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Formation of Aminoxy and Oxo Complexes from the Reaction of $Nb(NMe_2)_5$ with O_2 and the Crystal Structure of $Nb(NEt_2)_5$

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The reaction of $Nb(NMe_2)_5$ with O_2 gives three complexes: monomeric $(Me_2N)_nNb(\eta^2\text{-}ONMe_2)_{5-n}$ (n = 3, 4) and dimeric $(Me_2N)_4Nb_2[\eta^2\text{-}N(Me)CH_2NMe_2]_2(\mu\text{-}O)_2$. $Nb(NEt_2)_5$ was prepared in a mixture of pentane and THF, leading to its purification and characterization by single-crystal X-ray diffraction. Unlike $Nb(NMe_2)_5$, which adopts a square pyramidal structure, $Nb(NEt_2)_5$ is a distorted trigonal bipyramid. The reaction of $Nb(NEt_2)_5$ with O_2 gives an insoluble white solid.

Introduction

Chemical processes have been actively studied to make metal oxide thin films such as M_xO_y ($M = Ti, Zr, Hf, Nb, Ta$) as gate insulating materials for new generations of microelectronic devices.[1−4] SiO_2, the current gate insulating material, does not have the ability to insulate effectively when its film thickness is below 2 nm.[1] The use of metal oxides as gate insulating materials significantly reduces current leakage. Intel recently introduced a HfO_2-based microprocessor (Intel Atom processor).[5] Reactions of metal amides with O_2 in chemical vapor deposition (CVD) and atomic layer deposition (ALD) processes have been used to give metal oxide thin films in microelectronic devices.[2,3,6] Metal amides, especially homoleptic amides $M(NR_2)_n$, have been widely studied, including as CVD and ALD precursors, in part because they have demonstrated unique physical and chemical properties.[7−9] Among Group 5 amides, d^0 Nb and Ta dimethylamides $M(NMe_2)_5$ (M = Nb, **1**; Ta, **2**)[3,10a] and diethylamides $M(NEt_2)_5$ (M = Nb, **3**; Ta, **4**)[10b] have been used as precursors in CVD or ALD of metal nitrides and oxides.[10c−i] There is, however, little understanding of the reactivities of these d^0 amides toward O_2 and the pathways in the formation of metal oxides from the reactions.[11,12] In addition, it is not clear how different the reactivities of diethylamides **3** and **4** are from those of their dimethylamide

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analogs **1** and **2**. First prepared in the early 1960s, **3** and **4** were reported to be unstable and difficult to purify as they easily decomposed into liquid mixtures containing $M(NEt_2)_4$, $M(NEt_2)_5$, $M(=NEt)(NEt_2)_3$, and $M(\eta^2\text{-}Et-N=CH-CH_3)(NEt_2)_3$.[7d,10e,13,14] The single-crystal structure of **4** was not reported until 2006.[15] To our knowledge, the single-crystal structure of thermally unstable **3** has not been reported.[7b]

Reactions of d^0 metal complexes with O_2 are significantly different from those of d^n metal complexes with O_2. In the reactions of O_2 with d^n complexes at low oxidation states, the oxidation of metals is often a key step. Many reactions of O_2 with d^n metal complexes have been actively studied as they are often fundamental in biological processes and are used in catalytic reactions.[16] In comparison, there have been fewer studies of the reactions between O_2 and d^0 complexes. The metals in the complexes are at their highest oxidation states. Yet many of these d^0 early transition-metal complexes are often oxygen sensitive. In the reactions of O_2 with d^0 alkyl and silyl complexes, insertion of oxygen into M−R[11] and M−Si[12] bonds in d^0 alkyl and silyl complexes has been reported. O_2 has also been reported to play an important role in the syntheses of several d^0 complexes; for example, preparation of d^0 $Mo(NMe_2)_6$, $W(NMe_2)_6$, and WMe_6 requires adventitious O_2.[17]

We are interested in the nature of the reactions between metal amides and O_2 and the mechanistic pathways in the formation of metal oxides. Reactions of O_2 with d^0 Group 4 $M(NMe_2)_4$ (M = Zr, Hf) yield trinuclear complexes $M_3(NMe_2)_6(\mu\text{-}NMe_2)_3(\mu_3\text{-}O)(\mu_3\text{-}ONMe_2)$.[18] The reaction between d^0 **2** and O_2 gives several complexes: $(Me_2N)_4Ta(\eta^2\text{-}ONMe_2)$, $(Me_2N)_3Ta(\eta^2\text{-}ONMe_2)_2$, $(Me_2N)_4Ta_2[\eta^2\text{-}N(Me)CH_2NMe_2]_2(\mu\text{-}O)_2$, and $(Me_2N)_6Ta_3[\eta^2\text{-}N(Me)CH_2NMe_2]_2(\eta^2\text{-}ONMe_2)(\mu\text{-}O)_3$.[19] The d^0 silyl amides $(Me_2N)_4TaSiR_3$ [$R_3 = (SiMe_3)_3$,[20] Bu^tPh_2[21]] are also sensitive to O_2. The reactions yield $(Me_2N)_3Ta(\eta^2\text{-}ONMe_2)(OSiR_3)$, $(Me_2N)_4Ta(OSiBu^tPh_2)$, and $(Me_2N)_2(Ph_2Bu^tSiO)_2(\mu,\eta^2\text{-}Me_2NCH_2NMe)_2Ta_2(\mu\text{-}O)_2$.

