Amido-Imido Niobium Complexes with Chloro-Silyland Amino-Silyl-Functionalized Cyclopentadienyl Ligands

M. Isabel Alcalde, M. Pilar Gómez-Sal, and Pascual Royo*

Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario, E-28871 Alcalá de Henares, Spain

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The chloro–imido complex $[Nb(\eta^5-C_5H_4-SiMe_2Cl)(CH_2Ph)Cl(N^tBu)]$ undergoes selective substitution of the Nb–Cl bond when it is reacted with LiNH^tBu, giving $[Nb(\eta^5-C_5H_4-SiMe_2-$ Cl)(CH₂Ph)(NHⁱBu)(NⁱBu)], whereas preferential reaction at the Si–Cl bond occurs with $NH_2^{t}Bu$, giving $[Nb{\eta^5-C_5H_4-SiMe_2(NH^tBu)}(CH_2Ph)Cl(N^tBu)]$, which is then transformed into $[Nb{\eta^5-C_5H_4-SiMe_2(NH^tBu)}(CH_2Ph)(NH^tBu)(N^tBu)]$ on further reaction with NH₂^tBu. Chemical reactivity studies demonstrate that a spontaneous transformation of $[Nb(\eta^5-C_5H_4 SiMe_2Cl(CH_2Ph)(NH^{\dagger}Bu)(N^{\dagger}Bu)$ into $[Nb\{\eta^5-C_5H_4-SiMe_2(NH^{\dagger}Bu)\}(CH_2Ph)Cl(N^{\dagger}Bu)]$ takes place, via an intermolecular reaction, by attack of the silicon-bonded chlorine at the unsaturated niobium center. Benzylation of $[Nb{\eta^5-C_5H_4-SiMe_2(NH^tBu)}(CH_2Ph)Cl(N^tBu)]$ with Mg(CH₂Ph)₂·2THF gives $[Nb{\eta^5-C_5H_4-SiMe_2(NH^iBu)}(CH_2Ph)_2(N^iBu)]$, which also results from reaction of the chloro-silyl derivative $[Nb(\eta^5-C_5H_4-SiMe_2Cl)(CH_2Ph)_2(N^tBu)]$ with NH₂^tBu. The dichloro–imido complex [Nb(η^5 -C₅H₄-SiMe₂Cl)Cl₂(N^tBu)], readily obtained from $[Nb(\eta^5-C_5H_4-SiMe_2Cl)Cl_4]$, also reacts preferentially at the Si-Cl bond when treated with NH₂^tBu to give $[Nb{\eta^5-C_5H_4-SiMe_2(NH^tBu)}Cl_2(N^tBu)]$, which is further transformed into $[Nb{\eta^5-C_5H_4-SiMe_2(NH^tBu)}Cl(NH^tBu)(N^tBu)]$; the latter is alternatively prepared by reaction of $[Nb(\eta^5-C_5H_4-SiMe_2Cl)Cl_4]$ with a large excess of NH_2^tBu . The tetrachloro compound reacts with excess LiNH^tBu to give the constrained-geometry complex $[Nb{\eta^5-C_5H_4-SiMe_2(\eta^1 N^{t}Bu$ ($N^{t}Bu$), ($N^{t}Bu$), which is converted into the chloro–niobium derivative by reaction with SiMe₃Cl. These constrained-geometry complexes may also be obtained from the dichloro derivative $[Nb(\eta^5-C_5H_4-SiMe_2Cl)Cl_2(N^tBu)]$, by reaction with 3 or 2 equiv of LiNH^tBu, respectively. Thermal treatment of the benzyl compounds $[Nb{\eta^5-C_5H_4-SiMe_2(NH^tBu)}(CH_2-$ Ph)X(N^tBu)] (X = Cl, CH₂Ph) at 160 °C results in formation of the silyl-amido complexes $[Nb{\eta^5-C_5H_4-SiMe_2(\eta^1-N^tBu)}X(N^tBu)]$ (X = Cl, CH₂Ph) with elimination of toluene, whereas a similar transformation of the related iminoacyl complex $[Nb{\eta^5-C_5H_4-SiMe_2(NH^tBu)}]{\eta^2-C_5H_4-SiMe_2(NH^tBu)}$ $[C(CH_2Ph){N(2,6-Me_2C_6H_3)}](CH_2Ph)(N^tBu)]$ produces a simultaneous isomerization to give the vinylamido compound $[Nb{\eta^5-C_5H_4-SiMe_2(\eta^1-N^tBu)}]{N(CH=CHPh)(2,6-Me_2C_6H_3)}(N^t-Me_2C_6H_3)]$ Bu)]. Insertion of CN(2,6-Me₂C₆H₃) into the niobium-benzyl bonds of complexes $[Nb{\eta^{5}} C_{5}H_{4}$ -SiMe₂(NH^tBu)}(CH₂Ph)X(N^tBu)] (X = Cl, CH₂Ph) and [Nb{ η^{5} -C₅H₄-SiMe₂(η^{1} -N^tBu)}- $(CH_2Ph)(N^tBu)$] leads to the iminoacyl compounds $[Nb{\eta^5-C_5H_4-SiMe_2(NH^tBu)}{\eta^2-[C(CH_2Ph)-C_5H_4-SiMe_2(NH^tBu)]}$ $\{N(2,6-Me_2C_6H_3)\}\}X(N^tBu) (X = Cl, CH_2Ph) and [Nb{\eta^5-C_5H_4-SiMe_2(\eta^1-N^tBu)}{\eta^2-[C(CH_2-M_2-M_2)]}$ $Ph_{N(2,6-Me_2C_6H_3)}](N^tBu)$, respectively. All of the reported new compounds were characterized by elemental analyses and ¹H and ¹³C NMR spectroscopy, and the X-ray molecular structure of $[Nb{\eta^5-C_5H_4-SiMe_2(NH^tBu)}Cl_2(N^tBu)]$ was studied by diffraction methods.

Introduction

Silvl-substituted cyclopentadienyl rings have been extensively used to prepare Ziegler-Natta type olefin polymerization catalysts because the presence of the electron-withdrawing silvl substituent improves their catalytic activity.¹ The presence of additional functionalities, particularly chlorine, on these silvl groups not only allows their fixation on solid supports² but also offers new, direct synthetic strategies for constrainedgeometry catalysts with bidentate η^5 -cyclopentadienylsilyl- η^1 -amido ligands, in good yields.³ These constrained-geometry catalysts can also be fixed on silica supports if they contain one additional Si-Cl bond, such

^{*} To whom correspondence should be addressed. Tel.: 34-1-8854765.

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i.-LiNH^tBu, hexane, 1h. ii.- LiNH^tBu, 24h. iii.- 2NH₂^tBu, hexane, 12h. iv.- 4NH₂^tBu, hexane, 18h. or 2 LiNH^tBu, toluene, 18h. v.- Mg(CH ₂Ph)₂.2THF, hexane, 2h. vi.- 2NH₂^tBu, hexane, overnight.

as those obtained from initial silylcyclopentadienyl ligands which contain two Si–Cl bonds.⁴ The extended use of this type of ligand to prepare group 5 metal complexes has been scarcely studied, and only isolated examples of related constrained-geometry group 5 metal compounds have been reported.⁵

In contrast, high-valent group 5 metal imido cyclopentadienyl complexes isolobal⁶ with the very wellknown group 4 dicyclopentadienyl derivatives have been extensively studied in the last few years.⁷

