FULL PAPER

Dalton
www.rsc.org/dalton

The fixation of bis(2-pyridylimino)isoindolato (BPI) ligands to dendritic carbosilanes

Markus B. Meder, Isabelle Haller and Lutz H. Gade*

Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany. E-mail: lutz.gade@uni-hd.de

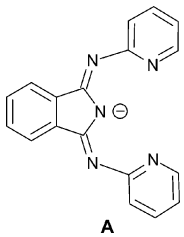
Received 21st January 2005, Accepted 3rd March 2005
First published as an Advance Article on the web 15th March 2005

Bis(2-pyridylimino)isoindolato (BPI) ligands, containing an alkynyl linker unit which allows their fixation to carbosilane dendrimers and dendrons, were synthesized by reaction of 4-nitrophthalodinitrile with 4-butynol giving the phthalodinitrile derivative **1** containing the linker. These were subsequently reacted with two molar equivalents of 2-amino-4-methylpyridine and 2-amino-4-^{t}butylpyridine yielding the respective BPI protioligands **2a** and **2b**. Lithiation with LDA and reaction with Si–Cl or Si–OTf (OTf = triflate) end groups in core or peripheral positions of dendritic carbosilanes gave the endodendrally and expdendrally functionalized dendrimers. Among these the first and second generation dendrimers $[G\text{-}1]_{8\text{-}exo}$-4-[C≡$CCH_2CH_2O$]-10-MeBPI (**8**), $[G\text{-}1]_{12\text{-}exo}$-4-[C≡$CCH_2CH_2O$]-10-MeBPI (**9**) and $[G\text{-}2]_{16\text{-}exo}$-4-[C≡$CCH_2CH_2O$]-10-MeBPI (**10**) were synthesized and fully characterized. The functional dendrimers were metallated by reaction with $[(PhCN)_2PdCl_2]$ in dichloromethane to give the corresponding pallada-dendrimers.

Introduction

Since the first reports of the dendrimer fixation of molecular catalysts,[1] a variety of ligands and catalytically active complexes have been immobilized on the inside and outside of dendritic polymers.[2] The aim of these research activities has been the development of catalytic phases which combine the virtues of homogeneous catalysis (high activity and selectivity, directed catalyst design) with those of heterogeneous catalysts (*e.g.* facile catalyst separation and recycling).[3] In principle, the position of catalytic sites in high density at the periphery of dendritic macromolecules may significantly alter the activity and selectivity in comparison with the respective mononuclear molecular catalysts.[4]

Leaching of the metal is a major practical problem, regardless of the method of catalyst fixation and the nature of the support material.[5] This may be suppressed to various degrees by using polydentate ligands which form thermally and kinetically stable complexes with the catalyst metal.



A

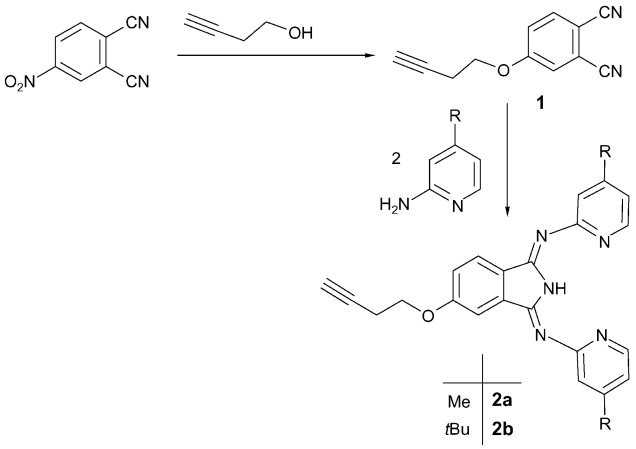
We have recently begun to investigate the catalytic activity of palladium complexes containing derivatives of the well established bis(2-pyridylimino)isoindolate (BPI) ligands (A),[6] which have been extensively studied previously in oxidation catalysis induced by the middle and late transition metals.[7–10] The novel BPI–palladium compounds have proved to be a promising new non-phosphine based class of molecular hydrogenation catalysts for alkenes, operating at ambient hydrogen pressure.[6]

In this paper we report the synthesis of BPI derivatives containing an alkynyl linker unit which allows their fixation to carbosilane dendrimers and dendrons. These are metallated to give the corresponding pallada-dendrimers.

Results and discussion

Synthesis of BPI-ligands (2a and 2b) containing an alkynyl-linker

Linker units are conveniently attached to the isoindole part of the bis(pyridylimino)isoindole protioligands (BPI's), however, their fixation has to be carried out at the phthalodinitrile level and prior to the assembly of the tricoordinate ligands. This was first noted by Siegl and coworkers[7] and Brewis *et al.* have shown in their synthesis of phthalocyanines at the core of polyarylether dendrimers,[11] that the coupling of the dendrons with the ligand or dendrimer core is readily achieved by the nucleophilic substitution of 4-nitrophthalodinitrile with the *in situ* generated alcoholates. Reaction of 4-nitrophthalodinitrile with 4-butynol cleanly gave the "tagged" phthalodinitrile derivative **1** (Scheme 1).



Scheme 1 Synthesis of a BPI ligand with an alkynyl linker for the immobilization on carbosilane dendrimers.

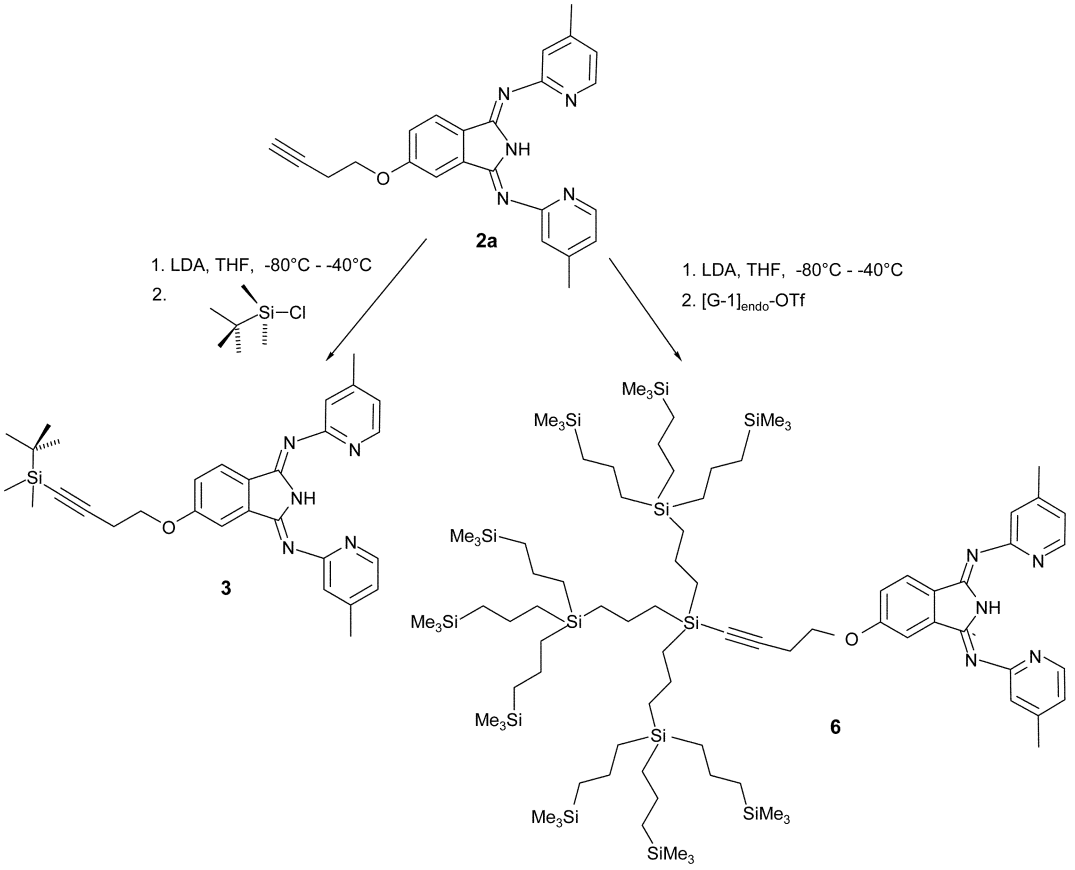
The synthesis of the BPI ligands derived from **1** was achieved by reaction with two molar equivalents of 2-amino-4-methylpyridine and 2-amino-4-^{t}butylpyridine in the presence of $CaCl_2$ in hexanol under reflux for 20 h to give the protioligands **2a** and **2b** as yellow microcrystalline solids.

DOI:10.1039/b501070e

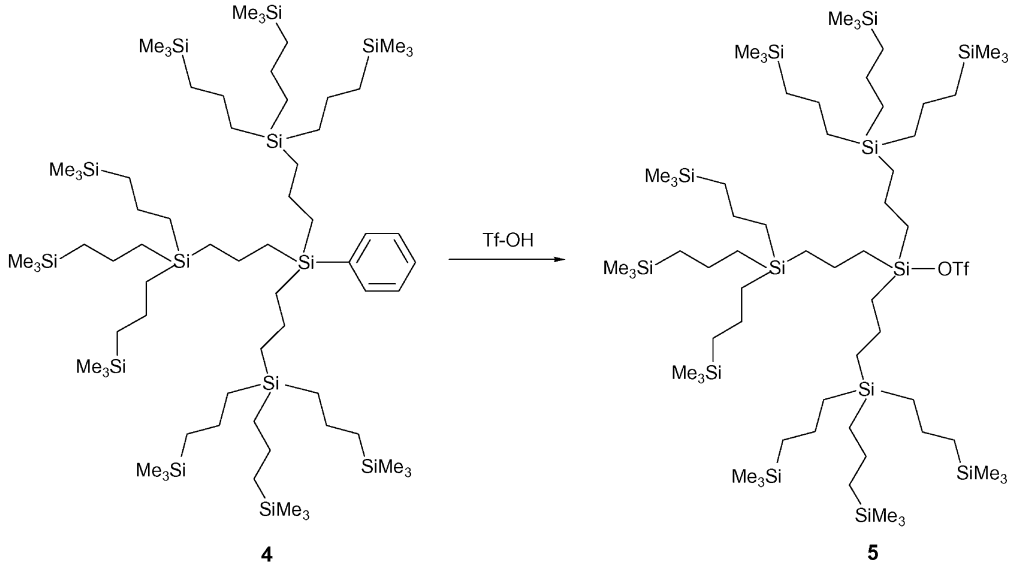
Silylation of the alkynyl-functionalized BPI-ligands and synthesis of their palladium(II) complexes

The reaction of acetylide anions with chlorosilanes as dendrimer end groups has been reported by Kim *et al.*[12] In their work, the alkynyl reagents were employed in excess and then removed *in vacuo* after reprotonation. Following this approach, phenylacetylene functionalized dendrimers containing relatively inert Si–C bonds were obtained. We took up this strategy of alkynyl fixation for the attachment of the BPI-linker units described above to carbosilane dendrimers, using LDA as the base for the deprotonation of the alkynyl linkers. In all cases two molar equivalents of base per BPI protioligand were required, since deprotonation of the isoindole-NH function preceded the H-abstraction from the alkynyl unit. The result was a doubly lithiated species which, due to the greater nucleophilicity of the acetylide anion selectively gave the desired Si–C-bonded products.

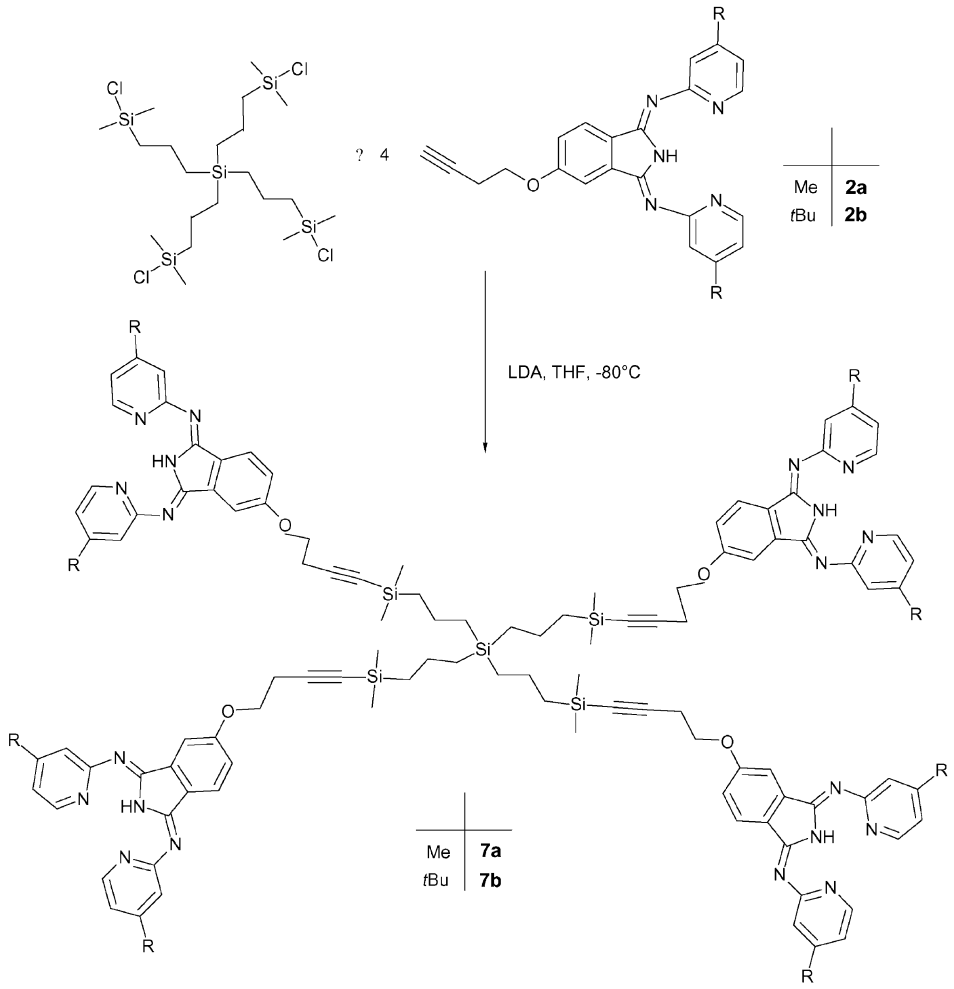
A first successful trial with $^{t}BuMe_2SiCl$, giving the silylated ligand **3** was followed up by the corresponding reaction with a dendritic triflate substituted carbosilane **5** to yield a core functionalized carbosilane dendrimer **6** (Scheme 2). The triflato derivative **5** was conveniently generated from the dendritic phenylsilane **4** by acidolytic treatment with triflic acid (see Scheme 3).[13] This transformation has been known for some



Scheme 2 Metallation of the BPI-linker unit **2a** with LDA in thf and subsequent silylation. In the synthesis of **6** this amounts to the core fixation of the protioligand to a dendritic carbosilane.



