

# Competitive Insertion of Isocyanide and Carbon Dioxide into Niobium– and Silicon–Amido Bonds

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

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

Received May 14, 2001

Reaction of the amido–niobium complex  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{NH}^t\text{Bu})\}(\text{N}^t\text{Bu})\text{Cl}(\text{NH}^t\text{Bu})]$  (**2**) with 1 equiv of  $\text{CNAr}$  ( $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ ) in hexane gave the iminocarbamoyl compound  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{NH}^t\text{Bu})\}(\text{N}^t\text{Bu})\text{Cl}\{\eta^2\text{-C}(\text{NH}^t\text{Bu})=\text{NAr}\}]$  (**5**) in quantitative yield at room temperature, whereas heating to 120 °C was required when similar reactions were carried out with the bridged silyl amido compounds  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\eta^1\text{-N}^t\text{Bu})\}(\text{N}^t\text{Bu})\text{Cl}]$  (**3**) and  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\eta^1\text{-N}^t\text{Bu})\}(\text{N}^t\text{Bu})(\text{NH}^t\text{Bu})]$  (**4**) to give the bridging  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{N}^t\text{Bu})\}\eta^2\text{-C}(\text{N}^t\text{Bu})=\text{NAr}]$  (**6**) and terminal iminocarbamoyl  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\eta^1\text{-N}^t\text{Bu})\}(\text{N}^t\text{Bu})\{\eta^2\text{-C}(\text{NH}^t\text{Bu})=\text{NAr}\}]$  (**7**) compounds, respectively. Benzoylation of **6** with  $\text{Mg}(\text{CH}_2\text{Ph})_2 \cdot 2\text{THF}$  provided the benzyl  $\eta^2$ -iminocarbamoyl compound  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{N}^t\text{Bu})\}\eta^2\text{-C}(\text{N}^t\text{Bu})=\text{NAr}]$  (**8**), which rearranges to the silyl- $\eta^1$ -amido  $\eta^2$ -iminoacyl derivative  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\eta^1\text{-N}^t\text{Bu})\}(\text{N}^t\text{Bu})\{\eta^2\text{-C}(\text{CH}_2\text{Ph})=\text{NAr}\}]$  (**9**) on heating its  $\text{C}_6\text{D}_6$  solution to 145 °C. Reaction of compound **2** with  $\text{CO}_2$  gave the dicarbamate complex  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\eta^1\text{-OOCNH}^t\text{Bu})\}(\eta^2\text{-OOCNH}^t\text{Bu})(\text{N}^t\text{Bu})\text{Cl}]$  (**10**), whereas the same reaction with  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{NH}^t\text{Bu})\}(\text{N}^t\text{Bu})\text{Cl}_2]$  (**1**) gave an unidentified mixture of products, which were transformed after heating to 130–140 °C into the oxo derivative  $[\{\text{Nb}(\text{N}^t\text{Bu})\text{Cl}_2\}_2\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-O-SiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4\}]$  (**11**), which was further benzylated to give  $[\{\text{Nb}(\text{N}^t\text{Bu})(\text{CH}_2\text{Ph})_2\}_2\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-O-SiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4\}]$  (**12**). Similar reaction of **3** with  $\text{CO}_2$  in toluene gave the oxo compounds  $[\text{Nb}(\text{N}^t\text{Bu})\text{Cl-}\mu\text{-}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta\text{-O})_2]$  (**13**) and  $[\{\text{Nb}(\text{N}^t\text{Bu})\text{Cl}\}_2(\mu\text{-O})\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-O-SiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4\}]$  (**14**). The molecular structure of **13** was determined by X-ray diffraction methods. Formation of the oxo complexes **11**, **13**, and **14** also resulted from hydrolysis of  $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})(\text{N}^t\text{Bu})\text{Cl}_2]$  in the presence of  $\text{NEt}_3$ .

## Introduction

Structural, synthetic, and catalytic aspects of the early transition metal cyclopentadienyl compounds have received considerable attention in recent years, because they are useful compounds that have found applications as reagents in organic chemistry and particularly as soluble Ziegler–Natta catalysts.<sup>1</sup> The cyclopentadienyl ring can be more than a mere spectator ligand, with different substituents introduced to modify the steric and electronic requirements of the central metal atom, particularly when such substituents contain reactive functional groups. Many studies on silyl-substituted ring compounds have been reported<sup>2</sup> comparing the reactivity of the Si–Cl bond of chlorosilyl–cyclopentadienyl complexes with the M–Cl bonds of group 4,<sup>3</sup> 5,<sup>4</sup> and 6<sup>5</sup> metal derivatives. Moreover, some chlorosilyl–cyclopentadienylmetal compounds have been used to isolate

chelated  $\eta^5$ -cyclopentadienyl- $\eta$ -amido metal derivatives when they are treated with alkali amides or amines under different conditions.<sup>3b,f,6</sup>

Cyclopentadienyl complexes of transition metals also containing imido ligands have been extensively reported,<sup>7</sup> and the reactivity and applications of those containing coordinatively unsaturated metal centers have been particularly studied.<sup>8</sup>

We recently<sup>4</sup> reported the isolation of the four types of amino-substituted cyclopentadienyl–imido niobium complexes shown in Scheme 1, which contain respec-

\* Corresponding author. Tel: 34-1-8854765. Fax: 34-1-8854683. E-mail: pascual.royo@uah.es.

(1) (a) Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon Press: New York, 1989. (b) Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds. *Comprehensive Organometallic Chemistry II*; Pergamon Press: New York, 1987. (c) Togni, A., Halterman, R. L., Eds. *Metallocenes. Synthesis, Reactivity, Applications*; Wiley-VCH: Weinheim, 1998; Vol. 1.

(2) Cuenca, T.; Royo, P. *Coord. Chem. Rev.* **1999**, 193–195, 447, and references therein.

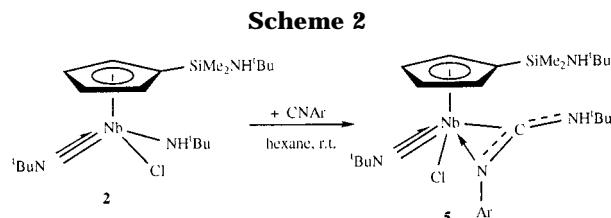
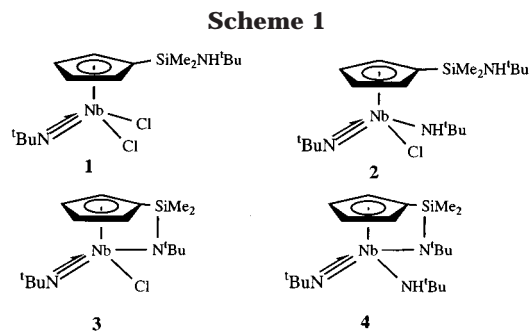
(3) (a) Ciruelos, S.; Cuenca, T.; Gómez-Sal, P.; Manzanero, A.; Royo, P. *Organometallics* **1995**, 14, 177. (b) Ciruelos, S.; Cuenca, T.; Gómez, R.; Gómez-Sal, P.; Manzanero, A.; Royo, P. *Organometallics* **1996**, 15, 5577. (c) Ciruelos, S.; Cuenca, T.; Gómez, R.; Gómez-Sal, P.; Manzanero, A.; Royo, P. *Polyhedron* **1998**, 17, 1055. (d) Ciruelo, G.; Cuenca, T.; Gómez, R.; Gómez-Sal, P.; Martín, A.; Rodríguez, G.; Royo, P. *J. Organomet. Chem.* **1997**, 547, 287. (e) Royo, B.; Royo, P.; Cadenas, L. M. *J. Organomet. Chem.* **1998**, 551, 293. (f) Gómez, R.; Gómez-Sal, P.; Martín, A.; Núñez, A.; Del Real, P. A.; Royo, P. *J. Organomet. Chem.* **1998**, 564, 93.

(4) (a) Alcalde, M. I.; Gómez-Sal, P.; Martín, A.; Royo, P. *Organometallics* **1998**, 17, 1144. (b) Alcalde, M. I.; Gómez-Sal, P.; Royo, P. *Organometallics* **1999**, 18, 546.

(5) De la Mata, F. J.; Giner, P.; Royo, P. *J. Organomet. Chem.* **1999**, 572, 155.

(6) Okuda, J.; Eberle, T.; Spaniol, T. P. *Chem. Ber.* **1997**, 130, 209.

(7) (a) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, 31, 123. (b) Nugent, W. A. *Inorg. Chem.* **1983**, 22, 965. (c) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, 42, 239.



reactivity of terminal Si–N, Nb–N, and bridging Si–N–Nb bonds leading to new  $\mu$ -oxo dinuclear compounds.

