A Bisphenylnitrene Complex of Molybdenum with a Bent Nitrene Ligand. Preparation and Structure of *cis*-$Mo(NC_6H_5)_2(S_2CN(C_2H_5)_2)_2$

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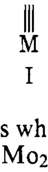
Abstract: The first bisnitrene complex of molybdenum, $Mo(NC_6H_5)_2(S_2CN(C_2H_5)_2)_2$, has been prepared in high yield by allowing an excess of phenyl azide to react with $Mo(CO)_2(S_2CN(C_2H_5)_2)_2$ in dry methylene chloride. Red-brown, solvent-free crystals of the complex were grown from methylene chloride-hexane. The structure of the complex was determined at −130 °C using X-ray diffraction techniques. The complex is monomeric and six coordinate with a somewhat distorted octahedral geometry caused by the small bite angles of the sulfur chelates, 67.60 (5) and 69.51 (4)°; the angle between the nitrene ligands is 103.5 (2)°. Of special import are the inequivalent phenylnitrene ligands. One nitrene is strongly bent at the nitrogen atom with Mo-N(1)-C(1) = 139.4 (4)° and Mo-N(1) = 1.789 (4) Å, and the other nitrene is nearly linear and has a shorter metal-nitrogen distance with Mo-N(3)-C(17) = 169.4 (4)° and Mo-N(3) = 1.754 (4) Å. Available structural evidence indicates that linear nitrene ligands exert little if any trans influence on trans ligands while the bent nitrene in the title complex has a significant trans influence. The Mo-S(4) distance of the sulfur atom trans to N(1) is 0.15 Å longer than that which is trans to N(3), and 0.30 Å longer than that which is trans to another sulfur. The title complex crystallizes in space group $P2_1/n$ with $a = 17.193$ (8) Å, $b = 10.194$ (4) Å, $c = 18.127$ (8) Å, $\beta = 123.59$ (1)°, and $Z = 4$. On the basis of 3518 unique reflections with $F_o^2 > 3\sigma(F_o^2)$, the structure was refined using full-matrix, least-squares methods to $R(F) = 0.042$ and $R_w(F) = 0.055$.

Introduction

The first nitrene complexes, $OsO_3(NR)$, were reported in 1959,[1] and several years later $Ta(NR)(NR_2)_3$ (1962),[2] $ReCl_3(NR)(PPhEt_2)_2$ (1962),[3] and $ReCl(NR)(RNH_2)_4^{2+}$ (1965)[4] were reported. In comparison to the number of carbene complexes, far fewer nitrene complexes are known. Although few in number, nitrene complexes include all second- and third-row transition metals of groups 4A, 5A, 6A, 7A, and 8 except Tc.

Nitrene ligands are of current scientific interest owing to their potential utility as stable sources of nitrenes in organic synthetic reactions. Furthermore, the metal in a nitrene complex can act as a variable source of electrons, thus allowing the NR group to react either as a nitrene or an imide.[5] The synthetic utility of nitrene complexes has not been fully exploited nor appreciated in the past because many of the more stable nitrene complexes are relatively inert toward reaction at the nitrogen atom of the NR group. This inertness is probably connected with the linear ligand geometry and short metal-nitrogen bond length. Recent work with certain osmium complexes has shown nucleophilic activity at the nitrene nitrogen atom.[1c] It is important to realize that the nitrene ligand can have amphoteric character similar to other N-ligating ligands such as NO, NNR, and NNR_2. Simple bonding theories suggest that nitrenes can act as linear four-electron donor ligands (I) or as bent two-electron donor ligands (II). The only nitrene complexes which have been structurally characterized in detail are $Cp_2Mo_2S_2(NR)_2$[6] and the very stable rhenium complexes, $ReCl_3(NR)(PR'_3)_2$ and $ReCl(NR)(RNH_2)_4^{2+}$;[7] in these complexes the nitrene ligands have a linear geometry with very short metal-nitrogen distances. Incomplete structural details of another molybdenum nitrene complex, $MoCl_2(NR)(PhC(O)N{=}NPh)(PPhMe_2)$, have been reported.[8]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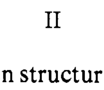
II

We now report the synthesis and structural characterization at low temperature of the molybdenum nitrene complex $Mo(NPh)_2(Et_2dtc)_2$, which was prepared by the action of PhN_3 on $Mo(CO)_2(Et_2dtc)_2$. This is the second bisnitrene complex which has been reported, and it is the first structurally characterized example of a complex containing a bent nitrene ligand. A bisnitrene complex of osmium, $OsO_2(NR)_2$, was recently described,[1c] and a brief report of the preparation of a bisaminonitrene complex, $Mo(NNPh_2)_2(Me_2dtc)_2$, has also appeared.[8]

Experimental Section

Crystal Preparation. The molybdenum complex was prepared by the method described subsequently. Crystals were grown from a solution of dry methylene chloride to which hexane had been added to create a nearly saturated solution at room temperature. The solution was placed in a refrigerator (−10 °C) for 12 h, and large, red-brown crystals formed. These crystals were separated from the supernatant and used in subsequent structural studies.

