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

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Received July 29, 1998

The chloro−imido complex [Nb(η^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(η^5-C_5H_4-$SiMe_2$Cl)(CH_2Ph)(NH^tBu)(N^tBu)], whereas preferential reaction at the Si−Cl bond occurs with $NH_2{}^tBu$, giving [Nb{η^5-C_5H_4-$SiMe_2$(NH^tBu)}(CH_2Ph)Cl(N^tBu)], which is then transformed into [Nb{η^5-C_5H_4-$SiMe_2$(NH^tBu)}(CH_2Ph)(NH^tBu)(N^tBu)] on further reaction with $NH_2{}^tBu$. Chemical reactivity studies demonstrate that a spontaneous transformation of [Nb(η^5-C_5H_4-$SiMe_2Cl$)(CH_2Ph)(NH^tBu)(N^tBu)] into [Nb{η^5-C_5H_4-$SiMe_2$(NH^tBu)}(CH_2Ph)Cl(N^tBu)] takes place, via an intermolecular reaction, by attack of the silicon-bonded chlorine at the unsaturated niobium center. Benzylation of [Nb{η^5-C_5H_4-$SiMe_2$(NH^tBu)}(CH_2Ph)Cl(N^tBu)] with $Mg(CH_2Ph)_2\cdot 2THF$ gives [Nb{η^5-C_5H_4-$SiMe_2$(NH^tBu)}$(CH_2Ph)_2$(N^tBu)], which also results from reaction of the chloro−silyl derivative [Nb(η^5-C_5H_4-$SiMe_2Cl$)$(CH_2Ph)_2$(N^tBu)] with $NH_2{}^tBu$. The dichloro−imido complex [Nb(η^5-C_5H_4-$SiMe_2Cl$)Cl_2(N^tBu)], readily obtained from [Nb(η^5-C_5H_4-$SiMe_2Cl$)Cl_4], also reacts preferentially at the Si−Cl bond when treated with $NH_2{}^tBu$ to give [Nb{η^5-C_5H_4-$SiMe_2$(NH^tBu)}Cl_2(N^tBu)], which is further transformed into [Nb{η^5-C_5H_4-$SiMe_2$(NH^tBu)}Cl(NH^tBu)(N^tBu)]; the latter is alternatively prepared by reaction of [Nb(η^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{η^5-C_5H_4-$SiMe_2$(η^1-N^tBu)}(NH^tBu)(N^tBu)], which is converted into the chloro−niobium derivative by reaction with $SiMe_3Cl$. These constrained-geometry complexes may also be obtained from the dichloro derivative [Nb(η^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{η^5-C_5H_4-$SiMe_2$(NH^tBu)}(CH_2Ph)X(N^tBu)] (X = Cl, CH_2Ph) at 160 °C results in formation of the silyl−amido complexes [Nb{η^5-C_5H_4-$SiMe_2$(η^1-N^tBu)}X(N^tBu)] (X = Cl, CH_2Ph) with elimination of toluene, whereas a similar transformation of the related iminoacyl complex [Nb{η^5-C_5H_4-$SiMe_2$(NH^tBu)}{η^2-[C(CH_2Ph){N(2,6-$Me_2C_6H_3$)}](CH_2Ph)(N^tBu)] produces a simultaneous isomerization to give the vinylamido compound [Nb{η^5-C_5H_4-$SiMe_2$(η^1-N^tBu)}{N(CH=CHPh)(2,6-$Me_2C_6H_3$)}(N^tBu)]. Insertion of CN(2,6-$Me_2C_6H_3$) into the niobium−benzyl bonds of complexes [Nb{η^5-C_5H_4-$SiMe_2$(NH^tBu)}(CH_2Ph)X(N^tBu)] (X = Cl, CH_2Ph) and [Nb{η^5-C_5H_4-$SiMe_2$(η^1-N^tBu)}(CH_2Ph)(N^tBu)] leads to the iminoacyl compounds [Nb{η^5-C_5H_4-$SiMe_2$(NH^tBu)}{η^2-[C(CH_2Ph){N(2,6-$Me_2C_6H_3$)}]}X(N^tBu)] (X = Cl, CH_2Ph) and [Nb{η^5-C_5H_4-$SiMe_2$(η^1-N^tBu)}{η^2-[C(CH_2Ph){N(2,6-$Me_2C_6H_3$)}]}(N^tBu)], respectively. All of the reported new compounds were characterized by elemental analyses and ^1H and ^{13}C NMR spectroscopy, and the X-ray molecular structure of [Nb{η^5-C_5H_4-$SiMe_2$(NH^tBu)}Cl_2(N^tBu)] was studied by diffraction methods.

Introduction

Silyl-substituted cyclopentadienyl rings have been extensively used to prepare Ziegler−Natta type olefin polymerization catalysts because the presence of the electron-withdrawing silyl substituent improves their catalytic activity.[1] The presence of additional functionalities, particularly chlorine, on these silyl groups not only allows their fixation on solid supports[2] but also offers new, direct synthetic strategies for constrained-geometry catalysts with bidentate η^5-cyclopentadienyl-silyl−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

