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Amide C−N Bond Cleavage and Formation of Nitride Promoted by a Niobium(II) Cluster

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Reaction of the diamagnetic cluster (TMEDA)$_2$Nb$_2$Cl$_5$Li(TMEDA) with the (3,5-Me$_2$Ph)(Ad)NLi (Ad = adamantyl) amide led to a rare case of C−N bond activation and formation of tetravalent, dinuclear, and diamagnetic {(3,5-Me$_2$Ph)(Ad)N]Nb(3,5-Me$_2$Ph)}$_2$(μ-NAd)$_2$·ether (**1**) containing a Nb−Nb single bond. Conversely, a similar reaction carried out with [Cy$_2$NLi]$_4$ (Cy = cyclohexyl) yielded dinuclear {[(Cy$_2$N)$_2$Nb]$_2$(μ-N)}(μ^3-N)Li(TMEDA) (**2**).

Introduction

The key to understanding the steady growth of interest in the reactivity of transition metals leading to cleavage of C−X bonds (X = O, S, N)[1] lies in the fact that understanding this type of behavior may lead to new chemical transformations with practical implications for several industrial processes. Dehydrodesulfurization,[2] -deoxygenation,[3] and -denitrogenation[4] of crude oil, catalytic degradation of halocarbons,[5] and catalysis and extrusion of nitrogen and ammonia from organic compounds[6] are the most prominent examples among a plethora of reactions which involve C−X bond cleavage. Although some of these processes are well understood, reactions leading to the cleavage of the C−N bonds are particularly challenging and information remains scarce.[7,8] The oxidative cleavage of C═N multiple bonds has been clearly identified in a few cases,[7] and the mechanism was elucidated in detail.[7a] There are also a few examples of cleavage of a C−N single bond which have been documented in the literature.[8] However, if we remove from this category the opening of strained rings such as aziridines or cleavage of amidinates, only two examples of amine C−N single bond cleavage remain.[8a,b] The first is an observation made in 1985 by Chisholm[8b] who isolated a carbide/imide cluster, probably originated by degradation of an amide ligand. More recently, Wolczanski has described a unique case of neat oxidative addition of a Ta(III) complex into the C−N bond of aniline to form a mixture of L$_3$Ta(H)(NHPh) and L$_3$Ta(Ph)(NH$_2$).[8a] In spite of this paucity in the literature, reactions leading to C−N bond cleavage have a tremendous synthetic potential.[9] For example, the Pd-catalyzed scrambling of alkyl groups between different amines is today a viable synthetic methodology for the preparation of a large number of amines.[10] Therefore, for synthetic purposes, it is important to understand this type of reactivity and to shed some light onto the factors which promote C−N bond cleavage.

In this paper, we describe the reaction of two anionic amides with the triply-bonded Nb(II) complex (TMEDA)$_2$Nb$_2$Cl$_5$Li(TMEDA).[11] Depending on the amide, the reaction yielded either a Nb(IV) imido-bridged diamagnetic amido/arene species, resulting from the cleavage of the amido C−N bond, or a nitrido-bridged mixed-valence species, possibly arising from dinitrogen activation.

Results and Discussion

The reaction of (TMEDA)$_2$Nb$_2$Cl$_5$Li(TMEDA) with (3,5-Me$_2$Ph)(Ad)NLi (Ad = adamantyl)[12] (Scheme 1) in boiling THF yielded dark orange crystals of diamagnetic {(3,5-Me$_2$Ph)(Ad)N]Nb(3,5-Me$_2$Ph)}$_2$(μ-NAd)$_2$·ether (**1**), which were isolated in a significant yield (32%) from

