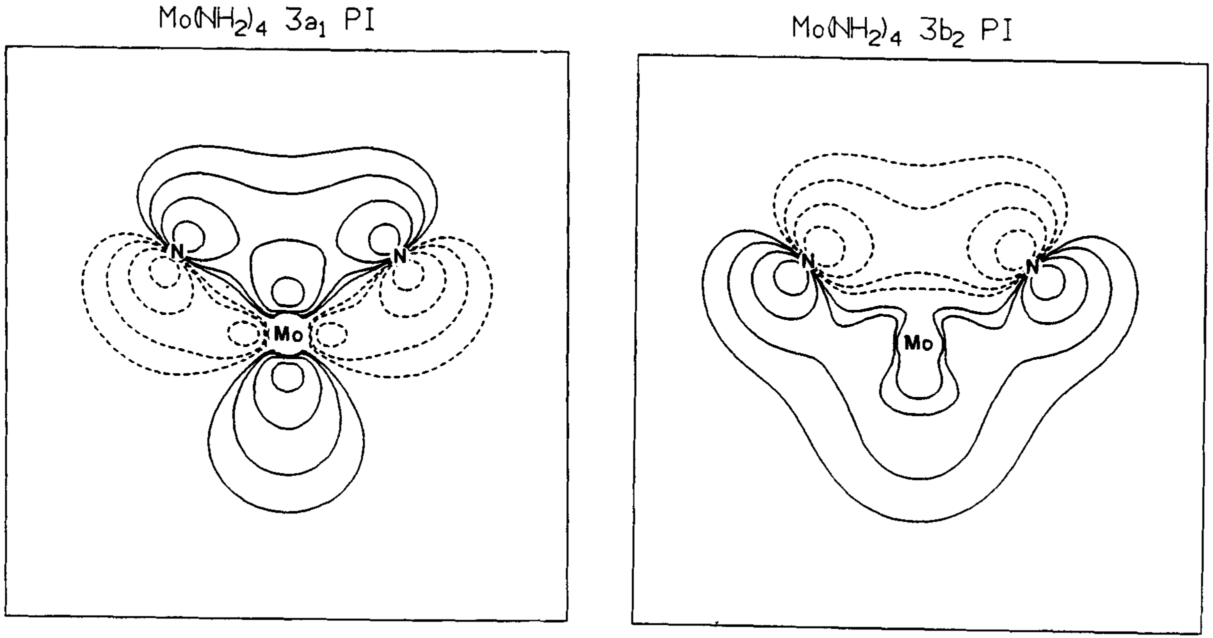


FIGURE 3 Contour plots of the $Mo(NH_2)_4$ $3a_1$ and $3b_2$ Mo-N π-bonding orbitals. These plots are in the horizontal mirror plane containing the Mo atom and two of the N atoms. Contour values are ± 0.02, ± 0.04, ± 0.08, and ± 0.16 e/A^3.

absence of steric effects.[12] Angles of 160–180° are very common for the aryloxide ligand.[13]

In most cases the structural changes observed in M-O distances and M-O-C angles can be traced directly to oxygen π interactions with the metal. Two-electron σ-donation from an alkoxide ligand can be supplemented by π-donation up to a maximum of π^4. Electron-deficient metal centers commonly found for complexes of the early transition metals[11] and actinides[14] typically exhibit extremely short M-O distances and large M-O-C angles implying a large degree of π-bonding. When there are no vacant d orbitals, or when the d orbitals are otherwise occupied in M-M bonding, then M-O bond distances approaching those anticipated for single bonds are observed with M-O-C angles close to 120° as in $Mo_2(OR)_4L_4$ compounds.[15] The extreme flexibility in M-O-C angles of aryloxide ligands can also be traced to oxygen π-bonding interactions. The aryl group can form π-bonds with oxygen, and this is the rationalization generally used to account for the higher acidity of phenols relative to aliphatic alcohols. A competition between the aryl group and the metal for electron density on oxygen will stabilize the linear M-O-Ar moiety and reduce the relative π donation to the metal. A theoretical analysis of π-bonding can be used in conjunction with this physical evidence to gain a better understanding of its causes and effects.