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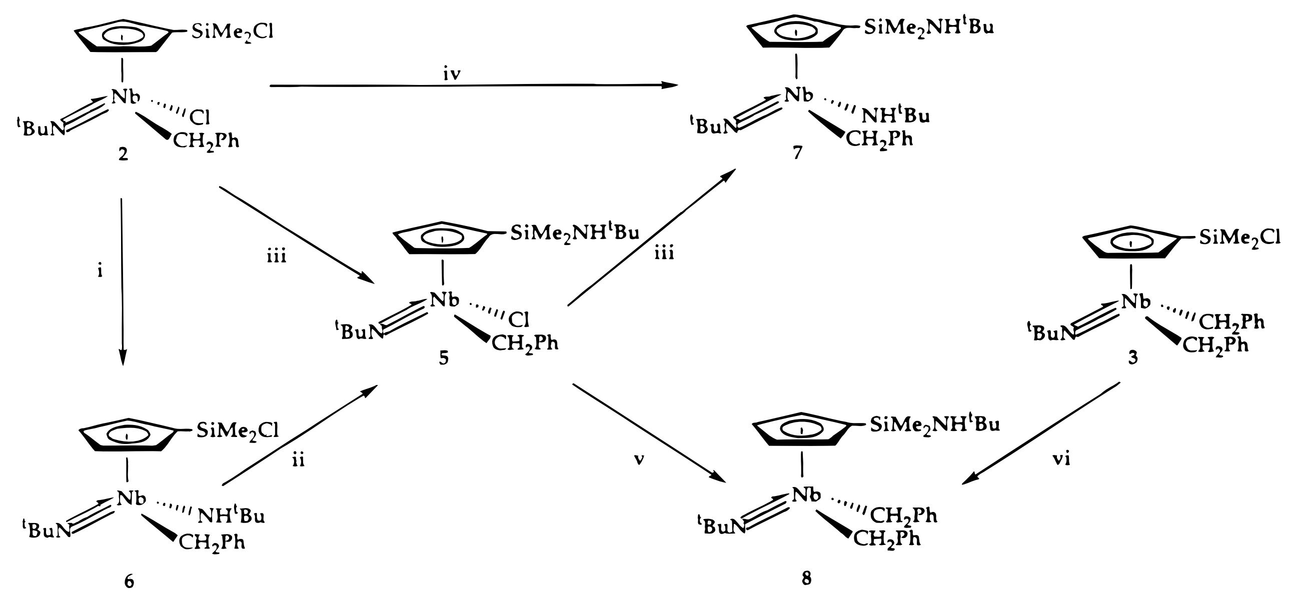
10.1021/om9806491 CCC: $18.00
Publication on Web 01/23/1999

Scheme 1



i.-LiNH^{t}Bu, hexane, 1h. ii.- LiNH^{t}Bu, 24h. iii.- 2NH$_2$^{t}Bu, hexane, 12h. iv.- 4NH$_2$^{t}Bu, hexane, 18h. or 2 LiNH^{t}Bu, toluene, 18h. v.- Mg(CH$_2$Ph)$_2$.2THF, hexane, 2h. vi.- 2NH$_2$^{t}Bu, 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 isolobal[6] with the very well-known group 4 dicyclopentadienyl derivatives have been extensively studied in the last few years.[7]

We have recently reported[8] the synthesis and characterization of new chlorosilyl-substituted cyclopentadienyl imido−dichloro ([Nb(η^5-C$_5$H$_4$-SiMe$_2$Cl)Cl$_2$(N^{t}Bu)], **1**), imido−chloro−benzyl ([Nb(η^5-C$_5$H$_4$-SiMe$_2$Cl)(CH$_2$Ph)Cl(N^{t}Bu)], **2**), imido−dibenzyl ([Nb(η^5-C$_5$H$_4$-SiMe$_2$Cl)(CH$_2$Ph)$_2$(N^{t}Bu)], **3**), and tetrachloro ([Nb(η^5-C$_5$H$_4$-SiMe$_2$Cl)Cl$_4$], **4**) niobium derivatives. We herein report their use as starting materials to obtain new ((aminosilyl)cyclopentadienyl)niobium chloro− and benzyl−imido ([Nb{η^5-C$_5$H$_4$-SiMe$_2$(NH^{t}Bu)}XY(N^{t}Bu)] (X, Y = Cl, Bz)), ((chlorosilyl)cyclopentadienyl)niobium amido−imido ([Nb(η^5-C$_5$H$_4$-SiMe$_2$Cl)Bz(NH^{t}Bu)(N^{t}Bu)]), and ((aminosilyl)cyclopentadienyl)niobium amido−imido ([Nb{η^5-C$_5$H$_4$-SiMe$_2$(NH^{t}Bu)}X(NH^{t}Bu)(N^{t}Bu)] (X = Cl, Bz)) compounds, used as precursors to prepare the new constrained-geometry niobium derivatives [Nb{η^5-C$_5$H$_4$-SiMe$_2$-η^1-N^{t}Bu)}X(N^{t}Bu)] (X = Cl, Bz, NH^{t}Bu, N(CH=CHPh)(2,6-Me$_2$C$_6$H$_3$)) and to study the insertion reactions of 2,6-dimethylphenyl isocyanide into their niobium−benzyl bonds.

Results and Discussion

Reactions with NH$_2$^{t}Bu. We reported[9] 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(η^5-C$_5$H$_4$-SiMe$_2$Cl)(CH$_2$Ph)Cl(N^{t}Bu)] (**2**) with 2 equiv of NH$_2$^{t}Bu in hexane at room temperature gave, after separation of the ammonium salt formed, the amino−silyl complex [Nb{η^5-C$_5$H$_4$-SiMe$_2$(NH^{t}Bu)}(CH$_2$Ph)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 NH$_2$^{t}Bu and 2 equiv of NEt$_3$ 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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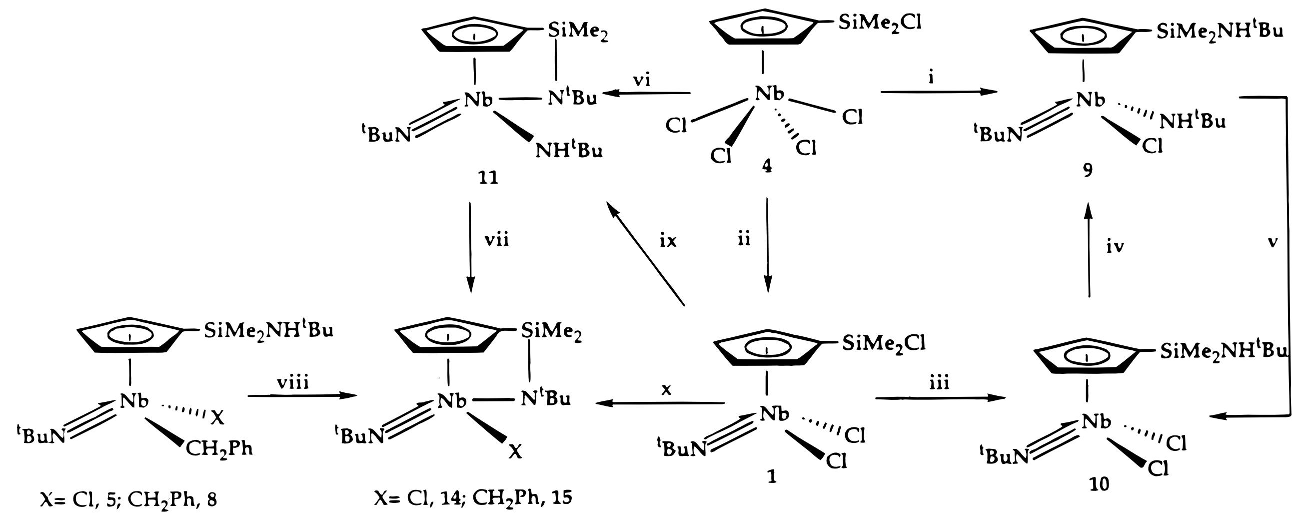
Scheme 2



