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Halide-Assisted Macrocyclic Ring Formation in Cyclometalated Carbosilane Dendrimers with 1-[$C_6H_3(CH_2NMe_2)$-4-(PdCl)-3] Peripheral Groups: Application as Aldol Condensation Catalysts

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A series of cyclopalladated carbosilane dendrimers functionalized with monoanionic $[C_6H_4(CH_2NMe_2)\text{-}4]^-$ (= CN) C,N-chelating ligands via a multiple and selective C−H bond activation process have been prepared. The structure of the support, i.e., the branching degree as well as the nature of the alkanediyl linkers present in the carbosilane dendrimer, was varied to investigate its influence on the dimer formation of the peripheral [CN−PdCl] complexes and on the catalytic performance of these Pd(II)-functionalized dendrimers. $Me_2Si\{(CH_2)_3SiMe_2{-}CN{-}PdCl\}_2$ (**4**) and $Si\{(CH_2)_2SiMe_2{-}CN{-}PdCl\}_4$ (**7a**) were characterized by a single X-ray crystal structure determination. In both cases a unique intramolecular halide-assisted macrocyclic ring structure was present. Variable-temperature NMR spectroscopic investigations indicated that in solutions of **4** and **7a** the *cis*-bridging mode of the peripheral dimers is predominant. For the two asymmetrically branched [G1] palladodendrimers $Si\{(CH_2)_2Si(Me)\{(CH_2)_2SiMe_2{-}CN{-}PdCl\}_2\}_4$ (**10a**) and $Si\{(CH_2)_3Si(Me)\{(CH_2)_3SiMe_2{-}CN{-}PdCl\}_2\}_4$ (**12a**) isomeric forms of the [CN−PdCl] dimeric units were observed. In addition, for the [G2] dendrimer $Si\{(CH_2)_3Si\{(CH_2)_3Si\{(CH_2)_3SiMe_2{-}CN{-}PdCl(pyr)\}_3\}_3\}_4$, **15b**, appended with a maximum of 36 [CN−PdCl(pyr)] complexes, a *cis*/*trans* isomerization of the peripheral [CN−PdCl(pyr)] groups is noted. The applicability of the cationic cyclopalladated carbosilane dendrimers, obtained by halide abstraction with $AgBF_4$, as Lewis acid catalysts in a model aldol condensation reaction was demonstrated. Their catalytic performance was compared to that of the parent mononuclear derivative $[Pd(C_6H_3\{CH_2NMe_2\}\text{-}2\text{-}(SiMe_3)\text{-}5)(pyr)(H_2O)]BF_4$ (**16**). The obtained catalytic data showed that up to generation [G2], the selectivity of the reaction is not affected. However, the rate of the reaction decreased with increasing steric congestion at the dendrimer periphery.

Introduction

The chemistry of C,N-chelated cyclometalated compounds has received much attention,[1] and recently the preparation of multi-cyclometalated systems has been reported.[2] These include systems such as (chiral) ferrocenylamine,[3] ferrocenylimine,[4] and primary and/or tertiary benzylamine ligands.[5] We are interested in the design of macromolecular (dendritic)[6] organometallics for application in catalysis[7] and sensor-type materials.[8] The application of dendritic metallodendrimers in membrane reactors has recently been attempted, and the feasibility of recycling these dendrimer catalysts by ultrafiltration techniques was shown.[9] We have also reported the selective conversion of dendritic carbosilanes functionalized with the monoanionic arylamine

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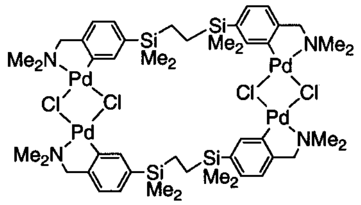

Figure 1. Schematic representation of a bis-palladated, dimeric carbosilane derivative.

ligands $[C_6H_3(CH_2NMe_2)_2\text{-}3,5]^-$ (NCN) and $[C_6H_4(CH_2NMe_2)\text{-}4]^-$ (CN) into synthetically useful, polylithiated ligand arrays[10] and their subsequent use for the preparation of a variety of group 8 metallodendritic compounds.[7d,11] As these polylithium reagents are sensitive toward hydrolysis, incomplete transmetalation is difficult to avoid. This prompted us to investigate the possibility of alternative and more direct methods for the introduction of metal sites into arylamine-functionalized carbosilane supports. In principle, this could overcome the problem of incomplete metalation.

Our earlier work had led to the preparation of a stable, macrocyclic cyclopalladated carbosilane which was structurally characterized by X-ray crystallography (Figure 1).[11] This palladated carbosilane exists as a dimeric aggregate in the solid state with a 26-membered-ring structure. Noteworthy is the fact that in this particular palladation reaction, unlike in previous reported work,[1c,12] the connected carbosilane backbone was not attacked by the metal reagent, showing that regioselective cyclopalladation of this type of dendritic carbosilanes with peripheral CN ligands is feasible.

Here, we present a general strategy for the incorporation of Pd(II) metal sites into the periphery of arylamine-functionalized carbosilane dendrimers by a multiple C−H bond activation. As an extension of our earlier efforts,[11] we have also studied the halide-assisted dimer formation at the periphery of these novel metallodendritic species by variation of the branching degree as well as the alkanediyl linking fragments present in the carbosilane dendrimer support (Figure 2). Study of these latter aspects is relevant because of our recent finding, which pointed to the effect of the number of organometallic catalytic sites at the periphery on the catalyst performance.[7d,e] We have employed the cyclopalladated carbosilane dendrimers as catalyst precursors in the aldol condensation reaction. The obtained catalytic data are compared with the parent model species and discussed.

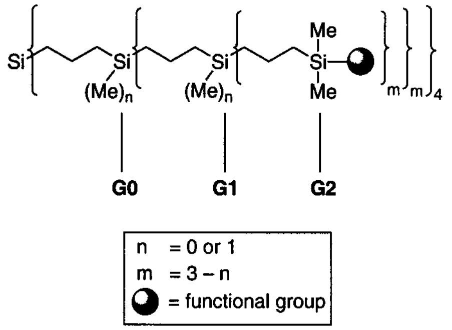

Figure 2. Schematic representation of the variation of the structure of the dendritic carbosilane support.

Results and Discussion

Synthesis of Cyclopalladated Compounds. The model dendritic compounds (viz., **4** and **5a**) were prepared to study the cyclopalladation and halide-assisted dimer formation in more detail. Treatment of diallyldimethylsilane with an excess of chlorodimethylsilane in the presence of a platinum catalyst (i.e., $(NBu_4)_2PtCl_6$) gave the hydrosilylated product **1** in quantitative yield (Scheme 1). Compound **1**, which is moisture sensitive, was converted to the moisture stable silicon hydride **2** in 74% yield by reduction of **1** in the presence of an excess of $LiAlH_4$ in Et_2O at 0 °C. Not only did the selective formation of **2** confirm the stoichiometry of its precursor **1**, but at the same time **2** itself is an interesting starting material for the synthesis of hyperbranched carbosilane polymers.[13] The CN-functionalized carbosilane $[G0]^{1/2}\text{-}(SiMe_2\text{−}CN)_2$ (**3**) was obtained in 76% yield by treatment of the silicon chloride **1** with an excess of $[Li(C_6H_4\{CH_2NMe_2\}\text{-}4)]$ (abbreviated as Li-[CN]) in Et_2O at −78 °C.[10] Cyclopalladation of **3** in the presence of $Pd(OAc)_2$ in MeOH at ambient temperature yielded the bis palladium chloride derivative $[G0]^{1/2}\text{-}(SiMe_2\text{−}CN\text{−}PdCl)_2$ (**4**) as a yellow-to-orange solid in 83% yield after addition of LiCl (Scheme 1). Crystals suitable for X-ray diffraction (vide infra) were obtained by layering a solution of **4** in benzene with pentane.

The [G0] dendrimers **5a** and **7a**, which differ with respect to the length of the alkanediyl spacer (viz., C_2 vs C_3), were prepared as reported for **4** (Scheme 2). Thus, addition of $Pd(OAc)_2$ to a stirred solution of $[G0]\text{-}(SiMe_2\text{−}CN)_4$[10] in MeOH followed by an appropriate workup yielded orange-colored $[G0]\text{-}(SiMe_2\text{−}CN\text{−}PdCl)_4$ (**5a**) in 51% yield (Scheme 2). The dendritic palladium complex **7a** was obtained by a two-step sequence. First, known $Si(CH_2CH_2SiMe_2Cl)_4$[14] (abbreviated as $[G0]^{\#}\text{-}(SiMe_2Cl)_4$, the symbol # denotes the presence of C_2 instead of C_3 branches/spacers in this compound) was treated with Li-[CN] (as described for **3**) to give $[G0]^{\#}$-

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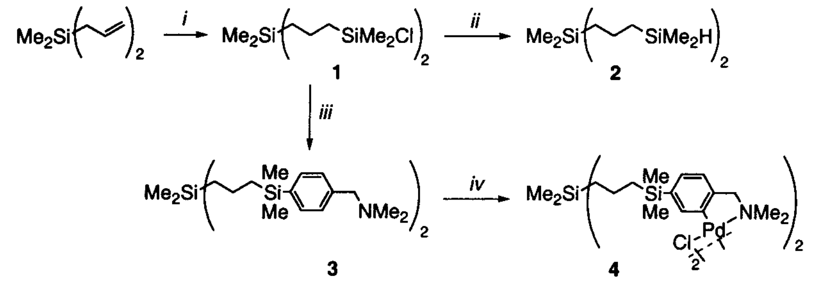
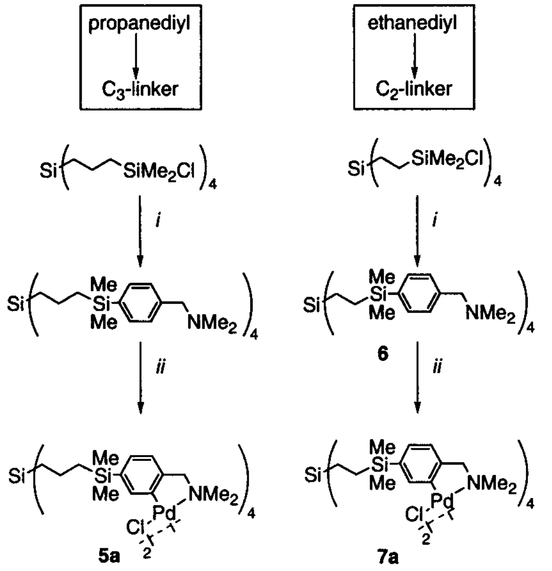
Scheme 1. Synthesis of the Model Derivative 4[a]



[a] Reagents and conditions: (i) neat $HSiMe_2Cl$, RT, $(NBu_4)_2PtCl_6$ as catalyst; (ii) excess $LiAlH_4$, Et_20, 0 °C; (iii) Li-[CN], Et_2O, −78 °C → RT; (iv) $Pd(OAc)_2$, MeOH; then LiCl, MeOH.

Scheme 2. Synthesis of the [G0] Dendrimers 5a and 7a[a]



[a] Reagents and conditions: (i) Li-[CN], Et_2O, −78 °C → RT; (ii) $Pd(OAc)_2$, MeOH; then LiCl, MeOH.

$(SiMe_2{-}CN)_4$, **6**, as a waxy white solid in 72% yield. Subsequent palladium incorporation as reported for **4** and **5** (Scheme 2) afforded $[G0]^{\#}$-$(SiMe_2{-}CN{-}PdCl)_4$, **7**, in good yield (91%). Unlike their [G1] generation analogues (vide infra), the [G0] generation dendrimers **5a** and **7a** as well as “dendritic” **4** are soluble in aromatic solvents such as benzene and toluene.

The synthesis of the [G1] generation dendrimers is outlined in Scheme 3. The derivative $[G1]^{\#}$-$(CH{=}CH_2)_8$ (**8**) was obtained in 63% yield by the vinylation of the known silicon chloride $[G0]^{\#}$-$(SiMeCl_2)_4$.[14] The olefinic derivative **8** was converted into the chlorosilane dendrimer $[G1]^{\#}$-$(SiMe_2Cl)_8$[14] by a hydrosilylation reaction with $HSiMe_2Cl$ using a platinum-based catalyst. The dendrimer ligand $[G1]^{\#}$-$(SiMe_2{-}CN)_8$ (**9**) was obtained in 84% yield by treatment of $[G1]^{\#}$-$(SiMe_2Cl)_8$ with an excess of the lithium reagent Li-[CN]. Likewise, [G1]-$(SiMe_2{-}CN)_8$ (**11**) was obtained as a yellow viscous oil in 78% yield by using an approach similar to that described for **9** (Scheme 3).[10] The [G1] generation palladodendrimers were prepared as described for the [G0] generation dendrimers **5a** and **7a** by a multiple C−H activation using $Pd(OAc)_2$ in MeOH. The [G1] derivatives $[G1]^{\#}$-$(SiMe_2{-}CN{-}PdCl)_8$ (**10a**), [G1]-$(SiMe_2{-}CN{-}PdCl)_8$ (**12a**), and [G1]-$(SiMe_2{-}CN{-}PdCl)_{12}$ (**13a**) were isolated as pale yellow-to-orange solids in 40−80% yield (Scheme 3).

The CN-functionalized dendrimer [G2]-$(SiMe_2{-}CN)_{36}$ (**14**) was obtained in a moderate yield (38%) by a procedure similar to the one used for the preparation of **9** and **11** starting from [G2]-$(SiMe_2Cl)_{36}$.[14] Preliminary investigations showed that the incorporation of Pd(II) sites on the periphery of [G2]-$(SiMe_2{-}CN)_{36}$ (**14**) by a multiple C−H activation using $Pd(OAc)_2$ as described for the [G0] and [G1] analogues afforded a yellow-to-brown, insoluble solid. The insolubility of the presumed product (i.e., [G2]-$(SiMe_2{-}CN{-}PdCl)_{36}$ (**15a**), Scheme 4) could be explained by a large increase in aggregational character in this intermediate species. The presumed product [G2]-$(SiMe_2{-}CN{-}PdCl)_{36}$ (**15a**) was converted into the corresponding pyridine adduct [G2]-$(SiMe_2{-}CN{-}PdCl\{pyr\})_{36}$ (**15b**) by an in situ preparation in CH_2Cl_2. Indeed, **15b** appeared to be more soluble and was isolated as a light yellow solid in 38% yield after appropriate workup (Scheme 4). The ^1H NMR spectrum of **15b** in $CDCl_3$ unambiguously showed that all the peripheral CN ligands had been cyclometalated, as indicated by the complete disappearance of the resonances corresponding to the CH_2N and NMe_2 fragments of the parent CN ligand at 3.40 and 2.22 ppm, respectively. Interestingly, two new resonance patterns were observed for several fragments of the [G2] pyridine adduct, of which the relative intensity ratio was temperature dependent (vide infra). The proposed stoichiometry of [G2]-$(SiMe_2{-}CN{-}PdCl\{pyr\})_{36}$ (**15b**) was further supported by elemental (including Pd and Cl) analyses.