We have found that the reaction of O_2 with d^0 **1** gives aminoxy complexes $(Me_2N)_4Nb(\eta^2\text{-}ONMe_2)$ (**5**), $(Me_2N)_3Nb(\eta^2\text{-}ONMe_2)_2$ (**6**), and an unusual dimer, $(Me_2N)_4Nb_2[\eta^2\text{-}N(Me)CH_2NMe_2]_2(\mu\text{-}O)_2$ (**7**), containing oxo and chelating ligands $[\eta^2\text{-}N(Me)CH_2NMe_2]$. This reaction is a rare case of the formation of oxo ligands in the reactions of d^0 complexes with O_2.[11i,19−21] **3** has been isolated, and its crystal structure has been determined. The reaction of **3** with O_2 has also been investigated.

Experimental Section

General Procedures. Manipulations were performed under a dry and oxygen-free nitrogen atmosphere with the use of glovebox or Schlenk techniques. Solvents were purified by distillation from potassium/benzophenone ketyl. Benzene-d_6 and toluene-d_8 were dried and stored over activated molecular sieves under nitrogen. $NbCl_5$ (Strem) was sublimed under vacuum prior to use. O_2 (National Welders Supply Co.) was dried by passing through a P_2O_5 column. $LiNMe_2$ (Aldrich) was used as received. $LiNEt_2$[22] and **1**[7b] were prepared according to the literature procedures. NMR spectra were recorded on a Bruker AMX-400 Fourier transform spectrometer. Elemental analyses were conducted by Complete Analysis Laboratories, Inc., Parsippany, NJ.

Preparation of 5−7. 1 (1.000 g, 3.191 mmol) was dissolved in toluene (35 mL) in a 74-mL Schlenk flask. The solution was frozen in a liquid nitrogen bath and thawed to remove gases. After the liquid nitrogen bath was removed and the frozen solid melt, 0.5 equiv of O_2 (39.0 mL, 1.0 atm, 1.6 mmol) was added. The flask was placed in a water bath and stirred at 23 °C for 30 min.

Volatiles were removed under a reduced pressure to give a brown sticky solid. Et_2O was added to the solid to form a mixture of a brown solution and a nearly white solid. After the brown solution was transferred to another Schlenk flask, the solid was dissolved in toluene. Both solutions were concentrated and then placed at −32 °C for crystallization.

Yellow crystals of **7** (0.015 g, 0.026 mmol, 2% yield based on O_2) were obtained from the toluene solution in a few days. ^{1}H NMR of **7** (benzene-d_6, 399.7 MHz, 23 °C) δ 3.93 (s, 4H, $2CH_2$), 3.42 (s, 24H, $4NMe_2$), 3.11 (s, 6H, $2MeNCH_2$), 2.31 (s, 12H, $2CH_2NMe_2$). ^{13}C NMR (benzene-d_6, 100.5 MHz, 23 °C) δ 84.6 (s, CH_2), 48.0 (s, NMe_2), 47.9 (s, CH_2NMe_2), 39.8 (s, $MeNCH_2$). Anal. calcd for C16H46N8Nb2O2: C, 33.81; H, 8.16; N, 19.71. Found: C, 33.66; H, 8.09; N, 19.52.

Yellow crystals of **6** (0.036 g, 0.10 mmol, 6% yield based on O_2) were obtained from the Et_2O solution. ^{1}H NMR of **6** (benzene-d_6, 399.97 MHz, 23 °C) δ 3.40 (s, 6H, equatorial NMe_2), 2.89 (s, 6H, axial $2NMe_aMe_b$), 2.85 (s, 6H, axial $2NMe_aMe_b$), 2.50 (s, 12H, $2ONMe_2$). ^{13}C NMR (benzene-d_6, 100.63 MHz, 23 °C) δ 50.2 (s, $ONMe_2$), 47.9 (s, NMe_2), 47.2 (s, NMe_2). Anal. calcd for C10H30N5NbO2: C, 34.79; H, 8.76; N, 20.28. Found: C, 34.68; H, 8.72; N, 20.06.

