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Synthesis, Characterization and Reactivity of New Dinuclear Guanidinate Diimidoniobium Complexes

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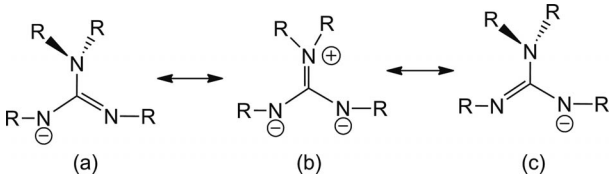
The guanidine proligands {2-[4-(*tert*-butyl)phenyl]-1,3-diisopropylguanidine} (**1**), [2-(4-methoxyphenyl)-1,3-diisopropylguanidine] (**2**) and [2-(4-bromophenyl)-1,3-diisopropylguanidine] (**3**) have been prepared by guanylation of anilines with diisopropylcarbodiimide, using [$MgBz_2(thf)_2$] as the catalyst at room temperature. These proligands react with the complex {[$Nb(CH_2SiMe_3)_3(CH_3CN)]_2(\mu$-1,4-$NC_6H_4N)$} (**4**) to afford new guanidinate-supported dialkyl niobium dinuclear complexes [{$Nb(CH_2SiMe_3)_2[(4$-*t*$BuC_6H_4)$-N=C(N*i*Pr)(NH*i*Pr)]}$_2(\mu$-1,4-$NC_6H_4N)$] (**5**), [{$Nb(CH_2SiMe_3)_2$-[(4-$MeOC_6H_4)$N=C(N*i*Pr)(NH*i*Pr)]}$_2(\mu$-1,4-$NC_6H_4N)$] (**6**) and [{$Nb(CH_2SiMe_3)_2[(4$-$BrC_6H_4)$N=C(N*i*Pr)(NH*i*Pr)]}$_2(\mu$-1,4-$NC_6H_4N)$] (**7**). Treatment of compounds **5**–**7** with 2 equiv. of 2,6-dimethylphenyl isocyanide gave the imido bis(iminoacyl) compounds [{$Nb(Me_3SiCH_2C$=Nxylyl)$_2[(4$-*t*$BuC_6H_4)$N=C-(N*i*Pr)(NH*i*Pr)]}$_2(\mu$-1,4-$NC_6H_4N)$] (**8**), [{$Nb(Me_3SiCH_2C$=Nxylyl)$_2[(4$-$MeOC_6H_4)$N=C(N*i*Pr)(NH*i*Pr)]}$_2(\mu$-1,4-$NC_6H_4N)$] (**9**) and [{$Nb(Me_3SiCH_2C$=Nxylyl)$_2[(4$-$BrC_6H_4)$N=C(N*i*Pr)-(NH*i*Pr)]}$_2(\mu$-1,4-$NC_6H_4N)$] (**10**). The molecular structures of compound **2** and complex **9** have been determined.

Introduction

The search for alternatives to cyclopentadienyl-based ligands has led to special interest in N-donor ligands in various fields of coordination and organometallic chemistry. In this context, guanidinate anions have generated significant interest as ligands[1] since the first report of a transition metal guanidinate complex by Lappert in 1970.[2] As illustrated in Scheme 1, guanidinate offers variable steric and electronic tunability through the ease of substituent modification within the "CN_3" core.



Scheme 1. Proposed resonance structures for monoanionic guanidinate ligands.

Guanidinate complexes of the main and transition metal groups have been actively studied in recent years for their application as catalysts and precatalysts in a variety of reactions.[3] In fact, *N*,*N*′,*N*′′-trisubstituted guanidines, $(RNH)_2C$=NR (R = alkyl or aryl), represent an interesting class of N-donor ligands. Recently, we described a new approach[4] for the catalytic synthesis of these organic molecules based on simple and cheap commercial catalysts. The resulting guanidines could coordinate, in an asymmetric mode,[5] through the alkylamino nitrogen and the arylimino nitrogen atom, which is a different mode from that found in previously reported complexes.

The quest for new dinuclear organometallic complexes in which the metal centres are linked by a bridging ligand that has a delocalized π system has become a subject of intense research. This is because of the important applications of such substances in the formation of new materials of low dimensionality or with interesting electrical or magnetic properties.[6] Aryldiimido ligands allow this electronic communication between the metallic centres in addition to the strong metal–imido interaction, which prevents dissociation in solution.[7] We previously described the preparation of niobium organodiimido complexes,[8] including bis- and monocyclopentadienyl derivatives. As a continuation of our research in this field, we describe here the preparation of alternative guanidinate alkyl diimidoniobium complexes in an effort to obtain new types of dinuclear complexes and to explore the relative influence that the guanidinate ligands have on isocyanide insertion migration into niobium–alkyl bonds.[9]