## Results and Discussion

**Insertion of Isocyanide.** The reaction of 1 equiv of the isocyanide CNAr (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) with the amido niobium compound [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>(NH<sup>t</sup>Bu)}(N<sup>t</sup>Bu)Cl(NH<sup>t</sup>Bu)] (**2**) proceeds immediately in hexane at room temperature. The  $\eta^2$ -iminocarbamoyl derivative [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>(NH<sup>t</sup>Bu)}(N<sup>t</sup>Bu)Cl{ $\eta^2$ -C(NH<sup>t</sup>Bu)=NAr}] (**5**) resulting from insertion of the isocyanide into the niobium–amido bond (Scheme 2) was isolated as a brown oil, which was characterized by elemental analysis and IR and NMR spectroscopy.

tively a single terminal NH<sup>t</sup>Bu group bound to silicon, **1**; two terminal NH<sup>t</sup>Bu groups bound to both silicon and niobium, **2**; one bridging N<sup>t</sup>Bu group between silicon and niobium, **3**; and the same complex containing one additional NH<sup>t</sup>Bu group bound to niobium, **4**. While insertion of isocyanides into Si–N bonds is not known due to the thermodynamic stability of Si–N compared with Si–C bonds, a few examples of insertion reactions of isocyanides into metal–amido bonds giving the first  $\eta^2$ -iminocarbamoyl derivatives were reported, initially for uranium<sup>9</sup> and molybdenum<sup>10</sup> complexes. More recently similar reactions have been reported for cyclopentadienyl titanium, zirconium, and tantalum compounds.<sup>11</sup> In contrast, the insertion of carbon dioxide into both silicon–amido and transition metal–amido bonds to afford carbamate compounds is well known.<sup>11a,12</sup> Similar CO<sub>2</sub> insertion reactions with  $\eta^5$ -cyclopentadienyl- $\eta$ -amido titanium and zirconium complexes to give oxo derivatives with elimination of the corresponding isocyanate have been reported.<sup>3b,13</sup>

In this paper we report our results from insertion reactions of 2,6-dimethylphenylisocyanide made to determine the comparative reactivity of terminal Nb–N and bridging Nb–N–Si bonds in compounds **1–4** to give new iminocarbamoyl derivatives. Analogous insertion reactions of carbon dioxide were studied to compare the

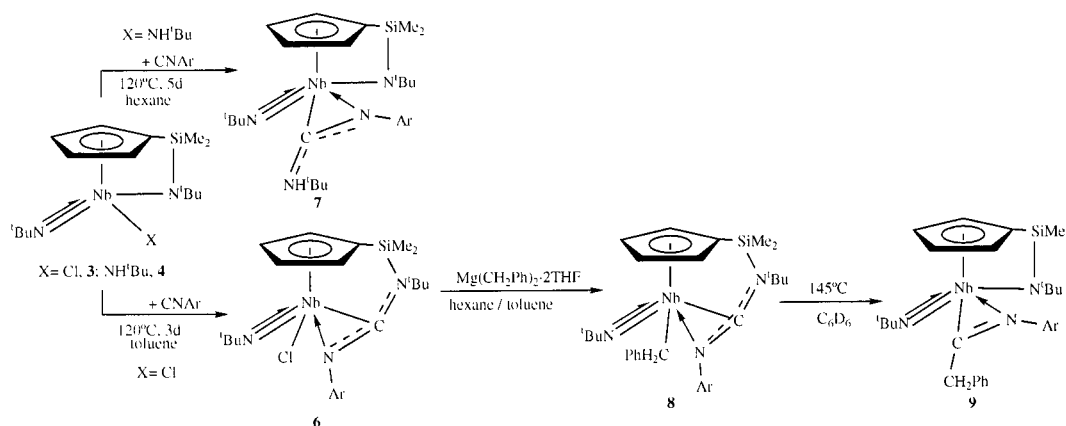
In contrast, insertion of CNAr into the bridging silylamido–niobium bond of [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>( $\eta^1$ -N<sup>t</sup>Bu)}(N<sup>t</sup>Bu)Cl] (**3**) (Scheme 3) required heating the toluene solution at 120 °C for 3 days. The isolated dark red product was the bridged silyl- $\eta^2$ -iminocarbamoyl derivative [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>(N<sup>t</sup>Bu)- $\eta^2$ -(C=NAr)}(N<sup>t</sup>Bu)Cl] (**6**), which was characterized by elemental analysis and IR and NMR spectroscopy. When a mixture of compound [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>( $\eta^1$ -N<sup>t</sup>Bu)}(N<sup>t</sup>Bu)(NH<sup>t</sup>Bu)] (**4**) and 1 equiv of isocyanide was heated in hexane at 120 °C, an even slower transformation was observed (Scheme 3). In this case, insertion into the terminal niobium–amido bond gave, after 5 days, a 75% yield of the  $\eta^2$ -iminocarbamoyl derivative [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>( $\eta^1$ -N<sup>t</sup>Bu)}(N<sup>t</sup>Bu){ $\eta^2$ -C(NH<sup>t</sup>Bu)=NAr}] (**7**), as a dark red oil. No insertion into the bridged silylamido–niobium bond was observed.

The values of the chemical shift difference ( $\Delta\delta$ ) between the quaternary and methyl carbons of the <sup>t</sup>Bu groups of different imido and amido ligands are given in Table 1. These differences may provide information about the  $\pi$ -bond contribution of these ligands.<sup>7,8</sup> The values of  $\Delta\delta$  found in complexes **1–4** for the niobium-bonded imido ligand indicate that its  $\pi$ -donor character decreases in the order **1** > **2** > **3** > **4**. Therefore, the imido ligand is a weaker  $\pi$ -donor when the number of competitive amido ligands (terminal and bridging) increases (**4**), consistent with what should be expected. It is also less  $\pi$ -donating with one bridging (**3**) than with one terminal (**2**) amido group. It can also be concluded that the  $\pi$ -character of the Nb–NH<sup>t</sup>Bu bonds is higher than that of the Si–NH<sup>t</sup>Bu bonds, consistent with the more electrophilic character of Nb. Similarly, the  $\pi$ -character of the Nb–NH<sup>t</sup>Bu bond is higher when no competitive amido ligand is present (**2** > **4**). In each case  $\Delta\delta$  is higher when the amido N<sup>t</sup>Bu group bridges two acidic centers (Si and Nb).

The ease of insertion into the amido–niobium bond of complexes **2–4** is governed not only by the availability of an empty orbital to accept isocyanide coordination but also by the degree of steric congestion due to the number of N<sup>t</sup>Bu groups bound to the metal. In addition, inser-

- (8) (a) Lee, S. Y.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 6396. (b) Schaller, C. P.; Cummins, C. C.; Wolczansky, P. T. *J. Am. Chem. Soc.* **1993**, *32*, 131. (c) de With, J.; Horton, A. D. *Organometallics* **1996**, *15*, 591. (d) Blake, R. E.; Antonelli, D. M.; Henling, L. M.; Schaefer, W. P.; Hardcastle, K. I.; Bercaw, J. E. *Organometallics* **1995**, *14*, 1901. (e) Royo, P.; Sánchez-Nieves, J. *J. Organomet. Chem.* **2000**, *597*, 61. (f) Castro, A.; Galakhov, M. V.; Gómez, M.; Sánchez, F. *J. Organomet. Chem.* **1999**, *580*, 161. (g) Antiñolo, A.; Fajardo, M.; Huertas, C.; Otero, A.; Prashar, S.; Rodríguez, A. M. *J. Organomet. Chem.* **1999**, *585*, 154. (h) Humphries, M. J.; Green, M. L. H.; Leech, M. A.; Gibson, V. C.; Jolly, M.; Williams, D. N.; Elsegood, M. R. J.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **2000**, 4044. (i) Humphries, M. J.; Green, M. L. H.; Douthwaite, R. E.; Rees, L. H. *J. Chem. Soc., Dalton Trans.* **2000**, 4555. (9) (a) Zanella, P.; Brianese, N.; Casellato, U.; Ossola, F.; Porchia, M.; Rosseto, G.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1987**, 2039. (b) Dormond, A.; Aaliti, A.; Moise, C. *J. Chem. Soc., Chem. Commun.* **1985**, 1231. (10) Chisholm, M. H.; Hammond, C. E.; Huffman, D.; Ho, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7860. (11) (a) Palacios, F. Doctoral Thesis, Universidad de Alcalá, 1998. (b) Galakhov, M. V.; Gómez-Sal, P.; Martín, A.; Mena, M.; Yélamos, C. *Eur. J. Inorg. Chem.* **1998**, 1319. (c) Sánchez-Nieves, J.; Royo, P.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **2000**, *19*, 3169. (d) Thirupathi, N.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2000**, *19*, 2573. (12) (a) Yin, X.; Moss, J. R. *Coord. Chem. Rev.* **1999**, *181*, 27. (b) Pandey, K. K. *Coord. Chem. Rev.* **1995**, *140*, 37. (c) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661. (d) Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* **1977**, *99*, 782. (e) Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* **1977**, *99*, 792. (f) Chisholm, M. H.; Tan, L.-S.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 4879. (g) Gómez-Sal, P.; Irigoyen, A. M.; Martín, A.; Mena, M.; Monge, M.; Yélamos, C. *J. Organomet. Chem.* **1995**, *494*, C19. (13) Kloppenburg, L.; Petersen, J. L. *Organometallics* **1996**, *15*, 7.

