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

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A new half-sandwich imido compound, $[Nb{\eta^5-C_5H_3(SiMe_3)_2}]$ - $Cl_2(NtBu)$] (1), was isolated by treatment of $[Nb{\eta^5} C_5H_3(SiMe_3)_2$ Cl₄] with 1 equiv. LiNHtBu in hexane. Alkvlimido derivatives $[Nb{\eta^5-C_5H_3(SiMe_3)_2}RR'(NtBu)]$ (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 $[Si_8O_{12}Cl(iBu)_7]$ (5a) can be obtained by treatment of [Si₇O₉(OH)₃(*i*Bu)₇] with 1 equiv. silicon tetrachloride in the presence of triethylamine. Ligand 5a reacts with $NH_3(q)$ at low temperatures to yield an amido derivative, $[Si_8O_{12}(NH_2)(iBu)_7]$ (5b), whereas the reaction of the trisilanol with excess BuLi leads to the corresponding lithium salt [Li₃Si₇O₁₂(*i*Bu)₇] (5c). A dichlorido(silsesquioxanylimido)niobium compound $[Nb{\eta^5-C_5H_3(SiXMe_2)(SiMe_3)}Cl_2 \{NSi_8O_{12}(iBu)_7\}$ (X = Cl **6a**, Me **6b**) can be prepared by reaction of 1 equiv. tetrachloridoniobium complex $[Nb{\eta^{5}} C_5H_3(SiXMe_2)(SiMe_3)$ (X = Cl, Me) and amidosilsesquioxane **5b**. From **6b**, three new alkyl derivatives, $[Nb{\eta^{5}} \mathrm{C_5H_3(SiMe_3)_2}\mathrm{XY(NSi_8O_{12}R_7)]}$ (R = $i\mathrm{Bu},\ \mathrm{X}$ = 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 $[Nb\{\eta^5-C_5H_3(SiXMe_2)(SiMe_3)\}Cl_4]$ (X = Cl) in the presence of triethylamine produces a dichlorido derivative, $[Nb{\eta^5-C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7-\kappa^2O_{\ell}O)]$ - Cl_2 (R = *i*Bu **10**), which can be transformed into an imido

complex, $[Nb{\eta^{5}-C_{5}H_{3}(SiMe_{3})(Me_{2}SiOSi_{7}O_{11}R_{7}-\kappa^{2}O,O)]$ -(N*t*Bu)] (R = *i*Bu **11**), by reaction with LiNH*t*Bu, whereas for X = Me, a chlorido complex, $[Nb{\eta^5-C_5H_3(SiMe_3)_2}Cl(Si_7O_{12}R_7 \kappa^{3}O(O,O)$] (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} - $C_5H_3(SiMe_3)_2R(NtBu)\{C(R')O-\kappa^2C_1O\}\}$ (R = Cl, R' = Me 16; $R = R' = Me \mathbf{17}$, $CH_2SiMe_3 \mathbf{18}$) and iminoacylimidoniobium $[Nb{\eta^{5}-C_{5}H_{3}(SiMe_{3})_{2}}R(NtBu){C(Me)NAr-\kappa^{2}C,N}]$ (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- $Me_2C_6H_3NC_1$ leading to enediolato $[Nb{\eta^5-C_5H_3(SiMe_3) (Me_2SiOSi_7O_{11}R_7-\kappa^2O,O)$ { $O(Me)C=C(Me)O-\kappa^2O,O$ } (R = *i*Bu **19**) and azaniobacyclopropane $[Nb{\eta^5-C_5H_3(SiMe_3) (Me_2SiOSi_7O_{11}R_7-\kappa^2O,O)$ (CMe_2NAr- κ^2C,N) (R = *i*Bu, Ar = 2,6-Me₂C₆H₃ 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, ¹H, ¹³C{¹H} and ²⁹Si{¹H} NMR spectroscopy and elemental analysis.

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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 chlor-

 [a] Departamento de Química Inorgánica, Universidad de Alcalá de Henares, Campus Universitario, 28871 Alcalá de Henares, Spain Fax: +34-91-885-46-83 E-mail: manuel.gomez@uah.es idosilylcyclopentadienyl 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 -C₅H₃(SiXMe₂)(SiMe₃); 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

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=NtBu 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 ²⁹Si 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, $[Nb{\eta^{5}-C_{5}H_{3}(SiMe_{3})_{2}}Cl_{2}(NtBu)]$ (1), can be synthesized when hexane solutions of the starting material, $[Nb{\eta^{5}-C_{5}H_{3}(SiMe_{3})_{2}}Cl_{4}]$, are treated at room temperature with LiNHtBu. Reactions of 1 with stoichiometric amounts of the alkylating reagent give solutions from which the alkylimido complex, $[Nb{\eta^{5}-C_{5}H_{3}(SiMe_{3})_{2}}RR'(NtBu)]$ (R = Cl, R' = Me 2; R = R' = Me 3, CH₂SiMe₃ 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 $[\tilde{v}_{\delta s}(CH_3)\approx 1250\,cm^{-1}]^{[3,17d,35]}$ and the Nb=N stretching vibration ($\tilde{\nu} \approx 1360 \text{ cm}^{-1}$).^[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 SiMe₃ substituents, respectively, due to the absence of local symmetry in the C₅H₃(SiMe₃)₂ moiety. However, the NMR spectroscopic data for the complexes 1, 3 and 4 show an A₂B spin system for the Cp ring protons, and consistently, three ring carbon resonances appear in the ${}^{13}C{}^{1}H$ 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 Si₇O₉R₇(OH)₃ (R = *i*Bu) by conventional methods. The chloro derivative $[Si_8O_{12}Cl($ *i* $Bu)_7]$ (**5a**) was obtained in high yield by reaction of $[Si_7O_9(OH)_3($ *i* $Bu)_7]$ with silicon tetrachloride in the presence of 3 equiv. triethylamine. The ammonolysis of **5a** in the presence of a large excess of NH₃(g) at -78 °C in dichloromethane led to the expected amido derivative $[Si_8O_{12}(NH_2)($ *i* $Bu)_7]$ (**5b**), whereas at 0 °C the reaction of trisilanol with excess BuLi gave the corresponding lithium salt $[Li_3Si_7O_{12}($ *i* $Bu)_7]$ (**5c**) (see Scheme 2). Compounds **5a–c** were found not to be airand moisture-sensitive and are soluble in hexane, chlorinated and aromatic solvents.

The IR and NMR (¹H, ¹³C{¹H}, ²⁹Si{¹H}) spectroscopic data are in agreement with the proposed structures. The ${}^{29}Si{}^{1}H$ 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 Si₇O₁₂ moiety, and the fourth signal can be assigned to the silicon atom directly bonded to the NH₂ 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_{3y} 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 (Si₇O₁₂) 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 Si₇O₁₂ unit and the other from a different one, forming a core of O₁₂Li₁₂. 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 $[Nb{\eta^{5}-C_{5}H_{3}(SiXMe_{2})(SiMe_{3})\}Cl_{4}]$ (X = Cl, Me) with 1 equiv. silsesquioxane reagent **5b** in the presence of triethylamine gave dichlorido(silsesquioxanylimido) derivatives $[Nb{\eta^{5}-C_{5}H_{3}(SiXMe_{2})(SiMe_{3})\}Cl_{2}{NSi_{8}O_{12}(iBu)_{7}}]$ (X = Cl **6a**, Me **6b**) (Scheme 3) with a silsesquioxanylimido group. In addition, chloridomethyl-, dimethyl- and bis(trimethylsilylmethyl)silsesquioxanylimido complexes $[Nb{\eta^{5}-$



Scheme 2.



Figure 1. ²⁹Si $\{^{1}H\}$ NMR spectrum of complex **5b** ([D₁]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(NSi₈O₁₂R₇)] (R = *i*Bu; X = Cl, Y = Me 7; X = Y = Me **8**, CH₂SiMe₃ **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 C₅H₃(SiClMe₂)(SiMe₃) ring, while in the spectrum of **6b**, two doublets at $\delta = 0.59$ and 0.52 ppm with observed vicinal (³J_{H,H}) SSCC values of 7.2 Hz can be assigned to the CH₂ protons of such groups, in agreement with the existence of a symmetric C₅H₃(SiMe₃)₂ ring. On the other hand, chiral chloridomethyl complex **7** shows the expected ¹H NMR spectroscopic behaviour with both nonequivalent SiMe₃ 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 -CH₂ protons of trimethylsilylmethyl groups. Additionally, an IR absorption band due to the Nb=N^[3a,17d] stretching vibration can be observed at $\tilde{v} \approx 1350$ cm⁻¹.

A series of chloridosilsesquioxanyl complexes was prepared in good yields by different methods (Scheme 4). $[Nb{\eta^{5}-C_{5}H_{3}(SiMe_{3})(Me_{2}SiOSi_{7}O_{11}R_{7}-\kappa^{2}O,O)]Cl_{2}]$ (R = *i*Bu 10) was synthesized by reaction of $[Nb{\eta^{5}} C_5H_3(SiMe_3)(SiClMe_2)$ with 0.5 equiv. $Si_7O_9(OH)_3$ - $(iBu)_7$ in the presence of NEt₃ or alternatively, by treatment of the tetrachlorido compound with lithium salt 5c. new imido derivative, $[Nb{\eta^5-C_5H_3(SiMe_3)(Me_2-$ A $SiOSi_7O_{11}R_7 - \kappa^2 O, O$ (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. LiNHtBu; in addition, 11 can be obtained by reaction between dichloridoimido derivative $[Nb{\eta^5-C_5H_3(SiClMe_2) (SiMe_3)$ $Cl_2(NtBu)$ ^[3a] and trisilanol $[Si_7O_9(iBu)_7(OH)_3]$ in the presence of triethylamine. Further, a chloridosilsesquioxanyl compound, $[Nb{\eta^5-C_5H_3(SiMe_3)_2}Cl(Si_7O_{12}R_7 \kappa^{3}O,O,O$] (R = *i*Bu 12), was prepared by reaction of tetra- $[Nb{\eta^{5}-C_{5}H_{3}(SiMe_{3})_{2}}Cl_{4}]$ chlorido derivative with Si₇O₉(OH)₃(*i*Bu)₇ and NEt₃.

