

Carbosilane dendrimers containing peripheral cyclopentadienyl niobium- and tantalum-imido complexes

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Abstract

Anilines $Gn-\{(C_6H_4)N(SiMe_3)_2\}_m$, based on simple or dendritic carbosilanes, have been used to synthesize (imido)tantalum compounds $Gn-\{(C_6H_4)NTaCl_2Cp^*\}_m$ (**1**, $n = 0$, $m = 1$; **2**, $n = 1$, $m = 4$; $Cp^* = \eta^5-C_5Me_5$), by the reaction with $[TaCl_4Cp^*]$ and elimination of $SiMe_3Cl$. (Imido)niobocene compounds of general formula $Gn-\{(C_6H_4)NNbClCp'_2\}_m$ (**3–5**; $n = 0, 1, 2$; $m = 1, 4, 8$, respectively) have been readily prepared from their corresponding half-sandwich complexes $Gn-\{(C_6H_4)NNbCl_2Cp'\}_m$ by the reaction with m equiv. of $LiCp'$ ($Cp' = \eta^5-C_5H_4SiMe_3$). Compounds **1–5** are all found to be exceedingly moisture sensitive, and in the case of the (imido)niobocene materials the hydrolytic reaction selectively leads to the formation of $[NbCl(O)Cp'_2]$ (**6**). The molecular structure of **6** has been determined by X-ray diffraction studies.

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1. Introduction

Metallodendrimer research has been steadily gaining ground during the last few years, a considerable number of dendritic macromolecules containing transition metals at their core, branches, or periphery have been prepared [1], and some of them studied in metal-based catalysis [2]. Much more limited is the number of examples describing dendrimers containing early transition metals [3–7a]. We have contributed with several works into the chemistry of carbosilane dendrimers containing early transition-metal complexes bonded to the dendritic periphery or focal point [4], usually through O- [5], or N-donor anchoring ligands [6]. Recently we have expanded the range of useful synthetic routes available to attach metal complexes to dendrimers, by using pyridylimine ligands in the synthesis of group 10 peripheral metallodendrimers, which showed rel-

evant dendritic effects on their polymerization catalyses [8], and also explored the application of poly(pyrazolyl)methane ligands in the field of metallodendritic chemistry [7].

Imido ligands have led to a prominent family of complexes in transition metal chemistry, being characterized by their capability to stabilize high-valent metal complexes due to their strong π -donor abilities [9,10], and with important uses such as stable ancillary ligands at early transition metal centers active in metathesis polymerization processes [11]. In our search for useful anchoring functionalities, we first identified the potential of terminal aniline groups to support early transition metal compounds through imido bonds on the periphery of carbosilane dendrimers [6a], and later tuned this approach for the synthesis of mono(cyclopentadienyl)niobium(V) carbosilane dendrimers with the metal complexes linked to the dendritic framework through arylimido–metal bonds [6b]. These previous results are used in this work for the synthesis of new carbosilane dendrimers with imido-supported complexes of niobium and tantalum at their periphery.

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2. Results and discussion

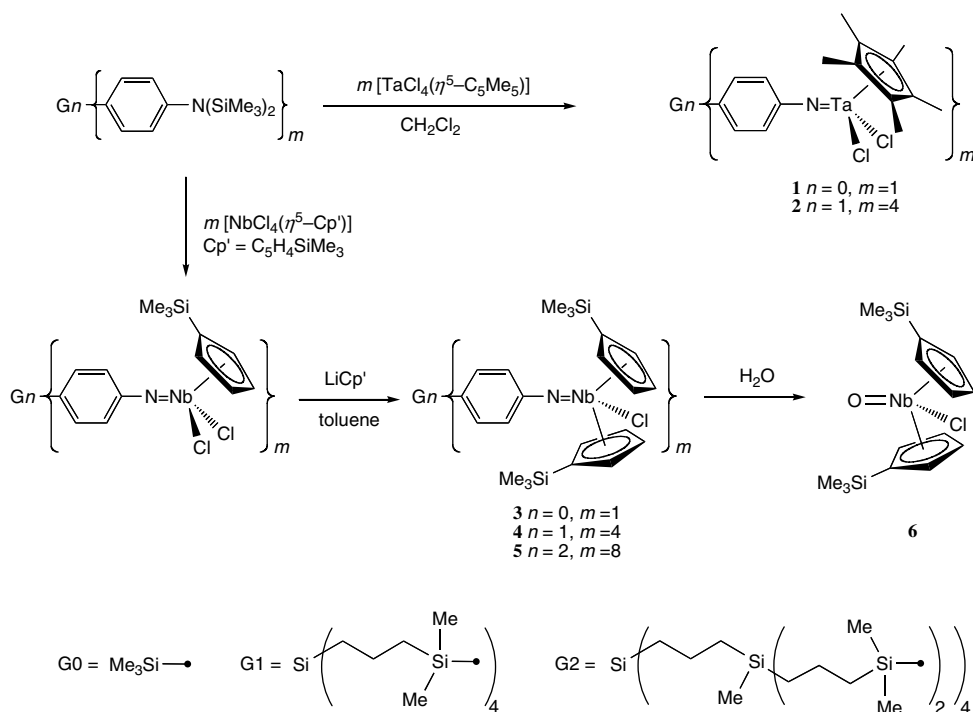
2.1. Synthesis of complexes

Preparative details and spectroscopic data for the new compounds are given in Section 4. Only selected data will be presented for this discussion. The cleavage of N–Si bonds has been previously employed as a route to form transition metal imido bonds [9,10]. Thus, we have quantitatively prepared new Ti and Nb imido complexes by reaction of *N,N*-bis(trimethylsilyl)-anilines with metal chlorides [6b]. Compared with other alternatives, such as amine deprotonation or amine/imido exchange reactions, the procedure is selective and particularly straightforward since the only by-product formed in the process is volatile SiMe₃Cl. These facts are essential because purification methods are far more limited for the synthesis of metallo-dendrimers than for simpler or smaller organometallic compounds, and they become impracticable for highly air-sensitive polymetallic dendritic species.

