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Carbosilane Molecules with Mono- and Bis(amino)arylmetal End Groups: Structures of $\{NiI[C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}SiMe_3\text{-}4]\}$ and Tetranuclear $\{[CH_2Si(Me)_2C_6H_3(CH_2NMe_2)\text{-}4\text{-}(PdCl)\text{-}3]_2\}_2$

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A set of model compounds have been designed in order to develop useful synthetic routes to novel dendritic carbosilane molecules functionalized with organometallic complexes derived from the monoanionic $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (=NCN) and $[C_6H_4(CH_2NMe_2)\text{-}2]^-$ (=CN) ligands. Selective electrophilic palladation of both $[C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}(SiMe_3)_2\text{-}1,4]$ (**1**) and $[C_6H_4(CH_2NMe_2)\text{-}4\text{-}SiMe_3\text{-}1]$ (**6**) using $Pd(OAc)_2$ afforded, after addition of LiCl, $[PdCl(C_6H_2\{CH_2NMe_2\}_2\text{-}2,6\text{-}SiMe_3\text{-}4)]$ (**2**) and dimeric $[PdCl(C_6H_3\{CH_2NMe_2\}\text{-}2\text{-}SiMe_3\text{-}5)]_2$ (**7**), respectively, in 98% and 84% yield. Lithiation of $[C_6H_3(CH_2NMe_2)_2\text{-}3,5\text{-}SiMe_3\text{-}1]$ followed by transmetalation using 1 equiv of $PtCl_2(SEt_2)_2$ in THF at room temperature yielded the platinated complex $[PtCl(C_6H_2\{CH_2NMe_2\}_2\text{-}2,6\text{-}SiMe_3\text{-}4)]$ (**3**). Reaction of the iodinated analogue of **1**, $[IC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}SiMe_3\text{-}4]$ (**4**), with an excess of $Ni(PPh_3)_4$ in THF at room temperature afforded the nickel complex $[NiI(C_6H_2\{CH_2NMe\}_2\text{-}2,6\text{-}SiMe_3\text{-}4)]$ (**5**). Similar synthetic approaches have also been applied to the (N)CN-substituted carbosilane ligand systems $[CH_2Si(Me)_2C_6H_3(CH_2NMe_2)_2\text{-}3,5]_2$ and $[CH_2Si(Me)_2C_6H_4(CH_2NMe_2)\text{-}4]_2$ to give the bismetalated species $[CH_2Si(Me)_2C_6H_2(CH_2NMe_2)_2\text{-}3,5\text{-}(MX)\text{-}4]_2$ (MX = PdCl (**9**), PtCl (**10**), PdI (**12**)) and $[CH_2Si(Me)_2C_6H_3(CH_2NMe_2)\text{-}4\text{-}(PdCl)\text{-}3]_2$ (**13**) in good yields. The molecular structures of **5** and bispalladated **13** have been determined. The molecular structure of **13** shows this species to be a centrosymmetric dimeric aggregate in the solid state, with the two bis(amino)arylpalladium carbosilane molecules held together via two terminal−terminal chlorine bridging atoms, thus forming a 26-membered macrocyclic ring.

Introduction

The incorporation of metals in dendrimers,[1] either in the skeleton or onto the periphery, may provide an opportunity to generate new macromolecules with interesting catalytic, redox-active, or liquid crystalline properties. In recent years much attention was focused on the synthesis of such materials and led to the preparation of a broad range of metallodendritic species. In many cases, the metals of choice were complexed on the dendrimer surface by suitable donor ligands such as phosphines[2−5] or chelating bipyridines,[6] but only few examples concerned the introduction of metals on the periphery via a direct metal-to-carbon bond.[7−11] Carbosilane dendrimers[12] are well-suited for this purpose because of their relatively easy synthesis and anticipated inertness for common organometallic reagents. In our group the monoanionic $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (=NCN) and $[C_6H_4(CH_2NMe_2)\text{-}2]^-$ (=CN) ligands have

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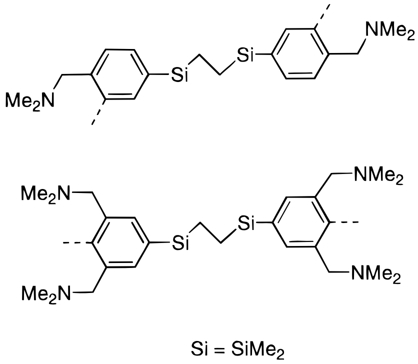

Figure 1. Schematic representation of the carbosilane molecules functionalized with the monoanionic (N)CN ligands.

been studied extensively[13] and several metal complexes were successfully applied as homogeneous catalysts in organic reactions. For instance, the $[NiX\{C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}R\text{-}4\}]$ compounds (X = Cl, Br, I; R = NH_2, MeO, H, Cl, MeC(O)) have proven to be effective catalyst systems in Kharasch addition chemistry[14] and were also immobilized on the surface of carbosilane dendrimers by using a carbamate linker.[11a] Recently we reported on the more facile synthesis of carbosilane molecules functionalized with NCN or CN moieties. These new ligand systems, in which the ligands are directly σ-bonded to the (peripherial) silicon atoms[15] (see Figure 1), were selectively lithiated without any decomposition of the carbosilane backbone.

Therefore, we have extended our studies, as the lithiation of these dendritic ligands could give rise to new and alternative synthetic concepts for the introduction of metal sites in carbosilane dendrimers. Here we present the syntheses of metal species derived from the carbosilanes substituted with CN or NCN ligands (vide supra), which serve as model compounds for their metallodendritic analogues. With the dilithiated ligand systems as the starting point, we have developed synthetic routes for the introduction of d^8-metal sites. This was accomplished via either oxidative addition, C−Si bond activation, or a lithiation/transmetalation sequence. Especially the last procedure provides a unique way for the introduction of σ-bonded metal atoms. Furthermore, we will show further evidence for an intermolecular aggregation between different organometallic end groups in metallodendrimers with CN- and NCN-metal end groups. These latter results will be evaluated and combined with our earlier results in this area.[15]

Results and Discussion

Syntheses and Characterization of Model Compounds. Treatment of 1-trimethylsilyl-3,5-bis[(dimethylamino)methyl]benzene[16] with excess *n*-butyllithium at ambient temperature and subsequently quenching the lithiated derivative in Et_2O with an excess of trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf)[17] afforded after workup the disilylated material 1,4-bis(trimethylsilyl)-2,6-bis[(dimethylamino)methyl]benzene (**1**) as a yellow oil in an almost quantitative yield (96%). Selective C−Si bond cleavage[17] was achieved by reaction of **1** with $Pd(OAc)_2$/LiCl in MeOH at room temperature to yield the palladated compound **2** in 98% yield. The *para*-positioned trimethylsilyl group was unaffected in this latter reaction, showing that direct, regioselective palladation of dendritic analogues of **1** could be feasible. The same selectivity accounts for the direct palladation of 1-trimethylsilyl-4-[(dimethylamino)methyl]benzene (**6**), which was obtained as a colorless liquid in 93% yield by reaction of 1-bromo-4-[(dimethylamino)methyl]benzene with 2 equiv of *tert*-butyllithium in THF at −78 °C followed by a quench reaction of the lithiated species with an excess of trimethylsilyl chloride. Selective cyclopalladation[18] of **6** using 1 equiv of $Pd(OAc)_2$ in MeOH gave the halide-bridged dimer $[PdCl(C_6H_3\{CH_2NMe_2\}\text{-}2\text{-}SiMe_3\text{-}5)]_2$, **7**, in 83% yield as a mixture of *cis*- and *trans*-isomers. Reaction of **7** with an excess of pyridine rapidly leads to the formation of the mononuclear pyridine adduct $[PdCl(C_6H_3\{CH_2NMe_2\}\text{-}2\text{-}SiMe_3\text{-}5)(C_5H_5N)]$, **8**, which was obtained quantitatively as a white solid (95%). The platinated analogue $[PtCl(C_6H_2\{CH_2NMe_2\}_2\text{-}2,6\text{-}SiMe_3\text{-}4]$ (**3**) was prepared in 61% yield by lithiation of 1-trimethylsilyl-3,5-bis[(dimethylamino)methyl]benzene with 1 equiv of *n*-BuLi in pentane followed by a transmetalation reaction in THF using a stoichiometric amount of $PtCl_2(SEt_2)_2$ (Scheme 1).