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

European Journal of Inorganic Chemistry



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 SiClMe₂ substituent, to give the reported^[3a] constrainedgeometry complex $[Nb{\eta^5-C_5H_3(SiMe_3)(SiMe_2NtBu-\kappa N)}Cl(NtBu)].$

On the other hand, in agreement with the reported ²⁹Si NMR spectroscopic studies,^[23a,28a] in the spectrum of complex **10** (see Figure 3) the resonance at $\delta = -3.57$ ppm can be assigned to the silicon atom of the *Si*Me₂O 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 $v \approx 635 \text{ cm}^{-1}$ can be assigned to the v_{Nb-O} stretching vibration.^[36]

Alkylation of 10 with 2 equiv. dimethylzinc at room temperature in hexane yields the expected dimethyl derivative $[Nb{\eta^{5}-C_{5}H_{3}(SiMe_{3})(Me_{2}SiOSi_{7}O_{11}R_{7}-\kappa^{2}O,O)]Me_{2}]$ (R = *i*Bu 13); however, treatment with 2 equiv. MgCl(CH₂SiMe₃) under rigorously anhydrous conditions at room temperature leads to the trimethylsilylmethylidene complex, $[Nb{\eta^5} C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7-\kappa^2O,O))(CHSiMe_3)]$ (R = *i*Bu 14), by a spontaneous α -hydrogen-abstraction process^[37] with formation of an unstable dialkyl intermediate and SiMe₄ elimination (Scheme 6). In addition, a methyl complex, $[Nb{\eta^5-C_5H_3(SiMe_3)_2}Me(Si_7O_{12}R_7-\kappa^3O,O,O)]$ (R = iBu 15), was isolated by reaction of the chloridosilsesquioxanyl complex 12 with excess (1 equiv.) ZnMe₂ in toluene. The reaction of 12 with the stoichiometric amount of ZnMe₂ (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 ¹H 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 $\delta = 0.35$ and 0.28 ppm can be assigned to the diastereotopic methyl groups of the SiMe₂ 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{v} 2717, 2625 cm⁻¹ can be assigned to v_{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 d⁰ 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 [D₆]benzene (NMR spectroscopic scale, see Exp. Sect.) to give chlorido-, methyl- and (trimethylsilylmethyl)imidoacyl $[Nb{\eta^{5}-C_{5}H_{3}(SiMe_{3})_{2}}R(NtBu){C(R')O-\kappa^{2}C,O}] (R = Cl,$ 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 (¹H 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, $[Nb{\eta^5-C_5H_3(SiMe_3) (Me_2SiOSi_7O_{11}R_7 \kappa^2 O, O) \{O(Me)C = C(Me)O \kappa^2 O, O\}$ (R



Figure 3. ²⁹Si{¹H} NMR spectrum of complex 10 ($[D_6]$ benzene).

iii- excess ZnMe2, toluene, r.t., 12 h



Me₂S

SiMe₃ iii

Scheme 6.



Scheme 7.

= *i*Bu **19**), is easily obtained when the corresponding [D₆]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 ¹H NMR spectroscopy.

On the other hand, when 1 equiv. 2,6-Me₂C₆H₃NC 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} -C₅H₃(SiMe₃)(Me₂SiOSi₇O₁₁R₇- $\kappa^{2}O$,*O*)}-(CMe₂NAr- $\kappa^{2}C$,*N*] (R = *i*Bu, Ar = 2,6-Me₂C₆H₃ **20**), was recovered as an orange solid. Previously, we reported^[17a,17e] the synthesis and the crystal structure of similar azametallacylopropane complexes, whose formation involves mi-

gration 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} - $C_{5}H_{3}(SiMe_{3})_{2}R(NtBu)\{C(Me)NAr-\kappa^{2}C,N\}\}$ (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-Ciminoacyl 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.

Me₂S

15

SiMe

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 $(v_{C-H} \approx 839 \text{ cm}^{-1})^{[33,34]}$ and for the SiMe₃ substituent $[\delta_{as}$ (CH₃) \approx 1253 cm⁻¹].^[3,17d,35] The formulation of **19** as an enediolato complex is supported by the IR spectra, which show $v_{C=C}$, v_{C-O} and v_{Nb-O} absorptions at $\tilde{v} = 1466$,^[17c,17d,43] 1150^[43] and 900^[36a,36c] cm⁻¹, respectively. Their ¹H NMR spectrum shows two resonances at $\delta = 1.76$ and 1.63 ppm, corresponding to the nonequivalent methyl substituents of the enediolato ligand, whereas the resonance assignable to the sp² 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 $[v_{C(Y)=O}]$ at 1587 cm⁻¹; such stretching vibrations in acyl derivatives range from $\tilde{v} \approx 1453$ 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 pseudosquare-pyramidal geometry found for similar chiral group 5 metal derivatives.^[17d] The iminoacyl carbon resonance appears at $\delta = 228$ 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 ¹³C 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 $\delta = 74$ ppm in the ¹³C NMR spectrum can be assigned to the C_a 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'(NtBu)] (R = Cl, R' = Me; R = R' = Me, CH₂SiMe₃) 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 $[Nb{\eta^{5}-C_{5}H_{3}(SiXMe_{2})(SiMe_{3})}Cl_{4}]$ (X = Cl, Me), by reaction with amidosilsesquioxane $[Si_8O_{12}(iBu)_7(NH_2)]$, a dichlorido(silsesquioxanylimido) compound, $[Nb{\eta^5} C_5H_3(SiXMe_2)(SiMe_3)$ $Cl_2\{NSi_8O_{12}(iBu)_7\}$ (X = Cl, Me), which reacts with alkylating reagents to yield the corresponding alkyl derivatives, $[Nb{\eta^5-C_5H_3(SiMe_3)_2}XY (NSi_8O_{12}R_7)]$ (R = *i*Bu; X = Cl, Y = Me; X = Y = Me, CH₂SiMe₃), 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: [D₆]benzene and hexane (Na/K alloy), [D₁]chloroform (NaH) and dicloromethane (P₄O₁₀). Starting materials [Nb{ η^5 -C₅H₃(SiXMe₂)(SiMe₃)}Cl₄] (X = Cl,Me),^[3a] [Nb-{ η^5 -C₅H₃(SiCIMe₂)(SiMe₃)}Cl₂(N*t*Bu)],^[3a] [Si₇O₉(OH)₃(*i*Bu)₇],^[45] LiNH*t*Bu^[46] and LiCH₂SiMe₃^[47] were prepared as described previously. Reagent grade CO and NH₃ (Air Líquide), BuLi (1.6 M in hexane), SiCl₄, MgCIMe (3 M in thf), MgCl(CH₂SiMe₃) (1 M in diethyl ether) and ZnMe₂ (2 M in toluene) (Aldrich), NEt₃ and 2,6-Me₂C₆H₃NC (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, ¹³C{¹H} and ²⁹Si{¹H} NMR spectra were recorded with Varian Unity 300 or Varian Unity 500 Plus spectrometers; chemical shifts were referenced to the ¹³C (δ = 128, 77 ppm) or residual ¹H (δ = 7.15, 7.24 ppm) resonances of the [D₆]benzene or [D₁]chloroform solvents, respectively, and for the ²⁹Si NMR spectra, they were referenced to the internal TMS resonance. C, H and N analyses were carried out with a LECO CHNS 932 microanalyzer.

 $[Nb{\eta^5-C_5H_3(SiMe_3)_2}Cl_2(NtBu)]$ (1): A mixture of LiNHtBu (0.20 g, 2.25 mmol) and $Nb\{\eta^5-C_5H_3(SiMe_3)_2\}Cl_4$ (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 $(2 \times 15 \text{ mL})$. Concentration and cooling of the filtrate produced 1 as an orange solid. Yield 0.80 g (80%). IR (KBr): $\tilde{v} = 2957$ (s), 1402 (m), 1375 (m), 1249 (vs), 1090 (s), 840 (vs), 451 (m) cm⁻¹. ¹H NMR (300 MHz, [D₁]chloroform, 25°C): $\delta = 6.93$ (m, 1 H), 6.76 [m, 2 H, C₅H₃(SiMe₃)₂], 1.27 [s, 9 H, NbN(CMe₃)], 0.29 [s, 18 H, C₅H₃(SiMe₃)₂] ppm. ¹³C{¹H} NMR (75 MHz, [D₁]chloroform, 25°C): $\delta = 129.6$ (Ci), 127.0, 121.8 [C₅H₃(SiMe₃)₂], 70.1 [NbN(CMe₃)], 30.4 [NbN(CMe₃)], -0.12 [C₅H₃(SiMe₃)₂] ppm. C₁₅H₃₀Cl₂NNbSi₂ (444.394): calcd. C 40.54, H 6.80, N 3.15; found C 40.65, H 6.85, N 3.09.

[Nb{\eta^{5-C_{5}H_{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 ZnMe₂ (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{v} = 2959 (s), 1406 (m), 1356 (m), 1251 (vs), 1084 (vs), 840 (vs), 471 (m), 397 (s) cm⁻¹. ¹H NMR (300 MHz, [D₆]benzene, 25°C): \delta = 6.55 (m, 1 H), 6.24 (br., 1 H), 6.17 [br., 1 H, C₅H₃(SiMe₃)₂], 1.26 [s, 9 H, NbN(CMe₃)], 1.24 (s, 3 H, NbMe),**



0.26 (s, 9 H), 0.23 [s, 9 H, $C_5H_3(SiMe_3)_2$] ppm. ¹³C{¹H} NMR (75 MHz, [D₆]benzene, 25°C): δ = 123.6, 122.9 (Ci), 121.3 (Ci), 118.7, 117.4 [C₅H₃(SiMe₃)₂], 70.5 [NbN(CMe₃)], 67.42 (NbMe), 31.3 [NbN(CMe₃)], 0.15, -0.06 [C₅H₃(SiMe₃)₂] ppm. C₁₆H₃₃CINNbSi₂ (423.976): calcd. C 45.33, H 7.85, N 3.30; found C 45.46, H 7.94, N 3.29.

 $[Nb{\eta^5-C_5H_3(SiMe_3)_2}Me_2(NtBu)]$ (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 MgCl₂ 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): $\tilde{v} = 2964$ (s), 1406 (m), 1354 (m), 1251 (vs), 1084 (vs), 838 (vs), 545 (m), 486 (m) cm⁻¹. ¹H NMR (300 MHz, [D₆]benzene, 25°C): $\delta = 6.34$ (s, 1 H), 6.17 [m, 2 H, $C_5H_3(SiMe_3)_2$, 1.41 [s, 9 H, NbN(CMe_3)], 0.60 (s, 6 H, NbMe_2), 0.28 [s, 18 H, $C_5H_3(SiMe_3)_2$] ppm. ¹³C{¹H} NMR (75 MHz, [D₆]benzene, 25°C): $\delta = 119.4$ (Ci), 118.9, 116.3 [C₅H₃(SiMe₃)₂], 70.0 $[NbN(CMe_3)], 70.0 (NbMe_2), 32.2 [NbN(CMe_3)], 0.21$ [C₅H₃(SiMe₃)₂] ppm. C₁₇H₃₆NNbSi₂ (403.558): calcd. C 50.60, H 8.99, N 3.47; found C 50.45, H 8.85, N 3.45.

 $[Nb{\eta^5-C_5H_3(SiMe_3)_2}(CH_2SiMe_3)_2(NtBu)]$ (4): A hexane (40 mL) solution of 1 (1.04 g, 2.40 mmol) was treated with a 1 M solution of MgCl(CH₂SiMe₃) in diethyl ether (0.48 mL, 4.80 mmol), and the mixture was stirred for 2 h. The suspension was decanted, the MgCl₂ 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): $\tilde{v} = 2956$ (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. ¹H NMR (300 MHz, [D₆]benzene, 25°C): δ = 6.64 (m, 1 H), 6.11 [m, 2 H, C₅H₃(SiMe₃)₂], 1.45 [s, 9 H, NbN(CMe₃)], 0.96, 0.71 $[AB, {}^{2}J_{H,H} = 10 \text{ Hz}, 4 \text{ H}, \text{Nb}(CH_{2}SiMe_{3})_{2}], 0.27 \text{ [s, } 18 \text{ H},$ $C_5H_3(SiMe_3)_2$, 0.26 [s, 18 H, Nb(CH₂SiMe₃)₂] ppm. ¹³C{¹H} NMR (75 MHz, [D₆]benzene, 25°C): δ = 129.8, 122.3 (Ci), 112.2 [C₅H₃(SiMe₃)₂], 66.0 [NbN(CMe₃)], 50.9 [Nb(CH₂SiMe₃)₂], 33.0 [NbN(CMe₃)], 3.2 [Nb(CH₂SiMe₃)₂], 0.50 [C₅H₃(SiMe₃)₂] ppm. C23H52NNbSi4 (547.922): calcd. C 50.42, H 9.57, N 2.56; found C 50.45, H 9.60, N 2.45.

