Acknowledgment. We thank the PHS for research support (Grant GM-27721) and the NSF Regional NMR Centers at the University of South Carolina (Grant CHE 78-18723) and Colorado State University (Grant GHE 78-18581) for their assistance.

Registry No. I, 40937-33-5; II, 86374-31-4.

Supplementary Material Available: Figures showing the unit cell of II and a dimer of I and listings of positional parameters, isotropic thermal parameters, anisotropic librational parameters, bond distances and angles, and observed and calculated structure amplitudes (62 pages). Ordering information is given on any current masthead page.

---

(55) Montgomery, H.; Lingafelter, E. C. *Acta Crystallogr.* **1966**, *20*, 728–730.

Contribution from the Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel, and Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843

New Preparative Route to Bi-oxo-capped Trinuclear Molybdenum(IV) Clusters by Reduction of Molybdate(VI). Structure of $[Mo_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]\cdot 16H_2O$

AMIRA BIRNBAUM,[1b] F. ALBERT COTTON,*[1a] ZVI DORI,*[1b] DAVID O. MARLER,[1a] GEORGE M. REISNER,[1b] WILLI SCHWOTZER,[1a] and MIRIAM SHAIA[1b]

Received January 27, 1983

It has been shown that the equilateral triangular, bi-oxo-capped type of trimolybdenum cluster compound can be obtained by reducing Na_2MoO_4 in acetic anhydride. Both $W(CO)_6$ and zinc dust have been used as reductants. A red solid was first isolated and shown to conform closely to the formula $Na[Mo_3O_2(O_2CCH_3)_9]$. In acid solution this is quickly hydrolyzed to replace the three equatorial acetate ions by H_2O molecules. In neutral water hydrolysis is slow, affording crystals of the compound $[Mo_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]\cdot 16H_2O$, which was characterized by X-ray crystallography. The compound forms monoclinic crystals in space group *C2/m* with the following unit cell dimensions: a = 18.825 (5) Å, b = 19.017 (6) Å, c = 10.871 (3) Å, β = 95.5 (1)°, V = 3873 (1) Å^3, Z = 4. The molecule is bisected by a crystallographic mirror plane and has Mo–Mo distances of 2.796 (1) Å (twice) and 2.773 (1) Å. Mo–OH bonds are shorter (ca. 1.98 Å) than Mo–OH_2 distances (ca. 2.11 Å). There is an inverse relationship between an Mo–O (equatorial) distance and the adjacent Mo–Mo distances, which accounts for the lack of 3-fold symmetry in the Mo_3 cluster. ^1H NMR studies show that the hydrolytic cleavage of equatorial acetate ligands is acid catalyzed and is about 90% complete in about 1 h.

Introduction

Over the last few years it has been well established that the reactions of $Mo(CO)_6$ or $W(CO)_6$ with acetic acid or mixtures of acetic acid and acetic anhydride lead to the formation of trinuclear bicapped metal cluster compounds.[2-9] Other carboxylic acids may also be used, and the general formula for the species produced is $[M_3X_2(O_2CR)_6L_3]^{n\pm}$. In such a unit there is a central trigonal-bipyramidal $M_3(\mu_3\text{-}X)_2$ unit, with two RCO_2^- groups bridging across each M–M edge and one additional unidentate ligand, L (most often H_2O), attached to each metal atom. For tungsten[7] the only capping groups so far identified are oxygen atoms and the only formal oxidation state for the metal atoms is +4. The behavior of molybdenum has been more varied, with CCH_3 groups as well as O atoms in the capping positions and mean formal oxidation numbers of $+4^1/_2$ and $+4^2/_3$ as well as +4.0. With tungsten, however, it has also been possible to obtain a hemicapped (μ_3-O) species[10] for which no molybdenum analogue is yet known.

In exploring this chemistry further, one of our goals has been to find other ways in which the bicapped cluster compounds might be prepared. In this paper we report that they can be obtained from sodium molybdate by using either zinc dust or $W(CO)_6$ as a reductant. In addition, it was found that the initial product of these preparative reactions, $Na[Mo_3O_2(O_2CCH_3)_9]$, hydrolyzes in aqueous solution to deposit well-formed crystals of a compound that has been shown by X-ray crystallography to be $[Mo_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]\cdot 16H_2O$. The hydrolysis reaction has been studied by NMR, and the structural consequence of the mixed ligand set, H_2O + 2 OH^-, in the final product are discussed.

