

100 μ s. The relaxation time for the decay of the autocorrelation function was measured and the corresponding translational diffusion constant calculated.²⁹ This, in turn, was related to the radius of the scattering particles by Stokes law.

A synthetic Ir colloid was prepared as described below. With a channel time of 3 μ s, this colloid gave a translational diffusion constant of 8.58×10^{-8} cm²/s, corresponding to a Stokes Radius of 250 Å. The preparation was diluted 10⁴-fold and still gave a readily detectable signal. Dilution a further 10⁴-fold led to the loss of signal. This allowed us to assign an approximate detection limit of 1 nM to the method.

The cooled alkane dehydrogenation solutions, in contrast, gave a completely flat autocorrelation function over the whole instrumental channel time range, implying that within the detection limits of the method, no particles were present. Further work is in progress on developing this technique as a general method for the detection of particulates in catalyst preparations.

Preparation of the Iridium Colloid. This preparation is a variant of that described by Dunsworth and Nord.³⁴ To an aqueous solution of poly(vinyl alcohol) (2 g of PVA in 90 mL of H₂O) was added 10 mL of a solution of (NH₄)₂IrCl₆ (40% Ir, 90 mg, 0.28 mmol) and N₂H₄·H₂O (25 mg, 0.5 mmol). The mixture was heated on a steam bath for 15 min, during which time it became gray-yellow. The cooled mixture was adjusted to pH 7 with 10% acetic acid and water added to make the whole up to 100 mL. Stable colloids could not be obtained without PVA, but the latter made very little contribution to the light scattering.

The synthetic colloids were completely clear to the eye, but the Tyndall effect light scattering could be easily seen at the focus of a small lens (2-cm diameter, 10-cm focal length) in bright sunlight.

We successfully repeated Dunsworth and Nord's³⁴ work on the reduction of nitrobenzene to aniline by the iridium colloid. Thirty cubic centimeters of H₂ (1 atm, 25 °C) was absorbed per minute. To the cooled alkane dehydrogenation reaction mixture in its original flask was

added nitrobenzene (1 mL) under H₂ (1 atm, 25 °C), and the mixture was stirred for 4 days. No trace of aniline was detected (GC), nor was metal precipitated.

The presence of bulk metal was eliminated as follows. The reaction mixtures were passed through a micropore filter, the flask washed with CH₂Cl₂ (5 × 5 mL), and the washings filtered. The micropore filter did not show traces of bulk metal (Zeiss microscope, 100 × magnification), nor did the filter catalyze cyclohexene hydrogenation (1 atm, 25 °C, 3 days, detection by GC) when returned to the original flask. This is a variant of the Maitlis²⁷ method.

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Registry No. 1a, 72414-17-6; 1b, 79792-57-7; 2, L = PPh₃, 38834-40-1; 3, L = PPh₃, 79792-58-8; 4, 79792-60-2; 5, 558-37-2; [Ir(η^5 -C₆H₇)H(PPh₃)₂]BF₄, 79792-62-4; [Ir(η^5 -C₇H₉)H(PPh₃)₂]BF₄, 79792-64-6; [Ir(C₈H₁₀)(PPh₃)₂]BF₄, 79792-66-8; [Ir(η^5 -cycloheptatrienyl)H(PPh₃)₂]BF₄, 79792-68-0; cyclopentene, 142-29-0; cyclopentadiene, 542-92-7; cyclohexene, 110-83-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; 1,5-cyclooctadiene, 111-78-4; [2.2.2]bicyclooctene, 931-64-6; styrene, 100-42-5; cyclopentane, 287-92-3; cyclooctane, 292-64-8; cycloheptane, 291-64-5.

A Second-Order Jahn–Teller Effect in a Tetranuclear Metal Atom Cluster Compound

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Abstract: The bonding in the type of compound exemplified by W₄(OC₂H₅)₁₆ (Chisholm et al., 1981) has been examined using Fenske–Hall calculations. It is shown that the low-symmetry (C₇) structure of this molecule can be understood as the result of a second-order Jahn–Teller distortion of a more regular (C_{2h}) structure; the more regular structure would require two more electrons, which would then permit the formation of the entire set of five metal–metal single bonds. Loss of two electrons from such a structure is shown to lead uniquely to the type of distortion observed and the calculations suggest that the molecule is stabilized by ca. 0.5 eV as a result of the distortion. It is noted that the analysis developed here applies directly to the newly reported compound Ba_{1.13}Mo₈O₁₆ which contains both nearly undistorted (C_{2h}) and strongly distorted (C₇) Mo₄ clusters.

Compounds containing triangular trinuclear metal atom clusters are being discovered and or recognized at a great rate these days¹⁻³ and the importance of these, especially among the early transition metals, is receiving increasing recognition.³ One of the important structure types is that shown in Figure 1a, in which there is a capping nonmetal atom (μ_3 -X) on one side of the plane of the M₃ triangle and three edge-bridging nonmetal atoms (μ -X) on the other side. In addition, there are three terminal (i.e., nonbridging) nonmetal atoms (X) also attached to each metal atom, completing a distorted MX₆ octahedron. This unit has the composition M₃X₁₃. It is known in the solid state context, where many of the X atoms

are shared between units, as well as in discrete molecular compounds. It is probably the structure of the aquo molybdenum(IV) species. The structure can be obtained simply by joining three MX₆ octahedra so that there is one vertex (the μ_3 -X or capping atom) common to all of them and three shared edges, all meeting at this unique vertex. This arrangement of fused octahedra constitutes one quarter of the Keggin structure found for a number of isopoly acids. It becomes a metal cluster structure when the metal atoms are drawn together by the formation of M–M bonds. In various cases the X atoms have been found to be O, S, F, Cl, or others and they need not all be the same in one molecule. Molecular orbital considerations, either simple⁵ or more sophisticated,⁶ suggest that this structure should be stable with three M–M bonds of formal order one when the cluster has 6 electrons

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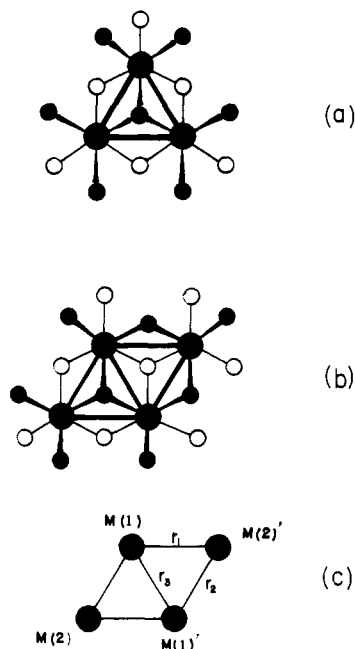


