Metal dπ–Ligand π Conflicts in Octahedral Oxo, Carbyne, and Carbonyl Complexes

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Abstract: Metal–ligand π interactions in group VI model compounds containing oxo, carbyne, and carbonyl ligands are probed with use of the extended Hückel method. The interplay between M=O π bonding optimization and the metal σ framework geometry in $[MoO_2H_4]^{2-}$ is examined first. The importance of oxygen's electronegativity for housing lone pairs in monomers containing terminal oxygens is noted and later contrasted with similar model compounds containing carbyne ligands. Calculations on $[W(CH)_2H_4]^{4-}$ confirm the qualitative expectation that a nonbonding carbon 2p orbital combination exists for both cis and trans isomers. Even though this orbital is not at particularly high energy for a filled frontier orbital, we anticipate that these carbyne carbons will be very nucleophilic if filled or very electrophilic if vacant; i.e., they will resemble a carbanion or a carbonium ion. A mixed oxocarbyne complex, such as $[W(CH)(O)H_4]^{3-}$, will exhibit a dπ conflict with the covalency requirements of the carbyne causing electron density to build up on the terminal oxygen. Competition for dπ orbitals also results when π-acid ligands are trans to π-donor ligands. Recognition of π-acid/π-donor dπ conflicts rationalizes the cis geometry of W(O)(CO) in d^2 $M(O)(CO)L_4$ octahedra.

Few theoretical studies address the electronic structure of metal carbyne complexes. Excellent papers by Kostic and Fenske have established the binding modes of carbynes in many coordination environments.[1] They conclude that CR^+ is a stronger π-acid than carbon monoxide and that the frontier orbitals dictate reactions of transition-metal carbyne complexes. Hoffmann, Wilker, and Eisenstein have examined biscarbyne model complexes as part of a ligand coupling study.[2] Employing the neutral CR formalism for assigning metal configurations they found that melding adjacent carbyne ligands into an alkyne was forbidden at d^6 metal centers, allowed but energetically unfavorable in d^4 complexes, and both allowed and energetically favorable in d^2 monomers. Experimentally numerous octahedral d^4 and several d^2 alkyne complexes are known,[3] while stable mononuclear octahedral biscarbynes of any electron count are rare.[4]

In contrast the d^0 MO_2 moiety is omnipresent for Mo and W and has been thoroughly characterized experimentally[5] and analyzed theoretically.[6] Tatsumi and Hoffmann have studied this fragment using the extended Hückel method and found that MoO_2^{2+} displays a strong preference for a bent geometry with an optimal angle near 110°.[7] This conclusion is in agreement with observed angles in octahedral Mo(VI) complexes (Table I) as well as the 105° O–M–O angle in the d^0 tetrahedral CrO_2Cl_2 molecule.[8] The dπ orbital utilization rationale for a cis preference in d^0 L_4MO_2 octahedra and a trans preference in d^2 L_4MO_2 has been discussed by Mingos using $MoO_2(PH_3)_4^{n+}$ ($n = 2, 0$).[9]

Dioxo derivatives represent one end of a continuum in which anionic ligands with lone pair electrons, in this case O^{2-}, bond to a metal center through both filled σ-donor and π-donor orbitals. Kubacek and Hoffmann have examined octahedral distortions in complexes containing linearly ligating π ligands at the other end of the spectrum: carbonyl groups with vacant π* orbitals.[10] There is a middle ground, dominated by metal ligand covalency and typified by the carbyne moiety, in which the energies of the ligand π functions are approximately equal to the metal dπ orbital energies (Figure 1). Metal carbyne complexes have been prepared for a variety of metals and d electron configurations,[11] as typified by the Fischer and Schrock examples, $Cr\equiv CPh(CO)_4Br^{12}$ and $(\pi-C_5Me_5)(PMe_3)_2Ta\equiv CPh(Cl)$,[13] respectively. The carbyne moiety has been considered a strong π-acceptor when counted as a cationic analogue of CO, $[:CR]^+$, or as a π-donor when counted as a trianion analogous to O^{2-}, $[:\ddot{C}-R]^{3-}$. Hoffmann has avoided the oxidation state formalism by considering the neutral carbyne as a building block, $:\dot{C}-R$, with two electrons arbitrarily assigned

Table I. Structural Parameters for d^0 MO_2^{2+} Complexes

M	X_2^{ℓ}	L_2^{ℓ}	M–O, Å	α	β	γ	ref
V		edta	1.65	107	76	202	5e
V		edtaH$_2$	1.64	107	75	201	5d
V		ox	1.64	104	78	208	5c
Mo	F	F	1.71	95	79	194	a
Mo	Br	Me$_2$SO	1.65	102	77	198	b
Mo	Br	dmf	1.68	102	76	200	c
Mo	Br	OPPh$_3$	1.71	103	77	193	20
Mo	Cl	OPPh$_3$	1.71	103	78	195	20
Mo	Br	bipyr	1.73	103	67	200	d
Mo	CH$_3$	bipyr	1.71	110	68	211	5a
Mo	PhacPhac		1.70	105	75	200	e
Mo	bu		1.66	105	79	215	20
Mo	Het		1.72	106	77	208	f
Mo	bz		1.73	103	79	204	g
Mo	Sbz		1.71	104	78	202	h
Mo	salen		1.71	103	80	204	i
Mo	dprtc		1.70	106	82	209	j
Mo	detc		1.63	114	80	211	k

