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Synthesis of Triamidoamine Complexes of Niobium

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Several vanadium[1−5] and tantalum[6−8] complexes that contain triamidoamine ligands of the type $[(\mathrm{Me_3SiNCH_2CH_2})_3\mathrm{N}]^{3-}$ ($[\mathrm{N_3N}]^{3-}$)[9,10] have been reported. It would seem likely that analogous triamidoamine complexes of niobium could be prepared, since although niobium complexes that contain one or more $[\mathrm{NR_2}]^-$ ligands are relatively rare, examples have been reported where R is an alkyl,[11−13] aryl,[14] or silyl[14,15] group. We report here the synthesis of several Nb[N$_3$N] complexes. Although we have not yet been able to manipulate these species to the degree that has been achieved in tantalum chemistry,[7,8,16] we believe this goal eventually will be realized.

Results

Reactions between $\mathrm{NbCl_5}$, $\mathrm{NbR_2Cl_3}$ complexes (R = Me,[17] $\mathrm{CH_2CMe_3}$[18]), or $\mathrm{NbCl_3(dme)}$[19] and $\mathrm{Li_3[N_3N]}$ afforded products that we have not been able to characterize. The reaction between $\mathrm{NbCl_4(THF)_2}$ and $\mathrm{Li_3[N_3N]}$ in tetrahydrofuran at −35 °C affords a brown-purple solid that is a mixture of $\mathrm{[N_3N]Nb{=}O}$ (*vide infra*) and an unknown species identified by broad resonances at ∼3.3, 0.0, and −6.0 ppm. While this unknown has a proton NMR spectrum similar to that for complexes of the type [N$_3$N]NbOR (*vide infra*), its isolation and complete characterization are hampered by its extreme solubility in common organic solvents. The failure of the reaction between $\mathrm{NbCl_4(THF)_2}$ and $\mathrm{Li_3[N_3N]}$ to yield [N$_3$N]NbCl cleanly is somewhat surprising, given the well-known reactions between $\mathrm{NbCl_4(THF)_2}$ and lithium amides to form niobium(IV) amido species.[14,20]

Only two reactions have yielded isolable Nb[N$_3$N] complexes so far. The reaction between $\mathrm{NbOCl_3(THF)_2}$[21] and $\mathrm{Li_3[N_3N]}$ in diethyl ether at −35 °C affords $\mathrm{[N_3N]Nb{=}O}$ (**1**) as a white crystalline solid in 81% yield (eq 1). The Nb═O stretch could not be located in the IR spectrum of **1**. (It is most likely obscured by N−Si absorptions in the 800−1000 cm^{-1} region.) $\mathrm{Nb(NSiMe_3)Cl_3(py)_2}$[22] reacts with $\mathrm{Li_3[N_3N]}$ in diethyl ether at −35 °C to afford white crystalline **2** in 53% yield (eq 2). Presumably these C_3-symmetric species contain pseudo-triply-bound oxo and imido ligands that utilize all three orbitals (d_{xz}, d_{yz}, d_{z^2} or a related σ orbital) that are available for stabilizing a metal−ligand triple or pseudo triple bond.[8,10,23−27]

$$\mathrm{NbOCl_3(THF)_2} \xrightarrow[\text{diethyl ether, − 35 °C}]{\mathrm{Li_3[N_3N]}} \underset{\mathbf{1}}{\mathrm{[N_3N]Nb{=}O}} \tag{1}$$

$$\mathrm{Nb(NSiMe_3)Cl_3(py)_2} \xrightarrow[\text{diethyl ether, −35 °C}]{\mathrm{Li_3[N_3N]}} \underset{\mathbf{2}}{\mathrm{[N_3N]Nb{=}NSiMe_3}} \tag{2}$$

$\mathrm{[N_3N]Nb{=}NSiMe_3}$ (0.01 M in diethyl ether) does not react with 1 equiv of methyl triflate, aniline, or pivaldehyde over a period of days at room temperature. It does react with 3 equiv of 2,6-lutidinium triflate, but no product could be identified.

