

CA spectra of the products of metastable decomposition were obtained by lowering the voltage of the first electric sector and the magnetic field to pass the products of metastable decompositions in the first field free region, colliding those ions in the third field free region and scanning the voltage of the second electric sector. Helium was used as the CA gas at a pressure of $1 \pm 0.1 \times 10^{-6}$ torr at the vacuum wall outside the collision chamber. Experiments were carried out at an electron energy of 70 eV and an ion source temperature of 200 °C.

Ethyl-1,1- d_2 butanoate was prepared by reaction of ethanol-1,1- d_2 with butanoyl chloride. The former compound was prepared by reducing acetic anhydride with LiAlD_4 . Butanol-4,4,4- d_3 , available from an earlier study,¹⁵ was oxidized to butanoic-4,4,4- d_3 acid with $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$

(15) Hudson, C. E.; McAdoo, D. J. *Org. Mass Spectrom.* 1979, 14, 109-113.

and converted to the acid chloride with excess SOCl_2 and to the ethyl ester with ethanol. Butanoic-2-2- d_2 acid was prepared by reduction of propanoic acid with LiAlD_4 , conversion to the bromide with $\text{HBr}/\text{H}_2\text{SO}_4$, and carbonation of the Grignard reagent. Butanoic-3,3- d_2 acid was prepared by treatment of ethanol-1,1- d_2 with $\text{HBr}/\text{H}_2\text{SO}_4$, followed by Grignard homologation with ethylene oxide. The resulting butanol-3,3- d_2 was oxidized with $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$. The acids were converted to the esters as described above.

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The Role of Ligand π -Donation in Electron-Deficient Organometallic Group 6 Complexes

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Abstract: Molecular orbital descriptions for six monomeric molybdenum complexes are presented as derived from extended Hückel calculations. The six model compounds were chosen to reflect the electronic features of both molybdenum and tungsten compounds of the types $\text{M}(\text{CO})(\text{RC}\equiv\text{CR})(\text{S}_2\text{CNR}'_2)_2$, $\text{M}(\text{CO})(\text{RC}\equiv\text{CR})(\pi\text{-C}_5\text{H}_5)(\text{R}')$, $\text{M}(\text{O})(\text{RC}\equiv\text{CR})(\text{S}_2\text{CNR}'_2)_2$, $\text{M}(\text{RC}\equiv\text{CR})_2(\text{S}_2\text{CNR}'_2)_2$, $\text{M}(\text{CO})_2(\text{OR})_2\text{L}_2$, and $\text{M}(\text{CO})_2(\text{S}_2\text{CNR}'_2)_2$. Each of these compounds is formally electron deficient with respect to the effective atomic number rule based on common electron bookkeeping procedures. The role of ligand π -donation in destabilizing the LUMO, which would be filled for analogous compounds obeying the inert gas formalism, is identified as a common phenomena which links each of these compounds to this single concept and accounts for their seemingly anomalous stability when compared to other coordinatively unsaturated group 6 carbonyl monomers.

Introduction

The majority of the numerous molybdenum(II) and tungsten(II) carbonyl complexes reported in the literature to date adhere to the effective atomic number (EAN) rule. Coordination of seven two-electron donor ligands to the central d^4 metal ion is typical and produces a total of 18 metal valence electrons in accord with expectations based on the inert gas formalism. Drew's comprehensive review of seven coordination, published in 1977, lists more than 100 seven-coordinate molybdenum(II) and tungsten(II) carbonyl derivatives.¹

Recently several six-coordinate molybdenum(II) and tungsten(II) carbonyl derivatives have been reported, and in cases where six two-electron donor ligands constitute the complete coordination sphere of a d^4 ion this produces a total of only 16 electrons in the metal valence shell. Such complexes would be expected to be highly electrophilic and display reactivity patterns typical of coordinatively unsaturated metal compounds. Experimental results are inconsistent with this simple scheme when an alkyne is one of the six ligands coordinated to Mo(II) or W(II).² The concept of four-electron donation from an alkyne ligand to a single metal center has been set forth by McDonald and co-workers based on EAN considerations and the observed reactivity,

or lack thereof, of $\text{M}(\text{CO})(\text{RC}\equiv\text{CR})(\text{S}_2\text{CNR}'_2)_2$ ($\text{M} = \text{Mo}$ or W) compounds.³ An empirical correlation between C-13 NMR chemical shifts for metal-bound alkyne carbons and the extent of electron donation to molybdenum or tungsten has been published.⁴

This article describes bonding interactions accessible to metal-alkyne moieties based on extended Hückel molecular orbital (EHMO) calculations, and as a consequence places the two-electron vs. four-electron question in perspective on a continuum molecular orbital basis. The resultant bonding picture provides information about the geometrical preferences exhibited by nonlinearly ligating (or single-faced π) alkyne ligands and predicts surprisingly accurate quantitative barriers for alkyne rotation processes.

Two additional six-coordinate molybdenum(II) carbonyl derivatives are considered in detail in the second part of this study. The trigonal prismatic structure reported for the coordinatively unsaturated $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNR}'_2)_2$ compound⁵ suggested that electronic factors were dictating the geometry of this six-coordinate d^4 complex, and indeed the octahedral structure of the 18-electron nitrosyl analogue, $\text{Mo}(\text{NO})_2(\text{S}_2\text{CNEt}_2)_2$,⁶ confirms this hypothesis. A molecular orbital description of this carbonyl complex has been generated from EHMO calculations and guided us to the conclusion that, as was the case for the metal-alkyne complexes, the role of ligand π -donation is crucial to the stability of this formally electron deficient molybdenum(II) carbonyl complex and is also

(1) Drew, M. G. B. *Prog. Inorg. Chem.* 1977, 23, 67.

(2) (a) Davidson, J. L.; Green, M.; Sharp, D. W. A.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* 1974, 706. (b) Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* 1976, 738. (c) Bottrill, M.; Green, M. *J. Am. Chem. Soc.* 1977, 99, 5795. (d) Faller, J. W.; Murray, H. H. *J. Organomet. Chem.* 1979, 172, 171. (e) Howard, J. A. K.; Stansfield, R. F. D.; Woodward, P. *J. Chem. Soc., Dalton Trans.* 1976, 246. (f) Davidson, J. L.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* 1975, 2531. (g) Davidson, J. L. *J. Chem. Soc., Chem. Commun.* 1980, 113. (h) Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* 1980, 102, 2698.

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Table I. Extended Huckel Calculation Parameters

atom	orbital	H_{ii} , eV	$\xi_1(C_1)^a$	$\xi_2(C_2)$	ref
H	1s	-13.60	1.000		b
C	2s	-21.40	1.625		c
	2p	-11.40	1.625		
N	2s	-26.00	1.950		c
	2p	-13.40	1.950		
O	2s	-36.30	2.275		c
	2p	-14.80	2.275		
S	3s	-28.79	2.000		d
	3p	-14.25	2.000		
Mo	5s	-9.66	2.330		e
	5p	-6.36	2.330		
	4d	-12.3	4.98 (0.6683)	2.07 (0.5422)	

^a C_1 and C_2 are coefficients in a double- ξ expansion. ^b Rein, R.; Fukuka, N.; Win, H.; Clarke, G. A.; Harris, F. E. *J. Chem. Phys.* 1966, 45, 4773. ^c Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* 1976, 98, 7240. ^d Carroll, D. G.; Armstrong, A. T.; McGlynn, S. P. *J. Chem. Phys.* 1966, 44, 1865. ^e Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* 1979, 101, 3821.

responsible for the observed geometry. A comparison with the molecular orbital rationale favoring the octahedral geometry reported by Chisholm, Huffman, and Kelly for $\text{Mo}(\text{CO})_2(\text{OBU}^t)_2(\text{py})_2$,⁷ also a six-coordinate molybdenum(II) dicarbonyl, is included in the discussion. The electronic structures of the Chisholm complex and several other six-coordinate d^4 complexes have been lucidly discussed by Kubáček and Hoffman.⁸

The final section of this article summarizes the impact of ligand π -basicity on the specific complexes considered herein prior to generalizing the structural and chemical implications of ligand π -donation. Conclusions are drawn concerning the role of π -base ligands in applications of the effective atomic number rule as a guide to the stoichiometries, geometries, and reactivities of mononuclear organometallic metal carbonyl complexes.