Figure 1. (a) The prototypal M_3X_{13} structure. Large filled circles represent M atoms; small filled and open circles represent X atoms above and below the M_3 plane. (b) The M_4X_{16} structure. (c) The M–M bond lengths in $W_4(OEt)_{16}$ are: $r_1 = 2.936$ (2) Å, $r_2 = 2.645$ (2) Å, $r_3 = 2.763$ (2) Å. Those used for the calculation on the model, $Mo_4(OH)_{16}$, were: 2.94 Å, 2.65 Å, 2.76 Å.

available, and not much less than one when 7 or 8 electrons are present. Real examples of all three situations are known. Those for the six-electron case are very numerous;⁴ the seven-electron case is exemplified by Nb_3Cl_8 ⁷ and the eight-electron case by $[Mo_3(\mu_3-O)(\mu-Cl)_3(O_2CCH_3)_3(H_2O)_3]^{2+}$.⁸

By fusing two such trinuclear units together, the tetranuclear structure shown in Figure 1b may be obtained. This structure was observed some time ago in the compounds MNb_4X_{11} where $M = Co, Rb$ and $X = Cl, Br$; it is not discrete in these compounds but part of an infinite solid state array.⁹ The same type of structure geometrically, but lacking M–M bonds, is found in several $[Ti(OR)_4]_4$ compounds.¹⁰ The symmetry is C_{2h} ($2/m$), with the two-fold axis passing through $M(1)$ and $M(1)'$ and the mirror plane through $M(2)$, $M(2)'$, and the two capping atoms. In the MNb_4X_{11} compounds, the number of electrons available per Nb₄ group is $4(5) + 1 - 11 = 10$. Thus five Nb–Nb single bonds, one between each adjacent pair of metal atoms, can be formed and the distances (in, e.g., $CsNb_4Cl_{11}$) $Nb(1)–Nb(1)' = 2.95$ Å and $Nb(1)–Nb(2) = 2.84$ Å indicate that this occurs.

Recently, Chisholm, Huffman, and Leonelli have reported the preparation and structural characterization of $W_4(OEt)_{16}$.¹¹ This molecule was found to have a distorted form of structure 1b, the metal skeleton of which is shown in Figure 1c. This structure has two long peripheral edges and two short ones, so arranged that from structure 1b only a center of symmetry remains; the C_2 axis and mirror plane are abolished. There are only $4(6) - 16 = 8$ electrons available for bond formation within the metal atom cluster. Clearly, the insufficiency of electrons has caused highly selective bond weakening, whereby two opposite peripheral bonds have been particularly affected.

The question posed by the structure of $W_4(OEt)_{16}$ is whether one can account for the particular way in which the symmetrical

Table I. Orbital Energies and Atomic Orbital Population for the 4d Valence Molecular Orbitals of $[Mo_4]^{14+}$

orbital	label (C_{2h} sym)	rel orbital energy, eV	% character ^a	
			M_1, M_1'	M_2, M_2'
M_{20}	$5a_u$	2.95	36.3 $d_z + 18.4 d_{x^2-y^2}$	37.5 d_{xz}
M_{19}	$4b_g$	2.10	63.7 d_{xz}	26.5 d_{xz}
M_{18}	$5b_u$	1.41	28.0 d_{xz}	65.4 d_z^2
M_{17}	$6a_g$	1.19	38.6 d_{xy}	60.6 d_{yz}
M_{16}	$3b_g$	1.09	80.9 d_{yz}	8.5 d_{xy}
M_{15}	$4a_u$	0.95	58.0 $d_z^2 + 44.6 d_{x^2-y^2}$	2.0 d_{xz}
M_{14}	$3a_u$	0.86	41.4 d_{xy}	58.6 d_{xy}
M_{13}	$5a_g$	0.78	34.3 $d_{x^2-y^2}$	8.5 $d_z^2 + 51.5 d_{x^2-y^2}$
M_{12}	$4b_u$	0.54	23.1 d_{yz}	75.8 d_{yz}
M_{11}	$4a_g$	0.45	24.0 d_z^2	49.0 $d_z^2 + 23.6 d_{x^2-y^2}$
M_{10}	$3b_u$	0.01	0.0	98.1 $d_{x^2-y^2}$
M_9	$2b_g$	0.01	17.5 d_{yz}	82.3 d_{xy}
M_8	$2a_u$	-0.38	58.6 d_{xy}	41.4 d_{xy}
M_7	$2b_u$	-0.67	76.6 d_{yz}	22.4 d_{yz}
M_6	$3a_g$	-0.73	60.4 d_{xy}	39.2 d_{yz}
M_5	$2a_g$	-1.29	6.0 $d_z^2 + 56.2 d_{x^2-y^2}$	10.6 $d_z^2 + 21.9 d_{x^2-y^2}$
M_4	$1b_g$	-1.38	33.8 d_{xz}	61.8 d_{xz}
M_3	$1a_g$	-1.79	72.4 d_z^2	17.3 d_z^2
M_2	$1a_u$	-2.09	7.9 $d_z^2 + 36.4 d_{x^2-y^2}$	49.7 d_{xz}
M_1	$1b_u$	-2.23	62.4 d_{xz}	32.1 d_z^2

^a Small contributions from high-lying 5s and 5p orbitals are not included.

(C_{2h}) structure that would have been expected if ten cluster electrons were present is distorted when only eight electrons are present. We show in this paper that this question can be answered in the affirmative and that the answer entails a novel but very clear and satisfying example of the second-order Jahn–Teller effect.¹²

Computational Procedures

We have proceeded essentially in the manner previously described,^{6,13} where the Fenske–Hall MO method is used to obtain numerical results. We have used Mo and OH rather than W and OEt to make the numerical calculations tractable. We have also handled the problem by the “clusters in molecules” formalism, in which we express the MO’s for the entire molecule in a basis set consisting of ligand atomic orbitals (AO’s) and molecular orbitals localized within the metal cluster. The forms of the metal cluster orbitals are determined by a calculation on the Mo_4^{9+} unit alone. There are 36 such orbitals, which are designated $M_1–M_{36}$, with the lowest 20 being formed mainly from the metal 4d orbitals. After the calculations on the entire molecule reach self-consistency, the results are transformed into the above basis set rather than into one consisting of metal AO’s as well as ligand AO’s. The energies of the localized cluster MO’s are then obtained for the cluster in the molecule and differ from the energies pertinent to the naked Mo_4^{9+} unit. In Tables I and III below, the energies listed are those for the “cluster in the molecule”.