We have recently reported⁸ the synthesis and characterization of new chlorosilyl-substituted cyclopentadienyl imido-dichloro ([Nb(η^5 -C₅H₄-SiMe₂Cl)Cl₂(N^tBu)], **1**), imido-chloro-benzyl ([Nb(η^5 -C₅H₄-SiMe₂Cl)(CH₂-Ph)Cl(N^tBu)], **2**), imido-dibenzyl ([Nb(η^5 -C₅H₄-SiMe₂-Cl)(CH₂Ph)₂(N^tBu)], **3**), and tetrachloro ([Nb(η^5 -C₅H₄-SiMe₂Cl)Cl₄], **4**) niobium derivatives. We herein report their use as starting materials to obtain new ((aminosilyl)cyclopentadienyl)niobium chloro– and benzyl–imido ([Nb{ η^{5} -C₅H₄-SiMe₂(NH^tBu)}XY(N^tBu)] (X, Y = Cl, Bz)), ((chlorosilyl)cyclopentadienyl)niobium amido–imido ([Nb- $(\eta^{5}$ -C₅H₄-SiMe₂Cl)Bz(NH^tBu)(N^tBu)]), and ((aminosilyl)cyclopentadienyl)niobium amido–imido ([Nb{ η^{5} -C₅H₄-SiMe₂(NH^tBu)}X(NH^tBu)(N^tBu)] (X = Cl, Bz)) compounds, used as precursors to prepare the new constrained-geometry niobium derivatives [Nb{ η^{5} -C₅H₄-SiMe₂- η^{1} -N^tBu)}X(N^tBu)] (X = Cl, Bz, NH^tBu, N(CH= CHPh)(2,6-Me₂C₆H₃)) and to study the insertion reactions of 2,6-dimethylphenyl isocyanide into their niobium–benzyl bonds.

Results and Discussion

Reactions with NH₂^tBu. We reported⁹ that preferential reaction at the Si-Cl bonds takes place when cyclopentadienylzirconium halides containing both Si-Cl and M-Cl bonds are reacted with an excess of less polar amines. As shown in Scheme 1, reaction of [Nb- $(\eta^5$ -C₅H₄-SiMe₂Cl)(CH₂Ph)Cl(N^tBu)] (**2**) with 2 equiv of NH₂^tBu in hexane at room temperature gave, after separation of the ammonium salt formed, the aminosilvl complex [Nb{n⁵-C₅H₄-SiMe₂(NH^tBu)}(CH₂Ph)Cl(N^t-Bu)] (5), which was isolated as a brown oil and characterized by NMR spectroscopy (see Experimental Section). The same reaction carried out using 1 equiv of NH₂^tBu and 2 equiv of NEt₃ also resulted in the formation of complex 5 instead of the constrained-geometry derivatives observed^{9b} in the reaction with the related group 4 metal complexes. Compound 5 was obtained when the hexane solution that gave 6, discussed below, was stirred for 24 h at room temperature (see Scheme 1).

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Scheme 2



i.- 15NH₂^tBu, toluene. ii.- 4NH₂^tBu, toluene. iii.- 2NH₂^tBu, hexane. iv.- 2NH₂^tBu, hexane. v.- SiMe₃Cl, toluene. vi.- 5 LiNH^tBu, ether. vii.- SiMe₃Cl, hexane. viii.- 160°C, 3 days, hexane. ix.-3 LiNH^tBu, ether. x.-2 LiNH^tBu, ether.

As shown in Scheme 1, reaction of **5** with 2 equiv of $NH_2^{t}Bu$ in hexane at room temperature afforded the corresponding amino-silyl complex $[Nb{\eta^5-C_5H_4-SiMe_2-(NH^{t}Bu)}(CH_2Ph)(NH^{t}Bu)(N^{t}Bu)]$ (**7**) in 83% yield. Complex **7** was isolated as a dark brown oil and characterized by NMR spectroscopy. Likewise, complex **7** can also be directly obtained by reaction of **2** with 4 equiv or excess $NH_2^{t}Bu$.

A selective reaction was also observed when the dibenzyl derivative $[Nb(\eta^5-C_5H_4-SiMe_2Cl)(CH_2Ph)_2(N^t-Bu)]$ (3), prepared as reported previously,⁸ was reacted with 2 equiv of the amine at room temperature in hexane to give the amino-silyl complex $[Nb\{\eta^5-C_5H_4-SiMe_2(NH^tBu)\}(CH_2Ph)_2(N^tBu)]$ (8) in 90% yield, after separation of the ammonium salt formed. The same compound was also isolated in high yield by benzylation of 5 using Mg(CH_2Ph)_2·2THF as alkylating agent. Complex 8 was isolated as a greenish solid and was characterized by elemental analysis, NMR spectroscopy, and mass spectrometry.

A similar reaction was carried out by adding a great excess of amine (15/1 molar ratio) to the tetrachloro complex [Nb(η^5 -C₅H₄-SiMe₂Cl)Cl₄] (**4**) in toluene (Scheme 2). After the mixture was stirred for **48** h at room temperature, the amino–silyl derivative [Nb{ η^5 -C₅H₄-SiMe₂(NH^tBu)}Cl(NH^tBu)(N^tBu)] (**9**) was isolated in 70% yield, after removal of the ammonium salt, as a pale yellow solid which was identified by elemental analysis and NMR spectroscopy. When the amine NH₂^t-Bu was added in a controlled manner, initially imido substitution occurred at two of the Nb–Cl bonds to give [Nb(η^5 -C₅H₄-SiMe₂Cl)Cl₂(N^tBu)] (**1**). The Si–Cl bond of **1** reacts further with the amine to give complex **10**, followed by reaction of the amine with another Nb–Cl bond to give **9** as the final product.

Transformation of the niobium chloro–amido complex **9** into the dichloro derivative $[Nb{\eta^5-C_5H_4-SiMe_2(NH^t-Bu)}Cl_2(N^tBu)]$ (**10**) was easily achieved in quantitative yield by reaction of **9** with 1 equiv of SiMe_3Cl in toluene at room temperature. Complex **10** was isolated as a dark yellow crystalline solid identified by elemental analysis, NMR spectroscopy, and X-ray diffraction methods.

The ¹H and ¹³C NMR spectra for complexes 8 and 10 show the expected singlet due to the equivalent methylsilyl groups and two singlets between δ 1.04 and 1.15 corresponding to the two types of Si-amine and Nbimido tert-butyl groups. Complex 8 shows two doublets due to the diastereotopic protons of the two niobiumbonded methylene benzyl moieties. The remaining amino-silyl compounds 5, 7, and 9 have a chiral metal center which causes the two silicon-bonded methyl groups to be inequivalent, appearing as two singlets in the high-field region between δ 0.31 and 0.43. Complex **5** and complexes **7–10** show either two or three types of tert-butyl groups, which can be easily identified by the C_{ipso} resonances in their ¹³C NMR spectra, shifted from δ 49–50 (Si–NH^tBu) to δ 56–57 (Nb–NH^tBu) and δ 65–70 (Nb=N^tBu).

The molecular structure of compound **10**, obtained by X-ray diffraction studies, is shown in Figure 1 with the atomic labeling scheme, and selected bond lengths and angles are presented in Table 1.

The structure is typical of half-sandwich imido complexes, and the structural parameters are comparable to those of related compounds, such as $[Nb(\eta^5-C_5H_5) Cl_2(NR)$] (R = Me, ^tBu, C₆H₅ⁱPr₂-2,6).^{6a} The Nb1-N1 distance of 1.748(8) Å is in the range expected for a triple bond and is very similar to those in other imidodichloro niobium compounds, for which the distances range from 1.744(3) to 1.761(6) Å; the imido group is also almost linear (169.1(8)°). The Nb-C(ring) distances vary slightly, ranging from 2.532(8) to 2.363(10) Å with a maximum deviation of 0.169 Å, where the longest distance corresponds to the substituted carbon atom. The centroid of the cyclopentadienyl ring is displaced 0.144 Å with respect to a point located in the direction perpendicular to the niobium center, one of the larger shifts described for this type of compound. The most interesting feature of this structure is the trans orientation of the silvl substituent with respect to the imido



Figure 1. View of the molecular structure of complex 10.