Scheme 3

Table 1. Values of  $\Delta\delta$  for Various Imido and Amido Ligands

compound	$\Delta\delta$				Nb–OC–NH <sup>t</sup> Bu Nb–C(NAr)–N <sup>t</sup> Bu
	Nb=N <sup>t</sup> Bu	Nb–NH <sup>t</sup> Bu	Nb–N <sup>t</sup> Bu–Si	Si–NH <sup>t</sup> Bu	
[Nb{ $\eta^5$ -C <sub>5</sub> H <sub>4</sub> SiMe <sub>2</sub> (NH <sup>t</sup> Bu)}(N <sup>t</sup> Bu)Cl <sub>2</sub> ] ( <b>1</b> ) <sup>4b</sup>	36.3			19.3	
[Nb{ $\eta^5$ -C <sub>5</sub> H <sub>4</sub> SiMe <sub>2</sub> (NH <sup>t</sup> Bu)}(N <sup>t</sup> Bu)Cl(NH <sup>t</sup> Bu)] ( <b>2</b> ) <sup>4b</sup>	33.4	23.6		18.0	
[Nb{ $\eta^5$ -C <sub>5</sub> H <sub>4</sub> SiMe <sub>2</sub> ( $\eta^1$ -N <sup>t</sup> Bu)}(N <sup>t</sup> Bu)Cl] ( <b>3</b> ) <sup>4b</sup>	32.1		25.7		
[Nb{ $\eta^5$ -C <sub>5</sub> H <sub>4</sub> SiMe <sub>2</sub> ( $\eta^1$ -N <sup>t</sup> Bu)}(N <sup>t</sup> Bu)(NH <sup>t</sup> Bu)] ( <b>4</b> ) <sup>4b</sup>	30.4	20.7	21.0		
[Nb{ $\eta^5$ -C <sub>5</sub> H <sub>4</sub> SiMe <sub>2</sub> (NH <sup>t</sup> Bu)}(N <sup>t</sup> Bu)Cl{ $\eta^2$ -C(NH <sup>t</sup> Bu)=NAr}] ( <b>5</b> )	33.6			18.1	21.7
[Nb{ $\eta^5$ -C <sub>5</sub> H <sub>4</sub> SiMe <sub>2</sub> (N <sup>t</sup> Bu)- $\eta^2$ -(C=NAr)}(N <sup>t</sup> Bu)Cl] ( <b>6</b> )	34.3				27.7
[Nb{ $\eta^5$ -C <sub>5</sub> H <sub>4</sub> SiMe <sub>2</sub> ( $\eta^1$ -N <sup>t</sup> Bu)}(N <sup>t</sup> Bu){ $\eta^2$ -C(NH <sup>t</sup> Bu)=NAr}] ( <b>7</b> )	30.2		21.4		22.0
[Nb{ $\eta^5$ -C <sub>5</sub> H <sub>4</sub> SiMe <sub>2</sub> (N <sup>t</sup> Bu)- $\eta^2$ -(C=NAr)}(N <sup>t</sup> Bu)(CH <sub>2</sub> Ph)] ( <b>8</b> )	31.8				27.2
[Nb{ $\eta^5$ -C <sub>5</sub> H <sub>4</sub> SiMe <sub>2</sub> ( $\eta^1$ -N <sup>t</sup> Bu)}(N <sup>t</sup> Bu){ $\eta^2$ -C(CH <sub>2</sub> Ph)=NAr}] ( <b>9</b> ) <sup>4b</sup>	30.4		21.7		
[Nb{ $\eta^5$ -C <sub>5</sub> H <sub>4</sub> SiMe <sub>2</sub> ( $\eta^1$ -OOCNH <sup>t</sup> Bu)}( $\eta^2$ -OOCNH <sup>t</sup> Bu)(N <sup>t</sup> Bu)Cl] ( <b>10</b> )	38.9				21.2; 21.6
[[Nb(N <sup>t</sup> Bu)Cl <sub>2</sub> ] <sub>2</sub> { $\eta^5$ -C <sub>5</sub> H <sub>4</sub> SiMe <sub>2</sub> -O-SiMe <sub>2</sub> - $\eta^5$ -C <sub>5</sub> H <sub>4</sub> }] ( <b>11</b> )	39.2				
[[Nb(N <sup>t</sup> Bu)(CH <sub>2</sub> Ph) <sub>2</sub> ] <sub>2</sub> { $\eta^5$ -C <sub>5</sub> H <sub>4</sub> SiMe <sub>2</sub> -O-SiMe <sub>2</sub> - $\eta^5$ -C <sub>5</sub> H <sub>4</sub> }] ( <b>12</b> )	34.7				
[Nb(N <sup>t</sup> Bu)Cl- $\mu$ -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> SiMe <sub>2</sub> - $\eta$ -O)] <sub>2</sub> ( <b>13</b> )	36.6				

tion occurs more easily for terminal than for bridging amido ligands. Consequently, insertion into the terminal Nb–NH<sup>t</sup>Bu group in compound **2** is easier (immediate at room temperature) than into the bridging silylamido ligand in compound **3** (3 days at 120 °C) and much easier (5 days at 120 °C) than in compound **4**, which contains three N<sup>t</sup>Bu systems. After the formation of the 18-electron compound **7**, which contains the  $\eta^2$ -imino-carbamoyl ligand, no further insertion reaction occurs.

Benzoylation of complex **6** with Mg(CH<sub>2</sub>Ph)<sub>2</sub>·2THF in toluene/hexane afforded the benzyl  $\eta^2$ -iminocarbamoyl derivative [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>(N<sup>t</sup>Bu)- $\eta^2$ -(C=NAr)}(N<sup>t</sup>Bu)-(CH<sub>2</sub>Ph)] (**8**), isolated in high yield as a brown solid (Scheme 3). Complex **8** is a rare example of a niobium compound containing a benzyl and an imino-carbamoyl ligand. It is unlikely that **8** could be prepared by reaction of the amido benzyl niobium derivative with CNAr, due to preferential insertion of the isocyanide into the niobium–benzyl bond to give the thermodynamically more stable iminoacyl compound [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>( $\eta^1$ -N<sup>t</sup>Bu)}(N<sup>t</sup>Bu){ $\eta^2$ -C(CH<sub>2</sub>Ph)=NAr}] (**9**), reported previously.<sup>4b</sup> Complex **8** therefore offered a unique opportunity to examine the comparative stability of iminoacyl and iminocarbamoyl species. When a C<sub>6</sub>D<sub>6</sub> solution of **8** was heated at 145 °C in a Teflon-valved NMR tube, almost quantitative formation of the reported iminoacyl **9** was observed (Scheme 3). Whereas deinsertion of CO and CO<sub>2</sub> from acyl and carbamate ligands, respectively, is a well-documented process,<sup>14</sup> deinsertion reactions of isocyanide from iminoacyl complexes have received less attention.<sup>11a,15</sup> Deinsertion of isocyanide was demonstrated under these conditions

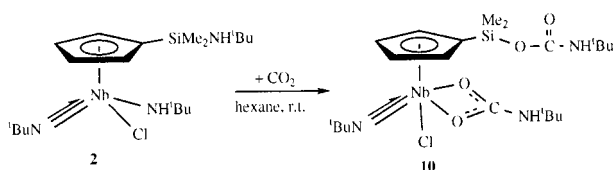
by the formation of an intermediate amido benzyl compound [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>( $\eta^1$ -N<sup>t</sup>Bu)}(N<sup>t</sup>Bu)(CH<sub>2</sub>Ph)], which was observed together with the same decomposition products identified when a sample of free isocyanide was heated at the same temperature. The amido benzyl species was the major component of the mixture obtained at higher temperature (160 °C), because the dissociated isocyanide completely decomposed during the reaction. However, **9** was the major component when free isocyanide was added before heating. It can thus be surmised that the reaction takes place by deinsertion of the isocyanide followed by its reinsertion with benzyl ligand migration.

The NMR data for all of the new  $\eta^2$ -iminocarbamoyl compounds described are consistent with that expected for asymmetric molecules. The <sup>1</sup>H NMR spectra show resonances consistent with an ABCD spin system for the cyclopentadienyl ring protons, two singlets for both nonequivalent silicon methyls, and one singlet for each type of *tert*-butyl group. The <sup>13</sup>C NMR spectra are particularly useful to differentiate the various types of *tert*-butyl group. The <sup>13</sup>C resonance of the quaternary *tert*-butyl carbon is observed between  $\delta$  64–68 when this group is bound to the imido ligand, at  $\delta$  49.7 when bound

(14) (a) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059. (b) Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* **1977**, *99*, 782. (c) Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* **1977**, *99*, 792 (d) Chisholm, M. H.; Tan, L.-S.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 4879.

(15) (a) Andrés, R.; Galakhov, M.; Gómez-Sal, M. P.; Martín, A.; Mena, M.; Santamaría, C. *Chem. Eur. J.* **1998**, *4*, 1206. (b) Pizzano, A.; Sánchez, L.; Altman, M.; Monge, A.; Ruiz, C.; Carmona, E. *J. Am. Chem. Soc.* **1995**, *117*, 1759. (c) Fandos, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 2665.

Scheme 4

Table 2. Chemical Shifts of the Carbamate Proton of **10**

	NH <sup>t</sup> Bu ( $\delta$ , C <sub>6</sub> D <sub>6</sub> )	
	carbamate group	
	bidentate	monodentate
25 °C	4.72	5.52
30 °C	4.72	5.36
40 °C	4.73	5.21
50 °C	4.75	5.08
60 °C	4.74	4.97
$3.6 \times 10^{-2}$ M	4.72	5.52
$7.2 \times 10^{-3}$ M	4.72	4.82

to the Si–NH<sup>t</sup>Bu amido ligand (**5**), and between  $\delta$  54 and **58** when bound to the Nb–NH<sup>t</sup>Bu amido ligand and is displaced to high field at  $\delta$  52.5 (**5**, **7**) when the NH<sup>t</sup>Bu group migrates to give the  $\pi$ -delocalized system of the  $\eta^2$ -iminocarbonyl ligand. However, no shift was observed for the *tert*-butyl group bound to the bridging iminocarbonyl ligand in complexes **6** and **8** compared with the values found<sup>4b</sup> for the bridging silyl–amido ligand of related complexes, despite chain lengthening and possible  $\pi$ -delocalization in the iminocarbonyl ligand. This chain lengthening is clearly evident in the <sup>29</sup>Si NMR spectra, with a downfield shift of the silicon resonance from  $\delta$  –17.1 for **3** to  $\delta$  8.8 for **6**. Similar comparison of the silicon resonance observed for complexes **4** ( $\delta$  –20.8) and **7** ( $\delta$  –22.0) confirms that insertion of isocyanide into the terminal Nb–NH<sup>t</sup>Bu bond occurred, rather than insertion into the bridging silyl–amido–Nb bond, which would resonate at ca.  $\delta$  8.0 as in complex **6**. The iminocarbonyl carbon resonance is observed between  $\delta$  190.0 and 199.0 for all the compounds bearing this ligand.

