for the one longest pair where the bond order is 1.06.

Thiourea contains a planar 3-coordinate carbon atom. That carbon atom is connected to two planar 3-coordinate nitrogen atoms and a sulfur atom. The SCN_2 fragment thus has six electrons in four π-symmetry orbitals. The π bonding may be highly delocalized although it has been estimated that for ethylenethiourea the resonance structure with a single bond to sulfur contributes approximately 80%.[14]

On complexation to Te(II) the thioureas should display even less C–S π bonding because this is a means to delocalize the positive charge on Te to the N atoms. Loss of electron density from the sulfur in such a process would imply a smaller sulfur atom and decreased C–S bond length while the loss of C–S π bonding implies increased C–S bond length. For the bridging thioureas the C–S bonds are relatively short and there seems no significant difference in the C–N bond lengths between terminal and bridging ligands.

A vibrational analysis of the Te_2S_6 core indicates the possible unimolecular dissociation modes available to the complex. For simplicity we consider the vibrations of hypothetical D_{2h} complexes. We further focus attention on the four modes, $A_{1g} + B_{2u} + B_{3u} + B_{1g}$, that could separate the dimers at the bridge bonds because it is the bridge bonds which are long and weak.

The A_{1g} and B_{2u} modes carried to dissociation lead to 2-coordinate Te(II) species and therefore seem unlikely. Complexes of Te(II) tend to be 4-coordinate except in those cases where the trans influence and electrostatic effects mitigate.

The B_{1g} vibration carried to dissociation preserves centrosymmetry, while separating a dimer into two T-shaped, 3-coordinate complexes. This is the distortion from D_{2h} symmetry of the four known hexakis(thiourea-*S*)ditellurium(II) cations. The products resulting from a complete separation along the B_{1g} coordinate, T-shaped Te(II) complexes, have precedent in the $C_6H_5TeL_2$ complexes where the extreme trans influence of the phenyl group essentially precludes a ligand trans to phenyl.[17]

The B_{3u} vibration lengthens both bonds to one bridge ligand and would lead to expulsion of one bridge ligand and retention of the other. The products here are two T-shaped Te(II) complexes linked by a bridging ligand. There is one example[18] of two 4-coordinate Te(II) complexes linked by a single bridge, and the B_{3u} distortion is seen in the monoclinic form of di-μ-bromo-bis[bis(ethylenethiourea-*S*)tellurium(II)] bromide.[19]

A linear combination of the B_{1g} and B_{3u} modes describes the distortions observed in $Se_2(SCN)_6^{2-}$ and $Se_2(SeCN)_6^{2-}$.[5,20,21]

We are beginning a variable-temperature ^{125}Te and ^{13}C NMR study of these ions in solution in the hopes of elucidating the true mechanism(s) of dissociation.

Registry No. Tris(ethylenethiourea)tellurium(II) perchlorate, 72672-41-4; tris(trimethylenethiourea)tellurium(II) perchlorate, 72672-43-6.

Supplementary Material Available: Listings of observed and calculated structure factors and of calculated hydrogen atom positions (64 pages). Ordering information is given on any current masthead page.

---

(17) Klaeboe, P.; Vikane, O. *Acta Chem. Scand., Ser. A* **1977**, *31*, 120 and references therein.
(18) Marøy, K., private communication, 1978.
(19) Herland, P.; Lundeland, M.; Marøy, K. *Acta Chem. Scand., Ser. A* **1976**, *30*, 719.
(20) Hauge, S.; Henriksen, P. A. *Acta Chem. Scand., Ser. A* **1975**, *29*, 778 and references therein.
(21) Hauge, S. *Acta Chem. Scand., Ser. A* **1975**, *29*, 843.

Contribution No. 3366 from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47405

Syntheses of $Mo(NC_6H_5)X_2(S_2CN(C_2H_5)_2)_2$ (X = Cl, Br) and the Structure of $Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2{\cdot}CHCl_3$

ERIC A. MAATTA, BARRY L. HAYMORE,* and R. A. D. WENTWORTH*

Received September 7, 1979

Stable nitrene complexes of the type $Mo(NC_6H_5)X_2(S_2CN(C_2H_5)_2)_2$ (X = Cl, Br) have been prepared via several different synthetic routes. The structure of $Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2{\cdot}CHCl_3$ has been determined at –150 °C by X-ray diffraction techniques. The complex crystallizes in the monoclinic space group $P2_1/c$ with lattice constants of $a = 9.356$ (4) Å, $b = 16.088$ (7) Å, $c = 19.008$ (7) Å, and $\beta = 106.48$ (1)°. The structure was solved by using 4162 unique reflections having $F_o^2 > 3\sigma(F_o)^2$ and refined by using full-matrix, least-squares techniques to yield final discrepancy indices of $R(F) = 0.040$ and $R_w(F) = 0.055$. The coordination geometry around the molybdenum atom is close to pentagonal bipyramidal with the NC_6H_5 ligand and a chlorine atom occupying the apical sites. The short Mo–N distance of 1.734 (4) Å and the near-linearity of the Mo–N–C linkage (166.8 (3)°) suggest that the molybdenum–nitrogen bond has triple-bond character. The axial and equatorial Mo–Cl distances are identical, indicating that the linear $-NC_6H_5$ group exerts no significant trans influence. This result contrasts with the unequal Mo–Cl bond lengths (0.09 Å difference) in the oxo analogue $MoOCl_2(S_2CN(C_2H_5)_2)_2$.