Infrared spectra were measured in Nujol mulls using a Perkin-Elmer 283 spectrometer and were calibrated using a polystyrene film. NMR spectra were measured in CD_2Cl_2 solution at ambient temperature using a Varian Associates HR-220 spectrometer. Spectra were calibrated using internal tetramethylsilane. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. $Mo(CO)_2(Et_2dtc)_2$ was prepared according to the literature method.[9] All reactions were performed in an inert atmosphere using dry, freshly distilled solvents. X-ray data collection was accomplished using a locally constructed diffractometer consisting of a Picker goniostat interfaced to a Texas Instruments TI980 computer. The attached low-temperature device has been described.[10]

Bis(phenylnitrene)bis(diethyldithiocarbamato)molybdenum. Freshly prepared $Mo(CO)_2(Et_2dtc)_2$ (0.50 g, 1.1 mmol) was allowed to react with 0.30 g of phenyl azide (2.5 mmol) in 25 mL of dry methylene chloride. After the solution was stirred at room temperature for 24 h, the volume of the solution was reduced to 10 mL, and 5 mL of dry hexane was added. After several minutes, the mixture was filtered to remove a yellow byproduct, and the solution was again concentrated in vacuo to a volume of 10 mL. More yellow byproduct was then removed by filtration. The remaining solution was allowed to stand overnight at −10 °C in order to crystallize the product from solution. The supernatant liquid was decanted and the product was washed with hexane to yield 0.32 g (50%) of deep red-brown crystals. In some instances, the above procedure produced an oil instead of crystals during the final crystallization step. The addition of 1-2 mL of methylene

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Table I. Summary of Crystallographic Data

compd	$Mo(NC_6H_5)_2(S_2CN(C_2H_5))_2$
formula	$C_{22}H_{30}MoN_4S_4$
formula weight	574.71
a, Å	17.193 (8)
b, Å	10.194 (4)
c, Å	18.127 (8)
β, deg	123.59 (1)
V, Å^3	2647
Z	4
space group	$C_{2h}{}^5$-$P2_1/n$
crystal size, mm	0.15 × 0.18 × 0.28
crystal volume	6.5×10^{-3} mm^3
crystal shape	monoclinic prism with {$\underline{1}$01}, {$\bar{1}$01}, and {111} faces
radiation	Mo Kα, λ 0.710 69, monochromatized using highly oriented graphite
density, g/cm^3	1.442 (calcd), 1.40 (1) obsd at 25 °C
temp	−130 (5) °C
μ	8.029 cm^{-1}
range of transmission factors	0.83–0.90
aperture	2.5 mm wide × 3.5 mm high
take-off angle	2.0°
scan speed	3.0 deg/min
scan range	0.85° below Kα_1 to 0.85° above Kα_2
background counting	10 s
2θ limits	4.0–50.0°
no. of variables	280
unique data with $I_0 > 3\sigma(I_0)$	3518
error in observation of unit weight	1.49 electrons
$R(F)$	0.042
$R_w(F)$	0.055

chloride followed by small amounts of hexane caused the solution to deposit crystals of the product. The infrared spectrum showed the normal diethyl dithiocarbamate bands and phenyl bands. The stretching frequency due to the $C\overset{...}{=}N$ group within the dithiocarbamate ligand was found at 1498 cm^{-1}. The ^1H NMR spectrum contained a methyl resonance at δ 1.24 (12 H, triplet, $J_{HH} = 7.2$ Hz), two methylene resonances at δ 3.74 (4 H, quartet, $J_{HH} = 7.1$ Hz) and 3.77 (4 H, quartet, $J_{HH} = 7.3$ Hz), and a complicated multiplet in the aromatic region near δ 7.0 (10 H). Anal. Calcd for $C_{22}H_{30}MoN_4S_4$: C, 45.98; H, 5.26; N, 9.75. Found: C, 45.77; H, 5.32; N, 9.54.

Crystallographic Data. The crystal of the Mo complex was mounted on the diffractometer, and monoclinic symmetry was immediately identified. Rapid data collection on the inner shell ($4° < 2\theta < 10°$) indicated extinctions ($h0l$, $h + l$ odd; $0k0$, k odd) characteristic of the space group $C2h^5$-$P2_1/n$. For reasons of convenience, the reduced monoclinic cell was not chosen. On the basis of a least-squares analysis of the angular positions of 12 strong, machine-centered reflections in diverse regions of reciprocal space ($21° < 2\theta < 25°$), accurate unit cell dimensions were determined. See Table I for pertinent crystal information and details of data collection. The crystal displayed acceptable mosaicity for the θ–2θ scan technique based upon ω scans of several reflections. Background counts were measured at both ends of the scan range with both the crystal and counter stationary. The intensities of three standard reflections were measured every 100 reflections and found to be absolutely constant within counting statistics during the entire data collection. The intensity data were corrected for background effects and for Lorentz polarizations effects. Though only marginally necessary, an absorption correction was performed using Gaussian integration.[11] A careful check of F_o and F_c in the final refined model showed that no extinction correction was necessary. Only reflections with $F_o{}^2 > 3\sigma(F_o{}^2)$ were used in least-squares calculations. The values of $\sigma(F_o)$ were estimated using the following formula with $p = 0.05$.