**Insertion of Carbon Dioxide.** A reaction flask containing a hexane solution of complex **2** was placed under an atmosphere of carbon dioxide. An immediate reaction occurred at room temperature to give the dicarbamate compound [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>( $\eta^1$ -OOCNH<sup>t</sup>Bu)}( $\eta^2$ -OOCNH<sup>t</sup>Bu)(N<sup>t</sup>Bu)Cl] (**10**) as a white solid in good yield (Scheme 4). Under these conditions the insertion of carbon dioxide occurred in both the Si–NH<sup>t</sup>Bu and Nb–NH<sup>t</sup>Bu bonds. The carbamate carbon resonance appeared at  $\delta$  153.3 in the <sup>13</sup>C NMR spectrum of **10**, confirming  $\eta^1$ -coordination of the silicon-bound carbamate substituent and supported by the  $\nu$ (COO) IR absorption observed at 1694 cm<sup>–1</sup>. In contrast, the <sup>13</sup>C NMR signal corresponding to the  $\eta^2$ -coordinate carbamate ligand bound to niobium was observed at lower field ( $\delta$  167.4), with a  $\nu$ (COO) IR absorption at 1587 cm<sup>–1</sup>. The <sup>1</sup>H NMR spectrum shows that the chemical shift of the amino proton of the monodentate carbamate ligand is temperature dependent (see Table 2), indicating a hydrogen bridge interaction between this proton and the oxygen of a second carbamate group. This resonance was displaced to higher field as the concentration of complex **10** was systematically reduced, evidence for the intermolecular nature of this interac-

tion. Interactions of this type have been reported for related organic substrates<sup>16</sup> and organometallic compounds.<sup>17</sup>

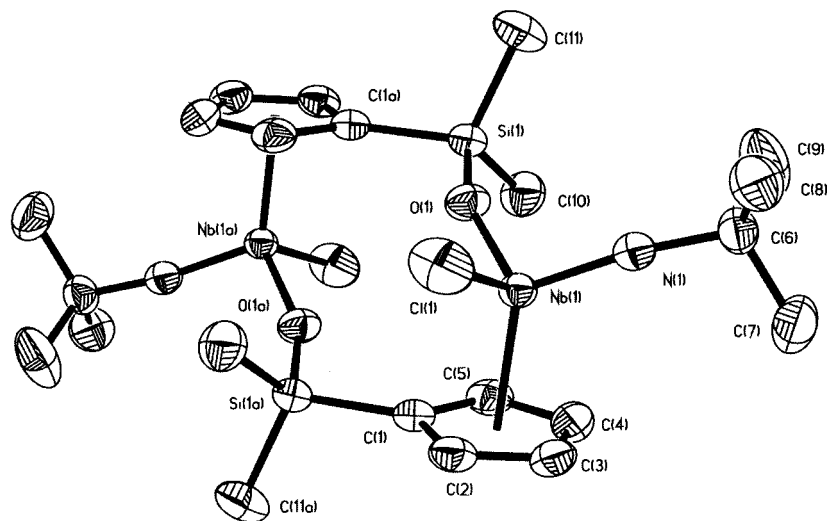
A similar insertion reaction should be expected for complex **1**, which contains only one Si–NH<sup>t</sup>Bu bond. However, the reaction of **1** with CO<sub>2</sub> at room temperature resulted in the formation of a mixture of unidentified compounds, which on heating at 130–140 °C afforded the  $\mu$ -oxo dinuclear complex [ $\{[Nb(N^tBu)Cl_2]_2\} \cdot \{\eta^5-C_5H_4SiMe_2-O-SiMe_2-\eta^5-C_5H_4\}$ ] (**11**). This transformation takes place with evolution of CO<sub>2</sub> and simultaneous elimination of *N,N*-di(*tert*-butyl)urea, (tBuNH)<sub>2</sub>CO, which was identified by comparing its spectroscopic data with those of a known sample.<sup>18</sup>

A mechanism involving the formation of an unstable intermediate carbamate compound resulting from insertion of CO<sub>2</sub> into the Si–NH<sup>t</sup>Bu bond with further intermolecular decomposition explains the behavior observed (Scheme 5). An alternative method to synthesize **11** is described below. Complex **11** shows the NMR data expected for a C<sub>2v</sub> symmetric molecule. The <sup>1</sup>H NMR spectrum exhibits an AA'BB' spin system for the ring protons and two singlets due to equivalent methylsilyl and *tert*-butyl groups. The IR absorption observed at 1080 cm<sup>–1</sup> due to the Si–O–Si bridge and the <sup>13</sup>C spectrum which showed the typical low-field resonance ( $\delta$  69.5) of the quaternary *tert*-butyl imido carbon confirmed this formulation. The value of  $\Delta\delta$  = 39.2 observed for this compound is slightly lower than that found<sup>4a</sup> for the related compound bearing the chlorodimethylsilyl moiety ( $\Delta\delta$  = 40.1). This formulation was also confirmed by preparing the tetrabenzyl derivative by treatment of a C<sub>6</sub>D<sub>6</sub> solution of **11** in a NMR tube with 4 equiv of Mg(CH<sub>2</sub>Ph)<sub>2</sub>·2THF. The resulting product [ $\{[Nb(N^tBu)(CH_2Ph)_2]_2\} \cdot \{\eta^5-C_5H_4SiMe_2-O-SiMe_2-\eta^5-C_5H_4\}$ ] (**12**) was characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The <sup>1</sup>H NMR spectrum shows the presence of the expected two doublets due to the diastereotopic benzylic protons of two equivalent benzyl groups bound to each metal center. The reaction of the bridged silyl–amido complex **3** with CO<sub>2</sub>, monitored at room temperature by <sup>1</sup>H NMR spectroscopy in C<sub>6</sub>D<sub>6</sub>, showed the presence of *tert*-butylisocyanate tBuNCO, characterized by comparing its spectroscopic data with those of a pure commercial sample. The same reaction was carried out in toluene at a preparative scale (Scheme 6) to give, after 6 days at room temperature, a solution from which the dinuclear compound [Nb(N<sup>t</sup>Bu)Cl- $\mu$ ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>- $\eta$ -O)]<sub>2</sub> (**13**) was isolated as a yellow crystalline solid, identified by elemental analysis, NMR and IR spectroscopy, and an X-ray diffraction study on a single crystal. Figure 1 shows a view of the molecular structure of **13** with the atomic labeling scheme, and Table 3 summarizes selected bond distances and angles.

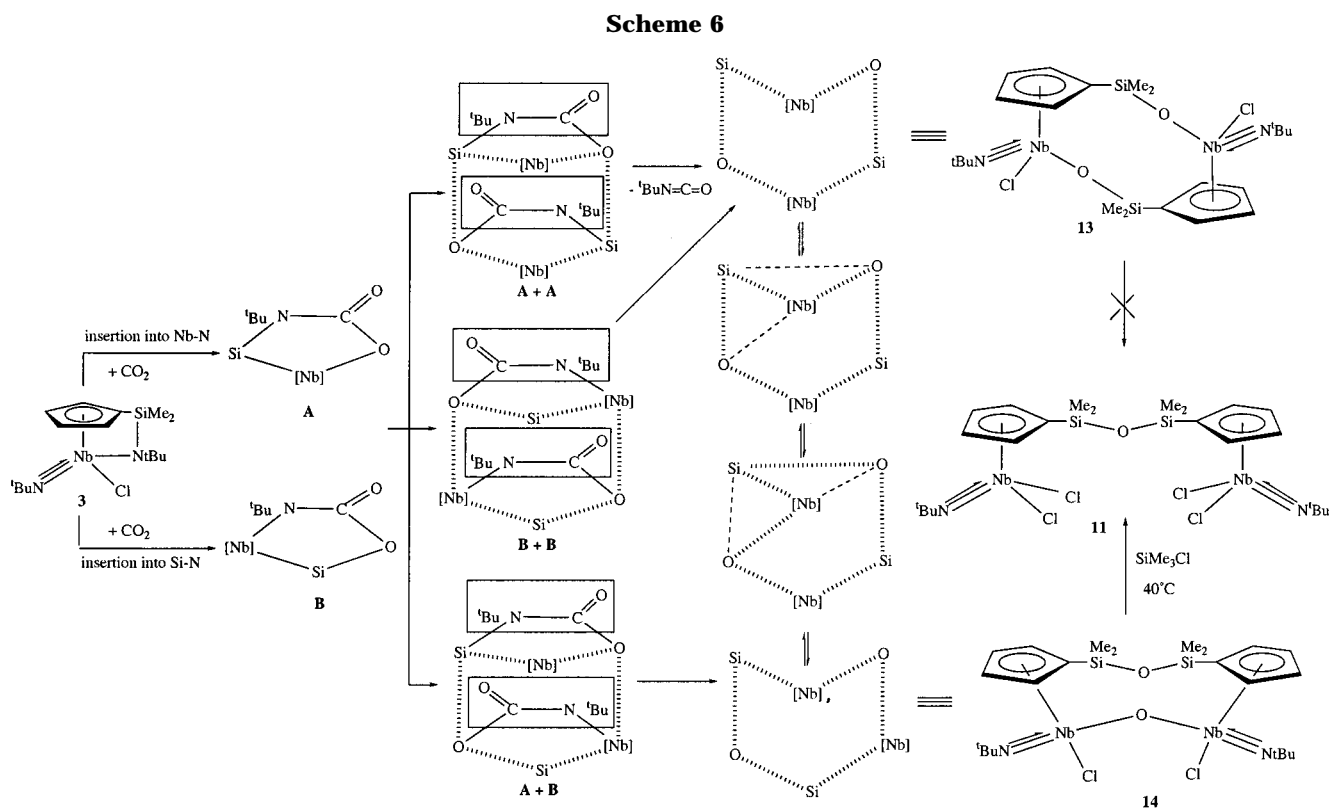
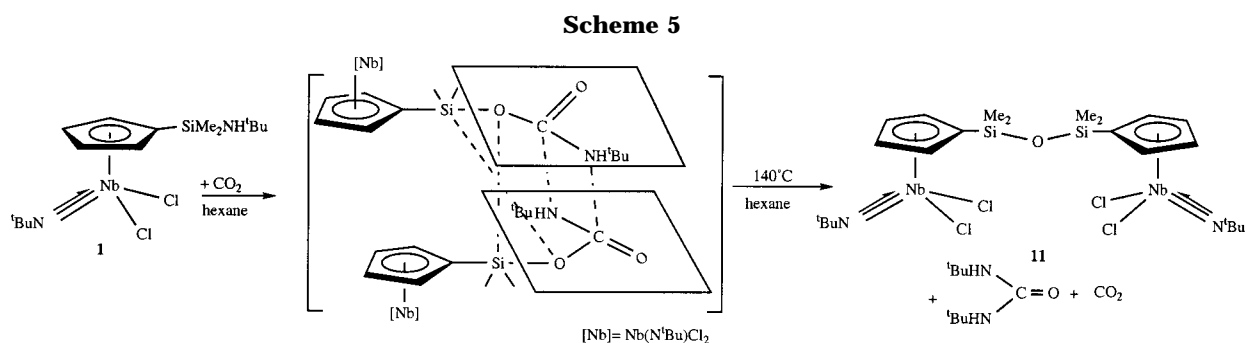
(16) (a) Gennari, G.; Gude, M.; Potenza, D.; Piarulli, U. *Chem. Eur. J.* **1998**, *4*, 1924. (b) Smith, M. D.; Claridge, T. D. W.; Tranter, G. E.; Sansom, M. S. P.; Fleet, G. W. J. *Chem. Commun.* **1998**, *18*, 2041. (c) Allott, C.; Adams, H.; Bernad, P. L., Jr.; Hunter, C. A.; Rotger, C.; Thomas, J. A. *Chem. Commun.* **1998**, *22*, 2449.

