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FACILE CLEAVAGE OF THE MO=MO BOND IN REACTIONS BETWEEN (MO2(OBU)-ETC(U)
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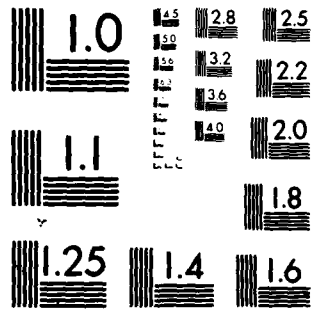
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FACILE CLEAVAGE OF THE $\text{Mo}=\text{Mo}$ BOND IN REACTIONS
BETWEEN $\text{Mo}_2(\text{OBU}^t)_6$ AND ARL AZIDES AND MOLECULAR OXYGEN

by

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John C. Huffman, Charles C. Kirkpatrick and Andrew Ratermann

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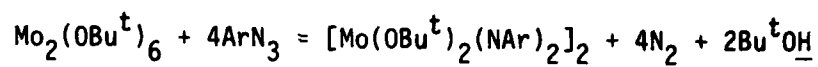
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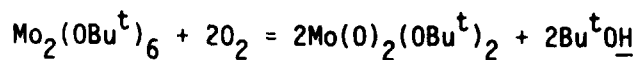
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Hydrocarbon solutions of Mo ₂ (OBU ^t) ₆ react with arylazides and molecular oxygen at room temperatures according to equations 1 and 2, shown below. I is structurally related to (MoMe ₂ (NBU ^t) ₂) ₂ recently characterized by Nujent and Harlow (J. Am. Chem. Soc. 1980, 102, 1759); II, the tert-butyl ester of molybdic acid, is the first molecule of its kind to be prepared for the group		

→ 6 transition elements. ←



I

where Ar = phenyl and p-tolyl



II

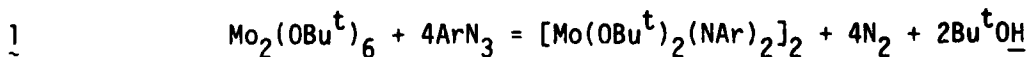
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FACILE CLEAVAGE OF THE Mo≡Mo BOND IN REACTIONS
BETWEEN Mo₂(OBU^t)₆ AND ARYL AZIDES AND MOLECULAR OXYGEN

Sir:

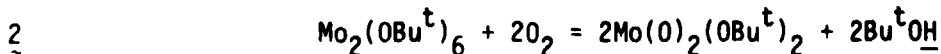
Recently, it has been shown that Mo-Mo multiple bonds can be cleaved under mild conditions by the addition of strong π -acceptor ligands. Specifically, Walton and coworkers¹⁻³ have shown that isocyanide ligands destroy the M≡M bond in a number of Mo₂⁴⁺ containing compounds yielding mononuclear Mo(CNR)₇²⁺ compounds and we have found related reactions involving the Mo≡Mo bond in Mo₂⁶⁺ containing compounds with carbon monoxide⁴ 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 Mo₂(OBU^t)₆.⁶ This work provides further evidence of the high susceptibility of the M≡M bond to attack by a wide variety of substrates⁷ and, in one of the present instances, leads to the formation of a mononuclear compound, Mo(O)₂(OBU^t)₂, which may be viewed as the tert-butyl ester of molybdic acid, the first molecule of its kind to be prepared for the group 6 transition elements.

Hydrocarbon solutions of Mo₂(OBU^t)₆ react⁸ with arylazides and molecular oxygen at room temperatures according to equations 1 and 2, shown below.



I

where Ar = phenyl and p-tolyl



II

The tert-butanol is evidently formed from a hydrogen atom abstraction reaction involving Bu^tO and solvent molecules: reaction 2, when carried out in 1,3-cyclohexadiene, yielded benzene and tert-butanol. The reaction between $\text{Mo}_2(\text{OBu}^t)_6$ and aryl azides has a parallel in the formation of the imido ligand with known reactions involving mononuclear transition metal complexes and aryl azides.⁹ A single crystal structural determination¹⁰ showed that I adopts a structure akin to that recently found¹¹ for $[\text{Mo}(\text{CH}_3)_2(\text{NBu}^t)_2]_2$ which provided the first structurally characterized example of a compound having unsymmetrical bridging imido ligands. A further comparison with the structures found for $\text{Mo}_2(\text{OPr}^i)_8$ ¹² and $\text{Mo}_2(\text{OPr}^i)_6(\text{NO})_2$ 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.

