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Molecular Rearrangements of a Low-Valent Niobium Amide: Ligand C−H Bond Oxidative Addition and Reductive Elimination

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Reaction of the dinuclear and divalent $\mathrm{(TMEDA)_2Nb_2Cl_5Li(TMEDA)}$ with $\mathrm{Ph_2NK}$ led to the formation of three different compounds. The first complex contains no amide ligands. It is a mixed-valence dinuclear and paramagnetic species with a typical face-sharing bioctahedral structure $\mathrm{Cl_2Nb_2}(\mu\text{-Cl})_3\mathrm{(TMEDA)_2}$ (**1**). The second complex, a trivalent and dinuclear $\{[(\mathrm{Ph_2N})_2\mathrm{Nb}]_2[\mu\text{-NPh}(\mu\text{-}\eta^1{:}\eta^2\text{-}\mathrm{C_6H_4})](\mu\text{-H})\}\{\mathrm{Li(TMEDA)_2}\}\cdot$toluene (**2**) with one hydride and one cyclometalated aromatic ring, is the result of oxidative addition of the two metal centers to the C−H bond. In a subsequent reaction step, the oxidative addition is followed by reductive elimination to restore the C−H bond to form the neutral, dinuclear, and diamagnetic $(\mathrm{Ph_2N})_2\mathrm{Nb}\{[\mu\text{-NPh}(\eta^6\text{-}\mathrm{C_6H_5})]_2\mathrm{Nb}\}\cdot$ether (**3**) containing the two metals in formal oxidation states of +4 and 0. Ab initio and EHMO calculations have been carried out in an attempt to clarify the nature of the Nb−Nb interaction in the three complexes.

Introduction

Among early transition metals in low oxidation states, Nb and Ta occupy a prominent position because of the very distinctive chemical behavior displayed by their derivatives. An exciting reactivity which spans from metal−metal multiple bonding[1] to activation of small molecules,[2] dehydrogenation reactions,[3] C−N bond cleavage,[4] and C−H bond activation[5] has been reported for the few cases where low-valent Nb and Ta complexes were either isolated[6] or in situ generated.[7] The homoleptic tris-silanolate derivatives $\mathrm{(silox)_3M}$ [M = Nb, Ta][2a,6f] reported by Wolczanski and the phenoxide systems described by Rothwell[6a−e] provide the only examples of trivalent noncyclopentadienyl systems successfully isolated and characterized and for which it was possible to extensively demonstrate the ability of the oxidation state +3 to perform molecular activation processes. In view of the caliber of the transformations accomplished by these species, it is interesting to investigate the reactivity of the oxidation state +2, for which an even more enhanced reactivity can be anticipated in analogy with the behavior of the vanadium congeners.[8] However, the chemistry of divalent niobium and tantalum is currently limited to the preparation and characterization of only a few Nb(II) salts.[1e,i,6a,b,7b,9] Only recently was a unique example of multiply bonded Nb(II) pyrimidinate described,[1g] while previous attempts to prepare similar amidinate complexes led to ligand fragmentation.[10] Despite that these results indeed indicate a high and promising reactivity, the

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chemical behavior of Nb(II) species remains so far unexplored.

Recently, we have described the convenient synthesis of $(TMEDA)_2Nb_2Cl_5Li$ (TMEDA)[11] and have used this complex as a starting point to investigate the chemistry of Nb(II). The preliminary results were encouraging. Simple chloride replacement by amide ligands formed highly reactive Nb(II) amides which either cleaved the amide C−N single bond or performed cleavage of the N−N bond of dinitrogen, forming dinuclear, high-valent derivatives.[12] Since these two desirable but diversified transformations were determined simply by the nature of the amide substituents, we have embarked on a systematic study in an attempt to understand how the amide substituents determine the type of reactivity exhibited by Nb(II) species. In this first paper, we describe the results of the intriguing reaction of $(TMEDA)_2Nb_2Cl_5Li(TMEDA)$ with Ph_2NK which led to the formation of three compounds. One of them arises from an intramolecular C−H bond oxidative addition process mediated by two transition metals.

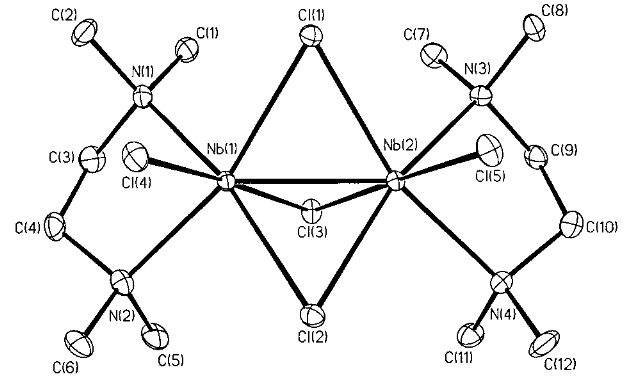
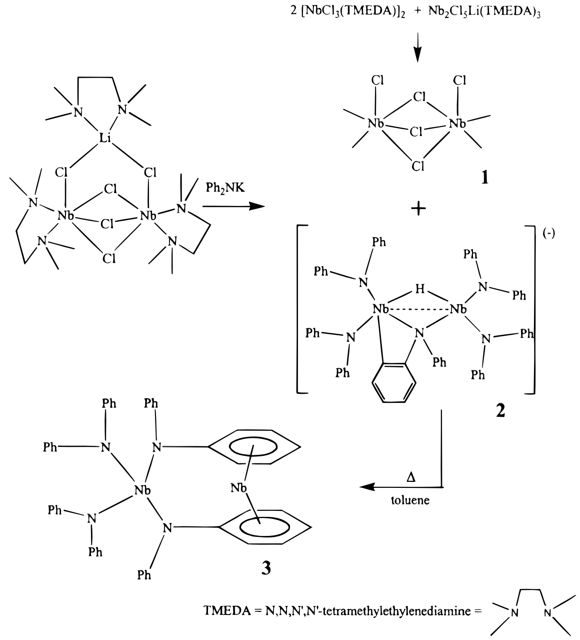


Figure 1. ORTEP drawing of **1**. Thermal ellipsoids are drawn at the 30% probability level.

Scheme 1



Results

The reaction of $(TMEDA)_2Nb_2Cl_5Li(TMEDA)$ with 4 equiv of Ph_2NK in THF gave a rapid reaction accompanied by color change. Three different compounds were isolated in crystalline form from the same reaction mixture after suitable work up (Scheme 1).