(17) (a) Biradha, K.; Desiraju, G. R.; Braga, D.; Grepioni, F. *Organometallics* **1996**, *15*, 1284. (b) Brammer, L.; Mareque Rivas, J. C.; Zhao, D. *Inorg. Chem.* **1998**, *37*, 5512. (c) Okamura, T.; Sakayue, K.; Ueyama, N.; Nakamura, A. *Inorg. Chem.* **1998**, *37*, 6731. (d) Carr, J. D.; Coles, S. J.; Hassan, W. W.; Hursthouse, M. B.; Abdul Malik, K. M.; Tucker, J. H. R. *J. Chem. Soc., Dalton Trans.* **1999**, 57.

(18) Legzdins, P.; Rettig, S. J.; Ross, K. J. *Organometallics* **1994**, *13*, 569.



**Figure 1.** Perspective view of complex **13** showing the atom-labeling scheme.



The molecular structure of **13** corresponds to a dinuclear compound in which the two moieties  $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2)(\text{N}^t\text{Bu})\text{Cl}]$  are related by an inversion center and are bonded by two oxygen bridges between silicon

and niobium atoms from different units. This bonding arrangement is similar to that observed for the related dinuclear titanium complex  $[\text{TiCl}_2\text{-}\mu\text{-(}\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta\text{-O)}_2]_2$ .<sup>3a</sup> The coordination around the niobium center in

**Table 3. Selected Bond Distances (Å) and Angles (deg) for 13**

Nb(1)–N(1)	1.7530(19)
Nb(1)–O(1)	1.9089(15)
Nb(1)–Cl(1)	2.3849(7)
Nb(1)–C(4)	2.412(2)
Nb(1)–C(3)	2.428(2)
Nb(1)–C(5)	2.463(2)
Nb(1)–C(2)	2.497(2)
Nb(1)–C(1)	2.543(2)
Si(1)–O(1)	1.6375(16)
Si(1)–C(11)	1.847(3)
Si(1)–C(10)	1.859(3)
Si(1)–C(1a)	1.868(2)
N(1)–C(6)	1.456(3)
Nb(1)–Cp(1)	2.156
N(1)–Nb(1)–O(1)	104.55(8)
N(1)–Nb(1)–Cl(1)	100.19(7)
O(1)–Nb(1)–Cl(1)	107.46(5)
Si(1)–O(1)–Nb(1)	156.32(11)
C(6)–N(1)–Nb(1)	171.77(17)
N(1)–Nb(1)–Cp(1)	118.94
Cl(1)–Nb(1)–Cp(1)	111.23
O(1)–Nb(1)–Cp(1)	112.86

each fragment is typical of half-sandwich imido complexes and could be described as a three-legged piano-stool structure with the bridging oxygen, the imido nitrogen, and the chloro ligand being the other three leg substituents. If the centroids of the silyl-substituted rings are considered as coordination sites, the central core of the dinuclear structure appears as an eight-membered cycle, with the two niobium and the two bridging oxygen atoms as the seat of a chair conformation. It is apparent from the bond distances that Nb–O and Si–O  $\pi$ -bond contributions exist. The Nb–O bond length (1.908(1) Å) is very similar to those found for Nb–O–Nb systems in dinuclear niobium(V) compounds without any other additional bridging groups, such as [(NbCp<sub>2</sub>Cl)<sub>2</sub>( $\mu$ -O)][BF<sub>4</sub>]<sub>2</sub><sup>19a</sup> (1.876 Å), [Nb{CpCl<sub>3</sub>(H<sub>2</sub>O)}<sub>2</sub>( $\mu$ -O)]<sup>19b</sup> (1.915 Å), and [Nb{(C<sub>5</sub>H<sub>4</sub>Me)Cl<sub>3</sub>(H<sub>2</sub>O)}<sub>2</sub>( $\mu$ -O)]<sup>19d</sup> (1.926 Å). The Si–O distance (1.637(1) Å) is larger than that found in the titanium derivative<sup>3a</sup> and similar to those found in siloxanes. The Nb–O–Si angle (156.3(1)°) is slightly smaller than that found for Ti–O–Si (160.2(1)°), and it is between those found for Si–O–Si (ca. 145°) and Nb–O–Nb (ca. 170–180°) in similar types of dinuclear compound.<sup>19</sup> The imido ligand is located trans to the silyl group and is in a staggered disposition similar to that in [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-SiMe<sub>2</sub>(NH<sup>t</sup>Bu)}Cl<sub>2</sub>(N<sup>t</sup>Bu)]<sup>4b</sup> rather than the usually eclipsed orientation found for most compounds of this type.<sup>8g,h,20</sup> The Nb(1)–N(1) distance of 1.7530(19) Å is in the range expected for a four-electron donor imido ligand and similar to those found in other imido niobium compounds. The imido group adopts an almost linear disposition (C(6)–N(1)–Nb(1), 171.7(1)°). A remarkable feature is the partial loss of the  $\eta^5$ -character of the Cp ligand, as evidenced by Nb–C distances, ranging from

the shorter 2.412(2) and 2.428(2) Å corresponding to the two carbon atoms trans to the silyl group to the longer 2.543(2) Å corresponding to the carbon bearing the silyl group. The Si atom is almost located in the Cp plane, with a distance to this plane of 0.011 Å, as expected for a Si–Csp<sup>2</sup> bond. It is important to notice that the Cp–Nb–L and L–Nb–L' angles are very similar to those found for the related monomeric [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-SiMe<sub>2</sub>(NH<sup>t</sup>Bu)}Cl<sub>2</sub>(N<sup>t</sup>Bu)]<sup>4b</sup> showing that the spatial distribution of the ligands is not affected by the formation of the dinuclear structure.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of C<sub>6</sub>D<sub>6</sub> solutions of compound **13** always show the presence of a second isomer in a molar ratio of ca. 1:3. Both isomers show similar sets of <sup>1</sup>H and <sup>13</sup>C NMR signals (see Experimental Section). Despite having two chiral centers, this second component cannot be identified as a diastereomer of **13** with the two chloro and N<sup>t</sup>Bu groups oriented to the same side in an eclipsed disposition, because this would be an asymmetric molecule with a very different NMR behavior. According to the <sup>1</sup>H and <sup>13</sup>C NMR spectra observed, this isomer has to be the dinuclear compound [(Nb(N<sup>t</sup>Bu)Cl)<sub>2</sub>( $\mu$ -O)]<sub>2</sub>{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>-O-SiMe<sub>2</sub>- $\eta^5$ -C<sub>5</sub>H<sub>4</sub>} (**14**). Simultaneous insertion of CO<sub>2</sub> into either the Nb–N or the Si–N bonds would lead to a mixture of two intermediates **A** and **B** (Scheme 6), which are further transformed by elimination of <sup>t</sup>BuN=C=O through an intermolecular reaction. Reaction between two **A** or two **B** units affords compound **13**, whereas formation of a mixture of **13** and **14** could result from the reaction of one **A** and one **B** unit. Therefore, complexes **13** and **14** could be generated during the insertion process, although concentration and crystallization only allows **13** to be recovered. This result could also be explained by accepting that only one of the two possible insertions into either the Nb–N or the Si–N bonds takes place to give **13** as the unique reaction product, which in solution could be transformed into **14** by the intramolecular rearrangement represented in Scheme 6. Actually, the NMR spectrum observed for a sample prepared with a selected crystal of **13** showed the presence of both **13** and **14** in approximately the same molar ratio 1:3. Moreover, when a mixture of both **13** and **14** was heated in the presence of ClSiMe<sub>3</sub>, a clean reaction occurred to give pure **11**. As **11** can only be formed by reaction of **14** with ClSiMe<sub>3</sub><sup>21</sup> and not from **13**, it can be concluded that conversion of **13** into **14** must happen in solution. Nevertheless none of these results negates the possibility that **14** is formed during the insertion reaction.

Both oxo complexes **13** and **14** contain two identical fragments related by one inversion center **13** and one plane of symmetry **14** each containing one chiral metal center, which makes the two methylsilyl groups and the four ring protons nonequivalent (ABCD spin system). The <sup>1</sup>H and <sup>13</sup>C NMR spectra (see experimental) always contain a mixture of both components in a molar ratio of ca. 1:3 and show two similar sets of signals which are consistent with this formulation, confirmed in the case of complex **13** by the X-ray diffraction study.

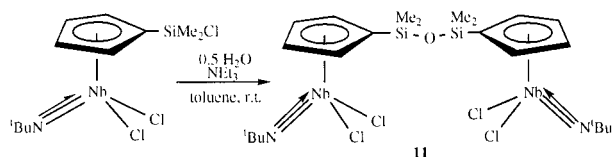
Complex **11** was also isolated by addition of 0.5 mol of water to a toluene solution of [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>Cl}]-

(19) (a) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sect. B* **1974**, *30*, 2290. (b) Bottomley, F.; Keizer, P. N.; White, P. S.; Preston, K. F. *Organometallics* **1990**, *9*, 1916. (c) Kirilova, N. I.; Lemenovskii, D. A.; Baukova, T. V.; Struchkov, Yu. T. *Koord. Khim.* **1977**, *3*, 1600. (d) Prout, K.; Daran, J. C. *Acta Crystallogr., Sect. B* **1979**, *35*, 2882. (e) Green, M. L. H.; Hughes, A. K.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1991**, 1407.