Introduction

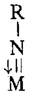
We have prepared a series of arylnitrene(1) complexes of molybdenum including $Mo(NAr)_2(Et_2dtc)_2$, $MoO(NAr)(Et_2dtc)_2$, $Mo(NAr)(Et_2dtc)_3^+$, $Mo(NAr)(Et_2dtp)_3$, and $Mo(NAr)Cl(Et_2dtp)_2$ in order to study the chemistry of the NR ligand and compare it to the oxo ligand in similar coordination environments.[2-4] The amphoteric nature of the

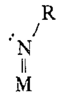
---

(1) (a) Although IUPAC rules suggest that the name "imido" be used, we use herein the more familiar "nitrene" terminology which has found widespread acceptance; see a recent review by: Cenini, S.; La Monica, G. *Inorg. Chim. Acta* **1976**, *18*, 279. (b) Abbreviations used herein: Ar = aryl; Ph = C_6H_5; Et = C_2H_5; R = alkyl; X = Cl or Br; $R_2dtc = S_2CNR_2$; $R_2dtp = S_2P(OR)_2$; Cp = η^5-C_5H_5.
(2) Haymore, B. L.; Maatta, E. A.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1979**, *101*, 2063.
(3) Maatta, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18* 2409.
(4) (a) Edelblut, A. W.; Wentworth, R. A. D., submitted for publication. (b) Maatta, E. A.; Haymore, B. L.; Wentworth, R. A. D. "Abstracts of Papers", 176th National Meeting of the American Chemical Society, Miami Beach, Fla., Sept 1978; American Chemical Society: Washington, D.C., 1978; INOR 38.

0020-1669/80/1319-1055$01.00/0

nitrene ligand allows it to function either as a linear, four-electron donor (**1**) or as a bent, two-electron donor (**2**).


1


2

Application of the EAN rule to the potential 20-electron complex $Mo(NPh)_2(Et_2dtc)_2$ suggests that this compound should act to relieve the electron excess either by forcing one of the dithiocarbamate ligands to become unidentate or by placing a pair of electrons on one of the ligating nitrogen atoms, causing bending to occur. An X-ray crystal structure of this complex revealed six-coordination around molybdenum and severe bending of one of the NPh groups (Mo–N–C = 139.4 (4)°).[2]

When $Mo(NPh)_2(Et_2dtc)_2$ is treated with gaseous HCl in CH_2Cl_2, a rapid reaction ensues which produces anilinium chloride and $Mo(NPh)Cl_2(Et_2dtc)_2$ in high yield. One of the two NPh groups is replaced by two one-electron donor chloro ligands; the remaining NPh ligand is inert to attack by acid under these conditions. This complex and others of the type $Mo(NAr)X_2(R_2dtc)_2$ seem to be particularly stable and easily formed because they can also be prepared by acidolysis of $MoO(NPh)(Et_2dtc)_2$ or by O/NPh exchange between $MoOCl_2(Et_2dtc)_2$ and tetraphenylphosphinimine. Recrystallization of $Mo(NPh)Cl_2(Et_2dtc)_2$ from chloroform affords the 1:1 solvate whose structure is presently reported. A preliminary report of this work has been given.[4b]

Experimental Section

All reactions were performed in freshly distilled, air-free solvents under an argon atmosphere; only freshly distilled $C_6H_5N_3$ was used. $MoOCl_2(S_2CNEt_2)_2$ was prepared according to a published procedure.[5] Infrared spectra were recorded in KBr pellets and Nujol mulls by using a Perkin-Elmer 283 spectrophotometer and calibrated with a polystyrene film. NMR spectra were recorded on a Varian HR-220 spectrometer at ambient temperatures in $CDCl_3$ solutions with tetramethylsilane as internal standard. The data crystal was grown by slow evaporation of a chloroform solution.

Reaction of $MoOCl_2(S_2CNEt_2)_2$ and $PhNPPh_3$. One millimole (0.48 g) of $MoOCl_2(S_2CNEt_2)_2$ was added to 35 mL of toluene and heated. When the solution became hot, 0.75 g (2 mmol) of $PhNPPh_3$ was added. The reaction mixture was heated to reflux for 3 h, and the color of the reaction was observed to darken somewhat from its original yellow color. After filtration of the hot solution to remove a small amount of solid, the volume was reduced to 15 mL and the solution was cooled with ice. A yellow powder separated from solution and was recrystallized from $CHCl_3/Et_2O$ to give yellow crystals. An infrared spectrum of this material showed the loss of ν(MoO) (945 cm^{-1} in $MoOCl_2(Et_2dtc)_2$). The recovered yield was 0.40 g (60%). The IR and NMR spectra of this material were identical with those of $Mo(NPh)Cl_2(S_2CNEt_2)_2 \cdot CHCl_3$ as prepared from $Mo(NPh)_2(S_2CNEt_2)_2$ and HCl.

