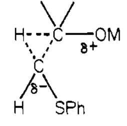
I the ratio of the C–H insertion to the formal C–Metal insertion rises with the increase of electron-donating substitution at the olefin or α-carbon site, and this validates the second factor for facilitating the C–H insertion (vide supra).



7

As to the formation of ether **3**, there are two possible mechanisms: (1) S_N2 attack of alkoxide anion on $ClCH_2SPh$ and (2) the insertion of (phenylthio)carbene into the oxygen–metal bond and subsequent protonation. In the absence of *t*-BuOK, sodium allylalkoxide reacts with $ClCH_2SPh$ very slowly at 0 °C, and only a trace amount of **3a** is produced together with the almost quantitative recovery of $ClCH_2SPh$ after reacting for 1 h. While this result suggests mechanism 2, there still remains at present a possibility of mechanism 1 where the addition of *t*-BuOK provides the corresponding potassium alkoxide as an active nucleophile. A reaction using *t*-BuONa in place of *t*-BuOK was performed, giving rise to the formation of **2a** and **3a** in 26% and 30% yield, respectively (entry 2, Table I). Thus, at least in this reaction, it is apparent that the formation of **3a** proceeds via the insertion of (phenylthio)carbene into the oxygen–sodium bond.

Work is in progress to disclose more precisely the nature and the synthetic potential of the present reaction.

Oxotrimolybdenum(IV) Alkoxides, $Mo_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu_2\text{-}OR)_3(OR)_6$ (R = $CH(CH_3)_2$ and $CH_2C(CH_3)_3$). Synthetic Considerations

M. H. Chisholm,* K. Folting, J. C. Huffman, and
C. C. Kirkpatrick

Department of Chemistry and Molecular Structure Center
Indiana University
Bloomington, Indiana 47405

Received May 18, 1981

Recently a large class of *triangulo*-M_3 complexes of molybdenum and tungsten have been discovered.[1] Some of these have involved 8–4 cluster electrons, though most commonly the number is 6. As yet little is known about the reaction pathways leading to these compounds, though they do appear to form very readily with a variety of ligands. For example, Bino, Cotton, and Dori recently reported[2] their characterization of six compounds of formula $[Mo_3(\mu_3\text{-}X)(\mu_3\text{-}Y)(OAc)_6(H_2O)_3]_x^{-}\cdot yH_2O$, where X = Y = O, X = Y = CCH_3, and X = O, Y = CCH_3. All of these were formed in the reaction between $Mo(CO)_6$, AcOH, and $(AcO)_2O$, which also yields the well-known dinuclear compound $Mo_2(OAc)_4$ ($M\overset{4}{—}M$). We wish here to report our discovery of oxotrimolybdenum(IV) alkoxides of formula $Mo_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu_2\text{-}OR)_3(OR)_6$, where R = isopropyl (*i*-Pr) and neopentyl (Ne), and furthermore to show that these compounds can be prepared in high yields by rational syntheses based on known reactivity patterns of metal–metal bonds.

During the course of studies of the reactions between $Mo_2(OR)_6$ compounds and molecular oxygen, which lead ultimately to $MoO_2(OR)_2$ compounds with cleavage of the Mo≡Mo bond,[3] we noted the formation of green intermediates when R = *i*-Pr and Ne (Ne = CH_2CMe_3). Indeed, from reactions involving $Mo_2(ONe)_6$ and O_2, we were able to isolate the green crystalline compound $Mo_3(O)(ONe)_{10}$, which was fully characterized by an X-ray study.[4] An ORTEP view of the central $Mo_3O(OC)_{10}$ skeleton of the molecule is shown in Figure 1 along with some pertinent bond distances.

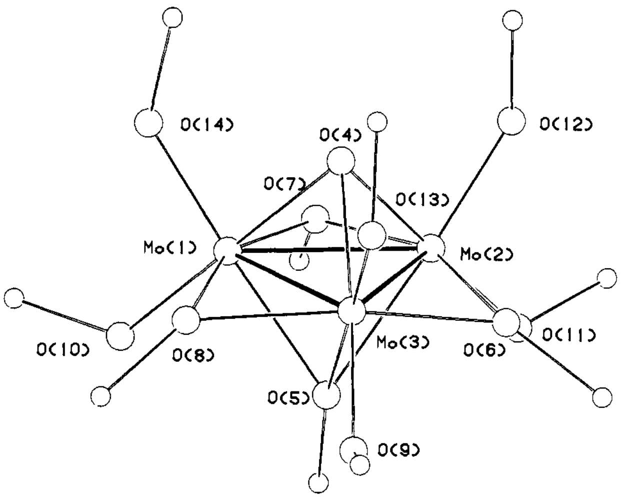


Figure 1. ORTEP view of the central $Mo_3O(OC)_{10}$ skeleton of the $Mo_3O(ONe)_{10}$ molecule. All atoms are assigned arbitrary thermal parameters. Each molybdenum atom is in a distorted octahedral environment with respect to six directly bonded oxygen atoms. Pertinent bond distances in Å (averaged) are Mo–Mo = 2.529 (9), Mo–μ_3O(oxo) = 2.03 (3), Mo–μ_3OR = 2.21 (3), Mo–μ_2OR = 2.02 (3), Mo–OR(terminal) trans to O(4) = 1.94 (2), Mo–OR(terminal) trans to μ_3-OR = 1.85 (3).