Scheme 3 Synthesis of the triflato carbosilane **5** by acidolysis of the "dummy" phenyl group at the core of **4**. This activates the core position in carbosilane dendrimers and allows the subsequent functionalization.



Scheme 4 Fixation of the ligand-linker units **2a,b** to the chain ends of a zeroth generation carbosilane dendrimer.

time[14] and, very recently, has been applied by us to carbosilane dendrimer chemistry.[13] The endodendrally functionalized dendrimer **6** was characterized by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy as well as a FAB mass spectrum which displays its molecular ion at $m/z = 1670.1$.

Fixation of the alkynyl-functionalized BPI-ligands at the periphery of carbosilane dendrimers

Having shown the feasibility of an "endodendral" fixation of the BPI ligand to dendritic carbosilanes we attempted the analogous functionalization of dendrimer end-groups ("exodendral fixation"). In order to avoid the formation of complex product mixtures a complete conversion of the Si–Cl end groups and thus an optimization of the coupling reaction were essential. Using the lithiated alkynyl-BPI derivatives **2a** and **2b** described in the previous section we first synthesized the two zeroth generation BPI functionalized dendrimers **7a** and **7b** (Scheme 4).

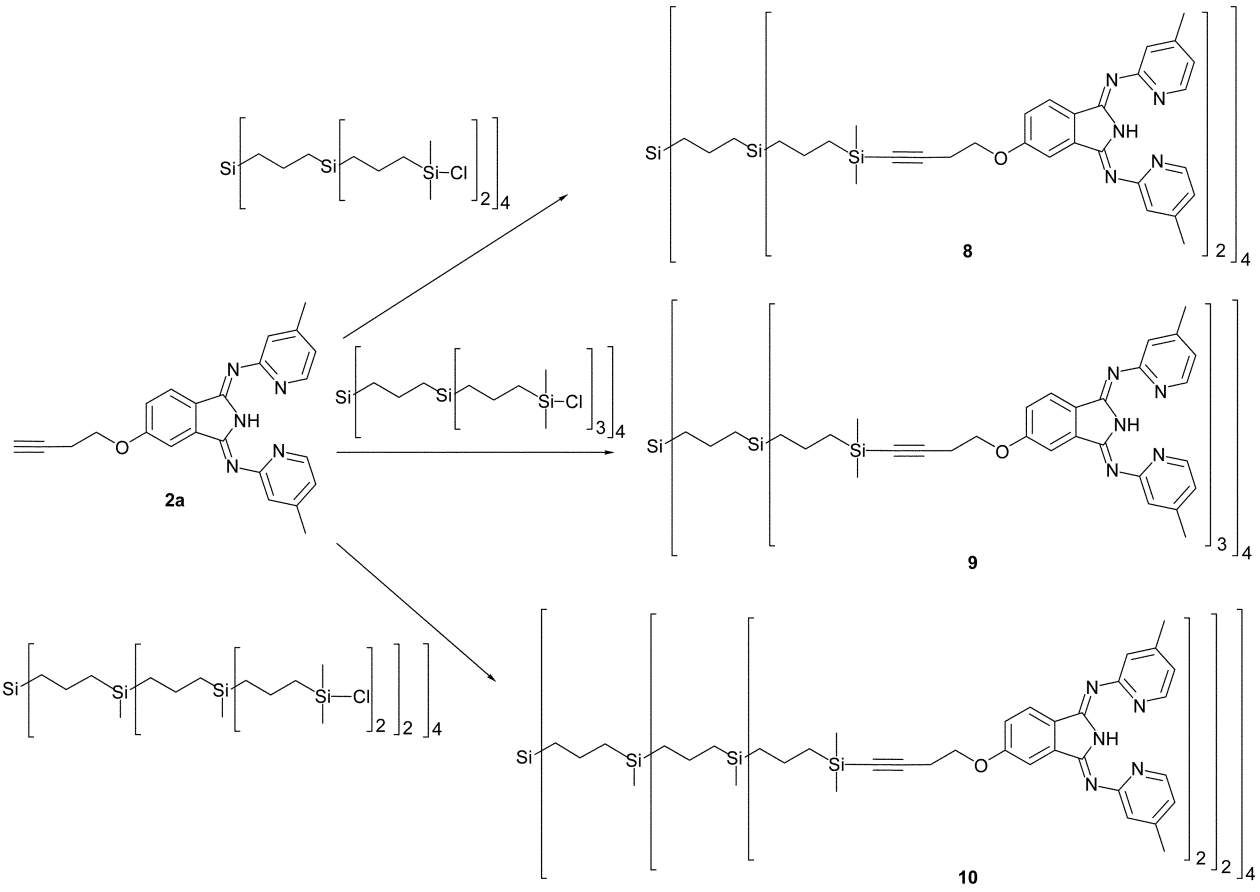
The complete functionalization of the silyl end groups is reflected in the observation of only a single singlet proton resonance for the $Si(CH_3)_2$-groups at 0.14 ppm, of the triplet at 2.74 ppm assigned to the methylene group adjacent to the C≡C triple bond as well as a single set of ^{13}C NMR resonances for the carbosilane core and the attached ligands. In the ^{29}Si-NMR spectra two resonances at −17.5 ppm (periphery) and 1.0 ppm (core) are observed while the identity of the reaction products $[G\text{-}0]_{4\text{-}exo}$-4-[C≡$CCH_2CH_2O$]-10-MeBPI (**7a**) and $[G\text{-}0]_{4\text{-}exo}$-4-[C≡$CCH_2CH_2O$]-10-^{t}BuBPI (**7b**) was confirmed by the detection of the molecular ion peaks in the FAB mass spectra at $m/z = 2006.6$ and 2344.4, respectively.

Following an analogous synthetic protocol as described above the BPI-functionalized first and second generation dendrimers $[G\text{-}1]_{8\text{-}exo}$-4-[C≡$CCH_2CH_2O$]-10-MeBPI (**8**), $[G\text{-}1]_{12\text{-}exo}$-4-[C≡$CCH_2CH_2O$]-10-MeBPI (**9**) and $[G\text{-}2]_{16\text{-}exo}$-4-[C≡$CCH_2CH_2O$]-10-MeBPI (**10**) were synthesized (Scheme 5).

The high molecular symmetry of the first generation carbosilane $[G\text{-}1]_{8\text{-}exo}$-4-[C≡$CCH_2CH_2O$]-10-MeBPI (**8**) (Fig. 1) is reflected in the simplicity of the signal patterns in its ^{1}H and ^{13}C NMR spectra. As expected, three signals are observed in the ^{29}Si NMR spectrum, the resonance at −17.7 ppm being again characteristic for the ^{29}Si nuclei adjacent to the C≡C-triple bond. The molecular ion peak was found at $m/z = 4326.7$ in the negative ion FAB mass spectrum and is associated with the dianion peak at $m/z = 2660.8$.

The NMR data of the other functionalized first generation dendrimer $[G\text{-}1]_{12\text{-}exo}$-4-[C≡$CCH_2CH_2O$]-10-MeBPI (**9**) are very similar to those of compound **8**. However, due to an accidental coincidence of the ^{29}Si NMR resonances of the inner Si nuclei only two signals at 17 ppm and 1 ppm are observed. The complete exodendral functionalization was confirmed by a MALDI-TOF spectrum displaying the molecular ion peak at $m/z = 6244.7$ and the absence of mass peaks due to incompletely converted species.

The synthesis of the exodendrally functionalized corresponding second generation dendrimer was achieved by reaction of the chlorosilane $[G\text{-}2]_{16\text{-}exo}$-Cl with the lithiated BPI derivative **2a** giving $[G\text{-}2]_{16\text{-}exo}$-4-[C≡$CCH_2CH_2O$]-10-MeBPI (**10**). The simple pattern of signals in the ^{1}H, ^{13}C and ^{29}Si NMR spectra of the highly symmetrical functionalized dendrimer (Fig. 2) are consistent with the complete conversion of the chlorosilane



Scheme 5 Exodendral fixation of the ligand-linker unit **2a** to first and second generation carbosilane dendrimers.

precursor. This formulation was substantiated by the observation of the molecular ion peak at $m/z = 8963.2$ in the MALDI-TOF mass spectrum and the absence of peaks attributable to defect structures.

Metallation of the functionalized dendrimers with palladium(II)

In view of the established catalytic hydrogenation activity of BPI–palladium complexes[6] and the facile accessibility of the square planar Pd and Pt complexes the palladation of the PBI-functionalized dendrimers was the principal aim of this work. In a first trial reaction of the simple silylated compound **3** with $[(PhCN)_2PdCl_2]$ in dichloromethane the Pd-complex **11** was obtained in high yield (Scheme 6). The conversion was clean and there was no indication of a partial cleavage of the Si–C(sp) bond.

Similarly, the metallation of the "endodendrally" functionalized second generation dendrimer $[G\text{-}2]_{1\text{-}endo}$-4-$[C{\equiv}CCH_2CH_2O]$-10-MeBPI (**6**) employing the same reaction conditions gave the second generation endodendral palladium complex $[G\text{-}2]_{1\text{-}endo}$-4-$[C{\equiv}CCH_2CH_2O]$-10-MeBPIPdCl (**12**). Its structure was established by the ^1H, ^{13}C and ^{29}Si NMR spectroscopic data and the observation of the molecular ion peak at $m/z = 1774.9$ in the negative ion FAB mass spectrum.

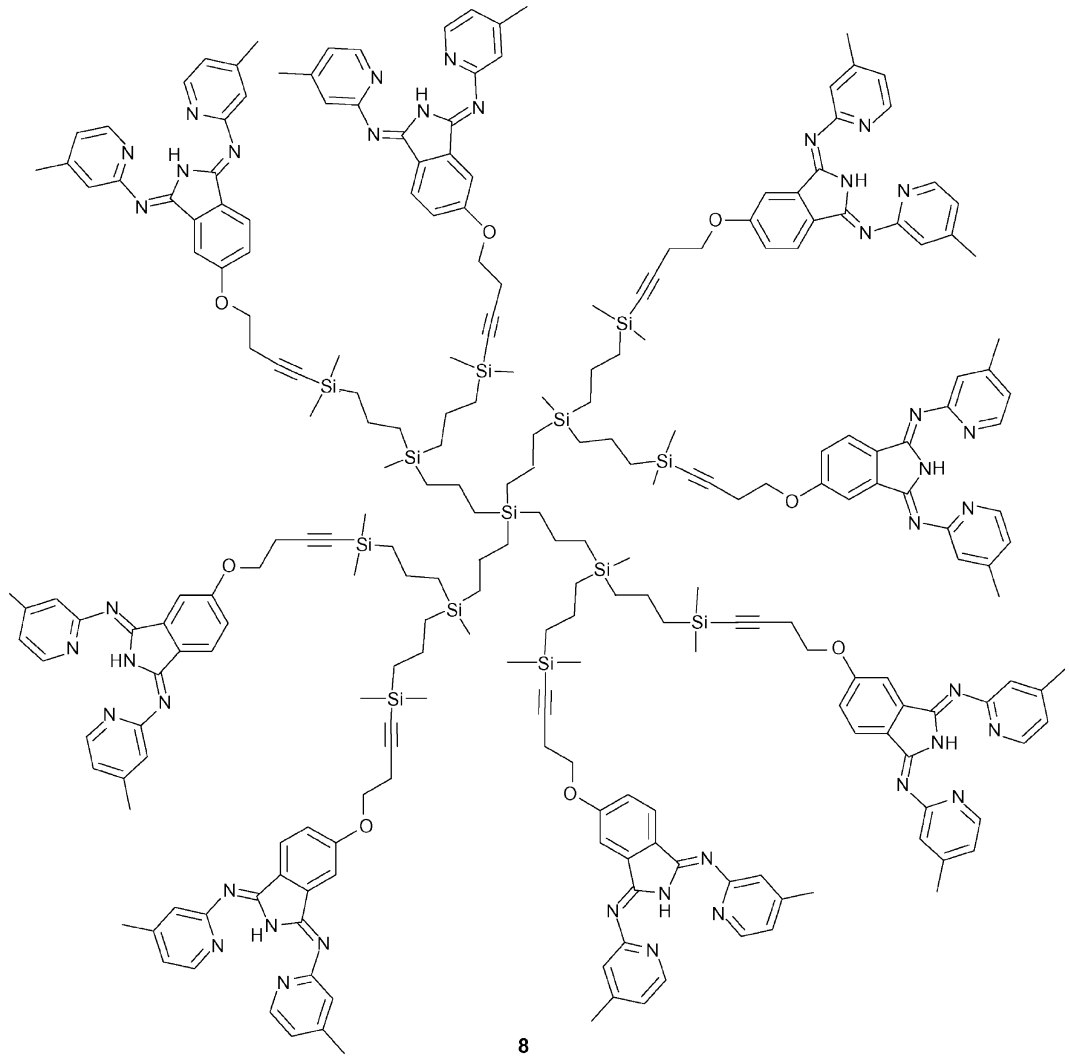
In the same way as for the systems discussed above, the palladation of the two "exodendrally" functionalized [G-0]-dendrimers **7a,b** gave the corresponding metalladendrimers **13a,b** (Scheme 7). A convenient probe for the metallation is the low field shift of the α-pyridyl protons in the BPI units from 8.5 to 9.5 ppm and the observation of a single set of resonances in the ^{13}C NMR spectrum. In the positive ion FAB mass spectrum of $[G\text{-}0]_{4\text{-}exo}$-4-$[C{\equiv}CCH_2CH_2O]$-10-MeBPIPdCl (**13a**) the base peak was observed at $m/z = 2534.5$ which corresponds to the fragment $[M - Cl^-]^+$ while the molecular ion peak of $[G\text{-}0]_{4\text{-}exo}$-4-$[C{\equiv}CCH_2CH_2O]$-10-^{t}BuBPIPdCl (**13b**) was found as expected at $m/z = 2869.7$.