Data Collection. Data were collected at −150 °C by using a locally constructed diffractometer employing a Picker four-circle goniostat interfaced with a TI Model 980B minicomputer; the low-temperature device has been described.[6] A preliminary examination of the data crystal revealed a diffraction pattern with monoclinic symmetry and systematic extinctions characteristic of the space group $P2_1/c$; ω scans showed acceptably narrow diffraction peaks. Accurate cell parameters were determined from a least-squares analysis of 12 strong, machine-centered reflections in diverse regions of reciprocal space (20° $< 2\theta <$ 35°). By use of the θ–2θ scan technique, a total of 5537 unique reflections were measured out to 2θ = 51.5°. The intensities of three standard reflections were periodically monitored throughout the data collection and found to be constant within counting errors. Background counts were measured at both ends of the scan range with both crystal and counter stationary. Corrections for Lorentz-polarization effects and background effects were applied to the intensity data. An absorption correction was deemed unnecessary because the range of transmission factors was 0.79–0.85. A small isotropic extinction correction, 5 (2) × 10^{-8} electron,[2] was applied in final least-squares calculations. A value of p = 0.05 was used to estimate the values of $\sigma(F_o)$ in the usual way.[2] Only reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in least-squares calculations.

Table I. Summary of Crystallographic Data

compd	$Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2 \cdot CHCl_3$
formula	$MoS_4C_{17}H_{26}N_3Cl_5$
fw	673.88
a, Å	9.356 (4)
b, Å	16.088 (7)
c, Å	19.008 (7)
β, deg	106.48 (1)
V, Å^3	2744
Z	4
space group	C_{2h}^5-$P2_1/c$
cryst size, mm	0.16 × 0.16 × 0.24
cryst vol, mm^3	6.9 × 10^{-3}
cryst shape	monoclinic prism with $\{0\bar{1}1\}$, $\{01\bar{1}\}$, and $\{100\}$ faces
radiation	Mo Kα, λ = 0.710 69 Å, monochromatized with highly oriented graphite
density, g/cm^3	1.631 (calcd), 1.65 (2) (obsd at 25 °C)
μ, cm^{-1}	12.632
range of transmission factors	0.79–0.85
temp, °C	−150 (5)
scan speed, deg/min	2.0
bkgd count, s	15
2θ limits, deg	4.0–51.5
aperture	2.5 mm wide × 3.5 mm high
takeoff angle, deg	2.0
scan range	1.0° below Kα_1 to 0.9 ° above Kα_2
no. of variables	272
unique data with $I_o > 3\sigma(I_o)$	4162
error in observn of unit wt, e	1.56
$R(F)$	0.040
$R_w(F)$	0.055

Structure Refinement. The molybdenum atom was located in a Patterson map, and the positions of all other atoms (including all 26 hydrogen atoms) were readily found in subsequent difference Fourier syntheses. The structure was refined by using full-matrix, least-squares techniques.[7] Atomic scattering factors were taken from the usual sources,[8] and the anomalous dispersion terms for Mo, S, and Cl were included in F_c. The 26 hydrogen atoms were introduced as fixed contributions (idealized geometries with C–H = 0.95 Å) in the final anisotropic refinements. The isotropic thermal parameters assigned to the hydrogen atoms were chosen to be 1.0 Å^2 larger than those of the attached carbon atoms. The quantity minimized in the refinement was $Q = \sum w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factor amplitudes and where the weights, w, are taken as $4F_o^2/\sigma^2(F_o^2)$.

The structure converged with 30 anisotropic nonhydrogen atoms to $R(F) = \sum||F_o| - |F_c||/\sum|F_o| = 0.040$ and $R_w(F) = (Q/\sum wF_o^2)^{1/2}$ = 0.055. A final difference Fourier synthesis revealed two peaks (of intensities 1.2 and 0.64 e/Å^3) located near one of the chlorine atoms of $CHCl_3$. There were no other peaks greater than 0.6 e/Å^3. A statistical analysis of Q as a function of F_o, diffractometer setting angles, and Miller indices exposed no anomalous trends, indicating

---

(5) Dirand, J.; Ricard, L.; Weiss, R. *J. Chem. Soc., Dalton Trans.* **1976**, 278.

(6) Huffman, J. C. Ph.D. Dissertation, Indiana University, Bloomington, Ind., 1974, p 10.

(7) In addition to various local routines for the CDC-6600 computer, modified versions of the following programs were employed: Zalkin's FORDAP Fourier summation program, Johnson's ORTEP thermal ellipsoid plotting program, Busing and Levy's ORFFE error function program, and the Northwestern full-matrix, least-squares program NUCLS, which, in its nongroup form, closely resembles the Busing and Levy ORFLS program.

(8) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table II. Positional and Thermal Parameters for the Atoms of (Phenylnitrene)bis(diethyldithiocarbamato)dichloromolybdenum, $MoCl_2(NC_6H_5)(S_2CN(C_2H_5)_2)_2$

