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Arylimido niobium(V) complexes: mononuclear and dendritic derivatives

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Abstract

The compound 4-LiC$_6$H$_4$N(SiMe$_3$)$_2$ reacted in tetrahydrofuran with SiMe$_3$Cl or with silicon-chloride groups located at the periphery of carbosilane dendrimers of first, second, and third generation to afford 4-SiMe$_3$C$_6$H$_4$N(SiMe$_3$)$_2$ (**3**) and functionalized dendrimers Si(CH$_2$CH$_2$CH$_2$SiMe$_2$C$_6$H$_4$N(SiMe$_3$)$_2$)$_4$ (**6**), Si(CH$_2$CH$_2$CH$_2$SiMe(CH$_2$CH$_2$CH$_2$SiMe$_2$C$_6$H$_4$N(SiMe$_3$)$_2$)$_2$)$_4$ (**7**), and Si(CH$_2$CH$_2$CH$_2$SiMe(CH$_2$CH$_2$CH$_2$SiMe(CH$_2$CH$_2$CH$_2$SiMe$_2$C$_6$H$_4$N(SiMe$_3$)$_2$)$_2$)$_2$)$_4$ (**8**). The *N,N*-bis(trimethylsilyl)aniline groups of **3** reacted with niobium pentachloride in acetonitrile or [NbCp′Cl$_4$] (Cp′ = η^5-C$_5$H$_4$SiMe$_3$) in dichloromethane to give imido mononuclear complexes [Nb(NC$_6$H$_4$SiMe$_3$-4)Cl$_3$(CH$_3$CN)$_2$] (**4**) and [NbCp′(NC$_6$H$_4$SiMe$_3$-4)Cl$_2$] (**5**), respectively. Reaction of dendrimers **6**–**8** and [NbCp′Cl$_4$] in CH$_2$Cl$_2$ afforded metallodendrimers [Si(CH$_2$CH$_2$CH$_2$SiMe$_2$C$_6$H$_4$N=NbCp′Cl$_2$)$_4$] (**9**), [Si(CH$_2$CH$_2$CH$_2$SiMe(CH$_2$CH$_2$CH$_2$SiMe$_2$C$_6$H$_4$N=NbCp′Cl$_2$)$_2$)$_4$] (**10**), and [Si(CH$_2$CH$_2$CH$_2$SiMe(CH$_2$CH$_2$CH$_2$SiMe(CH$_2$CH$_2$CH$_2$SiMe$_2$C$_6$H$_4$N=NbCp′Cl$_2$)$_2$)$_2$)$_4$] (**11**), in which the metal moieties are linked to the carbosilane framework through imido–metal bonds. The structure of complexes **4** and **5** has been determined by X-ray diffraction methods.
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1. Introduction

An increasing number of reports have been published on the incorporation of transition metals at the core, branches, or periphery of dendrimers [1]. Applications of these macromolecular systems in catalysis are being widely studied [2]. However, little attention has been paid to dendrimers containing early-transition metals [3]. We have focused our research work on the synthesis of dendrimers containing Group 4 complexes at their periphery [4] or at their focal point [5]. Recently, we have suggested that carbosilane dendrimers functionalized with aniline groups might support early-transition metal complexes at their periphery through imido bonds

[6]. Imido ligands are exceptionally suited for the stabilization of high-valent metal complexes due to their strong π-donor abilities [7].

In our previous report [6], the formation of metal–imido bonds from metal halides was carried out on mononuclear models or small dendritic molecules by means of deprotonation of aniline end-groups [7] or cleavage of nitrogen–silicon bonds in their *N,N*-bis(trimethylsilyl) derivatives [8]. The *ortho*- or *para*-carbon atoms of the aniline group were linked up with a dendritic silicon atom through an oxo bridge. This fact limited the scope of the reported procedures because of side-reactions between the Si–O bonds and the oxophilic early-transition metals. Here, we present the synthesis of new niobium(V) imido dendrimers obtained by reaction of metal chlorides with the *N,N*-bis(trimethylsilyl)aniline end-groups of oxygen-free dendrimers. Synthetic and structural studies on mononuclear models are in addition presented.

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2. Results and discussion

2.1. Synthesis and characterization of mononuclear complexes

Preparative details and spectroscopic data for all the new compounds are given in Section 4. Only selected data will be presented for discussion. Nitrogen-silylation in haloanilines is a typical reaction for the protection of amino groups [9]. For the preparation of 4-iodo-N,N-bis(trimethylsilyl)aniline (**2**, Scheme 1), we have followed a stepwise route in which the monosilylated compound **1** is synthesized as an intermediate. The preparation of **1** has been carried out in a decagram scale by the addition of SiMe$_3$Cl to 4-iodoaniline followed by dehydrohalogenation of the resulting ammonium salt with triethylamine [10]. In our hands, the alternative method [11], in which the aniline is deprotonated with one equivalent of n-BuLi and the amide anion reacted with SiMe$_3$Cl, was reliable for the preparation of **1** in only a small scale. Slow addition of one equivalent of n-BuLi to **1** in hexane at -78 °C gives a white solid that reacts with SiMe$_3$Cl in tetrahydrofuran (THF) at -78 °C to afford **2** in high yield (Scheme 1). In these conditions, only silylation at the amino group has been observed, although the selectivity of this route is highly sensitive to the experimental conditions. Thus, when the addition of n-BuLi was carried out in hexane at room temperature or in THF at -78 °C, **2** was isolated with different amounts of impurities mainly due to concurrent partial metallation at the iodo position. Further reaction of **2** with one equivalent of n-BuLi, now in pentane and at room temperature, lead to the formation of 4-LiC$_6$H$_4$N(SiMe$_3$)$_2$ as a white precipitate, which can be isolated in ca. 80% yield and stored in a dry-box or directly reacted with SiMe$_3$Cl in THF -78 °C to give the trisilylated compound **3** in quantitative yield [9].

Compounds **1**–**3** are liquids at room temperature and have been found to undergo hydrolysis of their nitrogen–silicon bonds upon exposure to air. Their ^{1}H-NMR spectra show downfield resonances for the aromatic ring protons (AA′BB′ spin systems), and a broad singlet for the N–H group in **1** (δ 3.47). The SiMe$_3$ groups give one (for **1** and **2**) or two (for **3**) singlets in [1]H-, ^{13}C{^{1}H}-, and ^{29}Si{^{1}H}-NMR. The ^{13}C chemical shift for the *ipso*-carbon in 4-position gives a spectroscopic handle to determine whether or not the iodo substitution occurred. After silylation, this resonance is shifted from higher (δ 78.3 for **1** and 87.6 for **2**) to much lower fields (δ 134.5 for **3**).

