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Monocyclopentadienyl(niobium) Compounds with Imido and Silsesquioxane Ligands: Synthetic, Structural and Reactivity Studies

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A new half-sandwich imido compound, [Nb{η^5-$C_5H_3(SiMe_3)_2$}Cl_2(N*t*Bu)] (**1**), was isolated by treatment of [Nb{η^5-$C_5H_3(SiMe_3)_2$}Cl_4] with 1 equiv. LiNH*t*Bu in hexane. Alkylimido derivatives [Nb{η^5-$C_5H_3(SiMe_3)_2$}RR′(N*t*Bu)] (R = Cl, R′ = Me **2**; R = R′ = Me **3**, CH_2SiMe_3 **4**) can be prepared by reaction of **1** with the appropriate alkylating reagent. Silsesquioxane ligand [$Si_8O_{12}Cl(i\text{Bu})_7$] (**5a**) can be obtained by treatment of [$Si_7O_9(OH)_3(i\text{Bu})_7$] with 1 equiv. silicon tetrachloride in the presence of triethylamine. Ligand **5a** reacts with NH_3 (g) at low temperatures to yield an amido derivative, [$Si_8O_{12}(NH_2)(i\text{Bu})_7$] (**5b**), whereas the reaction of the trisilanol with excess BuLi leads to the corresponding lithium salt [$Li_3Si_7O_{12}(i\text{Bu})_7$] (**5c**). A dichlorido(silsesquioxanylimido)-niobium compound [Nb{η^5-$C_5H_3(SiXMe_2)(SiMe_3)$}Cl_2-{$NSi_8O_{12}(i\text{Bu})_7$}] (X = Cl **6a**, Me **6b**) can be prepared by reaction of 1 equiv. tetrachloridoniobium complex [Nb{η^5-$C_5H_3(SiXMe_2)(SiMe_3)$}Cl_4] (X = Cl, Me) and amidosilsesquioxane **5b**. From **6b**, three new alkyl derivatives, [Nb{η^5-$C_5H_3(SiMe_3)_2$}XY($NSi_8O_{12}R_7$)] (R = *i*Bu, X = Cl, Y = Me **7**; X = Y = Me **8**, CH_2SiMe_3 **9**), were isolated by usual alkylation reactions. Alternatively, protonolysis reaction of trisilanol [$Si_7O_9R_7(OH)_3$] with [Nb{η^5-$C_5H_3(SiXMe_2)(SiMe_3)$}Cl_4] (X = Cl) in the presence of triethylamine produces a dichlorido derivative, [Nb{η^5-$C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7$-κ^2*O,O*)}-$Cl_2$] (R = *i*Bu **10**), which can be transformed into an imido complex, [Nb{η^5-$C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7$-κ^2*O,O*)}-(N*t*Bu)] (R = *i*Bu **11**), by reaction with LiNH*t*Bu, whereas for X = Me, a chlorido complex, [Nb{η^5-$C_5H_3(SiMe_3)_2$}Cl($Si_7O_{12}R_7$-κ^3*O,O,O*)] (R = *i*Bu **12**), can be isolated. Alkylation of **10** and **12** leads to dimethyl, trimethylsilylmethylidene and methyl derivatives **13**, **14** and **15**, respectively. Alkylimidoniobium complexes **2**–**4** react with carbon monoxide or xylyl isocyanide at room temperature to give acylimidoniobium [Nb{η^5-$C_5H_3(SiMe_3)_2$}R(N*t*Bu){C(R′)O-κ^2*C,O*}] (R = Cl, R′ = Me **16**; R = R′ = Me **17**, CH_2SiMe_3 **18**) and iminoacylimidoniobium [Nb{η^5-$C_5H_3(SiMe_3)_2$}R(N*t*Bu){C(Me)NAr-κ^2*C,N*}] (Ar = 2,6-$Me_2C_6H_3$; R = Cl **21**, Me **22**) compounds by simple insertion reactions. However, compound **13** reacts with CO and 2,6-$Me_2C_6H_3NC$, leading to enediolato [Nb{η^5-$C_5H_3(SiMe_3)$}-($Me_2SiOSi_7O_{11}R_7$-κ^2*O,O*)}{O(Me)C=C(Me)O-κ^2*O,O*}] (R = *i*Bu **19**) and azaniobacyclopropane [Nb{η^5-$C_5H_3(SiMe_3)$}-($Me_2SiOSi_7O_{11}R_7$-κ^2*O,O*)}(CMe_2NAr-κ^2*C,N*)] (R = *i*Bu, Ar = 2,6-$Me_2C_6H_3$ **20**) derivatives through intermolecular coupling between two acyl groups and by a double methyl migration processes, respectively. All new compounds have been characterized by IR spectrophotometry, ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectroscopy and elemental analysis.

Introduction

Structural and reactivity aspects of early transition metal cyclopentadienyl complexes have been extensively studied because of their role in numerous applications, as reagents in organic synthesis and also as soluble Ziegler–Natta catalysts.[1] Although a vast series of derivatives with ancillary cyclopentadienyl ligands has dominated this chemistry, the presence of electron-withdrawing silyl substituents improves catalytic activity, because steric and electronic properties can be tailored particularly when such substituents contain reactive functional groups.[2] We have recently reported a study comparing the reactivity of the Si–Cl bond of chloridosilylcyclopentadienyl ligands with the M–Cl bond of group 5 metal derivatives,[3] in which a series of methyl, dimethyl, trimethyl and tetramethyl compounds [$MCpCl_{4-x}Me_x$] {M = Nb, Ta; Cp = η^5-$C_5H_3(SiXMe_2)(SiMe_3)$; X = Cl, Me; x = 1, 2, 3, 4} has been isolated in good yields.

Recent years have witnessed an extensive development of imido group 5 metal chemistry[4] containing monofunctional,[5] tetradentate triamidoamine[6] and Cp ligands in mono-[7] and dicyclopentadienyl-type[8] complexes. Protonated lithium amides[9] have been extensively used to generate the imido ligand, but other synthetic strategies have been based on the deprotonation of cyclopentadiene by metal amides,[10] β-hydrogen elimination of amides, amines coordinated to metal(III) compounds[11] and oxidation of metal(III) complexes with azides,[11b] as more relevant synthetic processes. A lot of examples show that the development of nonmetallocene chemistry[1,12] is an area of constant activity. In this context, many neutral group 5 imido

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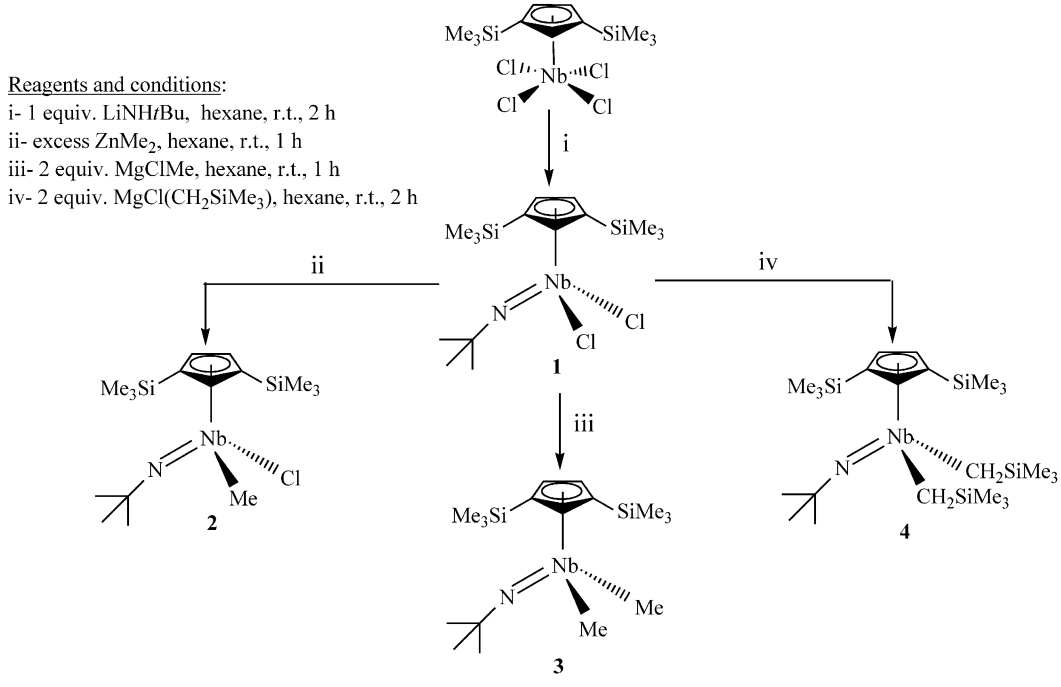
compounds have been synthesized,[4,13] and their functionalities were used as both ancillary ligands and reactive sites. As ancillary ligands, they have been compared electronically with cyclopentadienide,[14] but at the same time several stoichiometric transformations, such as protonations of tantalum amides,[15] additions of dihydrogen to tantalum–alkyl groups[16] and insertions of unsaturated molecules (CO, ArNC) into metal–alkyl bonds,[17] have been observed in the presence of niobium and tantalum–imido groups. However, in contrast with these cases, imine and carbodiimide metatheses, imido-to-oxo ligand exchange and the activation of benzene C–H bonds have been observed with Ta=N*t*Bu bonds.[18]

On the other hand, many researchers[19] have focused their attention on the chemistry of incompletely condensed polyhedral oligosilsesquioxanes (POSSs), as they are seen as attractive ligands with a sufficient degree of oligomerization so as to be relevant models for highly siliceous materials used to support heterogeneous catalysts. Furthermore, they may retain reactive Si–OH functionalities, which allow their use as ligands in a wide variety of main group and transition metal compounds.[20–22] Silsesquioxane is a general term for a type of spherosilicate with the general formula [$SiRO_{3/2}$] (R = H, organic group) and a random, ladder, cage or partial cage structure. The most familiar structure is that corresponding to the incompletely condensed POSS, which shows a hybrid organic–inorganic three-dimensional geometry with three silanol groups. A POSS ligand dictates the coordination geometry of the metal complexes[20e] much more effectively, and ^{29}Si NMR spectroscopy[23] is an essential tool in the structural study of a broad variety of silsesquioxane derivatives. Further, due to their geometric and electronic properties, they have been extensively studied for a number of years, either as an excellent model system for heterogeneous and homogeneous silica-supported catalysts,[20d,24] as building blocks for inorganic and hybrid materials[25] or as ligand backbones for transition metal complexes.[20c,20e] In the literature, a large number of complexes that contain silsesquioxane ligands with different condensation grades coordinated to metals have been reported.[20h–20i,22j,26–29] With respect to the group 5 metals, the vanadium[30] complexes are the most numerous, although in the last few years synthetic routes towards tantalum[28b,31] and niobium[32] derivatives have been described.

In this paper, we report the synthesis of several POSS ligands, their coordination to bis(silylcyclopentadienyl)niobium compounds and the comparative chemical behaviour between *tert*-butylimido and POSS derivatives in alkylation and insertion processes.

Results and Discussion

A pseudotetrahedral dichloridoimido compound, [Nb{η^5-$C_5H_3(SiMe_3)_2$}Cl_2(N*t*Bu)] (**1**), can be synthesized when hexane solutions of the starting material, [Nb{η^5-$C_5H_3(SiMe_3)_2$}Cl_4], are treated at room temperature with LiN*H*t*Bu. Reactions of **1** with stoichiometric amounts of the alkylating reagent give solutions from which the alkylimido complex, [Nb{η^5-$C_5H_3(SiMe_3)_2$}RR′(N*t*Bu)] (R = Cl, R′ = Me **2**; R = R′ = Me **3**, CH_2SiMe_3 **4**), can be isolated in good yields (Scheme 1). All of these complexes are soluble in most organic solvents, including saturated hy-



Scheme 1.

drocarbons. They are extremely air- and moisture-sensitive, and rigorously dried solvents and handling under an argon atmosphere were found to be imperative for successful preparations.

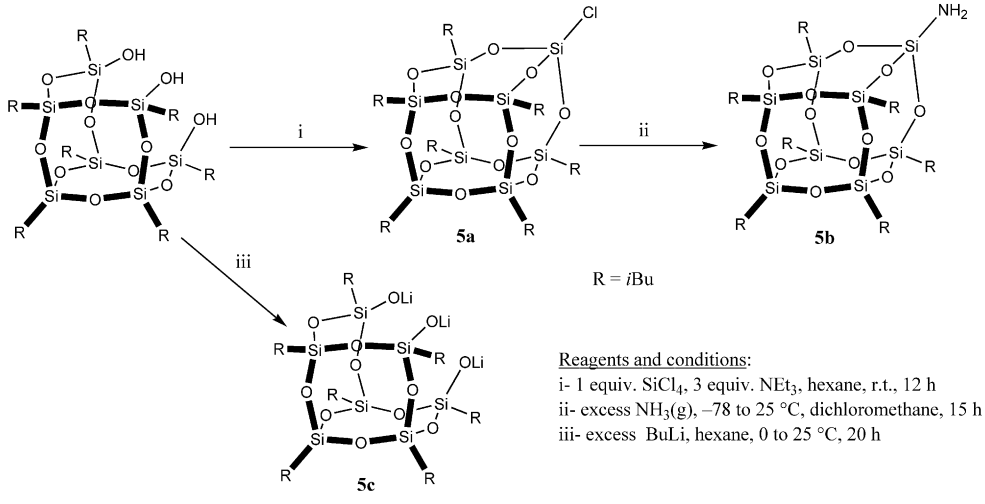
Compounds **1**–**4** were characterized by analytic and spectroscopic methods, and the data are in agreement with the proposed structures. The IR spectra of all complexes show the characteristic absorptions for bis(trimethylsilyl)cyclopentadienyl ($\tilde{\nu}_{C-H} \approx 839\ cm^{-1}$),[33,34] the trimethylsilyl substituent [$\tilde{\nu}_{\delta s}(CH_3) \approx 1250\ cm^{-1}$][3,17d,35] and the Nb=N stretching vibration ($\tilde{\nu} \approx 1360\ cm^{-1}$).[3a,17d] At room temperature, chiral complex **2** shows the expected ^1H NMR spectroscopic behaviour with three and two resonances for the protons of the disubstituted cyclopentadienyl ring and the $SiMe_3$ substituents, respectively, due to the absence of local symmetry in the $C_5H_3(SiMe_3)_2$ moiety. However, the NMR spectroscopic data for the complexes **1**, **3** and **4** show an A_2B spin system for the Cp ring protons, and consistently, three ring carbon resonances appear in the $^{13}C\{^1H\}$ NMR spectra in agreement with the existence of a metal centre in a characteristic three-legged piano-stool environment (C_s symmetry).[3a,33,34]

Silsesquioxane ligands **5a**–**c** were successively synthesized from trisilanol $Si_7O_9R_7(OH)_3$ (R = *i*Bu) by conventional methods. The chloro derivative $[Si_8O_{12}Cl(iBu)_7]$ (**5a**) was obtained in high yield by reaction of $[Si_7O_9(OH)_3(iBu)_7]$ with silicon tetrachloride in the presence of 3 equiv. triethylamine. The ammonolysis of **5a** in the presence of a large excess of NH_3(g) at –78 °C in dichloromethane led to the expected amido derivative $[Si_8O_{12}(NH_2)(iBu)_7]$ (**5b**), whereas at 0 °C the reaction of trisilanol with excess BuLi gave the corresponding lithium salt $[Li_3Si_7O_{12}(iBu)_7]$ (**5c**) (see Scheme 2). Compounds **5a**–**c** were found not to be air- and moisture-sensitive and are soluble in hexane, chlorinated and aromatic solvents.

