New Alkylimido Niobium Complexes Supported by Guanidinate Ligands: Synthesis, Characterization, and Migratory Insertion Reactions

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S Supporting Information

ABSTRACT: A series of guanidine proligands, 2-(4-(*tert*-butyl)phenyl)-1,3-diisopropylguanidine (1), 2-(4-bromophenyl)-1,3-diisopropylguanidine (2), 2-(4-methoxyphenyl)-1,3-diisopropylguanidine (3), and 2,2'-(1,4-phenylene)bis(2',3-diisopropylguanidine) (4), has been reacted with $[\text{NbBz}_2(\text{N}^t\text{Bu})]$ (5) through a protonolysis reaction to obtain new monoguanidinate-supported dibenzyl niobium complexes, $\{\text{NbBz}_2(\text{N}^t\text{Bu})[(4\text{-}^t\text{BuC}_6\text{H}_4)\text{N}=\text{C}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr})]\}$ (6), $\{\text{NbBz}_2(\text{N}^t\text{Bu})[(4\text{-BrC}_6\text{H}_4)\text{N}=\text{C}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr})]\}$ (7), $\{\text{NbBz}_2(\text{N}^t\text{Bu})[(4\text{-MeOC}_6\text{H}_4)\text{N}=\text{C}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr})]\}$ (8), and the dinuclear complex $\{[\text{NbBz}_2(\text{N}^t\text{Bu})]_2[(\text{C}_6\text{H}_4)(\text{N}=\text{C}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr}))_2]\}$ (9). Complexes 6, 8, and 9 were structurally characterized. These neutral complexes contain a η^2 -benzyl ligand coordinated to the metal center. Insertion migratory reactions with isocyanides resulted in the formation of bis- κ^2 -iminoacyl species, $\{\text{Nb}(\text{N}^t\text{Bu})(^t\text{BuN}=\text{CCH}_2\text{Ph})_2[(4\text{-}^t\text{BuC}_6\text{H}_4)\text{N}=\text{C}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr})]\}$ (10), $\{\text{NbBz}_2(\text{N}^t\text{Bu})(^t\text{BuN}=\text{CCH}_2\text{Ph})_2[(4\text{-BrC}_6\text{H}_4)\text{N}=\text{C}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr})]\}$ (11), $\{\text{Nb}(\text{N}^t\text{Bu})(^t\text{BuN}=\text{CCH}_2\text{Ph})_2[(4\text{-MeOC}_6\text{H}_4)\text{N}=\text{C}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr})]\}$ (12), and the dinuclear complex $\{[\text{Nb}(\text{N}^t\text{Bu})(^t\text{BuN}=\text{CCH}_2\text{Ph})_2]_2[(\text{C}_6\text{H}_4)(\text{N}=\text{C}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr}))_2]\}$ (13), when $^t\text{BuNC}$ was used. The analogous reaction using XyNC ($\text{Xy} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) led to the formation of vinylamido species, $\{\text{Nb}(\text{N}^t\text{Bu})[\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{CH}=\text{CHPh}][\text{BzC}=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)][(4\text{-}^t\text{BuC}_6\text{H}_4)\text{N}=\text{C}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr})]\}$ (14), $\{\text{Nb}(\text{N}^t\text{Bu})[\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{CH}=\text{CHPh}][\text{BzC}=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)][(4\text{-BrC}_6\text{H}_4)\text{N}=\text{C}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr})]\}$ (15), $\{\text{Nb}(\text{N}^t\text{Bu})[\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{CH}=\text{CHPh}][\text{BzC}=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)][(4\text{-MeOC}_6\text{H}_4)\text{N}=\text{C}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr})]\}$ (16), and $\{[\text{Nb}(\text{N}^t\text{Bu})[\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{CH}=\text{CHPh}][\text{BzC}=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)]_2[(\text{C}_6\text{H}_4)(\text{N}=\text{C}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr}))_2]\}$ (17), through a proposed 1,2-hydrogen shift mechanism from an iminoacyl intermediate similar to those obtained from the insertion of $^t\text{BuNC}$. Complex 17 was structurally characterized.

INTRODUCTION

The continued interest in new ligand systems that support metallic centers involved in, for example, catalytic processes has led to the design of increasingly elaborate compounds to accomplish this target.¹ In contrast, a series of simple organic molecules could satisfy the need for alternative ancillary ligands with diverse electronic and steric properties. In particular, guanidine derivatives have been widely used for the stabilization of different metal complexes.²

The ease of substituent modification within the guanidinate framework enables the variation of the interesting steric and electronic features of the ligand and its coordination to the metal center (Scheme 1). Among the direct methods for synthesizing N,N',N'' -trisubstituted guanidines, catalytic guanylation of amines with carbodiimides is a 100% atom-economic process.³

Numerous different examples of this reaction have been reported in recent years.⁴ For example, we described a new approach⁵ that involves the use of simple catalysts for the guanylation of amines (Scheme 2). These guanidines could coordinate, in a way different from that found in previously

Scheme 1. Resonance Structures for Monoanionic Guanidinate Ligands

described complexes, in an asymmetric manner by means of one alkylamino nitrogen and the arylimino nitrogen atom.

Imido ligands are suitable for the stabilization of metal complexes in high oxidation states.⁶ As a continuation of our interest in the area of imido complexes of group 5 metals,⁷ we have extended the relatively unexplored chemistry of guanidinate complexes of this group⁸ with the aim of obtaining alkylimido niobium(V) guanidinate derivatives and exploring their activity and the influence that these polydentate ligands

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Scheme 2. Catalytic Procedure To Obtain N,N',N'' -Trisubstituted Guanidines

have in isocyanide insertion migration into niobium–alkyl bonds.⁹

RESULTS AND DISCUSSION

We recently reported^{5,7a} that some commercially available products can be used as catalyst precursors for the guanylation of aromatic amines. This procedure was used to obtain the simple guanidine proligands 2-(4-*tert*-butylphenyl)-1,3-diisopropylguanidine (**1**),⁵ 2-(4-bromophenyl)-1,3-diisopropylguanidine (**2**),^{4b} and 2-(4-methoxyphenyl)-1,3-diisopropylguanidine (**3**)^{4a} in good yields using ZnEt_2 as catalyst. A direct method for the synthesis of biguanidines is the double catalytic addition reaction of diamines to carbodiimides. The reported catalytic procedure was extended successfully by the addition of 1,4-diaminobenzene to 2 equiv of $\text{iPrNCN}^{\text{iPr}}$. The reaction was complete after 2 h to afford quantitatively the corresponding biguanidine proligand 2,2'-(1,4-phenylene)bis(2',3-diisopropylguanidine) (**4**), which was previously obtained by means of complex titanium or lanthanide compounds.^{4f,m} This compound was used as a model system to study its potential to act as a bridge between two metal fragments.

Among the known routes to obtain new guanidinate complexes, the direct reaction between the proligand and a metal complex containing ligands that are susceptible to cleavage by protonolysis has been widely used. These reactions avoid the production of salt-containing byproduct and facilitate the isolation of the target compound.^{8,10} In group 4 chemistry, $\text{M}(\text{CH}_2\text{Ph})_4$ starting materials ($\text{M} = \text{Zr}, \text{Hf}$) are the compounds of choice. In a similar protocol, coordination of ligands **1–4** to niobium(V) was studied by treatment with $[\text{NbBz}_3(\text{N}^t\text{Bu})]$ (**5**).¹¹ The reaction of 1 equiv of **1**, **2**, or **3** with 1 equiv of **5**, or the reaction of **4** with 2 equiv of **5**, in toluene at room temperature, results in the formation of the corresponding dibenzyl complexes **6–9**, respectively, in good yields after recrystallization (^1H NMR spectroscopy showed complete conversion after a few seconds) (see Scheme 3). These complexes were stable for several weeks in solution under an inert atmosphere, at room temperature, and with exposure to light.