Calculations

The calculational method employed for this study was the extended Hückel approach described by Hoffmann.⁹ Program number QCPE 358 from the Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, was used for all the calculations reported here. Parameters for the calculations are listed in Table I. The crystallographic coordinates of $\text{W}(\text{CO})(\text{HC}\equiv\text{CH})(\text{S}_2\text{CNMe}_2)_2$ ¹⁰ were used to generate the geometry of $\text{Mo}(\text{CO})(\text{HC}\equiv\text{CH})(\text{S}_2\text{CNH}_2)_2$ with the N-H distances fixed at 1.02 Å. For $\text{Mo}(\text{CO})(\text{HC}\equiv\text{CH})(\pi\text{-C}_5\text{H}_5)(\text{CH}_3)$ the geometry was idealized with the molybdenum to cyclopentadienyl carbon distance fixed at 2.09 Å, the C-C separations in the ring at 1.43 Å, the Mo-C(CO) at 1.97 Å, C=O at 1.16, and Mo-C(CH₃) at 2.38 Å, and the C≡C bond distance was set at 1.29 Å with the center of the alkyne unit 1.91 Å from the molybdenum. A bent acetylene geometry was idealized with C-C-H angles of 135° and acetylene C-H distances of 1.07 Å for all the alkyne complexes investigated while all other C-H distances were fixed at 1.09 Å. Geometries for $\text{Mo}(\text{O})(\text{HC}\equiv\text{CH})(\text{S}_2\text{CNMe}_2)_2$ and $\text{Mo}(\text{HC}\equiv\text{CH})_2(\text{S}_2\text{CNH}_2)_2$ were idealized as pseudooctahedra with the same bond distances as in $\text{Mo}(\text{CO})(\text{HC}\equiv\text{CH})(\text{S}_2\text{CNH}_2)_2$ and a Mo-O distance of 1.70 Å. Atomic coordinates for $\text{Mo}(\text{CO})_2(\text{OMe})_2(\text{NH}_3)_2$ were derived from structural data reported for $\text{Mo}(\text{CO})_2(\text{OBU}^t)_2(\text{py})_2$ ⁷ with methyl hydrogen and ammine hydrogen distances set at 1.08 and 1.01 Å, respectively, for the model compound. Crystallographic coordinates for $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNPr}^i)_2$ ⁵ were used to generate atomic positions for $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNH}_2)_2$ with an N-H distance of 1.02 Å.

(7) Chisholm, M. H.; Huffman, J. C.; Kelly, R. L. *J. Am. Chem. Soc.* 1979, 101, 7615.

(8) Kubáček, P.; Hoffmann, R. *J. Am. Chem. Soc.* 1981, 103, 4320.

(9) Hoffmann, R. *J. Chem. Phys.* 1963, 39, 1397.

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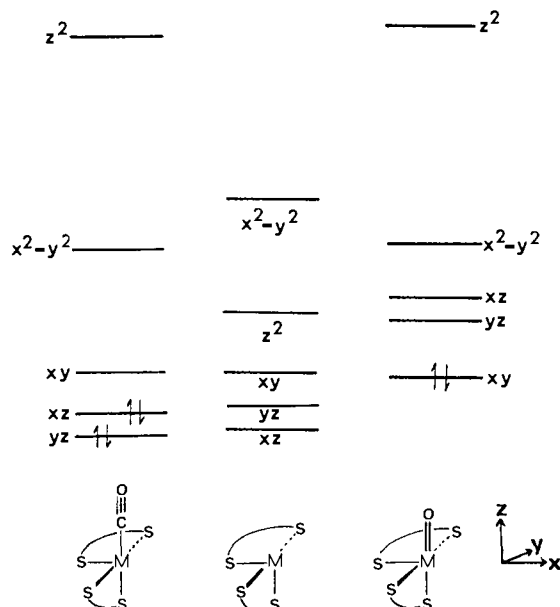
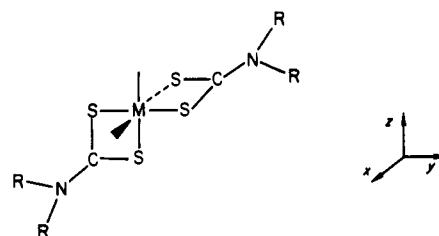


Figure 1. Energy diagrams for molecular orbitals dominated by d orbital contributions for three octahedral fragments: $\text{Mo}(\text{CO})(\text{S}_2\text{CNH}_2)_2$, $\text{Mo}(\text{S}_2\text{CNH}_2)_2$, and $\text{Mo}(\text{O})(\text{S}_2\text{CNH}_2)_2$.

Results and Discussion

Quantitative EHMO calculations were performed on four molybdenum alkyne model compounds which we consider to be representative of the following molybdenum and tungsten monomers: $\text{M}(\text{CO})(\text{RC}\equiv\text{CR})(\text{S}_2\text{CNR}'_2)_2$, $\text{M}(\text{CO})(\text{RC}\equiv\text{CR})(\pi\text{-C}_5\text{H}_5)(\text{R}')$, $\text{M}(\text{O})(\text{RC}\equiv\text{CR})(\text{S}_2\text{CNR}'_2)_2$, and $\text{M}(\text{RC}\equiv\text{CR})_2(\text{S}_2\text{CNR}'_2)_2$. The discussion will focus on an assessment of the electronic features which account for the geometric preferences and rotational barriers for these alkyne complexes prior to analyzing the molecular orbital schemes of two six-coordinate molybdenum(II) dicarbonyl compounds, $\text{Mo}(\text{CO})_2(\text{OBU}^t)_2(\text{py})_2$ and $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNPr}^i)_2$.

$\text{Mo}(\text{CO})(\text{HC}\equiv\text{CH})(\text{S}_2\text{CNH}_2)_2$ (1). The molecular orbital scheme appropriate for the $\text{Mo}(\text{S}_2\text{CNH}_2)_2$ fragment will be considered first in anticipation of the recurrence of this moiety in other complexes described below. The reference coordinate

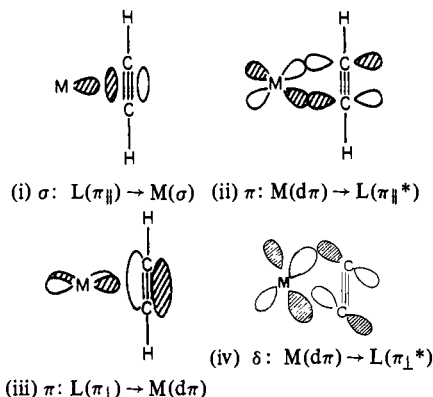


system has the two vacant cis-octahedral sites along the $+x$ and $+z$ axes with the planar dithiocarbamate ligands lying in the $-x, y$ and $-y, -z$ planes. The resultant energy levels of d orbital parentage are as shown in Figure 1. The expected correspondence between the classic octahedral orbital diagram and the fragment frontier orbitals is apparent since coordination of ligands along x and z will increase the σ^* character of $d_{x^2-y^2}$ and d_{z^2} to generate the familiar two above three pattern of $d\sigma^*$ (e_g) and $d\pi$ (t_{2g}). For a d^4 configuration, as in molybdenum(II) compounds, only two of the three low-lying $d\pi$ levels will be filled for diamagnetic complexes while diamagnetic d^2 $\text{Mo}(\text{IV})$ compounds will place electrons only in the lowest lying $d\pi$ orbital.

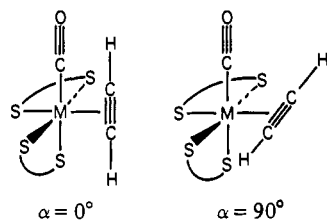
Let us initiate completion of the coordination sphere of **1** by addition of the carbon monoxide ligand to the $\text{Mo}(\text{S}_2\text{CNH}_2)_2$ fragment along the $+z$ axis. Since carbon monoxide is a linearly ligating ligand the impact of metal-ligand π bonding on both d_{xz} and d_{yz} will be similar. In view of the established π -acidity of carbonyl ligands one can qualitatively argue that the splitting pattern of the original nest of three $d\pi$ orbitals will be governed

by overlap with the vacant carbon monoxide π^* orbitals. The existence of retrodative π -bonding in the $\text{Mo}(\text{CO})(\text{S}_2\text{CNH}_2)_2$ fragment is evidenced by the near degeneracy of d_{xz} and d_{yz} approximately 0.3 eV below d_{xy} . Note that $d_{x^2-y^2}$ dominates the vacant metal σ -acceptor orbital directed toward the remaining unfilled octahedral site.