We began with the 10-electron system $[Mo_4(OH)_{16}]^{2-}$ and treated this with a structure of type 1b having the following bond lengths (Å): Mo–(μ_3 -O), 2.18; Mo–(μ -O), 2.02; Mo–O_t, 1.96; Mo–Mo, 2.76; and O–H, 1.00. Each metal atom was given approximately octahedral coordination angles, with slight distortions in those angles involving the capping and bridging ligands. A local right-handed Cartesian coordinate system was assigned to each metal atom, with the z axis pointing toward the center of the cluster, the x axis in the Mo_4 plane, and the y axis perpendicular to that plane.

The calculation was first carried out for the Mo_4^{14+} cluster. The lowest 20 valence orbitals, $M_1–M_{20}$, derived mainly from Mo 4d atomic orbitals, are listed in Table I along with their energies and their d orbital compositions. The cluster orbitals $M_1–M_5$ are occupied and provide Mo–Mo bonds. Schematic pictures of these orbitals are given in Figure

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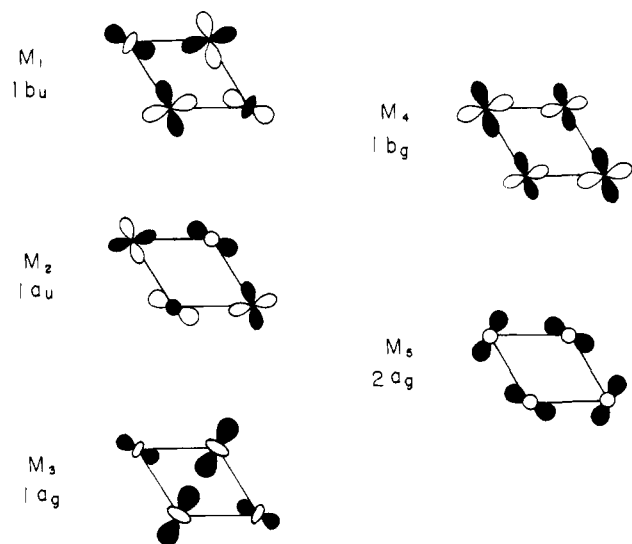


Figure 2. Schematic representations of the five metal cluster orbitals, M_1 – M_5 , that are principally responsible for M–M bonding in a M_4X_{16} species.

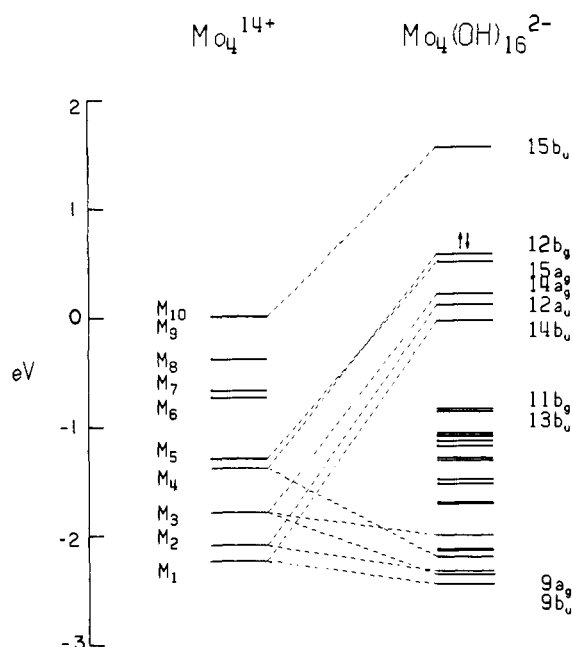


Figure 3. A partial energy level diagram for the $[Mo_4(OH)_{16}]^{2-}$ ion.

2. The main source of the $M(1)$ – $M(1)'$ bond is M_3 which makes a σ contribution; π , δ^* , π^* , and δ contributions from M_1 , M_2 , M_4 , and M_5 , respectively, tend to cancel out. The peripheral bonds are supplied by these last four M_i .

The Fenske–Hall calculation for the entire $[Mo_4(OH)_{16}]^{2-}$ unit gave the results listed in Table II. Some of these as well as the results for the cluster alone are represented in an energy level diagram in Figure 3. Between -26.5 and -24.0 eV are O–H bonding MO's of mainly oxygen 2s and hydrogen 1s character, having virtually no metal contribution. These 16 MO's are omitted from Table II and Figure 3 and have not been numbered. Between -11.4 and -7.6 eV we have a set of 16 MO's that are essentially Mo–O bonding, with metal contributions ranging from 12% to 22%. After another energy gap we find between -5.8 and -3.7 eV a set of twelve orbitals, eight of which are more weakly M–O bonding and also four that are mainly μ -O lone pairs. None of these orbitals is shown in Figure 3.

As shown in Figure 3 there is a set of 20 orbitals between -2.5 and -0.8 eV. These are mostly lone pair orbitals on terminal OH groups although there are significant metal cluster contributions to several of them.

Finally, between -0.1 and 0.6 eV we find a set of five MO's, $14b_u$, $12a_u$, $14a_g$, $15a_g$, and $12b_g$, that are strongly involved in Mo–Mo bonding, although they also have some Mo–OH bonding character. These five

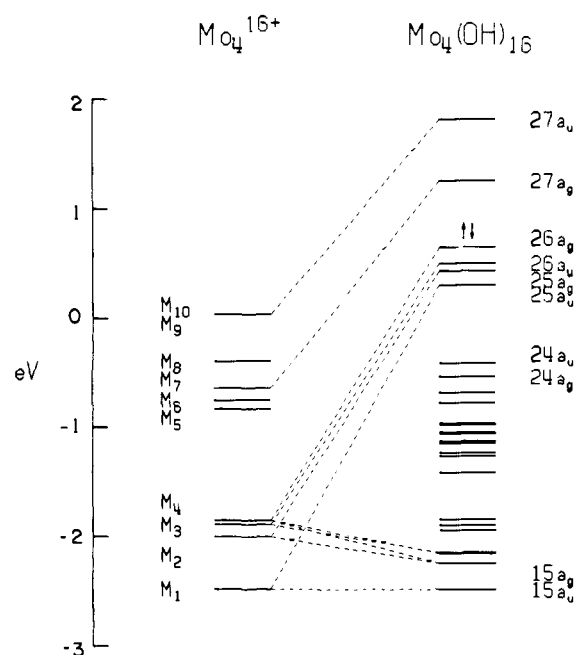


Figure 4. A partial energy level diagram for the $Mo_4(OH)_{16}$ molecule.

orbitals are filled in the $[Mo_4(OH)_{16}]^{2-}$ ion and significantly contribute to the existence of five Mo–Mo single bonds in the metal atom cluster. Because of the closeness in the calculated energies of the $12b_g$ and $15a_g$ orbitals, it is entirely possible their order could be reversed, with $15a_g$ being the HOMO.

