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Dendritic Carbosilanes Containing Silicon-Bonded 1-[$C_6H_2(CH_2NMe_2)_2$-3,5-Li-4] or 1-[$C_6H_3(CH_2NMe_2)$-4-Li-3] Mono- and Bis(amino)aryllithium End Groups: Structure of {[$CH_2SiMe_2C_6H_3(CH_2NMe_2)$-4-Li-3]$_2$}$_2$

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A useful synthetic procedure for the incorporation of the potentially multidentate monoanionic 1-[$C_6H_2(CH_2NMe_2)_2$-3,5]$^-$ (═NCN) and 1-[$C_6H_3(CH_2NMe_2)$-4]$^-$ (═CN) ligands via the *para*-position on the periphery of carbosilane (CS) dendrimers has been developed. Lithiation of suitable brominated precursors [$C_6H_3(CH_2NMe_2)_2$-3,5-Br-1], **1**, and [C_6H_4-(CH_2NMe_2)-4-Br-1], **2**, in Et_2O at −78 °C with 2 equiv of *t*-BuLi gives the monolithiated aminoaryl compounds Li[$C_6H_3(CH_2NMe_2)_2$-3,5], **1-Li**, and Li[$C_6H_4(CH_2NMe_2)$-4], **2-Li**, which can be subsequently treated in situ with the silicon chlorides $ClSiMe_2(CH_2)_nSiMe_2Cl$ (n = 2 or 6) to yield the functionalized CS-ligand systems [$CH_2SiMe_2C_6H_3(CH_2NMe_2)_2$-3,5]$_2$, **3**, and [$(CH_2)_nSiMe_2C_6H_4(CH_2NMe_2)$-4]$_2$ (for **4**, $n = 1$; for **5**, $n = 3$). The ligand systems **3**−**5** react with 2 equiv of *t*-BuLi to give the dilithiated derivatized carbosilane molecules [$CH_2SiMe_2C_6H_2$-($CH_2NMe_2)_2$-3,5-Li-4]$_2$ and [$(CH_2)_nSiMe_2C_6H_4(CH_2NMe_2)$-4-Li-3]$_2$ (**7**, $n = 1$) in good chemical yields. Quench reactions of the in situ prepared lithiated derivatives with either D_2O, Me_3SiCl/Me_3SiOTf, or MeSSMe clearly showed that the CS-ligand systems have been quantitatively converted into their lithiated derivatives. In addition, the functionalized carbosilane dendrimers G0−$SiMe_2$−(N)CN and G1−$SiMe_2$−(N)CN (**13**−**16**), which can be prepared in high yield by using the same synthetic approach used for the model compounds, can also be quantitatively converted into highly aggregated, polylithium derivatives. An X-ray molecular structure determination of **7** revealed this compound to be a unique dimeric aggregate {[$CH_2SiMe_2C_6H_3(CH_2NMe_2)$-4-Li-3]$_2$}$_2$ with their respective 2-electron−4-center (4c-2e) anionic C_{ipso} centers each bonded to a Li_3 face. As a result the $(Me)_2SiCH_2CH_2Si(Me)_2$ CS backbone exhibits a nonideal *trans* conformation with a vicinal dihedral angle of −161°.

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Introduction

During the last decade there has been a rapid development in the synthesis and application of highly branched molecules, viz., dendrimers,[1] with regular structures. Exciting new materials with interesting chemical, physical, and catalytic properties[2,3] can be prepared when these dendrimers function as carriers of organometallic entities. Recently we reported on carbosilane dendrimers[4] where the "pseudo" surfaces are covered with catalytic sites based on the monoanionic ligands [$C_6H_3(CH_2NMe_2)_2$-2,6]$^-$ (═NCN) and [$C_6H_4(CH_2NMe_2)$-2]$^-$ (═CN).[5] These metallodendritic catalysts were successfully applied as homogeneous catalysts in organic synthesis and showed a comparable activity with respect to their mononuclear complexes. However, a carbamate linker was used to introduce the NCN−metal catalytic sites onto the carbosilane dendritic surface, not only resulting in additional synthetic steps but also restricting the application of reactive

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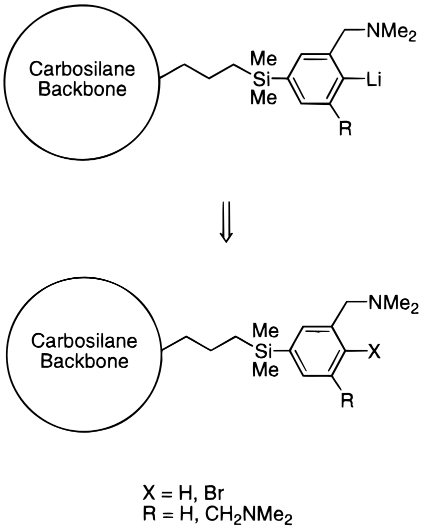

Figure 1. Schematic representation of the lithiation of dendritic carbosilane (N)CN derivatives.

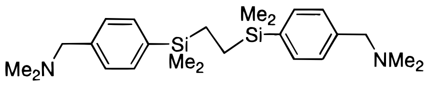

Figure 2. Schematic structure of the double CN-derivatized carbosilane model compound.

reagents as RLi or RMgX. This prompted us to try to simplify and improve the synthetic methodology for this type of metallodendrimers by connecting the catalytic NCN−metal moiety directly onto the silicon surface. This will greatly increase the accessibility of new metallodendritic catalysts.

In this report, we will show that dendritic carbosilanes functionalized with (N)CN−H or (N)CN−Br end groups (see Figure 1) can be selectively lithiated to give their multilithiated derivatives. In a separate paper we will show that this lithiation methodology can generate metal sites on a dendrimer surface in a unique way.[6a] The aggregate formation of these dendritic organolithium species was studied in more detail by using the synthesis and structural features of the bis(CN)-derivatized carbosilane depicted in Figure 2, which can be regarded as a model for two silane units within one wedge of a corresponding dendritic polylithiated species. This has led to the isolation and characterization of a unique bis(aryllithium) carbosilane (CS) compound that exists in the solid state as a dimeric bis(aryllithium) CS species with a Li_4C_4 core analogous to those encountered in the well-known structures of $Li_4Ph_4(Et_2O)_4$ and Li_4Ar_4 (Ar = $[C_6H_4(CH_2NMe_2)$-2]).[6b] A proposal for the two- and three-dimensional networks in these polylithiated carbosilanes[6c] with aminoaryl functionalities is described.

Results and Discussion

Preparation of Model Dendritic Ligand Systems. The bromine atom in **1** and **2**, respectively, is easily replaced by a lithium atom via a lithium/bromine exchange reaction using *tert*-butyllithium. This gives the lithiated species **1-Li** and **2-Li** in quantitative yields without any lithiation *ortho* to one of the amine substituents as is usually found in lithiation reactions involving Li/H exchange of the nonbrominated analogues of **1** and **2**. Alternatively, **2** could also be converted into the corresponding Grignard derivative **2-Mg** at 40 °C in the presence of THF as the solvent. These lithium and Grignard reagents can be used to introduce various other functionalities (see Scheme 1). It was shown that **1-Li** can be quantitatively converted into the silylated derivative $[C_6H_3(CH_2NMe_2)_2$-1,3-$SiMe_3$-5] by treatment with trimethylsilyl chloride (Me_3SiCl).[7] We anticipated that the reaction between the in situ prepared lithium reagents **1-Li** and **2-Li** and commercially available silicon chlorides with more than one reactive Si−Cl bond would selectively give the corresponding (N)CN-derivatized organosilicon compounds. These carbosilane molecules were chosen to serve as model compounds in order to develop and optimize a synthetic strategy for carbosilane dendrimers containing (N)CN ligands.

When either **1** or **2** is lithiated in situ with 1.8−1.9 equiv of *t*-BuLi at −78 °C followed by the addition of 0.8−0.9 equiv of the corresponding silicon chloride with respect to the theoretical amount of lithium reagent formed, the conversion to the target compounds (i.e., the carbosilane molecules **3**−**5**) is complete within 16−20 h (see Scheme 1). The unreacted starting bromide is then converted into the nonbrominated (N)CN derivatives by the addition of an extra amount of *t*-BuLi to the reaction mixture. After hydrolysis with excess H_2O, the crude products are isolated as viscous, yellow oils. Removal of free (N)CN ligand can be carried out using Kugelrohr distillation at elevated temperatures (100−140 °C) and reduced pressure (0.2 mmHg) to give the pure materials in excellent chemical yields (80−90%) (see synthesis of **3** for a general procedure, Experimental Section). The removed (N)CN ligands are easily recycled.[8]

The use of the Grignard reagent **2-Mg** in the derivatization of the carbosilane molecules with (N)CN ligands followed by a similar workup procedure (vide supra) leads to comparable isolated yields of **3**−**5** (see synthesis of **4** for a general procedure, Experimental Section). More importantly, the reagent **2-Mg** is more easy to handle in larger-scale experiments than the in situ prepared lithium reagents **1-Li** and **2-Li**.