The ^1H NMR spectra of the different guanidinate compounds **6–9** are quite similar. Methyl fragments of isopropyl groups of the guanidine ligands appear as two doublets close to δ 0.6 and 1 ppm, a finding that indicates an asymmetric disposition of the coordinated ligand (which is symmetric when free). One of the methine isopropyl groups is coupled with a doublet close to δ 3.5 ppm, and this signal is assigned to the remaining NH group from a noncoordinated isopropylamino group. NOESY-1D experiments give an indication of the proximity of the other isopropyl amino group to the imido moiety, which appears near δ 1.4 ppm. In addition, two coupled (ca. 8 Hz) doublets at around δ 2.3 and 3

Scheme 3. Synthesis of the Niobium Guanidinate Complexes **6–9**

ppm were observed for the diastereotopic methylene protons of the two benzyl ligands. The ^{13}C NMR spectra contain signals that are consistent with the proposed structures, including a single carbon resonance at δ 56 ppm correlated to both methylene doublets and a diagnostic signal close to δ 164 ppm for the central carbon of a κ^2 monoanionic chelating guanidinate.^{8g} The $^1J_{\text{CH}}$ value for the methylene group (ca. 134 Hz), the high-field chemical shift of the ipso carbon of the phenyl group ($\delta \sim 140$ ppm) and the methylene carbons ($\delta \sim 56$ ppm), and the germinal coupling constant ($^2J_{\text{HH}} \approx 8$ Hz) all suggest a η^2 coordination of the two equivalent benzyl groups. This type of η^2 coordinative behavior of the benzyl ligand in d^0 early transition metals is very common.^{7e,10f,11,12}

The spectroscopic features described above are indicative of a C_s -symmetric coordination that is consistent with a pseudo-bipyramidal geometry in which the strong donor imido ligand and the aromatic supporting nitrogen atom of the guanidinate ligand occupy the opposite axial positions, whereas the second coordinated nitrogen atom of the guanidinate, which bears an isopropyl moiety, and two equivalent benzyl groups are located in the equatorial positions.

X-ray single-crystal structure determinations were carried out for **6**, **8**, and **9**. The molecular structures and atomic numbering schemes are shown in Figures 1 and 2; selected bond lengths and angles are given in Table 1. Suitable X-ray-quality crystals were obtained from pentane (**6** and **8**) or tetrahydrofuran (**9**). Complex **6** crystallizes in the $Pbca$ space group. Complex **8** crystallizes in the $P\bar{1}$ space group. Finally, complex **9** crystallizes in the $C2/c$ space group. It is noteworthy that complex **9** is one of the few examples of a biguanidinate complex of a group 5 metal that has been structurally characterized^{8d} and, in this case, the biguanidine bridges two metal centers.

The distribution of the atoms around the niobium center in all three complexes is quite similar. A distorted-trigonal-bipyramidal geometry was found with an N2–Nb1–N3 angle of approximately 60° . The imido group occupies one of the axial positions, and the nitrogen atom bearing the aromatic group of the guanidinate occupies the other axial position. The equatorial plane contains the second coordinated nitrogen atom of the guanidinate ligand as well as the methylene fragments of the benzyl groups. The imido group is quasilinear with an Nb1–N1–C1 angle between $175.6(4)$ and $178.0(3)^\circ$ and an Nb1–N1 bond distance of 1.76 Å. The quoted values

Figure 1. ORTEP drawing of compounds **6** (a) and **8** (b). Hydrogen atoms are omitted for clarity, and thermal ellipsoids are shown at 30% probability.

Figure 2. ORTEP drawing of compound **9**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are shown at 30% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes **6**, **8**, and **9**

	6	8	9
Bond Lengths			
Nb1–N1	1.766(3)	1.765(4)	1.761(4)
Nb1–N2	2.091(3)	2.083(4)	2.089(4)
Nb1–N3	2.346(3)	2.368(4)	2.358(4)
Nb1–C12	2.201(4)	2.195(4)	2.190(6)
Nb1–C13	2.601(5)	2.573(5)	2.558(6)
Nb1–C31	2.229(4)	2.233(4)	2.229(5)
N2–C5	1.350(4)	1.365(5)	1.361(6)
N3–C5	1.328(4)	1.324(5)	1.336(6)
N4–C5	1.354(4)	1.362(6)	1.341(6)
Bond Angles (deg)			
N1–Nb1–N2	104.6(1)	103.8(2)	104.4(2)
N1–Nb1–N3	163.2(1)	162.6(1)	162.7(2)
N2–Nb1–N3	59.4(1)	59.6(1)	59.7(1)
Nb1–N1–C1	177.1(3)	178.0(3)	175.6(4)
N2–C5–N3	111.3(3)	111.8(4)	111.3(4)
N2–C5–N4	123.0(3)	122.1(4)	122.8(4)
N3–C5–N4	125.7(3)	126.1(4)	125.9(4)
Nb1–C12–C13	88.5(3)	86.8(3)	86.9(4)
Nb1–C31–C32	103.3(2)	107.3(3)	104.1(3)

for the angles and the distances are very close to those described for other imido complexes^{6,8a,11,13} and are consistent with the existence of a metal–nitrogen fragment with a triple bond and an sp-hybridized nitrogen atom. The ligand thus formally donates six electrons in total to the niobium center. The Nb1–N1 distance is slightly longer than in the case of the halide-containing complex [Nb(N^tBu)Cl₃(py)₂], with a value of 1.734 Å.^{13c} This difference can be explained by the higher donor strength of the guanidinate ligand compared with that of the chloro ligands.

Charge delocalization around the guanidinate atoms is postulated on the basis of the C–N distances (~1.35 Å for N2–C5, N3–C5 and N4–C5), which are intermediate between the values expected for C–N single and C=N double bonds,⁵ and the planarity of the “CN₃” core, which is evidenced by the sum of the bond angles around C5 (360°). The C5–N4 distance is also shorter than one would expect for a typical C–N single bond. These data imply that the guanidinate ligand acts as a strong donor toward the metal center in these complexes. Trans to the imido group, the Nb1–N3 bond is elongated compared to the Nb1–N2 bond ($\Delta(\text{Nb–N}) \approx 0.26$ Å), as one would expect due to the trans influence of the imido group.

The Nb1–C12–C13 angle of ~87° and the Nb1–C13 distance of ~2.6 Å both indicate that one benzyl group shows η^2 hapticity. In contrast, the Nb1–C31–C32 angle (~105°) and the Nb1–C32 distance (~3 Å) indicate that the second benzyl group shows η^1 hapticity. The results of the structural analyses are not consistent with the NMR results, which indicate that, in solution, the two equivalent benzyl groups have η^2 hapticity. It can therefore be deduced that the benzyl ligands pass uninterrupted from η^1 hapticity to η^2 hapticity (and vice versa). Unfortunately, this exchange could not be frozen in a ¹H NMR study in solution at low temperature (163 K).

The dinuclear complex **9** shows characteristics similar to those of mononuclear complexes **6** and **8**. The two metal centers are separated by 9.67 Å, and the dihedral plane formed by the metal guanidinate moiety and the central phenylene group is 61.6°.