As previously reported the reaction of *m* equiv. of [NbCl₄Cp'] (Cp' = η⁵-C₅H₄SiMe₃) with polyanilines based on carbosilane dendrimers up to the third generation Gn-((C₆H₄)N(SiMe₃)₂)_m (*n* = 0, 1, 2, 3; *m* = 1, 4, 8, 16, respectively) readily afforded half-sandwich niobium imido dendrimers Gn-((C₆H₄)NNbCl₂Cp')_m (Scheme 1), which were found to be stable solids under an inert atmosphere [6b]. However, when [TaCl₄Cp*] is used as the organometallic precursor (Cp* = η⁵-C₅Me₅), only the monometallic **1** and the first generation dendrimer **2** have been successfully prepared (Scheme 1), probably due to an exceedingly

moisture sensitivity of polymetallic dendrimers in higher generations. In fact, complexes **1** and **2** had to be prepared in sealed tubes using strictly dry solvents, otherwise decomposition was apparent by formation of some white-yellowish precipitate. It is worth noting that compounds of general formula [TaCl₂Cp*(NAr)] containing sterically demanding aryl-imido ligands, like *ortho*-disubstituted aryl ring [9c], are fairly stable, whereas those with *para*-substituted or plain phenyl rings on the imido ligand are known to be rather moisture-sensitive [10b,12]. Relative to the formation of half-sandwich niobium-imido compounds, the reactions leading to **1** and **2** required more severe conditions, and in order to facilitate the formation of **2** by removal of SiMe₃Cl, vacuum was briefly applied several times over the course reaction (see Section 4). Both compounds are isolated as an orange solid, soluble in chlorinated and aromatic solvents, but not in saturated hydrocarbons.

Complexes **1** and **2** were characterized by ¹H, ¹³C NMR, and IR spectroscopies. The [TaCl₂(Cp*)(NC₆H₄-4)] moiety is observed in the ¹H NMR spectra as an intense singlet at *ca.* 2.2 ppm due to the cyclopentadienyl ring, and an AA'XX' splitting pattern at lower field for the *para*-substituted aryl ring. The carbosilane part gives rise to a singlet for **1** (–SiMe₃), or a singlet and three multiplets (–CH₂CH₂CH₂SiMe₂–) for **2**, all in normal regions. ¹³C{¹H} NMR data are consistent with their proposed structures, and in the case of compound **2** are also in agreement with the equivalence of the four metallic terminal groups. The IR absorption due to the terminal imido groups was observed at *ca.* 1320–1340 cm^{–1}.



Scheme 1.

A limited number of procedures for the synthesis of niobocene-imido complexes has been reported so far [13]. A straightforward method consists in the reaction of niobium-imido halide precursors with alkali or alkaline earth metal cyclopentadienides [14]. Thus, niobocene-imido compounds up to the second generation $G_n\text{-}\{(C_6H_4)NNbClCp'_2\}_m$ ($n = 0, 1, 2; m = 1, 4, 8; \mathbf{3}\text{--}\mathbf{5}$) were prepared by the reaction of $G_n\text{-}\{(C_6H_4)NNbCl_2Cp'\}_m$ with m equiv. of $LiCp'$ in toluene (Scheme 1, Fig. 1). Compounds $\mathbf{3}\text{--}\mathbf{5}$ were isolated as an orange to red solid, with yields around 50% after work up as well as recrystallization, and were found to be soluble in all common solvents including alkanes.

The niobium compounds $\mathbf{3}\text{--}\mathbf{5}$ are stable under inert atmosphere, but they quickly decompose in the presence of traces of water to give complex $\mathbf{6}$, an chloro(oxo)niobocene previously synthesized by means of the oxidation of $[NbClCp'_2(CO)]$ with O_2 [15a]. The moisture-sensitivity of complexes $\mathbf{3}\text{--}\mathbf{5}$ increases with the metallic load on the dendritic molecule ($\mathbf{5} > \mathbf{4} > \mathbf{3}$). Even though mono- and dimetallic chloro(arylimido)niobocene complexes closely related to $\mathbf{3}\text{--}\mathbf{5}$, have been reported to be air-stable as solid materials [16], the formation of an oxoniobocene by selective hydrolysis of aryylimido–Nb bond has been preceded [17]. Compound $\mathbf{6}$ can be quantitatively prepared by dissolution of complex $\mathbf{3}$ in wet dichloromethane (or $CDCl_3$) giving free amine $4\text{-Me}_3Si\text{-C}_6H_4\text{-NH}_2$ [6b] as single by-product (1H NMR evidence). Other procedures for the

synthesis of oxoniobocene compounds comprise the oxidation of dichloro complexes [18], or olefin-hydride or alkyl- and halo-carbonyl niobocenes in their reaction with O_2 [15], or the decarbonylation of coordinated carbon dioxide [19].