Preparation of Lithiated Model Carbosilane Derivatives. Treatment of **3**−**5** with 2 equiv of *t*-BuLi

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(6) (a) The first preliminary report of these polylithiated species was presented during the ACS polymer division meeting in Chicago, August 5, 1996. (b) Jastrzebski, J. T. B. H.; van Koten, G.; Konijn, M.; Stam, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 5490. (c) Others have also reported the synthesis of lithiated carbosilanes. The main difference, however, is that these materials are less suitable for the introduction of metal sites on the periphery of the carbosilane backbone compared to the polylithiated carbosilane species presented in this paper. See: Vasilenko, N. G.; Getmanova, E. V.; Miakushev, V. D.; Rebrov, E. A.; Möller, M.; Muzafarov, A. M. *Polym. Sci.* **1997**, *39*, 9. Vasilenko, N. G.; Rebrove, E. A.; Muzafarov, A. M.; Esswein, B.; Striegel, B.; Möller, M. *Macromol. Chem. Phys.* **1998**, *199*, 889.

(7) Steenwinkel, P.; James, S. L.; Grove, D. M.; Veldman, N.; Spek, A. L.; van Koten, G. *Chem. Eur. J.* **1996**, *2*, 1440.

(8) The procedures described for the anchoring of the (N)CN ligands provide starting materials for a lot of our present research [5] as well as for related chemistry with PCP[9a−d] and SCS[9d,e] analogues of NCN.

(9) See for instance: (a) Dani, P.; Karlen, T.; Gossage R. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1997**, *119*, 11317. (b) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.***1995**, 1965; *J. Am. Chem. Soc.* **1995**, *117*, 9774. (c) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. G. *J. Am. Chem. Soc.* **1997**, *119*, 840. (d) Steenwinkel, P.; Dijkstra, H. P.; Grove, D. M.; Lutz, M.; Spek, A. L.; van Koten, G. To be published. (e) Loeb, S. J.; Shimizu, G. K. H. *J. Chem. Soc., Chem. Commun.* **1993**, 1395.

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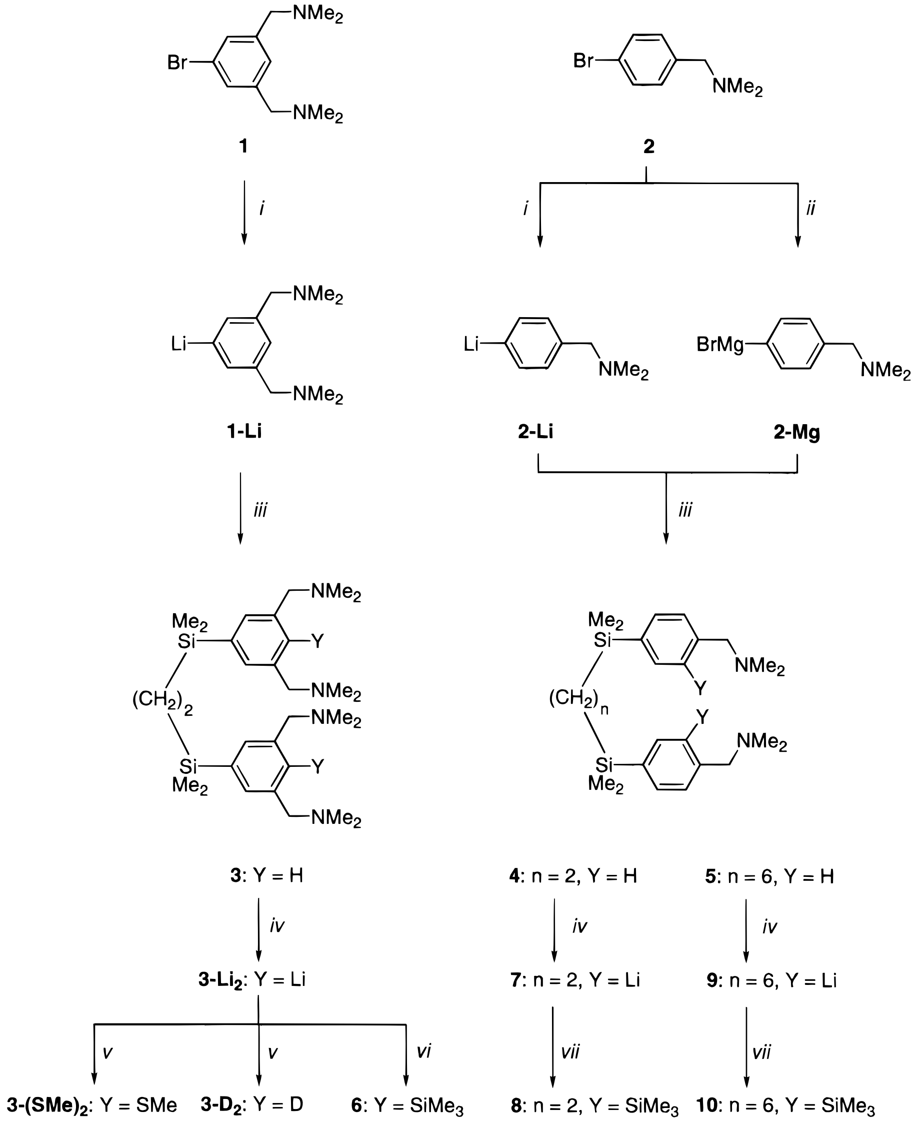
Scheme 1. Reagents and Conditions: (i) 2 equiv *t*-BuLi, Et_2O, −78 °C; (ii) Excess Mg, THF, 40 °C; (iii) 0.5 equiv $ClMe_2Si(CH_2)_nSiMe_2Cl$ (*n* = 2 or 6), Et_2O, −78 °C → rt; (iv) 2 equiv *t*-BuLi, Pentane; (v) D_2O or MeSSMe, Pentane; (vi) Me_3SiOTf, Et_2O; (vii) Me_3SiCl, THF



in pentane at room temperature for 18 h leads to the corresponding dilithiated species. Quench reactions were carried out to establish the conversion of the bisarenes into the respective bis(aryllithium) compounds. For example, treatment of a red-colored solution of the dilithiated species of **3** in hexane or pentane with either excess D_2O or dimethyl disulfide (MeSSMe) at room temperature leads to rapid decolorization of the reaction mixture. Analysis of the organic material(s) present by means of ^1H NMR spectroscopy and GC−MS revealed that in both cases a complete conversion of **3** was achieved to the bisdeuterium, **3-D$_2$**, and bis(methylthiolate), **3-(SMe)$_2$**, materials, respectively, which indicates that the complete and selective lithiation of **3** had occurred. Also, silylation of the dilithiated species of **3** with trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf)[10] in Et_2O at room temperature gave the disilylated compound **6** in 84% yield, whereas the bislithiated species of **4** and **5** could be converted into their corresponding bissilylated analogues **8** and **10** by treatment with Me_3SiCl under similar reaction conditions.

Preparation of Dendrimer Species. The syntheses of the corresponding dendritic species (see Scheme 2 and 3) can be described by the same routes as have been described for the model compounds (see Scheme 1). Thus, treatment of the carbosilanes G0−$SiMe_2Cl$ and G1−$SiMe_2Cl$[11] with the lithium reagents **1-Li** and **2-Li** gives the functionalized dendrimers **13**−**16**, while a similar reaction of $SiCl_4$ with **1-Li** yields the smallest NCN-derivatized organosilicon compound, **11**, possible. The organosilicon compound **11** and dendrimer species **13**−**16** were treated with an excess of *tert*-butyllithium in pentane at room temperature to give their multilithiated derivatives as amorphous, reddish solids which precipitate almost immediately from solution and are

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[10] It is must be emphasized that in this particular silylation reaction Me_3SiCl will fail to silylate the lithium derivative **6-Li$_2$**. See: Steenwinkel, P.; James, S. L.; Grove, D. M.; Kooijman, H.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 513.

[11] (a) van der Made, A. W.; van Leeuwen, P. W. M. N.; De Wilde, J. C.; Brandes, A. C. *Adv. Mater.* **1993**, *5*, (6), 466. (b) van der Made, A. W.; van Leeuwen, P. W. M. N. *J. Chem. Soc., Chem. Commun.* **1992**, 1400.