ATOM	X[a]	Y	Z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.86502(4)	0.24150(2)	0.05312(2)	40.4(5)	13.1(2)	8.5(1)	-1.0(2)	4.5(2)	0.1(1)
S(1)	0.64726(12)	0.30779(7)	0.08397(6)	43.6(14)	18.2(5)	10.3(3)	1.2(6)	3.0(5)	-1.7(3)
S(2)	0.94495(12)	0.31752(7)	0.17313(6)	43.8(14)	21.0(5)	13.2(4)	-0.3(6)	3.3(6)	-5.1(3)
S(3)	1.14021(12)	0.22039(7)	0.10795(6)	42.8(14)	19.6(5)	11.7(3)	-0.7(6)	4.3(5)	-3.4(3)
S(4)	0.96576(12)	0.13512(7)	-0.01594(6)	43.7(14)	19.2(5)	12.0(3)	-3.3(6)	5.9(5)	-3.6(3)
Cl(1)	0.81724(12)	0.12357(7)	0.12646(6)	62.6(15)	15.0(4)	11.8(3)	1.0(6)	9.1(6)	2.0(3)
Cl(2)	0.64761(12)	0.19134(7)	-0.04439(6)	43.9(13)	23.4(5)	11.1(3)	-2.9(6)	2.2(5)	-2.4(3)
Cl(3)	0.39365(23)	0.05047(13)	0.40637(11)	212.(4)	52.1(10)	38.2(7)	52.8(15)	4.6(12)	-16.3(7)
Cl(4)	0.25515(15)	0.17986(9)	0.46725(7)	91.2(18)	31.3(6)	21.5(4)	3.4(8)	15.1(7)	-1.5(4)
Cl(5)	0.23589(22)	0.18383(10)	0.31324(8)	220.(3)	37.3(7)	19.9(5)	-24.9(12)	18.3(10)	0.8(5)
C(1)	1.1420(5)	0.14875(26)	0.04059(24)	41.(5)	11.6(17)	11.6(13)	-5.5(24)	4.5(21)	1.6(12)
C(2)	1.2506(5)	0.0506(3)	-0.02621(28)	60.(6)	16.7(19)	21.5(17)	2.7(27)	17.9(26)	-1.8(14)
C(3)	1.4091(5)	0.1271(3)	0.08434(27)	41.(6)	22.8(21)	18.0(16)	-1.5(27)	9.8(24)	-1.3(15)
C(4)	1.4489(6)	0.0668(4)	0.1482(3)	74.(7)	45.(3)	22.0(19)	8.(4)	11.(3)	14.1(19)
C(5)	1.2678(6)	0.0931(3)	-0.09445(27)	78.(7)	21.6(21)	18.7(16)	-13.(3)	20.3(28)	-3.7(15)
C(6)	0.7618(5)	0.33886(26)	0.16683(24)	50.(5)	8.8(12)	13.9(15)	-0.9(22)	8.5(19)	1.1(12)
C(7)	0.5569(5)	0.3872(3)	0.21128(26)	57.(6)	25.9(22)	15.4(16)	-4.2(28)	11.3(25)	-4.6(14)
C(8)	0.8225(5)	0.3936(3)	0.29144(25)	68.(6)	23.8(21)	11.2(15)	-4.2(29)	7.1(24)	-4.5(14)
C(9)	0.8843(6)	0.4811(3)	0.29063(29)	82.(7)	24.9(22)	20.0(17)	-12.(3)	10.5(28)	-9.0(16)
C(10)	0.4484(6)	0.3185(4)	0.2450(3)	80.(7)	46.(3)	16.3(17)	-26.(4)	10.5(28)	-1.3(18)
C(11)	0.3479(6)	0.1567(4)	0.4011(3)	92.(8)	36.4(27)	20.1(18)	-13.(4)	18.(3)	-10.7(18)
C(12)	0.8584(5)	0.38262(29)	-0.05806(24)	39.(5)	19.7(19)	10.9(14)	-3.1(25)	4.4(22)	1.5(13)
C(13)	0.8651(6)	0.3562(3)	-0.12753(28)	106.(8)	25.8(23)	15.7(16)	5.(3)	15.(3)	-1.9(15)
C(14)	0.8435(6)	0.4141(4)	-0.18347(28)	103.(8)	43.(3)	12.0(16)	5.(4)	15.7(29)	3.2(17)
C(15)	0.8160(6)	0.4967(4)	-0.1704(3)	86.(8)	34.8(27)	18.6(18)	5.(4)	5.(3)	11.2(17)
C(16)	0.8094(6)	0.5218(3)	-0.1023(3)	89.(7)	20.9(21)	22.5(18)	-1.(3)	10.7(29)	5.5(16)
C(17)	0.8304(5)	0.4658(3)	-0.04508(27)	61.(6)	19.4(20)	16.3(16)	1.9(28)	6.2(25)	-0.4(14)
N(1)	1.2612(4)	0.11118(23)	0.03424(20)	42.(5)	15.4(15)	13.4(12)	1.9(21)	7.9(19)	-3.1(11)
N(2)	0.7160(4)	0.37166(23)	0.21967(20)	57.(6)	14.3(13)	11.8(14)	-4.8(21)	5.8(20)	-1.4(12)
N(3)	0.8785(4)	0.32403(23)	-0.00331(20)	49.(5)	17.4(15)	10.9(12)	-2.5(22)	6.9(19)	-1.8(11)

[a] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [b] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS $EXP[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

that the weighting scheme was adequate. In the final cycle of refinement, the largest parameter shift was only 10% of the estimated standard deviation. The standard deviation of an observation of unit weight was 1.56 e. A structure factor calculation with the use of the final model showed that the weak reflections ($F_o^2 < 3\sigma(F_o^2)$) were calculated correctly. Only six of these reflections had $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$ and none had $|F_o^2 - F_c^2| > 5\sigma(F_o^2)$. Table I summarizes the crystallographic data, and Table II lists the final positional and thermal parameters of the nonhydrogen atoms. Table III[9] presents the root-mean-square amplitudes of vibration, while the positional and thermal parameters of the hydrogen atoms are given in Table IV.[9] A listing of the observed and calculated structure amplitudes for those data used in the refinements is available.[9]

