

Synthesis of Molybdenum Complexes That Contain Silylated Triamidoamine Ligands. A μ -Dinitrogen Complex, Methyl and Acetylide Complexes, and Coupling of Acetylides

Keng-Yu Shih, Richard R. Schrock,* and Rhett Kempe

Department of Chemistry 6-331
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received May 2, 1994

Tetradentate "triamidoamine" ligands of the type $[(R_3\text{-SiNCH}_2\text{CH}_2)_3\text{N}]^{3-}$ ($R_3\text{Si} = \text{Me}_3\text{Si}$ or $t\text{-BuMe}_2\text{Si}$) have been found to form complexes with first-row metals Ti-Fe¹⁻⁴ and tantalum.⁵⁻⁷ This type of ligand forms relatively rigid distorted trigonal bipyramidal or pseudo-four-coordinate "trigonal monopyramidal" complexes in which the apical position is sterically protected to a significant degree by the $R_3\text{Si}$ groups. We have been interested in molybdenum complexes that contain triamidoamine ligands, in part in order to explore the binding and reduction of dinitrogen, and now have found conditions that allow some starting materials to be prepared simply, although so far in only moderate yield. The first results are reported here. They should be compared with a recent report of molybdenum complexes that contain pentafluorophenyl-substituted triamidoamine ligands⁸ and with reports of titanium, vanadium, and molybdenum complexes that contain the $[(\text{MeNCH}_2\text{CH}_2)_3\text{N}]^{3-}$ ligand.⁹⁻¹¹

Reactions between $\text{MoCl}_4(\text{THF})_2$ (in THF) and the $\text{Li}_3[\text{N}_3\text{N}]$ derivatives¹² shown in Scheme 1 yield the d^2 monochloro derivatives **1a** (26%), **1b** (38%), or **1c** (31%).¹³ These compounds, like $\text{Mo}[(\text{C}_6\text{F}_5\text{NCH}_2\text{CH}_2)_3\text{N}]\text{Cl}$,⁸ are paramagnetic, as evidenced by broad, shifted ligand resonances. We assume that their structures are analogous to those of $\text{Mo}[(\text{C}_6\text{F}_5\text{NCH}_2\text{CH}_2)_3\text{N}]\text{Cl}$ ⁸ and $\text{V}[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{Cl}$ ² and, therefore, that their paramagnetism can be ascribed to a degeneracy of the d_{xz} and d_{yz} orbitals (taking the z axis to be the pseudo 3-fold axis). Attempts to prepare $\text{Mo}[(t\text{-BuMe}_2\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{Cl}$ in a similar manner so far has yielded only traces (<5%) of that product.

(1) Cummins, C. C.; Lee, J.; Schrock, R. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *104*, 1501.

(2) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1992**, *11*, 1452.

(3) Cummins, C. C.; Schrock, R. R. *Inorg. Chem.* **1994**, *33*, 395.

(4) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448.

(5) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem.* **1993**, *115*, 758.

(6) Christou, V.; Arnold, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1450.

(7) Freundlich, J. S.; Schrock, R. R.; Cummins, C. C.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 6476.

(8) Kol, M.; Schrock, R. R.; Kempe, R.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 4382.

(9) Plass, W.; Verkade, J. G. *J. Am. Chem. Soc.* **1992**, *114*, 2275.

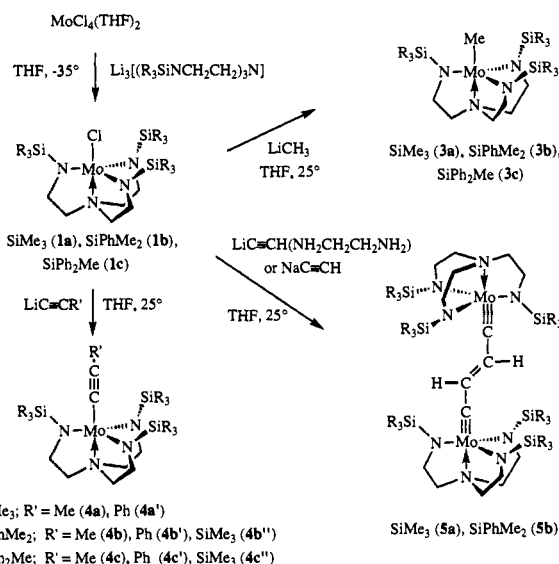
(10) Plass, W.; Verkade, J. G. *Inorg. Chem.* **1993**, *32*, 3762.