The IR and NMR (^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$) spectroscopic data are in agreement with the proposed structures. The $^{29}Si\{^1H\}$ NMR spectrum of complex **5b** (see Figure 1) shows four silicon resonances with relative intensities of 3:3:1:1; the first three signals can be assigned to the seven silicon atoms of the Si_7O_{12} moiety, and the fourth signal can be assigned to the silicon atom directly bonded to the NH_2 group. This NMR spectroscopic behaviour[20b,23] is also in agreement with that expected for totally condensed and cap-cornered silsesquioxanes with the same substituents (C_{3v} symmetry group).

Ligand **5c** was synthesized as shown in Scheme 1 (see Experimental Section), and afterwards, the slow evaporation of the reaction solvent (hexane) gave a small amount of crystals. The X-ray diffraction study of one of them showed in an unambiguous way that a new species **5c′** is present, but the bad quality of the crystal hindered a good refinement. This new species is the tetrameric unit of **5c**. The molecular structure and atom-labelling scheme of **5c′** are shown in Figure 2, and selected bond lengths and angles are given in the caption. Isobutyl groups are not shown for greater clarity. Compound **5c′** consists of four incomplete silsesquioxane cubes (Si_7O_{12}) bound through lithium–oxygen and lithium–lithium interactions. The structure of the core of the lithium atoms is a distorted icosahedron whose triangular faces are capped by oxygen atoms, and each lithium atom is bonded to three oxygen atoms. Two oxygen atoms are provided by one Si_7O_{12} unit and the other from a different one, forming a core of $O_{12}Li_{12}$. Every silicon atom is bonded to an isobutyl group. To the best of our knowledge, only one similar dimeric compound has been described[21d] in the literature with bond lengths and bond angles in the same range in both cases.

The treatment of hexane solutions of $[Nb\{\eta^5\text{-}C_5H_3(SiXMe_2)(SiMe_3)\}Cl_4]$ (X = Cl, Me) with 1 equiv. silsesquioxane reagent **5b** in the presence of triethylamine gave dichlorido(silsesquioxanylimido) derivatives $[Nb\{\eta^5\text{-}C_5H_3(SiXMe_2)(SiMe_3)\}Cl_2\{NSi_8O_{12}(iBu)_7\}]$ (X = Cl **6a**, Me **6b**) (Scheme 3) with a silsesquioxanylimido group. In addition, chloridomethyl-, dimethyl- and bis(trimethylsilylmethyl)silsesquioxanylimido complexes [Nb{η5-



Scheme 2.

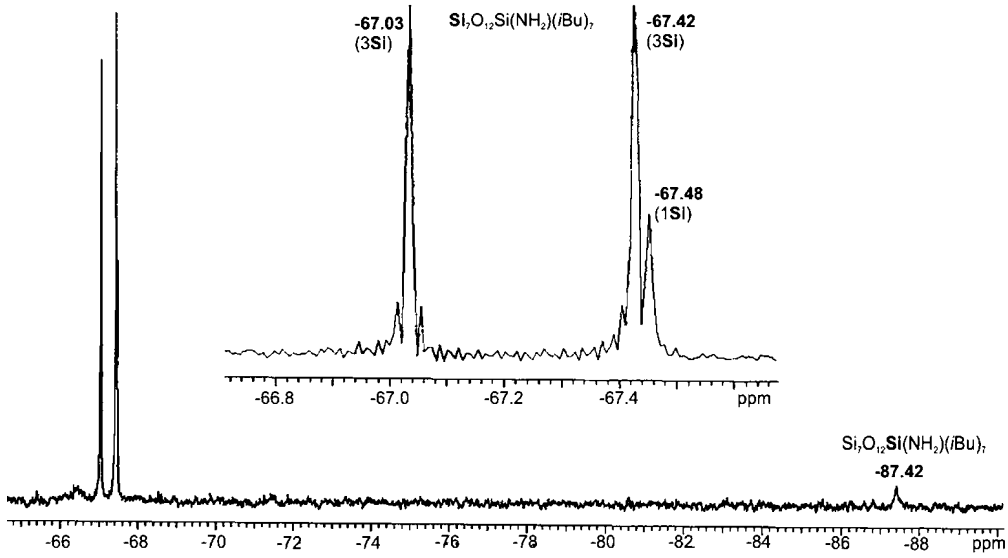


Figure 1. $^{29}Si\{^1H\}$ NMR spectrum of complex **5b** ([D$_1$]chloroform).

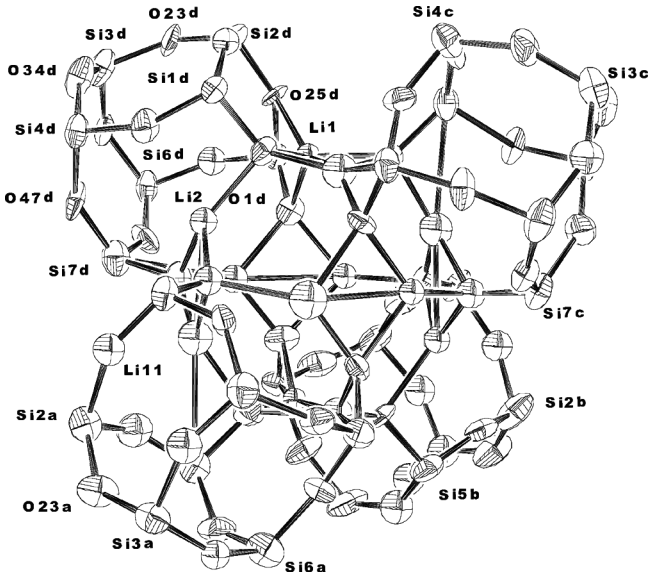


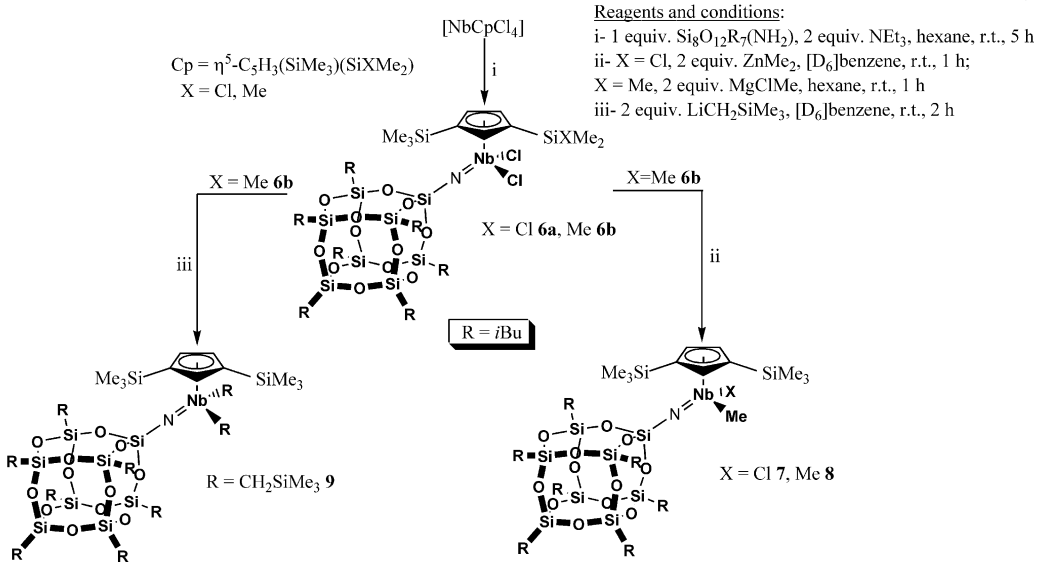
Figure 2. ORTEP view of **5c′**. Isobutyl groups have been omitted for clarity. Mean bond lengths [Å] and angles [°] are as follows. Mean distances [Å]: Si–C 1.83(1), Si–O 1.631(13) and Li–O 1.91(2). Mean angles [°]: Si–O–Si 145.3(9), O–Si–O 109.2(8).

$C_5H_3(SiMe_3)_2\}XY(NSi_8O_{12}R_7)]$ (R = *i*Bu; X = Cl, Y = Me **7**; X = Y = Me **8**, CH_2SiMe_3 **9**) can be prepared by treatment of **6b** with the appropriate alkylating reagent.

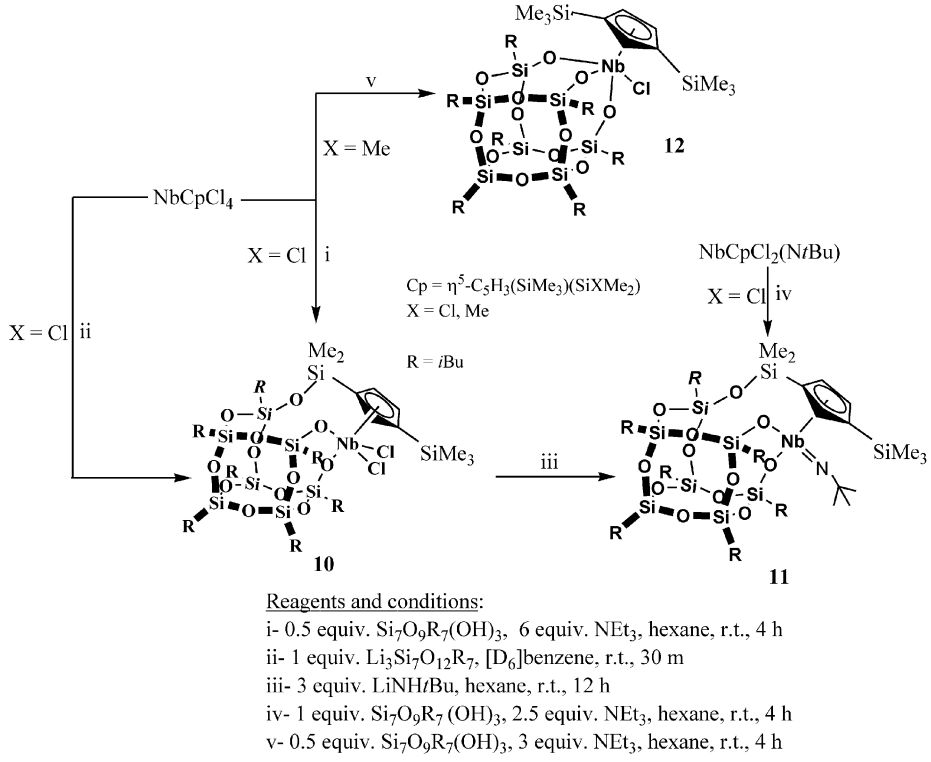
The complex **6a** shows a ^1H NMR spectrum in which the resonances corresponding to the *i*Bu substituents of the silsesquioxanyl moiety appear as multiplets due to the presence of an asymmetric $C_5H_3(SiClMe_2)(SiMe_3)$ ring, while in the spectrum of **6b**, two doublets at δ = 0.59 and 0.52 ppm with observed vicinal ($^3J_{H,H}$) SSCC values of 7.2 Hz can be assigned to the CH_2 protons of such groups, in agreement with the existence of a symmetric $C_5H_3(SiMe_3)_2$ ring. On the other hand, chiral chloridomethyl complex **7** shows the expected ^1H NMR spectroscopic behaviour with both nonequivalent $SiMe_3$ groups. All spectroscopic data for complexes **8** and **9** are in agreement with a C_s symmetry and with a metal centre in a characteristic three-legged piano-stool environment;[33] furthermore, complex **9** shows an AB spin system for diastereotopic α-CH_2 protons of trimethylsilylmethyl groups. Additionally, an IR absorption band due to the Nb=N[3a,17d] stretching vibration can be observed at $\tilde{\nu} \approx 1350\ cm^{-1}$.

A series of chloridosilsesquioxanyl complexes was prepared in good yields by different methods (Scheme 4). $[Nb\{\eta^5\text{-}C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7\text{-}\kappa^2O,O)\}Cl_2]$ (R = *i*Bu **10**) was synthesized by reaction of $[Nb\{\eta^5\text{-}C_5H_3(SiMe_3)(SiClMe_2)\}Cl_4]$ with 0.5 equiv. $Si_7O_9(OH)_3(iBu)_7$ in the presence of NEt_3 or alternatively, by treatment of the tetrachlorido compound with lithium salt **5c**. A new imido derivative, $[Nb\{\eta^5\text{-}C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7\text{-}\kappa^2O,O)\}(NtBu)]$ (R = *i*Bu **11**), whose structural study shows an unaltered silsesquioxanyl moiety and confirms that it is formed by the reaction of two Nb–Cl bonds, can be isolated by reaction of **10** with 3 equiv. LiN*t*Bu; in addition, **11** can be obtained by reaction between dichloridoimido derivative $[Nb\{\eta^5\text{-}C_5H_3(SiClMe_2)(SiMe_3)\}Cl_2(NtBu)]$[3a] and trisilanol $[Si_7O_9(iBu)_7(OH)_3]$ in the presence of triethylamine. Further, a chloridosilsesquioxanyl compound, $[Nb\{\eta^5\text{-}C_5H_3(SiMe_3)_2\}Cl(Si_7O_{12}R_7\text{-}\kappa^3O,O,O)]$ (R = *i*Bu **12**), was prepared by reaction of tetrachlorido derivative $[Nb\{\eta^5\text{-}C_5H_3(SiMe_3)_2\}Cl_4]$ with $Si_7O_9(OH)_3(iBu)_7$ and NEt_3.

