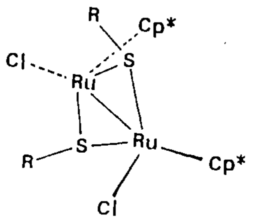

II

with two Cp* ligands in mutually cis positions from the ^{1}H NMR criteria. Furthermore, we favored the structure in which two R substituents are present in mutually syn positions with respect to the Ru_2S_2 core in consideration of the steric repulsion between the R groups and the methyl groups in the Cp* ligands.[3] However, we could not discern the details of the structure of complexes II because the isolation of the crystals suitable for an X-ray analysis was not successful.

Now an X-ray analysis of complex VIA has been performed, which is expected to have the same structure as complexes II. Although the R and R_w values after the final refinement were still 0.11 and 0.15 because of the poor character of the crystals obtained here,[14] the structure of complex VIA with the expected cis configuration of two Cp* ligands and the syn configuration of two *i*-Pr substituents has been clearly demonstrated, which is depicted in Figure 3. The positions of the hydride atoms were unable to be located, but the mutually cis terminal dihydride structure must be most plausible, if the coordination geometry of the Cp* and the thiolate ligands around the Ru atom is taken into consideration. The Ru–Ru distance of 2.784 (5) Å in this complex is significantly shorter than those in the diruthenium complexes without a Ru–Ru bond referred to above and even than that in complex IIIA, which is indicative of the presence of a Ru–Ru single bond in complex VIA. The Ru_2S_2 core is not planar but has a butterfly structure, and the dihedral angle between the plane including the Ru(1), Ru(2), and S(1) atoms and that defined by the Ru(1), Ru(2), and S(2) atoms is 150°.

The reaction of complex IIIA with PhC≡CH also gave the diamagnetic diruthenium complexes with alkynyl ligands [Cp*Ru(C≡CPh)(μ-S-*i*-Pr)$_2$RuCp*(C≡CPh)] (VIC). There appeared no ν_{Ru-H} bands in its IR spectra and no hydride resonances in its ^{1}H NMR spectra. Therefore we formulated this product as above, which might have the same structure as that of complex VIA. However, only a small amount of H_2 gas (<5%) was evolved from the reaction mixture and the formation of PhCH=CH$_2$ was not observed. Thus the fate of the acetylene hydrogen atom after the reaction is not yet clear.

Acknowledgment. This work was supported by The Ministry of Education of Japan. We thank Professor Yoshio Koike of The Kanagawa University for the permission to use an X-ray diffractometer and Mr. Takashi Murata of The University of Tokyo and Mr. Yuuki Abe of The Kanagawa University for their experimental assistance. We are grateful to Mr. Junichi Tsuchiya of The University of Tokyo for his enormous help in measuring EPR spectra and to Professor Hiroharu Suzuki of Tokyo Institute of Technology for recording mass spectra.

Supplementary Material Available: Tables of X-ray crystallographic data, bond distances and angles, positional and isotropic thermal parameters for hydrogen atoms, and anisotropic thermal parameters for non-hydrogen atoms for complex IIIA and a figure of the observed and calculated mass spectra around m/z = 537 generated by the fragmentation of [Cp*Ru(*t*-BuNC)(μ-SCy)$_2$RuCp*(*t*-BuNC)] (6 pages); a listing of observed and calculated structure factor amplitudes for complex IIIA (25 pages). Ordering information is given on any current masthead page.

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(14) Crystal data for complex VIA: $C_{26}H_{46}S_2Ru_2$; monoclinic, space group $P2_1/a$; a = 17.931 (5), b = 8.917 (3), c = 19.101 (9) Å; β = 110.30 (3)°; Z = 4. Data collection and structure solution and refinement were undertaken by the method analogous to that for complex IIIA. Final R and R_w values were 0.11 and 0.15, based on 2534 unique data ($F > 5\sigma(F)$).

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Synthesis, Structure, and Characterization of Chlorobis(diethyldithiocarbamato)((2-mercaptophenyl)imido)molybdenum(VI)[†]

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and Gottfried Huttner[§]

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The reaction of $MoOCl_2(S_2CN(C_2H_5)_2)_2$ with 2-aminothiophenol produces the imido complex $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$. The structure of this complex has been determined by X-ray crystallography. The crystals are monoclinic, of space group $P2_1/c$, with a = 8.565 (3) Å, b = 16.461 (5) Å, c = 20.542 (8) Å, β = 125.60 (2)°, and Z = 4. The structure was refined to R = 3.34% and R_w = 2.95% by using 1351 independent reflections. The geometry of the complex is distorted pentagonal bipyramidal. The molybdenum–imido nitrogen distance is 1.744 (6) Å, and the imido linkage (Mo–N(1)–C(11)) has an angle of 137.7 (7)°, indicating that the imido nitrogen acts as a two-π-electron donor. The Cl(1)–Mo–N(1) angle is 159.9 (4)°. The molybdenum–chloride distance is 2.455 (2) Å, showing no bond lengthening due to a trans effect of the molybdenum–imido nitrogen bond. The molybdenum–sulfur distances average 2.510 (6) Å. The complex has two reduction peaks in the cyclic voltammogram, one irreversible at –0.64 V and the other quasi-reversible at –0.87 V. When reduced with one electron at –0.7 V, the red-brown complex turns into a green Mo(V) monomer. The Mo(V) compound has an EPR signal with g_0 = 1.992. The frozen-solution EPR spectrum at 96 K has three different g values, indicating rhombic symmetry of the Mo(V) complex. The Mo(V) monomer can be reduced with one electron at –0.9 V to form a brown Mo(IV) complex, which can be reoxidized to the green, EPR-active Mo(V) monomer. The molybdenum center of $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$ has a ^{95}Mo NMR signal at 292 ppm; i.e., the ^{95}Mo nucleus is about 500 ppm more deshielded than in $Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2$ or $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2$. The imido nitrogen has a signal in the ^{14}N NMR spectrum at +70 ppm and is also more deshielded than the imido nitrogens in other seven-coordinate Mo(VI) imido complexes.