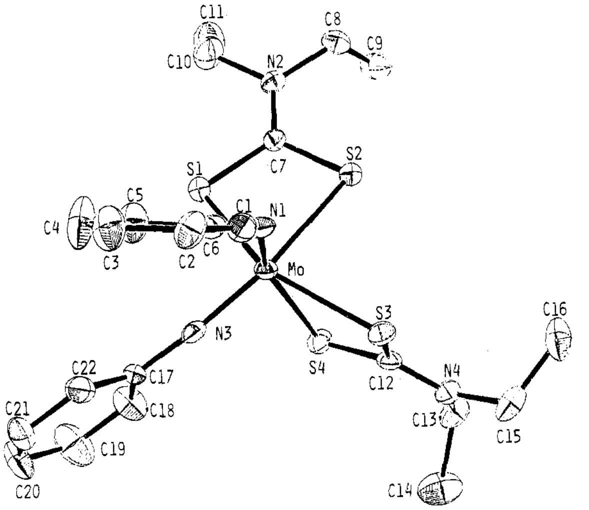


Figure 1. A drawing of a molecule of $Mo(NPh)_2(S_2CNEt_2)_2$. The hydrogen atoms have been omitted. Vibrational ellipsoids are drawn at the 50% probability level.

$$\sigma(F_o) = [S + 0.25(T_s/T_b)^2(B_1 + B_2) + p^2F_o{}^4]^{1/2}/2F_o$$

B_1 and B_2 are the background counts, T_b is the background counting time, S is the measured integrated scan count, T_s is the scan time, and F_o is $[S - (T_s/2T_b)(B_1 + B_2)]^{1/2}$. A total of 5117 unique reflections were collected out to 50° in 2θ. Owing to intermittent instrument failure, 56 reflections had to be discarded; no effort was made to recollect these data.

Structure Refinement. The structure was solved using a Patterson synthesis to locate the metal atom and difference Fourier syntheses to locate all the remaining atoms including all 30 hydrogen atoms. The structure was refined using full-matrix, least-squares techniques.[12] During the refinements, the quantity minimized was $q = \sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights, w, are taken as $4F_o{}^2/\sigma^2(F_o{}^2)$. Atomic scattering factors were taken from the usual sources,[13] and the anomalous dispersion terms for Mo and S were included in F_c. Although all 30 hydrogen atoms were easily located in difference Fourier syntheses, their positions were idealized, and they were included as fixed contributions in the final anisotropic refinements. The C–H distance was chosen to be 0.95 Å, and the isotropic thermal parameters for the hydrogen atoms were chosen to be 1.0 Å^2 larger than those of the respective carbon atoms to which they were attached.

The final structural model converged with 31 anisotropic nonhydrogen atoms to $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.042$ and $R_w(F) = (q/\sum wF_o{}^2)^{1/2} = 0.055$. A statistical analysis of the trends of q as a function of observed structure amplitudes, diffractometer setting angles, and Miller indices showed nothing unusual and indicated that the weighting scheme was adequate. A final difference Fourier synthesis showed no significant residual electron density; the largest peak at 0.6 e/Å^3 was located near the molybdenum atom. Of the reflections with $3\sigma(F_o{}^2) > F_o{}^2$, only five had $F_c{}^2 > 3\sigma(F_o{}^2)$ and none had $F_c{}^2 > 5\sigma(F_o{}^2)$.

The final positional and thermal parameters of the atoms appear in Table II and the root mean square amplitudes of vibration are given in Table III.[14] Table IV[14] contains the positional and thermal parameters for the hydrogen atoms. A listing of the observed and calculated structure amplitudes for those data used in the refinements is available.[14]

Discussion

Description of the Structure. The structure of $Mo(NPh)_2(Et_2dtc)_2$ consists of well-separated monomers. Figure 1 shows the complex to have a highly distorted octahedral geometry, partly caused by the small bite angles of the dithiocarbamate

Table II. Positional and Thermal Parameters for the Atoms of Bis(phenylnitrene)bis(diethyldithiocarbamato)molybdenum