i.- 15$NH_2{}^tBu$, toluene. ii.- 4$NH_2{}^tBu$, toluene. iii.- 2$NH_2{}^tBu$, hexane. iv.- 2$NH_2{}^tBu$, hexane. v.- $SiMe_3Cl$, toluene. vi.- 5 $LiNH^tBu$, ether. vii.- $SiMe_3Cl$, 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 $NH_2{}^tBu$ in hexane at room temperature afforded the corresponding amino–silyl complex [Nb{η^5-C_5H_4-$SiMe_2$-(NH^tBu)}(CH_2Ph)(NH^tBu)(N^tBu)] (**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 $NH_2{}^tBu$.

A selective reaction was also observed when the dibenzyl derivative [Nb(η^5-C_5H_4-$SiMe_2Cl$)$(CH_2Ph)_2$(N^tBu)] (**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{η^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 $Mg(CH_2Ph)_2{\cdot}2THF$ 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-C_5H_4-$SiMe_2Cl$)Cl_4] (**4**) in toluene (Scheme 2). After the mixture was stirred for 48 h at room temperature, the amino–silyl derivative [Nb{η^5-C_5H_4-$SiMe_2$(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 $NH_2{}^tBu$ was added in a controlled manner, initially imido substitution occurred at two of the Nb–Cl bonds to give [Nb(η^5-C_5H_4-$SiMe_2Cl$)Cl_2(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{η^5-C_5H_4-$SiMe_2$(NH^tBu)}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 ^{13}C NMR spectra for complexes **8** and **10** show the expected singlet due to the equivalent methyl–silyl groups and two singlets between δ 1.04 and 1.15 corresponding to the two types of Si–amine and Nb–imido *tert*-butyl groups. Complex **8** shows two doublets due to the diastereotopic protons of the two niobium-bonded 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 ^{13}C 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(η^5-C_5H_5)-Cl_2(NR)] (R = Me, ^{t}Bu, $C_6H_5{}^iPr_2$-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 imido–dichloro 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 silyl substituent with respect to the imido

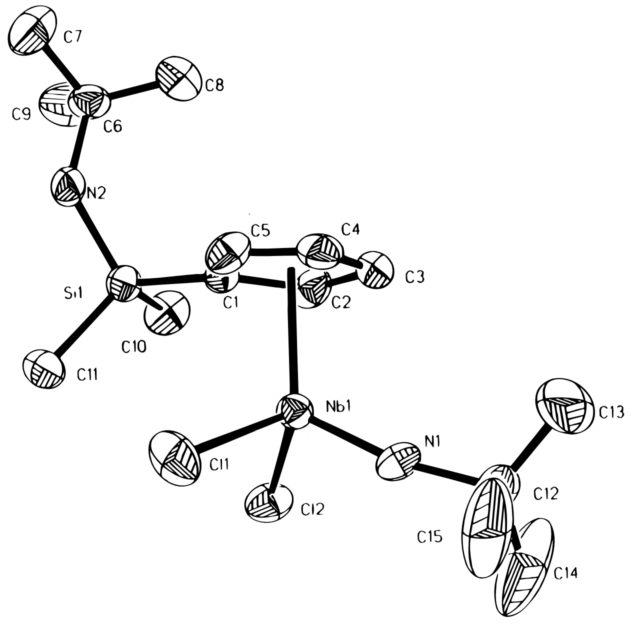


Figure 1. View of the molecular structure of complex **10**.

Table 1. Bond Lengths (Å) and Angles (deg) for 10

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)	113.59
C(10)−Si(1)−C(1)	105.8(5)	Cl(1)−Nb(1)−Cp(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 sp^2 and double-bond character of the Si−N bond.

Reactions with LiNH^{t}Bu. We also reported[9] 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 alkali-metal amides. As shown in Scheme 1, when [Nb(η^5-C_5H_4-$SiMe_2Cl$)(CH_2Ph)Cl(N^{t}Bu)] (**2**) was reacted with 1 equiv of LiNH^{t}Bu in hexane at room temperature for a limited period of time, the amido niobium complex [Nb(η^5-C_5H_4-$SiMe_2Cl$)(CH_2Ph)(NH^{t}Bu)(N^{t}Bu)] (**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{η^5-C_5H_4-$SiMe_2$(NH^{t}Bu)}(CH_2Ph)Cl(N^{t}Bu)] (**5**). The ^{1}H and ^{13}C 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 NH$_2$^{t}Bu could also be isolated using the amide LiNH^{t}Bu. Thus, reaction of complex **2** with 2 equiv of LiNH^{t}Bu 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 LiNH^{t}Bu 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^{t}Bu (see Scheme 2) resulted in complete substitution of the chlorine moieties to give the constrained-geometry complex [Nb{η^5-C_5H_4-$SiMe_2$(η^1-N^{t}Bu)}(NH^{t}Bu)(N^{t}Bu)] (**11**), which was easily, quantitatively transformed into the chloro derivative [Nb{η^5-C_5H_4-$SiMe_2$(η^1-N^{t}Bu)}Cl(N^{t}Bu)] (**14**; see below) by reaction with $SiMe_3Cl$ in hexane at room temperature. Complex **14** was also obtained from the reaction of complex **1** with 2 or 3 equiv of LiNH^{t}Bu, together with very small amounts of **9** and **11**, respectively, through deprotonation of the intermediate amido derivative[10] by LiNH^{t}Bu with elimination of NH$_2$^{t}Bu 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^{t}Bu takes place at room temperature in the complex [Nb(η^5-C_5H_4-$SiMe_2Cl$)(CH_2Ph)(NH^{t}Bu)(N^{t}Bu)] (**6**), which is quantitatively transformed in 24 h into [Nb{η^5-C_5H_4-$SiMe_2$(NH^{t}Bu)}(CH_2Ph)Cl(N^{t}Bu)] (**5**). This exchange between Si−Cl and Nb−NH^{t}Bu bonds is comparable to the well-known[11] use of Me_3Si−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 ^{1}H NMR spectroscopy formation of a mixture of complexes [Nb{η^5-C_5H_4-$SiMe_2$(NH^{t}Bu)} (CH_2Ph)(NH^{t}Bu)(N^{t}Bu)] (**7**) and [Nb(η^5-C_5H_4-$SiMe_2Cl$)(CH_2Ph)Cl(N^{t}Bu)] (**2**) was observed. Formation of **7** containing two NH^{t}Bu groups provides evidence of the intermolecular mechanism proposed in Scheme 3A. This mixture was further transformed into [Nb{η^5-C_5H_4-$SiMe_2$(NH^{t}Bu)}(CH_2Ph)Cl(N^{t}Bu)] (**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(η^5-C_5H_4-$SiMe_2Cl$)Cl_2(N^{t}Bu)] (**1**) were stirred in C_6D_6 (see Scheme 3B). In

