

NMR Spectroscopic and Theoretical Investigation of the Bonding in $W_3(OR)_9(\mu_3-CCH_3)$ and Its Comparison to $Co_3(CO)_9(\mu_3-CCH_3)$.

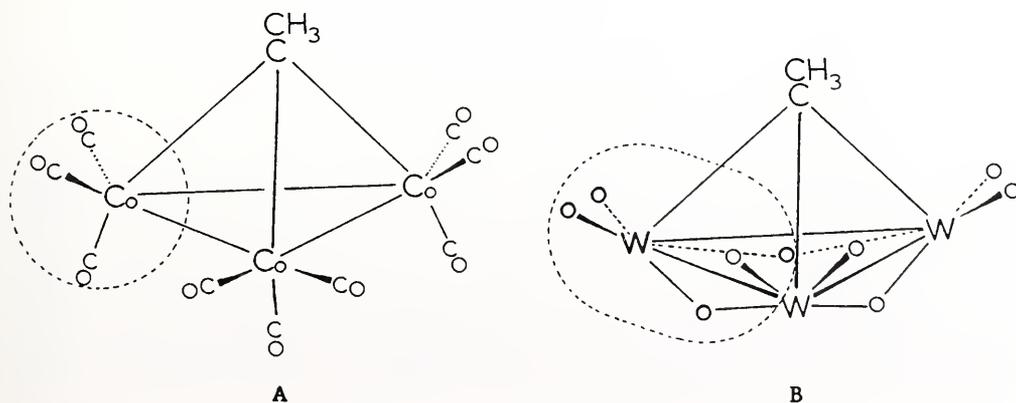
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Introduction

Metal clusters have in the last number of years been proposed to be models for the study of reactivity on metal surfaces. This proposed modeling of surfaces has been the driving force behind much synthetic and theoretical organometallic chemistry. Among the oldest, and most thoroughly studied organometallic clusters are the alkyldiyne capped tricobalt nonacarbonyls. Of particular interest with respect to such alkyldiyne capped trinuclear clusters is the nature of the bond between the metal cluster fragment, $M_3L_9^{3+}$, and the small organic fragment, the alkyldiyne. Theoretical studies (1) and the short C-C single bond distance (1.37 Å) from the crystal structure of $[(CO)_9Co_3C]_2$, (2) indicative of a butadiyne type conjugation of π systems, suggest that the apical carbon of the $Co_3(CO)_9(\mu_3-CR)$ clusters is approximately sp hybridized. While there is not yet such conclusive experimental evidence for the early transition metal complexes, $W_3(OR)_9(\mu_3-CR)$, alkyl like $^{13}C-^{13}C$ and $^{185}W-^{13}C$ one bond coupling constants, typical of an sp^3 hybridized apical carbon, suggest that some variation exists in the mode of alkyldiyne to metal cluster bonding between clusters of early and late transition metals. Fenske-Hall Molecular Orbital calculations of $Co_3(CO)_9(\mu_3-CCH_3)$ and $W_3(OH)_9(\mu_3-CCH_3)$ support this experimental trend. Beyond possible insight into the binding of small organic fragments to metal surfaces, an understanding of such a bonding variation between clusters of early and late transition metals may elucidate a range or limits to the isolobal analogy between organometallic and organic fragments.

Results and Discussion

The alkyldiyne capped tricobalt nonacarbonyl and tritungsten nonaalkoxide clusters are electronic and structural analogues. Electronically the metals Co^{+1} and W^{+4} may be related by a d^8-d^2 electron/hole formalism. Structurally the tungsten and cobalt clusters are related by their M_3C core. The arrangement of the supporting ligands, however, is different in each cluster. The nine carbonyl ligands of the cobalt cluster are terminally bound in such a way as to give the local pseudo-octahedral geometry about each cobalt seen in structure A. Thus one may visualize the $Co_3(CO)_9(\mu_3-CR)$ clusters as the assemblage of three ML_3 fragments capped by a triply bridging alkyldiyne. By contrast three of the



nine alkoxide ligands in the tungsten cluster bridge each of the three metal-metal bonds, the other six are terminal. This results in the pseudo-square based pyramidal geometry about each tungsten seen in structure B. A division of each bridging alkoxide allows the tungsten cluster to be visualized as the assemblage of three ML_4 fragments, capped by a triply bridging alkylidyne ligand.

