necessary for this oxidative addition to occur.

The tetrakis(phosphine) complexes MCl$_2$L$_4$ are crowded molecules, as demonstrated by the X-ray structures of MoCl$_2$(PMe$_3$)$_4$[10b] and WCl$_2$(PMePh$_2$)$_4$,[13a] and, for WCl$_2$L$_4$, undergo ligand substitution[11a] and oxidative addition[9c,13a] reactions via initial loss of L. These derivatives react with N$_3$SiMe$_3$ to form silylimido compounds. In contrast, the MCl$_4$L$_n$ derivatives have significantly less labile phosphine ligands and react with N$_3$SiMe$_3$, producing ClSiMe$_3$. Similarly, the lability of the phosphine ligands in **1**–**3** appears to be crucial in determining the course of further reaction with trimethylsilyl azide: **3**, with bulky, labile PMePh$_2$ ligands, reacts with a second equivalent of N$_3$SiMe$_3$ to produce **4**, whereas **1** and **2**, with smaller and therefore less labile PMe$_3$ ligands, yield trimethylsilyl chloride on further reaction with N$_3$SiMe$_3$. These observations parallel the substitution reactivity of the related oxo compounds W(O)Cl$_2$L$_3$ (L = PMe$_3$ or PMePh$_2$).[13]

Compound **4** is a rare example of a molecule with two terminal imido ligands in a five-coordinate structure. While a number of bis(imido) derivatives with coordination numbers of 4 and 6 are known,[16,17,22,24] significantly fewer M(NR)$_2$L$_3$ complexes have been reported.[18,25] The details of the structure of **4** are consistent with the trends observed for related compounds except for the long nitrogen–silicon bonds, which suggest that N–Si multiple bonding is less important in this compound than in silylamines and amides. While the size of the uncertainties in the bond distances calculated for **4** dictates caution in arguments based on these metrical data, the reactive nature of the N–Si bonds in **4** is consistent with weakened N–Si multiple bonding. Also consistent are the short W–N bond distances, since strong silylimido–tungsten $\pi$-donor interactions could weaken nitrogen–silicon $\pi$-bonding. The formal $C_s$ symmetry in **4** permits formation of four $\pi$-bonds between the filled nitrogen p orbitals and the empty tungsten d orbitals and results in formal electronic saturation at the tungsten(VI) center in the five-coordinate structure. Nonetheless, there does not appear to be any barrier to addition of ligands to form six-coordinate tungsten(VI) bis(silylimido) derivatives, as demonstrated by the reaction of **4** with bpy and Me$_2$bpy. Therefore, the unusual trigonal-bipyramidal geometry observed for **4** is likely a further reflection of the controlling influence of the phosphine ligand on structure and reactivity in this system.

## Conclusions

Trimethylsilyl azide can be used as a source of the (trimethylsilyl)imido ligand upon reaction with oxidizable metal chloride complexes. Coordinative unsaturation, which can be produced by loss of labile ligand(s), appears to be a prerequisite for this reaction, rather than the more usual formation of azido or nitrido derivatives, to occur.

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**Supplementary Material Available:** Tables of crystallographic data, anisotropic thermal parameters, hydrogen atom coordinates, bond distances and angles, torsional angles, and least-squares planes for **4** (7 pages); tables of observed and calculated structure factors for **4** (6 pages). Ordering information is given on any current masthead page.

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# Synthesis, Structure, and Characterization of ((2-Aminophenyl)imido)dichlorobis(diethyldithiocarbamato)molybdenum(VI)