Addition of an excess of pyridine to the dendritic palladium chloride compounds [G0]-$(SiMe_2{-}CN{-}PdCl)_4$ (**5a**), $[G0]^{\#}$-$(SiMe_2{-}CN{-}PdCl)_4$ (**7a**), $[G1]^{\#}$-$(SiMe_2{-}CN{-}PdCl)_8$ (**10a**), [G1]-$(SiMe_2{-}CN{-}PdCl)_8$ (**12a**), and [G1]-$(SiMe_2{-}CN{-}PdCl)_{12}$ (**13a**) in CH_2Cl_2 led to a rapid formation of their pyridine adducts [G0]-$(SiMe_2{-}CN{-}PdCl\{pyr\})_4$ (**5b**), $[G0]^{\#}$-$(SiMe_2{-}CN{-}PdCl\{pyr\})_4$ (**7b**), $[G1]^{\#}$-$(SiMe_2{-}CN{-}PdCl\{pyr\})_8$ (**10b**), [G1]-$(SiMe_2{-}CN{-}PdCl\{pyr\})_8$ (**12b**), and [G1]-$(SiMe_2{-}CN{-}PdCl\{pyr\})_{12}$ (**13b**), respectively. These pyridine adducts (Scheme 5) were isolated as off-white solids in excellent yields (84% to quantitative). The selective formation of the pyridine adducts became directly evident from the ^1H NMR spectra, in which the $Ar{-}H_{ortho}$ of the peripheral CN ligands shifts to higher field upon coordination of the

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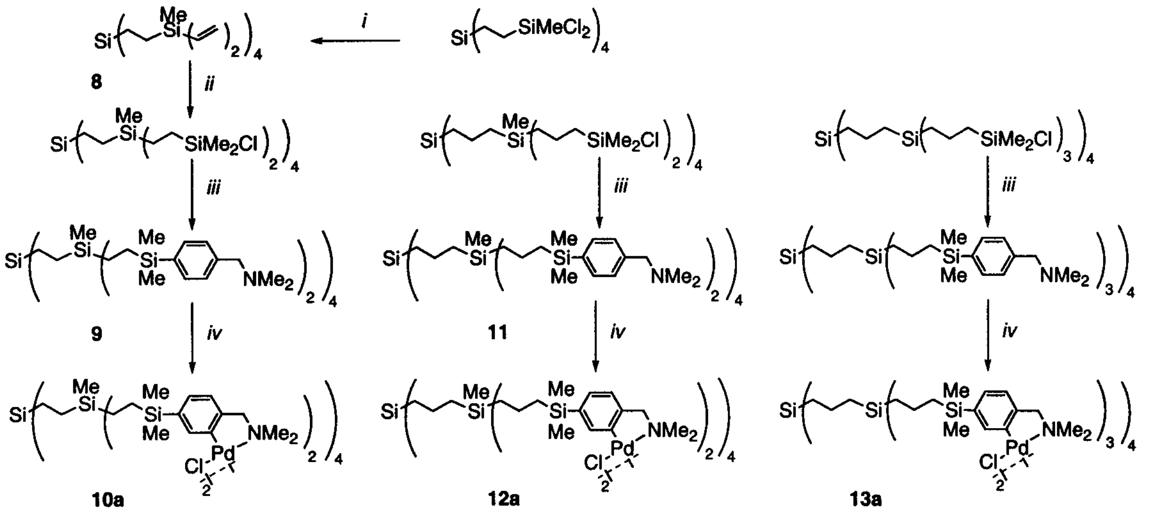
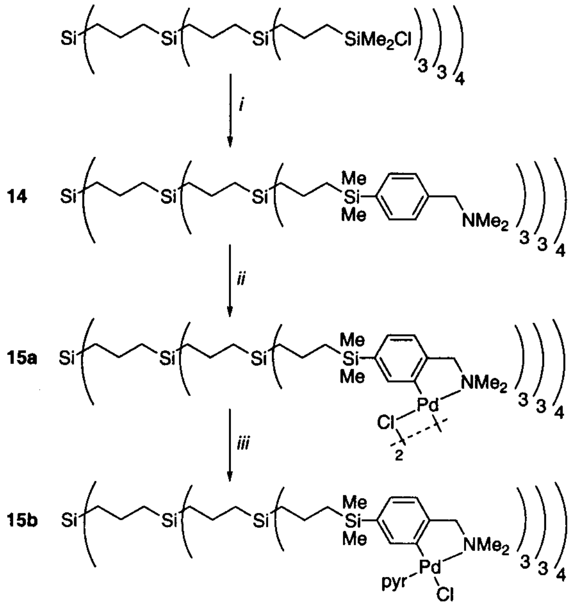
Scheme 3. Synthesis of the [G1] Dendrimers 10, 12a, and 13a[a]



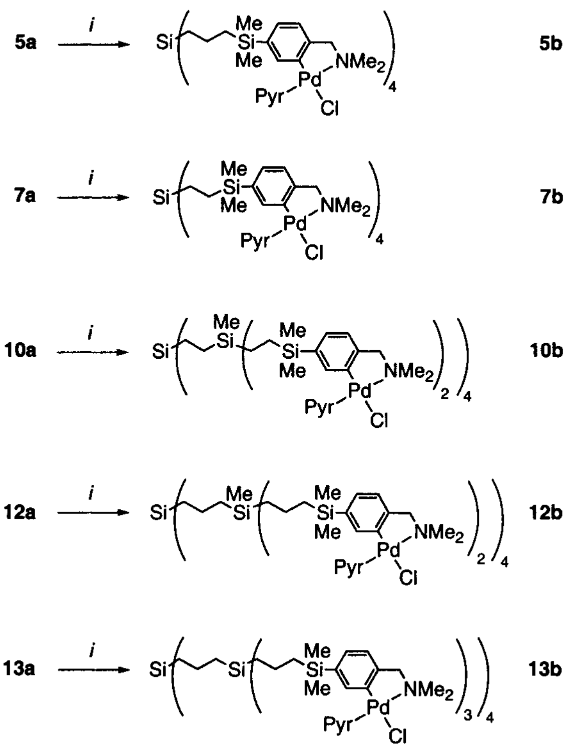
[a]Reagents and conditions: (i) excess VinylMgBr, THF, RT; (ii) neat $HSiMe_2Cl$, RT, $(NBu_4)_2PtCl_6$ as catalyst; (iii) Li-[CN], Et_2O, −78 °C → RT; (iv) $Pd(OAc)_2$, MeOH; then LiCl, MeOH.

Scheme 4. Synthesis of the [G2] Dendrimer 15b[a]



[a]Reagents and conditions: (i) Li-[CN], Et_2O, −78 °C → RT; (ii) $Pd(OAc)_2$, MeOH; then LiCl, MeOH; (iii) pyridine, CH_2Cl_2.

Scheme 5. Synthesis of the Dendrimer (Poly)pyridine Adducts[a]

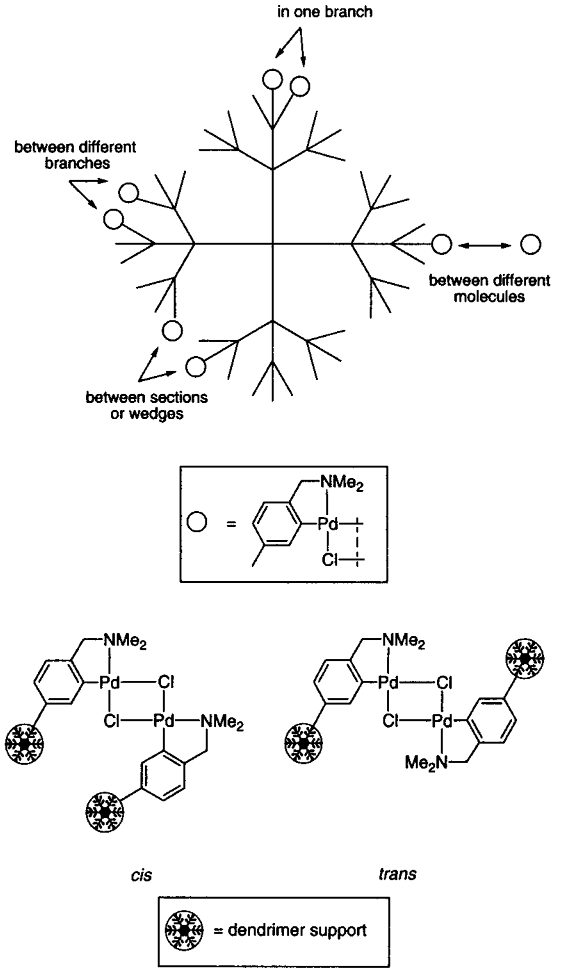


[a]Reagents and conditions: (i) pyridine, CH_2Cl_2.

pyridine ligand to the metal center (i.e., from ca. 7.3−7.4 ppm to 6.00−6.05 ppm). In addition, for the connecting $SiMe_2$ groups, a significant ^1H NMR shift from ca. 0.2 to −0.04 ppm was observed, pointing to a proximity effect between the coordinated pyridine ligand and the (*meta*) $SiMe_2$ groups. Moreover, the line widths of the resonances sharply decreased in the case of the pyridine adducts when compared to their chloride-bridged pallado-dendrimers. Finally, the combined analytical data of the pyridine adducts supported the selective and *quantitative* (cf., the nonquantitative lithiation/transmetalation protocol[7d,e]) palladation of the dendrimer ligands presented in Schemes 3 and 4. The pyridine adducts were used as starting materials for the preparation of homogeneous Lewis acid catalysts for the aldol condensation reaction (vide infra).

NMR Spectroscopic Analysis of the Metallodendrimer Species. In contrast with the sharp resonances observed in the ^1H NMR spectra of nearly all dendrimer ligands, spectra with relatively broad resonances were collected for the palladodendrimers [G0]-$(SiMe_2{-}CN{-}PdCl)_4$ (**5a**), [G0]$^\#$-$(SiMe_2{-}CN{-}PdCl$ (**7a**), [G1]$^\#$-$(SiMe_2{-}CN{-}PdCl)_8$ (**10a**), [G1]-$(SiMe_2{-}CN{-}PdCl)_8$ (**12a**), and [G1]-$(SiMe_2{-}CN{-}PdCl)_{12}$ (**13a**). Most probably this broadening arises from the halide-assisted dimer formation of the attached Pd(II)Cl complexes, which was clearly lost when a suitable Lewis base (i.e., pyridine) was added, resulting in spectra with relatively sharp resonances. It should be mentioned that this halide-assisted dimer formation leads in the case of the [G1] and [G2] species **10a**, **12a**, **13a**, and **15a** to the formation of several stereoisomers as schematically shown in

Scheme 6. Schematic Representation of the Stereoisomer Formation in the Cyclopalladated CN-Derivatized Carbosilane Dendrimers



Scheme 6. These stereoisomers can originate from dimer formation between [CN−PdCl] complexes of different branches, sections, or wedges. As illustrated in Scheme 6, the formation of *inter*molecular, large aggregates is not ruled out and the relatively low isolated yields of the higher generation species **13a** and **15a** may serve as indicative examples thereof. Due to the applied workup procedure(s), the insoluble, presumably polymeric fractions of the these chloride-bridged Pd(II) dendrimers were not isolated. We have intentionally only focused on the soluble, isolated materials that can be used in homogeneous catalytic applications and have undertaken no studies toward elucidation of the structures of the insoluble materials.

The occurrence of *cis* and *trans* isomeric forms[16] of the dimer has been well recognized for, for example, the parent species (μ-Cl-[PdCl(C$_6$H$_3${CH$_2$NMe$_2$}-2-SiMe$_3$-5)])$_2$ by means of ^{1}H and ^{13}C{^{1}H} NMR spectroscopy (isomer ratio ≈ 1.4, δ(^{1}H, CDCl$_3$, Ar−H$_{ortho}$) = 7.43 (*cis*), 7.33 (*trans*)).[11] Molecular modeling of both isomeric forms suggested a very small energy difference (i.e., 0.15 kcal/mol) between the *cis* and *trans* isomers of this particular compound in the gas phase.[17] Recently, Gül et al. described analogous *cis*/*trans* isomerization processes involving similar dimeric Pd(II)X complexes (X = halide) derived from simple (chiral) arylamines. The ratio between the *cis* and *trans* isomeric forms (ca. 1:1, calculated from the ^{1}H NMR spectra) of these complexes was temperature independent between 20 °C and the coalescence temperature (50−80 °C). From these data a $\Delta G^{\ddagger}_{298}$ of 15−16 (±0.5) kcal/mol was calculated for this isomerization process and the Gibbs activation energy was found to be practically solvent insensitive.[18]

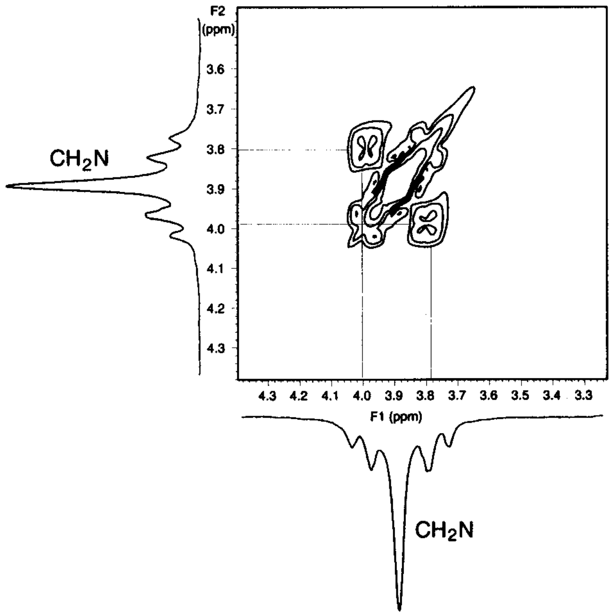


Figure 3. COSY (^{1}H, ^{1}H) spectrum recorded for **12a** in CDCl$_3$ at RT.