Silsesquioxane complexes were obtained as microcrystalline solids soluble in most organic solvents, but repeated attempts under different conditions (solvent, temperature)



Scheme 3.

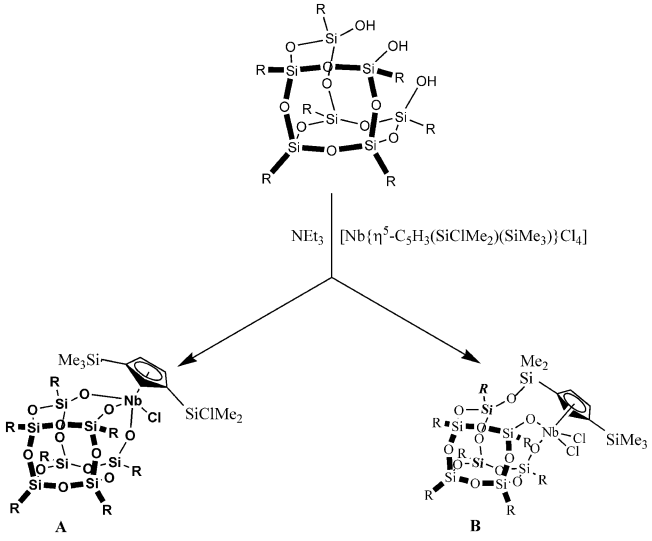


Scheme 4.

to prepare single crystals of adequate quality were unsuccessful. However, the spectroscopic and analytical data are in agreement with the proposed structures.

As illustrated in Scheme 5, we propose that the formation of compound **10** takes place by an alcoholysis process of three Nb–Cl (**A**) or two Nb–Cl and one Si–Cl (**B**) bonds. Although the spectroscopic data does not permit us to make a definitive structural assignment, we suggest structure **B**, because in the reaction of the original tetrachloridoniobium compound with tBuNH$_2$, the two Nb–Cl bonds react first, followed by the Si–Cl bond of the SiClMe$_2$ substituent, to give the reported[3a] constrained-geometry complex [Nb{η^5-C$_5$H$_3$(SiMe$_3$)(SiMe$_2$NtBu-κ*N*)}Cl(NtBu)].

On the other hand, in agreement with the reported ^{29}Si NMR spectroscopic studies,[23a,28a] in the spectrum of complex **10** (see Figure 3) the resonance at δ = –3.57 ppm can be assigned to the silicon atom of the *Si*Me$_2$O moiety, and complexes **10** and **11** therefore present a structure in which the cyclopentadienyl ring is bonded to the silsesquioxanyl



Scheme 5.

ligand across a silicon atom of a silyl substituent, and the observed IR absorption band at $\nu \approx 635\ cm^{-1}$ can be assigned to the ν_{Nb-O} stretching vibration.[36]

Alkylation of **10** with 2 equiv. dimethylzinc at room temperature in hexane yields the expected dimethyl derivative [Nb{η^5-$C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7$-κ^2*O*,*O*)}$Me_2$] (R = *i*Bu **13**); however, treatment with 2 equiv. $MgCl(CH_2SiMe_3)$ under rigorously anhydrous conditions at room temperature leads to the trimethylsilylmethylidene complex, [Nb{η^5-$C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7$-κ^2*O*,*O*)}$(CHSiMe_3)$] (R = *i*Bu **14**), by a spontaneous α-hydrogen-abstraction process[37] with formation of an unstable dialkyl intermediate and $SiMe_4$ elimination (Scheme 6). In addition, a methyl complex, [Nb{η^5-$C_5H_3(SiMe_3)_2$}Me($Si_7O_{12}R_7$-κ^3*O*,*O*,*O*)] (R = *i*Bu **15**), was isolated by reaction of the chloridosilsesquioxanyl complex **12** with excess (1 equiv.) $ZnMe_2$ in toluene. The reaction of **12** with the stoichiometric amount of $ZnMe_2$ (2:1 molar ratio) leads to a mixture of **12** and **15**, probably because of the mild alkylating character of this reagent.

At room temperature, the ^{1}H NMR spectrum of complex **13** shows a broad signal for both methyl groups, probably due to an intramolecular process that consists of the interconversion between two four-legged piano-stool enantiomeric ground states through a trigonal bipyramidal transition state, well known as Berry pseudorotation.[17b,17e,36b,38] However, the resonances at δ = 0.35 and 0.28 ppm can be assigned to the diastereotopic methyl groups of the $SiMe_2$ substituent. On the other hand, for some reported coordinatively unsaturated alkylidene complexes,[37] the stretching frequency corresponding to the C–H bond in the IR spectrum was assigned to absorption bands localized in the 2700–2350 cm^{-1} region, which are at a lower wavenumber than those for normal C–H stretches, probably as a result of the observed increase in the length of the C–H bond. In the case of the compound **14**, the absorption band localized at $\tilde{\nu}$ 2717, 2625 cm^{-1} can be assigned to ν_{C-H}. A high degree of deshielding is observed for the alkylidene proton (δ = 9.68 ppm) and carbon (δ = 235.7 ppm) resonances, which are comparable to other d^0 terminal (alkylidene)niobium and tantalum compounds.[37c,39,40]

The reactivity of the alkyl derivatives was studied in migratory insertion processes (Scheme 7). Chloridomethyl-, dimethyl- and bis(trimethylsilylmethyl)imido complexes **2**–**4** react with carbon monoxide (1 atm) at room temperature in [D$_6$]benzene (NMR spectroscopic scale, see Exp. Sect.) to give chlorido-, methyl- and (trimethylsilylmethyl)imidoacyl [Nb{η^5-$C_5H_3(SiMe_3)_2$}R(N*t*Bu){C(R′)O-κ^2*C*,*O*}] (R = Cl, R′ = Me **16**; R = R′ = Me **17**, CH_2SiMe_3 **18**) derivatives, as result of simple migration of an alkyl group bonded to the metal towards the electrophilic carbonyl atom of the previously coordinated CO. The treatment of [D$_6$]benzene solutions of the alkylsilsesquioxanylimido complexes **7**–**9** with carbon monoxide leads to an unidentified product mixture, but in the case of chloridomethyl compound **7**, we detected the formation of an unstable chloridoacyl derivative (^{1}H NMR: $\delta_{C(Me)O}$ = 2.58 ppm) when the reaction was followed by NMR spectroscopy. However, in contrast with this result, an enediolato complex, [Nb{η^5-$C_5H_3(SiMe_3)$-$(Me_2SiOSi_7O_{11}R_7$-κ^2*O*,*O*)}{O(Me)C=C(Me)O-κ^2*O*,*O*}] (R

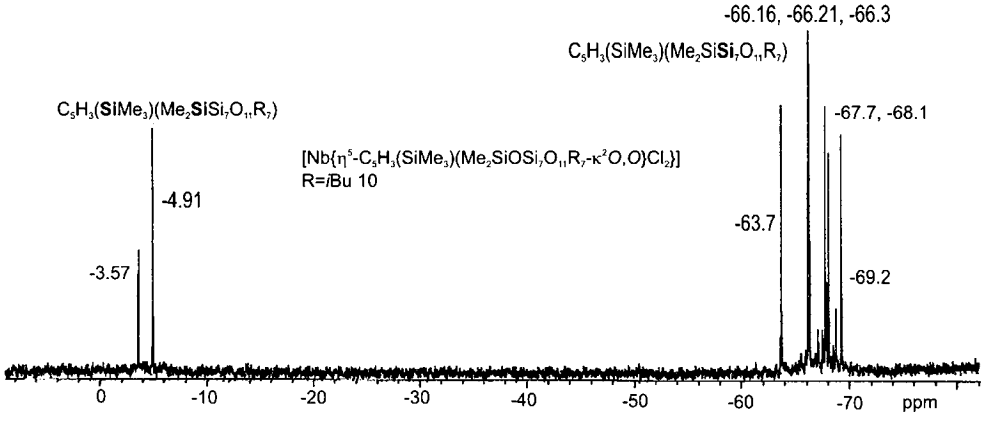
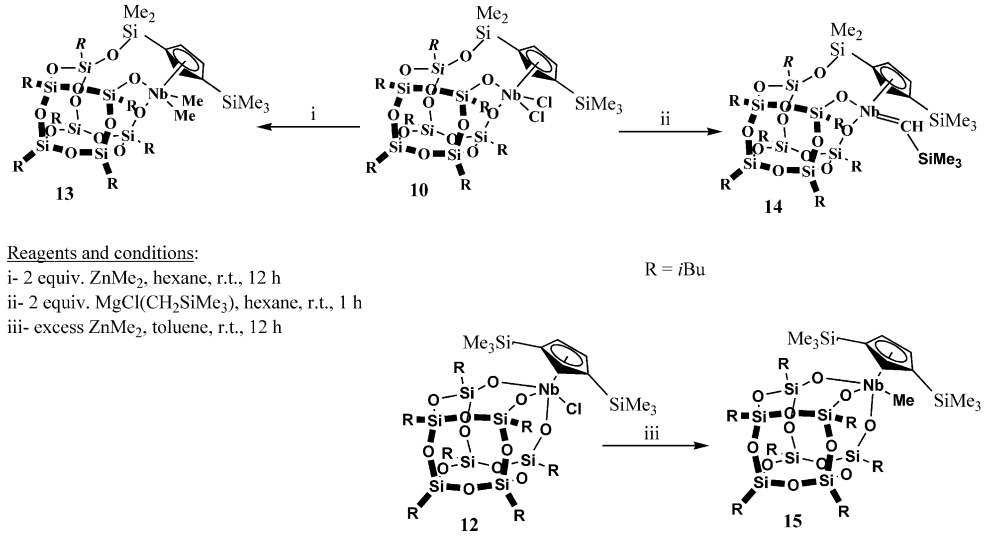
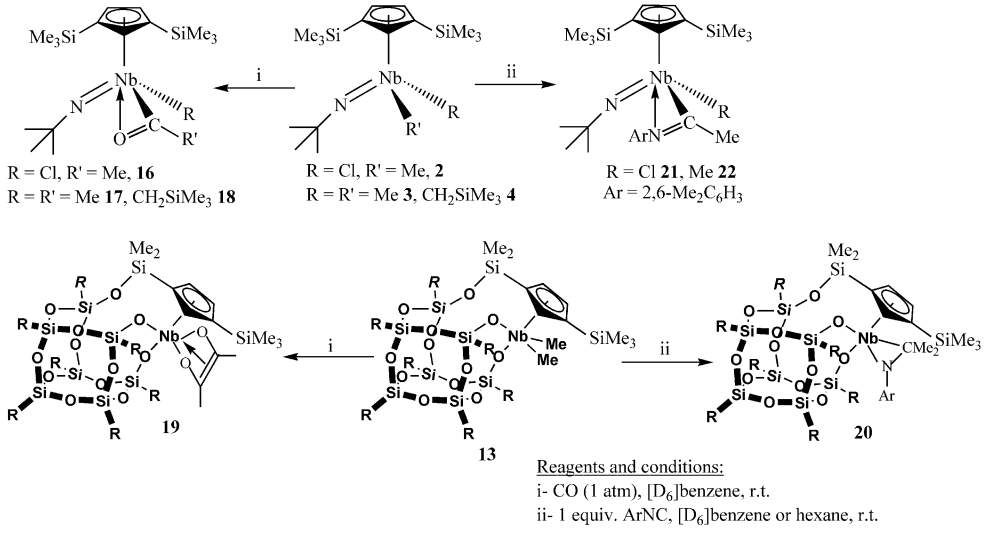


Figure 3. ^{29}Si{^{1}H} NMR spectrum of complex **10** ([D$_6$]benzene).



Scheme 6.



Scheme 7.

= *i*Bu **19**), is easily obtained when the corresponding [D_6]-benzene solution of dimethylsilsesquioxanyl compound **13** reacts with carbon monoxide under the same conditions. This reaction probably takes place by an intramolecular coupling process[17c,41] between two electrophilic acyl carbon atoms of the unstable bis(acyl) intermediate, which could not be observed when the reaction was followed by ^{1}H NMR spectroscopy.

On the other hand, when 1 equiv. 2,6-$Me_2C_6H_3NC$ is added to a solution of **13**, under rigorously anhydrous conditions, an instantaneous reaction takes place, leading to an orange solution from which an azaniobacyclopropane derivative, [Nb{η^5-$C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7$-$\kappa^2O,O$)}-($CMe_2$NAr-$\kappa^2C,N$] (R = *i*Bu, Ar = 2,6-$Me_2C_6H_3$ **20**), was recovered as an orange solid. Previously, we reported[17a,17e] the synthesis and the crystal structure of similar azametallacyclopropane complexes, whose formation involves migration of one methyl group to the electrophilic isocyanide carbon atom to give an iminoacyl intermediate, followed by nucleophilic attack of the second methyl group to the iminoacyl carbon atom to give an imine ligand. However, the treatment of solutions of alkylimido complexes **2**–**3** with 1 equiv. xylyl isocyanide under the same conditions leads to stable, 18-electron imidoiminoacyl compounds [Nb{η^5-$C_5H_3(SiMe_3)_2$}R(N*t*Bu){C(Me)NAr-κ^2C,N}] (R = Cl **21**, Me **22**). In the case of dimethylimido complex **3**, the migration of the second methyl group observed for dimethylsilsesquioxanyl complex **13** and other dimethyl derivatives[17e,42] does not take place, and the presence of excess isocyanide does not produce a second insertion reaction in the Nb–Me or Nb–$C_{iminoacyl}$ bond. Alkyl derivatives **4**, **7**–**9** and **15** also react with xylyl isocyanide, but insertion products cannot be isolated or detected by NMR spectroscopy, and the reaction leads to an unidentified mixture of products.