The Mulliken populations in the five lowest cluster orbitals are the following: M_1 , 1.72; M_2 , 1.62; M_3 , 1.78; M_4 , 1.67; and M_5 , 1.81. Thus, even though there is considerable mixing of cluster and ligand orbitals in the $[Mo_4(OH)_{16}]^{2-}$ ion, a set of five Mo–Mo single bonds based essentially on metal–metal d-orbital overlaps is present.

Calculations on the $Mo_4(OH)_{16}$ molecule were carried out in essentially the same way as for $[Mo_4(OH)_{16}]^{2-}$, using a model with C_i symmetry and the Mo–Mo distances shown in Figure 1c. All Mo–O and O–H distances were kept the same as before, and the local coordinate systems, basis sets, etc. were also the same. The results for the eight-electron $[Mo_4]^{16+}$ cluster are listed in Table III. Similarly, the results for the complete $Mo_4(OH)_{16}$ molecule are listed in Table IV and shown as an energy level diagram in Figure 4. The distribution of energies of Mo–O bonding orbitals and oxygen lone pair orbitals is not much different from that for $[Mo_4(OH)_{16}]^{2-}$ and, again, the numbering starts with orbitals above the sixteen O–H bonding orbitals. In C_i symmetry the a_g and b_g orbitals become a_g orbitals and the a_u and b_u orbitals have a_u symmetry. As before, there is a gap between the highest of the twenty t -OH lone-pair orbitals and the set of orbitals that are principally responsible for Mo–Mo bonding, these being, now, $25a_u$, $25a_g$, $26a_u$, and $26a_g$. The LUMO is $27a_g$ and the HOMO/LUMO gap is 0.61 eV. In Figure 5 we compare directly the pure cluster orbitals of the ten-electron Mo_4 cluster of C_{2h} symmetry in $[Mo_4(OH)_{16}]^{2-}$ and the eight-electron Mo_4 cluster of C_i symmetry in $Mo_4(OH)_{16}$.

Discussion

The $[Mo_4(OH)_{16}]^{2-}$ Species. This is a hypothetical ion, which we have analyzed as a basis for understanding the $Mo_4(OH)_{16}$ molecule, which is, in turn, our model for the real $W_4(OEt)_{16}$ molecule.¹¹ The anion itself has a sufficient number of electrons to allow the formation of five metal–metal single bonds and the calculations give a semiquantitative idea of the nature of these bonds. As shown in Figure 2, the five MO's that are principally responsible for the metal–metal bonds in the naked cluster are such that one, M_3 , is mainly confined to the $M(1)$ – $M(1)'$ bond while the other four all contribute to the set of symmetry-equivalent peripheral bonds. In the $[Mo_4(OH)_{16}]^{2-}$ species we find that some of the higher M_i , of appropriate symmetries, also contribute to the "Mo–Mo bonding orbitals", $14b_u$, $12a_u$, $14a_g$, $15a_g$, and $12b_g$, but to a smaller extent than M_1 – M_5 .

The results for $[Mo_4(OH)_{16}]^{2-}$ are not surprising, although it is satisfying to see that the qualitative expectation that a full set of Mo–Mo bonds would be formed if ten electrons are available is justified and articulated in detail by the calculations. The results

Table II. Molecular Orbital Symmetries, Energies, and Compositions for $[\text{Mo}_4(\text{OH})_{16}]^{2-}$