After the crystals of **6** were removed, the solution was further concentrated to give a yellow viscous liquid of **5** (0.310 g, 0.941 mmol, 30% yield based on O_2). ^{1}H NMR of **5** (benzene-d_6, 399.9 MHz, 23 °C) δ 3.15 (s, 24H, $4NMe_2$), 2.43 (s, 6H, $ONMe_2$). ^{13}C NMR (benzene-d_6, 100.6 MHz, 23 °C) δ 48.5 (s, NMe_2), 47.6 (s, $ONMe_2$). Anal. calcd for C10H30N5NbO: C, 36.48; H, 9.18; N, 21.27. Found: C, 36.04; H, 9.00; N, 20.97.

Preparation of 3. $NbCl_5$ (4.450 g, 16.47 mmol) dissolved in a mixture of pentane (30 mL) and THF (70 mL) was connected to

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an addition funnel containing 5 equiv of $LiNEt_2$ (6.512 g, 82.35 mmol). $LiNEt_2$ was slowly added in portions into the $NbCl_5$ solution within 1.5 h at 23 °C. The solution was then stirred at 23 °C for 18 h. Volatiles were removed in vacuo, and the viscous residue was extracted three times (40 mL/time) with freshly dried pentane. The dark-brown filtrate was concentrated and put in a freezer at −32 °C. Crystallization gave two crops of brown crystals of **3** (total weight: 1.221 g, 2.69 mmol, 16.3% yield). ^1H NMR of **3** (benzene-d_6, 399.8 MHz, 23 °C) δ 3.70 (q, 20H, CH_2CH_3), 1.12 (t, 30H, CH_2CH_3). ^{13}C NMR (benzene-d_6, 100.5 MHz, 23 °C) δ 47.9 (s, CH_2CH_3), 15.0 (s, CH_2CH_3). ^1H NMR of **3** (toluene-d_8, 399.8 MHz, 23 °C) δ 3.69 (q, 20H, CH_2CH_3), 1.12 (t, 30H, CH_2CH_3). ^{13}C NMR (toluene-d_8, 100.5 MHz, 23 °C) δ 48.0 (s, CH_2CH_3), 15.1 (s, CH_2CH_3).

Reaction of 3 with O_2. In a J. Young tube, **3** (0.041 g, 0.091 mmol) dissolved in benzene-d_6 (ca. 0.5 mL) was subject to a freeze−pump−thaw cycle using liquid nitrogen to remove gases in the NMR tube. When the frozen solid started to melt, 1 equiv of O_2 (2.2 mL, 1.0 atm, 0.091 mmol) was added. It was then shaken for 18 h, and a white solid precipitated at the bottom of the NMR tube. An NMR spectrum of the solution revealed that ca. 70% of **3** had not reacted. Only $HNEt_2$ could be identified by NMR. In 13 days, ca. 50% of **3** was left. Another 1 equiv of O_2 was added at this point, and, in 42 h, **3** completely disappeared to give a solid and $HNEt_2$. Small unidentified peaks were observed as well. The solid was essentially not soluble in benzene, $CHCl_3$, or THF.

Variable-Temperature NMR Studies of 6. ^1H NMR spectra of a solution of **6** (15.0 mg) in toluene-d_8 (0.5 mL) in a J. Young tube were taken at 288, 293, 303, 313, 323, 333, and 343 K, respectively. These spectra are given in Figure 2.

Determination of X-ray Crystal Structures of 3, 6, and 7. The data for the X-ray crystal structures of **3**, **6**, and **7** were collected on a Bruker-AXS APEX diffractometer that was equipped with a CCD area detector and fitted with an upgraded Nicolet LT-2 low-temperature device. The data were obtained by a graphite-monochromated Mo source (K_α radiation, 0.71073 Å). A suitable crystal was coated with paratone oil (Exxon) and mounted on loops under a stream of nitrogen at the temperature of the data collection. The structures were solved by direct methods.

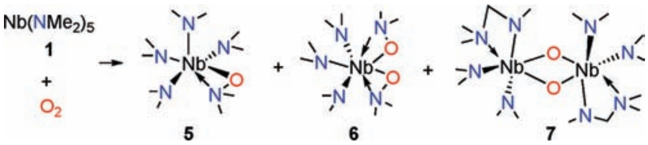
The solution in $C2/m$ yielded chemically reasonable and computationally stable results of **7**, where one molecule has a two-fold axis and a mirror plane. Each Nb atom is coordinated by two bridging O atoms, two terminal $-NMe_2$ ligands, and a chelating η^2-$N(Me)CH_2NMe_2$ ligand. One $-NMe_2$ ligand is disordered by the mirror plane with part of the chelating η^2-$N(Me)CH_2NMe_2$ ligand.