Addition of acetylene along the $+x$ axis completes the coordination sphere for 1. The σ bond formed by donation from the filled acetylene π orbital which lies in the MC_2 plane (π_{\parallel}) is the only one of the four possible metal-alkyne overlap quantities which is independent of the rotational orientation of the alkyne. Although the Dewar-Chart-Duncanson bonding model for olefins¹¹ is often considered adequate for monomeric metal alkyne complexes,¹² it is accurate only when π_{\parallel} σ -donation and π_{\parallel}^* π -acceptance (i and ii below) are present and significant interactions between the perpendicular alkyne π system and the metal (iii and iv below) are absent. Let us first deduce the geometrical consequences of the single-faced π_{\parallel}^* alkyne acceptor character for such a case.



Alkyne approach along the x axis selects d_{xy} and d_{xz} from the set of three $d\pi$ orbitals for potential nonzero overlap with π_{\parallel}^* . The rotational orientation of the alkyne partitions the π_{\parallel}^* interaction between these two orbitals. When the alkyne is parallel



to the metal carbonyl fragment ($\alpha = 0^\circ$), as is found for $\text{W}(\text{CO})(\text{HC}\equiv\text{CH})(\text{S}_2\text{CNEt}_2)_2$,¹⁰ π_{\parallel}^* lies in the xz plane and stabilizes the d_{xz} which is filled for the d^4 configuration based on carbonyl π -acid properties described above. This favorable overlap effectively creates a three-center two-electron bond with d_{xz} the low-lying filled orbital stabilized at the expense of both carbon monoxide and alkyne π -acceptor orbitals. The calculation indeed locates d_{xz} approximately 0.4 eV below the d_{yz} highest occupied molecular orbital (HOMO) in accord with this π_{\parallel}^* contribution. In contrast in the $\alpha = 90^\circ$ orientation with the alkyne entity normal to the $\text{M}-\text{C}\equiv\text{O}$ axis π_{\parallel}^* only stabilizes d_{xy} , but since d_{xy} houses no electrons in the $\text{M}(\text{CO})(\text{S}_2\text{CNH}_2)_2$ fragment no net energy gain is realized. A parallel orientation of the carbonyl and alkyne ligands is therefore predicted on the basis of metal $d\pi$ donation to the alkyne π_{\parallel}^* alone.

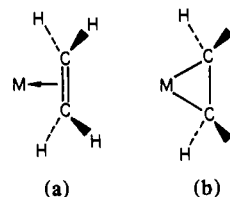
Analysis of the metal interaction with the π_{\perp} system follows similar reasoning. A comparison of metal olefin and metal carbonyl bonding features with metal-alkyne π_{\perp} interactions lends

Table II. Relative Magnitudes for Metal-Acetylene σ , π , and δ Overlap Values^a

metal orbital	$\pi_{\parallel}(\sigma)$	$\pi_{\parallel}^*(\pi)$	$\pi_{\perp}(\pi)$	$\pi_{\perp}^*(\delta)$
p_x	0.29	0	0	0
p_y	0	0	0.14	0
p_z	0	0.14	0	0
$d_{x^2-y^2}$	0.10	0	0	0
d_{z^2}	0.03	0	0	0
d_{xy}	0	0	0.11	0
d_{xz}	0	0.11	0	0
d_{yz}	0	0	0	0.04
total	0.42	0.25	0.25	0.04

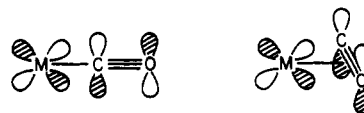
^a Based on alkyne approach to the metal along the x axis while oriented parallel to the z axis (as for $\alpha = 0$ in the text).

support to the hypothesis that the filled π_{\perp} alkyne orbital could influence the chemical behavior of monomeric metal-alkyne complexes. A continuum of bonding schemes from (a) to (b) is



accessible to metal olefin complexes, and the contribution of metal $d\pi$ to olefin π^* is generally accepted as an important component of the molecular orbital description.¹³ Surprisingly, calculations for metal-alkyne interactions i-iv revealed similar overlaps for both $d\pi \rightarrow \pi_{\parallel}^*$ and $\pi_{\perp} \rightarrow d\pi$ (ii and iii, respectively). Thus to the extent that metal donation to an alkyne π^* orbital influences chemical or physical properties of metal olefin complexes one could rationalize alkyne π_{\perp} donation to a vacant metal $d\pi$ orbital altering the chemistry of metal-alkyne monomers. Table II lists the overlap values for atomic orbitals responsible for bonding in a π -bound metal-alkyne moiety. In accord with intuitive expectations the σ donation (i) exhibits by far the largest overlap with both metal d and p orbitals while the δ overlap (iv) is small and clearly negligible in guiding qualitative chemical arguments. The near equality of $d\pi$ overlap for both π -acceptance and π -donation is matched by approximately equal metal p overlap with π_{\parallel}^* and π_{\perp} as well.

A second orbital comparison supporting the potential significance of π_{\perp} donation from an alkyne ligand stems from the utility of metal $d\pi$ to carbonyl π^* concepts for rationalizing and predicting the chemical behavior of metal carbonyl complexes.¹⁴ The orbitals contributing to the retrodative metal to carbon monoxide π -bond are derived from atomic orbitals which are indistinguishable in identity and orientation from those of the dative alkyne to metal π -bond (iii). The metal-carbon distances can



be comparable for group 6 complexes as in $\text{W}(\text{CO})(\text{HC}\equiv\text{CH})(\text{S}_2\text{CNEt}_2)_2$ ¹⁰ where $\text{W}-\text{C}(\text{O})$ is 1.94 Å and the two $\text{W}-\text{C}(\text{HC}\equiv\text{CH})$ bonds average 2.03 Å which places the center of the alkyne triple bond only 1.92 Å from the metal ion.

In the $\alpha = 0^\circ$ configuration the filled acetylene π_{\perp} orbital overlaps nicely with the vacant d_{xy} orbital to form a favorable two-center, two-electron bond with destabilization of d_{xy} creating a HOMO-LUMO gap of 1.12 eV. If one assumes retention of the carbonyl $d\pi$ level ordering scheme the $\alpha = 90^\circ$ rotamer

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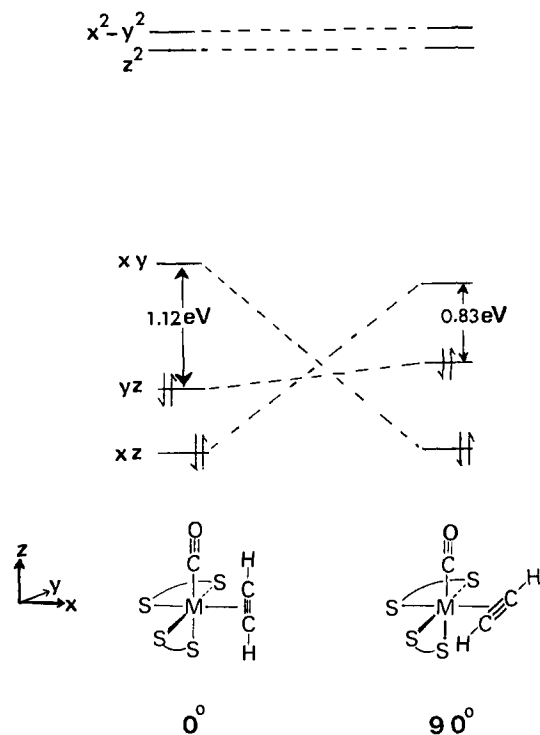


Figure 2. Relative frontier orbital energies for $\text{Mo}(\text{CO})(\text{HC}\equiv\text{C}-\text{H})(\text{S}_2\text{CNH}_2)_2$ as a function of the alkyne rotation angle α at 0 and 90°.

produces a repulsive four-electron, two-center $d\pi-\pi_{\perp}$ interaction with the filled d_{xz} orbital destabilized by overlap with π_{\perp} .