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to the σ-donor orbital and the remaining electron assigned to the two orthogonal carbon pπ orbitals.[2] Other formalisms are

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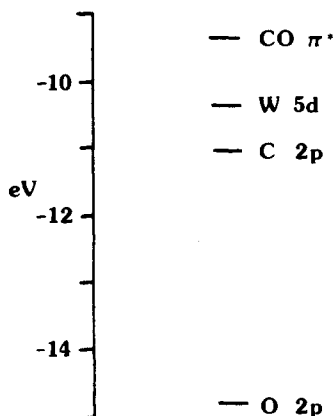[†] University of North Carolina.
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Figure 1. Atomic and molecular orbital energies.

Table II. Bond Lengths Used in MO Calculations

linkage	distance, Å	linkage	distance, Å
M–O (dioxo)	1.70	M–CH	1.90
M–H	1.70	C–O	1.20
M–CO	1.90	C–H	1.00

available which stress yet other aspects of M≡CR binding: ·Ç–R is primed for formation of three covalent bonds and [:C̈–R]⁻ can be considered to be crudely isolobal with RC≡CR, η^2-CH=CH$_2^-$ and η^2-C=CO⁻.[14]

This variety of formalisms regarding a sensible oxidation state convention reflects the range of metal dπ orbital energies available relative to the carbyne π orbitals: high oxidation state metals present low energy contracted dπ orbitals and encourage the CR moiety to function as a π-donor while low oxidation state, electron rich metals promote carbyne π-acid character.[15]

In earlier work we discussed the role of single-faced π-donor ligands in formally electron deficient octahedral group VI complexes containing π-acid ligands.[16] We now explore the electronic structure of biscarbyne complexes with the dioxo moiety serving as a useful point of departure. Conflicts apparent in the metal–ligand π-framework of biscarbynes have direct implications for octahedral monomers which bind both π-donor (O²⁻) and π-acceptor (CO) ligands.

These results are relevant to synthetic strategies designed to

Figure 2. Models and coordinate systems employed in the calculations.

Figure 3. Total energy of *cis*-[MoO$_2$H$_4$]²⁻ as a function of α, β, γ. The zero of energy is arbitrary.

cleave triple bonds in small molecules such as RC≡CR, RC≡N, and N≡N with mononuclear metal reagents. Microscopic reversibility addresses coupling reactions simultaneously. Some related coupling reactions have been achieved at single metal centers.[17] Although our considerations are limited to monomers we note that elegant dinuclear chemistry has succeeded in accomplishing direct alkyne and nitrile cleavage.[18]

Calculational Details. The extended Hückel molecular orbital program developed by Hoffmann was employed.[19] The metal–oxo

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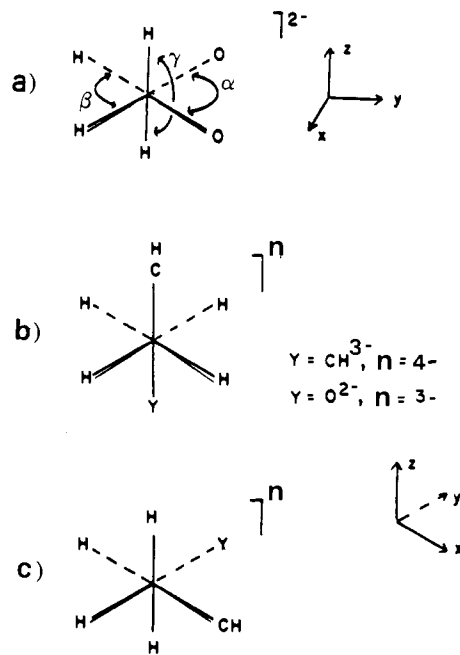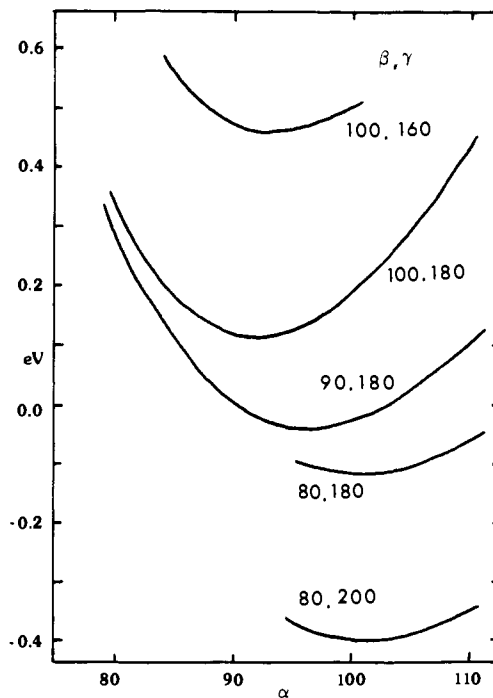(16) Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 7713.