atom	X^a	Y	Z	$B_{11}{}^b$	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
MC	0.086 060 (28)	0.284 51 (4)	0.347 327 (26)	25.36 (23)	31.9 (4)	16.69 (19)	0.29 (25)	14.25 (17)	0.07 (22)
S-1	−0.070 12 (8)	0.297 76 (12)	0.320 46 (8)	26.3 (6)	42.6 (13)	24.7 (6)	−8.1 (7)	15.5 (5)	−7.1 (7)
S-2	0.057 14 (8)	0.517 03 (12)	0.388 76 (8)	23.2 (6)	38.5 (12)	22.0 (5)	−2.5 (7)	14.3 (5)	−2.2 (6)
S-3	0.220 11 (8)	0.387 55 (12)	0.355 60 (8)	24.3 (6)	48.9 (13)	18.4 (5)	1.9 (7)	13.1 (5)	3.2 (7)
S-4	0.035 08 (8)	0.415 34 (12)	0.193 81 (8)	24.1 (6)	50.4 (13)	17.9 (5)	−3.8 (7)	12.1 (5)	1.9 (7)
C-1	0.1848 (3)	0.1133 (5)	0.5077 (3)	31.7 (27)	45. (5)	19.0 (22)	0. (3)	17.3 (21)	1.4 (27)
C-7	−0.0470 (3)	0.4557 (5)	0.3625 (3)	25.0 (25)	42. (5)	18.2 (21)	−5.1 (29)	13.8 (20)	−0.6 (26)
N-1	0.155 70 (28)	0.2300 (4)	0.459 86 (26)	30.6 (22)	51. (4)	21.4 (19)	6.9 (26)	19.2 (18)	3.7 (24)
N-2	−0.104 58 (26)	0.5216 (4)	0.375 96 (25)	19.7 (20)	51. (4)	22.4 (19)	0.7 (24)	13.7 (17)	0.3 (23)
C-2	0.2766 (4)	0.0978 (5)	0.5794 (3)	28.4 (26)	59. (6)	21.9 (23)	−7. (3)	14.0 (21)	−4. (3)
C-3	0.3057 (4)	−0.0199 (6)	0.6243 (3)	25.9 (28)	69. (6)	25.7 (25)	−1. (3)	12.1 (23)	12. (3)
C-4	0.2453 (4)	−0.1219 (6)	0.6012 (4)	51. (4)	51. (6)	37. (3)	0. (4)	19.6 (29)	16. (4)
C-5	0.1500 (4)	−0.1047 (6)	0.5316 (4)	42. (4)	87. (8)	34. (3)	−31. (4)	7.5 (28)	11. (4)
C-6	0.1219 (4)	0.0100 (6)	0.4856 (4)	36. (3)	68. (7)	30.0 (28)	−5. (4)	12.3 (26)	7. (4)
N-3	0.056 70 (27)	0.1386 (4)	0.286 16 (26)	30.4 (22)	43. (4)	27.7 (20)	−2.3 (25)	23.3 (18)	2.2 (24)
C-17	0.0172 (3)	0.0332 (5)	0.2285 (3)	26.7 (26)	37. (5)	27.0 (24)	−5.1 (29)	20.0 (21)	−9.2 (28)
C-18	−0.0456 (4)	0.0560 (6)	0.1381 (4)	42. (3)	66. (6)	29.2 (27)	7. (4)	13.5 (26)	−2. (3)
C-19	−0.0858 (5)	−0.0478 (6)	0.0807 (4)	62. (4)	88. (8)	26.8 (29)	5. (5)	8. (3)	−8. (4)
C-20	−0.0637 (5)	−0.1764 (6)	0.1126 (4)	57. (4)	54. (6)	40. (3)	−14. (4)	22. (3)	−21. (4)
C-21	−0.0011 (4)	−0.1984 (5)	0.2015 (4)	51. (4)	39. (6)	41. (3)	−5. (4)	28.9 (29)	−6. (3)
C-22	0.0389 (4)	−0.0939 (5)	0.2589 (3)	40. (3)	50. (5)	29.7 (26)	3. (3)	24.4 (25)	1. (3)
C-8	−0.0799 (3)	0.6537 (5)	0.4159 (3)	28.8 (27)	54. (5)	24.9 (24)	6. (3)	15.7 (22)	−3. (3)
C-9	−0.1069 (4)	0.7604 (5)	0.3486 (4)	45. (3)	59. (6)	30.5 (27)	9. (4)	23.9 (26)	5. (3)
C-10	−0.1900 (4)	0.4609 (6)	0.3616 (4)	27.6 (28)	79. (7)	46. (3)	0. (4)	22.1 (26)	0. (4)
C-11	−0.2756 (4)	0.5352 (6)	0.3008 (4)	35. (3)	86. (7)	56. (4)	−3. (4)	19. (3)	−4. (4)
N-4	0.185 58 (27)	0.5438 (4)	0.222 33 (25)	23.8 (21)	51. (4)	19.4 (18)	1.0 (25)	13.4 (17)	4.0 (23)
C-12	0.1495 (3)	0.4592 (5)	0.251 47 (29)	26.5 (25)	42. (5)	14.7 (20)	0.7 (28)	14.0 (19)	−2.0 (25)
C-13	0.1285 (4)	0.6063 (5)	0.1353 (3)	28.6 (26)	78. (6)	22.0 (23)	1. (3)	15.1 (22)	16. (3)
C-14	0.1411 (5)	0.5406 (7)	0.0676 (4)	56. (4)	153. (10)	21.6 (27)	13. (5)	20.7 (28)	11. (4)
C-15	0.2837 (3)	0.5849 (6)	0.2784 (4)	22.7 (26)	92. (7)	31.9 (27)	−2. (3)	15.7 (23)	16. (4)
C-16	0.2972 (4)	0.6968 (6)	0.3385 (4)	45. (3)	79. (7)	30.4 (28)	−27. (4)	11.9 (26)	−3. (4)

[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 $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. The quantities given in the table are the thermal coefficients $\times 10^4$.