(20) Williams, D. N.; Mitchell, J. P.; Poole, A. D.; Siemeling, U.; Clegg, W.; Hockless, D. C. R.; O'Neil, P. A.; Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1992**, 739.

(21) Antiñolo, A.; Carrillo-Hermosilla, F.; Fernández-Baeza, J.; Lanfranchi, M.; Lara-Sánchez, A.; Otero, A.; Palomares, E.; Pellinghelli, M. A.; Rodríguez, A. M. *Organometallics* **1998**, *17*, 3015.

Scheme 7



( $\text{N}^t\text{Bu}$ ) $\text{Cl}_2$ ] in the presence of  $\text{NEt}_3$  (Scheme 7), demonstrating that selective hydrolysis of the Si-Cl rather than the Nb-Cl bond occurs. This result is consistent with similar behavior found for reaction with a protic reagent such as  $\text{NH}_2^t\text{Bu}$ <sup>4b</sup> and contrasting with the reactivity observed for  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl}\}\text{Cl}_4]$ , when hydrolysis is not selective and takes place at both Nb-Cl and Si-Cl bonds simultaneously.<sup>4a</sup> The same hydrolysis carried out using a 1:1 compound **11**/ $\text{H}_2\text{O}$  molar ratio resulted in formation of a mixture of compounds **11**, **13**, and **14**. Two possible pathways can be proposed to explain the formation of **13**, namely, the selective conversion of all the Si-Cl into Si-OH bonds and their intermolecular reaction with the Nb-Cl bond of a second molecule with elimination of HCl, or a selective intermolecular hydrolysis to give **11** which requires 0.5 mol of water. Further intramolecular hydrolysis of the Nb-Cl bonds of **11** with a second 0.5 mol of water gave **13** and **14**.

### Conclusions

Insertion of isocyanide  $\text{CNAr}$  ( $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ ) into the terminal Nb-N bonds of amido complexes  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{NH}^t\text{Bu})\}(\text{N}^t\text{Bu})\text{Cl}(\text{NH}^t\text{Bu})]$  and  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{-SiMe}_2(\eta^1\text{-N}^t\text{Bu})\}(\text{N}^t\text{Bu})(\text{NH}^t\text{Bu})]$  is more favorable than insertion into the bridging Nb-N-Si amido system of compound  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\eta^1\text{-N}^t\text{Bu})\}(\text{N}^t\text{Bu})\text{Cl}]$ . The ease of insertion is controlled by the steric demands of the number of  $\text{N}^t\text{Bu}$  groups present in the molecule. These insertions lead to the formation of terminal  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{NH}^t\text{Bu})\}(\text{N}^t\text{Bu})\text{Cl}\{\eta^2\text{-C}(\text{NH}^t\text{Bu})=\text{NAr}\}]$ ,  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\eta^1\text{-N}^t\text{Bu})\}(\text{N}^t\text{Bu})\{\eta^2\text{-C}(\text{NH}^t\text{Bu})=\text{NAr}\}]$ , and bridging  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{N}^t\text{Bu})\text{-}\eta^2\text{-C}(\text{NH}^t\text{Bu})=\text{NAr}\}(\text{N}^t\text{Bu})\text{Cl}]$   $\eta^2$ -iminocarbonyl derivatives, respectively. The benzyl  $\eta^2$ -iminocarbonyl-amidosilyl compound  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{N}^t\text{Bu})\text{-}\eta^2\text{-C}(\text{NH}^t\text{Bu})=\text{NAr}\}(\text{N}^t\text{Bu})\text{-}(\text{CH}_2\text{Ph})]$  is transformed into the  $\eta^2$ -iminoacyl- $\eta^1$ -amidosilyl derivative  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\eta^1\text{-N}^t\text{Bu})\}(\text{N}^t\text{Bu})\{\eta^2\text{-C}(\text{CH}_2\text{Ph})=\text{NAr}\}]$  by heating its  $\text{C}_6\text{D}_6$  solution at 145 °C, one rare example of deinsertion of isocyanide.

Insertion of carbon dioxide takes place easily at room temperature into the terminal Si-N amido bond of compound  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{NH}^t\text{Bu})\}(\text{N}^t\text{Bu})\text{Cl}_2]$  to give an unidentified mixture, which is transformed by heating at 130–140 °C into the  $\mu$ -oxo dinuclear complex  $[\{\text{Nb}(\text{N}^t\text{Bu})\text{Cl}_2\}_2\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-O-SiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4\}]$  as a unique reaction product with elimination of *tert*-butylurea. Similar insertion takes place simultaneously into the terminal Nb-N and Si-N amido bonds of  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{NH}^t\text{Bu})\}(\text{N}^t\text{Bu})\text{Cl}(\text{NH}^t\text{Bu})]$  to give the dicarbamate derivative  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\eta^1\text{-OOCNH}^t\text{Bu})\}(\eta^2\text{-OOCNH}^t\text{Bu})(\text{N}^t\text{Bu})\text{Cl}]$ . A much slower insertion of  $\text{CO}_2$  was observed into the bridging Si-amido-Nb system of compound  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\eta^1\text{-N}^t\text{Bu})\}(\text{N}^t\text{Bu})\text{-Cl}]$ , which is transformed with elimination of  $\text{N}^t\text{BuN}=\text{C}=\text{O}$  in an intermolecular reaction to give a mixture of

two  $\mu$ -oxo dinuclear isomers,  $[\text{Nb}(\text{N}^t\text{Bu})\text{Cl}\text{-}\mu\text{-}(\eta^5\text{-C}_5\text{H}_4\text{-SiMe}_2\text{-}\eta\text{-O})_2]$  and  $[\{\text{Nb}(\text{N}^t\text{Bu})\text{Cl}\}_2(\mu\text{-O})\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-O-SiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4\}]$ . Both isomers were always present in solution; however X-ray diffraction methods identified the former complex as the unique solid reaction product.

### Experimental Section

**General Comments.** All manipulations were performed under an inert atmosphere of argon using standard Schlenk or drybox techniques. Solvents used were previously dried and freshly distilled under argon: toluene from sodium, hexane from sodium-potassium amalgam. Unless otherwise stated, reagents were obtained from commercial sources and used as received.  $\text{Mg}(\text{CH}_2\text{Ph})_2\cdot 2\text{THF}$ <sup>22</sup> and **1–4**<sup>4</sup> were prepared by reported methods.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Varian Unity FT-300 and Varian FT-500 Unity Plus instruments, and chemical shifts were measured relative to the residual  $^1\text{H}$  and  $^{13}\text{C}$  resonances of benzene- $d_6$  used as solvent,  $\delta$  7.15 ( $^1\text{H}$ ) and 128 ( $^{13}\text{C}$ ). IR spectra were recorded on a Perkin-Elmer 583 spectrophotometer (4000–200  $\text{cm}^{-1}$ ). C, H, and N analyses were carried out with a Perkin-Elmer 240 C analyzer. The elemental analysis for liquid compound **7**, which partially decomposed during sublimation, gave unacceptable deviation.

**Preparation of  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{NH}^t\text{Bu})\}(\text{N}^t\text{Bu})\text{Cl}\{\eta^2\text{-C}(\text{NH}^t\text{Bu})=\text{NAr}\}]$  (**5**) ( $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ ).** An equimolar mixture of  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{NH}^t\text{Bu})\}(\text{N}^t\text{Bu})\text{Cl}(\text{NH}^t\text{Bu})]$  (**2**) (0.80 g, 1.72 mmol) and isocyanide (0.22 g, 1.72 mmol) in hexane (50 mL) was stirred at room temperature for 12 h, and the solvent was then removed under vacuum to give a brown oil in quantitative yield, which was characterized as **5**.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ ): 0.56 (s, 3H,  $\text{SiMe}_2$ ), 0.62 (s, 3H,  $\text{SiMe}_2$ ), 0.98 (s, 9H,  $\text{CMe}_3$ ), 1.22 (s, 9H,  $\text{CMe}_3$ ), 1.23 (s, 9H,  $\text{CMe}_3$ ), 2.04 (s, 3H,  $\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{C}$ ), 2.09 (br s, 1H,  $\text{NHSi}$ ), 2.34 (s, 3H,  $\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{C}$ ), 5.43 (br s, 1H,  $\text{NHC}$ ), 5.96 (m, 1H,  $\text{C}_5\text{H}_4$ ), 6.33 (m, 1H,  $\text{C}_5\text{H}_4$ ), 6.45 (m, 1H,  $\text{C}_5\text{H}_4$ ), 6.80 (m, 1H,  $\text{C}_5\text{H}_4$ ), 6.90–6.98 (m, *Ph*).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ ): 3.2, 3.8 ( $\text{SiMe}_2$ ), 19.0, 19.1 ( $\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{C}$ ), 30.8 ( $\text{CNHCMe}_3$ ), 31.6 ( $\text{SiNHCMe}_3$ ), 33.9 ( $\text{NbNCMe}_3$ ), 52.5 ( $\text{CNHCMe}_3$ ), 49.7 ( $\text{SiNHCMe}_3$ ), 67.5 ( $\text{NbNCMe}_3$ ), 105.5, 107.4, 115.9, 118.3 ( $\text{C}_2\text{-C}_5$ ,  $\text{C}_5\text{H}_4$ ), 121.9 ( $\text{C}_{ipso}$   $\text{C}_5\text{H}_4$ ), 126.0–140.0 (*Ph*,  $\text{C}_6\text{H}_3$ ), 190.5 ( $\text{N}=\text{C-NHCMe}_3$ ). IR ( $\nu$   $\text{cm}^{-1}$ ): 3323, 1598, 1570, 1350. Anal. Calcd for  $\text{C}_{28}\text{H}_{48}\text{ClN}_4\text{SiNb}$ : C, 56.30; H, 8.12; N, 9.38. Found: C, 55.73; H, 7.86; N, 8.62.