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Table III. Degree of Bonding[a] as a Function of α, β, γ

α	β	γ	H_{eq}	H_{ax}	O	rel energy, eV
90	90	180	0.853	0.849	1.319	0.000
100	80	160	0.857	0.833	1.272	+0.206
100	80	180	0.860	0.847	1.331	-0.110
100	80	200	0.863	0.884	1.342	-0.395

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distance for $MoO_2H_4^{2-}$ was fixed at 1.70 Å (see Table I). The angles (α, β, γ) in $MoO_2H_4^{2-}$ were varied from (70, 70, 160) to (120, 110, 210), and the electronic structure was obtained for selected points in this space. Bond lengths for biscarbyne and oxo–carbyne calculations are collected in Table II. Coordinate systems employed in the calculations are shown in Figure 2.

Results and Discussion

Dioxo Complexes. Before considering carbyne complexes we will establish a framework for three-center ligand π–metal dπ interactions in octahedral complexes with two oxo ligands. Extensive rules governing ligand site occupation in d^0 $MO_2X_2L_2$ monomers have been published.[20] Weak π-donors occupy sites trans to terminal oxygens to minimize competition for dπ orbitals. The *cis*-MO_2 unit allows all three metal dπ orbitals to accept O^{2-} π-donation and is favored for d^0 configurations. *trans*-MO_2 moieties are favored for d^2 configurations (the metal electron pair can reside in the lone dπ orbital which is not destabilized by O^{2-} π-donation[9]). In addition to these basic dπ bonding concepts we need to consider angular distortions prior to analyzing the carbyne complexes of interest.

The total energy of *cis*-$MoO_2H_4^{2-}$ as a function of α, β, and γ is depicted in Figure 3. As β decreases, the minimum moves to lower energy and larger α. Making γ larger (moving the axial hydrides away from the oxo ligands) dramatically stabilizes the model complex. The global minimum in our calculations lies at (α, β, γ) = (101, 80, 200). Thus, despite the simplifications used to assemble the model, the calculations successfully mimic distortions evident in experimentally determined structures (see Table I).

The Walsh diagrams in Figure 4a,b track the frontier orbitals as β and γ are varied, respectively, for α = 100°. The d_{yz} orbital is restricted to purely π interactions when γ = 180°. Overlap between the axial hydrides and the d_{yz} orbital increases equally whether γ is increased or decreased from 180°. From this point of view there should be no energetic preference for $\gamma > 180°$, but substantial stabilization occurs as γ increases from 160° to 200°. The crucial factor is the d_{yz} orbital distribution among several s–p–d hybrids, and this *set* of interactions favors $\gamma > 180°$. These orbitals are sketched in Figure 4b for (α, β, γ) = (100, 80, 200). The $2b_2$ orbital is strongly hybridized toward the axial hydrides in a bonding fashion, and this interaction is enhanced as γ increases. The $3b_2$ orbital (chiefly d_{yz}) is hybridized so that its nodes lie along the Mo–axial hydride vectors. The lobes of this d_{yz} function balloon toward the oxygen p_z orbitals as γ increases and this enhances Mo–O π bonding. Note the increased degree of metal–ligand bonding as γ increases (Table III). For $\gamma < 180°$, the phase of mixing between Mo p_z and d_{yz} is reversed, the Mo–O π interaction in $3b_2$ is diminished, and the molybdenum bonds to the axial hydrides are weakened.