Reaction of the first generation dendrimer $[G\text{-}1]_{8\text{-}exo}$-4-$[C{\equiv}CCH_2CH_2O]$-10-MeBPI (**8**) with $[(PhCN)_2PdCl_2]$ gave the eightfold metallated product **14** (Fig. 3). The low yield of the isolated product of 25% is due to the loss incurred in the repeated extractions in order to remove the ammonium salts which strongly adhere to the dendrimer.

The ^1H, ^{13}C and ^{29}Si NMR spectra of dendrimer **14** display similarly simple signal patterns as those of **13a,b** indicating complete metallation. The peak at $m/z = 5419.9$ observed in the MALDI-TOF mass spectrum of **14** corresponds to the monocation $[M - Cl^-]^+$, thus establishing the identity of the pallada-dendrimer. All attempts to metallate the higher BPI-functionalized dendrimers $[G\text{-}1]_{12\text{-}exo}$-4-$[C{\equiv}CCH_2CH_2O]$-10-MeBPI (**9** and $[G\text{-}2]_{16\text{-}exo}$-4-$[C{\equiv}CCH_2CH_2O]$-10-MeBPI (**10**) in dichloromethane only gave insoluble materials which eluded adequate characterization.

Conclusions

We have developed a new class of BPI-ligands containing alkynyl linker units which allow their convenient grafting to carbosilane dendrimers both in endo- and exodendral positions. The choice of a carbon nucleophile and thus the formation of Si–C bonds between the carbosilane and the ligand-linker unit leads to kinetically inert functionalized dendrimers which may be metallated by reaction with palladium(II) complexes. The approach based on alkynyl linkers presented in this work may be generally applied in the immobilization of metal complexes, as we have previously shown for polydentate phosphines.[15] Current and future work will be devoted to the investigation of the catalytic properties of these systems with the aim of extending



8

Fig. 1 Structure of the functionalized first generation carbosilane dendrimer **8**.

our previous systematic investigation of "dendrimer effects" in hydrogenation and C–C coupling catalysis.[4,16]

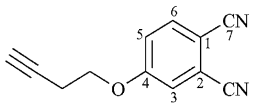
Experimental

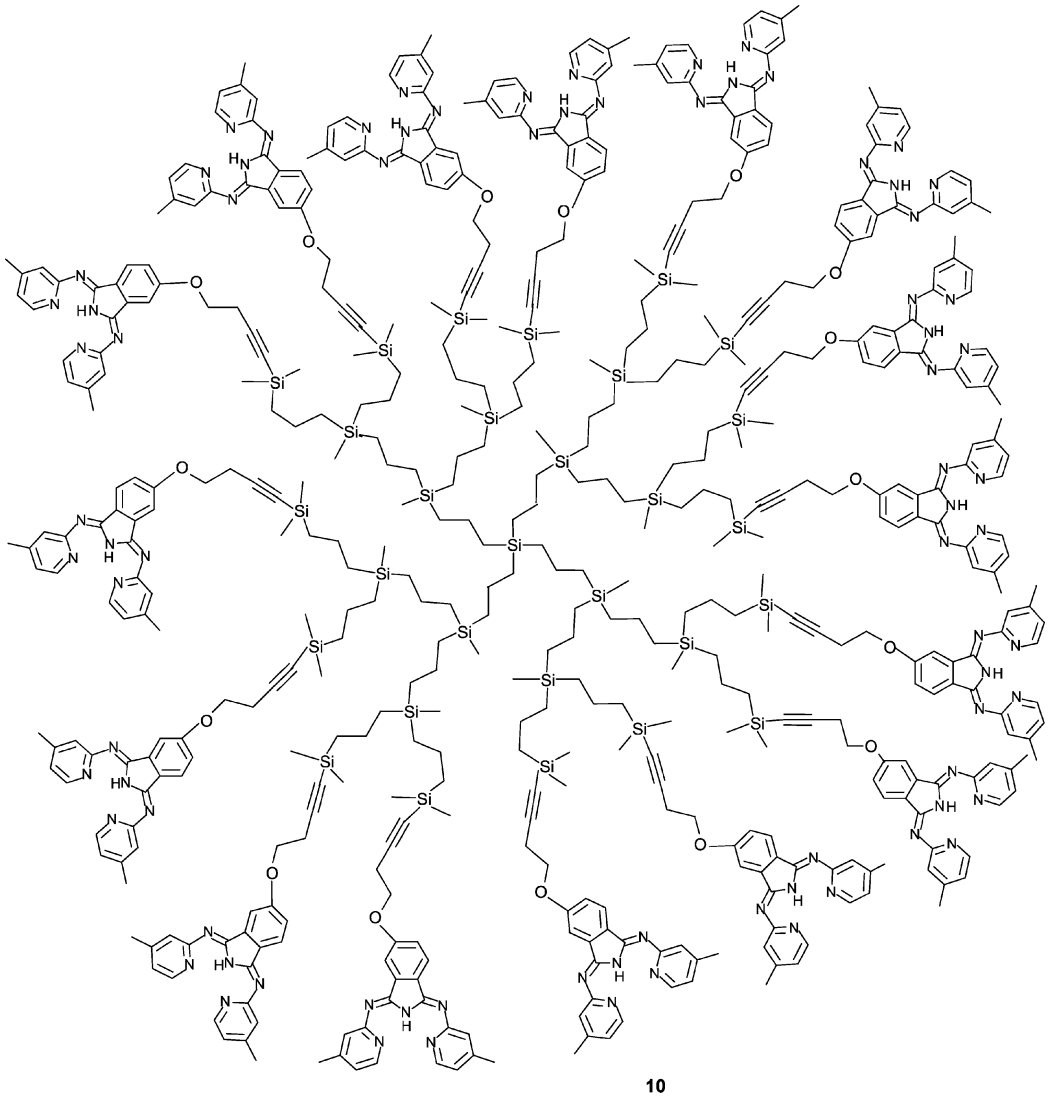
All manipulations were performed under nitrogen. Solvents were dried according to standard methods and saturated with nitrogen. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze–pump–thaw" cycles and stored over 4-Å molecular sieves. Solids were separated from suspensions by filtration through dried Celite or by centrifugation. The ^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on Bruker AC 200, Bruker Avance 250 and Bruker AMX 400 FT-NMR spectrometers (reference: tetramethylsilane), using the residual protonated solvent peak (^{1}H) or the carbon resonance (^{13}C). Infrared spectra were recorded on a Nicolet Magna IRTM 750 spectrometer. Elemental analyses were carried out by the microanalytical service at the chemistry department at Strasbourg. 2-Amino-4-*tert*-butylpyridine,[17] $[(PhCN)_2PdCl_2]$[18] and the chlorosilyl functionalized carbosilane dendrimers[19] were prepared according to published procedures. All other chemicals used as starting materials were obtained commercially and used without further purification.

Preparation of 4-(3-butynoxy)phthalodinitrile (1)

Solid K_2CO_3 (1.59 g = 11.5 mmol) was added to a solution of 4-nitrophthalodinitrile dissolved in DMF (15 ml) which was heated to 50 °C. To this mixture 3-butynol (0.81 g = 11.5 mmol) was added over a period of 30 min. After stirring for 20 h, the reaction mixture was cooled to room temperature. Upon addition of water, the solid reaction product precipitated. It was washed with 3 × 20 ml of water, re-dissolved in toluene and the solution dried over $MgSO_4$. Evaporation of the solvent gave pure 4-(3-butynoxy)phthalodinitrile (**1**) as a colourless solid.

Yield: 0.93 g (4.73 mmol, 82%). Mp: 97 °C. ^{1}H-NMR (400.16 MHz, $CDCl_3$, 298 K): δ = 2.04 (t, $^{4}J_{HH}$ = 2.6 Hz, 1 H, ≡CH), 2.71 (dt, $^{3}J_{HH}$ = 6.7 Hz, $^{4}J_{HH}$ = 2.6 Hz, 2 H, ≡CCH$_2$), 4.16 (t, $^{3}J_{HH}$ = 6.7 Hz, 2 H, OCH$_2$), 7.19 (dd, $^{3}J_{HH}$ = 8.8 Hz, $^{4}J_{HH}$ = 2.5 Hz, 1 H, H(5)), 7.26 (d, $^{4}J_{HH}$ = 2.5 Hz, 1 H, H(3)), 7.70 (d, $^{3}J_{HH}$ = 8.8 Hz, 1 H, H(6)). {^{1}H}^{13}C-NMR (100.6 MHz, $CDCl_3$, 295 K): δ = 19.3 (≡C*C*H$_2$), 67.0 (OCH$_2$), 70.7 (≡CH), 79.3 (*C*≡CH), 107.5 (C-1), 115.2, 115.6 (C-7), 117.4 (C-2), 119.6 (C-3), 120.1 (C-5), 135.3 (C-6), 161.6 (C-4). IR (KBr): ν [cm^{-1}] = 3306 (m), 3114 (w), 3083 (w), 3046 (w), 2956 (m), 2232 (s), 2127 (w), 1597 (s), 1507 (m), 1490 (w), 1473 (m), 1426 (w), 1413 (w), 1324 (s), 1262 (s), 1211 (w), 1180 (w), 1088 (m), 1021 (s), 929 (w), 868 (m), 856 (m), 739 (w), 645 (s). $C_{12}H_8N_2O$ (196.21 g mol^{-1}): calcd.: C 73.46, H 4.11, N 14.28; found: C 73.18, H 4.00, N 14.19.





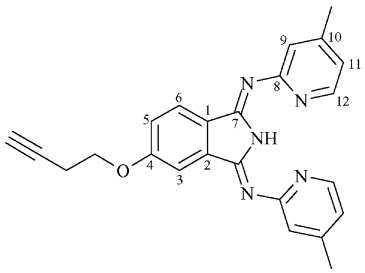
10

Fig. 2 Structure of the functionalized second generation carbosilane dendrimer **10**.

Preparation of 4-(3-butynoxy)-10-MeBPI (2a)

4-(3-Butynoxy)phthalodinitrile (**1**) (1.00 g = 5.10 mmol), 2-amino-4-methylpyridine (1.37 g = 12.7 mmol) and $CaCl_2$ (0.16 g = 1.36 mmol) were dissolved in 1-hexanol (50 ml) and heated under reflux for 72 h. Upon subsequent cooling to room temperature, the solid reaction product precipitated and was isolated by filtration. After washing the precipitate with 3 × 50 ml of water, it was dried over P_4O_{10} giving pure **2a** as a yellow solid.