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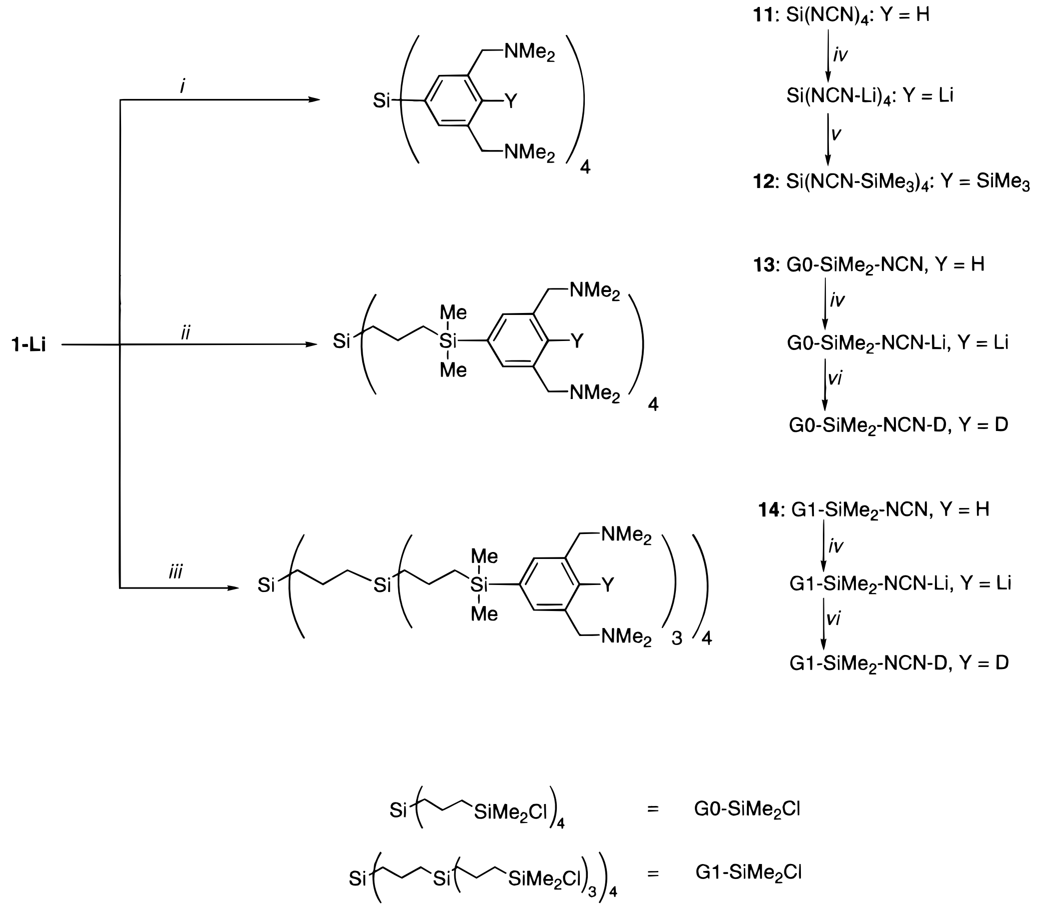
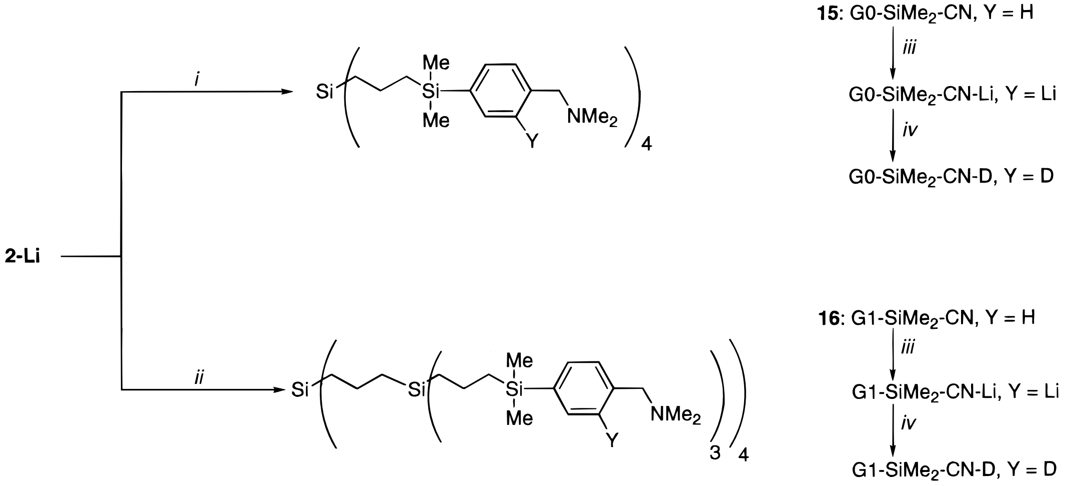
Scheme 2. Reagents and Conditions: (i) 0.25 equiv $SiCl_4$, Et_2O, −78 °C → rt; (ii) G0−$SiMe_2Cl$, Et_2O, −78 °C → rt; (iii) G1−$SiMe_2Cl$, Et_2O, −78 °C → rt; (iv) Excess *t*-BuLi, Pentane, 18 h; (v) Me_3SiOTf, Et_2O; (vi) D_2O, Pentane



Scheme 3. Reagents and Conditions: (i) G0−$SiMe_2Cl$, Et_2O, −78 °C → rt; (ii) G1−$SiMe_2Cl$, Et_2O, −78 °C → rt; (iii) excess *t*-BuLi, Pentane, 1 h; (iv) D_2O, Pentane



insoluble in all common organic solvents. The synthesis of multilithiated analogues can be confirmed by D_2O quench reactions. Thus, the addition of an excess of D_2O to a multilithiated derivative of one of the dendrimer species **13**−**16** rapidly led to a clear, almost colorless solution. After isolation of the deuterated species, ^1H and ^{13}C NMR spectroscopy clearly indicated that quantitative (>98%) and selective lithiation had occurred in all cases (see Schemes 2 and 3). The tetrasilylated compound **12** was prepared by treatment of **11-Li$_4$** with an excess of Me_3SiOTf as described for **6**. This latter reaction showed that a facile introduction of useful substituents between the N-donor atoms can be accomplished by using polylithiated precursors. All compounds were fully characterized by standard NMR techniques (^1H, $^{13}C\{^1H\}$), mass spectrometry (GC−MS, fast atom bombardment (FAB) MS, or MALDI-TOF-MS), and elemental microanalysis (see Experimental Section).

X-ray Molecular Structure of 7. The X-ray molec-

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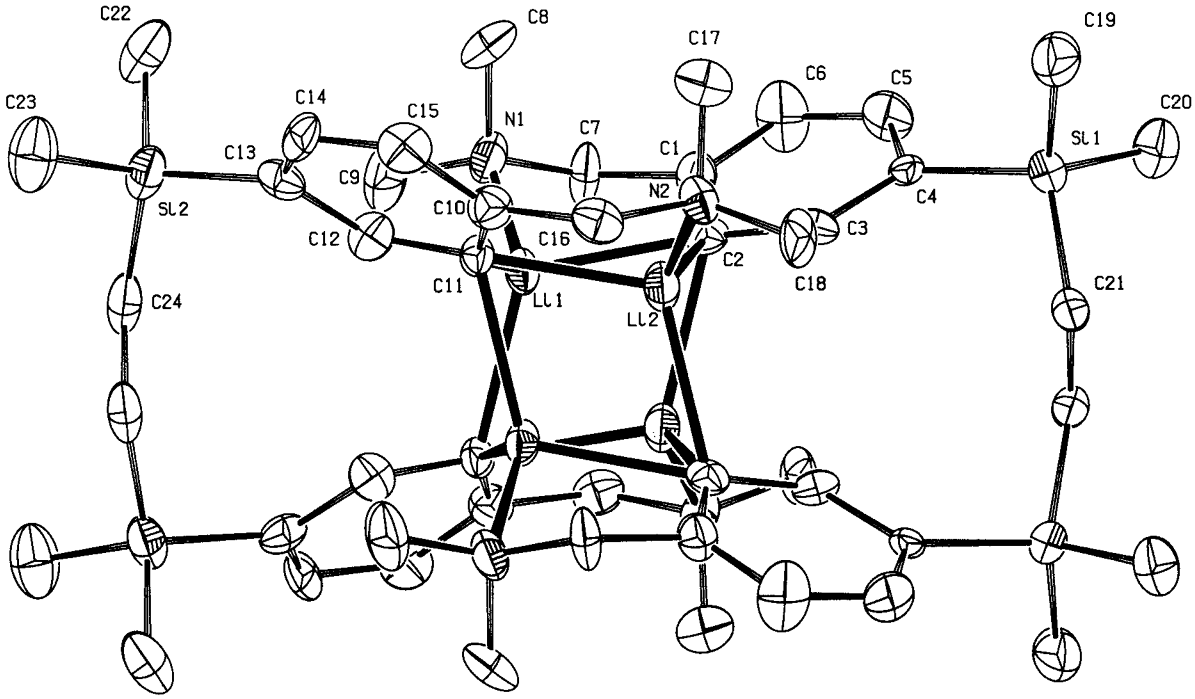

Figure 3. ORTEP drawing (thermal ellipsoids at 50% probability level) of the tetranuclear complex **7** together with the adopted numbering scheme (H atoms are omitted for clarity).