The molecular orbital interaction diagram of the $Co_3(CO)_9^{3+}$ and CCH_3^{3-} fragments is shown in Figure 1. On the left are the fragment orbitals resulting from the assemblage

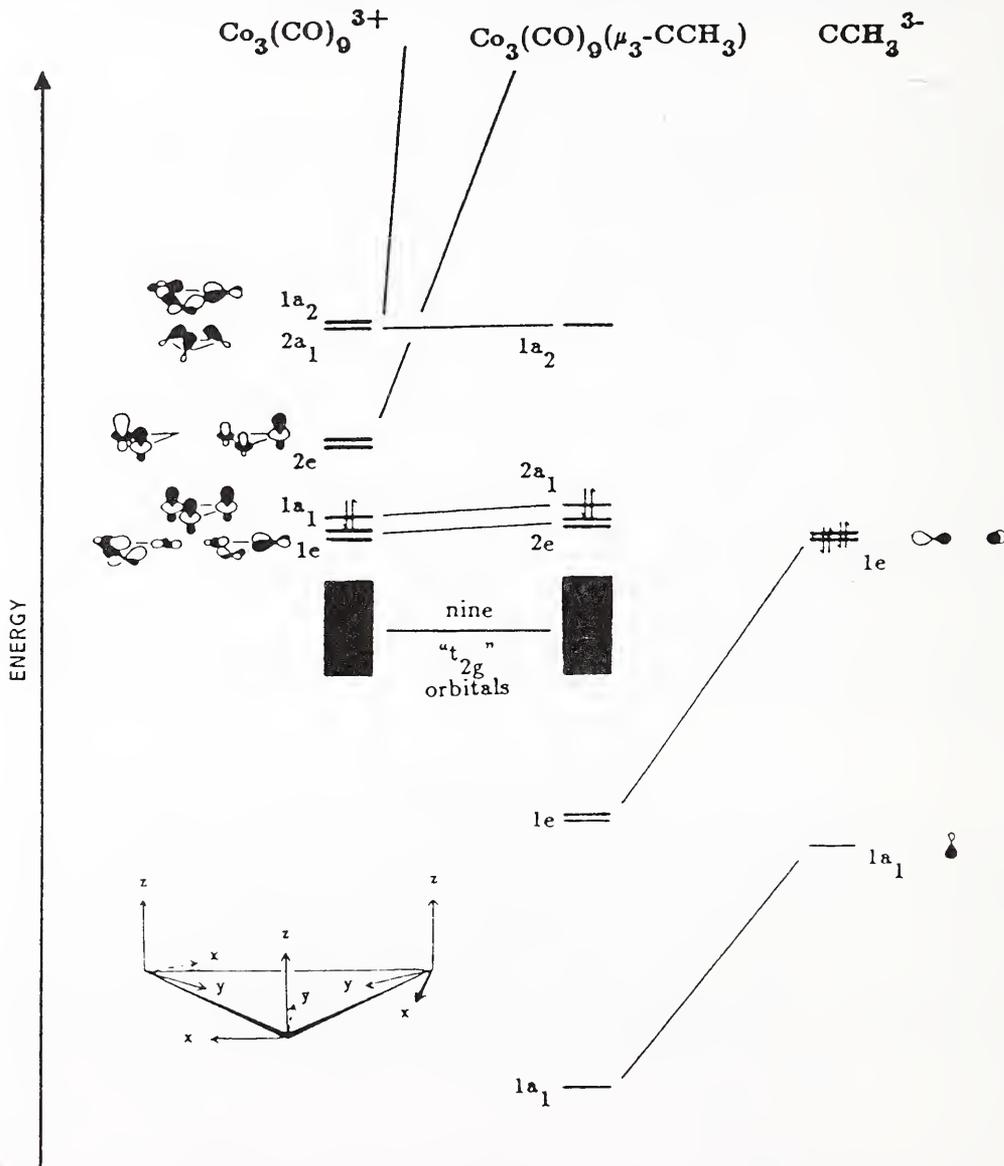


FIGURE 1: Interaction diagram for $Co_3(CO)_9(\mu_3-CCH_3)$.

of three ML_3 fragments. Of lowest energy are the nine pseudo- t_2 orbitals derived from linear combinations of the non-bonding t_2 orbitals of the ML_3 fragment. These orbitals have been stabilized by π -back bonding to the CO π^* orbitals, but undergo no further interaction with the cluster. The $1a_1$ and $1e$ metal cluster fragment orbitals, formally derived from metal-ligand σ -antibonding orbitals, form the metal-metal bonds leaving the $2e$, formally metal-metal and metal-ligand σ -antibonding, and the high lying $2a_1$, an spd hybrid, to interact with the incoming alkylidyne. This interaction is insufficient to in-

duce a rehybridization of the alkylidyne fragment orbitals. Instead the $1a_1$, sp-like hybrid of the alkylidyne is delocalized between all three metal atoms (1).