Non-hydrogen atoms were anisotropically refined. All hydrogen atoms were treated as idealized contributions. Empirical absorption correction was performed with SADABS.[23a] In addition, the global refinements for the unit cells and the data reductions of the structure were performed using the Saint program (version 6.02). All calculations were performed using SHELXTL (version 5.1) proprietary software package.[23b]

Results and Discussion

Preparation and Characterization of 5−7. These three complexes (**5**−**7**) were prepared from the reaction of **1** with O_2 (Scheme 1). The isolated yields were 30%, 6%, and 2%, respectively. For the reaction conducted in an NMR tube, the yields based on NMR integration were 70%, 10%, and 10%, respectively. In fact, it was difficult to separate the three compounds. Sometimes crystallization did not completely remove one product from another one. In the reaction of **2** with O_2, $(Me_2N)_4Ta(\eta^2$-$ONMe_2)$, which is analogous to **5**, was separated from $(Me_2N)_3Ta(\eta^2$-$ONMe_2)_2$ by sublimation.[19] Attempts to separate **5** from **6** through sublimation at 50−60 °C, however, failed, probably because **5** is not stable under heating. It was also found that the solubility of **5** was too high to obtain its crystals through crystallization. A successful approach to separate the three products involves first treating the reaction residue with Et_2O to remove **5** and **6**. The remaining solid, which was mostly dimer **7**, was dissolved in toluene. Cooling the toluene solution gave yellow crystals of **7**. Cooling the Et_2O solution containing **5** and **6** yielded yellow crystals of **6**. Removing volatiles from the supernatant Et_2O solution gave a yellow viscous liquid of **5**.

Scheme 1



In the reaction of **2** with O_2,[19] analogs of **5**−**7** and a Ta trinuclear complex $(Me_2N)_6Ta_3[\eta^2$-$N(Me)CH_2NMe_2]_2(\eta^2$-$ONMe_2)(\mu$-$O)_3$ (0.52% yield) were obtained. An analog of the trinuclar complex was not, however, observed in the reaction of **1** with O_2. We cannot, however, rule out its formation in a yield too small to be isolated or observed by NMR. It seems that there is a little difference between the reactions of **1** and **2** with O_2.

We have reported that the preparation of **1** from $NbCl_5$ and 5 equiv of $LiNMe_2$ gives a small amount of $Nb(NMe_2)_4[N(Me)CH_2NMe_2]$ as a byproduct.[24] We have found that this complex remains in the mixture of products in the reaction of **1** with O_2, suggesting it is perhaps stable to O_2.

By NMR and C, H and N analyses, **5** was characterized. Its ^1H NMR spectrum in benzene-d_6 shows two peaks at 3.15 and 2.43 ppm in a 4: 1 ratio. This is consistent with 24 protons from four $-NMe_2$ ligands and 6 protons from the single $-ONMe_2$ ligand in **5**. ^{13}C NMR spectrum of **5** also gives two peaks at 48.5 and 47.6 ppm, indicating two types of carbon from $-NMe_2$ and $-ONMe_2$, respectively.

Single-crystal X-ray structure of **6** and crystallographic data are given in Figure 1 and Table 1, respectively. In the solid state, **6** is a monomer and exhibits a distorted pentagonal bipyramidal structure with a nearly linear N(4)−Nb(1)−N(5) angle of 178.33(14)°. The axial Nb−N bond is almost vertical to the three equatorial Nb−N bonds with bond angles of 90.09(14)−90.50(14)°. The two Nb−O bond lengths are very close to each other [Nb(1)−O(2) 2.022(3), Nb(1)−O(1) 2.037(3) Å]. The N(2)−Nb(1) covalent bond length of 2.017(3) Å is the shortest in the molecule. The two Nb−N dative bond lengths [N(3)−Nb(1) 2.243(3), N(1)−Nb(1) 2.212(3) Å] are longer than the three Nb−N covalent bond lengths [N(2)−Nb(1) 2.017(3), N(4)−Nb(1) 2.068(4), N(5)−Nb(1) 2.075(4) Å]. The average Nb−N covalent

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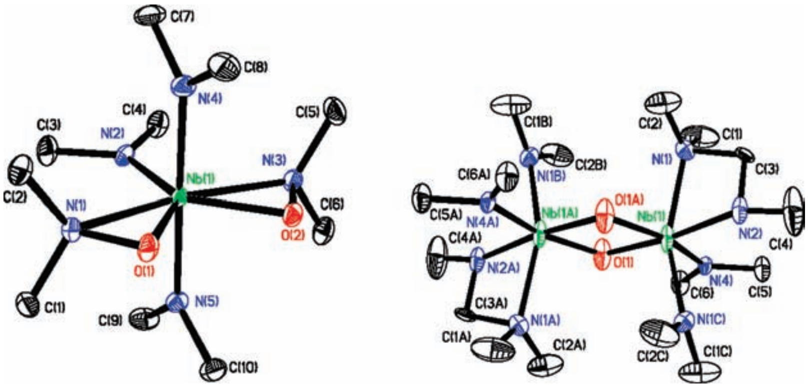