Analytical and spectroscopic data for insertion complexes **16**–**22** are in agreement with the stoichiometry proposed. IR spectra show characteristic absorptions for the trimethylsilylcyclopentadienyl ring ($\nu_{C-H} \approx 839\ cm^{-1}$)[33,34] and for the $SiMe_3$ substituent [δ_{as} (CH_3) ≈ 1253 cm^{-1}].[3,17d,35] The formulation of **19** as an enediolato complex is supported by the IR spectra,which show $\nu_{C=C}$, ν_{C-O} and ν_{Nb-O} absorptions at $\tilde{\nu}$ = 1466,[17c,17d,43] 1150[43] and 900[36a,36c] cm^{-1}, respectively. Their ^1H NMR spectrum shows two resonances at δ = 1.76 and 1.63 ppm, corresponding to the nonequivalent methyl substituents of the enediolato ligand, whereas the resonance assignable to the sp^2 C atoms appears at δ = 98.4 ppm. In addition, chiral pseudo-square-pyramidal acylimido complexes **16**–**18** show the characteristic absorption for the acyl moiety [$\nu_{C(Y)=O}$] at 1587 cm^{-1}; such stretching vibrations in acyl derivatives range from $\tilde{\nu} \approx$ 1453 to 1625 cm^{-1}, and the lowest frequencies occur for high-valent transition metals, which in our case can be attributed to the carbene character of the acyl carbon atom.

On the other hand, all structural data for iminoacyl complexes **21**–**22** are in agreement with the expected pseudo-square-pyramidal geometry found for similar chiral group 5 metal derivatives.[17d] The iminoacyl carbon resonance appears at δ = 228 ppm, and absorptions due to the C(R)=N–Ar and Nb=N–*t*Bu stretching vibrations are observed at 1645 and 1352 cm^{-1}, respectively. At room temperature, the ^1H and ^{13}C NMR spectra of **20** show two equivalent methyl groups and suggest an azaniobacyclopropane structure[17a,17b,17e] with the plane of the metallacycle perpendicular to the Cp ring. The resonance located at δ = 74 ppm in the ^{13}C NMR spectrum can be assigned to the C_α of the azaniobacyclopropane moiety, and the absorption band due to the C–N stretching vibration[44] was observed at 1365 cm^{-1} in the IR spectrum.

Conclusions

This article presents advances related to the chemistry of monocyclopentadienylniobium compounds. By conventional methods, new alkylimido complexes [Nb{η^5-$C_5H_3(SiMe_3)_2$}RR′(N*t*Bu)] (R = Cl, R′ = Me; R = R′ = Me, CH_2SiMe_3) have been isolated and several silsesquioxane ligands have been synthesized by treatment of trisilanol [$Si_7O_9(OH)_3(iBu)_7$] with the appropriate reagents. Starting from [Nb{η^5-$C_5H_3(SiXMe_2)(SiMe_3)$}Cl_4] (X = Cl, Me), by reaction with amidosilsesquioxane [$Si_8O_{12}(iBu)_7(NH_2)$], a dichlorido(silsesquioxanylimido) compound, [Nb{η^5-$C_5H_3(SiXMe_2)(SiMe_3)$}Cl_2{$NSi_8O_{12}(iBu)_7$}] (X = Cl, Me), which reacts with alkylating reagents to yield the corresponding alkyl derivatives, [Nb{η^5-$C_5H_3(SiMe_3)_2$}XY($NSi_8O_{12}R_7$)] (R = *i*Bu; X = Cl, Y = Me; X = Y = Me, CH_2SiMe_3), can be prepared, while by protonolysis with trisilanol, a new group of silsesquioxanyl complexes can be isolated with a POSS ligand bonded to niobium atom in a different coordination mode. The comparative chemical behaviour of all alkyl derivatives was studied in the insertion processes. Although alkylimido compounds react with carbon monoxide and xylyl isocyanide to give the expected acyl and iminoacyl derivatives, as a result of a simple insertion process, alkylsilsesquioxanyl complexes lead to enediolato and azaniobacyclopropane systems by coupling and double migration processes, respectively.

Experimental Section

General

All reactions and manipulations were carried out under a dry argon atmosphere by using standard Schlenk tube and cannula techniques or in a conventional argon-filled glove-box. The following solvents were refluxed over an appropriate drying agent and distilled and degassed prior to use: [D_6]benzene and hexane (Na/K alloy), [D_1]chloroform (NaH) and dicloromethane (P_4O_{10}). Starting materials [Nb{η^5-$C_5H_3(SiXMe_2)(SiMe_3)$}Cl_4] (X = Cl,Me),[3a] [Nb{η^5-$C_5H_3(SiClMe_2)(SiMe_3)$}Cl_2(N*t*Bu)],[3a] [$Si_7O_9(OH)_3(iBu)_7$],[45] LiNH*t*Bu[46] and $LiCH_2SiMe_3$[47] were prepared as described previously. Reagent grade CO and NH_3 (Air Líquide), BuLi (1.6 M in hexane), $SiCl_4$, MgClMe (3 M in thf), $MgCl(CH_2SiMe_3)$ (1 M in diethyl ether) and $ZnMe_2$ (2 M in toluene) (Aldrich), NEt_3 and 2,6-$Me_2C_6H_3NC$ (Fluka) were purchased from commercial sources and were used without further purification.

Infrared spectra were recorded with a Perkin–Elmer Spectrum 2000 spectrophotometer (4000–300 cm^{-1}) with samples as Nujol mulls between CsI plates or in KBr pellets. ^1H, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra were recorded with Varian Unity 300 or Varian Unity 500 Plus spectrometers; chemical shifts were referenced to the ^{13}C (δ = 128, 77 ppm) or residual ^1H (δ = 7.15, 7.24 ppm) resonances of the [D_6]benzene or [D_1]chloroform solvents, respectively, and for the ^{29}Si NMR spectra, they were referenced to the internal TMS resonance. C, H and N analyses were carried out with a LECO CHNS 932 microanalyzer.

[Nb{η^5-$C_5H_3(SiMe_3)_2$}Cl_2(N*t*Bu)] (1): A mixture of LiNH*t*Bu (0.20 g, 2.25 mmol) and Nb{η^5-$C_5H_3(SiMe_3)_2$}Cl_4 (1.00 g, 2.25 mmol) was dissolved in hexane (50 mL) under rigorously anhydrous conditions. The reaction mixture was stirred for 2 h at room temperature, and then the resulting suspension was decanted and filtered. The filtrate was concentrated to dryness, and the residue was extracted with hexane (2 × 15 mL). Concentration and cooling of the filtrate produced **1** as an orange solid. Yield 0.80 g (80%). IR (KBr): $\tilde{\nu}$ = 2957 (s), 1402 (m), 1375 (m), 1249 (vs), 1090 (s), 840 (vs), 451 (m) cm^{-1}. ^1H NMR (300 MHz, [D_1]chloroform, 25°C): δ = 6.93 (m, 1 H), 6.76 [m, 2 H, $C_5\mathbf{H}_3(SiMe_3)_2$], 1.27 [s, 9 H, NbN(C$\mathbf{Me}_3$)], 0.29 [s, 18 H, $C_5H_3(Si\mathbf{Me}_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D_1]chloroform, 25°C): δ = 129.6 (Ci), 127.0, 121.8 [$\mathbf{C}_5H_3(SiMe_3)_2$], 70.1 [NbN(**C**$Me_3$)], 30.4 [NbN(C$\mathbf{Me}_3$)], –0.12 [$C_5H_3(Si\mathbf{Me}_3)_2$] ppm. $C_{15}H_{30}Cl_2NNbSi_2$ (444.394): calcd. C 40.54, H 6.80, N 3.15; found C 40.65, H 6.85, N 3.09.

[Nb{η^5-$C_5H_3(SiMe_3)_2$}Cl(Me)(N*t*Bu)] (2): A hexane (50 mL) solution of **1** (0.80 g, 1.80 mmol) was treated at room temperature with $ZnMe_2$ (2 M in toluene, 1.10 mL, 0.90 mmol). The reaction mixture was stirred for 1 h, and the solvent was removed under reduced pressure. The resulting brown residue was extracted with hexane (2 × 15 mL), the solution was concentrated and cooled to –20 °C to give a brown microcrystalline solid, which was characterized as **2** (0.56 g, 74%). IR (KBr): $\tilde{\nu}$ = 2959 (s), 1406 (m), 1356 (m), 1251 (vs), 1084 (vs), 840 (vs), 471 (m), 397 (s) cm^{-1}. ^1H NMR (300 MHz, [D_6]benzene, 25°C): δ = 6.55 (m, 1 H), 6.24 (br., 1 H), 6.17 [br., 1 H, $C_5\mathbf{H}_3(SiMe_3)_2$], 1.26 [s, 9 H, NbN(C$\mathbf{Me}_3$)], 1.24 (s, 3 H, Nb**Me**),

0.26 (s, 9 H), 0.23 [s, 9 H, $C_5H_3(SiMe_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 123.6, 122.9 (Ci), 121.3 (Ci), 118.7, 117.4 [$C_5H_3(SiMe_3)_2$], 70.5 [NbN(**C**Me$_3$)], 67.42 (Nb**Me**), 31.3 [NbN(C**Me**$_3$)], 0.15, –0.06 [$C_5H_3(Si\mathbf{Me}_3)_2$] ppm. $C_{16}H_{33}ClNNbSi_2$ (423.976): calcd. C 45.33, H 7.85, N 3.30; found C 45.46, H 7.94, N 3.29.

[Nb{η^5-C$_5$H$_3$(SiMe$_3$)$_2$}Me$_2$(N*t*Bu)] (3): At room temperature, MgClMe (3 M in tetrahydrofuran, 1.20 mL, 3.60 mmol) was added to a hexane (30 mL) solution of **1** (0.80 g, 1.80 mmol), and the mixture was stirred for 1 h. The colour of the mixture changed quickly from orange to red. The resulting suspension was decanted, the $MgCl_2$ formed was removed by filtration, and the filtrate was concentrated to a volume of ca. 10 mL. Cooling to –40 °C overnight led to the deposition of **3** as a red microcrystalline solid. Yield 0.51 g (70%). IR (KBr): $\tilde{\nu}$ = 2964 (s), 1406 (m), 1354 (m), 1251 (vs), 1084 (vs), 838 (vs), 545 (m), 486 (m) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25°C): δ = 6.34 (s, 1 H), 6.17 [m, 2 H, $C_5\mathbf{H}_3(SiMe_3)_2$], 1.41 [s, 9 H, NbN(C**Me**$_3$)], 0.60 (s, 6 H, Nb**Me**$_2$), 0.28 [s, 18 H, $C_5H_3(Si\mathbf{Me}_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]-benzene, 25°C): δ = 119.4 (Ci), 118.9, 116.3 [$\mathbf{C}_5H_3(SiMe_3)_2$], 70.0 [NbN(**C**Me$_3$)], 70.0 (Nb**Me**$_2$), 32.2 [NbN(C**Me**$_3$)], 0.21 [$C_5H_3(Si\mathbf{Me}_3)_2$] ppm. $C_{17}H_{36}NNbSi_2$ (403.558): calcd. C 50.60, H 8.99, N 3.47; found C 50.45, H 8.85, N 3.45.

[Nb{η^5-C$_5$H$_3$(SiMe$_3$)$_2$}(CH$_2$SiMe$_3$)$_2$(N*t*Bu)] (4): A hexane (40 mL) solution of **1** (1.04 g, 2.40 mmol) was treated with a 1 M solution of $MgCl(CH_2SiMe_3)$ in diethyl ether (0.48 mL, 4.80 mmol), and the mixture was stirred for 2 h. The suspension was decanted, the $MgCl_2$ formed was filtered off, and the solution was concentrated to dryness to give a yellow solid identified as **4**. Yield 0.78 g (60%). IR (KBr): $\tilde{\nu}$ = 2956 (s), 2360 (w), 1610 (m), 1407 (m), 1355 (m), 1260 (vs), 1086 (vs), 838 (vs), 756 (s), 636 (m), 472 (m), 392 (s) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25°C): δ = 6.64 (m, 1 H), 6.11 [m, 2 H, $C_5\mathbf{H}_3(SiMe_3)_2$], 1.45 [s, 9 H, NbN(C**Me**$_3$)], 0.96, 0.71 [AB, $^2J_{H,H}$ = 10 Hz, 4 H, Nb(C$\mathbf{H}_2$SiMe$_3$)$_2$], 0.27 [s, 18 H, $C_5H_3(Si\mathbf{Me}_3)_2$], 0.26 [s, 18 H, Nb(CH$_2$Si**Me**$_3$)$_2$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 129.8, 122.3 (Ci), 112.2 [$\mathbf{C}_5H_3(SiMe_3)_2$], 66.0 [NbN(**C**Me$_3$)], 50.9 [Nb(**C**H$_2$SiMe$_3$)$_2$], 33.0 [NbN(C**Me**$_3$)], 3.2 [Nb(CH$_2$Si**Me**$_3$)$_2$], 0.50 [$C_5H_3(Si\mathbf{Me}_3)_2$] ppm. $C_{23}H_{52}NNbSi_4$ (547.922): calcd. C 50.42, H 9.57, N 2.56; found C 50.45, H 9.60, N 2.45.

[Si$_8$O$_{12}$(*i*Bu)$_7$Cl] (5a): A stirred solution of $Si_7O_9(i\mathrm{Bu})_7(OH)_3$ (1.77 g, 2.24 mmol) and NEt_3 (0.94 mL, 6.72 mmol) in hexane (60 mL) was treated with $SiCl_4$ (0.24 mL, 2.24 mmol) under rigorously anhydrous conditions for 12 h. The suspension was decanted, the ammonium salt [NHEt$_3$]Cl formed was removed by filtration, the filtrate was concentrated to ca. 5 mL and cooled to –20 °C to give **5a** as a white microcrystalline solid. Yield 1.62 g (85%). IR (KBr): $\tilde{\nu}$ = 2956 (vs), 1467 (s), 1402 (m), 1368 (m), 1334 (m), 1232 (s), 1107 (vs), 839 (s), 742 (s), 654 (s), 478 (s) cm^{-1}. ^{1}H NMR (300 MHz, [D$_1$]chloroform, 25°C): δ = 1.85 [m, 7 H, (Me$_2$C**H**CH$_2$)$_7$-Si$_8$O$_{12}$Cl], 0.96 [m, 42 H, (**Me**$_2$CHCH$_2$)$_7$Si$_8$O$_{12}$Cl], 0.68 [m, 14 H, (Me$_2$CHC**H**$_2$)$_7$Si$_8$O$_{12}$Cl] ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_1$]chloroform, 25°C): δ = 25.8–25.6 [(**Me**$_2$CHCH$_2$)$_7$Si$_8$O$_{12}$Cl], 23.9–23.7 [(Me$_2$CH**C**H$_2$)$_7$Si$_8$O$_{12}$Cl], 23.1–22.0 [(Me$_2$**C**HCH$_2$)$_7$Si$_8$O$_{12}$Cl] ppm. $^{29}Si\{^1H\}$ NMR (60 MHz, [D$_1$]chloroform, 25°C): δ = –90.2 [1Si, Si$_7$O$_{12}$**Si**(Cl)(*i*Bu)$_7$], –67.8 (1Si), –66.8 (3Si), –66.7 [3Si, Si$_7$O$_{12}$Si-(Cl)(*i*Bu)$_7$] ppm. $C_{28}H_{63}ClO_{12}Si_8$ (851.938): calcd. C 39.48, H 7.45; found C 39.83, H 7.25.