In contrast, both the ligand field and electron count of the tungsten cluster present a considerably different bonding picture, described in the interaction diagram of Figure 2. The important $W_3(OR)_9^{3+}$ fragment orbitals are pictured to the left of the interaction

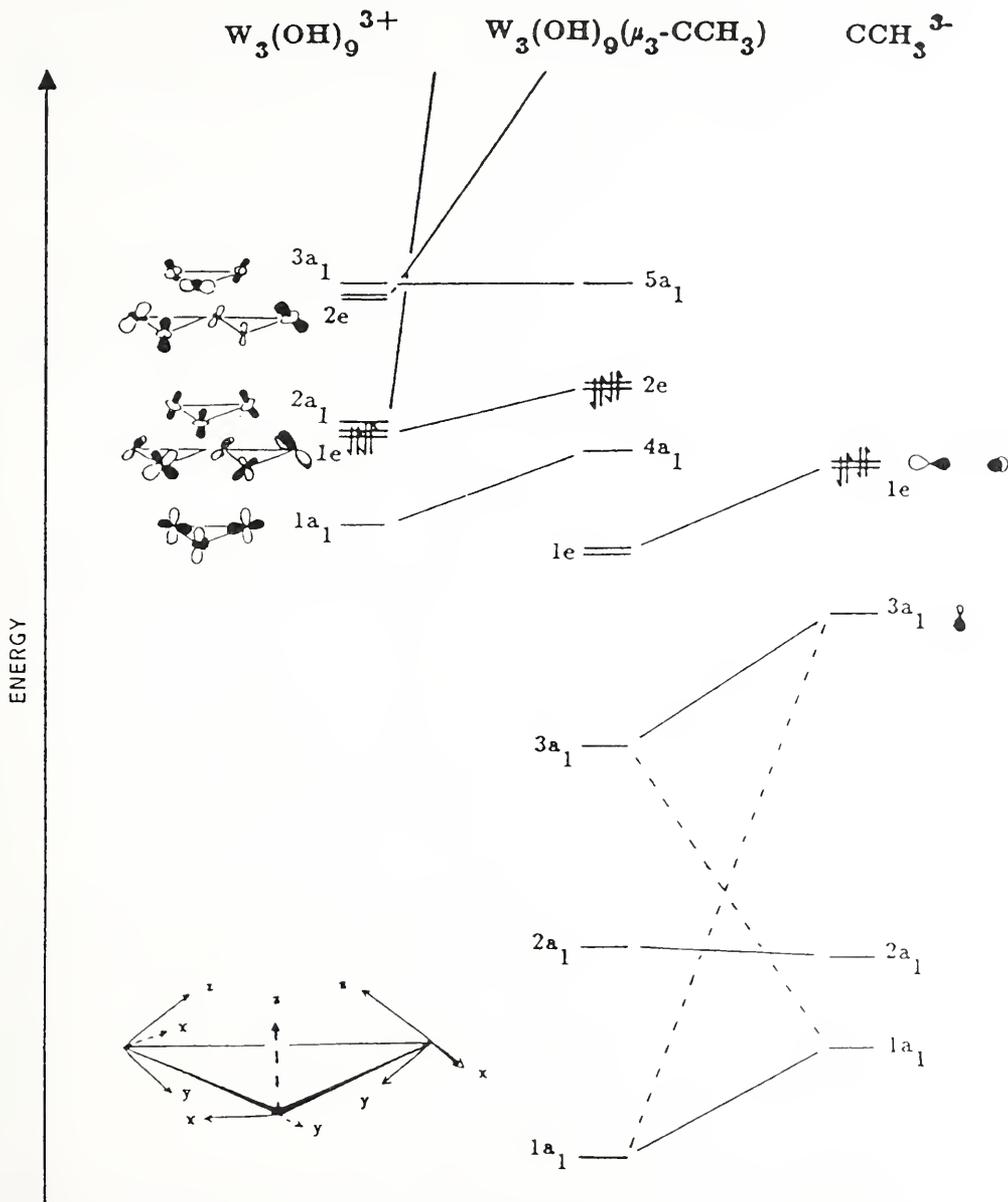


FIGURE 2: Interaction diagram for $W_3(OH)_9(\mu_3-CCH_3)$.