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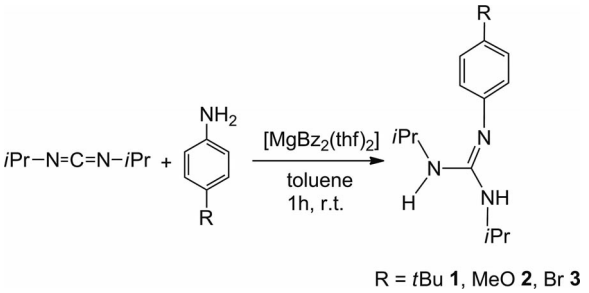
Results and Discussion

Several catalysts have been described that allow the addition of amines to carbodiimides in an atom-economical route.[10] Following our interest in the development of new, simple and efficient catalysts for the guanylation reaction of amines, we decided to explore the catalytic activity of $[MgBz_2(thf)_2]$,[11] an accessible crystalline compound. We found that in the presence of 1.5 mol-% of the aforementioned magnesium complex the guanylation reaction of a representative series of anilines, bearing electron-donating or electron-withdrawing substituents, with *N*,*N*′-diisopropylcarbodiimide took place in toluene at room temperature to afford quantitative yields of the corresponding guanidines in 1 h (Scheme 2). In contrast, $ZnEt_2$ or $MgBu_2$ required warming to 50 °C to attain the same performance.[4a] Further studies are underway that are aimed at thoroughly examining the use of $[MgBz_2(thf)_2]$ and to extend the scope of the reaction to other primary aromatic amines, secondary amines and heterocyclic amines.



Scheme 2. Catalytic addition of anilines to *N*,*N*′-diisopropylcarbodiimide with $[MgBz_2(thf)_2]$ as catalyst.

In the case of the previously described 2-(4-methoxyphenyl)-2,3-diisopropylguanidine (**2**),[10a] the molecular structure was established by X-ray diffraction (Figure 1). The crystal data are summarized in the Experimental Section. There are two molecules (A and B) in the asymmetric unit. The bond lengths in the CN_3 moiety indicate there is some charge delocalization, although the bond length C1–N3 of 1.315(3) Å and 1.306(3) Å, for molecules A and B, respectively, is slightly shorter, implying a greater double bond character.

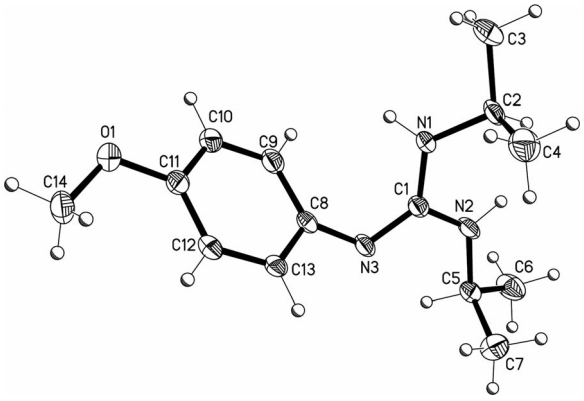
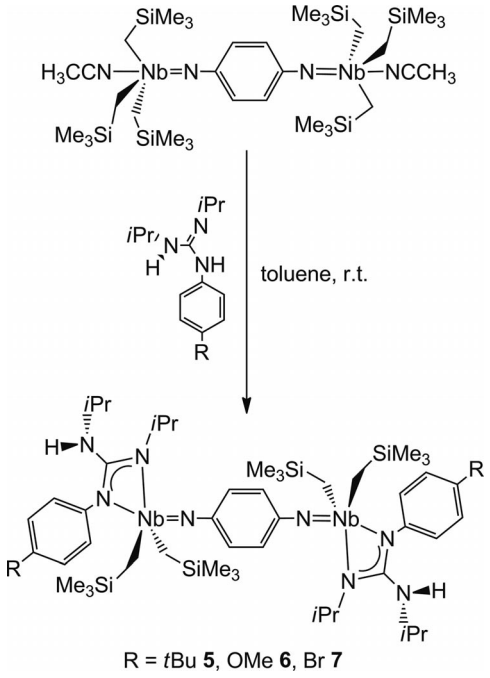


Figure 1. ORTEP drawing of compound **2**, with thermal ellipsoid at 20% probability. Selected bond lengths [Å] and angles [°] for molecule A: N1–C1 1.371(3); N2–C1 1.354(3); N3–C1 1.315(3); N1–C1–N2 116.7(2); N1–C1–N3 124.7(2); N2–C1–N3 118.6(2); molecule B: N1–C1 1.371(3); N2–C1 1.352(3); N3–C1 1.306(3); N1–C1–N2 117.1(2); N1–C1–N3 123.2(2); N2–C1–N3 119.5(2).

