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[Bis(pyrazolyl)methane]palladium Complexes with a Carbosilane Dendritic Structure

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A series of carbosilane dendritic ligands of general formula G*n*-[CH(3,5-Me_2pz)$_2$]$_m$ and their corresponding palladium(II) complexes G*n*-[CH(3,5-Me_2pz)$_2$Pd(X)Cl]$_m$ (X = Cl or Me) containing four (m = 1) or eight (m = 2) terminal bis(pyrazolyl)methane moieties, along with their corresponding monometallic counterparts (m = 0), have been synthesized. An appropriate choice of poly(pyrazolyl)methane ligand has allowed us to overcome the steric and solubility issues that previously limited the synthesis of polymetallic dendrimers containing (scorpionato)palladium complexes. The evaluation of these complexes as catalyst precursors in the Heck reaction between *p*-iodotoluene and methyl acrylate is also reported.

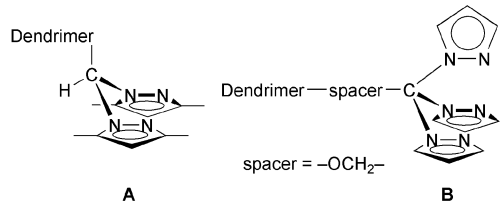
Introduction

Although a large variety of ligands have been used to anchor metal complexes to dendrimers,[1,2] [poly(pyrazol-1-yl)]metal complexes have rarely been used for this purpose. These ligands are a very versatile and important class of nitrogen donors in modern day coordination chemistry and have led to the development of the creative field of scorpionate chemistry.[3] Indeed, recent advances in this area have shown that poly(pyrazol-1-yl)alkane compounds[4,5] also have attractive applications in many interdisciplinary fields.[4,6]

In previous work, we evaluated the possible incorporation of scorpionate complexes into carbosilane metallodendritic complexes by taking advantage of the facile functionalization of the bridging methine carbon atom in tris(pyrazol-1-yl)methane,[7] as first demonstrated by Reger et al. in related studies.[8] A different approach to the synthesis of carbosilane dendrimers with peripheral [bis- or tris(pyrazolyl)borato]rhodium complexes was subsequently reported by Ciriano and Casado and their co-workers.[9]

After our preliminary study, in which we synthesized a tetranuclear compound with a carbosilane core along with four [tris(pyrazolyl)methane]molybdenum complexes, we concluded that a broader use of this type of N-heterocyclic donor in dendrimer chemistry would require modification of the ligand to reduce steric crowding and enhance the solubility of the final metallodendrimer.[7] Sterically demanding substituents bonded directly to the methine bridging carbon atom of tris(pyrazol-1-yl)methane units restrict the arrangement of the pyrazolyl rings and can suppress their coordination capability. Furthermore, poor solubility is a limiting factor commonly found in the synthesis of higher-generation polymetalated dendrimers.

In subsequent work, we focused on different strategies to overcome both the steric crowding in the ligand and the insolubility issue. In our first approach, we targeted a bis(pyrazol-1-yl)methane ligand with Fréchet's dendrons linked to the methylene bridge {G*n*-[HC(3,5-Me_2pz)$_2$]} (Scheme 1, **A**). These bidentate ligands at the focal point of the poly(benzyl ether) wedges are more flexible and lead to monometallic nickel(II)[10] and palladium(II)[11] complexes, the solubility of which is defined by the dendritic moiety and enhanced by the methyl substitutions on the pyrazolyl rings. Molybdenum(VI) and -(0) complexes containing the same bidentate ligands were also synthesized, and – in addition – we demonstrated that an –OCH_2– spacer between the poly(benzyl ether) dendrons and the methine carbon atom in the tris(pyrazol-1-yl)methane ligand (Scheme 1, **B**) results in suitable tridentate ligands for the preparation of either low- or high-oxidation-state molybdenum dendronized complexes.[12]



Scheme 1.

These synthetic studies have been complemented by others that aimed at gaining an understanding of the organization of the dendritic arms around the metal centers located at the core or focal point of the dendritic structures. Because this arrangement might modulate the properties of

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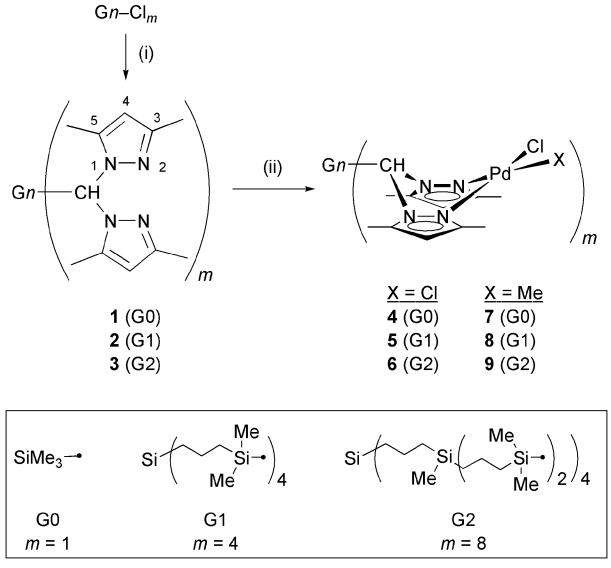
these metal centers, the catalytic behavior of these metallodendrimers has also been studied in processes such as oxidation, polymerization, and other carbon–carbon bond-formation reactions.[10–12]

We describe herein the next step in our ongoing research into dendrimers containing scorpionate complexes by reporting the preparation of polymetallic carbosilane dendrimers decorated with [bis(pyrazol-1-yl)methane]palladium(II) complexes at their periphery together with their catalytic performance in the Heck reaction.

