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Molybdenum(IV) Azamolybdatranes $ClMo(R_3SiNCH_2CH_2)_3N$ from an Unexpected Reaction

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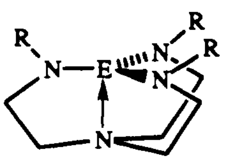
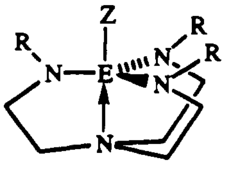
The azamolybdatranes $ClMo(Me_3SiNCH_2CH_2)_3N$, **2a**, and $ClMo(t\text{-}BuMe_2SiNCH_2CH_2)_3N$, **2b**, were prepared by the reaction of $MoCl_3(THF)_3$ and the corresponding lithiated tetramines. The μ_{eff} for **2a** is 2.35 μ_B. This compound was structurally characterized in the solid state by X-ray diffraction. Crystal data: cubic, $a = 17.199(1)$ Å, $V = 5087.6(11)$ Å^3, $Z = 8$, space group $Pa\bar{3}$, $R = 2.7\%$.

Azametallatranes and azanonmetallatranes of type **A** or **B** are typically formed in reactions of the corresponding tripodal triamine ligand as in transamination reactions with $E(NMe_2)_3$ or $E(NMe_2)_4$ ($Z = NMe_2$), respectively, or in reactions of the lithium triamide salt of the ligand with ECl_3 or $ZECl_3$ ($Z = Cl$, O, N), respectively.[1] In the case of **A**, the geometry around E can be either tetrahedral ($E = B^2$) or trigonal monopyramidal ($E = Al,^{2,3}$ $Ti,^4$ $V,^4$ $Cr,^4$ $Mn,^4$ Fe^4).



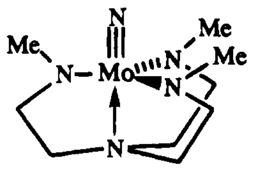
A



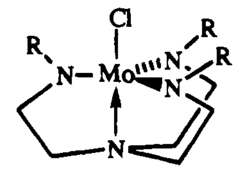
B

We have been investigating nucleophilic displacement reactions of Z substituents in **B**. For example, for E = Ti, the rate of displacement of $Z = NR'_2$ by alcohols and phenols proceeds in the unexpected order R′ = Et > Me and a rationale based on a protonated intermediate was substantiated experimentally.[5] Where E = Si in **B**, we have shown that Z = Cl can be nucleophilically displaced by carbanionic sources in the expected manner when R = H but that the product can possess Z = F or H arising from β elimination from the carbanion when the cage is adorned with more sterically hindering R groups.[6,7]

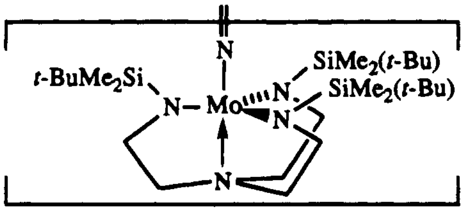
Following our earlier report of the nitrido Mo(VI) compound **1**,[8] we thought it would be interesting to synthesize a Mo(III) analogue of type **A** in order to oxidize it with a variety of reagents that would allow us to examine the reactivity of the Z substituent in the corresponding **B** structure. In a recent communication,[9] Schrock and co-workers reported that attempts to synthesize such a compound had failed and that, for example, only **2a** could be isolated in reaction 1 under dinitrogen. These investigators further disclosed that a similar reaction with $Li_3[(t\text{-}BuMe_2SiNCH_2CH_2)_3N]$ under dinitrogen gave purple **3**, whereas no product could be identified when the reaction was carried out under argon.[9]



1



2a, R = $SiMe_3$
2b, R = $t\text{-}BuMe_2Si$
2c, R = C_6F_5



3

$$MoCl_3(THF)_3 + Li_3[Me_3SiNCH_2CH_2)_3N] \rightarrow \mathbf{2a} \quad (1)$$

These results prompt us to report that our attempts to synthesize a Mo(III) complex of type **A** have also failed and that we too isolated **2a**, whose structure we also determined by X-ray means and characterized by magnetic susceptibility measurements. In addition, we report that when the analogous reaction is carried out with $Li_3[(t\text{-}BuMe_2SiNCH_2CH_2)_3N]$ under argon, **2b** can be isolated.