Earlier attempts to *ortho*-halogenate NCN derivatives quantitatively by reaction of the corresponding *ortho*-lithiated species[19] with halide sources such as 1,2-dibromoethane or molecular Br_2[20] failed and led to only partially halogenated materials. However, we found that lithiation of 1-trimethylsilyl-3,5-bis[(dimethylamino)-methyl]benzene with an excess of *n*-butyllithium in hexane followed by "titration" of the lithiated species with molecular I_2 dissolved in Et_2O selectively gave the iodine compound $[IC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}SiMe_3\text{-}4]$ (**4**). Evidence for a full iodination reaction was provided by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, GC−MS, and microanalysis. The iodinated compound **4** exhibits a characteristic $^{13}C\{^1H\}$ NMR upfield-shifted carbon resonance at 109.5 ppm. Oxidative addition of $Ni(PPh_3)_4$ to **4** in THF at room temperature gave the nickel species $[NiI(C_6H_2\{CH_2NMe_2\}_2\text{-}2,6\text{-}SiMe_3\text{-}4)]$ (**5**) (Scheme 1, see also ref 14b). Complex **5** is reasonably soluble in Et_2O at room temperature, and purification of **5** was accomplished by repeated crystallizations from Et_2O at −20 °C; as a consequence, the yield of **5** (35%) was low.

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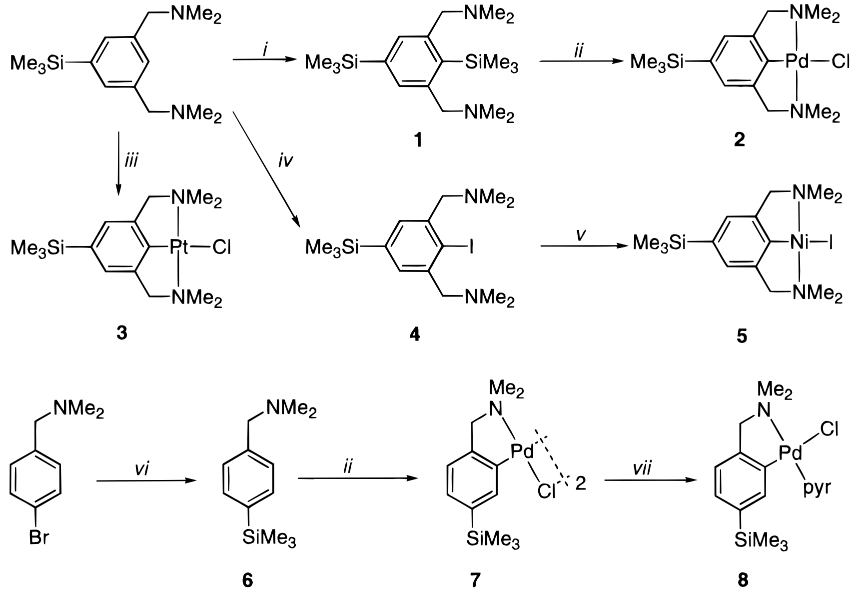
Scheme 1. Reagents and Conditions: (i) *t*-BuLi, Pentane; Me$_3$SiOTf, Et$_2$O; (ii) PdOAc$_2$, MeOH; Excess LiCl; (iii) *t*-BuLi, Pentane; PtCl$_2$(SEt$_2$)$_2$, THF; (iv) *t*-BuLi, Pentane; I$_2$, Et$_2$O; (v) Ni(PPh$_3$)$_4$, THF; (vi) 2 equiv *t*-BuLi, Et$_2$O, −78 °C; Me$_3$SiCl; (vii) Excess Pyridine, CH$_2$Cl$_2$



In general the nickel(II) center in this type of NCN−NiX complexes is particularly sensitive for oxidation, and the corresponding paramagnetic Ni(III) complexes give rise to severe line-broadening in their NMR spectra. Consequently, NMR solutions of **5** were prepared in an inert atmosphere, while possible line-broadening was reduced by bubbling CO(g) (reduction of Ni(III) to Ni(II)) through the NMR sample tube.

All discussed reactions (vide supra) gave nearly quantitative conversions, and compounds **1**−**8** were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, GC−MS or FAB mass spectrometry, elemental microanalysis, and in the case of **5**, X-ray analysis. The synthetic procedures described for these mononuclear compounds combined with their spectroscopic data provide a useful basis for the preparation of their dimetalated carbosilane analogues (vide infra).

Molecular Structure of 5. The molecular geometry of **5**, as a model for the NCN−metal species present at the periphery of carbosilane metallodendrimers, was established by means of X-ray crystal structure determination (see Experimental Section). The crystal structure of **5** comprises the packing of eight molecules in the unit cell. The asymmetric unit contains two crystallographically independent molecules A and B which are chemically identical, but which differ slightly but not significantly in structure. An ORTEP drawing of one of these molecules (A) is depicted in Figure 2 (for B: see Supporting Information and values between [ ] in the text, vide infra). Selected bond lengths and angles are listed in Table 1.

In **5** each nickel atom is coordinated by two nitrogen donor atoms and C$_{ipso}$ of the *para*-substituted, monoanionic η^3-*N,C,N*-bonded aryldiamine ligand, while an iodine atom trans to C$_{ipso}$ completes the ligand array. The nickel atoms in residues A and B are bonded in an approximately square-planar manner. Distortions from this ideal geometry are found for both residues. For **5** the angles N(1)−Ni(1)−N(2) and I(1)−Ni(1)−C(1) are 165.6 (2)° [165.4(2)°] and 177.0 (2)° [176.3(2)°]. As a result of these structural features, the nickel center is somewhat lifted from the plane defined by the aromatic ring, which is a distortion commonly found for d^8-metal−NCN complexes.[12,17,21]

Table 1. Selected Bond Distances (Å) and Angles (deg) of the Organonickel(II) Complex 5 (Residue A) with esd's in Parentheses

Bond Distances			
Ni(1)−C(1)	1.816(8)	Ni(1)−N(1)	1.989(6)
Ni(1)−N(2)	1.990(6)	Ni(1)−I(1)	2.5943(10)
C(4)−Si(1)	1.897(9)	C(13)−Si(1)	1.826(11)
C(14)−Si(1)	1.914(14)	C(15)−Si(1)	1.800(11)
Bond Angles			
I(1)−Ni(1)−C(1)	177.0(2)	C(1)−Ni(1)−N(1)	83.8(3)
C(1)−Ni(1)−N(2)	81.9(3)	N(1)−Ni(1)−N(2)	165.6(2)
Dihedral Angles			
Ni(1)−C(1)−C(2)−C(7)	−5.0(9)	Ni(1)−C(1)−C(6)−C(8)	−1.5(9)
C(1)−C(2)−C(7)−N(1)	21.1(9)	C(1)−C(6)−C(8)−N(2)	20.9(9)
C(6)−C(5)−C(4)−Si(1)	179.5(6)	C(2)−C(3)−C(4)−Si(1)	178.9(7)
C(1)−C(2)−C(3)−C(4)	1.8(12)	C(2)−C(3)−C(4)−C(5)	−2.0(13)
C(3)−C(4)−C(5)−C(6)	0.5(14)		

Syntheses of Bismetalated Carbosilanes. The syntheses of the ligand systems [CH$_2$Si(Me)$_2$C$_6$H$_4$(CH$_2$NMe$_2$)-4]$_2$ and [CH$_2$Si(Me)$_2$C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-3,5]$_2$ have been described elsewhere.[15] The incorporation of metal atoms was achieved using synthetic approaches similar to those described for the mononuclear compounds (vide supra).