The ^{1}H NMR spectra of the dendrimers [G1]$^{\#}$-(SiMe$_2$−CN−PdCl)$_8$ (**10a**) and [G1]-(SiMe$_2$−CN−PdCl)$_8$ (**12a**), which have lower branching multiplicity as compared with **5a**, **7a**, and **13a**, displayed two resonance patterns for the CH$_2$N groups of the attached [CN−PdCl] complexes (Figures 3 and 4). One pattern is represented by a singlet resonance, while the other is an AB type pattern (^2J(H$_a$−H$_b$) ≈ 13 Hz) for these protons. The assignment of this AB pattern was supported by ^{1}H decoupling experiments giving rise to *singlet* resonances for both doublets after selective irradiation of the presumed coupled spins. In addition, the COSY (^{1}H,^{1}H) NMR spectrum of **12a** (Figure 3) showed unambiguously that these doublets are correlated. Furthermore, the HETCOR (^{1}H,^{13}C) NMR spectrum of **12a** (Figure 4) clearly displayed a cross-peak between the CH$_2$ protons and the benzylic carbon atom.

Together, from these data we suggest the presence of more than one type of C,N-chelated Pd(II) complex for both **10a** and **12a** in solution, which is most probably due to different bridging modes between the peripheral Pd(II) complexes (Scheme 6). To our knowledge, these are the first characterized examples of isomeric forms

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[15] The halide-assisted dimer formation is reversible due to the presence of a number of different nucleophiles (see for instance: Hockless, D. C. R.; Gugger, P. A.; Leung, P. H.; Mayadunne, R. C.; Pabel, M.; Wild, S. B. *Tetrahedron* **1997**, *53*, 4083). This would allow (quantitative) dimer formation throughout the periphery of these dendrimers.

[16] The prefixes *cis* and *trans* refer to the relative positions of the NMe$_2$ groupings with respect to the Pd$_2$Cl$_2$ "square" unit, cf., Scheme 6.

[17] CAChe Molecular Mechanics using the implemented MM2 force field parameters, Cambridge Molecular Group.

[18] Gül, N.; Nelson, J. H. *Organometallics* **2000**, *19*, 91.

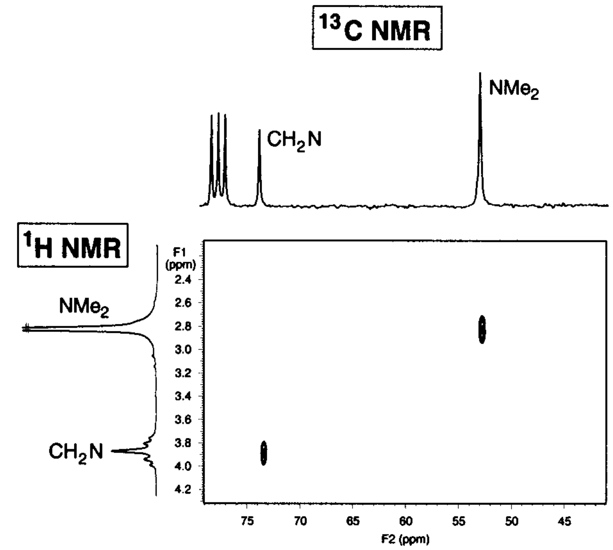


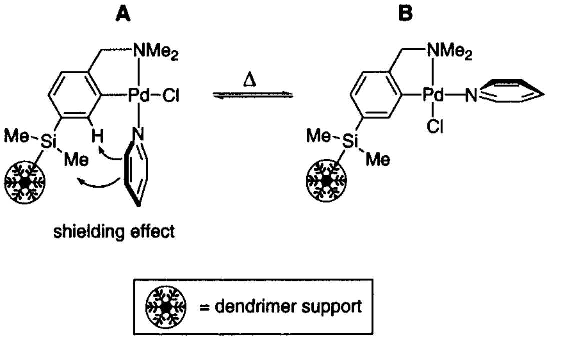
Figure 4. HETCOR (^{1}H, ^{13}C) spectrum recorded for **12a** in $CDCl_3$ at RT.

of dinuclear, d^8-metal complexes at the periphery of a dendrimer. Moreover, it seems likely that the asymmetric branching of the dendrimer support as well as the fact that in **10a** and **12a** the branches and wedges have more mobility is of importance for these observations. It should be noted that the mutual points of attachment of the CN ligands in the chloride-bridged Pd(II) carbosilane dendrimers (see for examples the structures of **4** and **7a**, vide infra) are responsible for the lower degree of symmetry in these [G1] generation molecules.

We started to investigate the isomerism behavior of the dendritic species **4**, **7a**, and **12a** as the results of earlier studies[11,18] suggested that *cis*/*trans* isomerism of these dimeric [CN−PdCl] complexes is a common feature. Therefore, variable-temperature (VT) NMR spectroscopy in CD_2Cl_2 was conducted for **12a**. In the temperature range −80 to +40 °C, no significant changes in relative intensities were observed for the AB pattern and the singlet resonance of the CH_2N groups. Interestingly, two distinct signals (partly overlapping) were noted for the Ar−H_{ortho} and $SiMe_2$ group of **12a** in CD_2Cl_2 in the same temperature range, whereas for the latter fragment, one coalesced signal was found in the temperature range 0 to +40 °C. It is important to emphasize that upon treatment of **12a** with pyridine, only *one* single resonance pattern was observed for all groups. This confirmed the complete conversion of the chloride-bridged, dinuclear into mononuclear, pyridine-ligated Pd(II) centers and unambiguously proved the proposed stoichiometry of **12a**.

To study the *temperature*-dependence of the isomer ratio of **4** and **7a**, VT ^{1}H NMR spectroscopy in toluene-d_8 was conducted. Interestingly, for both complexes only *one* (predominant) resonance pattern was observed in the temperature range −80 to +100 °C. For the CH_2N, $N(CH_3)_2$, and $Si(CH_3)_2$ groups, singlet resonances were found. From the VT ^{1}H NMR spectroscopic studies carried out for **4**, **7a**, and **12a**, we conclude that under these conditions the peripheral chloride-bridged Pd(II) dimers are stereochemically stable.[15] In addition, the NMR data suggested that in **4** and **7a** there is a higher degree of symmetry as compared with **10a** and **12a**.

Scheme 7. Schematic Representation of the Proposed Binding Mode of the Pyridine Ligand in 15b



For the [G2] dendrimer **15b**, two main, clearly different resonance patterns (partly overlapping) were observed for the $SiMe_2$, CH_2N, and NMe_2 groups, whereas for the pyridine ligand three broad signals were noted. For the Ar−H_{ortho} a broad, singlet resonance is found at δ 6.00 ppm, which supports the presence of peripheral Pd(II) complexes which are ligated by pyridine ligands as described for the [G0] and [G1] analogues (Scheme 7, **A**). The two signals for the $SiMe_2$ groups were found at δ 0.16 and −0.07 ppm, respectively (cf., ca. 0.20 ppm for the $SiMe_2$ groups in the chloride-bridged [CN−PdCl] complexes in the [G0] and [G1] Pd(II) dendrimers). The ^{1}H NMR signal integration for the two peaks observed for the $SiMe_2$ groups corresponds well with that of the NMe_2 groups. The resonance at −0.07 ppm further supported the formation of the isomer **A**. We ascribe the second resonance (i.e., at 0.16 ppm) to the presence of CN-chelated Pd(II) complexes, in which the proximity between the pyridine ligand and the $SiMe_2$ dendrimer-to-ligand connecting groups in $[G2]\text{-}(SiMe_2{-}CN{-}PdCl\{pyr\})_{36}$ (**15b**) is less as compared to isomer **A** (Scheme 7, **B**). VT ^{1}H NMR spectroscopy carried out for **15b** showed that at +60 °C the **A**/**B** ratio slightly changes in favor of **B** (**A**/**B** = 0.48). After cooling to ambient temperature, the original isomer ratio (**A**/**B** = 0.53) was again obtained. Similar ^{1}H NMR spectroscopic changes were noted for the NMe_2 and CH_2N groups.

Mass Spectrometric Analysis of the Dendrimer Species. Compounds **3**, **4**, **5a**, **6**, and **7a** (calcd molecular weight 526−1473) were analyzed using fast atom bombardment (FAB) mass spectrometry, while the metallodendrimers **8**, **9**, **10a**, **11**, **12a**, **13a**, and **14** (calcd molecular weight 636−9590) were studied by MALDI-TOF-MS. These results afforded unique additional proof for the monodisperse nature of the cyclometalated, dendritic species. For all cyclopalladated dendrimers, characteristic fragments ions $(M - Cl)^+$ were unambiguously identified (e.g., Figure 5).

MALDI-TOF-MS studies performed for the pyridine adducts **7b**, **10b**, **12b**, and **13b** were less conclusive, as no molecular ions for this type of species could be generated. Most likely this was due to a fast in situ loss of the pyridine ligands under the experimental conditions. For example, the MALDI-TOF mass spectrum of **7b** displayed the most intensive peak at *m*/*z* 1439.4, which was attributed to the fragment ion $[\mathbf{7b} - Cl - 4pyr]^+$.

Solid State Structures of 4 and 7a. The influence of the presence of different linkers (i.e., propanediyl vs

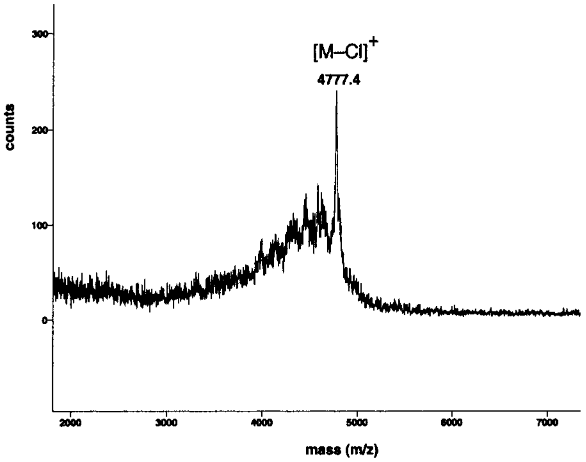


Figure 5. MALDI-TOF-MS spectrum of **13a**.

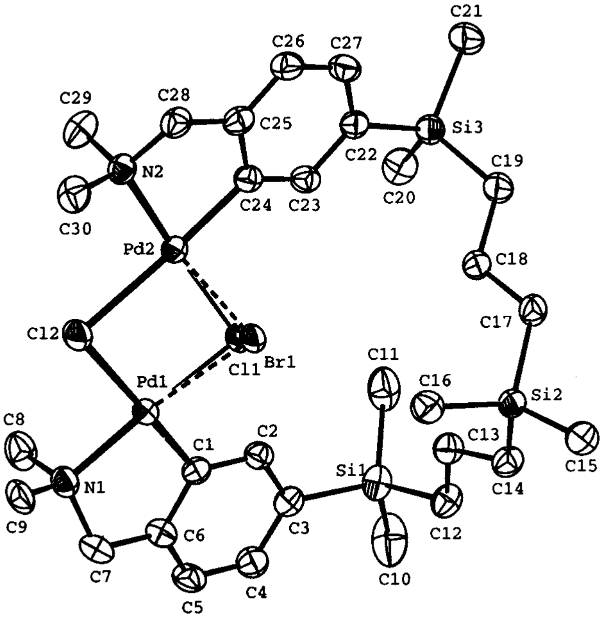


Figure 6. Displacement ellipsoid plot (50% probability) of the molecular structure of **4** showing a small halide disorder. Hydrogen atoms and cocrystallized benzene have been omitted for clarity.

ethanediyl, Scheme 2 and Figure 2) in the carbosilane dendrimer support on the halide-assisted dimer formation between peripheral [CN–PdCl] units was studied by determination of the structures of **4** (C_3-linker) and **7a** (C_2-linker) in the solid state. Moreover, the structures of these two molecules can serve as models for sections or wedges present in their corresponding higher generation dendritic analogues. The molecular structures of **4** and **7a** are depicted in Figures 6 and 7, respectively. Relevant bond lengths and distances are summarized in Table 1, while the crystallographic data for **4** and **7a** are given in Table 2.

The structures of **4**[19] and **7a** show the *monomeric*, i.e., *intra*molecular, halide-bridged, *cis*-isomers[16] unlike the dimeric, i.e., *inter*molecular, halide-bridged structure

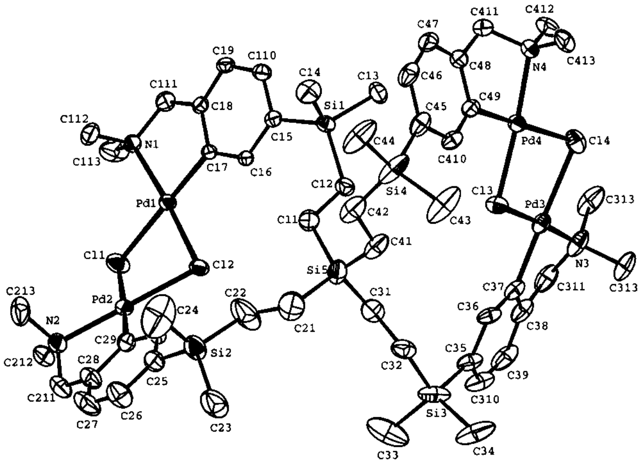


Figure 7. Displacement ellipsoid plot (50% probability) of the molecular structure of **7a**. Hydrogen atoms and cocrystallized pentane have been omitted for clarity.

found for $[CH_2SiMe_2(C_6H_3\{CH_2NMe_2\}\text{-}4\text{-}(PdCl)\text{-}3)]_2$ (abbreviated as CS-$[CN-PdCl]_2$, Figure 1).[11] The fact that in both **4** and **7a** *intra* rather than *inter* halide-assisted dimer formation takes place can be explained by the presence of a structurally different carbosilane backbone present in **4** and **7a** when compared with the carbosilane support in CS-$[CN-PdCl]_2$. Apparently, the conformations along the carbosilane support in **4** and **7a** enabled the pendant cyclopalladated complexes to come into each other's proximity to form an *intra*molecular bridge via the chloride anions. It is interesting to note that this intramolecular halide-bridging mode does not significantly affect the bond distances and angles found in both derivatives. The interatomic distances Pd–Cl(1), Pd–Cl(2), Pd–C, and Pd–N fall in the same range as was found for CS-$[CN-PdCl]_2$ (vide supra), although some bond lengths show (minor) deviations. The same applies for the bond angles, although it should be noted that in **7a** there were some marked differences found around the palladium metal center, e.g., expressed in the angle Cl(2)–Pd(1)–N(1) of 171.40(19)° (cf., 175.76(10)° for CS-$[CN-PdCl]_2$).[11] Additionally, in both structures some ring strain in the carbosilane interior is present. In **4**, the dihedral angles C(14)–Si(2)–C(17)–C(18) and C(17)–Si(2)–C(14)–C(13) are 73.2(3)° and −66.6(3)°, respectively, while in **7a** additional distortions are found in the torsion angles Si(5)–C(11)–C(12)–Si(1) and Si(5)–C(41)–C(42)–Si(4), which amounted to −157.6(5)° and −162.3(5)°. This increase in conformational distortion in the dendritic backbone of **4** and **7a** as compared with the close to ideal Si–C–C–Si dihedral angles in CS-$[CN-PdCl]_2$ of ca. 179° most probably has to be ascribed to the formation of *intra*- rather than *inter*molecular aggregates.