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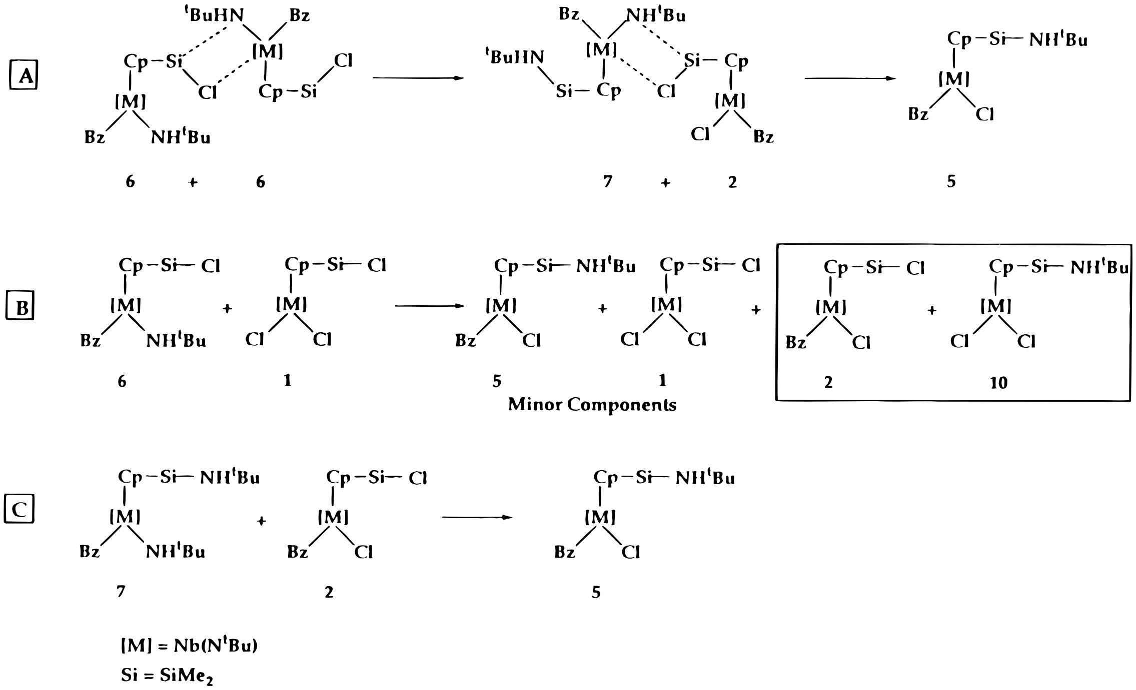
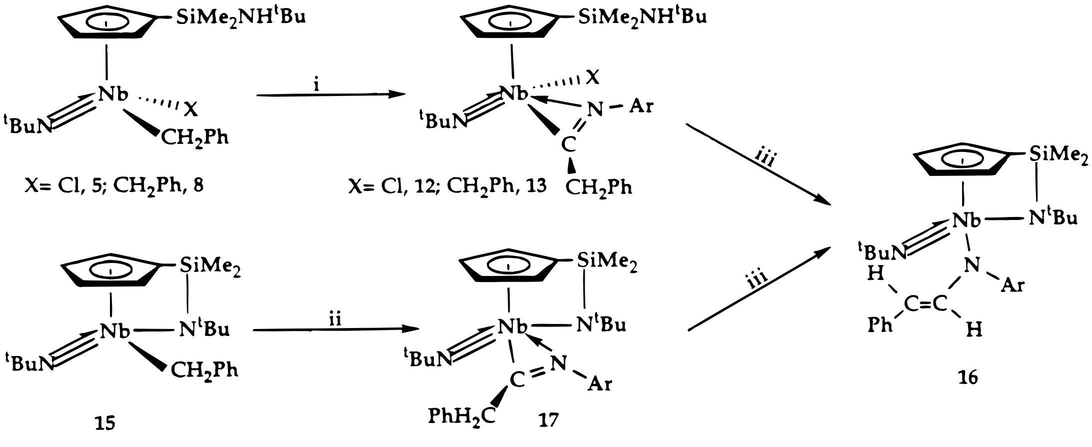
[11] (a) Herrmann, W. A.; Baratta, W.; Herdtweck, E. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1951. (b) Duchateau, R.; Lancaster, S. J.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **1997**, *16*, 4995.

Scheme 3



Scheme 4



i.- CN(2,6-Me$_2$C$_6$H$_3$), hexane, 1-2h. ii.- CN(2,6-Me$_2$C$_6$H$_3$), 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(η^5-C$_5$H$_4$-SiMe$_2$Cl)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$_6$D$_6$ (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-Me$_2$C$_6$H$_3$). Insertion of CN(2,6-Me$_2$C$_6$H$_3$)[8,12] into the niobium−benzyl bonds of the 16-electron mono- and dibenzyl complexes [Nb{η^5-C$_5$H$_4$-SiMe$_2$(NH^{t}Bu)}(CH$_2$Ph)X(N^{t}Bu)] (X = Cl (**5**), CH$_2$Ph (**8**)) readily took place when **5** and **8** were stirred for several hours in hexane at room temperature to give the iminoacyl derivatives [Nb{η^5-C$_5$H$_4$-SiMe$_2$(NH^{t}Bu)}{η^2-[C(CH$_2$Ph){N(2,6-Me$_2$C$_6$H$_3$)]}X(N^{t}Bu)] (X = Cl (**12**), CH$_2$Ph (**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 ^{13}C NMR spectra at δ 227.7 and 231.5 due to the iminoacyl carbon atom.

