AD-A045 818 PRINCETON UNIV N J DEPT OF CHEMISTRY F/G 7/2
REACTIONS OF METAL-TO-METAL MULTIPLE BONDS. 3. ADDITION OF NITR--ETC(U)
OCT 77 M H CHISHOLM, F A COTTON, M W EXTINE N00014-76-C-0826
UNCLASSIFIED TR-77-03 NL

| OF |
AD
A045818

END
DATE
FILMED
11-77
DDC

(12)

(15) OFFICE OF NAVAL RESEARCH
Contract N00014-76-C-0826
Task No. NR 056-625

B.S.

(9) TECHNICAL REPORT, NO. 77-03

(6) Reactions of Metal-to-Metal Multiple Bonds. 3.[1] Addition of Nitric Oxide to Hexakis(alkoxy)-dimolybdenum Compounds. Preparation and Properties of Bis(nitrosyl)hexakis(alkoxy)dimolybdenum Compounds and Structural Characterization of the Isoproproxy Derivative,

(10) by M.H. Chisholm[2a,3], F.A. Cotton[2b], M.W. Extine[2b], R.L. Kelly[2a]

Prepared for Publication
in
Journal of Inorganic Chemistry

Departments of Chemistry
Princeton University,
Princeton, New Jersey 08540
and
Texas A&M University
College Station, Texas 77843

(11) 4 October 1977

(12) 29 p.

(14) TR-77-03

1473
400 363

1B

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Reactions of Metal-to-Metal Multiple Bonds. 3. Addition of Nitric Oxide to Hexakis(alkoxy)-dimolybdenum Compounds.....		5. TYPE OF REPORT & PERIOD COVERED Technical Report, 1977
		6. PERFORMING ORG. REPORT NUMBER TR-77-03
7. AUTHOR(s) M.H. Chisholm, F.A. Cotton, M.W. Extine and R.L. Kelly		8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0826
9. PERFORMING ORGANIZATION NAME AND ADDRESS Departments of Chemistry Princeton University, Princeton, N.J. Texas A and M Univ., College Station Tx.		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy		12. REPORT DATE October 4, 1977
		13. NUMBER OF PAGES 26
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Metal-to-Metal Multiple Bonds, Nitric Oxide, Alkoxides

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
The reactions of $Mo_2(OR)_6$ compounds (R=Me_3C, Me_2CH and Me_3CCH_2) with nitric oxide yield a heretofore unrecognized class of metal nitrosyl complexes of empirical formula $Mo(OR)_3NO$. The latter show NO stretching frequencies at ca. 1640 cm^{-1} and are diamagnetic, dimeric and fluxional in solution. The compound $[Mo(OPr^i)_3NO]_2$ crystallized in space group $P\bar{1}$ with Z = 2 and unit cell dimensions a = 10.828(1)Å, b = 15.848(2)Å, c = 9.885(2)Å,

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 68 IS OBSOLETE
S/N 0102-LF-014-6601

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

$\alpha = 90.21(2)^0$, $\beta = 115.93(2)^0$, $\gamma = 82.42(1)^0$ and $V = 1509.4(4)\text{Å}^3$. There are two crystallographically independent molecules, one centered on the origin, the other at 1/2, 1/2, 1/2, which are essentially identical in structure. Each molybdenum atom is five coordinated in a trigonal bipyramidal manner and attains only a 14-valence shell electron configuration. The nitrosyl ligands occupy terminal axial positions and the two bridging OPr^i groups form short bonds in equatorial positions and long bonds in axial positions which are trans to the NO ligands. The Mo-N-O units are essentially linear (178^0) and the bond lengths therein are 1.754(7)Å for Mo-N and 1.19(1)Å for N-O. The Mo----Mo separation of 3.335(2)Å precludes metal-to-metal bonding. The M-M triple bonds that exist in $Mo_2(OR)_6$ compounds are thus shown to be cleaved by the addition of two NO ligands. The electronic structure in these new nitrosyl metal complexes can be formulated so that the highest filled MO is the e level responsible for Mo to NO π-bonding, made up of metal d_{xz}, d_{yz} and NO π^* orbitals. It is likely that other, similar $MX_3(NO)L$ molecules, where M is a group VI transition metal, X is a univalent group and L a two-electron donor, should be obtainable.

Reactions of Metal-to-Metal Multiple Bonds. 3[1] Addition of Nitric Oxide to Hexakis(alkoxy)-dimolybdenum Compounds. Preparation and Properties of Bis(nitrosyl)hexakis(alkoxy)dimolybdenum Compounds and Structural Characterization of the Isoproproxy Derivative.

M.H. Chisholm*[2a,3], F.A. Cotton*[2b], M.W. Extine[2b] and R.L. Kelly[2a]

Contribution from the Departments of Chemistry, Princeton University, Princeton, New Jersey 08540 and Texas A&M University, College Station, Texas 77843

Abstract

The reactions of $Mo_2(OR)_6$ compounds (R=Me_3C, Me_2CH and Me_3CCH_2) with nitric oxide yield a heretofore unrecognized class of metal nitrosyl complexes of empirical formula $Mo(OR)_3NO$. The latter show NO stretching frequencies at ca. 1640 cm^{-1} and are diamagnetic, dimeric and fluxional in solution. The compound $[Mo(OPr^i)_3NO]_2$ crystallizes in space group $P\bar{1}$ with Z = 2 and unit cell dimensions a = 10.828(1)Å, b = 15.848(2)Å, c = 9.885(2)Å, α = 90.21(2)°, β = 115.93(2)°, γ = 82.42(1)° and V = 1509.4(4)$Å^3$. There are two crystallographically independent molecules, one centered on the origin, the other at 1/2, 1/2, 1/2, which are essentially identical in structure. Each molybdenum atom is five coordinated in a trigonal bipyramidal manner and attains only a 14-valence shell electron configuration. The nitrosyl ligands occupy terminal axial positions and the two bridging OPr^i groups form short bonds in equatorial positions and long bonds in axial positions which are trans to the NO ligands. The Mo-N-O units

are essentially linear (178^0) and the bond lengths therein are 1.754(7)Å for Mo-N and 1.19(1)Å for N-O. The Mo----Mo separation of 3.335(2)Å precludes metal-to-metal bonding. The M-M triple bonds that exist in $Mo_2(OR)_6$ compounds are thus shown to be cleaved by the addition of two NO ligands. The electronic structure in these new nitrosyl metal complexes can be formulated so that the highest filled MO is the e level responsible for Mo to NO π-bonding, made up of metal d_{xz}, d_{yz} and NO π^* orbitals. It is likely that other, similar $MX_3(NO)L$ molecules, where M is a group VI transition metal, X is a univalent group and L a two-electron donor, should be obtainable.