Introduction

Molybdenum(VI) compounds are of special interest because of the importance of molybdenum(VI) as a catalytic center in molybdenum hydroxylases, a group of enzymes that catalyze two-electron reduction and oxidation reactions.[1] The synthesis

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[†] Dedicated to Professor Jack T. Spence on the occasion of his retirement.

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(1) (a) Coughlin, M. P., Ed. *Molybdenum and Molybdenum Containing Enzymes*; Pergamon Press: Oxford, U.K, 1980. (b) Spence, J. T. *Coord. Chem. Rev.* **1983**, *48*, 59. (c) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.

Table I. Crystallographic Data for $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$

chem formula	$MoClS_5N_3C_{16}H_{24}$	Z	4
fw	550.08	T	25 °C
space group	$P2_1/c$	λ	0.71073 Å
unit cell dimens	a = 8.565 (3) Å	ρ_{calcd}	1.55 g cm^{-3}
	b = 16.461 (5) Å	μ	1.10 mm^{-1}
	c = 20.542 (8) Å	final R indices (obs)	R = 3.34%
β	125.60 (2)°		R_w = 2.95%
volume	2354 $Å^3$		

and characterization of low molecular weight Mo(VI) compounds can help elucidate the role of molybdenum in enzymes. Molybdenum(VI) oxo[2-4] and nitride[2,5] complexes have been studied extensively, but only a few molybdenum(VI) imido complexes have been synthesized and characterized.[2,6-12] Molybdenum(VI) imido complexes are generally synthesized by reacting a molybdenum(VI) oxo complex with phenyl isocyanate, *N*-(triphenylphosphoranylidene)aniline, or related ligands. They can also be obtained through the reaction of molybdenum(VI) nitrido complexes with electrophilic benzene derivatives.[11] We recently reported the preparation of a molybdenum(VI) imido complex with an amine, 1,2-phenylenediamine, where one amine forms the imido bond and the other amine is uncoordinated.[12] In all molybdenum(VI) imido complexes reported so far, the imido ligand is monodentate. We report here the first example of a molybdenum(VI) imido complex with a chelating imido ligand, where the second binding site is a sulfur.

Experimental Part

All reactions were performed under an argon atmosphere by using 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.[13] 2-Aminothiophenol was purchased from Aldrich and used without further purification.

Preparation of $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$. A 2.0-g sample of $MoOCl_2(S_2CN(C_2H_5)_2)_2$ (4.2 mmol) was suspended in 80 mL of methanol. A 0.5-mL (4.7 mmol) aliquot of 2-aminothiophenol was added dropwise with a gastight syringe. The solution turned immediately from yellow to brown and then was refluxed for 7 h and filtered. After the volume of the filtrate was reduced to 20 mL under vacuum, it was cooled in an ice bath. A 1.5-g amount of red-brown solid was filtered off and dried under vacuum. The complex was then recrystallized from a CH_2Cl_2/hexanes mixture, yielding 1.0 g (42%) of pure product. Anal. Calcd for $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$: C, 34.94; H, 4.40; N, 7.64; Cl, 6.44. Found: C, 33.91; H, 4.29; N, 7.20; Cl, 6.31.

Table II. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å)