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Nb(1)-N(1)	1.748(8)	N(2)-C(6)	1.455(14)
Nb(1)-Cl(1)	2.352(3)	C(1) - C(5)	1.413(14)
Nb(1)-Cl(2)	2.358(3)	C(1) - C(2)	1.438(13)
Nb(1) - C(4)	2.363(10)	C(2) - C(3)	1.445(17)
Nb(1) - C(3)	2.398(10)	C(3) - C(4)	1.417(17)
Nb(1) - C(2)	2.442(10)	C(4) - C(5)	1.361(16)
Nb(1)-C(5)	2.459(10)	C(6) - C(8)	1.47(2)
Nb(1) - C(1)	2.532(8)	C(6) - C(7)	1.525(18)
Si(1)-N(2)	1.719(9)	C(6) - C(9)	1.533(19)
Si(1)-C(10)	1.849(13)	C(12)-C(13)	1.43(2)
Si(1)-C(11)	1.848(12)	C(12)-C(14)	1.46(2)
Si(1) - C(1)	1.862(9)	C(12)-C(15)	1.49(2)
N(1)-C(12)	1.478(14)	Nb(1)-Cp(1)	2.122
N(1) - Nb(1) - Cl(1)	101.5(3)	C(11) - Si(1) - C(1)	111.8(5)
N(1)-Nb(1)-Cl(2)	102.7(3)	C(12) - N(1) - Nb(1)) 169.1(8)
Cl(1)-Nb(1)-Cl(2)	105.39(13)	C(6) - N(2) - Si(1)	132.6(8)
N(2) - Si(1) - C(10)	114.8(6)	C(5) - C(1) - Si(1)	129.2(7)
N(2) - Si(1) - C(11)	105.1(5)	C(2) - C(1) - Si(1)	126.2(7)
C(10) - Si(1) - C(11)	109.1(7)	N(1) - Nb(1) - Cp(1)) 119.62
N(2)-Si(1)-C(1)	110.3(4)	Cl(2)-Nb(1)-Cp(1)	i) 113.59
C(10) - Si(1) - C(1)	105.8(5)	Cl(1)-Nb(1)-Cp(1)	1) 112.40
			-

ligand, which is located in a *staggered* disposition instead of the usually *eclipsed* orientation found for most compounds of this type. The very short Si1–N2 bond distance of 1.719(9) Å and the Si1–N2–C6 angle of 132.6(8)° indicate an important contribution of N sp² and double-bond character of the Si–N bond.

Reactions with LiNH^tBu. We also reported⁹ that preferential reaction of the M-Cl bonds takes place when cyclopentadienylmetal halides containing both Si-Cl and M-Cl bonds are reacted with polar alkalimetal amides. As shown in Scheme 1, when $[Nb(\eta^{5} C_5H_4$ -SiMe₂Cl)(CH₂Ph)Cl(N^tBu)] (2) was reacted with 1 equiv of LiNH^tBu in hexane at room temperature for a limited period of time, the amido niobium complex $[Nb(\eta^5-C_5H_4-SiMe_2Cl)(CH_2Ph)(NH^tBu)(N^tBu)]$ (6) was isolated as a brown oil which was characterized by NMR spectroscopy (see Experimental Section). The reaction time could not be extended for more than 1 h, because complex 6 underwent a further reaction, discussed above, and was finally transformed into the amino-silyl derivative $[Nb{\eta^5-C_5H_4-SiMe_2(NH^tBu)}(CH_2Ph)Cl(N^t-$ Bu)] (5). The ¹H and ¹³C NMR spectra of complex 6 showed the expected two singlets for the inequivalent Me–Si groups and two doublets for the methylenic benzyl protons, due to the asymmetry imposed by the chiral metal center. The presence of the metal-bonded *tert*-butylamido group was confirmed by its C_{ipso} resonance observed at δ 56.5.

Some of the compounds obtained by reactions with the amine NH₂^tBu could also be isolated using the amide LiNH^tBu. Thus, reaction of complex **2** with 2 equiv of LiNH^tBu in hexane gave complex 7 in high yield, although in diethyl ether a mixture of 7, 15, and other unidentified products was obtained. Similarly, reaction of 3 with 1 equiv of LiNHtBu gave lower yields of the dibenzyl derivative 8 (see Scheme 1). However, different reaction products were obtained in some cases; thus, reaction of the tetrachloro complex 4 with a 5 equiv excess of LiNH^tBu (see Scheme 2) resulted in complete substitution of the chlorine moieties to give the constrained-geometry complex $[Nb{\eta^5-C_5H_4-SiMe_2(\eta^1-$ N^tBu)}(NH^tBu)(N^tBu)] (11), which was easily, quantitatively transformed into the chloro derivative $[Nb{\eta^{5}}]$ C_5H_4 -SiMe₂(η^1 -N^tBu) Cl(N^tBu) (14; see below) by reaction with SiMe₃Cl in hexane at room temperature. Complex 14 was also obtained from the reaction of complex **1** with 2 or 3 equiv of LiNH^tBu, together with very small amounts of 9 and 11, respectively, through deprotonation of the intermediate amido derivative¹⁰ by LiNH^tBu with elimination of NH₂^tBu and LiCl. Both 11 and 14 are brown oils characterized by NMR spectroscopy.

Studies Related to the Transformation of Complex 6 into 5. We have discussed above that a slow exchange between the Si–Cl and Nb–NH^tBu takes place at room temperature in the complex [Nb(η^{5} -C₅H₄-SiMe₂Cl)(CH₂Ph)(NH^tBu)(N^tBu)] (6), which is quantitatively transformed in 24 h into [Nb{ η^{5} -C₅H₄-SiMe₂(NH^t-Bu)}(CH₂Ph)Cl(N^tBu)] (5). This exchange between Si– Cl and Nb–NH^tBu bonds is comparable to the wellknown¹¹ use of Me₃Si–Cl to halogenate metal–amido compounds. The transformation of **6** into **5** may be proposed to occur through intra- or intermolecular attack of the silicon-bonded chlorine on the unsaturated niobium center, as represented in Scheme 3 A.

We carried out several studies to distinguish between both intra- and intermolecular transformations. Initially we observed that this transformation was more rapid in THF than in toluene, C_6D_6 , or hexane and when it was monitored by ¹H NMR spectroscopy formation of a mixture of complexes [Nb{ η^5 -C₅H₄-SiMe₂(NH^tBu)} (CH₂-Ph)(NH^tBu)(N^tBu)] (7) and $[Nb(\eta^5-C_5H_4-SiMe_2Cl)(CH_2-$ Ph)Cl(N^tBu)] (2) was observed. Formation of 7 containing two NH^tBu groups provides evidence of the intermolecular mechanism proposed in Scheme 3A. This mixture was further transformed into $[Nb{\eta^5-C_5H_4-SiMe_2(NH^t-$ Bu}(CH₂Ph)Cl(N^tBu)] (5) in the same way. In a similar, but slower, reaction in C_6D_6 7 was also observed, although as a lower proportion of the reaction mixture. Further evidence was obtained when a 1/1 molar ratio of **6** and the dichloro derivative $[Nb(\eta^5-C_5H_4-SiMe_2Cl) Cl_2(N^tBu)$] (1) were stirred in C_6D_6 (see Scheme 3B). In

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i.- CN(2,6-Me₂C₆H₃), hexane, 1-2h. ii.- CN(2,6-Me₂C₆H₃), 50°C, 4h, hexane. iii.- 160°C, 3 days, hexane.

this reaction only a small amount of **6** was transformed into **5**, leaving an appropriate molar ratio of unreacted **1**; the major reaction products were **2** and **10**. This result is consistent with the same intermolecular attack by the silicon-bonded chlorine of $[Nb(\eta^5-C_5H_4-SiMe_2Cl)Cl_2(N^{t-}Bu)]$ on the niobium center of **6**. In a final experiment, a 1/1 molar ratio of complexes **7** and **2** were reacted in C_6D_6 (Scheme 3C). This reaction was faster than the transformation of **6** into **5**, probably because formation of **7** is unfavorable in this solvent, and rendered complex **5** in high yield.