Experimental Section

General Procedures. All reactions were carried out under argon using Schlenk or drybox techniques.[10] Solvents were dried over and distilled from Na/benzophenone under dinitrogen and stored over 4 Å molecular sieves under an argon atmosphere prior to use. $MoCl_3(THF)_3$[11] and $Li_3[(Me_3SiNCH_2CH_2)_3N]$[12] were prepared using literature methods.

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^1H NMR spectra were recorded at 20 °C on a Nicolet NT 300 or a Varian VXR 300 with deuterated solvents as internal locks. Mass spectra were obtained on a Finnigan 4000 low-resolution (70 eV, EI) and a Kratos MS-50 high resolution instrument. The masses are reported for the most abundant isotope present. IR spectra (4000–400 cm^{-1}) were taken on an IBM/Bruker IR-98 or a Digilab FTS-7 FTIR spectrometer as KBr pellets. Magnetic susceptibility measurements were performed in the range 6–300 K using a squid magnetometer. The susceptibilities have been corrected for the sample holder and the diamagnetic cores of **2a**. Elemental analyses were carried out by Desert Analytics. Melting points were measured in sealed capillaries with a Thomas-Hoover apparatus.

Compound 2a. A 100 mL Schlenk flask was charged with 0.760 g (2.00 mmol) of $Li_3[(Me_3SiCH_2CH_2)_3N$ and 0.850 g (2.03 mmol) of $MoCl_3(THF)_3$. With the flask cooled to −50 °C, 60 mL of pentane was added under argon. The reaction mixture was allowed to warm and then was stirred for 4 days at room temperature. A gray solid was filtered off and washed with 3 × 5 mL of pentane. The filtrate and the washings were combined, and the volume of the solution was reduced to about 5 mL. The solution was kept in a freezer for 2 days, which allowed red crystals to form. After filtration at −50 °C and washing with cold pentane, 0.196 g of crystalline **2a** was obtained in 20% yield. No melting point was observed up to 320 °C. ^1H NMR (C_6D_6, 20 °C): δ 6.20 (s, br, $\Delta\nu_{1/2}$ = 82 Hz, $Si(CH_3)_3$), −23.27 (s, br, $\Delta\nu_{1/2}$ = 390 Hz, CH_2). Low-resolution MS (EI), *m/z* (ion (M represents a group of peaks due to isotope distributions), relative intensity): 491 (M^+, 5.2), 476 ($M - CH_3^+$, 0.9), 456 ($M - Cl^+$, 2.0), 418 ($M - SiMe_3^+$, 0.2), 383 ($M - Cl - SiMe_3^+$, 2.2), 355 ($M - Cl - CH_2NSiMe_3$, 3.5), 171 (7.9), 157 (3.1), 147 (11.1), 130 (5.6), 116 ($CH_2CH_2NHSiMe_3^+$, 4.9), 102 ($CH_2NHSiMe_3^+$, 6.3), 73 ($SiMe_3^+$, 100). FTIR (KBr, cm^{-1}): 2951 s, 2901 s, 2860 s, 1595 m, 1447 m, 1406 w, 1244 s, 1132 w, 1063 m, 943 s, 914 s, 841 vs, 781 m, 756 m, 681 m, 473 w, 459 w. Anal. Calcd for $C_{15}H_{39}ClMoN_4Si_3$: C, 36.68; H, 8.00; N, 11.41. Found: C, 35.94; H, 8.21; N, 11.48. Attempts to isolate further product from the filtrate by SiO_2 column chromatography were unsuccessful.

Compound 2b. In 50 mL of pentane at −78 °C was dissolved 2.37 g (4.85 mmol) of $(t\text{-}BuMe_2SiNHCH_2CH_2)_3N$. To this was slowly added 5.84 mL (14.9 mmol) of 2.5 M *n*-BuLi in hexane. The solution was warmed to room temperature and stirred for 2 h. It was then transferred into a suspension of $MoCl_3(THF)_3$ (2.33 g, 5.57 mmol) in ~20 mL of pentane at −78 °C. The reaction mixture was allowed to warm gradually to room temperature and to stir for 2 days. LiCl was removed from the dark brown solution by filtration, and the volatile components were removed *in vacuo* to give an oily product, which was dissolved in *ca.* 7 mL of pentane. The solution was chilled to −40 °C for 2 days to give purple crystals. After filtration at −50 °C and washing with cold pentane, 0.308 g of **2b** was obtained in 10% yield; mp 123 °C dec. ^1H NMR (C_6D_6, 20 °C): δ 6.13 (s, br, $\Delta\nu_{1/2}$ = 121 Hz, $SiCH_3$), 3.83 (s, br, $\Delta\nu_{1/2}$ = 68 Hz, $C(CH_3)_3$). Low-resolution MS (EI), *m/z* (ion (M represents a group of peaks due to isotope distributions), relative intensity): 617 (M^+, 0.2), 344 (15.8), 313 (5.3), 213 (32.5), 199 (6.5), 187 (6.0), 185 (2.7), 158 (14.8), 132 (15.4), 95 (10.8), 93 (27.2), 75 (100). HRMS (EI), *m/z*: calcd for $C_{24}H_{57}ClMoN_4Si_3$ (M^+), 618.263 46; found, 618.262 22; error 2.00 ppm. FT-IR (KBr pellet, cm^{-1}): 2953 s, 2919 s, 2880 m, 2855 s, 1252 s, 1119 m, 934 s, 887 s, 832 vs, 7772 s, 672 m, 575 w.