$\mathrm{[N_3N]Nb{=}O}$ reacts with excess triethylaluminum in pentane at −35 °C to afford what we presume to be the C$_3$-symmetric monoadduct in 84% yield as white crystals (eq 3). The three equivalent ethyl groups on Al are characterized by triplet and quartet resonances at 1.67 and 0.44 ppm, respectively, in the ^{1}H NMR spectrum and quartet ($^1J_{\mathrm{CH}}$ = 123 Hz) and triplet ($^1J_{\mathrm{CH}}$ = 108 Hz) resonances at 12.1 and 5.1 ppm, respectively, in the ^{13}C NMR spectrum. An ^{27}Al NMR spectrum of **3** shows a broad singlet at 180 ppm (cf. 154 ppm for $\mathrm{AlEt_3}$).

$$\underset{\mathbf{1}}{\mathrm{[N_3N]Nb{=}O}} \xrightarrow[\text{pentane, −35 °C}]{\mathrm{AlEt_3}} \underset{\mathbf{3}}{\mathrm{[N_3N]Nb{=}O{\cdot}AlEt_3}} \tag{3}$$

Reactions between **1** and $\mathrm{Me_3SiX}$ (X = OTf, I) in dichloromethane afford **4a** and **4b** quantitatively (eq 4). Both siloxides are proposed to contain non-coordinated triflates, on the basis of their insolubility in diethyl ether, solubility in tetrahydrofuran and dichloromethane, and steric constraints within the apical "pocket" in triamidoamine complexes in general.[10] A 0.01 M solution of **1** in diethyl ether does not react with 5 equiv of trimethylchlorosilane after stirring the mixture for 1 day at room temperature. $\mathrm{[N_3N]Nb{=}O}$ reacts with methyl triflate to afford

$$\underset{\mathbf{1}}{\mathrm{[N_3N]Nb{=}O}} \xrightarrow[\mathrm{CH_2Cl_2},\ \text{−35 °C}]{\mathrm{Me_3SiX}} \underset{\mathrm{X\,=\,OTf\ (\mathbf{4a}),\ I\ (\mathbf{4b})}}{\mathrm{[N_3N]NbOSiMe_3{}^{+}X^{-}}} \tag{4}$$

$$\underset{\mathbf{1}}{\mathrm{[N_3N]Nb{=}O}} \xrightarrow[\mathrm{CH_2Cl_2},\ \text{−35 °C}]{\mathrm{MeOTf}} \underset{\mathbf{5}}{\mathrm{[N_3N]NbOMe^{+}OTf^{-}}} \tag{5}$$

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$[N_3N]NbOMe^+OTf^-$ (**5**) quantitatively (eq 5), although a 0.03 M solution of **1** in dichloromethane fails to react with 1 equiv of methyl iodide after 1 day at room temperature. No further reaction is observed in the presence of excess silylating or methylating reagent at 25 °C.

Reduction of **4a**, **4b**, or **5** with sodium amalgam in tetrahydrofuran yields blue-purple $[N_3N]NbOSiMe_3$ (**6a**) or blue $[N_3N]NbOMe$ (**6b**) in 82−91% yields (eq 6). Proton NMR spectra

$$\underset{\mathbf{4a},\ \mathbf{4b},\ \mathbf{5}}{[N_3N]NbOR^+X^-} \xrightarrow[\text{THF, } -35\ ^\circ\text{C}]{\text{Na/Hg}} \underset{R = SiMe_3\ (\mathbf{6a}),\ Me\ (\mathbf{6b})}{[N_3N]NbOR} \qquad (6)$$

of these species feature broad singlets in the +3 to −3 ppm window for TMS or methyl groups and one resonance for one of the two types of ligand methylene units. The resonance for the second set of ligand methylene hydrogens is apparently too broad to be observed. In comparison, both ligand methylene resonances can be observed in the proton NMR spectrum of $[N_3N]VCl$, but one of them is an extremely broad singlet ($\Delta\nu_{1/2}$ = 310 Hz) at −46.13 ppm.[1]