With the aid of Fenske–Hall calculations on a model system of formula $H_5Mo(OH)^{n-}$, the effects of varying Mo-O distance, Mo-O-H angle, and d^n electron count have been investigated.[8] The model can be decomposed into MoH_5 and OH^- fragment representations and the Mulliken populations of the canonical fragment orbitals employed as a relative measure of the magnitude of π-bonding for combinations of Mo-O distance and Mo-O-H angle. With this model, it is assured that the five Mo-H bonds are σ-only interactions, such that π-bonding can be isolated in the OH ligand.

The bonding interactions between the MoH_5 and OH fragments are most easily understood by first considering a linear Mo-O-H moiety. Defining the Mo-O vector as the z-axis, then the d_{xz} and d_{yz} "t_{2g}" fragment orbitals can be used to form Mo-O π-bonds with a set of degenerate sp hybrid orbitals on the oxygen atom as depicted qualitatively in Scheme III.

9

SCHEME III

For a formal d^2 electron count, π donation into the d_{xz} and d_{yz} acceptor orbitals destabilizes them above the $d_{x^2-y^2}$ "t_{2g}" orbital which in turn acquires the two metal electrons. The Mulliken populations of the d_{xz} and d_{yz} acceptor orbitals of the MoH_5 fragment in $MoH_5(OH)^{2-}$ are given in Table II. From this table it can be seen that for Mo-O-H angles of 180°, both d_{xz} and d_{yz} fragment orbitals accept an equivalent degree of π density for a given Mo-O distance. The decrease in Mulliken population (Table II) of d_{xz} and d_{yz} acceptor orbitals (from 0.275 to 0.175) with increasing Mo-O distance (from 1.82 to 2.13 Å) is consistent with a simple perturbation theory viewpoint that a decrease in the Mo-O distance

TABLE II

Selected Mulliken populations of the MoH_5 fragment in $MoH_5(OH)^{2-}$

Mo-O-H (Degrees)	Mo-O = 1.82 Å $d_{xz}(\sigma)$	Mo-O = 1.82 Å $d_{yz}(\pi)$	Mo-O = 2.13 Å $d_{xz}(\sigma)$	Mo-O = 2.13 Å $d_{yz}(\pi)$
180	0.275	0.275	0.175	0.175
170	0.271	0.276	0.172	0.172
160	0.260	0.278	0.163	0.177
150	0.244	0.281	0.149	0.180
140	0.222	0.286	0.132	0.184
130	0.197	0.292	0.113	0.189
120	0.173	0.300	0.095	0.195

increases Mo-O overlap, and increases the magnitude of the π interaction.

The population changes induced by the variation in bond angle can best be envisioned in terms of a rehybridization of the oxygen atom upon bending. When the Mo-O-H angle is 180°, sp hybridization at oxygen yields two degenerate π lone-pair orbitals which can π-bond to the metal equally, as evidenced by the equivalent Mulliken populations of the d_{xz} and d_{yz} acceptor orbitals (Table II). Upon bending, the in-plane orbital rehybridizes into a σ lone-pair, resulting in spatially and energetically inequivalent lone-pair orbitals at the limiting angle of 120°. The π lone-pair is now energetically closer to the d_{yz} orbital, maintains the best overlap, and forms the strongest π-bond. The σ lone-pair can still donate into the d_{xz} orbital, but it is spatially oriented such that overlap is small and the magnitude of π-bonding is diminished. This rehybridization is depicted qualitatively in Scheme IV.