The NMR characterization of all the complexes involved in these studies was made on the basis of the spectral behavior known for isolated samples of each component.

Reactions of Benzyl Complexes with CN(2,6-Me₂C₆H₃). Insertion of CN(2,6-Me₂C₆H₃)^{8,12} into the niobium–benzyl bonds of the 16-electron mono- and dibenzyl complexes [Nb{ η^{5} -C₅H₄-SiMe₂(NH^tBu)}(CH₂- Ph)X(N^tBu)] (X = Cl (**5**), CH₂Ph (**8**)) readily took place when **5** and **8** were stirred for several hours in hexane at room temperature to give the iminoacyl derivatives $[Nb{\eta^{5}-C_{5}H_{4}-SiMe_{2}(NH^{t}Bu)}{\eta^{2}-[C(CH_{2}Ph){N(2,6-Me_{2}C_{6}H_{3})}]X(N^{t}Bu)]$ (X = Cl (**12**), CH₂Ph (**13**)) in high yield (Scheme 4).

The iminoacyl derivatives **12** and **13** were isolated as a brown oil and a pale yellow solid, respectively, and were characterized by elemental analysis (**13**) and NMR spectroscopy. Both complexes are asymmetric molecules showing the expected inequivalency of all of their substituents, consistent with the proposed formulation (see Experimental Section for detailed assignments). The presence of the iminoacyl group was confirmed by the resonances observed in the ¹³C NMR spectra at δ 227.7 and 231.5 due to the iminoacyl carbon atom.

^{(12) (}a) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059. (b) Gómez, M.; Gómez-Sal, P.; Jiménez, G.; Martín, A.; Royo, P.; Sánchez-Nieves, J. *Organometallics* **1996**, *15*, 3579.

Complex **6** is a formally 18-electron species that does not react with isocyanide; instead, it is slowly transformed into **5** (see above), which then undergoes the insertion leading to complex **12**.

Thermal Conversion of Amino–Silyl Complexes [Nb{ η^5 -C₅H₄-SiMe₂(NH^tBu)}(CH₂Ph)X(N^tBu)] into Constrained Silyl–Amido Derivatives [Nb{ η^5 -C₅H₄-SiMe₂- η^1 -N^tBu)}X((N^tBu)]. [Ti(η^5 -C₅H₄-SiMe₂Cl)Cl₃] readily reacts with LiNH^tBu at room temperature to give the constrained-geometry complex [Ti{ η^5 -C₅H₄-SiMe₂(η^1 -N^tBu)Cl₂].⁹ In a similar reaction using the related zirconium complex, only very low yields were obtained and the reaction has never been observed for other transition-metal compounds.

We have described above the synthesis of constrained amido-silyl complexes and were interested in studying the accessibility of similar niobium complexes via the thermal transformation of appropriate benzyl complexes¹³ containing the (aminosilyl)cyclopentadienyl ligand. As shown in Scheme 2, when hexane solutions of $[Nb{\eta^5-C_5H_4-SiMe_2(NH^tBu)}(CH_2Ph)X(N^tBu)]$ (X = Cl (5), CH₂Ph (8)) were heated for 3 days at 160 °C in sealed tubes, elimination of toluene was observed and the constrained η^1 -amidosilyl- η^5 -cyclopentadienyl complexes $[Nb{\eta^5-C_5H_4-SiMe_2(\eta^1-N^tBu)}X(N^tBu)]$ (X = Cl (14), CH₂Ph (15)) were isolated as brown oils in high yields. Complex 15 can also be obtained in high yield via benzylation of 14 with Mg(CH₂Ph)₂·2THF. Not only does similar thermal treatment of the iminoacyl complex $[Nb{\eta^{5}-C_{5}H_{4}-SiMe_{2}(NH^{t}Bu)}{\eta^{2}-[C(CH_{2}Ph){N(2,6-Me_{2}-Me_{$ C₆H₃)]}(CH₂Ph)(N^tBu)] (**13**) eliminate toluene but also a further isomerization of the η^2 -iminoacyl group takes place to finally give the vinylamido derivative $[Nb{\eta^{5}}]$ C_5H_4 -SiMe₂(η^1 -N^tBu)}{N(CH=CHPh)(2,6-Me₂C₆H₃)}(N^t-Bu)] (16). This isomerization, which consists of a 1,2hydrogen shift,^{12a,14} was not perturbed by addition of pyridine as expected for a formally 18-electron η^2 iminoacyl-imido-Cp-silyl-amido intermediate compound isolated as **17** (see below), for which a β -hydrogen abstraction process is highly unlikely. No coordination of the eneamide moiety was observed. Although we have not carried out mechanistic studies for this process, the behavior observed could be better explained by invoking the amidocarbene resonance structure of the η^2 -iminoacyl group. Complexes 14 and 15 were characterized by NMR spectroscopy (see Experimental Section). These complexes showed two singlets for the inequivalent methyl groups bonded to silicon and four multiplets for the inequivalent ring protons (two overlapped for 14), due to the presence of the chiral niobium center. The diastereotopic benzyl methylenic protons of 15 were observed as two doublets with $J_{H-H} = 11.5$ Hz. The assignment of signals due to other groups and their ¹³C NMR spectra were consistent with the proposed formulation. The most relevant resonances observed for complex 16 were the two doublets at δ 4.90 and 8.82 $(J_{\rm H-H} = 14 \text{ Hz})$ due to the olefinic protons of the vinyl moiety, which appear in the ¹³C NMR spectrum as two singlets at δ 101.6 (J_{C-H} = 152 Hz) for the N-bound

carbon and at δ 150.9 (J_{C-H} = 165 Hz) for the terminal carbon, indicating the *trans* disposition of the two vinylic hydrogens.

As shown in Scheme 4, complex **15** reacted with CN-(2,6-Me₂C₆H₃) at 50 °C in hexane to give the related iminoacyl derivative [Nb{ η^5 -C₅H₄-SiMe₂(η^1 -N^tBu)}{ η^2 -[C(CH₂Ph){N(2,6-Me₂C₆H₃)]}(N^tBu)] (**17**), isolated after removal of the solvent as a brown oil, which was identified by NMR spectroscopy. The ¹H NMR spectrum of **17** showed two doublets due to the diastereotopic benzyl methylenic protons shifted to low field (δ 3.42, 3.58) and all the remaining signals expected for an asymmetric molecule with a chiral metal center (see Experimental Section). The ¹³C NMR spectrum shows the iminoacyl carbon resonance at δ 236.3. Thermal treatment of **17** for 3 days at 160 °C causes its isomerization to **16**, as shown in Scheme 4.