(11) Naitani, A. A.; Menge, W. M. P. B.; Verkade, J. G. *Inorg. Chem.* **1991**, *30*, 5009.

(12) $\text{Li}_3[(\text{PhMe}_2\text{SiNCH}_2\text{CH}_2)_3\text{N}]$ and $\text{Li}_3[(\text{Ph}_2\text{MeSiNCH}_2\text{CH}_2)_3\text{N}]$ were prepared in a manner analogous to that reported for $\text{Li}_3[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]$.⁴

(13) For example, for **1b**, $\text{MoCl}_4(\text{THF})_2$ (5.0 g, 12.8 mmol) was added to a 500 mL flask containing $\text{Li}_3[(\text{PhMe}_2\text{SiNCH}_2\text{CH}_2)_3\text{N}]\cdot\text{THF}$ (8.96 g, 14.0 mmol) in ~120 mL of THF at -35 °C. The reaction mixture was allowed to warm slowly to 25 °C and was stirred for 12 h. The resulting dark-brown solution was reduced in volume to ~5 mL, and ether (~30 mL) was added. After 30 min, the red product was collected by filtration and washed with cold ether (3 × 10 mL). The crude product was then extracted with dichloromethane (~120 mL), and the extract was filtered in order to remove LiCl. The dichloromethane was removed in vacuo to give 3.3 g of red, crystalline **1b** (38%): ¹H NMR (C_6D_6) δ 8.8 (br), 8.58 (s), 6.82 (s), 2.0 (s, br), -24.3 (s, br), -94.74 (s, br). Anal. Calcd for $\text{C}_{30}\text{H}_{45}\text{N}_4\text{ClMoSi}_3$: C, 53.20; H, 6.70; N, 8.27. Found: C, 52.93; H, 6.87; N, 8.09. Most other complexes reported here analyzed satisfactorily. See the supplementary material for full details.

Scheme 1



Attempts to prepare "trigonal monopyramidal" complexes,¹ $\text{Mo}[(R_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]$, so far have failed. For example, only **1a** (25% yield) could be isolated from the reaction between $\text{MoCl}_3(\text{THF})_3$ in ether and $\text{Li}_3[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]$ under dinitrogen, while the reaction between $\text{MoCl}_3(\text{THF})_3$ and $\text{Li}_3[(t\text{-BuMe}_2\text{SiNCH}_2\text{CH}_2)_3\text{N}]$ in pentane under dinitrogen gave a paramagnetic pentane-soluble purple complex (**2**) in ~10% yield. No products could be identified when the latter reaction was carried out under argon. An X-ray structure of **2**¹⁴ showed it to be a μ -diazenido(2-) complex of Mo(IV) (Figure 1; Table 1) or alternatively, a μ -dinitrogen complex of Mo(III). The Mo(1)-N(4) bond distance of 1.907 (8) Å, N(4)-N'(4) bond distance of 1.20(2) Å, and Mo(1)-N(4)-N'(4) bond angle of 178(1)° are all consistent with a formulation in which there is considerable π delocalization. These data should be compared with the N-N bond length [1.236(3) Å] and Mo-N bond length [1.819(2) and 1.821(3) Å] in the "hydrazido(4-)" complex, $\text{Cp}^*\text{Me}_3\text{-Mo=N-N=MoCp}^*\text{Me}_3$.¹⁵ The paramagnetism of **2** is consistent with the filling of three of the four pairs of degenerate Mo-N-N-Mo π MOs with 10 π electrons, leaving two unpaired electrons in the level that is antibonding with respect to Mo-N and bonding with respect to N-N.⁸ A significant feature of the structure of **2** is the degree to which the silyl groups are "bent back" (Mo-N-Si \approx 140°), presumably for steric reasons. M-N-Si angles in known monomeric triamidoamine complexes of V and Ta vary from 123° to 128°, and Mo-N-C angles in two pentafluorophenyl complexes⁸ vary from 127° to 128°.