The direct reaction between 2 equiv. of the guanidine proligands **1**–**3** and the trialkyl dinuclear bis(imido) complex $\{[Nb(CH_2SiMe_3)_3(CH_3CN)]_2(\mu\text{-}1,4\text{-}NC_6H_4N)\}$ (**4**)[8b] gave, through a protonolysis pathway, the corresponding guanidinate complexes $[\{Nb(CH_2SiMe_3)_2[(4\text{-}tBuC_6H_4)N{=}C(NiPr)(NHiPr)]\}_2(\mu\text{-}1,4\text{-}NC_6H_4N)]$ (**5**), $[\{Nb(CH_2SiMe_3)_2[(4\text{-}MeOC_6H_4)N{=}C(NiPr)(NHiPr)]\}_2(\mu\text{-}1,4\text{-}NC_6H_4N)]$ (**6**) and $[\{Nb(CH_2SiMe_3)_2[(4\text{-}BrC_6H_4)N{=}C(NiPr)(NHiPr)]\}_2(\mu\text{-}1,4\text{-}NC_6H_4N)]$ (**7**), which were isolated as air-sensitive dark yellow solids (Scheme 3). These complexes were characterized by ^1H NMR and ^{13}C NMR spectroscopy (see Exp. Sect.). The ^1H NMR spectra of **5**–**7** show the equivalence of the two metal environments and exhibit two doublets close to δ = 0.6 and 1.2 ppm, assigned to methyl fragments of isopropyl groups of the guanidinate ligands, a finding that indicates an asymmetric disposition of the coordinated ligand. The two methine groups appear as close multiplets near to δ = 3.2 ppm. One of these multiplets is coupled to a doublet at around δ = 3.7 ppm, and this signal is assigned to the remaining NH group from the noncoordinated isopropylamino moiety. In addition to the signals assigned to the phenylene and trimethylsilyl groups, at around δ = 7.4 and 0.3 ppm, respectively, an AB spin system ($\delta \approx 1.6$ ppm, $J_{AB} \approx 10$ Hz) is evident in the spectra. This system is assigned to the diastereotopic protons of the methylene groups, which appear as a result of the presence of a pro-chiral centre at the metal atom.



Scheme 3. Synthesis of the niobium diimido guanidinate complexes **5**–**7**.

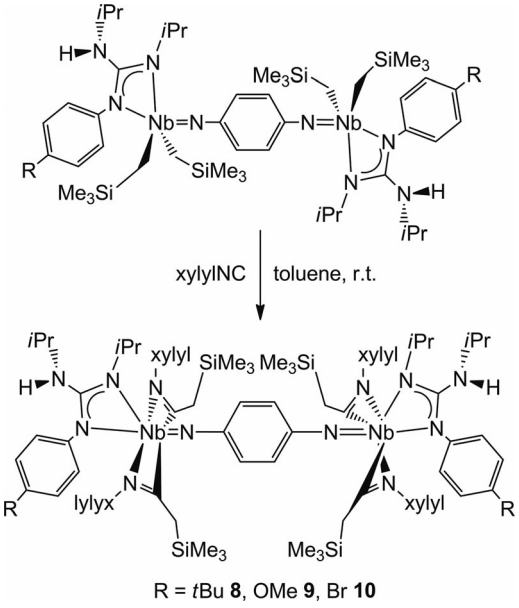
NOESY-1D experiments provided evidence for a coordination that is a pseudo-bipyramidal geometry in which the imido group and the aromatic substituted nitrogen atom of the guanidinate occupy the axial *trans* positions and the rest of the substituents are located in the equatorial plane.

The ^{13}C NMR spectra contain the appropriate signals for the proposed structures (see Exp. Sect.), including a single carbon resonance close to δ = 164 ppm for the central carbon of a κ^2-monoanionic chelating guanidinate ligand.[12]

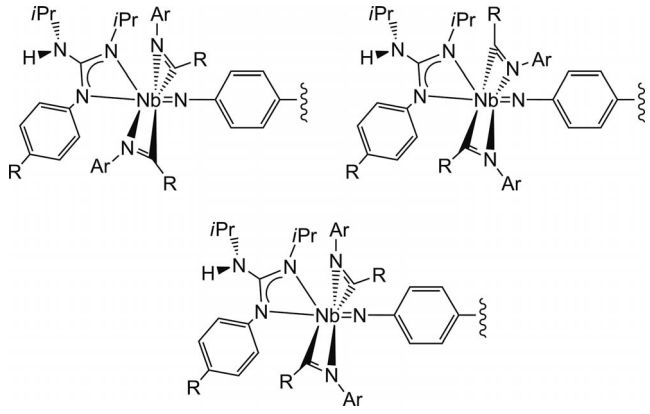
The migratory insertion of organic isocyanides into metal–alkyl bonds allows the formation of new iminoacyl groups. The product of these reactions typically adopts a κ^2-C,N-coordination mode through both the nitrogen and carbon atom.[9] Complexes **5**–**7** reacted readily in toluene at room temperature with 2,6-dimethylphenyl isocyanide (xylylNC) in a 1:4 molar ratio to give (in almost quantitative yield determined by NMR spectroscopy) the double bis(iminoacyl) derivatives [{Nb(Me_3SiCH_2C=Nxylyl)$_2$[(4-*t*BuC_6H_4)N=C(N*i*Pr)(NH*i*Pr)]}$_2$(μ-1,4-NC_6H_4N)] (**8**), [{Nb(Me_3SiCH_2C=Nxylyl)$_2$[(4-MeOC_6H_4)N=C(N*i*Pr)(NH*i*Pr)]}$_2$ (μ-1,4-NC_6H_4N)] (**9**) and [{Nb(Me_3SiCH_2C=Nxylyl)$_2$[(4-BrC_6H_4)N=C(N*i*Pr)(NH*i*Pr)]}$_2$(μ-1,4-NC_6H_4N)] (**10**), which were isolated as very air-sensitive yellow solids (Scheme 4). The final product is the result of the insertion of isocyanide molecules into the two niobium–carbon bonds at the two niobium moieties. Even when the stoichiometry was adjusted to favour the single insertion product at each niobium centre, evidence for the formation of this compound was not found and the double bis(iminoacyl) complexes described above were obtained together with unreacted starting materials. It is noteworthy that analogous half-sandwich bis(alkyl) diimido niobium complexes only undergo a single insertion reaction, evidencing the influence of the guanidinate ligand. This influence could be both steric and electronic, where these guanidinate ligands are less crowding and less donating than the cyclopentadienyl one, allowing more space for the coordination of the second isocyanide molecule, and enabling a greater concentration of electronic density on the metal centre from the second iminoacyl moiety. A similar result was observed when complex **4** undergoes a double migration insertion reaction of the isocyanide.[13] Also, in contrast with the reactivity of previously reported alkylimido guanidinate niobium complexes,[5] the evolution of these new bis(iminoacyl) compounds was not observed on warming at 50 °C for 1 d.