The successful synthesis of these Nb(V) and Nb(IV) complexes contrasts with our failure to prepare a niobium(III) trigonal-monopyramidal species. The successful preparation of a triamidoamine complex of niobium(III) may rest on the development of ligands more robust than $[N_3N]^{3-}$ (cage degradation has been observed for related tantalum complexes[7,8]) and/or new methods for placing these ligands on niobium(V) that avoid unproductive reduction of the metal or loss of a trimethylsilyl group to give trimethylchlorosilane.

Experimental Section

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques, unless otherwise noted. Reagent grade solvents were purified by standard methods. $NbOCl_3(THF)_2$,[21] $Nb(NSiMe_3)Cl_3(py)_2$,[22] and $Li_3[N_3N]$[2] were prepared according to literature methods.

^1H and ^{13}C NMR data are listed in parts per million downfield from TMS, while ^{19}F NMR data are listed in parts per million downfield from trifluoroacetic acid (δ −76.53) and ^{27}Al NMR data are listed in parts per million downfield from hexaaquoaluminum(III) (δ 0.00). Routine coupling constants are usually not reported; those listed are in units of Hz. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses (C, H, N) were performed by Oneida Research Services, Whitesboro, NY, or on-site using a Perkin-Elmer 2400 CHN analyzer.

[N$_3$N]Nb═O (1). $NbOCl_3(THF)_2$ (2.341 g, 6.51 mmol) and $Li_3[N_3N]\cdot THF_2$ (3.417 g, 6.51 mmol) were added to 100 mL of diethyl ether that had been cooled to −35 °C. The mixture was stirred for 24 h at room temperature and filtered through Celite. The brown filtrate was concentrated in vacuo to afford a solid that was recrystallized from pentane at −35 °C to give white crystals: yield 2.467 g (5.26 mmol, 81%); ^1H NMR (C_6D_6) δ 3.20 (t, 6, CH_2), 2.23 (t, 6, CH_2), 0.45 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 54.2 (t, $^1J_{CH}$ = 136, CH_2), 49.4 (t, $^1J_{CH}$ = 134, CH_2), 2.1 (q, $^1J_{CH}$ = 118, $SiMe_3$). Anal. Calcd for $NbSi_3N_4C_{15}H_{39}O$: C, 38.44; H, 8.39; N, 11.95. Found C, 38.26; H, 8.32; N, 11.98.

[N$_3$N]Nb═NSiMe$_3$ (2). A solution of $Nb(NSiMe_3)Cl_3(py)_2$ (366 mg, 0.823 mmol) in 20 mL of diethyl ether was cooled to −35 °C, and $Li_3[N_3N]\cdot THF_2$ (432 mg, 0.823 mmol) was added. The reaction mixture was stirred for 13 h at room temperature and filtered through Celite. The brown filtrate was taken to dryness in vacuo, and the residue was recrystallized from pentane at −35 °C to give white crystals: yield 555 mg (1.03 mmol, 53%): ^1H NMR (C_6D_6) δ 3.16 (t, 6, CH_2), 2.19 (t, 6, CH_2), 0.52 (s, 9, $SiMe_3$), 0.36 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 58.7 (t, $^1J_{CH}$ = 139, CH_2), 49.3 (t, $^1J_{CH}$ = 136, CH_2), 4.7 (q, $^1J_{CH}$ = 118, $SiMe_3$), 2.7 (q, $^1J_{CH}$ = 120, $SiMe_3$). Anal. Calcd for $NbSi_4N_5C_{18}H_{48}$: C, 40.05; H, 8.96; N, 12.97. Found: C, 40.10; H, 8.83; N, 12.81.