Results and Discussion

Synthesis of the Carbosilane Bis(pyrazolyl)methane Ligands 1–3

The same methodology as described previously for the preparation of $Me_3SiCH(Me_2pz)_2$ (**1**; Me_2pz = 3,5-dimethylpyrazol-1-yl) was applied to the synthesis of the dendritic ligands **2** and **3** (Scheme 2).[10] Thus, the straightforward functionalization of the bidentate ligand at the methylene bridge was achieved by treatment of the lithium salt $LiCH(3,5\text{-}Me_2pz)_2$ with the appropriate chlorocarbosilane Me_3Si-Cl (G0-Cl), G1-Cl_4, or G2-Cl_8 in thf. A slight excess of the lithium salt was added to ensure the complete reaction of the peripheral Si–Cl bonds in the synthesis of compounds **2** and **3**. The unreacted lithium salt was readily separated after hydrolysis by sublimation (10^{-2} Torr, 50 °C). Both dendrimers were isolated after workup as air-stable, yellowish oils in good yield (≥75%, see the Exp. Sect. for details) and, as is the case for **1**, they were found to be fairly soluble in all common organic solvents.



1 (G0)
2 (G1)
3 (G2)

X = Cl	X = Me
4 (G0)	**7** (G0)
5 (G1)	**8** (G1)
6 (G2)	**9** (G2)

Scheme 2. Synthesis of carbosilane ligands and complexes. Reagents and conditions (*m* equiv.): (i) $LiCH(3,5\text{-}Me_2pz)_2$ in thf; (ii) $[PdCl_2(cod)]$ in toluene or [PdClMe(cod)] in diethyl ether or toluene.

In the NMR spectra the $SiMe_2$ resonances shift from δ = 0.4 (^{1}H) and 0.2 ppm (^{13}C) in the starting chlorocarbosilanes to $\delta \approx 0.2$ (^{1}H) and –3.0 ppm (^{13}C) in **2** and **3**. A unique set of NMR resonances is observed for the pyrazolyl rings, which are also characterized by a strong ν_{as}(C=N) IR absorption at around 1554 cm^{-1}. Ligands **2** and **3** gave satisfactory elemental analyses, and their ESI$^+$-TOF mass spectra exhibit a peak corresponding to the protonated molecular ion $[M + H]^+$.

Synthesis of Palladium Complexes 4–9

The palladium dichloride complexes G*n*-$[CH(3,5\text{-}Me_2pz)_2\text{-}PdCl_2]_m$ (**4**–**6**) were synthesized by displacement of the diene ligand of $[PdCl_2(cod)]$ (cod = η^4-1,5-cyclooctadiene) with **1**–**3**, respectively (Scheme 2). However, whereas the formation of the mononuclear compound **4** was virtually quantitative after 2 h in toluene at reflux, the complexation of **5** and **6** did not go to completion under the same conditions, and further refluxing resulted in the partial decomposition and precipitation of Pd^0. These metalations did, however, go to completion in 3 h, with isolated yields ≥80%, when the temperature was lowered to 80 °C to avoid decomposition. Chlorido(methyl) complexes **7** and **8** precipitated from diethyl ether solutions containing a mixture of ligands **1**–**3** and [PdClMe(cod)] at room temperature in ≥80% yield. A partially metalated precipitate was obtained when dendrimer **3** was treated under the same conditions, but compound **9** (Figure 1) could be conveniently synthesized in toluene at 80 °C (80% yield). All compounds were isolated as orange (**4**–**6**) or white (**7**) to pale-grey (**8** and **9**) air-stable solids. The general solubility of the chlorido(methyl) derivatives is slightly superior to that of their dichlorido counterparts.[11b,13] Thus, complexes **4**–**6** are soluble in chlorinated and polar (acetone, acetonitrile) solvents and insoluble in diethyl ether, toluene, or alkanes, whereas compounds **7**–**9** are slightly soluble in toluene. As is often the case with surface-functionalized dendrimers,[13] the solubility diminishes as the number of metal complexes at the periphery increases. Note that our attempts to prepare similar palladium(II) complexes of related carbosilane dendrimers containing terminal tris(pyrazolyl)methane ligands (Scheme 1, **B**) failed due to the formation of intractable mixtures of insoluble solids. This observation highlights the importance of considering the solubility in the ligand design of metal dendrimers. It is also remarkable that, whereas chlorido(methyl) complexes usually decompose in chlorinated solvents by Pd–Me/Pd–Cl exchange and concomitant precipitation of Pd^0,[6f,13,14] compounds **7**–**9** are fairly stable in such solvents at room temperature.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of the complexes reflect the local symmetry around the palladium atoms. Thus, compounds **4**–**6** (C_s symmetry) show one set of signals for the chelate ligand, whereas the absence of a mirror plane in **7**–**9** (C_1 symmetry) means that the two pyrazolyl rings are nonequivalent. The resonance for the 3-Me protons ($\delta \approx$ 2.5 ppm for **4**–**6**) splits into two singles in the spectra of **7**–