Molecular mechanics calculations[17] carried out for **4** (Scheme 1) and the [G0] derivatives **5a** and **7a** (Scheme 2) clearly showed that the *cis*-bridging mode is more favored than the *trans*-bridging mode. The latter halide bridging mode leads to more conformational restraints in the Pd_2Cl_2 "square" units. These calculations were in line with those carried out for CS-$[CN-PdCl]_2$,[11] and the calculated structures of **4** and **7a** matched well with the results of the crystallographic studies. As compared with the molecular modeling carried out for the model species (μ-Cl-$[PdCl(C_6H_3\{CH_2NMe_2\}\text{-}2\text{-}SiMe_3\text{-}5)]$)$_2$[11] (vide

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(19) This compound showed a halide disorder in the solid state. We ascribe this to the presence of LiBr during the crystallization of **4** (see for refinement procedures the Experimental Section). In a separate experiment we prepared bromide-free **4**, the stoichiometry of which was spectroscopically and analytically supported (Experimental Section).

Table 1. Selected Interatomic Distances (Å), Bond Angles (deg), and Dihedral Angles (deg) for the Cyclopalladated Carbosilanes 4 and 7a

4		7a	
	Bond Distances		
Pd(1)−Cl(1)	2.305(6)	Pd(1)−Cl(1)	2.461(2)
Pd(1)−Cl(2)	2.462(2)	Pd(1)−Cl(2)	2.334(2)
Pd(1)−C(1)	1.978(4)	Pd(1)−C(17)	1.977(6)
Pd(1)−N(1)	2.068(3)	Pd(1)−N(1)	2.078(6)
Pd(2)−Cl(1)	2.314(6)	Pd(2)−Cl(1)	2.465(2)
Pd(2)−Cl(2)	2.462(2)	Pd(2)−Cl(2)	2.356(2)
Pd(2)−C(24)	1.961(4)	Pd(2)−C(29)	1.955(8)
Pd(2)−N(2)	2.073(3)	Pd(2)−N(2)	2.094(6)
	Bond Angles		
Cl(1)−Pd(1)−Cl(2)	86.20(14)	Cl(1)−Pd(1)−Cl(2)	85.72(7)
Cl(1)−Pd(1)−N(1)	177.32(17)	Cl(2)−Pd(1)−N(1)	171.40(19)
Cl(1)−Pd(1)−C(1)	95.05(18)	Cl(2)−Pd(1)−C(17)	96.62(19)
Cl(2)−Pd(1)−N(1)	95.62(9)	Cl(1)−Pd(1)−N(1)	94.76(16)
Cl(2)−Pd(1)−C(1)	175.94(11)	Cl(1)−Pd(1)−C(17)	176.09(19)
N(1)−Pd(1)−C(1)	83.26(14)	N(1)−Pd(1)−C(17)	83.4(2)
	Dihedral Angles		
C(14)−Si(2)−C(17)−C(18)	73.2(3)	Si(5)−C(12)−C(13)−Si(1)	−157.6(5)
C(17)−Si(2)−C(14)−C(13)	−6.6(3)	Si(5)−C(21)−C(22)−Si(2)	179.8(6)
C(17)−C(18)−C(19)−Si(3)	−177.4(3)	Si(5)−C(31)−C(32)−Si(3)	172.6(4)
Si(1)−C(12)−C(13)−C(14)	−177.4(2)	Si(5)−C(41)−C(42)−Si(4)	−162.3(4)

Table 2. Crystal Data and Details of the Structure Determination for 4 and 7a

	4	7
empirical formula	$C_{30}H_{52}N_2Si_3Pd_2Br_{0.15}Cl_{1.85}\cdot 0.5C_6H_6$	$C_{52}H_{84}N_4Si_4Pd_4Cl_4$
fw	854.48	1473.21
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$ (no. 14)	$Pbca$ (no. 61)
a/Å	12.746(9)	13.3571(2)
b/Å	14.627(4)	26.9874(4)
c/Å	23.890(16)	39.6304(5)
β/deg	109.50(5)	90
V/Å^3	4198(4)	14285.7(4)
Z	4	8
$D_{(calc)}$/[g/cm^3]	1.352	1.401
F(000)	1751	6102
μ(Mo Kα)/mm^{-1}	1.23	1.3
cryst size/mm	0.9 × 0.2 × 0.1	0.06 × 0.31 × 0.38
T/K	150	150
radiation/Å	Mo Kα, 0.71073	Mo Kα, 0.71073
θ min, max/deg	1.66, 27.47	1.5, 25.0
scan (type and range)/deg	$0.65 + 0.35\tan(\theta)$	
dataset	0.91:27.50; −16:16; −18:0;−20:30	0:15; 0:32; 0:47
no. of tot, unique data, R(int)	11 405, 9601, 0.0366	103609, 12559, 0.0628
no. obsd data [$I > 2.0\,\sigma(I)$]	7266	7941
N_{ref}, N_{par}	25, 393	0.0506, 0.1862, 0.995
R, wR2, S	0.039, 0.091, 0.998	0.056, 0.1862, 1.0
w^{-1}	$\sigma^2(F_o^2) + (0.044P^2)$	$\sigma^2(F_o^2) + (0.100P^2)$ and $P = (F_o^2 + 2F_c^2)/3$
max and av shift/error	0.002, 0.00	0.02, 0.00
min/max resd dens/[e/Å^3]	−0.61, 0.55	−0.90, 1.73

supra), these latter calculations, together with the crystallographic studies, indicate that, on the basis of geometrical considerations, the *cis* bridging mode in these peripheral halide-assisted Pd(II) dimers is more likely to occur. Furthermore, interconversion to the *trans* isomer seems unlikely, as the carbosilane support and the Pd_2Cl_2 "square" units then have to adopt rather strained conformations (cf., the conformation of the carbosilane support in the solid state structures of **4** and **7a**).

Cyclopalladated Dendrimers as Catalysts for the Aldol Condensation Reaction. The pyridine adducts **5b**, **7b**, **10b**, **12b**, **13b**, and **15b** were used as catalyst precursors in the aldol condensation reaction[20] of benzaldehyde with methyl isocyanoacetate (Figure 8).

Consequently, **5b**, **7b**, **10b**, **12b**, **13b**, and **15b** were converted in their corresponding (poly)cationic analogues **5c**, **7c**, **10c**, **12c**, **13c**, and **15c** by abstracting the

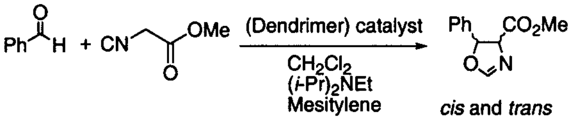

Figure 8. Catalyzed aldol condensation of benzaldehyde and methyl isocyanoacetate yielding oxazolines.

halide anion using $AgBF_4$ in wet acetone (Scheme 8). After appropriate workup involving a thorough filtration of the solutions containing the polycations through a path of Celite to remove the insoluble silver halide salt,[21]

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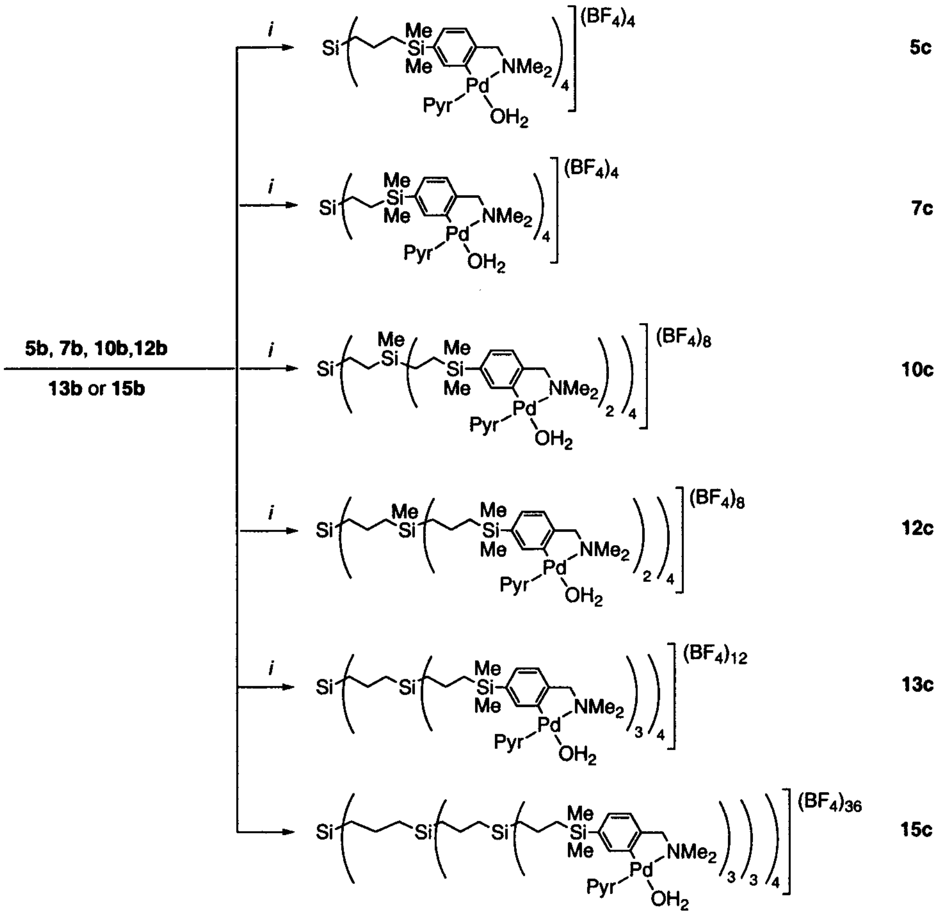
(20) For recent relevant examples concerning aldol condensation catalysis see: (a) Nesper, R.; Pregosin, P. S.; Püntener, K.; Wörle, M. *Helv. Chim. Acta* **1993**, *76*, 2239−2248. (b) Hayashi, T.; Sawamura, M.; Ito, Y. *Tetrahedron* **1999**, *48*, 1999−2012. (c) Longmire, J. M.; Zhang, X.; Shang, M. *Organometallics* **1998**, *17*, 4374−4379. (d) Gorla, F.; Togni, A.; Venanzi, L. M. *Organometallics* **1994**, *13*, 1607−1616. (e) Stark, M. A.; Jones, G.; Richards, C. J. *Organometallics* **2000**, *19*, 1282.

Scheme 8. Synthesis of the Polycationic Palladium(II) Dendrimers[a]



[a] Reagents and conditions: (i) $AgBF_4$, wet acetone.

Table 3. Aldol Condensation of Benzaldehyde and Methyl Isocyanoacetate Catalyzed by the Cationic Dendrimer Species and the Parent Model Complex 16[a]

catalyst	mol % Pd	time, h	conversion %[b]	% *trans*[b]	% *cis*[b]	TOF/Pd[c]	TON/Pd
5c, [G0]-Pd_4	0.99	24	>99	64	36	26	101
7c, [G0]#-Pd_4	1.04	24	97	64	36	20	93
10c, [G1]#-Pd_8	0.93	24	55	57	43	9	59
12c, [G1]-Pd_8	0.93	24	96	61	39	22	104
13c, [G1]-Pd_{12}	0.89	24	97	58	42	27	109
15c, [G2]-Pd_{36}	1.19	24	99	63	37	11	83
16, Pd_1	0.94	24	97	64	36	26	103
no catalyst		24	5	(n.d.)[d]	(n.d.)[d]		

[a] Reaction carried out in CH_2Cl_2 (10 mL) at RT with ca. 10 mol % Hünigs base (=NEt(i-Pr)$_2$). Selectivity for these reactions is ≥98% determined with mesitylene as an internal standard. [b] Calculated by specific ^1H NMR spectroscopic signal integration using the internal standard. [c] Per hour during the first hour. [d] Not determined.

these polycationic materials were isolated as rather insoluble and very hygroscopic, yellow to brown powders (isolated yields: 80% to quantitative). Identification of these cations was carried out by means of ^1H NMR spectroscopy in acetone-d_6.

Despite the low solubility of the polycationic dendritic species **5c**, **7c**, **10c**, **12c**, and **13c** in solvents such as $CHCl_3$, CH_2Cl_2, and benzene, these species dissolved readily in CH_2Cl_2 in the presence of methyl isocyanoacetate,[22] i.e., under the catalytic conditions. During the catalytic runs with the dendrimer catalysts *no* formation of palladium black was observed, which points to the increased stability of the cationic palladium complexes under the catalytic conditions.[23]

The catalytic results are presented in Table 3 and are compared with the activity of the corresponding mononuclear, model compound [Pd(C_6H_3{CH_2NMe_2}-2-($SiMe_3$)-5)(pyr)(H_2O)]BF_4 (**16**) (Scheme 9) as well as the uncatalyzed reaction. The parent model compound **16** was produced similarly to the dendrimer compounds starting from the known pyridine adduct [PdCl(C_6H_3{CH_2NMe_2}-2-($SiMe_3$)-5)(pyr)].[11]

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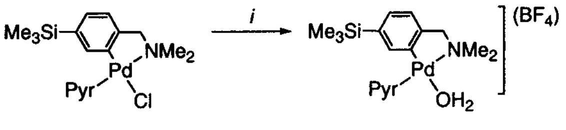
[21] This is important to note, as the precipitated silver salt can also act as a (heterogeneous) Lewis acid catalyst.

