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Facile Cleavage of the Mo≡Mo Bond in Reactions between $Mo_2(OBu\text{-}t)_6$ and Aryl Azides and Molecular Oxygen

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Recently, it has been shown that Mo–Mo multiple bonds can be cleaved under mild conditions by the addition of strong π-acceptor ligands. Specifically, Walton and co-workers[1–3] have shown that isocyanide ligands destroy the $M\overset{4}{—}M$ bond in a number of Mo_2^{4+}-containing compounds, yielding mononuclear $Mo(CNR)_7^{2+}$ compounds, and we have found related reactions involving the Mo≡Mo bond in Mo_2^{6+}-containing compounds with carbon monoxide[4] and nitric oxide.[5] We wish here to report two reactions of a different nature which proceed, under very mild conditions, to disrupt the Mo≡Mo bond in $Mo_2(OBu\text{-}t)_6$.[6] This work provides further evidence of the high susceptibility of the M≡M bond to attack by a wide variety of substrates[7] and, in one of the present instances, leads to the formation of a new compound, $Mo(O)_2(OBu\text{-}t)_2$, which may be viewed as the *tert*-butyl ester of molybdic acid.[8]

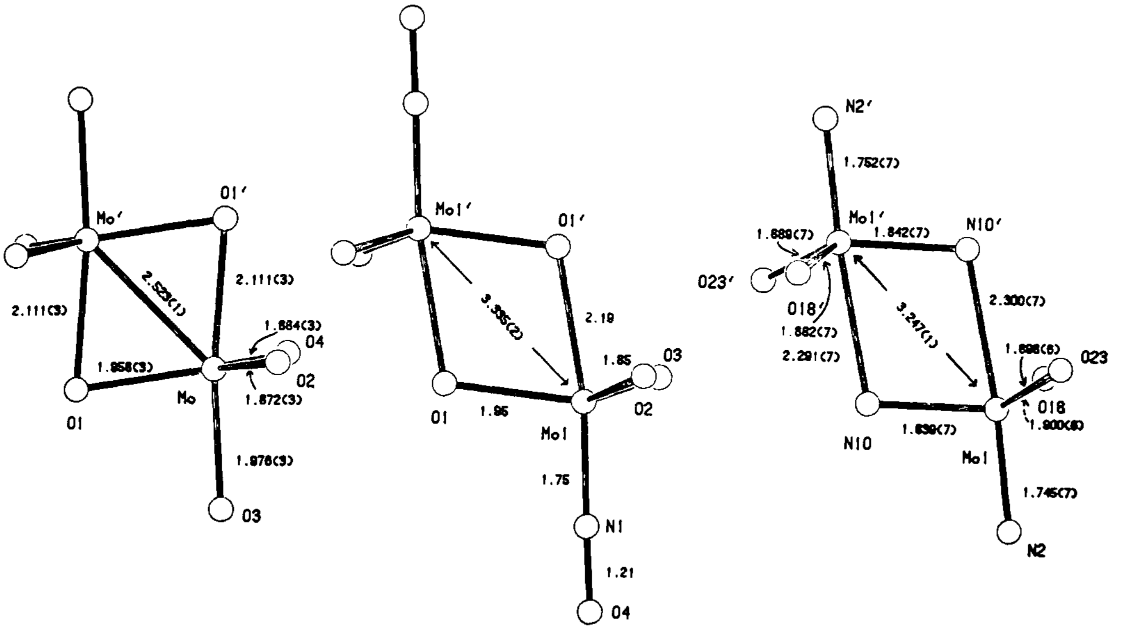

Figure 1. Comparison of the central skeletons of the $Mo_2(OPr\text{-}i)_8$ (left), $[Mo(NO)(OPr\text{-}i)_3]_2$ (center), and $[Mo(NC_7H_8)_2(OBu\text{-}t)_2]_2$ (right) molecules. The terminal imido ligands in $[Mo(NC_7H_8)_2(OBu\text{-}t)_2]_2$ have Mo–N–C angles = 175° (average); the Mo–N–O angle in $[Mo(NO)(OPr\text{-}i)_3]_2$ is 178°.