Introduction

The occurrence of compounds containing metal-to-metal multiple bonds is now a well documented facet of transition metal chemistry[1]. In this series we are studying the reactions of such compounds with regard to their ability (1) to undergo reactions of the type well documented in mononuclear chemistry[2] and (2) to act as building blocks for the systematic synthesis of new cluster (polynuclear) compounds[3]. Both have important catalytic implications.

In the compounds $Cp_2M_2(CO)_4$, where M=Mo or W, the formation of a metal-to-metal triple bond allows the metal atoms to achieve an 18-valence shell electron configuration[7]. In compounds of the type M_2L_6, where M=Mo and W, L=R(alkyl)[8,9], NR_2[10,11] and OR[12,13], which have metal-to-metal triple bonds and a central ethane-like M_2X_6 core (X=C,N,O), the metal atoms do not achieve an 18-valence shell electron configuration, even when ligand to metal π-bonding is important as is the case where L=NR_2 and OR[14]. The compounds $Cp_2M_2(CO)_4$ and M_2L_6 may be termed electronically saturated and unsaturated, respectively, and differences in their reactivity patterns may be expected. Some of these have already been observed.

All compounds containing metal-to-metal multiple bonds are inherently coordinatively unsaturated and $Cp_2M_2(CO)_4$ and M_2L_6 compounds react to expand the coordination number of the metal as shown in 1 through 4 below.

1[7] $Cp_2M_2(CO)_4+2L\rightarrow Cp_2M_2(CO)_4L_2$ where L=CO,PR_3.

2 $Cp_2M_2(CO)_4+un\rightarrow Cp_2M_2(CO)_4(un)$ where un=allene[15], RC≡CR,Me_2NCN[16]

3[12,16] $M_2(OR)_6+2L\rightleftarrows M_2(OR)_6L_2$ where =PR_3 or an amine

4[12,17] $M_2(OR)_6+2CO_2\rightleftarrows Mo_2(OR)_4(O_2COR)_2$

In reactions 1 and 2, the addition of 4 electrons to the electronically saturated M≡M moiety reduces the M-M bond order in $Cp_2M_2(CO)_4L_2$ and $Cp_2M_2(CO)_4$(un) compounds to a single M-M bond[18]. Addition of 2L(≡4 electrons) to $Mo_2(OR)_6$ compounds does not reduce the M-M bond order in the adducts The structural characterization of the dimethylamine adduct of hexakis (trimethylsiloxy)dimolybdenum, $Mo_2(OSiMe_3)_2(HNMe_2)_2$[16] and $Mo_2(OBu^t)_4(O_2COBu^t)_2$[17] reveal triple bonds between two four-coordinated molybdenum atoms with Mo-Mo distances of 2.242(1)Å and 2.244(1)Å respectively c.f.[12] Mo-Mo=2.222(1)Å in $Mo_2(OCH_2CMe_3)_6$.

The addition of 6 electrons, in the form of two nitrosyl ligands, to the electronically saturated M≡M moiety in $Cp_2M_2(CO)_4$ effects cleavage of the M-M triple bond with formation of two equivalents of a mononuclear complex, eq. 5.

5[19] $Cp_2M_2(CO)_4+2NO \rightarrow 2CpM(CO)_2NO$

This latter observation prompted us to examine the reactivity of the electronically unsaturated M≡M moiety in M_2L_6 compounds toward nitric oxide. We report here our studies of the reactions of $Mo_2(OR)_6$ compounds with NO.

Results and Discussion

Synthesis and Properties of $Mo_2(OR)_6(NO)_2$ Compounds:

Hydrocarbon solutions of $Mo_2(OR)_6$[12] compounds, where R=Me_3C, Me_2CH and Me_3CCH_2, react with NO (2 equiv) at room temperature according to eq. 6. The reaction is

6 $Mo_2(OR)_6+2NO \rightarrow Mo_2(OR)_6(NO)_2$

rapid, irreversible and seemingly quantitative. The nitrosyl compounds may be purified by sublimation (70^0 - 110^0C, 10^{-4} cm Hg). Analytical and other characterization data are recorded in the Experimental Section.

$Mo_2(OR)_6(NO)_2$ are yellow, crystalline, diamagnetic compounds, which, though thermally quite stable, are moisture and oxygen sensitive. They are soluble in hydrocarbon solvents, and a cryoscopic molecular weight determination in benzene confirmed the dinuclear nature of $Mo_2(OPr^i)_6(NO)_2$. The other compounds are assumed to be dinuclear in solution on the basis of their similar properties.

They show molecular ions $Mo_2(OR)_6(NO)_2^+$ followed by loss of NO in the mass spectrometer. Intense ions due to $Mo(OR)_3NO^+$ were also observed. The intensity of the latter is in sharp contrast with the mass spectra of $Mo_2(OR)_6$ compounds which show virtually only dinuclear ions (Mo_2-containing) in the mass spectrometer.

In the infrared spectra a single intense band at ca. 1640 cm^{-1} is attributed to $\upsilon_{Str}(NO)$ of a terminally bonded NO ligand. IR data are recorded in the Experimental Section.

NMR Studies

Variable temperature ^1H and ^{13}C nmr studies show that $Mo_2(OR)_6(NO)_2$ are fluxional molecules. The low temperature limiting spectra indicate the freezing out on the nmr time scale of a structure having two types of alkoxy-groups in 2:1 integral ratio: $Mo_2(OR)_2(OR')_4(NO)_2$. The rate of interconversion of alkoxy groups OR and OR' is dependent on the alkyl group: T_c=70°, 40° and -20°C for $OCMe_3$, $OCHMe_2$ and OCH_2CMe_3, respectively. The low temperature limiting ^{13}C nmr spectrum of the isoproproxide, corresponding to $Mo_2(OR)_2(OR')_4(NO)_2$, indicates that the R'-methyl carbons are diastereotopic. ^1H and ^{13}C nmr data are given in the Experimental Section.

Solid State Structure. There are two crystallographically independent molecules per unit cell, each possessing crystallographically imposed C_i symmetry. Table 1 lists the atomic

positional and thermal parameters. Bond distances and angles are given in Tables 2 and 3, respectively. An ORTEP view and a stereoview of Molecule I, showing the atom labelling scheme are shown in Figures 1 and 2. No views of Molecule II are shown since, as Tables 2 and 3 show, it is virtually identical to Molecule I. The labelling scheme used for Molecule II parallels that of Molecule I as can be deduced from Tables 2 and 3; for example O(5),..... O(8) in Molecule II correspond, in order, to O(1),..... O(4) in Molecule I. Figure 3 dipicts the coordination about the metal atoms and lists some pertinent bond distances averaged for both molecules and rounded off to 0.01Å.