The calculated barrier to alkyne rotation in **1** is 10.5 kcal mol⁻¹, fortuitously close to the range of experimental values determined for five $\text{M}(\text{CO})(\text{RC}\equiv\text{CR})(\text{S}_2\text{CNR}'_2)_2$ ($\text{M} = \text{Mo}$ or W) complexes of 11.1–11.9 kcal mol⁻¹.¹⁵ Total energy calculations at intermediate values of α indicate a smooth potential energy dependence on α with the minimum and maximum corresponding to $\alpha = 0$ and 90° producing the calculated energy barrier by difference. The surprisingly accuracy of the calculated rotational barrier is no doubt partially due to the absence of significant steric effects as the alkyne ligand rotates relative to the $\text{Mo}(\text{CO})(\text{S}_2\text{CNH}_2)_2$ fragment which was maintained as a rigid unit for calculational purposes.

In brief the $\alpha = 0^\circ$ orientation allows the filled d_{xz} metal orbital to be stabilized by both carbonyl and alkyne back-bonding, the filled d_{yz} to be stabilized by a carbonyl π^* interaction, and the lone vacant $d\pi$ orbital, d_{xy} , to stabilize the π_{\perp} alkyne electron pair by formation of a delocalized two-electron π system including the metal and both acetylenic carbon atoms. The compatibility of all the diverse metal–ligand π interactions present clearly identifies this arrangement as the preferred structure.

For $\alpha = 90^\circ$ the π effects of the carbonyl and alkyne ligand are in conflict as evidenced in the ordering of the three octahedral $d\pi$ levels which results. The π_{\parallel}^* acceptor alkyne orbital combines with d_{xy} to generate the lowest $d\pi$ orbital with d_{yz} the HOMO as a result of carbonyl back-bonding. The d_{xz} LUMO is destabilized by alkyne donation from π_{\perp} and stabilized by carbonyl π^* overlap effectively creating a three-center, two-electron subunit. The decreased HOMO–LUMO energy difference of 0.83 eV is 0.29 eV less than that for $\alpha = 0^\circ$ and reflects the discordant nature of the metal–ligand π -bonding features present for $\alpha = 90^\circ$. These results are presented in Figure 2.

Given that the $\alpha = 0^\circ$ geometry is obviously preferred even in the absence of π_{\perp} donation it is appropriate to list experimental results which indicate that π_{\perp} donation is a chemically significant factor in these molecules. (1) $\text{M}(\text{CO})(\text{RC}\equiv\text{CR})(\text{S}_2\text{CNR}'_2)_2$ compounds are not reactive electrophiles as demonstrated by the lack of reactivity toward added ligand in refluxing tetrahydro-

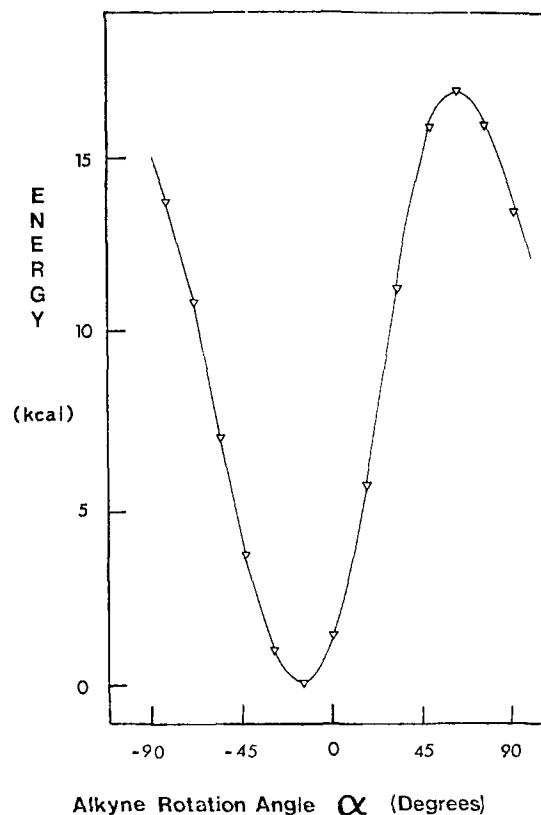
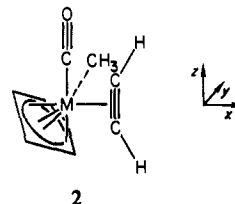


Figure 3. Relative calculated total energy vs. the alkyne rotation angle α for $\text{Mo}(\text{CO})(\text{HC}\equiv\text{CH})(\pi\text{-C}_5\text{H}_5)(\text{CH}_3)$.

furan.⁴ (2) Olefins do not form analogous compounds as would be expected if only π_{\parallel} and π_{\parallel}^* bonding were important.⁴ (3) Stabilization of the alkyne π_{\perp} orbital is observed upon coordination in both the $\alpha = 0$ and 90° calculations and the corresponding π^* mate, d_{xy} or d_{xz} , respectively, is significantly destabilized. (4) The magnitudes of the overlap for $d\pi-\pi_{\perp}$ and $d\pi-\pi_{\parallel}^*$ are similar.

Mo(CO)(HC≡CH)($\pi\text{-C}_5\text{H}_5$)(CH₃) (2). The coordinate system chosen for this molecule follows that employed for **1** and again places the carbon monoxide ligand along +z and the alkyne along +x. In a qualitative sense the ancillary $\pi\text{-C}_5\text{H}_5$ and CH₃ ligands of **2**, located in the -x,-y,-z octant and along +y, respectively, resemble the two dithiocarbamate chelates of **1** in formally occupying four coordination sites¹⁶ and leaving a d^4 configuration for the group 6 metal ion. This complex has been treated previously as a member of the general $\text{CpMo}(\text{CO})\text{L}(\text{acetylene})^+$ class by Schilling, Hoffmann, and Lichtenberger in a lucid article probing the electronic structures of $\text{CpM}(\text{CO})_2\text{L}$ compounds.¹⁷



The EHMO calculations for **2** reproduce a d orbital splitting pattern very similar to those described for **1** at $\alpha = 0$ and 90° with a difference of 12.3 kcal mol⁻¹ favoring the $\alpha = 0^\circ$ rotamer. However, unlike **1** where qualitative electronic analysis guides one to the correct ground state geometry with $\alpha = 0^\circ$ and also correctly predicts that the transition state will occur when $\alpha = 90^\circ$ in accord with EHMO results, a sampling of total energies for **2** at 15° intervals between -90 and +90° does not produce a symmetrical

(16) Raymond, K. N.; Eigenbrot, C. W. *Acc. Chem. Res.* **1980**, *13*, 276.

(17) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

plot with extrema at α values of 0 and 90° (see Figure 3). The calculation places the actual energy minimum and maximum at -20 and 60° as a function of the rotational orientation angle α . The true barrier to rotation is thus calculated to be 17.2 kcal mol⁻¹ based on this complete energy profile which compares very favorably with experimental literature values which are in the range 17–18 kcal mol⁻¹.¹⁸ Hoffmann has pointed out that the distinction between steric and electronic factors can be quite a subtle point,¹⁹ but in this case the two-center, four-electron repulsion between filled alkyne orbitals and the cyclopentadienyl and methyl ligands which contributes both to the high barrier and to the asymmetry of the potential energy function of **2** as compared to **1** can be conveniently classified as a steric effect. While it is possible that π -donation from the dithiocarbamate ligands in **1** could lower the energy of the transition state the similar energy differences between $\alpha = 0$ and 90° of 10.5 and 12.3 kcal mol⁻¹ for **1** and **2**, respectively, indicate this is at most a minor factor in determining the activation energy for alkyne rotation.

Mo(O)(HC≡CH)(S₂CNMe₂)₂ (3). The Mo(S₂CNH₂)₂ fragment employed for **1** also serves as a point of departure for constructing the molecular orbital description for **3**. Addition of a neutral oxo ligand along +z introduces a two-electron donor formally analogous to carbon monoxide for electron bookkeeping purposes. The molecular orbital scheme for the Mo(O)(S₂CNMe₂)₂ fragment reflects effective two-electron transfer with formation of molybdenum(IV) and coordinated oxide ion. In order to simplify the discussion one can consider the oxide as donating two electrons from an sp hybrid orbital to form a dative metal–oxygen σ bond while leaving a pair of filled oxide p_⊥ orbitals, p_x and p_y, to interact with the metal d_{xz} and d_{yz} orbitals. These two oxygen p_⊥ orbitals are stabilized at the expense of the two metal d π orbitals. Similar qualitative bonding diagrams have been presented previously for related complexes.²⁰ The logic applied to the d π splitting of **3** parallels that employed for **1**, but here the two d π orbitals overlapping the z-axis ligand π orbitals increase in energy since the oxo ligand is a π -donor rather than a π -acceptor. Clearly d_{xy} is left as the single low-energy d π orbital and will house the two electrons remaining in the d orbital manifold of the Mo⁴⁺ ion.

