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Chlorosilyl-Substituted Monocyclopentadienyl Niobium Chloro, Imido Chloro, and Benzyl Complexes. X-ray Molecular Structure of $[\{(NbCl_2)_2(\mu\text{-}O)(\mu\text{-}Cl)_2\}\{(\eta^5\text{-}C_5H_4)_2(Me_2SiOSiMe_2)\}]$

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We report the synthesis of 1-(chloromethylphenylsilyl)cyclopentadiene. The reaction of a toluene/CH_2Cl_2 suspension of $NbCl_5$ with 1-(SiClMeX)-1-($SiMe_3$)C_5H_4 (X = Me, Ph) leads to the monocyclopentadienyl derivatives $[M\{\eta^5\text{-}C_5H_4(SiClMeX)\}Cl_4]$ (X = Me, Ph) in 90 and 78% yields, respectively. Reaction of 1 equiv of water with $[M\{\eta^5\text{-}C_5H_4(SiClMe_2)\}Cl_4]$ in toluene takes place with elimination of HCl, resulting in formation of the dinuclear niobium oxo derivative $[\{(NbCl_2)_2(\mu\text{-}O)(\mu\text{-}Cl)_2\}\{(\eta^5\text{-}C_5H_4)_2(Me_2SiOSiMe_2)\}]$. Reaction of the complexes $[M\{\eta^5\text{-}C_5H_4(SiClMeX)\}Cl_4]$ with $LiNH^tBu$ and NEt_3 in toluene leads to the half-sandwich imido complexes $[Nb\{\eta^5\text{-}C_5H_4(SiClMeX)\}Cl_2(N^tBu)]$ (X = Me, Ph), which react at room temperature with 1 equiv of $Mg(CH_2Ph)_2(THF)_2$ to give the imido dibenzyl complexes $[Nb\{\eta^5\text{-}C_5H_4(SiClMeX)\}(CH_2Ph)_2(N^tBu)]$ (X = Me, Ph). The reaction of the chloro imido complexes $[Nb\{\eta^5\text{-}C_5H_4(SiClMeX)\}Cl_2(N^tBu)]$ with excess $Mg(CH_2Ph)_2(THF)_2$ on heating for 2−3 days to 80−90 and 50−60 °C, respectively, takes place, affording the totally alkylated complexes $[Nb\{\eta^5\text{-}C_5H_4[Si(CH_2Ph)MeX]\}(CH_2Ph)_2(N^tBu)]$ (X = Me, Ph). The chloro benzyl derivative $[Nb\{\eta^5\text{-}C_5H_4(SiClMe_2)\}(CH_2Ph)Cl(N^tBu)]$, which could not be prepared by addition of the stoichiometric amount of the alkylating agent, was isolated in quantitative yield by heating a mixture of the dichloro and dibenzyl complexes in toluene at 120 °C for 4 h. The 18-electron imido η^2-iminoacyl derivatives $[Nb\{(\eta^5\text{-}C_5H_4(SiMeXY)\}R(N^tBu)\{\eta^2\text{-}C(CH_2Ph){=}N\text{-}(2,6\text{-}Me_2C_6H_3)\}]$ (R = CH_2Ph, X = Cl, Y = Me, Ph; R = CH_2Ph, X = CH_2Ph, Y = Me, Ph; R = Cl, X = Cl, Y = Me) are formed when the isocyanide CN(2,6-$Me_2C_6H_3$) is added to a hexane solution of the benzylimido complexes. The molecular structure of the oxo complex $[\{(NbCl_2)_2(\mu\text{-}O)(\mu\text{-}Cl)_2\}\{(\eta^5\text{-}C_5H_4)_2(Me_2SiOSiMe_2)\}]$ has been determined by X-ray diffraction methods.

1. Introduction

The presence of different ring substituents in cyclopentadienylmetal complexes has significant steric and electronic effects on the metal center, whose behavior can also be modeled to the required objectives in bonding appropriate ligands in its coordination sphere. Trimethylsilyl-substituted rings have been extensively used[1] to transfer the ring to niobium and tantalum halides by elimination of chlorotrimethylsilane, providing one of the most convenient reactions to prepare monocyclopentadienyl-type metal compounds.

The imido group is a strong π-donor ligand that very conveniently stabilizes high-valent metal complexes,[2] and acting as a four-electron donor, it is isolobal with the cyclopentadienyl group,[3] thus providing group 5 metal complexes isoelectronic with the very well-known group 4 metal dicyclopentadienyl derivatives $[M(\eta^5\text{-}C_5R_5)_2X_2]$ (M = Ti, Zr, Hf) extensively used as Ziegler−Natta catalysts.

Reactions based on carbon−carbon bond formation have led to many important synthetic applications of organo group 5 metal complexes by migration of alkyl substituents to unsaturated carbonyl[4] and isocyanide[5] ligands through the intermediate formation of acyl- and (iminoacyl)metal complexes. This prompted us to extend our previous studies to the chemistry of niobium.

We report herein the synthesis of the new disilyl-substituted cyclopentadienyl ligand (SiClMePh)($SiMe_3$)-C_5H_4 and the use of this and the already reported ($SiClMe_2$)($SiMe_3$)C_5H_4 compound to isolate the tetra-

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[†] X-ray diffraction studies.

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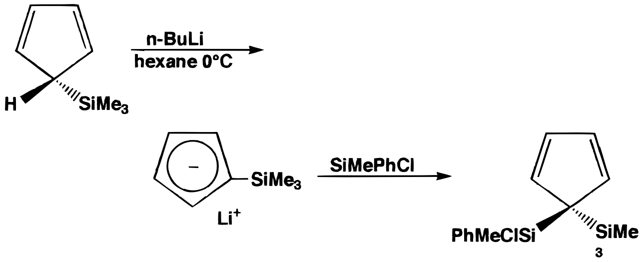
Scheme 1



chloro(η^5-cyclopentadienyl)niobium complexes [M{η^5-$C_5H_4(SiClMeX)$}Cl_4] (X = Me, Ph) and their *tert*-butylimido chloro and benzyl derivatives [Nb{η^5-C_5H_4(SiMeXY)}$R_2(N^tBu)$] (R = Cl, CH_2Ph; X = Me, Ph; Y = Cl, CH_2Ph). We report also the insertion reactions of isocyanides into niobium−benzyl bonds, leading to the iminoacyl complexes [Nb{(η^5-C_5H_4(SiMeXY)}R(N^tBu)-{η^2-C(CH_2Ph)=N(2,6-$Me_2C_6H_3$)}], and the X-ray molecular structure of the oxo derivative [{$(NbCl_2)_2(\mu$-O)(μ-$Cl)_2$}{(η^5-$C_5H_4)_2(Me_2SiOSiMe_2)$}], which results from the hydrolysis of the tetrachloro complex [M{η^5-C_5H_4($SiClMe_2$)}Cl_4].

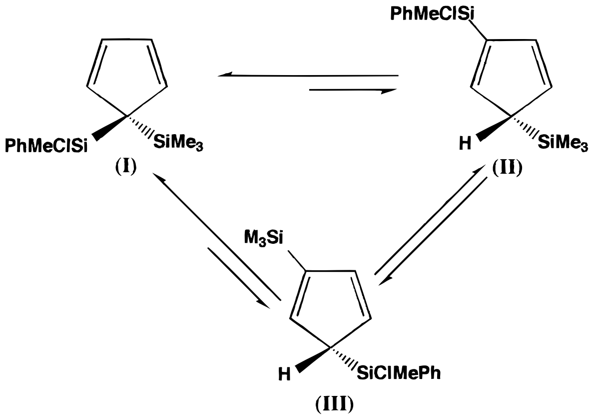
2. Results and Discussion

2.1. Synthesis of Silylcyclopentadiene Precursors. The synthesis of 1-(chlorodimethylsilyl)-1-(trimethylsilyl)cyclopentadiene (**1**) was effected by following the method previously reported,[6] which consists of the reaction of the lithium salt of the (trimethylsilyl)cyclopentadienyl anion with dichlorodimethylsilane, and a similar method was used to synthesize 1-(chloromethylphenylsilyl)-1-(trimethylsilyl)cyclopentadiene (**2**). The reaction of a solution of 1-(trimethylsilyl)cyclopenta-2,4-diene in hexane with *n*-butyllithium at 0 °C allowed us to obtain a suspension of a white insoluble lithium salt, which after addition of chloromethylphenylsilane reacted to yield a yellow liquid soluble in hexane (Scheme 1). The excess of the starting silane was removed by distillation (65 °C/1 × 10^{-2} mmHg) to give the required product as a yellow liquid which can be stored in the dark under an inert atmosphere for several months (yield 70%).