 $[Si_8O_{12}(iBu)_7Cl]$ (5a): A stirred solution of $Si_7O_9(iBu)_7(OH)_3$ (1.77 g, 2.24 mmol) and NEt₃ (0.94 mL, 6.72 mmol) in hexane (60 mL) was treated with SiCl₄ (0.24 mL, 2.24 mmol) under rigorously anhydrous conditions for 12 h. The suspension was decanted, the ammonium salt [NHEt₃]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): $\tilde{v} = 2956$ (vs), 1467 (s), 1402 (m), 1368 (m), 1334 (m), 1232 (s), 1107 (vs), 839 (s), 742 (s), 654 (s), 478 (s) cm⁻¹. ¹H NMR (300 MHz, [D₁]chloroform, 25°C): δ = 1.85 [m, 7 H, (Me₂CHCH₂)₇-Si₈O₁₂Cl], 0.96 [m, 42 H, (Me₂CHCH₂)₇Si₈O₁₂Cl], 0.68 [m, 14 H, (Me₂CHCH₂)₇Si₈O₁₂Cl] ppm. ¹³C{¹H} NMR (75 MHz, [D₁]chloroform, 25°C): $\delta = 25.8-25.6$ [(Me₂CHCH₂)₇Si₈O₁₂Cl], 23.9-23.7 [(Me₂CHCH₂)₇Si₈O₁₂Cl], 23.1–22.0 [(Me₂CHCH₂)₇Si₈O₁₂Cl] ppm. ²⁹Si{¹H} NMR (60 MHz, [D₁]chloroform, 25°C): δ = -90.2 [1Si, Si₇O₁₂Si(Cl)(*i*Bu)₇], -67.8 (1Si), -66.8 (3Si), -66.7 [3Si, Si₇O₁₂Si-(Cl)(*i*Bu)₇] ppm. C₂₈H₆₃ClO₁₂Si₈ (851.938): calcd. C 39.48, H 7.45; found C 39.83, H 7.25.

 $[Si_8O_{12}(iBu)_7(NH_2)]$ (5b): A solution of $Si_8O_{12}(iBu)_7Cl$ (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): v = 3432 (m), 2956 (vs), 1467 (m), 1232 (s), 1100 (vs), 911 (s), 839 (s), 743 (vs), 565 (s), 483 (vs), 432 (s) cm⁻¹. ¹H NMR (300 MHz, [D₁]chloroform, 25°C): $\delta = 1.83$ [m, 7 H, (Me₂CHCH₂)₇Si₈O₁₂(NH₂)], not observed [(Me₂CHCH₂)₇Si₈O₁₂- (NH_2)], 0.94 [dd, ${}^{3}J_{H,H} = 6.6$, ${}^{4}J_{H,H} = 1.8$ Hz, 42 H, Me₂CHCH₂₇- $Si_8O_{12}(NH_2)$], 0.59 [t, ${}^3J_{H,H}$ = 6.6 Hz, 14 H, $(Me_2CHCH_2)_7$ - $Si_8O_{12}(NH_2)$] ppm. ¹³C{¹H} NMR (75 MHz, [D₁]chloroform, 25°C): $\delta = 25.7, 25.64, 25.63 [3:1:3, (Me_2CHCH_2)_7Si_8O_{12}(NH_2)],$ $[(Me_2CHCH_2)_7Si_8O_{12}(NH_2)],$ 23.82 22.47, 22.44, 22.40[(Me₂CHCH₂)₇Si₈O₁₂(NH₂)] ppm. ²⁹Si{¹H} NMR (60 MHz, [D₁]chloroform, 25°C): $\delta = -87.4$ [1Si, Si₇O₁₂Si(NH₂)(*i*Bu)₇], -67.45 (1Si), -67.42 (3Si), -67 [3Si, Si₇O₁₂Si(NH₂)(*i*Bu)₇] ppm. C28H65NO12Si8 (832.508): calcd. C 40.40, H 7.87, N 1.68; found C 40.25, H 7.81, N 1.67.

[Li₃Si₇O₁₂(*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 Si₇O₉(***i***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): $\tilde{v} = 2955$ (vs), 1467 (s), 1367 (m), 1332 (m), 1230 (s), 1100 (vs), 971 (s), 836 (s), 739 (vs), 584 (s), 497 (s) cm⁻¹. ¹H NMR (300 MHz, [D₆]benzene, 25°C): *δ* = 2.21 [m, 7 H, (Me₂CHCH₂Si)₇O₁₂Li₃], 1.25 [m, 42 H, (Me₂CHCH₂Si)₇O₁₂Li₃], 1.10 [m, 14 H, (Me₂CHCH₂Si)₇O₁₂Li₃] ppm. ¹³C{¹H} NMR (75 MHz, [D₆]benzene, 25°C): *δ* = 26.7–25.5 [(Me₂CHCH₂Si)₇-O₁₂Li₃], 24.7–24.5 [(Me₂CHCH₂Si)₇O₁₂Li₃], 23.0 [(Me₂CHCH₂Si)₇-O₁₂Li₃] ppm. C₂₈H₆₃Li₃O₁₂Si₇ (809.223): calcd. C 41.56, H 7.85; found C 41.63, H 7.93.

[Nb{ η^{5} -C₅H₃(SiMe₃)(SiXMe₂)}Cl₂{NSi₈O₁₂(*i*Bu)₇}] (X = Cl 6a, Me 6b): Under rigorously anhydrous conditions, a hexane (25 mL) solution of [Nb{ η^{5} -C₅H₃(SiXMe₂)(SiMe₃)}Cl₄] (1.00 mmol; X = Cl, 0.465 g; X = Me, 0.444 g) was treated at room temperature with a solution of Si₈O₁₂(*i*Bu)₇(NH₂) (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): $\tilde{v} = 2954$ (vs), 1466 (vs), 1332 (s), 1260 (vs), 1076 (vs), 919 (s), 841 (vs), 737 (m), 568 (m), 507 (s) cm⁻¹. ¹H NMR (300 MHz, $[D_1]$ chloroform, 25°C): $\delta = 7.17$ (m, 1 H), 6.85 [m, 2 H, C₅H₃(SiClMe₂)(SiMe₃)], 1.81 [m, 7 H, NSi(Me₂CHCH₂Si)₇-O₁₂], 0.93 [m, 42 H, NSi(Me₂CHCH₂Si)₇O₁₂], 0.62 [m, 14 H, NSi-(Me₂CHCH₂Si)₇O₁₂], 0.294 [s, 9 H, C₅H₃(SiClMe₂)(SiMe₃)], 0.290 (s, 3 H), 0.03 [s, 3 H, C₅H₃(SiClMe₂)(SiMe₃)] ppm. ¹³C{¹H} NMR (75 MHz, $[D_1]$ chloroform, 25°C): δ = 131.1 (Ci), 127.1, 125.7 (Ci), 123.7, 123.6 [C₅H₃(SiClMe₂)(SiMe₃)], 25.7, 25.6 [NSi(Me₂-CHCH₂Si)₇O₁₂], 23.67, 23.71 [NSi(Me₂CHCH₂Si)₇O₁₂], 22.3, 22.2 [NSi(Me₂CHCH₂Si)₇O₁₂], 3.0, 2.1, [C₅H₃(SiClMe₂)(SiMe₃)], -0.55 [C₅H₃(SiClMe₂)(SiMe₃)] ppm. ²⁹Si{¹H} NMR (60 MHz, [D₆]benzene, 25°C): δ = 15.52 [C₅H₃(SiClMe₂)(SiMe₃)], -5.12 [C₅H₃(SiClMe₂)(SiMe₃)], -66.86, -66.88, -66.95, -67.82, -67.84, -67.86, -67.88 [NSi(Me₂CHCH₂Si)₇O₁₂], not observed [NSi- $(Me_2CHCH_2Si)_7O_{12}$ 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): $\tilde{v} = 2952$ (vs), 1464 (vs), 1332 (s), 1255 (vs), 1176 (vs), 919 (vs), 846 (s), 739 (s), 567 (m), 499 (s) cm⁻¹. ¹H

NMR (300 MHz, [D₁]chloroform, 25°C): δ = 7.03 (m, 1 H), 6.77 [m, 2 H, C₅H₃(SiMe₃)₂], 1.80 [m, 7 H, NSi(Me₂CHCH₂Si)₇O₁₂], 0.90 [m, 42 H, NSi(Me₂CHCH₂Si)₇O₁₂], 0.59 (d, ²J_{H,H} = 7.5 Hz, 7 H), 0.52 [d, ²J_{H,H} = 7.5 Hz, 7 H, NSi(Me₂CHCH₂Si)₇O₁₂], 0.25 [s, 18 H, C₅H₃(SiMe₃)₂] ppm. ¹³C{¹H} NMR (75 MHz, [D₁]chloroform, 25°C): δ = 131.0, 125.8, 123.7 [C₅H₃(SiMe₃)₂], 25.3, 25.1 [NSi(Me₂CHCH₂Si)₇O₁₂], 23.3 [NSi(Me₂CHCH₂Si)₇O₁₂], 22.0, 21.9 [NSi(Me₂CHCH₂Si)₇O₁₂], -0.89 [C₅H₃(SiMe₃)₂] ppm. C₃₉H₈₄Cl₂NNbO₁₂Si₁₀ (1203.758): calcd. C 38.91, H 7.03, N 1.16; found C 39.17, H 7.13, N 1.12.

$[Nb{\eta^5-C_5H_3(SiMe_3)_2}X(Me)(NSi_8O_{12}R_7)]$ (R = *i*Bu, X = Cl 7, Me 8)

7: In a sealed NMR tube and under rigorously anhydrous conditions, [D₆]benzene (0.70 mL) was added to a mixture of complex 6b (0.060 g, 0.050 mmol) and ZnMe₂ (2 м in toluene, 0.050 mL, 0.100 mmol). The colour of the mixture changed quickly from yellow to brown. The reaction was monitored by ¹H 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 $(2 \times 5 \text{ mL})$. 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): $\tilde{v} = 2950$ (vs), 1463 (s), 1365 (m), 1335 (m), 1245 (vs), 1109 (vs), 925 (s), 839 (s), 747 (m), 577 (m), 480 (m) cm⁻¹. ¹H NMR (300 MHz, [D₆]benzene, 25°C): $\delta = 6.70$ (m, 1 H), 6.43 (m, 1 H), 6.33 [m, 1 H, C₅H₃(SiMe₃)₂], 2.14 [m, 7 H, NSi-(Me₂CHCH₂Si)₇O₁₂], 1.47 (s, 3 H, NbMe), 1.12 [m, 42 H, NSi-(Me₂CHCH₂Si)₇O₁₂], 0.85 [m, 14 H, NSi(Me₂CHCH₂Si)₇O₁₂], 0.32 (s, 9 H), 0.29 [s, 9 H, C₅H₃(SiMe₃)₂] ppm. ¹³C{¹H} NMR (75 MHz, $[D_6]$ benzene, 25°C): $\delta = 129.3$ (Ci), 124.3 (Ci), 122.9, 120.6, 119.8 [C₅H₃(SiMe₃)₂], 48.2 (NbMe), 26.1, 25.9 [NSi(Me₂CHCH₂Si)₇O₁₂], 24.4 [NSi(Me₂CHCH₂Si)₇O₁₂], 23.1, 23.0 [NSi(Me₂CHCH₂Si)₇-O₁₂], -0.1, -0.2 [C₅H₃(SiMe₃)₂] ppm. C₄₀H₈₇ClNNbO₁₂Si₁₀ (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 MgCl₂ formed was separated by filtration. The volatiles were removed under reduced pressure, and the residue was extracted with hexane $(2 \times 10 \text{ mL})$. 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): v = 2955 (vs), 1466 (s), 1367 (m), 1333 (m), 1261 (s), 1111 (vs), 920 (s), 839 (vs), 742 (s), 567 (m), 484 (s) cm⁻¹. ¹H NMR (300 MHz, $[D_6]$ benzene, 25°C): $\delta = 6.46$ (m, 1 H), 6.27 [m, 2 H, C₅H₃-(SiMe₃)₂], 2.10 [m, 7 H, NSi(Me₂CHCH₂Si)₇O₁₂], 1.10 [m, 42 H, NSi(Me₂CHCH₂Si)₇O₁₂], 0.88 [m, 14 H, NSi(Me₂CHCH₂Si)₇O₁₂], 0.80 (s, 6 H, NbMe₂), 0.26 [s, 18 H, C₅H₃(SiMe₃)₂] ppm. ¹³C{¹H} NMR (75 MHz, [D₆]benzene, 25°C): δ = 125.4 (Ci), 119.7, 117.3 [C₅H₃(SiMe₃)₂], 38.6 (NbMe₂), 26.10, 25.94, 25.90 [NSi(Me₂-CHCH₂Si)₇O₁₂], 24.43, 24.40 [NSi(Me₂CHCH₂Si)₇O₁₂], 23.3, 23.0 $[NSi(Me_2CHCH_2Si)_7O_{12}],$ -0.06 $[C_5H_3(SiMe_3)_2]$ ppm. C₄₁H₉₀NNbO₁₂Si₁₀ (1162.922): calcd. C 42.35, H 7.80, N 1.20; found C 42.25, H 7.69, N 1.27.