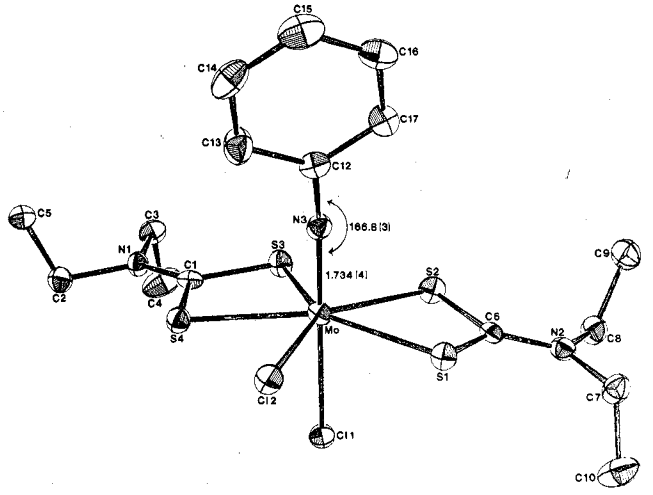


Figure 1. A drawing of a molecule of $Mo(NPh)Cl_2(S_2CNEt_2)_2$. The hydrogen atoms and the solvent molecule have been omitted for clarity. Vibrational ellipsoids are drawn at the 50% probability level.

Results and Discussion

Syntheses of $Mo(NPh)X_2(S_2CNEt_2)_2$ (X = Cl, Br). Complexes of the type $Mo(NPh)X_2(S_2CNEt_2)_2$ are accessible via several routes as indicated in eq 1–5.[3,10] It is important to

$$Mo(NPh)_2(S_2CNEt_2)_2 + 3HCl \rightarrow Mo(NPh)Cl_2(S_2CNEt_2)_2 + PhNH_3Cl \quad (1)$$

$$MoO(NPh)(S_2CNEt_2)_2 + 2HX \rightarrow Mo(NPh)X_2(S_2CNEt_2)_2 + H_2O \quad (2)$$

$$Mo(NPh)_2(S_2CNEt_2)_2 + 3CH_3Br \rightarrow Mo(NPh)Br_2(S_2CNEt_2)_2 + PhN(CH_3)_3Br \quad (3)$$

$$MoOCl_2(S_2CNEt_2)_2 + PhNPPh_3 \rightarrow Mo(NPh)Cl_2(S_2CNEt_2)_2 + OPPh_3 \quad (4)$$

$$MoOCl_2(S_2CNEt_2)_2 + PhNCO \rightarrow Mo(NPh)Cl_2(S_2CNEt_2)_2 + CO_2 \quad (5)$$

note that while the molybdenum precursors in eq 1–3 are electron rich, the progenitor in eq 4 and 5 is electron precise. It is also evident that all five reactions expel especially stable products; their stability provides a major driving force for the reactions. The $[Mo{\equiv}NPh]^{4+}$ unit also possesses considerable stability, as exemplified by its inertness toward acid. Furthermore, although the oxo ligand can be replaced by the NPh

---

[9] See paragraph at end of paper regarding supplementary material.

[10] Newton, W. E.; McDonald, J. W. "Abstracts of Papers", 176th National Meeting of the American Chemical Society, Miami Beach, Fla., Sept 1978; American Chemical Society: Washington, D.C., 1978; INOR 145.

Table V. Selected Bond Distances (Å) in $Mo(NPh)Cl_2(S_2CNEt_2)_2 \cdot CHCl_3$

Mo-N(3)	1.734 (4)	
Mo-Cl(1)	2.467 (1)	
Mo-Cl(2)	2.469 (1)	
Mo-S(1)	2.512 (1)	2.508[a]
Mo-S(2)	2.508 (1)	
Mo-S(3)	2.512 (1)	
Mo-S(4)	2.499 (1)	
S(1)-C(6)	1.709 (5)	1.715[a]
S(2)-C(6)	1.718 (5)	
S(3)-C(1)	1.726 (5)	
S(4)-C(1)	1.707 (4)	
C(1)-N(1)	1.304 (6)	1.307[a]
C(6)-N(2)	1.310 (6)	
C(12)-N(3)	1.377 (6)	
N(1)-C(2)	1.489 (6)	1.478[a]
N(1)-C(3)	1.463 (6)	
N(2)-C(7)	1.473 (6)	
N(2)-C(8)	1.485 (6)	
C(2)-C(5)	1.515 (7)	1.516[a]
C(3)-C(4)	1.515 (7)	
C(8)-C(9)	1.524 (7)	
C(7)-C(10)	1.509 (7)	
C(12)-C(13)	1.405 (6)	1.389[a]
C(13)-C(14)	1.385 (7)	
C(14)-C(15)	1.390 (8)	
C(15)-C(16)	1.373 (8)	
C(16)-C(17)	1.383 (7)	
C(17)-C(12)	1.398 (6)	
C(11)-Cl(3)	1.758 (6)	1.758[a]
C(11)-Cl(4)	1.758 (5)	
C(11)-Cl(5)	1.756 (6)	

[a] Average.