The $[Mo(OPr^i)_3NO]_2$ molecule consists of two equivalent (inversion-related) distorted trigonal bipyramidal $Mo(OR)_4NO$ units fused along a common axial-to-equatorial edge through the agency of bridging OPr^i groups. With a Mo-Mo distance of 3.335(2)Å it may be assumed that no significant direct Mo-Mo interaction exists. It will be shown later that the electronic structure can be understood quite satisfactorily without recourse to any such metal-to-metal interaction.

The distortions of the trigonal bipyramid are all understandable in terms of the nature and function of the ligands. The principal axis is slightly bent (171.9°), presumably because of stress imposed by the bridging system. The Mo(1)-O(1) and Mo(2)-O(5)' bonds, 1.95Å, are longer than the other equatorial Mo-O bonds, 1.85Å, since O(1) and O(5) are bridging atoms. The Mo(1)-O(1)' and Mo(2)-O(5)' bonds, 2.194Å, are much longer than any of the Mo-O equatorial bonds, which is entirely typical of the high trans influence normally encountered with the NO ligand.[20,21] Finally, the three equatorial Mo-O bonds are slightly bent away from the NO ligand and towards the long Mo-O axial bond, the N-Mo-O angles being 99 ±1°, which is an expected

steric consequence of closeness of the N and remoteness of the axial O atoms.

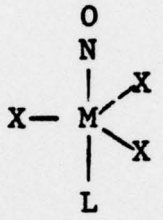
DISCUSSION

The work reported here is important because it implies the existence of a new and heretofore unrecognized, and potentially large, class of metal nitrosyl compounds. To appreciate the relationship of this compound to the known types of metal nitrosyls let us compare it with previously known trigonal bipyramidal complexes having the NO ligand in an axial position. According to the tabulation of Eisenberg and Meyer[21] there are only two of these, viz., $RuH(NO)(PPh_3)_3$[22] and $[IrH(NO)(PPh_3)_3]ClO_4$,[23] in each of which there is a formal 18-electron configuration for the metal atom. As is generally recognized, these 18 electrons can be assigned as shown in Fig. 4a.

It is then straightforward to assign the 14 electrons in the present case as shown in Fig. 4b. In this way the strong π interaction via the overlap between metal d_{xz} and d_{yz} orbitals with NO π^* orbitals is maintained and accounts for the short Mo-N distance and the low value of υ_{NO}. All that is lost in going from the configuration of Fig. 4a to that of Fig. 4b are the 2e electrons which are essentially nonbonding.

It may also be emphasized that the essential features of Fig. 4 are not dependent upon the precise fulfillment of trigonal bipyramidal geometry. In particular, the bending down of the equatorial bonds (i.e., away from NO), and the lengthening of the bond to the donor, L, trans to NO, even to the limit of eliminating L and having a four-coordinate structure of C_{3v} symmetry, do not invalidate the analysis. The monomeric diamagnetic compounds $Cr(NPr^i)_3NO$ and $Cr(NSi_2Me_6)_3NO$ provide examples of this limiting situation[24,25].

There would not seem to be any reason why discrete mononuclear complexes of the type 1, where X represents a univalent ligand, L a sigma donor and M any atom or ion isoelectronic with Mo(III) should not exist as a general class. In the particular context of the present case, the possibility of converting the dinuclear molecule to two molecules



1

of type 1 in which X = OPr^i by a bridge-splitting reaction with some neutral ligand, L, can be envisioned.

In a formal sense, the reaction of the $(RO)_3Mo{\equiv}Mo(OR)_3$ molecule with 2 NO to give two $(RO)_3MoNO$ units (which then associate via bridging RO groups) corresponds to the replacement of the Mo≡Mo triple bond (a σ bond plus two π bonds) by two Mo≡N-O: bonds. Again, there is a σ electron pair and two π electron pairs shared by the Mo atom and its partner, which is now the nitrogen atom instead of another molybdenum atom. Cleavage of the M-M triple bond in reaction 5 may be viewed in a similar manner. However, the detailed mechanism of the reaction which leads to cleavage of the M-M triple bond remains to be established.

Future work will be directed toward (i) the synthesis of monomeric compounds of the general formula $Mo(OR)_3(NO)L$, where L = a neutral donor ligand, and (ii) an elucidation of the fluxional properties of $Mo_2(OR)_6(NO)_2$ compounds.

Experimental Section

General procedures have been described previously[10]. All reactions were carried out under a dried and purified nitrogen atmosphere using standard Schlenk or vacuum-line procedures.

Preparation of $Mo_2(OR)_6(NO)_2$ Compounds where R=Me_3C, Me_2CH and Me_3CCH_2. All reactions were carried out in a similar manner, which is exemplified by the reaction described below.

$Mo_2(OPr^i)_6(NO)_2$: $Mo_2(OPr^i)_6$(0.38g, 0.7 mmol)

was dissolved in hexane (10 mL) in a 25 mL round-bottomed flask to give a pale yellow solution. The flask was cooled in liquid nitrogen, evacuated, and by use of a calibrated vacuum manifold, nitric oxide (1.4 mmol) was added. Upon warming to room temperature the solution darkened. After 12 hr the solvent was stripped yielding a light brown solid from which upon heating in vacuum (75°C, 10^{-3} cm Hg) gave the yellow compound $[Mo(OPr^i)_3NO]_2$ (0.15g, 36 % yield) by sublimation. In an nmr tube experiment the reaction between $Mo_2(OPr^i)_6$ and NO(2 equiv) to give $Mo_2(OPr^i)_6(NO)_2$ was seen to be rapid and apparently quantitative.

Analytical Data Found (calcd): $Mo_2(OPr^i)_6(NO)_2$: C, 35.36(35.65); H, 6.75(6.98); N, 4.56(4.62). $Mo_2(OBu^t)_6(NO)_2$: C, 41.49(41.74); H, 8.02(7.88); N, 4.22 (4.06). $Mo_2(OCH_2CMe_3)_6(NO)_2$: C, 46.34 (46.51); H, 8.29(8.59); H, 3.65(3.62).

Infrared Data in the range 2,000 - 400 cm^{-1} obtained from nujol mulls between KBr plates $Mo_2(OPr^i)_6(NO)_2$: 1640vs, 1330w, 1171w, 1132w, 1110s, 1022vw, 961s(br), 940s, 851m, 835m, 666m, 650m, 629w, 598m, 485w.

$Mo_2(OBu^t)_6(NO)_2$: 1632vs, 1310w, 1245m, 1163s(br), 976w, 950s, 938vs, 910m, 847s, 788s, 769s, 738m, 725m, 645s, 631s, 622m, 595m, 400w.