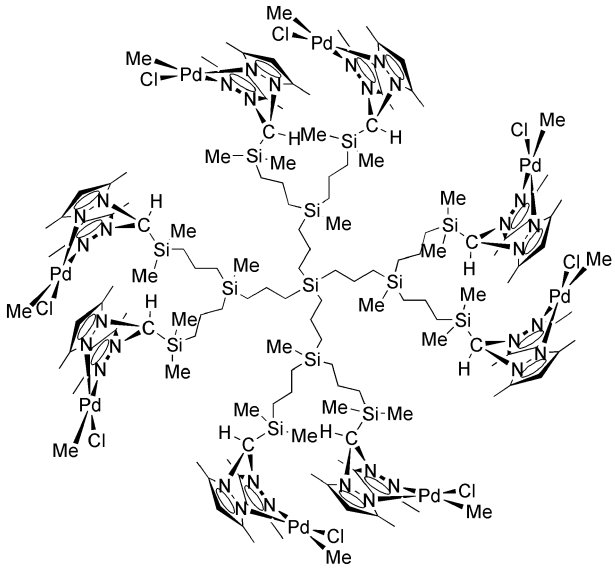


Figure 1. Metallodendrimer G2-[CH(Me$_2$pz)$_2$PdClMe]$_8$ (**9**).

9, with that at higher field ($\delta \approx 2.3$ ppm) corresponding to the 3-Me group adjacent to the Pd–Me moiety and that at lower field ($\delta \approx 2.5$ ppm) to the 3-Me group adjacent to the Pd–Cl bond. A similar splitting is observed for the 3-Me carbon atoms, the 5-Me groups, and, in the case of **9**, the C–H unit at the 4-position of the pyrazolyl rings. Additionally, a lack of symmetry is also observed in the $SiMe_2$ group bonded to the palladacycles in **8** and **9**. Coordination of the ligands usually shifts the ^{1}H and ^{13}C resonances of the CH(Me$_2$pz)$_2$ moieties (for instance, ca. 0.5 ppm for the 3-Me protons) and the $SiMe_2$ or $SiMe_3$ groups (ca. 0.4 ppm) downfield, whereas a significant upfield shift is observed for the ^{13}C resonance of the bridging methine carbon atom (ca. –4 ppm) as a result of the rigidity of the metallacycle formed.[10–12] Other resonances of the carbosilane framework remain basically unaltered upon coordination.

An absorption corresponding to the ν_{as}(C=N) vibration is found in the IR spectra of complexes **4**–**9** at around 1560 cm^{-1}. The ESI$^+$ or APCI$^+$ mass spectra of the G0- and G1-containing molecules (**4**, **5**, **7**, and **8**) show either the expected molecular ions or peaks derived from them, often resulting from the loss of Cl atoms or Me groups. In contrast, no peaks assignable to the molecular ions or to simple fragmentations are observed for the larger dendrimers **6** and **9**.

Structure of [Me$_3$SiCH(3,5-Me$_2$pz)$_2$PdCl$_2$] (4)

Figure 2 shows an ORTEP representation of the molecular structure of compound **4** in the solid state, as determined by single-crystal X-ray diffraction studies; selected structural data are given in Table 1. The structural parameters defining the –CH(3,5-Me$_2$pz)$_2$PdCl$_2$ moiety are fairly similar to those reported for other [bis(pyrazolyl)methane]-palladium(II) complexes[6f,11,14a,15] with the palladium atoms exhibiting a square-planar geometry. The Pd(NN)$_2$C palladacycle adopts a pronounced boat conformation, with the Me$_3$Si group occupying an axial position on the bridging atom C-11, thereby avoiding the steric hindrance that would arise from the adjacent methyl groups at the 5-position of the pyrazolyl ring in the equatorial positions. This steric repulsion confers rigidity on the metallacycle as no boat-to-boat conformational exchange is observed in solution.

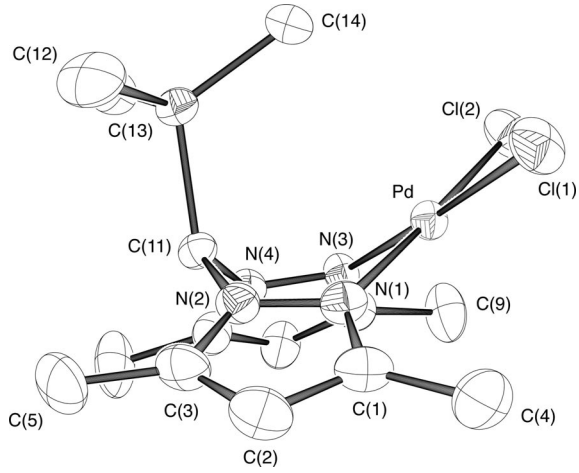


Figure 2. ORTEP diagram of the structure of compound **4** with thermal ellipsoids at the 50% probability level.