The migratory insertion reactions of CO or isocyanide ligands into alkyl groups allows the formation of new C–C bonds to give acyl or iminoacyl groups. In highly oxophilic d⁰ early transition metals, the iminoacyl group usually adopts a characteristic κ^2 -C,N coordination mode through both the nitrogen and carbon atoms of the double bond.⁹ This reaction represents an interesting way to approach fundamental research into these alkyl guanidinate niobium complexes in order to access a significant area in the organometallic chemistry of the group 5 metals.^{9b,12,14,15}

The reaction of the dibenzyl compounds **6**–**9** with *tert*-butyl isocyanide (^tBuNC) in an NMR tube gave the products {Nb(N^tBu)(^tBuN=CCH₂Ph)₂[(4-RC₆H₄)N=C(NⁱPr)-(NHⁱPr)]} (R = ^tBu (**10**), Br (**11**), OMe (**12**)) and {[Nb(N^tBu)(^tBuN=CCH₂Ph)₂](C₆H₄)(N=C(NⁱPr)-(NHⁱPr))₂] (**13**), respectively, in almost quantitative yield in a few minutes (Scheme 4).

These products originate from the migratory insertion of two isocyanide molecules into the two niobium–alkyl bonds. Even when the stoichiometry was adjusted to promote the single insertion, the final products were those described above together with unreacted starting materials. Compounds **10**–**13** were also isolated on a larger scale (see the Experimental Section) and were characterized by FT-IR and NMR

Scheme 4. Migratory Insertion Processes with ^tBuNC

spectroscopy. A characteristic band at ca. 1550 cm⁻¹ was assigned to the $\nu(\text{C}=\text{N})$ vibration of the κ^2 -iminoacyl groups.⁹ The ¹H NMR spectra of the complexes obtained from **6–8** indicate the formation of two products in an approximate ratio of 1:1. NOESY-1D experiments indicate that the relative coordination of the guanidinate ligand was retained in the new complexes. The insertion of the isocyanide compounds is suggested by the disappearance of the two doublets due to benzyl methylene protons and the appearance of two overlapped AB systems at ca. 4 ppm, corresponding to the diastereotopic benzylic protons. Four doublets of equal intensity, assigned to methyl groups on the isopropyl units, are observed along with four singlets, assigned to two *tert*-butyl imido and two *tert*-butyl iminoacyl groups, respectively, of relative intensity 1:2, in addition to other doubled signals of the corresponding guanidinate (see the Experimental Section). These signals lead us to propose the formation of two isomers with a C_s symmetry. The κ^2 binding mode of the iminoacyl groups in these complexes is also suggested by ¹³C NMR data, where two very similar resonances at $\delta \sim 220$ ppm^{9a} were assigned to the iminoacyl carbon atoms of two different isomers. The relative orientation of the two κ^2 -iminoacyl groups, as required to fit with the symmetry indicated by the NMR spectra, is shown in Scheme 5. These geometric isomers

Scheme 5. Relative Disposition of κ^2 -Iminoacyl Groups

are described as pseudo-bipyramidal complexes, in which the two κ^2 -iminoacyl groups formally occupy two coordination sites, with the nitrogen atoms both oriented proximal or distal to the guanidinate ligand. In the case of complex **9**, three isomers were obtained in an approximate 1:1:2 ratio and these correspond to the three possible configurations: i.e., distal–distal, proximal–proximal, and proximal–distal distribution of the two pairs of κ^2 -iminoacyl groups on each niobium atom of each dinuclear isomer, respectively.

In contrast to the situation outlined above for ^tBuNC and the reactivity observed for the parent compound **5**,¹⁴ the reaction of 2 equiv of 2,6-dimethylphenyl isocyanide, XyNC, with dibenzyl compounds **6–9** proceeded at room temperature to give a complex mixture of compounds. The ¹H NMR spectrum in C₆D₆ after several hours shows sharp and broad lines along with evidence for the presence of starting materials. In addition,

an AB system located close to δ 4 ppm can be assigned to a methylene group of an iminoacyl ligand that arises, as for complexes **10–13**, by a migratory insertion process. Surprisingly, this mixture was transformed in almost quantitative yield by gentle heating at 50 °C for 16 h into a single product on starting from complexes **6–8**; in the case of compound **9**, however, a 1:1 mixture of isomers was obtained. The ¹H NMR spectra of these new complexes contain two doublets, one at δ 5 ppm and the other downfield at δ 8 ppm. These resonances were attributed to the formation of a vinylamido group. The ³J_{HH} coupling constant between these two protons is 13 Hz, and this value is consistent with a *trans* arrangement of the olefinic moiety.^{16a} A close AB system was also observed at δ 3.7 ppm. This finding, along with the presence of a signal in the ¹³C NMR spectra at δ 240 ppm, allows us to propose the presence of an additional κ^2 -iminoacyl group (Scheme 6).

Scheme 6. Migratory Insertion Processes and Evolution to Vinylamido Derivatives

The resulting chiral environment around the metal center makes the isopropyl methyl groups diastereotopic, with the signals split into four doublets. Two sets of inequivalent methyl groups in the δ 1.5–2.5 ppm region indicate that the rotation of the two distinct 2,6-dimethylphenyl groups is hindered in these molecules. The presence of two chiral centers in **17**, obtained from complex **9**, results in the formation of two diastereoisomers in a 1:1 ratio, as mentioned above.

The formation of vinylamido ligands from isocyanides has already been observed for some group 4 metal complexes^{10a,b,d,16} and one niobium complex.¹⁷ A plausible mechanism for the formation of **14–17** would first involve reaction of the

Figure 3. ORTEP drawing of compound 17. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are shown at 20% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 17^a

bond length			bond angle		
Nb–N1	1.766(5)	1.752(5)	N1–Nb–N2	95.9(2)	95.7(2)
Nb–N2	2.174(5)	2.197(5)	N1–Nb–N5	102.9(2)	102.3(2)
Nb–N3	2.267(5)	2.224(5)	N1–Nb–N6	104.9(2)	106.2(2)
Nb–N5	2.097(5)	2.105(5)	N2–Nb–N3	59.4(2)	58.9(2)
Nb–N6	2.250(5)	2.235(5)	N2–Nb–N5	93.9(2)	92.6(2)
Nb–C41	2.133(6)	2.133(7)	N2–Nb–N6	157.6 (2)	157.5(2)
N1–C1	1.464(8)	1.443(8)	N3–Nb–N5	116.2(2)	120.7(2)
N2–C5	1.322(7)	1.315(8)	Nb1–N–C1	177.3(5)	174.9(5)
N3–C5	1.340(8)	1.355(8)	N2–C5–N3	111.5(6)	108.9(6)
N4–C5	1.371(8)	1.364(9)	N2–C5–N4	123.6(7)	125.9(7)
N5–C21	1.395(8)	1.368(7)	N3–C5–N4	124.8(7)	125.1(7)
N6–C41	1.262(7)	1.248(8)			
C21–C22	1.349(8)	1.342(8)			

^aEach data column corresponds to a different metal center in a single molecule (see the Experimental Section).

dibenzyl complex with 2 equiv of 2,6-dimethylphenyl isocyanide by a migratory insertion into the Nb–Bz bonds to form an intermediate bis(κ^2 -C,N-iminoacyl)-containing species. However, all attempts to isolate this intermediate were unsuccessful. Reaction of the parent compound **5** with 2 equiv of XyNC at 50 °C for more than 1 day, or in the presence of an excess of pyridine as an external donor ligand, did not give a vinylamido analogue, but the bis(iminoacyl) complex was obtained.¹⁴ This result indicates that the presence of the guanidinate ligand influences the reactivity of the metal center, probably due to greater electronic density on the niobium atom and, essentially, a steric influence on the probable iminoacyl intermediate.^{16c} This factor forces a 1,2-hydrogen shift to form the final vinylamido ligand from one of the iminoacyl groups, with the other one remaining intact. This situation is in contrast with that previously described for similar group 4 complexes, where both of the iminoacyl groups were transformed into vinylamido ligands. The guanidinate effect does not translate to complexes **10–13**, which contain less bulky iminoacyl ligands that do not undergo this further transformation on heating.

