Periphery-Palladated Carbosilane Dendrimers: Synthesis and Reactivity of Organopalladium(II) and -(IV) Dendritic Complexes. Crystal Structure of [PdMe(C_6H_4(OCH_2Ph)-4)(bpy)] (bpy = 2,2′-Bipyridine)

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Received February 22, 1999

A carbosilane dendrimer with 12 peripheral iodoarene groups, [Si{(CH_2)$_3$Si((CH_2)$_3$-$SiMe_2$($C_6H_4CH_2OC_6H_4$I-4))$_3$}$_4$] (G_1-ArI, **9**), and the corresponding G_0 model compound [Si-{(CH_2)$_3$$SiMe_2$($C_6H_4CH_2OC_6H_4$I-4)}$_4$] ($G_0$-ArI, **8**) have been prepared from [Si{(CH_2)$_3$Si((CH_2)$_3$-$SiMe_2$($C_6H_4CH_2$Br))$_3$}$_4$] (G_1-Br, **7**) and the corresponding G_0 model compound [Si{(CH_2)$_3$$SiMe_2$-($C_6H_4CH_2$Br)}$_4$] ($G_0$-Br, **6**). These dendritic species react with [Pd_2(dba)$_3$·dba/tmeda] (dba = dibenzylideneacetone, tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) to yield the periphery-palladated complexes [Si{(CH_2)$_3$$SiMe_2$($C_6H_4CH_2O$($C_6H_4$-4)PdI(tmeda))}$_4$] ($G_0$-ArPdI(tmeda), **10**) and [Si{(CH_2)$_3$Si((CH_2)$_3$$SiMe_2$($C_6H_4CH_2O$($C_6H_4$-4)PdI(tmeda))$_3$}$_4$] ($G_1$-ArPdI(tmeda), **11**). Complexes **10** and **11** react with LiMe and 2,2′-bipyridine (bpy) to yield the air-stable [Si-{(CH_2)$_3$$SiMe_2$($C_6H_4CH_2OC_6H_4$PdMe(bpy))}$_4$] ($G_0$-PdMe(bpy), **12**) and [Si{(CH_2)$_3$Si((CH_2)$_3$-$SiMe_2$($C_6H_4CH_2OC_6H_4$PdMe(bpy)))$_3$}$_4$] (G_1-ArPdMe(bpy), **13**). Complexes **12** and **13** undergo oxidative addition with benzyl bromide to form species containing Pd(IV) centers. These complexes can undergo subsequent reductive elimination at ambient temperature involving both Me−Ar and Me−CH_2Ph coupling on decomposition. Iodoarenes that model the arms of carbosilane-based dendrimers have been synthesized, and procedures have been developed for maximizing yields of organopalladium(II) and -(IV) derivatives of the iodoarenes as part of a program directed toward the isolation and study of organopalladium functionalized dendrimers. The iodoarenes RC_6H_4($CH_2OC_6H_4$I-4′)-4 (R = H (**1a**), $SiMe_3$ (**1b**)) were obtained and found to undergo facile oxidative addition to [Pd_2(dba)$_3$·dba/tmeda] to form [PdI(Ar)-(tmeda)] (**2a,b**), which react with LiMe to form [PdMe(Ar)(tmeda)] (**3a,b**). Bpy displaces tmeda to form [PdMe(Ar)(bpy)] (**4a,b**), and the latter complexes undergo oxidative addition with benzyl bromide to form the complexes [PdBrMeAr(CH_2Ph)(bpy)] (**5a,b**). The palladium-(IV) complex **5a** undergoes facile and clean reductive elimination at ambient temperature in $CDCl_3$ to form the coupling products Me-C_6H_4(OCH_2Ph)-4 (89%), PhCH_2-C_6H_4(OCH_2Ph)-4 (9%), and Me-CH_2Ph (2%). However, **5b** undergoes more complex behavior to form Me-C_6H_4-($OCH_2C_6H_4$($SiMe_3$)-4′)-4 (87%), Me-CH_2Ph (6%), and PhCH_2-CH_2Ph (7%) together with [$PdBr_2$(bpy)]. The complex [PdMe(C_6H_4(OCH_2Ph)-4)(bpy)] (**4a**) has been characterized by X-ray diffraction. The asymmetric unit contains two similar but crystallographically independent molecules. Each molecule has square-planar geometry for palladium with the aryl ring tilted by 76.2(4) and 67.1(3)° to the coordination plane, respectively. The crystal examined by X-ray diffraction exhibits significant substitutional disorder at one site: [PdX-(C_6H_4(OCH_2Ph)-4)(bpy)] (X = Me (71%), Cl (29%)).