This liquid was identified by ^1H NMR spectroscopy as an equilibrium mixture of the isomers shown in Scheme 2, in which 1-(chloromethylphenylsilyl)-1-(trimethylsilyl)cyclopentadiene (**I**) is the major component in a ratio of 80% with respect to **II** and **III**, identified by the broad and weak signals observed at ca. δ 3.2, corresponding to sp^3-C-bonded protons, along with other weak signals at δ −0.03 and δ 0.82 due to trimethylsilyl and chloromethylphenylsilyl protons.

2.2. Synthesis and Characterization of Niobium Chloro Cyclopentadienyl Complexes. Compounds **1** and **2** reacted with 1 equiv of $NbCl_5$ in toluene/dichloromethane at room temperature with elimination of $SiClMe_3$ to give the corresponding monocyclopentadienyl complexes [Nb{η^5-C_5H_4(SiClMeX)}Cl_4] (X = Me (**3**), Ph (**4**)) (see Scheme 3). The dark orange complexes **3** and **4** were isolated in 80−90% yield by cooling their red solutions at −20 °C.

Scheme 2



The ^1H NMR spectra of both complexes show the expected resonances for the methyl groups bonded to silicon. Two multiplets corresponding to an AA′BB′ spin system are observed for the cyclopentadienyl ring protons in complex **3**, whereas the presence of the chiral silicon atom is responsible for the four multiplets observed in complex **4** for the ring protons. These assignments were confirmed by the ^{13}C NMR spectra.

Compounds **3** and **4** were found to be moisture- and oxygen-sensitive compounds which can be stored for a long time in the solid state under an inert atmosphere. They are soluble in dichloromethane, chloroform, and aromatic solvents but insoluble in alkanes.

2.3. Hydrolysis of Complex 3. The different reactivities of the two different types of Si−Cl and Nb−Cl bonds were studied for complex **3** in relation to its hydrolysis. Addition of 1 equiv of water to its toluene solution at room temperature (see Scheme 3) led to the formation of an insoluble crystalline orange solid, which was identified as the oxo complex [{$(NbCl_2)_2(\mu$-O)(μ-$Cl)_2$}{(η^5-$C_5H_4)_2(Me_2SiOSiMe_2)$}] (**5**) by an X-ray diffraction study of its molecular structure, although its NMR characterization was prevented by its lack of solubility in appropriate solvents. The same compound was also formed when the quantity of water was limited to 0.5 equiv, leaving unreacted starting material. This behavior reveals that both Si−Cl and Nb−Cl bonds show similar reactivities and are simultaneously hydrolyzed.

Dinuclear complex **5** and toluene molecules of solvation are present in the crystals. The structure of **5** is shown in Figure 1 together with the atomic labeling scheme. Selected bond angles and distances are given in Table 1.

The structure of **5** shows two niobium atoms with slightly distorted pseudo-octahedral coordination, each niobium being bonded to one apical ring of the bridging [(η^5-$C_5H_4)_2(Me_2SiOSiMe_2)$] fragment in a slightly asymmetric η^5-fashion (the Nb(1)−C distances range from 2.389(4) to 2.469(3) Å; those of Nb(2)−C are in the range 2.396(4)−2.437(4) Å), two terminal and two bridging chlorine atoms, and one bridging oxygen. The two octahedra share one face defined by two chlorine atoms, each occupying one axial position trans to the cyclopentadienyl ring of one octahedron (Cp(1)−Nb(1)−Cl(3) and Cp(2)−Nb(2)−Cl(4) angles are 174.3 and 171.9°, respectively) and one equatorial position of the other, and the oxygen atom, which occupies one equatorial position of

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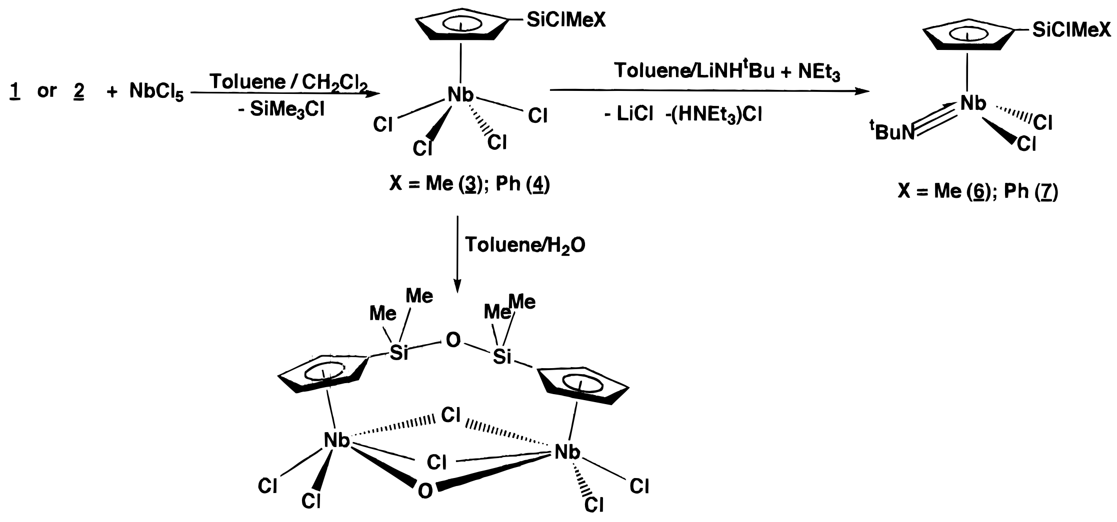
Scheme 3



5

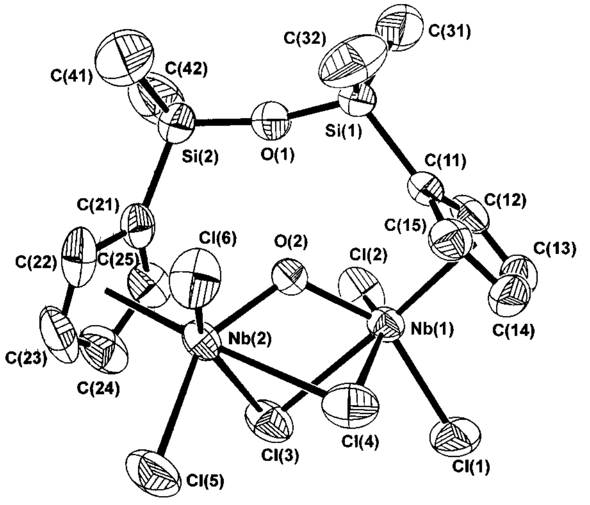


Figure 1. ORTEP drawing of the molecular structure of compound **5**$\cdot C_6H_5Me$ together with the atomic labeling scheme.