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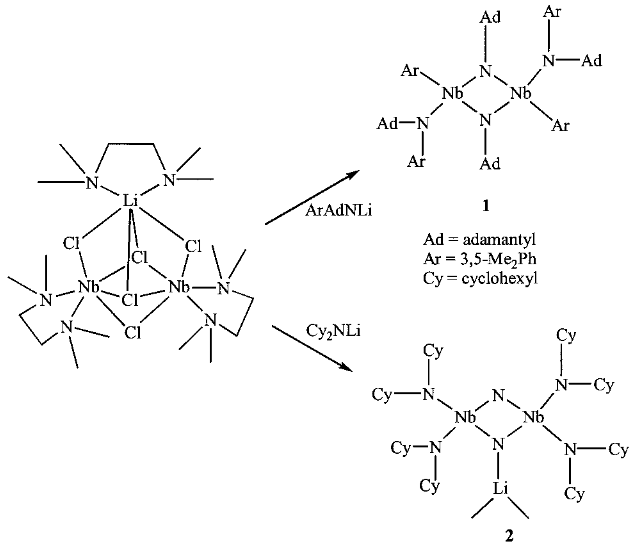
Scheme 1



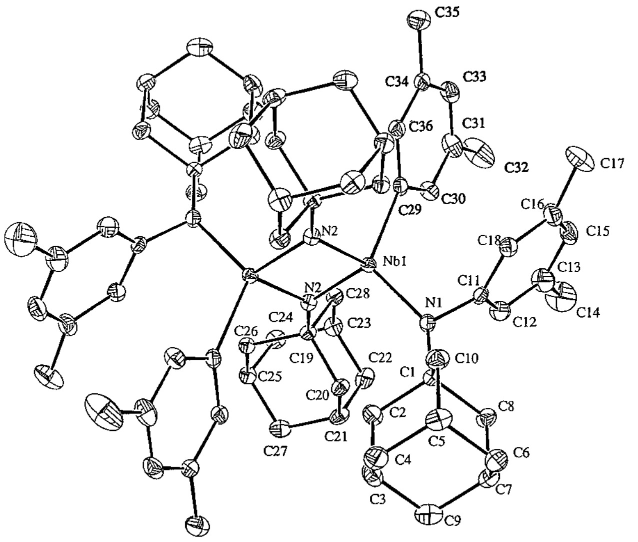


Figure 1. ORTEP drawing of **1**. Thermal ellipsoids are drawn at the 30% probability level.

ether solutions. A reflux in THF, even for a short period of time, appears to be important in obtaining an analytically pure compound. In the case of reactions carried out at room temperature and worked up as usual, complex **1** was only the minor component of a mixture predominantly containing dark brown crystals of a new compound. When this crystalline mixture was redissolved in THF and boiled for a few minutes, only orange crystals of **1** were obtained upon crystallization from ether. Unfortunately, efforts to characterize the brown compound were frustrated by several unfavorable factors, such as poor crystal quality and unavoidable contamination of the product by a substantial amount of the final orange product. The ^{1}H NMR spectrum clearly showed two different sets of phenyl ligands, one molecule of ether, and the absence of TMEDA. Combustion analysis data indicated a formula with two amide ligands and one molecule of ether per niobium atom. The complex is nonfluxional and thermally stable.

The molecular connectivity and the oxidation state of the metal were revealed by an X-ray crystal structure (Figure 1). The complex is binuclear and is formed by two identical tetrahedral niobium atoms bridged by two N−Ad imido groups. One 3,5-Me$_2$Ph moiety is directly connected to each metal center and, together with one intact amido group, completes the tetrahedral coordination geometry of each niobium atom. The two imido nitrogen atoms (Nb1−N2 = 1.984(3) Å) are distorted trigonal planar (Nb1−N2−C19 = 138.4(2)°, Nb1−N2−Nb1a = 84.4(1)°) and with the two Nb atoms form a planar Nb$_2$N$_2$ core. The Nb−N$_{\text{amide}}$ (Nb1−N1 = 2.008(2) Å) and Nb−C (Nb1−C29 = 2.223(3) Å) distances are normal and compare well with those of other Nb and Ta derivatives.[13]