 $[Nb{\eta^5-C_5H_3(SiMe_3)_2}(CH_2SiMe_3)_2\{NSi_8O_{12}(iBu)_7\}]$ (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 ¹H 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 $(2 \times 10 \text{ mL})$, 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): $\tilde{v} = 2954$ (vs), 1466 (s), 1333 (m), 1261 (s), 1111 (vs), 920 (s), 839 (vs), 742 (s), 484 (s) cm⁻¹. ¹H NMR (300 MHz, [D₆]benzene, 25°C): δ = 6.62 (br., 1 H), 6.35 [br., 2 H, C₅H₃(SiMe₃)₂], 2.13 [m, 7 H, NSi(Me₂CHCH₂Si)₇O₁₂], 1.15 [m, 42 H, NSi(Me₂CHCH₂Si)₇O₁₂], 0.86 [m, 14 H, NSi(Me₂CHCH₂Si)₇- O_{12}], 1.26, 0.58 [AB, ${}^{2}J_{H,H}$ = 11 Hz, 4 H, Nb(CH₂SiMe₃)₂], 0.36 [s, $18 \text{ H}, \text{ C}_5\text{H}_3(\text{SiMe}_3)_2$, 0.31 [s, 18 H, Nb(CH₂SiMe₃)₂] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, [D₆]benzene, 25°C): $\delta = 124.0$, 114.5, 110.4 (Ci, C₅H₃(SiMe₃)₂], 56.4 [Nb(CH₂SiMe₃)₂], 26.2, 26.0, 25.9 [NSi-(Me₂CHCH₂Si)₇O₁₂], 24.5, 24.4 [NSi(Me₂CHCH₂Si)₇O₁₂], 23.5, 23.0 [NSi(Me₂CHCH₂Si)₇O₁₂], 2.5 [Nb(CH₂SiMe₃)₂], 0.1 [C₅H₃(SiMe₃)₂] ppm. C₄₇H₁₀₆NNbO₁₂Si₁₂ (1307.286): calcd. C 43.18, H 8.17, N 1.07; found C 43.01, H 8.08, N 1.00.

 $[Nb{\eta^5-C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7-\kappa^2O, O)}Cl_2]$ (R = *i*Bu 10): The synthesis of complex 10 was carried out by two different methods.

Method A: $[Nb{\eta^5-C_5H_3(SiClMe_2)(SiMe_3)}Cl_4]$ (0.40 g, 0.86 mmol) was added to a hexane (50 mL) solution of Si₇O₉(*i*Bu)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 $[Nb{\eta^{5}-C_{5}H_{3}(SiClMe_{2})(SiMe_{3})}Cl_{4}]$ (0.25 g, 0.54 mmol) and [Li₃Si₇O₁₂(*i*Bu)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 ¹H 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 $(2 \times 10 \text{ mL})$. 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): $\tilde{v} = 2961$ (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. ¹H NMR (300 MHz, [D₁]chloroform, 25°C): δ = 7.05 (br., 2 H), 6.83 [m, 1 H, C₅H₃(SiMe₃)- $(Me_2SiOSi_7O_{11}R_7)$], 1.84 [m, 7 H, $C_5H_3(SiMe_3)$ {Me_2SiO(Me_2- $CHCH_2Si)_7O_{11}$], 0.94 [m, 42 H, $C_5H_3(SiMe_3)$ {Me₂SiO(Me₂-CHCH₂Si)₇O₁₁}], 0.58 [m, 14 H, C₅H₃(SiMe₃){Me₂SiO(Me₂-CHCH₂Si)₇O₁₁}], 0.43 (s, 3 H), 0.28 [s, 3 H, C₅H₃(SiMe₃)(Me₂-SiOSi₇O₁₁R₇)], 0.38 [s, 9 H, C₅H₃(SiMe₃)(Me₂SiOSi₇O₁₁R₇)] ppm. ¹³C{¹H} NMR (75 MHz, [D₁]chloroform, 25°C): δ = 142.7 (Ci), 135.5 (Ci), 132.1, 129.7, 127.0 [C₅H₃(SiMe₃)(Me₂SiOSi₇O₁₁R₇)], $26.6-25.6 [C_5H_3(SiMe_3) \{Me_2SiO(Me_2CHCH_2Si)_7O_{11}\}], 24.1, 24.0,$ 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 [C₅H₃(SiMe₃){Me₂SiO(Me₂CHCH₂Si)₇O₁₁}], 2.5, 0.6 [C₅H₃(SiMe₃)(Me₂SiOSi₇O₁₁R₇)], -0.5 [C₅H₃(SiMe₃)(Me₂-SiOSi₇O₁₁R₇)] ppm. ²⁹Si{¹H} NMR (60 MHz, [D₆]benzene, 25°C): $\delta = -69.2, -68.1, -67.7, -66.3, -66.21, -66.16, -63.7 [C_5H_3(SiMe_3)-$ (Me₂SiOSi₇O₁₁R₇)], -4.91 [C₅H₃(SiMe₃)(Me₂SiOSi₇O₁₁R₇)], -3.57 $[C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7)]$ ppm. C₃₈H₈₁Cl₂NbO₁₂Si₉ (1146.542): calcd. C 39.81, H 7.11; found C 39.90, H 7.18.

 $[Nb{\eta^5-C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7-\kappa^2O, O)}(NtBu)]$ (R = *i*Bu 11): Complex 11 was prepared by two different methods.

Method A: LiNH*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 micro-crystalline yellow solid identified as **11**. Yield 0.46 g (80%).

Method B: Hexane (60 mL) was added to a mixture of $[Nb{\eta^{5}}-$ C₅H₃(SiClMe₂)(SiMe₃)}Cl₂(NtBu)](0.24 g,0.51 mmol),Si₇O₉(iBu)₇-(OH)₃ (0.41 g, 0.51 mmol) and NEt₃ (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): $\tilde{v} = 2954$ (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. ¹H NMR (300 MHz, [D₆]benzene, 25°C): δ = 7.20 (m, 1 H), 7.00 (m, 1 H), 6.20 [m, 1 H, C₅H₃(Si-Me₃)(Me₂SiOSi₇O₁₁R₇)], 2.14 [m, 7 H, C₅H₃(SiMe₃){Me₂SiO-(Me₂CHCH₂Si)₇O₁₁}], 1.26 (s, 9 H, NbNCMe₃), 1.12 [m, 42 H, $C_5H_3(SiMe_3)\{Me_2SiO(Me_2CHCH_2Si)_7O_{11}\}], 0.85 [m, 14 H,]$ C₅H₃(SiMe₃){Me₂SiO(Me₂CHCH₂Si)₇O₁₁}], 0.62 (s, 3 H), 0.27 [s, 3 H, $C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7)$], 0.30 [s, 9 H, $C_5H_3(SiMe_3)$ - $(Me_2SiOSi_7O_{11}R_7)$] ppm. ¹³C{¹H} NMR (75 MHz, [D₆]benzene, 25°C): $\delta = 132.0$ (Ci), 131.8, 123.9 (Ci), 115.5, 113.73 [C₅H₃(SiMe₃)-(Me₂SiOSi₇O₁₁R₇)], 66.8 (NbNCMe₃), 32.2 (NbNCMe₃), 26.5– $26.2 [C_5H_3(SiMe_3){Me_2SiO(Me_2CHCH_2Si)_7O_{11}}], 25.0-24.5 [C_5H_3-26.2]$ $(SiMe_3){Me_2SiO(Me_2CHCH_2Si)_7O_{11}}], 24.0-23.0 [C_5H_3(SiMe_3) \{Me_2SiO(Me_2CHCH_2Si)_7O_{11}\}\], 3.63, -0.63 \[C_5H_3(SiMe_3)(Me_2-1)_7O_{11}\}\], 3.63, -0.63 \[C_5H_3(SiMe_3)(Me_2-1)_7O_{11}\], 3.63, -0.63 \[C_5H_3(SiMe_3)(Me_2-1)_7O_{11}\], 3.63, -0.63 \[C_5H_3(SiMe_3)(Me_3-1)_7O_{11}\], 3.63, -0.63 \[C_5Me_3)(Me_3-1)_7O_{11}\], 3.63, -0.63, -0.63 \], 3.63, -0.63, -0.63,$ $SiOSi_7O_{11}R_7$], -0.27 [C₅H₃(SiMe₃)(Me₂SiOSi₇O₁₁R₇)] ppm. C₄₂H₉₀NNbO₁₂Si₉ (1146.848): calcd. C 43.99, H 7.91, N 1.22; found C 43.82, H 7.74, N 1.09.

 $[Nb{\eta^{5}-C_{5}H_{3}(SiMe_{3})_{2}}Cl(Si_{7}O_{12}R_{7}-\kappa^{3}O,O,O)]$ (R = *i*Bu 12): A solution of $[Nb{\eta^5-C_5H_3(SiMe_3)_2}Cl_4]$ (0.33 g, 0.75 mmol) in hexane (20 mL) was added to a solution of Si₇O₉(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): $\tilde{v} = 2954$ (vs), 1465 (m), 1251 (s), 1228 (s), 1099 (vs), 998 (vs), 842 (vs), 756 (m), 634 (w), 464 (m), 391 (s) cm⁻¹. ¹H NMR (300 MHz, [D₁]chloroform, 25°C): $\delta = 6.92$ (br., 2 H), 6.83 [br., 1 H, $C_5H_3(SiMe_3)_2$], 1.78 [m, 7 H, (Me₂CHCH₂Si)₇O₁₂], 0.87 [m, 42 H, (Me₂CHCH₂Si)₇O₁₂], 0.52 [m, 14 H, (Me₂CHCH₂Si)₇O₁₂], 0.29 [s, 18 H, C₅H₃(SiMe₃)₂] ppm. ¹³C{¹H} NMR (75 MHz, [D₁]chloroform, 25°C): δ = 135.6, 133.9 (Ci), 129.4 [C₅H₃(SiMe₃)₂], 25.6, 25.5, 25.4 [(Me₂CHCH₂Si)₇O₁₂], 23.6, 23.5 [(Me₂CHCH₂Si)₇O₁₂], 23 [(Me₂CHCH₂Si)₇O₁₂], -1.1 [C₅H₃(SiMe₃)₂] ppm. C₃₉H₈₄ClNbO₁₂Si₉ (1126.213): calcd. C 41.59, H 7.52; found C 41.82, H 7.53.