[22] It is generally assumed that the initial step in this particular aldol condensation reaction is the replacement of the labile H_2O ligand by the isocyanoacetate substrate. For general mechanistic aspects concerning this kind of catalysis see: (a) Richard, J. P.; Nagorski, R. W. *J. Am. Chem. Soc.* **1999**, *121*, 4763–4770. (b) Saito, S.; Yamamoto, H. *Chem. Eur. J.* **1999**, *5*, 1959–1962.

[23] Though *during* the catalytic runs no palladium black formation was observed, the polycationic dendrimers are susceptible toward decomposition in (acetone) solution as well as in the solid state, as illustrated by darkening of the samples under these conditions.

Scheme 9. Synthesis of the Model Cationic Species 16[a]



16

[a] Reagents and conditions: (i) $AgBF_4$, wet acetone.

The smaller dendritic species and the model compound showed only minor differences when both the initial reaction rate (TOF) and total turnover number (TTN) after 24 h per Pd(II) site are compared. For the higher generation Pd-dendrimer catalysts **10c**, **12c**, and **13c** an almost negligible decrease in the *trans*/*cis* ratio of the oxazoline product formed in this particular aldol condensation reaction was observed. An interesting difference in reaction rate was noted between the [G1] generation species **10c** and **12c**. Apparently the more compact structure of **10c** due to the C_2-linkers instead of C_3-linkers present in **12c** has a distinct effect on the catalytic activity of the individual Pd(II) sites. These data are in line with the fact that also for the more crowded [G2] generation species **15c** a decrease in catalytic activity per Pd(II) site has been observed.

Conclusions

In summary, this work demonstrates that different generations of cyclometalated dendrimers can be readily prepared using a multiple C−H bond activation procedure. For the palladated dendrimers, a unique halide-assisted dimer formation between the peripheral Pd(II) complexes was encountered. For the [G1] dendrimers **10a** and **12a**, an unexpected formation of a temperature-independent ratio of isomeric forms of these dimeric Pd(II) complexes was observed, which was supported by VT and (2D) NMR spectroscopic studies. An unexpected isomerization of the peripheral pyridine ligands was proposed for the [G2] generation dendrimer **15b**, which is most likely due to steric congestion at the periphery of the dendrimer.

The Pd(II) metallodendrimers were successfully applied as homogeneous catalysts in the aldol condensation between benzaldehyde and methyl isocyanoacetate. The catalytic data indicated that more rigid/crowded dendritic catalysts become slower accompanied by a slight selectivity change in the *trans*/*cis* ratio of the oxazoline product. These novel Pd(II) dendrimers hold promise for a wide range of C−C or cross-coupling reactions.[24] Therefore, we are currently focused on the use of these Pd(II) dendrimers in a range of other (catalytic) applications.

Experimental Section

General Comments. All air-sensitive manupilations were carried out in an inert (nitrogen) atmosphere using standard Schlenk techniques. All solvents were carefully dried and distilled prior to use. Standard chemicals were purchased from Acros Chimica or Aldrich and used without further purification. Compounds [G0]-$(SiMe_2{-}CN)_4$,[10] [G1]-$(SiMe_2{-}CN)_{12}$,[10] $[G0]^{\#}$-$(SiMeCl_2)_4$,[14a,c] $[G1]^{\#}$-$(SiMe_2Cl)_8$,[14a] and [G2]-$(SiMe_2Cl)_{36}$[14b] were prepared according to previously reported procedures. ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectroscopic measurements were performed on a Varian Inova/Mercury 200 or 300 MHz spectrometer at RT, and chemical shifts (δ) are given in ppm with TMS as an external standard unless otherwise noted. The MALDI-TOF mass spectra were acquired using a Voyager-DE BioSpectrometry workstation (PerSeptive Biosystems Inc., Framingham, MA) mass spectrometer. Sample solutions with an approximate concentration of 20−30 mg/mL in THF or CH_2Cl_2 were prepared. The matrix was 3,5-dihydroxybenzoic acid (DHB) or 9-nitroanthracene (9-NA) with approximate concentrations of 20−30 mg/mL. A 0.2 μL portion of the sample 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. Elemental analyses were performed by Dornis und Kolbe, Mülheim a/d Ruhr, Germany.

$[G0]^{1/2}$-$(SiMe_2Cl)_2$ (1). To a mixture of dimethyldiallylsilane (2.60 g, 18.5 mmol) and chlorodimethylsilane (ca. 8 mL, 6.8 g, 72 mmol) were added some drops of a concentrated solution of $[Bu_4N]_2PtCl_6$ in EtOH. The reaction mixture was stirred and after ^1H NMR spectroscopy showed that the conversion into **1** was complete ($\leq$17 h). Excess $HSiMe_2Cl$ was removed under reduced pressure to give a clear, colorless liquid (6.08 g, 18.5 mmol, >99%). ^1H NMR (C_6D_6): δ 1.47−1.35 (m, 4H, $(CH_3)SiCH_2C\mathit{H}_2$), 0.79−0.71 (m, 4H, $C\mathit{H}_2Si(CH_3)_2Cl$), 0.60−0.49 (m, 4H, $(CH_3)SiC\mathit{H}_2CH_2$), 0.25 (s, 12H, $CH_2Si(C\mathit{H}_3)_2Cl$), −0.05 (s, 6H, $(C\mathit{H}_3)SiCH_2CH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 23.6, 19.5, 18.0 (3 × $\mathit{C}H_2$), 1.8 ($Si(\mathit{C}H_3)_2Cl$), −3.2 ($(\mathit{C}H_3)_2Si$). This compound was converted to the moisture stable hydride **2**.

$[G0]^{1/2}$-$(SiMe_2H)_2$ (2). A solution of **1** (1.77 g, 5.37 mmol) in Et_2O (30 mL) was slowly added to a suspension of $LiAlH_4$ (0.73 g, 19.2 mmol) in Et_2O (20 mL) at 0 °C. The reaction mixture was stirred at RT for 20 h and then cautiously treated with H_2O and 4 M HCl in order to dissolve most of the precipitated salts. After filtration, the H_2O layer was extracted with pentane (2 × 50 mL). The combined organic layers were dried on $MgSO_4$ and concentrated in vacuo. Flash distillation at reduced pressure gave a colorless liquid (1.03 g, 3.95 mmol, 74%). ^1H NMR (C_6D_6): δ 4.15−4.04 (m, 2H, $J = 3.5$ Hz, $CH_2Si(CH_3)_2\mathit{H}$), 1.53−1.37 (m, 4H, $(CH_3)SiCH_2C\mathit{H}_2$), 0.70−0.57 (m, 8H, $(CH_3)SiC\mathit{H}_2CH_2$ and $C\mathit{H}_2Si(CH_3)_2H$), 0.06 (d, 12H, $J = 3.7$ Hz, $CH_2Si(C\mathit{H}_3)_2H$), −0.01 (s, 6H, $(C\mathit{H}_3)SiCH_2CH_2{-}$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 19.8, 19.4, 19.0 (3 × $\mathit{C}H_2$), −3.1 ($(\mathit{C}H_3)_2Si$), −4.3 ($Si(\mathit{C}H_3)_2H$). GC−MS (EI): m/z 159 $(M - (CH_2)_3Si(CH_3)_2H)^+$. Anal. Calcd for $C_{12}H_{32}Si_3$: C 55.30, H 12.37, Si 32.33. Found: C 55.45, H 12.30, Si 32.46.

$[G0]^{1/2}$-$(SiMe_2\text{-}CN)_2$ (3). This compound was prepared using a previously reported method.[10] To a solution of 1-bromo-4-[(dimethylamino)methyl]benzene (1.99 g, 9.29 mmol) in Et_2O (25 mL) was added *t*-BuLi (ca. 10 mL of a 1.5 M solution in pentane, 15 mmol) at −78 °C. After stirring the white suspension for 15 min, a solution of **1** (1.13 g, 3.43 mmol) in Et_2O (30 mL) was added, and the resulting mixture was allowed to reach RT. After purification by Kugelrohr distillation (0.2 mmHg, 170−190 °C) a clear, yellow viscous oil was obtained (1.37 g, 2.60 mmol, 76%). ^1H NMR (C_6D_6): δ 7.54 (d, 4H, $J = 7.8$ Hz, Ar−H), 7.43 (d, 4H, $J = 7.6$ Hz, Ar−H), 3.30 (s, 4H, CH_2N), 2.11 (s, 12H, $N(CH_3)_2$), 1.52−1.40 (m, 4H, $(CH_3)_2SiCH_2C\mathit{H}_2$), 0.91−0.83 (m, 4H, $C\mathit{H}_2Si(CH_3)_2Ph$), 0.64−0.56 (m, 4H, $(CH_3)_2SiC\mathit{H}_2CH_2$), 0.29 (s, 12H, $CH_2Si(C\mathit{H}_3)_2Ph$), −0.03 (s, 6H, $(C\mathit{H}_3)_2SiCH_2CH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 140.8, 138.0, 134.0, 128.7 (4 × Ar−C), 64.6 ($\mathit{C}H_2N$), 45.5 ($N(\mathit{C}H_3)_2$), 20.8, 20.3, 19.0 (3 × $\mathit{C}H_2$), −2.6 ($Si(\mathit{C}H_3)_2Ph$), −3.0 ($(\mathit{C}H_3)_2Si$). FAB-MS: m/z 527 $(M + H)^+$, 525 $(M - H)^+$. Anal. Calcd for $C_{30}H_{54}N_2Si_3$: C 68.37, H 10.33, N 5.32, Si 15.99. Found: C 68.52, H 10.40, N 5.28, Si 15.83.

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[24] (a) Motoyama, Y.; Narusawa, H.; Nishiyama, H. *Chem. Commun.* **1999**, 131−132. (b) Motoyama, Y.; Mikami, Y.; Kawakami, H.; Aoki, K.; Nishiyama, H. *Organometallics* **1999**, *18*, 3584−3588. (c) Weissmann, H.; Milstein, D. *Chem. Commun.* **1999**, 1901−1902. (d) Leung, P. H.; Ng, K. H.; Li, Y.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1999**, 2435−2436. (e) Stark, M. A.; Richards, C. *Tetrahedron Lett.* **1997**, *38*, 5881−5884.

[G0]$^{1/2}$-(SiMe$_2$-CN−PdCl)$_2$ (4). Compound **3** (1.57 g, 2.98 mmol) was dissolved in MeOH (80 mL), and to this solution was added solid Pd(OAc)$_2$ (1.34 g, 5.96 mmol) and NaOAc (0.50 g, 6.10 mmol). The resulting mixture was stirred for 20 min, and during this time the color of the suspension changed from red-brown to black. The mixture was filtered through a path of Celite, and the resulting clear orange to red solution was treated with LiCl (0.33 g, 7.78 mmol). Immediately a yellow-orange suspension was obtained which was concentrated in vacuo. To the residue was added benzene (100 mL) and H$_2$O (100 mL). The organic layer was separated and the H$_2$O layer extracted with benzene (2 × 50 mL). The combined benzene layers were washed with saturated aqueous NaCl (2 × 50 mL) and then dried on K$_2$CO$_3$. After removal of the solvent under reduced pressure, the product was washed with pentane (2 × 50 mL) and dried in vacuo to give a yellow to orange solid (2.00 g, 2.47 mmol, 83%). Analytically pure **4** was obtained by slow diffusion of pentane into a concentrated solution of **4** in benzene. These crystals were suitable for an X-ray molecular structure determination. ^{1}H NMR (C$_6$D$_6$): δ 8.03 (s, 2H, Ar−H$_{ortho}$), 7.30 (d, 2H, J = 7.1 Hz, Ar−H), 6.74 (d, 2H, J = 7.2 Hz, Ar−H), 3.12 (s, 4H, CH$_2$N), 2.28 (s, 12H, N(CH$_3$)$_2$), 1.82−1.72 (m, 4H, (CH$_3$)$_2$SiCH$_2$C*H*$_2$), 0.99−0.91 (m, 4H, C*H*$_2$Si(CH$_3$)$_2$-Ph), 0.79−0.71 (m, 4H, (CH$_3$)$_2$SiC*H*$_2$CH$_2$), 0.38 (s, 12H, CH$_2$-Si(C*H*$_3$)$_2$Ph), 0.03 (s, 6H, (C*H*$_3$)$_2$SiCH$_2$CH$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 148.0, 143.9, 139.6, 137.0, 130.0, 121.3 (6 × Ar−C), 72.9 (*C*H$_2$N), 52.0 (N(*C*H$_3$)$_2$), 21.3, 20.8, 19.4 (3 × *C*H$_2$), −2.4 (Si(*C*H$_3$)$_2$Ph), −2.5 ((*C*H$_3$)$_2$Si). FAB-MS: *m/z* 808 (M)$^+$, 773 (M − Cl)$^+$. Anal. Calcd for crystalline C$_{30}$H$_{52}$N$_2$Si$_3$Pd$_2$Cl$_2$·C$_6$H$_6$: C 48.75, H 6.59, N 3.16, Si 9.50. Found: C 48.79, H 6.65, N 3.22, Si 9.63.

[G0]-(SiMe$_2$-CN-PdCl)$_4$ (5a). This compound was prepared in a way similar to that described for **4**. To a solution of [G0]-SiMe$_2$−CN (0.59 g, 0.61 mmol) in MeOH (40 mL) was added solid Pd(OAc)$_2$ (0.69 g, 3.07 mmol). The resulant red-colored mixture was stirred for 6 h, upon which LiCl (0.69 g, 16.3 mmol) was added. After workup, a yellow solid was isolated (0.47 g, 0.31 mmol, 51%). ^{1}H NMR (C$_6$D$_6$): δ 8.00 (s, 4H, Ar−H$_{ortho}$), 7.28 (d, 4H, J = 7.0 Hz, Ar−H), 6.71 (d, 4H, J = 7.2 Hz, Ar−H), 3.17 (s, 8H, CH$_2$N), 2.31 (s, 24H, N(CH$_3$)$_2$), 1.78−1.62 (m, 8H, SiCH$_2$C*H*$_2$CH$_2$), 1.01−0.93 (m, 8H, SiCH$_2$-CH$_2$C*H*$_2$), 0.84−0.76 (m, 8H, SiC*H*$_2$CH$_2$CH$_2$), 0.37 (s, 12H, Si(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 147.66, 143.77, 139.60, 137.39, 130.00, 121.17 (6 × Ar−C), 72.97 (*C*H$_2$N), 52.03 (N(*C*H$_3$)$_2$), 21.06, 19.38, 18.01 (3 × CH$_2$), −2.23 (Si(*C*H$_3$)$_2$). FAB-MS: *m/z* 1529.4 (M)$^+$, 1493.4 (M − Cl)$^+$. Anal. Calcd for C$_{56}$H$_{92}$N$_4$Si$_5$Pd$_4$Cl$_4$: C 43.98, H 6.06, N 3.66, Si 9.18. Found: C 43.82, H 6.15, N 3.83, Si 9.32.