Experimental Section

Preparations. The preparative procedures to be described below require the use of pure (freshly recrystallized) $Na_2MoO_4\cdot 2H_2O$. If material that has been on the shelf for long periods of time is used, an initial blue (rather than red) product may be obtained. If this is dissolved in water, the color changes to red. This red material can then be quantitatively adsorbed to a cation-exchange resin and eluted with 2 M CF_3SO_3H. The visible spectrum of the eluate corresponds in all respects to the one reported[8] for $[Mo_3O_2(CH_3COO)_6(H_2O)_3]^{2+}$. In addition, crystals of $[Mo_3O_2(CH_3COO)_6(H_2O)_3](CF_3SO_3)_2$ were grown by slow evaporation. Unit cell constants were identical with the ones reported elsewhere.[10] The blue compound is insoluble in dry nonprotic solvents. In Me_2SO that was dried over molecular sieves it forms initially a blue suspension that partly turns into a red solution over a period of ca. 3 h. This red solution shows NMR signals at 2.22 and 1.85 ppm (singlets, chemical shifts relative to Me_4Si). They can reasonably be assigned to bridging acetate ions in $[Mo_3O_2(CH_3COO)_6L_3]^{2+}$ (2.22 ppm), where L_3 = $(Me_2SO)_3$, $(H_2O)_3$, or a mixture of both, and to free acetate ion (1.85 ppm).

To purify $Na_2MoO_4\cdot 2H_2O$, about 7 g of commercially available product was dissolved in 30 mL of H_2O. A 30-mL portion of methanol was added to the filtered solution, and the precipitate was collected

---

(1) (a) Texas A&M University. (b) Technion-Israel Institute of Technology.

(2) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1978**, *100*, 5252.

(3) Bino, A.; Cotton, F. A.; Dori, Z. *Inorg. Chim. Acta* **1979**, *33*, L133.

(4) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1979**, *101*, 3842.

(5) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1981**, *103*, 243.

(6) Bino, A.; Cotton, F. A.; Dori, Z.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 5779.

(7) Bino, A.; Cotton, F. A.; Dori, Z.; Koch, S.; Küppers, H.; Millar, M.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3245.

(8) Ardon, M.; Bino, A.; Cotton, F. A.; Dori, Z.; Kaftory, M.; Reisner, G. *Inorg. Chem.* **1982**, *21*, 1912.

(9) Bino, A.; Gibson, D. *J. Am. Chem. Soc.* **1982**, *104*, 4383.

(10) Ardon, M.; Cotton, F. A.; Dori, Z.; Fang, A.; Kapon, M.; Reisner, G. M.; Shaia, M. *J. Am. Chem. Soc.* **1982**, *104*, 5394.

0020-1669/83/1322-2723$01.50/0 © 1983 American Chemical Society

Table I. Pertinent Information about Data Collection and Structure Refinement

space group	*C*2/*m*
a	18.825 (5) Å
b	19.017 (6) Å
c	10.871 (3) Å
β	95.5 (1)°
V	3874.1 Å^3
mol formula	$Mo_3C_{12}O_{33}H_{54}$
mol wt	1014.4
Z	4
ρ(calcd)	1.74 g cm^{-3}
radiation used for data collected	Mo Kα (λ = 0.710 69 Å)
scanning range for 2*θ*	$5° \le 2\theta \le 50°$
stds for intensity control	$[31\bar{1}; 0\bar{2}\bar{1}; \bar{2}2\bar{1}]$
scan mode	*ω*/2*θ*
scan speed	1.5°/min
scan width	1.2° (in *ω*)
no. of unique reflctns used in the last cycle of least-squares	2576
no. of variables	240
final *R*(*F*)[a]	0.055
final $R_w(F)$[b]	0.055

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ with $w = \sigma(F_o)^{-2}$.