The NCN moieties of [CH$_2$Si(Me)$_2$C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-3,5]$_2$ were functionalized between the two nitrogen donor arms (i.e., the 4-position in these carbosilane molecules) by using the dilithiated precursor [CH$_2$Si(Me)$_2$C$_6$H$_2$(CH$_2$NMe$_2$)$_2$-3,5-Li-4]$_2$,[15] which proved to be an excellent starting material for the introduction of

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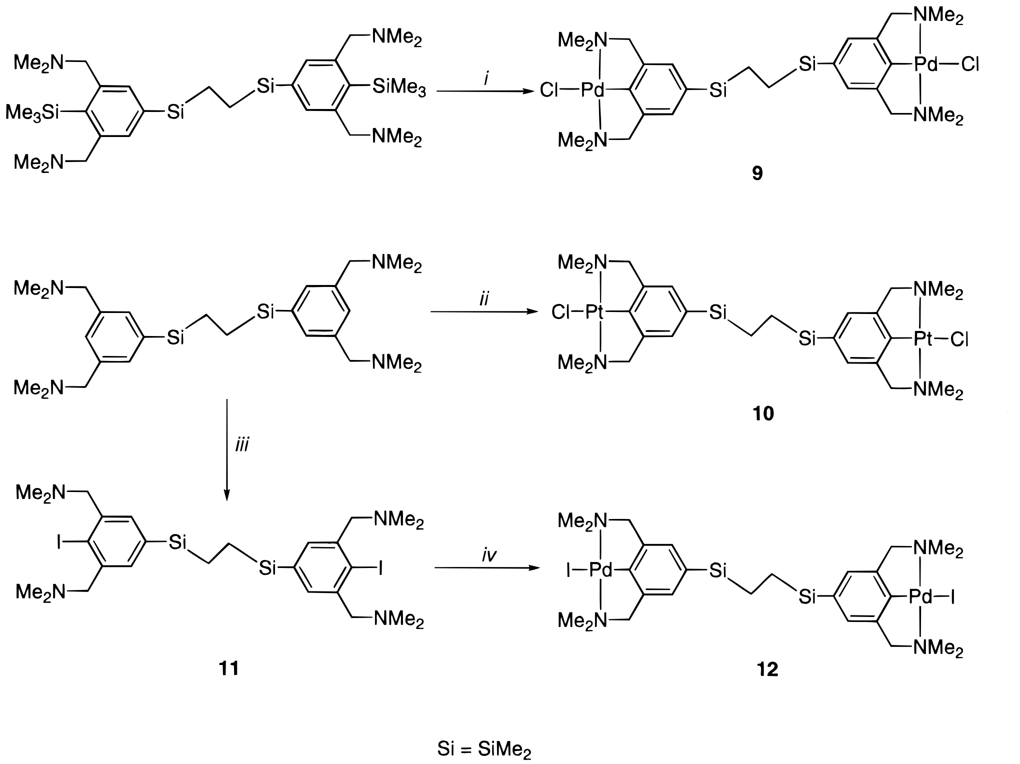
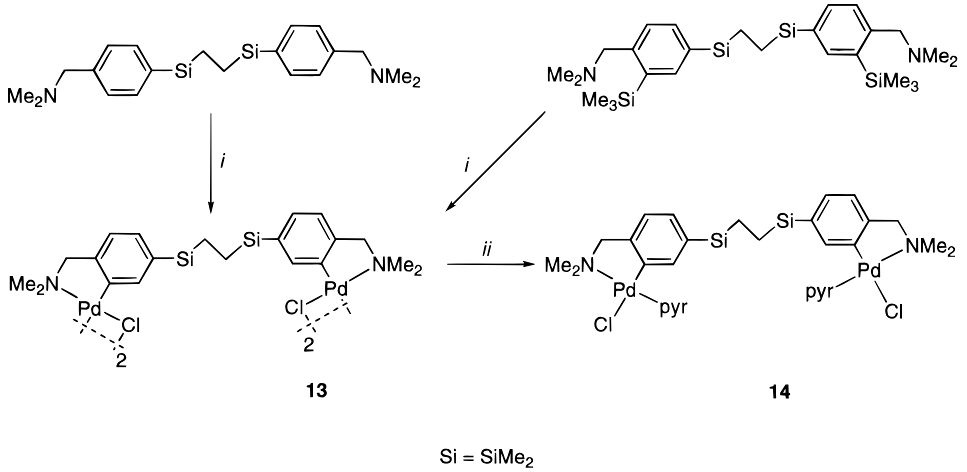
Scheme 2. Reagents and Conditions: (i) 2 equiv $PdOAc_2$, MeOH; Excess LiCl; (ii) 2 equiv *t*-BuLi, Pentane; 2 equiv $PtCl_2(SEt_2)_2$, THF; (iii) 2 equiv *t*-BuLi, Pentane; I_2, Et_2O; (iv) 2 equiv $Pd(dba)_2$, Benzene



Scheme 3. Reagents and Conditions: (i) 2 equiv $PdOAc_2$, MeOH; Excess LiCl; (ii) Excess Pyridine, CH_2Cl_2



metals employing the different approaches as illustrated in Scheme 1. Reaction of this dilithiated precursor with 2 equiv of $PtCl_2(SEt_2)_2$ affords the diplatinated species $[CH_2Si(Me)_2C_6H_2(CH_2NMe_2)_2\text{-}3,5\text{-}(PtCl)\text{-}4]_2$ (**10**) in 93% yield. To our knowledge, this is the first example of using a (multi)lithiated carbosilane for the introduction of metals and demonstrates a convenient, direct synthetic pathway to metallocarbosilane dendrimers. Reacting the dilithio compound with I_2 as described for **4** affords the diiodo compound $[CH_2Si(Me)_2C_6H_2(CH_2NMe_2)_2\text{-}3,5\text{-}I\text{-}4]_2$, **11**.

The direct metalation routes employed for the preparation of the mononuclear compounds proved also be applicable in the synthesis of their bismetallic analogues. The bispalladium chloride derivative **9** (Scheme 2) was prepared in 70% yield by a 2:1 molar reaction of $Pd(OAc)_2$ and disilylated $[CH_2Si(Me)_2C_6H_2(CH_2NMe_2)_2\text{-}3,5\text{-}SiMe_3\text{-}4]_2$ in MeOH, whereas the bispalladium iodide compound **12** (yield 71%) was obtained by reaction of the diiodide **11** with a slight excess of $Pd(dba)_2$ (dba = dibenzylideneacetone) in benzene at room temperature (Scheme 2).

Cyclopalladation of either $[CH_2Si(Me)_2C_6H_4(CH_2NMe_2)\text{-}4]_2$[15] or the disilylated precursor $[CH_2Si(Me)_2C_6H_3(CH_2NMe_2)\text{-}4\text{-}SiMe_3\text{-}3]_2$[15] with 2 equiv of $Pd(OAc)_2$ in MeOH was successfully carried out and gave the palladated derivative, after treatment with LiCl, $[CH_2Si(Me)_2C_6H_3(CH_2NMe_2)\text{-}4\text{-}(PdCl)\text{-}3]_2$ (**13**) (see Scheme 3) as a shiny, orange solid. Although in principle the two palladation reactions differ from each other (C−H vs C−Si bond activation), the crude yields (86 and 98%, respectively) are roughly the same as well as the selectivities (i.e., isomer ratio, vide infra) observed with ^1H NMR spectroscopy.

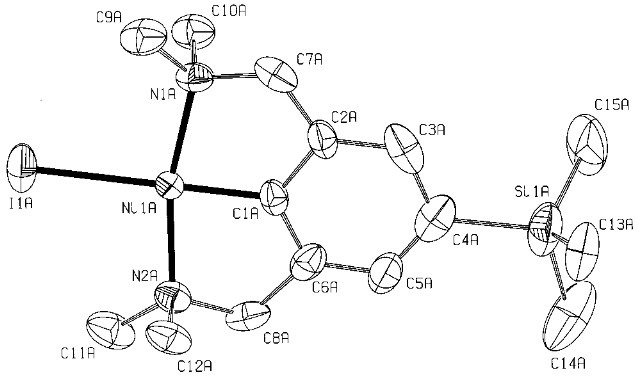


Figure 2. Displacement ellipsoid plot (ORTEP, 50% probability) of one of the two crystallographically independent molecules of $[NiI(C_6H_2\{CH_2NMe_2\}_2\text{-}2,6\text{-}SiMe_3\text{-}4)]$ (**5**) in the solid state together with the adopted numbering scheme. For a complete figure, see Supporting Information. Hydrogen atoms have been omitted for clarity.

The proton NMR spectrum of crude **13** recorded in $CDCl_3$ shows the presence of more than one species, as illustrated by the presence of several sets of signals. When excess pyridine is added, the spectrum collapses into *one* new pattern as a result of the chlorine bridge cleavage to form the dinuclear, bispyridine complex $[CH_2Si(Me)_2C_6H_3(CH_2NMe_2)\text{-}4\text{-}(PdCl\{C_6H_5N\})\text{-}3]_2$ (**14**) (Scheme 3), indicating that complete palladation of the starting material had occurred. Cooling down a saturated solution of **13** in CH_2Cl_2 at −20 °C afforded yellow block-shaped crystals which separated from the solution. The X-ray crystal structure of **13** confirmed its dimeric structure (vide infra) and unambiguously showed the presence of CH_2Cl_2 in the crystal lattice, which is in line with the microanalyses. Upon standing, this solvent slowly evaporates to give the solvent-free complex.

