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The First Triangular Trinuclear Cluster Compounds of Molybdenum with Nine Cluster Electrons: $[Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}O_2CCH_3)_3Cl_n(PR_3)_{3-n}]^{1-n}$, $n = 1\text{-}3$

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Abstract: The first four M_3X_{13} type molybdenum triangular trinuclear cluster compounds with nine cluster electrons are described in this paper: $(Bu_4N)_2[Mo_3OCl_6(OAc)_3]\cdot Me_2CO$ (**1**), $(Bu_4N)[Mo_3OCl_5(OAc)_3(PMe_3)]\cdot 2THF$ (**2**), $[Mo_3OCl_4(OAc)_3(PMe_3)_2]$ (**3**), and $[Mo_3OCl_4(OAc)_3(PMe_3)_2]\cdot THF$ (**4**). The first three compounds were obtained by chemical reduction of $(Bu_4N)[Mo_3OCl_6(OAc)_3]\cdot Me_2CO$, and the last one was prepared as a byproduct from a reaction mixture containing $MoCl_3(THF)_3$, Na/Hg, S, NaOAc, and PMe_3. In all four compounds, each metal atom has the formal oxidation state +3 and there are nine electrons for the metal cluster. Physical measurements indicated that these compounds are paramagnetic and have one unpaired electron, which is in good accord with theoretical calculations. In compound **1** the metal–metal bond distances are 2.617 (1), 2.598 (1), and 2.598 (1) Å. The crystals belong to the space group *Cc* with $Z = 4$. The unit cell dimensions are $a = 22.600$ (3) Å, $b = 12.031$ (2) Å, $c = 23.110$ (4) Å, $\beta = 113.51$ (1)°, $V = 5762$ (2) Å^3. In compound **2**, the metal–metal bond distances are 2.637 (1), 2.573 (1), and 2.567 (1) Å. It crystallized in the space group $P2_1/c$ with $Z = 4$ and the following unit cell dimensions $a = 13.419$ (3) Å, $b = 19.882$ (5) Å, $c = 18.630$ (5) Å, $\beta = 96.27$ (2)°, $V = 4940$ (2) Å^3. Compound **3** belongs to the space group $P2_1/c$ with $a = 10.381$ (3) Å, $b = 12.680$ (2) Å, $c = 19.402$ (2) Å, $\beta = 90.09$ (1)°, $V = 2553.6$ (8) Å^3, and $Z = 4$. The metal–metal bond distances are 2.5878 (5), 2.6117 (5), and 2.5764 (5) Å. Compound **4** forms triclinic crystals in the space group $P\bar{1}$ with the following unit cell dimensions: $a = 10.121$ (2) Å, $b = 11.013$ (2) Å, $c = 14.628$ (3) Å, $\alpha = 97.71$ (2)°, $\beta = 93.06$ (2)°, $\gamma = 104.62$ (2)°, $V = 1556.9$ (6) Å^3, and $Z = 2$. The metal–metal bond distances are 2.597 (1), 2.608 (1), and 2.5673 (9) Å.

Introduction

In a recent paper[1] we reported that not only molybdenum but also tungsten is capable of forming compounds of the type $[Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3]L_9$ in which there are eight electrons occupying molecular orbitals mainly confined to the M_3 cluster. As we pointed out, previous work,[2-4] both theoretical and experimental, had favored the idea that a six-electron configuration, $(1a_1)^2(1e)^4$, would be most favorable, corresponding as it does to the existence of a set of three M–M single bonds. However, this concept was implicitly based on experience with M_3O_4 cores, and, evidently, a change to the Mo_3OCl_3 core sufficiently lowers the energy of the next $(2a_1)$ orbital so that the $(1a_1)^2(1e)^4(2a_1)^2$ configuration becomes the favored one.

According to very approximate calculations, the LUMO for this eight-electron system would be the 2e orbital, and this would be expected to have a M–M antibonding nodal structure. It was not, therefore, anticipated that stable nine-electron species would exist. Nevertheless, by carrying out the preparations in a reducing preparation environment, several nine-electron compounds have now been prepared, isolated, and structurally characterized. In this paper, we describe four compounds containing the nine-electron Mo_3OCl_3 core, which, as expected, appear to have one unpaired electron in a degenerate orbital.

Experimental Section

All manipulations were carried out under an atmosphere of dry, oxygen-free argon with Schlenk techniques, unless otherwise noted. Solvents were dried and deoxygenated by refluxing over appropriate reagents before use. Zinc metal dust was purchased from Fisher Scientific Co. Trimethylphosphine was purchased from Aldrich Co. Sodium amalgam (Na/Hg) was prepared by dissolving Na metal (1.91 g, 68 mmol) in Hg (34 mL), and it was assumed to have a Na concentration of 2 mmol/mL. The starting material $(Bu_4N)[Mo_3OCl_6(OAc)_3]\cdot Me_2CO$ was made by a method similar to that used to prepare $(Me_4N)[Mo_3OCl_6(OAc)_3]\cdot 2HOAc$[1] except that a stoichiometric amount of Bu_4NBF_4 was used instead of Me_4NCl, and acetone was used for the recrystallization instead of acetic acid.

Preparation of $(Bu_4N)_2[Mo_3OCl_6(OAc)_3]\cdot Me_2CO$ (1). A mixture of $(Bu_4N)[MoOCl_6(OAc)_3]\cdot Me_2CO$ (0.60 g, 0.64 mmol), zinc metal dust (0.021 g, 0.32 mmol), and Bu_4NCl (0.21 g, 0.64 mmol) was stirred in THF solvent (20 mL) at 60 °C overnight. A mixture of green-brown solution and green-brown precipitate was formed. Then, the solution phase was filtered off. The green-brown precipitate was treated with acetone (20 mL) to give a brown solution and a grey precipitate. The mixture was filtered again, and the filtrate was layered with hexane. Crystals were formed after several days. Yield: 0.52 g, 66%.

Preparation of $(Bu_4N)[Mo_3OCl_5(OAc)_3(PMe_3)]\cdot 2THF$ (2). $(Bu_4N)[Mo_3OCl_6(OAc)_3]\cdot Me_2CO$ (2.0 g, 2.14 mmol), zinc metal dust (0.07 g, 1.07 mmol), and trimethylphosphine (0.22 mL, 2.14 mmol) were stirred in THF solvent (20 mL) for 36 h at room temperature. A mixture of brown solution and brown precipitate was formed. The mixture was filtered, and the filtrate was layered with hexane. Dark crystals were formed after the diffusion was complete. Yield: 0.33 g, 15%.