Table II. Final Positional Parameters (×10^5 for the Mo Atoms; and ×10^4 for the Light Atoms)

atom	*x*	*y*	*z*
Mo(1)	16613 (5)	0 (0)	23488 (9)
Mo(2)	19214 (3)	−7291 (3)	2041 (6)
O(1)	2458 (4)	0 (0)	1241 (6)
O(2)	1222 (3)	0 (0)	602 (6)
O(3)	858 (3)	−772 (3)	2402 (5)
O(4)	2367 (3)	−770 (3)	3192 (5)
O(5)	1455 (4)	0 (0)	4100 (7)
O(6)	2572 (3)	−1352 (3)	1480 (5)
O(7)	2047 (3)	−1654 (3)	−717 (5)
O(8)	2839 (3)	−583 (3)	−744 (5)
O(9)	1339 (3)	−584 (3)	−1529 (5)
O(10)	1067 (3)	−1354 (3)	687 (5)
C(1)	716 (4)	−1251 (4)	1606 (7)
C(2)	89 (4)	−1734 (4)	1787 (8)
C(3)	2673 (4)	−1245 (4)	2611 (8)
C(4)	3201 (5)	−1719 (5)	3367 (9)
C(5)	3126 (5)	0 (0)	−975 (10)
C(6)	3818 (7)	0 (0)	−1535 (16)
C(7)	1142 (5)	0 (0)	−2012 (11)
C(8)	684 (6)	0 (0)	−3209 (10)
O(11)	6516 (3)	2126 (2)	336 (5)
O(12)	2287 (3)	1418 (3)	6737 (6)
O(13)	7576 (5)	5000 (0)	5948 (10)
O(14)	3478 (4)	2297 (4)	7006 (7)
O(15)	3752 (4)	6620 (4)	5200 (6)
O(16)	5000 (0)	2608 (7)	5000 (0)
O(17)	9522 (4)	3705 (4)	937 (8)
O(18)	9003 (7)	5000 (0)	1875 (16)
O(19)	4722 (5)	1521 (5)	6719 (10)
O(201)	8856 (21)	5000 (0)	4679 (40)
O(202)	0 (0)	5657 (25)	5000 (0)
O(203)	1044 (18)	5315 (18)	4775 (32)
O(204)	−121 (36)	5000 (0)	3789 (66)

Table III. Bond Distances and Selected Bond Angles[a]

(A) Bond Distances (Å)

Mo(1)–Mo(2)	2.796 (1)	Mo(2)–O(9)	2.104 (5)
Mo(2)–Mo(2)′	2.773 (1)	Mo(2)–O(10)	2.106 (5)
Mo(1)–O(1)	2.012 (7)	O(3)–C(1)	1.267 (9)
Mo(2)–O(1)	1.999 (5)	O(4)–C(3)	1.276 (10)
Mo(1)–O(2)	1.997 (7)	O(6)–C(3)	1.242 (11)
Mo(2)–O(2)	1.989 (5)	O(8)–C(5)	1.270 (7)
Mo(1)–O(3)	2.112 (5)	O(9)–C(7)	1.269 (7)
Mo(1)–O(4)	2.125 (5)	O(10)–C(1)	1.265 (9)
Mo(1)–O(5)	1.979 (7)	C(1)–C(2)	1.525 (10)
Mo(2)–O(6)	2.121 (5)	C(3)–C(4)	1.519 (11)
Mo(2)–O(7)	2.049 (5)	C(5)–C(6)	1.490 (16)
Mo(2)–O(8)	2.113 (5)	C(7)–C(8)	1.489 (15)

(B) Bond Angles (deg)[b]

Mo(1)–Mo(2)–Mo(2)′	60.27 (2)	Mo(1)–O(2)–Mo(2)	89.1 (2)
Mo(2)–Mo(1)–Mo(2)′	59.46 (2)	Mo(2)–O(1)–Mo(2)′	87.9 (2)
Mo(1)–O(1)–Mo(2)	88.4 (2)	Mo(2)–O(2)–Mo(2)′	88.4 (2)

[a] Atoms labeled with primes are related to the reference atoms by mirror-plane symmetry. [b] A complete list of bond angles is available as supplementary material.

by filtration, washed with two portions of diethyl ether, and dried in a desiccator. The yield is 6.7 g of fine white crystalline powder.

Reduction with $W(CO)_6$. A mixture of sodium molybdate dihydrate (0.5 g), $W(CO)_6$ (1 g), and acetic anhydride (50 mL) was refluxed under N_2 for 4 h. When the mixture was cooled, a red precipitate was obtained, washed with ether, and dried. A sample that had been pumped at 25 °C for 5 h was analyzed, leading to assignment of the formula $Na[Mo_3O_2(O_2CCH_3)_9]$. Anal. Calcd for $C_{18}H_{27}O_{20}Mo_3Na$: C, 24.72; H, 3.09; Na, 2.63. Found: C, 23.8; H, 3.06; Na, 2.87. The dried red precipitate can be recrystallized from methanol.