Conclusions

Formation of the imido derivative is the first step in the reaction of $[Nb(\eta^5-C_5H_4-SiMe_2Cl)Cl_4]$ with LiNH^t-Bu or NH₂^tBu, whereas selective reactions of imido complexes $[Nb(\eta^5-C_5H_4-SiMe_2Cl)XCl(N^tBu)]$ (X = Cl, CH_2Ph) take place at the Nb–Cl bond, leading to amido-niobium compounds when LiNH^tBu is used, and at the Si-Cl bond, leading to amino-silyl derivatives when NH₂^tBu is employed. In the latter case, further reactions take place in the presence of excess amine to give amino-silyl-amido-niobium complexes. Intermolecular rearrangements between Si-Cl and Nb-NHt-Bu bonds are always observed, whatever the remaining substituents bonded to the metal center are, and lead to the thermodynamically more stable amino-silyl chloro-niobium derivatives. Deprotonation of protonated amido-niobium complexes with strongly basic solutions of LiNH^tBu in diethyl ether gives cyclopentadienylsilylamido-niobium complexes. These barely accessible constrained-geometry niobium compounds [Nb- $\{\eta^{5}-C_{5}H_{4}-SiMe_{2}(\eta^{1}-N^{t}Bu)\}X(N^{t}Bu)\}$ can also be obtained by heating the amino-silvl compounds at 160 °C. Insertion of CN(2,6-Me₂C₆H₃) into niobium-benzyl bonds is easily achieved for both open and cyclic compounds to give the corresponding iminoacyl derivatives. The η^2 -iminoacyl substituent in the constrained compounds is readily isomerized to the vinylamido derivatives through a 1,2-hydrogen shift by thermal treatment at 160 °C.

Experimental Section

General Comments. All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques or a drybox. Solvents used were previously dried and freshly distilled under argon: tetrahydrofuran from sodium benzophenone ketyl, toluene from sodium, hexane from sodium-potassium amalgam. Unless otherwise stated, reagents were obtained from commercial sources and used as received. NH2^tBu (Aldrich) was distilled before use and stored under argon. LiNH^tBu was prepared in hexane in almost quantitative yield from NH2^tBu and ⁿBuLi (Aldrich, 1.6 M in hexane). $[Nb(\eta^5-C_5H_4-SiMe_2Cl)Cl_2(N^tBu)]$ (1), $[Nb(\eta^5-C_5H_4-SiMe_2Cl)Cl_2(N^tBu)]$ $SiMe_2Cl$ (CH₂Ph)Cl(N^tBu)] (2), $[Nb(\eta^5-C_5H_4-SiMe_2Cl)(CH_2Ph)_2 (N^{t}Bu)$] (3), and $[Nb(\eta^{5}-C_{5}H_{4}-SiMe_{2}Cl)Cl_{4}]$ (4) were prepared by reported methods.⁸ IR spectra were recorded in Nujol mulls between CsI pellets, over the range 4000-200 cm⁻¹ on a Perkin-Elmer 583 spectrophotometer. ¹H and ¹³C NMR spectra

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^{(14) (}a) Beshouri, S. M.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1987**, *6*, 891. (b) Beshouri, S. M.; Chebi, D. E.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1990**, *9*, 2375.

were recorded on a Varian Unity VXR-300. Chemical shifts, in ppm, were measured relative to the residual ¹H and ¹³C resonances of benzene- d_6 used as solvent, δ 7.15 (¹H) and 128.0 (¹³C), and coupling constants are in Hz. C, H, and N analyses were carried out with a Perkin-Elmer 240 C analyzer for all the solid compounds. Compounds reported as oily products (5-7, 11, 12, 14-17) could not be purified by sublimation due to their limited thermal stability. Purification was carried out by extraction into pentane, filtration, and removal of solvent under vacuum, and the purity was confirmed by NMR spectroscopy. All attempts made to obtain acceptable analytical data for these oily products failed due to their air sensitivity, thermal transformation, and difficulties in the manipulation and weighting of samples. Therefore, the analytical values found for all these compounds which were ca. 1% (C) deviated are not included in the Experimental Section.

Preparation of [Nb(η^{5} -C₅H₄SiMe₂NH^tBu)(CH₂Ph)Cl-(N^tBu)] (5). The brown complex 5 was obtained by the procedure (2, 0.30 g, 0.67 mmol; LiNH^tBu; 0.053 g, 0.67 mmol; reaction time 24 h) described below for **6**.

5 was also obtained when a hexane solution of [Nb($\eta^{5-}C_5H_4$ -SiMe₂Cl)(CH₂Ph)Cl(N¹Bu)] (**2**; 0.30 g, 0.67 mmol) was treated with NH₂'Bu (0.098 g, 0.14 mL, 1.34 mmol). This mixture was stirred at room temperature for 12 h and was then filtered. The volatiles were removed under reduced pressure to give a brown oil which after purification by extraction into pentane, filtration, and removal of solvent under vacuum was characterized as 5 (0.26 g, 0.53 mmol, 80% yield).

Data for **5** are as follows. ¹H NMR (300 MHz, C_6D_6 , δ): 0.41 (s, 3H, Si*Me*₂), 0.42 (s, 3H, Si*Me*₂), 1.11 (s, 9H, C*Me*₃), 1.15 (s, 9H, C*Me*₃), 2.89 (d, 1H, *J*_{HH} = 8 Hz, C*H*₂Ph), 3.25 (d, 1H, *J*_{HH} = 8 Hz, C*H*₂Ph), 5.67 (m, 1H, C₅*H*₄), 5.88 (m, 1H, C₅*H*₄), 6.05 (m, 1H, C₅*H*₄), 6.19 (m, 1H, C₅*H*₄), 6.80–7.25 m, *Ph*). ¹³C NMR (75 MHz, C₆D₆, δ): 2.9, 3.0 (Si*Me*₂), 31.2 (C*Me*₃), 33.9 (C*Me*₃), 49.7 (CMe₃), 51.5 (CH₂Ph), 68.0 (CMe₃), 106.0, 111,1, 111.2, 120.6 (*C*₂-*C*₅, C₅H₄) (*C*_{ipso} not observed), 128.2, 128.4, 129.9, 131.7 (*Ph*). IR (*v*, cm⁻¹): 3339. MS: *m*/*z* [assignment, relative intensity (%)] 429 [(M⁺- ^tBu), 0.7]; 413 [(M⁺- NH^tBu), 2.7]; 393 [(M⁺- CH₂Ph), 5.9].

Preparation of [Nb(η^{5} -C₅H₄SiMe₂Cl)(CH₂Ph)(NH⁴Bu)-(N⁴Bu)] (6). A mixture of [Nb(η^{5} -C₅H₄SiMe₂Cl)(CH₂Ph)Cl(N⁴-Bu)] (2; 0.30 g, 0.67 mmol) and LiNH⁴Bu (0.053 g, 0.67 mmol) in 50 mL of hexane was stirred at room temperature for 1 h and then filtered. Solvent was removed from the resulting brown solution under vacuum, giving a brown oil which was purified by extraction into pentane, filtration, and removal of solvent under vacuum to be characterized as **6** (0.27 g, 0.56 mmol, 85% yield).

Data for **6** are as follows. ¹H NMR (300 MHz, C_6D_6 , δ): 0.37 (s, 3H, Si Me_2), 0.40 (s, 3H, Si Me_2 Cl), 1.22 (s, 9H, CMe_3), 1.29 (s, 9H, CMe_3), 2.64 (d, 1H, $J_{HH} = 10$ Hz, CH_2 Ph), 2.92 (d, 1H, $J_{HH} = 10$ Hz, CH_2 Ph), 5.70 (m, 1H, C_5H_4), 5.78 (m, 1H, C_5H_4), 5.88 (m, 1H, C_5H_4), 6.03 (m, 1H, C_5H_4), 6.90–7.30 (m, Ph), 7.41 (br s, 1H, NH). ¹³C NMR (75 MHz, C_6D_6 , δ): 3.2, 3.6 (Si Me_2 -Cl), 32.5 (CMe_3), 33.9 (CMe_3), 41.0 (CH_2 Ph), 56.5 (CMe_3), 66.0 (CMe_3), 107.3, 109.5, 112.3, 119.4 (C_2 – C_5 , C_5H_4) (C_{ipso} not observed), 121.4, 128.2, 128.4, 129.9, 131.8, 153.3 (Ph). IR (ν , cm⁻¹): 3286.