As discussed above, N,N-bis(trimethylsilyl)-substituted anilines are suitable starting materials for the synthesis of metal imido complexes from metal chlorides. In our experience, this procedure, which only produces volatile SiMe$_3$Cl by-product, is in general quantitative and cleaner than other alternatives employed for the formation of metal–imido bonds (e.g. deprotonation or exchange reactions). Purification methods are far more limited in dendrimers than in other areas of chemistry, making selectivity an essential question. Previously to the use of dendrimers, we have prepared related mononuclear complexes to prove selectivity and to determine optimal reaction conditions. Aniline **3** reacts smoothly with NbCl$_5$ in acetonitrile or with [NbCp′Cl$_4$] (Cp′ = η^5-C$_5$H$_4$SiMe$_3$) in dichloromethane affording imido complexes **4** and **5**, respectively (Scheme 1). Both reactions were quantitative (^{1}H-NMR evidence) although the final yield on **5** was reduced to 90% after recrystallization from pentane. ^{1}H- and ^{13}C-NMR data show the presence of two equivalent CH$_3$CN ligands in **4** at room temperature. This behavior contrasts with the solid-state structure determined by X-ray (see below) in which one of the ligands is coordinated *trans* to a chloride atom and the other to the imido fragment. Therefore, it should be assumed the
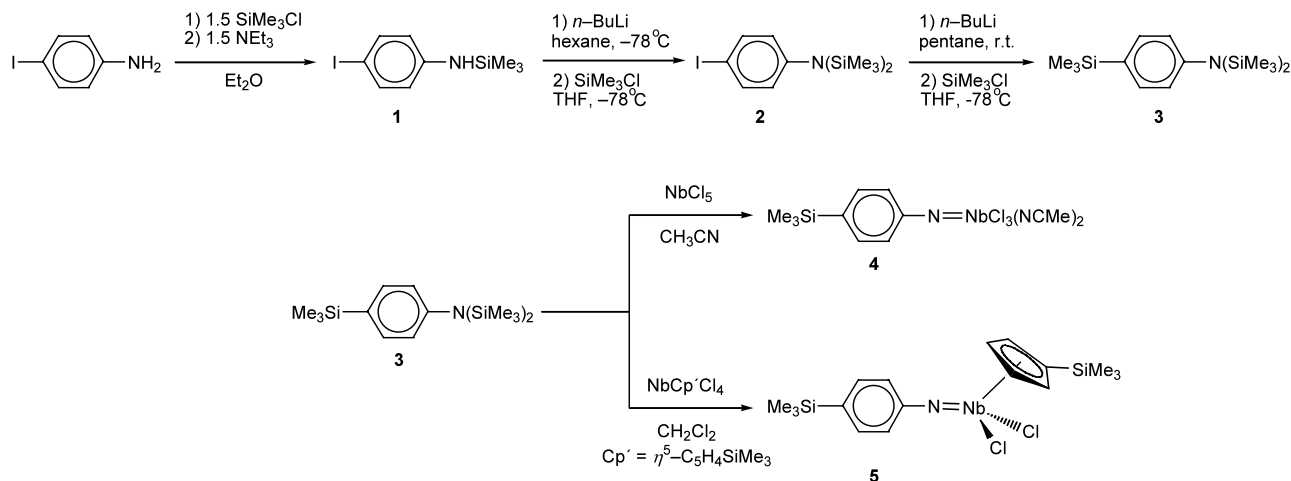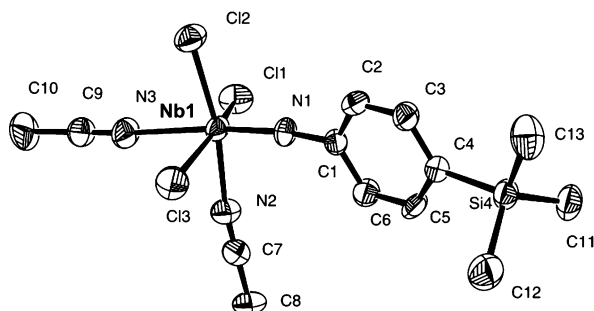

Scheme 1.

Fig. 1. View of the molecular structure of **4** with the atom-numbering scheme.

existence of either an isomerization or a rapid dynamical behavior of **4** in solution. The second interpretation has been confirmed by low-temperature ^{1}H-NMR spectra in which two resonances are observed at δ 2.37 and 2.43 (T_{coal} = 276 K, $\Delta G^{\ddagger}_{276}$ = 55 kJ mol^{-1}). The cyclopentadienyl ligand of complex **5** shows two sets of resonances at δ 6.75 and 6.98 (AA′BB′ spin system) due to the ring protons, and a singlet at δ 0.28 corresponding to the SiMe$_3$ group. IR bands at 1333 for **4** and 1320 cm^{-1} for **5** are within the characteristic range of terminal imido ligands (1200–1350 cm^{-1}). The terminal coordination mode of the ligand is a relevant point here, since imido bridges [12] might lead to undesired cross-linking of dendritic molecules.

2.2. Crystal structures of 4 and 5

Molecular structures of imido complexes **4** and **5** based on X-ray structural analyses are given in Figs. 1 and 2. Selected bond distances and angles are listed in Tables 1 and 2, respectively.

Compound **4** exhibits a *cis–mer* stereochemistry in an octahedral environment with three chloro atoms in the plane perpendicular to the Nb–N axis and the acetonitrile ligands mutually *cis* (Fig. 1). This is the first crystallographic evidence of *cis–mer* geometry in Group 5 complexes of general formula [M(NAr)X$_3$L$_2$] with L = monodentate ligand. Although this arrangement has previously been proposed for several complexes on the basis of their NMR data, the only structures

confirmed up to now by X-ray analysis correspond to niobium and tantalum complexes [M(NC$_6$H$_3^i$Pr$_2$-2,6)X$_3$L$_2$] (X = Cl, Br; L$_2$ = dimethoxyethane or tetramethyletilendiamine) for which the bidentate L$_2$ ligand forces the *cis* arrangement [13].