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(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 $[Nb\{\eta^5\text{-}C_5H_4\text{-}SiMe_2(NH^tBu)\}(CH_2Ph)X(N^tBu)]$ into Constrained Silyl−Amido Derivatives $[Nb\{\eta^5\text{-}C_5H_4\text{-}SiMe_2\text{-}\eta^1\text{-}N^tBu)\}X((N^tBu)]$. $[Ti(\eta^5\text{-}C_5H_4\text{-}SiMe_2Cl)Cl_3]$ readily reacts with $LiNH^tBu$ at room temperature to give the constrained-geometry complex $[Ti\{\eta^5\text{-}C_5H_4\text{-}SiMe_2(\eta^1\text{-}N^tBu)Cl_2]$.[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 complexes[13] containing the (aminosilyl)cyclopentadienyl ligand. As shown in Scheme 2, when hexane solutions of $[Nb\{\eta^5\text{-}C_5H_4\text{-}SiMe_2(NH^tBu)\}(CH_2Ph)X(N^tBu)]$ (X = Cl (**5**), CH_2Ph (**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 $[Nb\{\eta^5\text{-}C_5H_4\text{-}SiMe_2(\eta^1\text{-}N^tBu)\}X(N^tBu)]$ (X = Cl (**14**), CH_2Ph (**15**)) were isolated as brown oils in high yields. Complex **15** can also be obtained in high yield via benzylation of **14** with $Mg(CH_2Ph)_2{\cdot}2THF$. Not only does similar thermal treatment of the iminoacyl complex $[Nb\{\eta^5\text{-}C_5H_4\text{-}SiMe_2(NH^tBu)\}\{\eta^2\text{-}[C(CH_2Ph)\{N(2,6\text{-}Me_2C_6H_3)]\}(CH_2Ph)(N^tBu)]$ (**13**) eliminate toluene but also a further isomerization of the η^2-iminoacyl group takes place to finally give the vinylamido derivative $[Nb\{\eta^5\text{-}C_5H_4\text{-}SiMe_2(\eta^1\text{-}N^tBu)\}\{N(CH{=}CHPh)(2,6\text{-}Me_2C_6H_3)\}(N^tBu)]$ (**16**). This isomerization, which consists of a 1,2-hydrogen 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 ^{13}C 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 ($J_{H-H} = 14$ Hz) due to the olefinic protons of the vinyl moiety, which appear in the ^{13}C 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 $CN(2,6\text{-}Me_2C_6H_3)$ at 50 °C in hexane to give the related iminoacyl derivative $[Nb\{\eta^5\text{-}C_5H_4\text{-}SiMe_2(\eta^1\text{-}N^tBu)\}\{\eta^2\text{-}[C(CH_2Ph)\{N(2,6\text{-}Me_2C_6H_3)]\}(N^tBu)]$ (**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 ^{13}C 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 $[Nb(\eta^5\text{-}C_5H_4\text{-}SiMe_2Cl)Cl_4]$ with $LiNH^tBu$ or $NH_2{}^tBu$, whereas selective reactions of imido complexes $[Nb(\eta^5\text{-}C_5H_4\text{-}SiMe_2Cl)XCl(N^tBu)]$ (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 $NH_2{}^tBu$ 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 $Nb-NH^tBu$ 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 $[Nb\{\eta^5\text{-}C_5H_4\text{-}SiMe_2(\eta^1\text{-}N^tBu)\}X(N^tBu)]$ can also be obtained by heating the amino−silyl compounds at 160 °C. Insertion of $CN(2,6\text{-}Me_2C_6H_3)$ 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. $NH_2{}^tBu$ (Aldrich) was distilled before use and stored under argon. $LiNH^tBu$ was prepared in hexane in almost quantitative yield from $NH_2{}^tBu$ and ^nBuLi (Aldrich, 1.6 M in hexane). $[Nb(\eta^5\text{-}C_5H_4\text{-}SiMe_2Cl)Cl_2(N^tBu)]$ (**1**), $[Nb(\eta^5\text{-}C_5H_4\text{-}SiMe_2Cl)(CH_2Ph)Cl(N^tBu)]$ (**2**), $[Nb(\eta^5\text{-}C_5H_4\text{-}SiMe_2Cl)(CH_2Ph)_2(N^tBu)]$ (**3**), and $[Nb(\eta^5\text{-}C_5H_4\text{-}SiMe_2Cl)Cl_4]$ (**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 ^{13}C NMR spectra

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were recorded on a Varian Unity VXR-300. Chemical shifts, in ppm, were measured relative to the residual ^{1}H and ^{13}C resonances of benzene-d_6 used as solvent, δ 7.15 (^{1}H) and 128.0 (^{13}C), 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 $[Nb(\eta^5\text{-}C_5H_4SiMe_2NH^tBu)(CH_2Ph)Cl(N^tBu)]$ (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 $[Nb(\eta^5\text{-}C_5H_4SiMe_2Cl)(CH_2Ph)Cl(N^tBu)]$ (**2**; 0.30 g, 0.67 mmol) was treated with $NH_2{}^tBu$ (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. ^{1}H NMR (300 MHz, C_6D_6, δ): 0.41 (s, 3H, SiMe_2), 0.42 (s, 3H, SiMe_2), 1.11 (s, 9H, CMe_3), 1.15 (s, 9H, CMe_3), 2.89 (d, 1H, J_{HH} = 8 Hz, CH_2Ph), 3.25 (d, 1H, J_{HH} = 8 Hz, CH_2Ph), 5.67 (m, 1H, C_5H_4), 5.88 (m, 1H, C_5H_4), 6.05 (m, 1H, C_5H_4), 6.19 (m, 1H, C_5H_4), 6.80−7.25 m, *Ph*). ^{13}C NMR (75 MHz, C_6D_6, δ): 2.9, 3.0 (SiMe_2), 31.2 (CMe_3), 33.9 (CMe_3), 49.7 (CMe$_3$), 51.5 (CH$_2$Ph), 68.0 (CMe$_3$), 106.0, 111,1, 111.2, 120.6 (C_2-C_5, C_5H_4) (C_{ipso} not observed), 128.2, 128.4, 129.9, 131.7 (*Ph*). IR (υ, cm^{-1}): 3339. MS: *m/z* [assignment, relative intensity (%)] 429 [($M^+ - {}^tBu$), 0.7]; 413 [($M^+ - NH^tBu$), 2.7]; 393 [($M^+ - CH_2Ph$), 5.9].