Table 1. Selected Bond Distances (Å) and Bond Angles for the Tetralithio Aggregate 7

Bond Distances			
C(2)−Li(1)	2.276(12)	C(2)−Li(2)	2.248(14)
C(2)−Li(2a)	2.375(13)	N(1)−Li(1)	2.007(12)
C(11)−Li(1)	2.276(13)	C(11)−Li(2)	2.276(13)
C(11)−Li(1a)	2.372(13)	N(2)−Li(2)	2.001(13)
Bond Angles			
N(1)−Li(1)−C(2)	88.5(4)	N(2)−Li(2)−C(11)	89.3(5)
N(1)−C(7)−C(1)	113.3(6)	N(2)−C(16)−C(10)	113.6(6)
C(1)−C(2)−C(3)	111.3(6)	C(10)−C(11)−C(12)	112.4(6)
C(16)−N(2)−Li(2)	100.2(5)	C(7)−N(1)−Li(1)	99.4(5)
Dihedral Angles			
Si(9)−C(21)−C(21)A−Si(1)A	−161.7(3)		

ular structure of **7** is depicted in Figure 3, relevant bond distances and angles are summarized, in Table 1, and a summary of the crystallographic data is given in Table 2. In the solid state, the bis(aryllithium) compound **7** exists as a unique dimeric aggregate of stoichiometry $\{[CH_2SiMe_2C_6H_3(CH_2NMe_2)\text{-}4\text{-}Li\text{-}3]_2\}_2$. Each of the aryl anions of the CS ligand is face-centered bonded via a 4c−2e C−Li bond to a Li_3 face of the central Li_4 tetrahedron,[12] while intramolecular N−Li coordination completes the coordination sphere at each lithium atom.[13] As a consequence of this aggregation, the central $(Me)_2SiCH_2CH_2Si(Me)_2$ connecting chains have a *trans* conformation with a dihedral angle of −161° for the vicinal Si groupings (see Table 1).

Table 2. Summary of the Crystallographic Data for 7[a]

empirical formula	$C_{48}H_{76}Li_4N_4Si_4$
fw	849.25
cryst syst	Monoclinic
space group	C2/c (No. 15)
a/Å	16.8228(12)
b/Å	16.2206(11)
c/Å	19.6787(15)
β/deg	107.566(7)
V/Å^3	5119.4(7)
Z	4
D(calc)/[g/cm^3]	1.102
F(000)	1840
μ(Mo Kα)/mm^{-1}	0.2
cryst size/mm	0.12 × 0.12 × 0.38
T/K	100
radiation/Å	Mo Kα 0.71073
θ min., max./deg	1.8, 22.0
scan (type and range)/deg	0.54 + 0.35 Tan(θ)
dataset	−15: 21; −15: 21; −25: 24
no. of tot., unique data, R(int)	6528, 3149, 0.138
no. of obsd data [$I > 2.0\sigma(I)$]	1299
N_{ref}, N_{par}	3149, 281
R, wR_2, S	0.0754, 0.1121, 0.89
max. and av. shift/error	0.00, 0.00
min. and max. resd dens/[e/Å^3]	−0.25, 0.23

[a] $w^{-1} = \sigma^2(F_o^2) + (0.0177P)^2$, $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

Although the structures of **7** and the related Li_4Ar_4 (Ar = CN) have the C_4Li_4 central core in common, there are distinct differences between both structures which most likely originate from the presence of the connecting chains in **7**. A distinct lengthening of C(2)−Li(2a) and C(11)−Li(1a) to ca. 2.37−2.38 Å is observed in **7**, while in the Li_4Ar_4 tetramer the C−Li distances fall in the same range of 2.25−2.31 Å. Moreover, significantly reduced angles N(1)−Li(1)−C(2) and N(2)−Li(2)−C(11) amounting to 88.5(4)° and 89.3(5)°, respectively, are found, while these values in Li_4Ar_4 are ca. 99.5°.

In a Li_4Ar_4 arrangement with intramolecular N−Li coordination, two geometrically different isomers are

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[12] The overall structure of the $(CN\text{-}Li)_4$ core unit of **7** shows many similarities with previously reported structures of tetranuclear alkyl- and aryllithium aggregates in which the amine−N−Li coordination is replaced by coordination of a corresponding number of Et_2O molecules (cf. $Li_4Ph_4(OEt_2)_4$). See: (a) Weiss, E. *Angew. Chem., Int. Ed. Engl.* ***1993***, *32*, 1501. (b) Wijkens, P.; van Koten, E. M.; Janssen, M. D.; Jastrzebski, J. T. B. H.; Spek, A. L.; van Koten, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 219.

[13] Bond distances and angles in the $(CN−Li)_4$ core unit of the dimeric aggregate **7** are closely related to their analogues in the tetrameric $(CN−Li)_4$ complex[6b] except for the ones mentioned in the text.

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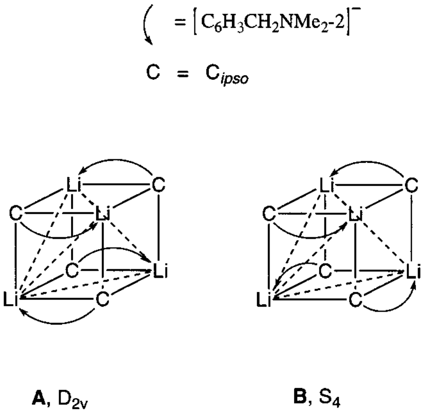


Figure 4. Schematic representation of the two possible isomeric tetramers of **7**.

possible, i.e. a Li_4Ar_4 isomer with D_{2v} and one with S_4 symmetry (see Figure 4). Klumpp and co-workers[14] reported on the tetrameric structure of 1-lithio-3-methoxypropane, and by means of ^1H NMR spectroscopic measurements in toluene-d_8 at low temperatures (173−253 K) they showed this alkyllithium compound to exist in solution as two isomeric forms depending on the actual O−Li coordination sequence (see Figure 4). At higher temperatures rapid interconversion of the two aggregated species is observed. In the solid state this alkyllithium species exists as only one isomer with D_{2v} symmetry (Figure 4, A).

An interesting aspect is the D_{2v} symmetry of **7** in the solid state. The presence of a connecting CS backbone in **7** could concievably limit the structure in solution to the one with D_{2v} symmetry. However, we could not confirm this assumption due to the low solubility of **7** in nonpolar solvents like toluene and CH_2Cl_2.

Structures of Polylithiated 13−16. The dimeric structure of monolithium species with a terdentate *N,C,N*-coordination motif (see Figure 5)[7,15] has been unambiguously established both in the solid state and in solution. One can imagine that the lithiated dendritic species **11-Li₄**, **13-Li₄**, and **14-Li₁₂**, with more than one NCN ligand present in one molecule, form polymeric aggregates via intra- and/or intermolecular self-assembly of monomeric NCN−Li units, which is schematically shown in Figure 5 for $Li(C_6H_3\{CH_2NMe_2\}_2$-2,6), **3-Li₂**, and the lithiated dendritic species. The same hypothesis is applicable for the lithiated CN derivatives of **15** and **16**, in which the CN−Li units now form tetrameric clusters as present in the solid-state structure of **7**. The formation of polymeric aggregates explains the very poor solubility characteristics of all these multilithiated species.

Incorporation of Metal Centers on a Carbosilane Dendrimer Surface via a Polylithiated Precursor. We have used the tetralithiated, NCN-derivatized first-generation carbosilane dendrimer G0−SiMe₂−NCN (**13**) (see Scheme 2) to illustrate that d⁸ platinum metal centers can be incorporated in the molecule. Treatment of freshly prepared G0−SiMe₂−NCN−Li (see Scheme 2) with a slight excess of $PtCl_2(SEt_2)_2$ in THF solution gives a 71% yield of the metalated dendrimer G0−SiMe₂−NCN−PtCl (**17**) (see Scheme 4).