orbital	energy, eV	metal	% contribution			
			Mo_4	$(\mu_3\text{-OH})_2$	$(\mu_2\text{-OH})_4$	$(t\text{-OH})_{10}$
14a _u	3.52	28M ₁₄ + 51M ₂₀	85.2	0.0	3.3	11.5
16b _u	2.97	8M ₁₀ + 22M ₁₂ + 43M ₁₈	78.9	5.0	3.0	12.8
13b _g	2.91	23M ₉ + 11M ₁₆ + 46M ₁₉	82.3	1.8	4.6	11.4
13a _u	2.82	62M ₅ + 8M ₈	75.5	7.6	0.9	15.9
17a _g	2.66	8M ₁₁ + 59M ₁₃	77.9	5.5	2.5	13.8
16a _g	1.81	39M ₁₁ + 15M ₁₃ + 16M ₁₇	75.3	0.2	3.6	21.0
15b _u	1.56	55M ₁₀ + 10M ₁₂	72.2	0.1	5.1	22.5
12b _g	0.58	43M ₄ + 4M ₉ + 9M ₁₆	57.4	1.4	1.3	39.8
15a _g	0.51	8M ₃ + 31M ₅ + 8M ₆	50.1	1.3	2.8	45.3
14a _g	0.21	23M ₃ + 15M ₅	40.0	0.1	0.6	59.1
12a _u	0.11	30M ₂ + 8M ₈	40.9	0.5	1.2	57.4
14b _u	-0.03	26M ₁ + 4M ₇	32.4	0.0	1.2	66.5
11b _g	-0.84		0.2	0.4	0.0	99.3
13b _u	-0.86		0.3	0.0	0.0	99.8
10b _g	-1.06	2M ₁₆ + 6M ₁₉	10.8	0.2	0.5	88.5
11a _u	-1.08		6.7	0.1	0.1	93.1
12b _u	-1.09		6.6	1.3	0.2	91.8
13a _g	-1.13	3M ₅ + 4M ₁₃	9.5	1.4	0.8	89.0
10a _u	-1.18	11M ₁₅	14.8	1.3	0.1	84.0
12a _g	-1.29	9M ₅	11.3	0.1	0.5	88.9
9b _g	-1.31	6M ₄	8.5	0.5	0.2	91.0
9a _u	-1.49	9M ₂ + 3M ₈	13.8	0.5	0.4	86.0
11b _u	-1.53	10M ₁ + 3M ₇	14.8	0.4	1.6	83.5
8b _g	-1.70		0.2	0.1	0.2	99.5
8a _u	-1.71		1.7	0.1	0.5	97.5
11a _g	-2.00	18M ₃ + 9M ₁₁ + 5M ₁₇	37.2	0.4	0.1	62.2
10a _g	-2.13	10M ₅ + 9M ₁₃	22.4	0.0	4.7	71.9
10b _u	-2.14	10M ₁₀ + 4M ₁₂	18.1	0.1	5.0	76.8
7b _g	-2.20	19M ₄	29.1	0.8	2.0	68.0
7a _u	-2.33	28M ₂ + 8M ₈	41.8	1.3	1.7	56.3
9a _g	-2.36	34M ₃ + 8M ₅	50.7	0.3	0.2	48.5
9b _u	-2.45	35M ₁ + 6M ₇ + 8M ₁₀	52.1	0.0	2.6	46.6
6b _g	-3.72		9.2	80.0	6.3	4.5
8b _u	-3.87		11.7	78.3	7.1	3.0
8a _g	-3.89		14.5	76.8	5.5	3.2
6a _u	-4.04	7M ₁₅	15.2	82.4	1.6	0.1
5a _u	-4.12		4.0	1.4	94.0	0.4
5b _g	-4.14		3.7	4.4	91.7	0.2
7b _u	-4.26		12.0	5.4	82.2	0.6
7a _g	-4.26		11.0	5.9	81.4	1.1
6b _u	-5.04	5M ₁₈	14.8	3.6	79.5	1.6
4b _g	-5.21	6M ₉ + 6M ₃₃	15.1	1.3	80.5	2.6
6a _g	-5.58		19.6	0.2	75.2	5.3
4a _u	-5.76	9M ₁₄ + 6M ₃₂	19.3	0.0	73.5	7.6
5a _g	-7.66	5M ₂₄	12.0	21.0	0.6	65.9
3a _u	-7.84	12M ₂₃	17.0	0.1	3.8	78.9
5b _u	-7.88	8M ₂₈	12.0	22.0	1.1	64.8
4a _g	-8.01	9M ₂₇	16.3	0.1	1.8	82.8
4b _u	-8.09	6M ₂₂	15.8	9.5	0.1	74.9
3b _g	-8.57	11M ₁₆	20.0	1.4	8.7	69.5
3a _g	-8.81	8M ₂₁	15.7	41.5	2.7	39.9
3b _u	-8.86	6M ₁₂	17.0	0.6	7.7	64.6
2b _g	-8.89	5M ₉	21.9	0.2	16.1	61.9
2a _u	-9.14	12M ₁₄ + 5M ₂₀	20.0	0.2	12.5	67.3
2a _g	-9.28	5M ₁₁ + 7M ₁₇	20.0	22.6	11.3	46.5
2b _u	-9.70	6M ₁ + 8M ₇	19.5	41.2	17.6	21.8
1b _u	-10.39	6M ₇ + 5M ₁₂	16.9	15.0	53.1	13.2
1b _g	-10.93	7M ₄ + 9M ₉	20.6	0.0	62.5	16.8
1a _g	-11.09	11M ₆	20.4	6.0	69.3	4.2
1a _u	-11.40	9M ₂ + 11M ₈	21.9	0.0	69.1	8.9

are in harmony with the experimental observations on the structures and diamagnetism of the $\text{MNb}_4\text{X}_{11}$ compounds.⁹ The results for the model system, $[\text{Mo}_4(\text{OH})_{16}]^{2-}$, also afford a direct prediction that the $\text{W}_4(\text{OEt})_{16}$ molecule should be susceptible to reduction to the $[\text{W}_4(\text{OEt})_{16}]^{2-}$ ion and that the ion should have a symmetrical (C_{2h}) structure. We believe that a reaction of $\text{W}_4(\text{OEt})_{16}$ with a reducing agent such as Na/Hg in the presence of a suitable large cation, perhaps $[\text{Ph}_3\text{PNPPh}_3]^+$, should allow the isolation of a compound such as $[\text{Ph}_3\text{PNPPh}_3]_2[\text{W}_4(\text{OEt})_{16}]^{2-}$.

One final observation based on the results for the $[\text{Mo}_4(\text{OH})_{16}]^{2-}$ ion itself is that removal of two electrons to give the neutral molecule $\text{Mo}_4(\text{OH})_{16}$ would not be expected to weaken the central $\text{Mo}(1)\text{-Mo}(1)'$ bond but rather the peripheral bonds. Each of

the two orbitals, either of which, according to the calculations, might be the HOMO of $[\text{Mo}_4(\text{OH})_{16}]^{2-}$, is involved entirely (12b_g) or primarily (15a_g) with the peripheral Mo-Mo bonds. It is only the third orbital down from the HOMO, 14a_g, that is a major contributor to the central bond. Thus, even in this straightforward way, we might confidently predict that whatever structural change should accompany the oxidation of $[\text{Mo}_4(\text{OH})_{16}]^{2-}$ to $\text{Mo}_4(\text{OH})_{16}$, it would not be a loss of the central bond but some form of weakening of the set of peripheral bonds.