SCHEME IV

We now differentiate between σ and π lone-pairs in Table II by denoting the acceptor orbitals as $d_{xz}(\sigma)$ and $d_{yz}(\pi)$ since they now accept density from σ or π lone-pairs, respectively. The change in Mulliken population of the $d_{xz}(\sigma)$ and $d_{yz}(\pi)$ orbitals is best illustrated graphically in Fig. 4, and effectively demonstrates that for Mo-O-H angles less than 180°, the π lone-pair is a stronger π-donor than the σ lone-pair.

We will now consider the effect of d^n electron count for a bent Mo-O-H moiety with a limiting angle of 120°. In general, an in-

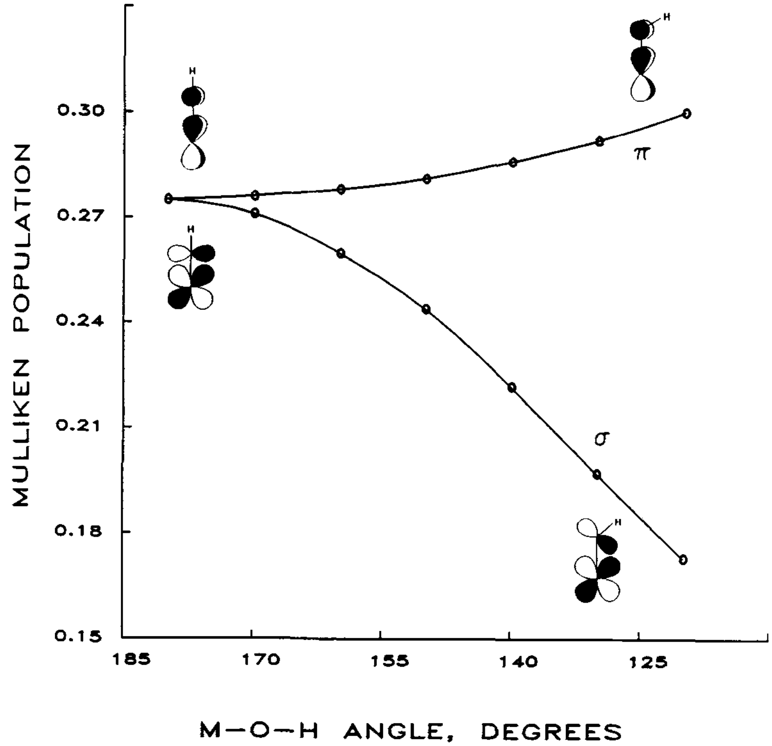


FIGURE 4 Graphical representation of the effect of Mo-O-H angle on Mulliken population of the Mo π-acceptor orbitals.

crease in the electron density on the metal results in a rise in energy of the metal d orbitals with concomitant increase in the energetic separation of metal d and oxygen pπ orbitals resulting in decreased π-bonding.[16] For a d^0 system where the "t_{2g}" orbitals are formally unoccupied, both $d_{xz}(\sigma)$ and $d_{yz}(\pi)$ acceptor orbitals show substantial population due to π interaction, while the $d_{x^2-y^2}$ orbital population remains at nearly 0.00 since it cannot be used to form a π-bond. The $d_{x^2-y^2}$ orbital becomes occupied in the d^2 case, but for a d^4 electron count, one of the $d_{xz}(\sigma)$ or $d_{yz}(\pi)$ orbitals must now become occupied, leaving the other for π-acceptance. Since the $d_{yz}(\pi)$ orbital can accept the maximum π-density from the OH ligand, it is destabilized more than the $d_{xz}(\sigma)$ by π-bonding and hence the $d_{xz}(\sigma)$ orbital acquires the next two d electrons in the d^4 system. Now the interaction of the σ lone-pair with the metal is repulsive and little mixing between σ lone-pair and metal is observed in contrast to the d^2 or d^0 systems.