[G0]-(SiMe$_2$-CN-PdCl{pyr})$_4$ (5b). To a solution of **5a** (62.1 mg, 0.0406 mmol) in CH$_2$Cl$_2$ (20 mL) was added an excess of pyridine (ca. 3 mL). The clear yellowish reaction mixture was stirred for 16 h. Then the volatiles were removed in vacuo, and the product was precipitated from CH$_2$Cl$_2$/pentane, washed with pentane (10 mL), and dried to give **5b** as an off-white solid (66.3 mg, 0.0359 mmol, 88%). ^{1}H NMR (CDCl$_3$): δ 8.87 (d, J = 3.6 Hz, 8H, pyr-H$_{ortho}$), 7.79 (br, 4H, pyr-H), 7.33 (br, 8H, pyr-H), 7.08 (d, J = 7.0 Hz, 4H, Ar−H), 6.94 (d, J = 7.0 Hz, 4H, Ar−H), 6.04 (s, 4H, Ar−H$_{ortho}$), 3.95 (s, 8H, CH$_2$N), 2.93 (s, 24H, N(CH$_3$)$_2$), 1.15 (br m, 8H, dendrimer CH$_2$), 0.55 (br m, 8H, dendrimer CH$_2$), 0.38 (br m, 8H, dendrimer CH$_2$), −0.04 (s, 24H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 153.90, 148.85, 148.45, 137.86, 137.29, 136.74, 129.83, 125.13, 121.30 (9 × Ar−C), 74.15 (*C*H$_2$N), 53.04 (N(*C*H$_3$)$_2$), 20.79, 18.66, 17.63 (3 × dendrimer CH$_2$), −2.75 (Si(CH$_3$)$_2$). Anal. Calcd for C$_{76}$H$_{112}$N$_8$Si$_5$Pd$_4$Cl$_4$·4CH$_2$Cl$_2$: C 43.97, H 5.53, N 5.13. Found: C 43.95, H 5.86, N 4.75.

[G0]$^{\#}$-(SiMe$_2$-CN)$_4$ (6). This compound was prepared using a previously reported method.[10] To a solution of 1-bromo-4-[(dimethylamino)methyl]benzene (4.61 g, 21.5 mmol) in Et$_2$O (40 mL) was added *t*-BuLi (ca. 26 mL of a 1.5 M solution in pentane, 39 mmol) at −78 °C. After stirring the white suspension for 15 min, a solution of [G0]$^{\#}$-(SiMe$_2$Cl)$_4$ (2.20 g, 4.28 mmol) in Et$_2$O (30 mL) was added, and the resulting mixture was allowed to reach room temperature and then stirred for 18 h. After purification by Kugelrohr distillation (0.2 mmHg, 130 °C) a clear, yellow viscous oil was obtained (2.79 g, 3.07 mmol, 72%), which solidified at RT. ^{1}H NMR (C$_6$D$_6$): δ 7.53 (d, 8H, J = 8.4 Hz, Ar−H), 7.41 (d, 8H, J = 8.1 Hz, Ar−H), 3.30 (s, 8H, CH$_2$N), 2.10 (s, 24H, N(CH$_3$)$_2$), 0.64 (m, 16H, SiC*H*$_2$C*H*$_2$Si, AA′BB′ pattern), 0.29 (s, 24H, Si(C*H*$_3$)). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 140.70, 137.71, 133.97, 128.69 (4 × Ar−C), 64.56 (*C*H$_2$N), 45.48 (N(*C*H$_3$)$_2$), 8.22, 3.01 (2 × *C*H$_2$), −3.3 (Si(*C*H$_3$)$_2$). FAB-MS: *m/z* 909.5 (M + H)$^+$. Anal. Calcd for C$_{52}$H$_{88}$N$_4$Si$_5$: C 68.65, H 9.75, N 6.16, Si 15.44. Found: C 68.70, H 9.84, N 6.10, Si 15.53.

[G0]$^{\#}$-(SiMe$_2$-CN-PdCl)$_4$ (7a). This compound was prepared analogously to **4**. To solution of **6** (0.50 g, 0.55 mmol) in MeOH (30 mL) was added Pd(OAc)$_2$ (0.55 g, 2.45 mmol), and the resultant red to orange colored mixture was stirred for 16 h followed by addition of LiCl (0.47 g, 11.1 mmol). After appropriate workup, a slightly yellow solid was obtained (0.73 g, 0.50 mmol, 91%). Crystals suitable for an X-ray molecular structure determination were obtained by slow diffusion of pentane into a solution of **6** in benzene. ^{1}H NMR (C$_6$D$_6$): δ 8.09 (s, 4H, Ar−H$_{ortho}$), 7.26 (d, 4H, J = 7.4 Hz, Ar−H), 6.71 (d, 4H, J = 7.2 Hz, Ar−H), 3.13 (s, 8H, CH$_2$N), 2.24 (s, 24H, N(CH$_3$)$_2$), 1.04−0.87 (m, 16H, SiC*H*$_2$C*H*$_2$Si, AA′BB′ pattern), 0.30 (s, 24H, Si(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 147.71, 143.99, 139.44, 137.38, 130.24, 121.22 (6 × Ar−C), 72.84 (*C*H$_2$N), 52.01 (N(*C*H$_3$)$_2$), 8.00, 3.71 (2 × *C*H$_2$), −2.55 (Si(*C*H$_3$)$_2$). FAB-MS: *m/z* 1472.7 (M)$^+$, 1437.0 (M − Cl)$^+$. Anal. Calcd for C$_{52}$H$_{84}$N$_4$-Si$_5$Pd$_4$Cl$_4$: C 42.40, H 5.75, N 3.80, Si 9.53. Found: C 42.58, H 5.66, N 3.72, Si 9.64.

[G0]$^{\#}$-(SiMe$_2$-CN-PdCl{pyr})$_4$ (7b). A mixture of **7a** (63.3 mg, 0.0430 mmol) and an excess of pyridine (3 mL) in CH$_2$Cl$_2$ (25 mL) was stirred for 19 h. Then the solvent was removed in vacuo and the product washed with pentane (50 mL) to give **7b** as a white solid. Yield: 66.0 mg (0.0369 mmol, 86%). ^{1}H NMR (CDCl$_3$): δ 8.79 (d, J = 5.2 Hz, 8H, pyr-H$_{ortho}$), 7.65 (t, J = 7.6 Hz, 4H, pyr-H), 7.15−7.06 (m, 12H, pyr-H + Ar−H), 6.95 (d, J = 7.0 Hz, 4H, Ar−H), 6.02 (s, 4H, Ar−H$_{ortho}$), 3.98 (s, 8H, CH$_2$N), 2.96 (s, 24H, N(CH$_3$)$_2$), 0.16 (m, 16H, dendrimer CH$_2$), −0.04 (s, 24H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 153.75, 148.97, 137.69, 137.44, 136.49, 129.80, 125.10, 121.40 (8 × Ar−C, one signal most probably coincident with another one), 74.10 (*C*H$_2$N), 53.11 (N(*C*H$_3$)$_2$), 8.02, 2.81 (2 × dendrimer CH$_2$), −3.48 (Si(*C*H$_3$)$_2$). Anal. Calcd for C$_{72}$H$_{104}$N$_8$Si$_5$Pd$_4$Cl$_4$: C 48.32, H 5.86, N 6.26, Cl 7.92. Found: C 48.39, H 5.93, N 6.17, Cl 8.06.

G1$^{\#}$-(CH=CH$_2$)$_8$ (8). To a solution of vinylmagnesium bromide (100 mL of a 1.0 M solution in THF, 100 mmol) was added dropwise [G0]$^{\#}$-(SiMeCl$_2$)$_4$ (2.72 g, 4.56 mmol) dissolved in THF (200 mL). The orange-colored mixture was stirred for 1.5 h, and ^{1}H NMR spectroscopy showed at this stage that the reaction was complete. The mixture was carefully quenched with H$_2$O, after which most of the THF was removed in vacuo. The product was extracted with pentane (250 mL) and the organic layer was washed with H$_2$O (2 × 250 mL), dried over Na$_2$SO$_4$, and filtered. After concentration under reduced pressure a clear yellow, viscous oil was obtained (1.53 g, 2.89 mmol, 63%). ^{1}H NMR (C$_6$D$_6$): δ 6.20 (dd, ^3J = 9.8 Hz, 8H, C*H*=CH$_2$), 5.99 (d, ^3J = 9.8 Hz, ^2J = 2.8 Hz, 8H, CH=C*H*$_2$), 5.76 (d, ^3J = 13.4 Hz, ^2J = 2.8 Hz, 8H, CH=C*H*$_2$), 0.67 (m, 16H, −CH$_2$CH$_2$−), 0.16 (s, 12H, SiCH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 137.01, 133.30 (*C*H=*C*H$_2$), 6.71, 3.11 (−*C*H$_2$*C*H$_2$−), −5.53 (Si*C*H$_3$). ^{29}Si{^{1}H} NMR (C$_6$D$_6$): δ 10.52 (*Si*$_{core}$), −10.82 (*Si*CH$_3$). MALDI-TOF-MS: *m/z* 635.08 and 637.00 (M+^{107}Ag/^{109}Ag)$^+$. Calcd for (M+^{107}Ag/^{109}Ag)$^+$: *m/z* 635.20 and 637.19. Anal. Calcd for C$_{28}$H$_{52}$Si$_5$: C 63.55, H 9.91, Si 26.54. Found: C 63.66, H 9.98, Si 26.36.

[G1]$^{\#}$-(SiMe$_2$-CN)$_8$ (9). This compound was prepared using a previously reported procedure.[10] To a solution of 1-bromo-4-[(dimethylamino)methyl]benzene (2.45 g, 11.4 mmol) in Et$_2$O

(25 mL) was added *t*-BuLi (ca. 14.5 mL of a 1.5 M solution in pentane, 21.8 mmol) at −78 °C. After stirring the white suspension for 15 min, a solution of [G1]$^{\#}$-(SiMe$_2$Cl)$_8$[14a] (1.14 g, 0.89 mmol) in Et$_2$O (30 mL) was added, and the resulting mixture was allowed to reach room temperature. After purification by Kugelrohr distillation (0.2 mmHg, 110−120 °C) a clear yellow, viscous oil was obtained (1.55 g, 0.75 mmol, 84%). ^{1}H NMR (C$_6$D$_6$): δ 7.57 (d, *J* = 7.8 Hz, 16H, Ar−H), 7.44 (d, *J* = 7.5 Hz, 16H, Ar−H), 3.32 (s, 16H, CH$_2$N), 2.11 (s, 48H, N(CH$_3$)$_2$), 0.73 (m, 48H, dendrimer −CH$_2$−), 0.32 (s, 48H, Si(CH$_3$)$_2$), 0.07 (s, 12H, SiCH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 140.81, 137.81, 134.11, 128.81 (4 × Ar−C), 64.69 (*C*H$_2$N), 45.59 (N(*C*H$_3$)$_2$), 8.51, 5.46, 5.17, 3.21 (4 × dendrimer *C*H$_2$), −3.08 (Si(*C*H$_3$)$_2$), −6.14 (Si*C*H$_3$). ^{29}Si{^{1}H} NMR (C$_6$D$_6$): δ 10.17 (*Si*$_{core}$), 8.56 (*Si*CH$_3$), −1.51 (*Si*(CH$_3$)$_2$). MALDI-TOF-MS: *m*/*z* 2076.21 (M$^+$). Calcd for M$^+$: *m*/*z* 2076.13. Anal. Calcd for $C_{116}H_{204}N_8Si_{13}$: C 67.11, H 9.90,N 5.40, Si 17.59. Found: C 67.27, H 9.96, N 5.54, Si 17.47.

[G1]$^{\#}$-(SiMe$_2$-CN-PdCl)$_8$ (10a). To a solution of **9** (0.34 g, 0.16 mmol) in MeOH (80 mL) was added solid Pd(OAc)$_2$ (0.36 g, 1.60 mmol). The resultant suspension was stirred for 23 h, after which LiCl (0.24 g, 5.80 mmol) was added. This mixture was then stirred for 0.5 h, and subsequently the solvent was removed in vacuo. The solid residue was extracted with CH$_2$Cl$_2$ (2 × 100 mL), washed with H$_2$O (75 mL), and dried on Na$_2$SO$_4$. After filtration and drying under reduced pressure, a light orange-colored solid was isolated (0.42 g, 0.13 mmol, 80%). ^{1}NMR (CDCl$_3$): δ 7.41 (s, 8H, Ar−H$_{ortho}$), 7.09 (d, *J* = 6.8 Hz, 8H, Ar−H), 6.84 (d, *J* = 7.2 Hz, 8H, Ar−H), 3.91 (s, 16H, CH$_2$N), 2.84 (s, 48H, N(CH$_3$)$_2$), 0.88−0.33 (br m, 48H, dendrimer −CH$_2$−), 0.18 (s, 48H, Si(CH$_3$)$_2$), −0.14 (s, 12H, SiCH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 147.44, 143.03, 138.81, 137.60, 130.27, 121.37 (6 × Ar−C), 73.45 (*C*H$_2$N), 52.97 (N(*C*H$_3$)$_2$), 7.94, 5.43, 2.87 (3 × dendrimer *C*H$_2$), −2.19, −2.89 (1 × dendrimer *C*H$_2$ + Si(*C*H$_3$)$_2$), −6.15 (Si*C*H$_3$). MALDI-TOF-MS: *m*/*z* 3168.12 (M − Cl)$^+$. Calcd for (M − Cl)$^+$: *m*/*z* 3167.54. Anal. Calcd for $C_{116}H_{196}N_8Si_{13}Pd_8Cl_8 \cdot 4CH_2Cl_2$: C 40.68, H 5.80, N 3.16. Found: C 40.80, H 5.84, N 3.09.