The $[NbCl(Cp')_2(NC_6H_4-4)]$ moiety is observed in the 1H NMR spectra of compounds $\mathbf{3}\text{--}\mathbf{5}$ as an ABCD spin system for the cyclopentadienyl rings (δ 5.5–6.5), together with an AA'XX' system for the aryl ring protons (δ 6.3–7.4), and an intense resonance at *ca.* 0.2 ppm for the Cp' substituent ($-\text{SiMe}_3$). When compared to the monocyclopentadienyl precursors, the presence of the second five-membered ring causes the lost of the symmetry plane that splits the Cp' ring, and as a result the four ring protons, as well the five carbons, of each Cp' group are now non-equivalent. Besides, the additional shielding introduced with the second ring makes the resonances for the *N-ortho* phenyl protons, and the average corresponding to the C_5H_4 protons to shift to higher field (0.4–0.5 ppm). Similarly, relevant shifts to higher field (up to 13 ppm) are noticeable in the $^{13}C\{^1H\}$ NMR data for the Cp' and phenyl ring carbons. On the contrary, the carbosilane framework is insignificantly affected by the formation of the niobocene complexes at their periphery, and therefore the general characteristics of their NMR spectra are almost identical to those described for the dendritic monocyclopentadienyl precursors [6b]. Thus, a singlet ($\mathbf{3}$) for the SiMe_3 group or three sets of signals attributed to the methylene groups ($\mathbf{4}$

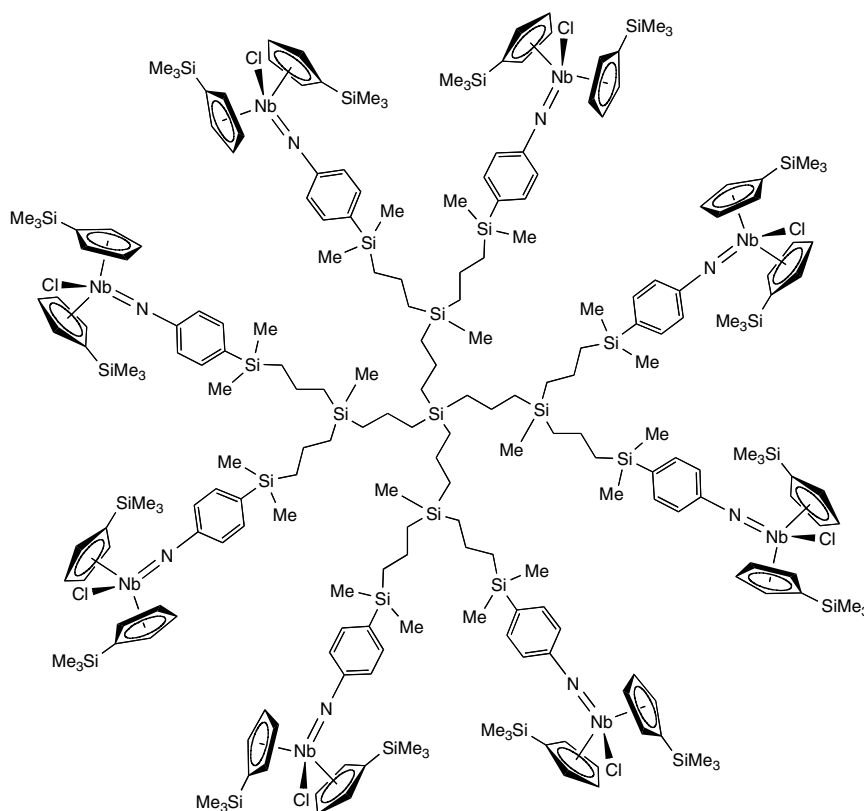


Fig. 1. (Imido)niobocene dendrimer $\mathbf{5}$.

and **5**) have been observed with the expected integration ratio. For the SiCH₂CH₂CH₂Si branches, the middle methylenes are located at *ca.* 1.25 ppm, and those directly bonded to silicon atoms are centered at *ca.* 0.45 ppm, except the outermost ones (CH₂SiMe₂Ph) that appear at *ca.* 0.75 ppm. Methylene carbon resonances are situated within the range 18–21 ppm. External SiMe₂ protons/carbons are located at about 0.17/–3.0 ppm and the internal SiMe groups in dendrimer **5** at –0.14/–5.0 ppm.

2.2. Structure of [NbCl(O)Cp'₂] (**6**)

Spectroscopic characterization of compound **6** has been reported elsewhere [15a]. Fig. 2 shows an ORTEP representation of the molecular structure found in the solid state by single crystal X-ray diffraction studies for compound **6**, while relevant bond lengths and angles are tabulated in Table 1. The crystal structure of **6** consists of a discrete molecule in a typical bent metallocene arrangement, where the niobium atom shows a pseudo-tetrahedral geometry, and binds to two Cp' rings, an oxygen atom and a chloro ligand.

Comparison with the structural information found in other oxoniobocene complexes [17,20,21], reveals the Cl–Nb–O (94.71(18)°) and Cp'–Nb–Cp' (126.31°) angles in **6** to be at the lower limits (95.6–99.7° and 126.5–131.0°,

respectively), whilst the Nb=O (1.816(5) Å) and Nb–Cl (2.418(2) Å) bond distances are somewhat longer and at the lower limits, respectively, than those previously reported (1.63–1.74 and 2.43–2.45 Å, respectively). For instance, in the closely related methyl-oxo compound [NbMe(O)(C₅H₄SiMe₃)₂] [15a], the Nb=O bond distance is 1.720(7) Å. The π donor capability of the chloro ligand in **6** must, in turn, weaken the π-bonding interaction with the oxo ligand elongating the Nb–O distance. The most distinctive feature in the structure of compound **6** is the *anti* positioning of the two C₅H₄SiMe₃ rings, therefore, making the niobium atom to be a stereogenic center in the solid state. In fact, the two *rac*-enantiomers are present in the unit cell (only one is depicted in Fig. 2). Compounds such as [NbCl(O)(C₅H₄Bu^t)(C₅H₄Me)] and [NbCl(O)(C₅H₄Prⁱ)₂] [21], [NbMe(O)(C₅H₄SiMe₃)₂] [15a], or [NbY(O)(C₅H₄Me)₂] (Y = Cl, CH₂SiMe₃) [19], all show crystal structures with a *syn*-conformation of the monosubstituted cyclopentadienyl ligands, where the rings are eclipsed or staggered and their substituents are on the side of the oxygen atom probably due to the presence of O···H-bonding type interactions. The different arrangement in **6** compare to the methyl-oxo analogous [15a], must be caused by weak stabilizing interactions in its crystal packing.