Figure 1. Molecular drawings of $(Me_2N)_3Nb(\eta^2\text{-}ONMe_2)_2$ (**6**, left) and $(Me_2N)_4Nb_2[\eta^2\text{-}N(Me)CH_2NMe_2]_2(\mu\text{-}O)_2$ (**7**, right). Selected bond lengths (Å) and angles (°) in **6**: N(1)−Nb(1), 2.212(3); N(2)−Nb(1), 2.017(3); N(3)−Nb(1), 2.243(3); N(4)−Nb(1), 2.068(4); N(5)−Nb(1), 2.075(4); Nb(1)−O(2), 2.022(3); Nb(1)−O(1), 2.037(3); O(2)−Nb(1)−O(1), 88.06(12); N(2)−Nb(1)−N(4), 90.09(14); O(2)−Nb(1)−N(4), 89.45(13); O(1)−Nb(1)−N(4), 88.87(14); N(2)−Nb(1)−N(5), 91.58(14); O(2)−Nb(1)−N(5), 89.30(13); O(1)−Nb(1)−N(5), 89.98(14); N(4)−Nb(1)−N(5), 178.33(14); N(2)−Nb(1)−N(1), 96.18(13); O(1)−Nb(1)−N(1), 39.32(11); N(4)−Nb(1)−N(1), 90.50(14); N(5)−Nb(1)−N(1), 89.38(14); N(2)−Nb(1)−N(3), 97.15(13); O(2)−Nb(1)−N(3), 39.32(12); N(4)−Nb(1)−N(3), 90.49(14); N(5)−Nb(1)−N(3), 89.25(14); and N(1)−Nb(1)−N(3), 166.64(12). Selected bond lengths (Å) and angles (°) in **7**: Nb(1)−O(1A), 1.936(9); Nb(1)−O(1), 1.942(9); Nb(1)−N(2), 1.977; Nb(1)−N(4), 2.036(10); Nb(1)−N(1), 2.207(8); Nb(1)−N(1C), 2.207(8); O(1)−Nb(1A), 1.936(9); O(1A)−Nb(1)−O(1), 77.1(4); O(1A)−Nb(1)−N(2), 103.8(5); O(1)−Nb(1)−N(2), 171.8(12); O(1A)−Nb(1)−N(2A), 103.8(5); O(1)−Nb(1)−N(2A), 171.8(12); O(1A)−Nb(1)−N(4), 160.7(4); O(1)−Nb(1)−N(4), 83.7(4); N(2)−Nb(1)−N(4), 95.3(5); O(1A)−Nb(1)−N(1), 91.7(2); O(1)−Nb(1)−N(1), 103.7(2); N(2)−Nb(1)−N(1), 68.2(13); N(4)−Nb(1)−N(1), 92.9(2); and O(1A)−Nb(1)−N(1C), 91.7(2).

Table 1. Crystallographic Data for $Nb(NEt_2)_5$ (**3**), $(Me_2N)_3Nb(\eta^2\text{-}ONMe_2)_2$ (**6**), and $(Me_2N)_4Nb_2[\eta^2\text{-}N(Me)CH_2NMe_2]_2(\mu\text{-}O)_2$ (**7**)

	3	**6**	**7**
empirical formula	$C_{20}H_{50}N_5Nb$	$C_{10}H_{30}N_5O_2Nb$	$C_{16}H_{46}N_8O_2Nb_2$
fw	453.56	345.30	568.40
temp (K)	173(2)	173(2)	173(2)
crystal system	triclinic	monoclinic	monoclinic
space group	$P1$	$P2(1)/n$	$C2/m$
a, Å	9.293(10)	8.272(2)	11.410(11)
b, Å	10.103(11)	13.052(3)	13.784(13)
c, Å	22.35(2)	16.254(4)	8.645(8)
α, °	82.456(13)		
β, °	83.912(13)	100.393(4)	107.856(9)
γ, °	65.483(12)		
V, Å^3	1890(3)	1726.1(7)	1294(2)
Z	3	4	2
D_{calc}, g/cm^3	1.196	1.329	1.438
crystal size (mm^3)	0.10 × 0.20 × 0.40	0.25 × 0.28 × 0.38	0.10 × 0.20 × 0.20
θ range (°)	0.92−27.60	2.01−28.37	2.39−22.48
reflections collected	18123	17519	4900
independent reflections	14213 [R(int) = 0.0430]	4205 [R(int) = 0.0694]	894 [R(int) = 0.1588]
completeness to θ	92.7%, 27.60°	97.3%, 28.37°	100.0%, 22.48°
GOF on F^2	1.093	1.052	1.257
final R indices	$R1$ = 0.0774	$R1$ = 0.0430	$R1$ = 0.0750
$[I > 2\sigma(I)]$ [a]	w$R2$ = 0.1973	w$R2$ = 0.1159	w$R2$ = 0.1811
R indices (all data)	$R1$ = 0.0995	$R1$ = 0.0575	$R1$ = 0.0752
	w$R2$ = 0.2327	w$R2$ = 0.1532	w$R2$ = 0.1812
largest diff. peak and hole, e·Å^{-3}	5.677 and −1.390	0.831 and −1.242	0.935 and −1.497