Reduction with Zinc. A mixture of $Na_2MoO_4 \cdot 2H_2O$ (2 g), zinc dust (2 g), and acetic anhydride (100 mL) was refluxed for 4 h. The red precipitate obtained on cooling was separated by filtration, washed with ether, and dried. Its behavior and spectrum indicated that it contains a trimolybdenum cluster similar to (or identical with) that in the red precipitate above. The two precipitates are not, however, entirely identical.

Hydrolysis of $Na[Mo_3O_2(O_2CCH_3)_9]$. Hydrolysis is very slow in neutral aqueous solution. When such a solution was slowly evaporated in room air at ca. 25 °C, excellent crystals of what was shown by X-ray crystallography (see below) to be $[Mo_3O_2(O_2CCH_3)_6(H_2O)(OH)_2] \cdot 16H_2O$ were obtained. In 0.1 M acid, hydrolysis is relatively rapid, as shown by NMR measurements made at probe temperature (26.1 °C) on a Varian spectrometer. By use of either method for reduction of the molybdate, the isolated yield after hydrolysis is about 75%.

Crystallographic Study of $[Mo_3O_2(O_2CCH_3)_6(H_2O)(OH)_2] \cdot 16H_2O$. The crystals were red plates that were stable in the mother liquor but decomposed rapidly when exposed to open air. A single crystal of dimensions 0.1 × 0.3 × 0.3 mm was placed in a Lindemann glass capillary that already contained a few drops of the mother liquor.

The data were collected on a Phillips PW-1100 four-circle diffractometer. Pertinent details are given in Table I. Accurate cell dimensions were determined by centering 25 strong high-angle reflections and are given in Table I. Lorentz and polarization corrections were made; absorption corrections were not applied. All data processing and other calculations were carried out by using the SHELX-77 system of programs.

The structure was solved by the heavy-atom technique. A three-dimensional Patterson map yielded the positions of the Mo atoms. All the remaining non-hydrogen atoms were located from successive difference Fourier maps. Anisotropic refinement of all the non-hydrogen atoms (except for the disordered water molecule, O(20), which was kept isotropic) converged to a final *R* factor of 0.055 (R_w = 0.055). The final statistical weights were $w = 1.2676/[\sigma^2(F_o) + 0.000982F_o^2]$. A 1.5 cutoff on F_o was used throughout the refinement. No unusually high correlations were noted between any variables in the final least-squares cycle. The atomic positional parameters are listed in Table II. The interatomic distances and angles are listed in Table IIIA,B, respectively. Observed and calculated structure factors are available as supplementary material. The structure of the neutral trimer and its atomic numbering scheme are shown in Figure 1.

Results and Discussion

Preparative Procedure. The generation of trinuclear molybdenum(IV) clusters of the bicapped type has now been accomplished simply by reduction of the molybdate ion; the reduction can be done by using such a classical and relatively cheap reducing agent as zinc. In all likelihood, this general approach is the simplest and cheapest that we can expect to have.

The particular conditions under which the reduction has been carried out lead initially to a triangulo cluster in which the three equatorial ligands, the L entities in $[Mo_3O_2(O_2CR)_6L_3]$, are carboxylate ions. A similar product containing tungsten, $Cs[W_3O_2(O_2CCH_3)_9] \cdot 3H_2O$, was reported[7]

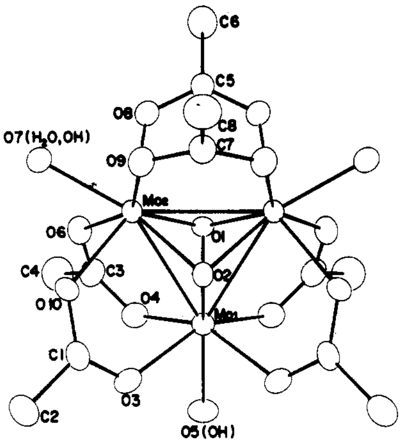


Figure 1. View of the $[Mo_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]$ molecule showing the atomic numbering scheme. A plane of symmetry passes through O(5), Mo(1), O(1), O(2), and C(5)–C(8).