Alkylations of **1a-c** yield the paramagnetic d^2 methyl complexes, **3a-c** (Scheme 1) in high yield, while lithium salts of substituted acetylides react smoothly to give the paramagnetic d^2 acetylide derivatives (**4**) in high yield. The acetylide C≡C stretch can be observed by IR in some cases, for example, at 2021 cm^{-1} in **4b**. When syntheses of Mo-C≡CH complexes are attempted, the products are diamagnetic yellow species derived from the parent acetylides via coupling of the β carbon atoms (Scheme 1). Carbon NMR spectra of **4a** reveal resonances for the alkylidyne-like carbon atom at 285 ppm¹⁶ and for the olefin-like carbon atom at 142 ppm with ¹J_{CH} = 153 Hz and ²J_{CH} = 6.1 Hz [cf. 256 ppm, 142 ppm, and 151 Hz, respectively, in *trans*-

(14) $a = 14.343(3)$ Å; $b = 21.486(5)$ Å; $c = 24.835(6)$ Å; $V = 7653.41$ Å³, $\text{FW} = 1191.89$, $Z = 4$, $\rho(\text{calcd}) = 1.034$ g/cm³, space group $Pbca$, $R = 0.066$; $R_w = 0.068$.

(15) Schrock, R. R.; Kolodziej, R. M.; Liu, A. H.; Davis, W. M.; Vale, M. G. *J. Am. Chem. Soc.* **1990**, *112*, 4338.

(16) Murdzek, J. S.; Schrock, R. R. In *Carbyne Complexes*; VCH: New York, 1988.

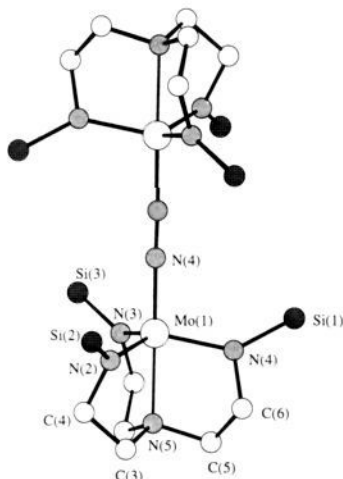


Figure 1. The structure of $[(t\text{-BuMe}_2\text{SiNCH}_2\text{CH}_2)_3\text{N}]_2\text{Mo}_2(\mu\text{-N}_2)$. The *t*-Bu and Me groups on Si have been omitted for clarity.

Table 1. Selected Bond Lengths and Bond Angles for **2**

distances (Å)		angles, (deg)	
Mo(1)–N(4)	1.907(8)	Mo(1)–N(4)–N'(4)	178(1)
Mo(1)–N(1)	2.00(1)	N(4)–Mo(1)–N(5)	179.5(4)
Mo(1)–N(2)	2.023(9)	N(1)–Mo(1)–N(3)	116.6(3)
Mo(1)–N(3)	2.010(9)	N(2)–Mo(1)–N(1)	116.3(4)
Mo(1)–N(5)	2.29(1)	N(3)–Mo(1)–N(2)	117.1(4)
N(4)–N'(4)	1.20(2)	N(1)–Mo(1)–N(5)	79.0(4)
N(1)–Si(1)	1.75(1)	N(2)–Mo(1)–N(5)	80.0(4)
N(2)–Si(2)	1.727(9)	N(3)–Mo(1)–N(5)	79.1(4)
N(3)–Si(3)	1.742(9)	Mo(1)–N(1)–Si(1)	139.7(6)