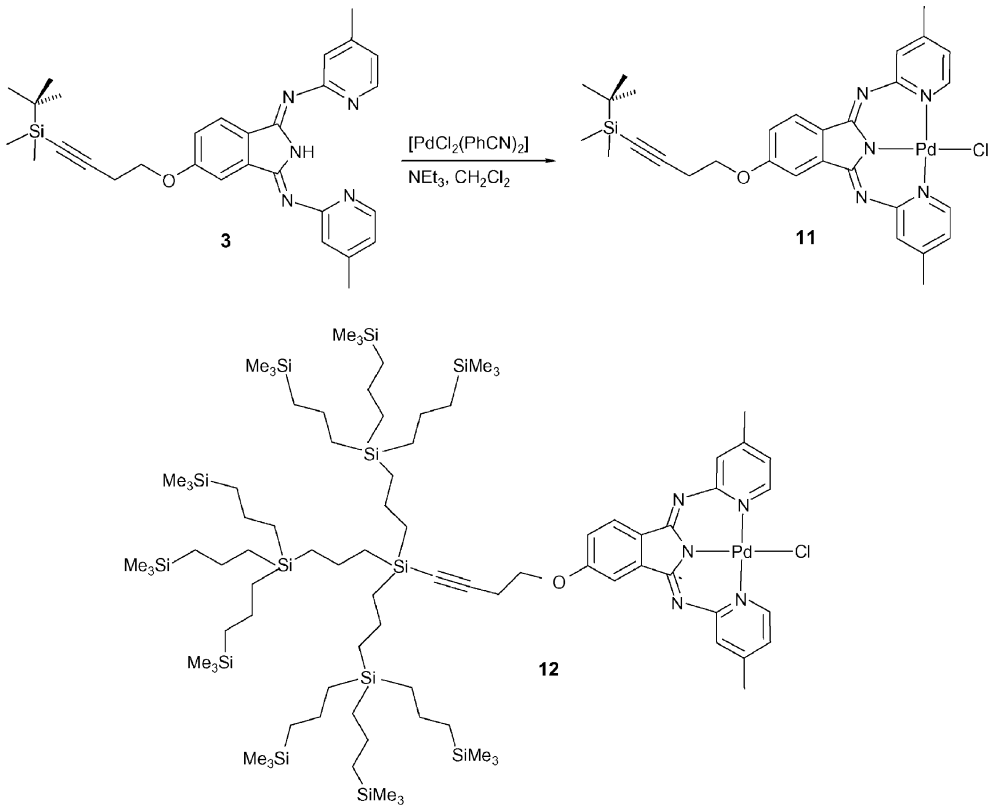
Yield: 1.35 g (3.42 mmol, 67%). Mp: 180 °C. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 298 K): δ = 2.06 (t, $^4J_{HH}$ = 2.8 Hz, 1 H, ≡CH), 2.38 (s, 6 H, 10-CH_3), 2.72 (dt, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 2.8 Hz, 2 H, ≡CCH_2–), 4.25 (t, $^3J_{HH}$ = 6.9 Hz, 2 H, –OCH_2–), 6.92 (m, 2 H, H(11)), 7.15 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.3 Hz, 1 H, H(5)), 7.28 (s, br, 2 H, H(9)), 7.52 (d, $^4J_{HH}$ = 2.3 Hz, 1 H, H(3)), 7.98 (d, $^3J_{HH}$ = 8.2 Hz, 1 H, H(6)), 8.43 (m, 2 H, 1H(2)), 13.85 (s, br, 1 H, NH). {^{1}H}^{13}C-NMR (100.6 MHz, $CDCl_3$, 298 K): δ = 19.8 (≡C*C*H_2–), 21.2 (10-CH_3), 66.8 (–OCH_2), 70.5 (–C≡*C*H), 80.3 (–*C*≡CH), 106.9 (C-3), 120.0 (C-5), 121.5/121.7 (C-9), 123.6/123.8 (C-11), 124.3 (C-6), 128.5 (C-1), 138.1 (C-2), 147.6/147.7 (C-12), 149.5 (C-10), 153.7 (C-7), 160.4 (C-8), 162.1 (C-4). IR (KBr): ν [cm^{-1}] = 3219 (m), 3049 (w), 2922 (w), 2130 (vw), 1627 (s), 1586 (s), 1540 (m), 1489 (m), 1465 (m), 1399 (w), 1358 (m), 1330 (m), 1291 (vw), 1274 (w), 1235 (s), 1191 (w), 1166 (m), 1151 (w), 1114 (m), 1041 (s), 936 (w), 816 (m), 718 (m), 681 (w). $C_{24}H_{21}N_5O$ (395.46 g.mol^{-1}): calcd.: C 72.89, H 5.35, N 17.71; found: C 72.66, H 5.54, N 17.31.



Preparation of 4-(3-butynoxy)-10-^{t}BuBPI (2b)

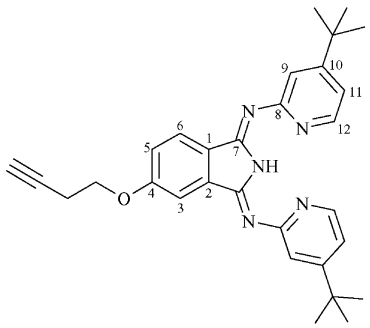
4-(3-Butynoxy)phthalodinitrile (**1**) (1.00 g = 5.10 mmol), 2-amino-4-^{t}butylpyridine (1.60 g = 10.6 mmol) and $CaCl_2$ (0.16 g = 1.36 mmol) were dissolved in 1-hexanol (50 ml) and heated under reflux for 36 h. Upon subsequent cooling to room temperature, the solid reaction product precipitated and was isolated by filtration. After washing the precipitate with 3 × 50 ml of water it was dried over P_4O_{10} giving pure **2b** as a yellow solid.

Yield: 1.35 g (3.42 mmol, 67%). Mp: 199 °C. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 298 K): δ = 1.34 (2·s, total of 18 H, 10-C(C*H*$_3$)$_3$), 2.06 (t, $^4J_{HH}$ = 2.6 Hz, 1 H, ≡CH), 2.74 (dt, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 2.6 Hz, 2 H, ≡CCH_2–), 4.26 (t, $^3J_{HH}$ = 7.0 Hz, 2 H, –OCH_2–), 7.08 (m, 2 H, H(11)), 7.13 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.2 Hz, 1 H, H(5)), 7.42 (m, br, 2 H, H(9)), 7.54 (d, $^4J_{HH}$ = 2.2 Hz, 1 H, H(3)), 7.94 (d, $^3J_{HH}$ = 8.4 Hz, 1 H, H(6)), 8.48 (m,



Scheme 6 Metallation of the protioligands **3** and **6** by reaction with $[PdCl_2(PhCN)_2]$.

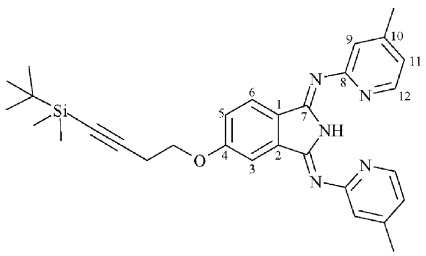
2 H, 1H(2)), 13.84 (s, br, 1 H, NH). $\{^1H\}^{13}C$-NMR (75.5 MHz, $CDCl_3$, 298 K): δ = 19.5 (≡C*C*H_2–), 30.5 (10-C(*C*H_3)$_3$), 34.8 (10-*C*(CH$_3$)$_3$), 66.5 (O*C*H_2), 70.1 (≡CH), 80.5 (–*C*≡CH), 106.5 (C-3), 117.4/117.6 (C-9), 119.7 (C-5), 119.8/119.9 (C-11), 123.8 (C-6), 128.4 (C-1), 137.9 (C-2), 147.5/147.6 (C-12), 153.5 (C-7), 160.5/160.6 (C-8), 161.9 (C-4), 162.3 (C-10). IR (KBr): ν [cm^{-1}] = 3312 (m), 2963 (s), 2126 (vw), 1633 (s), 1590 (s), 1534 (s), 1488 (m), 1466 (m), 1400 (m), 1365 (m), 1353 (m), 1326 (w), 1285 (m), 1264 (m), 1225 (m), 1107 (w), 1046 (m), 926 (vw), 894 (m), 859 (vw), 835 (m), 785 (vw), 719 (m), 622 (w), 495 (vw). $C_{30}H_{33}N_5O$ (479.63 g.mol^{-1}): calcd.: C 75.13, H 6.94, N 14.60; found: C 75.03, H 7.08, N 14.56.



Preparation of 4-(ᵗBuSi(CH$_3$)$_2$C≡CCH$_2$CH$_2$O–)-10-MeBPI (3)

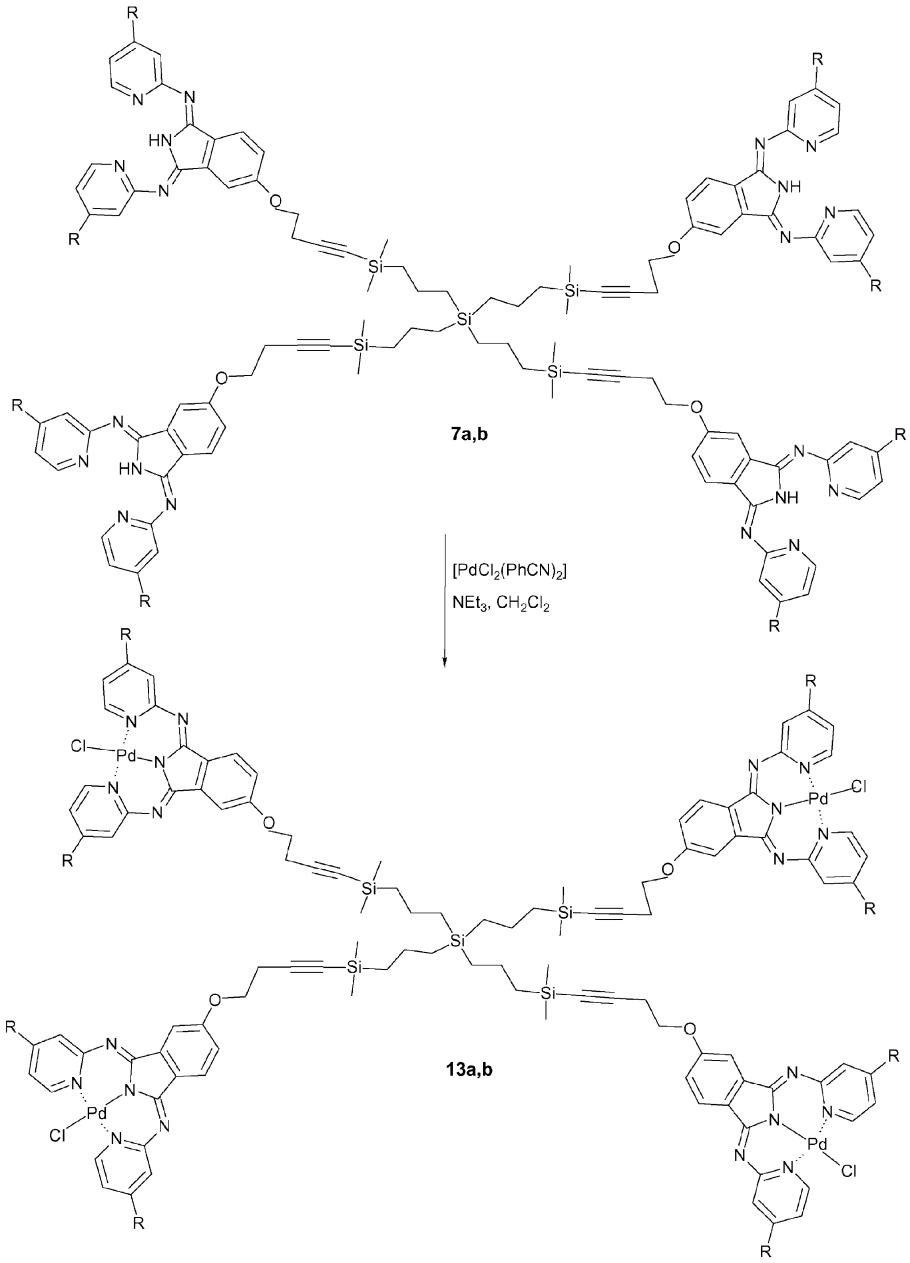
A solution of LDA in thf (2 M) (0.25 ml = 0.23 mmol) was slowly added to a solution of 4-(3-butynoxy)-10-MeBPI (**2a**) (91.0 mg = 0.23 mmol) in thf (10 ml), which was cooled to −80 °C. The mixture was warmed to −40 °C and then re-cooled to −80 °C. After addition of ᵗBuSi(CH$_3$)$_2$Cl (35.0 mg = 0.23 mmol) the reaction mixture was warmed to room temperature and then stirred for another 16 h. After removal of the volatiles *in vacuo*, the residue was washed with 3 × 10 ml of water and then recrystallized from CH$_3$Cl/*n*-hexane giving **3** as a yellow solid.

Yield: 87.0 mg (0.17 mmol, 74%). Mp: 184 °C. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 298 K): δ = −0.04 (s, 6 H, Si(CH$_3$)$_2$), 0.91 (s, 9 H, –SiC(CH$_3$)$_3$), 2.35 (s, 6 H, 10-CH$_3$), 2.76 (t, $^3J_{HH}$ = 6.7 Hz, 2 H, ≡CCH$_2$–), 4.21 (t, $^3J_{HH}$ = 6.7 Hz, 2 H, –OCH$_2$–), 6.90 (m, 2 H, H(11)), 7.13 (m, 1 H, H(5)), 7.23 (s, br, 2 H, H(9)), 7.50 (d, $^4J_{HH}$ = 2.0 Hz, 1 H, H(3)), 7.91 (d, $^3J_{HH}$ = 8.4 Hz, 1 H, H(6)), 8.44 (m, 2 H, 1H(2)), 12.61 (s, br, 1 H, NH). $\{^1H\}^{13}C$-NMR (100.6 MHz, $CDCl_3$, 298 K): δ = −4.5 (–Si(CH$_3$)$_2$–), 16.5 (Si*C*(CH$_3$)$_3$), 20.9 (10-CH$_3$), 21.0 (≡C*C*H$_2$–), 26.0 (SiC(*C*H$_3$)$_3$), 66.7 (–OCH$_2$–), 84.9 (CH$_2$*C*≡C), 102.7 (–C≡*C*Si), 106.5 (C-3), 119.8 (C-5), 121.2/121.4 (C-9), 123.4/123.5 (C-11), 123.9 (C-6), 128.2 (C-1), 137.9 (C-2), 147.4 (C-12), 149.3 (C-10), 153.7 (C-7), 160.3/160.4 (C-8), 161.9 (C-4). $\{^1H\}^{29}$Si-NMR (39.8 MHz, $CDCl_3$, 298 K): δ = −8.6 (–Si(CH$_3$)$_2$–). IR (KBr): ν [cm^{-1}] = 2954 (m), 2924 (m), 2179 (m), 1652 (m), 1635 (m), 1590 (s), 1489 (m), 1465 (m), 1386 (w), 1260 (m), 1191 (vw), 1105 (m), 1037 (w), 821 (m), 697 (m), 618 (w). $C_{30}H_{35}N_5OSi$ (509.72 g.mol^{-1}): calcd.: C 70.69, H 6.92, N 13.74; found: C 71.02, H 7.36, N 14.11.