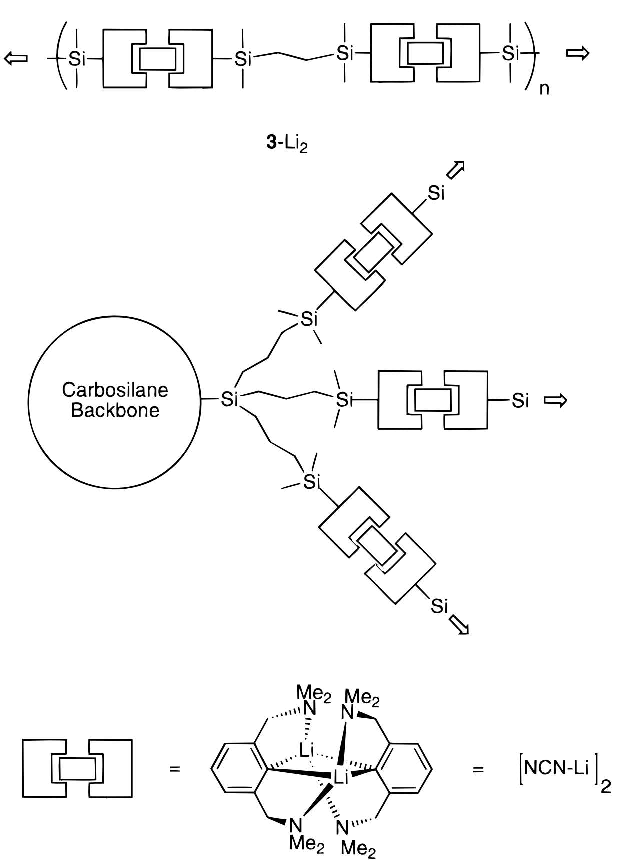
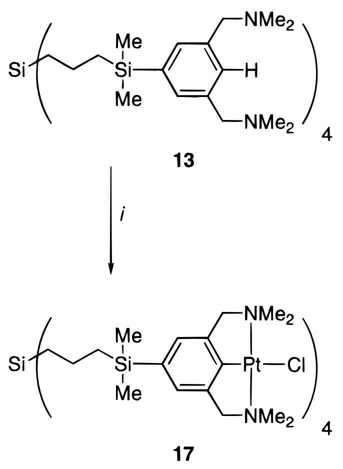


Figure 5. Schematic structures of the presumed highly aggregated **3-Li₂** and its polylithiated dendrimer analogues.

Scheme 4. Reagents and Conditions: (i) *t*-BuLi, Pentane, rt; PtCl₂(SEt₂)₂, THF, rt



Direct evidence for the formation **17** can be confirmed by the presence of platinum satellites in both the ^1H NMR as well as the ^{13}C NMR spectra. Furthermore, the FAB-MS spectrum for **17** shows characteristic isotope patterns at $m/z = 2111$ and 2076, which are attributed

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[14] Klumpp, G. W.; Geurink, P. J. A.; van Eikema Hommes, N. J. R.; De Kanter, F. J. J.; Vos, M. *Recl. Trav. Chim. Pays-Bays* **1986**, *105*, 398.

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[17] Sheldrick, G. M. *SHELXS86*, Program for crystal structure refinement; University of Göttingen, Göttingen, Germany, 1986.

[18] Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C-34.

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to the molecular ion M^+ and the corresponding fragment ion $(M - Cl)^+$. The isotopic patterns are consistent with their calculated ones.[19]

Conclusion

The present work represents the first example of multilithiated dendrimer systems with stable C−Li bonds[6a] which can be used to introduce various metals via lithiation/transmetalation sequences. As a proof of principle that these peripheral anions can be used for attachment of metal centers to these dendrimers, the transmetalation of G0−SiMe$_2$−NCN−Li (**13-Li$_4$**) with PtCl$_2$(SEt$_2$)$_2$ to G0−SiMe$_2$−NCN−PtCl (**17**) was successfully carried out (see Scheme 4 and Experimental Section). The structure of **7** is a model representing the silane arrangement of a polylithiated (N)CN-derivatized carbosilane dendrimer in one wedge. This shows that the overall solid-state structures of these multilithium species depend on the aggregation behavior of the separate monolithium units. Our future studies will focus on the synthesis of new metal-centered carbosilane dendrimers and their use as macromolecular homogeneous catalysts and aggregation behavior of metalated dendritic species.

Experimental Section

General Procedures. All sensitive organometallic syntheses were performed under a dry and deoxygenated dinitrogen atmosphere using standard Schlenk techniques unless otherwise stated. All solvents were carefully dried and distilled prior to use. All standard chemicals were purchased from Acros Chimica or Aldrich and used without further purification. The brominated precursor compounds 1-bromo-3,5-bis[(dimethylamino)methyl]benzene (**1**),[7] 1-bromo-4-[(dimethylamino)methyl]benzene (**2**),[7] and the dendritic silicon chlorides G0−SiMe$_2$Cl and G1−SiMe$_2$Cl[11b] were synthesized according to a literature procedures. ^{1}H (200 or 300 MHz) and ^{13}C (50 or 75 MHz) NMR spectra were recorded on a Bruker AC200 or Varian Inova 200/300 MHz spectrometer. Melting points are uncorrected. Chemical shifts are given in ppm using TMS as an external standard. Elemental analyses were performed by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

[CH$_2$Si(Me)$_2$C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-3,5]$_2$ (3): General Procedure. To a solution of 1-bromo-3,5-[(dimethylamino)methyl]benzene (2.25 g, 8.30 mmol) in Et$_2$O (25 mL) was added *t*-BuLi (21 mL of a 0.7 M solution in pentane, 15 mmol) at −78 °C. A white suspension, which formed immediately, was stirred for 20 min followed by the addition of 1,2-bis(chlorodimethylsilyl)ethane (0.74 g, 3.45 mmol) in Et$_2$O (40 mL). The yellow suspension was allowed to warm to room temperature and stirred for 18 h. Then an extra amount of *t*-BuLi (5 mL) was added followed by H$_2$O to hydrolyze the excess of lilthium reagents. The organic layer was separated and the aqueous layer extracted with pentane (2 × 50 mL). The combined organic layers were washed with H$_2$O (2 × 50 mL), dried over MgSO$_4$, filtered, and concentrated. The free 1,3-[(dimethylamino)methyl]benzene was removed by Kugelrohr distillation (100−140 °C, 0.1−0.2 mmHg) to yield a clear yellow, viscous oil (1.49 g, 2.83 mmol, 82% based on starting silicon compound). ^{1}H NMR (CDCl$_3$): δ 7.60 (s, 4H, Ar−H), 7.54 (s, 2H, ArH), 3.38 (s, 8H, CH$_2$N), 2.20 (s, 24H, N(CH$_3$)$_2$), 0.62 (s, 4H, −(CH$_2$)$_2$−), 0.21 (s, 12H, Si(CH$_3$)$_2$). ^{13}C NMR (CDCl$_3$): δ 139.2, 133.3, 130.7 (3 × Ar−C, one signal coincides with the solvent), 64.8 (Ar−*C*H$_2$), 45.5 (N(*C*H$_3$)$_2$), 8.5 (−(*C*H$_2$)$_2$−), −3.3 (Si(*C*H$_3$)$_2$). GC−MS (EI) *m*/*z* 525 (M^+). Anal. Calcd for C$_{30}$H$_{54}$Si$_2$: C 68.38, H 10.33, N 10.63, Si 10.66. Found: C, 68.32, H 10.28, N 10.61, Si 10.54.

[CH$_2$Si(Me)$_2$C$_6$H$_4$(CH$_2$NMe$_2$)-4]$_2$ (4): General Procedure. To a solution of 1,2-bis(chlorodimethylsilyl)ethane (4.89 g, 22.6 mmol) in THF (50 mL) was slowly added 4-[(dimethylamino)methyl]phenylmagnesium bromide (**2-Mg**) (68 mL of a 0.7 M solution in THF) at room temperature. The reaction mixture was stirred for 16 h, followed by addition of NH$_4$Cl until a clear two-phase system was obtained. The THF layer was separated and the H$_2$O layer extracted with one portion of pentane (40 mL). The combined organic layers were washed with H$_2$O (2 × 100 mL), dried over Na$_2$SO$_4$, and filtered. The filtrate was concentrated and the free (dimethylamino)methylbenzene was removed as described in the synthesis of **3** to yield a colorless crystalline solid (8.40 g, 20.3 mmol, 90% based on the starting silicon compound). Mp: 56−57 °C. ^{1}H NMR (C$_6$D$_6$): δ 7.49 (d, 4H, Ar−H, J = 7.8 Hz), 7.40 (d, 4H, ArH, J = 7.8 Hz), 3.29 (s, 4H, CH$_2$N), 2.09 (s, 12H, N(CH$_3$)$_2$), 0.74 (s, 4H, −(CH$_2$)$_2$−), 0.23 (s, 12H, Si(CH$_3$)$_2$). ^{13}C NMR (C$_6$D$_6$): δ 140.7, 137.7, 134.0, 128.7 (4 × Ar−C), 64.6 (*C*H$_2$N), 45.5 (N(*C*H$_3$)$_2$), 8.3 (−(*C*H$_2$)$_2$−), −3.3 (Si(*C*H$_3$)$_2$. GC−MS (EI): *m*/*z* 412 (M^+), 367 $(M - HNMe_2)^+$. Anal. Calcd for C$_{24}$H$_{40}$N$_2$Si$_2$: C 69.84, H 9.77, N 6.79, Si 13.61. Found: C 69.76, H 9.69, N 6.85, Si 13.76.