3. Conclusion

In summary, the synthetic strategy accounted in our previous report to synthesized (imido)niobium(V) carbosilane dendrimers, has been now extended to the preparation of related tantalum(V) compounds, as well as peripheral (arylimido)niobocene dendrimers. While half-sandwich compounds *Gn*-{(C₆H₄)NNbCl₂Cp'}_m described earlier were found to be easy-to-handle air-sensitive materials, the tantalum or biscyclopentadienyl derivatives of this work are remarkably moisture sensitive. Therefore, these studies demonstrate the efficiency of the procedures used for the synthesis of group 5 metal-imido dendrimers, without other limitation than the own stability of the final products. Thus, the hydrolysis of metal-imido bonds has prevented the preparation of higher generation metallodendrimers. In the case of the niobium compounds the hydrolytic reaction leads selectively to a structurally characterized chloro(oxo)niobocene compound.

4. Experimental

4.1. Reagents and general techniques

All operations were performed under an argon atmosphere using Schlenk or dry-box techniques. Unless otherwise stated, reagents were obtained from commercial sources and used as received. LiCp' (Cp' = η⁵-C₅H₄SiMe₃) [22], [TaCl₄Cp*] (Cp* = η⁵-C₅Me₅) [23], silylated anilines *Gn*-{(C₆H₄)N(SiMe₃)₂}_m, and niobium derivatives *Gn*-{(C₆H₄)NNbCl₂Cp'}_m (*n* = 0, 1, 2; *m* = 1, 4, 8, respectively) [6b] were prepared according to the literature procedures.

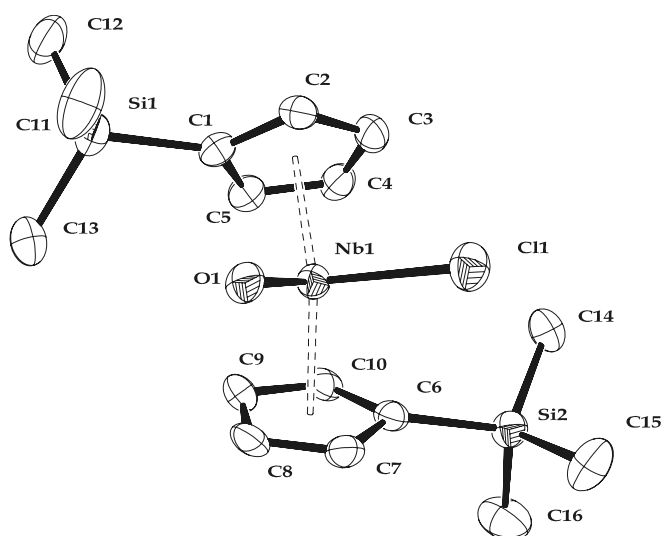


Fig. 2. ORTEP diagram of compound **6** with the atomic numbering scheme.

Table 1
Selected bond lengths [Å], and angles [°] for compound **6**^a

Nb(1)–O(1)	1.816(5)	Cp(1)–Nb(1)–Cp(2)	126.31
Nb(1)–Cl(1)	2.418(2)	O(1)–Nb(1)–Cp(1)	110.98
Nb(1)–Cp(1)	2.186	O(2)–Nb(1)–Cp(2)	109.00
Nb(1)–Cp(2)	2.186	Cl(1)–Nb(1)–Cp(1)	104.87
Nb(1)–C(Cp(1)) ^b	2.491(7)	Cl(1)–Nb(1)–Cp(2)	105.98
Nb(1)–C(Cp(2)) ^b	2.491(7)	Cl(1)–Nb(1)–O(1)	94.71(18)

^a Cp(1) and Cp(2) denote the cyclopentadienyl-centroid of C1–C5 and C6–C10 rings, respectively.

^b Average value.

Solvents were previously dried and distilled under argon as described elsewhere [24]. NMR spectra were recorded on Varian Unity 500+, Varian Unity VR-300 or Varian Unity 200 NMR spectrometers. Chemical shifts (δ) are reported in ppm referenced to SiMe₄ for ¹H and ¹³C. ¹H NMR integrated values for dendritic compounds are given relative to one of the four arms of the molecule. Elemental analyses were performed by Microanalytical Laboratories of the University of Alcalá on a Heraeus CHN-O-Rapid and Perkin–Elmer 2400 Series II C, H, N, S/O microanalyzers.

4.2. Preparation of G0- $\{(C_6H_4)NTaCl_2Cp^*\}$, dichloro(η^5 -pentamethylcyclopentadienyl)(4-trimethylsilylphenylimido)-tantalum(V) (1)

A solution of 4-trimethylsilyl-*N,N*-bis(trimethylsilyl)aniline (0.83 g, 2.68 mmol) in dichloromethane (30 mL), together with another solution of [TaCl₄Cp*] (1.22 g, 2.68 mmol) in toluene (30 mL) were introduced in an ampoule tube equipped with a PTFE valve. The tube was sealed and the mixture warmed up to 75 °C during 48 h. The resulting orange solution was filtered to a Schlenk tube, the solvent was removed *in vacuo* and the residue washed with pentane to give **1** as an orange solid (1.30 g, 88%). Anal. Calcd. for C₁₉H₂₈NSiCl₂Ta (550.38): C, 41.46; H, 5.13; N, 2.55. Found: C, 41.20; H, 5.27; N, 2.33%. ¹H NMR (CDCl₃): δ 0.21 (s, 9H, Si Me₃), 2.19 (s, 15H, C₅ Me₅), 6.73 (m, AA' part of an AA'XX' spin system, 2H, C₆H₄), 7.35 (m, XX' part of an AA'XX' spin system, 2H, C₆H₄). ¹³C{¹H} NMR (CDCl₃): δ -0.8 (Si Me₃), 11.6 (C₅ Me₅), 121.8 (C₅Me₅), 125.2 (C₆H₄), 132.9 (C₆H₄), 135.5 (*ipso* Si-C₆H₄), 154.4 (*ipso* N-C₆H₄). IR (KBr): ν 1321 cm⁻¹ (s, TaN), 1032 cm⁻¹ (s, Cp*).