Crystal Structure Determination of 2a. A red cubic crystal of **2a** was attached to the tip of a glass fiber and mounted on the P4RA diffractometer for data collection. The cell constants for the data collection were determined from reflections found from a rotation photograph. High-angle cell constants were determined from a subset of intense reflections in the range 35.0–50.0° 2θ. Lorentz and polarization corrections were applied. A nonlinear correction based on the decay in the standard reflections was applied to the data, and a series of azimuthal reflections was collected. A semiemperical absorption correction based on the azimuthal scans was applied to the data.

The space group was uniquely determined on the basis of systematic absences. This assumption proved to be correct as found by a successful direct-methods solution[13] and subsequent refinement. All non-hydrogen atoms were placed directly from the *E* map. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as riding atoms with C–H distances of 0.96 Å with individual isotropic displacement parameters, except that methyl groups were refined with a common parameter. Crystal data and experimental conditions for data collection, and structure refinement are listed in Table 1. The atomic coordinates and equivalent isotropic displacement parameters are collected in Table 2, and selected bond lengths and bond angles are given in Table 3.

Table 1. Crystal Data for **2a**

formula	$C_{15}H_{39}ClMoN_4Si_3$
fw	491.15
a (Å)	17.199(1)
V (Å^3)	5087.6(11)
Z	8
space group	$Pa\bar{3}$
T (°C)	-60 ± 1
d_{calcd} (g/cm^3)	1.281
μ (mm^{-1})	6.567
transm coeff	0.6064/0.8508
R^a	0.0272
$R_w{}^b$	0.0306

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = \sum(w^{1/2}(|F_o| - |F_c|))/\sum(w^{1/2}|F_o|)$; $w = 1/\sigma^2(|F_o|)$.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for **2a**

atom	*x*	*y*	*z*	$U_{eq}{}^a$
Mo	2039(1)	2039(1)	2039(1)	16(1)
Cl	2844(1)	2844(1)	2844(1)	36(1)
N(1)	1306(2)	1306(2)	1306(2)	24(1)
C(1)	507(2)	1618(2)	1355(3)	37(2)
C(2)	535(2)	2491(2)	1372(3)	35(2)
N(2)	1147(2)	2753(2)	1913(2)	24(1)
Si	1050(1)	3710(1)	2260(1)	32(1)
C(3)	1810(3)	4351(3)	1843(3)	50(2)
C(4)	97(3)	4110(3)	1954(3)	65(2)
C(5)	1067(3)	3744(3)	3340(3)	50(2)

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

Table 3. Selected Bond Distances (Å) and Angles (deg) for **2a**

	Distances		
Mo–Cl	2.398(2)	Mo–N(1)	2.185(5)
Mo–N(2)	1.976(3)	Mo–N(2A)	1.976(3)
Mo–N(2B)	1.976(3)		
	Angles		
Cl–Mo–N(1)	180.0(1)	C(2)–N(2)–Si	115.6(2)
N(1)–Mo–N(2)	81.2(1)	N(2)–Mo–N(2A)^a	117.7(1)
N(1)–Mo–N(2A)	81.2(1)	N(1)–Mo–N(2B)	81.2(1)
N(2)–Mo–N(2B)^a	117.7(1)	N(2A)–Mo–N(2B)^a	117.7(1)
Mo–N(2)–C(2)	115.7(2)	Mo–N(2)–Si	128.2(2)

^{a} N(2), N(2A), and N(2B) are related by a crystallographic 3-fold rotation, e.g., (*x*, *y*, *z*), (*y*, *z*, *x*), and (*z*, *x*, *y*) operations.