$\text{Mo}(\text{O})_2(\text{OBu}^t)_2$ 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 .¹³ This value is well within the range observed for terminal oxo-molybdenum(VI) groups. Indeed, according to the Miller and Wentworth¹⁴ correlation of ^{17}O chemical shifts with Mo-O bond distances, we calculate Mo-O = 1.71 Å for the oxo ligands in $\text{Mo}(\text{O})_2(\text{OBu}^t)_2$.¹⁵

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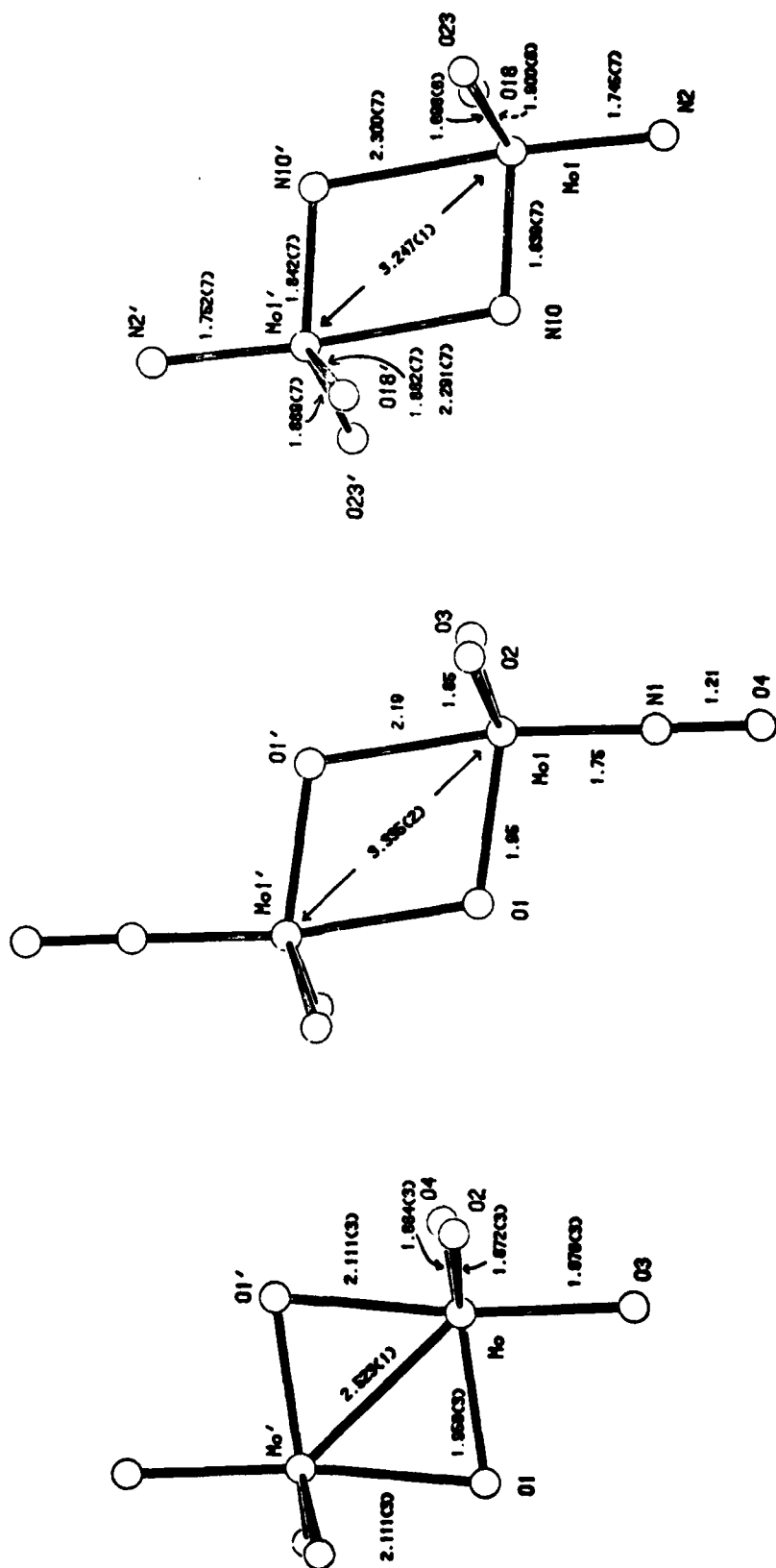
Contribution from the Department of Chemistry
and Molecular Structure Center
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3. The addition of NO to dichloromethane solutions of $\text{Mo}_2\text{X}_4\text{L}_4$ compounds, where X = Cl or Br and L = PEtPh_2 , PEt_3 or PBU^n_3 and $\text{Mo}_2\text{X}_4(\text{L-L})_2$ where X = Cl or NCS and LL = $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ (n = 1 or 2) gives the 18 electron mononuclear compounds $\text{Mo}(\text{NO})_2\text{X}_2\text{L}_2$ and $\text{Mo}(\text{NO})_2\text{X}_2(\text{L-L})$: Nimry, T.; Urbancic, M.A.; Walton, R.A. Inorg. Chem. 1979, 18, 691.
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8. 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. Evolution and uptake of gases were followed by gas-burette.
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10. Crystal data collected at -170°C using $\text{MoK}\alpha$ radiation gave the following: $a = 10.789(2)$, $b = 25.904(6)$, $c = 13.007(3)$ Å, $\alpha = 73.11(1)$, $\beta = 81.34(1)$, $\gamma = 91.25(1)^{\circ}$, $Z = 3$; $d_{\text{calcd}} = 1.314 \text{ g cm}^{-3}$. In the space group $P\bar{1}$, there are $1\frac{1}{2}$ unique molecules. Of 9734 reflections measured in the range $6^{\circ} \leq 2\theta \leq 45^{\circ}$, 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 non-hydrogen atoms isotropic parameters, converged to $R(F) = 0.076$ and $R_w(F) = 0.086$. The molecule shown in Figure 1 is the one possessing no crystallographic symmetry. Molecule 2, which possesses a center of symmetry, is virtually identical.
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15. For the absence of analogous compounds of the group 6 transition elements, see Cotton, F.A.; Wilkinson, G. "Advanced Inorganic Chemistry" 4th Ed., **1980**, John Wiley Interscience Publishers. We thank the Office of Naval Research, the National Science Foundation and the Wrubel Computing Center, Indiana University for financial support. MHC is the recipient of a Camille and Henry Dreyfus Teacher-Scholar Grant, 1979-84.