Preparation of PhSi[(CH$_2$)$_3$Si[(CH$_2$)$_3$SiMe$_3$]$_2$]$_3$ (4)

To a solution of 1.24 g (1.82 mmol) of **IV** in 60 ml of thf, which was cooled to −5 °C, were added 7.84 ml (23.5 mmol) of a 3.00 molar solution of methylmagnesium chloride over a period of 1.5 h. The reaction mixture was refluxed for 17 h and then poured into an ice cold aqueous solution of NH_4Cl (100 ml). After separation of the organic phase, the aqueous solution was twice extracted with 50 ml of hexane. The combined organic phases were washed with 50 ml of brine and then dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was purified



Scheme 7 Metallation of the zeroth generation dendrimers **7a,b** by reaction with $[PdCl_2(PhCN)_2]$.

by column chromatography (silica, hexane/ethyl acetate 6 : 1). Compound **4** was obtained as a colourless viscous oil. Yield: 59%. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 298 K): $\delta = -0.02$ (s, 81 H, 1H(7)), 0.55 (m, 48 H, 11-13-14-1H(6)), 1.32 (m, 24 H, 12-1H(5)), 7.32–7,47 (m, H(5), HPh). $\{^1H\}^{13}$C-NMR (75.5 MHz, $CDCl_3$, 298 K): $\delta = -1.4$ (C_{17}), 18.6 and 17.5 ($C_{11,13,14,16}$), 21.7 (C_{12}, C_{15}), 127.7, 128.7, 134.0; 137.8 (C-arom.). $\{^1H\}^{29}$Si-NMR (79.5 MHz, $CDCl_3$, 298 K): $\delta = -4.1$ (Si–Ph), 0.6 (CH_2–Si–CH_2), 0.5 (Si–Me_3). IR (KBr) = 2952 (s), 2911 (s), 2874 (s), 698 (m) cm^{-1}. $C_{69}H_{158}Si_{13}$ (1353 g.mol^{-1}): calcd.: C 61,25, H 11,77; found: C 61,29, H 11,83.

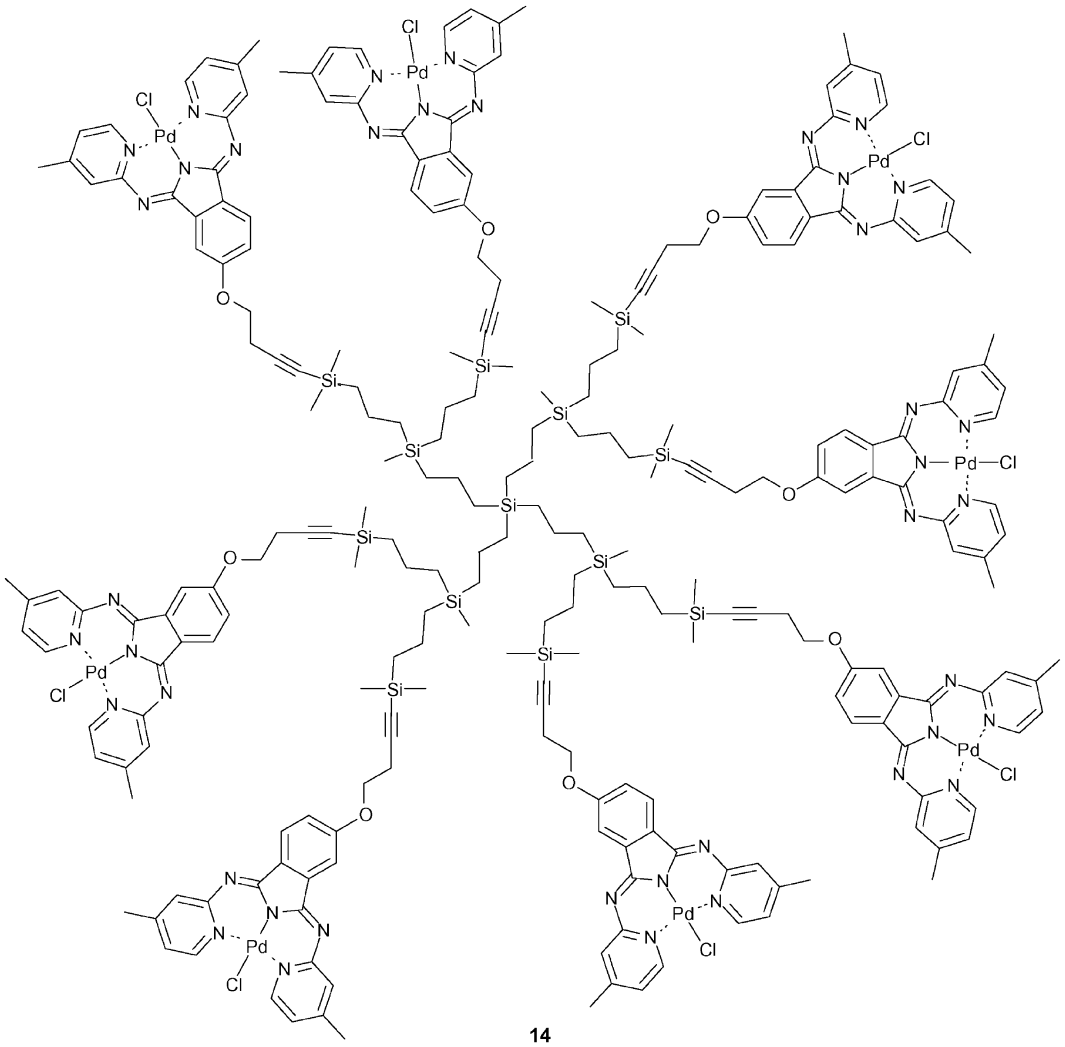
Preparation of (TfO)Si[$(CH_2)_3$Si[$(CH_2)_3SiMe_3]_3]_3$ (5)

To a solution of **4** 0,86 g (1,91 mmol) in 5 ml of toluene, which was cooled to −40 °C, were added 0,17 mL (1,91 mmol) of trifluoromethanesulfonic acid over a period of 10 min. The reaction mixture was stirred at −20 °C for 30 min and then at room temperature for another 55 min. After removal of the volatiles under high vacuum, compound **5** was obtained in quantitative yield as a pale yellow oil. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 298 K): $\delta = -0.03$ (s, 81 H, $SiMe_3$). 0.56 (m, 54 H, 11-13-14-1H(6)), 1.30 (m, 24 H, 12-1H(5)). $\{^1H\}^{13}$C-NMR (75.5 MHz, $CDCl_3$, 298 K): $\delta = 1.5$ (C_{17}), 17.5 ($C_{11–14}$), 18.6 ($C_{13–16}$), 21.7 ($C_{12–15}$), 118,4 (CF_3). $\{^1H\}^{29}$Si-NMR (79.5 MHz, $CDCl_3$, 298 K): $\delta = 40.2$ ($CF_3S(O)_2$–OSi), 0.8 (Si–Me_3). 0.6 (CH_2–Si–CH_2). IR (KBr) [cm^{-1}] = 1247 (m, C–F), 1350 (S = O). $C_{64}H_{153}O_3SSi_{13}F_3$ (1425.09 g mol^{-1}): calcd.: C 53,94, H 10,82; found: C 53.20, H 11.31.

Preparation of [G-2]$_{1\text{-endo}}$-4-[C≡CCH_2CH_2O]-10-MeBPI (6)

A solution of LDA in thf (2 M) (86.3 µl = 0.17 mmol) was slowly added to a solution of 4-(3-butynoxy)-10-MeBPI (**2a**) (60.0 mg = 86.3 µmol) in thf (15 ml), which was cooled to −80 °C. The mixture was warmed to −40 °C and then re-cooled to −80 °C. After the addition of [G-2]$_{1\text{-endo}}$-SiOTf (0.12 g = 86.3 µmol) the reaction mixture was warmed to room temperature and then stirred for another 16 h. After removal of the volatiles *in vacuo*, the residue was washed with 3 × 10 ml of water and then purified by column chromatography (silica, elution with pentane/CH_2Cl_2/Et_2O).

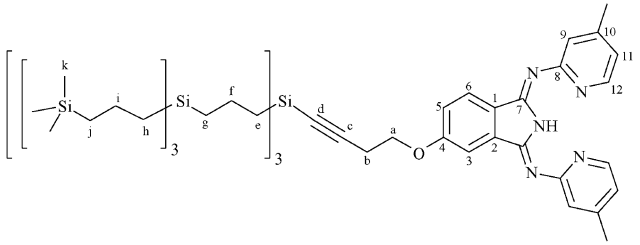
Yield: 0.10 g (61.3 µmol, 71%). ^{1}H-NMR (300.17 MHz, $CDCl_3$, 298 K): $\delta = -0.03$ (s, 81 H, H(k)), 0.56 (m, br, 48 H, H(e),



14

Fig. 3 Structure of the first generation pallada-dendrimer **8**.

H(g), H(h), H(j)), 1.33 (m, 24 H, H(f), H(i)), 2.39 (s, br, 6 H, 10-CH_3), 2.78 (t, $^3J_{HH} = 7.3$ Hz, 2 H, H(b)), 4.23 (t, $^3J_{HH} = 7.3$ Hz, 2 H, H(a)), 6.92 (m, 2 H, H(11)), 7.15 (dd,$^3J_{HH} = 8.2$ Hz, $^4J_{HH} = 2.1$ Hz, 1 H, H(5)), 7.25 (s, br, 2 H, H(9)), 7.51 (s, br, 1 H, H(3)), 7.94 (d, $^3J_{HH} = 8.2$ Hz, 1 H, H(6)), 8.43 (m, 2 H, 1H(2)), 10.88 (s, br, 1 H, NH). $\{^1H\}^{13}C$-NMR (75.5 MHz, $CDCl_3$, 298 K): $\delta = -1.7$ (C-k), 17.4/18.6 (C-e, C-g, C-h, C-j), 21.0 (10-CH_3), 21.7 (C-b, C-f, C-i), 66.6 (C-a), 84.7 (C-c), 103.0 (C-d), 106.5 (C-3), 119.5 (C-5), 121.3 (C-9), 123.6 (C-6/C-11), 128.4 (C-1), 138.0 (C-2), 147.5 (C-12), 149.1 (C-10), 153.5 (C-7), 160.6 (C-8), 162.3 (C-4). $\{^1H\}^{29}Si$-NMR (79.5 MHz, $CDCl_3$, 298 K): $\delta = -15.1$ (≡C–Si–), 0.6 ($(CH_3)_3Si$- and $Si(CH_2)_4$–). IR (neat): ν [cm^{-1}] = 2953 (s), 2911 (s), 2181 (vw), 1632 (m), 1592 (s), 1545 (w), 1467 (w), 1412 (m), 1330 (m), 1247 (s), 1141 (m), 1022 (m), 944 (w), 910 (m), 862 (s), 833 (s), 694 (m). MS (FAB): $m/z = 1670.1$ $[M]^+$. $C_{87}H_{173}N_5OSi_{13}$ (1670.48 g.mol^{-1}): calcd.: C 62.55, H 10.43, N 4.19; found: C 62.64, H 10.71, N 3.86.

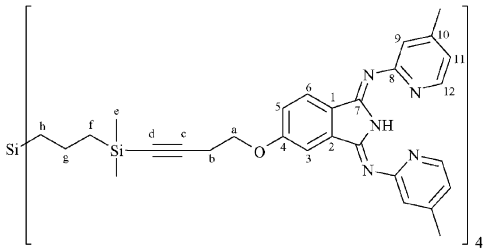


Preparation of $[G\text{-}0]_{4\text{-}exo}$-4-[C≡$CCH_2CH_2O$]-10-MeBPI (7a)

A solution of LDA in thf (2 M) (1.77 ml = 3.54 mmol) was slowly added to a solution of 4-(3-butynoxy)-10-MeBPI (**2a**) (0.70 g = 1.77 mmol) in thf (80 ml), which was cooled to −80 °C. The mixture was warmed to −40 °C and then re-cooled to −80 °C. After the addition of $[G\text{-}0]_{4\text{-}exo}$-Cl (0.23 g = 0.40 mmol) the reaction mixture was warmed to room temperature and then stirred for another 24 h. After removal of the volatiles *in vacuo*, the residue was washed with 3 × 10 ml of water and then extracted with *n-hexane* until the extracts were colourless. The pure reaction product was obtained as a yellow amorphous solid.