Compound **5** has a three-legged piano stool geometry with the phenyl ring of the imido ligand in a quasi reflection plane which roughly bisects the cyclopentadienyl ring and the Cl–Nb–Cl angle (Fig. 2). In other structurally characterized derivatives, the cyclopentadienyl ring is eclipsed with respect to the imido ligand [8a,12,14]. Instead, an *anti* conformation is adopted by the substituted Cp ring in **5** in such a way that C(1) is located *trans* to the imido group, in a position occupied by a ring C–C bond in closely related structures. This arrangement directs the SiMe$_3$ group away from the arylimido ligand, avoiding unfavorable steric interactions in the solid-state. On the other hand, the orientation of the aryl ring observed in comparable structures is either aligned or perpendicular to the reflection plane. The former is found in [Nb(η^5-C$_5$H$_5$){N(C$_6$H$_5^t$Bu-2)}Cl$_2$] [14b], and the latter in species of Nb and Ta with 2,6-disubstituted aryl rings [12,14a]. In these examples, the ring is arranged in order to minimize the steric congestion between the cyclopentadienyl ring and the aryl substituents in *ortho*. Interestingly, the *ortho* non-substituted ring in compound **5** is accommodated on the reflection plane of the molecule. By contrast, the dinuclear analog [{Nb(η^5-C$_5$H$_4$SiMe$_3$)Cl$_2$}$_2$(μ-*p*-N$_2$C$_6$H$_4$)}] [15] shows the perpendicular alignment of aryl ring and the eclipsed conformation of the cyclopentadienyl ligand. Clearly, it should be assumed that crystal-packing forces have a significant effect on the positioning of these groups in the solid-state structure of compound **5**.

In both complexes, the niobium–nitrogen distance lies within the range expected for a triple bond (1.754(4) for **4** and 1.740(9) Å for **5**) and the imido ligand is approximately linear (Nb–N–C$_{ipso}$: 167.6(4)° for **4** and 169.0(7)° for **5**) [12–14]. The *trans* influence of the imido ligand in **4** is manifested by a Nb–CH$_3$CN(*cis*) bond distance ca. 0.15 Å shorter than the Nb–CH$_3$CN(*trans*) one. In compound **5**, the *trans* influence gives rise to a
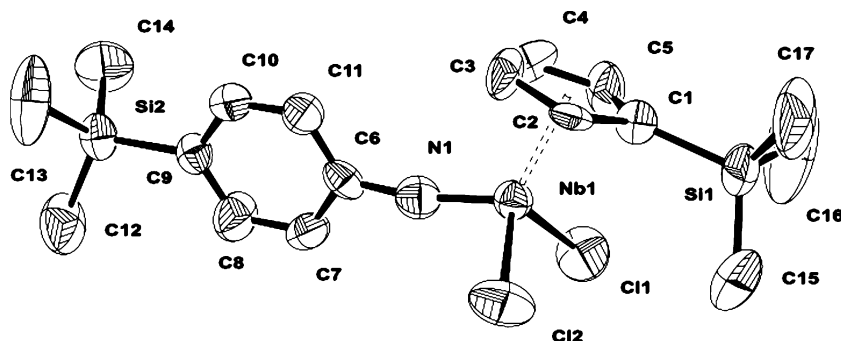

Fig. 2. View of the molecular structure of **5** with the atom-numbering scheme.

Table 1
Selected bond distances (Å) and angles (°) for **4**

Bond distances	
Nb(1)–N(1)	1.754(4)
Nb(1)–N(2)	2.260(6)
Nb(1)–N(3)	2.412(6)
Nb(1)–Cl(1)	2.388(2)
Nb(1)–Cl(2)	2.370(2)
Nb(1)–Cl(3)	2.388(2)
N(1)–C(1)	1.395(7)
N(2)–C(7)	1.139(8)
N(3)–C(9)	1.129(8)
C(7)–C(8)	1.442(9)
C(9)–C(10)	1.449(9)
Bond angles	
N(1)–Nb(1)–Cl(1)	100.99(17)
N(1)–Nb(1)–Cl(2)	99.07(17)
N(1)–Nb(1)–Cl(3)	95.66(17)
N(1)–Nb(1)–N(2)	91.9(2)
N(1)–Nb(1)–N(3)	174.2(2)
N(2)–Nb(1)–Cl(1)	82.98(14)
N(2)–Nb(1)–Cl(2)	169.04(14)
N(2)–Nb(1)–Cl(3)	82.36(14)
N(2)–Nb(1)–N(3)	84.02(19)
N(3)–Nb(1)–Cl(1)	82.69(15)
N(3)–Nb(1)–Cl(2)	85.04(14)
N(3)–Nb(1)–Cl(3)	79.69(15)
Cl(1)–Nb(1)–Cl(2)	95.16(7)
Cl(1)–Nb(1)–Cl(3)	158.11(7)
Cl(2)–Nb(1)–Cl(3)	96.15(7)
C(1)–N(1)–Nb(1)	167.6(4)
C(7)–N(2)–Nb(1)	170.5(6)
C(9)–N(3)–Nb(1)	170.9(6)
N(2)–C(7)–C(8)	179.4(7)
N(3)–C(9)–C(10)	177.8(8)

Table 2
Selected bond distances (Å) and angles (°) for **5**

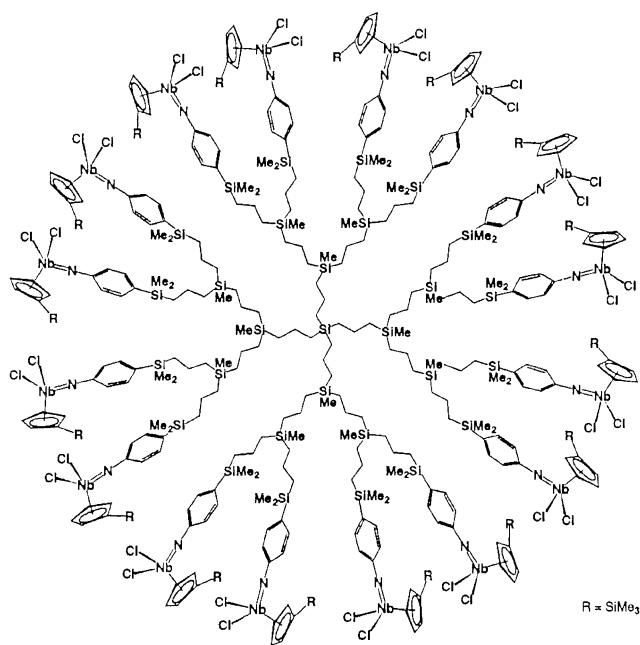| Bond distances	
Nb(1)–N(1)	1.740(9)
Nb(1)–Cl(1)	2.354(7)
Nb(1)–Cl(2)	2.323(6)
Nb(1)–Cp(1) [a]	2.128
Nb(1)–C(1)	2.526(10)
Nb(1)–C(2)	2.442(19)
Nb(1)–C(3)	2.39(2)
Nb(1)–C(4)	2.35(2)
Nb(1)–C(5)	2.46(2)
N(1)–C(6)	1.418(13)
Si(1)–C(1)	1.887(11)
C(1)–C(5)	1.35(2)
C(1)–C(2)	1.47(2)
C(2)–C(3)	1.43(2)
C(3)–C(4)	1.356(16)
C(4)–C(5)	1.40(3)
Bond angles	
N(1)–Nb(1)–Cl(1)	102.7(6)
N(1)–Nb(1)–Cl(2)	101.4(6)
N(1)–Nb(1)–Cp(1)	119.8
Cl(1)–Nb(1)–Cl(2)	106.08(18)
Cl(1)–Nb(1)–Cp(1) [a]	107.8
Cl(2)–Nb(1)–Cp(1) [a]	117.3
C(6)–N(1)–Nb(1)	169.0(7)