[N$_3$N]Nb═O·AlEt$_3$ (3). Triethylaluminum (197 μL, 1.44 mmol) was added to a −35 °C solution of $[N_3N]Nb{=}O$ (337 mg, 0.719 mmol) in 15 mL of pentane. A white precipitate formed immediately. After 28 h the cloudy white solution was taken to dryness in vacuo and the residue was extracted with 50 mL of diethyl ether. The solution was filtered through Celite, and the filtrate was concentrated in vacuo to afford white crystals: yield 354 mg (0.607 mmol, 84%); ^1H NMR (toluene-d_8) δ 3.05 (t, 6, CH_2), 2.14 (t, 6, CH_2), 1.67 (t, 9, CH_3), 0.44 (q, 6, CH_2), 0.26 (s, 27, $SiMe_3$); ^{13}C NMR (toluene-d_8) δ 60.4 (t, $^1J_{CH}$ = 135, CH_2), 51.3 (t, $^1J_{CH}$ = 137, CH_2), 12.1 (q, $^1J_{CH}$ = 123, $CH_2\mathit{CH_3}$), 5.1 (t, $^1J_{CH}$ = 108, $\mathit{CH_2}CH_3$), 1.6 (q, $^1J_{CH}$ = 119, $SiMe_3$); $^{27}Al\{^1H\}$ NMR (C_6D_6) δ 180. Anal. Calcd for $NbSi_3N_4OAlC_{21}H_{54}$: C, 43.28; H, 9.34; N, 9.61. Found: C, 42.80; H, 9.28; N, 9.76.

[N$_3$N]NbOSiMe$_3$$^+OTf^-$ (4a). Trimethylsilyl triflate (413 μL, 2.13 mmol) was added to a −35 °C solution of $[N_3N]Nb{=}O$ (1.00 g, 2.13 mmol) in 40 mL of dichloromethane. The colorless solution turned yellow immediately. After 24 h the yellow solution was concentrated in vacuo to provide a yellow solid that was washed with 10 mL of −35 °C diethyl ether and then dried in vacuo. Light yellow crystals were collected: yield 1.42 g (2.06 mmol, 97%); ^1H NMR (CD_2Cl_2) δ 3.82 (t, 6, CH_2), 3.13 (t, 6, CH_2), 0.43 (s, 9, $OSiMe_3$), 0.30 (s, 27, $NSiMe_3$); ^{13}C NMR (CD_2Cl_2) δ 62.7 (t, $^1J_{CH}$ = 138, CH_2), 54.5 (t, $^1J_{CH}$ = 139, CH_2), 3.6 (q, $^1J_{CH}$ = 118, $OSiMe_3$), 1.2 (q, $^1J_{CH}$ = 120, $NSiMe_3$); $^{19}F\{^1H\}$ NMR (CD_2Cl_2) δ −78.9; IR (Nujol, background subtracted) 1276 cm^{-1} (s, ν(OTf)). Anal. Calcd for $NbSi_4N_4O_4F_3SC_{19}H_{48}$: C, 33.03 H, 7.00; N, 8.11. Found: C, 33.34; H, 7.30; N, 8.36.

[N$_3$N]NbOSiMe$_3$$^+I^-$ (4b). Trimethylsilyl iodide (425 μL, 2.99 mmol) was added to a −35 °C solution of $[N_3N]Nb{=}O$ (700 mg, 1.49 mmol) in 30 mL of dichloromethane. The reaction mixture turned orange-red immediately. After 24 h the mixture was taken to dryness in vacuo and the residue was recrystallized from a mixture of pentane and dichloromethane (10:1) at −35 °C. Light yellow crystals were collected: yield 957 mg (1.43 mmol, 96%); ^1H NMR (CD_2Cl_2) δ 3.84 (t, 6, CH_2), 3.23 (t, 6, CH_2), 0.42 (s, 9, $OSiMe_3$), 0.30 (s, 27, $NSiMe_3$); ^{13}C NMR (CD_2Cl_2) δ 62.9 (t, $^1J_{CH}$ = 141, CH_2), 54.6 (t, $^1J_{CH}$ = 139, CH_2), 3.6 (q, $^1J_{CH}$ = 120, $OSiMe_3$), 1.3 (q, $^1J_{CH}$ = 120, $NSiMe_3$). Anal. Calcd for $NbSi_4N_4OC_{18}H_{48}I$: C, 32.33; H, 7.23; N, 8.38. Found: C, 32.52; H, 7.58; N, 8.22.