Yield: 0.67 g (0.33 mmol, 83%). Mp: 46 °C. ^1H-NMR (400.16 MHz, $CDCl_3$, 298 K): $\delta = 0.14$ (s, 24 H, H(e)), 0.68 (m, 16 H, H(f), H(h)), 1.42 (m, 8 H, H(g)), 2.34 (s, 24 H, 10-CH_3), 2.74 (t, $^3J_{HH} = 7.1$ Hz, 8 H, H(b)), 4.25 (t, $^3J_{HH} = 7.1$ Hz, 8 H, H(a)), 6.86 (m, 8 H, H(11)), 7.07 (m, 4 H, H(5)), 7.21 (s, br, 8 H, H(9)), 7.52 (d, $^4J_{HH} = 2.1$ Hz, 4 H, H(3)), 7.89 (d, $^3J_{HH} = 8.4$ Hz, 4 H, H(6)), 8.39 (m, 8 H, 1H(2)), 13.79 (s, br, 4 H, NH). $\{^1H\}^{13}C$-NMR (100.6 MHz, $CDCl_3$, 298 K): $\delta = -1.5$ (C-e), 17.1/18.5 (C-f, C-h), 20.9 (C-g), 21.0 (10-CH_3), 21.1 (C-b), 66.7 (C-a), 86.2 (C-c), 102.5 (C-d), 106.7 (C-3), 119.6 (C-5), 121.0/121.3 (C-9), 123.3/123.6 (C-11), 123.9 (C-6), 128.3 (C-1), 137.9 (C-2), 147.3/147.4 (C-12), 149.1 (C-10), 153.5 (C-7), 160.3 (C-8), 161.8 (C-4). $\{^1H\}^{29}Si$-NMR (79.5 MHz, $CDCl_3$, 298 K): $\delta = -17.6$ (≡C–Si), 1.0 ($Si(CH_2)$–). IR (KBr): ν [cm^{-1}] = 2917 (m), 2169 (w), 1633 (s), 1591 (s), 1544 (m), 1466 (m), 1359 (w), 1328 (w), 1242 (m), 1121 (w), 1039 (w), 821 (m). MS (FAB):

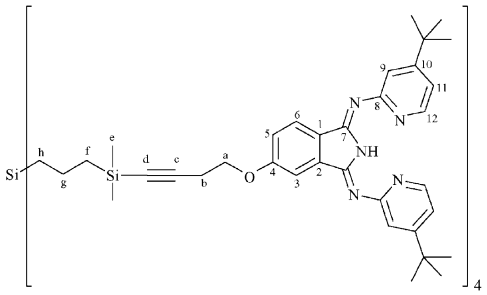
m/z = 2006.6 $[M]^-$. $C_{116}H_{128}N_{20}O_4Si_5$ (2006.85 g.mol^{-1}): calcd.: C 69.43, H 6.43, N 13.96; found: C 69.19, H 6.70, N 14.06.



Preparation of [G-0]$_{4\text{-exo}}$-4-[C≡CCH$_2$CH$_2$O]-10-^{t}BuBPI (7b)

A solution of LDA in thf (2 M) (0.67 ml = 1.34 mmol) was slowly added to a solution of 4-(3-butynoxy)-10-^{t}BuBPI (**2b**) (0.32 g = 0.67 mmol) in thf (50 ml), which was cooled to −80 °C. The mixture was warmed to −40 °C and then re-cooled to −80 °C. After the addition of [G-0]$_{4\text{-exo}}$-Cl (87.0 mg = 0.15 mmol) the reaction mixture was warmed to room temperature and then stirred for another 24 h. After removal of the volatiles *in vacuo*, the residue was washed with 3 × 10 ml of water and then extracted with *n*-hexane until the extracts were colourless. The pure reaction product was obtained as a yellow amorphous solid.

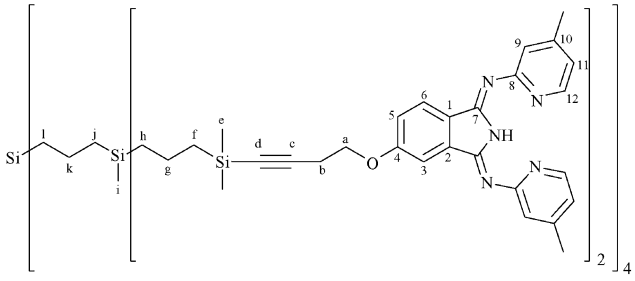
Yield: 0.30 g (0.13 mmol, 86%), Mp: 54 °C. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 298 K): δ = 0.15 (s, 24 H, H(e)), 0.69 (m, 16 H, H(f), H(h)), 1.42 (m, 8 H, H(g), 10-C(CH_3)$_3$), 2.78 (t, $^3J_{HH}$ = 7.3 Hz, 8 H, H(b)), 4.23 (t, $^3J_{HH}$ = 7.3 Hz, 8 H, H(a)), 7.11 (m, 12 H, H(5), H(11)), 7.41 (m, 8 H, H(9)), 7.54 (m, 4 H, H(3)), 7.92 (d, $^3J_{HH}$ = 8.1 Hz, 4 H, H(6)), 8.46 (m, 8 H, 1H(2)), 13.83 (s, br, 4 H, NH). {^{1}H}^{13}C-NMR (75.5 MHz, $CDCl_3$, 298 K): δ = −1.5 (C-e), 17.1/18.5 (C-f, C-h), 20.9 (C-g), 21.1 (C-b), 30.6 (10-C(CH_3)$_3$), 34.8 (10-C(CH_3)$_3$), 66.7 (C-a), 86.2 (C-c), 102.4 (C-d), 106.6 (C-3), 117.4/117.6 (C-9), 119.7 (C-5), 119.8/119.9 (C-11), 123.8 (C-6), 128.4 (C-1), 138.0 (C-2), 147.5/147.6 (C-12), 153.5 (C-7), 160.6/160.7 (C-8), 161.8 (C-4), 162.2 (C-10). {^{1}H}^{29}Si-NMR (79.5 MHz, $CDCl_3$, 298 K): δ = −17.7 (≡C–Si), 0.9 (Si(CH_2)–). IR (KBr): ν [cm^{-1}] = 2957 (m), 2912 (m), 2888 (m), 2172 (w), 1633 (s), 1588 (s), 1533 (s), 1478 (s), 1401 (m), 1367 (m), 1223 (m), 1285 (m), 1263 (m), 1224 (m), 1102 (w), 1042 (m), 1019 (w), 892 (w), 832 (m), 782 (w), 716 (w). MS (FAB): m/z = 2344.4 $[M]^+$. $C_{140}H_{176}N_{20}O_4Si_5$ (2343.50 g.mol^{-1}): calcd.: C 71.75, H 7.57, N 11.95; found: C 71.93, H 7.71, N 12.04.



Preparation of [G-1]$_{8\text{-exo}}$-4-[C≡CCH$_2$CH$_2$O]-10-MeBPI (8)

A solution of LDA in thf (2 M) (1.40 ml = 2.80 mmol) was slowly added to a solution of 4-(3-butynoxy)-10-MeBPI (**2a**) (0.56 g = 1.40 mmol) in thf (60 ml), which was cooled to −80 °C. The mixture was warmed to −40 °C and then re-cooled to −80 °C. After the addition of [G-1]$_{8\text{-exo}}$-Cl (0.23 g = 0.16 mmol). The reaction mixture was warmed to room temperature and then stirred for another 24 h. After removal of the volatiles *in vacuo*, the residue was washed with 3 × 10 ml of water and then extracted with *n*-hexane until the extracts were colourless. The pure reaction product was obtained as a yellow amorphous solid.

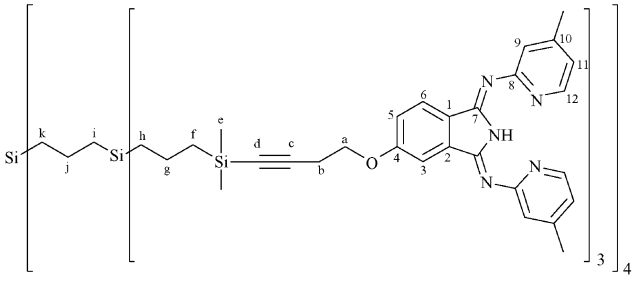
Yield: 0.57 g (0.13 mmol, 82%), Mp: 42 °C. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 298 K): δ = −0.03 (s, 12 H, H(i)), 0.14 (s, 48 H, H(e)), 0.68 (m, 48 H, H(f), H(h), H(j), H(l)), 1.42 (m, 24 H, H(g), H(k)), 2.33 (s, br, 48 H, 10-CH_3), 2.74 (t, $^3J_{HH}$ = 7.1 Hz, 16 H, H(b)), 4.25 (t, $^3J_{HH}$ = 7.1 Hz, 16 H, H(a)), 6.86 (m, 16 H, H(11)), 7.06 (m, 8 H, H(5)), 7.21 (s, br, 16 H, H(9)), 7.44 (s, br, 8 H, H(3)), 7.89 (d, $^3J_{HH}$ = 8.3 Hz, 8 H, H(6)), 8.39 (m, 16 H, 1H(2)), 13.76 (s, br, 8 H, NH). {^{1}H}^{13}C-NMR (75.5 MHz, $CDCl_3$, 298 K): δ = −4.9 (C-i), −1.5 (C-e), 17.6–20.8 (C-b, C-f, C-g, C-h, C-j, C-k, C-l), 20.9 (10-CH_3), 66.5 (C-a), 86.1 (C-c), 102.4 (C-d), 106.4 (C-3), 119.5 (C-5), 121.0/121.2 (C-9), 123.4/123.6 (C-11), 123.8 (C-6), 128.2 (C-1), 137.8 (C-2), 147.3/147.4 (C-12), 149.0 (C-10), 153.4/153.5 (C-7), 160.2/160.4 (C-8), 161.6 (C-4). {^{1}H}^{29}Si-NMR (79.5 MHz, $CDCl_3$, 298 K): δ = −17.7 (≡C–Si), 0.3 (Si(CH_2)–), 1.1 (–Si(CH_3)–). IR (KBr): ν [cm^{-1}] = 2959 (w), 2912 (m), 2875 (w), 2177 (w), 1632 (s), 1590 (s), 1544 (m), 1487 (m), 1466 (m), 1401 (vw), 1359 (w), 1328 (w), 1280 (m), 1242 (m), 1162 (m), 1040 (m), 910 (w), 820 (m), 716 (vw). MS (FAB): m/z = 4326.7 $[M]^-$, 2660.8 $[M]^{2-}$. $C_{248}H_{292}N_{40}O_8Si_{13}$ (4326.42 g.mol^{-1}): calcd.: C 68.84, H 6.80, N 12.95; found: C 69.19, H 6.83, N 13.06.



Preparation of [G-1]$_{12\text{-exo}}$-4-[C≡CCH$_2$CH$_2$O]-10-MeBPI (9)

A solution of LDA in thf (2 M) (1.85 ml = 3.70 mmol) was slowly added to a solution of 4-(3-butynoxy)-10-MeBPI (**2a**) (0.70 g = 1.85 mmol) in thf (60 ml), which was cooled to −80 °C. The mixture was warmed to −40 °C and then re-cooled to −80 °C. After addition of [G-1]$_{12\text{-exo}}$-Cl (0.27 g = 0.14 mmol) the reaction mixture was warmed to room temperature and then stirred for another 24 h. After removal of the volatiles *in vacuo*, the residue was washed with 3 × 10 ml of water and then extracted with *n*-hexane until the extract remains colourless. The pure reaction product was obtained as a yellow amorphous solid.

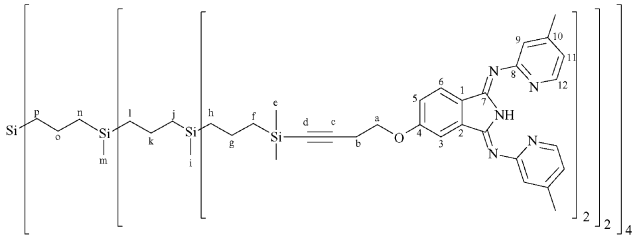
Yield: 0.69 g (0.11 mmol, 79%). Mp: 47 °C. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 298 K): δ = 0.18 (s, br, 72 H, H(e)), 0.73 (m, br, 64 H, H(f), H(h), H(i), H(k)), 1.42 (m, 32 H, H(g), H(j)), 2.27 (s, br, 72 H, 10-CH_3), 2.74 (m, br, 24 H, H(b)), 4.08 (m, br, 24 H, H(a)), 6.78 (m, 24 H, H(11)), 6.98–7.11 (m, br, 36 H, H(5), H(9)), 7.33 (s, br, 12 H, H(3)), 7.72 (s, br, 12 H, H(6)), 8.28 (m, br, 24 H, 1H(2)), 13.67 (s, br, 12 H, NH). {^{1}H}^{13}C-NMR (75.5 MHz, $CDCl_3$, 298 K): δ = −1.3 (C-e), 17.1–18.6 (C-f, C-g, C-h, C-i, C-j, C-k), 20.9 (10-CH_3), 21.2 (C-b), 66.5 (C-a), 86.1 (C-c), 102.5 (C-d), 106.4 (C-3), 119.2 (C-5), 121.0 (C-9), 123.4 (C-11), 123.6 (C-6), 128.3 (C-1), 137.8 (C-2), 147.2 (C-12), 148.7 (C-10), 153.4 (C-7), 160.2 (C-8), 161.5 (C-4). {^{1}H}^{29}Si-NMR (79.5 MHz, $CDCl_3$, 298 K): δ = −17.9 (≡C–Si), 0.7 (Si(CH_2)–). IR (KBr): ν [cm^{-1}] = 3420 (m, br), 2952 (w), 2914 (m), 2872 (w), 2177 (m), 1632 (s), 1590 (s), 1544 (m), 1488 (m), 1466 (m), 1400 (vw), 1359 (w), 1328 (w), 1280 (m), 1242 (m), 1162 (w), 1039 (m), 909 (w), 821 (m), 716 (vw), 457 (w). MS (MALDI-TOF): m/z = 6244.7 $[M]^-$. $C_{360}H_{408}N_{60}O_{12}Si_{17}$ (6245.05 g.mol^{-1}): calcd.: C 69.24, H 6.59, N 13.46; found: C 68.90, H 6.83, N 13.04.