Discussion

The formation of **2a** and **2b** from $MoCl_3(THF)_3$ and the lithium salts of the corresponding tripodal amine indicates the operation of a disproportionation reaction. Although XPS analysis for molybdenum oxidation states could not be carried out on the oily product mixture afforded by reaction 1, GC-MS analysis of the volatile components collected in a liquid-nitrogen-cooled trap revealed the presence of $(Me_3Si)_2O$, $C_4H_9OSiMe_3$, pentane, THF, and several unidentifiable species. The reactivity of THF that leads to the formation of the first two products suggests that it also may play a role in oxidizing Mo(III) to Mo(IV). Efforts to increase the 20% yield of **2a** by employing $MoCl_4(THF)_2$ instead of $MoCl_3(THF)_3$ resulted in a yield of only 16% for reasons that are not clear.

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[13] SHELXTL-PLUS, Siemens Analytical X-ray, Inc., Madison, WI.

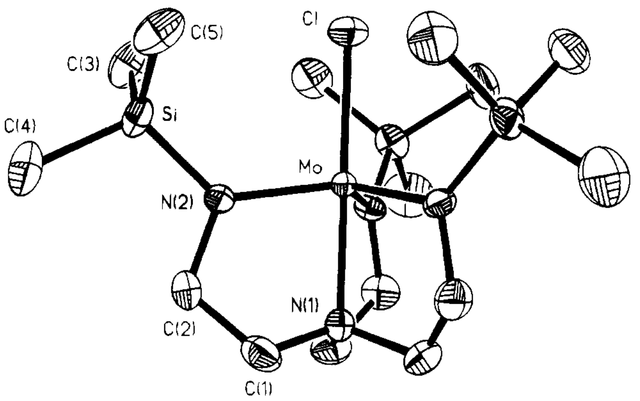
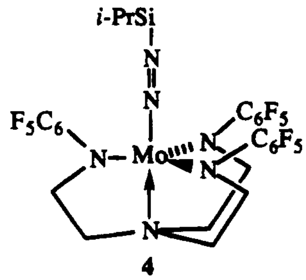


Figure 1. Molecular structure and atomic numbering scheme for **2a**, with ellipsoids drawn at the 50% probability level.

The paramagnetism of **2a** as evidenced by its broad and shifted ^1H NMR spectrum (see Experimental Section) is confirmed by its μ_{eff} of 2.35 μ_B (with a Curie–Weiss behavior above 100 K of $\Theta = 0.148$ K). This μ_{eff} value is close to that reported for $MoCl_4$ (2.1 μ_B[14]).

Although we were able to observe a parent peak for **2b** in its high-resolution mass spectrum, repeated elemental analyses for this crystalline, though highly air-sensitive, compound were unsatisfactory.

Crystal Structure of 2a. The slightly distorted TBP structure of **2a** shown in Figure 1 exhibits a transannular bond of 2.185(5) Å, which is considerably shorter than the average of the distances reported for Mo-coordinated tertiary amines (2.372 Å[15]), somewhat shorter than that in **3** (2.29(1) Å[9]), and comparable with this distance reported for **2c** (2.182(3) Å[16]) and **4** (2.218(9) Å[16]). The average $Mo-N_{eq}$ distance of 1.976(3) Å in **2a** is in the vicinity of that reported for **2c** (average 1.963(3) Å[16]) and **3** (average 2.011(9) Å[9]) though shorter than that in **4** (average 2.069(9) Å[16]). It had been suggested that the short $Mo-N_{ax}$ and $Mo-N_{eq}$ bond lengths in **2c** might be associated with the presence of the electronegative C_6F_5 substituents, but the comparable metrics we observe in **2a** render this suggestion somewhat doubtful.



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The Mo–Cl distance of 2.398(2) Å in **2a** is comparable to the average of 2.410 Å for this bond in other compounds[15] (albeit in a variety of molybdenum oxidation states), but it is longer than that recorded for **2c** (average 2.366(1) Å[16]). This may be attributed to steric repulsions between the chlorine and the $SiMe_3$ group in **2a** whereas in **2c** the C_6F_5 substituents form a "bowl" around the chlorine.[16] The protrusion of the Mo atom above the equatorial nitrogen plane in **2a** (0.302 Å) is virtually the same as that in **2c** (0.32 Å[16]). As is typical in azatrane structures, each equatorial nitrogen in **2a** possesses a quite planar stereochemistry, with the average sum of the angles around it equal to 359.5(2)°.

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Supplementary Material Available: Tables of complete crystal structure data, bond lengths and angles, anisotropic thermal parameters, and hydrogen coordinates and isotropic thermal parameters (7 pages). Ordering information is given on any current masthead page.

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