Structure of 13 in the Solid State and in Solution. An X-ray crystal structure determination revealed the structure of **13** to be dimeric (i.e., tetranuclear) in the solid state with the chlorine atoms acting as bridging ligands (see Figure 3). Relevant bond distances and angles are summarized in Table 2. The coordination plane around each palladium center is approximately square planar with interatomic distances to carbon, nitrogen, and both the chlorine atoms (see Table 2) comparable to those found for similar complexes.[22] The difference in the Pd−Cl bond lengths (see Table 2) can be explained by the *trans* influence of a tertiary N-donor atom vs an (aryl)C_{ipso}. This causes a weakening of the Pd−Cl bond *trans* to the Pd−C(σ) bond.

Moreover, the structure shows exclusively the *cis,cis*-isomer,[23] which indicates preferential crystallization of one of the three possible geometrical isomers. It is interesting to compare these results with those of, for example, Barr et al.,[22] who studied the molecular structures of dinuclear $[PdCl(C_6H_3\{CH_2NMe_2\}\text{-}2\text{-}MeO\text{-}y)]_2$ ($y = 3$, 4, or 5) by X-ray crystallography and found in all cases exclusively the *trans*-isomers. Most probably vicinal interactions in the carbosilane backbone of the dimeric structures of **13** affect the conformational energies of the *cis,cis*-, *cis,trans*-, and *trans,trans*-isomer in such a way that the *cis,cis*-isomer is the most stable one.

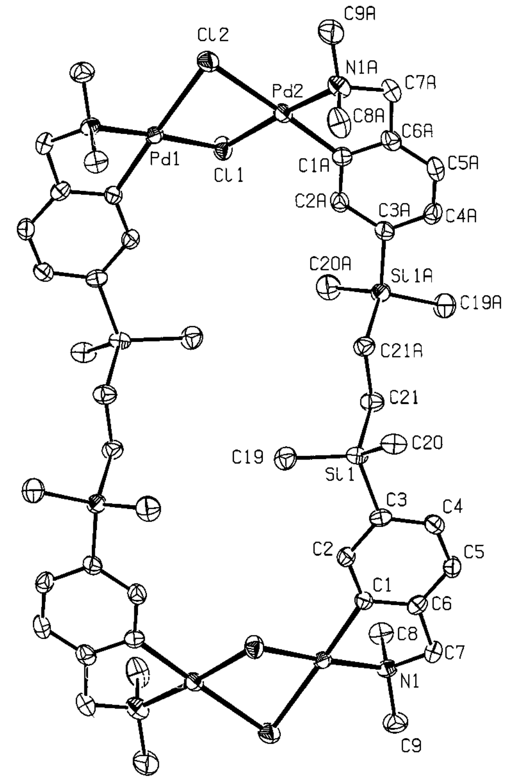


Figure 3. Displacement ellipsoid plot (ORTEP, 50% probability) of the molecular structure of complex **13** together with the adopted numbering scheme. Solvent molecules and hydrogen atoms have been omitted for clarity.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) with esd's in Parentheses for the Metal Carbosilane Complex 13

Bond Distances			
Pd(1)−Cl(1)	2.3154(15)	Pd(2)−Cl(1)	2.3105(14)
Pd(1)−Cl(2)	2.4747(14)	Pd(2)−Cl(2)	2.4732(15)
Pd(1)−C(1)	1.971(5)	Pd(1)−N(1)	2.075(5)
Pd(2)−C(1A)	1.977(5)	Pd(2)−N(1A)	2.072(5)

Bond Angles			
Cl(1)−Pd(1)−Cl(2)	85.54(5)	Cl(2)−Pd(1)−N(1)	98.52(11)
Cl(1)−Pd(1)−N(1)	175.76(10)	Cl(2)−Pd(1)−C(1)	178.33(12)
Cl(1)−Pd(1)−C(1)	94.09(16)	N(1)−Pd(1)−C(1)	81.89(19)

Dihedral Angles	
Cl(2)−Pd(1)−Cl(1)−Pd(2)	27.66(5)
C(1)−Pd(1)−Cl(1)−Pd(2)	−150.71(13)
Cl(1)−Pd(1)−Cl(2)−Pd(2)	−25.83(5)
Cl(1)−Pd(1)−C(1)−C(2)	23.2(4)
Cl(1)−Pd(1)−C(1)−C(6)	−158.4(3)
N(1)−Pd(1)−Cl(2)−Pd(2)	155.41(12)
Si(1)−C(21)−C(21A)−Si(1A)	178.9(2)

NMR Spectroscopy of the Novel Carbosilane Compounds. An interesting feature of these novel end group functionalized carbosilane compounds is that the metalated (N)CN moieties as well as the $SiMe_2$ and methylene protons of the carbosilane backbone give rise to single resonance patterns on the NMR time scale at room temperature, consistent with only one type of metal environment. As to be expected, compared to the mononuclear complexes (see Scheme 1), similar chemical shifts are found with respect to the dimetallocarbosilanes (Schemes 2 and 3). In general, the course of

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[22] The prefix *cis* refers to the relative positions of the NMe_2 groupings around the Pd_2Cl_2 unit.

[23] Barr, N.; Dyke, S. F.; Smith, G.; Kennard, C. H. L.; McKee, V. *J. Organomet. Chem.* **1985**, *288*, 109.

Table 3. Selected ^{1}H NMR Data for the Mononuclear Compounds and Bimetallic Carbosilanes

compound	X	SiMe	CH_2N	NMe_2	ArH
1^c	$SiMe_3$	0.29	3.56	2.03	7.67
		0.52			
2^b	PdCl	0.22	4.00	2.94	6.90
3^b	PtCl	0.22	3.08	4.03	6.94
4^c	I	0.26	3.55	2.16	7.66
5^c	NiI	0.29	3.07	2.50	6.73
7^b	PdCl	0.23	3.91	2.85	7.33^d
				2.87	7.42^d
9^b	PdCl	0.19	4.00	2.95	6.86
10^b	PtCl	0.20	4.03	3.09	6.90
11^c	I	0.28	3.53	2.15	7.64
12^c	PdI	0.36	3.31	2.67	6.87
13^b	PdCl	0.19	3.92	2.86	7.42^d
		0.21	3.96	2.96	7.63^d

[a] All signals are singlet resonances at room temperature unless otherwise stated and are given in ppm vs TMS as an external standard. [b] Recorded in $CDCl_3$. [c] Recorded in C_6D_6. [d] Aromatic *ortho*-hydrogen.

metalation can easily be monitored as the resonances of the aromatic protons of the ligand systems (7.6−7.7 ppm) and CH_2N moieties shift to higher field (6.8−6.9 ppm) (Table 3) together with a characteristic downfield shift for the signal corresponding to the NMe_2 fragments.

When *crystalline* **13** is dissolved in $CDCl_3$ at room temperature, the ^{1}H NMR spectrum of a mixture of two species in a nearly 1:3 ratio is obtained. Variable-temperature ^{1}H NMR measurements of **13** in $CDCl_3$ show an interesting interconversion between the two species. At low temperature (208 K), this ratio becomes ca. 1:8, while at high temperature (335 K) the ratio becomes close to 1:1. Upon mixing crystalline **13** and frozen $CDCl_3$ directly followed by analysis by ^{1}H NMR spectroscopy at −65 °C, mainly the resonance pattern belonging to one of these species is observed, while the resonance pattern belonging to the other species is only present in trace amounts. From this observation it may be concluded that the predominant resonance pattern belongs to the *cis*,*cis*-isomer as found in the solid state (vide supra).

There are a few possibilities that can explain the presence of two sets of resonances found for **13** in solution. The aggregation process to afford *cis*,*cis*-**13** probably proceeds via several equilibria as illustrated in Figure 4. Starting from two monomeric dipalladated molecules **13** (A in Figure 4), the dimeric species is generated in two steps. At first, one set of chlorine bridges (either *cis* or *trans*, A_2^c and A_2^t, respectively) is formed, after which the second set of chlorine bridges results in the dimeric molecules $A_4^{c,c}$, $A_4^{t,c}$, and $A_4^{t,t}$. Also, the formation of higher oligomers ($[A]_n$) via similar equilibria could be possible.

A separate, more detailed study is currently carried out concerning the aggregational behavior of **13** and related compounds in solution and in the solid state.

Molecular modeling of dimeric **13** using CAChe software (at the MM2 level) shows that within the dimeric $A_4^{t,c}$ and $A_4^{t,t}$ molecules the conformation of the carbosilane backbone is more strained as compared with the conformation of this backbone present in the $A_4^{c,c}$ isomer. Of the $A_4^{t,c}$ and $A_4^{t,t}$ isomers, the conformation of the carbosilane backbone in the latter is the most strained. This supports our findings in the crystallographic studies carried out for **13**.