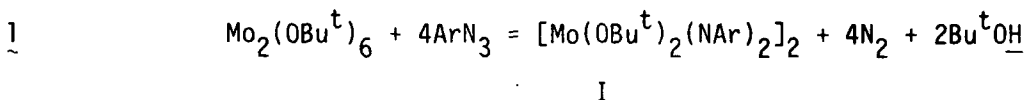
Caption to Figure 1: Comparison of the central skeletons of the $\text{Mo}_2(\text{OPr}^i)_8$ (left), $[\text{Mo}(\text{NO})(\text{OPr}^i)_3]_2$ (center) and $[\text{Mo}(\text{NC}_7\text{H}_8)_2(\text{OBu}^t)_2]_2$ (right) molecules. The terminal imido ligands in $[\text{Mo}(\text{NC}_7\text{H}_8)_2(\text{OBu}^t)_2]_2$ have Mo-N-C angles = 175° (average); the Mo-N-O angle in $[\text{Mo}(\text{NO})(\text{OPr}^i)_3]_2$ is 178° .



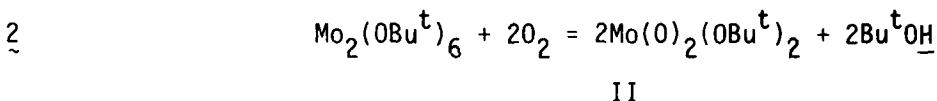
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Abstract

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I is structurally related to [MoMe₂(NBu^t)₂]₂ recently characterized by Nujent and Harlow (J. Am. Chem. Soc. 1980, 102, 1759); II, the tert-butyl ester of molybdic acid, is the first molecule of its kind to be prepared for the group 6 transition elements.