Table V. Selected Bond Distances (Å) in Mo(NPh)$_2$(Et$_2$dtc)$_2$

Mo-N(3)	1.754 (4)		C(1)-C(2)	1.391 (7)
Mo-N(1)	1.789 (4)		C(17)-C(18)	1.395 (7)
Mo-S(1)	2.453 (2)		C(2)-C(3)	1.380 (7)
Mo-S(3)	2.461 (2)		C(18)-C(19)	1.372 (8)
Mo-S(2)	2.602 (2)		C(3)-C(4)	1.362 (8)
Mo-S(4)	2.755 (2)		C(19)-C(20)	1.397 (9)
S(1)-C(7)	1.731 (5)		C(4)-C(5)	1.422 (8)
S(2)-C(7)	1.708 (5)		C(20)-C(21)	1.373 (9)
S(3)-C(12)	1.742 (5)		C(5)-C(6)	1.360 (8)
S(4)-C(12)	1.700 (5)		C(21)-C(22)	1.378 (7)
C(7)-N(2)	1.327 (6)	1.328 (av)	C(6)-C(1)	1.400 (8)
C(12)-N(4)	1.330 (6)		C(22)-C(17)	1.377 (7)
N(4)-C(13)	1.465 (6)	1.472 (av)		1.384 (av)
N(4)-C(15)	1.469 (6)			
N(2)-C(8)	1.476 (7)			
N(2)-C(10)	1.479 (7)			
C(10)-C(11)	1.470 (8)	1.498 (av)		
C(8)-C(9)	1.503 (8)			
C(13)-C(14)	1.515 (8)			
C(15)-C(16)	1.505 (9)			
N(1)-C(1)	1.392 (6)	1.389 (av)		
N(3)-C(17)	1.386 (6)			

ligands at 69.51 (4) and 67.60 (5)° (see Tables V and VI). The complex adopts the cis geometry, and the angle between the nitrogen atoms of the nitrene ligands is 103.5 (2)° (see Figure 2). There are no significant intermolecular nonbonded contacts in the unit cell; the shortest are H1C4-H2C10, H1C5-H1C8, and H2C8-N(1) at 2.4 Å. The complex is sterically unencumbered because the dithiocarbamate chelates are relatively small, and there are no unusual intramolecular contacts.

The dithiocarbamate ligands adopt the usual geometry seen for these groups. The average length of the C(7)-N(2) and C(12)-N(4) bonds at 1.33 Å is considerably shorter than the average of the four other C-N single bonds at 1.47 Å, but somewhat longer than the expected C-N double bond length of 1.27 Å. The geometries about C(7), C(12), N(2), and N(4) are planar within experimental error. Furthermore, both dithiocarbamate ligands (excluding the methyl groups) are very nearly planar; the dihedral angles about the C(7)-N(2) and C(12)-N(4) multiple bonds are 6.9 (5) and 4.5 (5)°, respectively. The methyl groups of one dithiocarbamate ligand are located on the same side of the ligand, while the methyl groups on the other ligand are located on opposite sides. There are no other unusual bond angles or distances in the dithiocarbamate ligands. The C(10)-C(11) distance at 1.470 (8) Å appears to be slightly shortened as a result of librational motion. The terminal methyl groups all seem to be well behaved, and there is no sign of any disorder.

Phenylnitrene Ligands. The most noticeable feature of the structure is the presence of a bent nitrene ligand and a nearly linear nitrene ligand in the same complex. The Mo-N(1)-C(1) and Mo-N(3)-C(17) angles are 139.4 (4) and 169.4 (4)°, respectively. The smaller angle is associated with a longer Mo-N(1) bond length of 1.789 (4) Å, and the larger angle is associated with the shorter Mo-N(3) bond length of 1.754 (4) Å. These values can be compared to Re-N distances of 1.69 Å and Re-N-C angles of 172° in the rhenium nitrene complexes ReCl$_3$(NMe)(PPh$_2$Me)$_2$ and ReCl$_3$(p-NC$_6$H$_4$COCH$_3$)(PPhEt$_2$)$_2$;[7] the corresponding distances and angles in Cp$_2$Mo$_2$S$_2$(NBu)$_2$ are 1.733 (4) Å and 176.3 (3)°.[6] The C(1) carbon atom of the bent nitrene is bent in the N(1)-Mo-N(3) plane toward the other nitrene ligand; the angle between the C(1)-N(1)-Mo and N(1)-Mo-N(3) planes is 5.5 (5)°. However, the entire phenyl group does not lie in the Mo-

Table VI. Selected Bond Angles and Interplanar Angles (deg) in $Mo(NPh)_2(Et_2dtc)_2$