$Mo_2(OCH_2CMe_3)_6(NO)_2$: 1643vs, 1300w, 1264w, 1218w, 1182w, 1168w, 1050s, 1040vs, 1016vs, 998s, 937m, 920w, 905w, 850w, 805w, 760w, 723w, 708w, 670m, 633w, 623m, 571m, 540m, 489w, 469w, 436w, 415w. ^{1}H nmr Data obtained in toluene-d_8, δ in ppm rel. to TMS, J in Hz. $Mo_2(OPr^i)_6(NO)_2$: T = 80°C, $\delta(CH_3)$ = 1.27, $\delta(CH)$ = 5.25, J = 6.5; T = 20°C, $\delta(CH_3)$ = 1.23, 1.40, $\delta(CH)$ = 4.98, 5.40, J = 6.5. $Mo_2(OBu^t)_6(NO)_2$: T = 80°, $\delta(CH_3)$ = 1.47; T = 20°C, $\delta(CH_3)$ = 1.40, 1.60. $Mo_2(OCH_2CMe_3)_6(NO)_2$: T = 20°C, $\delta(CH_2)$ = 4.75, $\delta(CH_3)$ = 0.92; T = -40°, $\delta(CH_2)$ = 4.61, 4.82, $\delta(CH_3)$ = 0.86, 1.01. Low temperature limiting ^{13}C nmr data corresponding to $Mo_2(OR)_2(OR')_4(NO)_2$ obtained in toluene-d_8, δ in ppm rel. TMS.
$Mo_2(OBu^t)_6(NO)_2$: δ(R-methyl) = 32.69 , δ(R-C tertiary) = 88.29.
δ(R'-methyl) = 33.10 , δ(R'-C tertiary) = 83.78.
$Mo_2(OPr^i)_6(NO)_2$: δ(R-methyl) = 25.69 , δ(R-CH) = 79.04,
δ(R'-methyl) = 26.75 , δ(R'-CH) = 81.01 .
$Mo_2(OCH_2CMe_3)_6(NO)_2$: δ(R-methyl) = 26.96, δ(R-C tertiary) = 34.09, $\delta(R\text{-}CH_2)$ = 91.61, δ(R'-methyl) = 26.60 , δ(R'-C tertiary) = 34.62, $\delta(R'\text{-}CH_2)$ = 91.50.

X-Ray Crystallography. A crystal of $Mo_2(OPr^i)_6(NO)_2$ measuring ca. 0.2 x 0.3 x 0.5 mm was wedged in a mineral oil filled capillary and mounted with the longest crystal dimension nearly coincident with ø. The ω-scans of several intense low-angle reflections had peak widths at half-height of ca. 0.2°. Cell constants indicated that the crystal belonged to the triclinic system with a = 10.828(1), b = 15.848(2), c = 9.885(2)Å α = 90.21(2)°, β = 115.93(2)°, γ = 82.42(1)°, V = 1509.4(4)Å. The observed volume was consistent with that expected for Z = 2. The space group was presumed to be $P\bar{1}$ (No. 2) and this was confirmed by the subsequent structure solution and refinement.

Data were collected at 24°C on a Syntex $P\bar{1}$ autodiffractometer using MoKα (λ= 0.710730) radiation with a graphite crystal mono-

chromator. The θ-2θ scan technique was used with scans ranging from 1.0^0 above to 1.0^0 below the calculated $K\alpha_1$, $K\alpha_2$ doublet, variable scan speeds from 4.0 to 24.0^0/min and a scan to background time ratio of 0.5. The intensities of three standard reflections were monitored frequently throughout data collection and showed a maximum decrease of 27%. A total of 4121 reflections having $0^0<2\theta(MoK\alpha)<45.0^0$ were collected. The intensities were reduced to a set of relative $|F_o|^2$ values and corrected for crystal decay[25]. The 2052 reflections having $|F_o|^2>3\sigma(|F_o|^2)$ were used in subsequent structure solution and refinement. In general, reflections of the type $hk\ell$, $h+k+\ell = 2n+1$ were weak. The data were not corrected for absorption (μ = 8.5 cm^{-1}). The structure was solved using conventional heavy atom methods,[25] and refined to convergence utilizing anisotropic thermal parameters for the Mo, O, and N atoms and isotropic thermal parameters for the remaining non-hydrogen atoms. The final residuals are

$$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.061$$

$$R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.093$$

A value of 0.07 was used for P in the calculation of the weights, w. The end of an observation of unit weight was 2.01. A final difference Fourier map showed no peaks of structural significance. A table of observed and calculated structure factors (9 pages) is available as supplementary material. See any current masthead page for ordering information.

Acknowledgements The financial support of the National Science Foundation (Grant MPS-73-05016) and the Office of Naval Research at Princeton University and the National Science Foundation (Grant CHE-75-05509) at Texas A and M University is gratefully acknowledged.

References Part 4.

1. Part 2, M.H. Chisholm, F.A. Cotton, M.W. Extine and L.A. Rankel, J. Am. Chem. Soc., Submitted for publication.
2. (a) Princeton University (b) Texas A&M University.
3. Alfred P. Sloan Fellow 1976-78.
4. F.A. Cotton, Chem. Soc. Rev., 4, 27 (1975).
5. C.A. Tolman, Chem. Soc. Rev., 1, 337 (1972).
6. (a) E.L. Muetterties, Bull. Soc. Chim. Belg. 84, 959 (1975). (b) R. Ugo, Catal. Rev., 11, 225 (1975).
7. R.J. Klinger, W. Butler and M.D. Curtis, J. Am. Chem. Soc., 97, 3535 (1975).
8. F. Huq, W. Mowat, A. Shortland, A.C. Skapski and G. Wilkinson, Chem. Commun., 1079 (1970).
9. M.H. Chisholm, F.A. Cotton, M.W. Extine and B.R. Stults, Inorg. Chem., 15, 2252 (1976).
10. M.H. Chisholm, F.A. Cotton, B.A. Frenz, W.W. Reichert, L.W. Shive and B.R. Stults, J. Am. Chem. Soc., 98, 4469 (1976).
11. M.H. Chisholm, F.A. Cotton, M.W. Extine and B.R. Stults, J. Am. Chem. Soc., 98, 4477 (1976).
12. M.H. Chisholm, F.A. Cotton, C.A. Murillo and W.W. Reichert, Inorg. Chem., 16, 1801 (1976).
13. M.H. Chisholm and M.W. Extine, J.Am.Chem. Soc., 97, 5625, (1975).
14. For a detailed electronic description of the Triple Bonds in $Mo_2(NMe_2)_6$ and $Mo_2(OR)_6$ Compounds See: F.A. Cotton, G.G. Stanley, B. Kalbacher, J.C. Green, E. Seddon and M.H. Chisholm, Proc. Natl. Acad. Sci., USA
15. W.I. Bailey, M.H. Chisholm, F.A. Cotton, C.A. Murillo and L.A. Rankel, J. Am. Chem. Soc., Submitted for publication.