both octahedra with a Nb(1)−O(2)−Nb(1) angle of 120.9(1)° and similar Nb(1)−O(2) and Nb(2)−O(2) distances to both niobium atoms (average 1.898(2) Å). In these octahedra Nb(1) is located 0.580 Å above the plane Cl(1)−Cl(2)−Cl(4)−O(2) (maximum deviation 0.110 Å for O(2)), which is almost parallel to the Cp(1) plane (1.13°) while Nb(2) is 0.592 Å above the plane O(2)−Cl(3)−Cl(5)−Cl(6) (maximum deviation 0.088 Å for O(2)), adopting an angle of 2.73° with the Cp(2) plane. This structural disposition is similar to that found for the dinuclear (μ-oxo)niobium complex $[\{Nb(\eta^5\text{-}C_5H_4SiMe_3)Cl_2\}_2(\mu\text{-}O)(\mu\text{-}Cl)_2]$,[7] containing a terminal instead of a bridging cyclopentadienyl system, whereas (pentamethylcyclopentadienyl)molybdenum $(\{Mo(\eta^5\text{-}C_5Me_5)Cl\}_2(\mu\text{-}O)(\mu\text{-}Cl)_2)$[8] and -zirconium $(\{Zr(\eta^5\text{-}C_5Me_5)Cl\}_3(\mu_3\text{-}O)(\mu_2\text{-}Cl)_4)$[9] derivatives, which also display similar face-sharing octahedral units, always have the bridging oxygen trans to the pentamethylcyclopentadienyl rings.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 5

Nb(1)−O(2)	1.908(2)	Nb(1)−Cl(1)	2.378(1)
Nb(1)−Cl(2)	2.390(1)	Nb(1)−Cl(3)	2.701(1)
Nb(1)−Cl(4)	2.554(1)	Nb(1)−Nb(2)	3.302(1)
Nb(2)−O(2)	1.888(2)	Nb(2)−Cl(3)	2.559(1)
Nb(2)−Cl(4)	2.774(1)	Nb(2)−Cl(5)	2.382(1)
Nb(2)−Cl(6)	2.378(1)	Si(1)−O(1)	1.604(3)
Si(2)−O(1)	1.611(3)	Nb(1)−Cp(1)	2.109
Nb(2)−Cp(2)	2.108		
O(2)−Nb(1)−Cl(1)	149.16(8)	O(2)−Nb(1)−Cl(2)	93.12(8)
Cl(1)−Nb(1)−Cl(2)	92.31(5)	O(2)−Nb(1)−Cl(4)	75.51(8)
Cl(1)−Nb(1)−Cl(4)	85.38(5)	Cl(2)−Nb(1)−Cl(4)	151.29(4)
O(2)−Nb(1)−Cl(3)	72.08(8)	Cl(1)−Nb(1)−Cl(3)	79.14(4)
Cl(2)−Nb(1)−Cl(3)	79.47(4)	Cl(4)−Nb(1)−Cl(3)	71.99(4)
O(2)−Nb(2)−Cl(6)	94.31(8)	O(2)−Nb(2)−Cl(5)	147.46(8)
Cl(6)−Nb(2)−Cl(5)	91.53(5)	O(2)−Nb(2)−Cl(3)	75.94(8)
Cl(6)−Nb(2)−Cl(3)	151.22(4)	Cl(5)−Nb(2)−Cl(3)	83.67(5)
O(2)−Nb(2)−Cl(4)	70.28(8)	Cl(6)−Nb(2)−Cl(4)	80.50(4)
Cl(5)−Nb(2)−Cl(4)	79.22(4)	Cl(3)−Nb(2)−Cl(4)	70.72(4)
O(1)−Si(1)−C(11)	112.1(2)	O(1)−Si(2)−C(21)	111.3(2)
Nb(2)−Cl(3)−Nb(1)	77.71(3)	Nb(1)−Cl(4)−Nb(2)	76.47(3)
Si(1)−O(1)−Si(2)	157.3(3)	Nb(2)−O(2)−Nb(1)	120.9(1)
Cp(1)−Nb(1)−Cl(1)	104.7	Cp(1)−Nb(1)−Cl(2)	104.4
Cp(1)−Nb(1)−Cl(3)	174.3	Cp(1)−Nb(1)−Cl(4)	103.9
Cp(1)−Nb(1)−O(2)	103.2	Cp(2)−Nb(2)−Cl(3)	103.2
Cp(2)−Nb(2)−Cl(4)	171.9	Cp(2)−Nb(2)−Cl(5)	105.9
Cp(2)−Nb(2)−Cl(6)	105.4	Cp(2)−Nb(2)−O(2)	103.3

The bridging tetramethylsiloxane group shows an open Si(1)−O(1)−Si(2) angle of 157.3(3)° with average C(11)-(C(21))−Si(1)(Si(2))−O(1) angles of 111.7(2)° and is long enough to allow the cyclopentadienyl ligands to behave as almost independent rings, allowing the structure to be similar to the dinuclear niobium complex $[\{Nb(\eta^5\text{-}C_5H_4SiMe_3)Cl_2\}_2(\mu\text{-}O)(\mu\text{-}Cl)_2]$[7] with independent rings.

The most remarkable features are the longer Nb−Cl distances observed for the bridging chlorine atoms trans to the cyclopentadienyl rings (Nb(1)−Cl(3), 2.701(1) Å; Nb(2)−Cl(4), 2.774(1) Å) in comparison with those corresponding to the equatorial chlorines (Nb(1)−Cl(4), 2.554(1) Å; Nb(2)−Cl(3), 2.559(1) Å), indicating the higher electron donation of the rings and providing asymmetric bridges. All of the terminal Nb−Cl bond distances are shorter, in the expected range between 2.377(1) and 2.390(1) Å. The same behavior was also observed for the dinuclear niobium complex mentioned above.

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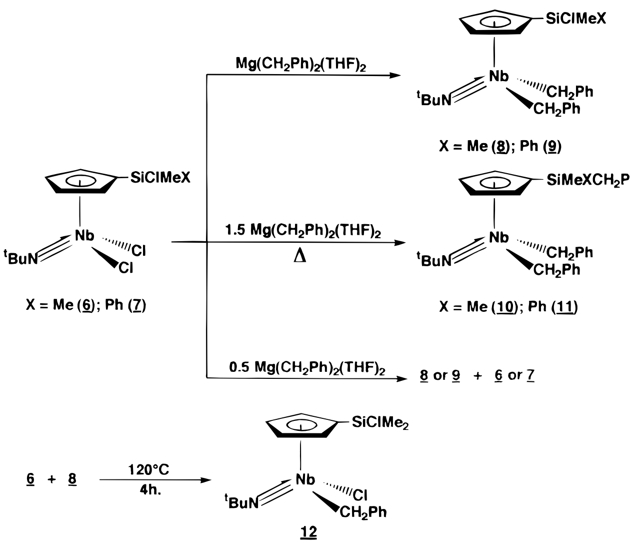
2.4. Synthesis and Characterization of Niobium Imido Cyclopentadienyl Complexes. A second strategy to compare the reactivities of the Si−Cl and Nb−Cl bonds was based on the study of reactions with secondary lithium amides. Related reactions with dicyclopentadienyltitanium dichloride have been reported[10] to lead to the formation of constrained monomeric cyclic species containing the pendant amido group of the cyclopentadienyl ligand coordinated to the metal center. Therefore, in this case, simultaneous substitution of both Ti−Cl and Si−Cl bonds by a bridging NR group takes place with elimination of LiCl and HCl. Reactions of complexes **3** and **4** with 1 equiv of the secondary amide LiNH^{t}Bu in the presence of NEt_3 in toluene (Scheme 3) also occur with elimination of LiCl and the ammonium salt $(NHEt_3)Cl$ to give solutions which after evaporation and convenient purification afford yellow crystalline solids characterized by elemental analyses as the corresponding substitution products containing the N^{t}Bu group, which could be formulated either as those related to the titanium analogues with the chelating cyclopentadienyl silylamido ligand of constrained geometry [Nb{η^5-C_5H_4[SiMeX(η^1-N^{t}Bu)]}Cl_3] or as imidoniobium complexes[11] containing the unreacted silyl group [Nb{η^5-C_5H_4(SiClMeX)}Cl_2(N^{t}Bu)]. The ^{1}H and ^{13}C NMR spectra of these compounds show a behavior similar to that discussed above for the tetrachloro complexes **3** and **4**, which does not provide a definitive answer about their stuctures (see Experimental Section). However, a definitive structural assignment as an imidoniobium complex was made for [Nb{η^5-C_5H_4(SiClMeX)}Cl_2(N^{t}Bu)] (X = Me (**6**), Ph (**7**)) on the basis of its ^{29}Si NMR spectrum which shows the silicon resonance at δ 8.34 and 6.53 ppm, respectively, in the same range observed for the starting chloro complex **3**, in comparison with the silicon resonance corresponding to silyl amido complexes of constrained geometry, which is observed[12] at higher field in the range of ca. δ 20 ppm.