A retrosynthetic analysis suggested that the *triangulo*-$Mo_3(\mu_3\text{-}O)$ unit could be constructed by the addition of an oxomolybdenum (6+) unit across the Mo≡Mo bond as in reaction 1. This bears analogy with the approach to cluster synthesis adopted by Stone and co-workers involving $M{=}CR_2$ and $M{\equiv}CR$ groups.[5]

$$Mo_3(\mu_3\text{-}O)(OR)_{10} \rightarrow Mo_2(OR)_6 + MoO(OR)_4 \quad (1)$$

The oxomolybdenum(6+) alkoxides, $MoO(OR)_4$, which were unknown, were viewed as the products of a simple replacement of a Mo═Mo bond[6] by two Mo═O bonds in the oxygenolysis reaction (2). Previously it had been shown[7] that the three electron

$$2MoO(OR)_4 \rightarrow Mo_2(OR)_8 + O_2 \quad (2)$$

ligand, NO, readily cleaves the Mo≡Mo bond to give two Mo–NO bonds, which may be formally viewed as M≡N—O.[7]

This synthetic strategy was successful: $Mo_2(OR)_8$ and molecular oxygen react to yield $MoO(OR)_4$ compounds which, in turn, react with $Mo_2(OR)_6$ compounds to yield $Mo_3O(OR)_{10}$ compounds in essentially quantitative reactions.[8]

---

(1) Muller, A.; Jostes, R.; Cotton, F. A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 875.

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

(3) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C.; Ratermann, A. L. *J. Am. Chem. Soc.* **1981**, *103*, 1305.

(4) Crystals suitable for X-ray work were grown from methylene chloride. Crystal data, collected at -161 °C, using Mo Kα radiation, gave the following: *a* = 35.56 (2), *b* = 18.97 (1), *c* = 19.34(1) Å; space group *Pbcn*; *Z* = 8; d_{calcd} = 1.295 g cm^{-3}. Of the 10379 reflections measured in the range 6 ≤ 2θ ≤ 40°, 6102 were unique. Only 55% of the unique data were observed using the criteria $F \geq 2.33\sigma(F)$. In retrospect, this was proven to be caused by loss of a solvent molecule (CH_2Cl_2) and disorder of one of the ONe ligands [O(5) in Figure 1] and high thermal motions of all the neopentyl groups. The structure was readily solved by direct methods and Fourier techniques and refined by full-matrix least squares. Only the largest 1500 reflections were used in the refinement. Molybdenum atoms were assigned anisotropic thermal parameters, and all other atoms were assigned isotropic parameters. Two peaks that occurred in a void in the crystal were assigned as chlorine atoms, whose occupancy refined to 0.33. The carbon of the CH_2Cl_2 molecule was not discernible. Final residuals are *R*(*F*) = 0.0752 and *Rw*(*F*) = 0.0759.

(5) Ashworth, T. V.; Chetcuti, M. J.; Farrugia, L. J.; Howard, J. A. K.; Jeffrey, J. C.; Mills, R.; Pain, G. N.; Stone, F. G. A.; Woodward, P. In "Reactivity of Metal–Metal Bonds"; Chisholm, M. H. Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 155, Chapter 15.

(6) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *Inorg. Chem.* **1978**, *17*, 2944.

(7) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 3354.

0002-7863/81/1503-5967$01.25/0

$Mo_3O(O\text{-}i\text{-}Pr)_{10}$ has been found to react separately with each of O_2 and $MoO_2(O\text{-}i\text{-}Pr)_2$ to form $Mo_6O_{10}(O\text{-}i\text{-}Pr)_{12}$ which has been structurally characterized and found to react further with O_2 to give $[MoO_2(O\text{-}i\text{-}Pr)_2]_n$. The details of this work will be the subject of a full paper. The thrust of this communication is to emphasize the potential of the generalized reaction 3 for syntheses of triangulo complexes of the type described here. A variety of X groups can be envisaged and conceivably this approach could be extended to include heterometallic systems.[9]