Given that oxygen π -donation is consistent with occupation of the d_{xy} orbital with d_{xz} vacant, orientation of the alkyne with $\alpha = 90^\circ$ will be preferable as it approaches along the +x axis. This rotamer allows d_{xy} to donate into $\pi_{||}^*$ while π_{\perp} can donate into d_{xz}, both compatible with oxo π effects. The d_{xz}, O p_x, and alkyne π_{\perp} orbitals produce a three-center, four-electron bond with d_{xz} driven above the d_{yz} LUMO which is destabilized only by O p_y π -donation. A large HOMO–LUMO energy gap of 1.11 eV reflects the impact of the various d π influences working in concert with one another as shown in Figure 4.

The conflicting d π interactions present when $\alpha = 0^\circ$ are readily apparent since $\pi_{||}^*$ overlaps the vacant d_{xz} and a four-electron repulsive interaction between π_{\perp} and d_{xy} also occurs. In fact the $\alpha = 0^\circ$ calculation indicates that d_{xy} becomes the highest energy d π level which is evidence of substantial donation from π_{\perp} . At the same time d_{xz} is stabilized by $\pi_{||}^*$ overlap and becomes the HOMO in spite of destabilization due to overlap with the oxygen p_x orbital. This three-center scheme has $\pi_{||}^*$ highest in energy, d_{xz} as the central orbital, and oxygen p_x as the lowest energy component. Although the effect of such a three-center interaction on the initial orbitals of highest and lowest energy is obvious, the movement of the central orbital is not easily predicted.⁸ Regardless of the final d π level ordering for $\alpha = 0^\circ$ the divergent d π bonding factors leave a HOMO–LUMO energy difference of 0.58 eV, and

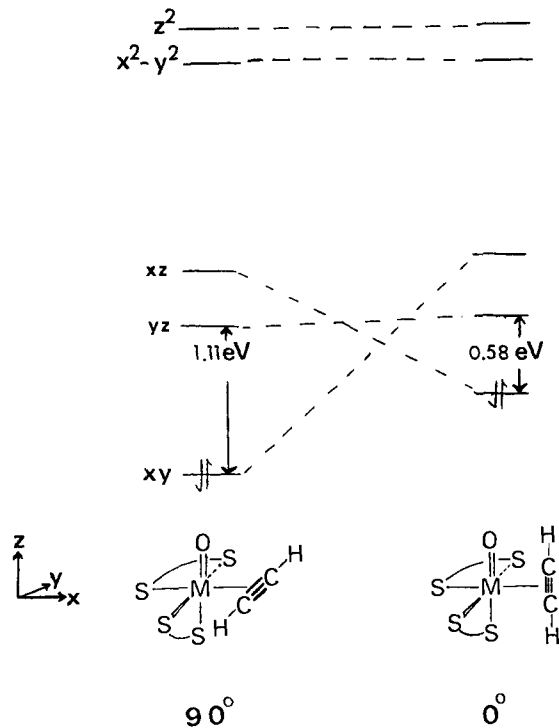
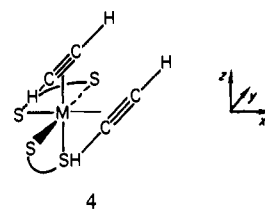


Figure 4. Relative frontier orbital energies for Mo(O)(HC≡CH)(S₂CNMe₂)₂ as a function of the alkyne rotation angle α at 90 and 0°.

the rotameric configuration with the alkyne perpendicular to the metal–oxo bond is 17.3 kcal mol⁻¹ lower in total energy than the parallel configuration. Recent DNMR studies of W(O)(RC≡CR)(S₂CNR')₂ are consistent with a rotational barrier greater than 16 kcal mol⁻¹, although the onset of a fluxional process involving the chelating dithiocarbamate ligands equilibrates the two ends of the alkyne ligand independently so that only a lower limit to the alkyne rotational activation energy is experimentally accessible.²¹

Mo(HC≡CH)₂(S₂CNH₂)₂ (4). The molecular orbital scheme for **4** is consistent with construction of a basic octahedral σ framework where each alkyne occupies one coordination site with formation of a dative σ bond utilizing the $\pi_{||}$ electron pair. Two of the three d π orbitals will be filled for this diamagnetic d⁴ complex, and optimization of metal-to-ligand π bonding can be realized when both alkynes are cis and parallel to one another. This geometry locates one vacant $\pi_{||}^*$ in the xy plane to overlap the filled d_{xy} orbital while the vacant $\pi_{||}^*$ orbital of the second alkyne lies in the yz plane and stabilizes the d_{yz} orbital which will be filled.



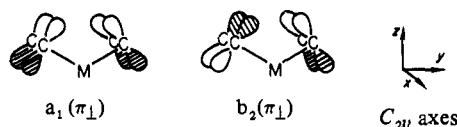
This arrangement allows both alkyne π_{\perp} orbitals to overlap with the only empty d π orbital, d_{xz}. The three-center, four-electron orbital scheme which results can be easily analyzed in terms of the local C_{2v} symmetry appropriate for the cis-M(HC≡CH)₂ unit. The two alkyne π_{\perp} orbitals are bases for a₁ and b₂ representations so that the d_{xz} orbital of a₁ symmetry produces a bonding orbital dominated by π_{\perp} and an antibonding counterpart, the LUMO, largely of d_{xz} character. The b₂(π_{\perp}) combination is rigorously

(18) Alt, H. G. *J. Organomet. Chem.* **1977**, *127*, 349.

(19) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

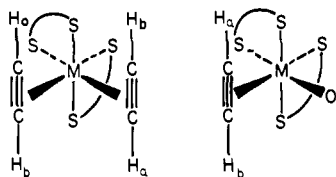
(20) (a) Newton, W. E.; McDonald, J. W.; Corbin, J. L.; Ricard, L.; Weiss, R. *Inorg. Chem.* **1980**, *19*, 1997. (b) Maatta, E. A.; Wentworth, R. A. D. *Ibid.* **1979**, *18*, 524. (c) Maatta, E. A.; Wentworth, R. A. D.; Newton, W. E.; McDonald, J. W.; Watt, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 1320. (d) Boki, N. G.; Gatilov, Yu. V.; Struchkov, Yu.; Ustynuk, N. A. *J. Organomet. Chem.* **1973**, *54*, 213. (e) Howard, J. A. K.; Stansfield, R. F. D.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1976**, 246.

(21) Templeton, J. L.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248.



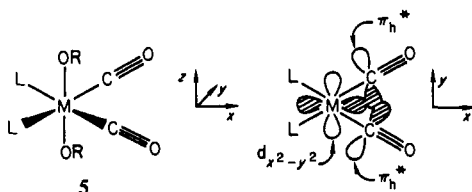
nonbonding due to the symmetry considerations which apply in this case. Note the similarity of this bonding picture to that of **3** where d_{xz} interacted with a filled oxygen p_x and a filled alkyne π_{\perp} orbital in a three-center, four-electron subsystem. The absence of any symmetry for **3** eliminates the rigorous intermediate nonbonding level and as a result all three orbitals can mix extensively. Nonetheless, since d_{xz} has the highest energy of the three interacting orbitals a similar result obtains for both **3** and **4**: the d_{xz} LUMO is substantially destabilized with filled ligand π orbitals concomitantly lowered in energy. The net result is effective donation of six electrons from the two alkynes as originally proposed by McDonald and co-workers.³

Rotation of one alkyne by 90° to a perpendicular orientation, i.e., the $+x$ $\text{HC}\equiv\text{CH}$ ligand rotated into the xz plane, increases the total energy by $40.3 \text{ kcal mol}^{-1}$. This extremely high rotation barrier suggests that the molecule is not fluxional at room temperature. Although we are not aware of any experimental studies which address this question only a single acetylene $^1\text{H NMR}$ signal has been reported³ even though the C_2 molecular symmetry of **4** places each end of the acetylene ligands in distinct magnetic environments due to the chelating dithiocarbamate ligands. The difference in chemical shifts should allow resolution based on analogy with analogues of **3** where a similar orientation of the acetylenic protons relative to the chelating ligands produces a shift differential of greater than 0.1 ppm .²¹