Compounds **8**–**10** were characterized by FTIR and NMR spectroscopy (see Experimental Section). A characteristic band at ca. 1630 cm^{-1} was assigned to the C=N vibration of the κ^2-iminoacyl groups.[9a] The ^1H NMR and ^{13}C NMR spectra are similar to those found for the parent complexes with regard to both the guanidinate and phenylene groups. Furthermore, the ^1H NMR spectra showed an AB spin system for the diastereotopic methylene protons of the inserted alkyl groups at ca. δ = 3 ppm, i.e. downfield with respect to the parent compounds **5**–**7**. Two inequivalent methyl groups in the δ = 2–2.5 ppm region indicate that rotation of the xylyl group is hindered in these complexes. The ^{13}C NMR spectra showed an upfield shift of the signals corresponding to the methylene carbons (ca. δ = 30 ppm) with respect to those of the parent compounds **5**–**7** (ca. δ = 60 ppm). The iminoacyl quaternary carbon atom signal was observed at ca. δ = 230 ppm, in good agreement with the presence of a unique type of κ^2-ligand.[9]

Complexes **8**–**10** are described as seven-coordinated niobium compounds or as a pseudo-bipyramidal structure where the κ^2-iminoacyl groups occupy one coordination site each.[14] This situation allows the possibility of two alternative arrangements of these groups (Scheme 5), i.e. with the nitrogen atom either proximal or distal to the equatorial nitrogen atom of the guanidinate ligand.



Scheme 4. Migratory insertion process with xylylNC.



Scheme 5. Possible isomers for compounds **8**–**10**.

NMR spectroscopy showed the presence of a single final product. This finding can be explained by rapid interchange, in solution, by the rotation of the κ^2-fragment about its midpoint or from κ^2–κ^2–κ^2 coordination ex-

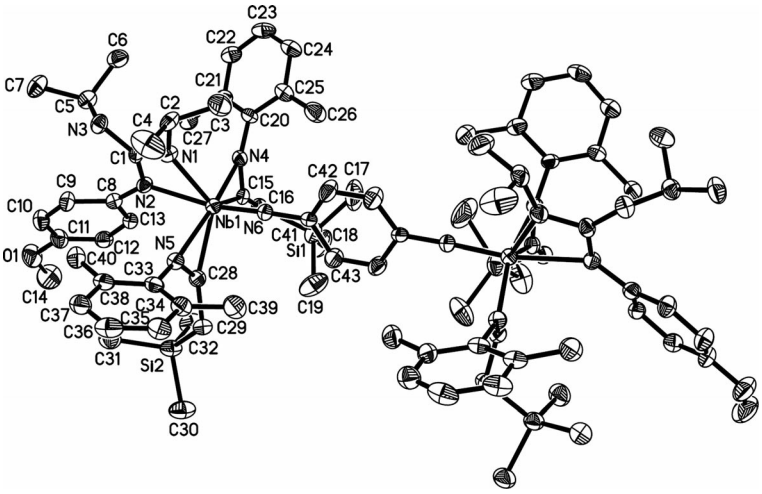


Figure 2. ORTEP drawing of compound **9**, with thermal ellipsoid at 20% probability. Hydrogen atoms are omitted for clarity.

change.[15] Unfortunately, this possible exchange could not be frozen even at low temperature (163 K) in a ^{1}H VT NMR study for these complexes.

In order to establish unequivocally the structural disposition of these complexes, an X-ray molecular analysis of complex **9** was carried out. The molecular structure and atomic numbering scheme are shown in Figure 2. The crystal data are summarized in the Exp. Sect. Selected bond lengths and angles for **9** are given in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] for complex **9**.