$$M{\equiv}M + M{\equiv}X \rightarrow M_3X \qquad (3)$$

---

(8) Preparation of $MoO(O\text{-}i\text{-}Pr)_4$. $Mo_2(O\text{-}i\text{-}Pr)_8$[6] (1.8 g) was dissolved in dry toluene (25 mL) in a 250-mL round-bottomed flask under a nitrogen atmosphere. The solution was frozen at −198 °C (liquid N_2), and the flask was evacuated and attached to a vacuum manifold. Dry molecular oxygen was added, and the solution was thawed and warmed to room temperature. The solution changed rapidly from blue to green to pale yellow and was stirred for 1 h at room temperature under 1 atm of O_2. The solvent was stripped, yielding a yellow viscous liquid $MoO(O\text{-}i\text{-}Pr)_4$. The compound was vacuum distilled (53 °C, 10^{-4} mmHg). Anal. Calcd for $MoO(O\text{-}i\text{-}Pr)_4$: C, 41.38; H, 8.10; N, 0.00. Found: C, 41.11; H, 7.90; N, 0.10. The ^1H NMR spectrum recorded in toluene-d_8 at 220 MHz, 16 °C, showed a septet at δ 4.77 and a doublet at δ 1.34 (δ in ppm relative to Me_4Si). The natural abundance ^{17}O NMR spectrum recorded at 30 °C in benzene showed a singlet at $\delta = 894$ with a peak width at half-height of 150 Hz ($\delta^{17}O$ relative to external $H_2{}^{17}O$). The narrow peak width is consistent with a terminal MoO group in a monomeric compound. A cryoscopic molecular weight determination in benzene also indicated that $MoO(O\text{-}i\text{-}Pr)_4$ is at least mostly monomeric in solution; $M_r = 410$ (calculated $M_r = 348$ for the monomer). Preparation of $Mo_3O(O\text{-}i\text{-}Pr)_{10}$. $MoO(O\text{-}i\text{-}Pr)_4$ (1.84 mmol) was dissolved in dry degassed toluene (25 mL) in a 50-mL round-bottomed flask fitted with a side arm and magnetic spin bar under a nitrogen atmosphere. $Mo_2(O\text{-}i\text{-}Pr)_6$ (1 g, 1.84 mmol) was added via the side-arm adaptor with stirring. The solution immediately turned from yellow to red and then to green. The solution was stirred for 1 h at room temperature and then the solvent was stripped and the green solids dissolved in CH_2Cl_2 (ca. 8 mL). The flask was placed in a refrigerator at ca. −15 °C for 12 h, during which time green crystals, $Mo_3O(O\text{-}i\text{-}Pr)_{10}$, formed which were collected by filtration and dried in vacuo; yield 1.5 g (ca. 80% based on Mo). Anal. Calcd for $Mo_3O(O\text{-}i\text{-}Pr)_{10}$: C, 40.27; H, 7.89; N, 0.00. Found: C, 40.17, H, 7.71; N, 0.07. The ^1H NMR spectrum recorded in toluene-d_8 at 220 MHz, 16 °C, showed septets at δ 5.67 (3 H), 5.42 (3 H), 4.64 (3 H), and 4.00 (1 H) and doublets at δ 1.64 (18 H), 1.57 (18 H), 1.19 (6 H), and 1.16 (18 H) with $J_{HH} = 7.0$ Hz; δ relative to Me_4Si. $MoO(ONe)_4$ and $Mo_3O(ONe)_{10}$ prepared in analogous reactions, are air-sensitive yellow and green crystalline solids, respectively. Both compounds gave satisfactory elemental analyses.

(9) We thank the Office of Naval Research for support. M.H.C. is the recipient of a Camille and Henry Dreyfus Teacher-Scholar Grant and C.C.K. is the 1980–1981 Indiana University SOHIO Fellow.

Raman Spectroscopy of Excited Electronic States of Photoactive Metal Complexes. 1. Nitroprusside Ion

John W. Schindler and Jeffrey I. Zink*

Department of Chemistry
University of California, Los Angeles
Los Angeles, California 90024

Received April 17, 1981

Knowledge of the structures and the bonding properties of electronic excited states is of primary importance in interpreting the photochemical reactions from these states. The current understanding of transition-metal photoreactions is based on predictions of both the bonding and the structural changes which occur after photoexcitation.[1-3] These predictions use ligand field and molecular orbital considerations. Experimental measures of these changes are rare. The primary experimental technique has been low-temperature electronic emission and/or absorption spectroscopic measurement of vibronic structure in concert with Franck–Condon calculations of the displacement along metal–ligand normal modes.[4-6] Optical spectra do not usually contain as detailed structural information as do vibrational spectra. Thus, an experimental measurement of the Raman spectra of metal complexes in their photoactive excited states could in principle provide direct measurements of the important bonding changes. The first such examples were recently obtained by using pulsed techniques.[7] We report here the first CW excited-state Raman spectrum of a photochemically active metal complex, that of the nitroprusside ion, $Fe(CN)_5NO^{2-}$.