Table 1. Selected bond lengths and angles for compound **4**.

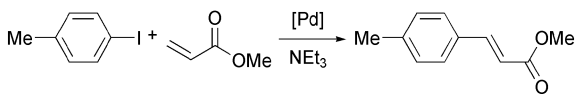
Bond lengths [Å]		Bond angles [°]	
Pd–Cl(1)	2.2869(11)	Cl(1)–Pd–Cl(2)	88.77(5)
Pd–Cl(2)	2.2881(11)	N(1)–Pd–N(3)	87.75(12)
Pd–N(1)	2.037(3)	N(1)–Pd–Cl(1)	91.70(9)
Pd–N(3)	2.032(3)	N(3)–Pd–Cl(2)	91.67(9)
N(1)–N(2)	1.375(4)	N(1)–Pd–Cl(2)	177.59(8)
N(3)–N(4)	1.375(4)	N(3)–Pd–Cl(1)	177.35(8)
N(2)–C(11)	1.460(4)	N(2)–C(11)–Si(1)	117.7(2)
N(4)–C(11)	1.455(4)	N(4)–C(11)–Si(1)	118.4(2)
C(11)–Si(1)	1.943(3)	N(2)–C(11)–N(4)	108.3(3)

A similar boat-type conformation of the six-membered metallacycle is found in structures of tetrahedral nickel(II)[10] and octahedral molybdenum(0)[12] complexes containing related bis(pyrazolyl)methane chelate ligands, although their different coordination environments yield broader or narrower N–M–N angles (ca. 94 and 79°, respectively) than those found in the structure of the square-planar Pd^{II} complex in this work (ca. 88°) or in previously reported structures.[6f,11,14a,15]

Evaluation of the Pd Dendrimers in the Heck Reaction

Complexes **4**–**9** were tested as catalytic precursors in the Heck coupling reaction of *p*-iodotoluene and methyl acrylate. The conversions attained after 23 h at 80 °C are summarized in Table 2 for all the catalysts, and the plots of conversion versus reaction time for the dichloride precursors **4**–**6** are shown in Figure 3 (analogous profiles were obtained for **7**–**9**).

Table 2. Conversion in the Heck reaction of *p*-iodotoluene with methyl acrylate catalyzed by **4**–**9**.[a]



Compounds	Conversions [%][b]		
	G0	G1	G2
G*n*-[L_2PdCl_2] **4**–**6**	61	82	89
G*n*-[$L_2PdMeCl$] **7**–**9**	81	90	88

[a] Conditions: 5 mL MeCN, *n*(Pd) = 5 μmol (1 mol-% based on Pd), [4-iodotoluene] = [methyl acrylate] = [NEt_3] = 0.1 M; t_r = 23 h; T_r = 80 °C. [b] Conversions were determined by GC.

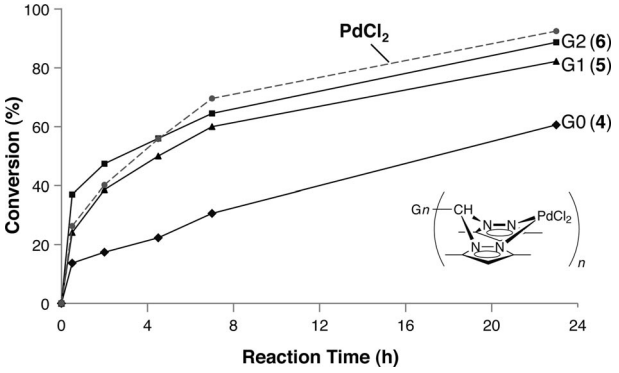


Figure 3. Reaction profiles for the G*n*-$[L_2PdCl_2]_m$ precursors **4**–**6** and $PdCl_2$ under the conditions described in Table 2. Conversions were determined by GC.

None of these precursors show significant advantages over $PdCl_2$ in the absence of the ligand under the same conditions (dashed line in Figure 3). As we have discussed previously,[11b] bis(pyrazolyl)methane ligands are barely efficient in stabilizing the molecular Pd species under the catalytic conditions and, in fact, precipitation of Pd black is always observed during the reaction. In any case, the dendrimer has a positive effect on the conversions, which follow the trend G2 (**6** and **9**) ≥ G1 (**5** and **8**) > G0 (**4** and **7**). This result may be related to the observation that polymetallic dendrimers tend often to be more resistant than monometallic complexes towards degradation and metal precipitation in Pd-catalyzed C–C coupling reactions.[16]

Conclusions

An appropriate choice of poly(pyrazolyl)methane ligand has allowed us to overcome the steric and solubility issues that previously limited the synthesis of polymetallic dendrimers containing scorpionate palladium complexes. Thus, by using $HC(3,5\text{-}Me_2pz)_2$ as a binding motif embedded in carbosilane structures, we have been able to synthesise palladium dendrimers up to the second generation, thereby highlighting the importance of ligand design in dendrimer chemistry.