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

bond length (2.053 Å) in **6** is slightly longer than that of **1** (2.029 Å).[25]

Variable-temperature ^{1}H NMR spectra of **6** in toluene-d_8 were obtained between 288 and 343 K (Figure 2) because **6** was found to be fluxional. At 288 K, two peaks at 2.88 and 2.79 ppm are assigned to two Me groups from the two axial $-NMe_2$ ligands: one for the Me groups [C(7) and C(9) in the structure of **6** in Figure 1] on both $-NMe_2$ ligands that are *trans* to the O atoms of $-ONMe_2$ ligands; the other for the Me groups [C(8) and C(10) in the structure of **6** in Figure 1] on the axial $-NMe_2$ ligands that are *cis* to the O atoms. These results are consistent with the crystal structure of **6** in Figure 1. When the temperature is increased, the peaks become broad, except the peak for the two $-ONMe_2$ ligands near 2.50 ppm. Two peaks in the middle of the spectrum (for the Me groups that are *trans*- and *cis*- to the O atoms) start to coalesce at 303 K. At 323 K, these two peaks coalesce into one broad peak at 2.82 ppm with a rate constant of 89 s^{-1} ($\Delta G_{323K}^{\ddagger}$ = 16 kcal/mol), indicating that two different methyl groups in each axial $-NMe_2$ ligand undergo a fast rotation at this temperature. At 343 K, the downfield peak of the equatorial $-NMe_2$ ligand and the peak at 2.82 ppm for the two axial $-NMe_2$ ligands coalesce with a rate constant of 227 s^{-1} ($\Delta G_{343K}^{\ddagger}$ = 16 kcal/mol), as a result of the fast equatorial−axial ligand exchange.

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Table 2. Comparison of Selected Bond Lengths (Å) and Bond Angles (°) in $Nb(NMe_2)_5$ (**1**), $Nb(NEt_2)_5$ (**3**), and $Ta(NEt_2)_5$ (**4**)[a]

1	**3**	**4**
Nb−N(1) (a) 1.977(17)	Nb(1)−N(1) (a) 2.092(12)	Ta(1)−N(1) (a) 2.093(10)
Nb−N(2) (b) 2.044(14)	Nb(1)−N(2) (a) 2.079(11)	Ta(1)−N(2) (a) 2.086(11)
Nb−N(3) (b) 2.040(15)	Nb(1)−N(3) (e) 1.952(9)	Ta(1)−N(3) (e) 1.917(9)
Nb−N(4) (b) 2.044(14)	Nb(1)−N(4) (e) 2.012(16)	Ta(1)−N(4) (e) 2.026(10)
Nb−N(5) (b) 2.040(15)	Nb(1)−N(5) (e) 2.023(12)	Ta(1)−N(5) (e) 2.238(9)
N(1)−Nb−N(2) 101.5(4)	N(1)−Nb(1)−N(2) 177.8(6)	N(1)−Ta(1)−N(2) 168.5(6)
N(1)−Nb−N(3) 109.1(4)	N(3)−Nb(1)−N(4) 122.5(5)	N(3)−Ta(1)−N(4) 128.1(6)
N(1)−Nb−N(4) 101.5(4)	N(3)−Nb(1)−N(5) 119.0(5)	N(3)−Ta(1)−N(5) 116.8(6)
N(1)−Nb−N(5) 109.1(4)	N(4)−Nb(1)−N(5) 118.5(5)	N(4)−Ta(1)−N(5) 115.1(5)
N(2)−Nb−N(3) 87.3(6)	N(2)−Nb(1)−N(3) 94.3(5)	N(2)−Ta(1)−N(3) 89.3(9)
N(2)−Nb−N(5) 86.1(6)	N(1)−Nb(1)−N(5) 94.1(5)	N(1)−Ta(1)−N(5) 100.1(5)
N(3)−Nb−N(4) 86.1(6)	N(1)−Nb(1)−N(4) 89.3(5)	N(1)−Ta(1)−N(4) 89.4(8)
N(4)−Nb−N(5) 87.3(6)	N(2)−Nb(1)−N(4) 88.5(5)	N(2)−Ta(1)−N(4) 89.1(8)
	N(1)−Nb(1)−N(3) 87.2(5)	N(1)−Ta(1)−N(3) 82.7(9)
	N(2)−Nb(1)−N(5) 86.5(5)	N(2)−Ta(1)−N(5) 90.8(5)

[a] See ref 25 for **1** and ref 15 for **4**. The following denote: (a) stands for the apical and axial positions in **1**, **3** and **4**, respectively; (b) stands for the basal positions in **1**; (e) stands for the equatorial positions in **3** and **4**.