[Nb{η⁵-C₅H₃(SiMe₃)(Me₂SiOSi₇O₁₁R₇-κ²O,O)}Me₂] (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 ZnMe₂ (0.80 mL, 1.60 mmol). After 12 h, the resulting suspension was decanted, and the ZnCl₂ 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): \tilde{v} = 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. ¹H NMR (300 MHz, [D₆]benzene, 25°C): \delta = 6.55 (m, 1 H), 6.33 [m, 2 H, C₅H₃(SiMe₃)(Me₂SiO(Me₂CHCH₂Si)₇O₁₁}], 1.13 [m, 42 H, C₅H₃(SiMe₃) {Me₂SiO(Me₂CHCH₂Si)₇O₁₁}], 0.86 [m, 14 H, C₅H₃(SiMe₃) {Me₂SiO-**

 $\begin{array}{l} (Me_2CHCH_2Si)_7O_{11} \}, 0.22 \ (s, 6 \ H, \ NbMe_2), 0.35 \ (s, 3 \ H), 0.28 \ [s, 3 \ H, \ C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7)], 0.27 \ [s, 9 \ H, \ C_5H_3(SiMe_3)-(Me_2SiOSi_7O_{11}R_7)] \ ppm. \ ^{13}C\{^{1}H\} \ NMR \ (75 \ MHz, \ [D_6]benzene, 25^{\circ}C): \delta = 132.6 \ (Ci), 126.4, 123.6 \ (Ci), 121.3, 119.8 \ [C_5H_3(SiMe_3)-(Me_2SiOSi_7O_{11}R_7)], 53.5, 53 \ (NbMe_2), 26.4-25.9 \ [C_5H_3(SiMe_3)-(Me_2SiO(Me_2CHCH_2Si)_7O_{11}], 24.8-24.5 \ [C_5H_3(SiMe_3)\{Me_2SiO(Me_2CHCH_2Si)_7O_{11}\}], 24.8-24.5 \ [C_5H_3(SiMe_3)\{Me_2SiO(Me_2CHCH_2Si)_7O_{11}\}], 24.7, 0.9 \ [C_5H_3(SiMe_3)(Me_2SiOSi_7-O_{11}R_7)], -0.4 \ [C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7)] \ ppm. \ C_{40}H_87Nb-O_{12}Si_9 \ (1105.795): \ calcd. C \ 43.45, H \ 7.93; \ found C \ 43.33, H \ 7.65. \end{array}$

 $[Nb{\eta^{5}-C_{5}H_{3}(SiMe_{3})(Me_{2}SiOSi_{7}O_{11}R_{7}-\kappa^{2}O,O)](CHSiMe_{3})]$ (R = **iBu 14):** A hexane (25 mL) solution of **10** (0.57 g, 0.50 mmol) was treated with a 1 M solution of MgCl(CH₂SiMe₃) 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): $\tilde{v} = 2954$ (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} . ¹H NMR $(300 \text{ MHz}, [D_6] \text{benzene}, 25^{\circ}\text{C}): \delta = 9.68 \text{ (s, 1 H, NbCHSiMe_3)}, 8.06$ (m, 1 H), 6.65 (m, 1 H), 6.38 [m, 1 H, C₅H₃(SiMe₃)(Me₂-SiOSi₇O₁₁R₇)], 2.07 [m, 7 H, C₅H₃(SiMe₃) {Me₂SiO(Me₂CH- $CH_2Si_7O_{11}$], 1.11 [m, 42 H, $C_5H_3(SiMe_3)$ { $Me_2SiO(Me_2-$ CHCH₂Si)₇O₁₁}], 0.88 [m, 14 H, C₅H₃(SiMe₃){Me₂SiO-(Me₂CHCH₂Si)₇O₁₁}], 0.385 (s, 3 H), 0.381 [s, 3 H, C₅H₃(SiMe₃)-(Me₂SiOSi₇O₁₁R₇)], 0.25 [s, 9 H, C₅H₃(SiMe₃)(Me₂SiOSi₇O₁₁R₇)], 0.21 (s, 9 H, NbCHSiMe₃) ppm. ¹³C{¹H} NMR (75 MHz, [D₆]benzene, 25°C): δ = 235.73 (NbCHSiMe₃), 129.6 (Ci), 124.5 (Ci), 120.3, 119.2, 112.43 [C₅H₃(SiMe₃)(Me₂SiOSi₇O₁₁R₇)], 26.4–25.9 [C₅H₃(SiMe₃){Me₂SiO(Me₂CHCH₂Si)₇O₁₁}], 24.9–24.1 [C₅H₃(Si- Me_3 { $Me_2SiO(Me_2CHCH_2Si)_7O_{11}$ }], 23.6, 23.3, 23.0 [C_5H_3 - $(SiMe_3){Me_2SiO(Me_2CHCH_2Si)_7O_{11}}], 3.7, 3.3 [C_5H_3(SiMe_3)-$ (Me₂SiOSi₇O₁₁R₇)], 2.36 (NbCHSiMe₃), -0.5 [C₅H₃(SiMe₃)(Me₂-SiOSi₇O₁₁R₇)] ppm. C₄₂H₈₉NbO₁₂Si₁₀ (1159.918): calcd. C 43.49, H 7.73; found C 43.38, H 7.78.

 $[Nb{\eta^5-C_5H_3(SiMe_3)_2}Me(Si_7O_{12}R_7-\kappa^3O,O,O)]$ (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 ZnMe₂ (2 м 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): $\tilde{v} = 2954$ (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. ¹H NMR (300 MHz, [D₆]benzene, 25°C): δ = 6.91 (br., 1 H), 6.63 [br., 2 H, C₅H₃(SiMe₃)₂], 2.13 [m, 7 H, (Me₂CHCH₂Si)₇O₁₂], 1.52 (br., 3 H, NbMe), 1.10 [m, 42 H, (Me₂CHCH₂Si)₇O₁₂], 0.85 [m, 14 H, (Me₂CHCH₂Si)₇O₁₂], 0.28 [s, 18 H, $C_5H_3(SiMe_3)_2$ ppm. ¹³C{¹H} NMR (75 MHz, [D₆]benzene, 25°C): $\delta = 133.0, 132.1, 127.1, 125.1, 123.5 [C_5H_3(SiMe_3)_2], 52.2$ $[(\mathbf{Me}_2\mathbf{CHCH}_2\mathbf{Si})_7\mathbf{O}_{12}],$ [NbMe], 26.1–25.9 24.5. 24.4[(Me₂CHCH₂Si)₇O₁₂], 23.5, 23.1 [(Me₂CHCH₂Si)₇O₁₂], -0.1 $[C_5H_3(SiMe_3)_2]$ 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{η⁵-C₅H₃(SiMe₃)₂}R(NtBu){C(Me)O- κ^2 C,O}] (R = Cl 16, Me 17): A [D₆]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 ¹H 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): $\tilde{v} = 2966$ (vs), 1577 (s), 1356 (s), 1248 (s), 1083 (s), 920 (s), 838 (vs), 756 (s), 635 (m), 546 (m), 473 (m) cm⁻¹. ¹H NMR (300 MHz, [D₆]benzene, 25°C): $\delta = 6.81$ (m, 1 H), 6.21 [m, 2 H, C₅H₃(SiMe₃)₂], 2.47 [s, 3 H, NbC(Me)O], 0.97 (s, 9 H, NbCMe₃), 0.44 (s, 9 H), 0.01 [s, 9 H, C₅H₃(SiMe₃)₂] ppm. ¹³C{¹H} NMR (75 MHz, [D₆]benzene, 25°C): $\delta = 295.2$ [C(Me)O], 122.3 (Ci), 122.0 (Ci), 116.5, 110.9, 110.7 [C₅H₃(SiMe₃)₂], 65.8 (NbNCMe₃), 29.4 (NbNCMe₃), 29.5 [C(Me)O], -0.15, -0.19 [C₅H₃(SiMe₃)₂] ppm. C₁₇H₃₃ClNNbOSi₂ (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): $\tilde{v} = 2960$ (vs), 1697 (s), 1405 (s), 1367 (m), 1261 (vs), 1086 (vs), 918 (s), 838 (vs), 694 (s), 634 (s) cm⁻¹. ¹H NMR (300 MHz, [D₆]benzene, 25°C): $\delta = 6.40$ (m, 1 H), 6.22 (m, 1 H), 6.12 [m, 1 H, C₅H₃(SiMe₃)₂], 2.54 [s, 3 H, NbC(Me)O], 1.19 (s, 3 H, NbMe), 1.08 (s, 9 H, NbCMe₃), 0.23 (s, 9 H), 0.14 [s, 9 H, C₅H₃(SiMe₃)₂] ppm. ¹³C{¹H} NMR (75 MHz, [D₆]benzene, 25°C): $\delta = 300.5$ [C(Me)O], 122.7 (Ci), 122.5 (Ci), 117.3, 114.9, 112.7 [C₅H₃(SiMe₃)₂], 67.8 (NbNCMe₃), 32.2 (NbNCMe₃), 31.5 (NbMe), 30.5 [C(Me)O], -0.18, -0.21 [C₅H₃(SiMe₃)₂] ppm. C₁₈H₃₆NNbOSi₂ (431.568): calcd. C 50.10, H 8.41, N 3.25; found C 49.59, H 8.35, N 3.18.