Experimental Section

General: All operations were performed under argon by using Schlenk or dry-box techniques. Unless otherwise stated, reagents were obtained from commercial sources and used as received. The ligand $Me_3Si\text{-}CH(3,5\text{-}Me_2pz)_2$ (**1**),[10] carbosilane dendrimers G*n*-Cl_m,[17] and metallic precursors [$PdCl_2$(cod)] and [PdClMe(cod)][18] were prepared according to literature procedures. $LiCH(3,5\text{-}Me_2pz)_2$ was prepared as a white solid by modifying[10] a previously reported procedure.[19] All solvents were dried and distilled prior to use under argon, as described elsewhere.[20] Alternatively, reagent-grade solvents (Baker and SDS) were purified by flash column chromatography and collected under argon by using an MBraun MB SPS solvent purification device. NMR spectra were recorded at room temperature with a Varian Unity VR-300 or -200 spectrometer. Chemical shifts (δ) are reported in ppm relative to $SiMe_4$ and are referenced with respect to the ^{13}C and residual ^1H resonances of the deuteriated solvents. Coupling constants (*J*) are given in Hz. ^1H NMR integrated values for dendritic compounds are given relative to one of the four arms of the molecule. The numbering scheme for the pyrazolyl ring atoms is given in Scheme 2. IR spectra were recorded with a Perkin-Elmer FT-IR Spectrum-2000 spectrophotometer. Elemental analyses were performed by the Microanalytical Laboratories of the University of Alcalá with a Heraeus CHN-O-Rapid microanalyzer, and mass spectra were recorded with a Thermoquest–Finnigan Automass Multi (APCI) or an Agilent G3250AA LC/MSD TOF Multi (ESI) mass spectrometer. Heck reactions were performed by using a procedure described elsewhere[11b] and monitored by GC on a Chrompack CP 9001 gas chromatograph using a CP-WAX 52 CB FS-capillary column (15 m, 0.25 mm i.d., 0.25 μm film thickness) under the following conditions: injector and detector temperatures: 250 and 260 °C, respectively; oven temperature program: 100 °C for 1 min, 10 °C/min ramp, 240 °C/10 min.

Synthesis of Ligands and Complexes

G1-[CH(3,5-Me$_2$pz)$_2$]$_4$ (2): *n*BuLi (2.9 mL, 1.6 M in hexanes, 4.6 mmol) was slowly added from a funnel equipped with a bubbler to a solution of $H_2C(3,5\text{-}Me_2pz)_2$ (934 mg, 4.6 mmol) in thf (40 mL) at –78 °C, and the mixture was stirred at that temperature for 2 h. A solution of carbosilane G1-Cl_4 (655 mg, 1.15 mmol) in thf (20 mL) was then added, and the reaction mixture was warmed to room temperature and stirred overnight. The resulting solution was diluted with diethyl ether (30 mL) and washed with water (40 mL). The aqueous layer was washed with diethyl ether (2 × 30 mL), and the combined organic extracts were dried with $MgSO_4$. The volatiles were removed under vacuum to give compound **2** as a yellow oil. Yield: 1.24 g (87%). ^1H NMR ($CDCl_3$): δ = 0.17 (s, 6 H, $SiMe_2$), 0.41 (m, 2 H, $SiCH_2$), 0.73 (m, 2 H, CH_2SiMe_2), 1.16 (m, 2 H, $CH_2CH_2CH_2$), 1.94 (s, 6 H, 3-Me_{pz}), 2.15 (s, 6 H, 5-Me_{pz}), 5.72 (s, 2 H, 4-H_{pz}), 5.85 (s, 1 H, CH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = –2.8 ($SiMe_2$), 10.9 (5-Me_{pz}), 13.6 (3-Me_{pz}), 17.2 (CH_2), 18.1 (CH_2), 19.6 (CH_2), 67.9 (CH), 106.1 (C-4_{pz}), 139.6 (C-5_{pz}), 146.6 (C-3_{pz}) ppm. IR (CsI/Nujol): $\tilde{\nu}$ = 1554 (s, C=N) cm^{-1}. MS (ESI^+-TOF, CH_2Cl_2/MeOH/NH_4HCOO 5 mM): *m*/*z* = 1241.78 $[M + H]^+$. $C_{64}H_{108}N_{16}Si_5$ (1242.1): calcd. C 61.89, H 8.76, N 18.04; found C 61.46, H 8.36, N 17.88.

G2-[CH(3,5-Me$_2$pz)$_2$]$_8$ (3): A solution of G2-Cl_8 (470 mg, 0.32 mmol) in thf (10 mL) at –78 °C was added to a suspension of $Li[HC(3,5\text{-}Me_2pz)_2]$ (544 mg, 2.59 mmol) in the same solvent and at the same temperature. The reaction mixture was then warmed to room temperature and stirred overnight. The volatiles were removed under vacuum, the residue extracted with diethyl ether (2 × 20 mL), and the resulting solution washed with water