Suitable X-ray-quality crystals of complex **17** were obtained from pentane. The molecular structure and atomic numbering scheme are shown in Figure 3; selected bond lengths and angles are given in Table 2. Complex **17** crystallizes in the $P2_1/n$ space group. The presence of a vinylamide group was confirmed by this analysis and also the presence of a κ^2 -C,N-iminoacyl ligand. Although this kind of complex has been observed previously for

a niobium compound,¹⁷ as mentioned above, complex **17** is the first such example that has been structurally characterized. The distribution of the atoms around the niobium center was altered in comparison to that in the parent compound **9** (the imido group is not in a trans disposition to the N3 guanidinate atom). In this case, a very distorted square pyramidal geometry is proposed, with the vinylamido group occupying the axial position and the base of the pyramid occupied by both coordinated nitrogen atoms of the guanidinate ligand, the imido group, and the fourth position occupied by the centroid of the κ^2 -iminoacyl ligand. The existence of this disposition can be explained in terms of the steric hindrance around the metal atom. The imido group is quasilinear with Nb–N1–C1 angles of 177.3(5) and 174.9(5)° for Nb1 and Nb2, respectively, and Nb–N1 distances of 1.766(5) and 1.752(5) Å for Nb1 and Nb2, respectively. The planarity of the “CN₃” core, which is evidenced by the sum of bond angles around C5 (360°), is in contrast with the three different distances found for the N–C bonds (~1.32 Å for N2–C5, ~1.35 Å for N3–C5, and ~1.37 Å for N4–C5). These data imply a different charge delocalization in this complex, with a less donating guanidinate ligand, probably due to the presence of other strong donors, such as vinylamide, in the coordination sphere of the metal atom.

CONCLUSIONS

The synthesis and characterization of new imidoguanidinate alkyl niobium(V) compounds were carried out. Guanidine

proligands, including a biguanidine compound, were prepared by a catalytic procedure and then reacted with an imido tribenzyl precursor. This process selectively gave monoanionic guanidinate mono- and dinuclear complexes $[\text{NbBz}_2(\text{N}^i\text{Bu})\text{-(guanH)}]$. These complexes were particularly stable in comparison with the starting compound $[\text{NbBz}_3(\text{N}^i\text{Bu})]$. The resulting dialkyl compounds contain a η^2 -benzyl group in the solid state, and this is in rapid exchange with the other η^1 -alkyl ligand in solution. Migratory insertion of $^i\text{BuNC}$ into niobium–benzyl bonds is easily achieved to give the corresponding bis(iminoacyl) derivatives. In contrast, insertion of XyNC gives rise, under mild conditions, to the isomerization of a proposed η^2 -iminoacyl group to vinylamido derivatives through a 1,2-hydrogen shift. The influence of the guanidinate ligand in this process is clear, as the same reaction does not take place on starting from the $[\text{NbBz}_3(\text{N}^i\text{Bu})]$ compound.

EXPERIMENTAL SECTION

General Procedures. All reactions were performed using standard Schlenk and glovebox techniques under an atmosphere of dry nitrogen. Solvents were purified by passage through a column of activated alumina (Innovative Technologies) and degassed under nitrogen before use. Microanalyses were carried out with a Perkin-Elmer 2400 CHN analyzer. NMR spectra were recorded on a Varian FT-400 spectrometer using standard VARIAN-FT software for NOESY-1D, COSY, g-HSQC, and g-HMBC. FT-IR spectra were recorded on a Bruker Tensor 27 spectrophotometer. Compounds 1–3 and 5 were prepared according to literature procedures.^{5,11} An alternative synthesis of the previously reported^{14f,m} 4 was used, following the procedure described for 1–3. NbCl_5 , ZnEt_2 , amines, isocyanides, and diisopropylcarbodiimide were purchased from Aldrich.

Synthesis of 2,2'-(1,4-Phenylene)bis(2',3'-diisopropylguanidine) (4). A Schlenk flask was charged with 1,4-phenylenediamine (1.30 g, 12.0 mmol), $\text{N,N}'$ -diisopropylcarbodiimide (3.70 mL, 24 mmol), 2 mol % of ZnEt_2 (1 M in hexanes), and 30 mL of THF. The solution was heated at 50 °C for 2 h. The resulting solution was separated by filtration, and the volatiles were removed under reduced pressure. The residue was washed with hexane and then dried to give 1 as a white solid. The identification was made by comparison with the NMR data previously reported in the literature. Yield: 4.10 g (94%).

Synthesis of $[\text{NbBz}_2(\text{N}^i\text{Bu})][\text{(4-}^i\text{BuC}_6\text{H}_4)\text{N}=\text{C}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr})]$ (6). 2-(4-*tert*-Butylphenyl)-1,3-diisopropylguanidine (0.19 g, 0.68 mmol) in toluene (30 mL) was added to a solution of $[\text{NbBz}_3(\text{N}^i\text{Bu})]$ (0.30 g, 0.68 mmol) in toluene (10 mL). The reaction mixture was stirred for 1 h at room temperature. The resulting yellow solution was evaporated to dryness in vacuo. The yellow solid was redissolved in pentane and cooled to –20 °C for crystallization, to afford yellow crystals of 6. Yield: 0.36 g (86%). ^1H NMR (400 MHz, C_6D_6): δ 0.63 (d, 6H, J = 6.3 Hz, Me_2CH), 0.98 (d, 6H, J = 6.3 Hz, Me_2CH), 1.26 (s, 9H, CMe_3), 1.41 (s, 9H, CMe_3), 2.40 (d, 2H, J = 7.7 Hz, CH_2Ph), 2.92 (d, 2H, J = 7.7 Hz, CH_2Ph); 3.17 (m, 1H, Me_2CH), 3.36 (m, 1H, Me_2CH), 3.58 (d, 1H, J = 9.2 Hz, NH), 6.98–7.27 (m, 14H, C_6H_4 and C_6H_5). ^{13}C NMR: δ 23.3 (Me_2CH), 24.5 (Me_2CH), 31.6 (CMe_3), 32.3 (CMe_3), 34.6 (CMe_3), 44.5 (Me_2CH), 47.7 (Me_2CH), 56.5 ($\text{CH}_2\text{-Ph}$), 65.9 (CMe_3), 123.9, 124.2, 131.1, 137.7, 138.5, 141.8, 145.1, and 146.2 (aromatic carbons), 164.2 (CN_3). Anal. Calcd for $\text{C}_{35}\text{H}_{51}\text{N}_4\text{Nb}$: C, 67.72; H, 8.28; N, 9.03. Found: C, 67.68; H, 8.34; N, 9.10.

Synthesis of $[\text{NbBz}_2(\text{N}^i\text{Bu})][\text{(4-BrC}_6\text{H}_4)\text{N}=\text{C}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr})]$ (7). The same procedure described for 6 was followed, using 2-(4-bromophenyl)-1,3-diisopropylguanidine (0.20 g, 0.68 mmol) in toluene (30 mL) and $[\text{NbBz}_3(\text{N}^i\text{Bu})]$ (0.30 g, 0.68 mmol) in toluene (10 mL) to afford 3 as a yellow solid, which was recrystallized from pentane at –20 °C. Yield: 0.37 g (84%). ^1H NMR (400 MHz, C_6D_6): δ 0.56 (d, J = 6.3 Hz, 6H, Me_2CH), 0.93 (d, J = 6.3 Hz, 6H, Me_2CH), 1.38 (s, 9H, CMe_3), 2.26 (d, J = 8.3 Hz, 2H, CH_2Ph), 2.81 (d, J = 8.3 Hz, 2H, CH_2Ph), 3.10 (m, 2H, Me_2CH), 3.46 (d, J = 9.3 Hz, NH), 6.74–7.30 (m, 14H, C_6H_4 and C_6H_5). ^{13}C NMR: δ 23.1 (Me_2CH),

24.3 (Me_2CH), 32.3 (CMe_3), 44.6 (Me_2CH), 47.7 (Me_2CH), 56.5 ($\text{CH}_2\text{-Ph}$), 65.9 (CMe_3), 114.7, 131.0, 132.1, 137.7, 137.9, and 148.3 (aromatic carbons), 164.2 (CN_3). Anal. Calcd for $\text{C}_{31}\text{H}_{42}\text{BrN}_4\text{Nb}$: C, 57.86; H, 6.58; N, 8.71. Found: C, 57.69; H, 6.62; N, 8.80.