2.5. Synthesis and Characterization of Niobium Benzyl Imido Complexes. The benzyl ligand can conveniently be introduced by reacting the chloro complexes **6** and **7** with 1 equiv of $Mg(CH_2Ph)_2(THF)_2$ in hexane, affording the dibenzyl complexes [Nb{η^5-C_5H_4(SiClMeX)}$(CH_2Ph)_2$(N^{t}Bu)] (X = Me (**8**), Ph (**9**)) as a brown solid and a dark yellow oil, respectively. This behavior indicates that preferential alkylation of the Nb−Cl bonds takes place, leaving the unmodified chlorosilyl group.[13] However, the Si−Cl bond can also be reacted when a toluene solution of **6** or a hexane solution of **7**, treated with an excess of $Mg(CH_2Ph)_2(THF)_2$, was heated for 2−3 days to 80−90 or 50−60 °C, respectively. Under these conditions slower alkylation of the Si−Cl bond takes place, affording the totally alkylated complexes [Nb{η^5-C_5H_4[Si(CH_2Ph)MeX]}$(CH_2Ph)_2$(N^{t}Bu)] (X = Me (**10**), Ph (**11**)) as brown oils after removal of the solvent and purification. Both are air-sensitive compounds very soluble in alkanes and thermally stable in refluxing toluene.

Scheme 4



The related monoalkylated complexes [Nb{η^5-C_5H_4(SiClMeX)}(CH_2Ph)Cl(N^{t}Bu)] could not be obtained by reaction of the dichloro derivatives with the stoichiometric amount (0.5 equiv) of the alkylating agent because their further alkylation is faster than that of the starting dichloro compounds and always led to a mixture of the dibenzyl derivatives **8** and **9** together with unreacted starting compounds (Scheme 4). However, a quantitative yield of [Nb{η^5-C_5H_4($SiClMe_2$)}(CH_2Ph)Cl(N^{t}Bu)] (**12**) was obtained when a mixture of the dichloro complex **6** and the corresponding dibenzyl compound **8** was heated in toluene at 120 °C for 4 h in a sealed tube. Complex **12** was isolated after removal of the solvent and extraction with hexane as an air-sensitive brown solid which easily retains solvent to become an oily solid. The benzyl complexes **8**−**12** were characterized by NMR spectroscopy (see Experimental Section). The diastereotopic methylene protons of both equivalent benzyl groups for complexes **8** and **10** are observed between δ 1.63 and 1.94 with coupling constants J_{H-H} = 8.0−8.2 Hz, whereas four doublets between δ 1.43 and 1.99 with coupling constants J_{H-H} = 7.5−8.2 Hz are observed for complexes **9** and **11** due to the presence of a silicon chiral center. Moreover, complex **10** shows one additional singlet for the methylene protons of the benzyl group bonded to silicon, whereas they are observed as one multiplet at δ 2.48 in $CDCl_3$ for complex **11** due to the chiral silicon.

The niobium atom in complex **12** is a chiral center which makes both methylsilicon and ring protons nonequivalent, the methylene protons of the benzyl ligand being observed as two doublets between δ 2.77 and 3.20 with the coupling constant J_{H-H} = 7.1 Hz.

2.6. Reactions of Benzyl Complexes with Isocyanide. When CN(2,6-$Me_2C_6H_3$) is added to hexane solutions of the alkylimido complexes **8**−**12**, an instantaneous insertion reaction takes place to give the 18-electron imido η^2-iminoacyl derivatives [Nb{(η^5-C_5H_4(SiMeXY)}R(N^{t}Bu){η^2-C(CH_2Ph)=N(2,6-$Me_2C_6H_3$)}] (R = CH_2Ph, X = Cl, Y = Me (**13**), Ph (**14**); R = CH_2Ph, X = CH_2Ph, Y = Me (**15**), Ph (**16**); R = Cl, X = Cl, Y = Me (**17**)) as shown in Scheme 5.

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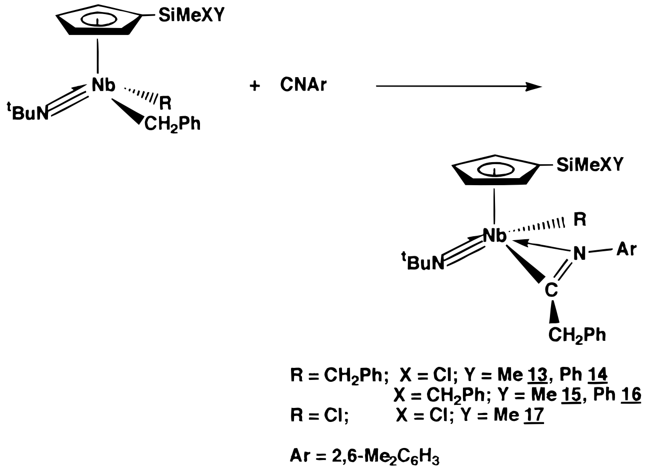
Scheme 5



The migration of the second benzyl group[14] does not take place, and the presence of an excess of isocyanide, at room temperature, does not produce a second insertion reaction in the Nb−CH$_2$Ph or Nb−C(iminoacyl) bonds.[4b,15] The presence of the η^2-iminoacyl group is confirmed by the ^{13}C resonance δ ~230 (η^2-PhH$_2$C-*C*═NAr) and the ν(C═N) IR band at 1624−1642 cm^{-1}. Complexes **14** and **16** have two chiral centers, and their ^{1}H NMR spectra show the signals expected for the two pairs of diastoreomers *RR*/*SS* and *RS*/*SR*.

3. Conclusions

Tetrachloro silyl-substituted cyclopentadienyl complexes of niobium are isolated by reaction of NbCl$_5$ with 1-(SiClMeX)-1-(SiMe$_3$)C$_5$H$_4$ (X = Me, Ph) with elimination of SiClMe$_3$. Unselective hydrolysis of both Si−Cl and Nb−Cl bonds takes place simultaneously in the presence of water to give the oxo derivative [{(NbCl$_2$)$_2$-(μ-O)(μ-Cl)$_2$}{(η^5-C$_5$H$_4$)$_2$(Me$_2$SiOSiMe$_2$)}], whose X-ray crystal structure reveals the presence of Si−O−Si and Nb−O−Nb bridged systems. Reaction of the tetrachloro monocyclopentadienyl complexes with LiNH^{t}Bu and NEt$_3$ leads to the corresponding imido compounds, which can be selectively alkylated by Mg(CH$_2$Ph)$_2$·2THF to give the dibenzylniobium derivatives, whereas the monobenzyl complex results from rearrangement between the dichloro and the dibenzyl complexes. Further alkylation of the Si−Cl bond requires heating in the presence of an excess of the alkylating agent. All of the benzyl−niobium compounds react rapidly with CN(2,6-Me$_2$C$_6$H$_3$) by insertion of the isocyanide into only one of the niobium−benzyl bonds to give 18-electron η^2-iminoacyl complexes. The structural characterization of all the new niobium compounds reported was made by ^{1}H and ^{13}C NMR spectroscopy.