Preparation of [Nb(η^{5} -C₅H₄SiMe₂NH^tBu)(CH₂Ph)(NH^t-Bu)(N^tBu)] (7). A solution of [Nb(η^{5} -C₅H₄SiMe₂Cl)(CH₂Ph)-Cl(N^tBu)] (2; 0.60 g, 1.34 mmol) in hexane (60 mL) was treated with NH₂^tBu (0.39 g, 0.56 mL, 5.36 mmol). The mixture was stirred at room temperature for 18 h and was then filtered. Solvent was completely removed from the resulting solution, giving a dark brown oil which was purified by extraction into pentane, filtration, and removal of solvent under vacuum to be characterized as 7 (0.58 g, 1.11 mmol, 83% yield).

Data for 7 are as follows. ¹H NMR (300 MHz, C_6D_6 , δ): 0.31 (s, 6H, Si Me_2), 0.62 (br s, 1H, NH), 1.07 (s, 9H, CMe_3), 1.26 (s, 9H, CMe_3), 1.33 (s, 9H, CMe_3), 2.60 (d, 1H, $J_{HH} = 10.6$ Hz, CH_2 Ph), 3.02 (d, 1H, $J_{HH} = 10.6$ Hz, CH_2 Ph), 5.71 (m, 2H,

C₅*H*₄), 5.95 (m, 1H, C₅*H*₄), 6.01 (m, 1H, C₅*H*₄), 6.80–7.25 (m, *Ph*). ¹³C NMR (75 MHz, C₆D₆, δ): 2.7, 3.3 (Si*Me*₂), 32.5 (C*Me*₃), 33.8 (C*Me*₃), 34.2 (C*Me*₃), 40.5 (CH₂Ph), 49.8 (CMe₃), 56.1 (CMe₃), 65.7 (CMe₃), 107.1, 108.9, 112.4, 119.7 (*C*₂–*C*₅, C₅H₄) (*C*_{*ipso*} not observed), 121.3, 128.2, 129.9, 130.4, 131.7, 153.8 (*Ph*). IR (ν , cm⁻¹): 3378, 3253.

Preparation of [Nb(η^{5} -C₅H₄SiMe₂NH^tBu)(CH₂Ph)₂(N^t-Bu)] (8). A solution of [Nb(η^{5} -C₅H₄SiMe₂Cl)(CH₂Ph)₂(N^tBu)] (3; 1.0 g, 1.99 mmol) in hexane (60 mL) was treated with NH₂^t-Bu (0.29 g, 0.42 mL, 3.98 mmol) at -78 °C. The mixture was then warmed to room temperature and stirred overnight. The resulting suspension was filtered and the solution concentrated (10 mL) and cooled to -40 °C to give a greenish solid which was characterized as **8** (0.97 g, 1.79 mmol, 90% yield).

Data for **8** are as follows. Anal. Calcd for $C_{29}H_{43}N_2SiNb$: C, 64.41; H, 8.03; N, 5.18. Found: C, 64.28; H, 8.01; N, 5.04. ¹H NMR (300 MHz, C_6D_6 , δ): 0.38 (s, 6H, Si Me_2), 0.72 (br s, 1H, NH), 1.11 (s, 9H, CMe_3), 1.15 (s, 9H, CMe_3), 1.70 (d, 2H, $J_{HH} = 8$ Hz, CH_2Ph), 1.96 (d, 1H, $J_{HH} = 8$ Hz, CH_2Ph), 5.52 (m, 2H, C_5H_4), 5.93 (m, 2H, C_5H_4), 6.90–7.06 (m, Ph). ¹³C NMR (75 MHz, C_6D_6 , δ): 3.0 (Si Me_2), 31.9 (CMe_3), 33.8 (CMe_3), 41.5 (CH_2Ph), 49.7 (CMe_3), 66.4 (CMe_3), 106.7, 113.7 (C_2-C_5 , C_5H_4), 115.8 (C_{ipso} C_5H_4), 124.9–140.1 (Ph). IR (ν , cm⁻¹): 3390. MS: m/z [assignment, relative intensity (%)] 449 [(M⁺ – CH₂Ph), 15]; 393 [(M⁺ – ^tBu), 5].

Preparation of [Nb(η^5 -C₅H₄SiMe₂NH⁴Bu)Cl(NH⁴Bu)-(N⁴Bu)] (9). A solution of [Nb(η^5 -C₅H₄SiMe₂Cl)Cl₄] (4; 1.50 g, 3.82 mmol) in toluene (100 mL) was treated with an excess of NH₂⁴Bu (4.19 g, 6.02 mL, 57.32 mmol), and the mixture was stirred at room temperature for 48 h. After complete removal of solvent, the residue was extracted into hexane (2 × 20 mL). The resulting extract was concentrated (10 mL) and cooled to -30 °C to give a pale yellow solid characterized as 9 (1.25 g, 2.67 mmol, 70% yield).

Data for **9** are as follows. Anal. Calcd for $C_{19}H_{39}N_3SiNb: C, 48.96; H, 8.45; N, 9.02. Found: C, 48.49; H, 8.20; N, 8.62. ¹H NMR (300 MHz, <math>C_6D_6$, δ): 0.42 (s, 3H, SiMe₂), 0.43 (s, 3H, SiMe₂), 1.13 (s, 9H, CMe_3), 1.22 (s, 9H, CMe_3), 1.33 (s, 9H, CMe_3), 6.06 (m, 1H, C_5H_4), 6.15 (m, 1H, C_5H_4), 6.19 (m, 1H, C_5H_4), 6.54 (m, 1H, C_5H_4), 8.08 (br s, 1H, NH). ¹³C NMR (75 MHz, C_6D_6 , δ): 2.7, 3.4 (SiMe₂), 31.9 (CMe_3), 33.6 (CMe_3), 33.8 (CMe_3), 49.9 (CMe_3), 57.2 (CMe_3), 67.2 (CMe_3), 105.9, 107.0, 116.6, 123.2 (C_2-C_5 , C_5H_4), 118.9 (C_{ipso} C_5H_4). IR (ν , cm⁻¹): 3347, 3267.

Preparation of [Nb(η^{5} -C₅H₄SiMe₂NH^tBu)Cl₂(N^tBu)] (10). SiMe₃Cl (0.30 g, 0.35 mL, 2.79 mmol) was added to a solution of **9** (1.30 g, 2.79 mmol) in toluene (50 mL). The reaction mixture was stirred for 2 h, and solvent was completely removed under vacuum. The resulting oily product was dissolved in a minimum amount of hexane (5 mL) and cooled to -30 °C to give a dark yellow crystalline product characterized as **10** (1.08 g, 2.51 mmol, 90%).

Data for **10** are as follows. Anal. Calcd for $C_{15}H_{29}N_2SiNb$: C, 41.96; H, 6.82; N, 6.52. Found: C, 42.57; H, 6.98; N, 6.52. ¹H NMR (300 MHz, C₆D₆, δ): 0.45 (s, 6H, Si*M*e₂), 1.04 (s, 9H, C*M*e₃), 1.08(s, 9H, C*M*e₃), 6.10 (m, 2H, C₅H₄), 6.49 (m, 2H, C₅H₄). ¹³C NMR (75 MHz, C₆D₆, δ): 2.2 (Si*M*e₂), 30.4 (C*M*e₃), 33.7 (C*M*e₃), 49.7 (CMe₃), 70.0 (CMe₃), 110.0, 123.1 (C₂-C₅, C₅H₄) (C_{ipso} not observed). IR (ν , cm⁻¹): 3374.