16. M.H. Chisholm, F.A. Cotton, M.W. Extine and W.W. Reichert, J. Am. Chem. Soc., in press.

17. M.H. Chisholm, F.A. Cotton, M.W. Extine and W.W. Reichert, J. Am. Chem. Soc., Submitted for publication.

18. The Mo-Mo distances in $Cp_2Mo_2(CO)_4(un)$ where un = HC≡CH, Me_2NCN, $CH_2{=}C{=}CH_2$, and 2CO are 2.984(1)Å, 3.056(1)Å, 3.117(1)Å and 3.27Å, respectively. These distances may be compared with Mo-Mo=2.48Å in $Cp_2Mo_2(CO)_4$ (ref. 7).

19. The reaction between the permethylated analog $(Me_5\text{-}C_5)_2Mo_2(CO)_4$ and 2NO was reported previously; R.B. King, A. Efratey and W.M. Douglas, J. Organometal. Chem. 60, 125 (1973). The reaction 5 has been found to occur very rapidly at room temperature and appears to be quantitative: M.H. Chisholm and L.A. Rankel, Unpublished results.

20. T.G. Appleton, H.C. Clark and L.E. Manzer, Coor. Chem. Rev. 10, 335(1973).

21. R. Eisenberg and C.D. Meyer, Accts. Chem. Res., 8, 26 (1975).

22. C.G. Pierpont and R. Eisenberg, Inorg. Chem., 11, 1094 (1972).

23. D.M.P. Mingos and J.A. Ibes, Inorg. Chem. 10, 1479 (1971).

24. D.C. Bradley, M.B. Hursthouse, C.W. Newing and A.J. Welch, J.C.S. Chem. Commun. 567 (1972).

25. D.C. Bradley and C.W. Newing, J.C.S. Chem. Commun., 219 (1972). It was noted here that $Cr(NPr^i_2)_3NO$ reacts with alcohols Bu^tOH and Pr^iOH to give $Cr(OR)_3NO$ compounds.

25. All computations were done on a PDP 11/45 computer at the Molecular Structures Corporation, College Station, Texas 77840, using the Enraf-Nonius structure determination package.

Fig. 1. An ORTEP view of Molecule I using 40% probability ellipsoids and showing the atom labelling scheme.

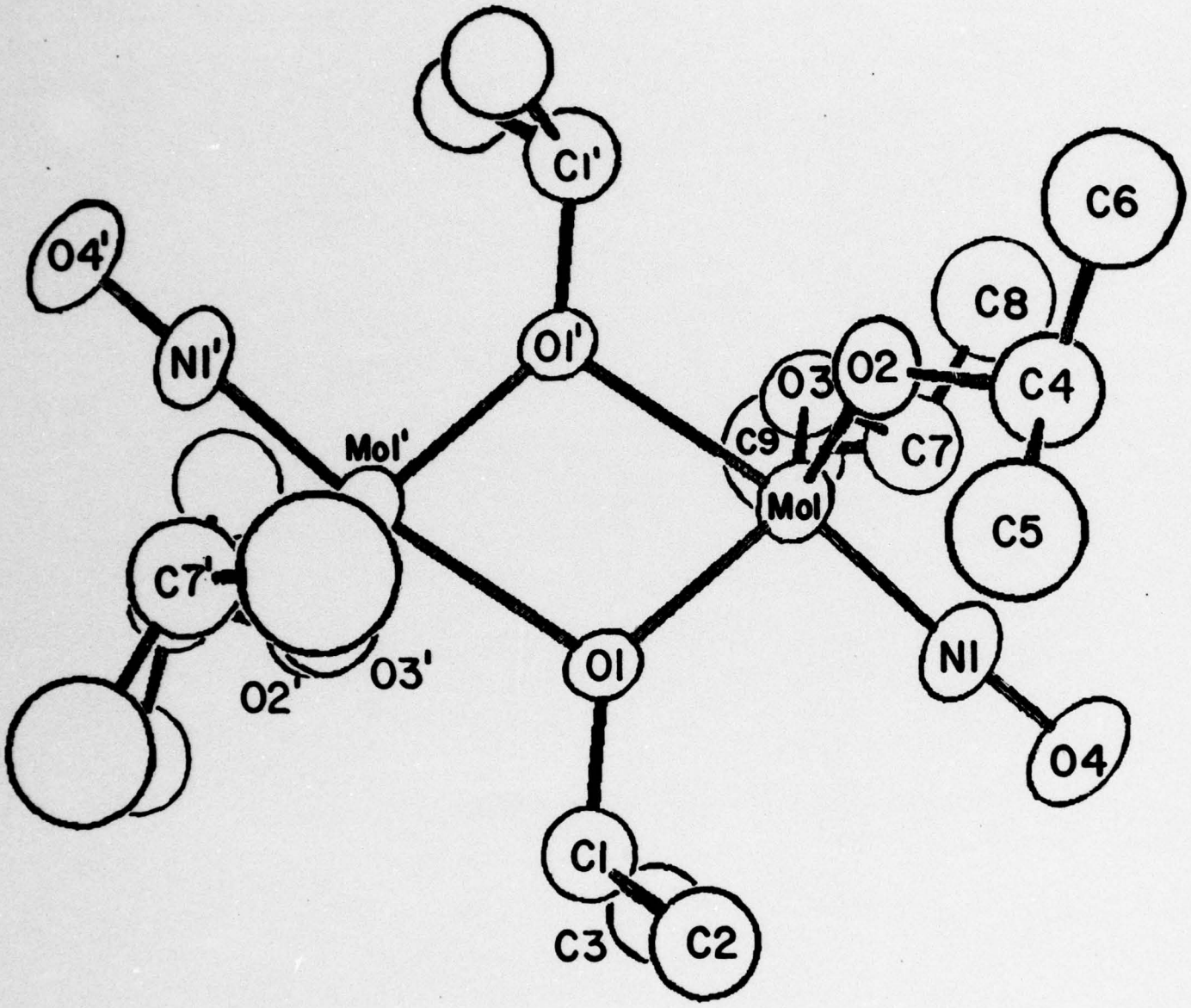
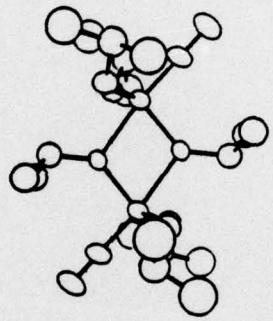

Cl'
O4'
C6
C8
Ni'
O1'
O3
O2
C4
Mo1'
C9
C7
Mo1
C5
C7'
O1
Ni
O2'
O3'
O4
Cl
C3
C2

Figure 2. A stereoview of Molecule I using 40% probability ellipsoids.



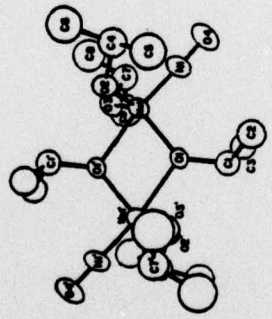


Figure 3. An ORTEP view showing the coordination geometry and average bond distances in the two essentially identical molecules.