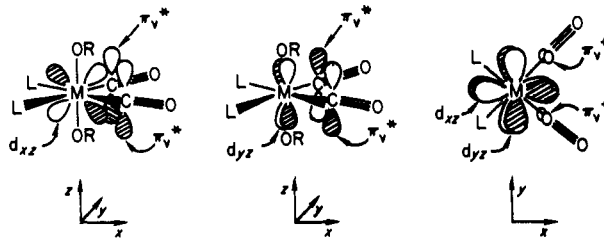


$\text{Mo}(\text{CO})_2(\text{OMe})_2(\text{NH}_3)_2$ (**5**). The pseudooctahedral geometry reported by Chisholm, Huffman, and Kelly for $\text{Mo}(\text{CO})_2(\text{O}i\text{Bu})_2(\text{py})_2$ ⁷ prompted us to include **5** in our calculations as a model for compounds of the type $\text{M}(\text{CO})_2(\text{OR})_2\text{L}_2$. Such compounds are electronically similar, at least in a formal bookkeeping sense, to the $\text{M}(\text{CO})_2(\text{S}_2\text{CNR}_2)_2$ ($\text{M} = \text{Mo}, \text{W}$) complexes under study in our laboratories.^{5,22} The gross structural differences between Chisholm's six-coordinate molybdenum(II) dicarbonyl derivative⁷ and the dicarbonylbis(dithiocarbamate)molybdenum(II) compound⁵ suggested that an informative comparison of molecular orbital features should be accessible. Rationalization of the octahedral disposition of ligands favored for **5** based on EHMO calculations provides a useful pedagogical strategy for elaborating the electronic origins of the trigonal prismatic structure found for $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNP}r_2)_2$.

The coordinate system chosen for **5** bisects the two carbonyl ligands with $+x$ such that the two amines are in the $-x, +y$ and $-x, -y$ quadrants. This somewhat unusual choice of coordinates, which is related to the common octahedral axes by a rotation of 45° around z , is preferable for **5** since each of the five d orbitals is a basis for a one-dimensional irreducible representation of the C_{2v} point group and this eliminates the need to form linear combinations as is required in the alternative coordinate system. A completely equivalent MO description results in either case.



σ bonds generate the familiar two above three octahedral d orbital pattern with $d_{x^2-y^2}$, d_{xz} , and d_{yz} constituting the $d\pi$ set. Considering the π effects of the two π -acid carbonyl ligands first it is apparent that $d_{x^2-y^2}$ will enjoy more stabilization than either d_{xz} or d_{yz} since both π_h^* carbonyl orbitals overlap $d_{x^2-y^2}$ quite effectively. Recognition that one of the $d\pi$ levels clearly lies below the other two may appear to contradict experimental data which require a two below one $d\pi$ splitting pattern, but the crux of the argument depends upon the disposition of the upper two $d\pi$ levels, d_{xz} and d_{yz} , as described below.



If the two carbonyl ligands lie along the $1,1,0$ and $1,\bar{1},0$ vectors the total overlap of d_{xz} and d_{yz} with the π_v^* orbitals of the two carbonyls would be equal and, neglecting the π influence of ancillary ligands, a degenerate pair of $d\pi$ orbitals would result and produce a triplet ground state. An acute angle of 74° is observed between the *cis*-carbonyl ligands in Chisholm's complex, however, and closure of this angle from 90° is accompanied by enhancement of π_v^* overlap with d_{xz} at the expense of decreasing the π -stabilization available to d_{yz} . Identification of d_{xz} as the HOMO and d_{yz} as the LUMO is a simple extension of the geometry observed for the $\text{M}(\text{CO})_2$ portion of Chisholm's complex.

The next bonding feature to be addressed stems from molecular orbital concepts derived from studies of the 16-electron alkyne complexes. For the alkyne complexes the contribution of the filled π_{\perp} orbital was essential and decreased the electrophilicity of **1**, **2**, and **4** compared to more reactive species such as $[(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]^+$ ²³ and $(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2\text{R}$,²⁴ also six-coordinate d^4 group 6 carbonyl derivatives. Although the geometries, physical properties, and EHMO calculations all reflect alkyne π -donation to some extent, it is the stability and moderate reactivity of the alkyne compounds that most emphatically underlines the impact of ligand π -donation in driving the LUMO to higher energy. The observed geometries can be easily deduced by simply seeking the alkyne orientation which is most effective for destabilizing the $d\pi$ LUMO. This principle of optimizing π -donation to vacant $d\pi$ orbitals can be generalized and applied to other formally electron-deficient monomers to account for unusual stability and predict structural features.

Having identified the d_{yz} orbital of **5** as the LUMO by analyzing carbonyl π^* factors one can proceed to identify and orient π -donor ligands to maximize overlap with d_{yz} . The ammine ligands were chosen to be π -innocent ligands in order to be consistent with the general absence of strong π interactions for metal-pyridine bonds²⁵ and thus mimic the electronic structure of $\text{Mo}(\text{CO})_2(\text{O}i\text{Bu})_2(\text{py})_2$. The alkoxy ligands are known to be good π -donors as exemplified by the Hammett σ_p^+ value of -0.78 .²⁶ Assuming sp^2 hybridization at oxygen simplifies the qualitative discussion since the lone pair housed in the lone p_{\perp} orbital will be a better match for $d\pi$ bonding than the sp^2 lone pair for both energetic and geometric reasons. Alkoxy p_{\perp} orbital donation couples with the d_{yz} LUMO to restrict the rotational orientation of the methoxy ligands to the xz plane. The R groups can reside between either the two carbonyl ligands or the two ammine ligands in order to leave p_{\perp} in the yz plane. The bulky *tert*-butyl groups of Chisholm's complex are located above and below the carbonyl ligands, perhaps avoiding

(23) Beck, W.; Schloter, K. *Z. Naturforsch.*, B **1978**, *33B*, 1214.(24) Kazlauskas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 1727.(25) (a) Glerup, J.; Monsted, O.; Schaffer, C. E. *Inorg. Chem.* **1976**, *15*, 1399. (b) Templeton, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4906.(26) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1957**, *79*, 1913.

steric problems between these large alkyl groups and the pyridine ligands. Our calculations for **5** favor this methoxy orientation by an energy difference of 7.9 kcal mol⁻¹ over the rotamer with both methyl groups in the yz plane. No experimental data bearing on alkoxy rotation processes are currently available. As summarized for the alkyne cases the geometry and chemical properties of **5** are easily rationalized in terms of destabilization of the $d\pi$ LUMO by ligand π -donation to the unsaturated metal center. Rotation of one methoxy by 90° produces a calculated rotation barrier of 5.0 kcal mol⁻¹.

Mo(CO)₂(S₂CNH₂)₂ (6). The molecular orbital analysis for **6** compared calculations utilizing the trigonal prismatic coordination geometry observed for Mo(CO)₂(S₂CNPr^t)₂ with an idealized octahedral arrangement with the same ligands. The salient distinction between the two MO schemes was the magnitude of the energy gap separating the HOMO and LUMO: 1.20 eV for the trigonal prism and only 0.20 eV for the octahedron. The unusual coordination geometry of **6** again follows from the general premise set forth above: maximize destabilization of the LUMO.

Consider first the octahedral ligand arrangement with the two cis carbonyls subtending an angle of 74° and a coordinate system analogous to that chosen for **5**. Again d_{yz} will be the LUMO since retrodative bonding to the carbonyls will parallel the behavior characterizing **5**. The question of what ligand orientation optimizes ligand π -donation into d_{yz} is a mute one since the chelating nature of the two dithiocarbamate ligands dictates the geometry. Unlike the case for **5** with alkoxy ligands which could rotate in order to influence $d\pi$ overlap there is no flexibility in the orientation of the dithiocarbamate delocalized π -system which is fixed perpendicular to the $\bar{1}, \bar{1}, z$ plane for one chelate and perpendicular to the $\bar{1}, \bar{1}, z$ plane for the other. The small splitting between d_{xz} and d_{yz} for the octahedral model manifests the poor and indiscriminatory $d\pi$ overlap for this case. This geometry leaves the LUMO near the HOMO in energy and one would anticipate very electrophilic behavior and/or a triplet ground state; neither is observed.