Table IV. ^1H NMR Data

		rel intens of signals of CH_3CO_2 group (δ rel to DSS[e])			
				free	
time,[a] min	solvent	bridging (2.28)	equatorial (2.18)	anion (1.91)	acid (2.09)
0–60	D_2O	6.00	2.65	0.23	
ca. 10	0.1 M DCl[d]	6.00[b]	1.48		1.49
15	0.1 M DCl[d]	6.00[c]	0.89		2.20
30	0.1 M DCl[d]	6.00	0.59		2.32
45	0.1 M DCl[d]	6.00	0.47		2.56
60	0.1 M DCl[d]	6.00	0.30		2.71

[a] Time from preparation of solution to recording of spectrum.
[b] Double peak; see Figure 2. [c] Broad single peak.
[d] Concentrated DCl diluted with D_2O. [e] DSS = 3-(trimethylsilyl)-propanesulfonic acid, sodium salt.

several years ago. In the present work, the initial product, $Na[Mo_3O_2(O_2CCH_3)_9]$, has not been studied structurally, although it probably could be, by using crystals obtained from a methanol solution. Instead, we have examined the product obtained when we attempted to recrystallize $Na[Mo_3O_2(O_2CCH_3)_9]$ from aqueous solution. The results of that structural work will be presented below. They demonstrate that in aqueous solution slow hydrolytic cleavage of the equatorial acetate ions takes place, allowing the slow growth of crystals of a compound containing the neutral molecule $[Mo_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]$.

We have studied the process of hydrolysis by spectroscopic means. It can be followed in the visible spectrum but ^1H NMR provides more detailed information. The spectrum of a fresh solution of $Na[Mo_3O_2(O_2CCH_3)_9]$ in D_2O is shown as (a) in Figure 2. The three signals (see Table IV for details) correspond to the bridging $CH_3CO_2^-$ groups, the equatorial $CH_3CO_2^-$ groups, and uncoordinated $CH_3CO_2^-$ ions, in order of decreasing intensities (and higher field location). Over a period of 1 h in neutral solution, changes in this spectrum were almost imperceptible. The ratio of the intensity of the lowest field peak to the sum of the intensities of the other two is very close to 2:1.

Hydrolysis is catalyzed by acid. After the period of about 10 min required to prepare a solution and record the spectrum in 0.1 M HCl (in D_2O), the spectrum shown as (b) in Figure 2 was obtained. Here the signal due to equatorial acetate groups has lost about half of its expected intensity based on the $[Mo_3O_2(O_2CCH_3)_9]^-$ structure, and there is an approximately equally intense signal for CH_3CO_2H. The sum of the latter two intensities is, as it should be, equal to half the intensity of the total signal for the bridging acetate groups.

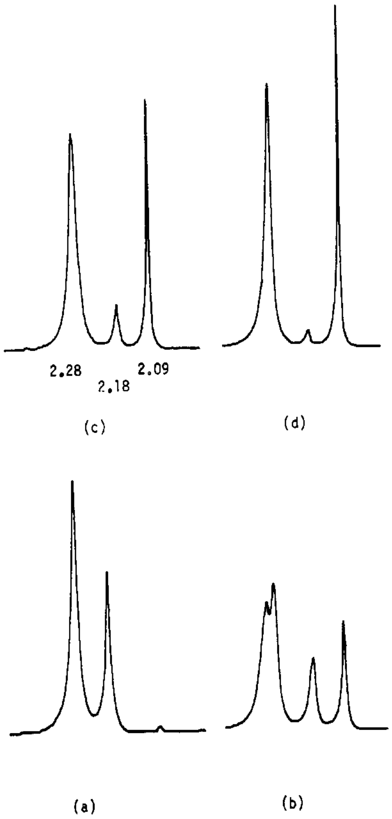
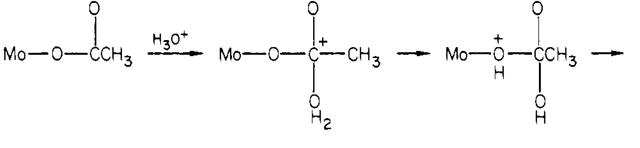


Figure 2. ^1H NMR spectra of $Na[Mo_3O_2(O_2CCH_3)_9]$: (a) in D_2O, 0–60 min; (b) in 0.1 M DCl, ca. 15 min after preparation of solution; (c) in 0.1 M DCl, ca. 30 min after preparation of solution; (d) in 0.1 M DCl, ca. 60 min after preparation of solution.