 $[Nb{\eta^{5}-C_{5}H_{3}(SiMe_{3})_{2}}R(NtBu){C(R)O-\kappa^{2}C,O}] (R = CH_{2}SiMe_{3})_{2}R(NtBu){C(R)O-\kappa^{2}C,O}]$ 18): A yellow solution of 4 (0.15 g, 0.27 mmol) in [D₆]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 ¹H NMR spectroscopy at room temperature. After 30 min, the formation of alkyl acyl complex 18 with a nearly quantitative yield was confirmed by ¹H and ¹³C NMR spectra. The solution was concentrated to dryness, giving 18 as a dark orange microcrystalline compound. Yield 0.135 g (85%). IR (KBr): $\tilde{v} = 2956$ (vs), 1577 (s), 1450 (s), 1357 (m), 1249 (s), 1084 (s), 840 (vs), 755 (s), 635 (m), 470 (m) cm⁻¹. ¹H NMR (300 MHz, [D₆]benzene, 25°C): δ = 6.35 (m, 2 H), 6.24 [m, 1 H, $C_5H_3(SiMe_3)_2$], 3.45, 2.73 [AB, ²J_{H,H} = 10 Hz, 2 H, C(CH₂SiMe₃)O], 1.20 [s, 9 H, NbN(CMe₃)], 0.97, 0.78 (AB, ${}^{2}J_{H,H}$ = 10 Hz, 2 H, NbCH₂SiMe₃), 0.53 [s, 9 H, C(CH₂SiMe₃)O], 0.10 (s, 9 H, NbCH₂SiMe₃), 0.31 (s, 9 H), 0.13 [s, 9 H, C₅H₃(SiMe₃)₂] ppm. ¹³C{¹H} NMR (75 MHz, [D₆]benzene, 25°C): $\delta = 298.0$ [C(CH₂SiMe₃)O], 122.1 (Ci), 121.9 (Ci), 117.4, 111.7, 110.9 $[C_5H_3(SiMe_3)_2]$, 65.6 $[NbN(CMe_3)]$, 42.3 [C(CH₂SiMe₃)O], 33.1 [NbN(CMe₃)], 29.6 (NbCH₂SiMe₃), 4.0 $[C(CH_2SiMe_3)O], \ 0.64 \ (NbCH_2SiMe_3), \ -0.1, \ -0.2 \ [C_5H_3(SiMe_3)_2]$ ppm. C₂₄H₅₂NNbOSi₄ (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} -C₅H₃(SiMe₃)(Me₂SiOSi₇O₁₁R₇- $\kappa^2 O$, *O*)}{O(Me)C=C(Me)-O- $\kappa^2 O$, *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 [D₆]-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 ¹H NMR spectroscopy until total conversion of the starting niobium complex was achieved. After 2 h, the formation of 19 in quantitative yield 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): $\tilde{v} = 2954$ (vs), 1466 (s), 1400 (s), 1253 (s), 1115 (vs), 1099 (vs), 839

(vs), 741 (s), 478 (s) cm⁻¹. ¹H NMR (300 MHz, [D₆]benzene, 25°C): $\delta = 7.24 \text{ (m, 1 H)}, 7.09 \text{ (m, 1 H)}, 5.15 \text{ [m, 1 H, } C_5H_3(\text{SiMe}_3)(\text{Me}_2-\text{Me}_3)$ SiOSi₇O₁₁R₇)], 2.12 [m, 7 H, C₅H₃(SiMe₃) {Me₂SiO(Me₂CH- $CH_2Si_7O_{11}$], 1.76 (s, 3 H), 1.63 [s, 3 H, O(Me)C=C(Me)O], 1.13 [m, 42 H, C₅H₃(SiMe₃){Me₂SiO(Me₂CHCH₂Si)₇O₁₁}], 0.81 [m, 14 H, C₅H₃(SiMe₃) {Me₂SiO(Me₂CHCH₂Si)₇O₁₁}], 0.53 (s, 3 H), 0.41 [s, 3 H, C₅H₃(SiMe₃) {Me₂SiO(Me₂CHCH₂Si)₇O₁₁}], 0.24 [s, 9 H, $C_5H_3(SiMe_3)$ {Me₂SiO(Me₂CHCH₂Si)₇O₁₁}] ppm. ¹³C{¹H} NMR (75 MHz, [D₆]benzene, 25°C): $\delta = 134.2$ (Ci), 130.8 (Ci), 126.7, 122.4, 111.8 $[C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7)]$, 98.4 [O(Me)C=C-(Me)O], 31.1, 30.8 [O(Me)C=C(Me)O], 26.5–25.8 $[C_5H_3(SiMe_3)-$ {Me₂SiO(Me₂CHCH₂Si)₇O₁₁}], 24.8–24.4 [C₅H₃(SiMe₃){Me₂SiO-(Me₂CHCH₂Si)₇O₁₁}]. 23.9–23.0 [C₅H₃(SiMe₃){Me₂SiO(Me₂-CHCH₂Si)₇O₁₁}], -0.3 [C₅H₃(SiMe₃)(Me₂SiOSi₇O₁₁R₇)], -0.5, -4.1 [C₅H₃(SiMe₃)(Me₂SiOSi₇O₁₁R₇)] ppm. C₄₂H₈₇NbO₁₄Si₉ (1161.815): calcd. C 43.42, H 7.55; found C 43.51, H 7.63.

 $[Nb{\eta^5-C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7-\kappa^2O,O)}(CMe_2NAr \kappa^2 C_{,N}$] (**R** = *i***Bu**, Ar = 2,6-Me₂C₆H₃ 20): Under rigorously anhydrous conditions, 2,6-Me₂C₆H₃NC (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): $\tilde{v} = 2953$ (vs), 2118 (s), 1466 (s), 1365 (w), 1253 (s), 1107 (vs), 921 (s), 838 (vs), 740 (s), 484 (m) cm⁻¹. ¹H NMR (300 MHz, [D₆]benzene, 25°C): δ = 7.02 (m, 3 H, $Me_2C_6H_3$), 7.43 (m, 1 H), 7.33 (m, 1 H), 5.65 [m, 1 H, C_5H_3 - $(SiMe_3)(Me_2SiOSi_7O_{11}R_7)]$, 2.12 [m, 7 H, $C_5H_3(SiMe_3){Me_2-1}$ SiO(Me₂CHCH₂Si)₇O₁₁}], 1.73 (s, 3 H), 1.69 (s, 3 H, Me₂C₆H₃), not observed (CMe₂NAr), 1.12 [m, 42 H, C₅H₃(SiMe₃){Me₂-SiO(Me₂CHCH₂Si)₇O₁₁}], 0.82 [m, 14 H, C₅H₃(SiMe₃){Me₂SiO-(Me₂CHCH₂Si)₇O₁₁}], 0.48 (s, 3 H), 0.39 [s, 3 H, C₅H₃(SiMe₃)-(Me₂SiOSi₇O₁₁R₇)], 0.34 [s, 9 H, C₅H₃(SiMe₃)(Me₂SiOSi₇O₁₁R₇)] ppm. ¹³C{¹H} NMR (75 MHz, [D₆]benzene, 25°C): δ = 151.83 (Ci), 135.0, 131.6, 129.2 (several phenyl, Me₂C₆H₃), 131.6 (Ci), 125.5, 125.2, 123.6 (Ci), 111.2 [C₅H₃(SiMe₃)(Me₂SiOSi₇O₁₁R₇)], 74.0 (CMe₂NAr), 30.3, 28.7 (CMe₂NAr), 26.9–25.9 [C₅H₃(SiMe₃)- $\{Me_2SiO(Me_2CHCH_2Si)_7O_{11}\}\}, 24.9-24.4 [C_5H_3(SiMe_3)\{Me_2SiO-V_$ $(Me_2CHCH_2Si)_7O_{11}$], 24.0–22.0 $[C_5H_3(SiMe_3)\{Me_2SiO(Me_2-1)\}]$ $CHCH_2Si_7O_{11}$], not observed (Me₂C₆H₃), 4.5, -0.2 [C₅H₃- $(SiMe_3)(Me_2SiOSi_7O_{11}R_7)], 0.05 [C_5H_3(SiMe_3)(Me_2SiOSi_7O_{11}R_7)]$ ppm. C₄₉H₉₆NNbO₁₂Si₉ (1236.973): calcd. C 47.58, H 7.82, N 1.13; found C 47.44, H 7.92, N 1.17.

 $[Nb{\eta^{5}-C_{5}H_{3}(SiMe_{3})_{2}}Cl(NtBu){C(Me)NAr-\kappa^{2}C,N}]$ (Ar = 2,6-Me₂C₆H₃ 21): A hexane (40 mL) solution of 2 (0.11 g, 0.26 mmol) was treated with a solution of 2,6-Me₂C₆H₃NC (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 $(2 \times 10 \text{ mL})$. 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): $\tilde{v} = 2967$ (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 $^{-1}$. 1H NMR (300 MHz, [D_6]benzene, 25°C): δ = 6.90 (m, 3 H, Me₂C₆H₃), 6.67 (m, 1 H), 6.25 (m, 1 H), 6.02 [m, 1 H, C₅H₃(SiMe₃)₂], 2.14 [s, 3 H, C(Me)NAr], 2.12 (s, 3 H), 1.77 (s, 3 H, Me₂C₆H₃), 1.18 [s, 9 H, NbN(CMe₃)], 0.52 (s, 9 H), 0.32 [s, 9 H, C₅H₃(SiMe₃)₂] ppm. ¹³C{¹H} NMR (75 MHz, [D₆]benzene, 25°C): δ = 227.3 [C(Me)NAr], 140.4 (Ci), 135.4 (Ci), 131.2, 129.8, 128.7, 126.4 (Me₂C₆H₃), 122.7 (Ci), 119.3, 119.2, 119.1, 117.3 (Ci, C₅H₃(SiMe₃)₂], 67.1 [NbN(CMe₃)], 31.5 [NbN(CMe₃)], 23.9 [C(Me)NAr], 18.7, 18.4 (Me₂C₆H₃), 0.95, -0.88



 $[C_{5}H_{3}(SiMe_{3})_{2}]$ ppm. $C_{25}H_{42}ClN_{2}NbSi_{2}$ (555.154): calcd. C 54.09, H 7.63, N 5.05; found C 53.85, H 7.54, N 4.88.