atom	x/a	y/b	z/c	U_{eq}
Mo	0.1534 (1)	0.25061 (4)	0.38240 (3)	
Cl(1)	−0.1124 (3)	0.2498 (1)	0.23950 (7)	
S(1)	0.3163 (5)	0.3662 (1)	0.3660 (1)	
S(2)	0.0102 (5)	0.3845 (1)	0.3805 (1)	
S(3)	0.1233 (6)	0.0988 (1)	0.3663 (1)	
S(4)	0.3991 (4)	0.1912 (1)	0.3668 (1)	
S(5)	−0.1110 (4)	0.2148 (1)	0.3976 (1)	
N(1)	0.275 (1)	0.2445 (3)	0.4861 (2)	0.030 (1)
N(2)	0.176 (2)	0.5129 (4)	0.3615 (3)	
N(3)	0.396 (2)	0.0284 (3)	0.3510 (3)	
C(1)	0.166 (1)	0.4332 (4)	0.3691 (3)	
C(2)	0.036 (2)	0.5672 (5)	0.3617 (4)	
C(3)	0.105 (2)	0.5906 (6)	0.4454 (5)	
C(4)	0.305 (2)	0.5496 (5)	0.3430 (5)	
C(5)	0.472 (2)	0.5751 (6)	0.4148 (5)	
C(6)	0.316 (2)	0.0937 (5)	0.3594 (3)	
C(7)	0.299 (1)	−0.0506 (4)	0.3434 (4)	
C(8)	0.375 (1)	−0.0902 (4)	0.4240 (4)	
C(9)	0.582 (5)	0.030 (1)	0.363 (1)	0.046 (6)
C(10)	0.526 (3)	0.030 (1)	0.278 (1)	0.089 (7)
C(9X)	0.550 (7)	0.032 (2)	0.325 (2)	0.07 (1)
C(10X)	0.710 (4)	0.005 (1)	0.401 (1)	0.057 (7)
C(11)	0.231 (1)	0.2274 (4)	0.5393 (3)	0.033 (2)
C(12)	0.368 (1)	0.2277 (4)	0.6247 (4)	0.040 (2)
C(13)	0.298 (2)	0.2088 (5)	0.6685 (4)	0.052 (2)
C(14)	0.107 (2)	0.1912 (5)	0.6331 (5)	0.070 (3)
C(15)	−0.030 (2)	0.1933 (5)	0.5492 (4)	0.059 (3)
C(16)	0.036 (2)	0.2110 (4)	0.5020 (4)	0.040 (2)

Table III. Bond Lengths (Å) in $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$

Mo–N(1)	1.744 (6)	N(3)–C(7)	1.558 (14)
Mo–Cl(1)	2.455 (2)	N(3)–C(9)	1.643 (28)
Mo–S(1)	2.496 (4)	C(2)–C(3)	1.520 (18)
Mo–S(2)	2.513 (4)	C(4)–C(5)	1.424 (14)
Mo–S(3)	2.513 (3)	C(7)–C(8)	1.553 (13)
Mo–S(4)	2.505 (5)	C(9)–C(10)	1.299 (24)
Mo–S(5)	2.524 (5)	N(1)–C(11)	1.366 (14)
S(1)–C(1)	1.726 (14)	S(5)–C(16)	1.754 (6)
S(2)–C(1)	1.664 (16)	C(11)–C(12)	1.395 (1)
S(3)–C(6)	1.715 (22)	C(12)–C(13)	1.395 (1)
S(4)–C(6)	1.728 (12)	C(13)–C(14)	1.395 (1)
C(1)–N(2)	1.357 (12)	C(14)–C(15)	1.395 (1)
C(6)–N(3)	1.389 (19)	C(15)–C(16)	1.395 (1)
N(2)–C(2)	1.484 (20)	C(16)–C(11)	1.395 (1)
N(2)–C(4)	1.505 (22)		

Table IV. Bond Angles (deg) in $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$

S(1)–Mo–S(2)	68.7 (2)	Mo–N(1)–C(11)	137.7 (7)
S(1)–Mo–S(4)	72.7 (1)	N(1)–C(11)–C(12)	126.6 (4)
S(4)–Mo–S(2)	141.3 (1)	N(1)–C(11)–C(16)	113.4 (4)
S(4)–Mo–S(3)	75.5 (2)	S(5)–C(16)–C(11)	116.2 (4)
S(1)–Mo–S(3)	139.9 (2)	S(5)–C(16)–C(15)	123.8 (4)
S(2)–Mo–S(3)	148.8 (2)	S(1)–C(1)–S(2)	112.8 (5)
S(5)–Mo–S(1)	143.7 (1)	S(3)–C(6)–S(4)	109.6 (8)
S(5)–Mo–S(3)	75.5 (2)	S(1)–C(1)–N(2)	121.4 (12)
S(5)–Mo–S(2)	75.0 (1)	S(2)–C(1)–N(2)	125.8 (12)
S(5)–Mo–S(4)	143.6 (1)	S(3)–C(6)–N(3)	132.0 (10)
S(5)–Mo–Cl(1)	82.7 (1)	S(4)–C(6)–N(3)	118.4 (14)
Cl(1)–Mo–S(2)	83.2 (1)	C(1)–N(2)–C(2)	118.9 (13)
Cl(1)–Mo–S(4)	96.3 (1)	C(1)–N(2)–C(4)	120.6 (12)
Cl(1)–Mo–S(1)	92.6 (1)	C(6)–N(3)–C(7)	109.5 (13)
Cl(1)–Mo–S(3)	83.3 (1)	C(6)–N(3)–C(9)	129.2 (10)
S(5)–Mo–N(1)	77.2 (4)	C(2)–N(2)–C(4)	119.9 (9)
Cl(1)–Mo–N(1)	159.9 (4)	C(7)–N(3)–C(9)	119.3 (9)
S(1)–Mo–N(1)	103.1 (3)	N(2)–C(2)–C(3)	112.2 (9)
S(2)–Mo–N(1)	90.8 (3)	N(2)–C(4)–C(5)	108.2 (12)
S(3)–Mo–N(1)	92.5 (2)	N(3)–C(7)–C(8)	112.4 (6)
S(4)–Mo–N(1)	100.4 (4)	N(3)–C(9)–C(10)	86.6 (15)

Structure Determination. For the crystal structure determination of $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$, a suitable crystal (0.2 × 0.2 × 0.3 mm) was fixed in a glass capillary and centered on a Siemens/Nicolet R3-diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The indexing of 24 centered reflections with 2θ between 15 and 25° indicated a monoclinic lattice. Axial photographs confirmed

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(2) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988.