[a] Cp(1) is the centroid of C(1)–C(5).

$\{(C_6H_4)NNbCp'Cl_2\}_x$ (**9–11**, Scheme 2, Fig. 3) were obtained in dichloromethane from **6** to **8** and [NbCp'Cl$_4$] in a quantitative reaction, as in the case of the model compound **5**. After crystallization, final yields were in the range 50–73%.

Organic dendrimers **6–8** were obtained as colorless oils whereas niobium derivatives **9–11** could be crystallized as red solids. All the new dendrimers are moisture sensitive. Niobium dendrimers are quite thermally stable as shown by the fact that solutions of **9** in CDCl$_3$ remained unchanged after 15 days at 70 °C in a PTFE-valved NMR tube. Nitrogen–silicon bonds in **6–8** are easily hydrolyzed. However, attempts to prepare NH$_2$-terminated dendrimers by reaction with mild acids failed to give pure products. This could be due to concurrent partial breaking of silicon–phenyl bonds, since small amounts of C$_6$H$_5$NH$_2$ are detected by ^{1}H-NMR in the crude of reaction. Although it is well known that aminophenyl–silicon bonds are sensitive to protic acids [17], it is noteworthy that hydrolysis of **3** in the same conditions produced its quantitative conversion into Me$_3$SiC$_6$H$_4$NH$_2$ (^{1}H-NMR evidence) [9a].

[1]H-, ^{13}C{^{1}H}-, and ^{29}Si{^{1}H}-NMR chemical shifts of terminal PhN(SiMe$_3$)$_2$ groups for **6–8** are comparable to those found for **3**. The replacement at the end of the dendritic branches of the chloride atom in dendrimers G$_n$–Cl by PhN(SiMe$_3$)$_2$ groups in **6–8** is confirmed, within the NMR resolution, by the shift of the SiMe$_2$ resonances from δ 0.38 (^{1}H) and 1.9 (^{13}C) to 0.19 (^{1}H)

distorted coordination of the cyclopentadienyl ring, with the niobium–carbon bond distances ranging from 2.526(10) Å for C(1) to 2.39(2) and 2.35(2) Å for C(3) and C(4), respectively.

2.3. Synthesis and characterization of dendrimers

The syntheses of dendrimers containing niobium centers at their periphery have been studied. For this purpose, chloro-terminated dendrimers of first, second, and third generation (Scheme 2) were synthesized according to previously reported methods [16]. These dendrimers containing peripheral Si–Cl bonds were converted into G$_n$–{(C$_6$H$_4$)N(SiMe$_3$)$_2$}$_x$ ($n = 1$, $x = 4$ (**6**); $n = 2$, $x = 8$ (**7**); $n = 3$, $x = 16$ (**8**)), which might be considered polyaniline analogues of **3**. These conversions (85–97% yield) were carried out by a parallel procedure to that described for model compound **3**, in which the appropriated chloro-terminated dendrimer G$_n$–Cl is used instead of SiMe$_3$Cl. Dendrimers **6–8** were used as supports for 4, 8, or 16 niobium centers that were anchored to the dendritic framework through imido bonds. Thus, niobium dendrimers G$_n$–

Scheme 2.

Fig. 3. Niobium dendrimer $G_3-\{(C_6H_4)NNbCp'Cl_2\}_{16}$ (**11**).

and -4.3 (^{13}C). The ^1H-NMR spectra of the carbosilane framework for dendrimers **6**–**8** show almost identical shifts for analogous nuclei in different generations. The overlapping of groups situated at different shells of a given dendrimer together with their restricted mobility, explain the typical peak broadening and loss of resolution observed in increasing the generation [18]. Three sets of signals attributed to the methylene groups of the $SiCH_2CH_2CH_2Si$ branches have been observed with the expected integration ratio. The middle methylenes are located at ca. δ 1.25, and those directly bonded

to silicon atoms are centered at ca. δ 0.50, except the outermost ones (CH_2SiMe_2Ph) that appear at ca. δ 0.75. In the ^{13}C-NMR spectra, the methylene carbon resonances are situated within the range δ 17–21. For the dendrimers of second and third generation, the three peaks due to the outer branches can be unambiguously assigned, although smaller signals, corresponding to the inner shells, are also observed. The external $SiMe_2$ protons are located at δ 0.19 but the internal SiMe groups are not observed probably because of overlapping with $N(SiMe_3)_2$ resonances.

Spectroscopic and analytical data for metallodendrimers **9**–**11** are consistent with their proposed structures shown in Scheme 2 and Fig. 3. IR spectra confirmed the terminal nature of their imido ligands (bands at ca. 1320 cm^{-1}). The presence of niobium complexes at the end of the dendritic branches was established by NMR. The proton and carbon atoms of the Cp' ring appear at the same positions that those in their mononuclear analog **5**. The carbosilane framework is insignificantly affected by the presence of niobium complexes at their periphery and therefore the general characteristics of the NMR spectra of dendrimers **9**–**11** are almost identical to that described above for metal-free dendrimers **6**–**8**.

3. Conclusion

In summary, a synthetic strategy that allows the anchoring of metal centers to the periphery of carbosilane dendrimers through imido ligands has been developed and applied to the synthesis of the first examples of niobium dendrimers. The formation of imido links is carried out via elimination of $SiMe_3Cl$ from metal

halides and *N,N*-bis(trimethylsilyl)aniline-ended dendrimers. This procedure has been shown to be suitable for the growing up to the third generation, although it could be useful for higher generations and for other metal complexes [19].