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*Received April 25, 1989*

The reaction of MoOCl$_2$(S$_2$CN(C$_2$H$_5$)$_2$)$_2$ with 1,2-phenylenediamine in the presence of 2 equiv of base produces the imido complex Mo(NC$_6$H$_4$NH$_2$)Cl$_2$(S$_2$CN(C$_2$H$_5$)$_2$)$_2$. The structure of Mo(NC$_6$H$_4$NH$_2$)Cl$_2$(S$_2$CN(C$_2$H$_5$)$_2$)$_2$·CH$_2$Cl$_2$ (I) has been determined by X-ray crystallography. The crystals are orthorhombic, of space group $Pc2_1n$, with $a$ = 11.847 (5) Å, $b$ = 13.836 (4) Å, and $c$ = 17.522 (4) Å. The structure was refined to $R$ = 7.13%, $R_w$ = 6.47% by using 2658 independent reflections. The geometry of the complex is pentagonal bipyramidal. The Mo–N(3)–C(11) angle is 178° and the molybdenum–nitrogen distance 1.70 Å, indicating triple-bond character of the molybdenum–nitrogen bond. Compared to that in the previously reported structure of the corresponding *N*-phenyl complex, Mo(NC$_6$H$_5$)Cl$_2$(S$_2$CN(C$_2$H$_5$)$_2$)$_2$·CHCl$_3$ (II), the molybdenum–nitrogen distance is slightly shorter in I and the molybdenum–imido linkage is closer to 180°. The molybdenum–chloride bond distances, which are equal in II, differ in I: the axial molybdenum–chloride bond trans to the nitrene ligand is 0.06 Å longer than the equatorial molybdenum–chloride bond, showing a trans effect of the –NC$_6$H$_4$NH$_2$ group. The molybdenum center in I has a $^{95}$Mo NMR signal at –164 ppm and is deshielded by 90 ppm compared to that of II. The imido nitrogen of I has a $^{14}$N NMR signal at –19 ppm. Both I and II show irreversible two-electron reduction peaks in their cyclic voltammograms. Complex I has an absorption band at 465 nm that is absent in the UV–vis spectrum of II.

## Introduction

Molybdenum(VI) compounds are of special interest due to the involvement of molybdenum(VI) in molybdenum hydroxylases, a group of enzymes that catalyze two-electron reduction or oxidation processes.[1] Molybdenum(VI) dioxo[2,3] and molybdenum(VI) monooxo complexes[2,4–6] have been studied extensively.

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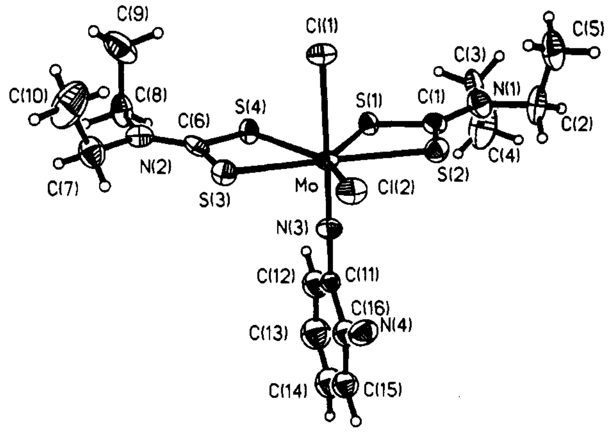

**Figure 1.** Molecular structure of $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2$.

Molybdenum(VI) nitride complexes have also been reported,[2,7] but only a few molybdenum(VI) imido and bis(imido) compounds have been characterized.[5,8-13] There are numerous methods of synthesizing molybdenum(VI) imido complexes: they can be obtained by reacting $MoOCl_2(S_2CN(C_2H_5)_2)_2$ with $PhNPPh_3$ or PhNCO; the reaction of $MoO(S_2CN(C_2H_5)_2)_2$ or $Mo(CO)_2(S_2CN(C_2H_5)_2)_2$ with aryl azide produces an oxoimido and a diimido complex;[10] the reaction of a nitrido complex such as $MoN(S_2CNR_2)_3$ with electrophilic 2,4-dinitrochlorobenzene produces $Mo(NC_6H_5)(S_2CNR_2)_3$.[12] While imido complexes of other transition metals have also been synthesized with amines as starting materials,[8] no molybdenum(VI) imido complexes have been synthesized via this route. We report here the first synthesis of a molybdenum(VI) imido complex using an amine as starting material. The new $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2$ complex is considerably different in structure and properties from the $Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2$ analogue.

## Experimental Section

All reactions were performed under an argon atmosphere by standard Schlenk techniques unless otherwise mentioned. The solvents were dried and distilled prior to use. $MoOCl_2(S_2CN(C_2H_5)_2)_2$ was synthesized according to the method of Weiss et al.[6] 1,2-Phenylenediamine dihydrochloride was purchased from SIGMA Chemical Co. and used without further purification. Triethylamine was purchased from Aldrich, dried over sodium, and distilled before use.