4. Experimental Section

All manipulations were performed under an inert atmosphere (argon) using Schlenk and high-vacuum-line techniques or a VAC Model HE 453 glovebox. Solvents were purified by distillation from an appropiate drying/deoxygenating agent (phosphorus pentoxide for dichloromethane, sodium for toluene, and sodium/potassium alloy for hexane). C$_5$H$_5$SiMe$_3$ and Mg(CH$_2$Ph)$_2$(THF)$_2$ were prepared according to literature procedures. *n*-BuLi, ^{t}BuNH$_2$, SiMe$_2$Cl$_2$, SiMePhCl$_2$, CNR (R = 2,6-Me$_2$C$_6$H$_3$), and NbCl$_5$ were obtained commercially. ^{1}H and ^{13}C NMR spectra were recorded on Varian Unity FT-300 and Varian FT-500 Unity Plus instuments, and chemical shifts were measured relative to residual ^{1}H and ^{13}C resonances in the deuterated solvents C$_6$D$_6$ (δ 7.15), CDCl$_3$ (δ 7.24) and C$_6$D$_6$ (δ 128), CDCl$_3$ (δ 77), respectively. IR spectra were recorded on a Perkin-Elmer 583 spectrophotometer (4000−200 cm^{-1}) as Nujol mulls between CsI pellets. Mass spectra were recorded on an HP 5988 A instrument. C, H, and N analyses were carried out with a Perkin-Elmer 240C microanalyzer. Elemental analyses for liquid compounds **9**−**11** and **14**−**16**, which partially decompose by sublimation, gave unacceptable deviations (1.5−2.0% for C).

4.1. Preparation of 1-(SiClMePh)-1-(SiMe$_3$)C$_5$H$_4$ (2). A 1.6 M hexane solution of *n*-butyllithium (50.0 mL, 80.0 mmol) was added dropwise at 0 °C to a solution of freshly distilled C$_5$H$_5$SiMe$_3$ (13.4 mL, 11.1 g, 80.0 mmol) in hexane (200 mL). The reaction mixture was slowly warmed to room temperature and stirred for 3 h to afford a white precipitate, which after filtration was washed with hexane (3 × 30 mL). A suspension of this white solid in hexane (200 mL) was inmediately treated with SiCl$_2$MePh (13.0 mL, 15.3 g, 80.0 mmol) at room temperature, and the reaction mixture was stirred for 12 h. After filtration the solvent was removed by evaporation under vacuum to give a yellow oil, which was characterized as compound **2** (16.4 g, 55.9 mmol, 70% yield). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, δ): −0.17 (s, 9H, Si*Me$_3$*, major component), −0.03 (s, 9H, Si*Me$_3$*, minor component), 0.36 (s, 3H, SiCl*Me*Ph, major component), 0.83 (s, 3H, SiCl*Me*Ph, minor component), 6.50−6.80 (m, C$_5$*H$_4$*), 7.30−7.70 (m, SiClMe*Ph*). ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C, δ): −2.2, −1.7, −1.1 (Si*Me$_3$*, SiCl*Me*Ph), 48.4, 57.8 (*C$_5$*H$_4$ *ipso*), 127.1, 127.5, 127.9, 129.7, 129.8, 131.2, 132.5, 133.2, 133.4, 133.6, 134.6, 140.9, 146.2 (*C$_5$*H$_4$, *Ph*).

4.2. Preparation of [Nb{η^5-C$_5$H$_4$(SiClMeX)}Cl$_4$] (X = Me, 3; X = Ph, 4). 1-(SiClMeX)-1-(SiMe$_3$)(C$_5$H$_4$) (X = Me, 4.26 mL, 3.84 g, 16.66 mmol; X = Ph, 4.87 g, 16.66 mmol) was added to a suspension of NbCl$_5$ (4.50 g, 16.66 mmol) in toluene (100 mL). The reaction mixture was stirred for 3 h at room temperature. After filtration the resulting solution was concentrated (20 mL) and cooled to −20 °C to give a dark orange solid, which was characterized as **3** (X = Me, 7.39 g, 18.83 mmol, 90% yield) and **4** (X = Ph, 5.90 g, 12.98 mmol, 78% yield), respectively.

Data for **3** are as follows. Anal. Calcd for C$_7$H$_{10}$Cl$_5$SiNb: C, 21.41; H, 2.55. Found: C, 21.40; H, 2.60. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C, δ): 0.54 (s, 6H, SiCl*Me$_2$*), 6.20 (m, 2H, C$_5$*H$_4$*), 6.24 (m, 2H, C$_5$*H$_4$*). ^{13}C NMR (75 MHz, C$_6$D$_6$, 25 °C, δ): 2.7 (SiCl*Me$_2$*), 131.5, 131.9 (*C$_2$*-*C$_5$*, C$_5$H$_4$) (C$_{ipso}$ not observed). ^{29}Si NMR (toluene, 25 °C, δ): 8.99 (*Si*ClMe$_2$).

Data for **4** are as follows. Anal. Calcd for C$_{12}$H$_{12}$Cl$_5$SiNb: C, 31.70; H, 2.64. Found: C, 31.65; H,2.67. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C, δ): 0.92 (s, 3H, SiCl*Me*Ph), 6.15 (m, 1H, C$_5$*H$_4$*), 6.21 (m, 1H, C$_5$*H$_4$*), 6.32 (m, 1H, C$_5$*H$_4$*), 6.48 (m, 1H, C$_5$*H$_4$*), 7.07−7.51 (m, 5H, SiClMe*Ph*). ^{13}C NMR (75 MHz, C$_6$D$_6$, 25 °C, δ): 0.5 (SiCl*Me*Ph), 128.6, 129.2, 131.7, 134.6 (*C$_5$*H$_4$, *Ph*).

4.3. Preparation of [{(NbCl$_2$)$_2$(μ-O)(μ-Cl)$_2$}{(η^5-C$_5$H$_4$)$_2$-(Me$_2$SiOSiMe$_2$)}] (5). Water (55 μL, 3.05 mmol) was added to a solution of [Nb{η^5-C$_5$H$_4$(SiClMe$_2$)}Cl$_4$] (**3**; 1.19 g, 3.05 mmol) in 50 mL of toluene. The reaction mixture was stirred at room temperature for 2 h. After filtration, the resulting orange solution was concentrated (10 mL) and cooled to −20

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°C to give single crystals for X-ray diffraction. Anal. Calcd for **5**, $C_{14}H_{20}Cl_6O_2Si_2Nb_2\cdot C_7H_8$: C, 32.87; H, 3.65. Found: C, 32.45; H, 3.47.

4.4. Preparation of $[Nb\{\eta^5\text{-}C_5H_4(SiClMeX)\}Cl_2(N^tBu)]$ (X = Me, 6; X = Ph, 7). A mixture of $[Nb\{\eta^5\text{-}C_5H_4(SiClMeX)\}Cl_4]$ (**3**; 1.00 g, 2.55 mmol; **4**; 1.16 g, 2.55 mmol), $LiNH^tBu$ (0.20 g, 2.55 mmol), and NEt_3 in 50 mL of toluene was stirred at room temperature overnight and then filtered. After evaporation under vacuum to dryness a brown solid was obtained, which was extracted with hexane (30 mL). The resulting extract was concentrated and cooled to −30 °C to give a yellow solid characterized as **6** (X = Me, 0.70 g, 1.78 mmol, 70% yield) and **7** (X = Ph, 0.83 g, 1.83 mmol, 72% yield).