Preparation of $[Nb(\eta^5\text{-}C_5H_4SiMe_2Cl)(CH_2Ph)(NH^tBu)(N^tBu)]$ (6). A mixture of $[Nb(\eta^5\text{-}C_5H_4SiMe_2Cl)(CH_2Ph)Cl(N^tBu)]$ (**2**; 0.30 g, 0.67 mmol) and $LiNH^tBu$ (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. ^{1}H NMR (300 MHz, C_6D_6, δ): 0.37 (s, 3H, SiMe_2), 0.40 (s, 3H, SiMe_2Cl), 1.22 (s, 9H, CMe_3), 1.29 (s, 9H, CMe_3), 2.64 (d, 1H, J_{HH} = 10 Hz, CH_2Ph), 2.92 (d, 1H, J_{HH} = 10 Hz, CH_2Ph), 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, N*H*). ^{13}C NMR (75 MHz, C_6D_6, δ): 3.2, 3.6 (SiMe_2Cl), 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 $[Nb(\eta^5\text{-}C_5H_4SiMe_2NH^tBu)(CH_2Ph)(NH^tBu)(N^tBu)]$ (7). A solution of $[Nb(\eta^5\text{-}C_5H_4SiMe_2Cl)(CH_2Ph)Cl(N^tBu)]$ (**2**; 0.60 g, 1.34 mmol) in hexane (60 mL) was treated with $NH_2{}^tBu$ (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. ^{1}H NMR (300 MHz, C_6D_6, δ): 0.31 (s, 6H, SiMe_2), 0.62 (br s, 1H, N*H*), 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_2Ph), 3.02 (d, 1H, J_{HH} = 10.6 Hz, CH_2Ph), 5.71 (m, 2H, C_5H_4), 5.95 (m, 1H, C_5H_4), 6.01 (m, 1H, C_5H_4), 6.80−7.25 (m, *Ph*). ^{13}C NMR (75 MHz, C_6D_6, δ): 2.7, 3.3 (SiMe_2), 32.5 (CMe_3), 33.8 (CMe_3), 34.2 (CMe_3), 40.5 (CH$_2$Ph), 49.8 (CMe$_3$), 56.1 (CMe$_3$), 65.7 (CMe$_3$), 107.1, 108.9, 112.4, 119.7 (C_2−C_5, C_5H_4) (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 $[Nb(\eta^5\text{-}C_5H_4SiMe_2NH^tBu)(CH_2Ph)_2(N^tBu)]$ (8). A solution of $[Nb(\eta^5\text{-}C_5H_4SiMe_2Cl)(CH_2Ph)_2(N^tBu)]$ (**3**; 1.0 g, 1.99 mmol) in hexane (60 mL) was treated with $NH_2{}^tBu$ (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. ^{1}H NMR (300 MHz, C_6D_6, δ): 0.38 (s, 6H, SiMe_2), 0.72 (br s, 1H, N*H*), 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*). ^{13}C NMR (75 MHz, C_6D_6, δ): 3.0 (SiMe_2), 31.9 (CMe_3), 33.8 (CMe_3), 41.5 (CH$_2$Ph), 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 [($M^+ - CH_2Ph$), 15]; 393 [($M^+ - {}^tBu$), 5].

Preparation of $[Nb(\eta^5\text{-}C_5H_4SiMe_2NH^tBu)Cl(NH^tBu)(N^tBu)]$ (9). A solution of $[Nb(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_4]$ (**4**; 1.50 g, 3.82 mmol) in toluene (100 mL) was treated with an excess of $NH_2{}^tBu$ (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. ^{1}H NMR (300 MHz, C_6D_6, δ): 0.42 (s, 3H, SiMe_2), 0.43 (s, 3H, SiMe_2), 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, N*H*). ^{13}C NMR (75 MHz, C_6D_6, δ): 2.7, 3.4 (SiMe_2), 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 $[Nb(\eta^5\text{-}C_5H_4SiMe_2NH^tBu)Cl_2(N^tBu)]$ (10). $SiMe_3Cl$ (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. ^{1}H NMR (300 MHz, C_6D_6, δ): 0.45 (s, 6H, SiMe_2), 1.04 (s, 9H, CMe_3), 1.08(s, 9H, CMe_3), 6.10 (m, 2H, C_5H_4), 6.49 (m, 2H, C_5H_4). ^{13}C NMR (75 MHz, C_6D_6, δ): 2.2 (SiMe_2), 30.4 (CMe_3), 33.7 (CMe_3), 49.7 (CMe$_3$), 70.0 (CMe$_3$), 110.0, 123.1 (C_2−C_5, C_5H_4) (C_{ipso} not observed). IR (ν, cm^{-1}): 3374.

Preparation of $[Nb(\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta^1\text{-}N^tBu)(NH^tBu)(N^tBu)]$ (11). A diethyl ether (30 mL) solution of $LiNH^tBu$ (0.5 g, 6.27 mmol) was slowly added to a suspension of $[Nb(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_4]$ (**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. ^{1}H NMR (300 MHz, C_6D_6, δ): 0.48 (s, 3H, SiMe_2), 0.52 (s, 3H, SiMe_2), 1.24 (s, 9H, CMe_3), 1.25 (s, 9H, CMe_3), 1.36 (s, 9H, CMe_3), 5.63 (br s, 1H, N*H*), 5.93 (m, 1H,

C_5H_4), 6.06 (m, 1H, C_5H_4), 6.22 (m, 1H, C_5H_4), 6.37 (m, 1H, C_5H_4). ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$, δ): 2.7, 3.2 (SiMe_2), 32.8 (CMe_3), 34.1 (CMe_3), 34.7 (CMe_3), 53.8 ($C\mathrm{Me}_3$), 54.8 ($C\mathrm{Me}_3$), 65.1 ($C\mathrm{Me}_3$), 107.5, (C_{ipso} $\mathrm{C_5H_4}$), 108.0, 109.0, 115.6, 116.2 (C_2–C_5, $\mathrm{C_5H_4}$). IR (ν, cm^{-1}): 3291.