Hydrocarbon solutions of $Mo_2(OBu\text{-}t)_6$ react[9] with aryl azides and molecular oxygen at room temperatures according to eq **1** and **2**:

$$Mo_2(OBu\text{-}t)_6 + 4ArN_3 = \underset{\mathrm{I}}{[Mo(OBu\text{-}t)_2(NAr)_2]_2} + 4N_2 + 2t\text{-}BuOH \quad (1)$$

where Ar = phenyl and *p*-tolyl.

$$Mo_2(OBu\text{-}t)_6 + 2O_2 = \underset{\mathrm{II}}{2Mo(O)_2(OBu\text{-}t)_2} + 2t\text{-}BuOH \quad (2)$$

The *tert*-butyl alcohol is evidently formed from a hydrogen-atom abstraction reaction involving *t*-BuO· and solvent molecules: reaction 2, when carried out in 1,4-cyclohexadiene, yielded benzene and *tert*-butyl alcohol. The reaction between $Mo_2(OBu\text{-}t)_6$ and aryl azides has a parallel in the formation of the imido ligand with known reactions involving mononuclear transition-metal complexes and aryl azides.[10] A single-crystal structural determination[11] showed that I adopts a structure akin to that recently found[12] for $[Mo(CH_3)_2(NBu\text{-}t)_2]_2$ which provided the first structurally characterized example of a compound having unsymmetrical bridging imido ligands. A further comparison with the structures

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(1) Brant, P.; Cotton, F. A.; Sekutowski, J. C.; Wood, T. E.; Walton, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 6588.

(2) Wood, T. E.; Deaton, J. C.; Corning, J.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* **1980**, *19*, 2614.

(3) The addition of NO to dichloromethane solutions of $Mo_2X_4L_4$ compounds where X = Cl or Br and L = $PEtPh_2$, PEt_3, or $PBu\text{-}n_3$ and $Mo_2X_4(L\text{–}L)_2$ where X = Cl or NCS and L–L = $Ph_2P(CH_2)_nPPh_2$ (n = 1 or 2) gives the 18 electron mononuclear compounds $Mo(NO)_2X_2L_2$ and $Mo(NO)_2X_2(L\text{–}L)$: Nimry, T.; Urbancic, M. A.; Walton, R. A. *Inorg. Chem.* **1979**, *18*, 691.

(4) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7645.

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

(6) Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *Inorg. Chem.* **1977**, *16*, 1801.

(7) For recent reviews of the chemistry surrounding the Mo_2^{6+} unit, see: Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 356. Chisholm, M. H. *Transition Met. Chem. (Weinheim, Ger.)* **1978**, *3*, 351.

(8) For earlier attempted syntheses, see: Nebelung, von A.; Jahr, F. K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1964**, *19B*, 654. Rosenheim, A.; Bertheim, A. *Z. Anorg. Chem.* **1903**, *34*, 437. The related chromium compound $CrO_2(OBu\text{-}t)_2$ is known: Behr, W. J.; Fuchs, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1973**, *28B*, 597. The tungsten compound $WO(OBu\text{-}t)_4$ has been reported: Bradley, D. C.; Chisholm, M. H.; Extine, M. W.; Stager, M. E. *Inorg. Chem.* **1977**, *16*, 1794.

(9) Anhydrous solvents and dry and oxygen-free atmospheres were maintained for (1); dry solvents and dried molecular oxygen were used in (2). The compounds I and II are highly moisture sensitive and must be handled under rigorously anhydrous conditions. Satisfactory elemental analyses were obtained for I and II. Evolution and uptake of gases were followed by gas burette.

(10) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123 and references therein.