**Preparation of $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2{\cdot}CH_2Cl_2$ (I).** A 2.0-g sample of $MoOCl_2(S_2CN(C_2H_5)_2)_2$ (4.2 mmol) was suspended in 40 mL of methanol. A solution of 0.80 g of 1,2-phenylenediamine dihydrochloride (4.4 mmol) and 1.3 mL of triethylamine (10 mmol) in 40 mL of methanol was added dropwise over 30 min to the suspension. The solution turned red-brown and was refluxed for 7 h. The solution was then filtered, and the solvent was taken off under vacuum. The crude product was redissolved in $CH_2Cl_2$ in air, and the solution was extracted with water until the water fraction, which initially turned yellow, was clear. Addition of hexanes to the $CH_2Cl_2$ solution produced orange-red crystals overnight, yield 0.5 g (18%). Anal. Calcd for $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2{\cdot}CH_2Cl_2$: C, 31.20; H, 4.31; Cl, 21.67. Found: C, 31.47; H, 4.33; Cl, 20.63.

**Table I.** Crystallographic Data for $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2{\cdot}CH_2Cl_2$

| | |
|---|---|
| chem formula | $C_{16}H_{26}N_4S_4MoCl_2{\cdot}CH_2Cl_2$ |
| fw | 654.4 |
| space group | orthorhombic, $Pc2_1n$ |
| unit cell dimens | $a$ = 11.847 (5) Å<br>$b$ = 13.836 (4) Å<br>$c$ = 17.522 (4) Å |
| vol | 2872.0 (17) $Å^3$ |
| $Z$ | 4 |
| $T$ | 21 °C |
| $\lambda$ | 0.71073 Å |
| $\rho_{calcd}$ | 1.513 g $cm^{-3}$ |
| $\mu$ | 1.114 $mm^{-1}$ |
| transm coeff | 0.578 (max)/0.535 (min) |
| final $R$ indices (obs) | $R$ = 7.13%, $R_w$ = 6.47% |

**Table II.** Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)

| | $x$ | $y$ | $z$ | $U$(eq)[a] |
|---|---|---|---|---|
| Mo | 2325 (1) | 1255 (15) | 8276 (1) | 36 (1) |
| S(1) | 2473 (3) | −228 (15) | 9101 (2) | 44 (1) |
| S(2) | 759 (4) | 79 (15) | 8025 (2) | 56 (1) |
| S(3) | 3167 (3) | 2920 (15) | 8193 (2) | 51 (1) |
| S(4) | 3856 (3) | 1517 (15) | 9248 (2) | 47 (1) |
| Cl(1) | 1055 (4) | 1930 (15) | 9280 (2) | 55 (1) |
| Cl(2) | 1136 (4) | 2061 (15) | 7331 (2) | 56 (1) |
| Cl(3) | 7406 (9) | 3070 (16) | 3055 (8) | 227 (3) |
| Cl(4) | 7559 (11) | 1233 (19) | 3625 (11) | 308 (4) |
| C(1) | 1248 (13) | −663 (19) | 8711 (8) | 48 (3) |
| C(2) | −300 (15) | −1803 (20) | 8585 (12) | 84 (4) |
| C(3) | 1208 (15) | −2096 (19) | 9517 (11) | 73 (4) |
| C(4) | 1917 (20) | −2847 (20) | 9207 (14) | 132 (4) |
| C(5) | −1341 (15) | −1403 (22) | 8949 (12) | 93 (4) |
| C(6) | 4015 (12) | 2678 (19) | 8925 (9) | 53 (3) |
| C(7) | 4863 (16) | 4287 (19) | 8930 (12) | 73 (4) |
| C(8) | 5411 (12) | 3062 (20) | 9942 (10) | 65 (3) |
| C(9) | 4829 (17) | 3233 (23) | 10667 (10) | 106 (4) |
| C(10) | 4140 (22) | 5030 (21) | 9259 (13) | 136 (4) |
| C(11) | 3983 | 405 | 7104 | 36 (3) |
| C(12) | 4922 (8) | −86 (16) | 7389 (5) | 73 (4) |
| C(13) | 5713 | −477 | 6887 | 98 (5) |
| C(14) | 5567 | −378 | 6101 | 90 (5) |
| C(15) | 4628 | 114 | 5817 | 64 (4) |
| C(16) | 3837 | 505 | 6318 | 61 (4) |
| C(17) | 6869 (23) | 1867 (30) | 3042 (18) | 308 (4) |
| N(1) | 715 (12) | −1453 (18) | 8935 (8) | 61 (3) |
| N(2) | 4723 (11) | 3313 (18) | 9253 (7) | 57 (3) |
| N(3) | 3231 (10) | 794 (17) | 7617 (7) | 47 (3) |
| N(4) | 2906 (11) | 970 (18) | 6044 (7) | 67 (3) |