4. Experimental

4.1. Reagents and general techniques

All operat ions were performed under an Ar atmosphere using Schlenk or dry-box techniques. Unless otherwise stated, reagents were obtained from commercial sources and used as received. [NbCp′Cl$_4$] [20], and carbosilane dendrimers G$_n$–Cl (*n* = 1–3) [16] were prepared according to literature procedures; the purity of dendrimers was checked by GPC analysis of the G$_n$–(allyl) intermediates. Solvents were previously dried and distilled under Ar as described elsewhere [21]. NMR spectra were recorded on Varian Unity 300 or 500 Plus spectrometers. Chemical shifts (δ, ppm) are reported in ppm referenced to SiMe$_4$ for ^{1}H, ^{13}C and [29]Si. IR spectra were recorded in Nujol mulls on a Perkin–Elmer FT-IR Spectrum-2000 spectrophotometer. Elemental analyses were performed by Microanalytical Laboratories of the University of Alcalá on a Heraeus CHN-O-Rapid mycroanalyzer.

4.2. Preparation of 4-iodo-N-trimethylsilylaniline (1)

This compound was synthesized by adapting a literature procedure relating the monosilylation reaction of aromatic amines [10b]. A solution of 4-IC$_6$H$_4$NH$_2$ (29.40 g, 134.2 mmol) in Et$_2$O (250 ml) was treated with an excess of SiMe$_3$Cl (25.5 ml, 201 mmol) at 0 °C. The resulting suspension of white precipitate was stirred for 30 min and Et$_3$N (28.1 ml, 201 mmol) was slowly added also at 0 °C. The reaction mixture was allowed to warm up to room temperature (r.t.) and was stirred for 5 h. After filtration of the solution, the remaining solid was washed with C$_5$H$_{12}$ (2 × 50 ml). The filtrates were combined and the volatiles removed in vacuo to give crude 1 as a yellow–brownish sticky liquid. The monosilylated aniline was purified by crystallization in C$_5$H$_{12}$ (ca. 70 ml) at −78 °C, leading to 1 as a white solid (32.80 g, 84%) which melts back at r.t. Anal. Calc. for C$_9$H$_{14}$INSi: C, 37.1; H, 4.8; N, 4.8. Found: C, 36.9; H, 4.8; N, 5.3%. ^{1}H-NMR (CDCl$_3$): δ 0.28 (s, 9H, Si*Me$_3$*), 3.47 (broad s, 1H, N*H*), 6.45 (AA′ part of an AA′BB′ spin system, 2H, C$_6$H$_4$), 7.38 (BB′ part of an AA′BB′ spin system, 2*H*, C$_6$*H$_4$*). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ −0.1 (Si*Me$_3$*), 78.3 (*ipso* I–C$_6$H$_4$), 118.4 (C$_6$H$_4$), 137.8 (C$_6$H$_4$), 147.1 (*ipso* N–C$_6$H$_4$). ^{29}Si{^{1}H}-NMR (CDCl$_3$): δ 3.3 (*Si*Me$_3$).

4.3. Preparation of 4-iodo-N,N-bis(trimethylsilyl)aniline (2)

One equivalent of *n*-BuLi (14.5 ml, 1.6 M in hexanes, 23.2 mmol) was slowly added from a funnel, equipped with a bubbler, to a solution of compound 1 (6.74 g, 23.1 mmol) in C$_6$H$_{14}$ (50 ml) at −78 °C. When the addition was completed, the mixture was allowed to warm up to r.t. and stirred overnight. Then, the resulting white precipitate was separated from the solution by filtration, washed with C$_5$H$_{12}$ (2 × 25 ml), dried, dissolved in THF (50 ml), and reacted with SiMe$_3$Cl (3.0 ml, 23.7 mmol) at −78 °C. The reaction mixture was stirred for 2 h at r.t., the solvent was removed under reduced pressure, and the oily residue extracted with C$_5$H$_{12}$ (2 × 25 ml). Removal of the C$_5$H$_{12}$ afforded spectroscopically pure 2 (7.23 g, 86%) as a pale-yellow liquid, which could be distilled under vacuum (70–73 °C, 10^{-3} mmHg). Anal. Calc. for C$_{12}$H$_{22}$INSi$_2$: C, 39.7; H, 6.1; N, 3.9. Found: C, 40.0; H, 6.1; N, 4.4%. ^{1}H-NMR (CDCl$_3$): δ 0.04 (s, 18H, Si*Me$_3$*), 6.63 (AA′ part of an AA′BB′ spin system, 2H, C$_6$H$_4$), 7.48 (BB′ part of an AA′BB′ spin system, 2H, C$_6$H$_4$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 2.0 (Si*Me$_3$*), 87.6 (*ipso* I–C$_6$H$_4$), 132.3 (C$_6$H$_4$), 137.5 (C$_6$H$_4$), 148.1 (*ipso* N–C$_6$H$_4$). ^{29}Si{^{1}H}-NMR (CDCl$_3$): δ 5.3 (*Si*Me$_3$).

4.4. Preparation of 4-trimethylsilyl-N,N-bis(trimethylsilyl)aniline (3)

n-BuLi (7.2 ml, 1.6 M in hexanes, 11.5 mmol) was added from a syringe to a solution of compound 2 (4.16 g, 11.4 mmol) in C$_5$H$_{12}$ (10 ml) at r.t. The solution turned slowly to a suspension of white solid. The mixture was stirred overnight and then filtered to separate the *n*-BuI by-product from the white precipitate that was washed with C$_5$H$_{12}$ (2 × 15 ml) and dried under vacuum. The lithiated compound 4-LiC$_6$H$_4$N(SiMe$_3$)$_2$ thus obtained, which can be stored in a dry-box, was subsequently treated with SiMe$_3$Cl (1.50 ml, 11.8 mmol) in THF (15 ml) at −78 °C. The reaction mixture was stirred for 4 h at r.t., the solvent was removed under reduced pressure, and the residue extracted with C$_5$H$_{12}$ (2 × 25 ml). Removal of the solvent in vacuo gave 3 as a pale-yellow liquid (2.59 g, 73%). Anal. Calc. for C$_{15}$H$_{31}$NSi$_3$: C, 58.2; H, 10.1; N, 4.5. Found: C, 58.3; H, 10.2; N, 5.5%. ^{1}H-NMR (CDCl$_3$): δ 0.06 (s, 18H, N−Si*Me$_3$*), 0.24 (s, 9H, Ph−Si*Me$_3$*), 6.86 (AA′ part of an AA′BB′ spin system, 2H, C$_6$H$_4$), 7.32 (BB′ part of an AA′BB′ spin system, 2H, C$_6$H$_4$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ −0.9 (Ph−Si*Me$_3$*), 2.1 (N−Si*Me$_3$*), 129.5 (C$_6$H$_4$), 133.5 (C$_6$H$_4$), 134.5 (*ipso* Si−C$_6$H$_4$), 148.5 (*ipso* N−C$_6$H$_4$). ^{29}Si{^{1}H}-NMR (CDCl$_3$): δ −4.4 (Ph−*Si*Me$_3$), 4.7 (N−*Si*Me$_3$).