diagram. Not represented are the higher lying metal based orbitals, destabilized by π donation of the alkoxide ligands, and the highest metal-ligand antibonding orbitals. The $1a_1$, $2a_1$, and $1e$ cluster fragment orbitals, with six electrons, form the metal-metal bonds. These as well as the slightly higher $2e$ orbitals have been derived from linear combinations of the formally non-bonding orbitals of the ML_4 fragments, providing a more favorable energy match with the alkylidyne fragment than was provided by the antibonding orbitals of the cobalt fragment. The net result of this interaction is a severe rehybridiza-

tion of the sp-like $3a_1$ alkylidyne fragment orbital such that in the final $W_3(OR)_9(\mu_3-CCH_3)$ cluster the $C2s$ character of the former sp-like hybrid is now in the $1a_1$ cluster orbital, leaving the alkylidyne component of the $3a_1$ cluster orbital to be 99.9% $C2p_z$.

This separation of the $C2s$ and $C2p_z$ character is reminiscent of the molecular orbital description of the classical sp^3 -hybrid, methane. When viewed from the perspective of C_3 symmetry, both a classical sp and an sp^3 hybridized carbon should have two molecular orbitals of a_1 symmetry and one set of orbitals of e symmetry. Both a_1 orbitals of the sp hybrid should contain an approximately 50:50 mixture of the $C2s$ and $C2p_z$, whereas the sp^3 hybrid should have the $C2s$ character localized in the $1a_1$ orbital and the $C2p_z$ character localized in the $2a_1$ orbital. Thus we suggest that the apical carbon of $Co_3(CO)_9(\mu_3-CCH_3)$ is hybridized in an sp -like fashion while the apical carbon of $W_3(OR)_9(\mu_3-CCH_3)$ is hybridized in an sp^3 -like manner.

We had hoped to make use of the correlation established for organic systems (3) between the hybridization of carbon atoms and their one bond coupling constants. Unfortunately the ethylidyne one bond carbon-carbon coupling constants of both clusters were found to be virtually identical, and of the magnitude expected for an sp^3 - sp^3 interaction (see Table 1). Furthermore the ethylidyne coupling constant ($^1J_{13C-13C}$) of the

Table 1. A Comparison of $^1J_{13C-1H}$, $^1J_{13C-13C}$, $^1J_{183W-13C}$, and the Total $C2s$ - $C2s$ Overlap Population.

	$^1J_{13C-1H}$	$^1J_{183W-13C}$	$^1J_{13C-13C}$	$C2s-C2s$ O.P.
$W_3(O^iPr)_9(\mu_3-CCH_3)$	126.4	136.9	36.1	0.141
$(^tBuO)_3W \equiv CCH_3$	126.8	302.1	32.2	0.129
$Co_3(CO)_9(\mu_3-CCH_3)$	127.7	—	31.2	0.119
$HC \equiv CCH_3$	131	—	67.4	—
$HC \equiv CH$	248.7	—	170.6	—
$(^tBuO)_3W \equiv CH$	150	289	—	—

tungsten alkylidyne monomer, $(^tBuO)_3W \equiv CCH_3$, is 32.2 Hz rather than the approximately 60 Hz coupling expected for an sp - sp^3 interaction as seen in $HC \equiv CCH_3$. This suggests that a one bond carbon-carbon coupling constant analysis is not a valid measure of the hybridization of a metal bound carbon. Nonetheless, the direct correlation between the one bond carbon-carbon coupling constants and the calculated total $C2s$ - $C2s$ overlap population suggests that one can legitimately infer the polarization of the $C2s$ orbital from the coupling constants.

Conclusion

While the one bond carbon-carbon coupling constants have been shown to be an ineffective probe into the bonding between alkylidyne and trinuclear metal fragments, Fenske-Hall Molecular Orbital calculations have shown a variation to exist between the bonding of the $Co_3(CO)_9(\mu_3-CCH_3)$ and $W_3(OR)_9(\mu_3-CCH_3)$ clusters. Current experimental work is anticipated to confirm this trend. The significance of this bonding variation is best explained by the contrasting isolobal analogies presented by these two clusters (Figure 3). With an sp -like hybridization of its apical carbon the alkylidyne tricobalt nonacarbonyl cluster is isolobal to acetylene, thus the $Co_3(CO)_9$,³⁺ fragment may be considered isolobal to CH^3+ . By contrast the alkylidyne tritungsten nonaalkoxide cluster, with an sp^3 -like hybridization of its apical carbon, is isolobal to a carbon tetrahedrane, C_4H_4 , and the $W_3(OR)_9$,³⁺ fragment is isolobal to the π orbitals of C_3H_3 ,³⁺.