The first compound (**1**) was obtained in analytically pure form as dark purple, paramagnetic, and moderately air-sensitive crystals (yield 23%) upon allowing the reaction mixture to stand overnight at room temperature. The IR spectrum and combustion analysis data clearly ruled out the presence of the amide ligand. Qualitative analytical tests excluded the presence of lithium, while the presence of TMEDA was clearly identified in the NMR spectrum of samples previously exposed to air. Combustion analysis and X-ray fluorescence data confirmed the formulation of **1** as a mixed-valence $Cl_2Nb_2(\mu\text{-}Cl)_3(TMEDA)_2$ (**1**) complex as elucidated by an X-ray crystal structure (Figure 1). The magnetic moment was also in agreement with the presence of one unpaired electron per dimeric unit [$\mu_{eff} = 1.81\ \mu_B$].

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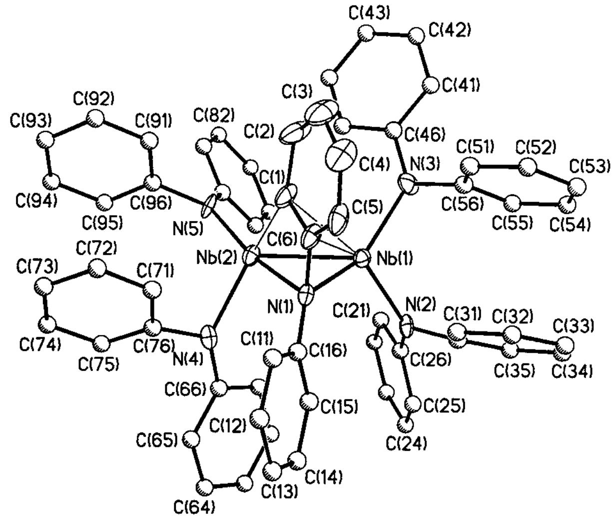

Figure 2. ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 30% probability level.

Complex **1** is insoluble in most common organic solvents including pyridine. Therefore, after filtration of the original reaction mixture and replacement of the solvent with toluene, it was possible to isolate a second species (**2**) in acceptable yield (33%) and analytically pure form. The IR and NMR spectra of this diamagnetic compound clearly indicated the presence of both the amide ligand and TMEDA. The complex tested positive for the presence of lithium, while the presence of noncoordinated toluene, probably interstitial, was clearly indicated by the NMR spectra. The amount of interstitial toluene was not always reproducible, thus indicating a tendency of the solid samples to spontaneously lose solvent. This, together with a particularly enhanced air-sensitivity and thermal instability, was probably responsible for the difficulties encountered in obtaining reproducible analytical data and sufficient quality crystals. The formulation of compound **2** as $\{[(Ph_2N)_2Nb]_2[\mu\text{-}NPh(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_4)]\}\{Li(TMEDA)_2\}\cdot$toluene was elucidated by an X-ray crystal structure (Figure 2). According to the positions of the heavy atoms, the structure of **2** arose from the complete substitution of the five chlorine atoms of the starting $(TMEDA)_2Nb_2Cl_5Li(TMEDA)$ by five Ph_2N. In addition, one of the two phenyl rings of the bridging amide is metalated in the *ortho* position and forms a σ-bond with one of the two niobium atoms, thus indicating a Nb(II)/Nb(III) mixed-valence species. This formulation necessarily requires the complex to be paramagnetic, whereas complex **2** is diamagnetic in both solid state and solution. Therefore, the formulation of **2** as a dinuclear d^2 Nb(III) hydride $\{[(Ph_2N)_2Nb]_2[\mu\text{-}NPh(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_4)](\mu\text{-}H)\}\{Li\ (TMEDA)_2\}^{(-)}$ remains the sole possibility. A difference Fourier map yielded one residual peak on the side of the Nb–Nb vector opposite that of the bridging nitrogen atom at a distance of 1.83 Å from each of the niobium atoms and at 2.71 Å from the cyclometalated carbon atom. However, given the poor crystal quality and the presence of heavy atoms in the structure, we prefer not to draw definite conclusions from the diffraction data about the presence of the hydride. Conversely, the hydride was clearly shown by NMR. The ^1H NMR spectrum showed the presence of a broad singlet [$\delta = -8.24$ ppm] which did not correlate with any carbon atom in HQMC experiments. The resonance integrated correctly for the Nb–H moiety of the proposed formulation. The resonance assigned to the bridging hydride rapidly decreased in intensity upon exposure of a THF solution of **2** to D_2 gas. At the same time, both the characteristic triplet of DH and the singlet of H_2 appeared at 4.55 and 4.70 ppm, respectively, while the resonance of the corresponding deuteride was present at −8.24 ppm of the ^2H NMR spectrum. The chemical shift of the hydride is unusually upfield while comparing to Nb and Ta hydride derivatives[2,3,13a–h] in oxidation states +4 and +5 but is in agreement with the resonances of $Cp_2NbH(L)$ [L = phosphine, phosphite] derivatives.[13i] No resonance was observed in the region 2500–1690 cm^{-1} of the IR spectrum that could be conclusively be assigned to terminal Nb–H. A broad and intense band, which instead may tentatively be assigned to the bridging hydride, is present at 1070 cm^{-1} in the IR spectrum. The poor thermal stability of **2** prevented isotopic labeling experiments to conclusively identify the Nb–H resonance in the IR spectrum. The aromatic region of the ^1H NMR spectrum, albeit rather complicated, was informative, and through COSY experiments it was possible to obtain a reasonable interpretation of the spectral features. The spectrum clearly shows the signals of three different types of aromatic rings correctly integrating in the ratio 4:5:40. The signals of the cyclometalated ring are well resolved as two doublets at 7.71 and 6.80 ppm and one multiplet (double doublet) at 6.84 ppm. The terminal ring of the bridging amide presents two distinctive doublets (8.38 and 7.30 ppm) and one pseudoquadruplet (6.78 ppm). The terminal amide ring resonances consist of two large pseudotriplets (6.64 and 6.43 ppm) and one broad feature partially overlapping with one of the two triplets. The quaternary carbon atoms and the carbon attached to the Nb atom also display unusual chemical shifts (157.5 ppm).