4.5. Preparation of bis(acetonitrile)trichloro(4-trimethylsilylphenylimido)niobium(V) (4)

A solution of **3** (2.09 g, 6.75 mmol) in MeCN (25 ml) was added to NbCl$_5$ (1.824 g, 6.75 mmol) in MeCN (25 ml) at r.t. The solution turned quickly from clear-yellow to red. The stirring was kept for 90 min. Solvent evaporation afforded a foamy purple–red solid which was treated with C$_5$H$_{12}$ (2 × 40 ml) and dried in vacuo to give pure **4** (2.88 g, 96%) as a purple–red powder. Anal. Calc. for C$_{13}$H$_{19}$Cl$_3$N$_3$NbSi: C, 35.1; H, 4.3; N, 9.4. Found: C, 34.8; H, 4.3; N, 9.1%. ^{1}H-NMR (CDCl$_3$): δ 0.21 (s, 9H, Ph–SiMe_3), 2.31 (s broad, 6H, MeCN), 7.27 (AA′ part of an AA′BB′ spin system, 2H, C$_6$H$_4$), 7.44 (BB′ part of an AA′BB′ spin system, 2H, C$_6$H$_4$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ −1.2 (SiMe_3), 3.2 (s, MeCN), 120.1 (s very broad, MeCN), 124.5 (C$_6$H$_4$), 133.1 (C$_6$H$_4$), 140.2 (ipso Si–C$_6$H$_4$), 154.6 (ipso N–C$_6$H$_4$). ^{29}Si{^{1}H}-NMR (CDCl$_3$): δ −3.7 (SiMe_3). IR (Nujol, CsI): ν 1333 cm^{-1} (NbN).

4.6. Preparation of dichloro(η^5-trimethylsilylcyclopentadienyl)(4-trimethylsilylphenylimido)niobium(V) (5)

A solution of [NbCp′Cl$_4$] (1.60 g, 4.30 mmol) in CH$_2$Cl$_2$ (40 ml) was added to a solution of compound **3** (1.33 g, 4.30 mmol) in CH$_2$Cl$_2$ (40 ml) at r.t. The solution was stirred overnight, and the solvent was removed in vacuo. The residue was dissolved in C$_5$H$_{12}$ (ca. 40 ml), and the solution was concentrated and stored at −20 °C overnight. Complex **5** precipitated as a microcrystalline orange solid that was filtered and dried in vacuo (1.80 g, 90%). Anal. Calc. for C$_{17}$H$_{26}$Cl$_2$NNbSi$_2$: C, 44.0; H, 5.6; N, 3.0. Found: C, 43.9; H, 5.8; N, 2.7%. ^{1}H-NMR (CDCl$_3$): δ 0.22 (s, 9H, Ph–SiMe_3), 0.28 (s, 9H, Cp–SiMe_3), 6.62 (AA′ part of an AA′BB′ spin system, 2H, C$_5$H$_4$), 6.75 (BB′ part of an AA′BB′ spin system, 2H, C$_5$H$_4$), 6.98 (AA′ part of an AA′BB′ spin system, 2H, C$_6$H$_4$), 7.39 (BB′ part of an AA′BB′ spin system, 2H, C$_6$H$_4$). ^{13}C{^{1}H}-NMR (C$_6$D$_6$): δ −1.1 (Ph–SiMe_3), −0.6 (Cp–SiMe_3), 114.2 (C$_5$H$_4$), 122.0 (C$_5$H$_4$), 123.7 (C$_6$H$_4$), 125.5 (ipso C$_5$H$_4$), 133.80 (C$_6$H$_4$), 138.5 (ipso Si–C$_6$H$_4$), 156.4 (ipso N–C$_6$H$_4$). ^{29}Si{^{1}H}-NMR (C$_6$D$_6$): δ −5.2 (C$_5$H$_4$$SiMe_3$), −4.1 (Ph$SiMe_3$). IR (Nujol, CsI): ν 1321 cm^{-1} (NbN).

4.7. Preparation of G$_1$–{(C$_6$H$_4$)N(SiMe$_3$)$_2$}$_4$ (6)

A solution of 4-LiC$_6$H$_4$N(SiMe$_3$)$_2$ (1.12 g, 4.60 mmol) in THF (30 ml), prepared as for **3**, was added to G$_1$–Cl (0.66 g, 1.15 mmol) at −78 °C. The solution was allowed to reach r.t., stirred overnight, and evaporated to dryness. The residue was extracted with C$_5$H$_{12}$ (30 ml) and filtered. The colorless oil obtained after solvent evaporation was characterized as **6** (1.34 g, 85%). Anal.

Calc. for C$_{68}$H$_{136}$N$_4$Si$_{13}$: C, 59.4; H, 10.0; N, 4.1. Found: C, 59.2; H, 10.3; N, 4.2%. ^{1}H-NMR (CDCl$_3$): δ 0.03 (s, 18H, SiMe_3), 0.19 (s, 6H, SiMe_2), 0.50 (m, 2H, SiCH_2), 0.76 (m, 2H, CH_2SiMe$_2$), 1.28 (m, 2H, CH$_2$CH_2CH$_2$), 6.83 (AA′ part of an AA′BB′ spin system, 2H, C$_6$H$_4$), 7.27 (BB′ part of an AA′BB′ spin system, 2H, C$_6$H$_4$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ −2.7 (SiMe_2), 2.2 (SiMe_3), 17.3 (CH$_2$), 18.6 (CH$_2$), 20.9 (CH$_2$), 129.5 (C$_6$H$_4$), 133.7 (C$_6$H$_4$), 134.8 (ipso Si–C$_6$H$_4$), 148.5 (ipso N–C$_6$H$_4$). ^{29}Si{^{1}H}-NMR (CDCl$_3$): δ −4.4 (SiMe_2), 0.8 (central Si), 4.4 (SiMe_3).