4.3. Preparation of G1- $\{(C_6H_4)NTaCl_2Cp^*\}_4$ (2)

Using a dry-box, a solution of [TaCl₄Cp*] (0.86 g, 1.88 mmol) and G1- $\{(C_6H_4)N(SiMe_3)_2\}_4$ (0.65 g, 0.47 mmol) in a dichloromethane/toluene solvent mixture (1:1, 60 mL) was poured and sealed into an ampoule-tube like that described above. Again warming was kept 48 h, and now vacuum was periodically applied briefly through the PTFE valve. After filtration of the solution and removal of the volatiles, the resulting residue was washed in portions with pentane to give an orange solid characterized as compound **2** (0.70 g, 64%). Anal. Calcd. for C₈₄H₁₂₆N₄Si₅Cl₈Ta₄ (2339.79): C, 43.12; H, 5.43; N, 2.39. Found: C, 41.93; H, 5.35; N, 1.96%. ¹H NMR (CDCl₃): δ 0.18 (s, 6H, Si Me₂), 0.48 (m, 2H, SiCH₂), 0.74 (m, 2H, CH₂SiMe₂), 1.30 (m, 2H, CH₂CH₂CH₂), 2.18 (s, 15H, C₅ Me₅), 6.70 (m, AA' part of an AA'XX' spin system, 2H, C₆H₄), 7.34 (m, XX' part of an AA'XX' spin system, 2H, C₆H₄). ¹³C{¹H} NMR (CDCl₃): δ -2.7 (Si Me₃), 11.6 (C₅ Me₅), 17.4 (CH₂), 18.6 (CH₂), 20.9 (CH₂), 121.7 (C₅Me₅), 125.1 (C₆H₄), 133.1 (C₆H₄), 134.8 (*ipso* Si-C₆H₄), 154.3 (*ipso* N-C₆H₄). IR (KBr): ν 1341 cm⁻¹ (s, TaN), 1030 cm⁻¹ (s, Cp*).

4.4. Preparation of G0- $\{(C_6H_4)NNbCp'_2Cl\}$, chloro(*bis*- η^5 -trimethylsilylcyclopentadienyl)(4-trimethylsilylphenylimido)-niobium(V) (3)

Solid compounds [(4-Me₃Si-C₆H₄)NNbCl₂Cp'] (0.50 g, 1.07 mmol) and LiCp' (158 mg, 1.09 mmol) were weighed and introduced into a Schlenk tube, toluene (35 mL) was added and the mixture stirred 18 h at room temperature. Then the solvent was removed *in vacuo* and the residue extracted with pentane (2 × 15 mL). After elimination of the solvent, complex **3** is obtained as an orange solid that could be recrystallized from pentane solutions (0.32 g, 53%). Anal. Calcd. for C₂₅H₃₉NSi₃ClNb (566.21): C, 53.03; H, 6.94; N, 2.47. Found: C, 52.76; H, 7.19; N, 2.22%. ¹H NMR (CDCl₃): δ 0.22 (s, 9H, Ph-Si Me₃), 0.27 (s, 18H, Cp-Si Me₃), 5.52 (m, ABCD spin system, 2H, C₅H₄), 5.99 (m, ABCD spin system, 2H, C₅H₄), 6.25 (m, ABCD spin system, 2H, C₅H₄), 6.38 (m, ABCD spin system, 2H, C₅H₄), 6.58 (m, AA' part of an AA'XX' spin system, 2H, C₆H₄), 7.43 (m, XX' part of an AA'XX' spin system, 2H, C₆H₄). ¹³C{¹H} NMR (CDCl₃): δ -0.9 (Ph-Si Me₃), 0.1 (Cp-Si Me₃), 111.2 (C₅H₄), 110.5 (C₆H₄), 116.9 (C₅H₄), 119.2 (*ipso* C₅H₄), 120.9 (C₆H₄), 126.3 (C₅H₄), 133.2 (C₅H₄, and *ipso* Si-C₆H₄ overlapping), 159.9 (*ipso* N-C₆H₄). IR (KBr): ν 1329 cm⁻¹ (NbN).