(2 × 20 mL) and dried with $MgSO_4$. Removal of the solvent gave compound **3** as a yellow oil. Yield: 670 mg (75%). ^{1}H NMR ($CDCl_3$): δ = –0.17 (s, 3 H, SiMe), 0.18 (s, 12 H, $SiMe_2$), 0.47 (m, 8 H, SiCH_2), 0.74 (m, 4 H, CH_2SiMe_2), 1.20 (m, 6 H, $CH_2CH_2CH_2$), 1.94 (s, 12 H, 3-Me_{pz}), 2.14 (s, 12 H, 5-Me_{pz}), 5.72 (s, 4 H, 4-H_{pz}), 5.86 (s, 2 H, CH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = –5.1 (SiMe), –2.7 ($SiMe_2$), 10.8 (5-Me_{pz}), 13.6 (3-Me_{pz}), 17.7 (CH_2), 18.1 (CH_2), 18.6 (CH_2), 19.1 (CH_2), 19.5 (CH_2), 67.9 (CH), 106.1 (C-4$_{pz}$), 139.5 (C-5$_{pz}$), 146.5 (C-3$_{pz}$) ppm. IR (CsI/Nujol): $\tilde{\nu}$ = 1553 (s, C=N) cm^{-1}. MS (ESI$^+$/TOF, CH_2Cl_2/MeOH/NH_4HCOO 5 mM): *m*/*z* = 2794.70 [M + H]$^+$, 1397.89 [M]$^{2+}$. $C_{144}H_{252}N_{32}Si_{13}$ (2796.9): calcd. C 61.84, H 9.08, N 16.03; found C 61.01, H 9.45, N 15.45.

Me_3Si-[CH(3,5-Me_2pz)$_2$PdCl$_2$] (4): [$PdCl_2$(cod)] (78 mg, 0.27 mmol) and bis(3,5-dimethylpyrazolyl)(trimethylsilyl)methane (**1**; 83 mg, 0.30 mmol) were placed in a Schlenk tube with toluene (30 mL), and the resulting yellow suspension was heated at reflux for 2 h. The orange solution was then cooled to room temperature, the solvent removed in vacuo, and the residue washed with pentane (2 × 15 mL) to give **4** as a clear brownish solid, which was recrystallized from dichloromethane/pentane to give an orange crystalline solid. Yield: 120 mg (97%). ^{1}H NMR ($CDCl_3$): δ = 0.68 (s, 9 H, $SiMe_3$), 2.32 (s, 6 H, 5-Me_{pz}), 2.58 (s, 6 H, 3-Me_{pz}), 5.85 (s, 1 H, CH), 5.90 (s, 2 H, 4-H_{pz}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = –0.3 ($SiMe_3$), 11.7 (5-Me_{pz}), 15.3 (3-Me_{pz}), 65.0 (CH), 108.1 (C-4$_{pz}$), 140.1 (C-5$_{pz}$), 153.9 (C-3$_{pz}$) ppm. IR (KBr): $\tilde{\nu}$ = 1557 (s, C=N) cm^{-1}. MS (APCI, MeOH): *m*/*z* = 871 [M_2 – Cl]$^+$, 450 [M – Cl + MeOH]$^+$, 277 [**1** + H]$^+$. $C_{14}H_{24}Cl_2N_4PdSi$ (453.78): calcd. C 37.06, H 5.33, N 12.35; found C 37.36, H 5.32, N 12.08.

G1-[CH(3,5-Me_2pz)$_2$PdCl$_2$]$_4$ (5): Dendritic compound **5** was synthesized as described above for **4**, starting from **2** (67 mg, 0.054 mmol) and [$PdCl_2$(cod)] (65 mg, 0.228 mmol) in toluene (20 mL). In this case, the reaction mixture was kept in the dark for 3 h, whilst heating at 80 °C. Compound **5** was isolated as an orange solid after workup. Yield: 92 mg (87%). ^{1}H NMR ($CDCl_3$): δ = 0.37 (m, 2 H, SiCH_2), 0.68 (s, 6 H, $SiMe_2$), 1.08 (m, 2 H, CH_2SiMe_2), 1.26 (m, 2 H, $CH_2CH_2CH_2$), 2.35 (s, 6 H, 5-Me_{pz}), 2.54 (s, 6 H, 3-Me_{pz}), 5.88 (s, 1 H, CH), 5.95 (s, 2 H, 4-H_{pz}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = –1.1 ($SiMe_2$), 12.1 (5-Me_{pz}), 15.4 (3-Me_{pz}), 16.6 (CH_2), 17.6 (CH_2), 19.6 (CH_2), 64.6 (CH), 108.2 (C-4$_{pz}$), 140.8 (C-5$_{pz}$), 153.4 (C-3$_{pz}$) ppm. IR (KBr): $\tilde{\nu}$ = 1559 (s, C=N) cm^{-1}. MS (ESI$^+$/TOF, CH_2Cl_2/MeOH/NH_4HCOO 5 mM): *m*/*z* = 1966.16 [M + H_2O]$^+$, 1241.78 [**2** + H]$^+$, 994.57 [M + K]$^{2+}$. $C_{64}H_{108}Cl_8N_{16}Pd_4Si_5$ (1951.4): calcd. C 39.39, H 5.58, N 11.48; found C 40.03, H 5.35, N 10.59.