The trigonal prismatic σ bonds generate a two above three d orbital energy level pattern.²⁷ With the z axis passing through both trigonal faces and $+x$ between the two carbon monoxide ligands the $d\pi$ set consists of d_{xz} , d_{xy} , and $d_{x^2-y^2}$ with d_{zx} and d_{yz} σ antibonding. Both carbonyl π_v^* orbitals are nicely accom-

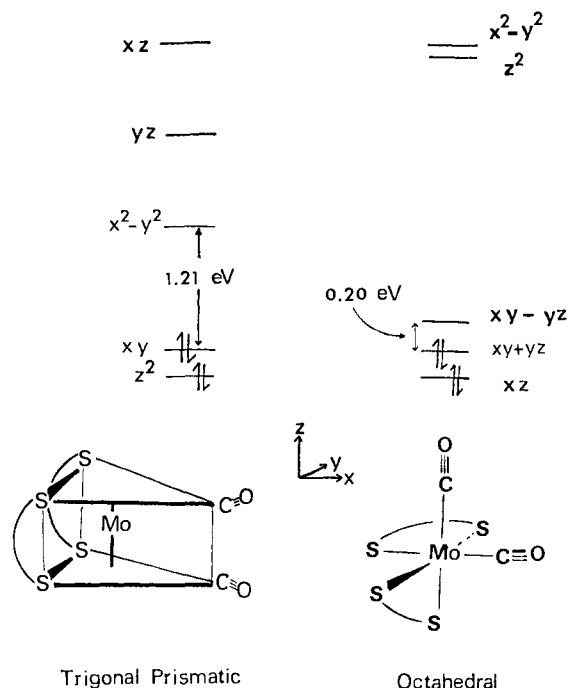
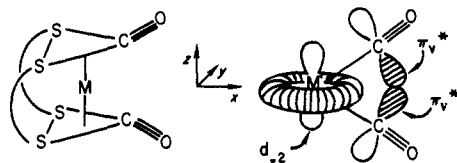


Figure 5. Calculated d orbital energy diagrams for Mo(CO)₂(S₂CNH₂)₂ as a trigonal prism and as a pseudooctahedron.

evident in the comparative calculations for the trigonal prism and octahedron. The π -donor potential of both dithiocarbamate ligands is efficiently directed into the $d_{x^2-y^2}$ LUMO in the trigonal prism and drives it more than 1 eV above the HOMO (see Figure 5). Concomitant stabilization of the chelate π system is difficult to specify since the effect is dispersed among several filled orbitals.

The total energy calculated for the idealized Mo(CO)₂(S₂CNH₂)₂ octahedron is 0.09 eV (2.1 kcal mol⁻¹) below that of the trigonal prism, underlining the hazards and limitations of the EHMO method. This discrepancy may reflect inaccuracies in total energy calculations based on the one-electron Hückel approximation or, conceivably, packing effects in the solid state could account for the observed trigonal prismatic molecular structure.

If one considers analogous d^6 compounds such as Mo(NO)₂(S₂CNR₂)₂⁶ or Fe(CO)₂(S₂CNR₂)₂²⁹ where all three $d\pi$ orbitals would be populated the trigonal prism is more than 20 kcal mol⁻¹ above the octahedron due to occupancy of the high-energy $d_{x^2-y^2}$ orbital. Indeed these 18-electron complexes are known to exhibit an octahedral arrangement of the six ligating atoms.

Conclusions

The role of ligand π -donation in the six model compounds chosen for molecular orbital analysis is evident in the calculated geometrical preferences which are in complete accord with available experimental data. The excellent agreement between observed and calculated alkyne rotational barriers is no doubt fortuitous, but nonetheless the quantitative distinction between barriers for **1** and **2** certainly supports a greater steric role for the ancillary ligands in the alkyne rotation process for **2** and related Mo(CO)(R(C \equiv CR))(π -C₂H₅)(R) compounds. Furthermore the calculated rotational barrier of 17.3 kcal mol⁻¹ for the oxo acetylene derivative is consistent with the recent interpretation of ¹H DNMR spectra which invokes only a rearrangement of the two chelating dithiocarbamate ligands to average the magnetic environment of the two ends of the alkyne in the absence of rotation.²¹

The possibility of altering chemical properties by incorporation of π -donor ligands into metal carbonyl complexes is not limited to alkyne ligands. The geometries of both **5** and **6** manifest substantial π -basicity for both alkoxide and dithiocarbamate ligands. No doubt numerous other ligands, particularly those with

modated by d_{z^2} overlap and lie near the upper and lower nodal cones which are separated by 70.5° (cf. the angle subtended by the cis carbonyls of 74°). One would intuitively anticipate maximum π overlap when the carbon is located in the d_{z^2} nodal cone, but calculations indicate no significant change in metal-to-ligand π bonding between β values of 74–90°. A second factor favoring the nodal cone location is the minimization of carbon σ -donor overlap with the filled d_{z^2} orbital.²⁸ An additional π -bonding feature fostering the acute β angle is overlap between the carbonyl π_b^* orbitals and d_{xy} which increases monotonically as β decreases from 90°. Since π_b^* overlap with $d_{x^2-y^2}$ is rigorously zero it is left as the LUMO for this d^4 Mo(II) complex.

Identification of d_{z^2} and d_{xy} as the $d\pi$ orbitals stabilized by the two carbon monoxide π -acid ligands accounts for the diamagnetism of Mo(CO)₂(S₂CNPr^t)₂. Isolation of this group of unsaturated compounds suggests that the empty $d\pi$ level is effectively destabilized by ligand π -donation, and indeed such an effect is

(27) For a general treatment of the comparative bonding in several six-coordinate geometries see: Hoffmann, R.; Howell, J. M.; Rossi, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 2484 and references contained therein.

(28) This aspect of the bonding was pointed out by Professor C. E. Schäffer.

(29) Ricci, J. S.; Eggers, C. A.; Bernal, I. *Inorg. Chim. Acta* **1972**, *6*, 97.

first row donor atoms such as C, N, O, and F, can donate significant π electron density to a metal center. Certainly the $\text{Mo}(\text{NPh})_2(\text{S}_2\text{CNET}_2)_2$ complex described in detail by Haymore, Maatta, and Wentworth³⁰ provides an example where the lowest unoccupied orbitals are π^* in character. The geometries and orientation of the nitrene ligands are consistent with π -donation from the two NPh^{2-} ligands into the vacant $d\pi$ orbitals as elucidated by these workers.³⁰

The $\text{W}(\text{CO})(\text{RC}\equiv\text{CR})_3$ compound³¹ is formally a 14-electron complex, but π -donation from the three alkyne ligands destabilizes two additional d orbitals as accurately described by King some years ago.³² A similar analysis applies for $\text{Mo}(\text{NO})(\text{py})(\text{OBU}^+)_3$ ³³ where once again C_{3v} molecular symmetry limits π -donation from three ligands to destabilization of only two d orbitals. As noted by Chisholm, Cotton, Extine, and Kelly the linear nitrosyl ligand is an excellent π -acid and hence d_{xz} and d_{yz} will be filled as the lowest lying d orbitals.³³ This leaves d_{xy} and $d_{x^2-y^2}$ as vacant d orbitals which can interact with the three oxygen p_\perp orbitals only when they lie in the xy plane. Indeed the observed geometry has the R groups in vertical planes which would correspond to the optimal orientation for alkoxy donation into d_{xy} and $d_{x^2-y^2}$. Although steric factors probably dictate this structure as well the surprising stability of this 14-electron complex and the compatibility of the observed structure with optimal oxygen p to metal d π -bonding strongly supports the importance of ligand π -basicity in this electron-deficient monomer.

It is appropriate to summarize the results reported herein by placing the role of ligand π -donation in perspective relative to the EAN rule. The molecular orbital foundation for the EAN rule has been lucidly described by other workers.³⁴ The formation of n σ -antibonding orbitals invariably occurs for ML_n complexes for accessible integral values of n . This leaves $9 - n$ nonbonding levels among the metal s, p, and d valence orbitals which combine with the n ligand based σ bonding orbitals to house a total of 18 electrons while the antibonding orbitals remain vacant.

The prominence of π -acid ligands such as carbon monoxide in monomers which adhere to the EAN rule is not coincidental. Often the $9 - n$ nonbonding metal valence orbitals are of π character relative to the metal-ligand framework. The energy considerations responsible for filling all metal based orbitals which are not of σ^* character are substantially enhanced by the conversion of nonbonding levels to π -bonding orbitals which accompanies coordination of π -acid ligands. Thus the general effect of additional π -acid ligands is to augment the applicability of the inert gas formalism.