Synthesis of $[\text{NbBz}_2(\text{N}^i\text{Bu})][\text{(4-MeOC}_6\text{H}_4)\text{N}=\text{C}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr})]$ (8). The same procedure described for 6 was followed, using 2-(4-methoxyphenyl)-1,3-diisopropylguanidine (0.17 g, 0.68 mmol) in toluene (30 mL) and $[\text{NbBz}_3(\text{N}^i\text{Bu})]$ (0.30 g, 0.68 mmol) in toluene (10 mL) to afford 8 as a yellow solid, which was recrystallized from pentane at –20 °C. Yield: 0.41 g (79%). ^1H NMR (400 MHz, C_6D_6): δ 0.66 (d, 6H, J = 6.4 Hz, Me_2CH), 1.01 (d, 6H, J = 6.4 Hz, Me_2CH), 1.39 (s, 9H, CMe_3), 2.35 (d, 2H, J = 7.8 Hz, CH_2Ph), 2.95 (d, 2H, J = 7.8 Hz, CH_2Ph), 3.25 (m, 2H, Me_2CH), 3.34 (s, 3H, $-\text{OCH}_3$), 3.54 (d, 1H, J = 9.4 Hz, NH), 6.75–7.25 (m, 14H, C_6H_4 and C_6H_5). ^{13}C NMR: δ 23.5 (Me_2CH), 24.8 (Me_2CH), 32.6 (CMe_3), 44.5 (Me_2CH), 48.1 (Me_2CH), 54.9 (OCH_3), 56.9 (CH_2Ph), 65.8 (CMe_3), 114.6, 124.0, 125.6, 131.1, 138.9, 141.9 and 155.8 (aromatic carbons), 164.5 (CN_3). Anal. Calcd for $\text{C}_{32}\text{H}_{45}\text{N}_4\text{NbO}$: C, 64.64; H, 7.63; N, 9.42. Found: C, 64.52; H, 7.57; N, 9.46.

Synthesis of $[\text{NbBz}_2(\text{N}^i\text{Bu})]_2[(\text{C}_6\text{H}_4)(\text{N}=\text{C}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr}))_2]$ (9). Bis(2-(*p*-phenyl)-1,3-diisopropylguanidine) (0.12 g, 0.34 mmol) in THF (20 mL) was added to a solution of $[\text{NbBz}_3(\text{N}^i\text{Bu})]$ (0.30 g, 0.68 mmol) in THF (10 mL). The reaction mixture was stirred for 1 h. The resulting yellow mixture was filtered, and the solution was evaporated to dryness in vacuo. The yellow solid was redissolved in THF and cooled to –20 °C for crystallization, to afford yellow crystals of 9. Yield: 0.31 g (87%). ^1H NMR (400 MHz, C_6D_6): δ 0.77 (d, 6H, J = 6.3 Hz, Me_2CH), 1.02 (d, 6H, J = 6.5 Hz, Me_2CH), 1.43 (s, 9H, CMe_3), 2.38 (d, 2H, J = 7.8 Hz, CH_2Ph), 3.02 (d, 2H, J = 7.8 Hz, CH_2Ph), 3.25 (m, 1H, Me_2CH), 3.49 (m, 1H, Me_2CH), 3.64 (d, 1H, J = 9.1 Hz, NH), 7.03–7.30 (m, 24H, C_6H_4 and C_6H_5). ^{13}C NMR: δ 23.2 (Me_2CH), 24.2 (Me_2CH), 32.1 (CMe_3), 44.2 (Me_2CH), 47.9 (Me_2CH), 56.3 (CH_2Ph), 65.4 (CMe_3), 123.6, 125.0, 128.2, 130.8, 138.4, and 143.4 (aromatic carbons), 163.4 (CN_3). Anal. Calcd for $\text{C}_{56}\text{H}_{80}\text{N}_8\text{Nb}_2$: C, 63.99; H, 7.67; N, 10.66. Found: C, 64.11; H, 7.75; N, 10.80.

Synthesis of $[\text{Nb}(\text{N}^i\text{Bu})(^i\text{BuN}=\text{CCH}_2\text{Ph})_2][\text{(4-}^i\text{BuC}_6\text{H}_4)\text{N}=\text{C}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr})]$ (10). In a glovebox, $^i\text{BuNC}$ (0.20 mL, 1.80 mmol) was added to a solution of 6 (0.60 g, 0.97 mmol) in toluene (10 mL). The reaction mixture was stirred for 10 min and evaporated to dryness in vacuo. The brown oily material was redissolved in pentane and cooled to –20 °C for crystallization, to afford brown crystals of 10. Yield: 0.27 g (38%). ^1H NMR (400 MHz, C_6D_6): δ 0.61 (d, 3H, J = 6.3 Hz, Me_2CH), 0.81 (d, 3H, J = 6.3 Hz, Me_2CH), 0.88 (d, 3H, J = 6.3 Hz, Me_2CH), 1.19 (s, 9H, CMe_3), 1.34 (s, 9H, CMe_3), 1.36 (s, 9H, CMe_3), 1.44 (s, 18H, CMe_3), 1.49 (s, 18H, CMe_3), 1.62 (d, 3H, J = 6.3 Hz, Me_2CH), 3.03 (m, 1H, Me_2CH), 3.42 (d, 1H, NH), 3.43 (m, 1H, Me_2CH), 3.59 (m, 1H, Me_2CH), 4.02–4.21 (m, CH_2Ph), 6.55–7.76 (m, C_6H_4 and C_6H_5). ^{13}C NMR: δ 23.9 (Me_2CH), 24.3 (Me_2CH), 25.1 (Me_2CH), 26.8 (Me_2CH), 30.1 (Me_3C), 31.6 (Me_3C), 32.8 (Me_3C), 33.2 (Me_3C), 41.6 (CH_2Ph), 43.9 (Me_2CH), 44.2 (Me_2CH), 44.3 (Me_2CH), 45.2 (Me_2CH), 58.5 (Me_3C), 59.2 (Me_3C), 123.9, 124.5, 125.6, 125.8, 129.6, 138.5, 138.7, 139.8, 141.0, 147.7, and 149.3 (aromatic carbons), 159.0 (CN_3), 160.1 (CN_3), 222.4 ($^i\text{BuN}=\text{CCH}_2\text{Ph}$), 223.4 ($^i\text{BuN}=\text{CCH}_2\text{Ph}$). Anal. Calcd for $\text{C}_{45}\text{H}_{69}\text{N}_6\text{Nb}$: C, 68.68; H, 8.84; N, 10.68. Found: C, 68.52; H, 8.75; N, 10.78.