[a] Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

**Table III.** Bond Lengths (Å) for I

| | | | |
|---|---|---|---|
| Mo–N(3) | 1.700 (16) | Mo–Cl(1) | 2.497 (12) |
| Mo–Cl(2) | 2.442 (14) | Mo–S(1) | 2.516 (24) |
| Mo–S(2) | 2.507 (19) | Mo–S(3) | 2.514 (27) |
| Mo–S(4) | 2.515 (6) | S(1)–C(1) | 1.713 (19) |
| S(2)–C(1) | 1.683 (23) | S(3)–C(6) | 1.663 (17) |
| S(4)–C(6) | 1.714 (31) | N(1)–C(1) | 1.323 (32) |
| N(2)–C(6) | 1.343 (28) | N(3)–C(11) | 1.375 (19) |
| N(4)–C(16) | 1.364 (21) | N(1)–C(2) | 1.435 (25) |
| N(1)–C(3) | 1.473 (28) | N(2)–C(7) | 1.471 (34) |
| N(2)–C(8) | 1.497 (22) | C(2)–C(5) | 1.494 (28) |
| C(3)–C(4) | 1.443 (35) | C(9)–C(8) | 1.466 (25) |
| C(7)–C(10) | 1.457 (35) | | |

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(3) Representative examples: (a) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1. (b) Bruce, A.; Corbin, J. L.; Dahlstrom, P. L.; Hyde, J. R.; Minelli, M.; Stiefel, E. I.; Spence, J. T.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 917. (c) Harlan, E. W.; Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6992.

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**Table IV.** Bond Angles (deg) for I

| | | | |
|---|---|---|---|
| S(1)-Mo-S(2) | 67.8 (6) | S(4)-Mo-S(3) | 67.7 (6) |
| S(1)-Mo-S(4) | 71.2 (5) | S(1)-Mo-S(3) | 138.8 (3) |
| S(4)-Mo-S(2) | 138.2 (8) | S(2)-Mo-S(3) | 151.5 (6) |
| Cl(1)-Mo-S(1) | 86.7 (5) | Cl(1)-Mo-S(2) | 85.4 (4) |
| Cl(1)-Mo-S(3) | 86.4 (7) | Cl(1)-Mo-S(4) | 84.5 (3) |
| Cl(1)-Mo-Cl(2) | 87.7 (5) | Cl(2)-Mo-S(1) | 143.3 (7) |
| Cl(2)-Mo-S(2) | 75.6 (5) | Cl(2)-Mo-S(3) | 76.8 (7) |
| Cl(2)-Mo-S(4) | 144.0 (11) | Cl(1)-Mo-N(3) | 177.8 (5) |
| Cl(2)-Mo-N(3) | 94.3 (5) | S(1)-Mo-N(3) | 92.3 (10) |
| S(2)-Mo-N(3) | 96.0 (9) | S(3)-Mo-N(3) | 93.1 (9) |
| S(4)-Mo-N(3) | 93.4 (5) | Mo-N(3)-C(11) | 178.0 (11) |
| N(3)-C(11)-C(12) | 118.3 (7) | N(3)-C(11)-C(16) | 121.7 (7) |
| S(1)-C(1)-S(2) | 111.2 (15) | S(3)-C(6)-S(4) | 112.1 (13) |
| S(1)-C(1)-N(1) | 125.2 (14) | S(2)-C(1)-N(1) | 123.5 (13) |
| S(3)-C(6)-N(2) | 125.1 (20) | S(4)-C(6)-N(2) | 122.8 (14) |
| C(1)-N(1)-C(2) | 123.5 (17) | C(1)-N(1)-C(3) | 121.0 (15) |
| C(6)-N(2)-C(7) | 120.4 (16) | C6)-N(2)-C(8) | 122.1 (21) |
| C(7)-N(2)-C(8) | 117.5 (18) | N(1)-C(2)-C(5) | 112.6 (19) |
| N(1)-C(3)-C(4) | 113.9 (17) | N(2)-C(7)-C(10) | 115.3 (18) |
| N(2)-C(8)-C(9) | 113.9 (15) | N(4)-C(16)-C(11) | 119.7 (6) |
| N(4)-C(16)-C(15) | 120.3 (7) | | |