The third compound (**3**) present in the reaction mixture was isolated in rather poor yield (18%) from the mother liquor after replacement of the solvent by ether, followed by filtration and cooling. This third compound, also diamagnetic, tested negative for chlorine and lithium. The IR clearly indicated the presence of the amide ligand, while combustion analysis data were in good agreement with the formulation $(Ph_2N)_2Nb\{[\mu\text{-}NPh(\eta^6\text{-}C_6H_5)]_2Nb\}\cdot$ether (**3**) as revealed by an X-ray crystal structure (Figure 3). No significant features were observed in the ^1H NMR spectrum other than the presence of the aromatic amide resonances. The rings engaged in the formation of the metallocenic structure presented three distinctive bands: two pseudotriplets at 5.25 and 4.09 ppm, and one pseudodoublet at 4.85 ppm. The ^{13}C NMR spectrum was also consistent with

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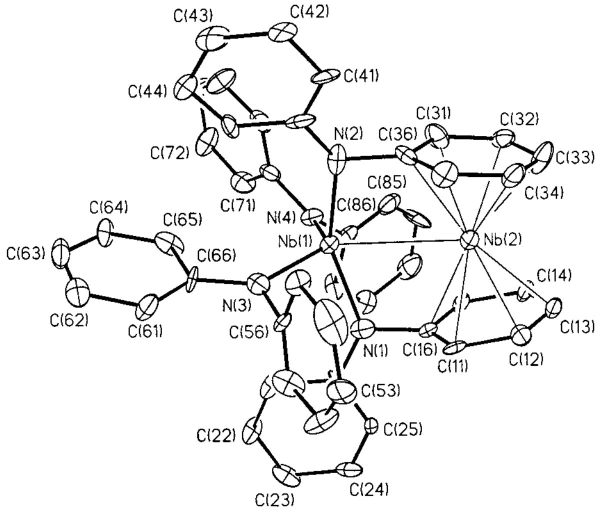

Figure 3. ORTEP drawing of **3**. Thermal ellipsoids are drawn at the 30% probability level.

these observations. The other aromatic signals of the molecule were observed in the usual range.

Structural Considerations

Suitable crystals were mounted with cooled viscous oil on thin glass fibers. Data were collected on a Bruker AG SMART 1k CCD diffractometer using a proprietary hemisphere scan routine. Cell constants were calculated from reflection data obtained from 60 data frames collected at different parts of the Ewald sphere. The data for **1** were corrected for absorption effects using redundant data at different effective azimuthal angles. No absorption corrections were applied to the data sets for **2** and **3**. The reflection data for **1** were consistent for $Pna2_1$ and *Pnam* (*Pnma*); however, only the acentric option yielded chemically reasonable and computationally stable results of refinement. The reflection data for **2** and **3** were uniquely consistent with the reported space groups. The structures were solved by direct methods, completed with subsequent Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2. A molecule of solvent of crystallization was located in the asymmetric unit for **2** and **3**. All non-hydrogen atoms, excluding the atoms of the cocrystallized solvent molecule of **2**, were refined with anisotropic displacement coefficients. Phenyl groups were refined as idealized, flat, rigid hexagons. Hydrogen atoms were assigned with idealized geometry and constrained with an isotropic, riding model. Crystallographic details are presented in Table 1. Selected bond distances and angles are given in Table 2. Additional information is given as Supporting Information. All scattering factors are contained in the SHELXTL 5.03 program library (Sheldrick, 1994, WI).

Complex 1. The crystal structure of **1** showed the molecule to be composed of two niobium atoms, five chlorine atoms, and two molecules of TMEDA, organized in an overall face-sharing bioctahedral geometry (Figure 1). Three chlorine atoms are bridging the two metal centers [Nb(1)−Cl(1) = 2.530(2) Å, Nb(1)−Cl(2) = 2.536(3) Å, Nb(1)−Cl(3) = 2.540(2) Å], while the other two are terminally bonded [Nb(1)−Cl(4) = 2.467(2) Å, Nb(2)−Cl(5) = 2.474(2) Å]. The distorted octahedral coordination geometry around each Nb atom [Cl(1)−Nb(1)−Cl(2) = 110.26(7)°, Cl(1)−Nb(1)−Cl(3) = 92.60(6)°, Cl(2)−Nb(1)−Cl(3) = 85.15(5)°, Cl(1)−Nb(1)−Cl(4) = 88.72(6)°, Cl(2)−Nb(1)−Cl(4) = 89.81(5)°, Cl(3)−Nb(1)−Cl(4) = 174.94(5)°, N(1)−Nb(1)−N(2) = 80.6(2)°, N(1)−Nb(1)−Cl(4) = 97.62(13)°, N(1)−Nb(1)−Cl(3) = 87.38(13)°, N(1)−Nb(1)−Cl(2) = 164.36(12)°, N(1)−Nb(1)−Cl(1) = 83.77(13)°] is completed by the two nitrogen atoms of the chelating TMEDA [Nb(1)−N(1) = 2.337(5) Å, Nb(1)−N(2) = 2.347(5) Å]. The Nb−Nb distance [Nb(1)−Nb(2) = 2.545(1) Å] is in the M−M bonding range but is significantly longer than that observed in $(TMEDA)_2Nb_2Cl_5Li$ (TMEDA)[9] despite the close structural similarity.

Complex 2. Spontaneous loss of solvent, conformational disorder of the interstitial molecule of toluene, and elevated thermal motions of the TMEDA molecules coordinated to lithium in the cationic unit were responsible for the relatively high values of the agreement factors. However, the anionic part of the molecule was well behaved with normal thermal parameters for all the atoms, thus allowing a reliable determination of the connectivity. The molecule is formed by two separate ionic moieties (Figure 2). The cationic unit is composed of one lithium atom surrounded by two TMEDA molecules [Li(1)−N(101) = 2.12(3) Å, Li(1)−N(102) = 2.16(4) Å, N(101)−Li(1)−N(102) = 100(2) Å]. The anionic moiety features a dinuclear unit composed by two almost identical $(Ph_2N)_2Nb$ moieties connected by one bridging amide group [Nb(1)−N(1) = 2.177(9) Å, Nb(2)−N(1) = 2.377(9) Å]. The two terminal amides are rather normal with usual bond distances [Nb(1)−N(2) = 2.107(9) Å, Nb(1)−N(3) = 2.108(10) Å] and the characteristic trigonal planar coordination geometry around the nitrogen atoms [Nb(2)−N(4)−C(66) = 136.1(7)°, Nb(2)−N(4)−C(76) = 103.1(6)°, C(66)−N(4)−C(76) = 120.3(8)°]. Conversely, the bridging amide [Nb(1)−N(1) = 2.177(9) Å, Nb(2)−N(1) = 2.377(9) Å, Nb(1)−N(1)−Nb(2) = 68.5(3)°] has some unique features. One of the two phenyl rings attached to the bridging nitrogen is normal and points away from the two Nb atoms [N(1)−C(16) = 1.448(11) Å, Nb(1)−N(1)−C(16) = 138.2(7)°, Nb(2)−N(1)−C(16) = 128.2(6)°]. The second one is bent toward both Nb atoms [Nb(1)−N(1)−C(6) = 87.1(7)°, Nb(2)−N(1)−C(6) = 93.3(6)°], showing two different types of interaction with the two metals. This is emphasized by the presence of a short bonding contact between one metal center and one of the two ring *ortho* carbon atoms [Nb(2)−C(1) = 2.197(12) Å]. This short contact is consistent with the presence of a Nb−C σ-bond, thus indicating metalation of the aromatic ring. Furthermore, the metal is nearly coplanar with the ring [torsion angle Nb(2)−N(1)−C(6)−C(1) = 7.1°]. The same ring carbon atom and the adjacent quaternary are also engaged in the formation of rather short contacts with the second Nb atom [Nb(1)−C(1) = 2.573(12) Å, Nb(1)−C(6) = 2.549(16) Å], which is elevated above the plane of the aromatic ring [2.026 Å] and nearly perpendicular to the C−C bond [Nb(1)−C(1)−C(6) = 72.9(7)°, Nb(1)−C(6)−C(1) = 105.0(9)°, torsion angles Nb(1)−N(1)−C(6)−C(5) = 117.1°, Nb(1)−N(1)−C(6)−C(1) = 61.1°]. This indicates the presence of a significant π-interaction of a portion of the aromatic ring with the metal center not engaged in the *ortho* metalation.