(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. J.; Holm, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6992.

(4) Representative examples: (a) Gheller, S. F.; Newton, W. E.; Pabon de Majid, L.; Bradbury, J. R.; Schultz, F. A. *Inorg. Chem.* **1988**, *27*, 359. (b) Bond, M. A.; Broomhead, J. A.; Hollenkamp, A. F. *Inorg. Chem.* **1988**, *27*, 978. (c) Wieghardt, K.; Holzbach, W.; Hofer, E.; Weiss, *J. Chem. Ber.* **1981**, *114*, 2700. (d) Bristow, S.; Enemark, J. H.; Garner, C. D.; Minelli, M.; Morris, G. A.; Ortega, R. B. *Inorg. Chem.* **1985**, *24*, 4070. (e) Young, C. G.; Broomhead, J. A.; Boreham, C. J. *J. Chem. Soc., Dalton Trans.* **1983**, 2135.

(5) Representative examples: (a) Chatt, J.; Dilworth, J. R. *J. Indian Chem. Soc.* **1977**, *54*, 13. (b) Dehnicke, K.; Prinz, H.; Kafitz, W.; Kujanek, R. *Liebigs Ann. Chem.* **1981**, 20. (c) Noble, M. E.; Folting, K.; Huffman, J. C.; Wentworth, R. A. D. *Inorg. Chem.* **1982**, *21*, 3722.

(6) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

(7) Maatta, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 2409.

(8) Haymore, B. L.; Maatta, E. A.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1979**, *101*, 2063.

(9) Maatta, E. A.; Haymore, B. L.; Wentworth, R. A. D. *Inorg. Chem.* **1980**, *19*, 1055.

(10) Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Neaves, B. D.; Dahlstrom, P.; Hyde, J.; Zubieta, J. *J. Organomet. Chem.* **1981**, *213*, 109.

(11) Chou, C. Y.; Devore, D. D.; Huckett, S. C.; Maatta, E. A.; Huffman, J. C.; Takusagawa, F. *Polyhedron* **1986**, *5*, 301.

(12) Minelli, M.; Carson, M. R.; Whisenhunt, D. W., Jr.; Hubbard, J. L. *Inorg. Chem.* **1990**, *29*, 442.

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

symmetry down the *b* axis. Check reflections (taken every 50 reflections) indicated negligible decomposition during the data collection. The centric space group $P2_1/c$ was deduced from the systematic absences. The structure was solved by direct methods and refined by full-matrix least-squares techniques. The 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 (merging $R = 0.0324$ (before correction) and 0.0162 (after correction); maximum transmission factor = 0.964, minimum transmission factor = 0.803). All remaining non-hydrogen atoms were located in subsequent difference Fourier maps. All atoms were refined anisotropically, except atoms N1 and C(9)–C(16), which were refined isotropically. There is some disorder in one of the nitrogen-bound ethyl groups (C(9), C(10)). The alternative positions that are found for 40% of the molecule are given as C(9X), C(10X). The coordinated nitrogen had to be refined in the isotropic model: anisotropic refinement led to physically impossible thermal parameters, and it is assumed that the *o*-phenylene derivative shows some degree of disorder corresponding to an exchange of N vs S and vice versa. It was not possible to further substantiate the model by refinement of the site-occupation numbers of two superimposed rigid group models for this ligand. Hydrogen atoms were generated in idealized positions with fixed (0.08) thermal parameters. All computations used the SHELXTL PLUS package of programs (SHELXTL PLUS, G. Sheldrick, Universitaet Goettingen, West Germany, 1988). Table I provides the crystallographic data. Fractional atomic coordinates and equivalent isotropic displacement parameters (Table II), bond lengths (Table III), and bond angles (Table IV) are also provided. Complete lists of the crystallographic data, anisotropic displacement parameters, 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 $^1H/^{13}C$ probe head was used. ^{14}N and ^{95}Mo NMR spectra were measured on a 10-mm broad-band probe head (^{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 spectra); 2 M Na_2MoO_4 in D_2O, basic (^{95}Mo NMR spectra). The concentrations of the solutions were about 0.1 M.

EPR Spectra. The EPR spectra were measured on a Varian E-109 X-band spectrometer. Samples from the solutions of the reduced species were withdrawn with a gastight syringe and transferred from the coulometer cell to an EPR flat cell under nitrogen or to a 5-mm quartz EPR tube, which was frozen immediately in liquid nitrogen for the frozen-solution spectra.

Electronic Spectra. The electronic spectra were recorded on a Beckman 5260 spectrophotometer using 1-cm cells and on a Varian 635 spectrophotometer using 0.1-cm cells.