**Preparation of $Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2 \cdot CHCl_3$ (II).** The complex, used for comparative NMR, UV-vis, and electrochemical measurements, was synthesized according to the method of Young et al.[5]

**Structure Determination.** For the crystal structure determination of I, a suitable crystal (0.14 × 0.15 × 0.45 mm) was fixed vertically on a glass fiber with epoxy cement and centered on a Nicolet R3m/v single-crystal diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). The indexing of 24 centered reflections with 2$\theta$ between 15 and 25° indicated a primitive orthorhombic lattice. Axial photographs confirmed symmetry down each of the axes. Check reflections (taken every 50 reflections) indicated negligible decomposition during the data collection. The acentric space group $Pc2_1n$ was deduced from the systematic absences and Wilson plot analysis. The structure was solved by direct methods and refined by full-matrix least-squares techniques. Due to the relatively low number of observed data, the six-membered phenyl ring was refined as a rigid isotropic group. An empirical absorption correction, which models the crystal as a pseudoellipsoid, was applied to the data. All remaining non-hydrogen atoms were located in subsequent difference Fourier maps and refined anisotropically. Hydrogen atoms were generated in idealized positions with fixed (0.08) thermal parameters. Hydrogens on N(4) were not generated. All computations used the SHELXTL PLUS package of programs (Nicolet Corp., Madison, WI). Table I provides the crystal data collection and refinement parameters. Fractional atomic coordinates and equivalent isotropic displacement parameters (Table II), bond lengths (Table III), and bond angles (Table IV) are also provided. Anisotropic displacement parameters, H atom coordinates, and isotropic parameters and structure factors are available as supplementary material.

**NMR Spectra.** The NMR spectra were measured on an IBM NR 300-MHz NMR spectrometer. For the $^1H$ and $^{13}C$ NMR spectra, a 5-mm dual $^1H/^{13}C$ probehead was used. $^{14}N$ and $^{95}Mo$ NMR spectra were measured on a 10-mm broad-band probehead ($^{109}Ag$–$^{31}P$) with digital tuning. For the $^1H$ and $^{13}C$ NMR spectra, the residual solvent was used as an internal reference. For the other nuclei, external standards were used: nitromethane, neat ($^{14}N$ NMR); 2 M $Na_2MoO_4$ in $D_2O$, basic (pH ~ 11) ($^{95}Mo$ NMR). The concentrations of the solutions were about 0.1 M.

**Electronic Spectra.** The electronic spectra were recorded on a Beckman 5260 spectrophotometer using 1-cm cells.

**Electrochemistry.** The cyclic voltammograms were measured on an IBM EC 225 voltammetric analyzer. A three-electrode cell configuration with a Pt-disk working electrode, a Pt-wire auxiliary electrode, and an Ag/AgCl reference electrode was used. The solutions were $5 \times 10^{-4}$ M in DMF and $CH_3CN$ with 0.1 M tetraethylammonium chloride or tetrabutylammonium tetrafluoroborate as electrolyte. A sweep rate of 100 mV/s was used to record the cyclic voltammograms. For the coulometry, a PAR 175 universal programmer, a PAR 174A polarographic analyzer, a PAR 173 potentiostat, and a platinum-gauze working electrode were used.

## Results and Discussion

The reaction of $MoOCl_2(S_2CN(C_2H_5)_2)_2$ with 1,2-phenylenediamine dihydrochloride in the presence of 2 equiv of base produces the imido complex $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2$ (I). To our knowledge this is the first report of the synthesis of a molybdenum(VI) imido complex with an amine as starting material.