An interesting feature of the structure of complex **1** is the presence of a short Nb−Nb distance (Nb1−Nb1a = 2.679(1) Å), which is even shorter than that observed in doubly-bonded Nb(III) derivatives[14] and comparable to that of one triply-bonded Nb(II) complex.[15] This relatively short distance, together with the diamagnetism, is perhaps indicative of the presence of a Nb−Nb single bond. Extended Hückel MO calculations were carried out on a model compound with the atomic coordinates as obtained from the crystal structure. For simplicity reasons, the adamantyl groups were transformed into *t*-Bu groups by replacing the unnecessary carbon atoms with hydrogen atoms introduced at their idealized positions. Similarly, the two methyls of the 3,5-Me$_2$Ph groups were replaced by hydrogen atoms. The calculation showed a substantial HOMO−LUMO gap (0.8 eV) which is certainly sufficient to account for the observed diamagnetism. The HOMO (−11.7 eV) is metal−metal bond-centered with strong σ character (Figure 2). It is formed by two identical hybrid orbitals of each niobium atom (arising from the mixing of d_{z^2} (0.52) and $d_{x^2-y^2}$ (0.33)) which undergo overlap of the two lobes lying on the intermetallic vector. However, the molecular orbital also requires a minor but significant participation of the bridging nitrogen p_y orbitals (perpendicular to the intermetallic vector which was choosen as the *z* axis) which overlap *side-on* with the perpendicular lobes of the d hybrid orbitals, thus forming two lobes on the two sides of the intermetallic vector connecting the two metal centers and encompassing the bridging nitrogen atoms. The bond between the bridging imido nitrogen atoms and the metal centers is provided by a molecular orbital located at −13.0 eV (HOMO-13), which is formed by the mixing of the d_{yz} orbitals of the two niobium atoms with the two bridging nitrogen p_z orbitals (Figure 2).

The structure of **1** shows that one C−N bond of one amide ligand was cleaved during the chlorine replacement reaction of (TMEDA)$_2$Nb$_2$Cl$_5$Li(TMEDA) by (3,5-Me$_2$Ph)(Ad)NLi. The complex is the result of an oxidation of the metal which provides the two electrons necessary to cleave the C−N bond to form the aryl and imido moieties. Since the final complex contains niobium in the formal oxidation state +4, it is rather tempting to envision the process by assuming the

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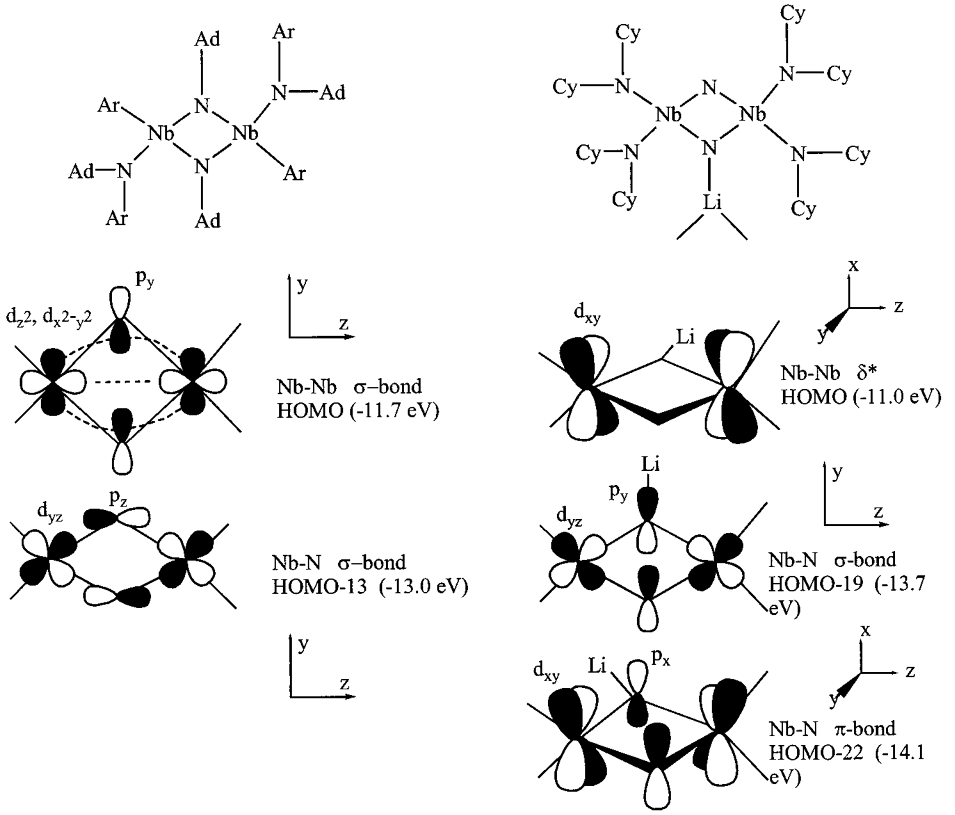