4.5. Preparation of G1- $\{(C_6H_4)NNbClCp'_2\}_4$ (4)

Solid LiCp' (144 mg, 1.00 mmol) and G1- $\{(C_6H_4)N-NbCl_2Cp'\}_4$ (0.50 g, 0.25 mmol) were placed into a Schlenk tube together with toluene as a solvent (25 mL). The reddish solution was stirred over a 48 h period, observing the formation of white precipitate. The LiCl by-product was eliminated by filtration, and the solvent under reduced pressure, affording compound **4** as a red solid. The niobodendrimer was recrystallized from toluene solutions by cooling at -20 °C during several days (0.30 g, 50%). Anal. Calcd. for C₁₀₈H₁₆₈N₄Si₁₃Cl₄Nb₄ (2401.10): C, 54.02; H, 7.05; N, 2.33. Found: C, 54.42; H, 6.91; N, 2.70%. ¹H NMR (CDCl₃): δ 0.17 (s, 6H, Si Me₂), 0.19 (s, 18H, Cp-Si Me₃), 0.42 (m, 2H, SiCH₂), 0.75 (m, 2H, CH₂SiMe₂), 1.24 (m, 2H, CH₂CH₂CH₂), 6.00 (m, ABCD spin system, 2H, C₅H₄), 6.34 (m, AA' part of an AA'XX' spin system, 2H, C₆H₄), 6.39 (m, ABCD spin system, 2H, C₅H₄), 6.44 (m, ABCD spin system, 2H, C₅H₄), 6.47 (m, ABCD spin system, 2H, C₅H₄), 7.24 (m, XX' part of an AA'XX' spin system, 2H, C₆H₄). ¹³C{¹H} NMR (CDCl₃): δ -2.7 (Si Me₂), 0.0 (Si Me₃), 17.8 (CH₂), 18.5 (CH₂), 20.9 (CH₂), 110.4 (C₆H₄), 111.2 (C₅H₄), 116.9 (C₅H₄), 119.1 (*ipso* C₅H₄), 120.7 (C₆H₄), 126.3 (C₅H₄), 133.3 (C₅H₄), 133.6 (*ipso* Si-C₆H₄), 159.8 (*ipso* N-C₆H₄).

4.6. Preparation of G2- $\{(C_6H_4)NNbCp'_2Cl\}_8$ (5)

Dendritic compound **5** was synthesized as described above for **4** starting from G2- $\{(C_6H_4)NNbCl_2Cp'\}_8$ (0.55 g, 0.13 mmol) and LiCp' (150 mg, 1.04 mmol) in

toluene (25 mL). Compound **5** was isolated as a oily red solid that solidified by repeating freezing/vacuum operations, and was recrystallized from cold toluene (0.33 g, 50%). Anal. Calcd. for $C_{232}H_{372}N_8Si_{29}Cl_8Nb_8$ (5114.91): C, 54.47; H, 7.33; N, 2.19. Found: C, 54.40; H, 7.94; N, 2.35%. 1H NMR ($CDCl_3$): δ -0.14 (s, 3H, Si *Me*), 0.17 (s, 12H, Si *Me*₂), 0.19 (s, 36H, Cp-Si *Me*₃), 0.51 (m, 8H, SiCH₂), 0.76 (m, 4H, CH₂SiMe₂), 1.30 (m, 6H, CH₂CH₂CH₂), 6.00 (m, ABCD spin system, 4H, C₅H₄), 6.34 (m, AA' part of an AA'XX' spin system, 4H, C₆H₄), 6.39 (m, ABCD spin system, 4H, C₅H₄), 6.44 (m, ABCD spin system, 4H, C₅H₄), 6.47 (m, ABCD spin system, 4H, C₅H₄), 7.24 (m, XX' part of an AA'XX' spin system, 4H, C₆H₄). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ -5.4 (Si *Me*), -3.1 (Si *Me*₂), 0.4 (Si *Me*₃), 18.1 (CH₂), 18.3 (CH₂), 20.2 (CH₂), 20.3 (CH₂), 110.1 (C₆H₄), 110.8 (C₅H₄), 116.5 (C₅H₄), 118.7 (*ipso* C₅H₄), 120.3 (C₆H₄), 125.9 (C₅H₄), 132.9 (C₅H₄), 134.3 (*ipso* Si-C₆H₄), 159.4 (*ipso* N-C₆H₄).

4.7. Preparation of $[NbCl(O)Cp_2']$, chloro(oxo)(bis- η^5 -trimethylsilyl-cyclopentadienyl)niobium(V) (**6**)

This compound was prepared by treatment of imido complex **3** (0.20 g, 0.35 mmol) with wet dichloromethane (10 μ L/100 mL) over night. After evaporation of the solvent and washing with pentane (10 mL), complex **6** is isolated as yellow-orange microcrystalline solid in quantitative yield (147 mg). Anal. Calcd. for $C_{16}H_{26}Si_2ClONb$ (418.91): C, 45.87; H, 6.26. Found: C, 45.70; H, 6.45%. 1H NMR ($CDCl_3$): δ 0.26 (s, 18H, Cp-Si *Me*₃), 6.14 (m, ABCD spin system, 2H, C₅H₄), 6.38 (m, ABCD spin system, 2H, C₅H₄), 6.50 (m, ABCD spin system, 2H, C₅H₄), 6.59 (m, ABCD spin system, 2H, C₅H₄). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 0.2 (Cp-Si *Me*₃), 115.1 (C₅H₄), 115.7 (C₅H₄), 120.3 (C₅H₄), 125.2 (*ipso* C₅H₄), 126.9 (C₅H₄). IR (KBr): ν 920 cm^{-1} (NbO).

4.8. X-ray crystallographic studies

Suitable monocrystals of **6** were obtained by slow diffusion of a pentane layer into a dichloromethane solution of the niobium complex at room temperature. A summary of crystal data, data collection, and refinement parameters for the structural analysis is given in Table 2.