**Preparation of  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{N}^t\text{Bu})\text{-}\eta^2\text{-C}(\text{NH}^t\text{Bu})=\text{NAr}\}(\text{N}^t\text{Bu})\text{Cl}]$  (**6**) ( $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ ).** A mixture of  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{-SiMe}_2(\eta^1\text{-N}^t\text{Bu})\}(\text{N}^t\text{Bu})\text{Cl}]$ , (**3**) (0.75 g, 1.91 mmol) and isocyanide (0.25 g, 1.91 mmol) in toluene (50 mL) was warmed to 120 °C for 3 days in a Teflon-valved Schlenk. The solvent was removed under vacuum, and the resulting dark oil was washed with hexane ( $2 \times 10$  mL) to give a dark red solid characterized as **6**. Concentration of the mother liquor and subsequent cooling to –30 °C gave a second crop of **6** (0.85 g, 1.82 mmol, 85% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ ): 0.39 (s, 3H,  $\text{SiMe}_2$ ), 0.41 (s, 3H,  $\text{SiMe}_2$ ), 0.92 (s, 9H,  $\text{CMe}_3$ ), 1.19 (s, 9H,  $\text{CMe}_3$ ), 1.89 (s, 3H,  $\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{C}$ ), 2.37 (s, 3H,  $\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{C}$ ), 5.12 (m, 1H,  $\text{C}_5\text{H}_4$ ), 6.23 (m, 1H,  $\text{C}_5\text{H}_4$ ), 6.35 (m, 1H,  $\text{C}_5\text{H}_4$ ), 6.61 (m, 1H,  $\text{C}_5\text{H}_4$ ), 6.90–7.00 (m, *Ph*).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ ): 0.0, 3.0 ( $\text{SiMe}_2$ ), 19.3, 19.5 ( $\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{C}$ ), 30.0 ( $\text{SiNHCMe}_3$ ), 32.0 ( $\text{NbNCMe}_3$ ), 57.7 ( $\text{SiNHCMe}_3$ ), 66.3 ( $\text{NbNCMe}_3$ ), 99.8 ( $\text{C}_2\text{-C}_5$ ,  $\text{C}_5\text{H}_4$ ), 103.5 ( $\text{C}_{ipso}$   $\text{C}_5\text{H}_4$ ), 109.1, 109.3, 125.5 ( $\text{C}_2\text{-C}_5$ ,  $\text{C}_5\text{H}_4$ ), 126.4–142.7 (*Ph*,  $\text{C}_6\text{H}_3$ ) ( $\text{N}=\text{C-NHCMe}_3$  not observed).  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C,  $\delta$ ): 8.8. IR ( $\nu$   $\text{cm}^{-1}$ ): 1650, 1586, 1368. Anal. Calcd for  $\text{C}_{24}\text{H}_{37}\text{ClN}_3\text{SiNb}$ : C, 55.00; H, 7.13; N, 8.02. Found: C, 55.96; H, 7.11; N, 7.88.

**Preparation of  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\eta^1\text{-N}^t\text{Bu})\}(\text{N}^t\text{Bu})\{\eta^2\text{-C}(\text{NH}^t\text{Bu})=\text{NAr}\}]$  (**7**) ( $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ ).** An equimolar mixture of  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\eta^1\text{-N}^t\text{Bu})\}(\text{N}^t\text{Bu})(\text{NH}^t\text{Bu})]$  (**4**)

(0.90 g, 2.09 mmol) and isocyanide (0.27 g, 2.09 mmol) in hexane (50 mL) was heated to 120 °C for 5 days in a sealed tube. The volatiles were removed under reduced pressure, and the residue was extracted into pentane (2 × 20 mL). The solvent was removed under vacuum from the solution to give a dark red oil characterized as **7** (0.88 g, 1.75 mmol, 75% yield). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, δ): 0.63 (s, 3H, SiMe<sub>2</sub>), 0.73 (s, 3H, SiMe<sub>2</sub>), 1.02 (s, 9H, CMe<sub>3</sub>), 1.25 (s, 9H, CMe<sub>3</sub>), 1.26 (s, 9H, CMe<sub>3</sub>), 2.09 (s, 3H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=C), 2.11 (s, 3H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=C), 5.29 (br s, 1H, NH), 5.84 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 6.14 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 6.63 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 6.70 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 6.80–7.10 (m, Ph). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, δ): 4.2, 4.5 (SiMe<sub>2</sub>), 18.2, 19.4 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=C), 31.1 (CNHCM<sub>3</sub>), 32.7 (Si, Nb-NCM<sub>3</sub>), 35.4 (NbNCMe<sub>3</sub>), 52.5 (CNHCM<sub>3</sub>), 54.7 (Si, Nb-NCM<sub>3</sub>), 65.6 (NbNCMe<sub>3</sub>), 104.6, 109.4 (C<sub>2</sub>-C<sub>5</sub>, C<sub>5</sub>H<sub>4</sub>), 110.1 (C<sub>ipso</sub> C<sub>5</sub>H<sub>4</sub>), 114.5, 116.8 (C<sub>2</sub>-C<sub>5</sub>, C<sub>5</sub>H<sub>4</sub>), 125.4–143.2 (Ph, C<sub>6</sub>H<sub>3</sub>), 196.7 (N=C-NHCM<sub>3</sub>). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, δ): –22.0.

**Preparation of [Nb{η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>(N<sup>t</sup>Bu)-η<sup>2</sup>-(C=NR)}-(N<sup>t</sup>Bu)(CH<sub>2</sub>Ph)] (8) (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).** A mixture of [Nb{η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>(N<sup>t</sup>Bu)-η<sup>2</sup>-(C=NR)}(N<sup>t</sup>Bu)Cl] (**6**) (0.50 g, 0.95 mmol) and Mg(CH<sub>2</sub>Ph)<sub>2</sub>·2THF (0.67 g, 1.90 mmol) in hexane/toluene (50:10 mL) was stirred at room temperature for 24 h. After removal of the solvent under vacuum the residue was extracted into hexane (2 × 20 mL) and the filtrate was concentrated to 10 mL. Cooling to –30 °C gave a brown oily product, which was characterized as **8** (0.41 g, 0.71 mmol, 75% yield). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, δ): 0.43 (s, 3H, SiMe<sub>2</sub>), 0.49 (s, 3H, SiMe<sub>2</sub>), 1.05 (s, 9H, CMe<sub>3</sub>), 1.20 (s, 9H, CMe<sub>3</sub>), 1.72 (s, 3H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=C), 2.20 (d, 1H, J<sub>HH</sub> = 10.2 Hz, CH<sub>2</sub>Ph), 2.27 (s, 3H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=C), 3.22 (d, 1H, J<sub>HH</sub> = 10.2 Hz, CH<sub>2</sub>Ph), 4.84 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 5.72 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 6.11 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 6.21 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 6.80–7.40 (m, Ph). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, δ): 0.3, 3.1 (SiMe<sub>2</sub>), 19.1, 19.3 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=C), 30.1 (Si-NCM<sub>3</sub>), 32.8 (NbNCMe<sub>3</sub>), 38.2 (CH<sub>2</sub>Ph), 57.3 (Si-NCM<sub>3</sub>), 64.6 (NbNCMe<sub>3</sub>), 99.9 (C<sub>2</sub>-C<sub>5</sub>, C<sub>5</sub>H<sub>4</sub>), 102.8 (C<sub>ipso</sub> C<sub>5</sub>H<sub>4</sub>), 106.8, 109.5, 119.8 (C<sub>2</sub>-C<sub>5</sub>, C<sub>5</sub>H<sub>4</sub>), 122.2–156.1 (Ph, C<sub>6</sub>H<sub>3</sub>), 198.6 (N=C-NCM<sub>3</sub>). IR (ν cm<sup>-1</sup>): 1648, 1570, 1368. Anal. Calcd for C<sub>31</sub>H<sub>44</sub>N<sub>3</sub>SiNb: C, 64.21; H, 7.66; N, 7.25. Found: C, 64.44; H, 7.62; N, 7.23.

**Preparation of [Nb{η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>(η<sup>1</sup>-OOCNH<sup>t</sup>Bu)}(η<sup>2</sup>-OOCNH<sup>t</sup>Bu)(N<sup>t</sup>Bu)Cl] (10).** A solution of [Nb{η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>-SiMe<sub>2</sub>(NH<sup>t</sup>Bu)}(N<sup>t</sup>Bu)Cl(NH<sup>t</sup>Bu)] (**2**) (1.50 g, 3.22 mmol) in hexane (50 mL) was stirred overnight at room temperature under a CO<sub>2</sub> atmosphere. The solution was concentrated (15 mL) and cooled to –30 °C to give a gelatinous product. After filtration, pentane (5–10 mL) was added to give a white solid, which was characterized as **10**. Concentration of the mother liquor and subsequent cooling to –30 °C gave a second crop of product (1.51 g, 2.73 mmol, 85% yield). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, δ): 0.72 (s, 3H, SiMe<sub>2</sub>), 0.74 (s, 3H, SiMe<sub>2</sub>), 1.12 (s, 9H, CMe<sub>3</sub>), 1.13 (s, 9H, CMe<sub>3</sub>), 1.15 (s, 9H, CMe<sub>3</sub>), 4.72 (br s, 1H, NH), 5.52 (br s, 1H, NH), 6.33 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 6.64 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 6.90 (m, 1H, C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, δ): –0.9, –0.5 (SiMe<sub>2</sub>), 28.7 (CNHCM<sub>3</sub>), 29.1 (CNHCM<sub>3</sub>), 30.4 (NbNCMe<sub>3</sub>), 49.9 (CNHCM<sub>3</sub>), 50.7 (CNHCM<sub>3</sub>), 69.3 (NbNCMe<sub>3</sub>), 105.7, 107.5, 116.4, 126.6 (C<sub>2</sub>-C<sub>5</sub>, C<sub>5</sub>H<sub>4</sub>) (C<sub>ipso</sub> not observed), 153.3, 167.4 (CO<sub>2</sub>NH). IR (ν cm<sup>-1</sup>): 3390, 3323, 1694, 1587, 1367. Anal. Calcd for C<sub>21</sub>H<sub>39</sub>ClN<sub>3</sub>O<sub>4</sub>SiNb: C, 45.52; H, 7.11; N, 7.58. Found: C, 45.08; H, 7.23; N, 7.25.