S(1)-Mo-S(2)	69.51 (4)		C(1)-C(2)-C(3)	120.2 (5)	120.0 (av)
S(3)-Mo-S(4)	67.60 (5)		C(2)-C(3)-C(4)	121.1 (5)	
S(1)-Mo-S(4)	94.08 (5)		C(3)-C(4)-C(5)	119.2 (5)	
S(2)-Mo-S(3)	84.79 (5)		C(4)-C(5)-C(6)	119.6 (5)	
S(1)-Mo-S(3)	150.92 (5)		C(5)-C(6)-C(1)	121.0 (5)	
S(2)-Mo-S(4)	80.45 (5)		C(6)-C(1)-C(2)	118.6 (5)	
N(1)-Mo-N(3)	103.5 (2)		C(17)-C(18)-C(19)	120.0 (5)	
N(1)-Mo-S(4)	160.1 (1)		C(18)-C(19)-C(20)	120.1 (6)	
N(3)-Mo-S(2)	156.1 (1)		C(19)-C(20)-C(21)	119.7 (5)	
N(1)-Mo-S(1)	102.2 (1)		C(20)-C(21)-C(22)	120.0 (5)	
N(1)-Mo-S(2)	94.5 (1)		C(21)-C(22)-C(17)	120.9 (5)	
N(1)-Mo-S(3)	92.8 (1)		C(22)-C(17)-C(18)	119.2 (5)	
N(3)-Mo-S(1)	91.2 (1)		C(7)-N(2)-C(8)	120.7 (4)	121.4 (av)
N(3)-Mo-S(3)	109.4 (1)		C(7)-N(2)-C(10)	121.7 (4)	
N(3)-Mo-S(4)	87.3 (1)		C(12)-N(4)-C(13)	121.9 (4)	
Mo-N(1)-C(1)	139.4 (4)		C(12)-N(4)-C(15)	121.3 (4)	
Mo-N(3)-C(17)	169.4 (4)		C(8)-N(2)-C(10)	117.2 (4)	117.0 (av)
N(2)-C(7)-S(1)	122.6 (4)		C(13)-N(4)-C(15)	116.7 (4)	
N(2)-C(7)-S(2)	123.4 (4)		N(1)-C(1)-C(2)	120.7 (5)	
N(4)-C(12)-S(3)	120.3 (4)		N(1)-C(1)-C(6)	120.7 (5)	
N(4)-C(12)-S(4)	124.2 (4)		N(3)-C(17)-C(18)	119.7 (5)	
S(1)-C(7)-S(2)	114.0 (3)		N(3)-C(17)-C(22)	121.1 (5)	
S(3)-C(12)-S(4)	115.6 (3)		Mo-S(1)-C(7)	90.2 (2)	
N(2)-C(10)-C(11)	113.6 (5)	112.5 (av)	Mo-S(2)-C(7)	85.9 (2)	
N(2)-C(8)-C(9)	112.7 (4)		Mo-S(3)-C(12)	92.6 (2)	
N(4)-C(13)-C(14)	111.7 (5)		Mo-S(4)-C(12)	83.9 (2)	
N(4)-C(15)-C(16)	112.1 (5)				
Mo-S(1)-S(2) Mo-S(3)-S(4)	99.20 (5)		Mo-S(1)-S(2) Mo-N(1)-N(3)	77.8 (1)	
			Mo-S(3)-S(4) Mo-N(1)-N(3)	−110.5 (1)	

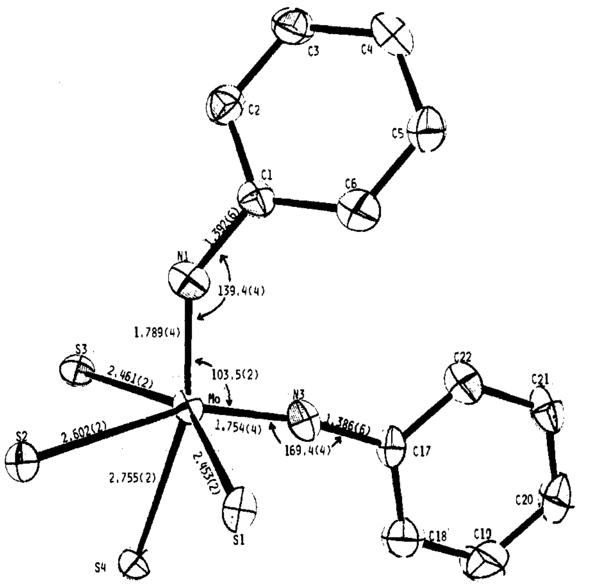
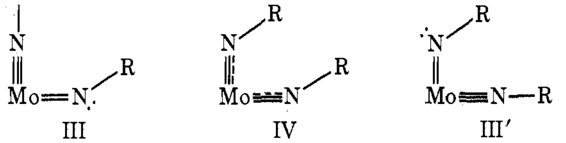


Figure 2. The coordination sphere of $Mo(NPh)_2(S_2CNEt_2)_2$. The phenyl hydrogen atoms and all but the sulfur atoms of the dithiocarbamate ligands have been omitted. Vibrational ellipsoids are drawn at the 50% probability level.

N(1)-C(1) plane, and the dihedral angle about the N(1)-C(1) bond is 43.4 (5)°.

In Table VII, certain structural parameters of the dioxo complex, the oxoaminonitrene complex, and the bisnitrene complex are compared. All are six-coordinate, bisdithiocarbamate complexes of molybdenum and have the same number of bonding electrons at molybdenum. The average Mo-S distances (S trans to S) at 2.46 Å, and the average Mo-S distances (S trans to N, O) at 2.66 Å are essentially the same for all three complexes. The 0.20-Å difference is the average trans lengthening caused by the combined effect of the oxo and/or nitrene ligands. Based on a comparison of available structural data, we would expect the Mo-NR bond length to be about 0.06 Å longer than the analogous Mo-O bond length. This is near the observed average difference seen in $Mo(NPh)_2(Et_2dtc)_2$ and $MoO_2(Pr_2dtc)_2$[15] (0.076-Å difference) and in $Cp_2Mo_2S_2(NBu)_2$ and $Cp_2Mo_2S_2O_2$[16] (0.054-Å difference).