Preparation of [Nb(η^5-$\mathrm{C_5H_4SiMe_2NH^tBu}$){$\eta^2$-[C($\mathrm{CH_2Ph}$)-{N(2,6-$\mathrm{Me_2C_6H_3}$)}]}Cl($\mathrm{N^tBu}$)] (12). A mixture of [Nb(η^5-$\mathrm{C_5H_4SiMe_2NH^tBu}$)($\mathrm{CH_2Ph}$)Cl($\mathrm{N^tBu}$)] (**5**; 0.6 g, 1.24 mmol) and CN(2,6-$\mathrm{Me_2C_6H_3}$) (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. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, δ): 0.53 (s, 3H, SiMe_2), 0.59 (s, 3H, SiMe_2), 1.05 (s, 9H, CMe_3), 1.20 (s, 9H, CMe_3), 1.86 (s, 3H, $Me_2\mathrm{C_6H_3N{=}C}$), 2.16 (s, 3H, $Me_2\mathrm{C_6H_3N{=}C}$), 3.58 (br s, 2H, PhCH_2C=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*). ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$, δ): 3.3, 3.6 (SiMe_2), 18.6 ($Me_2\mathrm{C_6H_3N{=}C}$), 18.9 ($Me_2\mathrm{C_6H_3N{=}C}$), 31.6 (CMe_3), 33.9 (CMe_3), 43.3 (Ph$C\mathrm{H_2}$C=N), 49.7 ($C\mathrm{Me}_3$), 67.1 ($C\mathrm{Me}_3$), 103.9, 108.0, 113.4, 119.1 (C_2–C_5, $\mathrm{C_5H_4}$) (C_{ipso} not observed), 126.4–140.6, (*Ph*), 227.7 ($\mathrm{PhCH_2}C$=N). IR (ν, cm^{-1}): 3329, 1640.

Preparation of [Nb(η^5-$\mathrm{C_5H_4SiMe_2NH^tBu}$){$\eta^2$-[C($\mathrm{CH_2Ph}$)-{NC (2,6-$\mathrm{Me_2C_6H_3}$)}]($\mathrm{CH_2Ph}$)($\mathrm{N^tBu}$)] (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 $\mathrm{C_{38}H_{52}N_3SiNb}$: C, 67.92; H, 7.82; N, 6.25. Found: C, 67.76; H, 7.78; N, 5.77. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, δ): 0.49 (s, 3H, SiMe_2), 0.52 (s, 3H, SiMe_2), 0.98 (br s, 1H, NH), 1.14 (s, 9H, CMe_3), 1.15 (s, 9H, CMe_3), 1.62 (s, 3H, $Me_2\mathrm{C_6H_3N{=}C}$), 1.69 (s, 3H, $Me_2\mathrm{C_6H_3N{=}C}$), 2.90 (d, 1H, J_{HH} = 9.1 Hz, NbCH_2Ph), 3.19 (d, 1H, J_{HH} = 9.1 Hz, NbCH_2Ph), 3.64 (m, 2H, PhCH_2C=N), 5.37 (m, 1H, C_5H_4), 5.71 (m, 1H, C_5H_4), 6.00 (m, 1H, C_5H_4), 6.09 (m, 1H, C_5H_4), 6.80–7.20 (m, 13H, *Ph*). ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$, δ): 3.3, 3.6 (SiMe_2), 18.3 ($Me_2\mathrm{C_6H_3N{=}C}$), 18.7 ($Me_2\mathrm{C_6H_3N{=}C}$), 32.8 (CMe_3), 33.8 (CMe_3), 37.1 (Nb$C\mathrm{H_2Ph}$), 43.5 (Ph$C\mathrm{H_2}$C=N), 49.8 ($C\mathrm{Me}_3$), 65.6 ($C\mathrm{Me}_3$), 106.7, 109.1, 110.7, 116.8 (C_2–C_5, $\mathrm{C_5H_4}$) (C_{ipso} not observed), 126.4–140.6 (Ph), 231.5 ($\mathrm{PhCH_2}C$=N). IR (ν, cm^{-1}): 3344, 1620.

Preparation of [Nb(η^5-$\mathrm{C_5H_4SiMe_2}$-η^1-$\mathrm{N^tBu}$)Cl($\mathrm{N^tBu}$)] (14). Method A. $\mathrm{SiMe_3Cl}$ (0.60 mL, 4.75 mmol) was added to a solution of [Nb(η^5-$\mathrm{C_5H_4SiMe_2}$-η^1-$\mathrm{N^tBu}$)($\mathrm{NH^tBu}$)($\mathrm{N^tBu}$)] (**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 yield.

Method B. A hexane (50 mL) solution of [Nb(η^5-$\mathrm{C_5H_4SiMe_2NH^tBu}$)($\mathrm{CH_2Ph}$)Cl($\mathrm{N^tBu}$)] (**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. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, δ): 0.27 (s, 3H, SiMe_2), 0.37 (s, 3H, SiMe_2), 1.20 (s, 9H, CMe_3), 1.37 (s, 9H, CMe_3), 5.70 (m, 1H, C_5H_4), 6.35 (m, 1H, C_5H_4), 6.43 (m, 2H, C_5H_4). ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$, δ): 1.2, 1.5 (SiMe_2), 32.1 (CMe_3), 33.9 (CMe_3), 57.8 ($C\mathrm{Me}_3$), 66.0 ($C\mathrm{Me}_3$), 107.7, 109.7, 120.1, 121.8 (C_2–C_5, $\mathrm{C_5H_4}$) (C_{ipso} not observed).