Bond length		Bond angle	
Nb1–N1	2.193(4)	N1–Nb1–N2	58.0(1)
Nb1–N2	2.358(4)	N2–Nb1–N6	167.7(2)
Nb1–N4	2.182(4)	Nb1–N6–C41	173.7(4)
Nb1–N5	2.176(5)	N1–C1–N2	111.9(5)
Nb1–N6	1.787(4)	N1–C1–N3	120.8(5)
N1–C1	1.349(6)	N2–C1–N3	127.4(5)
N2–C1	1.321(6)		
N3–C1	1.385(6)		
N4–C15	1.273(6)		
N5–C28	1.272(6)		

The presence of two κ^2-C,N-iminoacyl ligands was confirmed by X-ray analysis and, although the crystal structures of some bis(iminoacyl) group 5 complexes have been reported,[16] to the best of our knowledge, this is the first example of a bis(iminoacyl) niobium compound that has been structurally characterized and one of the rare examples of iminoacyl niobium derivatives to be structurally characterized.[5,17] The structure of **9** consists of a dinuclear complex and each metal atom is bound to the guanidinate ligand in a κ^2-mode, to two iminoacyl groups in a κ^2-mode and to the nitrogen atom from the imido group in a distorted-trigonal-bipyramidal geometry, with two equatorial positions occupied by the centroid of the κ^2-iminoacyl ligands. The two κ^2-iminoacyl groups are coplanar with mutually *cis*-carbon atoms, as observed in the aforementioned vanadium and tantalum derivatives, with the nitrogen atoms proximal to the equatorial nitrogen atom of the guanidinate ligand. The Nb1–N6 distance of 1.787(4) Å is normal for imido ligands, although slightly longer than in the case of the trialkyl compound **4**, with a value of 1.762 Å,[8b] probably because of the presence of strong donors in the coordination sphere of the metal. The angle at the imido nitrogen atom is in the range normally associated with linear imido ligands [Nb1–N6–C41 173.7(4)°].[8] Similar results were found in cyclopentadienyl analogues.[8d,13] The planarity of the "CN_3" core was evidenced by the sum of the bond angles around C1 (360.1°). This is in contrast with the three different distances found for the N–C bonds [N1–C1 1.349(6) Å, N2–C1 1.321(6) Å, N3–C1 1.385(6) Å]. These data imply a less strongly donating character of the guanidinate ligand (resonance structures *a* and *c* in Scheme 1). As in previously described monoimido guanidinato niobium complexes,[5] the nitrogen atom N2 is placed *trans* to the imido group and the N6–Nb1–N2 angle of 167.7(2)° is close to linearity. The small angle of 15.6° between the plane of the guanidinate core and that of the phenylene group could indicate some electronic delocalization along these ligands through the metal atom.

Conclusions

In this paper we report a straightforward method to obtain *N*,*N*′,*N*′′-trisubstituted guanidines using [$MgBz_2(thf)_2$] as the catalyst under very mild conditions. The synthesis of new dinuclear guanidinato niobium imido complexes is also reported, along with their reactivity towards xylyl isocyanide in migratory insertion reactions to form bis(iminoacyl) derivatives. The first example of the molecular structure of a bis(iminoacyl) niobium complex has been described.

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 Tech.) and degassed under nitrogen before use. Microanalyses were carried out with a Perkin–Elmer 2400

CHN analyzer. NMR spectra were recorded with a Varian FT-400 spectrometer using standard VARIAN-FT software for NOESY-1D, COSY, g-HSQC and g-HMBC. FTIR spectra were recorded with a Bruker Tensor 27 spectrophotometer. $[MgBz_2(thf)_2]$ and $\{[Nb(CH_2SiMe_3)_3(CH_3CN)]_2(\mu\text{-}1,4\text{-}NC_6H_4N)\}$ were prepared according to literature procedures.[8b,11] Amines, diisopropylcarbodiimide and 2,6-dimethylphenyl isocyanide were purchased from Aldrich.

General Procedure for the Synthesis of Guanidines: In a glovebox, amine (12.00 mmol), carbodiimide (12.00 mmol), 1.5%mol of $[MgBz_2(thf)_2]$ and toluene (10 mL) were added to a Schlenk tube. The Schlenk tube was taken outside the glovebox and the reaction was carried out at room temperature for 1 h. The solvent was removed under reduced pressure and the residue was extracted with diethyl ether, filtered to give a clear solution and the solution was cooled to –40 °C to provide the solid guanidines as crystalline products. Identification was carried out by comparison with the NMR spectroscopic data previously reported in the literature. Yields close to 95% were obtained in ppm.