ligand in isoelectronic molybdenum complexes, the reverse reaction (displacement of NPh by O) has not been realized. An analogous situation exists for Re complexes.[11]

Structure of $Mo(NPh)Cl_2(S_2CNEt_2)_2$. The unit cell contains well-separated molecules of $Mo(NPh)Cl_2(S_2CNEt_2)_2$ and $CHCl_3$. There are no significant intramolecular or intermolecular contacts, the shortest being about 2.4 Å (calculated by using C–H = 1.08 Å). The closest approach of the $CHCl_3$ to the Mo complex occurs between H1C11 and C(12) at a distance of 2.7 Å. Figure 1 shows the structure of the complex with the hydrogen atoms and the $CHCl_3$ molecule omitted for clarity. The molybdenum atom is seven-coordinate, and the NPh ligand and one chlorine atom occupy the apexes of a slightly distorted pentagonal bipyramid. The remaining chlorine atom and the four sulfur atoms of the dithiocarbamate ligands are roughly coplanar. As expected, the molybdenum atom is displaced out of the equatorial plane toward the nitrogen atom by 0.17 Å.

Important distances and angles are given in Tables V and VI. The geometric parameters within the dithiocarbamate ligands are similar to those commonly found for these groups; the average length of the C(1)–N(1) and C(6)–N(2) multiple bonds at 1.31 Å is much shorter than the average length of the C–N single bonds in these ligands (1.48 Å). The respective distances in $Mo(NPh)_2(S_2CNEt_2)_2$ are 1.33 and 1.47 Å.[2] The N(3)–C(12) distance (1.38 Å) is normal for a C–N single bond between multiply bonded atoms. The four Mo–S distances are all about the same with an average value of 2.51 Å, which is similar to these distances in $MoOCl_2(S_2CNEt_2)_2$[5] (average 2.50 Å) and $Mo(NPh)_2(S_2CNEt_2)_2$ (2.46 Å, S trans to S).[2]

If the terminal methyl groups are neglected, each dithiocarbamate ligand is planar; the dihedral angles about the C(1)–N(1) and C(6)–N(2) bonds are 1.0 (4) and 3.0 (4)°, respectively. The dithiocarbamate ligands are not mutually coplanar; however, they are folded away from the NPh group such that the angle between the S(1)–C(6)–S(2) and the S(3)–C(1)–S(4) planes is 16.6 (3)°.

In the present complex, the Mo–N bond length of 1.734 (4) Å is very close to the same distances in $Cp_2Mo_2(NC(CH_3)_3)_2(\mu\text{-}S)_2$ (1.733 (4) Å)[12] and in $Mo(NC_7H_7)Cl_2(PhCON{=}NC_6H_4CH_3)(PMe_2Ph)$ (1.726 (9) Å).[13] All three molybdenum–nitrene complexes can be considered as 18-electron compounds (EAN rule) with the –NR ligand acting as a four-electron donor, and despite differing coordination environments, all three have the same Mo–N distance of 1.73 Å, which now seems to be firmly established as the Mo≡N triple-bond distance in nitrene complexes. By comparison, the Mo≡N triple bond in molybdenum–nitrido complexes is 0.05–0.09 Å shorter.[14] The same shortening is observed in rhenium–nitrido complexes as compared to rhenium nitrene complexes.[15] The structure of $Mo(NPh)_2(S_2CNEt_2)_2$ displays distinctly longer Mo–N distances of 1.754 (4) and 1.789 (4) Å; however, this compound possesses two more electrons (EAN

Table VI. Selected Bond Angles and Interplanar Angles (Deg) in $Mo(NPh)Cl_2(S_2CNEt_2)_2 \cdot CHCl_3$

S(1)-Mo-S(2)	68.47 (4)	
S(3)-Mo-S(4)	68.30 (4)	
S(1)-Mo-S(3)	139.85 (4)	
S(1)-Mo-S(4)	149.92 (4)	
S(2)-Mo-S(4)	138.79 (4)	
S(2)-Mo-S(3)	71.49 (4)	
Cl(1)-Mo-S(1)	84.59 (4)	
Cl(1)-Mo-S(2)	85.19 (5)	
Cl(1)-Mo-S(3)	89.44 (4)	
Cl(1)-Mo-S(4)	85.75 (5)	
Cl(1)-Mo-Cl(2)	85.99 (4)	
Cl(2)-Mo-S(1)	76.34 (5)	
Cl(2)-Mo-S(2)	144.33 (4)	
Cl(2)-Mo-S(3)	142.87 (4)	
Cl(2)-Mo-S(4)	74.62 (5)	
N(3)-Mo-Cl(1)	173.9 (1)	
N(3)-Mo-Cl(2)	88.6 (1)	
N(3)-Mo-S(1)	91.5 (1)	
N(3)-Mo-S(2)	97.7 (1)	
N(3)-Mo-S(3)	96.6 (1)	
N(3)-Mo-S(4)	95.5 (1)	
Mo-N(3)-C(12)	166.8 (3)	
N(3)-C(12)-C(13)	118.1 (4)	
N(3)-C(12)-C(17)	120.9 (4)	
C(12)-C(13)-C(14)	118.8 (5)	120.0[a]
C(13)-C(14)-C(15)	120.0 (5)	
C(14)-C(15)-C(16)	120.6 (5)	
C(15)-C(16)-C(17)	121.1 (5)	
C(16)-C(17)-C(12)	118.5 (5)	
C(17)-C(12)-C(13)	121.0 (5)	
S(1)-C(6)-S(2)	111.0 (2)	110.5[a]
S(3)-C(1)-S(4)	110.0 (2)	
S(1)-C(6)-N(2)	124.6 (3)	124.7[a]
S(2)-C(6)-N(2)	124.3 (4)	
S(3)-C(1)-N(1)	124.5 (3)	
S(4)-C(1)-N(1)	125.5 (3)	
C(6)-N(2)-C(8)	121.3 (4)	121.4[a]
C(6)-N(2)-C(7)	121.7 (4)	
C(1)-N(1)-C(2)	120.2 (4)	
C(1)-N(1)-C(3)	122.3 (4)	
N(1)-C(2)-C(5)	111.4 (4)	111.8[a]
N(1)-C(3)-C(4)	112.5 (4)	
N(2)-C(8)-C(9)	111.6 (4)	
N(2)-C(7)-C(10)	111.6 (4)	