Preparation of [Nb(η^5-$\mathrm{C_5H_4SiMe_2}$-η^1-$\mathrm{N^tBu}$)($\mathrm{CH_2Ph}$)($\mathrm{N^tBu}$)] (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. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, δ): 0.29 (s, 3H, SiMe_2), 0.31(s, 3H, SiMe_2), 1.26 (s, 9H, CMe_3), 1.38 (s, 9H, CMe_3), 2.67 (d, 1H, J_{HH} = 11.5 Hz, CH_2Ph), 2.98 (d, 1H, J_{HH} = 11.5 Hz, CH_2Ph), 5.57 (m, 1H, C_5H_4), 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*). ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$, δ): 1.0, 1.5 (SiMe_2), 32.8 (CMe_3), 34.7 (CMe_3), 46.8 (Nb$C\mathrm{H_2Ph}$), 56.8 ($C\mathrm{Me}_3$), 65.0 ($C\mathrm{Me}_3$), 104.1 (C_{ipso} $\mathrm{C_5H_4}$), 107.6, 107.9, 117.2, 121.6 (C_2–C_5, $\mathrm{C_5H_4}$), 123.0, 127.4, 128.5, 153.0 (*Ph*).

Table 2. Crystal Data and Structure Refinement for 10

empirical formula	$\mathrm{C_{15}H_{29}C_{12}N_2NbSi}$
fw	429.30
temp	293(2) K
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	$P2_12_12_1$
unit cell dimens	
a	11.795(2) Å
b	12.828(3) Å
c	14.227(3) Å
V	2152.6(8) Å^3
Z	4
density (calcd)	1.325 g/cm^3
abs coeff	0.860 mm^{-1}
F(000)	888
cryst size	0.30 × 0.25 × 0.20 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
R indices (all data)	R1 = 0.1029, wR2 = 0.2449
weighting scheme	calc $w = 1/[\sigma^2(F_o^2) + (0.2000P)^2]$[a]
largest diff peak and hole	1.052 and −1.141 e/Å^3

[a] $P = (F_o^2 + F_c^2)/3$.

Preparation of [Nb(η^5-$\mathrm{C_5H_4SiMe_2}$-η^1-$\mathrm{N^tBu}$){N(CH=CH-Ph) (2,6-$\mathrm{Me_2C_6H_3}$)}($\mathrm{N^tBu}$)] (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. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, δ): 0.35 (s, 3H, SiMe_2), 0.42 (s, 3H, SiMe_2), 1.31 (s, 9H, CMe_3), 1.42 (s, 9H, CMe_3), 2.28 (s, 3H, $Me_2\mathrm{C_6H_3NCH{=}CHPh}$), 2.30 (s, 3H, $Me_2\mathrm{C_6H_3NCH{=}CHPh}$), 4.90 (d, 1H), 8.82 (d, 1H, J_{HH} = 14 Hz, $\mathrm{Me_2C_6H_3NC}H$=CHPh), 5.43 (m, 1H, C_5H_4), 5.65 (m, 1H, C_5H_4), 5.79 (m, 1H, C_5H_4), 6.32 (m, 1H, C_5H_4), 6.80–7.30 (m, *Ph*). ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$, δ): 2.0, 2.2 (SiMe_2), 18.7 ($Me_2\mathrm{C_6H_3NCH{=}CHPh}$), 19.5 ($Me_2\mathrm{C_6H_3NCH{=}CHPh}$), 32.9 (C$Me_3$), 34.2 (C$Me_3$), 56.9 ($C\mathrm{Me}_3$), 66.3 ($C\mathrm{Me}_3$), 101.6 (d, J_{CH} = 152 Hz, $\mathrm{Me_2C_6H_3NCH{=}}C$HPh), 107.3 ($C_{ipso}$ $\mathrm{C_5H_4}$), 108.2, 108.6, 119.4, 120.8 (C_2–C_5, $\mathrm{C_5H_4}$), 123.0–151.3 (*Ph*), 150.9 (d, J_{CH} = 165 Hz, $\mathrm{Me_2C_6H_3N}C$H=CHPh).

Preparation of [Nb(η^5-$\mathrm{C_5H_4SiMe_2}$-η^1-$\mathrm{N^tBu}$){η^2-[C($\mathrm{CH_2Ph}$)-{N(2,6-$\mathrm{Me_2C_6H_3}$)}]($\mathrm{N^tBu}$)] (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. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, δ): 0.50 (s, 3H, SiMe_2), 0.67 (s, 3H, SiMe_2), 1.16 (s, 9H, CMe_3), 1.30 (s, 9H, CMe_3), 1.93 (s, 3H, $Me_2\mathrm{C_6H_3N{=}C}$), 1.97 (s, 3H, $Me_2\mathrm{C_6H_3N{=}C}$), 3.42 (d, 1H, J_{HH} = 16.1 Hz, PhCH_2C=N), 3.58 (d, 1H, J_{HH} = 16.1 Hz, PhCH_2C=N), 5.31 (m, 1H, C_5H_4), 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*). ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$, δ): 3.9, 4.3 (SiMe_2), 18.0 ($Me_2\mathrm{C_6H_3N{=}C}$), 18.9 ($Me_2\mathrm{C_6H_3N{=}C}$), 32.7 (CMe_3), 35.1 (CMe_3), 43.9 (Ph$C\mathrm{H_2}$C=N), 54.4 ($C\mathrm{Me}_3$), 65.5 ($C\mathrm{Me}_3$), 105.1, 107.9 (C_2−C_5, C_5H_4), 109.7 (C_{ipso}, C_5H_4), 113.3, 114.7 (C_2−C_5, C_5H_4), 125.7−144.9 (*Ph*), 236.3 ($PhCH_2C{=}N$). IR (ν, cm^{-1}): 1632.

Crystal Structure Determination of [Nb(η^5-$C_5H_4SiMe_2NH^tBu$)Cl_2 (N^tBu)] (10). Yellow crystals of compound **10** were obtained by crystallization from dry hexane at −30 °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 Kα radiation ($\lambda = 0.710\ 73$ Å). 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 refined by least squares against F^2 (SHELXL 97).[16] All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced from geometrical calculations and refined using a riding model with fixed thermal parameters.

Acknowledgment. We acknowledge the DGICYT (project PB97-0776) for financial support.

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

OM9806491

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