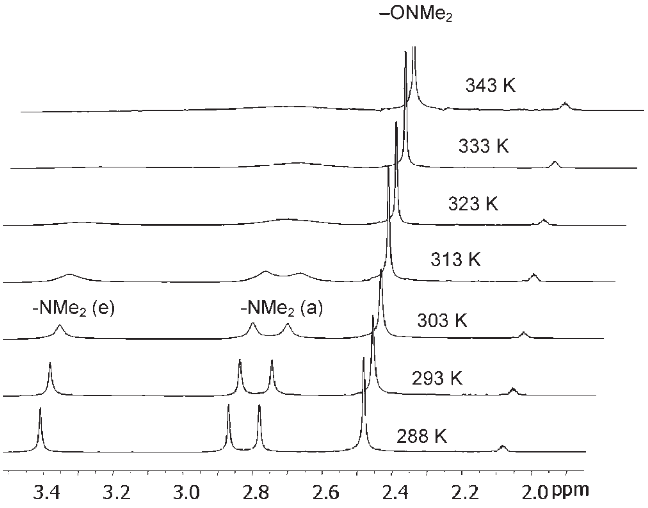
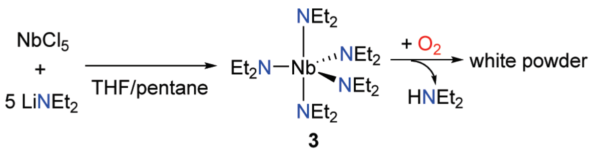


Figure 2. Variable-temperature (VT) ^1H NMR spectra of $(Me_2N)_3Nb(\eta^2\text{-}ONMe_2)_2$ (**6**) in toluene-d_8; (a) and (e) stand for axial and equatorial, respectively.

Scheme 2



An alternative explanation is that there is only one exchange of the ligands: axial−equatorial exchange of the $-NMe_2$ ligands. As the equatorial $-NMe_2$ ligand moves to the axial position, its two methyl groups move to the Me_a and Me_b positions. The fact that the activation free energies ($\Delta G_{323K}^{\ddagger}$ and $\Delta G_{343K}^{\ddagger}$) are equal suggests that the three amide ligands are exchanging via the same process.

By X-ray crystallography, **7** has been characterized. Figure 1 shows that the molecule is a dimer in the solid state. Unlike **6**, **7** does not have $-ONMe_2$ ligands. There are two oxo ligands bridging the two Nb atoms. There is a two-fold symmetry axis and a mirror plane in the molecule. One $-NMe_2$ ligand is disordered by the mirror plane with part of the chelating $\eta^2\text{-}N(Me)CH_2NMe_2$ ligand. The crystal structure of **7** is in agreement with its NMR spectra. Two bridging Nb−O bond lengths are almost the same [Nb(1)−O(1A) 1.936(9), Nb(1)−O(1) 1.942(9) Å]. The core unit consists of Nb(1), O(1), Nb(1A), and O(1A). O(1) and O(1A) form nearly straight angles of 171.8(12)° and 160.7(4)° with their *trans* atoms N(2) and N(4) through Nb(1). O(1A)−Nb(1) devides N(1)−Nb(1)−N(1C) into two equal angles 91.7(2)°. A mirror disorder makes Nb−N bond lengths identical [Nb(1)−N(1) 2.207(8), Nb(1)−N(1C) 2.207(8) Å]. Two covalent bond lengths [Nb(1)−N(4) 2.036(10), Nb(1)−N(2) 1.977(15)] are slightly different. Both are, however, shorter than the dative bond lengths [Nb(1)−N(1) and Nb(1)−N(1C)].

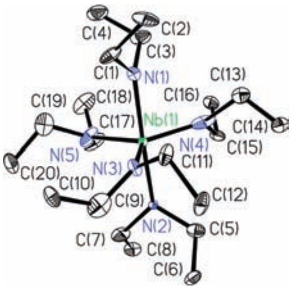


Figure 3. Molecular structure of $Nb(NEt_2)_5$ (**3**).

Preparation and Crystal Structure of 3 and Its Reaction with O_2. The complex **3** was prepared through the reaction of $NbCl_5$ with $LiNEt_2$ in mixed solvents of pentane and THF (Scheme 2). This complex has been used as a precursor in the preparation of metal oxides and nitrides.[10a,b,i−k] It has also been used as a catalyst for the preparation of polyesters.[26] Although **3** was first prepared in 1962,[7b] to our knowledge, pure, solid **3** has not been reported. It usually exists as a liquid mixture containing $Nb(NEt_2)_4$. In chemical vapor deposition, purity of a precursor is an important issue. Crystals of **3** have been isolated, and its structure determined by X-ray diffraction in the current work. For reasons not clear to us, mixed solvents in the current work play a critical role in the crystallization of **3**, as in the preparation of pure crystalline **4**.