(11) Crystal data collected at −170 °C using Mo Kα radiation gave the following: a = 10.789 (2), b = 25.904 (6), c = 13.007 (3) Å; α = 73.11 (1), β = 81.34 (1), γ = 91.25 (1)°; Z = 3; d_{calcd} = 1.314 g cm^{-3}. In the space group $P\bar{1}$, there are 1.5 unique molecules. Of 9734 reflections measured in the range 6° ≤ 2θ ≤ 45°, 8946 were unique. The structure was solved by Patterson and Fourier techniques. Full matrix refinement, in which the metal atoms were assigned anisotropic thermal parameters and all other nonhydrogen atoms isotropic parameters, converged to $R(F)$ = 0.076 and $Rw(F)$ = 0.086. The molecule shown in Figure 1 is the one possessing no crystallographic symmetry. Molecule 2, which possesses a center of symmetry, is virtually identical.

(12) Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 1759.

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found for $Mo_2(OPr\text{-}i)_8$[13] and $Mo_2(OPr\text{-}i)_6(NO)_2$[5] is interesting (see Figure 1). In all three compounds, the molybdenum atoms are in distorted trigonal-bipyramidal environments and the bridging ligands form alternately long (axial) and short (equatorial) bonds.

$Mo(O)_2(OBu\text{-}t)_2$ is a yellow liquid at room temperature, which distills in vacuo at 55 °C (10^{-4} torr) and is monomeric in benzene as determined by a cryoscopic molecular weight determination. The monomeric nature of this compound in benzene is further supported by the natural abundance ^{17}O NMR spectrum which shows a single sharp signal (width at half-height ~90 Hz) at 862 ppm relative to $H_2{}^{17}O$.[14] This value is well within the range observed for terminal oxomolybdenum(VI) groups. Indeed, according to the Miller and Wentworth[15] correlation of ^{17}O chemical shifts with Mo–O bond distances, we calculate Mo–O = 1.71 Å for the oxo ligands in $Mo(O)_2(OBu\text{-}t)_2$.[16]

Supplementary Material Available: Fractional coordinates and isotropic and anisotropic thermal parameters for $[Mo(OBu\text{-}t)_2(NC_7H_8)_2]_2$ (3 pages). Ordering information is given on any current masthead page.

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

(14) Klemperer, W. G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 246.

(15) Miller, K. F.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 984.

(16) We thank the Office of Naval Research, the National Science Foundation, and the Wrubel Computing Center, Indiana University, for financial support. M.H.C. is the recipient of a Camille and Henry Dreyfus Teacher–Scholar grant, 1979–1984. C.C.K. is the 1980/81 Indiana University SOHIO Graduate Fellow.

*Book Reviews**

Medical Botany. Plants Affecting Man's Health. Walter H. Lewis (Missouri Botanical Garden) and Memory P. F. Elvin-Lewis (Department of Dental Microbiology, Washington University, St. Louis, Missouri). John Wiley and Sons, New York, London, Sydney, Toronto. 1977. xv + 515 pp. $29.50.

Biologists, pharmacologists, physicians, and anyone interested in how plants affect the body will find this book fascinating and informative. The first section, titled injurious plants, discusses internal poisons, allergy, and cell modifiers. This is followed by a section which is concerned with medicinal plants and which gives examples of plant remedies for cancer, the nervous system, heart and circulation, metabolism, eye and ear, oral hygiene, gastrointestinal tract, respiratory system, urogenital system, and skin. Antibiotics, antiseptics, pesticides, and universal remedies complete this section. The final section is devoted to stimulants, hallucinogens, and depressants. The survey is extensive and includes the folk lore of plants as well as references to scientific studies and uses by orthodox medicine. Extensive descriptions of disease states as well as the physiological effects of medicinal plants are included. References, a glossary, and an index complete the book.

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Nutrition and Environmental Health: The Influence of Nutritional Status on Pollutant Toxicity and Carcinogenicity. By Edward James Calabrese (School of Public Health, University of Massachusetts, Amherst, Massachusetts). John Wiley and Sons, New York. 1980. xix + 585 pp. $60.00.