[N$_3$N]NbOMe$^+$OTf$^-$ (5). Methyl triflate (241 μL, 2.13 mmol) was added to a −35 °C solution of $[N_3N]Nb{=}O$ (500 mg, 1.07 mmol) in 20 mL of dichloromethane. The colorless solution turned yellow. After 24 h the yellow solution was taken to dryness in vacuo and the resulting yellow solid was recrystallized from a mixture of pentane and dichloromethane (10:1) at −35 °C. Lemon yellow crystals were collected: yield 651 mg (1.03 mmol, 96%); ^1H NMR ($CDCl_3$) δ 4.43 (s, 3, OMe), 3.79 (t, 6, CH_2), 3.20 (t, 6, CH_2), 0.16 (s, 27, $SiMe_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 65.9 (OMe), 59.4 (CH_2), 53.4 (CH_2), 1.0 ($SiMe_3$); $^{19}F\{^1H\}$ NMR (CD_2Cl_2) δ −78.9; IR (Nujol, background subtracted) 1276 cm^{-1} (s, ν(OTf)). Anal. Calcd for $NbSi_3N_4O_4F_3SC_{17}H_{42}$: C, 32.27; H, 6.69; N, 8.85. Found: C, 31.97; H, 6.84; N, 8.58.

[N$_3$N]NbOSiMe$_3$ (6a). (a) From [N$_3$N]NbOSiMe$_3$$^+OTf^-$. Sodium amalgam (0.5 wt % Na, 2.32 mmol) was added to a −35 °C solution of $[N_3N]NbOSiMe_3^+OTf^-$ (800 mg, 1.16 mmol) in 40 mL of tetrahydrofuran. The yellow-orange solution turned purple after approximately 2 min. After 6 h, the purple solution was decanted from the remaining amalgam and was concentrated to dryness in vacuo. The purple solid was extracted with 25 mL of pentane, and the extract was filtered through Celite. The blue-purple filtrate was concentrated and cooled to −35 °C to yield blue-purple crystals: yield 571 mg (1.05 mmol, 91%); ^1H NMR (C_6D_6) δ 3.23 (br s, 27, $NSiMe_3$), 1.28 (br s, 9, $OSiMe_3$), −3.23 (br s, 6, CH_2). Anal. Calcd for $NbSi_4N_4OC_{18}H_{48}$: C, 39.90; H, 8.93; N, 10.34. Found: C, 40.17; H, 9.22; N, 10.35.

(b) From [N$_3$N]NbOSiMe$_3$$^+I^-$. Sodium amalgam (0.5 wt % Na, 1.76 mmol) was added to a −35 °C solution of $[N_3N]NbOSiMe_3^+I^-$ (590 mg, 0.882 mmol) in 20 mL of tetrahydrofuran. The yellow-orange solution turned purple after approximately 2 min. The product was isolated as described in (a): yield 391 mg (0.726 mmol, 82%).

[N$_3$N]NbOMe (6b). Sodium amalgam (0.5 wt % Na, 1.25 mmol) was added to a −35 °C solution of $[N_3N]NbOMe^+OTf^-$ (394 mg, 0.623 mmol) in 20 mL of tetrahydrofuran. The yellow solution turned blue after 2 min. The blue, crystalline product was isolated as described for **6a**: yield 268 mg (0.554 mmol, 89%); ^{1}H NMR (C_6D_6) δ 3.37 (br s, 27, NSiMe$_3$), 1.25 (br s, 3, OMe), −0.43 (br s, 6, CH$_2$). Anal. Calcd for $NbSi_3N_4OC_{16}H_{42}$: C, 39.73; H, 8.75; N, 11.58. Found: C, 39.66; H, 8.37; N, 12.01.

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