[(CH$_2$)$_3$Si(Me)$_2$C$_6$H$_4$(CH$_2$NMe$_2$)-4]$_2$ (5). This compound was synthesized as described for **3**. The product was isolated in quantitative yield and distilled (bp 250 °C/0.1 mmHg), to yield a colorless oil. $n^{22.5}{}_D = 1.5220$. ^{1}H NMR (CDCl$_3$): δ 7.48 (d, 4H, J = 8.0 Hz, Ar−H), 7.30 (d, 4H, J = 8.0 Hz, Ar−H), 3.44 (s, 4H, CH$_2$N), 2.27 (s, 12H, N(CH$_3$)$_2$), 1.31 (br s, 0.68 (s, 4H, CH$_2$), 0.26 (s, 12H, Si(CH$_3$)$_2$). ^{13}C NMR (CDCl$_3$): δ 139.4, 138.2, 133.6, 128.4 (Ar−C), 64.4 (*C*H$_2$N), 45.5 (N(*C*H$_3$)$_2$), 33.2, 23.8, 15.8 (Si*C*H$_2$*C*H$_2$*C*H$_2$), −2.8 (Si(*C*H$_3$)$_2$). GC−MS (EI): *m*/*z* 468 (M^+). Anal. Calcd for C$_{28}$H$_{48}$N$_2$Si$_2$: C 71.72, H 10.32, N 5.97, Si 11.98. Found: C 71.62, H 10.28, N 6.10, Si 11.92.

[CH$_2$Si(Me)$_2$C$_6$H$_2$(CH$_2$NMe$_2$)$_2$-3,5-SiMe$_3$-4]$_2$ (6). Compound **3** (0.64 g, 1.21 mmol) was dissolved in hexane (20 mL), and to this solution was added *t*-BuLi (2.3 mL of a 1.5 M solution in pentane, 3.5 mmol) at room temperature. The resulting suspension was stirred for 18 h and then quenched with Me$_3$SiOTf (1.7 mL, 8.8 mmol). The solvent was evaporated, and HCl (4 M, 30 mL) and pentane (50 mL) were added. The organic layer was separated, the H$_2$O layer was washed with pentane (50 mL), and then NaOH pellets were added until pH 14. The basified layer was extracted with pentane (3 × 50 mL), and the combined organic layers were washed with H$_2$O (3 × 50 mL), dried over MgSO$_4$, and filtered. The filtrate was concentrated in vacuo to give a slightly yellow waxy solid, which was crystallized in MeOH at −20 °C (0.68 g, 1.01 mmol, 84%). ^{1}H NMR (C$_6$H$_6$): δ 7.65 (s, 4H, Ar−H), 3.55 (s, 8H, CH$_2$N), 2.04 (s, 24H, N(CH$_3$)$_2$), 0.63 (s, 4H, −(CH$_2$)$_2$−), 0.51 (s, 18H, Si(CH$_3$)$_3$), 0.31 (s, 12H, Si(CH$_3$)$_2$). ^{13}C NMR (C$_6$H$_6$): δ 146.0 (Ar−C), 139.6, 139.2 (2 × Ar−C−Si), 134.5 (Ar−C), 66.2 (*C*H$_2$N), 45.1 (N(*C*H$_3$)$_2$), 8.4 (−(*C*H$_2$)$_2$−), 3.4 (Si(*C*H$_3$)$_3$), −3.4 (Si(*C*H$_3$)$_2$). GC−MS (EI): *m*/*z* 656 $(M - CH_3)^+$. Anal. Calcd for C$_{36}$H$_{70}$N$_4$Si$_4$: C 64.41, H 10.51, N 8.35, Si 16.74. Found: C 64.70, H 10.50, N 8.20, Si 16.86.

[CH$_2$Si(Me)$_2$C$_6$H$_3$(CH$_2$NMe$_2$)-4-Li-3]$_2$ (7). To a solution of **4** (0.67 g, 1.62 mmol) in hexane (100 mL) was added *t*-BuLi (2 mL, 1.7 M in hexane, 3.4 mmol) at −78 °C. The unstirred homogeneous reaction mixture was allowed to warm to room temperature, and after 12 h, crystals were obtained. The solvent was removed by decantation and the slightly orange-colored crystals were washed with a minimum amount of

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[19] As a consequence of the workup procedure used for the hygroscopic, tetralithiated derivative G0−SiMe$_2$−NCN−Li, some hydrolysis takes place prior to the transmetalation reaction. This is clearly shown by NMR spectroscopy, in which resonances are found which are attributed to nonmetalated NCN sites. By means of signal integration, the percentage of metalation could be calculated (95%). This incomplete metalation was confirmed by both elemental analyses and FAB mass spectrometry (see Experimental Section).

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pentane and dried in vacuo. Yield: 0.41 g, 0.97 mmol, 60%. ^{1}H NMR (THF-d_8): δ 8.19 (br s, 2H, Ar−H), 6.97 (d, 2H, J = 7.0 Hz, Ar−H), 6.73 (d, 2H, J = 7.0 Hz, Ar−H), 3.45 (s, 4H, CH_2N), 2.17 (br s, 12H, $N(CH_3)_2$), 0.68 (s, 4H, (CH_2), 0.16 (s, 12H, $Si(CH_3)_2$). ^{13}C NMR (THF-d_8): δ 152.7, 148.8, 131.6, 129.5 and 124.4 (Ar−C), 72.2 (CH_2N), 46.0 (N $CH_3)_2$), 9.6 (CH_2), −2.7 ($Si(CH_3)_2$). Anal. Calcd for $C_{24}H_{38}N_2Si_2Li_2$: C 67.88, H 9.02, N 6.60, Si 13.23. Found: C 67.73, H 8.97, N 6.68, Si 13.35.

$[CH_2Si(Me)_2C_6H_3(CH_2NMe_2)$-4-$SiMe_3-3]_2$ (8). To **4** (0.70 g, 1.70 mmol) dissolved in pentane (20 mL) was added t-BuLi (3.0 mL of a 1.5 M solution in pentane, 4.5 mmol) at room temperature. The initially formed orange suspension was stirred for 18 h, after which the solvent was removed in vacuo and THF (25 mL) was added. Then an excess of trimethylsilyl chloride (4.0 mL, 32 mmol) was added, whereupon the solution decolorized. After stirring for 0.5 h, the solvent was removed under reduced pressure, and the product was extracted with pentane (50 mL), filtered through Celite, and concentrated to give a white, crystalline solid (0.83 g, 1.49 mmol, 88%). ^{1}H NMR ($CDCl_3$): δ 7.76 (s, 2H, Ar−H), 7.55 (dd, 4H, J = 8.0 Hz, Ar−H), 3.60 (s, 4H, CH_2N), 2.30 (s, 12H, $N(CH_3)_2$), 0.80 (s, 4H, CH_2), 0.42 (s, 18H, $Si(CH_3)_3$), 0.32 (s, 12H, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 146.0, 140.2, 137.6, 136.6, 134.6, 128.1 (ArC), 64.7 (CH_2N), 45.5 ($N(CH_3)_2$), 8.1 (CH_2), 3.4 $Si(CH_3)_3$), 0.7 ($Si(CH_3)_2$). Anal. Calcd for $C_{30}H_{56}N_2Si_4$: C 64.67, H 10.13, N 5.03, Si 20.17. Found: C 64.78, H 10.06, N 4.89, Si 20.26.