Electrochemistry. For cyclic voltammetry and coulometry a PAR 175 universal programmer, a PAR 174A polarographic analyzer, and a PAR 173 potentiostat were used. The three-electrode electrochemical cell for cyclic voltammetry consisted of a Pt-disk working electrode, a Pt-wire auxiliary electrode, and a standard calomel reference electrode. For coulometry a platinum gauze electrode served as working electrode. The solvent, CH_3CN, was purchased from Burdick & Jackson and used without further purification. Tetrabutylammonium tetrafluoroborate (TBATFB) and tetraethylammonium chloride ((TEA)Cl) were used as electrolytes. TBATFB was purchased from Southwestern Analytical Chemicals Inc., dried in a vacuum oven, and stored in a desiccator. (TEA)Cl was purchased from Aldrich, recrystallized three times, and stored in a desiccator. The concentration of the complex was generally 5×10^{-4} M with 0.1 M electrolyte. A sweep rate of 100 mV/s was used to record the cyclic voltammograms.

Results and Discussion

$MoOCl_2(S_2CN(C_2H_5)_2)_2$ reacts with 2-aminothiophenol to form the complex $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$. To our knowledge, this is the first molybdenum(VI) imido complex with a chelating imido ligand. In the previously reported reaction of $MoOCl_2(S_2CN(C_2H_5)_2)_2$ with 1,2-phenylenediamine, which forms $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2$, the imido ligand is monodentate and the second amino group is uncoordinated.[12]

Structure. The structure of the complex has been determined by X-ray crystallography. The geometry of the complex is distorted pentagonal bipyramidal with five sulfur atoms in the equatorial plane and the imido nitrogen and the chloride in the axial positions. If an idealized plane is imposed on the atoms S(1), S(2), S(3), S(4), and S(5), the following deviations from this plane are observed: S(1), −0.0165 Å; S(2), −0.0669 Å; S(3), −0.140 Å; S(4), 0.103 Å; S(5), 0.121 Å. It is therefore possible to assume an almost planar configuration of the atoms S(1)–S(5). The Cl(1)–Mo–N(1) angle of 159.9 (4)° also supports a pentagonal bipyramidal geometry. The deviation from the ideal angle of 180° is due to the fixed ring system Mo–S(5)–C(11)–C(16)–N(1). A drawing of the complex is shown in Figure 1. The bond lengths are listed in Table III; the bond angles, in Table IV.

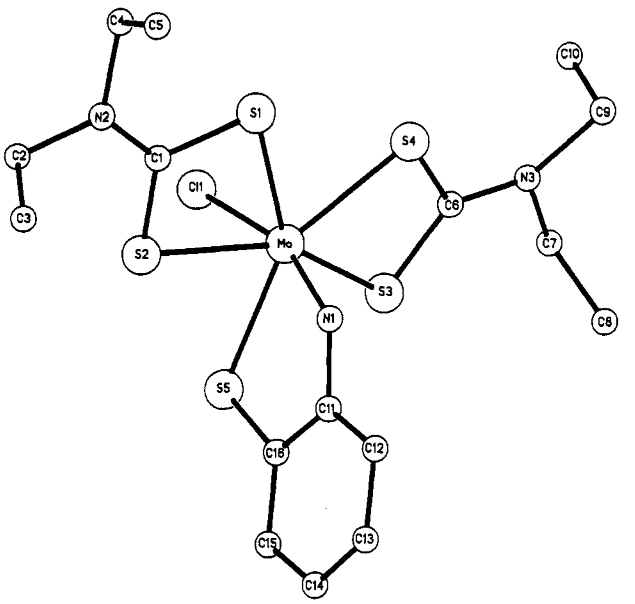


Figure 1. Molecular structure of $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$.

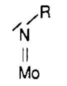
Table V. NMR Properties of $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$ (Chemical Shifts in ppm; Line Widths in Parentheses in Hz)

$^{95}Mo^a$	292 (300)	^{13}C (imido L)^b	170.3
^{14}N (imido N)^a	70 (500)		150.2
^{14}N (free L)^a	−324 (550)		128.7
^{13}C $(S_2CN(C_2H_5)_2)^b$	194.9		128.1
	43.6		121.8
	42.7		116.7
	12.7		
	12.4		

^{a}In CH_2Cl_2. ^{b}In $CDCl_3$.

Two Lewis structures have been proposed for the metal–nitrogen bond in imido complexes.[9] In structure **1**, the nitrogen acts as a four-π-electron donor and a Mo–N–R angle close to 180° is expected; in structure **2**, the nitrogen acts as a two-π-electron donor and the Mo–N–R linkage is bent.

1


2


The imido ligand in $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$ is bidentate, forcing the Mo–N–R linkage into a bent position with an angle of 137.7 (7)°. The nitrogen therefore acts as a two-π-electron donor according to structure **2**. In related complexes with monodentate imido ligands, angles closer to 180° are found, 166.8 (3)° in $Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2$[9] and 178.0 (11)° in $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2$.[12] The molybdenum–nitrogen distance is 1.744 (6) Å compared to 1.734 (4) Å in $Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2$[9] and 1.700 (16) Å in $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2$.[12] The imido nitrogen–aromatic carbon bond (N(1)–C(11)) is 1.366 (14) Å; the corresponding bonds in the other two complexes are approximately 1.38 Å.[9,12] The Cl–Mo–N angle is 159.9 (4)°; the molybdenum–chloride distance is 2.455 (2) Å and does not show any trans effect from the imido bond as found in $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2$, where the molybdenum–chloride bond trans to the imido bond is 2.497 (12) Å. The molybdenum–sulfur bonds average 2.5 Å and do not differ from comparable bond lengths reported previously.