Introduction

Dendrimers are currently generating enormous interest in diverse areas of science and technology due to their precisely defined nanoscale, often globular, molecular structure. For example, exciting potential applications are being developed in areas such as micelle mimicry, magnetic resonance imaging, immunodiagnostics, and targeted gene delivery.[1−13] There also has

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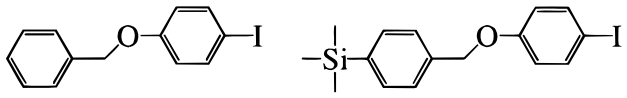
10.1021/om9901269 CCC: $18.00
Publication on Web 07/08/1999

been an explosive interest in the chemistry of dendrimers incorporating transition metals into their structure, as part of the dendrimeric skeleton[14−26] and/or as peripheral functionalization.[27−42] Periphery-functionalized dendrimers have immense potential in areas such as organic synthesis and homogeneous catalysis, where well-defined and easily accessible reaction sites (or their precursors) are essential. Furthermore, their nanoscale macromolecular architecture should allow simple removal of the catalytic species from product streams. Recently an organonickel dendrimer containing 12 nickel atoms σ-bonded to the peripheral carbon atoms of a carbosilane dendrimer was shown to be catalytically active for the Kharasch addition of polyhalogenoalkanes to carbon−carbon double bonds.[29]



1a **1b**

Figure 1.

The development of organopalladium(IV) chemistry is also a relatively recent phenomenon,[43,44] and the observed or suspected intermediacy of Pd(IV) complexes in various stoichiometric and catalytic organic transformations has generated numerous studies aimed at elucidating mechanisms and reactivity trends in related reactions. Interesting examples of selectivity in C−C bond formation in reductive elimination from triorganopalladium(IV) complexes have been documented.[43−54] For complexes containing structurally simple organic groups, $[Pd^{IV}MeAr(CH_2Ph)(N\sim N)]$, exclusive Ar−Me bond formation has been observed when the bidentate nitrogen donor is 2,2′-bipyridine (bpy) with less selectivity observed for the more rigid 1,10-phenanthroline (phen).[52,54] This has been ascribed to the increased rigidity of phen, hindering the necessary rearrangement(s) of organic groups at the Pd(IV) center and/or the formation of other transition states.

Recently, we have prepared carbosilane dendrimers with terminal iodoarene functionality, derived from polyols, and incorporating an ester group.[55] These dendrimers were functionalized with organopalladium groups at their periphery, via the oxidative addition of the C−I bond to Pd(0). However, as determined by studies on a model compound, the ester function in the molecule appeared to prevent the transmetalation of the complex to a diorganopalladium(II) complex. The emerging importance of organopalladium(IV) complexes has prompted us to attempt the synthesis of dendrimers containing organo groups that are expected to be both ideal for palladium functionalization and transmetalation and suitable for incorporation as part of the dendrimer synthesis prior to palladium functionalization. In view of recent work showing that transmetalation is possible when there is a methoxy substituent on the aryl group of [PdI(Ar)(tmeda)],[54] we report here the synthesis of a carbosilane dendrimer with peripheral functionality identical with those of **1a**,**b** (see Figure 1)

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and developed the organopalladium chemistry of **1a**,**b** as model chemistry for the incorporation of palladium into the dendrimer.

Groups **1a**,**b** are suitable periphery groups, since iodoarenes undergo facile oxidative addition reactions with palladium(0) substrates (eq 1)[54,56,57] and there is an emerging synthetic chemistry for carbosilane-based dendrimers.[8,25,28,29,32] These studies were undertaken to

$$Pd(dba)_2 + tmeda + ArI \longrightarrow PdIAr(tmeda) + 2dba \quad (1)$$

dba = dibenzylideneacetone,
tmeda = *N,N,N′,N′*-tetramethylethylenediamine

determine the most efficient reaction conditions for periphery palladation of dendrimers containing terminal ArI moieties, since (at least near) quantitative reactions are required in practical dendrimer syntheses to minimize laborious purification procedures. To assess the impact of the increase in steric bulk around the palladium center, X-ray crystallographic studies were undertaken on one such Pd(II) complex. Of particular interest in this study was the effect of the large *para* substituents on the synthesis and structure of Pd(II) and Pd(IV) complexes, including selectivity in reductive elimination compared with smaller methoxy substituents already studied,[54] since this should be expected to give useful information toward developing dendrimer chemistry containing Pd−C σ-bonds. Studies of the model chemistry indicated suitable conditions for the synthesis of a periphery-palladated dendrimer, followed by a NMR investigation of the formation and decomposition of Pd(IV) centers at the periphery of a dendrimer.