Figure 2. Pictorial view of most relevant MO's for complex **1** and **2**.

formation of an intermediate "(amide)$_2$Nb" complex, perhaps dinuclear, which rearranges into the final tetravalent product by simply performing oxidative addition into the N-C bond.

In an attempt to substantiate this speculation, we have attempted similar reactions with different amides. Unfortunately, employement of *i*-Pr$_2$NLi, Ph$_2$NK, 1,2-[(*i*-Pr)N]$_2$C$_6$H$_8$Li$_2$, 2,2′,6,6′-Me$_4$C$_5$H$_3$NLi, and (Me$_3$Si)$_2$NLi only led to intractable or not well-characterized materials. However, in the case of [Cy$_2$NLi]$_4$, the reaction with (TMEDA)$_2$Nb$_2$Cl$_5$Li(TMEDA) in THF under N$_2$ gave a new paramagnetic product, moderately air-sensitive, which was isolated from ether solutions as a bright orange homogeneous crystalline material in a rather poor but reproducible yield. Attempts to improve the yield by usual work up with solvents revealed the presence, in the mother liquor, of a substantial amount of unreacted (TMEDA)$_2$Nb$_2$Cl$_5$Li(TMEDA) starting material. Reactions carried out with larger amounts of [Cy$_2$NLi]$_4$, with the aim to complete the conversion, surprisingly gave only intractable mixtures. Qualitative analytical tests on the orange crystalline compound showed the absence of chlorine and the presence of lithium. Combustion analysis data were consistent with the formula (Cy$_2$N)$_4$Nb$_2$N$_2$Li(TMEDA) (**2**), indicative of the formation of a mixed-valence complex, probably containing dinitrogen. The presence of TMEDA was revealed by the NMR spectrum of this paramagnetic species. The magnetic moment ($\mu_{\text{eff}} = 1.76\mu_{\text{B}}$) was consistent with the presence of one unpaired electron per unit formula. Since the crystals were of sufficient quality, we have undertaken an X-ray crystal structure determination of this new product.

The X-ray analysis revealed a dinuclear structure composed two identical (Cy$_2$N)$_2$Nb units linked togheth-er by two bridging nitride atoms (Figure 3). One of the two bridging nitride atoms is also bonded to a Li-(TMEDA) unit (N2–Li = 1.99(1) Å) forming a Nb$_2$N$_2$Li planar core. The coordination geometry around each niobium is distorted tetrahedral (N1–Nb–N2 = 86.3(2)°, N1–Nb1–N3 = 116.1(2)°, N1–Nb1–N4 = 110.3(1)°, N3–Nb1–N4 = 110.0(2)°) and is defined by two nitrogen atoms of the terminal amide (Nb1–N3 = 2.040(4), Nb1–N4 = 2.032(4) Å) and two bridging nitrides. The two bridging nitrides form comparable bond distances (Nb1–N1 = 1.893(4), Nb1–N2 = 1.965(4), Nb2–N1 = 1.937(4), Nb2–N2 = 1.943(4) Å) and angles (Nb1–N1–Nb2 = 95.1(2)°, Nb1–N2–Nb2 = 92.6(2)°) with the two niobium metal centers in spite of the coordination of the alkali cation to only one of them and compare well with those of a Mo–N cluster reported in the