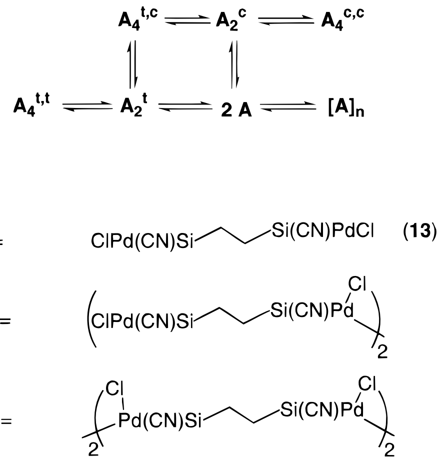

Figure 4. Possible aggregation modes and isomeric forms for the (CN)PdCl-dimeric units in the dipalladium carbosilane compound **13**.

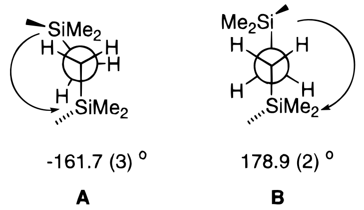

Figure 5. Newman projections along the C−*C* axis in the carbosilane backbone of dilithiated $[CH_2Si(Me)_2C_6H_3(CH_2NMe_2)\text{-}4]_2$ and **13**.

Due to the low solubility of **13** in organic solvents ($CHCl_3$, THF, benzene) suitable for colligative measurements, analysis of the dimer (A_4) vs polymeric $(A)_n$ aggregate formation by molecular weight determination (cryoscopy) was hampered. FAB-MS spectroscopic analysis of **13** (direct inlet in a *m*-NBA matrix) showed the presence of both the monomeric unit $(M - Cl)^+$ (*m*/*z* 659) and the dimeric units M_2^+ and $(M_2 - Cl)^+$ (*m*/*z* 1388 and 1353, respectively) with isotope patterns consistent with their calculated ones. Higher oligomers could not be detected.

The flexible behavior of the carbosilane backbone used in this work (viz., $Me_2SiCH_2CH_2SiMe_2$) was earlier illustrated by the solid-state structure of dimeric $\{[CH_2Si(Me)_2C_6H_3(CH_2NMe_2)\text{-}4\text{-}Li\text{-}3]_2\}_2$,[15] in which the dihedral angle Si−C−C−Si in the alkanedisilyl skeleton is −161.7(3)°, resulting in a distorted *anti* conformation (see Figure 5, A). In this way, the lithiated ligands of the two monomeric units are brought in close approximity to each other to form a stable Li_4-tetrahedron, which is regarded as the main driving force in the formation of this tetralithio aggregate. The carbosilane backbone in the solid-state structure of **13**, however, shows an almost ideal conformation reflected in the dihedral angle between the bulky Si substituents, Si(1)−C(21)−C(21A)−Si(1A), of 178.9(2)° (Figure 5, B).

Concluding Remarks

This investigation has led to the isolation and characterization of novel bimetallic compounds derived from carbosilane molecules functionalized with monoanionic

CN or NCN end groups. We have successfully demonstrated that the use of these dilithiated carbosilanes provides new synthetic approaches to (catalytically active) metal-containing carbosilane dendrimers. In addition we can state that the carbosilane backbone used in this work exhibits a flexible, conformational behavior governed by the aggregation of the organometallic end groups. A further study toward possible aggregation between different end groups in metallodendritic species will be carried out. In this respect, it is interesting to see that the use of the $SiC_6H_3(CH_2NMe_2)$-4-(PdCl)-3 end groups in **13** leads to the formation of a stable 26-membered macromolecular ring structure. Future work will also be focused on both the application of the presented synthetic concepts in the generation of metal-centered organosilicon dendrimers and their utility as homogeneous catalysts.

Experimental Section

General. All sensitive, organometallic manupilations 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 precursor materials 1-bromo-3,5-[(dimethylamino)methyl]benzene, 1-bromo-[(dimethylamino)methyl]-benzene, 1-trimethylsilyl-3,5-[(dimethylaminomethyl)]benzene,[16] and the carbosilanes $[CH_2Si(Me)_2C_6H_3(CH_2NMe_2)_2\text{-}3,5]_2$, $[CH_2Si(Me)_2C_6H_2(CH_2NMe_2)_2\text{-}3,5\text{-}SiMe_3\text{-}4]_2$, $[CH_2Si(Me)_2C_6H_4(CH_2NMe_2)\text{-}4]_2$, and $[CH_2Si(Me)_2C_6H_3(CH_2NMe_2)\text{-}4\text{-}SiMe_3\text{-}3]_2$[15] were prepared according to previously reported procedures. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC200/AC300 MHz or a Varian Inova 300 MHz spectrometer. Chemical shifts are given in ppm using TMS as an external standard. Melting points are uncorrected. FAB-MS 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. Elemental analyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

[$C_6H_2(CH_2NMe_2)_2$-2,6-$(SiMe_3)_2$-1,4] (1). *n*-BuLi (4 mL, 1.6 M solution in pentane, 6.4 mmol) was added to a solution of 1-trimethylsilyl-3,5-bis[(dimethylamino)methyl]benzene (1.63 g, 6.16 mmol) in pentane (25 mL) at room temperature. The solution was stirred for 18 h, and then Me_3SiOTf (2.2 mL, 11.4 mmol) was added. The solution decolorized immediately, and after 25 min of additional stirring, all volatiles were removed in vacuo. Pentane (50 mL) and NaOH pellets were added (to pH 14), and the organic layer was separated. The water layer was extracted with pentane (2 × 50 mL), the combined organic layers were dried on K_2CO_3 and filtered, and the filtrate was evaporated to dryness, affording a clear yellow oil (1.99 g, 5.91 mmol, 96%). ^1H NMR (C_6H_6): δ 7.67 (s, 2H, Ar−H), 3.56 (s, 4H, Ar−CH_2), 2.03 (s, 12H, $N(CH_3)_2$), 0.52 (s, 9H, $Si(CH_3)_3$), 0.29 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6H_6): δ 146.1 (Ar−C), 140.3, 139.7 (2 × Ar−C−Si), 134.1 (Ar−C), 66.2 (Ar−CH_2), 45.1 ($N(CH_3)_2$), 3.4 ($Si(CH_3)_3$), −1.0 ($Si(CH_3)_3$). GC−MS: *m/z* 322 $(M - CH_3)^+$. Anal. Calcd for $C_{18}H_{36}N_2Si_2$: C 64.21, H 10.78, N 8.32, Si 16.69. Found: C 64.08, H 10.82, N 8.42, Si 16.55.

[$PdCl(C_6H_2\{CH_2NMe_2\}_2$-2,6-$(SiMe_3)$-4)] (2). Bissilylated **1** (0.53 g, 1.57 mmol) in MeOH (30 mL) was treated with $Pd(OAc)_2$ (0.35 g, 1.56 mmol). The orange solution was stirred for 1 h, and subsequently LiCl (0.14 g, 3.30 mmol) was added, upon which the color of the solution changed to green-yellow. The solvent was removed in vacuo, and the solid residue was extracted with CH_2Cl_2 (100 mL). The organic layer was washed with H_2O (3 × 50 mL) and dried on $MgSO_4$. After filtration and removal of all volatiles under reduced pressure, a salmon-colored solid was isolated (0.63 g, 1.55 mmol, 98%). White needles were obtained by crystallization of the product in CH_2Cl_2/Et_2O. ^1H NMR ($CDCl_3$): δ 6.90 (s, 2H, Ar−H), 4.00 (s, 4H, Ar−CH_2), 2.94 (s, 12H, $N(CH_3)_2$), 0.22 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 158.1 (C_{ipso}), 144.7 (Ar−C), 136.0 (Ar−C−Si), 124.4 (Ar−C), 74.8 (Ar−CH_2), 53.1 ($N(CH_3)_2$), −0.9 ($Si(CH_3)_2$). Anal. Calcd for $C_{17}H_{27}N_2SiPdCl$: C 44.45, H 6.71, N 6.91. Found: C 44.32, H 6.65, N 7.04.