The doubling of the bridging acetate signal is understandable because the expected intermediates in the total process of hydrolysis, $[Mo_3O_2(\mu\text{-}O_2CCH_3)_6(O_2CCH_3)_2(H_2O)]$ and $[Mo_3O_2(\mu\text{-}O_2CCH_3)_6(O_2CCH_3)(H_2O)_2]^+$, each have two kinds of $\mu\text{-}O_2CCH_3$ groups.

Figure 2 also shows spectra recorded after approximately 30 and 60 min, and the data for these and other times are listed in Table IV. Evidently, in 0.1 M acid after about 1 h the hydrolysis is about 90% complete.

The catalytic effect of acid on the hydrolysis and the extreme slowness of hydrolysis in the absence of acid can be understood in the following way. Bimolecular displacement of $CH_3CO_2^-$ from the molybdenum atom by direct attack of OH^- or H_2O on the latter is not an important path since the metal atoms in these species are nine-coordinate. Therefore, the preferred pathway is probably similar to the well-established one for acid-catalyzed ester hydrolysis, namely



The Structure. The structure consists of $[Mo_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]$ molecules linked into an elaborate network of hydrogen bonds through intervening water molecules. The 64 water molecules per unit cell are accounted for as follows. O(11), O(12), O(14), O(15), O(17), and O(19) represent water molecules on general (8×) positions. O(13), O(16), and O(18) reside on positions of mirror or twofold symmetry (4×). In this way 48 + 12 = 60 water molecules are accounted for. The sets of general positions partially occupied by O(20), viz. O(201)–O(204), with occupancies of 0.1, 0.125, 0.175, and

0.1, respectively, provide the remaining four water molecules per cell. Each of the water molecules forms two to four hydrogen bonds, mostly among themselves but also to the equatorial OH and H_2O groups of the cluster molecule. The O···O distances range from 2.56 to 2.92 Å. A complete tabulation of hydrogen bonds is available as supplementary material.

The metal cluster unit deviates slightly but significantly from threefold symmetry. We believe that these deviations can be understood in the following way. O(5) represents an equatorial OH group. The Mo(1)-O(5) distance, 1.979 (7) Å, is appreciably shorter than the Mo-OH_2 distances previously reported,[11] which run from 2.083 [10] to 2.144 [4] Å. Evidently, OH^- is a significantly stronger donor in this context than H_2O. The Mo(2)-O(7) and Mo(2)′-O(7)′ bond lengths are each considered to represent an equal-weighted average of Mo-OH and Mo-OH_2 bonds, and the observed bond distance, 2.049 (5) Å compares favorably with the average of ca. 1.98 and ca. 2.11 Å, the typical Mo-OH and Mo-OH_2 distances.

If we then make the reasonable assumption that the stronger the Mo-O (equatorial) bond the weaker will be the adjacent Mo-Mo bonds, we can account for the observed pattern of Mo-Mo bond lengths. The Mo(1)-Mo(2) and Mo(1)-Mo(2)′ bonds, which always have OH^- at one end and have OH^- at the other end half the time, are longer, 2.796 (1) Å, than the Mo(2)-Mo(2)′ bond, which is always of the HO-Mo-Mo-OH_2 type (though disordered) and is shorter at 2.773 (1) Å. In cases containing only axial Mo-OH_2 bonds, the Mo-Mo bond lengths are shorter than either of the above, running from 2.752 [2] Å to 2.766 (2) Å.[10]

The effect of replacing Mo-OH_2 by Mo-OH in lengthening adjacent Mo-Mo bonds (by an amount that can be estimated to be about 0.040-0.050 Å on going from all Mo-OH_2 to all Mo-OH) is not surprising, since the Mo-OH bonds are evidently appreciably stronger than Mo-OH_2 bonds. It is, however, important to be cognizant that such a change in Mo-Mo distances can occur even when the nominal bond order (i.e., number of electrons formally available in the cluster for Mo-Mo bonding) is not changed.

The Mo-(μ_3-O) bond lengths average 1.998 [3] Å, which is not different from values found in other bi-oxo-capped Mo_3 cluster species, where they are in the range[11] 1.984 [4]-2.004 [6] Å.

Acknowledgment. We thank the U.S. National Science Foundation and the U.S.-Israeli Binational Science Foundation for financial support.