The use of the Mulliken populations has given us a measure of the relative magnitude of π-bonding of the alkoxide ligand for varying M-O distances and M-O-H angles. The result that the larger M-O-H angle and shorter M-O distance yields the highest magnitude of π-bonding for any given d^n electron count is consistent with the physial evidence amassed from structural studies. The π-bonding properties of the alkoxide ligand can have profound effects on the bonding and chemical reactivity of neighboring ligands.

π-DONOR EFFECTS OF ALKOXIDES ON NEIGHBORING LIGANDS

The influence of the π-donor ligands may be seen in both the reactivity and the spectroscopic properties of ancillary ligands. The presence of π-donor ligands may enhance π back-bonding to adjacent π-acid ligands such as carbonyl or nitrosyl. In $W(OBu^t)_3(NO)(py)$,[17] extensive π back-bonding to the nitrosyl is evident from the extremely short W-NO distance and the exceedingly low value of ν(N-O), 1555 cm^{-1}, for a terminal NO ligand. In $Mo(OBu^t)_2(py)_2(CO)_2$,[18] unusually low values of ν(C-O), 1906 and 1776 cm^{-1}, for a *cis* dicarbonyl may be understood in part by the ability of the alkoxides to enhance π back-bonding to the carbonyl π^* orbitals.

A more quantitative measure of the enhanced π back-bonding to adjacent ligands can be seen in a series of related compounds of formula $W_2(OBu^t)_6(\mu\text{-}CX)$ where X = O and NR. A characteristic spectroscopic feature of the μ-CX ligands is the exceptionally low values of ν(C-O) for a μ_2-CO moiety (1598 cm^{-1})[19] and ν(C-N) for a μ_2-CNR moiety (1530 and 1525 cm^{-1} when R = Bu^t and 2,6-dimethylphenyl, respectively).[20] These low values of ν(C-O) and ν(C-N) imply a large degree of reduction in the μ-CO and μ-CNR ligands, and the nature of reduction has been investigated via Fenske–Hall calculations on model systems.

The calculations indicate that the weakening of the C-X bonds (X = O, NH) upon interaction with the strongly reducing dinuclear centers can be attributed primarily to the degree of π back-bonding in the M_2 (μ-CX) moiety.[20,21] A measure of the relative magnitude of π back-bonding was obtained from the Mulliken populations of the canonical orbitals of the CX ligand, and a linear correlation was found to exist between the occupation of antibonding carbonyl orbitals and C-O stretching frequencies.[21] Most significantly, the calculations indicate that π-donation from the alkoxide ligands is extremely important in rationalizing the high reducing strength of the W≡W bond on the μ-CX ligands.

This point needs some amplification. The π-bonding interactions of the alkoxide ligands in the model compounds $M_2(\mu\text{-CO})(OH)_6$ have been discussed in detail elsewhere.[21] Through the use of our frozen π-orbital method we can now examine those population changes induced in the CO ligand as a direct result of π-donation from the hydroxide ligands. To accomplish this, we reconverge a calculation on the model compound $Mo_2(\mu\text{-CO})(OH)_6$ with linear Mo-O-H angles, as this greatly simplifies the mechanics of the frozen π-orbital method.

The results of freezing the π lone-pair orbitals of the hydroxide ligands in the canonical basis are quite revealing. Table III lists the Mulliken populations of the canonical orbitals of the CO ligand in $Mo_2(\mu\text{-CO})(OH)_6$. As a reference point, we notice that for the free CO ligand, the 5σ (carbon lone-pair) orbital is doubly occupied and the 2π orbitals (π*) are unoccupied. The synergistic nature of $M_2(\mu\text{-CO})$ bonding is revealed in the Mulliken populations. That is to say that CO 5σ donation to the dimetal center is revealed

TABLE III

Selected Mulliken populations of the canonical orbitals of free CO, and the CO moiety in $Mo_2(\mu\text{-CO})$ $(OH)_6$ with and without frozen OH π-orbitals