$[\{Nb(CH_2SiMe_3)_2[(4\text{-}tBuC_6H_4)N{=}C(NiPr)(NHiPr)]\}_2(\mu\text{-}1,4\text{-}NC_6H_4N)]$ (5): 2-(4-*tert*-Butylphenyl)-1,3-diisopropylguanidine (0.18 g, 0.66 mmol) in toluene (10 mL) was added to a solution of $\{[Nb(CH_2SiMe_3)_3(CH_3CN)]_2(\mu\text{-}1,4\text{-}NC_6H_4N)\}$ (0.30 g, 0.33 mmol) in toluene (10 mL). The reaction mixture was stirred for 1 h at room temperature. The resulting dark 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 **5**, yield 0.31 g (80%). ^1H NMR (400 MHz, C_6D_6): δ = 0.29 (s, 36 H, $SiMe_3$), 0.67 [d, $^3J_{HH}$ = 6.2 Hz, 12 H, $CH(CH_3)_2$], 1.26 [d, $^3J_{HH}$ = 5.7 Hz, 12 H, $CH(CH_3)_2$], 1.29 (s, 18 H, *t*Bu), 1.60, 1.67 (AB, $^2J_{HH}$ = 10.0 Hz, 8 H, CH_2SiMe_3), 3.27 [m, 2 H, $CH(CH_3)_2$], 3.49 [m, 2 H, $CH(CH_3)_2$], 3.74 (d, $^3J_{HH}$ = 9.0 Hz, NH), 7.28–7.32 (m, 8 H, C_6H_4), 7.35 (s, 4 H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ = 2.96 ($SiMe_3$), 23.12 [$CH(CH_3)_2$], 25.10 [$CH(CH_3)_2$], 31.60 [$C(CH_3)_3$], 34.26 [$C(CH_3)_3$], 44.58 [$CH(CH_3)_2$], 47.40 [$CH(CH_3)_2$], 63.60 (CH_2SiMe_3), 123.38, 125.78, 125.87, 144.96, 145.47, 152.75 (C_6H_4), 164.11 (CN_3) ppm. $C_{56}H_{106}N_8Nb_2Si_4$ (1189.65): calcd. C 56.54, H 8.98; found C 56.66, H 9.01.

$[\{Nb(CH_2SiMe_3)_2[(4\text{-}MeOC_6H_4)N{=}C(NiPr)(NHiPr)]\}_2(\mu\text{-}1,4\text{-}NC_6H_4N)]$ (6): The same procedure described for **5** was followed, using 2-(4-methoxyphenyl)-1,3-diisopropylguanidine (0.16 g, 0.66 mmol) and $\{[Nb(CH_2SiMe_3)_3(CH_3CN)]_2(\mu\text{-}1,4\text{-}NC_6H_4N)\}$ (0.30 g, 0.33 mmol) to afford yellow crystals of **6**, yield 0.33 g (89%). ^1H NMR (400 MHz, C_6D_6): δ = 0.31 (s, 36 H, $SiMe_3$), 0.70 [d, $^3J_{HH}$ = 6.3 Hz, 12 H, $CH(CH_3)_2$], 1.27 [d, $^3J_{HH}$ = 5.8 Hz, 12 H, $CH(CH_3)_2$], 1.60, 1.68 (AB, $^2J_{HH}$ = 9.8 Hz, 8 H, CH_2SiMe_3), 3.27 [m, 2 H, $CH(CH_3)_2$], 3.37 (s, 6 H, OMe), 3.40 [m, 2 H, $CH(CH_3)_2$], 3.69 (d, $^3J_{HH}$ = 10.0 Hz, NH), 6.82 (d, $^3J_{HH}$ = 7.8 Hz, 4 H, C_6H_4), 7.21 (d, $^3J_{HH}$ = 7.8 Hz, 4 H, C_6H_4), 7.41 (s, 4 H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ = 3.11 ($SiMe_3$), 23.21 [$CH(CH_3)_2$], 25.23 [$CH(CH_3)_2$], 44.58 [$CH(CH_3)_2$], 47.48 [$CH(CH_3)_2$], 55.01 (O*Me*), 65.85 (CH_2SiMe_3), 114.73, 125.07, 126.34, 141.44, 153.16, 156.09 (C_6H_4), 164.50 (CN_3) ppm. $C_{50}H_{94}N_8Nb_2O_2Si_4$ (1137.49): calcd. C 52.79, H 8.33; found C 52.84, H 8.40.