S(1)-C(6)-S(2)	S(3)-C(1)-S(4)	16.6 (3)
C(12)-N(3)-Mo	N(3)-Mo-Cl(2)	8 (1)
C(2)-N(1)-C(3)	S(3)-C(1)-S(4)	1.0 (4)
C(7)-N(2)-C(8)	S(1)-C(6)-S(2)	3.0 (4)
Mo-N(3)-C(12)	N(3)-C(12)-C(17)	112 (1)

[a] Average.

---

(11) La Monica, G; Cenini, S. *Inorg. Chim. Acta* **1978**, *29*, 183.

(12) Dahl, L. F.; Frisch, P. D.; Gust, G. R. *J. Less-Common Met.* **1974**, *36*, 255.

(13) Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Hursthouse, M. B.; Jayaweera, S.; Amarasiri, A.; Quick, A. *J. Chem. Soc., Dalton Trans.* **1979**, 914.

(14) (a) The distances in Table VII may be compared to those in $MoN(Et_2dtc)_3$ (Mo≡N = 1.641 (9) Å),[14b] $MoNCl_3$ (two independent Mo≡N distances of 1.64 (1) and 1.67 (1) Å)[14c] and $MoNCl_3(OPCl_3)$ (Mo≡N = 1.659 (5) Å).[14d] (b) Hursthouse, M. B.; Motevalli, M. *J. Chem. Soc., Dalton Trans.* **1979**, 1362. (c) Strahle, J. *Z. Anorg. Allg. Chem.* **1970**, *375*, 238. (d) Strahle, J.; Weiher, U.; Dehnicke, K. *Z. Naturforsch., B* **1978**, *33*, 1347.

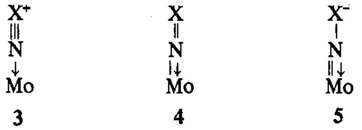
Table VII. Structural Data for Terminal Nitrene Complexes of Molybdenum

complex[a]	R	Mo-N, Å	Mo-N-R, deg	ref
$Mo_2(NR)_2Cp_2(\mu\text{-}S)_2$	$C(CH_3)_3$	1.733 (4)	176.3 (3)	12
$Mo(NR)Cl_2(PhCONNC_6H_4CH_3)(PMe_2Ph)$	$C_6H_4CH_3$	1.726 (9)	177 (1)	13
$Mo(NR)Cl_2(S_2CNEt_2)_2\cdot CHCl_3$	C_6H_5	1.734 (4)	166.8 (3)	this work
$Mo(NR)_2(S_2CNEt_2)_2$	C_6H_5	1.754 (4)	169.4 (4)	2
		1.789 (4)	139.4 (4)	
$Mo(NR)OCl_2(OPEtPh_2)_2$	H	1.70 (1)	157 (10)	16

[a] Abbreviations: Ph = C_6H_5; Et = C_2H_5; Cp = $\eta^5\text{-}C_5H_5$; Me = CH_3.

rule) than $Mo(NPh)Cl_2(S_2CNEt_2)_2$, and the longer bond lengths are consistent with the expected average bond order of 2.5 for the two Mo–N bonds.[2]

It is noteworthy that $Mo(NO)(S_2CNBu_2)_3$ (Mo–N = 1.731 (8) Å)[20] and $Mo(NS)(S_2CNMe_2)_3$ (Mo–N = 1.738 (11) Å)[14b] possess molybdenum–nitrogen distances which are the same as those found in linear nitrene complexes. Compounds of the type $Mo(NR)(S_2CNR'_2)_3^+$ are known, but their structure are unknown. Notwithstanding, the Mo–N distances are probably close to 1.73 Å as in the present complex, $MoCl_2(NPh)(S_2CNEt_2)_2$. Thus, attaching R^+, O, or S to the nitride in $MoN(S_2CNR'_2)_3$ results in a significant lengthening of the Mo–N distance from 1.64 to 1.73 Å in all three cases.[14b] Furthermore, these data suggest that formalism **5** contributes



X = O, S

significantly (if not exclusively) to the ground-state geometry of the coordinated nitrosyl and thionitrosyl ligands in these Mo complexes.