The optimal value of α and the total energy are both sensitive to β. Figure 4a shows that the effect of varying β is concentrated in one filled orbital, $3a_1$. This orbital is Mo–H bonding and good overlap between molybdenum and the equatorial hydrides occurs for small values of β. Hybridization of $d_{x^2-y^2}$ occurs into $1a_1$ as β decreases. This distortion increases the π interaction with the oxygens only slightly as $1a_1$ drops by less than 0.05 eV as β decreases from 100° to 80°. At (β, γ) = (100, 180), the $d_{x^2-y^2}$
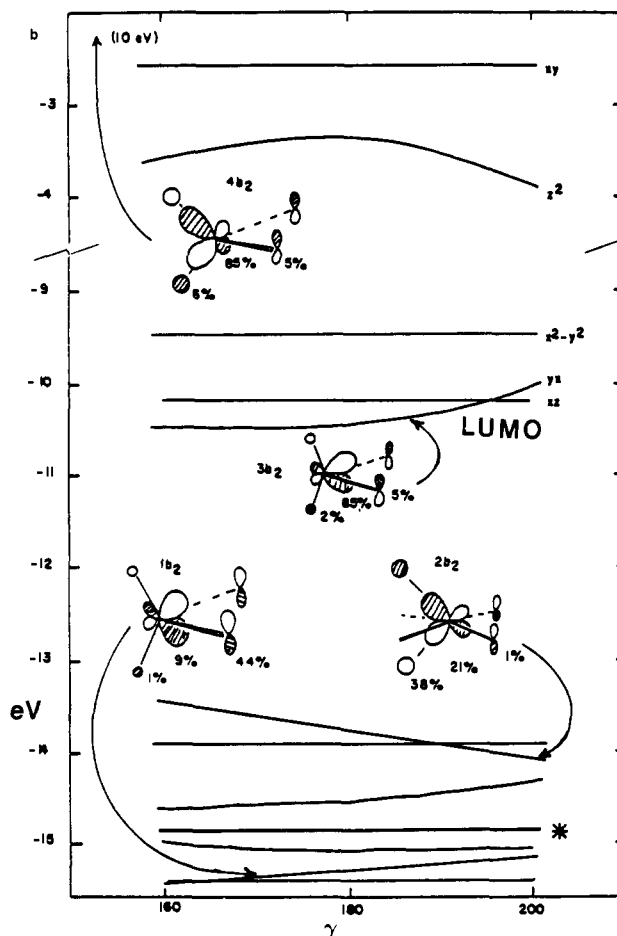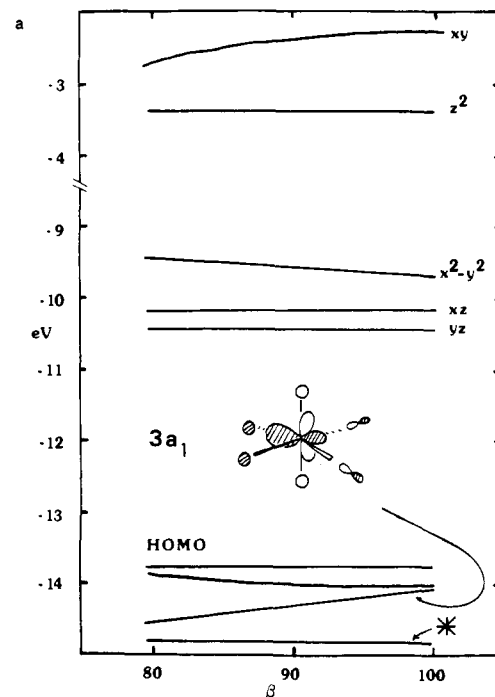
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Figure 4. (a) Walsh diagram for $[MoO_2H_4]^{2-}$ as a function of β. α is fixed at 100° and γ at 180°. The orbital marked with an asterisk is the nonbonding 2p orbital combination. (b) Walsh diagram for $[MoO_2H_4]^{2-}$ as a function of γ. α is fixed at 100° and β at 80°. The orbital marked with an asterisk is the nonbonding O 2p orbital combination.

π interaction with oxygens is diminished by a destructive admixture of p_y. However, the phase of mixing reverses when β passes through 90° and closes to 80°, once again allowing optimal π bonding between this orbital and the oxygens.
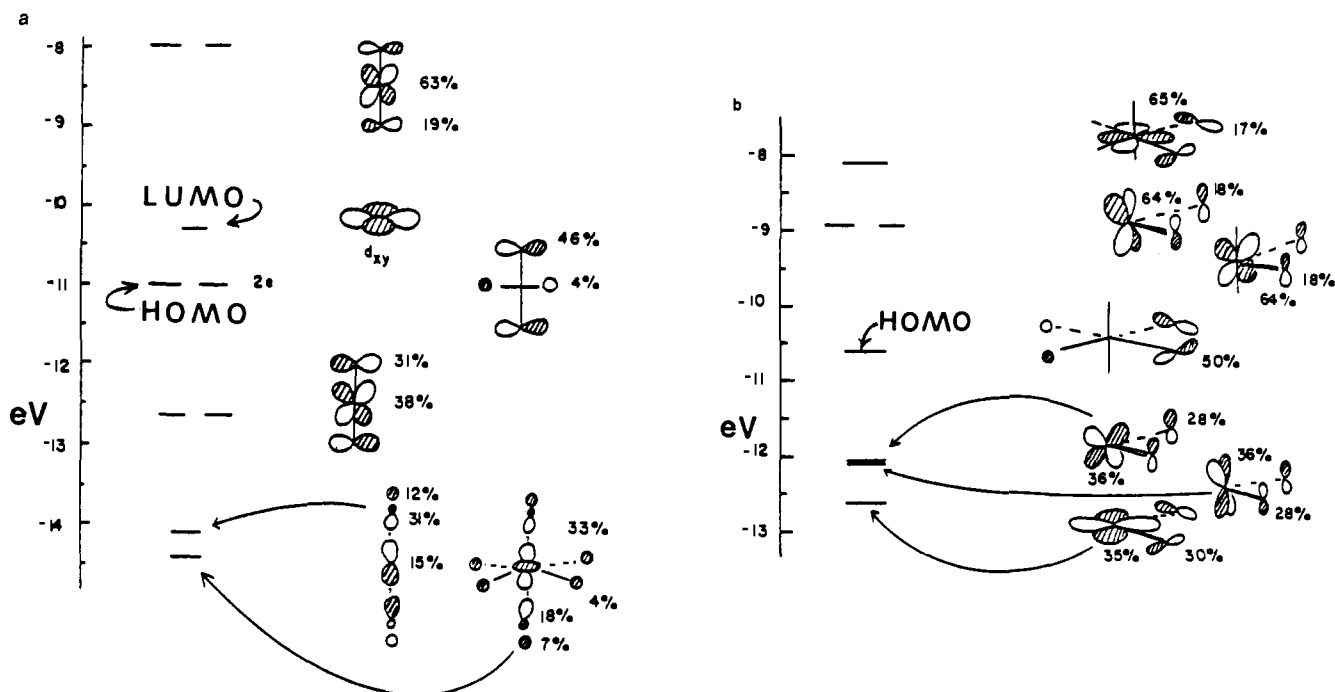
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Figure 5. (a) Orbital energy diagram for *trans*-[W(CH)$_2$H$_4$]$^{4-}$. Some low-lying functions (−14 to −15 eV) have been omitted for clarity. (b) Orbital energy diagram for *cis*-[W(CH)$_2$H$_4$]$^{4-}$. Some low-lying functions (−12 to −14 eV) have been omitted for clarity.