Preparation of $[G\text{-}2]_{16\text{-}exo}$-4-[C≡CCH$_2CH_2$O]-10-MeBPI (10)

A solution of LDA in thf (2 M) (0.76 ml = 1.52 mmol) was slowly added to a solution of 4-(3-butynoxy)-10-MeBPI (**2a**) (0.30 g = 0.76 mmol) in thf (30 ml), which was cooled to −80 °C. The mixture was warmed to −40 °C and then re-cooled to −80 °C. After the addition of $[G\text{-}2]_{16\text{-}exo}$-Cl (0.14 g = 43.3 μmol) the reaction mixture was warmed to room temperature and then stirred for another 24 h. After removal of the volatiles *in vacuo*, the residue was washed with 3 × 10 ml of water and then extracted with *n*-hexane until the extracts were colourless. The pure reaction product was obtained as a yellow amorphous solid.

Yield: 0.29 g (32.9 μmol, 76%). Mp: 54 °C. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 298 K): δ = −0.05 (s, 12 H, H(m)), −0.04 (s, 24 H, H(i)), 0.15 (s, 96 H, H(e)), 0.68 (m, 112 H, H(f), H(h), H(j), H(l), H(n), H(p)), 1.42 (m, 56 H, H(g), H(k), H(o)), 2.33 (s, br, 96 H, 10-CH_3), 2.74 (m, br, 32 H, H(b)), 4.17 (m, br, 32 H, H(a)), 6.86 (m, br, 32 H, H(11)), 7.07 (m, br, 16 H, H(5)), 7.20 (s, br, 32 H, H(9)), 7.44 (s, br, 16 H, H(3)), 7.85 (m, br, 16 H, H(6)), 8.38 (m, br, 32 H, 1H(2)), 13.79 (s, br, 16 H, NH). {^{1}H}^{13}C-NMR (75.5 MHz, $CDCl_3$, 298 K): δ = −4.9 (C-i, C-m), −1.5 (C-e), 18.3–19.9 (C-f, C-g, C-h, C-j, C-k, C-l, C-n, C-o, C-p), 20.8 (C-b), 20.9 (10-CH_3), 66.5 (C-a), 86.1 (C-c), 102.4 (C-d), 106.4 (C-3), 119.4 (C-5), 120.9/121.1 (C-9), 123.4/123.5 (C-11), 123.6 (C-6), 128.4 (C-1), 137.9 (C-2), 147.3 (C-12), 148.9 (C-10), 153.4 (C-7), 160.3/160.5 (C-8), 161.7 (C-4). {^{1}H}^{29}Si-NMR (79.5 MHz, $CDCl_3$, 298 K): δ = −17.7 (≡C–Si), 0.8/0.9/1.1 (Si(CH_2)$_4$–, Si(CH_3)–). IR (KBr): ν [cm^{-1}] = 3428 (m, br), 2912 (m), 2875 (w), 2177 (m), 1633 (s), 1590 (s), 1543 (m), 1487 (m), 1465 (m), 1401 (vw), 1358 (w), 1328 (w), 1280 (w), 1242 (m), 1162 (m), 1039 (m), 910 (w), 818 (m), 716 (vw). MS (MALDI-TOF): m/z = 8963.2 [M]$^-$. $C_{512}H_{620}N_{80}O_{16}Si_{29}$ (8965.56 g.mol^{-1}): calcd.: C 68.59, H 6.97, N 12.49; found: C 68.60, H 7.16, N 12.37.

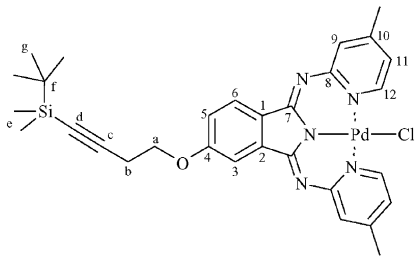


General procedure for the preparation of the palladium complexes 11–14

The BPI-substituted carbosilane (0.05 mmol) was dissolved in 5 ml of CH_2Cl_2 and 1.5 molar equivalents of triethylamine per BPI-ligand were added to this solution. Subsequently, 1.5 molar equivalents of [(PhCN)$_2$PdCl$_2$] were added for every BPI-equivalent and the reaction mixture then stirred at room temperature for 24 h. After removal of the volatiles *in vacuo* the yellow–ochre residue was washed with 3 × 10 ml of water and 3 × 10 ml of *n*-hexane. The crude product was taken up in CH_2Cl_2, filtered through Celite and the filtrate dried over $MgSO_4$. After removal of the solvent *in vacuo*, the product palladium complex was obtained as an analytically pure yellow oil (**11**) or amorphous solid (**12**–**14**).

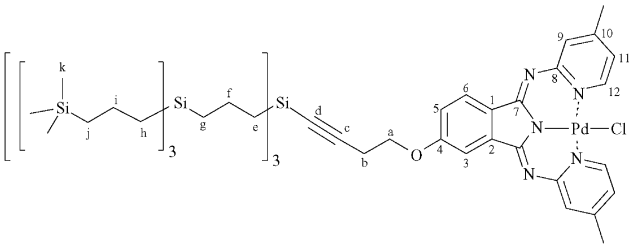
4-[^{t}BuSi(CH$_3$)$_2$C≡CCH$_2$CH$_2$O]-10-MeBPIPdCl (11)

Yield: 10.0 mg (19.2 μmol, 65%). Mp: 140 °C. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 298 K): δ = 0.11 (s, 6 H, H(e)), 0.95 (s, 9 H, H(g)), 2.40 (s, 6 H, 10-CH_3), 2.79 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, H(b)), 4.23 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, H(a)), 6.85 (m, 2 H, H(11)), 6.97 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.5 Hz, 1 H, H(5)), 7.26 (m, 2 H, H(9)), 7.45 (d, $^4J_{HH}$ = 2.5 Hz, 1 H, H(3)), 7.82 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, H(6)), 9.64 (m, 2 H, 1H(2)). {^{1}H}^{13}C-NMR (75.5 MHz, $CDCl_3$, 298 K): δ = −4.52 (C-e), 16.3 (C-f), 20.6 (10-CH_3), 20.9 (C-b), 26.1 (C-g), 66.7 (C-a), 92.7 (C-c), 105.7 (C-d), 106.8 (C-3), 119.0 (C-5), 121.2 (C-9), 123.6 (C-6), 126.4 (C-11), 130.4 (C-1), 139.9 (C-2), 151.1 (C-10), 151.5 (C-7/C-8), 152.7 (C-12), 153.6 (C-7/C-8), 161.7 (C-4). {^{1}H}^{29}Si-NMR (79.5 MHz, $CDCl_3$, 298 K): δ = −8.7 (≡C–Si). IR (KBr): ν [cm^{-1}] = 2954 (w), 2922 (w), 2857 (w), 2164 (vw), 1582 (s), 1519 (m), 1470 (s), 1405 (vw), 1364 (m), 1329 (vw), 1296 (w), 1232 (w), 1188 (w), 1106 (w), 1088 (vw), 1020 (w), 933 (vw), 885 (vw), 825 (m), 808 (m), 776 (w), 679 (vw). $C_{30}H_{34}ClN_5OPdSi$ (650.58 g.mol^{-1}): calcd.: C 55.39, H 5.27, N 10.76; found: C 54.93, H 4.91, N 10.45.



$[G\text{-}2]_{1\text{-}endo}$-4-[C≡CCH$_2CH_2$O]-10-MeBPIPdCl (12)

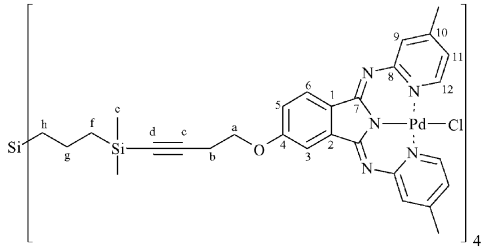
Yield: 55.0 mg (30.1 μmol, 56%). ^{1}H-NMR (300.17 MHz, CD_2Cl_2, 298 K): δ = −0.02 (s, 81 H, H(k)), 0.57 (m, br, 48 H, H(e), H(g), H(h), H(j)), 1.35 (m, 24 H, H(f), H(i)), 2.42 (s, br, 6 H, 10-CH_3), 2.79 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, H(b)), 4.24 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, H(a)), 6.90 (m, 2 H, H(11)), 7.15 (d, br,$^3J_{HH}$ = 8.1 Hz, 1 H, H(5)), 7.36 (m, br, 2 H, H(9)), 7.50 (s, br, 1 H, H(3)), 7.87 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, H(6)), 9.63 (m, 2 H, 1H(2)). {^{1}H}^{13}C-NMR (100.6 MHz, CD_2Cl_2, 298 K): δ = −1.4 (C-k), 17.8–19.0 (C-e, C-g, C-h, C-j), 20.7 (10-CH_3), 22.1 (C-b, C-f, C-i), 67.0 (C-a), 84.9 (C-c), 100.4 (C-d), 107.2 (C-3), 118.7 (C-5), 121.2 (C-9), 123.6 (C-6), 125.4 (C-11), 135.8 (C-1), 140.2 (C-2), 151.5 (C-10), 151.8 (C-7/C-8), 152.7 (C-12), 153.6 (C-7/C-8), 161.9 (C-4). {^{1}H}^{29}Si-NMR (79.5 MHz, $CDCl_3$, 298 K): δ = −21.9 (≡C–Si), 0.3 ((CH$_3$)$_3$Si–). IR (neat): ν [cm^{-1}] = 2953 (s), 2921 (s), 2854 (s), 2180 (vw), 1584 (m), 1469 (m), 1408 (m), 1336 (w), 1259 (s), 1246 (s), 1138 (m), 1096 (s), 1021 (s), 910 (m), 861 (s), 834 (s), 799 (s), 693 (m). MS (FAB): m/z = 1774.9 [M − Cl]$^+$. $C_{87}H_{172}ClN_5OPdSi_{13}$ (1811.34 g.mol^{-1}): calcd.: C 57.69, H 9.57, N 3.87; found: C 57.99, H 9.97, N 3.42.



$[G\text{-}0]_{4\text{-}exo}$-4-[C≡CCH$_2CH_2$O]-10-MeBPIPdCl (13a)

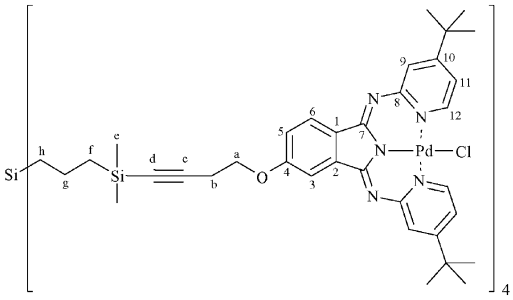
Yield: 14.5 mg (5.65 μmol, 63%), Mp: 88 °C. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 298 K): δ = 0.19 (s, 24 H, H(e)), 0.73 (m, 16 H, H(f), H(h)), 1.51 (m, 8 H, H(g)), 2.35 (s, br, 24 H, 10-CH_3), 2.78 (t, $^3J_{HH}$ = 7.4 Hz, 8 H, H(b)), 4.09 (t, $^3J_{HH}$ = 7.4 Hz, 8 H, H(a)), 6.75 (m, 8 H, H(11)), 6.86 (m, 4 H, H(5)), 7.15–7.19 (m, br, 12 H, H(3), H(9)), 7.67 (d, $^3J_{HH}$ = 8.1 Hz, 4 H, H(6)), 9.50 (m, 8 H, 1H(2)). {^{1}H}^{13}C-NMR (100.6 MHz, $CDCl_3$, 298 K): δ = −1.4 (C-e), 17.1/18.7/20.8 (C-f, C-g, C-h), 20.9 (10-CH_3), 21.0 (C-b), 66.7 (C-a), 86.3 (C-c), 102.6 (C-d), 107.2 (C-3), 118.8 (C-5), 121.4/121.5 (C-9), 124.4 (C-6), 125.6 (C-11), 126.4 (C-1), 139.0 (C-2), 150.3 (C-10), 151.3/151.4 (C-7/C-8), 152.9 (C-12), 154.1 (C-7/C-8), 161.7 (C-4). {^{1}H}^{29}Si-NMR (79.5 MHz, $CDCl_3$, 298 K): δ = −17.4 (≡C-Si), 1.2 (–Si(CH_3)$_2$–). IR (neat): ν [cm^{-1}] = 2950 (w), 2906 (w), 2883 (w), 2174 (w), 1581 (s), 1519 (m), 1470 (s), 1403 (vw), 1364 (w), 1331 (w), 1288 (m), 1231 (m), 1189 (w), 1102 (w), 1085 (w), 1020 (w), 815 (m). MS (FAB): m/z = 2534.5 [M − Cl]$^+$, 1249.4

$[M - 2{\cdot}Cl]^{2+}$. $C_{116}H_{124}Cl_4N_{20}O_4Pd_4Si_5$ (2570.31 g.mol^{-1}): calcd.: C 54.21, H 4.86, N 10.90; found: C 53.89, H 4.67, N 10.55.