Data for **6** are as follows. Anal. Calcd for $C_{11}H_{19}Cl_3NSiNb$: C, 33.63; H, 4.84; N, 3.57. Found: C, 33.93; H, 4.95; N, 3.33. ^1H NMR (300 MHz, C_6D_6, 25 °C, δ): 0.59 (s, 6H, SiClMe_2), 1.02 (s, 9H, N^tBu), 5.98 (m, 2H, C_5H_4), 6.34 (m, 2H, C_5H_4). ^{13}C NMR (75 MHz, C_6D_6, 25 °C, δ): 1.9 (SiClMe_2), 29.7 ($C(CH_3)_3$), 69.8 ($C(CH_3)_3$), 110.3, 121.7 (C_2-C_5, C_5H_4) (C_{ipso} not observed). ^{29}Si NMR (toluene, 25 °C, δ): 8.34 (SiClMe_2).

Data for **7** are as follows. Anal. Calcd for $C_{16}H_{21}Cl_3NSiNb$: C, 42.26; H, 4.66; N, 3.08. Found: C, 42.87; H, 4.70; N, 2.81. ^1H NMR (300 MHz, C_6D_6, 25 °C, δ): 0.94 (s, 3H, SiClMePh), 0.99 (s, 9H, N^tBu), 5.95 (m, 1H, C_5H_4), 6.00 (m, 1H, C_5H_4), 6.25 (m, 1H, C_5H_4), 6.61 (m, 1H, C_5H_4), 7.12−7.64 (m, SiClMePh). ^{13}C NMR (75 MHz, C_6D_6, 25 °C, δ): 1.6 (SiClMePh), 30.0 ($C(CH_3)_3$), 70.5 ($C(CH_3)_3$), 111.2, 111.3, 122.9, 123.3 (C_2−C_5, C_5H_4), 120.0 (C_{ipso}, C_5H_4), 128.5, 131.1, 133.6, 134.4 (SiClMePh). ^{29}Si NMR (C_6D_6, 25 °C, δ): 6.53 (SiClMePh).

4.5. Preparation of $[Nb\{\eta^5\text{-}C_5H_4(SiClMeX)\}(CH_2Ph)_2(N^tBu)]$ (X = Me, 8; X = Ph, 9). A mixture of $[Nb\{\eta^5\text{-}C_5H_4(SiClMe_2)\}Cl_2(N^tBu)]$ (**6**; 0.50 g, 1.27 mmol) and $Mg(CH_2Ph)_2(THF)_2$ (0.45 g, 1.27 mmol) in 50 mL of hexane was stirred at room temperature for 3 h and then filtered. The filtrate was evaporated to dryness to give a light brown solid, which was characterized as **8** (0.56 g, 1.11 mmol, 88% yield). Compound **9** was synthesized from $[Nb\{\eta^5\text{-}C_5H_4(SiClMePh)\}Cl_2(N^tBu)]$ (**7**; 0.58 g, 1.27 mmol), in a manner analogous to that descrived for the preparation of **8**, and isolated as a dark yellow oil.

Data for **8** are as follows. Anal. Calcd for $C_{25}H_{33}ClNSiNb$: C, 59.57; H, 6.61; N, 2.78. Found: C, 59.36; H, 6.59; N, 2.78. ^1H NMR (300 MHz, C_6D_6, 25 °C, δ): 0.46 (s, 6H, SiClMe_2), 1.09 (s, 9H, N^tBu), 1.64 (d, 2H, J_{H-H} = 8.20 Hz, CH_2Ph), 1.94 (d, 2H, J_{H-H} = 8.20 Hz, CH_2Ph), 5.51 (m, 2H, C_5H_4), 5.93 (m, 2H, C_5H_4), 6.98−7.05 (m, 10H, Ph). ^{13}C NMR (75 MHz, C_6D_6, 25 °C, δ): 3.6 (SiClMe_2), 31.8 ($C(CH_3)_3$), 41.3 (CH_2Ph), 66.1 ($C(CH_3)_3$), 106.6, 113.9 (C_2−C_5, C_5H_4) (C_{ipso} not observed), 125.2, 128.8, 130.5, 139.6 (Ph).

Data for **9** are as follows. ^1H NMR (300 MHz, C_6D_6, 25 °C, δ): 0.75 (s, 3H, SiClMePh), 1.07 (s, 9H, N^tBu), 1.59 (d, 1H, J_{H-H} = 8.25 Hz, CH_2Ph), 1.66 (d, 1H, J_{H-H} = 8.25 Hz, CH_2Ph), 1.98 (m, 2H, CH_2Ph), 5.51 (m, 1H, C_5H_4), 5.57 (m, 1H, C_5H_4), 5.98 (m, 1H, C_5H_4), 6.15 (m, 1H, C_5H_4), 6.85−7.14, 7.58 (m, Ph). ^{13}C NMR (75 MHz, C_6D_6, 25 °C, δ): 2.2 (SiClMePh), 31.7 ($C(CH_3)_3$), 41.6 (CH_2Ph), 66.8 ($C(CH_3)_3$), 105.6, 106.3, 114.9, 115.4 (C_2−C_5, C_5H_4) (C_{ipso} not observed), 125.0, 125.3, 128.7, 130.5, 130.7, 134.0, 138.9, 140.1 (Ph).

4.6. Preparation of $[Nb[\eta^5\text{-}C_5H_4Si(CH_2Ph)MeX](CH_2Ph)_2(N^tBu)]$ (X = Me, 10; X = Ph, 11). A mixture of $[Nb\{\eta^5\text{-}C_5H_4(SiClMe_2)\}Cl_2(N^tBu)]$ (**6**; 0.50 g, 1.27 mmol) and $Mg(CH_2Ph)_2(THF)_2$ (0.67 g, 1.91 mmol) in toluene (50 mL) was warmed to 80−90 °C for 3 days. After evaporation to dryness the resudue was extacted with ether or hexane and the filtrate was again evaporated to dryness to give a brown oil, which was characterized as **10**. A mixture of $[Nb(\eta^5\text{-}C_5H_4SiClMePh)Cl_2(N^tBu)]$ (**7**; 0.50 g, 1.10 mmol) and $Mg(CH_2Ph)_2(THF)_2$ (0.58 g, 1.65 mmol) in hexane (50 mL) was heated to 50−60 °C for 2 days. The resulting suspension was filtered, and then the volatiles were removed under reduced pressure. The brown oil obtained was characterized as **11**.

Data for **10** are as follows. ^1H NMR (300 MHz, C_6D_6, 25 °C, δ): 0.20 (s, 6H, Si(CH_2Ph)Me_2), 1.11 (s, 9H, N^tBu), 1.63 (d, 2H, J_{H-H} = 8.06 Hz, CH_2Ph), 1.89 (d, 2H, J_{H-H} = 8.06 Hz, CH_2Ph), 2.13 (s, 2H, Si(CH_2Ph)Me_2), 5.51 (m, 2H, C_5H_4), 5.70 (m, 2H, C_5H_4), 6.80−7.15 (m, Ph). ^{13}C NMR (75 MHz, C_6D_6, 25 °C, δ): −2.3 (SiClMe_2), 28.1 ($SiMe_2CH_2Ph$), 31.9 ($C(CH_3)_3$), 41.3 (CH_2Ph), 66.5 ($C(CH_3)_3$), 107.4, 113.3 (C_2−C_5, C_5H_4) (C_{ipso} not observed), 124.6, 124.9, 128.5, 128.6, 128.7, 130.3, 139.6, 140.0 (Ph).