$[\{Nb(CH_2SiMe_3)_2[(4\text{-}BrC_6H_4)N{=}C(NiPr)(NHiPr)]\}_2(\mu\text{-}1,4\text{-}NC_6H_4N)]$ (7): The same procedure described for **5** was followed, using 2-(4-bromophenyl)-1,3-diisopropylguanidine (0.19 g, 0.66 mmol) and $\{[Nb(CH_2SiMe_3)_3(CH_3CN)]_2(\mu\text{-}1,4\text{-}NC_6H_4N)\}$ (0.30 g, 0.33 mmol) to afford yellow crystals of **7**, yield 0.37 g (90%). ^1H NMR (400 MHz, C_6D_6): δ = 0.25 (s, 36 H, $SiMe_3$), 0.61 [d, $^3J_{HH}$ = 6.2 Hz, 12 H, $CH(CH_3)_2$], 1.20 [d, $^3J_{HH}$ = 6.1 Hz, 12 H, $CH(CH_3)_2$], 1.59, 1.61 (AB, $^2J_{HH}$ = 10.2 Hz, 8 H, CH_2SiMe_3), 3.17 [m, 2 H, $CH(CH_3)_2$], 3.24 [m, 2 H, $CH(CH_3)_2$], 3.63 (d, $^3J_{HH}$ = 9.4 Hz, NH), 7.01 (d, $^3J_{HH}$ = 7.5 Hz, 4 H, C_6H_4), 7.32 (d, $^3J_{HH}$ = 7.5 Hz, 4 H, C_6H_4), 7.44 (s, 4 H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ = 2.96 ($SiMe_3$), 22.90 [$CH(CH_3)_2$], 25.25 [$CH(CH_3)_2$], 44.97 [$CH(CH_3)_2$], 46.62 [$CH(CH_3)_2$], 64.76 (CH_2SiMe_3), 115.05, 125.40, 126.37, 132.30, 147.55, 153.17 (C_6H_4), 164.52 (CN_3) ppm. $C_{48}H_{88}Br_2N_8Nb_2Si_4$ (1235.23): calcd. C 46.67, H 7.18; found C 46.75, H 7.25.

$[\{Nb(Me_3SiCH_2C{=}Nxylyl)_2[(4\text{-}tBuC_6H_4)N{=}C(NiPr)(NHiPr)]\}_2(\mu\text{-}1,4\text{-}NC_6H_4N)]$ (8): In a glovebox, xylylNC (0.13 g, 1.00 mmol) was added to a solution of **5** (0.30 g, 0.25 mmol) in toluene (10 mL). The reaction mixture was stirred for 30 min and the solvents evaporated to dryness in vacuo. The yellow oily material was redissolved in pentane and cooled to –20 °C to afford yellow crystals of **8**, yield 0.34 g (80%). ^1H NMR (400 MHz, C_6D_6): δ = 0.14 (s, 36 H, $SiMe_3$), 0.69 [d, $^3J_{HH}$ = 6.1 Hz, 12 H, $CH(CH_3)_2$], 1.32 [d, $^3J_{HH}$ = 6.0 Hz, 12 H, $CH(CH_3)_2$], 1.29 (s, 18 H, *t*Bu), 2.10 (s, 12 H, $Me_2C_5H_3$), 2.47 (s, 12 H, $Me_2C_5H_3$), 3.06, 3.11 (AB, $^2J_{HH}$ = 10.0 Hz, 8 H, CH_2SiMe_3), 3.38 [m, 2 H, $CH(CH_3)_2$], 3.47 (d, $^3J_{HH}$ = 10.6 Hz, NH), 3.51 [m, 2 H, $CH(CH_3)_2$], 6.83–7.25 (m, 24 H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ = 0.31 ($SiMe_3$), 19.54 ($Me_2C_5H_3$), 19.85 ($Me_2C_5H_3$), 23.41 [$CH(CH_3)_2$], 25.15 [$CH(CH_3)_2$], 31.51 [$C(CH_3)_3$], 32.58 (CH_2SiMe_3), 33.77 [$C(CH_3)_3$], 44.83 [$CH(CH_3)_2$], 46.06 [$CH(CH_3)_2$], 115.50, 121.10, 123.50, 124.66, 125.11, 130.76, 130.99, 140.19, 145.63, 145.96, 151.52 (C_6H_4), 161.60 (CN_3), 230.84 (xylylN=CCH_2SiMe_3) ppm. $C_{92}H_{142}N_{12}Nb_2Si_4$ (1714.35): calcd. C 64.46, H 8.35; found C 64.66, H 8.50.

$[\{Nb(Me_3SiCH_2C{=}Nxylyl)_2[(4\text{-}MeOC_6H_4)N{=}C(NiPr)(NHiPr)]\}_2(\mu\text{-}1,4\text{-}NC_6H_4N)]$ (9): The same procedure described for **8** was followed, using **6** (0.30 g, 0.26 mmol) and 2,6-$Me_2C_6H_3NC$ (0.13 g, 1.05 mmol), yield 0.38 g (88%). ^1H NMR (400 MHz, C_6D_6): δ = 0.14 (s, 36 H, $SiMe_3$), 0.71 [d, $^3J_{HH}$ = 5.8 Hz, 12 H, $CH(CH_3)_2$], 1.33 [d, $^3J_{HH}$ = 6.2 Hz, 12 H, $CH(CH_3)_2$], 2.09 (s, 12 H, $Me_2C_5H_3$), 2.47 (s, 12 H, $Me_2C_5H_3$), 3.02, 3.09 (AB, $^2J_{HH}$ = 10.3 Hz, 8 H, CH_2SiMe_3), 3.36 [m, 2 H, $CH(CH_3)_2$], 3.44 (s, 6 H, O*Me*), 3.53 [m, 2 H, $CH(CH_3)_2$], 3.55 (m, NH), 6.58–7.06 (m, 24 H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ = –0.09 ($SiMe_3$), 19.75 ($Me_2C_5H_3$), 20.15 ($Me_2C_5H_3$), 23.56 [$CH(CH_3)_2$], 25.41 [$CH(CH_3)_2$], 32.83 (CH_2SiMe_3), 45.03 [$CH(CH_3)_2$], 46.21 [$CH(CH_3)_2$], 55.19 (O*Me*), 113.78, 115.05, 122.29, 123.71, 124.15, 125.31, 131.16, 142.05, 146.13, 151.61, 153.11 (C_6H_4), 161.80 (CN_3), 231.07 (xylylN=CCH_2SiMe_3) ppm. $C_{86}H_{130}N_{12}Nb_2O_2Si_4$ (1662.19): calcd. C 62.14, H 7.88; found C 62.25, H 7.95.