4.8. Preparation of G$_2$–{(C$_6$H$_4$)N(SiMe$_3$)$_2$}$_8$ (7)

4-LiC$_6$H$_4$N(SiMe$_3$)$_2$ (1.16 g, 4.8 mmol) and G$_2$–Cl (0.87 g, 0.60 mmol) were reacted in THF as described above for **6** to give **7** as a colorless oil (1.78 g, 97%). Anal. Calc. for C$_{152}$H$_{308}$N$_8$Si$_{29}$: C, 59.6; H, 10.1; N, 3.7. Found: C, 58.8; H, 9.9; N, 4.0%. ^{1}H-NMR (CDCl$_3$): δ −0.19 (s, 3H, SiMe), 0.02 (s, 36H, SiMe_3), 0.19 (s, 12H, SiMe_2), 0.48 (m, 8H, SiCH_2), 0.73 (m, 4H, CH_2SiMe$_2$), 1.25 (m, 6H, CH$_2$CH_2CH$_2$), 6.81 (AA′ part of an AA′BB′ spin system, 4H, C$_6$H$_4$), 7.27 (BB′ part of an AA′BB′ spin system, 4H, C$_6$H$_4$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ −5.1 (SiMe), −2.7 (SiMe_2), 2.1 (SiMe_3), 18.5 (CH$_2$), 18.6 (CH$_2$), 20.7 (CH$_2$), 129.4 (C$_6$H$_4$), 133.7 (C$_6$H$_4$), 134.7 (ipso Si–C$_6$H$_4$), 148.4 (ipso N–C$_6$H$_4$). ^{29}Si{^{1}H}-NMR (CDCl$_3$): δ −4.3 (SiMe_2), 1.0 (SiMe), 4.4 (SiMe_3), central Si not observed.

4.9. Preparation of G$_3$–{(C$_6$H$_4$)N(SiMe$_3$)$_2$}$_{16}$ (8)

4-LiC$_6$H$_4$N(SiMe$_3$)$_2$ (3.32 g, 13.6 mmol) and G$_3$–Cl (2.74 g, 0.85 mmol) were reacted in THF as described above for **6** to give **8** as a colorless oil (4.85 g, 89%). Anal. Calc. for C$_{320}$H$_{652}$N$_{16}$Si$_{61}$: C, 59.7; H, 10.2; N, 3.5. Found: C, 59.1; H, 10.0; N, 3.7%. ^{1}H-NMR (CDCl$_3$): δ −0.19 (s, 9H, SiMe), 0.02 (s, 72H, SiMe_3), 0.19 (s, 24H, SiMe_2), 0.50 (m, 20H, SiCH_2), 0.73 (m, 8H, CH_2SiMe$_2$), 1.26 (m, 14H, CH$_2$CH_2CH$_2$), 6.82 (AA′ part of an AA′BB′ spin system, 8H, C$_6$H$_4$), 7.27 (BB′ part of an AA′BB′ spin system, 8H, C$_6$H$_4$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ −5.1 (SiMe, only one peak can be distinguished), −2.7 (SiMe_2), 2.1 (SiMe_3), 18.5 (CH$_2$), 18.6 (CH$_2$), 20.8 (CH$_2$), 129.5 (C$_6$H$_4$), 133.7 (C$_6$H$_4$), 134.8 (ipso Si–C$_6$H$_4$), 148.5 (ipso N–C$_6$H$_4$). ^{29}Si{^{1}H}-NMR (CDCl$_3$): δ −4.3 (SiMe_2), 1.1 (G$_2$–SiMe), 4.4 (SiMe_3), G$_1$–SiMe and central Si not observed.

4.10. Preparation of G$_1$–{(C$_6$H$_4$)NNbCp′Cl$_2$}$_4$ (9)

A solution of [NbCp′Cl$_4$] (1.04 g, 2.80 mmol) in CH$_2$Cl$_2$ (30 ml) was added to **6** (0.96 g, 0.70 mmol), and stirred for 12 h. Then, the solvent was removed in vacuo to dryness. The red oil thus obtained was crystallized by washing twice with cold C$_5$H$_{12}$ (2 × 15 ml) to give

dendrimer **9** as a red solid that was filtered and dried in vacuo (0.70 g, 50%). Anal. Calc. for $C_{76}H_{116}Cl_8N_4Nb_4Si_9$: C, 45.8; H, 5.9; N, 2.8. Found: C, 44.4; H, 5.9; N, 2.7%. ^1H-NMR (CDCl₃): δ 0.20 (s, 6H, Si*Me₂*), 0.28 (s, 9H, Si*Me₃*), 0.48 (m, 2H, SiC*H₂*), 0.75 (m, 2H, C*H₂*SiMe₂), 1.26 (m, 2H, CH₂C*H₂*CH₂), 6.60 (AA′ part of an AA′BB′ spin system, 2H, C_5H_4), 6.75 (BB′ part of an AA′BB′ spin system, 2H, C_5H_4), 6.97 (AA′ part of an AA′BB′ spin system, 2H, C_6H_4), 7.36 (BB′ part of an AA′BB′ spin system, 2H, C_6H_4). $^{13}C\{^1H\}$-NMR (CDCl₃): δ −2.9 (Si*Me₂*), −0.5 (Si*Me₃*), 17.4 (*CH₂*), 18.5 (*CH₂*), 20.6 (*CH₂*), 113.9 (C_5H_4), 122.1 (C_5H_4), 123.2 (C_6H_4), 126.1 (*ipso* C_5H_4), 133.6 (C_6H_4), 138.0 (*ipso* Si–C_6H_4), 156.3 (*ipso* N–C_6H_4). $^{29}Si\{^1H\}$-NMR (CDCl₃): δ −4.8 (*Si*Me₃), −4.6 (*Si*Me₂), central *Si* not observed. IR (Nujol, CsI): ν 1320 cm^{-1} (NbN).