NMR Spectra. The multinuclear NMR data for $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$ are listed in Table V. The molybdenum

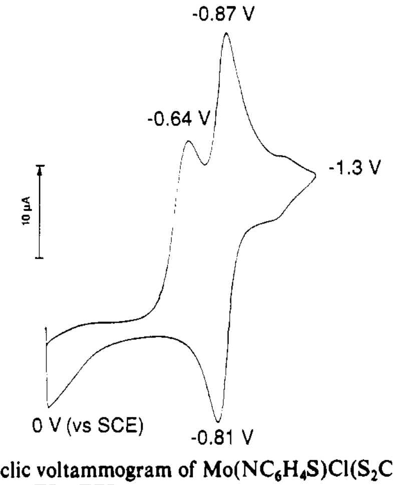


Figure 2. Cyclic voltammogram of $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$ in CH_3CN, 0.1 M TBATFB.

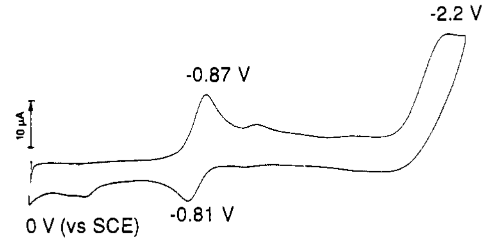


Figure 3. Cyclic voltammogram of $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$ after $1e^-$ reduction in CH_3CN, 0.1 M TBATFB.

center has a ^{95}Mo NMR signal at +292 ppm, a region where generally Mo(VI) oxo complexes are found.[14] This signal is deshielded by acout 500 ppm compared to those of the other molybdenum(VI) imido complexes whose ^{95}Mo NMR chemical shifts are known: $(Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2$, −254 ppm (480 Hz);[15] $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2$, −164 ppm (400 Hz).[12] The deshielding can be attributed to the different geometry and the larger number of sulfur atoms present in $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$. The imido nitrogen absorbs at +70 ppm, at the deshielded end of the chemical shift range for imido nitrogens.[16] It is more deshielded by about 90 ppm compared to those of the other two complexes. It has been found for several groups of complexes that deshielding of the metal center is accompanied by deshielding of the atoms coordinated to the metal center.[17-20]

The ^{13}C NMR data for the dithiocarbamate ligands are not significantly different from those measured for $Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2$ and $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2$.[12] The methylene carbons and the methyl carbons show two different peaks due to their different environments in the complex in solution. The most deshielded peak of the aryl carbons in the imido ligand at 170.3 ppm is assigned to the carbon that binds the sulfur. The peak at 150.2 ppm is assigned to the carbon that binds the nitrogen. In $Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2$ and $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2$, this carbon is more shielded (139 ppm).[12] The carbon–nitrogen distances in these complexes are about 1.38 Å compared to 1.36 Å in $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$. The distance between the free amine nitrogen and the aryl carbon in $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2$ is 1.364 (21) Å, comparable to the imido nitrogen–carbon distance in $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$ (1.366 (14) Å). The carbons in both cases show ^{13}C NMR signals at 150 ppm.

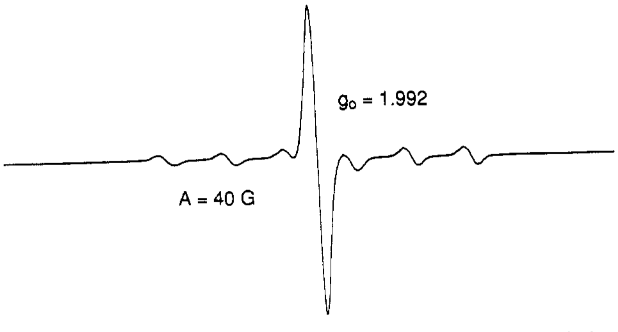


Figure 4. Room-temperature EPR spectrum of $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$ after $1e^-$ reduction in CH_3CN, 0.1 M TBATFB.

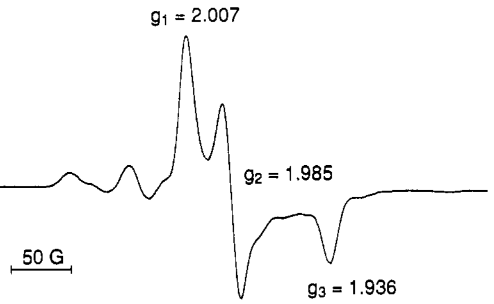


Figure 5. EPR spectrum of $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$ at 96 K after $1e^-$ reduction in CH_3CN, 0.1 M TBATFB.