[$PtCl(C_6H_2\{CH_2NMe_2\}_2$-2,6-$(SiMe_3)$-4)] (3). To a solution of 1-(trimethylsilyl)-3,5-bis[(dimethylamino)methyl]benzene (0.47 g, 1.78 mmol) in pentane (25 mL) was added *n*-BuLi (1.2 mL of a 1.4 M solution in pentane, 1.7 mmol) at room temperature. After stirring the reaction mixture for 16 h, the solvent was removed in vacuo, and $PtCl_2(SEt_2)_2$ (0.81 g, 1.81 mmol) in THF (30 mL) was added. The resulting yellow to brown solution was stirred for 1 h and subsequently the solvent evacuated under reduced pressure. The solid residue was washed with Et_2O (2 × 40 mL) and then extracted with CH_2Cl_2 (60 mL), filtered through Celite, and concentrated to afford a cream-colored powder (0.54 g, 1.09 mmol, 61%). Analytically pure **3** was obtained by crystallization in CH_2Cl_2/Et_2O. ^1H NMR ($CDCl_3$): δ 6.94 (s, 2H, Ar−H), 4.03 (s, 4H, $J(Pt-H) = 46.0$ Hz, Ar−CH_2), 2.94 (s, 12H, $J(Pt-H) = 37.9$ Hz, $N(CH_3)_2$), 0.22 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.6 (C_{ipso}), 143.1 (Ar−C), 134.2 (Ar−C−Si), 123.8 (Ar−C, $^2J(Pt-C) = 34.6$ Hz), 77.7 (Ar−CH_2, $^2J(Pt-C) = 65.9$ Hz), 54.4 ($N(CH_3)_2$), −0.9 ($Si(CH_3)_2$, $^1J(Si-C) = 136$ Hz). Anal. Calcd for $C_{17}H_{27}N_2SiPtCl$: C 36.47, H 5.51, N 5.67, Si 5.69. Found: C 36.49, H 5.61, N 5.60, Si 5.66.

[$IC_6H_2(CH_2NMe_2)_2$-2,6-$(SiMe_3)$-4] (4). *t*-BuLi (2.5 mL of a 1.5 M solution in pentane, 3.8 mmol) was added to a solution of 1-trimethylsilyl-3,5-bis[(dimethylamino)methyl]benzene (0.70 g, 2.65 mmol) in pentane (25 mL) at room temperature. The solution was stirred for 18 h, and then the lithiated material was titrated with an excess of I_2 (1.21 g, 4.77 mmol) in Et_2O (30 mL) until the color of the solution turned dark red-brown. Then H_2O (30 mL) and Na_2SO_3 were added, and the mixture was stirred until decolorization was almost complete. The organic layer was separated, and the H_2O was extracted with hexane (2 × 40 mL). The combined organic layers were dried on K_2CO_3, filtered, and concentrated under reduced pressure. The slightly yellow viscous oil that was obtained solifidied upon standing (0.88 g, 2.25 mmol, 85%). ^1H NMR (C_6D_6): δ 7.66 (s, 2H, Ar−H), 3.55 (s, 4H, CH_2N), 2.16 (s, 12H, $N(CH_3)_2$), 0.26 (s, 9H, $Si(CH_3)_3$, $J = 6.7$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 141.7 (Ar−C), 139.2 (Ar−C−Si), 134.2 (Ar−C), 109.5 (Ar−C−I), 69.5 (Ar−CH_2), 45.5 ($N(CH_3)_2$), −1.0 ($Si(CH_3)_2$). GC−MS: *m/z* 263 $(M - I)^+$. Anal. Calcd for $C_{15}H_{27}N_2SiI$: C 46.15, H 6.97, N 7.18, Si 7.20. Found: C 46.08, H 7.06, N 7.09, Si 7.29.

[$NiI(C_6H_2\{CH_2NMe_2\}$-2,6-$(SiMe_3)$-4)] (5). To a solution of **4** (0.27 g, 0.69 mmol) in THF (30 mL) was added $Ni(PPh_3)_4$ (1.14 g, 1.03 mmol) in THF (20 mL). The brown solution was stirred for 18 h at room temperature. ^1H NMR spectroscopy showed at this stage that the conversion of **4** into **5** was complete. The solvent was removed in vacuo, and the crude product was extracted with Et_2O (2 × 25 mL) was added. Colloidal Ni^0 that was formed during the reaction was centrifuged off. Then the combined Et_2O layers were cooled to −20 °C to afford dark orange to red, needle-shaped crystals (0.11 g, 0.24 mmol, 35%). ^1H NMR (C_6D_6): δ 6.73 (s, 2H, Ar−H), 3.07 (s, 4H, CH_2N), 2.50 (s, 12H, $N(CH_3)_2$), 0.29 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 155.7 (C_{ipso}), 147.1 (Ar−C), 136.1 (Ar−C−Si), 123.6 (Ar−C), 72.8 (Ar−CH_2), 53.2 ($N(CH_3)_2$), −0.7 ($Si(CH_3)_2$). FAB-MS: *m*/*z* 447.9 (M^+), 321.0 $(M - I)^+$. Anal. Calcd for $C_{15}H_{27}N_2SiNiI$: C 40.12, H 6.06, N 6.24, Si 6.25. Found: C 39.86, H 6.10, N 6.18, Si 6.31.

[$C_6H_4(CH_2NMe_2)$-1-($SiMe_3$)-4] (6). 1-Bromo-4-bis[(dimethylamino)methyl]benzene (4.43 g, 20.7 mmol) was dissolved in THF (30 mL) and subsequently cooled to −78 °C. Then *t*-BuLi (42 mL of a 1.5 M solution in pentane, 63 mmol) was slowly added. The clear orange solution was stirred for 10 min, after which an excess of trimethylsilyl chloride (10 mL, 8.6 g, 79 mmol) was added, affording a clear colorless mixture. The solution was allowed to reach room temperature, upon which a white solid precipitated. The suspension was stirred for an additional 45 min. HCl (4 M) was added until pH 1, and the organic layer was separated. The H_2O layer was extracted with Et_2O (2 × 100 mL), and then NaOH (4 M) was added until pH 14. The H_2O layer was extracted with Et_2O (2 × 100 mL), and the combined organic layers were dried on K_2CO_3 and filtered. The filtrate was concentrated in vacuo, and after short-path distillation of the crude product a clear, colorless liquid was isolated (4.00 g, 19.3 mmol, 93%). ^1H NMR (C_6D_6): δ 7.50 (d, 2H, Ar−H, *J* = 7.9 Hz), 7.41 (d, 2H, ArH, *J* = 7.9 Hz), 3.30 (s, 2H, CH_2N), 2.10 (s, 6H, $N(CH_3)_2$), 0.22 (s, 9H, $Si(CH_3)_3$, *J* = 6.56 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 140.7, 138.7, 133.7, 128.7 (4 × Ar−C), 64.6 (Ar−CH_2), 45.5 ($N(CH_3)_2$), −1.0 ($Si(CH_3)_2$). GC−MS: *m*/*z* 207 (M^+). Anal. Calcd for $C_{12}H_{21}NSi$: C 69.50, H 10.21, N 6.75, Si 13.54. Found: C 69.38, H 10.29, N 6.65, Si 13.64.

[PdCl($C_6H_3\{CH_2NMe_2\}$-2-($SiMe_3$)-5)]$_2$ (7). To a solution of **6** (0.74 g, 3.57 mmol) in MeOH (20 mL) was added $Pd(OAc)_2$ (0.81 g, 3.61 mmol), and the initial red suspension was stirred for 18 h. Then excess LiCl (0.26 g, 6.13 mmol) was added to the solution, and almost immediately a green suspension was obtained. After stirring the mixture for 1 h, the solvent was removed by decantation and the solid residue washed with MeOH (2 × 25 mL). After drying under reduced pressure a green solid was obtained (1.03 g, 2.96 mmol, 83%). Analytically pure **7** was obtained by slow diffusion of Et_2O into a concentrated solution of the product in CH_2Cl_2 affording yellow-green plate-shaped crystals. ^1H NMR ($CDCl_3$, mixture of isomers): δ 7.42 (s, 2H, Ar−H_{ortho}, major isomer), 7.33 (s, 2H, Ar−H_{ortho}, minor isomer), 7.11 (d, 2H, ArH, *J* = 7.2 Hz), 6.86 (d, 2H, ArH, *J* = 7.2 Hz), 3.91 (s, 4H, CH_2N), 2.87 (s, 12H, $N(CH_3)_2$, minor isomer), 2.85 (s, 12H, $N(CH_3)_2$, major isomer), 0.23 (s, 18H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, mixture of isomers): δ 147.6, 147.5, 143.1, 142.9 (4 × Ar−C), 138.2, 138.0, 137.8, 137.7 (Ar−C), 129.7 (Ar−C), 121.2 (Ar−C), 73.2 (Ar−CH_2), 53.0, 52.7 (2 × $N(CH_3)_2$), −0.9, −1.0 (2 × $Si(CH_3)_2$). Anal. Calcd for $C_{24}H_{40}N_2Si_2Pd_2Cl_2$ (dimer): C 41.39, H 5.79, N 4.02, Si 8.07. Found: C 41.35, H 5.86, N 3.98, Si 8.04.