$[(CH_2)_3Si(Me)_2C_6H_3(CH_2NMe_2)$-4-Li-3$]_2$ (9). A similar procedure was used as described for **7**. Compound **5** (0.55 g, 1.20 mmol) was treated with t-BuLi (3.7 mL of a 0.65 M solution in pentane, 2.40 mmol). The dilithio compound was isolated as a microcrystaline solid and isolated as a white powder after drying in vacuo. ^{1}H NMR (THF-d_8): δ 8.23 (br s, 2H, Ar−H), 7.03 (d, 2H, J = 7.0 Hz, Ar−H), 6.79 (d, 2H, J = 7.0 Hz, Ar−H), 3.50 (s, 4H, CH_2N), 2.12 (br s, 12H, $N(CH_3)_2$), 1.32 (br s, 8H, ($SiCH_2CH_2CH_2$), 0.74 (m, 4H, $SiCH_2$), 0.22 (s, 12H $Si(CH_3)_2$). ^{13}C NMR (THF-d_8): δ 153.1, 148.8, 131.6, 129.5 and 124.6 (Ar−C), 72.3 (CH_2N), 46.1 ($N(CH_3)_2$), 34.8 ($SiCH_2CH_2CH_2$), 17.6 ($SiCH_2$), −2.0 ($Si(CH_3)_2$). Anal. Calcd for $C_{28}H_{46}N_2Si_2Li_2$: C 69.96, H 9.64, N 5.83, Si 11.69. Found: C 69.76, H 9.71, N 5.83, Si 11.78.

$[(CH_2)_3Si(Me)_2C_6H_3(CH_2NMe_2)$-4-$SiMe_3-3]_2$ (10). This compound was obtained by using an experimental procedure similar to that described for **8**. Compound **5** (0.97 g, 2.05 mmol) was treated with t-BuLi (2.96 mL of a 1.4 M solution in pentane, 4.14 mmol) and subsequently treated with excess $SiMe_3Cl$ to yield a colorless oil (0.75 g, 1.22 mmol, 60%). The product crystallized upon standing. Mp: 51 °C. ^{1}H NMR ($CDCl_3$): δ 7.32 (s, 2H, Ar−H), 7.49 (dd, 4H, J = 8.0 Hz, ArH), 3.56 (s, 4H, CH_2N), 2.27 (s, 12H, $N(CH_3)_2$), 1.38 (m, 8H (CH_2CH_2), 0.80 (s, 4H, $SiCH_2$), 0.42 (s, 12H, $Si(CH_3)_3$), 0.32 (s, 18H ($Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 145.8, 140.0, 137.5, 136.8, 134.4 and 128.0 (Ar−C), 64.6 (CH_2N), 45.4 ($N(CH_3)_2$), 33.3, 23.9, 15.8 (3 × CH_2), 0.60 ($Si(CH_3)_3$), −2.9 ($Si(CH_3)_2$). GC−MS (EI): m/z 612 (M^+). Anal. Calcd for $C_{34}H_{64}N_2Si_4$: C 66.57, H 10.52, N 4.57, Si 18.32. Found: C 66.65, H 10.58, N 4.65, Si 18.22.

Si{NCN}$_4$ (11). To a solution of 1-bromo-3,5-bis[(dimethylamino)methyl]benzene (4.39 g, 16.2 mmol) in Et_2O (40 mL) was added t-BuLi (18 mL of a 1.7 M solution in pentane, 30.6 mmol) at −78 °C. After stirring the white suspension for ca. 10 min, $SiCl_4$ (0.4 mL, 0.59 g, 3.49 mmol) was added, and the resultant suspension was allowed to reach room temperature. After the same workup as described for **3** the crude product was obtained in quantitative yield. Purification by crystallization in hexane at −30 °C gave analytically pure **11** as white needles. Mp: 145−146 °C. ^{1}H NMR (C_6D_6): δ 7.88 (s, 8H, Ar−H), 7.65 (s, 4H, Ar−H), 3.28 (s, 16H, CH_2N), 2.09 (s, 48H, $N(CH_3)_2$). ^{13}C NMR (C_6D_6): δ 139.3, 136.3, 135.0, 131.5 (4 × Ar−C), 64.5 (CH_2N), 45.4 ($N(CH_3)_2$). FAB-MS: m/z 793.4 ($M + H)^+$. Anal. Calcd for $C_{48}H_{76}N_8Si$: C 72.68, H 9.66, N 14.13, Si 3.54. Found: C 72.54, H 9.57, N 14.08, Si 3.62.

Si{NCN−SiMe$_3$}$_4$ (12). This compound was prepared as described for **6**. To a solution of **11** (1.35 g, 1.71 mmol) in Et_2O (20 mL) was added t-BuLi (6.8 mL of a 1.5 M solution in pentane, 10.2 mmol) at 0 °C. After stirring the red to brown colored suspension for 15 min, an excess of Me_3SiOTf (2.3 mL, 12.0 mmol) was added. After workup, a yellow solid was isolated (1.69 g, 1.51 mmol, 89%). Analytically pure **12** was obtained by crystallization in pentane at −30 °C. Mp: 155 °C. ^{1}H NMR (C_6D_6): δ = 7.88 (s, 8H, Ar−H), 3.44 (s, 16H, CH_2N), 2.00 (s, 48H, $N(CH_3)_2$), 0.49 (s, 36H, $SiMe_3$). ^{13}C NMR (C_6D_6): δ 146.3, 140.7, 137.6, 135.1 (4 × Ar−C), 66.0 (CH_2N), 45.0 ($N(CH_3)_2$), 3.3 ($Si(CH_3)_3$). FAB-MS: m/z 1081.7 ($M + H)^+$. Anal. Calcd for $C_{60}H_{108}N_8Si_5$: C 66.60, H 10.06, N 10.36, Si 12.98. Found: C 66.66, H 10.11, N 10.25, Si 12.84.

G0−SiMe$_2$−NCN (13). To a solution of 1-bromo-3,5-bis[(dimethylamino)methyl]benzene (2.30 g, 8.48 mmol) in Et_2O (25 mL) was added t-BuLi (10 mL, 1.5 M solution in pentane, 15 mmol) at −78 °C. After stirring the white suspension for 20 min G0-SiMe$_2$Cl (1.00 g, 1.75 mmol) was added, and the mixture was stirred for 18 h. After hydrolysis with H_2O and the same isolation and purification sequence used for **3**, a clear yellow viscous oil was obtained (1.80 g, 1.51 mmol, 86). ^{1}H NMR (C_6D_6): δ 7.64 (s, 8H, Ar−H), 7.56 (s, 4H, Ar−H), 3.40 (s, 16H, CH_2N), 2.16 (s, 48H, N()CH$_3$)$_2$), 1.58−1.52 (m, 8H, $SiCH_2CH_2$−), 0.98−0.90 (m, 8H, −$CH_2Si(CH_3)_2$−), 0.71−0.63 (m, 8H, $SiCH_2CH_2$−), 0.35 (s, 24H, $Si(CH_3)_2$). ^{13}C NMR (C_6D_6): δ 139.5, 139.2, 133.1, 130.7 (4 × Ar−C), 64.8 (CH_2N), 45.6 ($N(CH_3)_2$), 21.1, 19.1, 17.8 (3 × CH_2), −2.5 ($Si(CH_3)_2$). FAB-MS: m/z 1194.0 ($M + H)^+$. Anal. Calcd for $C_{68}H_{124}N_8Si_5$: C 68.39, H 10.47, N 9.38, Si 11.76. Found: C 68.26, H 10.39, N 9.48, Si 11.58.

G1−SiMe$_2$−NCN (14). To a solution of 1-bromo-3,5-bis[(dimethylamino)methyl]benzene (5.03 g, 18.5 mmol) in Et_2O (40 mL) was added t-BuLi (22 mL, 1.5 M solution in pentane, 33 mmol) at −78 °C. The resultant white suspension was stirred for 1 h, and then G1−SiMe$_2$Cl (1.68 g, 0.87 mmol) in Et_2O (25 mL) was added at 0 °C. After hydrolysis and the same isolation and purification sequence used for **2** (Kugelrohr, 200 °C), a clear orange, very viscous oil was obtained (2.54 g, 0.67 mmol, 77%). ^{1}H NMR (C_6D_6): δ 7.63 (s, 8H, Ar−H), 7.57 (s, 4H, Ar−H), 3.42 (s, 16H, CH_2N), 2.18 (s, 48 H, $N(CH_3)_2$), 1.75−1.52 (m, 8H, $SiCH_2CH_2$−), 1.05−0.97 (m, 8H, −$CH_2Si(CH_3)_2$−), 0.91−0.77 (m, 8H, $SiCH_2CH_2$−), 0.40 (s, 24H, $Si(CH_3)_2$). ^{13}C NMR (C_6D_6): δ 139.1, 138.6, 132.9, 130.4 (4 × Ar−C), 64.6 (CH_2N), 45.3 ($N(CH_3)_2$), 21.0, 19.0, 18.5, 18.3, 17.6 (*inner* and *outer* CH_2), −2.6 ($Si(CH_3)_2$). MALDI-TOF-MS: m/z 3804.22 (calcd for $(M + H)^+$: 3803.78). Anal. Calcd for $C_{216}H_{396}N_{24}Si_{17}$: C 68.14, H 10.48, N 8.83, Si 12.54. Found: C 68.30, H 10.38, N 8.94, Si 12.25.