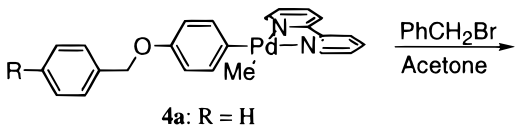
Results

Synthesis and Reactivity of Palladium(II) and -(IV) Complexes. In the preparation of completely functionalized organopalladium dendrimers, it is crucial to develop experimental procedures which prevent the formation of metallic palladium wherever possible. The synthetic procedure for the preparation of phenylpalladium(II) compounds, developed by de Graaf et al.,[56,57] shown to be useful for substituted iodoarenes[54] and used in the preparation of palladated dendrimers,[55] was successfully modified to give high-yield preparations of new arylpalladium(II) complexes from **1a**,**b**. Palladium(IV) complexes were prepared by oxidative addition of benzyl bromide to an acetone solution of these Pd(II) precursors.

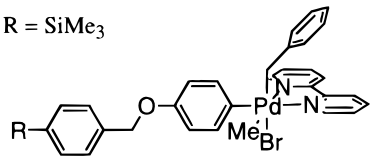
The reaction of $[Pd_2(dba)_3{\cdot}dba/tmeda]$ with ArI is typically performed at 50 °C in benzene and 80 °C in tetrahydrofuran. However, reduced temperatures were necessary for the reaction of $[Pd_2(dba)_3{\cdot}dba/tmeda]$ with **1a**,**b** in order to prevent extensive decomposition to metallic palladium. Thus, the reaction of **1a** with $[Pd_2(dba)_3{\cdot}dba/tmeda]$ occurred quantitatively at room temperature in benzene and in 95% yield in tetrahydrofuran at room temperature to give the tmeda complex $[PdI(C_6H_4(OCH_2Ph)\text{-}4)(tmeda)]$ (**2a**). The reaction of **1b** with $[Pd_2(dba)_3{\cdot}dba/tmeda]$ occurred in 95% yield in benzene at 8 °C and in 50% yield in benzene at room temperature to give $[PdI(C_6H_4(OCH_2C_6H_4SiMe_3\text{-}4')\text{-}4)(tmeda)]$ (**2b**).

Reaction of excess LiMe with the arylpalladium iodide complexes **2a**,**b** gave the methyl(aryl)palladium(II) complexes **3a**,**b** without formation of metallic palladium. Due to the intrinsic thermal instability of **3a**,**b** (slow decomposition occurs even at −30 °C in solution) these compounds were only characterized by ^1H and $^{13}C\{^1H\}$ spectroscopy (see Experimental Section). However, subsequent exchange of the tmeda ligand by bpy afforded in quantitative yield the corresponding bpy analogues **4a**,**b** respectively, which are temperature- and air-stable and have been fully characterized.

The oxidative addition of benzyl bromide to acetone solutions of **4a**,**b** was performed at 0 °C, and isolation of the triorgano−Pd(IV) complexes (**5a**,**b**; see eq 2) as white powders was carried out at low temperature by means of a dry ice cooled microfilter.



4a: R = H
4b: R = $SiMe_3$



(2)

5a: R = H
5b: R = $SiMe_3$

Once isolated, the Pd(IV) complexes could be handled for short periods in the solid state at 0 °C. In the absence of X-ray crystallographic data, the structures of the Pd(IV) complexes have been assigned the configuration as shown in eq 2 from comparison of spectra with earlier ^1H and $^{13}C\{^1H\}$ NMR spectroscopic studies of related complexes. These have shown that the chemical shift of $Pd^{IV}Me$ resonances in the ^1H NMR spectrum depends on the position of the methyl group relative to nitrogen and halogen, with Me trans to N appearing at low-field (∼2.3 ppm) and Me trans to X (X = Br, I) at higher field (∼1.7 ppm).[52] For complexes $[PdXMe(Ph)(CH_2Ph)(bpy)]$ (X = Br, I), $^{13}C\{^1H\}$ NMR spectroscopic studies have shown that the CH_2Ph and X groups are most likely mutually trans.[52] Small-scale NMR studies have shown that the oxidative addition of organohalides to $[PdMe_2(bpy)]$ is quantitative,[47,48,58] although the Pd(IV) complexes thus formed are generally isolated in moderate yield (52−71%). The results presented herein indicate that it is possible to isolate these thermally unstable organopalladium(IV) complexes of bpy in higher yield (∼80%).