The $\text{Mo}_4(\text{OH})_{16}$ Species. Based on the results of our calculation, and other considerations, we regard the symmetrical (C_{2h}) structure of the $[\text{Mo}_4(\text{OH})_{16}]^{2-}$ ion as a secure starting point for understanding the distorted (C_i) structure of the $\text{Mo}_4(\text{OH})_{16}$

Table III. Orbital Energies and Atomic Orbital Population for the 4d Valence Molecular Orbitals of $[Mo_4]^{16+}$

orbital	label (C_i sym)	rel orbital energy, eV	% character ^a	
			M_1, M_1'	M_2, M_2'
M_{20}	$10a_u$	3.01	$35 d_{z^2} +$ $18 d_{x^2-y^2}$	$39 d_{xz}$
M_{19}	$10a_g$	2.06	$3 d_{x^2-y^2} +$ $60 d_{xz}$	$6 d_{z^2} + 1 d_{x^2-y^2} +$ $20 d_{xz}$
M_{18}	$9a_u$	1.47	$28 d_{xz}$	$66 d_{z^2}$
M_{17}	$9a_g$	1.33	$36 d_{xy} + 3 d_{yz}$	$4 d_{xy} + 56 d_{yz}$
M_{16}	$8a_u$	1.10	$38 d_{xy} + 3 d_{yz}$	$40 d_{xy} + 18 d_{yz}$
M_{15}	$8a_g$	1.03	$2 d_{xy} + 83 d_{yz}$	$10 d_{xy} + 4 d_{yz}$
M_{14}	$7a_u$	0.97	$46 d_{z^2} +$ $40 d_{x^2-y^2}$	$4 d_{x^2-y^2} + 3 d_{xz}$
M_{13}	$7a_g$	0.76	$31 d_{x^2-y^2}$	$4 d_{z^2} + 59 d_{x^2-y^2}$
M_{12}	$6a_g$	0.47	$18 d_{z^2} +$ $3 d_{x^2-y^2}$	$51 d_{z^2} +$ $11 d_{x^2-y^2} +$ $11 d_{xz}$
M_{11}	$6a_u$	0.35	$2 d_{xy} + 16 d_{yz}$	$24 d_{xy} + 58 d_{yz}$
M_{10}	$5a_g$	0.04	$12 d_{yz}$	$83 d_{xy} + 4 d_{yz}$
M_9	$5a_u$	0.04	$2 d_{z^2}$	$92 d_{x^2-y^2} + 3 d_{xz}$
M_8	$4a_u$	-0.39	$55 d_{xy} +$ $10 d_{yz}$	$34 d_{xy}$
M_7	$4a_g$	-0.64	$19 d_{x^2-y^2} +$ $26 d_{xz}$	$18 d_{x^2-y^2} +$ $33 d_{xz}$
M_6	$3a_u$	-0.75	$71 d_{yz} + 5 d_{xy}$	$22 d_{yz}$
M_5	$3a_g$	-0.83	$61 d_{xy}$	$35 d_{yz} + 3 d_{xy}$
M_4	$2a_g$	-1.85	$78 d_{z^2}$	$11 d_{z^2}$
M_3	$2a_u$	-1.89	$7 d_{z^2} +$ $30 d_{x^2-y^2} +$ $13 d_{xz}$	$4 d_{z^2} + 40 d_{xz}$
M_2	$1a_g$	-2.00	$39 d_{x^2-y^2} +$ $9 d_{xz}$	$15 d_{z^2} +$ $7 d_{x^2-y^2} +$ $21 d_{xz}$
M_1	$1a_u$	-2.48	$7 d_{x^2-y^2} +$ $50 d_{xz}$	$27 d_{z^2} + 7 d_{xz}$

^a All orbitals contain small contributions from 5s and 5p orbitals.

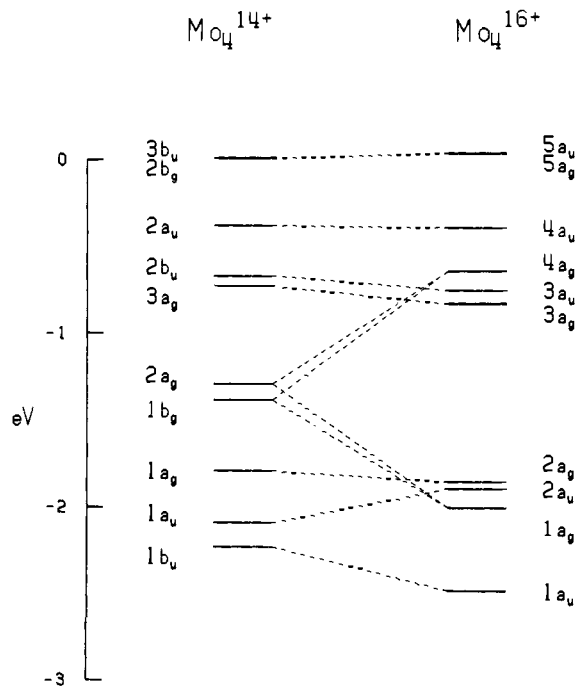


Figure 5. A comparison of the M_4 cluster orbitals in the region of the HOMO/LUMO gap for $[Mo_4(OH)_{16}]^{2-}$ and $Mo_4(OH)_{16}$. The energy scales have been adjusted to give the same energy to a pure 4d AO in each species.

molecule. The least that one might hope to do would be to show that for the 8-electron case the C_i structure should be more stable than the C_{2h} structure. To do this rigorously is not easy, and perhaps not possible since, rigorously, the two total energies must

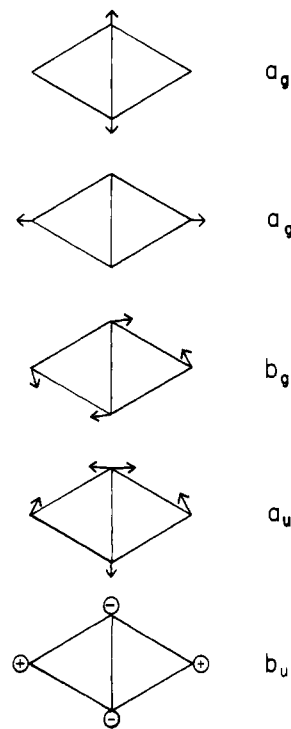


Figure 6. The types and qualitative forms of the five normal vibrations of the M_4 cluster with C_{2h} symmetry.

be calculated and compared. However, in a more heuristic approach, it may be assumed that the change in energy from the C_{2h} structure to the C_i structure, with an 8-electron population for each, would be dominated by the energy changes of those orbitals mainly responsible for metal-metal bonding. It then seems clear from Figures 3 and 4 that the energy is lower for the C_i structure.