Complex **3** is also dinuclear (Figure 3). It is formed

Table 1. Crystal Data and Structure Analysis Results

	1	**2**	**3**
formula	$C_{12}H_{32}Cl_5N_4Nb_2$	$C_{79}H_{90}N_9Nb_2Li$	$C_{52}H_{50}N_4Nb_2O$
fw	595.49	1358.36	932.78
space group	*Pna*2(1)	*P*21/*n*	*P*2(1)2(1)2(1)
a (Å)	19.843(9)	13.4635(8)	14.1827(7)
b (Å)	8.509(9)	39.259(2)	15.5713(8)
c (Å)	13.218(7)	14.4635(9)	19.2238(9)
β (deg)		94.936(1)	
V (Å^3)	2232(3)	7597.0(8)	4245.4(4)
Z	4	4	4
radiation (Kα, Å)	0.709 30	0.709 30	0.709 30
T (°C)	−153	−153	−153
D_{calcd} (g cm^{-3})	1.772	1.188	1.459
μ_{calcd} (cm^{-1})	16.28	3.48	5.84
R, wR^2, GoF[a]	0.022, 0.046, 1.05	0.091, 0.250, 1.01	0.021, 0.056, 1.01

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

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

1	**2**	**3**
Nb1−Nb2 = 2.545(1)	Nb1−Nb2 = 2.569(12)	Nb1···Nb2 = 3.0250(2)
Nb1−Cl1 = 2.530(2)	Nb1−N1 = 2.177(9)	Nb1−N1 = 2.071(2)
Nb1−Cl2 = 2.536(3)	Nb1−N2 = 2.107(9)	Nb1−N2 = 2.099(2)
Nb1−Cl3 = 2.540(2)	Nb1−N3 = 2.108(10)	Nb1−N3 = 2.037(2)
Nb1−Cl4 =2.467(2)	Nb1−C1 = 2.573(12)	Nb1−N4 = 2.027(2)
Nb2−Cl5 = 2.474(2)	Nb1−C6 = 2.549(12)	Nb2−CentrA = 1.864
Nb2−Cl1 = 2.533(3)	Nb2−N1 = 2.377(9)	Nb2−CentrB = 1.865
Nb2−Cl2 = 2.524(2)	Nb2−N4 = 2.155(10)	N1−Nb1−N2 = 149.93(6)
Nb2−Cl3 = 2.542(2)	Nb2−N5 =2.108(9)	N1−Nb1−N3 = 105.94(6)
Nb1−N1 = 2.337(5)	Nb2−C1 = 2.197(12)	N1−Nb1−N4 = 95.99(6)
Nb1−N2 = 2.347(5)	Li1−N101 = 2.12(3)	N2−Nb1−N3 = 95.63(6)
Nb2−N3 = 2.347(4)	Li1−N102 = 2.16(4)	N2−Nb1−N4 = 91.06(6)
Nb2−N4 = 2.367(5)	N101−Li1−N102 = 100(2)	N3−Nb1−N4 = 119.65(5)
Cl1−Nb1−Cl2 = 110.26(7)	Nb1−N1−Nb2 = 68.5(3)	CentrA−Nb2−CentrB = 163.5
Cl1−Nb1−Cl3 = 92.60(6)	N1−Nb1−N3 = 139.6(4)	Nb1−N1−C6 = 101.40(11)
Cl1−Nb1−Cl4 = 88.72(6)	N1−Nb1−N2 = 107.5(4)	Nb1−N1−C12 = 138.13(12)
Cl1−Nb1−N1 = 83.77(13)	N2−Nb1−N3 =106.4(4)	C6−N1−C12 = 117.25(14)
Cl1−Nb1−N2 = 163.76(12)	N1−Nb2−N4 =86.6(3)	
Cl2−Nb1−Cl3 = 85.15(5)	N1−Nb2−N5 =166.6(3)	
Cl2−Nb1−Cl4 = 89.81(5)	N1−Nb2−C1 =59.5(4)	
Cl2−Nb1−N1 = 164.36(12)	N4−Nb2−N5 = 104.7(4)	
Cl2−Nb1−N2 = 85.80(13)	N4−Nb2−C1 = 136.9(4)	
Cl3−Nb1−Cl4 = 174.94(5)	N5−Nb2−C1 = 107.2(4)	
Cl3−Nb1−N1 = 87.38(13)	N1−C6−C1 = 105.0(9)	
Cl3−Nb1−N2 = 91.17(13)	N1−C6−C5 =130.4(11)	
Cl4−Nb1−N1 = 97.62(13)	N1−C16−C11 = 122.7(8)	
Cl4−Nb1−N2 = 88.91(13)	N1−C16−C15 =117.0(8)	
N1−Nb1−N2 = 80.6(2)	Nb2−N4−C66 =136.1(7)	
Nb1−Cl1−Nb2 = 60.36(5)	Nb2−N4−C76 = 103.1(6)	
Nb1−Cl2−Nb2 = 60.40(6)	C66−N4−C76 = 120.3(8)	
Nb1−Cl3−Nb2 = 60.11(4)		