Physicians and investigators in the fields of environmental and occupational health will find this an informative book. The vitamins A, B, C, D, and E are dealt with in relation to a variety of pollutants and toxic agents. It is suggested that an inadequate diet may predispose one to experience the adverse effects of certain toxic materials, while vitamin supplements may provide some protection from these substances. Extensive references and an index are included.

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Renewable Resources, A Systematic Approach. Edited by Enrique Campos-Lōpez (Centro de Investigacion en Quimica Aplicada, Saltillo, Coahuila, Mexico). Academic Press, New York. 1980. x + 410 pp. $29.50.

The seventeen papers which make up this book were originally presented at the CIQA International Conference in Saltillo, Coahuila, Mexico, in August 1979. The first part is devoted to systems and models and includes such titles as, systems analysis models in forest utilization, socioeconomic models in renewable natural resource utilization, global systematization of resource depletion in terms of nonrenewable factors, and others. The second part is titled scientific and technological trends. Some of the papers in this section are concerned with biomass for energy, trends in microbial technology for developing countries, future prospects for steroid drugs from botanical sources, and conversion of renewable resources into chemical feedstocks. A case study of guayule is also presented. This book will be useful to workers in the area of resource management. References and an index are included.

M. C. W. Smith, *Ann Arbor, Michigan*

Chemical Bonding. 2nd Edition. By Audrey L. Companion (University of Kentucky). McGraw-Hill, New York. 1979. x + 179 pp. $5.95 (paperback).

This book in its new edition remains an excellent supplement for undergraduates introducing quantum theory and chemical bonding.

Thermochemical Kinetics. 2nd Edition. By S. W. Benson (University of Southern California). John Wiley & Sons, New York. 1976. xi + 320 pp. $22.50.

Methods for empirical estimation of thermodynamic functions and rate parameters for gas-phase systems.

Physics of Quantum Electronics. Volume 7. Free-Electron Generators of Coherent Radiation. Edited by S. F. Jacobs, H. S. Pilloff, M. Sargent III, M. O. Scully, and R. Spitzer. Addison-Wesley, Reading, Massachusetts. 1980. xix + 813 pp. $36.50.

This volume is based on a series of lectures sponsored by the Office of Naval Research in 1979 at Telluride, Colorado, and is primarily of interest to physicists.

Theoretical Chemistry, Advances and Perspectives. Volume 3. Edited by H. Eyring and D. Henderson. Academic Press, New York. 1978. xi + 239 pp. $25.00.

This volume contains five essentially unrelated reviews of topics of current research interest: Theoretical Studies of Negative Molecular Ions (J. Simons); Geometrical Aspects of Equilibrium Thermodynamics (F. Weinhold); A Model of the Liquid State (M. S. John and H. Eyring); Structure of Fluid ^4He (R. D. Murphy); Proton Transfer Reactions and Kinetics in Water (F. H. Stillinger).

Progress in Liquid Physics. Edited by C. A. Croxton (University of Newcastle, New South Wales, Australia). Wiley-Interscience, New York. 1978. vii + 592 pp. $63.00.

A collection of 14 articles by 18 contributors covering recent advances in the statistical-mechanical theory of liquids. Emphasized topics include quantum fluids, critical phenomena, irreversibility, transport processes, phase transitions, polymeric systems, liquid crystals, and triplet correlations.

Perchloric Acid and Perchlorates. By Alfred A. Schilt (Northern Illinois University). G. Frederick Smith Chemical Co., Columbus, Ohio. 1979. ix + 189 pp. $15.00 hardbound, $8.00 paperbound.

This book is a comprehensive review of the chemistry of perchlorates and includes a nearly complete bibliography through 1977 (papers on their use in explosives and propellants are generally omitted, however). There are chapters on preparation, properties, applications, analysis biological effects, and safety and environmental concerns. A substantial appendix tabulates references to equilibrium data for binary, ternary, and

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*Unsigned book reviews are by the Book Review Editor.