Synthesis of $[\text{Nb}(\text{N}^i\text{Bu})(^i\text{BuN}=\text{CCH}_2\text{Ph})_2][\text{(4-BrC}_6\text{H}_4)\text{N}=\text{C}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr})]$ (11). The same procedure described for 10 was followed, using $^i\text{BuNC}$ (0.21 mL, 1.86 mmol) and 7 (0.60 g, 0.93 mmol). Yield: 0.38 g (51%). ^1H NMR (400 MHz, C_6D_6): δ 0.54 (d, 3H, J = 6.3 Hz, Me_2CH), 0.78 (d, 3H, J = 6.3 Hz, Me_2CH), 0.81 (d, 3H, J = 6.3 Hz, Me_2CH), 1.12 (s, 9H, CMe_3), 1.16 (s, 9H, CMe_3), 1.37 (s, 18H, CMe_3), 1.41 (s, 18H, CMe_3), 1.56 (d, 3H, J = 6.3 Hz, Me_2CH), 2.89 (m, 1H, Me_2CH), 3.16 (d, 1H, J = 10.7 Hz, NH), 3.29 (m, 1H, Me_2CH), 3.50 (m, 1H, Me_2CH), 3.53 (d, 1H, J = 10.7 Hz, NH), 3.99–4.18 (m, CH_2Ph), 6.31–7.59 (m, C_6H_4 and C_6H_5). ^{13}C NMR: δ 23.8 (Me_2CH), 24.2 (Me_2CH), 24.8 (Me_2CH), 26.5 (Me_2CH), 30.1 (Me_3C), 32.7 (Me_3C), 33.1 (Me_3C), 41.6 (CH_2Ph), 41.7 (CH_2Ph), 44.1 (Me_2CH), 44.2 (Me_2CH), 44.5 (Me_2CH), 45.2 (Me_2CH), 58.4 (Me_3C), 59.1 (Me_3C), 108.9, 110.4, 122.9, 125.6,

Table 3. Crystal Data and Structure Refinement Details for Complexes 6, 8, 9, and 17

	6	8	9	17
empirical formula	C ₃₅ H ₃₁ N ₄ Nb	C ₃₂ H ₄₅ N ₄ NbO	C ₅₆ H ₈₀ N ₈ Nb ₂ ·2C ₄ H ₈ O	C ₉₂ H ₁₁₆ N ₁₂ Nb ₂ ·2C ₅ H ₁₂
M _w	620.71	594.63	1195.31	1720.08
temp (K)	230(2)	230(2)	230(2)	230(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	orthorhombic	triclinic	monoclinic	monoclinic
space group	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>C2/c</i>	<i>P2₁/n</i>
<i>a</i> (Å)	12.881(1)	8.453(1)	29.609(3)	13.08(1)
<i>b</i> (Å)	16.646(1)	12.223(1)	15.569(1)	22.92(1)
<i>c</i> (Å)	32.319(2)	16.960(1)	16.647(1)	33.05(2)
α (deg)	90	104.483(5)	90	90
β (deg)	90	97.859(5)	121.992(2)	90
γ (deg)	90	108.605(3)	90	90
<i>V</i> (Å ³)	6929.7 (9)	1562.6(2)	6508(1)	9911(9)
<i>Z</i>	8	2	4	4
calcd density (g/cm ³)	1.190	1.264	1.220	1.153
abs coeff (mm ⁻¹)	0.374	0.414	0.398	0.281
<i>F</i> (000)	2640	628	2536	3672
cryst size (mm ³)	0.222 × 0.096 × 0.058	0.556 × 0.112 × 0.035	0.530 × 0.473 × 0.452	0.237 × 0.077 × 0.049
index ranges	−17 ≤ <i>h</i> ≤ 17 −22 ≤ <i>k</i> ≤ 18 −44 ≤ <i>l</i> ≤ 43	−12 ≤ <i>h</i> ≤ 12 −17 ≤ <i>k</i> ≤ 15 −24 ≤ <i>l</i> ≤ 24	−42 ≤ <i>h</i> ≤ 41 −16 ≤ <i>k</i> ≤ 22 −17 ≤ <i>l</i> ≤ 23	−18 ≤ <i>h</i> ≤ 16 −31 ≤ <i>k</i> ≤ 31 −43 ≤ <i>l</i> ≤ 43
no. of rflns collected	53 410	24 517	22 551	84 423
no. of indep rflns	8862 (<i>R</i> (int) = 0.1366)	9505 (<i>R</i> (int) = 0.1236)	9858 (<i>R</i> (int) = 0.1250)	25 676 (<i>R</i> (int) = 0.2296)
no. of obsd rflns	4368	3990	3899	8177
no. of data/restraints/params	8862/0/380	9505/0/365	9858/0/374	25 676/0/1079
goodness of fit on <i>F</i> ²	0.977	0.883	0.922	0.921
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]				
<i>R</i> 1	0.0615	0.0696	0.0787	0.0956
<i>wR</i> 2	0.1211	0.1099	0.1447	0.1639
largest diff peak, hole (e Å ⁻³)	0.377, −0.471	0.430, −0.571	0.445, −0.734	0.398, −0.5

125.8, 129.5, 129.6, 130.5, 130.6, 138.2, 138.3, 149.5, and 151.6 (aromatic carbons), 159.0 (CN₃), 160.0 (CN₃), 221.9 (¹BuN=CCH₂Ph), 223.2 (¹BuN=CCH₂Ph). Anal. Calcd for C₄₁H₄₀BrN₆Nb: C, 60.81; H, 7.47; N, 10.38. Found: C, 60.70; H, 7.35; N, 10.42.

Synthesis of {Nb(N^tBu)(^tBuN=CCH₂Ph)₂[(4-MeOC₆H₄)N=C(NⁱPr)(NHⁱPr)]} (12). The same procedure described for **10** was followed, using ^tBuN=C (0.22 mL, 2.00 mmol) and **8** (0.60 g, 1.00 mmol). Yield: 0.31 g (41%). ¹H NMR (400 MHz, C₆D₆): δ 0.62 (d, 3H, *J* = 6.3 Hz, Me₂CH), 0.84 (d, 3H, *J* = 6.3 Hz, Me₂CH), 0.89 (d, 3H, *J* = 6.3 Hz, Me₂CH), 1.18 (s, 9H, CMe₃), 1.19 (s, 9H, CMe₃), 1.47 (s, 18H, CMe₃), 1.49 (s, 18H, CMe₃), 1.63 (d, 3H, *J* = 6.3 Hz, Me₂CH), 3.01 (m, 1H, Me₂CH), 3.44 (s, 3H, OMe), 3.46 (s, 3H, OMe), 3.53 (d, 1H, NH), 3.61 (m, 1H, Me₂CH), 4.03–4.23 (m, CH₂Ph), 6.55–7.73 (m, C₆H₄ and C₆H₅). ¹³C NMR: δ 23.3 (Me₂CH), 24.3 (Me₂CH), 24.8 (Me₂CH), 25.4 (Me₂CH), 30.5 (Me₃C), 33.2 (Me₃C), 33.5 (Me₃C), 41.9 (CH₂Ph), 44.1 (Me₂CH), 44.6 (CH₂Ph), 45.5 (Me₂CH), 55.0 (OMe), 55.1 (OMe), 58.8 (Me₃C), 59.5 (Me₃C), 113.6, 113.8, 115.2, 122.8, 124.2, 125.3, 125.9, 126.1, 130.0, 138.7, 139.0, 144.2, 145.7, 153.0, and 153.7 (aromatic carbons), 159.6 (CN₃), 160.3 (CN₃), 222.8 (¹BuN=CCH₂Ph), 223.9 (¹BuN=CCH₂Ph). Anal. Calcd for C₄₂H₆₃N₆NbO: C, 66.30; H, 8.35; N, 11.04. Found: C, 66.20; H, 8.38; N, 11.12.