[Si$_8$O$_{12}$(*i*Bu)$_7$(NH$_2$)] (5b): A solution of $Si_8O_{12}(i\mathrm{Bu})_7Cl$ (0.34 g, 0.40 mmol) in dichloromethane (50 mL) was placed in an ampoule under rigorously anhydrous conditions. The ampoule was cooled to –78 °C, and then the inert atmosphere was replaced with NH_3 (g). The solution was warmed to room temperature and stirred vigorously for 15 h. After the ampoule was opened, the ammonium salt formed was removed by filtration, and the filtrate was concentrated to a volume of ca. 10 mL. Cooling at –40 °C led to the deposition of a white microcrystalline solid identified as **5b**. Yield 0.31 g (90%). IR (KBr): $\tilde{\nu}$ = 3432 (m), 2956 (vs), 1467 (m), 1232 (s), 1100 (vs), 911 (s), 839 (s), 743 (vs), 565 (s), 483 (vs), 432 (s) cm^{-1}. ^{1}H NMR (300 MHz, [D$_1$]chloroform, 25°C): δ = 1.83 [m, 7 H, (Me$_2$C**H**CH$_2$)$_7$Si$_8$O$_{12}$(NH$_2$)], not observed [(Me$_2$CHCH$_2$)$_7$Si$_8$O$_{12}$-(N**H**$_2$)], 0.94 [dd, $^3J_{H,H}$ = 6.6, $^4J_{H,H}$ = 1.8 Hz, 42 H, **Me**$_2$CHCH$_2$-Si$_8$O$_{12}$(NH$_2$)], 0.59 [t, $^3J_{H,H}$ = 6.6 Hz, 14 H, (Me$_2$CHC**H**$_2$)$_7$-Si$_8$O$_{12}$(NH$_2$)] ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_1$]chloroform, 25°C): δ = 25.7, 25.64, 25.63 [3:1:3, (**Me**$_2$CHCH$_2$)$_7$Si$_8$O$_{12}$(NH$_2$)], 23.82 [(Me$_2$CH**C**H$_2$)$_7$Si$_8$O$_{12}$(NH$_2$)], 22.47, 22.44, 22.40 [(Me$_2$**C**HCH$_2$)$_7$Si$_8$O$_{12}$(NH$_2$)] ppm. $^{29}Si\{^1H\}$ NMR (60 MHz, [D$_1$]-chloroform, 25°C): δ = –87.4 [1Si, Si$_7$O$_{12}$**Si**(NH$_2$)(*i*Bu)$_7$], –67.45 (1Si), –67.42 (3Si), –67 [3Si, **Si**$_7$O$_{12}$Si(NH$_2$)(*i*Bu)$_7$] ppm. $C_{28}H_{65}NO_{12}Si_8$ (832.508): calcd. C 40.40, H 7.87, N 1.68; found C 40.25, H 7.81, N 1.67.

[Li$_3$Si$_7$O$_{12}$(*i*Bu)$_7$] (5c): BuLi (1.6 M in hexane, 0.82 mL, 1.32 mmol) was added dropwise at 0 °C to a hexane (60 mL) solution of $Si_7O_9(i\mathrm{Bu})_7(OH)_3$ (0.35 g, 0.44 mmol). The reaction mixture was then warmed to room temperature and stirred for 20 h. The LiCl formed was filtered off, and the volatiles were partially removed at reduced pressure to give **5c** as a white microcrystalline solid. Yield 0.27 g (76%). IR (KBr): $\tilde{\nu}$ = 2955 (vs), 1467 (s), 1367 (m), 1332 (m), 1230 (s), 1100 (vs), 971 (s), 836 (s), 739 (vs), 584 (s), 497 (s) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25°C): δ = 2.21 [m, 7 H, (Me$_2$C**H**CH$_2$Si)$_7$O$_{12}$Li$_3$], 1.25 [m, 42 H, (**Me**$_2$CHCH$_2$Si)$_7$O$_{12}$Li$_3$], 1.10 [m, 14 H, (Me$_2$CHC**H**$_2$Si)$_7$O$_{12}$Li$_3$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 26.7–25.5 [(**Me**$_2$CHCH$_2$Si)$_7$-O$_{12}$Li$_3$], 24.7–24.5 [(Me$_2$**C**HCH$_2$Si)$_7$O$_{12}$Li$_3$], 23.0 [(Me$_2$CH**C**H$_2$Si)$_7$-O$_{12}$Li$_3$] ppm. $C_{28}H_{63}Li_3O_{12}Si_7$ (809.223): calcd. C 41.56, H 7.85; found C 41.63, H 7.93.

[Nb{η^5-C$_5$H$_3$(SiMe$_3$)(SiXMe$_2$)}Cl$_2${NSi$_8$O$_{12}$(*i*Bu)$_7$}] (X = Cl 6a, Me 6b): Under rigorously anhydrous conditions, a hexane (25 mL) solution of [Nb{η^5-C$_5$H$_3$(SiXMe$_2$)(SiMe$_3$)}Cl$_4$] (1.00 mmol; X = Cl, 0.465 g; X = Me, 0.444 g) was treated at room temperature with a solution of $Si_8O_{12}(i\mathrm{Bu})_7(NH_2)$ (0.83 g, 1.00 mmol) and triethylamine (0.20 g, 2.00 mmol) in hexane (15 mL) for 5 h. The suspension was decanted, and the ammonium salt was filtered off. Afterwards, the volatiles were removed under reduced pressure to give **6a/6b** as microcrystalline yellow solids. Yields **6a** (0.98 g, 80%) and **6b** (1.08 g, 90%).

6a: IR (CsI/Nujol mull): $\tilde{\nu}$ = 2954 (vs), 1466 (vs), 1332 (s), 1260 (vs), 1076 (vs), 919 (s), 841 (vs), 737 (m), 568 (m), 507 (s) cm^{-1}. ^{1}H NMR (300 MHz, [D$_1$]chloroform, 25°C): δ = 7.17 (m, 1 H), 6.85 [m, 2 H, $C_5\mathbf{H}_3(SiClMe_2)(SiMe_3)$], 1.81 [m, 7 H, NSi(Me$_2$C**H**CH$_2$Si)$_7$-O$_{12}$], 0.93 [m, 42 H, NSi(**Me**$_2$CHCH$_2$Si)$_7$O$_{12}$], 0.62 [m, 14 H, NSi-(Me$_2$CHC**H**$_2$Si)$_7$O$_{12}$], 0.294 [s, 9 H, $C_5H_3(SiClMe_2)(Si\mathbf{Me}_3)$], 0.290 (s, 3 H), 0.03 [s, 3 H, $C_5H_3(SiCl\mathbf{Me}_2)(SiMe_3)$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_1$]chloroform, 25°C): δ = 131.1 (Ci), 127.1, 125.7 (Ci), 123.7, 123.6 [$\mathbf{C}_5H_3(SiClMe_2)(SiMe_3)$], 25.7, 25.6 [NSi(**Me**$_2$-CHCH$_2$Si)$_7$O$_{12}$], 23.67, 23.71 [NSi(Me$_2$CH**C**H$_2$Si)$_7$O$_{12}$], 22.3, 22.2 [NSi(Me$_2$**C**HCH$_2$Si)$_7$O$_{12}$], 3.0, 2.1, [$C_5H_3(SiCl\mathbf{Me}_2)(SiMe_3)$], –0.55 [$C_5H_3(SiClMe_2)(Si\mathbf{Me}_3)$] ppm. $^{29}Si\{^1H\}$ NMR (60 MHz, [D$_6$]benzene, 25°C): δ = 15.52 [$C_5H_3(\mathbf{Si}ClMe_2)(SiMe_3)$], –5.12 [$C_5H_3(SiClMe_2)(\mathbf{Si}Me_3)$], –66.86, –66.88, –66.95, –67.82, –67.84, –67.86, –67.88 [NSi(Me$_2$CHCH$_2$**Si**)$_7$O$_{12}$], not observed [N**Si**-(Me$_2$CHCH$_2$Si)$_7$O$_{12}$] ppm. $C_{38}H_{81}Cl_3NNbO_{12}Si_{10}$ (1224.176): calcd. C 37.28, H 6.67, N 1.14; found C 37.48, H 6.65, N 1.20.

6b: IR (CsI/Nujol mull): $\tilde{\nu}$ = 2952 (vs), 1464 (vs), 1332 (s), 1255 (vs), 1176 (vs), 919 (vs), 846 (s), 739 (s), 567 (m), 499 (s) cm^{-1}. ^{1}H

NMR (300 MHz, [D$_1$]chloroform, 25°C): δ = 7.03 (m, 1 H), 6.77 [m, 2 H, $C_5H_3(SiMe_3)_2$], 1.80 [m, 7 H, $NSi(Me_2CHCH_2Si)_7O_{12}$], 0.90 [m, 42 H, $NSi(Me_2CHCH_2Si)_7O_{12}$], 0.59 (d, $^2J_{H,H}$ = 7.5 Hz, 7 H), 0.52 [d, $^2J_{H,H}$ = 7.5 Hz, 7 H, $NSi(Me_2CHCH_2Si)_7O_{12}$], 0.25 [s, 18 H, $C_5H_3(SiMe_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_1$]chloroform, 25°C): δ = 131.0, 125.8, 123.7 [$C_5H_3(SiMe_3)_2$], 25.3, 25.1 [$NSi(Me_2CHCH_2Si)_7O_{12}$], 23.3 [$NSi(Me_2CHCH_2Si)_7O_{12}$], 22.0, 21.9 [$NSi(Me_2CHCH_2Si)_7O_{12}$], –0.89 [$C_5H_3(SiMe_3)_2$] ppm. $C_{39}H_{84}Cl_2NNbO_{12}Si_{10}$ (1203.758): calcd. C 38.91, H 7.03, N 1.16; found C 39.17, H 7.13, N 1.12.

[Nb{η^5-C$_5$H$_3$(SiMe$_3$)$_2$}X(Me)(NSi$_8$O$_{12}$R$_7$)] (R = *i*Bu, X = Cl 7, Me 8)

7: In a sealed NMR tube and under rigorously anhydrous conditions, [D$_6$]benzene (0.70 mL) was added to a mixture of complex **6b** (0.060 g, 0.050 mmol) and $ZnMe_2$ (2 M in toluene, 0.050 mL, 0.100 mmol). The colour of the mixture changed quickly from yellow to brown. The reaction was monitored by ^{1}H NMR spectroscopy, and after 1 h, the spectrum showed the total conversion of **6** into chloridomethyl derivative **7** in quantitative yield. The suspension was decanted and filtered. The filtrate was concentrated to dryness, and the residue was extracted with hexane (2 × 5 mL). The resulting solution was concentrated to ca. 1 mL and cooled to –40°C to give **7** as a microcrystalline brown solid. Yield 0.047 g (80%). IR (CsI/Nujol mull): $\tilde{\nu}$ = 2950 (vs), 1463 (s), 1365 (m), 1335 (m), 1245 (vs), 1109 (vs), 925 (s), 839 (s), 747 (m), 577 (m), 480 (m) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25°C): δ = 6.70 (m, 1 H), 6.43 (m, 1 H), 6.33 [m, 1 H, $C_5H_3(SiMe_3)_2$], 2.14 [m, 7 H, $NSi(Me_2CHCH_2Si)_7O_{12}$], 1.47 (s, 3 H, Nb**Me**), 1.12 [m, 42 H, $NSi(Me_2CHCH_2Si)_7O_{12}$], 0.85 [m, 14 H, $NSi(Me_2CHCH_2Si)_7O_{12}$], 0.32 (s, 9 H), 0.29 [s, 9 H, $C_5H_3(SiMe_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 129.3 (Ci), 124.3 (Ci), 122.9, 120.6, 119.8 [$C_5H_3(SiMe_3)_2$], 48.2 (Nb**Me**), 26.1, 25.9 [$NSi(Me_2CHCH_2Si)_7O_{12}$], 24.4 [$NSi(Me_2CHCH_2Si)_7O_{12}$], 23.1, 23.0 [$NSi(Me_2CHCH_2Si)_7O_{12}$], –0.1, –0.2 [$C_5H_3(SiMe_3)_2$] ppm. $C_{40}H_{87}ClNNbO_{12}Si_{10}$ (1183.34): calcd. C 40.60, H 7.41, N 1.18; found C 40.80, H 7.64, N 1.93.