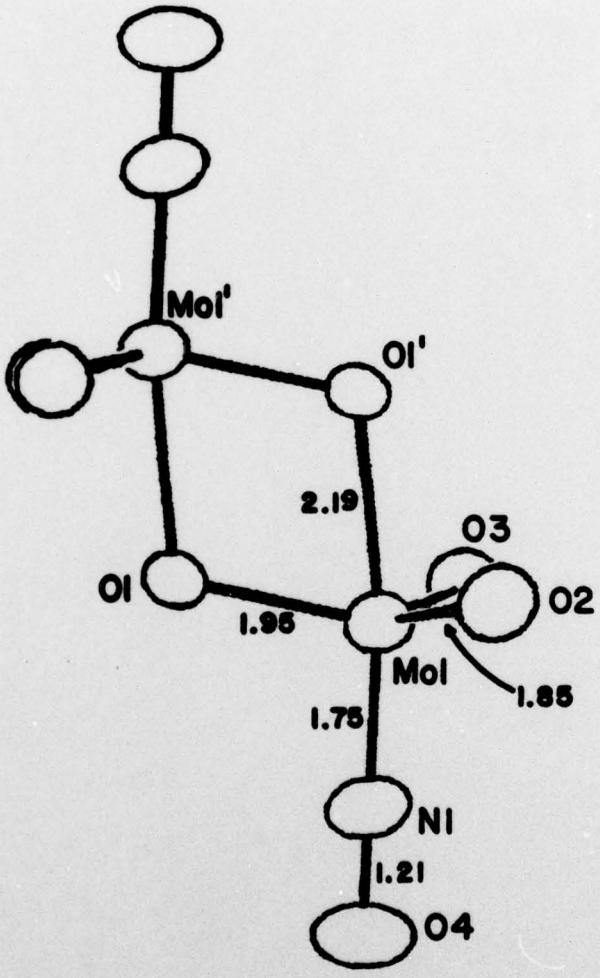
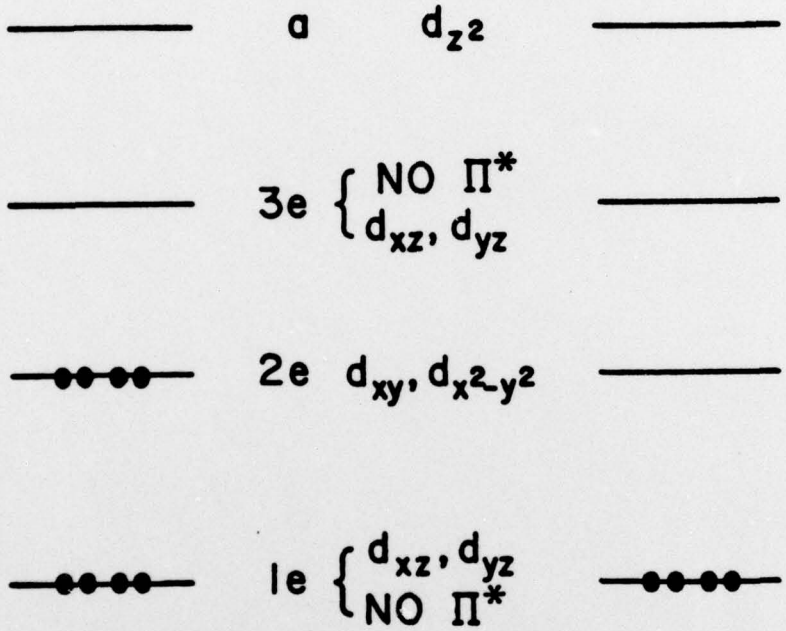

Mo1'
O1'
2.19
O3
O1
O2
1.95
Mo1
1.85
1.75
N1
1.21
O4

Fig. 4. MO diagrams, showing only the highest filled and lowest unfilled orbitals, for trigonal bipyramidal molecules of the type $MX_3L(NO)_1$ where L and NO are axial, for (a) the 18-electron case and (b) the 14-electron case.



10 electrons in M-ligand σ-bonds

a b

Table 1. POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS.[a]

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	-0.1085(1)	0.05358(8)	0.0592(1)	0.0133(1)	0.00683(6)	0.0181(1)	-0.0010(1)	0.0164(2)	0.0008(2)
Mo(2)	0.3931(1)	0.55137(8)	0.5638(1)	0.0140(1)	0.00647(6)	0.0197(2)	-0.0028(2)	0.0138(2)	-0.0004(2)
O(1)	0.0053(7)	-0.0572(5)	0.0883(8)	0.0133(8)	0.0058(4)	0.018(1)	-0.001(1)	0.017(1)	0.004(1)
O(2)	-0.0235(9)	0.1478(6)	0.1392(9)	0.0199(11)	0.0075(5)	0.020(1)	-0.003(1)	0.019(2)	-0.004(1)
O(3)	-0.2702(8)	0.0760(6)	-0.1203(9)	0.0124(9)	0.0088(5)	0.022(1)	-0.004(1)	0.012(2)	0.002(1)
O(4)	-0.2279(10)	0.0250(8)	0.2695(11)	0.0302(13)	0.0154(9)	0.036(1)	-0.001(2)	0.049(2)	0.007(2)
O(5)	0.4039(7)	0.5251(5)	0.3764(8)	0.0094(9)	0.0085(5)	0.015(1)	-0.001(1)	0.003(2)	0.001(1)
O(6)	0.4957(10)	0.6310(6)	0.6820(11)	0.0242(14)	0.0083(6)	0.027(2)	-0.006(1)	0.020(2)	-0.006(2)
O(7)	0.3676(8)	0.4652(6)	0.6717(9)	0.0164(10)	0.0080(5)	0.025(1)	-0.005(1)	0.020(2)	0.000(1)
O(8)	0.1159(11)	0.6538(7)	0.4427(13)	0.0214(14)	0.0106(7)	0.040(2)	0.009(2)	0.024(3)	0.008(2)
N(1)	-0.181(1)	0.0355(8)	0.182(1)	0.021(1)	0.0113(8)	0.024(1)	0.004(2)	0.030(2)	0.004(2)
N(2)	0.226(1)	0.6108(7)	0.489(1)	0.017(1)	0.0085(7)	0.026(2)	0.000(2)	0.021(2)	0.002(2)
C(1)	0.034(1)	-0.1349(9)	0.182(2)	7.7(4)					
C(2)	0.100(2)	-0.1130(11)	0.357(2)	9.6(5)					
C(3)	-0.103(2)	-0.1690(11)	0.139(2)	9.4(5)					
C(4)	-0.011(2)	0.1915(11)	0.274(2)	9.3(5)					
C(5)	0.121(2)	0.1494(14)	0.416(2)	13.4(7)					
C(6)	-0.003(2)	0.2814(14)	0.250(2)	13.9(7)					
C(7)	-0.113(2)	0.0696(11)	-0.140(2)	10.3(5)					
C(8)	-0.495(2)	0.1504(16)	-0.212(3)	16.2(8)					
C(9)	-0.470(3)	0.0096(17)	-0.290(3)	17.7(10)					
C(10)	0.309(2)	0.5507(10)	0.215(2)	8.8(4)					
C(11)	0.175(2)	0.5100(13)	0.173(2)	12.4(6)					
C(12)	0.289(2)	0.6457(13)	0.196(2)	12.0(6)					
C(13)	0.454(2)	0.7252(14)	0.698(2)	13.6(7)					
C(14)	0.492(3)	0.7677(18)	0.596(3)	18.9(10)					
C(15)	0.494(4)	0.7357(22)	0.859(4)	23.8(13)					