The obtuse O–M–O angle in concert with distortions of the remaining ligand positions reflect an interplay between σ and π interactions. In very qualitative terms the observed distortions provide more "metal orbitals" for the two π-bonding oxo ligands at the expense of the four σ-only ligands.

Biscarbyne Complexes. *cis*- and *trans*-[W(CH)$_2$H$_4$]$^{4-}$ were assigned a net charge consistent with a d^0 metal configuration, formally W^{6+}, with CH arbitrarily assigned as CH^{3-} analogous to O^{2-}. Energy level diagrams for the two biscarbyne isomers are shown in Figure 5. The *trans*-[W(CH)$_2$H$_4$]$^{4-}$ diagram contains three nonbonding orbitals: d$_{xy}$ dominates the LUMO and degenerate carbon 2p combinations constitute the HOMO. The trans isomer is thermodynamically favored for a d^2 metal which fills the d$_{xy}$ level; the rationale is the same as in the dioxo d^2 case. Regardless of configuration, however, the crucial issue is the reactivity anticipated for the strictly nonbonding carbon based orbitals near −11 eV. Although a nonbonding metal d orbital in this energy range is acceptable for modelling a real molecule, the inherent potential for exothermic reaction associated with a carbon 2p orbital indicates that isolation of a *trans*-W(CR)$_2$L$_4$ complex, either d^0 or d^2, is unlikely. When filled this degenerate 2e set will be nucleophilic, crudely resembling a carbanion. Furthermore no perturbation of the four equatorial ligands enhances the stability of the axial carbynes. As a referee noted the plus combination of trans π ligand orbitals simply has no metal orbital mate. A carbon with only three bonds is not a viable chemical option.

A similar orbital deficiency at the metal, now three dπ orbitals to satisfy four carbyne 2p orbitals, characterizes the *cis*-[W-(CH)$_2$H$_4$]$^{4-}$ isomer. Here the minus combination of ligand π orbitals is isolated with no suitable metal dπ mate. Thus the cis case is also subject to electrophilic attack at the carbon based HOMO. Related arguments apply regardless of electron count; removal of electrons from the carbyne based HOMO of either the cis or trans isomer generates an electrophilic reagent, crudely resembling a carbonium ion.

Note that similar ligand based orbital combinations exist for *cis*-dioxo and *cis*-dicarbonyl complexes, but the functions either lie very low in energy and are happily filled (the oxo case) or are high in energy and remain empty (the carbonyl case).

Oxo–Carbyne Complexes. The electronic structure of *trans*-[W(CH)(O)H$_4$]$^{3-}$ is shown in Figure 6. The HOMO–LUMO gap, 1.44 eV, is adequate for a stable complex, but the presence of a vacant metal-localized nonbonding level, d$_{xy}$, indicates that the full binding potential of the metal has not been exploited. The
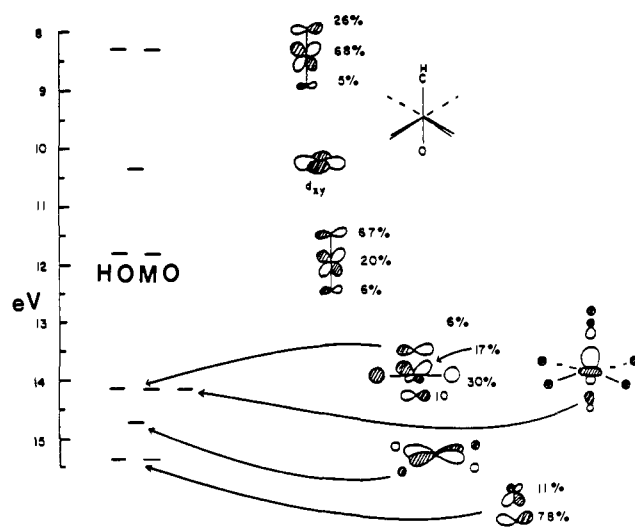