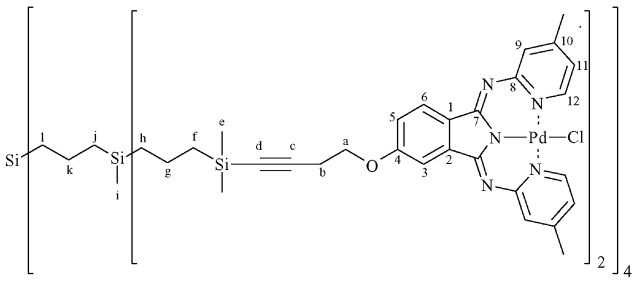
[G-0]$_{4\text{-exo}}$-4-[C≡CCH$_2$CH$_2$O]-10-^{t}BuBPIPdCl (13b)

Yield: 20.0 mg (6.96 μmol, 65%), Mp: 100 °C (dec.). ^{1}H-NMR (300.17 MHz, $CDCl_3$, 298 K): $\delta = 0.17$ (s, 24 H, H(e)), 0.72 (m, 16 H, H(f), H(h)), 1.51 (m, 80 H, H(g), 10-^{t}Bu), 2.81 (t, $^3J_{HH} = 7.4$ Hz, 8 H, H(b)), 4.21 (t, $^3J_{HH} = 7.4$ Hz, 8 H, H(a)), 6.99 (m, 12 H, H(5), H(11)), 7.32–7.44 (m, br, 12 H, H(3), H(9)), 7.70 (d, $^3J_{HH} = 8.1$ Hz, 4 H, H(6)), 9.59 (m, 8 H, 1H(2)). {^{1}H}^{13}C-NMR (100.6 MHz, $CDCl_3$, 298 K): $\delta = -1.4$ (C-e), 17.1/18.6/20.9 (C-b, C-f, C-g, C-h), 30.2 (10-C(CH_3)$_3$), 34.9 (10-C(CH$_3$)$_3$), 66.6 (C-a), 86.2 (C-c), 102.5 (C-d), 106.7 (C-3), 117.7 (C-9), 118.6 (C-5), 122.9 (C-11), 123.4 (C-6), 128.3 (C-1), 139.9 (C-2), 151.7 (C-7/C-8), 152.7 (C-12), 153.2 (C-7/C-8), 161.5 (C-4), 163.5 (C-10). {^{1}H}^{29}Si-NMR (79.5 MHz, $CDCl_3$, 298 K): $\delta = -17.5$ (≡C–Si), 1.1 (–Si(CH$_3$)$_2$–). IR (neat): ν [cm^{-1}] = 2996 (m), 2820 (w), 2867 (w), 2166 (vw), 1605 (m), 1573 (s), 1509 (m), 1479 (s), 1398 (m), 1366 (m), 1329 (w), 1297 (w), 1281 (w), 1249 (w), 1222 (m), 1207 (m), 1185 (m), 1143 (w), 1106 (m), 1079 (m), 1016 (w), 946 (vw), 920 (w), 888 (w), 824 (m), 716 (vw). MS (FAB): m/z = 2869.7 $[M - Cl]^+$, 2834.2 $[M - 2{\cdot}Cl]^+$. $C_{140}H_{172}Cl_4N_{20}O_4Pd_4Si_5$ (2906.96 g.mol^{-1}): calcd.: C 57.85, H 5.96, N 9.64; found: C 57.69, H 5.55, N 10.03.



[G-1]$_{8\text{-exo}}$-4-[C≡CCH$_2$CH$_2$O]-10-MeBPIPdCl (14)

Yield: 7.00 mg (1.26 μmol, 25%). Mp: 103 °C. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 298 K): $\delta = 0.03$ (s, 12 H, H(i)), 0.19 (s, 48 H, H(e)), 0.77 (m, 48 H, H(f), H(h), H(j), H(l)), 1.43 (m, 24 H, H(g), H(k)), 2.33 (s, br, 48 H, 10-CH$_3$), 2.75 (t, $^3J_{HH} = 6.8$ Hz, 16 H, H(b)), 4.25 (t, $^3J_{HH} = 6.8$ Hz, 16 H, H(a)), 6.72 (m, 16 H, H(11)), 6.83 (m, br, 8 H, H(5)), 7.09 (s, br, 16 H, H(9)), 7.17 (s, br, 8 H, H(3)), 7.59 (m, br, 8 H, H(6)), 9.48 (m, br, 16 H, 1H(2)). {^{1}H}^{13}C-NMR (75.5 MHz, $CDCl_3$, 298 K): $\delta = -4.8$ (C-i), -1.4 (C-e), 17.1/18.4/18.6/19.2 (C-f, C-g, C-h, C-j, C-k, C-l), 20.5 (C-b), 20.8 (10-CH$_3$), 66.3 (C-a), 86.1 (C-c), 102.5 (C-d), 106.1 (C-3), 118.2 (C-5), 120.7 (C-9), 123.1 (C-6), 126.4 (C-11), 130.1 (C-1), 139.5 (C-2), 150.4 (C-10), 151.2 (C-7/C-8), 152.5 (C-12), 152.7 (C-7/C-8), 160.9 (C-4). {^{1}H}^{29}Si-NMR (79.5 MHz, $CDCl_3$, 298 K): $\delta = -17.6$ (≡C–Si), 0.5 (Si(CH$_2$)$_4$–), 1.2 (–Si(CH$_3$)–). IR (neat): ν [cm^{-1}] = 2963 (w), 2906 (m), 2852 (w), 2173 (w), 1579 (s), 1517 (m), 1468 (m), 1397 (vw), 1364 (w), 1261 (s), 1228 (w), 1188 (m), 1103 (s), 1019 (s), 803 (s). MS (MALDI-TOF): $m/z = 5416.9$ $[M - Cl]^+$. $C_{248}H_{284}Cl_8N_{40}O_8Pd_8Si_{13}$ (5453.34 g.mol^{-1}): calcd.: C 54.62, H 5.25, N 10.27; found: C 54.42, H 5.47, N 10.48.



Acknowledgements

We thank the Deutsche Forschungsgemeinschaft for funding and Wacker Chemie AG for generous gifts of basic chemicals.

References

1 (*a*) J. W. J. Knapen, A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwen, P. Wijkens, D. M. Grove and G. van Koten, *Nature*, 1994, **372**, 659; (*b*) R. A. Gossage, L. A. van de Kuil and G. van Koten, *Acc. Chem. Res.*, 1998, **31**, 423; (*c*) A. W. Kleij, H. Kleijn, J. T. B. H. Jastrzebski, W. J. J. Smeets, A. L. Spek and G. van Koten, *Organometallics*, 1999, **18**, 268; (*d*) A. W. Kleij, H. Kleijn, J. T. B. H. Jastrzebski, A. L. Spek and G. van Koten, *Organometallics*, 1999, **18**, 277; (*e*) R. A. Gossage, J. T. B. H. Jastrzebski, J. van Ameijde, S. J. E. Mulders, A. J. Brouwser, R. M. J. Liskamp and G. van Koten, *Tetrahedron Lett*, 1999, **40**, 1413.

2 For reviews of dendrimer catalysis, see: (*a*) G. E. Oosterom, J. N. H. Reek, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Angew. Chem. Int. Ed.*, 2001, **40**, 1828; (*b*) D. Astruc and F. Chardac, *Chem. Rev.*, 2001, **101**, 2991; (*c*) A. M. Caminade, V. Maraval and J.-P. Majoral, *Curr. Org. Chem.*, 2002, **6**, 739; (*d*) For a general overview of the current state of the field: D. Astruc, *C. R. Chim.*, 2003, **6**(8–10).

3 (*a*) B. C. Gates, *Catalytic Chemistry*, Wiley, New York, 1982; (*b*) C. Lecuyer, F. Quignard, A. Choplin, D. Olivier and J.-M. Basset, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1660; (*c*) T. A. Budzichowski, S. T. Chacon, M. H. Chisholm, F. J. Feher and W. Streib, *J. Am. Chem. Soc.*, 1991, **113**, 689.

4 For a review, see for example:Y. Ribourdouille, G. D. Engel and L. H. Gade, *C. R. Chim.*, 2003, **6**, 1087.

5 (*a*) F. R. Hartley, *Supported Metal Complexes- A New Generation of Catalysts*, D. Reidel Publishing Company, Dortrecht, 1989; (*b*) Yu. I. Yermakov, B. N. Kuznetsov and V. A. Zakharov, *Catalysis by Supported Complexes*, Elsevier, Amsterdam, 1981; (*c*) W. A. Herrmann and C. W. Kohlpaintner, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1524.

6 B. Siggelkow, M. B. Meder, C. H. Galka and L. H. Gade, *Eur. J. Inorg. Chem.*, 2004, 3424.

7 (*a*) W. O. Siegl, *J. Org. Chem.*, 1977, **42**, 1872; (*b*) W. O. Siegl, *Inorg. Nucl. Chem. Lett.*, 1974, **10**, 825; (*c*) W. O. Siegl, F. C. Ferris and P. A. Mucci, *J. Org. Chem.*, 1977, **42**, 3442; (*d*) W. O. Siegl, *J. Heterocyclic Chem*, 1981, **18**, 1613; (*e*) R. R. Gagné, W. A. Marritt, D. N. Marks and W. O. Siegl, *Inorg. Chem.*, 1981, **20**, 3260; (*f*) R. R. Gagné, R. S. Gall, G. C. Lisensky, R. E. Marsh and L. M. Speltz, *Inorg. Chem.*, 1979, **18**, 771; (*g*) D. N. Marks, W. O. Siegl and R. P. Gagné, *Inorg. Chem.*, 1982, **21**, 3140.

8 (*a*) A. W. Addison, P. J. Burke and K. Henrick, *Inorg. Chem.*, 1982, **21**, 60; (*b*) E. Balogh-Hergovich, J. Kaiser, G. Speier, G. Huttner and A. Jacobi, *Inorg. Chem.*, 2000, **39**, 4224; (*c*) E. Balogh-Hergovich, G. Speier, M. Réglier, M. Giorgi, E. Kuzmann and A. Vértes, *Eur. J. Inorg. Chem.*, 2003, 1735; (*d*) O. P. Anderson, A. La Cour, A. Dodd, A. D. Garrett and M. Wicholas, *Inorg. Chem.*, 2003, **42**, 4513; (*e*) R. D. Bereman, G. D. Shields, J. R. Dorfman and J. Bordner, *J. Inorg. Biochem.*, 1983, **19**, 75; (*f*) D. M. Baird, W. P. Maehlmann, R. D. Bereman and P. Singh, *J. Coord. Chem.*, 1997, **42**, 107.

9 (*a*) C. A. Tolman, J. D. Druliner, P. J. Krusic, M. J. Nappa, W. C. Seidel, I. D. Williams and S. D. Ittel, *J. Mol. Catal.*, 1988, **48**, 129; (*b*) L. Saussine, E. Brazi, A. Robine, H. Mimoun, J. Fischer and R. Weiss, *J. Am. Chem. Soc.*, 1985, **107**, 3534; (*c*) E. T. Farinas, C. V. Nguyen and P. K. Mascharak, *Inorg. Chim. Acta*, 1997, **263**, 17; (*d*) F. A. Chavez and P. K. Mascharak, *Acc. Chem. Res.*, 2000, **33**, 539.

10 (*a*) M. B. Meder and L. H. Gade, *Eur J. Inorg. Chem.*, 2004, 2716; (*b*) M. B. Meder, B. A. Siggelkow and L. H. Gade, *Z. Anorg. Allg. Chem.*, 2004, **630**, 1962.

11 M. Brewis, G. J. Clarkson, A. M. Holder and N. B. McKeown, *Chem. Commun.*, 1998, 969.

12 (*a*) C. Kim and M. Kim, *J. Organomet. Chem.*, 1998, **563**, 43; (*b*) C. Kim and I. Jung, *J. Organomet. Chem.*, 1999, **588**, 8; (*c*) C. Kim and I. Jung, *J. Organomet. Chem.*, 2000, **599**, 208; (*d*) C. Kim and S. Son, *J. Organomet. Chem.*, 2000, **599**, 123.
13 A. Tuchbreiter, H. Werner and L. H. Gade, *Dalton Trans.*, 2005, 10.1039/b501069a.
14 (*a*) K. Matyjaszewski and Y. L. Chen, *J. Organomet. Chem.*, 1988, **340**, 7; (*b*) W. Uhlig, *Chem. Ber.*, 1992, **125**, 47.
15 (*a*) R. A. Findeis and L. H. Gade, *J. Chem. Soc., Dalton Trans.*, 2002, 3952; (*b*) R. A. Findeis and L. H. Gade, *Dalton Trans.*, 2003, 249.
16 Y. Ribourdouille, G. D. Engel, M. Richard-Plouet and L. H. Gade, *Chem. Commun.*, 2003, 1228.
17 P. J. Domaille, R. L. Harlow, S. D. Ittel and W. G. Peet, *Inorg. Chem.*, 1983, **22**, 3944.
18 (*a*) F. R. Hartley, *Organomet. Chem. Rev.*, 1960, **6**, 119; (*b*) M. S. Kharasch, R. C. Seyler and F. R. Mayo, *J. Am. Chem. Soc.*, 1938, **60**, 882; (*c*) J. R. Doyle, P. E. Slade and H. B. Jonassen, *Inorg. Synth.*, 1960, **6**, 218; (*d*) E. Kuljian and H. Frye, *Z. Naturforsch. (B)*, 1964, **19**, 651.
19 (*a*) A. W. van der Made and P. W. N. M. van Leeuwen, *J. Chem. Soc. Chem. Commun.*, 1992, 1400; (*b*) A. W. van der Made, P. W. N. M. van Leeuwen, J. C. de Wilde and R. A. C. Brandes, *Adv. Mater.*, 1993, **5**, 466; (*c*) L.-L. Zhan and J. Roovers, *Macromolecules*, 1993, **26**, 963; (*d*) J. Roovers, P. M. Toporowski and L.-L. Zhan, *Polym. Prepr. (Am. Chem. Sci. Div. Polym. Chem.)*, 1992, **23**, 182; (*e*) A. M. Muzafarov, O. B. Gorbatsevich, E. A. Rebrov, G. M. Ignat'eva, T. B. Myakushev, A. F. Bulkin and V. S. Papkov, *Polym. Sci. Ser. A*, 1993, **35**, 1575; (*f*) D. Seyferth, D. Y. Son, A. L. Rheingold and R. L. Ostrander, *Organometallics*, 1994, **13**, 2682.