$(t\text{-BuO})_3\text{W}\equiv\text{CCH}=\text{CHC}\equiv\text{W}(\text{O}-t\text{-Bu})_3^{17}$]. We assume for steric reasons that the configuration about the C=C bond is *trans*, although we have no data that confirm that proposal. This coupling reaction is most closely related to that observed when d^2 tantalum and niobium chlorides react with acetonitrile,^{18,19} and the products are related to those formed from alkyldiyne complexes and enediyne via metathesis reactions.¹⁷ At the present time we assume that coupling of d^2 acetylide complexes is slow when C_β in the acetylide is substituted. Although there are many examples of acetylide couplings,^{20,21} we could find no other example of this "tail-to-tail" type in which each metal is oxidized by two electrons in the process.

(17) Krouse, S. A.; Schrock, R. R. *J. Organomet. Chem.* **1988**, *355*, 257.

(18) Finn, P. A.; King, M. S.; Kilty, P. A.; McCarley, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 220.

(19) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1978**, *17*, 3525.

(20) Evans, W. T.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1993**, *12*, 2618.

(21) Shutowski, D. G.; Stucky, G. D. *J. Am. Chem. Soc.* **1976**, *98*, 1376.

Table 2. Oxidation Potentials for Complexes **1**, **3**, and **4**^a

compound	$E_{1/2}(\text{ox})$ (V)
Me ₃ Si/Cl (1a)	0.05
Me ₂ PhSi/Cl (1b)	0.13
MePh ₂ Si/Cl (1c)	0.25
Me ₃ Si/Me (3a)	−0.36
Me ₂ PhSi/Me (3b)	−0.18
MePh ₂ Si/Me (3c)	−0.03
Me ₃ Si/C≡CMe (4a)	−0.13
Me ₃ Si/C≡CPh (4a')	−0.01
Me ₂ PhSi/C≡CMe (4b)	−0.06
Me ₂ PhSi/C≡CPh (4b')	0.03
Me ₂ PhSi/C≡CSiMe ₃ (4b'')	0.06
MePh ₂ Si/C≡CMe (4c)	0.17
MePh ₂ Si/C≡CPh (4c')	0.16
MePh ₂ Si/C≡CSiMe ₃ (4c'')	0.25

^a In dichloromethane under dinitrogen using 0.1 M $[\text{NBu}_4]^+\text{PF}_6^-$ as the electrolyte and ferrocene as the internal reference (0.47 V). Data were acquired at 200 mV s^{-1} scan speed using a Pt bead electrode. In all cases $i_{p,a} \approx i_{p,c}$ and $E_{p,a} - E_{p,c}$ values are in the range 90–120 mV.

Preliminary electrochemical studies for the chloride, methyl, and acetylide complexes reveal that oxidation is relatively facile and reversible in each case (Table 2). The trends are those expected on the basis of the qualitative relative electron-withdrawing abilities of the SiR_3 groups or X in the $\text{Mo}[(\text{R}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]_2\text{X}$ species, i.e., the ease of oxidation for a given SiR_3 group is $\text{X} = \text{Me} > \text{C}\equiv\text{CMe} > \text{Cl}$, and for a given X the ease of oxidation follows the trend $\text{SiR}_3 = \text{SiMe}_3 > \text{SiMe}_2\text{Ph} > \text{SiMePh}_2$. Preliminary studies suggest that these are one-electron oxidations and that in some cases the cations can be isolated at 25 °C.

The chemistry described here is the first involving high oxidation state Mo complexes that contain silylated triamidoamine ligands. We are continuing to explore the potential utility of triamidoamine ligands for organometallic chemistry and dinitrogen chemistry of the earlier, heavier transition metals in mid to high oxidation states.

Acknowledgment. We thank the National Institutes of Health (GM 31978) and the National Science Foundation (CHE 91 22827) for supporting this research.

Supplementary Material Available: Experimental details for selected compounds, experimental details for the structure study of **2**, an ORTEP representation of **2**, and final positional and final thermal parameters for **2** (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.