Reductive Elimination from Pd(IV) Complexes. The Pd(IV) complexes decompose cleanly in $CDCl_3$ to give Pd(II) complexes and no metallic palladium. While organic group coupling is predominantly between Ar and Me groups, it is exclusive for neither of the Pd(IV) complexes. For **5a** the reductive elimination products

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arise from Me−Ar, Ar−CH_2Ph, and Me-CH_2Ph coupling, in 89%, 9%, and 2% yields, respectively (eq 3). For

$$\underset{\textbf{5a}}{[PdBrMe(C_6H_4(OCH_2Ph)\text{-}4)(CH_2Ph)(bpy)]} \xrightarrow[RT]{CDCl_3}$$

$$\begin{aligned} &0.89\{[PdBr(CH_2Ph)(bpy)] + Me\text{-}C_6H_4(OCH_2Ph)\text{-}4\} + \\ &0.09\{[PdBrMe(bpy)] + PhCH_2\text{-}C_6H_4(OCH_2Ph)\text{-}4\} + \\ &0.02\{[PdBr(C_6H_4(OCH_2Ph)\text{-}4)(bpy)] + Me\text{-}CH_2Ph\} \end{aligned} \quad (3)$$

complex **5b** the decomposition products arise from Me−Ar, $PhCH_2$−Br, and Me−CH_2Ph coupling in 92%, 3%, and 3% yields, respectively. For this complex 2% of the organic products were identified by GC-MS as the $PhCH_2$−CH_2Ph coupling product (vide infra).

Earlier studies of selectivity in reductive elimination from related triorganopalladium(IV) complexes have used integration of signals in ^{1}H NMR spectra to determine the ratios of products.[52,54] In this study, although the corresponding organopalladium(II) complexes were observable in the ^{1}H NMR spectra, their precipitation in the NMR tube rendered unsuitable the use of NMR integration. In these cases stoichiometry was determined by GC-MS analysis of NMR samples after complete disappearance of Pd(IV) signals and silica gel chromatography to remove Pd(II) products.

The decomposition of [PdBrMe{C_6H_4(OCH_2Ph)-4}-(CH_2Ph)(bpy)] (**5a**) was also examined in the presence of $PhCH_2$Br, and products different from those of eq 3 were detected. Although Me−Ar (87%) and Me−CH_2-Ph (6%) were detected as for eq 3, $PhCH_2$−CH_2Ph (7%) was also observed and an orange crystalline precipitate of [$PdBr_2$(bpy)] was formed. No palladium metal was formed.

Light-Induced Decomposition of Diorganopalladium(II) bpy Complexes 4a,b. To test the robustness of the Pd(II) moiety and both the Si−C and C−O bonds present in the molecules, solid-state and solution decomposition studies were undertaken. After exposure to light at ambient temperature for 1 week, bright yellow samples of **4a**,**b** became dark brown, and GC-MS analysis of a diethyl ether extract of the solid residues revealed the presence of Me−Ar coupling products only, i.e., Me-C_6H_4(OCH_2Ph)-4 and Me-C_6H_4-($OCH_2C_6H_4(SiMe_3)$-4′)-4 for **4a**,**b**, respectively. Thus, the solid-state decomposition of the organopalladium(II) complexes reported here occurs via a reductive elimination process. Chlorine incorporation into the molecule occurred during recrystallization from $CDCl_3$, either via direct reaction of the Pd(II) complex with $CDCl_3$ or with DCl/HCl present in $CDCl_3$. An acetone solution of **4a** decomposed over 1 week to yield orange crystals, which were analyzed by X-ray crystallography. The crystals contain both the starting material **4a** and [PdCl-(C_6H_4(OCH_2Ph)-4)(bpy)] (vide infra).