**Preparation of [Nb(N<sup>t</sup>Bu)Cl]<sub>2</sub>{η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>-O-SiMe<sub>2</sub>-η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>} (11).** Method A. Water (25 μL, 1.27 mmol) was added to a solution of [Nb(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>Cl)(N<sup>t</sup>Bu)Cl]<sub>2</sub> (1.00 g, 2.55 mmol) and NEt<sub>3</sub> (0.35 mL, 2.55 mmol) in toluene (50 mL). The reaction mixture was stirred at room temperature for 12 h. After removal of the solvent under vacuum, the residue was extracted into hexane (2 × 20 mL) and the solvent was again removed to give a yellow solid characterized as **11** (0.65 g, 0.89 mmol, 70% yield).

**Method B.** A solution of [Nb(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>NH<sup>t</sup>Bu)(N<sup>t</sup>Bu)Cl]<sub>2</sub> (**1**) (1.00 g, 2.33 mmol) in toluene (50 mL) was stirred for 6 h at 140 °C under CO<sub>2</sub> atmosphere in a sealed tube. The

**Table 4. Crystal, Experimental Data, and Structure Refinement Procedures for Compound 13**

formula	C <sub>22</sub> H <sub>38</sub> Cl <sub>2</sub> O <sub>2</sub> N <sub>2</sub> Si <sub>2</sub> Nb <sub>2</sub>
M <sub>w</sub>	675.44
cryst habit	prismatic
color	yellow
cryst size	0.22 × 0.25 × 0.30 mm
symmetry	triclinic, P1
unit cell dimens	
a (Å)	7.437(1)
b (Å)	8.818(1)
c (Å)	11.819(1)
α (deg)	78.24(1)
β (deg)	80.97(1)
γ (deg)	81.65(1)
V, Å <sup>3</sup>	744.25(15)
Z	1
D <sub>calc</sub> , g cm <sup>-3</sup>	1.507
F(000)	344
μ, cm <sup>-1</sup>	10.50
scan mode	ω/2θ, 2.38 < θ < 24.97
no. of reflns	
measd	2840
indep	2620
obsd	2471 (I > 2σ(I))
range of hkl	0 < h < 8, –10 < k < 10, –13 < l < 14
standard reflns	3 every 200 reflns
refinement method	full matrix least squares on F <sup>2</sup>
final R indices all data <sup>a</sup>	R1 = 0.0240, wR2 = 0.0604
final R indices I > 2σ(I)	R1 = 0.0219, wR2 = 0.0591
weighting scheme params <sup>b</sup>	
x	0.0402
y	0.3461
largest diff peak	0.88
and hole e/Å <sup>3</sup>	–0.87
goodness of fit on F <sup>2</sup>	1.011

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

resulting solution was cooled to room temperature to give a white crystalline solid, which was characterized as (NH<sup>t</sup>Bu)<sub>2</sub>CO. After filtration the solvent was removed under vacuum and the residue was extracted into hexane (4 × 25 mL). Removal of the solvent under vacuum gave a yellow solid, which was characterized as **11** (0.64 g, 0.88 mmol, 75% yield). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, δ): 0.45 (s, 12H, SiMe<sub>2</sub>), 1.07 (s, 18H, CMe<sub>3</sub>), 6.08 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 6.47 (m, 4H, C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, δ): 1.6 (SiMe<sub>2</sub>), 30.3 (NbNCMe<sub>3</sub>), 69.5 (NbNCMe<sub>3</sub>), 109.9, 122.5 (C<sub>2</sub>-C<sub>5</sub>, C<sub>5</sub>H<sub>4</sub>), 125.3 (C<sub>ipso</sub> C<sub>5</sub>H<sub>4</sub>). IR (ν cm<sup>-1</sup>): 1370, 1080. Anal. Calcd for C<sub>22</sub>H<sub>38</sub>Cl<sub>4</sub>N<sub>2</sub>Si<sub>2</sub>ONb<sub>2</sub>: C, 36.18; H, 5.24; N, 3.84. Found: C, 36.22; H, 5.50; N, 4.03.

**Preparation of [Nb(N<sup>t</sup>Bu)(CH<sub>2</sub>Ph)<sub>2</sub>]{η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>-O-SiMe<sub>2</sub>-η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>} (12).** C<sub>6</sub>D<sub>6</sub> was added to a mixture of [Nb(N<sup>t</sup>Bu)Cl]<sub>2</sub>{η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>-O-SiMe<sub>2</sub>-η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>} (**11**) (0.020 g, 0.028 mmol) and Mg(CH<sub>2</sub>Ph)<sub>2</sub>·2THF (0.039 g, 0.11 mmol) in a Teflon-valved NMR tube. After 3 h at room temperature the formation of **12** was demonstrated by the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the solution. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, δ): 0.38 (s, 12H, SiMe<sub>2</sub>), 1.12 (s, 18H, CMe<sub>3</sub>), 1.67 (d, 4H, J<sub>HH</sub> = 8.1 Hz, CH<sub>2</sub>Ph), 1.97 (d, 4H, J<sub>HH</sub> = 8.1 Hz, CH<sub>2</sub>Ph), 5.55 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 5.97 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 6.85–7.50 (m, Ph). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, δ): 2.13 (SiMe<sub>2</sub>), 31.8 (NbNCMe<sub>3</sub>), 41.2 (CH<sub>2</sub>Ph), 66.5 (NbNCMe<sub>3</sub>), 106.4, 113.5 (C<sub>2</sub>-C<sub>5</sub>, C<sub>5</sub>H<sub>4</sub>), 113.1 (C<sub>ipso</sub> C<sub>5</sub>H<sub>4</sub>), 125.0, 128.7, 130.3, 139.9 (Ph).

**Preparation of [Nb(N<sup>t</sup>Bu)Cl-μ-(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>-η-O)]<sub>2</sub> (13) + [Nb(N<sup>t</sup>Bu)Cl]<sub>2</sub>{μ-O}{η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>-O-SiMe<sub>2</sub>-η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>} (14).** A solution of [Nb{η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>(η<sup>1</sup>-N<sup>t</sup>Bu)}(N<sup>t</sup>Bu)Cl] (**3**) (1.50 g, 3.82 mmol) in toluene (50 mL) was stirred for 6 days at room temperature under CO<sub>2</sub> atmosphere. The solvent was removed under vacuum, and the residue was extracted into hexane (3 × 25 mL). The filtrate was concentrated (15 mL) under reduce pressure and cooled to –30 °C to give yellow crystals, which were characterized as **13** (1.10 g, 1.62 mmol, 85% yield). Anal. Calcd for C<sub>22</sub>H<sub>38</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Si<sub>2</sub>Nb<sub>2</sub>: C, 39.11; H,



5.68; N, 4.15. Found: C, 38.84; H, 5.99; N, 4.10. Solutions of **13** contain a mixture of two isomers in a ratio 1:3. Data for the major component:  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ ): 0.40 (s, 6H,  $\text{SiMe}_2$ ), 0.57 (s, 6H,  $\text{SiMe}_2$ ), 1.13 (s, 18H,  $\text{CMe}_3$ ), 6.16 (m, 2H,  $\text{C}_5\text{H}_4$ ), 6.40 (m, 2H,  $\text{C}_5\text{H}_4$ ), 6.47 (m, 2H,  $\text{C}_5\text{H}_4$ ), 6.51 (m, 2H,  $\text{C}_5\text{H}_4$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ ): 0.9, 1.9 ( $\text{SiMe}_2$ ), 31.3 ( $\text{CMe}_3$ ), 67.9 ( $\text{CMe}_3$ ), 107.2, 111.2, 117.5, 125.2 ( $\text{C}_2\text{-C}_5$ ,  $\text{C}_5\text{H}_4$ ), 123.8 ( $\text{C}_{\text{ipso}}$   $\text{C}_5\text{H}_4$ ). Data for the minor component:  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ ): 0.43 (s, 6H,  $\text{SiMe}_2$ ), 0.44 (s, 6H,  $\text{SiMe}_2$ ), 1.15 (s, 18H,  $\text{CMe}_3$ ), 6.29 (m, 4H,  $\text{C}_5\text{H}_4$ ), 6.51 (m, 2H,  $\text{C}_5\text{H}_4$ , overlapped), 6.55 (m, 2H,  $\text{C}_5\text{H}_4$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ ): 1.1, 1.5 ( $\text{SiMe}_2$ ), 31.3 ( $\text{CMe}_3$ ) overlapped, 67.9 ( $\text{CMe}_3$ ) overlapped, 108.6, 113.4, 116.6, 124.6 ( $\text{C}_2\text{-C}_5$ ,  $\text{C}_5\text{H}_4$ ), 123.5, ( $\text{C}_{\text{ipso}}$   $\text{C}_5\text{H}_4$ ).

**Crystal Structure Determination of 13.** Yellow crystals of compound **13** were obtained by crystallization from toluene at  $-30^\circ\text{C}$ , and a suitable sized crystal was sealed under argon in a Lindemann capillary tube and mounted in an Enraf-Nonius CAD 4 automatic four-circle diffractometer with graphite-monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Crystallographic and experimental details are summarized in Table 4. Data were collected at room temperature. 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 (SHELXS 97)<sup>23</sup> and refined by least squares against  $F^2$  (SHELXL 97).<sup>23</sup> All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced from geometrical calculations and refined using a riding model with thermal parameters equivalent to that of the C atom to which they were attached. The final  $R$  values and other interesting X-ray structural analysis data are presented in Table 2.

**Acknowledgment.** We thank the Dirección General de Enseñanza Superior e Investigación Científica (DGE-SIC) for financial support of this work (Project PB97-0776).

**Supporting Information Available:** Tables of positional parameters and estimated standard deviations, bond distances and angles, anisotropic displacement parameters, and hydrogen coordinates for **13**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0103963

(23) Sheldrick, G. M. *SHELX-97, Programs for Crystal Structure Analysis (Release 97-2)*; Universität Göttingen: Göttingen, Germany, 1998.