8: At room temperature, a tetrahydrofuran solution of MgClMe (3 M, 0.33 mL, 1.00 mmol) was added to a hexane (40 mL) solution of **6b** (0.60 g, 0.50 mmol). After 1 h, the resulting brown suspension was decanted, and the $MgCl_2$ formed was separated by filtration. The volatiles were removed under reduced pressure, and the residue was extracted with hexane (2 × 10 mL). The solution was filtered, concentrated to ca. 5 mL and cooled to –40°C to give **8** as a microcrystalline brown solid. Yield 0.29 g (50%). IR (CsI/Nujol mull): $\tilde{\nu}$ = 2955 (vs), 1466 (s), 1367 (m), 1333 (m), 1261 (s), 1111 (vs), 920 (s), 839 (vs), 742 (s), 567 (m), 484 (s) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25°C): δ = 6.46 (m, 1 H), 6.27 [m, 2 H, $C_5H_3(SiMe_3)_2$], 2.10 [m, 7 H, $NSi(Me_2CHCH_2Si)_7O_{12}$], 1.10 [m, 42 H, $NSi(Me_2CHCH_2Si)_7O_{12}$], 0.88 [m, 14 H, $NSi(Me_2CHCH_2Si)_7O_{12}$], 0.80 (s, 6 H, Nb$Me_2$), 0.26 [s, 18 H, $C_5H_3(SiMe_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 125.4 (Ci), 119.7, 117.3 [$C_5H_3(SiMe_3)_2$], 38.6 (NbMe_2), 26.10, 25.94, 25.90 [$NSi(Me_2CHCH_2Si)_7O_{12}$], 24.43, 24.40 [$NSi(Me_2CHCH_2Si)_7O_{12}$], 23.3, 23.0 [$NSi(Me_2CHCH_2Si)_7O_{12}$], –0.06 [$C_5H_3(SiMe_3)_2$] ppm. $C_{41}H_{90}NNbO_{12}Si_{10}$ (1162.922): calcd. C 42.35, H 7.80, N 1.20; found C 42.25, H 7.69, N 1.27.

[Nb{η^5-C$_5$H$_3$(SiMe$_3$)$_2$}(CH$_2$SiMe$_3$)$_2$(NSi$_8$O$_{12}$(*i*Bu)$_7$)] (9): In a valved NMR tube, a [D$_6$]benzene (0.70 mL) solution of **6b** (0.30 g, 0.25 mmol) was treated with a slight excess of $LiCH_2SiMe_3$ (0.52 g, 0.55 mmol). The reaction was checked by ^{1}H NMR spectroscopy. After 2 h the spectrum showed the transformation of **6b** into dialkyl compound **9** with a nearly quantitative yield. The suspension was decanted, filtered, and the solvent was removed under reduced pressure. The residue was extracted with hexane (2 × 10 mL), and the solution was concentrated to ca. 5 mL and cooled overnight to –40°C, giving **9** as a microcrystalline yellow solid. Yield 0.22 g (70%). IR (CsI/Nujol mull): $\tilde{\nu}$ = 2954 (vs), 1466 (s), 1333 (m), 1261 (s), 1111 (vs), 920 (s), 839 (vs), 742 (s), 484 (s) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25°C): δ = 6.62 (br., 1 H), 6.35 [br., 2 H, $C_5H_3(SiMe_3)_2$], 2.13 [m, 7 H, $NSi(Me_2CHCH_2Si)_7O_{12}$], 1.15 [m, 42 H, $NSi(Me_2CHCH_2Si)_7O_{12}$], 0.86 [m, 14 H, $NSi(Me_2CHCH_2Si)_7O_{12}$], 1.26, 0.58 [AB, $^2J_{H,H}$ = 11 Hz, 4 H, $Nb(CH_2SiMe_3)_2$], 0.36 [s, 18 H, $C_5H_3(SiMe_3)_2$], 0.31 [s, 18 H, $Nb(CH_2SiMe_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 124.0, 114.5, 110.4 (Ci, $C_5H_3(SiMe_3)_2$], 56.4 [$Nb(CH_2SiMe_3)_2$], 26.2, 26.0, 25.9 [$NSi(Me_2CHCH_2Si)_7O_{12}$], 24.5, 24.4 [$NSi(Me_2CHCH_2Si)_7O_{12}$], 23.5, 23.0 [$NSi(Me_2CHCH_2Si)_7O_{12}$], 2.5 [$Nb(CH_2SiMe_3)_2$], 0.1 [$C_5H_3(SiMe_3)_2$] ppm. $C_{47}H_{106}NNbO_{12}Si_{12}$ (1307.286): calcd. C 43.18, H 8.17, N 1.07; found C 43.01, H 8.08, N 1.00.

[Nb{η^5-C$_5$H$_3$(SiMe$_3$)(Me$_2$SiOSi$_7$O$_{11}$R$_7$-κ^2*O*,*O*)}Cl$_2$] (R = *i*Bu 10): The synthesis of complex **10** was carried out by two different methods.

Method A: [Nb{η^5-$C_5H_3(SiClMe_2)(SiMe_3)$}Cl_4] (0.40 g, 0.86 mmol) was added to a hexane (50 mL) solution of $Si_7O_9(iBu)_7(OH)_3$ (0.34 g, 0.42 mmol) and triethylamine (0.26 g, 2.58 mmol). The mixture was stirred for 4 h, and the suspension was then decanted. The ammonium salt formed was filtered off, and the solution was concentrated to ca. 10 mL. Cooling of the solution to –40 °C gave **10** as a microcrystalline yellow solid. Yield 0.88 g (90%).

Method B: In a standard experiment, a solution in [D$_6$]benzene (0.70 mL) of [Nb{η^5-$C_5H_3(SiClMe_2)(SiMe_3)$}Cl_4] (0.25 g, 0.54 mmol) and $[Li_3Si_7O_{12}(iBu)_7]$ (0.45 g, 0.57 mmol) was transferred to a valved NMR tube. The colour of the mixture changed quickly from dark red to yellow, and the reaction was monitored for 30 min by ^{1}H NMR spectroscopy until quantitative conversion of the niobium starting complex to **10** was observed. The solvent was removed in vacuo, and the residue was extracted into hexane (2 × 10 mL). The hexane solution was concentrated to ca. 5 mL and cooled to –40°C to give **10** as a microcrystalline yellow solid. Yield 0.46 g (75%). IR (CsI/Nujol mull): $\tilde{\nu}$ = 2961 (vs), 1465 (vs), 1401 (vs), 1366 (vs), 1332 (vs), 1260 (vs), 1233 (s), 1095 (s), 967 (s), 739 (s), 634 (m), 584 (m), 471 (vs) cm^{-1}. ^{1}H NMR (300 MHz, [D$_1$]-chloroform, 25°C): δ = 7.05 (br., 2 H), 6.83 [m, 1 H, $C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7)$], 1.84 [m, 7 H, $C_5H_3(SiMe_3)\{Me_2SiO(Me_2CHCH_2Si)_7O_{11}\}$], 0.94 [m, 42 H, $C_5H_3(SiMe_3)\{Me_2SiO(Me_2CHCH_2Si)_7O_{11}\}$], 0.58 [m, 14 H, $C_5H_3(SiMe_3)\{Me_2SiO(Me_2CHCH_2Si)_7O_{11}\}$], 0.43 (s, 3 H), 0.28 [s, 3 H, $C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7)$], 0.38 [s, 9 H, $C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7)$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_1$]chloroform, 25°C): δ = 142.7 (Ci), 135.5 (Ci), 132.1, 129.7, 127.0 [$C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7)$], 26.6–25.6 [$C_5H_3(SiMe_3)\{Me_2SiO(Me_2CHCH_2Si)_7O_{11}\}$], 24.1, 24.0, 23.9, 23.8 [$C_5H_3(SiMe_3)\{Me_2SiO(Me_2CHCH_2Si)_7O_{11}\}$], 23.21, 22.9, 22.3, 22.2, 22.1 [$C_5H_3(SiMe_3)\{Me_2SiO(Me_2CHCH_2Si)_7O_{11}\}$], 2.5, 0.6 [$C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7)$], –0.5 [$C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7)$] ppm. $^{29}Si\{^1H\}$ NMR (60 MHz, [D$_6$]benzene, 25°C): δ = –69.2, –68.1, –67.7, –66.3, –66.21, –66.16, –63.7 [$C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7)$], –4.91 [$C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7)$], –3.57 [$C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7)$] ppm. $C_{38}H_{81}Cl_2NbO_{12}Si_9$ (1146.542): calcd. C 39.81, H 7.11; found C 39.90, H 7.18.

[Nb{η^5-C$_5$H$_3$(SiMe$_3$)(Me$_2$SiOSi$_7$O$_{11}$R$_7$-κ^2*O*,*O*)}(N*t*Bu)] (R = *i*Bu 11): Complex **11** was prepared by two different methods.

Method A: LiN*t*Bu (0.10 g, 1.50 mmol) was added at room temperature to a hexane (20 mL) solution of **10** (0.57 g, 0.50 mmol),

and the mixture was stirred for 12 h. The LiCl formed was removed by filtration, and the filtrate was concentrated to a volume of ca. 5 mL. Cooling at –40 °C overnight led to the deposition of a microcrystalline yellow solid identified as **11**. Yield 0.46 g (80%).

Method B: Hexane (60 mL) was added to a mixture of [Nb{η^5-$C_5H_3(SiClMe_2)(SiMe_3)$}Cl_2(N*t*Bu)](0.24 g,0.51 mmol),Si_7O_9(*i*Bu)$_7$-$(OH)_3$ (0.41 g, 0.51 mmol) and NEt_3 (0.27 mL, 1.24 mmol), and the mixture was stirred for 4 h. The resulting suspension was decanted and filtered. The solution was concentrated to ca. 5 mL and cooled to –40 °C to give **11** as a microcrystalline yellow solid. Yield 0.50 g (85%). IR (CsI/Nujol mull): ṽ = 2954 (vs), 1465 (vs), 1366 (s), 1331 (s), 1251 (vs), 1228 (vs), 1103 (vs), 978 (vs), 919 (vs), 839 (s), 740 (s), 609 (s), 536 (m), 478 (s) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25°C): δ = 7.20 (m, 1 H), 7.00 (m, 1 H), 6.20 [m, 1 H, $C_5\mathbf{H}_3$(SiMe$_3$)$(Me_2SiOSi_7O_{11}R_7)$], 2.14 [m, 7 H, $C_5H_3(SiMe_3)$}{Me_2SiO-$(Me_2C\mathbf{H}CH_2Si)_7O_{11}$}], 1.26 (s, 9 H, NbNC**Me**$_3$), 1.12 [m, 42 H, $C_5H_3(SiMe_3)$}{Me_2SiO(**Me**$_2$$CHCH_2Si)_7O_{11}$}], 0.85 [m, 14 H, $C_5H_3(SiMe_3)$}{$Me_2SiO(Me_2CHC\mathbf{H}_2Si)_7O_{11}$}], 0.62 (s, 3 H), 0.27 [s, 3 H, $C_5H_3(SiMe_3)$(**Me**$_2$$SiOSi_7O_{11}R_7$)], 0.30 [s, 9 H, C_5H_3(Si**Me**$_3$)-$(Me_2SiOSi_7O_{11}R_7)$] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 132.0 (Ci), 131.8, 123.9 (Ci), 115.5, 113.73 [**C**$_5$H$_3$(SiMe$_3$)-$(Me_2SiOSi_7O_{11}R_7)$], 66.8 (NbN**C**Me$_3$), 32.2 (NbNC**Me**$_3$), 26.5–26.2 [$C_5H_3(SiMe_3)$}{Me_2SiO(**Me**$_2$$CHCH_2Si)_7O_{11}$}], 25.0–24.5 [$C_5H_3$-$(SiMe_3)$}{$Me_2SiO(Me_2CH\mathbf{C}H_2Si)_7O_{11}$}], 24.0–23.0 [$C_5H_3(SiMe_3)$-}{$Me_2SiO(Me_2\mathbf{C}HCH_2Si)_7O_{11}$}], 3.63, –0.63 [$C_5H_3(SiMe_3)$(**Me**$_2$-$SiOSi_7O_{11}R_7$)], –0.27 [$C_5H_3$(Si**Me**$_3$)$(Me_2SiOSi_7O_{11}R_7)$] ppm. $C_{42}H_{90}NNbO_{12}Si_9$ (1146.848): calcd. C 43.99, H 7.91, N 1.22; found C 43.82, H 7.74, N 1.09.

[Nb{η^5-$C_5H_3(SiMe_3)_2$}Cl($Si_7O_{12}R_7$-κ^3*O*,*O*,*O*)] (R = *i*Bu 12): A solution of [Nb{η^5-$C_5H_3(SiMe_3)_2$}Cl_4] (0.33 g, 0.75 mmol) in hexane (20 mL) was added to a solution of $Si_7O_9(OH)_3$(*i*Bu)$_7$ (0.30 g, 0.37 mmol) and triethylamine (0.23 g, 2.25 mmol) in hexane (10 mL) at room temperature. The reaction mixture was stirred for 4 h. The supernatant solution was separated from the solid by filtration, and the filtrate was concentrated to dryness. The residue was extracted with cool hexane (2 × 10 mL). The resulting solution was filtered, and the solvent was partially removed under reduced pressure to give a microcrystalline yellow solid identified as **12**. Yield 0.71 g (85%). IR (KBr): ṽ = 2954 (vs), 1465 (m), 1251 (s), 1228 (s), 1099 (vs), 998 (vs), 842 (vs), 756 (m), 634 (w), 464 (m), 391 (s) cm^{-1}. ^{1}H NMR (300 MHz, [D$_1$]chloroform, 25°C): δ = 6.92 (br., 2 H), 6.83 [br., 1 H, $C_5\mathbf{H}_3(SiMe_3)_2$], 1.78 [m, 7 H, $(Me_2C\mathbf{H}CH_2Si)_7O_{12}$], 0.87 [m, 42 H, (**Me**$_2$$CHCH_2Si)_7O_{12}$], 0.52 [m, 14 H, $(Me_2CHC\mathbf{H}_2Si)_7O_{12}$], 0.29 [s, 18 H, C_5H_3(Si**Me**$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_1$]chloroform, 25°C): δ = 135.6, 133.9 (Ci), 129.4 [**C**$_5$H$_3$(SiMe$_3$)$_2$], 25.6, 25.5, 25.4 [(**Me**$_2$$CHCH_2Si)_7O_{12}$], 23.6, 23.5 [$(Me_2CH\mathbf{C}H_2Si)_7O_{12}$], 23 [$(Me_2\mathbf{C}HCH_2Si)_7O_{12}$], –1.1 [$C_5H_3$(Si**Me**$_3$)$_2$] ppm. $C_{39}H_{84}ClNbO_{12}Si_9$ (1126.213): calcd. C 41.59, H 7.52; found C 41.82, H 7.53.