In the foregoing paragraph, average metal-ligand distances were used; however, careful scrutiny shows that the individual values are sometimes very different. Simple electron counting using the EAN rule shows that all three complexes are 20-electron complexes if the nitrene and oxo ligands donate the maximum of four electrons each. Assuming that a 20-electron configuration is unfavorable, the complex may reduce the number to 18 electrons by causing one of the dithiocarbamate ligands to become monodentate or by placing a pair of electrons in a nonbonding nitrene ligand orbital. In the latter case, a double-bonded nitrene ligand should form, and significant bending at the nitrene nitrogen should become evident. Because two amphoteric ligands are present, several possibilities must be considered. One possible structure is the localized, linear-bent form (III and III′). The other is the symmetric, delocalized double half-bent form (IV). Although the Mo-S distances (S trans to O) at 2.621 (2) and 2.681 (2) Å in $MoO_2(Pr_2dtc)_2$ are similar but not quite equal, this complex has identical Mo-O distances and closely approximates the delocalized form analogous to IV. However, $Mo(NPh)_2(Et_2dtc)_2$ in the solid state does not seem to be properly described by either III or IV,



III IV III′

Table VII. Comparison of Bond Distances (Å) in Some Bisdithiocarbamate complexes of Mo

compd[a]	Mo-S (S trans to S)	Mo-S A	Mo-S B	Mo-O,N C	Mo-O,N D
$MoO_2(Pr_2dtc)_2$[d]	2.446 (2), 2.457 (2) 2.452 (av)	2.621 (2) 2.651 (av)	2.681 (2)	1.696 (5) 1.696 (av)	1.695 (5)
$MoO(NNMe_2)(Me_2dtc)_2$[e]	2.43 (1), 2.52 (1) 2.47 (av)	2.58 (1) 2.65 (av)	2.72 (1)	1.80 (1)[b]	1.71 (1)[c]
$Mo(NPh)_2(Et_2dtc)_2$[f]	2.453 (2), 2.461 (2) 2.457 (av)	2.602 (2) 2.679 (av)	2.755 (2)	1.754 (4) 1.772 (av)	1.789 (4)

[a] Abbreviations: Pr = *n*-propyl, Et = ethyl, Me = methyl, Ph = phenyl, dtc = dithiocarbamate. Bond A is trans to bond C and bond B is trans to bond D. [b] Mo-N distance. [c] Mo-O distance. [d] See ref 15. [e] See ref 8. [f] This work.

but rather something partway between the two forms. The Mo-N-C angles at 169.4 (4) and 139.4 (4)° lie between those values expected for IV (~150, ~150°) and III (180, 120°). The two Mo-N distances at 1.754 (4) and 1.789 (4) Å are definitely not the same, yet differ by less than the 0.10-0.16 Å expected for III. It is important to note here that both localized and delocalized forms (III and IV) may exist for molybdenum dioxo complexes. Although the structural precision is not particularly good in $MoBr_2O_2(bpy)$ (trans bromine and cis oxygen ligands), there are two significantly different Mo-O bond lengths at 1.64 and 1.83 Å,[17] while an analogous complex, $MoO_2(Pr_2dtc)_2$, contains two equal Mo-O lengths at 1.70 Å.[15] In light of this contrast, the former structure deserves to be investigated in more detail.

In $Mo(NPh)_2(Et_2dtc)_2$, the nitrene ligands exert a strong trans influence on the sulfur ligands. Using the Mo-S distances with S trans to S as references, the more linear nitrene lengthens the Mo-S(2) bond by 0.15 Å and the more bent nitrene lengthens the Mo-S(4) bond by 0.30 Å. Thus the more bent nitrene with the *longer* Mo-N length exerts the *larger* trans influence. This contrasts with the common observation in structures of 18-electron oxo complexes in which the shorter Mo-O bond usually has the larger trans influence.[18] This apparent contrast bears some comment. First, in the $ReCl_3(NR)(PR'_3)_2$ structures,[7] there is absolutely no trans influence operating to change the length of the Re-Cl bonds in these 18-electron complexes. If this is a general phenomenon, it differs markedly from the structures of 18-electron oxo and nitrido complexes.[18] Apparently, the electrons nominally described as lone pairs in the Mo≡N: and Mo≡O: formalisms act in a weakly bonding fashion with metal σ orbitals to shorten the metal-O,N triple bond and bring about the lengthening of the trans metal-ligand bond.[19] Second, the present molybdenum nitrene complex has a maximum electron count of 20 electrons, although we can formally call it an 18-electron complex with two half-bent nitrenes or with one linear and one bent nitrene. Two electrons must be removed from the metal and placed out on the nitrene ligands thus causing them to bend. Those two electrons on the bent nitrene nitrogen atom in III may compete to some extent with the electron pair donated by the trans sulfur ligand and thus weaken the sulfur-metal bond in order to preserve the electron count at the metal. In one extreme, the pair of electrons on the bent nitrene nitrogen atom will win out, the bent nitrene will become linear, and the trans sulfur ligand will dissociate itself from the metal; in the other extreme, the pair of sulfur electrons will win out, and there will be no lengthening of the molybdenum-sulfur bond due to the trans, bent nitrene. We would thus expect that the unknown complexes, $Mo(NPh)_2(Et_2dtc)_2{}^{2+}$ and $Mo(NPh)(NMePh)(Et_2dtc)_2{}^{+}$, would show a greatly reduced trans influence operating because the two electrons in question (on the former bent nitrene) either have been removed by oxidation or have been completely tied up in bonding with the methyl group. Similarly, the known electron precise[20] complexes, $ReCl(NPh)(Et_2dtc)_2$[21] and $W(CO)(NPh)(Et_2dtc)_2$,[22] should contain linear nitrene ligands which exert little if any trans influence.