by a $(Ph_2N)_4Nb$ unit with the niobium atom placed in the center of a rather distorted coordination tetrahedron [N(1)−Nb(1)−N(2) = 149.93(6)°, N(1)−Nb(1)−N(3) = 105.94(6)°, N(1)−Nb(1)−N(4) = 95.99(6)°, N(2)−Nb(1)−N(3) = 95.63(6)°, N(2)−Nb(1)−N(4) = 91.06(6)°, N(3)−Nb(1)−N(4) = 119.65(5)°] defined by the four nitrogen atoms of four amide groups [Nb(1)−N(1) = 2.071(2) Å, Nb(1)−N(2) = 2.099(2) Å, Nb(1)−N(3) = 2.037(2) Å, Nb(1)−N(4) = 2.027(2) Å]. A second niobium atom is placed between the two nearly parallel aromatic rings of two different amides and is symmetrically connected to the two aromatic rings [Nb(2)−C(1) = 2.365(2) Å, Nb(2)−C(2) = 2.337(2) Å, Nb(2)−C(3) = 2.346(2) Å, Nb(2)−C(4) = 2.344(2) Å, Nb(2)−C(5) = 2.324(2) Å, Nb(2)−C(6) = 2.345(2) Å], thus forming a bis-arene niobium structure [[Nb(2)−CentrA = 1.864 Å, Nb(2)−CentrB = 1.875 Å]. The Nb−Nb distance [Nb(1)···Nb(2) = 3.0250(2) Å] is rather long and perhaps not in agreement with the formation of significant M−M bonding interaction. However, there is a rather pronounced distortion in the coordination geometry of the two metal centers. Both metal atoms are pushed toward the center of the molecule [N(1)−Nb(1)−N(2) = 149.93(6)°, CentrA−Nb(2)−CentrB = 163.5°] as responding to a significant attractive force between the two metal centers.

Molecular Orbital Calculations

Ab initio HF calculations with an STO-3G basis were carried out on complex **1** using a Silicon Graphics workstation and the Spartan 4.0 software package.[14] Given the molecular complexity, simple EHMO calculations were performed on complexes **2** and **3**. In these two cases, calculations were carried out with a Pentium-PRO 266 computer using the Quantum CaCHE 2.0

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(14) All the calculations were performed with the software package *SPARTAN 4.0*; Wavefunction, Inc.: 18401 Von Karman Ave., #370, Irvine, CA 92715, 1995.

Chart 1

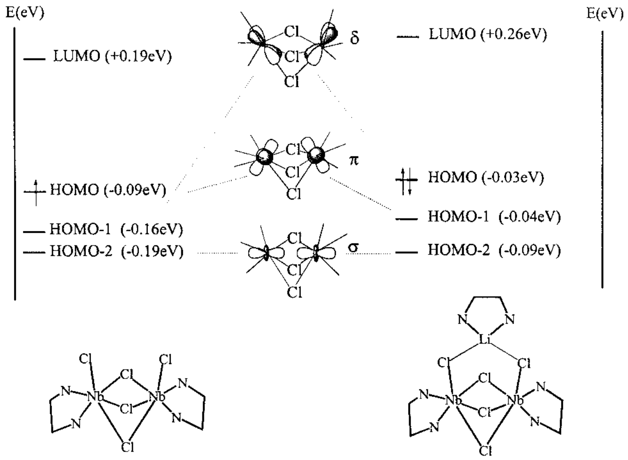
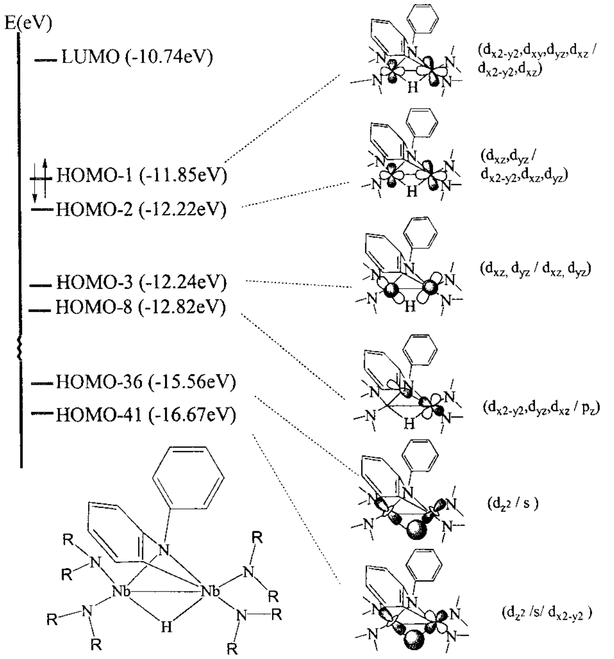


Chart 2



software package.[15] The program's default parameters were used for both calculations. The fractional atomic coordinates of the crystal structures were converted to the corresponding Cartesian coordinates by using the XP program of the SHELXTL program library.

The comparison between the geometry of **1** with that of the starting (TMEDA)$_2$Nb$_2$Cl$_5$Li(TMEDA) complex is somewhat interesting. The most visible difference lies in the absence of the lithium cation and the value of the Nb−Nb distances [respectively 2.545(1) and 2.401(5) Å for **1** and the starting material]. The deviation from the regular octahedral coordination geometry of the metal center is rather similar in the two complexes and only slightly more pronounced in complex **1** [Cl3−Nb1−Cl4 angle is 174.94(5)° against the value of 179.43(3)° of the (TMEDA)$_2$Nb$_2$Cl$_5$Li(TMEDA) complex], despite the absence of coordinated lithium. The absence in complex **1** of the attractive force applied by the lithium cation between the two vertexes of the two octahedra of the starting material might well be a critical factor in determining the elongation of the intermetallic vector of **1**. However, it is also possible that given that complex **1** is a mixed-valence species, the absence of one electron with respect to the starting Nb(II) complex depopulates the HOMO (a MO with some Nb−Nb δ-bond character), thus decreasing the formal Nb−Nb bond order and ultimately lengthening the Nb−Nb distance.