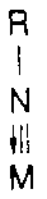
**Table V.** Bond Lengths (Å) and Angles (deg) in $Mo(L)Cl_2(S_2CN(C_2H_5)_2)_2$

| | L = $NC_6H_5$ (II)[a] | L = $NC_6H_4NH_2$ (I)[b] |
|---|---|---|
| Mo-N(3) | 1.734 (4) | 1.700 (16) |
| N(3)-C(11) | 1.377 (6) | 1.375 (19) |
| N(4)-C(16) | | 1.364 (21) |
| Mo-Cl(1) | 2.467 (1) | 2.497 (12) |
| Mo-Cl(2) | 2.469 (1) | 2.442 (14) |
| Mo-S(1) | 2.512 (1) | 2.516 (24) |
| Mo-S(2) | 2.508 (1) | 2.507 (19) |
| Mo-N(3)-C(11) | 166.8 (3) | 178.0 (11) |
| N(3)-Mo-Cl(1) | 173.9 (1) | 177.8 (5) |

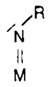
[a] Measured at −150 °C. [b] Measured at +21 °C.

The molecular geometry of the complex is pentagonal bipyramidal. A drawing of the complex is shown in Figure 1. The $CH_2Cl_2$ solvent molecule is not included in Figure 1. Bond lengths are listed in Table III; bond angles, in Table IV.

Two Lewis structures have been proposed for the metal-nitrogen bond in imido complexes.[10] In structure **1**, the nitrogen acts as a four-$\pi$-electron donor and a M-N-R angle close to 180° is expected. In structure **2**, the nitrogen acts as a two-$\pi$-electron donor and the M-N-R linkage should be bent.



**1**



**2**

**Structure.** The X-ray structural data of I suggest that the imido coordination is closest to Lewis structure **1**. The Mo-N(3)-C(11) angle is 178.0°, indicating a formal molybdenum-nitrogen bond with triple-bond character. The molybdenum-nitrogen distance is 1.700 (16) Å. A comparison of I with the X-ray structure reported by Haymore et al. for II[11] (Table V) shows that the molybdenum-nitrogen bond in I is slightly shorter and the Mo-N(3)-C(11) angle is closer to 180°. The distances between the imido nitrogen and the ring carbon are about equal in I and II and are typical for an aromatic carbon-nitrogen single bond (1.38 Å).[11] The bond between the free amine nitrogen, N(4), and the aromatic carbon, C(16), is shorter, 1.364 (21) Å, suggesting some double-bond character. While the molybdenum-chloride distances are equal in II, the bond between the molybdenum and the chloride trans to the imido ligand is 0.06 Å longer than the molybdenum-equatorial chloride bond in I. This is the result of a slight trans effect of the $-NC_6H_4NH_2$ ligand in I that is not seen in II. The N(3)-Mo-Cl(1) angle in I is 178° compared to 174° in II. The molybdenum-sulfur distances are similar between I and II, averaging 2.5 Å. One particularly striking feature in the structure of I is the alignment of N(4) toward Cl(2). The dihedral angle between Cl(1)-Mo-Cl(2) and the plane containing the phenyl ring is 5.1°. It is possible that some interaction (perhaps H-bonding) between Cl(2) and N(4) gives rise to the observed "locked" conformation.

**NMR Data.** The NMR data for I and II are listed in Table VI. The $^{95}Mo$ NMR chemical shifts show that the molybdenum nucleus in I is deshielded by 90 ppm compared to the molybdenum nucleus in II.[14] Both nuclei absorb at the shielded end of the chemical shift range for Mo(VI) compounds.[15] The deshielding of the molybdenum nucleus from II to I supports the assumption that the triple-bond character of the molybdenum-nitrogen bond increases. Although the $^{95}Mo$ NMR chemical shift value for $[MoNCl_2(S_2CN(C_2H_5)_2)_2]^-$ is not available, a comparison of the $^{95}Mo$ NMR chemical shifts of $[Mo(NC_6H_5)(S_2CN(C_2H_5)_2)_3]BF_4$ (−294 ppm) and $MoN(S_2CN(C_2H_5)_2)_3$ (−103 ppm)[14] shows that molybdenum becomes more deshielded as the triple-bond character of the molybdenum-nitrogen bond increases. Compared to that in the oxo complex, $MoOCl_2(S_2CN(C_2H_5)_2)_2$ (+137 ppm), the