[Nb{η^5-$C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7$-κ^2*O*,*O*)}$Me_2$] (R = *i*Bu 13): At room temperature, a stirred hexane (30 mL) solution of **10** (0.92 g, 0.80 mmol) was treated with a 2 M toluene solution of $ZnMe_2$ (0.80 mL, 1.60 mmol). After 12 h, the resulting suspension was decanted, and the $ZnCl_2$ formed was separated by filtration. The volatiles were removed under reduced pressure to give **13** as a microcrystalline brown solid. Yield 0.62 g (70%). IR (KBr): ṽ = 2954 (vs), 1465 (s), 1402 (m), 1331 (m), 1259 (vs), 1228 (s), 1099 (vs), 990 (vs), 839 (vs), 741 (s), 479 (s), 392 (m) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25°C): δ = 6.55 (m, 1 H), 6.33 [m, 2 H, $C_5\mathbf{H}_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7)$], 2.14 [m, 7 H, $C_5H_3(SiMe_3)$-}{$Me_2SiO(Me_2C\mathbf{H}CH_2Si)_7O_{11}$}], 1.13 [m, 42 H, $C_5H_3(SiMe_3)$ {Me_2-SiO(**Me**$_2$$CHCH_2Si)_7O_{11}$}], 0.86 [m, 14 H, $C_5H_3(SiMe_3)$ {Me_2SiO-$(Me_2CHC\mathbf{H}_2Si)_7O_{11}$}], 0.22 (s, 6 H, Nb**Me**$_2$), 0.35 (s, 3 H), 0.28 [s, 3 H, $C_5H_3(SiMe_3)$(**Me**$_2$$SiOSi_7O_{11}R_7$)], 0.27 [s, 9 H, C_5H_3(Si**Me**$_3$)-$(Me_2SiOSi_7O_{11}R_7)$] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 132.6 (Ci), 126.4, 123.6 (Ci), 121.3, 119.8 [**C**$_5$H$_3$(SiMe$_3$)-$(Me_2SiOSi_7O_{11}R_7)$], 53.5, 53 (Nb**Me**$_2$), 26.4–25.9 [$C_5H_3(SiMe_3)$ {Me_2SiO(**Me**$_2$$CHCH_2Si)_7O_{11}$}], 24.8–24.5 [$C_5H_3(SiMe_3)$}{$Me_2SiO$-$(Me_2CH\mathbf{C}H_2Si)_7O_{11}$}], 24.0, 23.8, 23.1, 23.0 [$C_5H_3(SiMe_3)$}{Me_2-$SiO(Me_2\mathbf{C}HCH_2Si)_7O_{11}$}], 2.7, 0.9 [$C_5H_3(SiMe_3)$(**Me**$_2$$SiOSi_7$-$O_{11}R_7$)], –0.4 [$C_5H_3$(Si**Me**$_3$)$(Me_2SiOSi_7O_{11}R_7)$] ppm. $C_{40}H_{87}Nb$-$O_{12}Si_9$ (1105.795): calcd. C 43.45, H 7.93; found C 43.33, H 7.65.

[Nb{η^5-$C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7$-κ^2*O*,*O*)}(CHSi$Me_3$)] (R = *i*Bu 14): A hexane (25 mL) solution of **10** (0.57 g, 0.50 mmol) was treated with a 1 M solution of $MgCl(CH_2SiMe_3)$ in diethyl ether (1.00 mL, 1.00 mmol), and the colour of the mixture changed quickly from yellow to dark orange. The resulting suspension was stirred for 1 h, the magnesium chloride formed was then removed by filtration, and the filtrate was concentrated to a volume of ca. 5 mL. Cooling at –40 °C yielded **14** as a microcrystalline orange solid. Yield 0.44 g (77%). IR (KBr): ṽ = 2954 (vs), 2717 (w), 2625 (w), 1465 (s), 1365 (m), 1331 (m), 1252 (vs), 1228 (s), 1115 (vs), 983 (s), 839 (vs), 740 (s), 686 (m), 631 (m), 477 (s) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25°C): δ = 9.68 (s, 1 H, NbC**H**SiMe$_3$), 8.06 (m, 1 H), 6.65 (m, 1 H), 6.38 [m, 1 H, $C_5\mathbf{H}_3(SiMe_3)(Me_2$-$SiOSi_7O_{11}R_7)$], 2.07 [m, 7 H, $C_5H_3(SiMe_3)$ {$Me_2SiO(Me_2C\mathbf{H}$-$CH_2Si)_7O_{11}$}], 1.11 [m, 42 H, $C_5H_3(SiMe_3)$ {Me_2SiO(**Me**$_2$-$CHCH_2Si)_7O_{11}$}], 0.88 [m, 14 H, $C_5H_3(SiMe_3)$}{Me_2SiO-$(Me_2CHC\mathbf{H}_2Si)_7O_{11}$}], 0.385 (s, 3 H), 0.381 [s, 3 H, $C_5H_3(SiMe_3)$-(**Me**$_2$$SiOSi_7O_{11}R_7$)], 0.25 [s, 9 H, C_5H_3(Si**Me**$_3$)$(Me_2SiOSi_7O_{11}R_7)$], 0.21 (s, 9 H, NbCHSi**Me**$_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]-benzene, 25°C): δ = 235.73 (Nb**C**HSiMe$_3$), 129.6 (Ci), 124.5 (Ci), 120.3, 119.2, 112.43 [**C**$_5$H$_3$(SiMe$_3$)$(Me_2SiOSi_7O_{11}R_7)$], 26.4–25.9 [$C_5H_3(SiMe_3)$}{Me_2SiO(**Me**$_2$$CHCH_2Si)_7O_{11}$}], 24.9–24.1 [$C_5H_3$(Si-$Me_3$)}{$Me_2SiO(Me_2CH\mathbf{C}H_2Si)_7O_{11}$}], 23.6, 23.3, 23.0 [$C_5H_3$-$(SiMe_3)$}{$Me_2SiO(Me_2\mathbf{C}HCH_2Si)_7O_{11}$}], 3.7, 3.3 [$C_5H_3(SiMe_3)$-(**Me**$_2$$SiOSi_7O_{11}R_7$)], 2.36 (NbCHSi**Me**$_3$), –0.5 [$C_5H_3$(Si**Me**$_3$)$(Me_2$-$SiOSi_7O_{11}R_7)$] ppm. $C_{42}H_{89}NbO_{12}Si_{10}$ (1159.918): calcd. C 43.49, H 7.73; found C 43.38, H 7.78.

[Nb{η^5-$C_5H_3(SiMe_3)_2$}Me($Si_7O_{12}R_7$-κ^3*O*,*O*,*O*)] (R = *i*Bu 15): Under rigorously anhydrous conditions, a toluene (20 mL) solution of **12** (0.84 g, 0.75 mmol) was treated with excess $ZnMe_2$ (2 M in toluene, 0.37 mL, 0.75 mmol), and the mixture was stirred at room temperature for 12 h. The resulting suspension was decanted and filtered. The solution was concentrated to ca. 5 mL and cooled to –40°C to give **15** as a microcrystalline brown solid. Yield 0.58 g (70%). IR (KBr): ṽ = 2954 (vs), 1466 (s), 1402 (m), 1332 (m), 1252 (s), 1229 (s), 1097 (vs), 997 (s), 838 (vs), 741 (s), 634 (m), 467 (s), 388 (m) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25°C): δ = 6.91 (br., 1 H), 6.63 [br., 2 H, $C_5\mathbf{H}_3(SiMe_3)_2$], 2.13 [m, 7 H, $(Me_2C\mathbf{H}CH_2Si)_7O_{12}$], 1.52 (br., 3 H, Nb**Me**), 1.10 [m, 42 H, (**Me**$_2$$CHCH_2Si)_7O_{12}$], 0.85 [m, 14 H, $(Me_2CHC\mathbf{H}_2Si)_7O_{12}$], 0.28 [s, 18 H, C_5H_3(Si**Me**$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 133.0, 132.1, 127.1, 125.1, 123.5 [**C**$_5$H$_3$(SiMe$_3$)$_2$], 52.2 [Nb**Me**], 26.1–25.9 [(**Me**$_2$$CHCH_2Si)_7O_{12}$], 24.5, 24.4 [$(Me_2CH\mathbf{C}H_2Si)_7O_{12}$], 23.5, 23.1 [$(Me_2\mathbf{C}HCH_2Si)_7O_{12}$], –0.1 [$C_5H_3$(Si**Me**$_3$)$_2$] ppm. $C_{40}H_{87}NbO_{12}Si_9$ (1105.795): calcd. C 43.45, H 7.93; found C 43.57, H 8.02.

[Nb{η^5-$C_5H_3(SiMe_3)_2$}R(N*t*Bu){C(Me)O-κ^2*C*,*O*}] (R = Cl 16, Me 17): A [D$_6$]benzene (0.70 mL) solution of **2** (0.21 g, 0.50 mmol) or **3** (0.20 g, 0.50 mmol) was placed in a valved NMR tube, and the argon atmosphere was replaced by carbon monoxide (1 atm). The solution was shaken until it was homogeneous, and the colour of the mixture changed from dark brown to orange. The reaction was

monitored by ^{1}H NMR spectroscopy, and after 30 min the complete conversion of the starting niobium complex into the acyl derivative was confirmed. The resulting solution was then concentrated to dryness to give an orange microcrystalline solid identified as **16** (R = Cl) or **17** (R = Me).

16: IR (KBr): $\tilde{\nu}$ = 2966 (vs), 1577 (s), 1356 (s), 1248 (s), 1083 (s), 920 (s), 838 (vs), 756 (s), 635 (m), 546 (m), 473 (m) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25°C): δ = 6.81 (m, 1 H), 6.21 [m, 2 H, C$_5$**H**$_3$(SiMe$_3$)$_2$], 2.47 [s, 3 H, NbC(**Me**)O], 0.97 (s, 9 H, NbC**Me**$_3$), 0.44 (s, 9 H), 0.01 [s, 9 H, C$_5$H$_3$(Si**Me**$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 295.2 [**C**(Me)O], 122.3 (Ci), 122.0 (Ci), 116.5, 110.9, 110.7 [**C**$_5$H$_3$(SiMe$_3$)$_2$], 65.8 (NbN**C**Me$_3$), 32.4 (NbNC**Me**$_3$), 29.5 [C(**Me**)O], –0.15, –0.19 [C$_5$H$_3$(Si**Me**$_3$)$_2$] ppm. C$_{17}$H$_{33}$ClNNbOSi$_2$ (451.986): calcd. C 45.17, H 7.36, N 3.10; found C 44.92, H 7.30, N 3.25.

17: IR (KBr): $\tilde{\nu}$ = 2960 (vs), 1697 (s), 1405 (s), 1367 (m), 1261 (vs), 1086 (vs), 918 (s), 838 (vs), 694 (s), 634 (s) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25°C): δ = 6.40 (m, 1 H), 6.22 (m, 1 H), 6.12 [m, 1 H, C$_5$**H**$_3$(SiMe$_3$)$_2$], 2.54 [s, 3 H, NbC(**Me**)O], 1.19 (s, 3 H, Nb**Me**), 1.08 (s, 9 H, NbC**Me**$_3$), 0.23 (s, 9 H), 0.14 [s, 9 H, C$_5$H$_3$(Si**Me**$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 300.5 [**C**(Me)O], 122.7 (Ci), 122.5 (Ci), 117.3, 114.9, 112.7 [**C**$_5$H$_3$(SiMe$_3$)$_2$], 67.8 (NbN**C**Me$_3$), 32.2 (NbNC**Me**$_3$), 31.5 (Nb**Me**), 30.5 [C(**Me**)O], –0.18, –0.21 [C$_5$H$_3$(Si**Me**$_3$)$_2$] ppm. C$_{18}$H$_{36}$NNbOSi$_2$ (431.568): calcd. C 50.10, H 8.41, N 3.25; found C 49.59, H 8.35, N 3.18.

[Nb{η^5-C$_5$H$_3$(SiMe$_3$)$_2$}R(N*t*Bu){C(R)O-κ^2*C*,*O*}] (R = CH$_2$SiMe$_3$ 18): A yellow solution of **4** (0.15 g, 0.27 mmol) in [D$_6$]benzene (0.8 mL) was placed into a valved NMR tube, and the argon atmosphere was replaced by carbon monoxide (1 atm). The reaction was monitored by ^{1}H NMR spectroscopy at room temperature. After 30 min, the formation of alkyl acyl complex **18** with a nearly quantitative yield was confirmed by ^{1}H and ^{13}C NMR spectra. The solution was concentrated to dryness, giving **18** as a dark orange microcrystalline compound. Yield 0.135 g (85%). IR (KBr): $\tilde{\nu}$ = 2956 (vs), 1577 (s), 1450 (s), 1357 (m), 1249 (s), 1084 (s), 840 (vs), 755 (s), 635 (m), 470 (m) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25°C): δ = 6.35 (m, 2 H), 6.24 [m, 1 H, C$_5$**H**$_3$(SiMe$_3$)$_2$], 3.45, 2.73 [AB, $^2J_{H,H}$ = 10 Hz, 2 H, C(C**H**$_2$SiMe$_3$)O], 1.20 [s, 9 H, NbN(C**Me**$_3$)], 0.97, 0.78 (AB, $^2J_{H,H}$ = 10 Hz, 2 H, NbC**H**$_2$SiMe$_3$), 0.53 [s, 9 H, C(CH$_2$Si**Me**$_3$)O], 0.10 (s, 9 H, NbCH$_2$Si**Me**$_3$), 0.31 (s, 9 H), 0.13 [s, 9 H, C$_5$H$_3$(Si**Me**$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 298.0 [**C**(CH$_2$SiMe$_3$)O], 122.1 (Ci), 121.9 (Ci), 117.4, 111.7, 110.9 [**C**$_5$H$_3$(SiMe$_3$)$_2$], 65.6 [NbN(**C**Me$_3$)], 42.3 [C(**C**H$_2$SiMe$_3$)O], 33.1 [NbN(C**Me**$_3$)], 29.6 (Nb**C**H$_2$SiMe$_3$), 4.0 [C(CH$_2$Si**Me**$_3$)O], 0.64 (NbCH$_2$Si**Me**$_3$), –0.1, –0.2 [C$_5$H$_3$(Si**Me**$_3$)$_2$] ppm. C$_{24}$H$_{52}$NNbOSi$_4$ (575.932): calcd. C 50.05, H 9.10, N 2.43; found C 49.87, H 8.96, N 2.37.