Preparation of [Nb(η^5 -C₅H₄SiMe₂- η^1 -N^tBu)(NH^tBu)-(N^tBu)] (11). A diethyl ether (30 mL) solution of LiNH^tBu (0.5 g, 6.27 mmol) was slowly added to a suspension of [Nb(η^5 -C₅H₄-SiMe₂Cl)Cl₄] (2; 0.49 g, 1.25 mmol) in diethyl ether (50 mL), and the reaction mixture was stirred overnight. The solvent was removed from the resulting suspension under vacuum, and the residue was extracted into hexane (50 mL). Removal of the solvent under vacuum gave an oily brown product which was characterized as **11** (0.43 g, 1.00 mmol, 80%). Data for **11** are as follows. ¹H NMR (300 MHz, C₆D₆, δ): 0.48 (s, 3H, SiMe₂), 0.52 (s, 3H, SiMe₂), 1.24 (s, 9H, CMe₃), 1.25 (s, 9H, CMe₃), 1.36 (s, 9H, CMe₃), 5.63 (br s, 1H, NH), 5.93 (m, 1H, C₅H₄), 6.06 (m, 1H, C₅H₄), 6.22 (m, 1H, C₅H₄), 6.37 (m, 1H, C₅H₄). ¹³C NMR (75 MHz, C₆D₆, δ): 2.7, 3.2 (SiMe₂), 32.8 (CMe₃), 34.1 (CMe₃), 34.7 (CMe₃), 53.8 (CMe₃), 54.8 (CMe₃), 65.1 (CMe₃), 107.5, (C_{ipso} C₅H₄), 108.0, 109.0, 115.6, 116.2 (C₂- C_5 , C₅H₄). IR (ν , cm⁻¹): 3291.

Preparation of $[Nb(\eta^5-C_5H_4SiMe_2NH^tBu)\{\eta^2-[C(CH_2Ph) \{N(2,6-Me_2C_6H_3)\}]$ Cl(N^tBu)] (12). A mixture of $[Nb(\eta^5-C_5H_4-$ SiMe₂NH^tBu)(CH₂Ph)Cl(N^tBu)] (5; 0.6 g, 1.24 mmol) and CN(2,6-Me₂C₆H₃) (0.16 g, 1.24 mmol) in hexane (50 mL) was stirred for several hours. Solvent was completely removed in vacuo to give an oily brown product in quantitative yield which was purified by extraction into pentane, filtration, and removal of solvent under vacuum to be characterized as 12.

Data for **12** are as follows. ¹H NMR (300 MHz, C_6D_6 , δ): 0.53 (s, 3H, SiMe2), 0.59 (s, 3H, SiMe2), 1.05 (s, 9H, CMe3), 1.20 (s, 9H, CMe3), 1.86 (s, 3H, Me2C6H3N=C), 2.16 (s, 3H, Me₂C₆H₃N=C), 3.58 (br s, 2H, PhCH₂C=N), 5.47 (m, 1H, C_5H_4), 6.05 (m, 2H, C_5H_4), 6.60 (m, 1H, C_5H_4), 6.80-7.25 (m, Ph). ¹³C NMR (75 MHz, C₆D₆, δ): 3.3, 3.6 (SiMe₂), 18.6 (Me₂C₆H₃N=C), 18.9 (Me₂C₆H₃N=C), 31.6 (CMe₃), 33.9 (CMe₃), 43.3 (PhCH₂C=N), 49.7 (CMe₃), 67.1 (CMe₃), 103.9, 108.0, 113.4, 119.1 (C_2 - C_5 , C_5H_4) (C_{ipso} not observed), 126.4–140.6, (*Ph*), 227.7 (PhCH₂*C*=N). IR (ν , cm⁻¹): 3329, 1640.

Preparation of $[Nb(\eta^5-C_5H_4SiMe_2NH^tBu){\eta^2-[C(CH_2Ph)-$ {NC (2,6-Me₂C₆H₃)}](CH₂Ph)(N^tBu)] (13). 13 was synthesized from 8 (0.6 g, 1.11 mmol) and isocyanide (0.14 g, 1.11 mmol) in a manner analogous to that described for 12 and isolated as a white solid after recrystallization from pentane (0.67 g, 1.00 mmol, 90%).

Data for 13 are as follows. Anal. Calcd for C₃₈H₅₂N₃SiNb: C, 67.92; H, 7.82; N, 6.25. Found: C, 67.76; H, 7.78; N, 5.77. ¹H NMR (300 MHz, C_6D_6 , δ): 0.49 (s, 3H, SiMe₂), 0.52 (s, 3H, SiMe₂), 0.98 (br s, 1H, NH), 1.14 (s, 9H, CMe₃), 1.15 (s, 9H, CMe3), 1.62 (s, 3H, Me2C6H3N=C), 1.69 (s, 3H, Me2C6H3N= C), 2.90 (d, 1H, $J_{HH} = 9.1$ Hz, Nb CH_2 Ph), 3.19 (d, 1H, $J_{HH} =$ 9.1 Hz, NbCH2Ph), 3.64 (m, 2H, PhCH2C=N), 5.37 (m, 1H, C₅H₄), 5.71 (m, 1H, C₅H₄), 6.00 (m, 1H, C₅H₄), 6.09 (m, 1H, C_5H_4), 6.80–7.20 (m, 13H, Ph). ¹³C NMR (75 MHz, C_6D_6 , δ): 3.3, 3.6 (SiMe2), 18.3 (Me2C6H3N=C), 18.7 (Me2C6H3N=C), 32.8 (CMe3), 33.8 (CMe3), 37.1 (NbCH2Ph), 43.5 (PhCH2C=N), 49.8 (CMe₃), 65.6 (CMe₃), 106.7, 109.1, 110.7, 116.8 (C₂-C₅, C₅H₄) (Cipso not observed), 126.4-140.6 (Ph), 231.5 (PhCH₂C=N). IR $(\nu, \text{ cm}^{-1})$: 3344, 1620.

Preparation of $[Nb(\eta^5-C_5H_4SiMe_2-\eta^1-N^tBu)Cl(N^tBu)]$ (14). Method A. SiMe₃Cl (0.60 mL, 4.75 mmol) was added to a solution of $[Nb(\eta^5-C_5H_4SiMe_2-\eta^1-N^tBu)(NH^tBu)(N^tBu)]$ (11; 1.0 g, 2.33 mmol) in hexane (50 mL). The reaction mixture was stirred for 24 h, and the solvent was removed under vacuum to give 14 as an oily brown product in quantitative vield.

Method B. A hexane (50 mL) solution of $[Nb(n^5-C_5H_4SiMe_2-$ NH^tBu)(CH₂Ph)Cl(N^tBu)] (5; 0.70 g, 1.44 mmol), in a sealed tube, was heated to 160 °C for 3 days. The volatiles were removed under reduced pressure to give an oily brown product which after purification by extraction into pentane, filtration, and removal of solvent under vacuum was characterized as 14 (0.40 g, 1.01 mmol, 70% yield).

Data for 14 are as follows. ¹H NMR (300 MHz, C_6D_6 , δ): 0.27 (s, 3H, SiMe2), 0.37 (s, 3H, SiMe2), 1.20 (s, 9H, CMe3), 1.37 (s, 9H, CMe₃), 5.70 (m, 1H, C₅H₄), 6.35 (m, 1H, C₅H₄), 6.43 (m, 2H, C₅H₄). ¹³C NMR (75 MHz, C₆D₆, δ): 1.2, 1.5 (SiMe₂), 32.1 (CMe₃), 33.9 (CMe₃), 57.8 (CMe₃), 66.0 (CMe₃), 107.7, 109.7, 120.1, 121.8 (*C*₂-*C*₅, C₅H₄) (*C*_{ipso} not observed).