Figure 6. Orbital energy diagram for *trans*-[W(CH)(O)H$_4$]$^{3-}$. Some low-lying functions have been omitted for clarity.

Table IV. Energy Partitioning and HOMO Energy for Equatorial Distortion of *trans*-[W(CH)(O)H$_4$]$^{3-}$ (eV)

inter-action	distortion, deg						
	toward carbyne 20	10	5	0	5	toward 10	oxo 20
Mo–H	−4.96	−4.99	−5.01	−5.02	−5.02	−5.00	−4.89
Mo–C	−8.00	−10.02	−10.67	−11.16	−11.52	−11.77	−12.02
Mo–oxo	−9.71	−9.37	−9.20	−9.02	−8.81	−8.56	−7.82
HOMO	−10.64	−11.36	−11.62	−11.82	−11.96	−12.05	−12.13

degenerate HOMO pair at −11.81 eV results from competition between the oxo ligand and the carbyne for π bonding. In contrast to the biscarbyne case, however, it is possible to stabilize this ligand-based p-orbital combination. Moving the hydrides toward the oxo ligand causes the metal d orbital contribution in this degenerate e set to balloon toward the carbyne ligand and enhances M≡CH bonding. This stabilization, predicted by Bennett and Mason[21] and by Elian and Hoffmann[22] for distortions of equatorial
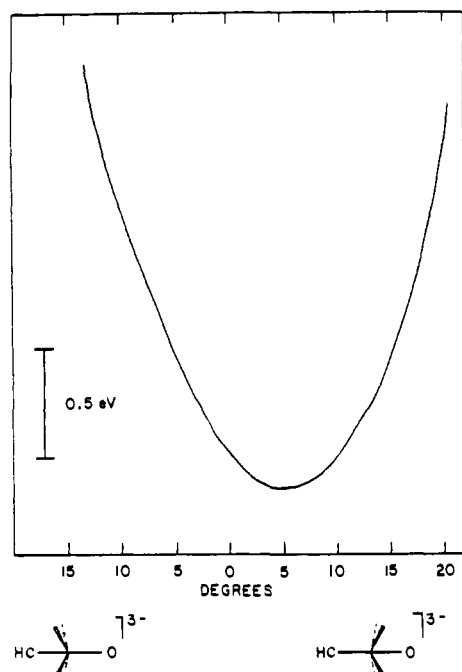
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(22) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

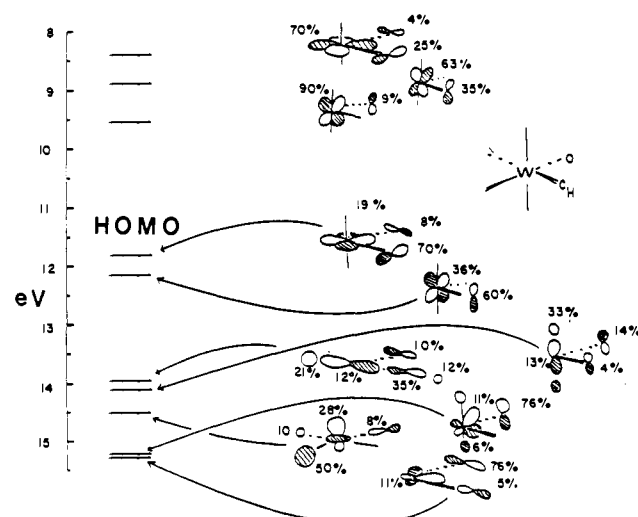**Figure 7.** Total energy of *trans*-[W(CH)(O)H₄]³⁻ as a function of distortions in the equatorial positions.

Figure 8. Orbital energy diagram for *cis*-[W(CH)(O)H₄]³⁻. Some low-lying orbitals have been omitted for clarity.

carbonyl groups, is confirmed for small deformations as shown in Figure 7. As expected, the degenerate HOMO set is chiefly responsible for the decline in total energy which occurs as the hydrides are moved toward the oxygen (Table IV). In contrast the total energy rises sharply when the hydrides are bent toward the carbyne ligand as this distortion diminishes the W≡CH π interaction.