[G1]$^{\#}$-(SiMe$_2$-CN-PdCl{pyr})$_8$ (10b). To a solution of **10a** (0.19 g, 0.059 mmol) in CH$_2$Cl$_2$ (10 mL) was added an excess of pyridine (0.5 mL). The mixture was stirred for 10 min and then evaporated to dryness. The solid residue was washed with pentane (20 mL) and dried in vacuo to yield a slightly salmon colored powder (>99%). ^{1}H NMR (CDCl$_3$): δ 8.83 (br, 16H, pyr-H$_{ortho}$), 7.76 (br m, 8H, pyr-H), 7.34 (br m, 16H, pyr-H), 6.04 (s, 8H, Ar−H$_{ortho}$), 3.98 (br s, 16H, CH$_2$N), 2.95, 2.85 (2 × s, 48H, N(CH$_3$)$_2$), 0.25 (br, dendrimer −CH$_2$−), −0.04 (br s, 48H, Si(CH$_3$)$_2$), −0.16, −0.22 (br, 12H, SiCH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 147.44, 143.03, 138.81, 137.60, 130.27, 121.37 (6 × Ar−*C*), 73.45 (*C*H$_2$N), 52.97 (N(*C*H$_3$)$_2$), 7.93, 5.43, 2.87 (3 × dendrimer *C*H$_2$), −2.19, −2.88 (Si*C*H$_3$ + Si(*C*H$_3$)$_2$), −6.15 (dendrimer *C*H$_2$). Anal. Calcd for $C_{156}H_{236}N_{16}Si_{13}Pd_8Cl_8$: C 48.85, H 6.20, N 5.84, Cl 7.39. Found: C 48.72, H 6.25, N 5.78, Cl 7.31.

[G1]-(SiMe$_2$-CN)$_8$ (11). This compound was prepared using a method described in the literature.[10] To a solution of 4-bromo-[(dimethylamino)methyl]benzene (2.33 g, 10.9 mmol) in Et$_2$O was added *t*-BuLi (14 mL of a 1.5 M solution in pentane, 21 mmol) at −78 °C. The resultant suspension was stirred for 10 min, whereupon [G1]-(SiMe$_2$Cl)$_8$ (1.42 g, 0.98 mmol) was added as a solution in Et$_2$O (30 mL). After appropriate workup and further purification by Kugelrohr distillation (130−140 °C, 2−3 h) a bright yellow, viscous oil was obtained (1.70 g, 0.76 mmol, 78%). ^{1}H NMR (C$_6$D$_6$): δ 7.55 (d, 16H, *J* = 8.0 Hz, Ar−H), 7.42 (d, 16H, *J* = 7.6 Hz, Ar−H), 3.31 (s, 16H, CH$_2$N), 2.11 (s, 48H, N(CH$_3$)$_2$), 1.55 (m, −CH$_2$−, dendrimer support), 0.92 (m, −CH$_2$-, dendrimer support), 0.72 (m, −CH$_2$−, dendrimer support), 0.31 (s, 48H, Si(C*H*$_3$)), 0.06 (s, 12H, SiCH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 141.08, 138.36, 134.29, 129.08 (4 × Ar−C), 65.02 (*C*H$_2$N), 45.93 (N(*C*H$_3$)$_2$), 21.38, 19.57, 19.52 (3 × outer −*C*H$_2$−, dendrimer support), 20.14, 19.75, 18.74 (3 × inner −*C*H$_2$−, dendrimer support), −2.07 (Si(*C*H$_3$)$_2$), −4.17 (Si*C*H$_3$). ^{29}Si{^{1}H} NMR (C$_6$D$_6$): δ 1.44 (*Si*(CH$_3$)$_2$), 1.04 (*Si*CH$_3$), −3.86 (*Si*-aryl). MALDI-TOF-MS: *m*/*z* 2245.81 (M + H)$^+$. Calcd: 2245.47 (M + H)$^+$. Anal. Calcd for $C_{128}H_{228}N_8Si_{13}$: C 68.50, H 10.24, N 4.99, Si 16.27. Found: C 68.50, H 10.29, N 5.06, Si 16.20.

[G1]-(SiMe$_2$-CN-PdCl)$_8$ (12a). This compound was prepared as described for **10**. To a solution of **11** (0.46 g, 0.21 mmol) in MeOH (60 mL) was added Pd(OAc)$_2$ (0.50 g, 2.21 mmol). Within 10 min a suspension was observed, which was stirred for 2 h, and subsequently LiCl (0.23 g, 5.56 mmol) was added. After a workup similar to that described for **11**, a yellow to orange solid was isolated (0.45 g, 0.13 mmol, 65%). ^{1}H NMR (CDCl$_3$, mixture of isomers): δ 7.41 (br s, 8H, Ar−H$_{ortho}$), 7.08 (br d, *J* = 5.0 Hz, 8H, Ar−H), 6.83 (br d, *J* = 6.8 Hz, 8H, Ar−H), 3.99 (d, *J*(A−B) = 14.0 Hz, CH$_2$N), 3.90 (br s, CH$_2$N), 3.80 (d, *J*(A−B) = 13.8 Hz, CH$_2$N), 2.83 (br s, 48H, N(CH$_3$)$_2$), 1.31 (br, −CH$_2$−, dendrimer backbone), 0.76 (br, −CH$_2$−, dendrimer backbone), 0.55 (br, −CH$_2$−, dendrimer backbone), 0.22 (br s, 48H, Si(CH$_3$)$_2$), −0.13 (br s, 12H, SiCH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 147.44, 142.93, 138.92, 137.76, 129.94, 121.29 (6 × Ar−*C*), 73.43 (*C*H$_2$N), 52.87 (N(*C*H$_3$)$_2$), 20.93, 20.69, 19.89, 18.95, 18.76, 17.89 (6 × −*C*H$_2$−, dendrimer backbone), −2.38 (Si(*C*H$_3$)$_2$), −4.32 (Si*C*H$_3$). MALDI-TOF-MS: *m*/*z* 3335.45 (M − Cl)$^+$. Calcd: *m*/*z* 3335.92 (M − Cl)$^+$. Anal. Calcd for $C_{128}H_{220}N_8Si_{13}Pd_8Cl_8$: C 45.60, H 6.58,N 3.32, Cl 8.41. Found: C 45.46, H 6.47, N 3.24, Cl 8.52.

[G1]-(SiMe$_2$-CN-PdCl{pyr})$_8$ (12b). To a solution of **12a** (0.17 g, 0.050 mmol) in CH$_2$Cl$_2$ (10 mL) was added an excess of pyridine (0.5 mL). The mixture was stirred for 20 min and then evaporated to dryness. The solid residue was washed with pentane (20 mL) and dried in vacuo to yield a slightly yellow powder (>99%). ^{1}H NMR (CDCl$_3$): δ 8.88 (br, 16H, pyr-H$_{ortho}$), 7.78 (br, 8H, pyr-H), 7.32 (br, 16H, pyr-H), 7.07 (br, 8H, Ar−H), 6.95 (br, 8H, Ar−H), 6.04 (s, 8H, Ar−H$_{ortho}$), 3.94 (s, 16H, CH$_2$N), 2.92 (s, 48H, N(CH$_3$)$_2$), 1.80 (br m, 8H, dendrimer CH$_2$), 1.20 (br m, 16H, dendrimer CH$_2$), 0.82 (br m, 8H, dendrimer CH$_2$), 0.55 (br m, 16H, dendrimer CH$_2$), 0.44 (br m, 16H, dendrimer CH$_2$), 0.21 (br m, 8H, dendrimer CH$_2$), −0.04 (s, 48H, Si(CH$_3$)$_2$), −0.17 (s, 12H, SiCH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 153.87, 148.85, 148.52, 137.81, 137.30, 136.82, 129.81, 125.13, 121.30 (9 × Ar−C), 74.14 (*C*H$_2$N), 53.02 (N(*C*H$_3$)$_2$), 20.64, 19.51, 18.91, 18.76, 18.63, 17.93 (6 × dendrimer CH$_2$), −2.69 (Si(*C*H$_3$)$_2$), −4.68 (Si*C*H$_3$). Anal. Calcd for $C_{168}H_{260}N_{16}Si_{13}Pd_8Cl_8$: C 50.39, H 6.55, N 5.60, Cl 7.08. Found: C 50.47, H 6.61, N 5.52, Cl 7.07.

[G1]-(SiMe$_2$-CN-PdCl)$_{12}$ (13a). This compound was prepared as described for **10**. To a stirred solution of [G1]-(SiMe$_2$−CN)$_{12}$ (0.66 g, 0.21 mmol) in MeOH was added Pd(OAc)$_2$ (0.65 g, 2.89 mmol). Gradually an orange-brown colored suspension was observed, which was stirred for 21 h. Then LiCl (0.53 g, 12.5 mmol) was added and this mixture stirred for ca. 2 h. After a similar workup as described for **10**, a light yellow to orange powder was isolated (0.40 g, 0.083 mmol, 40%). ^{1}H NMR (CDCl$_3$): δ 7.40 (br, 12H, Ar−H$_{ortho}$), 7.08 (br, 12H, Ar−H), 6.83 (br, 12H, Ar−H), 3.88 (br, 24H, CH$_2$N), 2.83 (br s, 72H, N(CH$_3$)$_2$), 1.29 (br m, −CH$_2$−, dendrimer backbone), 0.76 (br m, −CH$_2$−, dendrimer backbone), 0.53 (br m, −CH$_2$−, dendrimer backbone), 0.21 (br s, 72H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 147.47, 143.02, 138.82, 137.60, 129.99, 121.39 (6 × Ar−C), 73.45 (*C*H$_2$N), 52.91 (N(*C*H$_3$)$_2$), 21.22, 20.82, 18.91, 17.89 (−CH$_2$− dendrimer backbone, several signals coincide with each other), −2.33 (Si(*C*H$_3$)$_2$). MALDI-TOF-MS: *m*/*z* 4777.4 (M − Cl)$^+$. Calcd: *m*/*z* 4777.02 (M − Cl)$^+$. Anal. Calcd for $C_{180}H_{300}N_{12}Si_{13}Pd_{12}Cl_{12}$: C 44.92, H 6.28, N 3.49, Cl 8.84. Found: C 44.86, H 6.15, N 3.41, Cl 8.68.

[G1]-(SiMe$_2$-CN-PdCl{pyr})$_{12}$ (13b). To a solution of **13a** (0.16 g, 0.033 mmol) in CH$_2$Cl$_2$ (10 mL) was added an excess of pyridine (0.5 mL). The yellow-colored mixture was stirred for 5 min and then evaporated to dryness. The solid residue was washed with pentane (20 mL) and dried in vacuo to yield a slightly yellow powder (0.16 g, 0.028 mmol, 84%). ^{1}H NMR (CDCl$_3$): δ 8.88 (br, 16H, pyr-H$_{ortho}$), 7.78 (br, 8H, pyr-H), 7.32 (br, 16H, pyr-H), 7.07 (br, 8H, Ar−H), 6.95 (br, 8H, Ar−H), 6.04 (s, 8H, Ar−H$_{ortho}$), 3.94 (s, 16H, CH$_2$N), 2.92 (s, 48H, N(CH$_3$)$_2$), 1.80 (br m, 8H, dendrimer CH$_2$), 1.20 (br m, 16H, dendrimer CH$_2$), 0.82 (br m, 8H, dendrimer CH$_2$), 0.55 (br m, 16H, dendrimer CH$_2$), 0.44 (br m, 16H, dendrimer CH$_2$), 0.21 (br m, 8H, dendrimer CH$_2$), −0.04 (s, 48H, Si(CH$_3$)$_2$), −0.17 (s, 12H, SiCH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 153.83, 148.86, 148.59, 137.84, 137.25, 136.74, 129.77, 125.13, 121.31 (9 × Ar−C), 74.10 (*C*H$_2$N), 53.01 (N(*C*H$_3$)$_2$), 20.82, 18.73, 17.93, 17.63 (4 × dendrimer CH$_2$, 2 signals are coincident), −2.66 (Si(*C*H$_3$)$_2$). Anal. Calcd for $C_{240}H_{360}N_{24}Si_{17}Pd_{12}Cl_{12}$: C 50.03, H 6.30, N 5.83, Cl 7.38. Found: C 49.92, H 6.21, N 5.77, Cl 7.49.

[G2]-(SiMe$_2$-CN)$_{36}$ (14). This compound was prepared using a literature procedure[10] by treatment of [G2]-SiMe$_2$Cl (1.42 g, 0.235 mmol) with an excess of the in situ prepared lithium reagent [Li(C$_6$H$_4${CH$_2$NMe$_2$}-4)] (ca. 16 mmol). After appropriate workup using Kugelrohr distillation (180−200 °C), the product was isolated as an extremely viscous brown oil (0.86 g, 0.090 mmol, 38%). ^{1}H NMR (C$_6$D$_6$): δ 7.54 (br, 72H, Ar−H), 7.44 (br, 72H, Ar−H), 3.30 (br s, 72H, CH$_2$N), 2.10 (br s, 216H, N(CH$_3$)$_2$), 1.59 (br m, −CH$_2$−, dendrimer support), 0.86 (br m, −CH$_2$−, dendrimer support), 0.32 (br s, 216H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 140.97, 138.36, 134.29, 129.13 (4 × Ar−C), 64.96 (*C*H$_2$N), 45.87 (N(*C*H$_3$)$_2$), 21.50, 19.60, 18.85, 18.30 (4 × −*C*H$_2$−, dendrimer support with the other signals most probably coicident), −2.07 (Si(*C*H$_3$)$_2$). ^{29}Si{^{1}H} NMR (C$_6$D$_6$): δ 1.37, 1.08, 0.90 (inner *Si*), −3.92 (outer *Si*). MALDI-TOF-MS: *m/z* ca. 7200−9930 (br, M^{+} region), ca. 4250−6250 (br, M^{2+} region), ca. 2000−3500 (br, M$^{3/4+}$ region). Anal. Calcd for $C_{552}H_{960}N_{36}Si_{53}$: C 69.13, H 10.09, N 5.26, Si 15.52. Found: C 69.07, H 10.02, N 5.15, Si 15.43.

[G2]-(SiMe$_2$-CN-PdCl)$_{36}$ (15a). To a solution of **14** (0.30 g, 0.0313 mmol) in MeOH (40 mL) was added Pd(OAc)$_2$ (0.25 g, 1.13 mmol). The resultant yellow-brown suspension was stirred for 16 h. The solvent was then decanted and the solid residue washed with one portion of MeOH (60 mL). The chloride-bridged intermediate species proved to be insoluble in the common organic solvents. Therefore, compound **15a** was converted into its soluble pyridine adduct in situ without further purification.