Preparation of $[Mo_3OCl_4(OAc)_3(PMe_3)_2]$ (3). $(Bu_4N)[Mo_3OCl_6(OAc)_3]\cdot Me_2CO$ (2.0 g, 2.14 mmol), zinc metal dust (0.07 g, 1.07 mmol), and trimethylphosphine (0.44 mL, 4.28 mmol) were stirred in THF solvent (20 mL) for 36 h at room temperature. The major product was a dark brown precipitate, which was separated from the solution phase by filtration and treated with acetone (20 mL). A mixture of brown solution and grey precipitate was formed. The mixture was filtered, and the filtrate was layered with hexane. Crystals were formed after several days of standing. Yield: 1.1 g, 63%.

Preparation of $[Mo_3OCl_4(OAc)_3(PMe_3)_2]\cdot THF$ (4). Compound **4** was obtained in the attempt to synthesize molybdenum eight-electron trinuclear compounds with capping sulfur and terminal phosphine ligands. $MoCl_3(THF)_3$ (0.20 g, 0.48 mmol), S_8 (0.01 g, 0.08 mmol), and NaOAc (0.066 g, 0.8 mmol) were placed in a three-necked flask and stirred in THF (20 mL) at 70 °C overnight. Na/Hg (0.08 mL, 0.16 mmol) and PMe_3 (0.10 mL, 0.96 mmol) were added. A mixture of a brown solution and a grey precipitate was formed after stirring overnight, which was then filtered, and the filtrate was layered with hexane. Crystals were formed after the diffusion was complete.

Electronic Spectroscopy. The electronic spectra of compounds **1**, **2**, and **3** were obtained on a Cary-17 spectrophotometer. They are shown in Figure 1. Although the spectra of these three compounds have not been assigned, they can be used to identify them.

NMR Spectroscopy. The ^1H NMR spectrum of **3** in acetone-d_6 was measured on a Varian XL-200 NMR spectrometer. The ^{31}P spectra of **3** at temperatures between −78 °C and 20 °C in solvent CH_2Cl_2 were

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[1] Cotton, F. A.; Shang, M.; Sun, Z. S. *J. Am. Chem. Soc.* **1991**, *113*, 3007–3011.

[2] Cotton, F. A. *Inorg. Chem.* **1964**, *3*, 1217.

[3] Bursten, B. E.; Cotton, F. A.; Hall, M. B.; Najjar, R. C. *J. Am. Chem. Soc.* **1982**, *21*, 302.

[4] Cotton, F. A. *Polyhedron* **1986**, *5*, 3.

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also measured on the Varian XL-200 NMR spectrometer.

EPR Spectroscopy. The spectra of compound **3** in solvent CH_2Cl_2 were recorded on a Bruker ESP-300 with Oxford 910 Cryostat equipment. EPR conditions: (A) 10 K sample temperature, 0.126 mw microwave power, 9.43 GHz microwave frequency, 5.116 G modulation amplitude; (B) 298 K sample temperature, 126 mw microwave power, 9.45 GHz microwave frequency, 5.01 G modulation amplitude. The EPR spectrum of compound **3** in the solid phase was also measured on the same spectrometer at room temperature.

Magnetic Measurement. The magnetic susceptibility measurement on compound **3** was carried out on a Johnson Matthey magnetic susceptibility balance at 25 °C.

Electrochemical Measurements. The cyclic voltammogram was recorded on a BAS-100 Electronic Analyzer in the range −1.8 to 1.8 V for compound **3** with sweep rates 20–200 mV/s. Platinum electrodes were used as the auxiliary and working electrodes, and a Ag/AgCl electrode was used as the reference electrode. A solution of 0.2 M tetrabutylammonium tetrafluoroborate and 10^{-3} M compound **3** in acetonitrile was degassed with a nitrogen flow for at least 5 min prior to making measurements.

X-ray Crystallography. The basic crystallographic procedures have been fully described elsewhere.[5] Because all the compounds are air stable, no special precautions were taken when mounting the crystals. Typically, the crystals were mounted on the top of thin glass fibers with the use of epoxy cement. The intensity data of compounds **1** and **4** were collected on a Syntex-P3 equivalent diffractometer, while those of compounds **2** and **3** were collected on an Enraf-Nonius CAD-4 diffractometer. On both diffractometers, Mo Kα radiation (λ_α = 0.71073 Å) was used as the incident beam. Unit cell dimensions were determined by accurately centering 25 reflections in the 2θ range of 28–36°. Intensity data were measured by the ω-2θ scan method. Data reductions and corrections were conducted by the methods which are standard in this laboratory.[6] In each case, no significant decay was observed. Empirical absorption corrections were applied based on the ψ scan data of seven reflections with their χ angles near 90°. The positions of the three independent molybdenum atoms in four compounds were all derived by the Patterson method (SHELXS-86). The other atoms were then found by a combination of least-squares refinement and difference Fourier syntheses. Table I lists important crystallographic data for compounds **1**–**4**.

Compound 1. Systematic absences indicated that the possible space groups were *Cc* or *C*2/*c*. Crystal structure analysis was carried out assuming that the space group was accentric *Cc* because the unit cell could accommodate only four cluster molecules for its size and the *C*2/*c* space group would impose unacceptable symmetry elements, such as an inversion center or 2-fold axis on the cluster anion so as to reduce the multiplicity of these molecules. This choice was later fully confirmed by the successful location of all atoms and satisfactory structure refinement. All non-hydrogen atoms were refined anisotropically except for the carbon atoms of one of the tetrabutylammonium cations, which were refined only isotropically. Some carbon atoms from a butyl group in the first Bu_4N^+ cation (C(19)–C(22)) and from the second Bu_4N^+ cation (C(23)–C(38)) showed rather large isotropic or equivalent isotropic thermal parameters (>20 Å^2) or had some irregular C–C single bond lengths, such as a little larger than 1.65 or less than 1.40 Å. These results were indicative of slight disorder of these atoms, which were therefore refined with constrained bond distances by using the SHELX-76 crystallographic package (C–C, 1.54 Å; C–N, 1.48 Å). The five highest peaks in the final difference Fourier map were around the N(2) atom with a distance range from 1.386 to 1.582 Å, which indicated that part of the central tetrahedral structural units formed by the N(2) and the four α carbon atoms from the four butyl chains had different orientations from those of the major part. However, this kind of orientation disorder was not serious since the highest residual electron density was only 0.624 e/Å^3 and the thermal parameters for the four α carbon atoms with full site occupancy were reasonable. Therefore, no further effort was made to take explicit account of the disorder.