Electrochemistry. The cyclic voltammogram of $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$ shows two reduction peaks, at −0.64 and 0.87 V (Figure 2). The first reduction is irreversible; the second is quasi-reversible with an oxidation peak at −0.81 V. The red-brown Mo(VI) complex can be reduced coulometrically with one electron at 0.7 V to form a green Mo(V) monomer. The cyclic voltammogram of this complex retains the reduction peak at 0.87 V and the oxidation peak at −0.81 V (Figure 3). The Mo(V) monomer can be reversibly reduced to a brown Mo(IV) complex that has a cyclic voltammogram identical with that of the Mo(V) monomer. The first reduction at −0.64 V is probably irreversible due to the loss of a ligand and a rearrangement of the coordination sphere. The additional electron increases the electron density on the seven-coordinate metal center sufficiently that one ligand, probably the chloride, comes off. The coordination sphere changes with the loss of a ligand so that the reduction, even in the presence of chloride as an electrolyte, is irreversible. When the scan rate for the cyclic voltammograms is increased, the peak at −0.64 V collapses into the peak at −0.87 V at a scan rate of 500 mV/s. The electrochemical behavior of this molybdenum(VI) imido complex is different from that of $Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2$ and $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2$. Both of these complexes show an irreversible two-electron reduction peak in their cyclic voltammograms. When $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2$ is reduced with two electrons, no peaks for the reduced product are observed in the cyclic voltammogram.[12]

EPR Spectra. The Mo(V) monomer that results from the one-electron reduction of $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$ has a room-temperature EPR spectrum with a g_0 value of 1.992 (Figure 4). The high *g* value is due to the large number of sulfurs in the coordination sphere. Both sulfur and chloride in the coordination sphere of molybdenum tend to increase the *g* value toward that of a free electron, 2.0023.[21] The *A* value (40 G) is small and confirms that the electron is delocalized. The frozen-solution EPR spectrum has three different *g* values (Figure 5). This indicates a rhombic symmetry for the Mo(V) monomer. Pariyadath et al. reported a similar g_0 value (1.990) and *A* value (38 G) for the complex $Mo(S_2CN(C_2H_5)_2)(NHC_6H_4S)_2$. The

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(14) Minelli, M.; Enemark, J. H.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Coord. Chem. Rev.* **1985**, *68*, 169.

(15) Minelli, M.; Young, C. G.; Enemark, J. H. *Inorg. Chem.* **1985**, *24*, 1111.

(16) Mason, J. *Chem. Br.* **1983**, 654.

(17) Minelli, M.; Hubbard, J. L.; Christensen, K. A.; Enemark, J. H. *Inorg. Chem.* **1983**, *22*, 2652.

(18) Minelli, M.; Hubbard, J. L.; Lichtenberger, D. L.; Enemark, J. H. *Inorg. Chem.* **1984**, *23*, 2721.

(19) Young, C. G.; Minelli, M.; Enemark, J. H.; Hussain, W.; Jones, C. J.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1987**, 619.

(20) Minelli, M.; Maley, W. J. *Inorg. Chem.* **1989**, *28*, 2954.

(21) Stiefel, E. I. In *Molybdenum and Molybdenum Containing Enzymes*; Coughlin, M. P., Ed.; Pergamon Press: Oxford, U.K., 1980; p 41.

authors do not report the properties of the frozen-solution spectrum for this complex.[22]

Visible Spectra. $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$ has a charge-transfer band in the visible spectrum at 530 nm with an ϵ value of 1000 M^{-1} cm^{-1}. When the Mo(VI) complex is reduced with one electron to the green Mo(V) monomer, two bands are observed in the visible spectrum, one at 610 nm with an ϵ value of 2300 M^{-1} cm^{-1} and a second band at 400 nm with an ϵ value of 15000 M^{-1} cm^{-1}. The Mo(V) monomer can be reduced with one electron to a brown Mo(IV) complex that has a band at 445 nm (ϵ = 10000 M^{-1} cm^{-1}) in the visible spectrum.

Conclusions. The new complex, $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$, is the first example of a molybdenum(VI) complex with a chelating imido ligand. The geometry of the complex is distorted pentagonal bipyramidal. The molybdenum nucleus in this complex, as observed by ^{95}Mo NMR spectroscopy, is deshielded by about 500 ppm; the imido nitrogen, observed by ^{14}N NMR spectroscopy, is deshielded by about 90 ppm compared to that of other seven-coordinate Mo(VI) imido complexes. In contrast to other seven-coordinate Mo(VI) imido compounds, the complex can be reduced with one electron to yield a Mo(V) monomer. The Mo(V) complex can be reversibly reduced with a second electron to a Mo(IV) species. We are currently working on the synthesis of related complexes with different Mo(VI) starting materials to see if a complex with a reversible two-electron redox pathway, as found for molybdenum in hydroxylases, can be isolated.

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Supplementary Material Available: Tables listing the complete structure determination summary, atomic coordinates and equivalent isotropic and anisotropic displacement coefficients for all atoms including H atoms, bond lengths, and bond angles (8 pages); a table of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

(22) (a) Pariyadath, N.; Newton, W. E.; Stiefel, E. I. *J. Am. Chem. Soc.* **1976**, *98*, 5388.