Synthesis of {[Nb(N^tBu)(^tBuN=CCH₂Ph)₂][(C₆H₄)N=C(NⁱPr)(NHⁱPr)]} (13). The same procedure described for **10** was followed, using ^tBuN=C (0.26 mL, 2.30 mmol) and **9** (0.60 g, 0.57 mmol). Yield: 0.34 g (43%). ¹H NMR (400 MHz, C₆D₆): δ 0.63 (d, 3H, *J* = 6.3 Hz, Me₂CH), 0.67 (d, 3H, *J* = 6.3 Hz, Me₂CH), 0.82 (d, 3H, *J* = 6.3 Hz, Me₂CH), 0.86 (d, 3H, *J* = 6.3 Hz, Me₂CH), 0.98 (d, 3H, *J* = 6.3 Hz, Me₂CH), 1.01 (d, 3H, *J* = 6.3 Hz, Me₂CH), 1.15 (s, 9H, CMe₃), 1.19 (s, 9H, CMe₃), 1.25 (s, 9H, CMe₃), 1.52 (s, 9H, CMe₃), 1.53 (s, 9H, CMe₃), 1.55 (s, 9H, CMe₃), 1.66 (d, 3H, *J* = 6.3 Hz, Me₂CH), 1.70 (d, 3H, *J* = 6.3 Hz, Me₂CH), 3.04 (m, 1H, Me₂CH), 3.11 (m, 1H, Me₂CH), 3.34 (d, 1H, NH), 3.62 (d, 1H, NH), 3.69 (m,

1H, Me₂CH), 3.81 (m, 1H, Me₂CH), 4.00–4.27 (m, CH₂Ph), 6.45–7.74 (m, C₆H₄ and C₆H₅). ¹³C NMR: δ 23.0 (Me₂CH), 23.1 (Me₂CH), 24.1 (Me₂CH), 24.2 (Me₂CH), 24.5 (Me₂CH), 24.6 (Me₂CH), 25.1 (Me₂CH), 25.2 (Me₂CH), 30.2 (Me₃C), 30.3 (Me₃C), 30.4 (Me₃C), 32.8 (Me₃C), 33.0 (Me₃C), 33.1 (Me₃C), 41.5 (CH₂Ph), 41.6 (CH₂Ph), 43.3 (Me₂CH), 43.4 (Me₂CH), 43.9 (Me₂CH), 44.1 (Me₂CH), 44.2 (Me₂CH), 58.2 (Me₃C), 59.2 (Me₃C), 59.3 (Me₃C), 121.6, 122.0, 122.7, 142.1, 125.3, 125.7, 129.6, 138.3, 138.7, 138.9, 141.6, 142.4, and 143.7 (aromatic carbons), 159.3 (CN₃), 160.0 (CN₃), 160.1 (CN₃), 222.6 (¹BuN=CCH₂Ph), 223.5 (¹BuN=CCH₂Ph), 223.7 (¹BuN=CCH₂Ph). Anal. Calcd for C₇₆H₁₁₆N₁₂Nb₂: C, 65.97; H, 8.45; N, 12.15; Nb, 13.43. Found: C, 66.17; H, 8.54; N, 11.85.

Synthesis of {Nb(N^tBu)[(2,6-Me₂C₆H₃)NCH=CHPh][BzC=N(2,6-Me₂C₆H₃)][(4-^tBu-C₆H₄)(N=C(NⁱPr)(NHⁱPr)]} (14). 2,6-Me₂C₆H₃NC (0.06 g, 0.46 mmol) in toluene (5 mL) was added to a solution of **6** (0.14 g, 0.23 mmol) in toluene (5 mL). The reaction mixture was stirred and heated to 50 °C for 16 h. The resulting dark brown solution was evaporated to dryness in vacuo. The dark solid was redissolved in pentane and cooled to −20 °C for crystallization, to afford dark brown crystals of **14**. Yield: 0.08 g (38%). ¹H NMR (400 MHz, C₆D₆): δ 0.65 (d, 3H, *J* = 6.3 Hz, Me₂CH), 0.68 (d, 3H, *J* = 6.3 Hz, Me₂CH), 1.03 (s, 9H, CMe₃), 1.23 (s, 9H, CMe₃), 1.26 (d, 3H, *J* = 6.3 Hz, Me₂CH), 1.31 (d, 3H, *J* = 6.3 Hz, Me₂CH), 1.64 (s, 3H, Me₂C₆H₃), 2.17 (s, 3H, Me₂C₆H₃), 2.49 (s, 3H, Me₂C₆H₃), 2.54 (s, 3H, Me₂C₆H₃), 3.16 (m, 1H, Me₂CH), 3.61 (d, 1H, *J* = 9.2 Hz, NH), 3.70 (d, 2H, *J* = 5.6 Hz, CH₂Ph), 4.11 (m, 1H, Me₂CH), 4.99 (d, 1H, *J* = 13.7 Hz, PhCH=CH), 6.85–7.35 (m, 20H, C₆H₃, C₆H₄, and C₆H₅), 8.40 (d, 1H, *J* = 13.9 Hz, PhCH=CH). ¹³C NMR: δ 18.2 (Me₂C₆H₃), 18.7 (Me₂C₆H₃), 19.0 (Me₂C₆H₃), 19.3 (Me₂C₆H₃), 23.0 (Me₂CH), 23.1 (Me₂CH), 23.7 (Me₂CH), 23.9 (Me₂CH), 31.3 (Me₃C), 31.9 (Me₃C), 33.9 (Me₃C), 42.9 (CH₂Ph), 44.5 (Me₂CH), 49.4 (Me₂CH), 66.8 (Me₃C), 98.6 (PhCH=CH), 122.6, 124.1, 125.1,

129.7, 133.6, 134.3, 136.1, and 140.9 (aromatic carbons), 145.7 (PhCH=CH), 164.4 (CN₃), 240.9 (ArN=CCH₂Ph). Anal. Calcd for C₅₃H₆₉N₆Nb: C, 72.09; H, 7.88; N, 9.52. Found: C, 72.19; H, 7.928; N, 9.55.

Synthesis of {Nb(NⁱBu)[(2,6-Me₂C₆H₃)NCH=CHPh][(BzC=N-(2,6-Me₂C₆H₃))[(4-Br-C₆H₄)(N=C(NⁱPr)(NHⁱPr))]} (15). The same procedure described for **14** was followed, using **7** (0.15 g, 0.23 mmol) and 2,6-Me₂C₆H₃NC (0.06 g, 0.46 mmol). Yield: 0.08 g (40%). ¹H NMR (400 MHz, C₆D₆): δ 0.60 (d, 3H, *J* = 6.2 Hz, Me₂CH), 0.66 (d, 3H, *J* = 6.2 Hz, Me₂CH), 0.99 (s, 9H, CMe₃), 1.19 (d, 3H, *J* = 6.9 Hz, Me₂CH), 1.29 (d, 3H, *J* = 6.9 Hz, Me₂CH), 1.75 (s, 3H, Me₂C₆H₃), 2.16 (s, 3H, Me₂C₆H₃), 2.46 (s, 3H, Me₂C₆H₃), 2.52 (s, 3H, Me₂C₆H₃), 3.00 (m, 1H, Me₂CH), 3.52 (d, 1H, *J* = 9.5 Hz, NH), 3.72 (d, 2H, *J* = 3.6 Hz, CH₂Ph), 4.04 (m, 1H, Me₂CH), 4.93 (d, 1H, *J* = 13.9 Hz, PhCH=CH), 6.51–7.29 (m, 20H, C₆H₃, C₆H₄ and C₆H₅), 8.15 (d, 1H, *J* = 13.9 Hz, PhCH=CH). ¹³C NMR: δ 18.5 (Me₂C₆H₃), 18.6 (Me₂C₆H₃), 19.0 (Me₂C₆H₃), 19.2 (Me₂C₆H₃), 22.7 (Me₂CH), 23.1 (Me₂CH), 23.2 (Me₂CH), 24.1 (Me₂CH), 32.2 (Me₃C), 43.2 (CH₂Ph), 44.7 (Me₂CH), 49.5 (Me₂CH), 67.1 (Me₃C), 99.4 (PhCH=CH), 115.1, 123.2, 124.5, 128.9, 130.0, 132.2, 136.3, and 140.8 (aromatic carbons), 145.0 (PhCH=CH), 164.5 (CN₃), 240.2 (ArN=CCH₂Ph). Anal. Calcd for C₄₉H₆₀BrN₆Nb: C, 64.97; H, 6.68; N, 9.28. Found: C, 65.10; H, 6.70; N, 9.22.