Compound 2. From systematic absences the space group was determined to be *P*2$_1$/*c*. All atoms were refined anisotropically except for the atoms from the interstitial THF solvent, which were refined only isotropically. The oxygen atom was arbitrarily assigned to that ring atom in the THF group which showed the lowest thermal parameter after these ring atoms were all refined as carbon atoms. Some of these ring atoms showed also rather large thermal parameters (>20 Å^2) and had anomalously short bond distances (<1.4 Å), which indicated that the solvent molecule was slightly disordered. Therefore, in the final refinement these atoms were refined with constrained C–C bond distances (1.54 Å), with the SHELX-76 crystallographic package. The highest residual electron density in a final difference Fourier map was 0.773 e/Å^3. The six highest peaks were all around the THF group. However, as these peaks were not significant, no effort was made to define more precisely the disorder mode.

Compound 3. All non-hydrogen atoms were refined anisotropically in the uniquely determined space group *P*2$_1$/*c*. All hydrogen atoms were then found by a difference Fourier synthesis and were refined isotropically in the final refinement. The final difference Fourier map was featureless with the highest residual electron density 0.318 e/Å^3.

Compound 4. The structure was solved and refined successfully by assuming the centric space group *P*$\bar{1}$. The oxygen atom for the interstitial THF solvent was assigned in the same way as in compound **2**. In the final refinement all non-hydrogen atoms were refined anisotropically,

Figure 1. The electronic spectra of compounds **1**, **2** (dot-dashed line), and **3** (dashed line).

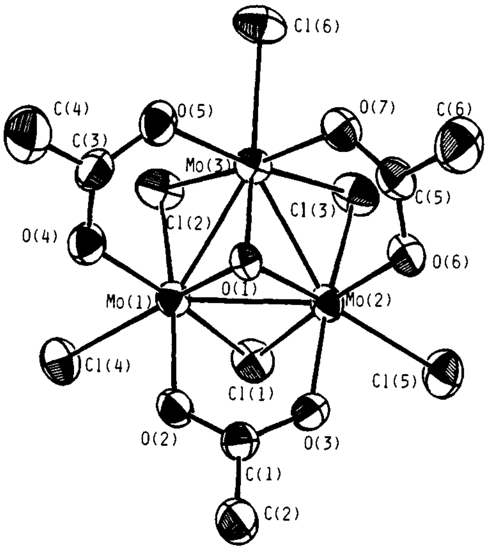

Figure 2. An ORTEP drawing of the anion of **1**. The thermal ellipsoids are at the 50% probability level.

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[5] (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

[6] Calculations were done on a Local Area VAX cluster (VMS V4.6), with the programs SHELX-76, SHELXS-86, and the commercial package SDP/V V3.0.

Table I. Crystallographic Data for Compounds **1-4**

compd	1	2	3	4
formula	$Mo_3Cl_6O_8N_2C_{41}H_{87}$	$Mo_3Cl_5PO_9NC_{33}H_{70}$	$Mo_3Cl_4P_2O_7C_{12}H_{27}$	$Mo_3Cl_4P_2O_8C_{16}H_{35}$
fw	1236.70	1120.99	774.92	838.67
space group	*Cc*	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	22.600 (3)	13.419 (3)	10.381 (3)	10.121 (2)
b, Å	12.031 (2)	19.882 (5)	12.680 (2)	11.013 (2)
c, Å	23.110 (4)	18.630 (5)	19.402 (2)	14.628 (3)
α, deg				97.71 (2)
β, deg	113.51 (1)	96.27 (2)	90.09 (1)	93.06 (2)
γ, deg				104.62 (2)
V, $Å^3$	5762 (2)	4940 (2)	2553.6 (8)	1556.9 (6)
Z	4	4	4	2
d_{calc}, g/cm^3	1.426	1.507	2.015	1.789
radiation (monochromated in incident beam)		Mo Kα (λ_α = 0.71073 Å)		
R	0.047	0.045	0.023	0.038
R_w	0.068	0.062	0.032	0.063
temp, °C		20		

Table II. Selected Bond Distances (Å) and Angles (deg) for $(Bu_4N)_2[Mo_3OCl_6(OAc)_3]\cdot Me_2CO$[a]

atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance
Mo(1)	Mo(2)	2.617 (1)	Mo(1)	O(4)	2.105 (8)	Mo(2)	O(6)	2.106 (8)
Mo(1)	Mo(3)	2.598 (1)	Mo(2)	Mo(3)	2.598 (2)	Mo(3)	Cl(2)	2.434 (4)
Mo(1)	Cl(1)	2.439 (4)	Mo(2)	Cl(1)	2.430 (3)	Mo(3)	Cl(3)	2.442 (4)
Mo(1)	Cl(2)	2.429 (4)	Mo(2)	Cl(3)	2.442 (4)	Mo(3)	Cl(6)	2.463 (4)
Mo(1)	Cl(4)	2.479 (4)	Mo(2)	Cl(5)	2.469 (4)	Mo(3)	O(1)	1.976 (8)
Mo(1)	O(1)	1.997 (8)	Mo(2)	O(1)	1.979 (8)	Mo(3)	O(5)	2.117 (9)
Mo(1)	O(2)	2.11 (1)	Mo(2)	O(3)	2.126 (9)	Mo(3)	O(7)	2.112 (9)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Mo(2)	Mo(1)	Mo(3)	59.77 (5)	Cl(1)	Mo(2)	Cl(5)	88.9 (1)	Cl(2)	Mo(3)	O(5)	89.2 (3)
Cl(1)	Mo(1)	Cl(2)	89.0 (1)	Cl(1)	Mo(2)	O(1)	106.6 (2)	Cl(2)	Mo(3)	O(7)	172.6 (3)
Cl(1)	Mo(1)	Cl(4)	89.4 (1)	Cl(1)	Mo(2)	O(3)	90.5 (2)	Cl(3)	Mo(3)	Cl(6)	89.1 (1)
Cl(1)	Mo(1)	O(1)	105.7 (2)	Cl(1)	Mo(2)	O(6)	173.2 (2)	Cl(3)	Mo(3)	O(1)	106.5 (3)
Cl(1)	Mo(1)	O(2)	89.5 (3)	Cl(3)	Mo(2)	Cl(5)	89.3 (1)	Cl(3)	Mo(3)	O(5)	173.7 (3)
Cl(1)	Mo(1)	O(4)	174.4 (2)	Cl(3)	Mo(2)	O(1)	106.4 (3)	Cl(3)	Mo(3)	O(7)	89.1 (2)
Cl(2)	Mo(1)	Cl(4)	89.5 (1)	Cl(3)	Mo(2)	O(3)	173.3 (3)	Cl(6)	Mo(3)	O(1)	157.5 (2)
Cl(2)	Mo(1)	O(1)	106.3 (3)	Cl(3)	Mo(2)	O(6)	89.1 (3)	Cl(6)	Mo(3)	O(5)	84.6 (3)
Cl(2)	Mo(1)	O(2)	173.2 (2)	Cl(5)	Mo(2)	O(1)	157.8 (3)	Cl(6)	Mo(3)	O(7)	84.0 (3)
Cl(2)	Mo(1)	O(4)	90.5 (3)	Cl(5)	Mo(2)	O(3)	84.0 (3)	O(1)	Mo(3)	O(5)	79.6 (4)
Cl(4)	Mo(1)	O(1)	158.0 (2)	Cl(5)	Mo(2)	O(6)	84.7 (3)	O(1)	Mo(3)	O(7)	80.4 (3)
Cl(4)	Mo(1)	O(2)	83.9 (2)	O(1)	Mo(2)	O(3)	80.2 (3)	O(5)	Mo(3)	O(7)	90.4 (3)
Cl(4)	Mo(1)	O(4)	85.1 (2)	O(1)	Mo(2)	O(6)	80.1 (3)	Mo(1)	Cl(1)	Mo(2)	65.02 (9)
O(1)	Mo(1)	O(2)	80.4 (3)	O(3)	Mo(2)	O(6)	91.2 (4)	Mo(1)	Cl(2)	Mo(3)	64.6 (1)
O(1)	Mo(1)	O(4)	79.7 (3)	Mo(1)	Mo(3)	Mo(2)	60.47 (4)	Mo(2)	Cl(3)	Mo(3)	64.28 (9)
O(2)	Mo(1)	O(4)	90.4 (4)	Cl(2)	Mo(3)	Cl(3)	90.6 (1)	Mo(1)	O(1)	Mo(2)	82.3 (3)
Mo(1)	Mo(2)	Mo(3)	59.77 (4)	Cl(2)	Mo(3)	Cl(6)	88.6 (1)	Mo(1)	O(1)	Mo(3)	81.7 (3)
Cl(1)	Mo(2)	Cl(3)	88.5 (1)	Cl(2)	Mo(3)	O(1)	106.8 (2)	Mo(2)	O(1)	Mo(3)	82.1 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

except for the atoms of the interstitial THF molecule, which were refined isotropically. The highest peak in a final difference Fourier map was 0.594 e/$Å^3$ and located in the vicinity of the Mo(1) atom.

Results and Discussion

Structure. The crystal structure of **1** consists of four formula units of $[Bu_4N]_2[Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OAc)_3Cl_3]\cdot Me_2CO$ per unit cell. An ORTEP diagram, Figure 2, shows the structure of the molybdenum trinuclear dianion, in which the three molybdenum atoms form a triangle. One capping oxygen atom and three bridging acetate groups are above the plane of the triangle and three chloride atoms are below it. Each Mo atom has a pseudooctahedral coordination environment. The bond distances between molybdenum atoms are 2.617 (1), 2.598 (1), and 2.598 (2) Å with a mean value of 2.604 [9] Å. Compared with the Mo-Mo bond distances 2.572 (1), 2.572 (1), and 2.566 (1) Å with a mean value of 2.570 [2] Å in its eight-electron counterpart, $[Mo_3OCl_6(OAc)_3]^-$,[1] reduction of the oxidation state has apparently caused a slight lengthening of the Mo-Mo bonds. The core structure is basically the same as that of its eight-electron analogue except for a somewhat large deviation from C_{3v} symmetry. Table II lists some important bond distances and bond angles of compound **1**.

The crystal structure of **2** has four formula units of $(Bu_4N)[Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OAc)_3Cl_2(PMe_3)]\cdot 2THF$ in the unit

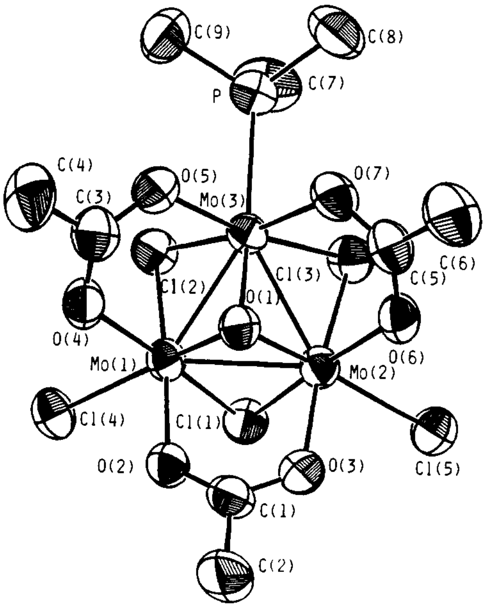

Figure 3. An ORTEP drawing of the anion of **2**. The thermal ellipsoids are at the 50% probability level.

Table III. Selected Bond Distances (Å) and Angles (deg) for $(Bu_4N)[Mo_3OCl_5(OAc)_3(PMe_3)]\cdot 2THF$

atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance
Mo(1)	Mo(2)	2.6365 (9)	Mo(1)	O(4)	2.111 (5)	Mo(2)	O(6)	2.093 (5)
Mo(1)	Mo(3)	2.5730 (9)	Mo(2)	Mo(3)	2.5670 (9)	Mo(3)	Cl(2)	2.432 (2)
Mo(1)	Cl(1)	2.430 (2)	Mo(2)	Cl(1)	2.430 (2)	Mo(3)	Cl(3)	2.425 (2)
Mo(1)	Cl(2)	2.448 (2)	Mo(2)	Cl(3)	2.447 (2)	Mo(3)	P	2.575 (2)
Mo(1)	Cl(4)	2.459 (2)	Mo(2)	Cl(5)	2.445 (2)	Mo(3)	O(1)	1.990 (5)
Mo(1)	O(1)	1.987 (5)	Mo(2)	O(1)	1.974 (5)	Mo(3)	O(5)	2.098 (6)
Mo(1)	O(2)	2.099 (5)	Mo(2)	O(3)	2.097 (5)	Mo(3)	O(7)	2.095 (5)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Mo(2)	Mo(1)	Mo(3)	59.03 (2)	Cl(1)	Mo(2)	Cl(3)	89.36 (7)	Cl(2)	Mo(3)	P	84.36 (8)
Cl(1)	Mo(1)	Cl(2)	88.96 (7)	Cl(1)	Mo(2)	Cl(5)	89.45 (8)	Cl(2)	Mo(3)	O(1)	107.8 (1)
Cl(1)	Mo(1)	Cl(4)	89.97 (7)	Cl(1)	Mo(2)	O(1)	105.4 (1)	Cl(2)	Mo(3)	O(5)	89.1 (2)
Cl(1)	Mo(1)	O(1)	104.9 (1)	Cl(1)	Mo(2)	O(3)	89.0 (1)	Cl(2)	Mo(3)	O(7)	170.8 (2)
Cl(1)	Mo(1)	O(2)	88.6 (2)	Cl(1)	Mo(2)	O(6)	174.8 (2)	Cl(3)	Mo(3)	P	85.53 (8)
Cl(1)	Mo(1)	O(4)	175.1 (1)	Cl(3)	Mo(2)	Cl(5)	87.13 (8)	Cl(3)	Mo(3)	O(1)	107.6 (1)
Cl(2)	Mo(1)	Cl(4)	87.95 (7)	Cl(3)	Mo(2)	O(1)	107.4 (2)	Cl(3)	Mo(3)	O(5)	170.7 (2)
Cl(2)	Mo(1)	O(1)	107.3 (2)	Cl(3)	Mo(2)	O(3)	172.9 (2)	Cl(3)	Mo(3)	O(7)	88.3 (2)
Cl(2)	Mo(1)	O(2)	173.0 (1)	Cl(3)	Mo(2)	O(6)	89.2 (2)	P	Mo(3)	O(1)	161.3 (2)
Cl(2)	Mo(1)	O(4)	89.4 (2)	Cl(5)	Mo(2)	O(1)	159.1 (1)	P	Mo(3)	O(5)	85.3 (2)
Cl(4)	Mo(1)	O(1)	158.5 (2)	Cl(5)	Mo(2)	O(3)	86.0 (2)	P	Mo(3)	O(7)	86.5 (2)
Cl(4)	Mo(1)	O(2)	85.4 (1)	Cl(5)	Mo(2)	O(6)	85.5 (2)	O(1)	Mo(3)	O(5)	80.9 (2)
Cl(4)	Mo(1)	O(4)	85.4 (2)	O(1)	Mo(2)	O(3)	79.7 (2)	O(1)	Mo(3)	O(7)	80.8 (2)
O(1)	Mo(1)	O(2)	79.7 (2)	O(1)	Mo(2)	O(6)	79.8 (2)	O(5)	Mo(3)	O(7)	89.4 (2)
O(1)	Mo(1)	O(4)	79.9 (2)	O(3)	Mo(2)	O(6)	91.8 (2)	Mo(1)	Cl(1)	Mo(2)	65.71 (6)
O(2)	Mo(1)	O(4)	92.5 (2)	Mo(1)	Mo(3)	Mo(2)	61.72 (2)	Mo(1)	Cl(2)	Mo(3)	63.64 (5)
Mo(1)	Mo(2)	Mo(3)	59.25 (2)	Cl(2)	Mo(3)	Cl(3)	91.68 (7)	Mo(2)	Cl(3)	Mo(3)	63.60 (6)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $Mo_3OCl_4(OAc)_3(PMe_3)_2$

atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance
Mo(1)	Mo(2)	2.5878 (5)	Mo(1)	O(4)	2.113 (3)	Mo(2)	O(6)	2.104 (3)
Mo(1)	Mo(3)	2.6117 (5)	Mo(2)	Mo(3)	2.5764 (5)	Mo(3)	Cl(2)	2.420 (1)
Mo(1)	Cl(1)	2.442 (1)	Mo(2)	Cl(1)	2.418 (1)	Mo(3)	Cl(3)	2.434 (1)
Mo(1)	Cl(2)	2.431 (1)	Mo(2)	Cl(3)	2.431 (1)	Mo(3)	P(2)	2.588 (1)
Mo(1)	Cl(4)	2.430 (1)	Mo(2)	P(1)	2.574 (1)	Mo(3)	O(1)	1.989 (2)
Mo(1)	O(1)	1.985 (2)	Mo(2)	O(1)	2.002 (3)	Mo(3)	O(5)	2.079 (3)
Mo(1)	O(2)	2.118 (3)	Mo(2)	O(3)	2.093 (3)	Mo(3)	O(7)	2.119 (3)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Mo(2)	Mo(1)	Mo(3)	59.40 (1)	Cl(1)	Mo(2)	P(1)	85.08 (4)	Cl(2)	Mo(3)	O(5)	88.82 (8)
Cl(1)	Mo(1)	Cl(2)	89.34 (4)	Cl(1)	Mo(2)	O(1)	107.23 (7)	Cl(2)	Mo(3)	O(7)	173.54 (8)
Cl(1)	Mo(1)	Cl(4)	88.12 (4)	Cl(1)	Mo(2)	O(3)	88.46 (8)	Cl(3)	Mo(3)	P(2)	88.76 (4)
Cl(1)	Mo(1)	O(1)	106.88 (8)	Cl(1)	Mo(2)	O(6)	171.94 (8)	Cl(3)	Mo(3)	O(1)	107.65 (8)
Cl(1)	Mo(1)	O(2)	87.90 (8)	Cl(3)	Mo(2)	P(1)	88.01 (4)	Cl(3)	Mo(3)	O(5)	171.14 (8)
Cl(1)	Mo(1)	O(4)	173.74 (7)	Cl(3)	Mo(2)	O(1)	107.30 (8)	Cl(3)	Mo(3)	O(7)	88.32 (8)
Cl(2)	Mo(1)	Cl(4)	89.87 (4)	Cl(3)	Mo(2)	O(3)	170.95 (8)	P(2)	Mo(3)	O(1)	158.60 (8)
Cl(2)	Mo(1)	O(1)	105.89 (8)	Cl(3)	Mo(2)	O(6)	88.48 (8)	P(2)	Mo(3)	O(5)	82.41 (8)
Cl(2)	Mo(1)	O(2)	173.91 (8)	P(1)	Mo(2)	O(1)	159.74 (7)	P(2)	Mo(3)	O(7)	86.75 (8)
Cl(2)	Mo(1)	O(4)	87.78 (7)	P(1)	Mo(2)	O(3)	82.95 (8)	O(1)	Mo(3)	O(5)	81.1 (1)
Cl(4)	Mo(1)	O(1)	158.04 (8)	P(1)	Mo(2)	O(6)	86.86 (8)	O(1)	Mo(3)	O(7)	80.3 (1)
Cl(4)	Mo(1)	O(2)	84.62 (8)	O(1)	Mo(2)	O(3)	81.4 (1)	O(5)	Mo(3)	O(7)	91.8 (1)
Cl(4)	Mo(1)	O(4)	86.32 (8)	O(1)	Mo(2)	O(6)	80.5 (1)	Mo(1)	Cl(1)	Mo(2)	64.34 (3)
O(1)	Mo(1)	O(2)	80.1 (1)	O(3)	Mo(2)	O(6)	90.6 (1)	Mo(1)	Cl(2)	Mo(3)	65.16 (3)
O(1)	Mo(1)	O(4)	79.3 (1)	Mo(1)	Mo(3)	Mo(2)	59.83 (1)	Mo(2)	Cl(3)	Mo(3)	63.95 (3)
O(2)	Mo(1)	O(4)	94.4 (1)	Cl(2)	Mo(3)	Cl(3)	90.04 (4)	Mo(1)	O(1)	Mo(2)	80.92 (9)
Mo(1)	Mo(2)	Mo(3)	60.76 (1)	Cl(2)	Mo(3)	P(2)	86.97 (4)	Mo(1)	O(1)	Mo(3)	82.16 (9)
Cl(1)	Mo(2)	Cl(3)	91.19 (4)	Cl(2)	Mo(3)	O(1)	106.18 (7)	Mo(2)	O(1)	Mo(3)	80.40 (9)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