Preparation of $[Nb(\eta^5-C_5H_4SiMe_2-\eta^1-N^tBu)(CH_2Ph)-$ (NtBu)] (15). 15 was synthesized from 8 (0.80 g, 1.48 mmol) in a manner analogous to that described for the preparation of 14 (method B) and isolated as a brown oil (0.48 g, 1.08 mmol, 73% yield).

Data for **15** are as follows. ¹H NMR (300 MHz, C_6D_6 , δ): 0.29 (s, 3H, SiMe2), 0.31(s, 3H, SiMe2), 1.26 (s, 9H, CMe3), 1.38 (s, 9H, CMe3), 2.67 (d, 1H, J_{HH} = 11.5 Hz, CH2Ph), 2.98 (d,

Table 2.	Crystal Data and Structure R	efinement
for 10		

	л 10
empirical formula	$C_{15}H_{29}C_{12}N_2NbSi$
fw	429.30
temp	293(2) K
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	$P2_12_12_1$
unit cell dimens	
а	11.795(2) Å
b	12.828(3) Å
С	14.227(3) Å
V	2152.6(8) Å ³
Ζ	4
density (calcd)	1.325 g/cm ³
abs coeff	0.860 mm^{-1}
<i>F</i> (000)	888
cryst size	$0.30\times0.25\times0.20~mm$
θ range for data collection	2.14-25.04°
index ranges	-13 < h < 0, -15 < k < 0,
-	-16 < l < 16
no. of rflns collected	4134
no. of obsd rflns $(I > 2\sigma(I))$	3389
abs cor	N/A
refinement method	full-matrix least squares on F ²
no. of data/restraints/params	3773/0/190
goodness of fit on F^2	1.113
final R indices $(I > 2\sigma(I))$	R1 = 0.0897, $wR2 = 0.2358$
<i>R</i> indices (all data)	R1 = 0.1029, $wR2 = 0.2449$
weighting scheme	calc $W = 1/[\sigma^2(F_0^2) + (0.2000P)^2]^2$
largest diff peak and hole	1.052 and -1.141 e/Å ³

^a $P = (F_0^2 + F_c^2)/3.$

1H, $J_{\text{HH}} = 11.5$ Hz, CH_2 Ph), 5.57 (m, 1H, C₅H₄), 5.76 (m, 1H, C_5H_4), 5.88 (m, 1H, C_5H_4), 6.05 (m, 1H, C_5H_4), 6.82–7.25 (m, Ph). ¹³C NMR (75 MHz, C₆D₆, δ): 1.0, 1.5 (SiMe₂), 32.8 (CMe₃), 34.7 (CMe3), 46.8 (NbCH2Ph), 56.8 (CMe3), 65.0 (CMe3), 104.1 (C_{ipso} C₅H₄), 107.6, 107.9, 117.2, 121.6 (C₂-C₅, C₅H₄), 123.0, 127.4, 128.5, 153.0 (Ph).

Ph) (2,6-Me₂C₆H₃)}(N^tBu)] (16). 16 was synthesized from 13 (2.0 g, 2.98 mmol) in a manner analogous to that described for the preparation of 14 (method B) and isolated as a brown oil in quantitative yield.

Data for **16** are as follows. ¹H NMR (300 MHz, C_6D_6 , δ): 0.35 (s, 3H, SiMe₂), 0.42 (s, 3H, SiMe₂), 1.31 (s, 9H, CMe₃), 1.42 (s, 9H, CMe3), 2.28 (s, 3H, Me2C6H3NCH=CHPh), 2.30 (s, 3H, Me₂C₆H₃NCH=CHPh), 4.90 (d, 1H), 8.82 (d, 1H, J_{HH} = 14 Hz, $Me_2C_6H_3NCH=CHPh$), 5.43 (m, 1H, C_5H_4), 5.65 (m, 1H, C₅H₄), 5.79 (m, 1H, C₅H₄), 6.32 (m, 1H, C₅H₄), 6.80-7.30 (m, Ph). ¹³C NMR (75 MHz, C_6D_6 , δ): 2.0, 2.2 (SiMe₂), 18.7 $(Me_2C_6H_3NCH=CHPh)$, 19.5 $(Me_2C_6H_3NCH=CHPh)$, 32.9 (CMe₃), 34.2 (CMe₃), 56.9 (CMe₃), 66.3 (CMe₃), 101.6 (d, J_{CH} = 152 Hz, Me₂C₆H₃NCH=*C*HPh), 107.3 (*C*_{ipso} C₅H₄), 108.2, 108.6, 119.4, 120.8 (C_2 - C_5 , C_5H_4), 123.0-151.3 (*Ph*), 150.9 (d, J_{CH} = 165 Hz, $Me_2C_6H_3NCH=CHPh$).

Preparation of $[Nb(\eta^5-C_5H_4SiMe_2-\eta^1-N^tBu)\{\eta^2-[C(CH_2Ph)-$ {N(2,6-Me₂C₆H₃)}](N^tBu)] (17). A mixture of 15 (0.90 g, 2.01 mmol) and isocyanide (0.26 g, 2.01 mmol) in hexane (50 mL) was heated to 50 °C and stirred for 4 h. The solvent was evaporated in vacuo, and the resulting brown oil was purified by extraction into pentane, filtration, and removal of solvent under vacuum to be characterized as 17 in quantitative yield.

Data for **17** are as follows. ¹H NMR (300 MHz, C_6D_6 , δ): 0.50 (s, 3H, SiMe₂), 0.67 (s, 3H, SiMe₂), 1.16 (s, 9H, CMe₃), 1.30 (s, 9H, CMe3), 1.93 (s, 3H, Me2C6H3N=C), 1.97 (s, 3H, $Me_2C_6H_3N=C$), 3.42 (d, 1H, $J_{HH} = 16.1$ Hz, Ph $CH_2C=N$), 3.58 (d, 1H, $J_{HH} = 16.1$ Hz, Ph*CH*₂C=N), 5.31 (m, 1H, C₅H₄), 5.98 $(m, 1H, C_5H_4), 6.08 (m, 1H, C_5H_4), 6.39 (m, 1H, C_5H_4), 6.90 -$ 7.20 (m, Ph). ¹³C NMR (75 MHz, C₆D₆, δ): 3.9, 4.3 (SiMe₂), 18.0 (Me₂C₆H₃N=C), 18.9 (Me₂C₆H₃N=C), 32.7 (CMe₃), 35.1 (CMe₃), 43.9 (PhCH₂C=N), 54.4 (CMe₃), 65.5 (CMe₃), 105.1, **Crystal Structure Determination of [Nb**(η^{s} -**C**₅**H**₄**SiMe**₂ **NH**^t**Bu**)**Cl**₂ (**N**^t**Bu**)] (10). Yellow crystals of compound 10 were obtained by crystallization from dry hexane at $-30 \,^{\circ}$ C, and a suitable sized crystal was introduced, under argon, in a Lindemann tube and mounted in an Enraf-Nonius CAD 4 automatic four-circle diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.710 \, 73 \,^{\circ}$). Crystallographic and experimental details are summarized in Table 2. Data were collected at room temperature (25 °C). Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made. The structure was solved by direct methods (SHELXL 90)¹⁵ and

(15) Sheldrick, G. M. Acta Crystallogr., Sect. A 1990, 46, 467.

refined by least squares against F^2 (SHELXL 97).¹⁶ All nonhydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced from geometrical calculations and refined using a riding model with fixed thermal parameters.

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Supporting Information Available: Tables giving positional and thermal parameters and bond distances and angles for **10** and figures giving ¹H NMR spectra for complexes **5**–**7**, **11**, **12**, and **14–17** (35 pages). Ordering information is given on any current masthead page.

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