Synthesis of {Nb(NⁱBu)[(2,6-Me₂C₆H₃)NCH=CHPh][(BzC=N-(2,6-Me₂C₆H₃))[(4-MeOC₆H₄)(N=C(NⁱPr)(NHⁱPr))]} (16). The same procedure described for **14** was followed, using **8** (0.14 g, 0.23 mmol) and 2,6-Me₂C₆H₃NC (0.06 g, 0.46 mmol). Yield: 0.08 g (39%). ¹H NMR (400 MHz, C₆D₆): δ 0.67 (d, 3H, *J* = 6.3 Hz, Me₂CH), 0.75 (d, 3H, *J* = 6.3 Hz, Me₂CH), 1.03 (s, 9H, CMe₃), 1.24 (d, 3H, *J* = 6.3 Hz, Me₂CH), 1.33 (d, 3H, *J* = 6.3 Hz, Me₂CH), 1.79 (s, 3H, Me₂C₆H₃), 2.21 (s, 3H, Me₂C₆H₃), 2.53 (s, 3H, Me₂C₆H₃), 2.56 (s, 3H, Me₂C₆H₃), 3.16 (m, 1H, Me₂CH), 3.34 (s, 3H, OMe), 3.60 (d, 1H, *J* = 9.4 Hz, NH), 3.76 (d, 2H, *J* = 2.0 Hz, CH₂Ph), 4.08 (m, 1H, Me₂CH), 4.98 (d, 1H, *J* = 13.8 Hz, PhCH=CH), 6.66–7.35 (m, 20H, C₆H₃, C₆H₄ and C₆H₅), 8.26 (d, 1H, *J* = 13.8 Hz, PhCH=CH). ¹³C NMR: δ 18.5 (Me₂C₆H₃), 18.7 (Me₂C₆H₃), 19.0 (Me₂C₆H₃), 19.3 (Me₂C₆H₃), 23.0 (Me₂CH), 23.3 (Me₂CH), 23.7 (Me₂CH), 24.3 (Me₂CH), 32.3 (Me₃C), 43.0 (CH₂Ph), 44.5 (Me₂CH), 49.3 (Me₂CH), 54.5 (OMe), 66.6 (Me₃C), 98.5 (PhCH=CH), 114.2, 122.3, 124.3, 125.5, 129.8, 134.2, 136.0, and 140.7 (aromatic carbons), 145.6 (PhCH=CH), 165.0 (CN₃), 240.7 (ArN=CCH₂Ph). Anal. Calcd for C₅₀H₆₃N₆NbO: C, 70.08; H, 7.41; N, 9.81. Found: C, 70.15; H, 7.39; N, 9.92.

Synthesis of {[Nb(NⁱBu)[N(2,6-Me₂C₆H₃)CH=CHPh][BzC=N-(2,6-Me₂C₆H₃)]₂[(C₆H₄)(N=C(NⁱPr)(NHⁱPr))₂]} (17). The same procedure described for **14** was followed, using **9** (0.10 g, 0.09 mmol) and 2,6-Me₂C₆H₃NC (0.05 g, 0.36 mmol). Yield: 0.06 g (41%). ¹H NMR (400 MHz, C₆D₆): δ 0.64–0.72 (m, Me₂CH), 1.03 (s, CMe₃), 1.06 (s, CMe₃), 1.26–1.33 (m, Me₂CH), 1.54 (s, Me₂C₆H₃), 1.60 (s, Me₂C₆H₃), 2.03 (s, Me₂C₆H₃), 2.05 (s, Me₂C₆H₃), 2.28 (s, Me₂C₆H₃), 2.33 (s, Me₂C₆H₃), 2.52 (s, Me₂C₆H₃), 2.74 (s, Me₂C₆H₃), 3.16 (m, Me₂CH), 3.63 (m, Me₂CH), 4.04 (m, Me₂CH), 4.15 (m, Me₂CH), 3.42–3.65 (m, CH₂Ph), 4.95–5.00 (m, PhCH=CH), 6.75–7.32 (m, C₆H₃, C₆H₄, and C₆H₅), 8.71–8.77 (m, PhCH=CH). ¹³C NMR: δ 18.9 (Me₂C₆H₃), 19.0 (Me₂C₆H₃), 19.3 (Me₂C₆H₃), 19.5 (Me₂C₆H₃), 23.3 (Me₂CH), 23.6 (Me₂CH), 23.7 (Me₂CH), 23.9 (Me₂CH), 32.3 (Me₃C), 32.4 (Me₃C), 42.6 (CH₂Ph), 44.5 (CH₂Ph), 48.6 (Me₂CH), 48.9 (Me₂CH), 67.6 (Me₃C), 67.8 (Me₃C), 98.6 (PhCH=CH), 98.7 (PhCH=CH), 122.6, 124.1, 124.3, 125.5, 125.8, 126.0, 126.7, 129.2, 130.1, 134.1, 134.5, 136.2, 137.7, and 141.5 (aromatic carbons), 146.5 (PhCH=CH), 146.9 (PhCH=CH), 165.1 (CN₃), 241.3 (ArN=CCH₂Ph), 241.5 (ArN=CCH₂Ph). Anal. Calcd for C₉₂H₁₁₆N₁₂Nb₂: C, 70.12; H, 7.42; N, 10.67. Found: C, 70.25; H, 7.68; N, 10.85.

X-ray Structure Determination for Complexes 6, 8, 9, and 17. Crystals of complexes **6**, **8**, and **17** were obtained from pentane solution, and complex **9** was crystallized from THF solution. Crystals of complexes were mounted at low temperature in inert oil on a glass fiber. Data were collected on a Bruker X8 APPEX II CCD-based diffractometer, equipped with a graphite-monochromated Mo *K*α radiation source (λ = 0.710 73 Å).

The crystal data, data collection, structural solution, and refinement parameters for the complexes are summarized in Table 3. Data were integrated using SAINT,¹⁸ and an absorption correction was performed with the program SADABS.¹⁹ The structures were solved by direct methods using SHELXTL²⁰ and refined by full-matrix least-squares methods based on *F*². All non-hydrogen atoms were refined with anisotropic thermal parameters. All H atoms were computed and refined with an overall isotropic temperature factor using a riding model—except for H4, which was located in the difference electron density map and then refined. There are some atoms in a disordered position for complexes **6**, **8**, and **9**. Complexes **9** and **17** have two THF and two pentane solvent molecules, respectively.

The small size of the crystals of **17** prevented the structure from being solved in a higher symmetry system. We repeated data collection with different crystals but were unable to obtain better data. However, considering the importance of the structure, it was solved despite the aforementioned problems.

■ ASSOCIATED CONTENT

Supporting Information

CIF files giving full crystallographic data for **6**, **8**, **9**, and **17**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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