cell. The configuration of the molybdenum trinuclear anion is shown in Figure 3, and selected bond distances and bond angles are listed in Table III. The anion of this complex is homologous to that in **1** with substitution of one of the terminal chloride atoms in **1** by trimethylphosphine. Three molybdenum atoms form a triangle with metal–metal bond distances of 2.637 (1), 2.567 (1), and 2.573 (1) Å with a mean value of 2.59 [3] Å. The two metal–metal bonds that intercept the Mo–P bond are shorter than the third, whereas steric factors resulting from the substitution of a chloride ligand by a bulkier phosphine would be expected to increase the metal–metal bond length.

Compounds 3 and 4 both have exactly the same core structure, $[Mo_3OCl_4(OAc)_3(PMe_3)_2]$. The geometric configuration of the core structure is schematically shown in Figure 4. This molecule can be considered to result from the replacement of one more terminal chloride ligand in **2** by a trimethylphosphine ligand. There are only slight differences in crystal structure details between compounds **3** and **4**, which may, presumably, be attributed to different packing effects in the two different crystal environments. The metal–metal bond distances for **3** are 2.6117 (5), 2.5878 (5), and 2.5764 (5) Å with a mean value of 2.592 [15] Å, and those for **4** are 2.608 (1), 2.597 (1), and 2.5673 (9) Å with a mean value of 2.591 [17] Å. Again, the shortest Mo–Mo bond is the one that intercepts the most Mo–P bonds, contrary to what might have been expected on steric grounds. Tables IV and V list some important bond distances and bond angles for compounds **3** and **4**.

Chemistry. Our earlier results from cyclic voltammetry[1] showed that it is possible to reduce eight-electron molybdenum trinuclear triangular clusters with the Mo_3OCl_3 core. Later, successful

Table V. Selected Bond Distances (Å) and Angles (deg) for $Mo_3OCl_4(OAc)_3(PMe_3)_2{\cdot}THF$

atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance
Mo(1)	Mo(2)	2.597 (1)	Mo(1)	O(4)	2.087 (6)	Mo(2)	O(6)	2.085 (7)
Mo(1)	Mo(3)	2.608 (1)	Mo(2)	Mo(3)	2.5673 (9)	Mo(3)	Cl(2)	2.424 (3)
Mo(1)	Cl(1)	2.448 (2)	Mo(2)	Cl(1)	2.427 (3)	Mo(3)	Cl(3)	2.428 (3)
Mo(1)	Cl(2)	2.449 (2)	Mo(2)	Cl(3)	2.433 (3)	Mo(3)	P(2)	2.609 (3)
Mo(1)	Cl(4)	2.448 (3)	Mo(2)	P(1)	2.589 (3)	Mo(3)	O(1)	1.988 (6)
Mo(1)	O(1)	1.979 (6)	Mo(2)	O(1)	1.992 (5)	Mo(3)	O(5)	2.079 (6)
Mo(1)	O(2)	2.105 (6)	Mo(2)	O(3)	2.086 (6)	Mo(3)	O(7)	2.097 (7)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Mo(2)	Mo(1)	Mo(3)	59.10 (3)	Cl(1)	Mo(2)	P(1)	85.64 (9)	Cl(2)	Mo(3)	O(5)	87.3 (2)
Cl(1)	Mo(1)	Cl(2)	89.79 (8)	Cl(1)	Mo(2)	O(1)	106.8 (2)	Cl(2)	Mo(3)	O(7)	171.6 (2)
Cl(1)	Mo(1)	Cl(4)	88.10 (9)	Cl(1)	Mo(2)	O(3)	88.6 (2)	Cl(3)	Mo(3)	P(2)	85.68 (9)
Cl(1)	Mo(1)	O(1)	106.5 (2)	Cl(1)	Mo(2)	O(6)	171.3 (2)	Cl(3)	Mo(3)	O(1)	107.8 (2)
Cl(1)	Mo(1)	O(2)	88.9 (2)	Cl(3)	Mo(2)	P(1)	85.47 (9)	Cl(3)	Mo(3)	O(5)	170.4 (2)
Cl(1)	Mo(1)	O(4)	173.4 (2)	Cl(3)	Mo(2)	O(1)	107.4 (2)	Cl(3)	Mo(3)	O(7)	87.5 (2)
Cl(2)	Mo(1)	Cl(4)	89.47 (9)	Cl(3)	Mo(2)	O(3)	171.5 (2)	P(2)	Mo(3)	O(1)	160.3 (2)
Cl(2)	Mo(1)	O(1)	105.9 (2)	Cl(3)	Mo(2)	O(6)	87.7 (2)	P(2)	Mo(3)	O(5)	84.7 (2)
Cl(2)	Mo(1)	O(2)	174.1 (2)	P(1)	Mo(2)	O(1)	161.5 (2)	P(2)	Mo(3)	O(7)	84.5 (2)
Cl(2)	Mo(1)	O(4)	87.8 (2)	P(1)	Mo(2)	O(3)	86.0 (2)	O(1)	Mo(3)	O(5)	81.8 (2)
Cl(4)	Mo(1)	O(1)	158.6 (2)	P(1)	Mo(2)	O(6)	85.6 (2)	O(1)	Mo(3)	O(7)	81.8 (2)
Cl(4)	Mo(1)	O(2)	84.7 (2)	O(1)	Mo(2)	O(3)	80.8 (2)	O(5)	Mo(3)	O(7)	92.6 (2)
Cl(4)	Mo(1)	O(4)	85.7 (2)	O(1)	Mo(2)	O(6)	81.7 (2)	Mo(1)	Cl(1)	Mo(2)	64.39 (6)
O(1)	Mo(1)	O(2)	80.0 (2)	O(3)	Mo(2)	O(6)	91.2 (3)	Mo(1)	Cl(2)	Mo(3)	64.72 (7)
O(1)	Mo(1)	O(4)	80.1 (2)	Mo(1)	Mo(3)	Mo(2)	60.23 (3)	Mo(2)	Cl(3)	Mo(3)	63.76 (7)
O(2)	Mo(1)	O(4)	92.8 (2)	Cl(2)	Mo(3)	Cl(3)	91.19 (9)	Mo(1)	O(1)	Mo(2)	81.7 (2)
Mo(1)	Mo(2)	Mo(3)	60.67 (3)	Cl(2)	Mo(3)	P(2)	87.1 (1)	Mo(1)	O(1)	Mo(3)	82.2 (2)
Cl(1)	Mo(2)	Cl(3)	91.20 (9)	Cl(2)	Mo(3)	O(1)	106.5 (2)	Mo(2)	O(1)	Mo(3)	80.3 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