G0−SiMe$_2$−CN (15). To a solution of 1-bromo-4-[(dimethylamino)methyl]benzene (1.68 g, 7.85 mmol) in Et_2O (25 mL) was added t-BuLi (19 mL of a 0.7 M solution in pentane, 13.3 mmol) at −78 °C, and the resulting suspension was stirred for 15 min, whereupon G0−SiMe$_2$Cl (0.87 g, 1.52 mmol) in Et_2O (20 mL) was added. After purification by Kugelrohr distillation as described for **3**, a bright yellow, viscous oil was obtained (1.32 g, 1.37 mmol, 90%). ^{1}H NMR (C_6D_6): δ 7.55 (d, 8H, J = 7.9 Hz, Ar−H), 7.44 (d, 8H, J = 7.8 Hz, Ar−H), 3.31 (s, 8H, CH_2N), 2.11 (s, 24H, $N(CH_3)_2$), 1.54−1.42 (m, 8H, $SiCH_2CH_2$−), 0.91−0.82 (m, 8H, −$CH_2CH_2Si(CH_3)_2$), 0.68−0.60 (m, 8H, $SiCH_2CH_2$−), 0.30 (s, 24H, J(Si−H) = 28.9 Hz, $Si(CH_3)_2$. ^{13}C NMR (C_6D_6): δ 140.8, 138.1, 134.0, 128.7 (4 × Ar−C), 64.6 (CH_2N), 45.5 ($N(CH_3)_2$), 21.0, 19.2, 17.6 (3 × CH_2), −2.6 ($Si(CH_3)_2$). FAB-MS m/z 965.8 ($M + H)^+$. Anal. Calcd for $C_{56}H_{96}N_4Si_5$: C 69.64, H 10.02, N 5.80, Si 14.54. Found: C 69.57, H 9.99, N 5.87, Si 14.39.

G1−SiMe$_2$−CN (16). This compound was prepared as described for 3 by using a similar approach. To a solution of 1-bromo-4-[(dimethylamino)methyl]benzene (2.70 g, 12.61 mmol) in Et_2O (35 mL) was added t-BuLi (12 mL of a 1.7 M solution in pentane, 20.4 mmol) at −78 °C, and the resultant suspen-

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sion was stirred for 10 min, whereupon G1−$SiMe_2Cl$ (1.05 g, 0.54 mmol) in Et_2O (30 mL) was added. After workup (Kugelrohr 170−190 °C) a viscous, yellow oil was isolated (1.29 g, 0.41 mmol, 76%). ^1H NMR (C_6D_6): δ 7.57 (d, 24H, J = 7.5 Hz, Ar−H), 7.45 (d, 24H, J = 7.5 Hz, Ar−H), 3.33 (s, 24H, CH_2N), 2.12 (s, 72H, $N(CH_3)_2$), 1.59 (m, 32H, $SiCH_2CH_2-$), 0.97−0.86 (m, 32H, $-CH_2CH_2Si(CH_3)_2$), 0.86−0.75 (m, 32H, $SiCH_2$-CH_2-), 0.34 (s, 72H, $Si(CH_3)_2$). ^{13}C NMR (C_6D_6): δ 140.3, 137.6, 133.5, 128.3 (4 × Ar−C), 64.2 (CH_2N), 45.1 ($N(CH_3)_2$), 20.7, 18.8, 18.3, 18.1, 17.6, 17.2 (6 × CH_2), −2.9 ($Si(CH_3)_2$). MALDI−TOF−MS: m/z 3120.94 (calcd for $(M + H)^+$: 3119.09). Anal. Calcd for $C_{180}H_{312}N_{12}Si_{17}$: C 69.25, H 10.07, N 5.38, Si 15.30. Found: C 69.16, H 10.09, N 5.20, Si 15.22.

G0−$SiMe_2$−NCN−PtCl (17). To a solution of G0−$SiMe_2$−NCN (**13**) (0.71 g, 0.59 mmol) in hexane (40 mL) was added *t*-BuLi (4.0 mL of a 0.65 M solution in pentane, 2.6 mmol). A reddish suspension, which formed immediately, was stirred for 1 h, and the solid was isolated by centrifugation and washed with hexane (40 mL). Then a solution of $PtCl_2(SEt_2)_2$ (1.05 g, 2.36 mmol) in THF (40 mL) was added and the resultant clear, yellow solution stirred for 2 h. The solvent was evaporated in vacuo and the solid extracted with CH_2Cl_2 and filtered through a layer of Celite. The solvent was removed under reduced pressure and the product washed with Et_2O (4 × 30 mL) to yield a cream-colored powder (0.89 g, 0.42 mmol, 71%). ^1H NMR (C_6D_6): δ 7.01 (s, 8H, Ar−H), 3.49 (s, J(Pt−H) = 43.8 Hz, 16H, CH_2N), 2.77 (s, J(Pt−H) = 31.7 Hz, 48 H, $N(CH_3)_2$), 1.70−1.64 (m, 8H, $SiCH_2CH_2-$), 1.11−0.99 (m, 8H, $-CH_2Si(CH_3)_2-$), 0.87−0.82 (m, 8H, $SiCH_2CH_2-$), 0.42 (s, 24 H, $Si(CH_3)_2$). ^{13}C NMR (C_6D_6): d 149.7 (^1J(Pt−C) = 1047 Hz, Ar−C_{ipso}), 143.9 (^3J(Pt−C) = 75.9 Hz, Ar−C_{meta}), 133.0 (Ar−C), 124.2 (^2J(Pt−C) = 35.5 Hz, Ar−C_{ortho}), 77.5 (J(Pt−C) = 60.3 Hz, CH_2N), 54.1 ($N(CH_3)_2$), 21.6, 19.4, 18.1 (3 × CH_2), −2.1 ($Si(CH_3)_2$). FAB-MS: m/z 2111 (Pt_4Cl_4: M^+), 2076 (Pt_4Cl_4: $(M - Cl)^+$), 1882 (Pt_3Cl_3: (M^+)), 1846 (Pt_3Cl_2: $(M - Cl)^+$). Anal. Calcd for 95% platinated $C_{68}H_{120}N_8Si_5Pt_4Cl_4$: C 40.05, H 5.97, N 5.50, Cl 6.37. Found: C 39.84, H 6.00, N 5.34, Cl 5.89.

FAB Mass Spectrometry. The FAB mass spectra were recorded on two different machines: (1) a JEOL JMS SX/SX 102A four-sector mass spectrometer, operated at 10 kV accelerating voltage, equipped with a JEOL MS-FAB 10 D FAB gun operated at a 5 mA emission current, producing a beam of 6 keV xenon atoms; (2) a JEOL JMS AX 505 spectrometer, operated at 3 kV accelerating voltage, equipped with a JEOL MS-FAB 10 D FAB gun operated at a 10 mA emission current, producing a beam of 6 keV xenon. Data acquisition and processing were accomplished using JEOL Complement software. The spectra were obtained from the Analytical Chemical Department of the University of Utrecht.

MALDI-TOF Mass Spectrometry. The MALDI-TOF mass spectra obtained for **14** and **16** were acquired using a Voyager-DE BioSpectrometry Workstation (PerSeptive Biosystems Inc., Framingham, MA) mass spectrometer equipped with a nitrogen laser emitting at 337 nm. The instrument was operated in the linear mode at an accelerating voltage in the range 23 000−25 000 V. External calibration was performed using insulin (bovine). Detection was done by means of a linear detector and a digitizing oscilloscope operating at 500 MHz. Sample solutions with an approximate concentration of 30 mg/mL in THF were prepared. The matrix was 3,5-dihydroxybenzoic acid in THF (36 mg/mL). A 0.2 μL sample of the solution and 0.2 μL of the matrix solution were combined and placed on a golden MALDI target and analyzed after evaporation of the solvents.

Crystal Structure Solution and Refinement for 7. X-ray data were collected on a Enraf-Nonius CAD4T diffractometer (Rotating Anode, graphite monochromator) for a colorless transparent crystal taken from the mother liquor, covered with protective inert oil, and transferred into the cold dinitrogen stream. The structure was solved by direct methods using ShElXS86[16] and refined on F^2 by full-matrix least-squares with ShElXL93.[17] Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. All geometrical calculations and the ORTEP illustration were done with PLATON.[18] Numerical details on the data collection and refinement have been collected in Table 2 (see Results and Discussion section).

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Supporting Information Available: A listing of tables of atomic coordinates, bond lengths and angles, and thermal parameters for **7** (12 pages). See any current masthead page for Internet access instructions.

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