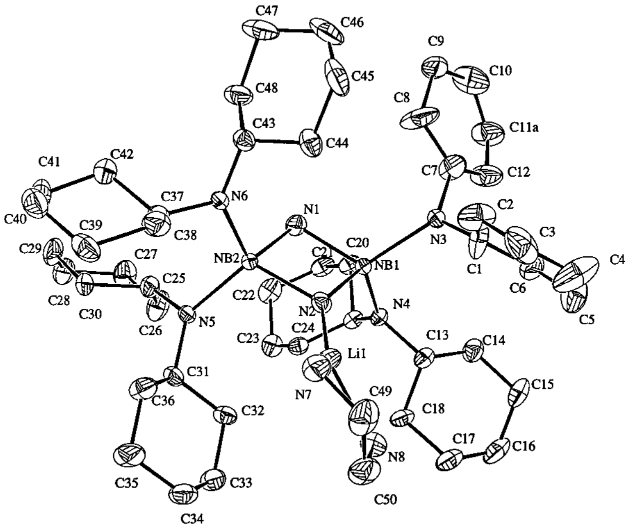

Figure 3. ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 30% probability level.

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Table 1. Crystal Data and Structure Analysis Results

	1	2
formula	$C_{40}H_{58}N_2NbO$	$C_{54}H_{104}N_8Nb_2Li$,
fw	675.81	1058.21
space group	$P2_1/c$	$P2_1/c$
a (Å)	12.5969(2)	12.9901(1)
b (Å)	14.3835(1)	21.0577(4)
c (Å)	20.3103(3)	21.1299(4)
β (deg)	104.223(1)	101.206(1)
V (Å^3)	3567.17(8)	5669.7(2)
Z	4	4
radiation (Mo Kα, Å)	0.709 30	0.709 30
T (°C)	−153	−153
D_{calcd} (g cm^{-3})	1.258	1.240
μ_{calcd} (cm^{-1})	3.7	4.4
R, R_w, GOF	0.045, 0.057, 1.05	0.055, 0.056, 1.52

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

Table 2. Selected Bond Distances (Å) and Angles (deg)

1	2
Nb1−Nb1a = 2.6792(5)	Nb1−Nb2 = 2.8252(6)
Nb1−N1 = 2.008(2)	Nb1−N1 =1.893(4)
Nb1−N2 = 1.984(3)	Nb1−N2 = 1.965(4)
Nb1−C29 = 2.223(3)	Nb1−N3 = 2.040(4)
N1−C1 = 1.494(4)	Nb1−N4 = 2.032(4)
N1−C11 = 1.438(4)	Nb2−N1 = 1.937(4)
N1−Nb1−N2 = 112.1(1)	Nb2−N2 = 1.943(4)
N1−Nb1−N2a = 112.4(1)	N1−Nb1−N2 = 86.3(2)
N1−Nb1−C29 = 119.5(1)	N1−Nb1−N3 = 116.1(2)
N2−Nb1−C29 = 105.4(1)	N1−Nb1−N4 = 110.3(2)
N2−Nb1−N2a = 95.6(1)	N2−Nb1−N3 = 116.4(2)
Nb1−N2−Nb1a = 84.4(1)	N2−Nb1−N4 = 115.9(2)
Nb1−N1−C1 = 140.3(2)	N3−Nb1−N4 = 110.0(2)
Nb1−N1−C11 = 98.7(2)	Nb1−N1−Nb2 = 95.2(1)
C1−N1−C11 = 120.4(2)	Nb1−N2−Nb2 = 92.6(2)
	Nb1−N2−Li1 = 144.5(4)
	Nb2−N2−Li1 = 112.9(4)
	N2−Li1−N7 = 141.9(6)
	N2−Li−N8 = 131.0(6)
	N7−Li1−N8 = 85.9(4)
	Nb1−N3−C1 = 118.8(4)
	Nb1−N3−C7 = 124.7(4)
	C1−N3−C7 =116.4(5)

literature.[8b] The distorted trigonal coordination geometry of the alkali cation is completed by one molecule of TMEDA (N2−Li1−N8 = 131.0(6)°, N2−Li1−N7 = 141.9(6)°). The geometry around the amide nitrogen atoms is trigonal planar as usual (Nb1−N3−C1 = 118.8(4)°, Nb1−N3−C7 = 124.7(4)°).