4.11. Preparation of G_2–{$(C_6H_4)NNbCp'Cl_2$}₈ (**10**)

[NbCp′Cl₄] (1.02 g, 2.74 mmol) and **7** (1.05 g, 0.34 mmol) were reacted in CH₂Cl₂ as described above for **9** to give **10** as a red solid (0.98 g, 67%). Anal. Calc. for $C_{168}H_{268}Cl_{16}N_8Nb_8Si_{21}$: C, 46.9; H, 6.3; N, 2.6. Found: C, 47.0; H, 6.5; N, 2.7%. ^1H-NMR (CDCl₃): δ −0.14 (s, 3H, Si*Me*), 0.19 (s, 12H, Si*Me₂*), 0.27 (s, 18H, Si*Me₃*), 0.51 (m, 8H, SiC*H₂*), 0.74 (m, 4H, C*H₂*SiMe₂), 1.29 (m, 6H, CH₂C*H₂*CH₂), 6.60 (AA′ part of an AA′BB′ spin system, 4H, C_5H_4), 6,74 (BB′ part of an AA′BB′ spin system, 4H, C_5H_4), 6.95 (AA′ part of an AA′BB′ spin system, 4H, C_6H_4), 7.35 (BB′ part of an AA′BB′ spin system, 4H, C_6H_4). $^{13}C\{^1H\}$-NMR (CDCl₃): δ −5.0 (Si*Me*), −2.8 (Si*Me₂*), −0.5 (Si*Me₃*), 18.4 (*CH₂*), 18.7 (*CH₂*), 20.4 (*CH₂*), 113.9 (C_5H_4), 122.1 (C_5H_4), 123.2 (C_6H_4), 126.1 (*ipso* C_5H_4), 133.6 (C_6H_4), 138.0 (*ipso* Si–C_6H_4), 156.3 (*ipso* N–C_6H_4). $^{29}Si\{^1H\}$-NMR (C₆D₆): δ −5.0 (*Si*Me₃), −3.8 (*Si*Me₂), 1.0 (*Si*Me), central Si not observed. IR (Nujol, CsI): ν 1321 cm^{-1} (NbN).

4.12. Preparation of G_3–{$(C_6H_4)NNbCp'Cl_2$}₁₆ (**11**)

[NbCp′Cl₄] (0.59 g, 1.59 mmol) and **8** (0.64 g, 0.10 mmol) were reacted in CH₂Cl₂ as described above for **9** to give **11** as a red solid (0.65 g, 73%). Anal. Calc. for $C_{352}H_{572}Cl_{32}N_{16}Nb_{16}Si_{45}$: C, 47.4; H, 6.5; N, 2.5. Found: C, 46.7; H, 6.7; N, 2.4%. ^1H-NMR (CDCl₃): δ −0.14 (s broad, 9H, Si*Me*, only one peak can be distinguished), 0.19 (s, 24H, Si*Me₂*), 0.27 (s, 36H, Si*Me₃*), 0.51 (m, 20H, SiC*H₂*), 0.73 (m, 8H, C*H₂*SiMe₂), 1.28 (m, 14H, CH₂C*H₂*CH₂), 6.59 (AA′ part of an AA′BB′ spin system, 8H, C_5H_4), 6.74 (BB′ part of an AA′BB′ spin system, 8H, C_5H_4), 6.96 (AA′ part of an AA′BB′ spin system, 8H, C_6H_4), 7.36 (BB′ part of an AA′BB′ spin system, 8H, C_6H_4). $^{13}C\{^1H\}$-NMR (CDCl₃): δ −4.9 (Si*Me*, only one peak can be distinguished), −2.8 (Si*Me₂*), −0.5 (Si*Me₃*), 18.5

(*CH₂*), 18.7 (*CH₂*), 20.5 (*CH₂*), 114.0 (C_5H_4), 122.2 (C_5H_4), 123.2 (C_6H_4), 126.1 (*ipso* C_5H_4), 133.6 (C_6H_4), 138.0 (*ipso* Si–C_6H_4), 156.3 (*ipso* N–C_6H_4). $^{29}Si\{^1H\}$-NMR (CDCl₃): δ −5.5 (*Si*Me₃), −3.9 (*Si*Me₂), 1.2 (G_2–*Si*Me), G_1–*Si*Me and central *Si* not assigned. IR (Nujol, CsI): ν 1321 cm^{-1} (NbN).

4.13. Crystal structure determinations

Purple crystals of compound **4** were obtained by cooling a concentrated solution in MeCN at −20 °C. Orange crystals of **5** were obtained by slow concentration of a C_6H_{14} solution. Suitable sized crystals were sealed under Ar in a Lindemann tube and mounted in an Enraf−Nonius CAD 4 automatic four-circle diffractometer with graphite monochromated Mo−K$_\alpha$ radia-

Table 3
Crystallographic details for **4** and **5**

	4	**5**
Chemical formula	$C_{13}H_{19}Cl_3N_3NbSi$	$C_{17}H_{26}Cl_2NNbSi_2$
Habit	Prismatic	Prismatic
Formula weight	444.66	464.38
Temperature (K)	293(2)	293(2)
λ (Mo−K$_\alpha$) (Å)	0.71069	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$Pna2_1$
a (Å)	7.173(5)	24.389(3)
b (Å)	9.874(5)	8.848(1)
c (Å)	14.665(5)	10.502(1)
α (°)	74.230(5)	
β (°)	86.600(5)	
γ (°)	86.650(5)	
V (Å³)	996.8(9)	2266.2(4)
Z	2	4
D_{calc} (g cm^{-3})	1.481	1.361
μ (cm^{-1})	10.62	8.71
Crystal size (mm)	0.30 × 0.27 × 0.27	0.35 × 0.27 × 0.20
θ Limits (°)	1.44–22.97	2.45–24.99
Limiting indices	−7 < h < 7,	0 < h < 28,
	−10 < h < 10,	0 < k < 10,
	0 < k < −16	−12 < l < 0
Reflections collected	2962	2312
Reflections unique	2762 [R_{int} = 0.04]	2108
Reflections observed [$I > 2\sigma(I)$]	2095	1294
Data/restraints/ parameters	2762/0 /230	2108/0 /121
R [[$I > 2\sigma(I)$]; wR^2 [a]	0.0439; 0.1038	0.0534; 0.1163
Goodness-of-fit indicator	1.031	1.014
Max peak in final difference map (e Å^{-3})	0.661	0.815
Min peak in final difference map (e Å^{-3})	−0.501	−0.399

[a] $R = \Sigma\ ||F_o| - |F_c||/\Sigma\ |F_o|]$; $wR^2 = [\Sigma\ w(F_o^2 - F_c^2)^2/\Sigma\ w(F_o^2)^2]^{1/2}$.

tion. Crystallographic and experimental details are summarized in Table 3. Data were collected at r.t. Intensities were corrected for Lp effects in the usual manner. No absorption or extinction corrections were made. The structure was solved by direct methods (SHELXL-90) [22] and refined by least-squares against F^2 (SHELXL-97) [23]. All non hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced from geometrical calculations and refined using a riding model. Compound **5** could be solved in the centersymmetric *Pnma* group with a crystallographic symmetry plane. In that case the whole molecule is well defined but the SiMe$_3$ group bonded to the Cp group, and two phenyl carbon atoms appear seriously disordered.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 188939–188940 for compounds **4** and **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk/conts/retrieving.html).

Acknowledgements

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