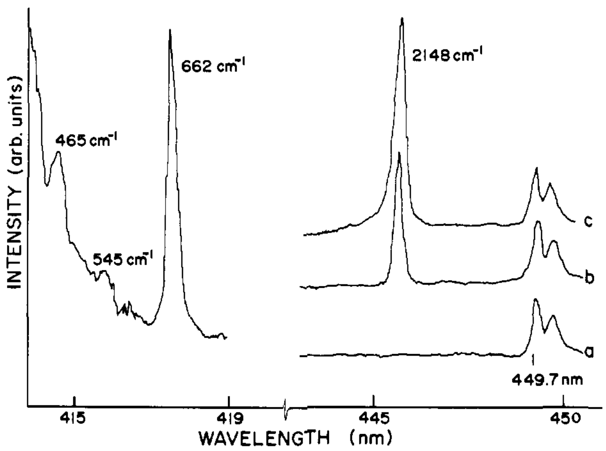


Figure 1. Raman spectra of aqueous $K_2Fe(CN)_5NO$. (a) Low laser power (or unfocused laser beam); (b) 0.1-W laser power, tightly focused; (c) 0.5-W laser power, tightly focused.

The 406.7-nm line of a krypton ion laser with maximum power of 0.5 W was used to excite the nitroprusside ion into its $^1A_1$ electronic excited state. This transition corresponds to a metal d orbital (d_{xz}, d_{yz}) to nitrosyl π^*, metal-to-ligand charge-transfer transition.[8] The laser beam was tightly focused to a diameter of about 6 μm by using a 44 power microscope objective as the final focussing element. Plasma lines and the 413.1-nm line were removed (vide infra) by passing the beam through two dispersing prisms and an iris diaphragm. The *E* vector of the laser beam was adjusted to be either parallel or perpendicular to the line of the entrance optics. The Raman signals were collected by using an optical system containing a collecting lens, a right angle diaphragm, and a focusing lens and passed through a $^1/_2$-m monochrometer to a PAR optical multichannel analyzer. In a typical experiment, data were collected over 15-min interval using a delay time on the OMA of 15 s. A saturated solution of $K_2Fe(CN)_5NO$ (ca. 1 M) was circulated by using a peristaltic pump through a 250-μm hyperdermic needle to produce a roughly 200-μm diameter jet stream of solution at the point of the laser focus. The calculated residence time in the focused laser beam ranged between 6 and 83 μs. The collecting optics allowed the tightly focused laser spot to be visually observed in the jet stream. All parts of the stream except that containing the most tightly focused spot were shuttered out. Under nearly optimum conditions of focus and laser power, the flux was about 1.02×10^{18} photons per second on an irradiated volume of 6.2×10^{-12} L. Given a calculated residence time per molecule for this situation of 77 μs, we estimate the photon-to-metal ratio to be 21 photons per molecule.

The metal–ligand and C–N stretching regions of the Raman spectrum obtained under tight focus and high power conditions are shown in Figure 1. The major peak of interest is the 2148 cm^{-1} peak arising from a C–N stretching mode.[9,10] The peak at

---

(1) Zink, J. I. *J. Am. Chem. Soc.* **1972**, 94, 8039; Inorg. Chem. **1973**, *12*, 1018; **1973**, *12*, 1957; *J. Am. Chem. Soc.* **1974**, *96*, 4464.

(2) (a) Wrighton, M.; Gray, H. B.; Hammond, G. S. *Mol. Photochem.* **1973**, *5*, 165. (b) Geoffroy, G.; Wrighton, M. "Organometallic Photochemistry"; Wiley: New York, 1980.

(3) Van Quickenbourne, H. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1977**, *99*, 2208; **1978**, *100*, 475.

(4) Hipps, K. W.; Merrell, G.; Crosby, G. A. *J. Phys. Chem.* **1976**, *80*, 2232.

(5) Wilson, R. B.; Solomon, E. I. *Inorg.* Chem. **1978**, *17*, 1729.

(6) Yersin, H.; Otto, H.; Zink, J. I.; Gliemann, G. *J. Am. Chem. Soc.* **1980**, *102*, 951.

(7) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391; Dallinger, R. F.; Miskowski, V. M.; Gray, H. B.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 1595.

(8) Monoharan, P. T.; Gray, H. B. *J. Am. Chem. Soc.* **1965**, *87*, 3340.

(9) Khanna, R. K.; Brown, C. W.; Jones, L. H. *Inorg. Chem.* **1969**, *8*, 2195.

(10) Bates, J. B.; Khanna, R. K. *Inorg. Chem.* **1970**, *6*, 1376.

0002-7863/81/1503-5968$01.25/0