The intemetallic distance in complex **2** is rather long (Nb1−Nb2 = 2.8252(6) Å) and unlikely in agreement with the presence of a significant M−M bonding interaction. Extended Hückel MO calculations were carried out on the geometrical parameters obtained from the crystal structure and confirmed the absence of M−M-centered bonding molecular orbitals. While the HOMO−LUMO gap appears to be rather modest (0.4 eV), the HOMO is well above all the other occupied molecular orbitals (gap HOMO/HOMO-1 = 2.2 eV). The singly occupied HOMO, located at −11.0 eV, is mainly a δ^* M−M antibonding orbital and is originated by the out-of-phase combination of the two parallel d_{xy} atomic orbitals of the two niobium atoms. The bonding between the two niobium atoms and the two bridging nitrides is provided by two MOs located well below in energy and are, respectively, the Nb−N σ (HOMO −19 at −13.7eV) and π (HOMO-22 at −14.1 eV bonds (Figure 2). The first is originated by the overlap of the two d_{yz} orbitals of the two niobium atoms lying on the Nb_2N_2 plane with the in-plane p_y orbitals of the two bridging nitrides. The second is formed by the combination of the d_{xy} metal orbitals with the nitride p_x orbitals perpendicular to the molecular plane.

Complex **2** is a mixed-valence Nb(V)/Nb(IV) species which, in agreement with the magnetic measurement, possesses one unpaired electron per unit formula. The origin of the bridging nitride (C−N cleavage or N_2 activation) could not be conclusively demonstrated in this case. However, we observed that identical reactions carried out under Ar atmosphere are remarkably different and form products of different nature, perhaps indicating that complex **2** is originated by N_2 activation.

Experimental Section

All operations were performed under an inert atmosphere by using standard Schlenck techniques. $(TMEDA)_2Nb_2Cl_5Li(TMEDA)$,[11] $[3,5\text{-}Me_2PhN(Ad)]Li\cdot Et_2O$ (Ad = adamantyl),[12] and $(Cy_2NLi)_4$[16] were prepared according to published procedures. Solvents were dried with the appropriate drying agents and distilled prior to use. Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were prepared inside a drybox and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moments were calculated by standard methods,[17] and corrections for underlying diamagnetism were applied to the data.[18] Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer.

Preparation of $\{(3,5\text{-}Me_2Ph)(Ad)N]Nb(3,5\text{-}Me_2Ph)\}_2(\mu\text{-}NAd)_2\cdot$ether (1). A solution of $Nb_2Cl_5Li(TMEDA)_3$ (1.0 g, 1.4 mmol) in THF (70 mL) was treated with $(3,5\text{-}Me_2Ph)(Ad)NLi$ (1.8 g, 5.5 mmol). The mixture was stirred at room temperature overnight and then boiled for a few minutes. The solvent was removed *in vacuo*, and the solid residue was redissolved in ether (100 mL). A small amount of insoluble material was filtered off, and the solution was concentrated to a small volume. Dark orange-red crystals of **1** separated upon standing overnight at room temperature (0.60 g, 0.44 mmol, 32%). Anal. Calcd (found) for $C_{40}H_{58}N_2NbO$: C, 71.09 (70.84); H, 8.65 (8.64); N, 4.15 (4.09). IR (Nujol, KBr plates, cm^{-1}) ν: 1592 (m), 1575 (m), 1302 (m), 1090 (s), 1025 (s), 950 (m), 923 (m), 801 (s), 720 (m), 684 (m). ^1H NMR (C_6D_6, 500 MHz, 25 °C) δ: 7.20 (s, 2H, Ph_{ortho}), 6.77 (s, 1H, Ph_{para}), 6.46 (s, 2H, Ph_{ortho}), 6.35 (s, 1H, Ph_{para}), 2.47 (s, 6H, CH_{2Ad}), 2.33 (br s, 3H, CH_{Ad}), 2.17 (s, 6H, CH_3), 1.98 (s, 6H, CH_3), 1.89 (m, 6H, CH_{2Ad}), 1.51 (m, 3H, CH_{Ad}), 1.30−1.14 (dd, 6H, CH_{2Ad}), 1.24 (br s, 6H, CH_{2Ad}). ^{13}C NMR (C_6D_6, 125 MHz, 25 °C) δ: 139.8 (quat Ph), 135.8 (quat Ph), 133.9 (quat Ph), 133.4 and 131.9 (CH_{ortho} Ph), 130.6 and 127.7 (CH_{para} Ph), 120.6 (quat Ph), 58.5 and 47.6 (quat Ad), 48.77 and 46.0 (CH_2 Ad), 38.0 and 37.33 (CH_2 Ad), 32.0 and 30.73 (CH Ad), 21.5 and 21.3 (Me Ph).