The foregoing observations and explanations are exactly analogous to the molecular orbital descriptions which are used to explain the bonding in electron-rich dinitrosyl complexes.[23] The nitrosyl analogue of the present molybdenum nitrene complex is the hypothetical ruthenium compound, *cis*-$Ru(NO)_2(Et_2dtc)_2$. Using this compound as a model (pseudooctahedral geometry with C_{2v} symmetry) and considering initially only the interaction of the metal d orbitals with the π orbitals on the nitrogen ligands, one obtains nine molecular orbitals. With regard to the nitrogen-metal interaction, three of them ($1a_1$, $1a_2$, $1b_2$) are bonding orbitals and three others are the antibonding partners ($3a_1$, $2a_2$, $2b_2$). The remaining three orbitals, $2a_1$, $1b_1$, and $2b_1$, have a nonbonding interaction between metal and nitrogen ligand. The a_2 and b_2 orbitals involve π interactions perpendicular to the N-Mo-N plane and the a_1 and b_1 orbitals are located in the N-Mo-N plane. Since there are eight π electrons, the three bonding orbitals and one nonbonding orbital are filled. Owing to unfavorable antibonding σ interactions, Enemark and Feltham argue that the $2a_1$ orbital is higher in energy than one or both b_1 orbitals. This is a quite reasonable assumption and, if it is correct, the highest occupied molecular orbital would be $1b_1$ which is nonbonding with regard to the metal-nitrogen interaction, but *antibonding* with regard to the in-plane σ interaction between the metal and those ligands trans to the nitrogen atoms. The above MO description correlates nicely with the above delocalized model (IV): two equal Mo-N bonds of bond order 2.5 and a lengthening of the Mo-S bonds trans to the nitrenes. It might be expected that electrons in the $1b_1$ orbital would have stereochemical consequences and would cause a partial bending of the nitrene ligands in the N-Mo-N plane. If we relax the C_{2v} symmetry restrictions, and allow one nitrene to bend more than the other, the HOMO (formerly $1b_1$) will be localized mainly on the more bent nitrene, its trans ligand, and the metal. Thus, the more bent nitrene will exert the stronger trans influence. Furthermore, the metal-nitrogen distance for the more bent nitrene is expected to increase owing to reduced overlap in the bonding $1a_1$ orbital. The less bent nitrene will respond in an opposite manner, and, in the extreme case, the complex would adopt a fully localized geometry (III) with the two electrons in the HOMO being represented as the lone pair of electrons on the bent nitrene in the valence bond description. In fact, no 20-electron, six-coordinate dinitrosyl complexes are known; however, structures of several 20-electron mononitrosyl complexes are known ($Co(NCS)(NO)(diars)_2{}^{+}$, $Co(NO)(NH_3)_5{}^{2+}$), and they adopt the expected localized geometry with fully bent nitrosyl ligands which appear to exert a strong trans influence.

Two salient structural features can now be predicted. First, based on observations in electron-precise nitrene complexes,[7] we expect to find essentially linear nitrene ligands with short metal-nitrogen bond lengths and no trans influence. Second, if the number of electrons in the complex is increased, we expect as a general phenomenon that bending of the nitrene and lengthening of the metal–nitrogen bond will occur, and that the trans weakening influence of the bent nitrene will become evident. Returning now to the present molybdenum bisnitrene complex, we would expect an unsymmetric lengthening of the Mo–S bonds (trans to N) by zero and ca. 0.4 Å in formalism III or a symmetric lengthening of the same bonds by 0.20 Å in formalism IV. Here again we see that $Mo(NPh)_2(Et_2dtc)_2$ is best described by something between formalisms III and IV.

This study has demonstrated a number of important results. We have shown that more than one nitrene ligand can be readily placed on one metal, that ordinary aromatic azides in addition to perfluoroalkyl azides are good sources of nitrene ligands, that stable bent nitrene ligands can be prepared, that the EAN rule is useful in predicting when a bent nitrene is present in a given complex, and that a bent nitrene in an electron-rich complex exerts a strong trans influence. Indeed, a structural comparison of $ReCl_3(NR)(PPh_3)_2$[3] and $RhCl_2(CH_3CO)(NR)(PPh_3)_2$,[24,25] would represent a good way to test some of the ideas which have been expressed here.

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Supplementary Material Available: A listing of observed and calculated structure factor amplitudes, Tables III and IV (34 pages). Ordering information is given on any current masthead page.

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