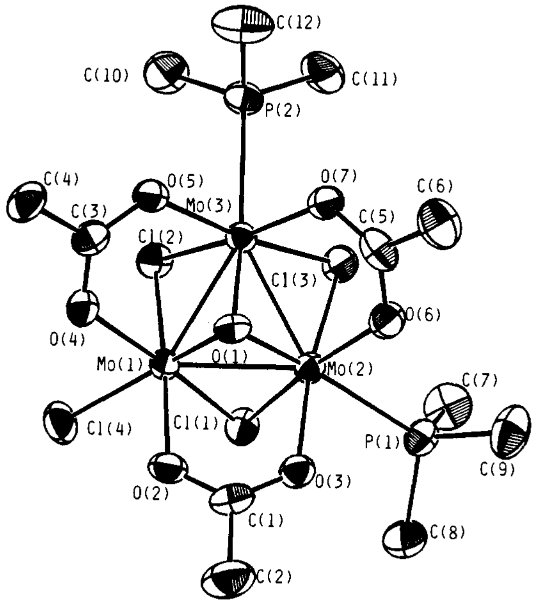

Figure 4. An ORTEP drawing of the anion of **3** and **4**. The thermal ellipsoids are at the 50% probability level.

characterization of compound **4**, which was obtained unexpectedly in the attempt to synthesize sulfur-capped trinuclear species fully confirmed the existence of the nine-electron cluster. These results then led us to conduct a series of investigations aimed at developing designed syntheses of nine-electron trinuclear clusters by reduction of eight-electron clusters. One of the synthetic efforts was to synthesize a nine-electron molybdenum trinuclear compound with exactly the same geometry as its eight-electron counterpart. Synthesis of compound **1** was achieved by the following reaction

$$(Bu_4N)[Mo_3OCl_6(OAc)_3] + {}^1\!/_2Zn + Bu_4NCl \rightarrow (Bu_4N)_2[Mo_3OCl_6(OAc)_3] + {}^1\!/_2ZnCl_2 \quad (1)$$

in which zinc powder served as a mild reductant in the one-electron reduction reaction of the eight-electron molybdenum trimer. The geometric configuration of the cluster did, indeed, remain intact, as hoped, with no extra ligand involved in the reaction.

In an earlier report,[7] terminal ligands, such as H_2O, in the M_3X_{13} type molybdenum trinuclear compounds with Mo_3O_4 core were labile and could be substituted. However, our experiments showed that the terminal chloride ligands in the Mo_3X_{13} type molybdenum trinuclear compound with an Mo_3OCl_3 core, $[Mo_3OCl_6(OAc)_3]^-$, were more inert to substitution reaction, and no such substitution has so far been observed, although several attempts have been made and the existence of another type of terminal ligand was reported more than a decade ago.[8] Synthesis of compound **4** with terminal phosphine ligands had led us to speculate, however, that during the process of reduction one or two of the terminal chloride ligands of the molybdenum trinuclear species might become liable to substitution. This has been verified by the synthesis of compounds **2** and **3** according to the following reactions:

$$(Bu_4N)[Mo_3OCl_6(OAc)_3] + {}^1\!/_2Zn + PMe_3 \rightarrow (Bu_4N)[Mo_3OCl_5(OAc)_3(PMe_3)] + {}^1\!/_2ZnCl_2 \quad (2)$$

$$(Bu_4N)[Mo_3OCl_6(OAc)_3] + {}^1\!/_2Zn + 2PMe_3 \rightarrow [Mo_3OCl_4(OAc)_3(PMe_3)_2] + {}^1\!/_2ZnCl_2 + Bu_4NCl \quad (3)$$

In these reactions one or two terminal chloride atoms were replaced by phosphine ligands, although the exact reason for the increased lability of the terminal chloride ligands during reduction is not yet clear.

It is interesting to note that synthetic efforts to obtain a nine-electron molybdenum trinuclear compound with three terminal trimethylphosphine ligands have so far failed, even though a large excess of phosphine has been used. From **1** to **3** the average bond distances between molybdenum and terminal chloride atoms are 2.470 [7], 2.452 [7], and 2.430 (1) Å, respectively. The strength of the bonds between molybdenum and terminal chloride atoms apparently increases with increase of the number of terminal trimethylphosphine ligands, and this increase of the Mo–Cl bond strength would inevitably hamper further substitution of the third terminal chloride ligand.