Preparation of $\{[(Cy_2N)_2Nb]_2(\mu\text{-}N)\}(\mu^3\text{-}N)Li(TMEDA)$ (2). A solution of $(TMEDA)_2Nb_2Cl_5Li(TMEDA)$ (1.0 g, 1.4 mmol) in THF (75 mL) was treated with freshly prepared $[Cy_2NLi]_4$ (1.0 g, 1.4 mmol). The mixture was stirred at room temperature overnight, after which the solvent was removed *in vacuo*. The addition of ether (40 mL) allowed the elimination on unreacted starting material which separated as a fine yellow microcrystalline solid. The ether mother liquor was concentrated to a small volume and allowed to stand at room

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temperature, upon which orange crystals of **2** separated (0.18 g, 0.17 mmol, 12%). Anal. Calcd (found) for $C_{54}H_{104}N_8Nb_2Li$: C, 61.29 (61.15); H, 9.91 (9.85); N, 10.59 (10.41). I.R (nujol, cm^{-1}) ν: 1330 (sh), 1255 (s), 1143 (m), 1130 (m), 1109 (s), 1060 (m), 1036 (s), 990 (m), 954 (s), 889 (s), 835 (m), 799 (m), 771 (s), 760 (m), 720 (s), 689 (m). $\mu_{eff} = 1.76\ \mu_B$.

X-ray Crystallography. Data were collected at −153 °C for suitable air-sensitive crystals mounted on glass fibers inside a drybox and transferred under the liquid nitrogen stream of the cooling system of a Siemens CCD X-ray diffractometers. The $\omega - 2\theta$ scan technique was used. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 centered reflections. The intensities of three standard reflections, measured after every 150 reflections, showed no statistically significant decay over the duration of the data collections. Data were corrected for Lorentz and polarization effects and for absorption (ψ-scan). The structures were solved by direct methods resulting in locating all the non-hydrogen atoms. Their positions were refined anisotropically. Hydrogen atom positions were calculated but not refined. In the case of **2**, refinement was attempted by replacing the two nitrides with oxygen atoms. The higher values of the residuals supported the formulation indicated by combustion analysis data. The data were processed using the NRCVAX software packages on a Silicon Graphics workstation. Refinements were carried out by using full-matrix least-squares techniques on F minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o2/\sigma2(F_o{}^2)$ and F_o and F_c are the observed and calculated structure factors. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources (Cromer & Waber).[19] Details on the data collections and structure refinement are listed in Table 1. The final atomic coordinates are given as Supporting Information. Selected bond distances and angles are given in Table 2.

Molecular Orbital Calculations. All molecular orbital calculations were performed on a Pentium computer by using the software package Quantum CaCHE 2.0.[20] The program's default parameters were used in the extended Hückel calculations. The fractional atomic coordinates of the crystal structures were converted to the corresponding Cartesian coordinates by using a special device of the NRCVAX program. The adamantyl groups were converted to *t*-Bu groups and the cyclohexyl to *i*-Pr for simplicity. Hydrogen atoms were introduced at their idealized positions. The intermetallic vector was selected as a *z* axis.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles, text giving X-ray crystal data, and packing diagrams for **1** and **2** (26 pages). Ordering information is given on any current masthead page.

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