[PdCl($C_6H_3\{CH_2NMe_2\}$-2-$SiMe_3$-5)(C_5H_5N)] (8). Reaction of **7** (0.25 g, 0.36 mmol) with an excess of pyridine in CH_2Cl_2 yielded the monomeric complex **8** as a white solid after evaporation of all volatiles and washing the product with pentane (20 mL) (0.29 g, 0.68 mmol, 95%). ^1H NMR ($CDCl_3$): δ 8.91 (d, 2H, pyr−H, *J* = 6.3 Hz), 7.84 (t, 1H, pyr−H, *J* = 7.4 Hz), 7.38 (t, 2H, pyr−H, *J* = 6.4 Hz), 7.14 (d, 1H, ArH, *J* = 7.3 Hz), 6.96 (d, 1H, ArH, *J* = 7.2 Hz), 6.06 (s, 1H, Ar−H_{ortho}), 3.96 (s, 2H, CH_2N), 2.94 (s, 6H, $N(CH_3)_2$), 0.02 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.8, 148.6, 148.2, 137.8, 137.6, 137.0, 129.5, 125.0, 121.1 (Ar−C), 74.0 (Ar−CH_2), 52.8 ($N(CH_3)_2$), −1.2 ($Si(CH_3)_2$). Anal. Calcd for $C_{17}H_{25}N_2SiPdCl$: C 47.78, H 5.90, N 6.56, Si 6.57. Found: C 47.59, H 5.98, N 6.64, Si 6.46.

[$CH_2Si(Me)_2C_6H_2(CH_2NMe_2)_2$-3,5-(PdCl)-4]$_2$ (9). Experimental conditions are similar to those described for **2**. [$CH_2Si(Me)_2C_6H_2(CH_2NMe_2)_2$-3,5-$SiMe_3$-4]$_2$ (0.22 g, 0.33 mmol) was suspended in MeOH (40 mL), and to this solution was added $Pd(OAc)_2$ (0.20 g, 0.89 mmol). In addition, the CH_2Cl_2 solution of **9** was filtered through Celite. A light brown solid was formed (0.19 g, 0.23 mmol, 70%). ^1H NMR ($CDCl_3$): δ 6.86 (s, 4H, Ar−H), 4.00 (s, 8H, Ar−CH_2), 2.95 (s, 24H, $N(CH_3)_2$), 0.60 (s, 4H, $-(CH_2)_2-$), 0.19 (s, 12H, $Si(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 158.2 (C_{ipso}), 144.7 (Ar−C), 135.0 (Ar−C−Si), 124.6 (Ar−C), 74.8 (Ar−CH_2), 53.1 ($N(CH_3)_2$), 8.0 ($-(CH_2)_2-$), −3.4 ($Si(CH_3)_2$). FAB-MS: *m*/*z* 807.9 (M^+), 772.9 $(M - Cl)^+$. Anal. Calcd for $C_{30}H_{52}N_4Si_2Pd_2Cl_2$: C 44.56, H 6.48, N 6.93, Si 6.95. Found: C 44.32, H 6.46, N 6.88, Si 7.01.

[$CH_2Si(Me)_2C_6H_2(CH_2NMe_2)_2$-3,5-(PtCl)-4]$_2$ (10). This compound was prepared in a similar way as described for **3**. *t*-BuLi (2.0 mL of a 1.5 M solution in pentane, 3.0 mmol) was added to a solution of [$CH_2Si(Me)_2C_6H_3(CH_2NMe_2)_2$-3,5]$_2$ (0.76 g, 1.44 mmol) in pentane (20 mL) and stirred for 18 h at room temperature. A cream-colored powder was formed (1.31 g, 1.33 mmol, 92%). ^1H NMR ($CDCl_3$): δ 6.90 (s, 4H, Ar−H), 4.03 (s, 8H, Ar−CH_2, *J*(Pt−H) = 45.3 Hz), 3.09 (s, 24H, $N(CH_3)_2$, *J*(Pt−H) = 37.2 Hz), 0.62 (s, 4H, $-(CH_2)_2-$), 0.20 (s, 12H, $Si(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.7 (Ar−C), 143.1 (Ar−C, ^2J(Pt−C) = 76.2 Hz), 133.3 (Ar−C−Si), 124.2 (Ar−C, *J*(Pt−C) = 35.1 Hz), 77.7 (Ar−CH_2, *J*(Pt−C) = 67.3 Hz), 54.5 ($N(CH_3)_2$), 8.1 ($-(CH_2)_2-$), −3.4 ($Si(CH_3)_2$). Mp > 200 °C. FAB-MS: *m*/*z* 986 (M^+), 949 $(M - Cl)^+$. Anal. Calcd for $C_{30}H_{52}N_4Si_2Pt_2Cl_2$: C 36.54, H 5.32, N 5.68, Si 5.70. Found: C 36.68, H 5.39, N 5.55, Si 5.72.

[$CH_2Si(Me)_2C_6H_2(CH_2NMe_2)_2$-3,5-I-4]$_2$ (11). Experimental conditions are similar to those described for **4**. To a solution of [$CH_2Si(Me)_2C_6H_3(CH_2NMe_2)_2$-3,5]$_2$ (1.19 g, 2.26 mmol) was added *t*-BuLi (3.5 mL of a 1.7 M solution in pentane, 6.0 mmol) at room temperature. The lithiated species was “titrated” with I_2 (1.64 g, 6.46 mmol) in Et_2O (40 mL). The combined organic extraction layers were washed with saturated Na_2SO_3 solution (2 × 50 mL) and H_2O (2 × 50 mL). An orange, very viscous oil, which solidifies after several weeks, was produced (1.50 g, 1.93 mmol, 85%). ^1H NMR (C_6D_6): δ 7.64 (s, 4H, Ar−H), 3.53 (s, 8H, CH_2N), 2.15 (s, 24H, $N(CH_3)_2$), 0.79 (s, 4H, $-(CH_2)_2-$), 0.28 (s, 12H, $Si(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 141.7 (Ar−C), 138.1 (Ar−C−Si), 134.6 (Ar−C), 109.6 (Ar−C−I), 69.5 (Ar−CH_2), 45.5 ($N(CH_3)_2$), 8.4 ($-(CH_2)_2-$), −3.4 ($Si(CH_3)_2$). FAB-MS: *m*/*z* 779 $(M + H)^+$. Anal. Calcd for $C_{30}H_{52}N_4Si_2I_2$: C 46.27, H 6.73, N 7.19, Si 7.21. Found: C 46.18, H 6.67, N 7.26, Si 7.28.

[$CH_2Si(Me)_2C_6H_2(CH_2NMe_2)_2$-3,5-(PdI)-4]$_2$ (12). To a stirred solution of **11** (0.32 g, 0.41 mmol) in benzene (40 mL) was added an excess of $Pd(dba)_2$ (0.56 g, 0.97 mmol) at room temperature. The dark-colored mixture was then stirred until ^1H NMR spectroscopy showed the reaction to be complete (=48 h). The reaction mixture was filtered through Celite and the solvent removed under reduced pressure. The solid residue was washed with acetone (30 mL), and the first fraction (0.12 g) was isolated. The acetone layer was then cooled to −20 °C, and the precipitated solid was isolated by decantation and dried in vacuo to give a second fraction (0.17 g) of a beige-colored solid (total yield 0.29 g, 0.29 mmol, 71%). ^1H NMR (C_6D_6): δ 6.87 (s, 4H, Ar−H), 3.31 (s, 8H, CH_2N), 2.67 (s, 24H, $N(CH_3)_2$), 0.87 (s, 4H, $-(CH_2)_2-$), 0.36 (s, 12H, $Si(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 162.3 (Ar−C_{ipso}), 145.7, 134.6, 124.7 (3 × Ar−C), 74.0 (Ar−CH_2), 54.7 ($N(CH_3)_2$), 8.8 ($-(CH_2)_2-$), −3.1 ($Si(CH_3)_2$). FAB-MS: *m*/*z* 865 $(M - I)^+$. Anal. Calcd for $C_{30}H_{52}N_4Si_2Pd_2I_2$: C 36.34, H 5.29, N 5.65, Si 5.67. Found: C 36.42, H 5.36, N 5.61, Si 5.79.