[G2]-(SiMe$_2$-CN-PdCl{pyr})$_{36}$ (15b). To an unpurified sample of **15a** (vide supra) was added an excess of pyridine (ca. 5 mL), and immediately solubilization of the solid material occurred. The dark solution was stirred for 16 h and then filtered through a path of Celite to remove traces of palladium black and then concentrated to a volume of ca. 10 mL. The product was precipitated by adding pentane (50 mL), collected by centrifugation, and washed again with pentane (50 mL) and acetone (50 mL). Drying in vacuo gave a white solid (0.21 g, 0.0120 mmol, 38% overall). ^{1}H NMR (CDCl$_3$, mixture of isomers): δ 8.83 (br m, 72H, pyr-H$_{ortho}$), 7.70 (br m, 36H, pyr-H), 7.40 (br m, 72H, pyr-H), 7.05 (br m, 72H, Ar−H), 6.90−6.86 (br m, 72H, Ar−H), 6.01 (br s, 36H, Ar−H$_{ortho}$), 3.93 and 3.88 (2 × br s, 72H, CH$_2$N), 2.91 and 2.81 (2 × br s, 216H, N(CH$_3$)$_2$), 1.27, 0.84, 0.82, 0.53 (br m, all dendrimer CH$_2$), 0.16 and −0.07 (2 × s, 216H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, mixture of isomers): δ 153.81, 153.53, 148.86, 148.74, 148.55, 148.43, 138.75, 138.40, 137.94, 137.27, 136.74, 129.87, 125.21, 121.42 (all Ar−C + pyr-C), 74.15, 73.44 (CH$_2$N), 53.05 (N(CH$_3$)2), 20.85, 18.08, 17.66, 16.14 (partly overlapping dendrimer CH$_2$), −2.20, −2.54 (Si(CH$_3$)$_2$). Anal. Calcd for $C_{732}H_{1104}N_{72}Si_{53}Pd_{36}Cl_{36}$: C 50.21, H 6.36, N 5.76, Cl 7.29, Pd 21.88. Found: C 50.18, H 6.28, N 5.71, Cl 7.34, Pd 21.76.

Preparation of Aldol Condensation Catalysts. General procedure: A mixture of [PdCl(C$_6$H$_3${CH$_2$NMe$_2$}-2-(SiMe$_3$)-4)(Pyr)][11] (60.0 mg, 0.14 mmol) and a slight excess of AgBF$_4$ (32.3 mg, 0.17 mmol) in acetone (25 mL) was stirred for 16 h at RT. Then the precipitated silver salt was thoroughly removed by filtration through a path of Celite to give a clear, yellow-colored filtrate. The solvent was removed in vacuo and the product precipitated from a acetone/pentane mixture to yield [Pd(C$_6$H$_3${CH$_2$NMe$_2$}-2-(SiMe$_3$)-4)(H$_2$O)(Pyr)] (**16**), as a solid material (75.1 mg, 0.15 mmol). The dendrimer species **5c**, **7c**, **10c**, **12c**, **13c**, and **15c** were prepared analogously. It should be mentioned that the dendrimer precursor compounds **5b** **7b**, **10b**, **12b**, **13b**, and **15b** are rather insoluble in acetone, but dissolve upon treatment with AgBF$_4$. *All* cationic species are extremely hygroscopic and were used immediately after isolation and ^{1}H spectroscopic analysis in the catalytic experiments. For **16** (off-white solid, yield >99%): ^{1}H (CDCl$_3$): δ 8.84 (d, *J* = 5.2 Hz, 2H, pyr-H$_{ortho}$), 7.92 (t, *J* = 7.8 Hz, 1H, pyr-H), 7.48 (t, *J* = 7.2 Hz, 2H, pyr-H), 7.15 (d, *J* = 7.0 Hz, 1H, Ar−H), 6.93 (d, *J* = 7.4 Hz, 1H, Ar−H), 5.99 (s, 1H, Ar−H$_{ortho}$), 3.94 (s, 2H, CH$_2$N), 3.13 (br s, 2H, H$_2$O), 2.84 (s, 6H, N(CH$_3$)$_2$), 0.02 (s, 9H, Si(CH$_3$)$_3$).

For **5c** (off-white solid, yield >99%): ^{1}H (acetone-*d*$_6$): δ 8.95 (d, *J* = 5.2 Hz, 8H, pyr-H$_{ortho}$), 8.15 (t, *J* = 8.0 Hz, 4H, pyr-H), 7.73 (t, *J* = 7.6 Hz, 8H, pyr-H), 7.14 (d, *J* = 6.6 Hz, 4H, Ar−H), 6.97 (d, *J* = 7.8 Hz, 4H, Ar−H), 6.03 (s, 4H, Ar−H$_{ortho}$), 4.11 (s, 8H, CH$_2$N), 2.96 (s, 24H, N(CH$_3$)$_2$), 1.45, 0.75, 0.58 (3 × m, 8H, dendrimer CH$_2$), −0.04 (s, 24H, Si(CH$_3$)$_2$).

For **7c** (light yellow solid, yield >99%): ^{1}H (acetone-*d*$_6$): δ 8.90 (br, 8H, pyr-H$_{ortho}$), 8.04 (br, 4H, pyr-H), 7.64 (br, 8H, pyr-H), 7.14 (d, *J* = 7.2 Hz, 4H, Ar−H), 7.04 (d, *J* = 6.8 Hz, 4H, Ar−H), 6.06 (s, 4H, Ar−H$_{ortho}$), 4.14 (s, 8H, CH$_2$N), 3.42 (br s, 8H, H$_2$O), 2.82 (s, 24H, N(CH$_3$)$_2$), 0.27 (br m, 16H, dendrimer CH$_2$), −0.01 (s, 24H, Si(CH$_3$)$_2$).

For **10c** (light yellow solid, yield 56%): ^{1}H (acetone-*d*$_6$): δ 8.90 (br, 16H, pyr-H$_{ortho}$), 8.08 (br, 8H, pyr-H), 7.64 (br, 16H, pyr-H), 7.12 (d, *J* not resolved, 8H, Ar−H), 7.01 (d, *J* = 7.2 Hz, 8H, Ar−H), 6.06 (s, 8H, Ar−H$_{ortho}$), 4.11 (s, 16H, CH$_2$N), 3.36 (br s, 16H, H$_2$O), 2.83 (s, 48H, N(CH$_3$)$_2$), 0.38 (br m, dendrimer CH$_2$), 0.18 (br m, dendrimer CH$_2$), −0.04 (s, 48H, Si(CH$_3$)$_2$), −0.14 (s, 12H, SiCH$_3$).

For **12c** (off-white solid, yield 91%): ^{1}H (acetone-*d*$_6$): δ 8.93 (d, *J* = 4.8 Hz, 16H, pyr-H$_{ortho}$), 8.12 (t, 8H, pyr-H$_{ortho}$), 7.69 (t, *J* ≈ 8 Hz, 16H, pyr-H), 7.16 (d, *J* ≈ 7 Hz, 8H, pyr-H), 7.14 (d, *J* ≈ 7 Hz, 8H, Ar−H), 7.02 (d, *J* ≈ 7 Hz, 8H, Ar−H), 6.03 (s, 8H, Ar−H$_{ortho}$), 4.11 (s, 16H, CH$_2$N), 3.22 (br s, 16H, H$_2$O), 2.84 (s, 48H, N(CH$_3$)$_2$), 1.30 (br m, dendrimer CH$_2$), 0.65−0.55 (br m, dendrimer CH$_2$), −0.04 (s, 48H, Si(CH$_3$)$_2$), −0.11 (s, 12H, SiCH$_3$).

For **13c** (yellow to brown solid, yield 80%): ^{1}H (acetone-*d*$_6$): δ 8.92 (br, 24H, pyr-H$_{ortho}$), 8.12 (br, 12H, pyr-H), 7.64 (br, 24H, pyr-H), 7.14 (br, 12H, Ar−H), 7.02 (br, 12H, Ar−H), 6.06 (br s, 12H, Ar−H$_{ortho}$), 4.11 (br s, 24H, CH$_2$N), 3.28 (br s, 24H, H$_2$O), 2.84 (br s, 72H, N(CH$_3$)$_2$), 1.42−1.23 (br m, dendrimer CH$_2$), 0.85 (br m, dendrimer CH$_2$), 0.62 (br m, dendrimer CH$_2$), 0.27 (br m, dendrimer CH$_2$), 0.22 (br m, dendrimer CH$_2$), −0.01 (br s, 72H, Si(CH$_3$)$_2$).

For **15c** (light brown, sticky solid, yield 78%): ^{1}H (acetone-*d*$_6$): δ 8.88 (br, 72H, pyr-H$_{ortho}$), 8.06 (br, 36H, pyr-H), 7.63 (br, 72H, pyr-H), 7.12 (br, 36H, Ar−H), 6.98 (br, 36H, Ar−H), 6.06 (s, 36H, Ar−H$_{ortho}$), 4.09 (br s, 144H, CH$_2$N), 3.16 (br, H$_2$O), 2.81 (br s, 432H, N(CH$_3$)$_2$), 1.40−0.13 (br, dendrimer CH$_2$), −0.02 (br s, 216H, Si(CH$_3$)$_2$).

Protocol for the Catalytic Aldol Condensation Reaction. A mixture of benzaldehyde (0.26 g, 2.4 mmol), methyl isocyanoacetate (0.16 g, 1.6 mmol), ethyl-*N*,*N*-diisopropylamine (cocatalyst, 0.03 g), mesitylene (internal standard, 0.19 g, 1.6 mmol), and CH$_2$Cl$_2$ (10 mL) was prepared and added to 1 mol % of catalyst species (vide supra). From the clear and completely homogeneous, stirred reaction mixture samples were taken after regular time intervals and analyzed with ^{1}H spectroscopy in CDCl$_3$ after *careful* removal of the solvent. ^{1}H NMR (CDCl$_3$, oxazoline product): δ 7.38−7.23 (m, Ar−H), 7.10 (d, ^{4}J = 2.2 Hz, (*H*)C═N, *cis* or *trans* isomer, other signal not visible due to overlap), 5.73 (d, ^{3}J = 7.4 Hz, Ar−C(*H*)-O, *cis* isomer), 5.68 (d, ^{3}J = 5.2 Hz, Ar−C(*H*)−O, *trans* isomer), 5.08

(d, $^3J = 11.0$ Hz, $^4J = 1.8$ Hz, $-C(H)CO_2CH_3$, *cis* isomer), 4.62 (d, $^3J = 7.8$ Hz, $^4J = 2.2$ Hz, $-C(H)CO_2CH_3$, *trans* isomer), 3.83 (s, $-C(H)CO_2CH_3$, *trans* isomer), 3.19 (s, $-C(H)CO_2CH_3$, *cis* isomer).

Crystal Structure Determination for 4 and 7a. For **4**: $C_{30}H_{52}Br_{0.15}Cl_{1.85}N_2Pd_2Si_3^{-}\cdot 1/2C_6H_6$, $M_r = 854.48$, yellow, needle-shaped crystals (0.1 × 0.2 × 0.9 mm), cut from a larger aggregate, monoclinic, space group $P2_1/c$ (no. 14) with $a = 12.746(9)$, $b = 14.627(4)$, $c = 23.890(16)$ Å, $\beta = 109.50(5)°$, $V = 4198(4)$, $Z = 4$, $D_x = 1.352$ g/cm^3, $F(000) = 1751$, μ(Mo Kα) = 1.23 mm^{-1}. All data, where relevant, are given without disordered solvent contribution (vide infra); 11 405 reflections measured, 9601 independent reflections, $R_{int} = 0.0366$ ($1.66° < \theta < 27.47°$, ω scan, $T = 150$ K, Mo Kα radiation, graphite monochromator, $\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 Turbo diffractometer on a rotating anode. The structure was solved by direct methods (SHELXS86)[25] and refined on F^2 using SHELXL-96.[26] One of the bridging Cl atoms is substitutionally disordered with Br. A disorder model was introduced; the occupancy of the Cl component was refined to 0.850(3). Besides the disordered benzene solvate area, the unit cell contains two symmetry-related cavities (220 Å^3 each), filled with disordered solvent. No satisfactory model could be refined; the disordered density was therefore taken into account with the PLATON/SQUEEZE procedure.[27] A total electron count of 74 per unit cell was found and corrected for. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The displacement parameters of the Br atom were set equal to those of the corresponding Cl atom. Hydrogen atoms were refined with a fixed isotropic displacement parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms. Refinement of 393 parameters resulted in a final wR2 value of 0.091, $w = 1/[\sigma^2(F^2) + (0.0440P)^2]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$, R1 = 0.0393 (for 7266 $I > 2\sigma(I)$), $S = 0.998$, $-0.61 < \Delta\rho < 0.55$ e/Å^3.

For **7a**: $C_{52}H_{84}Cl_4N_4Pd_4Si_5\cdot 0.4CH_2Cl_2$, fw = 1507.05, yellow plate, 0.38 × 0.31 × 0.06 mm^3, orthorhombic, *Pbca* (no. 61), $a = 13.3571(2)$, $b = 26.9874(4)$, $c = 39.6304(5)$ Å, $V = 14285.7(4)$ Å^3, $Z = 8$, $D_x = 1.401$ g/cm^3, $\mu = 1.29$ mm^{-1}; 103 609 reflections were measured on a Nonius KappaCCD diffractometer with a rotating anode ($\lambda = 0.71073$ Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)\max = 0.59$ Å^{-1}. The data were merged using the program SORTAV;[28] 12 559 reflections were unique ($R_{int} = 0.063$). An absorption correction was not considered necessary. The structure was solved with direct methods (SHELXS97)[29] and refined with SHELXL97[30] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined as rigid groups. The dichloromethane molecules were refined on two postions with a total occupancy of 0.4 with respect to the main molecule: 666 refined parameters, 109 restraints. R values [$I > 2\sigma(I)$]: R1 = 0.0506, wR2 = 0.1659. R values [all reflns]: R1 = 0.0762, wR2 = 0.1862. GoF = 0.995. The remaining electron density was between −0.90 and 1.73 e/Å^3. Molecular illustration, structure checking, and calculations were performed with the PLATON package.[27]

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Supporting Information Available: Crystallographic details of the structure determination of **4** and **7a** including thermal parameters. This information is available free of charge via the Internet at http://pubs.acs.org.

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