Table VII summarizes the structural data for molybdenum complexes that contain terminal nitrene ligands. The first three 18-electron complexes all contain essentially linear Mo–N–C angles. These observations are consistent with the description of the Mo–N bonds as triple bonds. The last two 20-electron complexes, $Mo(NPh)_2(S_2CNEt_2)_2$ and $Mo(NH)OCl_2(OPPh_2Et)_2$,[16] contain distinctly bent nitrene ligands which correlate with the reduced Mo–N bond order expected in these complexes. The actual Mo–N–C angle in $Mo(NPh)Cl_2(S_2CNEt_2)_2$ deviates from linearity by 13°, which is more than the 1–8° deviation from linearity observed in structures of other "linear" –NR ligands. We attribute this extra bending of the –NPh ligand to the unsymmetric π bonding in the pentagonal plane. Almost all of the bending of the –NPh group occurs in the Cl(2)–Mo–N(3) plane toward Cl(2); the dihedral angle Cl(2)–Mo–N(3)–C(12) is 8 (1)°. The six phenyl carbon atoms form a rigorous plane which is neither in (180° angle) nor perpendicular to (90° angle) the plane (Mo–N(3)–C(12)) of bending; the dihedral angle about N(3)–C(12) is 112 (1)°. This intermediate dihedral angle coupled with the dispositions of the four methyl groups on the dithiocarbamate ligands is the major structural feature which prevents the complex from having C_s symmetry in the solid state.

Finally, the structure of $Mo(NPh)Cl_2(S_2CNEt_2)_2$ may be compared to that of the analogous oxo complex $MoOCl_2(S_2CNEt_2)_2$.[5] The overall atomic dispositions within the complexes are very similar; both complexes have slightly distorted pentagonal-bipyramidal structures with a chlorine atom and a multiply bonded (oxygen or NC_6H_5) ligand occupying the apical positions. The only major difference between the two structures arises in a comparison of the axial and equatorial Mo–Cl bond lengths within each complex. In $MoOCl_2(Et_2dtc)_2$, the axial Mo–Cl bond length of 2.504 (1) Å is about 0.09 Å longer than the equatorial Mo–Cl distance of 2.417 (1) Å. In $Mo(NPh)Cl_2(Et_2dtc)_2$, the equatorial Mo–Cl distance of 2.469 (1) Å is identical with the axial Mo–Cl distance of 2.467 (1) Å. Despite the short metal–nitrogen distance, the equal Mo–Cl distances in $MoCl_2(NPh)(S_2CNEt_2)_2$ indicate the absence of a significant trans influence caused by the –NPh ligand; although there is no ligand formally trans to Cl(2), sulfur donor atoms rarely exert any appreciable trans influence. These observations parallel the absence of a trans influence in the three $Re(NR)Cl_2(PR_3)_2$ structures.[15d] On the other hand, this observation contrasts with the significant trans influence observed in $MoOCl_2(S_2CNEt_2)_2$,[5] $MoO(S_2CNEt_2)_2^+$,[17] $MoN(S_2CNEt_2)_3$,[14b] and $Mo(NPh)_2(S_2CNEt_2)_2$.[2] The presence of the two extra electrons in the bis(nitrene) complex seems to be responsible for the trans influence in that molecule. However, other explanations must be sought in order to understand the trans influence in the oxo and nitrido complexes.[18,19]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also acknowledge support from NSF Grant CHE 75-08188-A01, a grant-in-aid from Indiana University, and the Marshall H. Wrubel Computing Center for use of computing facilities.

Registry No. $Mo(NPh)Cl_2(S_2CNEt_2)_2\cdot CHCl_3$, 72882-13-4; $MoOCl_2(S_2CNEt_2)_2$, 57146-54-0; $PhNPPh_3$, 2325-27-1.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes and Tables III and IV giving rms amplitudes of vibration and positions and thermal parameters for H atoms (21 pages). Ordering information is given on any current masthead page.

---

(15) (a) The Re–N distances in $ReNCl_2(PPh_3)_2$ (1.602 (9) Å)[15b] and in $ReN(Et_2dtc)_2$ (1.656 (8) Å)[15c] may be compared to the Re–N distances of 1.69 Å found in the $Re(NR)Cl_3(PR_3)_2$ structures.[15d] The Re–N bond length of 1.788 (11) Å observed in $ReNCl_2(PEt_2Ph)_3$[15e] is an unusual case wherein the Re–N distance approaches a double-bond value. (b) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204. (c) Fletcher, S. R.; Rowbottom, J. F.; Skapski, A. C.; Wilkinson, G. *Chem. Commun.* **1970**, 1572. Fletcher, S. R.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1972**, 1079. (d) Bright, D.; Ibers, J. A. *Inorg. Chem.* **1968**, *7*, 1099; **1969**, *8*, 703. (e) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

(16) Chatt, J.; Choukraun, R.; Dilworth, J. R.; Hyde, J.; Vella, P.; Zubieta, J. *Transition Met. Chem.* **1979**, *4*, 59.

(17) Dirand, J.; Richard, L.; Weiss, R. *Transition Met. Chem.* **1976**, *1*, 2.

(18) See, for example, the brief discussion in ref 2.

(19) Shustorovich, E. M.; Porai-Koshits, M. A.; Buslaer, Y. A. *Coord. Chem. Rev.* **1975**, *17*, 1.

(20) Brennan, T. F.; Bernal, I. *Inorg. Chim. Acta* **1973**, *7*, 283.