Magnetic Properties. No signal was observed during the attempted measurement of ^1H NMR of **3** at room temperature and ^{31}P NMR at both room temperature and −78 °C, thus supporting

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[7] Richens, D. T.; Helm, L.; Pittet, P.; Merbach, A. E.; Nicolo, F.; Chapuis, G. *Inorg. Chem.* **1989**, *28*, 1394.

[8] Bino, A.; Cotton, F. A.; Dori, Z. *Inorg. Chim. Acta* **1979**, *33*, L3.

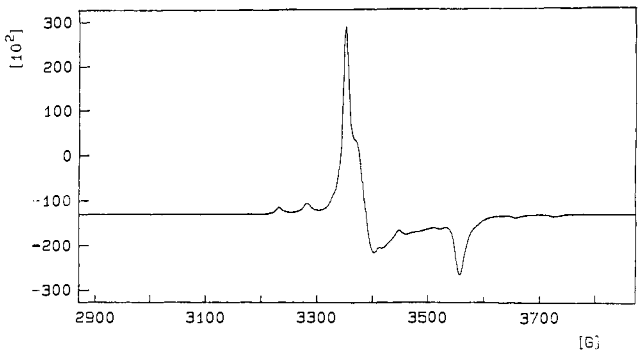

Figure 5. EPR spectrum of compound **3** in CH_2Cl_2 at 10 K.

the conclusion that the nine-electron molybdenum trinuclear compounds are paramagnetic, which is in full accord with the crystallographic results. The EPR measurements of compound **3** were carried out in the solid phase at room temperature and in solution at both room temperature and 10 K. At room temperature, because of rapid T_1 relaxation, no signal was observed. The EPR spectrum recorded at 10 K showed a complicated signal, which cannot be assigned right now. However, it is indicative of the paramagnetic nature of the compound. Figure 5 shows the EPR spectrum of compound **3** in solvent dichloromethane at 10 K. The magnetic susceptibility of compound **3** was also measured. The μ_{eff} value was 1.49 μ_B after the diamagnetism correction, which is a little lower than the calculated value, 1.73 μ_B, for one unpaired spin-only electron, but this could be due to spin-orbit coupling effects.

Electrochemical Properties. Cyclic voltammetry of **3** showed a quasi-reversible reduction wave at −1.2 V (the separation is 0.12 V) and a reversible oxidation wave at 0.43 V (separation is 0.06 V). The CV results imply that the nine-electron molybdenum trimer might be further reduced to molybdenum trimer with ten electrons and clearly show that, as expected, it can be oxidized to one with eight electrons. On the basis of the combination of CV data of both nine- and eight-electron molybdenum trinuclear compounds, a redox equilibrium reaction between the eight-electron molybdenum trimer and the nine-electron one is shown below:

$$Mo_2^{III}Mo^{IV} \rightleftarrows Mo_3^{III}$$

Although a similar equilibrium reaction has been reported for the Mo_3O_4 type cluster,[9,10] so far no such nine-electron species has been synthesized. Our synthetic work on these first nine-electron Mo_3OCl_3 type clusters confirms that the equilibrium not only exists in the thermodynamic sense but also is feasible kinetically. Furthermore, the CV data suggest the possibility of the existence of ten-electron trinuclear species, which is now under intensive investigation.

Discussion. In the earliest discussion of bonding in M_3X_{13} type clusters, both theory and empirical fact seemed to suggest a rather simple picture, namely, that there would be two bonding MOs, $1a_1$ and 1e (in C_{3v} symmetry), and that the filling of these with six electrons would provide the equivalent of three M–M single bonds. The possibility that the next orbital ($2a_1$), which was believed to have approximately nonbonding character, might be occupied without prejudice to the stability of the structure was also recognized, thus making seven- and eight-electron species seem possible but not necessarily likely.

It is now clear that from a general point of view this picture was an oversimplification because it was based, both theoretically and empirically, on results for Mo_3O_4 type cores. We now know that changing either the metal atoms, the four intimate nonmetal atoms, (i.e., the X atoms in the M_3X_4 core) or both can change the nature of the MOs pertinent to M–M interactions so that populations other than six are favored.[11]

For the $Mo_3OCl_3^{n+}$ system, theory shows that the first three orbitals $1a_1$, 1e, and $2a_1$ are Mo–Mo bonding orbitals thus making the favored population the eight-electron one. The LUMO then is found to be the 2e orbital which is somewhat Mo–Mo antibonding in character but not very high in energy. Thus, the existence of these nine-electron species is not inconsistent with theory but not predicted explicitly. The presence of an electron in a weakly antibonding orbital does, however, raises two points: (1) how much should the Mo–Mo distances be lengthened and (2) how much of a Jahn–Teller (J–T) distortion should be observed. Both of these effects are at best slight and possibly unobserved in the nine-electron species reported here. Is this reasonable? We believe that it is.

One slightly antibonding electron spread over three bonds cannot exert a large effect. Moreover, since the mean oxidation state of the Mo atoms goes from +3.33 for the eight-electron case to +3.0 for the nine-electron case, it is likely that some enhancement of the bonding effect of the $(1a_1)^2(1e)^4(2a_1)^2$ configuration could occur, thus mitigating the antibonding effect of the single 2e electron.

As for the J–T effect, it is impossible to say for certain whether one occurs in **2**, **3**, and **4** because the symmetry-breaking pattern of the outer ligands could also be responsible for the occurrence of two bonds slightly longer than the third. Even if the differences could be attributed to a J–T effect they are small, which is again consistent with only one electron spread over the three bonds operating to induce the J–T effect. Compound **1**, however, provides a more direct approach. Here, we have only a tiny difference between one of the Mo–Mo bonds and the other two, and this is barely significant in the statistical sense. Moreover, even though the outer set of ligands is now uniform (i.e., all Cl^-) the $[Mo_3OCl_3(OAc)_3Cl_3]^{2-}$ ion resides on a general position in the crystal, where different Mo–Mo bonds are subject to different packing forces. A small difference such as that observed could easily be caused by an imbalance of such forces.

Acknowledgment. We thank Dr. Judith Eglin for her help with NMR and EPR measurements. We thank the National Science Foundation for financial support.

Supplementary Material Available: Tables of positional parameters, bond lengths, bond angles, and anisotropic displacement parameters and ORTEP drawings of unit cell contents for **1–4** (47 pages); tables of observed and calculated structure factors for **1–4** (73 pages). Ordering information is given on any current masthead page.

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