[Nb{η^5-C$_5$H$_3$(SiMe$_3$)(Me$_2$SiOSi$_7$O$_{11}$R$_7$-κ^2*O*,*O*)}{O(Me)C=C(Me)-O-κ^2*O*,*O*}] (R = *i*Bu 19): In a standard experiment, a sample of **13** (0.55 g, 0.50 mmol) was placed in a valved NMR tube, and [D$_6$]-benzene was (0.70 mL) added. Subsequently, the inert atmosphere was replaced by carbon monoxide, and the colour of the mixture changed from gold-plated to yellow. The reaction was monitored by ^{1}H NMR spectroscopy until total conversion of the starting niobium complex was achieved. After 2 h, the formation of **19** in quantitative yield was confirmed by its ^{1}H NMR spectrum. The [D$_6$]benzene solution was concentrated to dryness, and the yellow oily residue was extracted with hexane (2 × 10 mL). The solution was filtered, concentrated to ca. 5 mL and cooled to –40°C to give **19** as a microcrystalline yellow solid. Yield 0.46 g (80%). IR (KBr): $\tilde{\nu}$ = 2954 (vs), 1466 (s), 1400 (s), 1253 (s), 1115 (vs), 1099 (vs), 839 (vs), 741 (s), 478 (s) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25°C): δ = 7.24 (m, 1 H), 7.09 (m, 1 H), 5.15 [m, 1 H, C$_5$**H**$_3$(SiMe$_3$)(Me$_2$-SiOSi$_7$O$_{11}$R$_7$)], 2.12 [m, 7 H, C$_5$H$_3$(SiMe$_3$) {Me$_2$SiO(Me$_2$C**H**-CH$_2$Si)$_7$O$_{11}$}], 1.76 (s, 3 H), 1.63 [s, 3 H, O(**Me**)C=C(**Me**)O], 1.13 [m, 42 H, C$_5$H$_3$(SiMe$_3$){Me$_2$SiO(**Me**$_2$CHCH$_2$Si)$_7$O$_{11}$}], 0.81 [m, 14 H, C$_5$H$_3$(SiMe$_3$) {Me$_2$SiO(Me$_2$CHC**H**$_2$Si)$_7$O$_{11}$}], 0.53 (s, 3 H), 0.41 [s, 3 H, C$_5$H$_3$(SiMe$_3$) {**Me**$_2$SiO(Me$_2$CHCH$_2$Si)$_7$O$_{11}$}], 0.24 [s, 9 H, C$_5$H$_3$(Si**Me**$_3$){Me$_2$SiO(Me$_2$CHCH$_2$Si)$_7$O$_{11}$}] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 134.2 (Ci), 130.8 (Ci), 126.7, 122.4, 111.8 [**C**$_5$H$_3$(SiMe$_3$)(Me$_2$SiOSi$_7$O$_{11}$R$_7$)], 98.4 [O(Me)**C**=**C**-(Me)O], 31.1, 30.8 [O(**Me**)C=C(**Me**)O], 26.5–25.8 [C$_5$H$_3$(SiMe$_3$)-{Me$_2$SiO(**Me**$_2$CHCH$_2$Si)$_7$O$_{11}$}], 24.8–24.4 [C$_5$H$_3$(SiMe$_3$){Me$_2$SiO-(Me$_2$CH**C**H$_2$Si)$_7$O$_{11}$}]. 23.9–23.0 [C$_5$H$_3$(SiMe$_3$){Me$_2$SiO(Me$_2$-**C**HCH$_2$Si)$_7$O$_{11}$}], –0.3 [C$_5$H$_3$(Si**Me**$_3$)(Me$_2$SiOSi$_7$O$_{11}$R$_7$)], –0.5, –4.1 [C$_5$H$_3$(SiMe$_3$)(**Me**$_2$SiOSi$_7$O$_{11}$R$_7$)] ppm. C$_{42}$H$_{87}$NbO$_{14}$Si$_9$ (1161.815): calcd. C 43.42, H 7.55; found C 43.51, H 7.63.

[Nb{η^5-C$_5$H$_3$(SiMe$_3$)(Me$_2$SiOSi$_7$O$_{11}$R$_7$-κ^2*O*,*O*)}(CMe$_2$NAr-κ^2*C*,*N*)] (R = *i*Bu, Ar = 2,6-Me$_2$C$_6$H$_3$ 20): Under rigorously anhydrous conditions, 2,6-Me$_2$C$_6$H$_3$NC (0.065 g, 0.50 mmol) was added at room temperature to a hexane (30 mL) solution of **13** (0.55 g, 0.50 mmol). The reaction mixture was stirred vigorously for 30 min and then filtered. The filtrate was concentrated to ca. 5 mL and cooled to –40 °C to give **20** as a dark orange microcrystalline solid. Yield 0.49 g (80%). IR (KBr): $\tilde{\nu}$ = 2953 (vs), 2118 (s), 1466 (s), 1365 (w), 1253 (s), 1107 (vs), 921 (s), 838 (vs), 740 (s), 484 (m) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25°C): δ = 7.02 (m, 3 H, Me$_2$C$_6$**H**$_3$), 7.43 (m, 1 H), 7.33 (m, 1 H), 5.65 [m, 1 H, C$_5$**H**$_3$-(SiMe$_3$)(Me$_2$SiOSi$_7$O$_{11}$R$_7$)], 2.12 [m, 7 H, C$_5$H$_3$(SiMe$_3$){Me$_2$-SiO(Me$_2$C**H**CH$_2$Si)$_7$O$_{11}$}], 1.73 (s, 3 H), 1.69 (s, 3 H, **Me**$_2$C$_6$H$_3$), not observed (C**Me**$_2$NAr), 1.12 [m, 42 H, C$_5$H$_3$(SiMe$_3$){Me$_2$-SiO(**Me**$_2$CHCH$_2$Si)$_7$O$_{11}$}], 0.82 [m, 14 H, C$_5$H$_3$(SiMe$_3$){Me$_2$SiO-(Me$_2$CHC**H**$_2$Si)$_7$O$_{11}$}], 0.48 (s, 3 H), 0.39 [s, 3 H, C$_5$H$_3$(SiMe$_3$)-(**Me**$_2$SiOSi$_7$O$_{11}$R$_7$)], 0.34 [s, 9 H, C$_5$H$_3$(Si**Me**$_3$)(Me$_2$SiOSi$_7$O$_{11}$R$_7$)] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 151.83 (Ci), 135.0, 131.6, 129.2 (several phenyl, Me$_2$**C**$_6$H$_3$), 131.6 (Ci), 125.5, 125.2, 123.6 (Ci), 111.2 [**C**$_5$H$_3$(SiMe$_3$)(Me$_2$SiOSi$_7$O$_{11}$R$_7$)], 74.0 (**C**Me$_2$NAr), 30.3, 28.7 (C**Me**$_2$NAr), 26.9–25.9 [C$_5$H$_3$(SiMe$_3$)-{Me$_2$SiO(**Me**$_2$CHCH$_2$Si)$_7$O$_{11}$}], 24.9–24.4 [C$_5$H$_3$(SiMe$_3$){Me$_2$SiO-(Me$_2$CH**C**H$_2$Si)$_7$O$_{11}$}], 24.0–22.0 [C$_5$H$_3$(SiMe$_3$){Me$_2$SiO(Me$_2$-**C**HCH$_2$Si)$_7$O$_{11}$}], not observed (**Me**$_2$C$_6$H$_3$), 4.5, –0.2 [C$_5$H$_3$-(SiMe$_3$)(**Me**$_2$SiOSi$_7$O$_{11}$R$_7$)], 0.05 [C$_5$H$_3$(Si**Me**$_3$)(Me$_2$SiOSi$_7$O$_{11}$R$_7$)] ppm. C$_{49}$H$_{96}$NNbO$_{12}$Si$_9$ (1236.973): calcd. C 47.58, H 7.82, N 1.13; found C 47.44, H 7.92, N 1.17.

[Nb{η^5-C$_5$H$_3$(SiMe$_3$)$_2$}Cl(N*t*Bu){C(Me)NAr-κ^2*C*,*N*}] (Ar = 2,6-Me$_2$C$_6$H$_3$ 21): A hexane (40 mL) solution of **2** (0.11 g, 0.26 mmol) was treated with a solution of 2,6-Me$_2$C$_6$H$_3$NC (0.034 g, 0.26 mmol) in hexane (5 mL). The reaction mixture was stirred vigorously for 1 h, and then the solution was filtered. The volatiles were removed by vacuum, and the brown residue was extracted with hexane (2 × 10 mL). The solution was concentrated to ca. 5 mL and cooled to –40 °C to give **21** (0.10 g, 69%) as a brown microcrystalline solid. IR (KBr): $\tilde{\nu}$ = 2967 (vs), 2111 (s), 1650 (s), 1474 (s), 1427 (s), 1353 (m), 1249 (s), 1080 (s), 920 (s), 837 (vs), 762 (s), 637 (m), 541 (m), 499 (m) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]-benzene, 25°C): δ = 6.90 (m, 3 H, Me$_2$C$_6$**H**$_3$), 6.67 (m, 1 H), 6.25 (m, 1 H), 6.02 [m, 1 H, C$_5$**H**$_3$(SiMe$_3$)$_2$], 2.14 [s, 3 H, C(**Me**)NAr], 2.12 (s, 3 H), 1.77 (s, 3 H, **Me**$_2$C$_6$H$_3$), 1.18 [s, 9 H, NbN(C**Me**$_3$)], 0.52 (s, 9 H), 0.32 [s, 9 H, C$_5$H$_3$(Si**Me**$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 227.3 [**C**(Me)NAr], 140.4 (Ci), 135.4 (Ci), 131.2, 129.8, 128.7, 126.4 (Me$_2$**C**$_6$H$_3$), 122.7 (Ci), 119.3, 119.2, 119.1, 117.3 (Ci, **C**$_5$H$_3$(SiMe$_3$)$_2$], 67.1 [NbN(**C**Me$_3$)], 31.5 [NbN(C**Me**$_3$)], 23.9 [C(**Me**)NAr], 18.7, 18.4 (**Me**$_2$C$_6$H$_3$), 0.95, –0.88

$[C_5H_3(SiMe_3)_2]$ ppm. $C_{25}H_{42}ClN_2NbSi_2$ (555.154): calcd. C 54.09, H 7.63, N 5.05; found C 53.85, H 7.54, N 4.88.

[Nb{η⁵-$C_5H_3(SiMe_3)_2$}Me(N*t*Bu){C(Me)NAr-κ²*C*,*N*}] (Ar = 2,6-$Me_2C_6H_3$ 22): In a standard experiment, **3** (0.15 g, 0.372 mmol), 2,6-$Me_2C_6H_3NC$ (0.049 g, 0.372 mmol) and [D_6]benzene (0.8 mL) were placed in a valved NMR tube. The reaction was monitored by ^{1}H NMR spectroscopy until the starting material was totally transformed and no further change was observed. The formation of iminoacyl compound **22** was confirmed by its ^{1}H NMR spectrum. When the solvent was removed by vacuum, **22** was isolated as a brown microcrystalline solid. Yield 0.17 g (86%). IR (KBr): $\tilde{\nu}$ = 2961 (vs), 1634 (s), 1442 (s), 1351 (m), 1250 (vs), 1080 (vs), 921 (vs), 836 (vs), 757 (s), 640 (m), 539 (m) cm^{-1}. ^{1}H NMR (300 MHz, [D_6]benzene, 25°C): δ = 6.91 (m, 3 H, $Me_2C_6\mathbf{H}_3$), 6.31 (m, 1 H), 6.00 (m, 1 H), 5.59 [m, 1 H, $C_5\mathbf{H}_3(SiMe_3)_2$], 2.18 [s, 3 H, C(**Me**)NAr], 1.96 (s, 3 H), 1.67 (s, 3 H, $\mathbf{Me}_2C_6H_3$), 1.20 [s, 9 H, NbN(C**Me**$_3$)], 0.67 (s, 3 H, Nb**Me**), 0.26 (s, 9 H), 0.11 [s, 9 H, $C_5H_3(Si\mathbf{Me}_3)_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D_6]benzene, 25°C): δ = 230.1 [**C**(Me)NAr], 141.7 (Ci), 134.2 (Ci), 130.47, 129.8, 125.9 (several phenyl, $Me_2\mathbf{C}_6H_3$), 122.8 (Ci), 119.0 (Ci), 117.2, 115.9, 113.7 [$\mathbf{C}_5H_3(SiMe_3)_2$], 69.9 [NbN(**C**Me$_3$)], 64.62 (Nb**Me**), 32.4 [NbN(C**Me**$_3$)], 23.9 [C(**Me**)NAr], 18.2, 18.1 ($\mathbf{Me}_2C_6H_3$), 1.08, –0.93 [$C_5H_3(Si\mathbf{Me}_3)_2$] ppm. $C_{26}H_{45}N_2NbSi_2$ (534.736): calcd. C 58.40, H 8.48, N 5.24; found C 58.25, H 8.35, N 5.18.

X-ray Structure Determination of 5c′

A crystal of **5c′** suitable for X-ray analysis was obtained by the slow concentration of a hexane solution of **5c**. The crystal was then covered with mineral oil and mounted in the N_2 stream of a Bruker-Nonius Kappa CCD diffractometer. Data was collected by using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collection was performed at 150 K with an exposure time of 76 s per frame (11 sets, 1021 frames). Raw data was corrected for Lorentz and polarization effects.

The structure was solved by direct methods, completed by subsequent difference Fourier techniques and refined by full-matrix least-squares on F^2 (SHEXL-97).[48] Due to the bad quality of the crystal, only some of the atoms could be refined anisotropically; most of them were refined with isotropic thermal parameters, and in some cases it was necessary to fix them. Hydrogen atoms were included in geometrical calculations and refined by using a riding model. Some other different space groups were checked, but the results were not satisfactory. All the calculations were performed with the WINGX system.[49]

Crystal data: $C_{112}H_{252}Li_{12}O_{48}Si_{28}$; M_w = 3236.89; orthorhombic; space group $Pna2_1$; a = 28.260(6) Å, b = 21.764(6) Å, c = 31.558(9) Å; V = 19410(9) Å^3; 124325 reflections collected, 22506 unique reflections (R_{int} = 0.1834), final R_1 = 0.2185 [$I > 2\sigma(I)$].

CCDC-683456 contains the supplementary crystallographic data (excluding structure factors) for **5c′**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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