Ab initio Hartree−Fock calculations were carried out at the geometrical parameters of **1** as determined by the crystal structure. The frontier orbitals (HOMO, HOMO-1, and HOMO-2) are basically the same as those calculated for the (TMEDA)$_2$Nb$_2$Cl$_5$Li(TMEDA) complex (Chart 1) with a comparable HOMO−LUMO gap. As for the starting material, these orbitals are mainly Nb−Nb centered MOs with a metal atom contribution mainly of d-orbital character and a significant contribution from the bridging chlorine p-orbitals. For both complexes, the orbitals are originated by the same hybrid combinations of d-orbitals. In the case of complex **1**, the contribution of the bridging halide p orbitals to the formation of the M−M bonds is even higher than in the starting material. The most visible difference between the two complexes arises from the fact that the orbital that has the higher δ-character in complex **1** is more stable than the "π" orbital and becomes the HOMO. As a probable result of an increased involvement of the bridging ligand orbitals in complex **1** and of the potential depopulation of the HOMO, the formal Nb−Nb bond order decreased from 2.76 to 1.45. It is tempting at this stage to conclude that the partial depopulation of the HOMO, rather than the absence of the lithium cation, is the factor that determines the lengthening of the Nb−Nb distance.

The Nb−Nb distance in the trivalent **2** [Nb(1)−Nb(2) = 2.569(12) Å] and the diamagnetism may indicate the presence of a significant Nb−Nb bonding interaction.

The results of the EHMO calculation carried out on the anionic moiety of **2** showed a HOMO−LUMO gap (0.46 eV) sufficient to account for the observed diamagnetism. There are six MOs of interest (Chart 2). The Nb−Nb σ-interaction is realized via two MOs: the HOMO-1 (−11.85 eV) and HOMO-2 (−12.24 eV). Both orbitals are mainly Nb−Nb centered and are originated by hybrid combinations of Nb d orbitals which overlap their lobes placed on the intermetallic vector to form weak Nb−Nb bonds of mainly σ-character. The HOMO-3 arises from two identical hybrid combinations of d orbitals of the two metal atoms which overlap two lobes on one side of the intermetallic vector. This orbital, which is somewhat reminiscent of a π orbital, is very similar in shape to the HOMO of complex **1**. These three orbitals together account for a calculated Nb−Nb bond order of 1.63. The next MO of interest is HOMO-8 (−12.82 eV). This orbital is a simple Nb−C σ-bond and is formed by the overlap of a $d_{x^2-y^2}$, d_{xz}, d_{yz} hybrid combination of the metal atom with the p_z orbital of the carbon atom. The Nb−H−Nb bridging interaction is realized with two orbitals. The first, HOMO-36 (−15.56 eV), is formed via the overlap of the Nb d_{z^2} orbitals with the hydrogen s orbital. The second, HOMO-41 (−15.98 eV), is very similar to the previous one except that it is constructed by two different orbitals of the two different Nb atoms (d_{z^2} and $d_{x^2-y^2}$ respectively).

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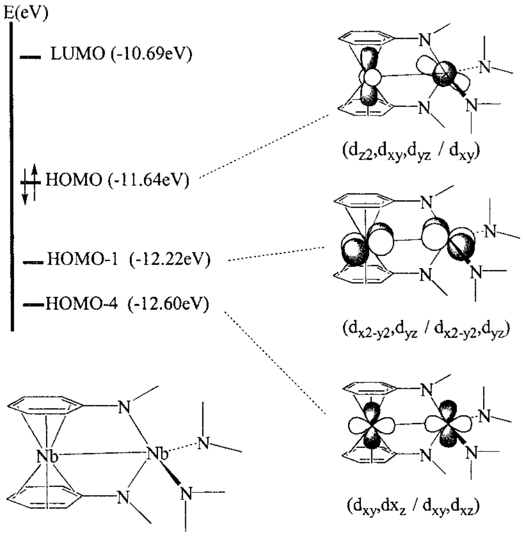
[15] Quantum CAChe 2.0 for Windows software package; Oxford Molecular Group, 1997.

Chart 3



Compound **3** may be regarded either as a Nb(IV)/Nb(0) mixed-valence species or as a Nb(II) derivative. The coordination geometry of the amide nitrogen atoms, invariably trigonal planar, indicates that each amide ligand acts as a four-electron donor. In the hypothesis of a mixed-valence formulation, each niobium atom will possess a 17-electron configuration. Therefore, the presence of a simple Nb−Nb bond will provide a formal 18-electron configuration that would explain the observed diamagnetism. Conversely, in the case of the formulation as a Nb(II) derivative the formal electron count will be of 19 and 15 electrons for the two Nb atoms, respectively. The fairly large HOMO−LUMO gap (1.05 eV) accounts well for the observed diamagnetism (Chart 3). Three frontier orbitals (HOMO, HOMO-1, and HOMO-4) have a significant Nb−Nb bond character. The HOMO (−11.64 eV) is originated by the overlap of one lobe of the d_{z^2}, d_{xy}, d_{yz} hybrid used by the “metallocenic” niobium for bonding the two aromatic rings, with one lobe of the d_{xy} orbital of the second niobium atom. The resulting MO consists of a large lobe symmetrically distributed along the Nb−Nb vector. The next MO (HOMO-1, −12.22 eV) is a regular π orbital and is originated by the overlap of two identical $d_{x^2-y^2}$, d_{yz} hybrid combinations. The orbital has two lobes symmetrically placed on the two sides of the Nb−Nb vector with a nodal plane bisecting the two parallel aromatic rings π-bonded to the second niobium atom. The next MO with a significant Nb−Nb bond character is the HOMO-4 (−12.60 eV). The orbital is also mainly d-centered with a weak but significant Nb−Nb σ-bond character. It is formed by the overlap of two lobes of two identical d_{xy}, d_{xz} hybrid combinations of each Nb atom forming a lobe symmetrically placed along the intermetallic vector. The calculated Nb−Nb bond order (0.83) is surprisingly high and might suggest the presence of a significant Nb−Nb single bond. The partial Mulliken atomic charges calculated for the two niobium atoms are consistent with the mixed-valence Nb(IV)/Nb(0) formulation.

Discussion

The complexity of the reaction of $(TMEDA)_2Nb_2Cl_5$-Li(TMEDA) with Ph_2NK poses some puzzling mechanistic questions. The formation of the mixed-valence niobium compound **1** as a significant component of the reaction mixture occurs despite using a rigorous stoichiometric amide/Nb ratio of 2:1 and has no explanation at this stage. Probably, its formation occurs via disproportionation of some intermediate able to generate a “$NbCl_3$(TMEDA)” unit. This species is rapidly scavenged by the Nb(II) starting material to form the highly insoluble mixed valence **1,** as indicated by the fact that the direct reaction of $(TMEDA)_2Nb_2Cl_5Li$(TMEDA) with $Nb_2Cl_6(TMEDA)_2$ led to the nearly quantitative formation of **1** through a rapid reaction (Scheme 1). It is interesting to observe that similar reactions of MCl_2-$(TMEDA)_2$ [M = V, Ti][16] with Ph_2NK also form halogenated clusters $[M_3Cl_5(TMEDA)_3]^{(+)}$, triangular and cationic in these particular cases. The counteranions of these species are $[(Ph_2N)_2M\{[\mu\text{-}NPh(\eta^6\text{-}C_6H_5)]_2M\}]^{(-)}$ anions [M = V,[17] Ti] possessing structures related to that of **3**.