Table 1. (continued)

Atom	x	y	z	β_{11}
C(16)	0.239(2)	0.4529(11)	0.686(2)	10.4(5)
C(17)	0.237(3)	0.3565(17)	0.682(3)	16.8(9)
C(18)	0.245(2)	0.4828(16)	0.825(3)	15.6(8)

The form of the anisotropic thermal parameter is: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}\ell^2+\beta_{12}hk+\beta_{13}h\ell+\beta_{23}k\ell)]$.

Table 2. Bond Distances (Å).

Molecule I		Molecule II	
Atoms	Distance	Atoms	Distance
Mo(1)-Mo(1)'	3.334(2)	Mo(2)-Mo(2)'	3.337(2)
-O(1)	1.951(6)	-O(5)	1.946(6)
-O(1)'	2.195(6)	-O(5)'	2.194(6)
-O(2)	1.850(7)	-O(6)	1.849(8)
-O(3)	1.861(6)	-O(7)	1.857(7)
-N(1)	1.747(9)	-N(2)	1.761(10)
N(1)-O(4)	1.205(11)	N(2)-O(8)	1.184(11)
C(1)-O(1)	1.46(1)	C(10)-O(5)	1.50(1)
-C(2)	1.61(2)	-C(11)	1.55(2)
-C(3)	1.53(2)	-C(12)	1.49(2)
C(4)-O(2)	1.46(2)	C(13)-O(6)	1.53(2)
-C(5)	1.56(2)	-C(14)	1.44(2)
-C(6)	1.47(2)	-C(15)	1.47(3)
C(7)-O(3)	1.49(2)	C(16)-O(7)	1.49(2)
-C(8)	1.44(2)	-C(17)	1.53(2)
-C(9)	1.68(2)	-C(18)	1.42(2)

Table 3. Bond Angles (Deg).

Molecule I				Molecule II			
Atoms			Angle	Atoms			Angle
Mo(1)′	Mo(1)	O(1)	39.1(2)	Mo(2)′	Mo(2)	O(5)	38.9(2)
Mo(1)′	Mo(1)	O(1)	34.1(2)	Mo(2)′	Mo(2)	O(5)	33.8(2)
Mo(1)′	Mo(1)	O(2)	102.8(2)	Mo(2)′	Mo(2)	O(6)	102.8(3)
Mo(1)′	Mo(1)	O(3)	101.4(2)	Mo(2)′	Mo(2)	O(7)	102.6(2)
Mo(1)′	Mo(1)	N(1)	137.9(3)	Mo(2)′	Mo(2)	N(2)	138.0(3)
O(1)	Mo(1)	O(1)′	73.1(3)	O(5)	Mo(2)	O(5)′	72.7(3)
O(1)	Mo(1)	O(2)	119.3(3)	O(5)	Mo(2)	O(6)	119.1(3)
O(1)	Mo(1)	O(3)	117.3(3)	O(5)	Mo(2)	O(7)	118.6(3)
O(1)	Mo(1)	N(1)	98.8(4)	O(5)	Mo(2)	N(2)	99.1(4)
O(1)′	Mo(1)	O(2)	84.4(3)	O(5)′	Mo(2)	O(6)	84.6(3)
O(1)′	Mo(1)	O(3)	83.8(3)	O(5)′	Mo(2)	O(7)	84.6(3)
O(1)′	Mo(1)	N(1)	171.9(4)	O(5)′	Mo(2)	N(2)	171.9(4)
O(2)	Mo(1)	O(3)	115.1(3)	O(6)	Mo(2)	O(7)	114.2(3)
O(2)	Mo(1)	N(1)	100.8(4)	O(6)	Mo(2)	N(2)	100.0(4)
O(3)	Mo(1)	N(1)	99.5(4)	O(7)	Mo(2)	N(2)	99.4(4)
Mo(1)′	O(1)	Mo(1)	106.9(3)	Mo(2)′	O(5)	Mo(2)	107.3(3)
Mo(1)	O(1)	C(1)	134.8(6)	Mo(2)	O(5)	C(10)	132.8(6)
Mo(1)′	O(1)	C(1)	118.3(6)	Mo(2)′	O(5)	C(10)	119.8(6)
Mo(1)	O(2)	C(4)	129.9(7)	Mo(2)	O(6)	C(13)	131.1(9)
Mo(1)	O(3)	C(7)	125.7(7)	Mo(2)	O(7)	C(16)	128.5(8)
Mo(1)	N(1)	O(4)	178(1)	Mo(2)	N(2)	O(8)	177(1)
O(1)	C(1)	C(2)	109.3(9)	O(5)	C(10)	C(11)	108(1)
O(1)	C(1)	C(3)	108.1(9)	O(5)	C(10)	C(12)	108(1)
C(2)	C(1)	C(3)	110(1)	C(11)	C(10)	C(12)	116(1)

Table 3. (continued)

Molecule I			
Atoms			Angle
O(2)	C(4)	C(5)	111(1)
O(2)	C(4)	C(6)	108(1)
C(5)	C(4)	C(6)	111(1)
O(3)	C(7)	C(8)	105(1)
O(3)	C(7)	C(9)	101(1)
C(8)	C(7)	C(9)	99(2)

Molecule II			
Atoms			Angle
O(6)	C(13)	C(14)	103(2)
O(6)	C(13)	C(15)	107(2)
C(14)	C(13)	C(15)	130(2)
O(7)	C(16)	C(17)	105(1)
O(7)	C(16)	C(18)	111(1)
C(17)	C(16)	C(18)	111(2)