$[\{Nb(Me_3SiCH_2C{=}Nxylyl)_2[(4\text{-}BrC_6H_4)N{=}C(NiPr)(NHiPr)]\}_2(\mu\text{-}1,4\text{-}NC_6H_4N)]$ (10): The same procedure described for **8** was followed, using **7** (0.30 g, 0.24 mmol) and 2,6-$Me_2C_6H_3NC$ (0.12 g, 0.97 mmol), yield 0.37 g (89%). ^1H NMR (400 MHz, C_6D_6): δ = 0.09 (s, 36 H, $SiMe_3$), 0.61 [d, $^3J_{HH}$ = 5.6 Hz, 12 H, $CH(CH_3)_2$], 1.25 [d, $^3J_{HH}$ = 5.7 Hz, 12 H, $CH(CH_3)_2$], 1.95 (s, 12 H, $Me_2C_5H_3$), 2.43 (s, 12 H, $Me_2C_5H_3$), 2.96, 3.02 (AB, $^2J_{HH}$ = 10.5 Hz, 8 H, CH_2SiMe_3), 3.17 [m, 2 H, $CH(CH_3)_2$], 3.28 (d, $^3J_{HH}$ = 10.8 Hz, NH), 3.39 [m, 2 H, $CH(CH_3)_2$], 6.60–7.24 (m, 24 H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ = 0.00 ($SiMe_3$), 19.60 ($Me_2C_5H_3$), 20.14 ($Me_2C_5H_3$), 23.65 [$CH(CH_3)_2$], 25.20 [$CH(CH_3)_2$], 32.92 (CH_2SiMe_3), 45.36 [$CH(CH_3)_2$], 46.30 [$CH(CH_3)_2$], 110.04, 123.21, 123.83, 125.59, 128.77, 131.03, 131.11, 145.98, 147.80, 151.77 (C_6H_4), 161.80 (CN_3), 230.73 (xylylN=CCH_2SiMe_3) ppm. $C_{84}H_{124}Br_2N_{12}Nb_2Si_4$ (1759.93): calcd. C 57.33, H 7.10; found C 57.50, H 7.20.

X-ray Structure Determination for Compounds 2 and 9: Crystals of compounds **2** and **9** were mounted at low temperature in inert oil on a glass fibre. Data were collected with a Bruker X8 APPEX II CCD-based diffractometer, equipped with a graphite monochromated Mo-K_α (radiation source λ = 0.71073 Å).

The crystal data, data collection, structural solution and refinement parameters for the complexes are summarized in Table 2. 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 SHELXTL,[20] 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. In complex **9**, solvent molecules were severely disordered and were removed using the SQUEEZE procedure implemented in PLATON.[21]

Table 2. Crystal data and structure refinement for compounds **2** and **9**.

	2	**9**
Empirical formula	$C_{14}H_{23}N_3O$	$C_{43}H_{63}N_6NbOSi_2$
Temperature [K]	220(2)	250(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	*Pnma*
a [Å]	9.351(1)	24.463(3)
b [Å]	16.081(1)	29.082(3)
c [Å]	19.495(2)	17.152(2)
α [°]	90	90
β [°]	90	90
γ [°]	90	90
V [Å^3]	2931.5(5)	12203(2)
Z	8	8
$\rho_{calcd.}$ [g cm^{-3}]	1.130	0.904
μ [mm^{-1}]	0.073	0.265
F(000)	1088	3528
Crystal size [mm]	0.48 × 0.13 × 0.10	0.63 × 0.54 × 0.46
Index ranges	$-12 \le h \le 12$	$-33 \le h \le 33$
	$-22 \le k \le 22$	$-39 \le k \le 39$
	$-26 \le l \le 27$	$-16 \le l \le 23$
Reflections collected	29262	99230
Independent reflections	8094	16158
	[*R*(int) = 0.1235]	[*R*(int) = 0.1765]
Observed reflections	2626	4588
Data/restraints/parameters	8094/0/335	16158/0/478
Goodness-of-fit on F^2	0.712	0.756
Final *R* indices	R_1 = 0.0626	R_1 = 0.0652
	wR_2 = 0.1228	wR_2 = 0.1569
$\Delta\rho_{max/min}$ [e Å^{-3}]	0.258 and –0.238	0.277 and –0.294

CCDC-916804 (for **2**) and -916805 (for **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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