The formation of **2** may be regarded as the result of chlorine replacement of the divalent $(TMEDA)_2Nb_2Cl_5$-Li(TMEDA) by five $Ph_2N^{(-)}$ anions. The resulting $Nb_2(NPh_2)_5Li$ intermediate, also divalent, forms compound **2** via oxidative addition of the two Nb(II) centers to the C−H σ-bond of one aromatic ring. The one-electron oxidation of each of the two metal centers provides the two electrons necessary for the C−H bond cleavage and formation of the trivalent **2.** The reaction may be also regarded as a formal metathesis of the Nb−Nb triple bond, perhaps present in $(TMEDA)_2Nb_2Cl_5$-Li(TMEDA) (calculated Nb−Nb bond order 2.76), with the ligand C−H bond to form a Nb−Nb doubly bonded Nb(III) complex (calculated Nb−Nb bond order 1.63). This behavior is in striking contrast with that of similar reactions performed with different amides, where similar cooperative interaction of the two Nb atoms gave instead C−N bond cleavage.[12]

Examples of transformations involving intermediate C−H bond activation are abundant in the literature,[18] while examples of oxidative addition of metal centers to C−H bonds to form characterizable alkyl/hydride derivatives remain relatively few.[19] Although we do not know the mechanism for the formation of complex **2**, from the formal point of view this species is the result of the oxidative addition performed by the attack of two group 5 metals on the same C−H bond, forming a stable alkyl hydride compound.[20]

A relatively complex reorganization of complex **2** (dissociation of amide Li and shift of one of the two Nb atoms) is at the origin of **3** (Scheme 2). However, with this reaction the amide ligand is restored, thus indicating that both the hydride and the metalated ring were reductively eliminated by the metal center. Accordingly, we did not observe during this process hydrogen evolu-

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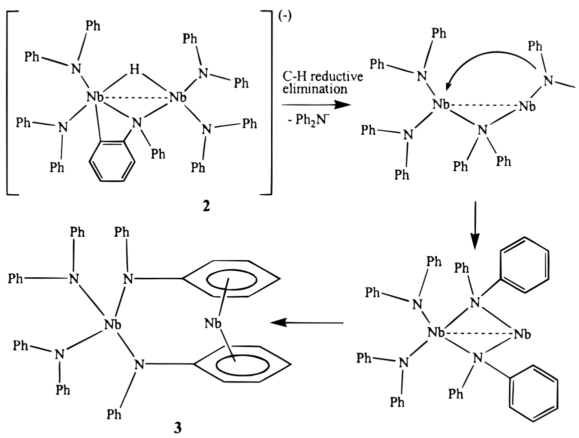
[16] Edema, J. J. H.; Duchateau, R.; Gambarotta, S.; Bensimon, C. *Inorg. Chem.* **1991**, *30*, 3585.

[17] Song, J.; Gambarotta, S. Manuscript in preparation.

[18] See for example: (a) Dani, P. Karlen, T.; Gossage, R. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1997**, *119*, 11317, and references cited therein. (b) Liou, S. Y.; Gozin, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1965. (c) Gozin, M.; Aizenberg, M.; Liou, S. Y.; Weismann, A.; Ben-David, Y.; Milstein, D. *Nature* **1994**, *370*, 42. (d) Fryzuk, M. D.; Montogomery, C. D.; Rettig, S. J. *Organometallics* **1991**, *10*, 467. (e) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020. (f) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840. (g) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235.

Scheme 2



tion, which could possibly indicate alternative pathways. The overall transformation implies an internal redox process and does not require electrons to be added to or removed from **2**. In agreement with the proposal that **3** is a product of the evolution of **2**, thermolysis of an analytically pure sample of **2** in toluene afforded higher yield (60%) of complex **3**. The conversion of **2** to **3** may also be monitored by NMR during a reaction that is slow at room temperature (about 5 days) but much faster at high temperature. NMR tube experiments clearly indicate that the formation of **3** is also accompanied by the appearance of a new thermally stable hydride, probably high-valent ($\delta = +9.8$ ppm not correlated with any carbon resonance). Unfortunately, attempts to isolate this fourth species were so far unsuccessful.

Experimental Part

All operations were performed under an inert atmosphere by using standard Schlenck techniques. (TMEDA)$_2$Nb$_2$Cl$_5$Li(TMEDA)[11,12] was prepared according to published procedures. Ph$_2$NK was prepared in situ by treating the corresponding amine (Aldrich) with KH. 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,[21] and corrections for underlying diamagnetism were applied to the data.[22] 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 [(TMEDA)NbCl]$_2$(μ-Cl)$_3$ (1). Method A. A solution of (TMEDA)$_2$Nb$_2$Cl$_5$Li(TMEDA) (1.0 g, 1.4 mmol) in THF (70 mL) was treated with Ph$_2$NK (1.55 g, 5.6 mmol). The homogeneous solution was allowed to stand at room temperature overnight without stirring, upon which dark purple crystals of **1** separated (0.18 g, 0.32 mmol, 23%). El. Anal. Calcd (found) for C$_{12}$H$_{32}$N$_4$Nb$_2$Cl$_2$: C 24.20 (24.61), H 5.42 (5.71), N 9.41 (9.23). IR (Nujol, KBr plates, cm^{-1}): ν 1407 (w), 1287 (m), 1261 (m), 1240 (m), 1194 (w), 1120 (m), 1100 (w), 1064 (m), 1040 (m), 1014 (s), 994 (m), 951 (s), 918 (m), 793 (s), 766 (m), 722 (w). $\mu_{\mathrm{eff}} = 1.81\mu_{\mathrm{B}}$.

Method B. A solution of (TMEDA)$_2$Nb$_2$Cl$_5$Li(TMEDA) (1.0 g, 1.4 mmol) in THF (70 mL) was treated with Nb$_2$Cl$_6$(TMEDA)$_2$ (0.88 g, 1.4 mmol) under vigorous stirring. The color changed immediately, and a dark purple microcrystalline solid started to separate. Stirring was continued for 2 h, and microcrystalline **1** was isolated (0.76 g, 1.25 mmol, 90%) and identified by comparison of the spectroscopic, analytical, and magnetic properties with those of an analytically pure sample prepared according to method A.