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**Table VI.** NMR Data for $Mo(L)Cl_2(S_2CN(C_2H_5)_2)_2$ (Chemical Shifts in ppm; Line Widths in Hz in Parentheses)

| nucleus | L = $NC_6H_5$ (II) | L = $NC_6H_4NH_2$ (I) |
|---|---|---|
| $^{95}Mo^a$ | −254 (480)[d] | −164 (400) |
| $^{14}N$ (imido)[a] | −14 (200) | −19 (360) |
| $^{14}N$ (free L) | −336 (210)[a] | −333 (900)[b] |
| $^{13}C$ ($S_2CN(C_2H_5)_2$)[c] | 197.9 | 197.8 |
|  | 43.9 | 44.0 |
|  | 43.1 | 43.1 |
|  | 12.6 | 12.62 |
|  | 12.4 | 12.56 |
| $^{13}C$ (L)[c] | 139.3 | 151.8 |
|  | 130.4 | 139.9 |
|  | 128.7 | 131.9 |
|  | 128.0 | 129.3 |
|  | 122.5 | 117.6 |
|  | 119.7 | 116.0 |

[a] In $CH_2Cl_2$. [b] In $H_2O$. [c] In $CDCl_3$. [d] Reference 14.

molybdenum in the imido complexes is more shielded, giving a shielding order O < N < NR.

The $^{14}N$ NMR signals lie within the chemical shift range proposed for imido nitrogens.[16] In molybdenum nitrosyl complexes the $^{14}N$ chemical shift change generally parallels the chemical shift change of the metal; i.e., if the metal becomes more shielded, the nitrogen will become more shielded, too.[17–19] In molybdenum carbonyl–isocyanide complexes the same trend is found for the carbons bound to the metal center.[20] This trend is reversed in I and II, where the more shielded metal in II has the more deshielded nitrogen. While the amino groups of the free 1,2-phenylenediamine ligand show a broad signal at −333 ppm, no $^{14}N$ NMR signal was detected for the free amino group in I, probably due to broadening of the line width.

The $^{13}C$ NMR chemical shifts of the dithiocarbamate ligands do not differ significantly between I and II. The methylene and methyl carbons show two distinct peaks in I and II. The methyl peaks are separated by 0.2 ppm in II and by less than 0.1 ppm in I in $CDCl_3$ as well as $CD_2Cl_2$. All carbons of the imido ligand absorb at different frequencies. We assign the most deshielded aryl carbon peak in the $^{13}C$ NMR spectrum of I (151.8 ppm) to C(16), which binds the free amine nitrogen N(4). The carbon–nitrogen distance is 1.364 (21) Å, indicating some double-bond character of the C(16)–N(4) bond. The $^{13}C$ NMR chemical shifts of the carbons attached to the imido nitrogen, C(11), are similar; the carbon in I is slightly deshielded.

**Electrochemistry.** The cyclic voltammograms of I and II show irreversible two-electron reductions at −0.82 V (I) and −1.18 V (II). I has two oxidation peaks at −0.21 and +0.48 V; II has two oxidation peaks at +0.58 and +0.73 V. The linear imido linkage in I provides more electron density to the molybdenum center and makes the reduction potential more positive. I can be reduced coulometrically with two electrons. The resulting brown species has an absorption maximum at 415 nm ($\epsilon$ = 10000) and does not show any redox activity from +0.5 to −1.8 V in the cyclic voltammogram. Irreversible redox behavior is also found for the corresponding seven-coordinate Mo(VI) monooxo complex, $MoOCl_2(S_2CN(C_2H_5)_2)_2$, which has a two-electron reduction at −0.4 V.[21] This shows that the exchange of a terminal oxo ligand by an imido ligand shifts the reduction potential to a more negative value.

**Electronic Spectra.** The electronic spectrum of I has an absorption peak at 465 nm ($\epsilon$ = 6700) that is not present in the electronic spectrum of II. The high $\epsilon$ value suggests a charge-transfer band that may be attributed to the more linear imido linkage.

The comparison of I and II shows that the *o*-amino group has a significant influence on the structure and properties of the complex. Attempts to synthesize II by simply using aniline and 2 equiv of base were unsuccessful. We are currently studying the reaction of $MoOCl_2(S_2CN(C_2H_5)_2)_2$ with aniline derivatives that have electron-donating substituents in the ortho or para position to determine if properly substituted aromatic amines generally form imido complexes under the conditions applied.

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**Supplementary Material Available:** Tables of the complete structure determination summary, the atomic coordinates and equivalent isotropic displacement coefficients, bond lengths, bond angles, the anisotropic displacement coefficients, and H atom coordinates and isotropic displacement coefficients (6 pages); a listing of the observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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