[$CH_2Si(Me)_2C_6H_3(CH_2NMe_2)$-4-(PdCl)-3]$_2$ (13). *Method 1*: [$CH_2Si(Me)_2C_6H_4(CH_2NMe_2)$-4]$_2$ (0.46 g, 1.11 mmol) in MeOH (20 mL) was treated with $Pd(OAc)_2$ (0.52 g, 2.32 mmol). After stirring the red-colored solution for 3 h, excess LiCl (0.15 g, 3.54 mmol) was added to afford a yellow suspension, which was stirred for 18 h. The solvent was removed in vacuo, and CH_2Cl_2 (100 mL) and H_2O (100 mL) were added. The organic layer was separated and the H_2O layer extracted with CH_2Cl_2 (50 mL). The combined organic layers were filtered through Celite and evaporated to yield a bright orange solid (0.66 g, 0.95 mmol, 86%). *Method 2:* To a solution of [$CH_2Si(Me)_2C_6H_3(CH_2NMe_2)$-4-$SiMe_3$-3]$_2$ (0.37 g, 0.66 mmol) in MeOH (30 mL) was added $Pd(OAc)_2$ (0.32 g, 1.43 mmol), which was stirred for 1 h, and subsequently LiCl (0.12 g, 2.83 mmol) was added. After the same purification and isolation sequence described in method 1, an orange solid was obtained (0.45 g, 98%). The low solubility of **13** in the common organic solvents hampered the analysis by $^{13}C\{^1H\}$ NMR spectroscopy. Yellow block-shaped crystals suitable for an X-ray analysis were obtained by cooling a saturated solution of the product in CH_2Cl_2 to −20 °C. ^1H NMR ($CDCl_3$, crystalline material, mixture of isomers): δ 7.63 (s, 2H, Ar−H_{ortho}, minor isomer), 7.42 (s, 2H, Ar−H_{ortho}, major isomer), 7.11 (d, 2H, ArH, $J = 7.2$ Hz, minor isomer), 7.10 (d, 2H, ArH, $J = 7.2$ Hz, major isomer), 6.88 (d, 2H, ArH, $J = 7.2$ Hz, minor isomer), 6.86 (d, 2H, ArH, $J = 7.2$ Hz, major isomer), 3.96 (s, 4H, CH_2N, minor isomer), 3.92 (s, 4H, CH_2N, major isomer), 2.96 (s, 12H, $N(CH_3)_2$, minor isomer), 2.86 (s, 12H, $N(CH_3)_2$, major isomer), 0.91 (s, 4H, $-(CH_2)_2-$, minor isomer), 0.56 (s, 4H, $-(CH_2)_2-$, major isomer), 0.21 (s, 18H, $Si(CH_3)_3$, minor isomer), 0.19 (s, 18H, $Si(CH_3)_3$, major isomer). FAB-MS: m/z 659 ($(M - Cl)^+$, monomer), 1388 (M^+, dimer) 1353 ($(M - Cl)^+$, dimer). Anal. Calcd for $C_{24}H_{40}N_2Si_2Pd_2Cl_2{\cdot}1.5CH_2Cl_2$: C 37.40, H 5.01, N 3.41. Found: C 37.28, H 5.03, N 3.41.

$[CH_2Si(Me)_2C_6H_3(CH_2NMe_2)$-4-$\{PdCl(C_5H_5N)\}-3]_2$ (14). Reaction of crystalline **13** (0.24 g, 0.29 mmol) with an excess of pyridine in CH_2Cl_2 (see synthesis of **8**) yielded **14** as a white solid (0.22 g, 0.26 mmol, 89%). ^1H NMR ($CDCl_3$): δ 8.85 (d, 4H, pyr−H, $J = 5.0$ Hz), 7.77 (t, 2H, pyr−H, $J = 7.3$ Hz), 7.28 (t, 4H, pyr−H, $J = 6.4$ Hz), 7.05 (d, 2H, ArH, $J = 7.1$ Hz), 6.95 (d, 2H, ArH, $J = 7.2$ Hz), 6.00 (s, 2H, Ar−H_{ortho}), 3.94 (s, 4H, CH_2N), 2.91 (s, 12H, $N(CH_3)_2$), 0.29 (s, 4H, $-(CH_2)_2$), −0.08 (s, 12H, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 153.7, 148.6, 148.3, 137.8, 137.3, 136.6, 129.8, 125.0, 121.1 (Ar−C), 74.0 (Ar−CH$_2$), 52.9 (N(CH$_3$)$_2$), 7.7 ($-(CH_2)_2$), −3.7 (Si(CH$_3$)$_2$). Anal. Calcd for $C_{34}H_{48}N_4Si_2Pd_2Cl_2$: C 47.89, H 5.67, N 6.57, Si 6.59. Found: C 47.70, H 5.45, N 6.27, Si 6.70.

Table 4. Crystal Data and Details of the Structure Determination for 5 and 13

	5	**13**
empirical formula	$C_{15}H_{27}IN_2NiSi$	$C_{48}H_{76}Cl_4N_4Pd_4Si_4$, 3($CH_2Cl_2$)
fw	449.07	1643.75
cryst syst	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P1$ (No. 2)
a/Å	10.2695(7)	10.8029(10)
b/Å	27.914(2)	11.5113(7)
c/Å	13.7232(11)	14.7454(19)
α/deg	90	100.130(8)
β/deg	101.171(6)	105.530
γ/deg	90	100.963(6)
V/Å^3	3859.4(5)	1683.9(3)
Z	8	1
D(calc)/[g/cm^3]	1.546	1.621
F(000)	1808	826
μ(Mo Kα)/mm^{-1}	2.7	1.6
cryst size/mm	0.10 × 0.15 × 0.55	0.15 × 0.15 × 0.35
T/K	225	150
radiation/Å	Mo Kα 0.71073	Mo Kα 0.71073
θ min., max./deg	1.5, 27.5	1.5, 27.5
scan (type and range)/deg	$0.64 + 0.35 \tan(\theta)$	$1.02 + 0.35 \tan(\theta)$
dataset	−12: 13; 0: 36; −17: 17	−14: 13; 0: 14; −19: 18
no. of tot, unique data, R(int)	16 105, 8861, 0.048	8088, 7705, 0.050
no. of obsd data [$I > 2.0\sigma(I)$]	4408	5568
N_{ref}, N_{par}	8861, 375	7705, 351
R, wR_2, S[a]	0.0638, 0.1666, 1.02	0.0452, 0.0985, 1.02
w^{-1}	$\sigma^2(F_o^2) + (0.0606P^2) + 1.6816P$ where $P = (F_o^2 + 2F_c^2)/3$	$\sigma^2(F_o^2) + (0.0370P^2) + 1.5120P$
max. and av. shift/error	0.01, 0.00	0.02, 0.00
min./max. resd dens/[e/Å^3]	−1.17, 2.20	−0.69, 1.02

[a] $R = \sum|F_o| - |F_c|/\sum|F_o|$, $wR_2 = \{\sum w(|F_o|^2 - |F_c|^2/\sum w|F_o^2|^2\}^{-1/2}$.

Crystal Structure Determinations for 5 and 13. General. Crystal data collection and refinement parameters are given in Table 4. X-ray data were collected at low temperature (inert oil technique) on an Enraf Nonius CAD4T diffractometer (Rotating Anode, Mo Kα radiation, graphite monochromator). Both structures were refined on F^2 by full-matrix least-squares (SHELXL96).[24] All geometrical calculations including the ORTEP illustrations were done with PLATON.[25] For **5***:* Needle-shaped orange crystal. The structure was solved by direct methods using SHELXS86.[26] Correction for absorption was done with a semiempirical ψ-scan-based technique (PLATON/ABSPSI).[25] The monoclinic unit cell contains two similar but crystallographically independent molecules of **5**. A test for higher symmetry using PLATON/ADDSYM[25] was negative apart from an indication for a pseudotranslation in the b-axis direction. Most residual density is found near iodine, indicating some residual absorption artifacts. Molecule A containing Ni1A contains some unresolved disorder as indicated by a few larger than usual displacement ellipsoids and residual density near Si1A. For **13**: Block-shaped yellowish crystal. The structure was solved by automated Patterson techniques (DIRDIF).[27] Correction for absorption was done with an empirical correction procedure (PLATON/DELABS).[25] One of the CH_2Cl_2 molecules is disordered over an inversion center.

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Supporting Information Available: A listing of tables of atomic coordinates, bond lengths and angles, and thermal parameters for **5** and **13** and complete Figure 2 (11 pages). See any current masthead page for Internet access instructions.

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