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Dr. D. A. Vroom Intelcom Rad Tech. P.O. Box 80817 San Diego, California 92138	1
Dr. P. R. Antoniewicz University of Texas Department of Physics Austin, Texas 78712	1
Dr. W. D. McCormick University of Texas Department of Physics Austin, Texas 78712	1
Dr. G. A. Somorjai University of California Department of Chemistry Berkeley, California 94720	1
Dr. L. N. Jarvis Surface Chemistry Division 4555 Overlook Avenue, S.W. Washington, D.C. 20375	1
Dr. W. M. Risen, Jr. Brown University Department of Chemistry Providence, Rhode Island 02912	1
Dr. Bruce Wagner, Jr. Northwestern University Materials Research Center Evanston, Illinois 60201	1
~~Dr. M. H. Chisholm~~ ~~Chemistry Department~~ ~~Princeton University~~ ~~Princeton, New Jersey 08540~~	1
Dr. J. B. Hudson Rensselaer Polytechnic Institute Materials Division Troy, New York 12181	1
Dr. John T. Yates National Bureau of Standards Department of Commerce Surface Chemistry Section Washington, D.C. 20234	1
Dr. Theodore E. Madey Department of Commerce National Bureau of Standards Surface Chemistry Section Washington, D.C. 20234	1
Dr. J. M. White University of Texas Department of Chemistry Austin, Texas 78712	1
Dr. R. W. Vaughan California Institute of Technology Division of Chemistry & Chemical Engineering Pasadena, California 91125	1
Dr. Keith H. Johnson Massachusetts Institute of Technology Department of Metallurgy and Materials Science Cambridge, Massachusetts 02139	1
Dr. M. S. Wrighton Massachusetts Institute of Technology Department of Chemistry Cambridge, Massachusetts 02139	1
Dr. J. E. Demuth IBM Corp. Thomas J. Watson Research Center P.O. Box 218 Yorktown Heights, New York 10598	1
Dr. C. P. Flynn University of Illinois Department of Physics Urbana, Illinois 61801	1
Dr. W. Kohn Department of Physics University of California (San Diego) La Jolla, California 92037	
Dr. R. L. Park Director, Center of Materials Research University of Maryland College Park, Maryland 20742	1

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Dr. W. T. Peria Electrical Engineering Department University of Minnesota Minneapolis, Minnesota 55455	1
Dr. Narkis Tzoar City University of New York Convent Avenue at 138th Street New York, New York 10031	1
Dr. Chia-wei Woo Northwestern University Department of Physics Evanston, Illinois 60201	1
Dr. D. C. Mattis Physics Department Yeshiva University Amsterdam Avenue & 185th Street New York, New York 10033	1
Dr. Leonard Wharton Department of Chemistry James Franck Institute 5640 Ellis Avenue Chicago, Illinois 60637	1
Dr. M. G. Lagally Department of Metallurgical and Mining Engineering University of Wisconsin Madison, Wisconsin 53706	1
Dr. Robert Gomer Department of Chemistry James Franck Institute 5640 Ellis Avenue Chicago, Illinois 60637	1
Dr. R. F. Wallis Department of Physics University of California (Irvine) Irvine, California 92664	1

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Dr. W. N. Lipscomb Department of Chemistry Harvard University Cambridge, Massachusetts 02138	1
Dr. R. M. Grimes Department of Chemistry University of Virginia Charlottesville, Virginia 22903	1
Dr. M. Tsutsui Department of Chemistry Texas A&M University College Station, Texas 77843	1
Dr. C. Quicksall Department of Chemistry Georgetown University 37th & O Streets Washington, D.C. 20007	1
Dr. M. F. Hawthorne Department of Chemistry University of California Los Angeles, California 90024	1
Dr. D. B. Brown Department of Chemistry University of Vermont Burlington, Vermont 05401	1
Dr. Alan Siedle National Bureau of Standards Department of Commerce Chemistry Section Washington, D.C. 20375	1
Dr. W. B. Fox Naval Research Laboratory Chemistry Division Code 6130 Washington, D.C. 20375	1
Dr. R. J. Lagow University of Texas Department of Chemistry Austin, Texas 78712	1

	No. Copies
Dr. A. Cowley University of Texas Department of Chemistry Austin, Texas 78712	1
Dr. W. Hatfield University of North Carolina Department of Chemistry Chapel Hill, North Carolina 27514	1
Dr. D. Seyferth Massachusetts Institute of Technology Department of Chemistry Cambridge, Massachusetts 02139	1
~~Dr. M. F. Chisholm~~ ~~Princeton University~~ ~~Department of Chemistry~~ ~~Princeton, New Jersey 08540~~	1
Dr. B. Foxman Department of Chemistry Brandeis University Waltham, Massachusetts 02154	1

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Office of Naval Research Arlington, Virginia 22217 Attn: Code 472	2
Office of Naval Research Arlington, Virginia 22217 Attn: Code 102IP	6
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. George Sandoz	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1
ONR Branch Office 760 Market Street, Rm. 447 San Francisco, California 94102 Attn: Dr. P. A. Miller	1
ONR Branch Office 495 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1
Director, Naval Research Laboratory Washington, D.C. 20390 Attn: Library, Code 2029 (ONRL) Technical Info. Div. Code 6100, 6170	6 1 1
The Asst. Secretary of the Navy (R&D) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1
Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20360 Attn: Code 310C (H. Rosenwasser)	1

	No. Copi
Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
U.S. Army Research Office P.O. Box 12211 Research Triangle Park, North Carolina 27709 Attn: CRD-AA-IP	
Commander Naval Undersea Research & Development Center San Diego, California 92132 Attn: Technical Library, Code 133	1
Naval Weapons Center China Lake, California 93555 Attn: Head, Chemistry Division	1
Naval Civil Engineering Laboratory Port Hueneme, California 93041 Attn: Mr. W. S. Haynes	1
Professor O. Heinz Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	
Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Dr. M. A. El-Sayed University of California Department of Chemistry Los Angeles, California 90024	1
Dr. M. W. Windsor Washington State University Department of Chemistry Pullman, Washington 99163	
Dr. E. R. Bernstein Colorado State University Department of Chemistry Fort Collins, Colorado 80521	
Dr. C. A. Heller Naval Weapons Center Code 6059 China Lake, California 93555	1
Dr. G. Jones, II Boston University Department of Chemistry Boston, Massachusetts 02215	
~~Dr. M. H. Chisholm~~ ~~Chemistry Department~~ ~~Princeton, New Jersey 08540~~	1
Dr. J. R. MacDonald Code 6110 Chemistry Division Naval Research Laboratory Washington, D.C. 20375	1
Dr. G. B. Schuster Chemistry Department University of Illinois Urbana, Illinois 61801	1
Dr. E. M. Eyring University of Utah Department of Chemistry Salt Lake City, Utah 84112	1
Dr. A. Adamson University of Southern California Department of Chemistry Los Angeles, California 90007	1
Dr. M. S. Wrighton Massachusetts Institute of Technology Department of Chemistry Cambridge, Massachusetts 02139	1