 $[Nb{\eta^{5}-C_{5}H_{3}(SiMe_{3})_{2}}Me(NtBu){C(Me)NAr-\kappa^{2}C,N}]$ (Ar = 2,6- $Me_2C_6H_3$ 22): In a standard experiment, 3 (0.15 g, 0.372 mmol), 2,6-Me₂C₆H₃NC (0.049 g, 0.372 mmol) and [D₆]benzene (0.8 mL) were placed in a valved NMR tube. The reaction was monitored by ¹H 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 ¹H NMR spectrum. When the solvent was removed by vacuum, 22 was isolated as a brown microcrystalline solid. Yield 0.17 g (86%). IR (KBr): v = 2961 (vs), 1634 (s), 1442 (s), 1351 (m), 1250 (vs), 1080 (vs), 921 (vs), 836 (vs), 757 (s), 640 (m), 539 (m) cm⁻¹. ¹H NMR (300 MHz, $[D_6]$ benzene, 25°C): $\delta = 6.91$ (m, 3 H, Me₂C₆H₃), 6.31 (m, 1 H), 6.00 (m, 1 H), 5.59 [m, 1 H, C₅H₃(SiMe₃)₂], 2.18 [s, 3 H, C(Me)-NAr], 1.96 (s, 3 H), 1.67 (s, 3 H, Me₂C₆H₃), 1.20 [s, 9 H, NbN(CMe₃)], 0.67 (s, 3 H, NbMe), 0.26 (s, 9 H), 0.11 [s, 9 H, $C_5H_3(SiMe_3)_2$ ppm. ¹³C{¹H} NMR (75 MHz, [D₆]benzene, 25°C): $\delta = 230.1$ [C(Me)NAr], 141.7 (Ci), 134.2 (Ci), 130.47, 129.8, 125.9 (several phenyl, Me₂C₆H₃), 122.8 (Ci), 119.0 (Ci), 117.2, 115.9, 113.7 [C₅H₃(SiMe₃)₂], 69.9 [NbN(CMe₃)], 64.62 (NbMe), 32.4 [NbN(CMe₃)], 23.9 [C(Me)NAr], 18.2, 18.1 (Me₂C₆H₃), 1.08, -0.93 $[C_5H_3(SiMe_3)_2]$ 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 **5**c' suitable for X-ray analysis was obtained by the slow concentration of a hexane solution of **5**c. The crystal was then covered with mineral oil and mounted in the N₂ stream of a Bruker-Nonius Kappa CCD diffractometer. Data was collected by using graphite monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ 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) Å³; 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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- [1] V. C. Gibson, S. K. Spitzmeseer, Chem. Rev. 2003, 103, 283– 315.
- [2] a) T. Cuenca, P. Royo, *Coord. Chem. Rev.* 1999, *193–195*, 447–498 and references cited therein; b) M. I. Alcalde, P. Gómez-Sal, P. Royo, *Organometallics* 1999, *18*, 546–554.
- [3] a) M. Gómez, P. Gómez-Sal, J. M. Hernández, *Eur. J. Inorg. Chem.* 2006, 5106–5114; b) M. Gómez, P. Gómez-Sal, J. M. Hernández, *J. Organomet. Chem.* 2007, 692, 2291–2298.
- [4] M. Gómez, Eur. J. Inorg. Chem. 2003, 3681-3697.
- [5] P. J. Stewart, A. J. Blake, P. Mountford, *Inorg. Chem.* 1997, 36, 1982–1986.
- [6] J. S. Freundlich, R. R. Schrock, W. M. Davis, J. Am. Chem. Soc. 1996, 118, 3643–3655.
- [7] a) S. Schmidt, J. Sundermeyer, J. Organomet. Chem. 1994, 472, 127–138; b) S. Schmidt, J. Sundermeyer, F. Möller, J. Organomet. Chem. 1994, 475, 157–166; c) W. A. Herrmann, W. Baratta, J. Organomet. Chem. 1996, 506, 357–361; d) L. Djakovitch, W. A. Herrmann, J. Organomet. Chem. 1998, 562, 71–78; e) M. I. Alcalde, P. Gómez-Sal, A. Martín, P. Royo, Organometallics 1998, 17, 1144–1150; f) A. Antiñolo, M. Fajardo, C. Huertas, A. Otero, S. Prashar, A. M. Rodríguez, J. Organomet. Chem. 1999, 585, 154–161; g) A. Schorn, J. Sundermeyer, Eur. J. Inorg. Chem. 2001, 2947–2955.
- [8] a) W. A. Herrmann, W. Baratta, E. Herdtweck, Angew. Chem. Int. Ed. Engl. 1996, 35, 1951–1953; b) G. Proulx, R. G. Bergman, Organometallics 1996, 15, 684–692.
- [9] T. C. Baldwin, S. R. Huber, M. A. Bruck, D. E. Wigley, *Inorg. Chem.* 1993, 32, 5682–5686.
- [10] V. C. Gibson, A. D. Poole, J. Chem. Soc., Chem. Commun. 1995, 2261–2262.
- [11] a) D. M. Antonelli, W. P. Schaefer, G. Parkin, J. E. Bercaw, J. Organomet. Chem. 1993, 462, 213–220; b) A. Antiñolo, P. Espinosa, M. Fajardo, P. Gómez-Sal, C. López-Mardomingo, A. Martín, A. Otero, J. Chem. Soc., Dalton Trans. 1995, 1007– 1013.
- [12] a) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* 2000, 100, 1169–1204; b) W. E. Piers, D. J. H. Emslie, *Coord. Chem. Rev.* 2002, 233–234, 131–155; c) D. W. Stephan, *Organometallics* 2005, 24, 2548–2560; d) P. D. Bolton, P. Mountford, *Adv. Synth. Catal.* 2005, 347, 355.
- [13] a) S. M. Pugh, D. J. M. Trosch, M. E. G. Skinner, L. H. Gade, P. Mountford, *Organometallics* **2001**, *20*, 3531–3542; b) K. R. Gust, M. J. Heeg, C. H. Winter, *Polyhedron* **2001**, *20*, 805–813.
- [14] a) J. Sundermeyer, D. Runge, Angew. Chem. Int. Ed. Engl. 1994, 33, 1255–1257; b) V. C. Gibson, J. Chem. Soc., Dalton Trans. 1994, 1607–1618.
- [15] W. A. Herrmann, W. Baratta, E. Herdtweck, J. Organomet. Chem. 1997, 541, 445–460.
- [16] a) J. Gavenonis, T. D. Tilley, J. Am. Chem. Soc. 2002, 124, 8536–8537; b) U. Burckhardt, G. L. Casty, J. Gavenonis, T. D. Tilley, Organometallics 2002, 21, 3108–3122.
- [17] a) M. V. Galakhov, M. Gómez, G. Jiménez, P. Royo, M. A. Pellinghelli, A. Tiripicchio, Organometallics 1995, 14, 1901–1910; b) M. V. Galakhov, M. Gómez, G. Jiménez, P. Royo, M. A. Pellinghelli, A. Tiripicchio, Organometallics 1995, 14, 2843–2854; c) M. Gómez, P. Gómez-Sal, G. Jiménez, A. Martín, P. Royo, J. Sánchez-Nieves, Organometallics 1996, 15, 3579–3587; d) A. Castro, M. V. Galakhov, M. Gómez, P. Gómez-Sal, A. Martín, F. Sánchez, J. Organomet. Chem. 2000, 595, 36–53; e) A. Castro, M. V. Galakhov, M. Gómez, P. Gómez-Sal, A. Martín, F. Sánchez, P. Velasco, Eur. J. Inorg. Chem. 2000, 2047–2054; f) J. Sánchez-Nieves, P. Royo, M. A. Pellinghelli, A. Tiripicchio, Organometallics 2000, 19, 3161–3169; g) S. Prashar, M. Fajardo, A. Garcés, I. Dorado, A. Antiñolo, A. Otero, I. López-Solera, C. López-Mardomingo, J. Organomet. Chem. 2004, 689, 1304–1314.
- [18] P. Royo, J. Sánchez-Nieves, J. Organomet. Chem. 2000, 597, 61– 68.

- [19] a) F. J. Feher, T. A. Budzichowski, R. L. Blanski, K. J. Weller, J. W. Ziller, *Organometallics* 1991, 10, 2526–2528; b) R. H. Baney, M. Itoh, A. Sakakibara, T. Suzuki, *Chem. Rev.* 1995, 95, 1409–1430; c) F. J. Feher, R. Terroba, J. W. Ziller, *Chem. Commun.* 1999, 2153–2154.
- [20] a) F. J. Feher, S. L. Gonzales, J. W. Ziller, Inorg. Chem. 1988, 27, 3442-3446; b) E. Popowski, I. Hillert, H. Kelling, H. Jancke, Z. Anorg. Allg. Chem. 1991, 601, 133-143; c) F. J. Feher, T. A. Budzichowski, J. W. Ziller, Inorg. Chem. 1992, 31, 5100-5105; d) F. J. Feher, T. A. Budzichowski, Polyhedron 1995, 14, 3239-3253; e) R. Murugavel, A. Voigt, M. G. Walawalkar, H. W. Roesky, Chem. Rev. 1996, 96, 2205-2236; f) F. J. Feher, S. H. Phillips, J. Organomet. Chem. 1996, 521, 401-403; g) H. C. L. Abbenhuis, Chem. Eur. J. 2000, 6, 25-32; h) V. Lorenz, A. Fischer, S. Gießmann, J. W. Gilje, Y. Gun'ko, K. Jacob, F. T. Edelmann, Coord. Chem. Rev. 2000, 206-207, 321-368; i) V. Lorenz, A. Fischer, F. T. Edelmann, Inorg. Chem. Commun. 2000, 3, 292-295; j) R. Duchateau, Chem. Rev. 2002, 102, 3525-3542; k) R. W. J. M. Hanssen, R. A. van Santen, H. C. L. Abbenhuis, Eur. J. Inorg. Chem. 2004, 675-683; 1) V. Lorenz, F. T. Edelmann, Z. Anorg. Allg. Chem. 2004, 630, 1147; m) V. Lorenz, F. T. Edelmann, Adv. Organomet. Chem. 2005, 53, 101-153.
- [21] a) E. G. Shockey, A. G. Bolf, P. F. Jones, J. J. Schwab, K. P. Chaffee, T. S. Haddad, J. D. Lichtenhan, *Appl. Organomet. Chem.* 1999, 13, 311–327; b) J. Annand, H. C. Aspinall, A. Steiner, *Inorg. Chem.* 1999, 38, 3941–3943; c) Z. Fei, K. Ibrom, F. T. Edelmann, Z. Anorg. Allg. Chem. 2002, 628, 2109–2112; d) V. Lorenz, S. Giessmann, Y. K. Gun'ko, A. K. Fischer, J. W. Gilje, F. T. Edelmann, Angew. Chem. Int. Ed. 2004, 43, 4603–4606; e) Y. Gao, A. Eguchi, K. Kakehi, Y. C. Lee, Org. Lett. 2004, 6, 3457–3460; f) R. Unno, R. Tanaka, S. Tanaka, T. Takenchi, S. Kyushin, H. Matsumoto, Organometallics 2005, 24, 765–768; g) G. Ionescu, J. I. van der Vlugt, H. C. L. Abbenhuis, D. Vogt, Tetrahedron: Asymmetry 2005, 16, 3970–3975.
- [22] a) F. J. Feher, T. A. Budzichowski, K. Rahimian, J. W. Ziller, J. Am. Chem. Soc. 1992, 114, 3859-3866; b) W. A. Herrmann, R. Anwander, V. Dufaud, W. Scherer, Angew. Chem. Int. Ed. Engl. 1994, 33, 1285–1286; c) H. C. L. Abbenhuis, A. D. Burrows, H. Kooijman, M. Lutz, M. T. Palmer, R. A. van Santen, A. L. Spek, Chem. Commun. 1998, 2627-2628; d) M. Crocker, R. H. M. Herold, A. G. Orpen, M. T. A. Overgaag, J. Chem. Soc., Dalton Trans. 1999, 3791-3804; e) J. Annand, H. C. Aspinall, J. Chem. Soc., Dalton Trans. 2000, 1867-1872; f) M. Chabanas, E. A. Quadrelli, B. Fenet, C. Coperet, J. Thivolle-Cazat, J. M. Basset, A. Lesage, L. Emsley, Angew. Chem. Int. Ed. 2001, 40, 4493-4496; g) P. L. Arnold, A. J. Blake, S. N. Hall, B. D. Ward, C. Wilson, J. Chem. Soc., Dalton Trans. 2001, 488–491; h) N. Maxim, A. Overweg, P. J. Kooijman, R. A. van Santen, H. C. L. Abbenhuis, J. Mater. Chem. 2002, 12, 3792; i) J. I. van der Vlugt, M. M. P. Grutters, J. Ackerstaff, R. W. J. H. Hanssen, H. C. L. Abbenhuis, D. Vogt, Tetrahedron Lett. 2003, 44, 8301-8305; j) N. Mintcheva, M. Tanabe, K. Osakada, Organometallics 2006, 25, 3776-3783; k) K. Suyama, T. Gunji, K. Arimitsu, Y. Abe, Organometallics 2006, 25,5587-5593; l) N. Tohnai, Y. Mizobe, M. Doi, S. Sukata, T. Hinoue, T. Yuge, I. Hisaki, Y. Matsukawa, M. Miyata, Angew. Chem. Int. Ed. 2007, 46, 2220-2223; m) E. Lucenti, F. J. Feher, J. W. Ziller, Organometallics 2007, 26, 75-82.
- [23] a) S. D. Kinrade, T. W. Swaddle, *Inorg. Chem.* 1988, 27, 4253–4259; b) H. Jancke, J. Schulz, E. Popowski, H. Kelling, *J. Organomet. Chem.* 1988, 354, 23–29; c) B. Bussemer, K.-P. Schröder, J. Sauer, *Solid State Nucl. Magn. Reson.* 1997, 9, 155–164; d) R. Wolff, H. Jancke, R. Radeglia, *Solid State Nucl. Magn. Reson.* 1997, 9, 177–189; e) S. D. Kinrade, C. T. G. Knight, D. L. Pole, R. T. Syvitski, *Inorg. Chem.* 1998, 37, 4272–4277; f) T. M. Alam, M. Henry, *Phys. Chem. Chem. Phys.* 2000, 2, 23–28.
- [24] a) F. J. Feher, D. A. Newman, J. F. Walzer, J. Am. Chem. Soc.
 1989, 111, 1741–1748; b) F. T. Edelmann, Angew. Chem. Int. Ed. Engl. 1992, 31, 586–587; c) F. J. Feher, J. J. Schwab, S. H.