Compound	5σ	$2\pi_x$[a]	$2\pi_y$[b]
CO	2.000	0.000	0.000
$Mo_2(\mu\text{-CO})$ $(OH)_6$	1.274	0.468	0.742
$Mo_2(\mu\text{-CO})$ $(OH)_6$ (frozen)	1.339	0.471	0.499

[a] $2\pi_x$ is the π* orbital perpendicular to the M-M axis.
[b] $2\pi_y$ is the π* orbital parallel to the M-M axis.

via a loss of electron density from the 5σ orbital of CO, and 2π acceptance is revealed via a gain of electron density into the 2π orbitals of CO. From the Mulliken populations in Table III it is clear that when the π lone-pair orbitals of the hydroxide ligands are frozen, a dramatic decrease in the CO 2π population is observed. Thus π-donation from the alkoxide ligands enhances π back-bonding to the carbonyl as evidenced by an increase in the CO 2π population relative to those when the alkoxide π lone-pair orbitals are frozen. Thus we reiterate that the metal-based orbitals are destabilized by strong π-donor interactions with alkoxide ligands, which in turn enhances π back-bonding to the π^* orbitals of the μ-CO and μ-CNR ligands, and indeed these compounds exhibit the lowest ν(C-O) and ν(C-N) values in the current literature for μ_2-(CX) moieties in neutral compounds.[22]

CONCLUDING REMARKS

Application of M.O. calculations employing the Fenske–Hall method and analyses of Mulliken orbital populations provide valuable insight into the electronic structure of transition metal complexes containing π-donor ligands such as amides and alkoxides. (1) A simple electron-counting procedure for a molecule such as $Mo(NMe_2)_4$ might lead one to the view that the molybdenum atom attains 18 valence electrons: Mo(IV) d^2; Me_2N^- $(\sigma^2 + \pi^2) \times 4 = 16$. However, the Mulliken populations clearly show that certain of the π-M.O.s are ligand-centered even though they have the correct symmetry to interact with molybdenum atomic d orbitals. (2) Using the "frozen π-orbital method" one can investigate the role of π-bonding as a distinct perturbation to the σ-bonding in the molecule. (3) The M.O. approach adopted here shows Mo-OR π-bonding is sensitive to Mo-O distance, Mo-O-C(H) angle, and the d^n configuration. (4) The influence of π-bonding on ancillary π-acceptor ligands is easily demonstrated.

Finally, we mention that this MO. approach also provides insight into likely modes of reactivity. (1) For compounds with M-X π-bonds that are ligand-centered, the π^* M.O.s will be low-lying and metal-centered, thus nucleophilic attack at the metal is a plausible reaction mode, in addition to electrophilic attack on the ligand centered π-orbital. (2) π-donation into filled metal d orbitals or occupied M-M bonds will have a destabilizing influence on the d^n electrons or the M-M bond. The compounds will then be labilized toward oxidation. Though the actual calculated energies may not be reliable, the trends within a series of related compounds can reasonably be understood, such as the correlation of Mulliken orbital occupations of antibonding orbitals in μ-CO ligands with ν(C-O) values.

APPENDIX

Molecular orbital calculations were performed using the Fenske–Hall method which has been described in detail elsewhere.[1] All the calculations were obtained at the Indiana University Computational Chemistry Center using a Vax/11 780 computer system, and contour plots were done on a TALARIS 800 laser printer.

All atomic wave functions were generated by a best fit to Herman–Skillman atomic calculations using the method of Bursten, Jensen and Fenske.[23] Contracted double-ζ representations were used for Mo 4d AOs as well as C, O, and N 2p AOs. Basis functions for the Mo atom were derived for a + 1 oxidation state with valence s and p exponents fixed at 1.8. An exponent of 1.16 was used for the H 1s atomic orbital.[24] The coordinates for $Mo(NH_2)_4$ were idealized to D_{2d} point symmetry, but otherwise were taken from the crystal structure of $Mo(NMe_2)_4$.[7]

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