However, we should like to have, if possible, a more complete, sophisticated and, as it were, predictive understanding. We should like to answer the following question: *What is the form of distortion, from the C_{2h} structure, to be expected when two electrons are removed from the HOMO of the $[Mo_4(OH)_{16}]^{2-}$ ion?* We have already noted that a simple loss of the central bond is not likely. It should also be recognized that the set of μ_3 -OH and μ_2 -OH ligands covering the edges and face of the Mo_4 cluster will impose some restraint on the distortions available to the cluster. We would not, therefore, expect total loss of any one bond in the periphery but rather some kind of concerted weakening, and lengthening, of some set of two or more bonds. The question we are asking then deals with the type of phenomena called Jahn-Teller effects. Since in the C_{2h} symmetry there are no rigorous degeneracies, we should expect our question to come under the heading of second-order Jahn-Teller effects.¹²

A necessary condition for the occurrence of a second-order Jahn-Teller effect in a symmetrical structure is that a low-lying excited state be coupled to the ground state by one of the normal vibrations of the symmetrical molecule; the distortion will then take the form of the vibration that couples the two states. To couple the two states, the vibration must belong to the same representation as the direct product of the ground state and the excited state. The normal modes of vibration of the Mo_5 unit with C_{2h} symmetry are listed and illustrated in Figure 6.

According to Table II and Figure 2, the HOMO of $[Mo_4(OH)_{16}]^{2-}$ is either the $12b_g$ or the $15a_g$ orbital. Loss of two electrons from the HOMO will then leave a totally symmetric (A_g) ground state with a very low-lying state of B_g symmetry based on either a $\cdots b_g a_g$ or a $\cdots a_g b_g$ electron configuration. Since the direct product $A_g \times B_g$ is B_g , we expect the second-order Jahn-Teller distortion to take the form of some b_g normal vibration. As Figure 6 shows, there is only one b_g vibration and it leads to precisely the type of distortion that is observed, namely, one that destroys all symmetry elements except the inversion center, by

Table IV. Molecular Orbital Symmetries, Energies, and Composition for Mo₄(OH)₁₆

orbital	energy, eV	metal	% contribution			
			Mo ₄	(μ ₃ -OH) ₂	(μ ₂ -OH) ₄	(t-OH) ₁₀
30a _u	3.86	16M ₁₁ + 43M ₂₀	79.8	2.9	4.3	13.0
30a _g	3.51	13M ₉ + 14M ₁₃ + 7M ₁₇ + 32M ₁₉	77.0	5.0	4.9	13.0
29a _u	3.18	33M ₁₄ + 11M ₁₆ + 19M ₁₈	74.0	6.3	1.0	18.6
28a _u	2.75	10M ₉ + 25M ₁₄ + 7M ₁₆ + 21M ₁₈	76.7	4.1	2.3	16.9
29a _g	2.38	55M ₁₃ + 10M ₁₉	77.8	2.2	3.2	16.8
28a _g	2.02	5M ₁₀ + 44M ₁₂ + 11M ₁₇	69.1	0.9	3.3	26.7
27a _u	1.82	47M ₉ + 7M ₁₁	66.8	0.1	5.6	27.5
27a _g	1.26	5M ₅ + 46M ₇	61.9	1.0	2.6	31.5
26a _g	0.65	24M ₄	30.3	0.7	0.4	68.6
26a _u	0.50	27M ₃ + 6M ₈	42.6	0.6	1.1	54.9
25a _g	0.43	26M ₂	29.1	0.6	0.8	69.5
25a _u	0.30	17M ₁	21.1	0.1	0.8	78.1
24a _u	-0.41		4.4	0.5	0.0	95.1
24a _g	-0.54		4.2	0.2	0.0	95.6
23a _g	-0.69	7M ₂	16.3	1.6	1.8	80.4
23a _u	-0.78		11.7	1.1	1.0	86.2
22a _g	-0.97		2.5	0.0	0.1	97.3
22a _u	-0.98		4.7	0.2	0.0	95.1
21a _u	-1.05		6.8	0.2	0.9	91.9
21a _g	-1.06		5.2	0.5	0.0	84.2
20a _u	-1.13	8M ₁₄	11.8	2.1	0.3	85.8
20a _g	-1.15		11.8	0.5	0.6	87.0
19a _u	-1.24		3.9	0.1	0.1	95.9
19a _g	-1.27		5.7	0.1	1.7	92.5
18a _u	-1.42	7M ₃	16.1	1.0	2.8	80.0
18a _g	-1.85	9M ₁₂	20.9	0.4	3.5	75.0
17a _u	-1.90	8M ₉	18.1	0.1	8.3	73.5
17a _g	-1.95	9M ₇ + 8M ₁₃	27.4	0.6	3.5	67.4
16a _u	-2.15	19M ₃	40.9	1.6	2.0	55.4
16a _g	-2.16	22M ₄ + 10M ₂	51.4	1.5	4.2	42.7
15a _g	-2.25	21M ₄ + 33M ₂	62.3	1.0	0.4	36.0
15a _u	-2.49	40M ₁ + 6M ₉	61.5	0.9	8.4	28.6
14a _g	-3.42		10.3	69.5	15.7	4.4
14a _u	-3.55		11.6	56.5	29.2	2.7
13a _g	-3.63		17.2	66.7	12.3	3.8
13a _u	-3.64		8.8	16.9	73.0	1.2
12a _g	-3.64		7.3	14.1	77.6	1.0
12a _u	-3.77		18.6	68.8	11.1	1.5
11a _g	-3.83		14.8	13.5	70.2	1.5
11a _u	-3.86		18.5	17.0	62.6	1.9
10a _u	-4.61	5M ₁₈	16.6	5.3	76.4	1.8
10a _g	-4.76	5M ₃₃ + 6M ₁₀	16.6	1.8	78.4	3.2
9a _g	-5.21		20.9	0.3	72.7	6.1
9a _u	-5.40	5M ₁₆ + 7M ₃₂	20.6	0.1	69.9	9.5
8a _g	-7.23	7M ₂₄	13.4	19.5	1.2	65.9
8a _u	-7.32	10M ₂₃	17.1	7.6	3.6	71.7
7a _u	-7.53	10M ₂₈	13.8	10.6	2.2	73.4
7a _g	-7.58	11M ₂₇	16.2	0.8	2.2	81.0
6a _u	-7.78	5M ₂₂	15.2	14.2	0.9	68.7
6a _g	-8.16	5M ₁₅	17.5	7.9	15.5	59.0
5a _g	-8.42	6M ₂₁	14.9	31.6	11.1	42.4
5a _u	-8.44		18.1	0.7	20.4	60.8
4a _g	-8.52	7M ₁₅	21.9	4.5	4.7	68.9
4a _u	-8.76	8M ₁₆	20.8	0.7	18.7	59.9
3a _g	-8.92	7M ₁₇	20.8	20.7	14.2	44.3
3a _u	-9.29	5M ₆	20.5	31.4	22.9	25.3
2a _u	-9.90	9M ₆	20.9	23.1	39.5	16.5
2a _g	-10.37	7M ₁₀	22.4	1.1	60.0	16.5
1a _g	-10.54	9M ₅	21.0	6.9	64.5	7.6
1a _u	-10.82	9M ₃ + 10M ₈	22.7	0.1	67.0	10.2

making the lengths of the peripheral bonds become alternately long and short. This prediction is unique and unambiguous. Such a distortion of the cluster is clearly possible, up to a considerable amplitude, within the constraints imposed by the bridging and capping OH groups.