An orange suitable sized crystal were sealed under argon in a Lindemann capillary tube and mounted in an Enraf Nonius CAD 4 automatic four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Intensities were collected at room temperature and were corrected for Lorenz and polarization effects in the usual manner. No extinction or absorption correction were made. Structure was solved by direct methods, completed by the subsequent difference Fourier techniques and refined by full-matrix least squares on F^2 (SHELXL-97) [25]. Anisotropic thermal parameters were used in the last cycles of refinement for the non hydrogen atoms. The hydrogen atoms were included from geometrical calcula-

Table 2

Crystal data and structure refinement for compound **6**

Empirical formula	$C_{16}H_{26}ClONbSi_2$
Formula weight	418.91
Color	Orange
Temperature (K)	293.0(2)
Wavelength (Å)	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	
<i>a</i> (Å)	6.550(5)
<i>b</i> (Å)	12.955(5)
<i>c</i> (Å)	13.315(5)
α (°)	64.281(5)
β (°)	83.774(5)
γ (°)	76.888(5)
Volume (Å ³)	991.3(9)
Z, Calculated density (g/cm ³)	2, 1.403
Absorption coefficient (mm ⁻¹)	0.860
<i>F</i> (000)	432
Crystal size (mm)	0.22 × 0.20 × 0.18
θ Ranges (°)	1.70–22.97
Limiting indices	$-7 \leq h \leq 7$, $-14 \leq k \leq 0$, $-14 \leq l \leq 13$
Reflections collected/unique [<i>R</i> (int)]	2967/2753 [0.0312]
Reflections observed	1960 [$I > 2\sigma(I)$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2753/0/190
Goodness-of-fit on F^2	1.044
Final R^a indices [$I > 2\sigma(I)$]	$R_1 = 0.0501$, $wR_2 = 0.1119$
<i>R</i> indices (all data)	$R_1 = 0.0993$, $wR_2 = 0.1278$
Largest difference in peak and hole ($e/\text{Å}^3$)	1.130 and -0.377

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = \{[\sum \omega(F_o^2 - F_c^2)] / [\sum \omega(F_o^2)]\}^{1/2}.$$

tions and refined using a riding model. All the calculations were made using the WINGX system [26].

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Appendix A. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 602652 for compound **6**. Copies of this information can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: (int. code) +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk; or www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.009.

References

- [1] (a) For example see: C. Gorman, Adv. Mater. 10 (1998) 295; (b) G.R. Newkome, E. He, C.N. Moorefield, Chem. Rev. 99 (1999) 1689; (c) I. Cuadrado, M. Morán, C.M. Casado, B. Alonso, J. Losada, Coord. Chem. Rev. 193–195 (1999) 395;