G2-[CH(3,5-Me_2pz)$_2$PdCl$_2$]$_8$ (6): Dendritic compound **6** was synthesized as described above for **4**, starting from **3** (200 mg, 0.071 mmol) and [$PdCl_2$(cod)] (163 mg, 0.571 mmol), and was isolated as an orange solid. Yield: 236 mg (79%). ^{1}H NMR ($CDCl_3$): δ = –0.19 (s, 3 H, SiMe), 0.53 (m, 8 H, SiCH_2), 0.68 (s, 12 H, $SiMe_2$), 1.26 (m, 10 H, CH_2SiMe_2 and $CH_2CH_2CH_2$ overlapping), 2.37 (s, 12 H, 5-Me_{pz}), 2.54 (s, 12 H, 3-Me_{pz}), 5.92 (br. s, 6 H, 4-H_{pz} and CH overlapping) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = –5.1 (SiMe), –1.4 ($SiMe_2$), 12.2 (5-Me_{pz}), 15.3 (3-Me_{pz}), 17.8 (CH_2), 18.4 (CH_2), 18.5 (CH_2), 19.9 (CH_2), 64.5 (CH), 108.2 (C-4$_{pz}$), 141.1 (C-5$_{pz}$), 153.4 (C-3$_{pz}$) ppm. IR (KBr): $\tilde{\nu}$ = 1559 (s, C=N) cm^{-1}. $C_{144}H_{252}Cl_{16}N_{32}Pd_8Si_{13}$ (4215.5): calcd. C 41.03, H 6.03, N 10.63; found C 40.50, H 6.02, N 9.87.

Me_3Si-[CH(3,5-Me_2pz)$_2$PdClMe] (7): Diethyl ether (30 mL) was added to [PdClMe(cod)] (56 mg, 0.21 mmol) and ligand **1** (65 mg, 0.30 mmol) in a Schlenk tube at room temperature to give a clear yellowish solution. After 15 min, a white precipitate started to appear. The mixture was stirred for 2 h, and then the solvent was removed under vacuum, and the excess of ligand and cod byproduct were removed by washing the residue with pentane (2 × 15 mL). Compound **7** was isolated as a white solid. Yield: 87 mg (96%). ^{1}H NMR ($CDCl_3$): δ = 0.47 (s, 9 H, $SiMe_3$), 0.88 (s, 3 H, PdMe), 2.26 (s, 3 H, 3-Me_{pz} aside PdMe) 2.31 (s, 3 H, 5-Me_{pz}), 2.32 (s, 3 H, 5-Me_{pz}), 2.47 (s, 3 H, 3-Me_{pz} aside PdCl), 5.78 (s, 2 H, 4-H_{pz}), 5.91 (s, 1 H, CH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = –5.1 (PdMe), –0.2 ($SiMe_3$), 11.4 (5-Me_{pz}), 12.0 (5-Me_{pz}), 14.1 (3-Me_{pz}), 15.0 (3-Me_{pz}), 63.9 (CH), 106.8 (C-4$_{pz}$), 107.4 (C-4$_{pz}$), 137.7 (C-5$_{pz}$), 139.4 (C-5$_{pz}$), 151.4 (C-3$_{pz}$), 151.5 (C-3$_{pz}$) ppm. IR (KBr): $\tilde{\nu}$ = 1558 (s, C=N) cm^{-1}. MS (APCI, MeOH): *m*/*z* = 450 [M – Me + MeOH]$^+$, 433 [M]$^+$, 277 [**1** + H]$^+$. $C_{15}H_{27}ClN_4PdSi$ (433.36): calcd. C 41.57, H 6.28, N 12.93; found C 41.44, H 6.26, N 12.80.

G1-[CH(3,5-Me_2pz)$_2$PdClMe]$_4$ (8): Compound **8** was synthesized as described above for **7** starting from **2** (67 mg, 0.054 mmol) and [PdClMe(cod)] (60 mg, 0.226 mmol) in diethyl ether (20 mL). A white solid precipitated after a few minutes. Stirring was maintained for 3 h, and then the solid was filtered off and washed with pentane to give compound **5** as a pale-grey solid. Yield: 91 mg (90%). ^{1}H NMR ($CDCl_3$): δ = 0.38 (m, 2 H, SiCH_2), 0.43 (s, 3 H, $SiMe_2$), 0.46 (s, 3 H, $SiMe_2$), 0.85 (s, 3 H, PdMe), 1.10 (m, 4 H, $CH_2CH_2SiMe_2$), 2.28 (s, 3 H, 3-Me_{pz} aside PdMe), 2.30 (s, 3 H, 5-Me_{pz}), 2.33 (s, 3 H, 5-Me_{pz}), 2.45 (s, 3 H, 3-Me_{pz} aside PdCl), 5.79 (s, 2 H, 4-H_{pz}) 5.93 (s, 1 H, CH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = –5.2 (PdMe), –1.4 ($SiMe_2$), 11.6 (5-Me_{pz}), 12.2 (5-Me_{pz}), 14.2 (3-Me_{pz}), 15.1 (3-Me_{pz}), 17.0 (CH_2), 17.9 (CH_2), 20.3 (CH_2), 63.5 (CH), 106.8 (C-4$_{pz}$), 107.5 (C-4$_{pz}$), 138.0 (C-5$_{pz}$), 139.8 (C-5$_{pz}$), 151.2 (C-3$_{pz}$) ppm. IR (KBr): $\tilde{\nu}$ = 1559 (s, C=N) cm^{-1}. MS (ESI$^+$/TOF, CH_2Cl_2/MeOH/NH_4HCOO 5 mM): *m*/*z* = 1853.35 [M – Me]$^+$, 1241.78 [**2** + H]$^+$, 905.15 [M – 4 Me]$^{2+}$. $C_{68}H_{120}Cl_4N_{16}Pd_4Si_5$ (1869.7): calcd. C 43.68, H 6.47, N 11.99; found C 43.26, H 6.27, N 11.22.