Data for **11** are as follows. ^1H NMR (300 MHz, C_6D_6, 25 °C, δ): 0.50 (s, 3H, Si(CH_2Ph)MePh), 1.07 (s, 9H, N^tBu), 1.43 (d, 1H, J_{H-H} = 8.06 Hz, CH_2Ph), 1.56 (d, 1H, J_{H-H} = 7.50 Hz, CH_2Ph), 1.72 (d, 1H, J_{H-H} = 8.06 Hz, CH_2Ph), 1.99 (d, 1H, J_{H-H} = 7.50 Hz, CH_2Ph), 2.40 (br s, 2H, Si(CH_2Ph)MePh), 5.55 (m, 2H, C_5H_4), 5.80 (m, 1H, C_5H_4), 5.91 (m, 1H, C_5H_4), 6.70−7.47 (m, Ph). ^1H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 0.55 (s, 3H, Si(CH_2Ph)MePh), 1.07 (s, 9H, NBu^t), 1.22 (d, 1H, J_{H-H} = 8.06 Hz, CH_2Ph), 1.38 (d, 1H, J_{H-H} = 7.69 Hz, CH_2Ph), 1.52 (d, 1H, J_{H-H} = 8.06 Hz, CH_2Ph), 1.83 (d, 1H, J_{H-H} = 7.69 Hz, CH_2Ph), 2.48 (m, 2H, Si(CH_2Ph)MePh), 5.53 (m, 1H, C_5H_4), 5.55 (m, 1H, C_5H_4), 5.90 (m, 1H, C_5H_4), 5.99 (m, 1H, C_5H_4), 6.65−7.45 (m, Ph). ^{13}C NMR (75 MHz, C_6D_6, 25 °C, δ): −4.6 (Si(CH_2Ph)MePh), 27.4 (Si(CH_2Ph)MePh), 31.8 ($C(CH_3)_3$), 41.4 (CH_2Ph), 69.0 ($C(CH_3)_3$), 106.2, 107.0 (C_2−C_5, C_5H_4), 111.3 (C_{ipso}, C_5H_4), 113.9, 114.9 (C_2−C_5, C_5H_4), 124.6, 124.8, 125,1, 128.2, 128.6, 128.7, 129.0, 129.8, 130.2, 130.3, 130.5, 134.4, 134.9, 136.4, 138.9, 139.0, 141.1 (Ph).

4.7. Preparation of $[Nb\{\eta^5\text{-}C_5H_4(SiClMe_2)\}(CH_2Ph)Cl(N^tBu)]$ (12). A mixture of $[Nb\{\eta^5\text{-}C_5H_4(SiClMe_2)\}Cl_2(N^tBu)]$ (**6**; 0.50 g, 1.27 mmol) and $[Nb\{\eta^5\text{-}C_5H_4(SiClMe_2)\}(CH_2Ph)_2(N^tBu)]$ (**8**; 0.64 g, 1.27 mmol) in toluene (50 mL) was warmed to 120 °C for 4 h. After evaporation under vacuum to dryness, an oil was obtained, which was dissolved in hexane (20 mL). The resulting solution was concentrated and cooled to −40 °C to give a brown solid, which was characterized as **12** (0.51 g, 1.15 mmol, 90% yield). Data for **12** are as follows. Anal. Calcd for $C_{18}H_{26}ClNSiNb$: C, 48.21; H, 5.86; N, 3.12. Found: C, 48.00; H, 5.98; N, 3.15. ^1H NMR (300 MHz, C_6D_6, 25 °C, δ): 0.57 (s, 3H, SiClMe_2), 0.67 (s, 3H, SiClMe_2), 1.08 (s, 9H, N^tBu), 2.77 (d, 1H, J_{H-H} = 7.10 Hz, CH_2Ph), 3.20 (d, 1H, J_{H-H} = 7.10 Hz, CH_2Ph), 5.65 (m, 1H, C_5H_4), 5.87 (m, 2H, C_5H_4), 6.13 (m, 1H, C_5H_4), 6.75−7.29 (m, Ph). ^{13}C NMR (75 MHz, C_6D_6, 25 °C, δ): 2.7 (SiClMe_2), 3.6 (SiClMe_2), 31.0 ($C(CH_3)_3$), 48.6 (CH_2Ph), 68.3 ($C(CH_3)_3$), 105.8, 109.7, 110.9, 118.9 (C_2−C_5, C_5H_4) (C_{ipso} not observed), 130.1, 130.4, 132.4 (Ph).

4.8. Preparation of $[Nb\{\eta^5\text{-}C_5H_4(SiMeXY)\}R(N^tBu)\{\eta^2\text{-}C(CH_2Ph){=}N(2,6\text{-}Me_2C_6H_3)\}]$ (R = CH₂Ph, X = Cl, Y = Me (13), Ph (14); R = CH₂Ph, X = CH₂Ph, Y = Me (15), Ph (16); R = Cl, X = Cl, Y = Me (17)). An equimolar mixture of the corresponding alkyl complex and isocyanide in hexane was stirred at room temperature for 1 h and was then evaporated to dryness. The oily products obtained were characterized as the corresponding iminoacyl complexes **13**−**17**.

Data for **13** are as follows. Anal. Calcd for $C_{34}H_{42}ClN_2SiNb$: C, 64.28; H, 6.68; N, 4.41. Found: C, 63.69; H, 6.78; N, 4.37. ^1H NMR (300 MHz, C_6D_6, 25 °C, δ): 0.52 (s, 3H, SiClMe_2), 0.58 (s, 3H, SiClMe_2), 1.09 (s, 9H, N^tBu), 1.67 (s, 6H, $C{=}NMe_2C_6H_3$), 2.97 (m, 2H, Nb−CH_2Ph), 3.62 (m, 2H, PhCH_2C=N), 5.48 (m, 1H, C_5H_4), 5.68 (m, 1H, C_5H_4), 5.98 (m, 1H, C_5H_4), 6.03 (m, 1H, C_5H_4), 6.82−7.20 (m, Ph). ^{13}C NMR (75 MHz, C_6D_6, 25 °C, δ): 3.8 (SiClMe_2), 4.0 (SiClMe_2), 18.5 ($C{=}NMe_2C_6H_3$), 18.8 ($C{=}NMe_2C_6H_3$), 32.6 ($C(CH_3)_3$), 37.0 (Nb−CH_2Ph), 43.3 (PhCH_2C=N), 66.0 ($C(CH_3)_3$), 107.8, 109.2, 112.2, 115.0 (C_2−C_5, C_5H_4) (C_{ipso} not observed), 120.7−154.7 (Ph), 230.6 ($PhCH_2C{=}N$). IR (Nujol mull; ν, cm^{-1}): 1626, 1240.

Data for **14** are as follows. ^1H NMR (300 MHz, C_6D_6, 25 °C, δ): 0.81, 0.87 (s, 3H, SiClMePh), 1.03, 1.13 (s, 9H, N^tBu), 1.62, 1.69, 1.71, 1.76 (s, 3H, $C{=}NMe_2C_6H_3$), 3.00−3.08 (m, 2H, Nb−CH_2Ph), 3.56 (d, 1H, J_{H-H} = 15.4 Hz, PhCH_2C=N), 3.64

(d, 1H, $J_{H-H} = 9.7$ Hz, PhCH_2C═N), 3.67 (d, 1H, $J_{H-H} = 9.7$ Hz, PhCH_2C═N), 3.74 (d, 1H, $J_{H-H} = 15.4$ Hz, PhCH_2C═N), 5.48, 5.63, 5.67, 5.78, 5.97, 6.04, 6.17, 6.20 (m, 1H, C_5H_4), 6.82−7.58 (m, *Ph*). ^{13}C NMR (75 MHz, C_6D_6, 25 °C, δ): 2.2, 2.6 (SiCl*Me*Ph), 18.4, 18.6, 18.6, 19.1 (C═N$Me_2C_6H_3$), 32.5, 32.6 (C(CH_3)$_3$), 36.9 (br s, Nb−CH_2Ph), 43.2, 43.3 (PhCH_2C═N), 66.1 (*C*(CH_3)$_3$), 107.0, 108.2, 109.2, 110.0, 112.9, 114.7, 115.0, 115.3 (C_2−C_5, C_5H_4), 120.6−154.9 (*Ph*), 230.4 (PhCH_2*C*═N). IR (Nujol mull; ν, cm^{-1}): 1625, 1240.