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Steric Control of Tricoordination in Univalent Coinage Metal Complexes: Crystal Structure of Tris(cyclopentyldiphenylphosphine)silver(I) Tetrafluoroborate

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Eighteen complexes of general formula $[M(PR_2R')_3]X$ (M = Cu, Ag, Au; X = BF_4, ClO_4; R = Ph, Cy, C_5H_9) have been isolated and characterized. In the majority of cases, the infrared spectra of the anions indicate that they are not coordinated or, at most, very weakly coordinated. Thus three-coordination is indicated. This intermediate coordination number for univalent coinage metals is produced by steric limitations of the tertiary phosphine ligands. The PR_2R' ligands employed are intermediate in size between tricyclohexylphosphine, which forms two-coordinate complexes, and triphenylphosphine, which forms four-coordinate complexes. Crystals of $[Ag\{PPh_2(C_5H_9)\}_3][BF_4]$ belong to the trigonal space group $P\bar{3}1c$, with a = 13.398 (6) Å, c = 30.509 (10) Å, and Z = 4. The structure refinement converged at R = 0.0551. The structure consists of nonplanar three-coordinate Ag-phosphine complexes and disordered BF_4^- anions. The silver ions are located on sites of 3-fold symmetry (Ag-P = 2.545 (3) Å, P-Ag-P = 117.4 (1)°). The $Ag(PR_2R')_3$ cations are found in pairs about a single disordered BF_4^- anion. Weak Ag-BF_4 interactions (Ag$\cdots$F = 2.54 (2) Å) induce the deformation of the AgP_3 core from planarity.

Introduction

It has been the aim of the research investigations in one of our laboratories to study the role of size and ligation properties of tertiary phosphines (as well as tertiary arsines) upon the stereochemistry of cationic, univalent coinage metal complexes. Prior to this work the only unambiguously characterized, three-coordinate complexes containing three group VB ligands were the $[Au(PPh_3)_3]X$ (X = BPh_4, $B_9H_{12}S$) complexes.[1,2] Triphenylphosphine, despite its cone angle of 145°,[3] forms four-coordinate $[M(PPh_3)_4]^+$ (M = Cu, Ag) cations,[4] but it has been shown recently that larger tertiary phosphine or arsine ligands form two-coordinate complexes with univalent coinage metals.[5] These complexes are frequently distorted from linear coordination because of weak interactions between the anions and the cations. Thus they are effectively precursors of three-coordinate acido complexes. It was believed that if somewhat smaller ligands of this type were to be employed, it should then be possible to prepare three-coordinate, cationic complexes. Construction of molecular models suggested that cycloalkyldiphenylphosphines would be able to form the desired $[M(PRPh_2)_3]^+$ cations. Indeed, that has been observed, and in this paper, we present the results on the new complexes prepared of this type, as well as the structure of one specific compound, $[Ag\{PPh_2(C_5H_9)\}_3]BF_4$.

Table I. Physical Properties of Complexes Containing Three Tertiary Alkylphosphine Ligands

complex	conductivity[a]/S	anion peaks[b]/cm^{-1}	anion symmetry
$[Cu\{PPh(C_5H_9)_2\}_3][ClO_4]$	26.7	1100, 625	T_d
$[Cu(PPhCy_2)_3][BF_4]$	29.4	1050	T_d
$[Cu(BF_4)(PPh_2Cy)_3]$	25.7	1085, 980	C_{3v}
$[Cu(ClO_4)(PPh_2Cy)_3]$	25.5	1115, 1050, 625	C_{3v}
$[Cu\{P(C_5H_9)Ph_2\}_3][BF_4]$	27.6	1050	T_d
$[Cu\{P(C_5H_9)Ph_2\}_3][ClO_4]$	26.7	1090, 620	T_d
$[Cu(BF_4)\{P(C_7H_{13})Ph_2\}_3]$	23.8	1080, 975	C_{3v}
$[Cu\{P(C_7H_{13})Ph_2\}_3][ClO_4]$	25.6	1100, 615	T_d
$[Ag(PCy_2Ph)_3][BF_4]$	26.6	1050	T_d
$[Ag(PCy_2Ph)_3][ClO_4]$	26.6	1085, 620	T_d
$[Ag(PCyPh_2)_3][BF_4]$	24.7	1050	T_d
$[Ag(PCyPh_2)_3][ClO_4]$	26.3	1090	T_d
$[Ag\{P(C_5H_9)Ph_2\}_3][BF_4]$	26.0	1055	T_d
$[Ag\{P(C_7H_{13})Ph_2\}_3][BF_4]$	27.0	1050	T_d
$[Ag\{P(C_7H_{13})Ph_2\}_3][ClO_4]$	26.7	1095, 620	T_d
$[Ag\{P(C_5H_9)Ph_2\}_3][ClO_4]$	26.8	1090, 1070, 620	T_d
$[Au\{PPh_2(C_5H_9)\}_3][ClO_4]$		1090	T_d
$[Au\{PPh_2(Cy)\}_3][ClO_4]$		1100	T_d

[a] Determined on all nitrobenzene solutions. [b] Nujol mull spectra.

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