G2-[CH(3,5-Me_2pz)$_2$PdClMe]$_8$ (9): Compound **9** was synthesized as described above for **7**, starting from **3** (255 mg, 0.091 mmol) and [PdClMe(cod)] (194 mg, 0.732 mmol), but in hot toluene (20 mL, 80 °C, 3 h). The volatiles were removed under vacuum, and the residue was washed with pentane to give compound **9** as a pale-grey solid. Yield: 295 mg (80%). ^{1}H NMR ($CDCl_3$): δ = –0.19 (s, 3 H, SiMe), 0.44 (s, 6 H, $SiMe_2$), 0.47 (s, 6 H, $SiMe_2$), 0.40 (m, 8 H, SiCH_2), 0.85 (s, 6 H, PdMe), 1.11 (m, 10 H, CH_2SiMe_2 and $CH_2CH_2CH_2$ overlapping), 2.28 (s, 6 H, 3-Me_{pz} aside PdMe) 2.30 (s, 6 H, 5-Me_{pz}), 2.33 (s, 6 H, 5-Me_{pz}), 2.44 (s, 6 H, 3-Me_{pz} aside PdCl), 5.78 (s, 2 H, 4-H_{pz}), 5.80 (s, 2 H, 4-H_{pz}), 5.93 (s, 2 H, CH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = –5.4 (PdMe), –5.3 (SiMe), –1.5 ($SiMe_2$), –1.7 ($SiMe_2$), 11.5 (5-Me_{pz}), 12.1 (5-Me_{pz}), 14.0 (3-Me_{pz}), 15.0 (3-Me_{pz}), 17.8 (CH_2), 18.5 (CH_2), 18.8 (CH_2), 20.3 (CH_2), 63.4 (CH), 106.8 (C-4$_{pz}$), 107.5 (C-4$_{pz}$), 138.1 (C-5$_{pz}$), 139.9 (C-5$_{pz}$), 151.3 (C-3$_{pz}$) ppm. IR (KBr): $\tilde{\nu}$ = 1559 (s, C=N) cm^{-1}. $C_{152}H_{276}Cl_8N_{32}Pd_8Si_{13}$ (4052.2): calcd. C 45.05, H 6.87, N 11.06; found C 44.23, H 6.27, N 10.56.

X-ray Crystallographic Studies: Single crystals of **4** suitable for X-ray diffraction studies were obtained by slow diffusion of pentane into a dichloromethane solution of the palladium complex at room temperature. A summary of the crystal data, data collection and refinement parameters is given in Table 3. A suitable crystal was covered with mineral oil and mounted in the N_2 stream of a Bruker–Nonius Kappa-CCD diffractometer equipped with an area detector and an Oxford Cryostream 700 unit; data were collected by using graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å) at 200 K with an exposure time of 10 s per frame (7 sets; 354 frames; ϕ and ω scans, 2° scan width). Raw data were corrected

for Lorentzian and polarization effects. The structure was solved by direct methods, completed by subsequent difference Fourier techniques, and refined by full-matrix least squares on F^2 with SHELXL-97.[21] Anisotropic thermal parameters were used in the last cycles of refinement for the non-hydrogen atoms. Hydrogen atoms were found in the difference Fourier map and refined with isotropic parameters. All calculations were performed by using the WinGX program.[22] CCDC-742206 (for **4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystal data and structure refinement for compound **4**.

Empirical formula	$C_{14}H_{24}Cl_2N_4PdSi$
Formula mass	453.76
Color	orange
Temperature [K]	200.0(2)
Wavelength [Å]	0.71069
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a [Å]	9.152(5)
b [Å]	16.471(5)
c [Å]	13.208(5)
β [°]	90.608(7)
Volume [Å^3]	1940.3(14)
Z	4
$P_{calcd.}$ [g/cm^3]	1.553
μ [mm^{-1}]	1.295
$F(000)$	920
Crystal size [mm]	$0.54 \times 0.45 \times 0.36$
θ range [°]	5.08–27.49
Limiting indices	$-11 \le h \le 11$
	$-21 \le k \le 21$
	$-17 \le l \le 17$
Reflections collected/unique	36924/4420 (R_{int} = 0.1304)
Reflections observed	3455 [$I > 2\sigma(I)$]
Completeness to θ [%]	99.3
Refinement method	full-matrix least squares on F^2
Data/restraints/parameters	4420/0/295
Goodness of fit on F^2	1.147
Final R[a] indices [$I > 2\sigma(I)$]	R_1 = 0.0378, wR_2 = 0.0899
R indices (all data)	R_1 = 0.0583, wR_2 = 0.1059
Largest diff. peak and hole [e/Å^3]	0.697 and –1.288

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

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