Registry No. $[Mo_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]\cdot xH_2O$, 86709-53-7; $Na[Mo_3O_2(O_2CCH_3)_9]$, 86695-77-4; Na_2MoO_4, 7631-95-0.

Supplementary Material Available: Tables of structure factors, thermal parameters, and bond angles and nonbonded contacts less than 3.0 Å (19 pages). Ordering information is given on any current masthead page.

---

(11) Cotton, F. A.; Dori, Z.; Marler, D. O.; Schwotzer, W., submitted for publication in *Inorg. Chem.*

Contribution from the Department of Chemistry, Guelph-Waterloo Centre for Graduate Work in Chemistry,
Waterloo Campus, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

Chemistry of Multisite-Bound Ligands. Addition of Amines to μ-η^2-Acetylides: Dipolar, Electron-Rich μ-η^1- and μ-η^2-Alkylidene and μ-η^1-Vinylidene Diiron Hexacarbonyl Complexes

GRAHAM N. MOTT and ARTHUR J. CARTY*

Received October 28, 1982

As part of a major effort to explore and establish patterns of reactivity for multisite-bound unsaturated ligands, the reactions of the μ-η^2-acetylides $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$ (**1**) (R = C_6H_5, *p*-$MeOC_6H_4$, *p*-BrC_6H_4, C_6H_{11}, $C(CH_3)_3$) toward primary, secondary, and tertiary amines have been investigated. Three types of addition products have been isolated and characterized by microanalysis and infrared, ^1H and ^{31}P NMR, and Mössbauer spectroscopy. Solid-state structures by X-ray crystallography are available for several of the adducts. Attack at the β-carbon of the acetylide affords zwitterionic μ-vinylidene compounds $Fe_2(CO)_6[C{=}C\{NHR^1R^2\}R][P(C_6H_5)_2]$ (**4**); attack at the β-carbon atom by primary or secondary amines with hydrogen transfer yields dipolar μ-alkylidene derivatives $Fe_2(CO)_6[CHC\{NR^1R^2\}R][P(C_6H_5)_2]$ (**3**) with a single carbon atom bridge between iron atoms. Attack at the α-carbon atom of the μ-η^2-acetylide with hydrogen migration gives the μ-η^2-alkylidene derivatives $Fe_2(CO)_6[C\{NR^1R^2\}CR][P(C_6H_5)_2]$ (**2**) where a two-carbon three-electron ligand is present. ^{31}P NMR and Mössbauer studies permit facile differentiation of the three structural types; in particular $\delta(^{31}P)$ shifts show a systematic variation with M-P-M angle and M- - -M bond length, with larger, downfield shifts corresponding to greater Fe-P-Fe angles. Factors affecting the electrophilicity of the multisite-bound acetylides in **1** and the regiospecificity of nucleophilic attack have been probed via ^{13}C NMR studies of the precursors and variable-temperature ^{31}P studies of reactions of **1** with a variety of nucleophiles. Multisite coordination confers enhanced reactivity toward nucleophilic attack with the site of attachment of the nitrogen nucleophile determined principally by polarization in the μ triple bond, the steric bulk of the substituent R in **1**, and the incoming nucleophile.

Introduction

There is now abundant evidence that multisite coordination of unsaturated molecules to two or more metals in polynuclear transition-metal clusters frequently leads to ligand activation and novel types of chemical reactivity.[1] Particular attention has recently focused on the reactivity of highly coordinated carbon monoxide[2] and carbidic carbon atoms[3] in carbonyl clusters and on the chemistry of certain proposed model intermediates[4] such as μ-methylidyne, μ-methylene, μ-vinylidene, and formyl and hydroxymethyl complexes possibly implicated

---

(1) For recent reviews of metal cluster chemistry see: (a) Johnson, B. F. G.; Lewis, J. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 225. (b) Johnson, B. F. G., Ed. "Transition Metal Clusters"; Wiley: New York, 1980. (c) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207. (d) Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1980**, *25*, 145.

(2) (a) Holt, E. M.; Whitmire, K.; Shriver, D. F. *J. Chem. Soc., Chem. Commun.* **1980**, 778. (b) Dawson, P. A.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *Ibid.* **1980**, 781.

(3) Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4541. (b) Bradley, J. S.; Ansell, G. B.; Hill, M. E. *Ibid.* **1979**, *101*, 7417.

(4) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479.

0020-1669/83/1322-2726$01.50/0 © 1983 American Chemical Society