The electronic structure of *cis*-[W(CH)(O)H₄]³⁻ is shown in Figure 8. The undistorted d^0 cis isomer (−398.2 eV) is favored relative to the undistorted d^0 trans isomer (−398.0 eV). Utilization of all three dπ orbitals is possible in the cis case while the equatorial dπ orbital is π-innocent in the trans complex. The large HOMO–LUMO gap, 2.18 eV, and the absence of nonbonding orbitals suggest that the cis model could represent a stable molecule. The LUMO1 and LUMO2 orbitals are W–O and W–C π* functions, respectively. The greater covalency of the carbyne-metal interaction is evident in the much greater ligand component in LUMO2. The HOMO orbitals, also O and C 2p combinations, lie near −12 eV, and ligand distortions could further stabilize them. In the Mo(VI) dioxo calculations, the natural distortion coordinates retained the C_{2v} symmetry of the model.

Table V. Relative Total Energies and Energies of Frontier Orbitals of *cis*-[W(CH)(O)H₄]³⁻ (eV)

| distortion	rel energy	LUMO	HOMO1	HOMO2
none, octahedral axial hydrides	0.00	−9.57	−11.75	−12.11
10° away from CH	−0.24	−9.57	−11.75	−12.27
10° toward CH	+0.76	−9.58	−11.63	−11.75
10° away from O	−0.15	−9.30	−11.75	−12.13
10° toward O equatorial hydrides	+0.35	−9.66	−11.75	−12.12
100°	+0.21	−9.57	−11.70	−12.12

Scheme I
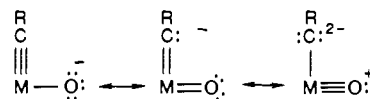
In this case the symmetry is much lower (C_s), but we chose to explore only two axial hydride modes: (1) movement in the metal–oxo plane and (2) movement in the metal–carbyne plane. Since the HOMO consists of a tungsten–carbyne d_{xz}–pπ interaction, it will be sensitive to motion in the *xz* plane. The metal–oxo interaction will be less sensitive to changes in molecular geometry; the bonding is less covalent. As shown in Table V, the total energy of the complex is reduced by 0.24 eV when the axial hydrides bend 10° away from the carbyne ligand in the *xz* plane, largely due to stabilization of the HOMO2. A smaller reduction in the total energy, 0.15 eV, results when the hydrides are bent away from the oxo ligand in the *yz* plane. The behavior of the LUMO orbital, which is destabilized by 0.27 eV, shows that the trend in total energy along the second distortion mode derives chiefly from changes in W–O π bonding. Stabilization occurs along both distortion coordinates because interactions among filled orbitals are enhanced when the axial hydrides bend away from either the carbyne or oxo ligand.

Moving the equatorial hydrides together, as in the dioxo case, reduces the total energy as expected by analogy (Table V). The stabilization of 0.07 eV that results at an equatorial hydride angle of 80° can be traced to a lower energy HOMO. Ballooning the metal d_{xy} orbital toward the carbyne ligand enhances both π bonding to CH and π antibonding to O; for small deformations the bonding effect dominates.

The calculations suggest that *cis*-(oxo–carbyne) complexes may be preparable. They indicate that a d^0 configuration will be optimal, again counting the carbyne as CR³⁻ (or alternatively a d^4 configuration with CR⁺), since all filled orbitals are net bonding. Some weakening of the metal–oxo interaction occurs due to occupation of the HOMO1 which has an antibonding admixture of an oxygen pπ function. However, the carbyne–metal bond is substantially weakened if these electrons are removed. In the dioxo case a similar conflict is resolved by retaining the lone pair character of oxygen p electrons as a filled, nonbonding O 2p orbital combination at low energy (see Figure 4). For two carbynes the inherent reactivity of the free carbon 2p orbitals makes 3-center interactions unattractive whether the nonbonding ligand-based level is filled or vacant as discussed above. For the intermediate oxo–carbyne case the resolution of the conflict may be framed qualitatively from simple resonance arguments (Scheme I). Oxygen will tolerate localization of electron pairs and sacrifice some of the shared dπ orbital to meet the covalent needs of the adjacent carbyne.

Distant analogues of the model M≡CR(O)L₄ complexes proposed here are the XM(CO)₄(CR) complexes prepared by Fischer and co-workers,[12] all containing *trans*-halide–carbyne arrangements. Calculations by Kostic and Fenske[1b] show that the halide is a negligible contributor to π bonding. Counting the carbyne moiety as [CR]³⁻ gives the metal center a formal 4+ charge in the Fischer complexes, a d^2 configuration. We wish to assess the properties of oxo–carbyne complexes which place different demands on the energy and occupancy of the dπ orbitals. The high degree of covalency in the carbyne–metal interaction