Data for **15** are as follows. ^{1}H NMR (300 MHz, C_6D_6, 25 °C, δ): 0.29 (s, 3H, SiMe_2CH_2Ph), 0.34 (s, 3H, SiMe_2CH_2Ph), 1.11 (s, 9H, N^{t}Bu), 1.61 (s, 3H, C═N$Me_2C_6H_3$), 1.67 (s, 3H, C═N$Me_2C_6H_3$), 2.22 (s, 2H, SiMe_2CH_2Ph), 2.85 (d, 1H, $J_{H-H} = 10.0$ Hz, Nb−CH_2Ph), 3.11 (d, 1H, $J_{H-H} = 10.0$ Hz, Nb−CH_2-Ph), 3.57 (m, 2H, PhCH_2C═N), 5.40 (m, 1H, C_5H_4), 5.71 (m, 1H, C_5H_4), 5.79 (m, 1H, C_5H_4), 5.90 (m, 1H, C_5H_4), 6.81−7.28 (m, *Ph*). ^{13}C NMR (75 MHz, C_6D_6, 25 °C, δ): −1.9 (SiMe_2CH_2-Ph), 18.4 (C═N$Me_2C_6H_3$), 18.6 (C═N$Me_2C_6H_3$), 28.2 (SiMe_2CH_2-Ph), 32.8 (C(CH_3)$_3$), 37.1 (Nb−CH_2Ph), 43.4 (PhCH_2C═N), 65.7 (*C*(CH_3)$_3$), 106.6, 109.4, 110.7, 116.1 (C_2−C_5, C_5H_4), 120.4−154.8 (*Ph*), 231.3 (PhCH_2*C*═N). IR (Nujol mull; ν, cm^{-1}): 1624, 1242.

Data for **16** are as follows. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ): 0.60, 0.64 (s, 3H, Si*Me*PhCH_2Ph), 1.00, 1.05 (s, 9H, N^{t}Bu), 1.52, 1.53, 1.56, 1.59 (s, 3H, C═N$Me_2C_6H_3$), 2.46−2.56 (m, 4H, CH_2Ph), 2.77−2.82 (m, 2H, CH_2Ph), 3.06−3.11 (m, 2H, CH_2Ph), 3.48−3.50 (m, 4H, PhCH_2C═N), 5.38, 5.43, 5.69, 5.75 (m, 1H, C_5H_4), 5.83 (m, 2H, C_5H_4), 5.95, 6.00 (m, 1H, C_5H_4), 6.54−7.43 (m, *Ph*). ^{13}C NMR (75 MHz, C_6D_6, 25 °C, δ): −3.6, −3.8 (SiCl*Me*Ph), 18.2, 18.3, 18.5 (C═N$Me_2C_6H_3$), 27.1, 27.3 (SiCH_2Ph), 32.6 (C(CH_3)$_3$), 37.1, 37.2 (Nb−CH_2Ph), 43.3 (PhCH_2C═N), 65.6 (*C*(CH_3)$_3$), 106.5, 107.0, 109.5, 109.9, 110.2, 110.6, 116.2 (C_2−C_5, C_5H_4), 120.4−154.8 (*Ph*), 230.9, 231.0 (PhCH_2*C*═N). IR (Nujol mull; ν, cm^{-1}): 1625, 1241.

Data for **17** are as follows. Anal. Calcd for $C_{27}H_{35}ClN_2SiNb$: C, 55.95; H, 6.10; N, 4.83. Found: C, 56.05; H, 6.21; N, 4.73. ^{1}H NMR (300 MHz, C_6D_6, 25 °C, δ): 0.85 (s, 3H, SiClMe_2), 0.97 (s, 3H, SiClMe_2), 0.97 (s, 9H, N^{t}Bu), 1.74 (s, 3H, C═N$Me_2C_6H_3$), 2.07 (s, 3H, C═N$Me_2C_6H_3$), 3.54 (br s, 2H, PhCH_2C═N), 5.46 (m, 1H, C_5H_4), 5.81 (m, 1H, C_5H_4), 5.87 (m, 1H, C_5H_4), 6.61 (m, 1H, C_5H_4), 7.00−7.45 (m, *Ph*). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ): 0.78 (s, 3H, SiClMe_2), 0.88 (s, 3H, SiClMe_2), 1.05 (s, 9H, N^{t}Bu), 1.94 (s, 3H, C═N$Me_2C_6H_3$), 2.16 (s, 3H, C═N$Me_2C_6H_3$), 4.04 (m, 2H, PhCH_2C═N), 5.69 (m, 1H, C_5H_4), 5.92 (m, 1H, C_5H_4), 6.08 (m, 1H, C_5H_4), 6.66 (m, 1H, C_5H_4), 6.85−7.10 (m, *Ph*). ^{13}C NMR (75 MHz, C_6D_6, 25 °C, δ): 2.91 (SiClMe_2), 3.96 (SiClMe_2), 18.4 (C═N$Me_2C_6H_3$), 18.8 (C═N$Me_2C_6H_3$), 31.5 (C(CH_3)$_3$), 43.0 (PhCH_2C═N), 67.3 (*C*(CH_3)$_3$), 103.5, 110.6, 111.9, 116.9 (C_2−C_5, C_5H_4), 115.8 (C_{ipso}, C_5H_4), 126.6−140.3 (*Ph*), 226.9 (PhCH_2*C*═N). IR (Nujol mull; ν, cm^{-1}): 1642, 1244.

4.9. Crystal Structure Determination of 5·C_6H_5Me. Crystals suitable for X-ray study were obtained by recrystallization from toluene, and the dinuclear complex **5** crystallized with one molecule of toluene. The crystallographic data for **5**·C_6H_5Me are summarized in Table 2.

Table 2. Crystal Data and Structure Refinement Details for 5

empirical formula	$C_{14}H_{20}Cl_6Nb_2O_2Si_2 \cdot C_7H_8$
fw	767.13
temp; wavelength	293(2) K; 0.710 73 Å
cryst syst; space group	monoclinic; $P2_1/c$
a, *b*, *c*	12.040(2), 12.230(2), 20.041(4) Å
β	93.80(3)°
V; *Z*	2944.5(9) Å^3; 4
density (calcd)	1.730 g/cm^3
abs coeff	1.423 mm^{-1}
F(000)	1528
no. of rflns collected	5190
no. of indep rflns	4963 ($R_{int} = 0.1185$)
abs cor	ψ scan
max and min transmissn	0.276 and 0.228
refinement method	full-matrix least squares on F^2
goodness of fit on F^2	1.068
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0307, wR2 = 0.0764
R indices (all data)	R1 = 0.0458, wR2 = 0.0908
weighting scheme	calcd $w = 1/[\sigma^2(F_o^2) + (0.0372P)^2 + 3.9258P]$; $P = (F_o^2 + 2F_c^2)/3$
largest diff peak and hole	0.656 and −0.455 e/Å^3

Data were collected at room temperature (25 °C) on an Enraf-Nonius CAD 4 automatic four-circle diffractometer. Intensity measurements were performed by ω scans in the range $2° < 2\theta < 50°$ on a crystal of dimensions 0.40 × 0.32 × 0.28 mm. A total of 4963 of the 5190 measured reflections were independent; the largest minimum and maximum in the final difference Fourier synthesis were 0.455 and 0.656 e Å^{-3}, respectively. R1 = 0.031, and wR2 = 0.076 (for 4083 reflections with $F > 4\sigma(F)$). The values of R1 and wR2 are defined as $R1 = \Sigma||F_o| - |F_c||/[\Sigma|F_o|]$ and $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$. The structure was solved by direct methods and refined by least-squares against F^2 (SHELX-97).[16] All non-hydrogen atoms were anisotropically refined and the hydrogen atoms positioned geometrically and refined by using a riding model in the last cycles of refinement.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates and isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and least-squares planes (7 pages). Ordering information is given on any current masthead page.

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[16] Sheldrick, G. M. SHELX-97 Package; University of Göttingen, Göttingen, Germany, 1997.