Numerous exceptions to the EAN rule are known and explanations for various cases have been presented by other workers.³⁵ The six "exceptions" treated in this article can be readily understood in terms of ligand π -donation. The influence of ligand π -basicity on EAN guidelines is diametrically opposed to that of π -acid ligands. As the π -basicity of the ligand complement increases π^* character encroaches on the nominally nonbonding d orbitals. The accompanying increase in energy for these d orbitals is in conflict with the EAN rule which requires occupancy of all $d\pi$ levels. Since ligand π -basicity can exert considerable influence on the chemistry of metal complexes it provides a convenient variable which can range from negligible to substantial depending on the nature of the ligands. At one extreme π -donation can selectively drive a $d\pi$ level sufficiently high in energy so that it remains vacant in the isolated molecule as is the case for compounds 1 through 6 (see Figure 6). For electron-counting purposes

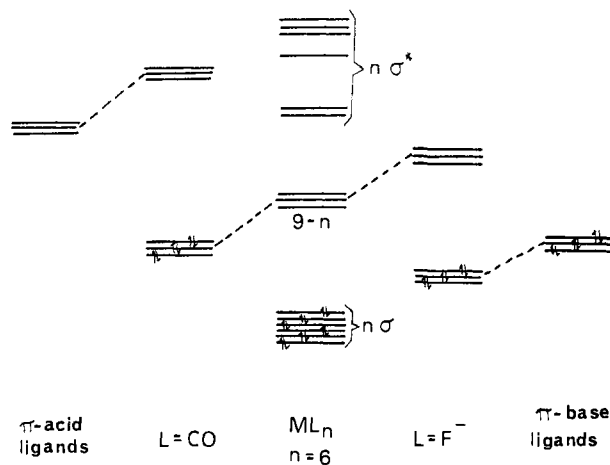


Figure 6. Idealized orbital diagram depicting the general impact of π -acid and π -base ligands on the metal $d\pi$ orbital energy levels.

π -donation from a single ligand orbital to one vacant $d\pi$ level is analogous to a σ interaction, and one could arrive at an 18-electron total in such simple cases by treating the π -donor electron pair as equivalent to a σ -donor electron pair. In practice this is not a useful procedure. Unlike σ bonds where there is invariably a one-to-one correspondence between ligand donor and metal acceptor orbitals for all common monomeric coordination numbers and geometries, π interactions are often restricted by the number of available metal orbitals and the geometry of the complex. Complexes 3, 4, 5, and 6 provide examples where more than one potential π -donor ligand interacts with only one vacant $d\pi$ orbital.

The role of ligand π -donation in the above complexes is particularly apparent since they appear anomalous in terms of the EAN rule. This singularity guided us to the π^* character of the LUMO, which would be filled for analogous 18-electron compounds, as the key feature of the molecular orbital structure of these unsaturated monomers and allows their isolation as relatively unreactive monomers. The impact of ligand π -basicity is not restricted to isolated compounds, however, and it seems probable that as the π -donor ability of the ligands decreases coordination of a seventh ligand to a six-coordinate d^4 monomer would occur with conversion to seven vacant σ^* levels and two occupied $d\pi$ orbitals. This ligand addition indeed occurs readily for $\text{M}(\text{CO})_2(\text{S}_2\text{CNR}_2)_2$ ($\text{M} = \text{Mo}, \text{W}$) compounds.³⁶

Likewise ligand dissociation from a saturated metal carbonyl complex should be more facile in cases where π -base ligands could stabilize the unsaturated intermediate or activated complex. The relative rates of carbon monoxide dissociation from MnCO_5X ($\text{Cl} > \text{Br} > \text{I}$)³⁷ are consistent with the halogen π -donor ability as reflected in σ_p^{+26} and $\Delta_{\pi_j}^{25a}$ values. The cis-labilization phenomenon has been thoroughly treated both experimentally³⁸ and theoretically³⁹ by Brown, Atwood, and Lichtenberger. The stabilization of unsaturated species by π -donor ligands was cited by these workers as a central factor in determining the rate of carbon monoxide dissociation. It is interesting to note that extrapolation of this series suggests that the fluoro derivatives should be most reactive and in fact both $\text{Mn}(\text{CO})_5\text{F}$ and $[\text{Mo}(\text{CO})_5\text{F}]^-$ have proved to be extremely elusive, although $\text{Re}(\text{CO})_5\text{F}^{40}$ and $[\text{W}(\text{CO})_5\text{F}]^-^{41}$ are known.

A common orbital theme among the compounds considered in this work is the mutual compatibility of all the $d\pi$ interactions present in any given complex. The π -acid and π -base ligands

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invariably find a match among filled and vacant $d\pi$ orbitals, respectively, in compounds 1-6. The experimental and theoretical results to date lead us to hypothesize that numerous new compounds containing both π -acid and π -base ligands in the coordination sphere should be accessible. Synthetic efforts to realize this chemistry where segregation of empty $d\pi$ orbitals overlapping with π -donor ligands will complement retrodative metal-to-ligand bonding to π -acid ligands are continuing in our laboratory.

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Molybdenum Sites of Sulfite Oxidase and Xanthine Dehydrogenase. A Comparison by EXAFS

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Abstract: The molybdenum enzymes sulfite oxidase and xanthine dehydrogenase have been investigated by fluorescence-detected EXAFS using synchrotron radiation, and the results have been interpreted with improved EXAFS analysis procedures. A new treatment of EXAFS amplitudes has been developed which allows the extraction of meaningful Debye-Waller factors using experimentally derived functions. A search profile procedure has also been developed to aid in the treatment of minor EXAFS components. These methods have been used for a more detailed analysis of sulfite oxidase molybdenum EXAFS. They have also been used for analysis of the EXAFS of intact and cyanolyzed xanthine dehydrogenase, in both oxidized and reduced forms. Although the results are in qualitative agreement with recent work by Bordas et al., some significant quantitative differences are found. For oxidized sulfite oxidase, the analysis revealed two oxygens at 1.68 Å and two or three sulfurs at 2.41 Å, changing to one oxygen at 1.69 Å and three sulfurs at 2.38 Å upon reduction. For oxidized, intact xanthine dehydrogenase the prediction was one oxygen at 1.70 Å, one sulfur at 2.15 Å, and two sulfurs at 2.47 Å, changing to one oxygen at 1.68 Å and three sulfurs at 2.38 Å upon reduction. Finally, in cyanolyzed xanthine dehydrogenase, two oxygens at 1.67 Å and two sulfurs at 2.46 Å were found, which upon reduction changed to one oxygen at 1.66 Å and two or three sulfurs at 2.33 Å. In all cases there may be extra ligands which complete the molybdenum coordination sphere but contribute only weakly to the EXAFS.

Molybdenum enzymes exhibit a broad range of chemical and spectroscopic behavior,¹ and comprehending the structural basis for this diversity is a prerequisite for understanding and synthetically modeling their catalytic mechanisms. Previous results from X-ray absorption spectroscopy have suggested that the Mo sites of these enzymes can be classified as either "cluster" type such as in nitrogenase²⁻⁴ or "oxo" type such as contained in xanthine oxidase,⁵⁻⁷ sulfite oxidase,⁸ and nitrate reductase.⁹ Specifically, the EXAFS studies of nitrogenase have shown that the molybdenum is present in an Fe,Mo,S cluster, whereas the other Mo enzymes appear to have a Mo site with both sulfur donor and terminal oxo ligands. The structural differences between these two types of sites may be related to the fact that nitrogenase possesses an iron-molybdenum cofactor ("FeMo-co"),¹⁰ whereas the other enzymes cited contain a molybdenum cofactor ("Mo-co") which is free of iron but contains a novel pterin component.¹¹

Even within the class of oxo-type Mo proteins there are substantial differences in properties. Xanthine oxidase, xanthine dehydrogenase, and aldehyde oxidase all have relatively low Mo redox potentials¹² and a unique "cyanolyzable" sulfur.¹ Upon treatment of these enzymes with cyanide, SCN^- is released and "desulfo" Mo proteins are formed which have no catalytic activity and even lower redox potentials. A molybdenum protein from *Desulfovibrio gigas* has properties similar to these desulfo proteins.¹³ In contrast, sulfite oxidase¹⁴ and nitrate reductase¹⁵ have substantially higher Mo redox potentials, and although they are inhibited by cyanide in their reduced states, this process is re-

versible by oxidation and no SCN^- is released.¹⁶ Thus, a distinction can be made between low potential and high potential

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