Scheme II
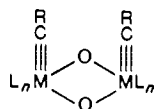
Scheme III
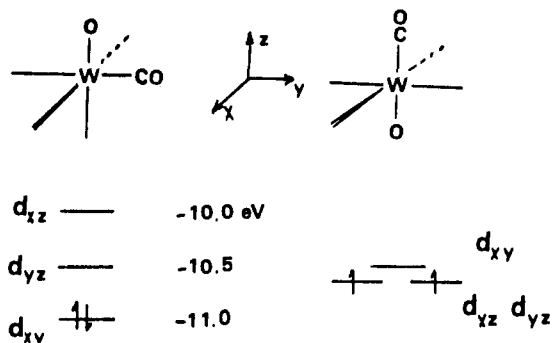
limits the utility of conventional oxidation state descriptions in any case. Nonetheless it is accurate to depict the proposed d^0 cis-(oxo–carbyne) (O^{2-},CR^{3-}) complexes as electron rich at oxygen. One attractive reaction path available to such a monomer is dimer formation as shown in Scheme II. This removes the π-bonding requirement of the oxo ligand and cancels the $d\pi$-orbital conflict responsible for excessive electron density on the terminal oxygen in the monomer.

Oxo–Carbonyl Complexes. A d^2 octahedral oxocarbonyl derivative, $W(O)(CO)(PPh_2Me)_2Cl_2$, has recently been reported by Rheingold, Mayer, and co-workers.[23] Given that the conflict

characterizing identical π ligands trans to one another (either π-acidic or π-basic) can be eliminated by replacing one with a π-innocent ligand, what is the effect of a strong π-donor trans to a strong π-acceptor?

The isolated $d\pi$ orbital energies (Scheme III) for cis and trans d^2 $[M(O)(CO)H_4]^{2-}$ model compounds answer this question and also reveal why the cis isomer is favored. Clearly π-acid and π-base ligands prefer to avoid sharing $d\pi$ orbitals. In terms of three-center $d\pi$–ligand π interactions, the shared $d\pi$ orbital is pushed up by π-donation and down by π-acceptance. The two effects nearly cancel one another in the $M(O)(CO)$ case, and this cancellation leads to a net nonbonding result.

The trans $O{=}M{—}CO$ arrangement produces three nearly degenerate $d\pi$ orbitals. The d_{xy} orbital is π-innocent and conflicting oxygen 2p donation and CO π^* acceptance leave d_{xz} and d_{yz} near their original energies. The cis-$M(O)(CO)$ moiety allows for two constructive 2-center 2-electron π bonds: stabilization of the lone filled $d\pi$ level by CO π^*_x and destabilization of the vacant d_{xz} by O p_x. The remaining $d\pi$ orbital is shared by O^{2-} and CO and is nearly nonbonding. It is vacant in the d^2 tungsten monomer which has been isolated. A d^4 configuration would bind the CO more tightly but the confrontation of the oxide p_y with a filled d_{yz} would weaken the $M{=}O$ bond and create a nucleophilic terminal oxygen analogous to the $M(CO)(CR)L_4$ d^0 monomer discussed above.

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Nuclear Magnetic Resonance Proton Relaxation in Bimetallic Complexes Containing Cobalt(II)

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Abstract: The ^1H NMR spectra of $CoM(PMK)_3^{4+}$, where M is Zn^{2+}, Co^{2+}, Ni^{2+}, or Cu^{2+}, and PMK = 2,5-bis(2-pyridyl)-3,4-diazahexa-2,4-diene, have been analyzed with the aim of understanding nuclear and electron relaxation rates. Very short electron relaxation rates have been found for $CoZn(PMK)_3^{4+}$ and $Co_2(PMK)_3^{4+}$. The cobalt(II) has a significant influence on the electronic relaxation times of copper and nickel in the $CoCu(PMK)_3^{4+}$ and $CoNi(PMK)_3^{4+}$ complexes, thereby dramatically sharpening their ^1H NMR peaks as compared to those of the $ZnCu(PMK)_3^{4+}$ and $ZnNi(PMK)_3^{4+}$ complexes. Modifications of the Solomon equations are proposed to interpret the relaxation rates in magnetically coupled equations. We find that a magnetic coupling constant slightly larger than the maximum dipolar coupling between Cu(II) and Co(II) is capable of making the signals of protons on ligands bound to Cu(II) essentially as sharp as those bound to the high-spin, six-coordinate, cobalt(II). Supporting magnetic and variable-temperature T_1 data are included.

The understanding of nuclear relaxation induced by paramagnetic metal ions can, in principle, provide information on the structure of (Figure 1), under investigation and on the time-dependent phenomena concerning the resonating nucleus.[1-4] A theoretical description of the coupling between the nucleus and the unpaired electron has been proposed under a variety of conditions.[5-16] The contributions to nuclear relaxation have been identified and their magnitudes predicted on the basis of appropriate spin Hamiltonians.[12-16] Such treatments pertain, however, to isolated paramagnetic metal ions or to two magnetically coupled $S = 1/2$ ions.[17a] No theory and almost no experimental data are

described for other heterobimetallic systems where both metal ions are paramagnetic and magnetically coupled.

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