If we turn now to the computational results, as they are shown in Figure 5, we see that they correspond very well with the prediction of the foregoing second-order Jahn-Teller analysis. The HOMO and LUMO, which are of b_g and a_g symmetry (or vice versa), in the C_{2h} structure both become a_g orbitals in C_i symmetry, and they split apart in energy. The HOMO in C_i symmetry at the distances used is thus more stable, by about 0.5 eV, than the HOMO in C_{2h} symmetry.

The Mo₄ Clusters in Ba_{1.13}Mo₈O₁₆. After the completion of the work described above, we were kindly informed in advance of publication of the results of Torardi and McCarty on Ba_{1.13}-Mo₈O₁₆. These results are now published in preliminary form.¹⁴ This remarkable compound contains two Mo₄ cluster species of the same types we had been concerned with in our calculations. Torardi and McCarty have shown that in both of them the symmetry is distorted from C_{2h} in the sense required by the b_g vibration, but in one case the distortion is very slight, Figure 7a, while in the other it is about as great as in W₄(OEt)₁₆, Figure 7b. For the two species there is a total of 18.26 electrons available

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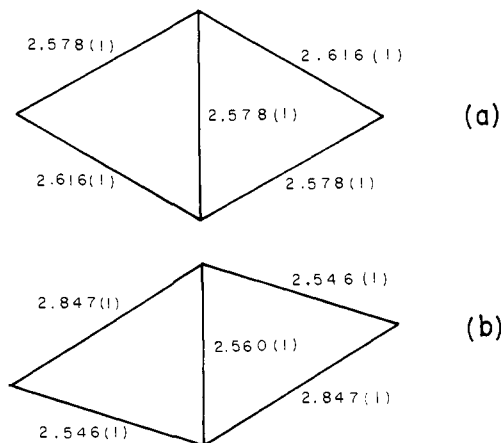


Figure 7. The Mo-Mo distances in the two Mo₄ clusters found in Torardi and McCarley's Ba_{1.13}Mo₈O₁₆.

for Mo-Mo bonding according to the formula given. Torardi and McCarley propose to consider one of the clusters a 10-electron species and the other an 8.26-electron species. On the basis of our work we would not necessarily disagree with this, but would only remark that perhaps the slight distortion of the more symmetrical cluster implies that it has slightly less than 10 electrons,

with the other one having slightly more than 8.26 electrons. However, we do not at all insist on this notion since the very small distortion in the first one, even though it has the correct form for a Jahn-Teller distortion, may well have some other cause.

The preliminary values of the Mo-O bond lengths available to us when this manuscript was written^{14,15} were not of sufficient precision or apparent accuracy to warrant a consideration of the possible role of Mo-O π bonding in the deformation process. Professor R. E. McCarley has subsequently informed us that the final values, which have esd's of 0.006 Å, lead him to conclude that the distortion from the 10-electron to the 8-electron cluster structure is probably aided by an increase in the strength of two Mo-O π bonds that tends to offset the decrease in the strength of the two opposite Mo-Mo bonds that become elongated. The two Mo-O bond lengths in question change from 2.022 (6) Å to 1.894 (6) Å on going from the undistorted to the distorted cluster. We are entirely in agreement with this suggestion.

Acknowledgment. We thank the National Science Foundation for financial support.

Registry No. W₄(OC₂H₅)₁₆, 78166-59-3.

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Electrophilic Attack on a Metal Alkynyl by Carbon Disulfide: Preparation and Structure of [Fe(C₂MeCS₂Me)(dppe)(Cp)]I·MeOH, a Cationic Vinylidene Complex

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Abstract: The electron-rich metal alkynyl complex [Fe(C≡CMe)(dppe)(Cp)] (Fp'C≡CMe, I) undergoes (2 + 2) cycloaddition with carbon disulfide to form [Fe(C≡CMeC(S)S)(dppe)(Cp)] (II) containing a 2*H*-thiete-2-thione functional group. This CS₂ adduct is subsequently alkylated by iodomethane to yield [Fe(C₂MeCS₂Me)(dppe)(Cp)]I·MeOH (III), a cationic vinylidene complex. The products were investigated by spectroscopic means and, in the case of III, by an X-ray crystal structure analysis: space *P*2₁/*c*, *a* = 11.625 (3) Å, *b* = 20.609 (4) Å, *c* = 15.490 (2) Å, β = 103.25 (2)°, *V* = 3612.4 Å³, *Z* = 4, ρ (calcd) = 1.487 g·cm⁻³. Refinement on 2552 reflections with $F^2 \geq 3\sigma(F^2)$ yielded the final discrepancy indices *R* = 0.058 and *R_w* = 0.070. The substituted vinylidene ligand of complex III is bonded to the iron atom by a very short Fe-C bond, 1.74 (2) Å, and the Fe-C1-C2 bond angle is nearly linear, 176 (1)°. Spectroscopic and structural evidence suggest that 2-(dithiocarbomethoxy)propenylidene is a very large strong π -acid ligand.

Electron-rich transition-metal alkynyl complexes react with protic acids or alkylating agents to form cationic metal vinylidene complexes.¹ This behavior is attributed to a buildup of electron density on the alkynyl β -carbon atom by back-bonding from filled metal orbitals, resulting in nucleophilic character at that carbon atom. A few instances of additions of more complex electrophiles² to metal alkynyls have been reported, involving addition of tetracyanoethylene or hexafluoroacetone to [Fe(C≡CPh)(CO)₂-

(Cp)], [Fe(C≡CPh)(CO)(PPh₃)(Cp)],³ and [Ru(C≡CPh)(PPh₃)₂(Cp)].⁴

Carbon disulfide is an unsaturated electrophile with an extensive organic and organometallic chemistry.⁵ Typically, CS₂ reacts with metal alkyls or hydrides by insertion, forming dithio-

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