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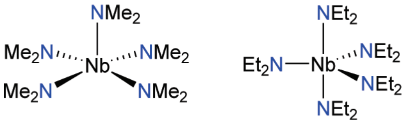
(26) (a) Okuzumi, Y., US Patent US 3962193, **1976**. (b) Goodyear Tire and Rubber Co. British Patent GB 1227474, **1971**.

Chart 1



1 3

The steric effect in **3** may have helped its conversion to $Nb(NEt_2)_4$ during the previous attempts to purify **3** through distillation at 120 °C.[7b] Bradley and Thomas have reported that the order of the steric effect in $Nb(NR_2)$ (R = Bu^n, Pr^n, Et, and Me) is $Bu^n{}_2N > Pr^n{}_2N > Et_2N \gg Me_2N$.[7b]

Single-crystal X-ray structure, crystallographic data, and selected bond lengths and angles of **3** are listed in Figure 3 and Tables 1 and 2. A comparison of bond lengths and angles in **3** with those in its dimethylamide analog **1** and Ta analog **4** is given in Table 2 as well. In the solid state, **3** is a monomer. It displays distorted trigonal bipyramidal (TBP) geometry with a nearly linear axial N(1)−Nb(1)−N(2) angle of 177.8(6)°. This is similar to the structure of **4**, in which the axial N(1)−Ta(1)−N(2) angle is 168.5(6)°.[15] The central [Nb(1)] and equatorial [N(3), N(4), and N(5)] atoms are coplanar, as in **4**. To our knowledge, this is a rare case. Bond angles formed by both axial and equatorial bonds are close to 90°. Both axial bond lengths [Nb(1)−N(1) 2.092(12), Nb(1)−N(2) 2.079(11) Å] are nearly identical and are similar to those in **4** [Ta(1)−N(1) 2.093(10), Ta(1)−N(2) 2.086(11) Å].[15] However, both are slightly larger than three equatorial bond lengths [Nb(1)−N(3) 1.952(9), Nb(1)−N(4) 2.012(16), Nb(1)−N(5) 2.023(12) Å]. In **4**, two equatorial Ta−N bond lengths [Ta(1)−N(3) 1.917(9), Ta(1)−N(4) 2.026(10) Å] are similar to those in **3**. One, Ta(1)−N(5) 2.238(9) Å, is, however, significantly longer than that in the Nb analog **3** and other Ta−N bonds. It is not clear why this is the case.[15]

The structure of **3** is different from that of **1**.[25] As shown in Chart 1, **1** adopts square-pyramidal (SP) geometry,[25] while **3** is a TBP. The SP structure may allow the apical N atom in **1** to have significant π-bonding interaction with the Nb atom.[25] In fact, the $M-N_{apical}$ bonds in both **1**[25] and **2**[27] are significantly shorter than $M-N_{basal}$ bonds. The Nb−N apical and basal bond lengths in **1** are 1.977(17) and 2.040(14/15)−2.044(14/15) Å, respectively. In the more bulky **3** and **4**, ligand−ligand repulsion leads to the TBP structures. In ^1H and ^{13}C NMR spectra of both **1** or **2** and **3** or **4** at 23 °C, only one peak is observed, suggesting that the molecules perhaps undergo fast Berry pseudorotations between the SP and TBP structures and that the energy differences between the two structures are not large. It should be also pointed out that the average Nb−N bond lengths in both **1** and **3** are close (2.029 in **1** and 2.032 Å in **3**).

The reactivity of **3** toward O_2 was studied in a J. Young NMR tube. The reaction appears to be slower than that of **1**. ^1H NMR spectra of the reaction mixture show that two peaks of **3** keep dropping, while the peaks of $HNEt_2$ increase with the formation of a white solid. The solid is essentially not soluble in solvents (benzene, CH_3Cl, and THF) we have tested. When the solid was placed in benzene-d_6, two broad peaks were observed around 1.2 and 3.5 ppm with very low intensities. Several quartets and triplets were observed around the peaks at 1.2 and 3.5 ppm, respectively, suggesting that some −Et groups are present on the solid. The insoluble solid is probably a Nb polymer containing bridging oxo (=O) and $-NEt_2$ ligands.

The mechanistic pathways in the formation of **5**−**7** from the reaction of **1** with O_2 is probably similar to those in the reaction of **2** with O_2, which have been studied in detail.[19] It is, however, not clear what leads to the difference in the reactions of **1** and **3** with O_2.

In the current work on the reaction of d^0 **1** with O_2, anionic amide ligands undergo oxidation, yielding $-ONMe_2$ and oxo ligands. Unlike **1**, which adopts a SP structure, **3** is a TBP. The reaction of **3** with O_2 apparently gives products that are different from those of the reaction of **1** with O_2.

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Supporting Information Available: Complete list of reference 4 and crystallographic data for **3**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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