Phillips, A. Eklund, E. Martínez, Organometallics 1995, 14, 4452–4453; d) T. W. Dijkstra, R. Duchateau, R. A. van Santen, A. Meetsma, G. P. A. Yap, J. Am. Chem. Soc. 2002, 124, 9856–9864; e) L. Li, M. V. Metz, H. Li, M.-C. Chen, T. J. Marks, L. Liable-Sands, A. L. Rheingold, J. Am. Chem. Soc. 2002, 124, 12725–12741; f) P. Belanzoni, M. Rosi, A. Sgamellotti, THEO-CHEM 2002, 579, 181–189; g) R. Duchateau, T. W. Dijkstra, R. A. van Santen, G. P. A. Yap, Chem. Eur. J. 2004, 10, 3979–3990; h) R. Y. Kannan, H. J. Salacinski, P. E. Butler, A. M. Seifalian, Acc. Chem. Res. 2005, 38, 879–884; i) A. Fina, H. C. L. Abbenhuis, D. Tabuani, A. Frache, G. Camino, Polym. Degrad. Stab. 2006, 91, 1064–1070.

- [25] a) F. J. Feher, R. Terroba, R. Z. Jin, K. D. Wyndham, S. Lucke, R. Brutchey, F. Nguyen, *Polym. Mater. Sci. Eng.* 2000, *82*, 301;
 b) N. Maxim, P. C. M. M. Magusin, P. J. Kooyman, J. H. M. C. van Wolput, R. A. van Santen, H. C. L. Abbenhuis, *Chem. Mater.* 2001, *13*, 2958–2964; c) J. Choi, J. Harcup, A. F. Yee, Q. Zhu, R. M. Laine, *J. Am. Chem. Soc.* 2001, *123*, 11420–11430.
- [26] a) U. Schubert, P. Jutzi, Silicon Chemistry: From the Atom to Extended Systems, Wiley-VCH, 2003; b) R. W. J. M. Hanssen, R. A. van Santen, H. C. L. Abbenhuis, Eur. J. Inorg. Chem. 2004, 675–683.
- [27] a) R. Duchateau, R. J. Harmsen, H. C. L. Abbenhuis, R. A. van Santen, A. Meetsma, S. K. H. Thiele, M. Kranenburg, *Chem. Eur. J.* **1999**, *5*, 3130–3135; b) G. Gerritsen, R. Duchateau, R. A. van Santen, G. P. A. Yap, *Organometallics* **2003**, *22*, 100–110.
- [28] a) M. D. Skowronska-Ptasinska, M. L. W. Vorstenbosch, R. A. van Santen, H. C. L. Abbenhuis, *Angew. Chem. Int. Ed.* 2002, *41*, 637–639; b) Z. F. Fei, S. Busse, F. T. Edelmann, *J. Chem. Soc., Dalton Trans.* 2002, 2587–2589; c) K. Wada, N. Itayama, N. Watanabe, M. Bundo, T. Kondo, T. Mitsudo, *Organometallics* 2004, *23*, 5824–5832.
- [29] a) R. Duchateau, H. C. L. Abbenhuis, R. A. van Santen, A. Meetsma, S. K. H. Thiele, M. F. H. van Tol, Organometallics 1998, 17, 5663–5673; b) R. Duchateau, U. Cremer, R. J. Harmsen, S. I. Mohamud, H. C. L. Abbenhuis, R. A. van Santen, A. Meetsma, K.-H. Thiele, M. F. H. van Tol, M. Kranenburg, Organometallics 1999, 18, 5447–5459; c) F. T. Edelmann, S. Giessmann, A. Fischer, J. Organomet. Chem. 2001, 620, 80–89; d) J. R. Severn, R. Duchateau, R. A. van Santen, D. D. Ellis, A. L. Spek, G. P. A. Yap, Dalton Trans. 2003, 2293–2302; e) J. M. Fraile, J. I. Garcia, J. A. Mayoral, E. Vispe, J. Catal. 2005, 233, 90–99.
- [30] a) F. J. Feher, J. F. Walzer, *Inorg. Chem.* 1991, 30, 1689–1694;
 b) F. J. Feher, J. F. Walzer, R. L. Blanski, *J. Am. Chem. Soc.* 1991, 113, 3618–3619;
 c) F. J. Feher, R. L. Blanski, *J. Am. Chem. Soc.* 1992, 114, 5886–5887;
 d) K. Wada, M. Nakashita, A. Yamamoto, H. Wada, T. Mitsudo, *Chem. Lett.* 1997, 1209–1210.
- [31] a) H.-J. Gosink, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, E. Irmer, R. Herbst Irmer, *Organometallics* 1994, 13, 3420– 3426; b) M. Lazell, M. Motevalli, S. A. A. Shah, A. C. Sullivan, J. Chem. Soc., Dalton Trans. 1997, 3363–3366.
- [32] V. Lorenz, S. Blaurock, H. Görls, F. T. Edelmann, Organometallics 2006, 25, 5922–5926.
- [33] A. Castro, M. V. Galakhov, M. Gómez, F. Sánchez, J. Organomet. Chem. 1999, 580, 161–168.
- [34] A. Castro, M. V. Galakhov, M. Gómez, P. Gómez-Sal, A. Martín, P. Royo, J. Organomet. Chem. 1998, 554, 185–194.
- [35] A. Castro, M. V. Galakhov, M. Gómez, P. Gómez-Sal, A. Martín, *Eur. J. Inorg. Chem.* 2002, 1336–1342.
- [36] a) J. de la Mata, R. Fandos, M. Gómez, P. Gómez-Sal, S. Martínez-Carrera, P. Royo, *Organometallics* 1990, *9*, 2846–2850; b)
 I. de Castro, M. V. Galakhov, M. Gómez, P. Gómez-Sal, A. Martín, P. Royo, *J. Organomet. Chem.* 1996, *514*, 51–58; c) D. Laurencin, R. Thouvenot, K. Boubekeur, A. Proust, *Dalton Trans.* 2007, 1334–1345.
- [37] a) I. de Castro, J. de la Mata, M. Gómez, P. Gómez-Sal, P. Royo, J. M. Selas, *Polyhedron* **1992**, *11*, 1023–1027; b) J. M.



Boncella, M. L. Cajigal, K. A. Abboud, *Organometallics* **1996**, *15*, 1905–1912; c) M. V. Galakhov, M. Gómez, P. Gómez-Sal, P. Velasco, *Eur. J. Inorg. Chem.* **2006**, 4242–4253.

- [38] M. V. Galakhov, M. Gómez, P. Gómez-Sal, P. Velasco, Organometallics 2005, 24, 3552–3560.
- [39] a) K. C. Wallace, W. M. Davis, R. R. Schrock, *Inorg. Chem.* 1990, 29, 1104–1106; b) D. H. Berry, T. S. Koloski, P. J. Carroll, *Organometallics* 1990, 9, 2952–2962; c) J. S. Freundlich, R. R. Schrock, C. C. Cummins, W. M. Davis, *J. Am. Chem. Soc.* 1994, 116, 6476–6477; d) H. C. L. Abbenhuis, M. H. P. Rietveld, H. F. Haarman, M. P. Hogerheide, A. L. Spek, G. van Koten, *Organometallics* 1994, 13, 3259–3268; e) D. Y. Dawson, J. Arnold, *Organometallics* 1997, 16, 1111–1113; f) M. H. P. Rietveld, W. Teunissen, H. Hagen, L. van der Water, D. M. Grove, P. A. van der Schaaf, A. Mühlebach, H. Kooijman, W. J. Smeets, N. Veldman, A. L. Spek, G. van Koten, *Organometallics* 1997, 16, 1674–1684; g) M. H. P. Rietveld, E. G. Klumpers, J. T. B. H. Jastrzebski, D. M. Grove, N. Veldman, A. L. Spek, G. van Koten, *Organometallics* 1997, 16, 4260–4267.
- [40] a) M. C. W. Chan, J. M. Cole, V. C. Gibson, J. A. K. Howard, C. Lehmann, A. D. Poole, U. Siemeling, J. Chem. Soc., Dalton Trans. 1998, 103–112; b) K. Mashima, M. Kaidzu, Y. Tanaka, Y. Nakayama, A. Nakamura, J. G. Hamilton, J. J. Rooney, Organometallics 1998, 17, 4183–4195; c) R. Baumann, R. Stumpf, W. M. Davis, L.-C. Liang, R. R. Schrock, J. Am. Chem. Soc. 1999, 121, 7822–7836; d) S. Courtenay, D. W. Stephan, Organometallics 2001, 20, 1442–1450; e) P. J. Chirik, D. L. Zubris, L. J. Ackerman, L. M. Henling, M. W. Day, J. E. Bercaw, Organometallics 1998, 121, 7822–7836; d) S. Courtenay, J. E. Bercaw, Organometallics 2001, 20, 1442–1450; e) P. J. Chirik, D. L. Zubris, L. J. Ackerman, L. M. Henling, M. W. Day, J. E. Bercaw, Organometallics 1998, 121, 7822–7836; d) S. Courtenay, J. E. Bercaw, Organometallics 2001, 20, 1442–1450; e) P. J. Chirik, D. L. Zubris, L. J. Ackerman, L. M. Henling, M. W. Day, J. E. Bercaw, Organometallics 2001, 20, 2001, 20, 2001, 20, 2001, 20, 2001, 20, 2001, 20, 2001, 2

metallics **2003**, *22*, 172–187; f) K. Mashima, H. Yonekura, T. Yamagata, K. Tani, *Organometallics* **2003**, *22*, 3766–3772.

- [41] a) L. Kloppenburg, J. L. Petersen, Organometallics 1997, 16, 3548–3556; b) J. H. Hardesty, T. A. Albright, S. Kahlal, Organometallics 2000, 19, 4159–4168; c) F. de Angelis, A. Sgamellotti, N. Re, S. Fantacci, Organometallics 2005, 24, 1876–1885.
- [42] a) E. Carmona, J. M. Marín, P. Palma, M. L. Poveda, J. Organomet. Chem. 1989, 377, 157–169; b) A. C. Filippou, W. Grünleitner, C. Völkl, P. Kiprof, J. Organomet. Chem. 1991, 413, 181–203; c) A. C. Filippou, C. Völkl, P. Kiprof, J. Organomet. Chem. 1991, 415, 375–394.
- [43] T. Y. Meyer, L. R. Garner, N. C. Baenziger, L. Messerle, *Inorg. Chem.* 1990, 29, 4045–4050.
- [44] P. Legzdins, P. J. Lundmark, S. J. Rettig, Organometallics 1996, 15, 2988–2993.
- [45] F. J. Feher, R. Terroba, J. W. Ziller, Chem. Commun. 1999, 2309–2310.
- [46] LiNHtBu was prepared in situ by reaction of NH₂tBu and LinBu in an 1:1 molar ratio with hexane as solvent or by the method described in P. Jutzi, R. Sauner, J. Organomet. Chem. 1973, 50, C29–C30.
- [47] C. Tessiers-Youngs, O. T. Beachley Jr, Inorg. Synth. 1986, 24, 95–97.
- [48] G. M. Sheldrick, SHELX-97, Program for Crystal Structure Analysis, University of Göttingen, Göttingen, Germany, 1998.
- [49] L. J. Farrugia WINGX, J. Appl. Crystallogr. 1999, 32, 837–838. Received: June 22, 2009
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