- (d) F.J. Stoddart, T. Welton, *Polyhedron* 18 (1999) 3575;
(e) M.A. Hearshaw, J.R. Moss, *Chem. Commun.* (1999) 1;
(f) H.-J. van Manen, F.C.J.M. van Veggel, D.N. Reinhoudt, *Top. Curr. Chem.* 217 (2001) 121;
(g) K. Onitsuka, S. Takahashi, *Top. Curr. Chem.* 228 (2003) 39;
(h) P.A. Chase, R.J.M.K. Gebbink, G. van Koten, *J. Organomet. Chem.* 689 (2004) 4016.
- [2] (a) G.E. Oosterom, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, *Angew. Chem., Int. Ed.* 40 (2001) 1828;
(b) D. Astruc, F. Chardac, *Chem. Rev.* 101 (2001) 2991;
(c) R. Kreiter, A.W. Kleij, R.J.M.K. Gebbink, G. van Koten, *Top. Curr. Chem.* 217 (2001) 163;
(d) R. van Heerbeek, P.C.J. Kamer, P.W.N.M. van Leeuwen, J.N.H. Reek, *Chem. Rev.* 102 (2002) 3717;
(e) G.S. Smith, R. Chen, S.F. Mapolie, *J. Organomet. Chem.* 673 (2003) 111;
(f) Z.-J. Zheng, J. Chen, Y.-S. Li, *J. Organomet. Chem.* 689 (2004) 3040;
(g) C. Müller, L.J. Ackerman, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, *J. Am. Chem. Soc.* 126 (2004) 14960;
(h) M.J. Overett, R. Meijboom, J.R. Moss, *Dalton Trans.* (2005) 551.
- [3] (a) D. Seyferth, R. Wryrwa, U.W. Franz, S. Becke, *PCT Int. Appl. WO 97/32908*, 1997; *Chem Abstr.* 127 (1997) 263179;
(b) K. Brüning, H. Lang, *J. Organomet. Chem.* 575 (1999) 153;
(c) V. Cadierno, A. Igau, B. Donnadiu, A.M. Caminade, J.P. Majoral, *Organometallics* 18 (1999) 1580;
(d) D. Seebach, R.E. Marti, T. Hintermann, *Helv. Chim. Acta* 79 (1996) 1710;
(e) P.B. Rheiner, H. Sellner, D. Seebach, *Helv. Chim. Acta* 80 (1997) 2027;
(f) H. Sellner, D. Seebach, *Angew. Chem., Int. Ed.* 38 (1999) 1918;
(g) P.B. Rheiner, D. Seebach, *Chem. Eur. J.* 5 (1999) 3221.
- [4] (a) R. Andrés, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, *Eur. J. Inorg. Chem.* (2002) 2281;
(b) R. Andrés, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, *J. Organomet. Chem.* 690 (2005) 939;
(c) V. Amo, R. Andrés, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, P. Gómez-Sal, J.F.C. Turner, *Organometallics* 24 (2005) 2331;
(d) R. Andrés, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, *Eur. J. Inorg. Chem.* (2005) 3742.
- [5] (a) S. Arévalo, J.M. Benito, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, *J. Organomet. Chem.* 602 (2000) 208;
(b) S. Arévalo, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, *Organometallics* 20 (2001) 2583;
(c) S. Arévalo, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, P. Gómez-Sal, P. Ortega, S. Vigo, *Organometallics* 22 (2003) 5109;
(d) K.T. Welch, S. Arévalo, J.F.C. Turner, R. Gómez, *Chem. Eur. J.* 11 (2005) 1217.
- [6] (a) J.M. Benito, S. Arévalo, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, *J. Organomet. Chem.* 610 (2000) 42;
(b) J.M. Benito, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, P. Gómez-Sal, *J. Organomet. Chem.* 664 (2002) 258.
- [7] (a) A. Sánchez-Méndez, G.F. Silvestri, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, P. Gómez-Sal, *Eur. J. Inorg. Chem.* (2004) 3287;
(b) A. Sánchez-Méndez, J.M. Benito, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, P. Gómez-Sal, *Dalton Trans.* (submitted for publication).
- [8] (a) J.M. Benito, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, *Chem. Commun.* (2005) 5217;
(b) J.M. Benito, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, P. Gómez-Sal, *Organometallics* (in press);
(c) J.M. Benito, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, *Organometallics* 25 (2006) 3045.
- [9] (a) W.A. Nugent, B.L. Haymore, *Coord. Chem. Rev.* 31 (1980) 123;
(b) V.C. Gibson, D.N. Williams, W. Clegg, C.R. Hockless, *Polyhedron* 8 (1989) 1819;
(c) D.N. Williams, J.P. Mitchell, A.D. Poole, U. Siemeling, W. Clegg, D.C.R. Hockless, P.A. O'Neil, V.C. Gibson, *J. Chem. Soc., Dalton Trans.* (1992) 739;
(d) D.E. Wigley, *Prog. Inorg. Chem.* 42 (1994) 239;
(e) T.I. Gountchev, T.D. Tilley, *J. Am. Chem. Soc.* 119 (1997) 12831.
- [10] (a) I. Dorado, A. Garcés, C. López-Mardomingo, M. Fajardo, A. Rodríguez, A. Antiñolo, A. Otero, *J. Chem. Soc., Dalton Trans.* (2000) 2375;
(b) A. Antiñolo, I. Dorado, M. Fajardo, A. Garcés, I. López-Solera, C. López-Mardomingo, M.M. Kubicki, A. Otero, S. Prashar, *Eur. J. Inorg. Chem.* (2004) 1299;
(c) A. Antiñolo, I. Dorado, M. Fajardo, A. Garcés, M.M. Kubicki, C. López-Mardomingo, A. Otero, S. Prashar, *J. Organomet. Chem.* 691 (2006) 1361.
- [11] (a) R.R. Schrock, *Acc. Chem. Res.* 23 (1990) 158;
(b) R. Torecki, R.R. Schrock, *J. Am. Chem. Soc.* 112 (1990) 2448;
(c) O. Fujimura, F.J. de la Mata, R.H. Grubbs, *Organometallics* 15 (1996) 1865.
- [12] M. Gómez, P. Gómez-Sal, M.P. Nicolás, P. Royo, *J. Organomet. Chem.* 491 (1995) 121.
- [13] A. Antiñolo, M. Fajardo, A. Otero, S. Prashar, *Eur. J. Inorg. Chem.* (2003) 17.
- [14] (a) M.L.H. Green, J.T. James, A.N. Chernega, *J. Chem. Soc., Dalton Trans.* (1997) 1719;
(b) A. Antiñolo, M. Fajardo, C. Huertas, A. Otero, S. Prashar, A.M. Rodríguez, *J. Organomet. Chem.* 585 (1999) 154;
(c) M.J. Humphries, R.E. Douthwaite, M.L.H. Green, L.H. Rees, *J. Chem. Soc., Dalton Trans.* (2000) 4555.
- [15] (a) A. Antiñolo, J. Martínez de Iarduya, A. Otero, P. Royo, A.M.M. Lanfredi, A. Tiripicchio, *J. Chem. Soc., Dalton Trans.* (1988) 2685;
(b) A. Antiñolo, I. del Hierro, I. López-Solera, S. García-Yuste, A. Otero, M. Fajardo, A. Rodríguez, *J. Organomet. Chem.* 598 (2000) 167.
- [16] A. Antiñolo, F. Carrillo-Hermosilla, A. Otero, M. Fajardo, A. Garcés, P. Gómez-Sal, C. López-Mardomingo, A. Martín, C. Miranda, *J. Chem. Soc., Dalton Trans.* (1998) 59.
- [17] A. Antiñolo, I. López-Solera, A. Otero, S. Prashar, *J. Organomet. Chem.* 631 (2001) 151.
- [18] R. Broussier, J.D. Oliver, B. Gautheron, *J. Organomet. Chem.* 251 (1983) 307.
- [19] (a) P.-f. Fu, M.A. Khan, K.M. Nicholas, *Organometallics* 11 (1992) 2607;
(b) P.-f. Fu, M.A. Khan, K.M. Nicholas, *J. Organomet. Chem.* 506 (1996) 49.
- [20] H. Brunner, J.-C. Leblanc, D. Lucas, W. Meier, C. Moise, Y. Mugnier, B. Nuber, S. Rigny, A. Sadorge, J. Wachter, *J. Organomet. Chem.* 566 (1998) 203.
- [21] E. Kolehmainen, K. Laihia, M. Nissinen, J. Linnanto, A. Perjéssy, B. Gaytheron, R. Broussier, *J. Organomet. Chem.* 613 (2000) 7.
- [22] P. Jutzi, R. Saver, *J. Organomet. Chem.* 50 (1973) C29.
- [23] (a) W.A. Herrmann, W. Kalcher, H. Bierseck, J. Bernal, M. Creswick, *Chem. Ber.* 114 (1981) 3558;
(b) R.D. Sanner, S.T. Carter, W.J. Bruton, *J. Organomet. Chem.* 240 (1982) 157.
- [24] D.P. Perrin, W.L.F. Armarego, third ed. *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1988.
- [25] G.M. Sheldrick, *SHELXL_97*. Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
- [26] L.J. Farrugia, *WinGX System, J. Appl. Cryst.* 32 (1999) 837.