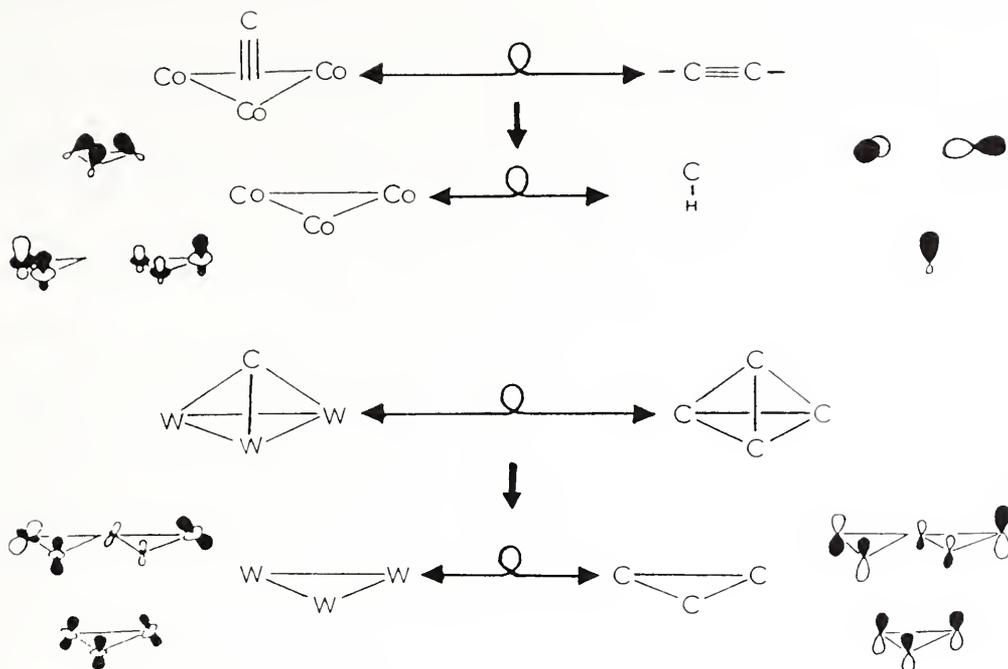


FIGURE 3: The contrasting isolobal analogies of $\text{Co}_3(\text{CO})_9(\mu_3\text{-CCH}_3)$ and $\text{W}_3(\text{OH})_9(\mu_3\text{-CCH}_3)$.

It is predicted that such contrasting limits of many such isolobal analogies may be articulated by the comparison of transition metal complexes of early and late transition metals.

Experimental

The coordinates for the model compounds $\text{Co}_3(\text{CO})_9(\mu_3\text{-CCH}_3)$ and $\text{W}_3(\text{OH})_9(\mu_3\text{-CCH}_3)$ were taken from the crystal structures of $\text{Co}_3(\text{CO})_9(\mu_3\text{-CCH}_3)$ (4) and $\text{W}_3(\text{O}^i\text{Pr})_9(\mu_3\text{-CCH}_3)$ (5) and idealized to C_{3v} symmetry.

Molecular orbital calculations were performed using the Fenske-Hall method described elsewhere (6). All calculations were performed using the VAX 11/780 computer at the Indiana University Computational Chemistry Center. Atomic basis functions were generated by a best fit to Herman Skillman atomic calculations (7). Contracted double- ζ representations were used for Co 3d and W 5d AO's as well as C and O 2p AO's. Basis functions for the metal atoms were generated for a +1 oxidation state with valence s and p exponents fixed at 2.00 for Co 4s and 4p, and 1.80 for W 6s and 6p.

All ^1H NMR spectra were recorded in benzene- d_6 or toluene- d_8 on a Nicolet-360 spectrometer at 360 MHz. ^{13}C NMR spectra of the tungsten complexes were recorded in benzene- d_6 or toluene- d_8 on a Varian XL-300 spectrometer at 75 MHz. ^{13}C NMR spectra of $\text{Co}_3(\text{CO})_9(\text{CCH}_3)$ was recorded in C_6D_{12} on a modified Nicolet-200 spectrometer at 50.3 MHz.

Acknowledgment

We would like to thank Professor Adam Allerhand and Steve Maple for determining the ethynyl coupling constant of $\text{Co}_3(\text{CO})_9(\mu_3\text{-CCH}_3)$, and Professor Odile Eisenstein for many helpful discussions.

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