Preparation of {[(Ph$_2$N)$_2$Nb]$_2$[μ-NPh(μ-η^1:η^2-C$_6$H$_4$)](μ-H)}{Li(TMEDA)$_2$}·toluene (2). The mother liquor of the above reaction, as described in method A, was evaporated to dryness. The residual solid was redissolved in toluene (250 mL), and the resulting solution was filtered to remove a small amount of insoluble material. The resulting solution was allowed to stand at −30 °C overnight, upon which dark orange crystals of **2** separated (0.36 g, 0.28 mmol, 33%). Anal. Calcd (found) for C$_{79}$H$_{90}$N$_9$Nb$_2$Li: C 69.85 (69.36), H 6.68 (6.61), N 9.28 (9.01). IR [Nujol, cm^{-1}]: ν 1589 (s), 1307 (m), 1287 (m), 1261 (s), 1172 (m), 1079 (m), 1027 (s), 921 (m), 887 (m), 856 (m), 798 (s), 748 (s), 727 (s), 694 (s). ^{1}H NMR [500 MHz, THF-d_8, 23 °C]: δ 8.38 (doublet, 1H, bridging amide terminal aromatic ring), 7.71 (doublet, 1H, bridging amide metalated ring), 7.30 (doublet, 2H, bridging amide terminal aromatic ring), 7.17 (multiplet, 5H, toluene), 6.84 (multiplet, 2H, bridging amide metalated ring), 6.80 (doublet, 1H, bridging amide metalated ring), 6.78 (pseudoquadruplet, 2H, bridging amide terminal aromatic ring), 6.64 and 6.43 (pseudotriplet, 40H, terminal amides rings), 2.31 (singlet, 8H, CH$_2$ TMEDA), 2.15 (singlet, 24H, CH$_3$ TMEDA), 2.08 (singlet, 3H, toluene), −8.24 (broad singlet, 1H, hydride). ^{13}C NMR [127.7 MHz, THF-d_8, 23 °C]: δ 157.5, 154.6, 154.4, 152.5, 151.2 (quaternary carbon), 142.4, 121.7, 120.9 (bridging amide terminal aromatic ring), 122.7, 127.9, 126.0, 124.6 (bridging amide metalated ring), 123.9−119.7 (series of lines, aromatic ring terminal amides), 137.5, 128.8, 128.0, 125.2 (toluene), 58.93 (CH$_2$ TMEDA), 46.18 (CH$_3$ TMEDA), 20.04 (CH$_3$ toluene).

Preparation of (Ph$_2$N)$_2$Nb{[μ-NPh(η^6-C$_6$H$_5$)]$_2$Nb}·ether (3). Method A. The toluene solution obtained from the preparation of complex **2** was evaporated to dryness. The residual solid was redissolved in ether (70 mL), and the resulting solution was filtered to remove a small amount of insoluble material. The solution was allowed to stand for 4 days at room temperature, upon which dark brown crystals of **3** separated (0.14 g, 0.16 mmol, 12%). Anal. Calcd (found) for C$_{52}$H$_{50}$N$_4$Nb$_2$O: C 66.96 (66.86), H 5.40 (5.13), N 6.01 (5.75). IR [Nujol, cm^{-1}]: ν 1587 (s), 1572 (w), 1421 (m), 1326 (w), 1291 (s), 1267 (s), 1227 (m), 1194 (m), 1167 (s), 1120 (m), 1079 (m), 1027 (m), 991 (m), 959 (m), 870 (s), 840 (m), 751 (s), 696 (s). ^{1}H NMR [500 MHz, THF-d_8, 23 °C]: δ 6.94 (multiplet, 20H, aromatic rings terminal amide), 6.74 (multiplet, 10H, terminal aromatic rings bridging amides), 5.25 (pseudotriplet, 4H,

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(19) See for example: (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (c) Hoyano, G. J.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190. (d) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620. (e) Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436. (f) Gregory, T.; Harper, P.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7915. (g) *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; Collman, J. P., Hegedus, L. S., Norton, J. R., Finke, R. G., Eds.; University Science Books: Mill Valley, CA, 1987. (h) Blau, R. J.; Chisholm, M. H.; Eichborn, B. W.; Huffman, J. C.; Kramer, K. S.; Lobkovsky, E. B.; Streib, W. E. *Organometallics* **1995**, *14*, 1855. (i) Green, J. C.; Green, M. L. H.; O'Hare, D.; Watson, R. R.; Bandy, J. A. *J. Chem. Soc., Dalton Trans.* **1987**, 391. (j) Arndsten, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (k) Bromberg, S. E.; Yang, H.; Asplund, M. C.; Lian, T.; Mcnamara, B. K.; Kotz, K. T.; Yeston, J. S.; Wilkens, M.; Frei, H.; Bergman, R. G.; Harris, C. B. *Science* **1997**, *278*, 260.

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(22) Foese, G.; Gorter, C. J.; Smits, L. J. *Constantes Selectionnées Diamagnetisme, Paramagnetisme, Relaxation Paramagnetique*; Masson: Paris 1957.

π-bonded aromatic ring *meta* C−H), 4.85 (pseudodoublet, π-bonded aromatic ring *ortho* C−H, 4H), 4.09 (pseudotriplet, aromatic rings π-bonded aromatic ring *para* C−H, 2H), 3.39 (quadruplet, CH_2 ether, 4H), 1.12 (triplet, CH_3 ether, 6H). ^{13}C NMR [127.7 MHz, THF-d_8, 23 °C]: δ 154.2 (ring quaternary C), 152.4 (ring quaternary C), 129.4, 125.4, 119.5 (CH ring terminal amide) 129.1, 124.4, 119.6 (CH ring bridging amide), 98.9 (quaternary C π-ring), 88.5 (*ortho* CH π-ring), 82.5 (*meta* CH π-ring), 73.4 (*para* CH π-ring)

Method B. A sample of analytically pure **2** (1.0 g, 0.75 mmol) was added to toluene (70 mL) and heated for 15 min at 100 °C. The solvent was then removed by evaporation in vacuo, and the residual solid redissolved in ether. The solution was filtered to remove a small amount of insoluble material and allowed to stand at room temperature for 4 days, upon which dark brown crystals of **3** separated (0.42 g, 0.45 mmol, 60%). The compound was identified by comparison of the analytical and spectroscopic properties with those of an analytically pure sample.

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Supporting Information Available: Listings of atomic coordinates, thermal parameters, and bond distances and angles for **1, 2** and **3** (31 pages). Ordering information can be found on any current masthead page.

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