Structural Study of Crystals Obtained during Decomposition of 4a. The crystal examined has two independent molecules in the asymmetric unit. Crystallographic data and related bond length and angles are presented in Tables 1 and 2. One of these is [PdMe-(C_6H_4(OCH_2Ph)-4)(bpy)] (**4a**) (molecule 1) (Figure 2), and the other ("molecule 2") is substantially disordered such that 29% of the molecules are [PdCl(C_6H_4(OCH_2-Ph)-4)(bpy)] instead of the methylpalladium(II) complex.

Table 1. Crystal Data and Details of the Structure Determination of PdMe(C_6H_4(OCH_2Ph)-4)(bipy) (4a)

empirical formula	$C_{24}H_{22}N_2OPd\cdot C_{24-x}H_{22-3x}N_2OPdCl_x$ ($x = 0.289$)
fw	927.64
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, b, c, (Å)	10.6985(8), 11.8973(8), 17.5225(14)
α, β, γ (deg)	103.495(6), 92.797(6), 114.671(8)
V_{calcd} (Å^3)	1943.6(3)
Z	2
D_{calcd} (g/cm^3)	1.585
F(000) (e)	941
μ(Mo Kα) (cm^{-1})	9.9
cryst size (mm)	0.05 × 0.08 × 0.63
temp (K)	150
radiation, Mo Kα (graphite monochromated) (Å)	0.710 73
θ_{min}, θ_{max} (deg)	1.2, 25.0
scan type	ω
scan (deg)	0.86 + 0.35 tan θ
ref rflns	3, no decay
data set	−12 to +13; −15 to +13; −22 to +22
total, unique no of data	12 298, 6837
no. of obsd data ($I > 2.0\sigma(I)$)	4062
N_{ref}, N_{par}	6837, 553
R, R_w, S	0.0592, 0.1356, 1.00
weighting scheme	$w = 1/(\sigma^2(F_o^2) + (0.0516P)^2)$
max, av shift/error	0.00, 0.00
min, max resd intensity (e/Å^3)	−1.20, 0.87

"Molecule 2" has bond lengths and angles similar to those of molecule 1 (Table 1), and the geometry at palladium is very similar to that reported for the two polymorphs of [PdMePh(bpy)].[57,59]

The conformation of the arylpalladium(II) group is of particular interest, as it provides one indication of the possible geometry to be obtained in periphery-palladated carbosilane dendrimers. The aryl group bonded to palladium forms dihedral angles of 76.2(4)° (molecule 1) and 67.1(3)° ("molecule 2") with the "PdC_2N_2" mean planes, compared to 78.7(2)° in one polymorph of [PdMePh(bpy)][57] and 65.7(11), 70.7(10), 75.3(11), and 75.7(12)° in the four independent molecules in a second polymorph of [PdMePh(bpy)].[59] The variation in the values between the two molecules in the crystal is reflected also in dihedral angles between the phenyl rings in each [$PdC_6H_4OCH_2C_6H_5$] unit (54.3(4)° (molecule 1), 67.9(4)° ("molecule 2")) and in the torsion angles between the outer phenyl ring and the "OCC_{ipso}" group (−179.2(7)° (molecule 1), 172.0(6)° ("molecule 2")).

Synthesis and Characterization of G_0-ArI and G_1-ArI. The dendritic alkyl bromide intermediates **6** and **7** were synthesized in high (80%) or moderate (55%) overall yields by starting from the corresponding polyols.[60] The ^{1}H NMR spectra show an AA′BB′ pattern for the aromatic protons on the disubstituted benzene ring of **6** and **7** in the range 7.4−7.6 ppm. Benzylic protons appear at 4.49 and 4.46 ppm, respectively. The methylene protons appear for G_0 (24) and G_1 (72) as three well-resolved resonances. The ^{13}C{^{1}H} NMR spectra show characteristic signals for the benzylic carbon at 34.1 and 33.8 ppm. Only two of the inner core methylene

(59) Spek, A. L.; Janssen, M. D.; Markies, B. A.; van Koten, G. *Acta Crystallogr., Sect. C* **1996**, *52*, 868.
(60) Hovestad, N. J.; Jastrzebski, J. T. B. H.; van Koten, G. *Polym. Mater. Sci. Eng.* **1999**, *80*, 53.

Table 2. Selected Bond Distances (Å) and Angles (deg) and Other Data for the Ordered and Disordered Molecules of [PdMe(C_6H_4(OCH_2Ph)-4)(bpy)] (4a)

	ordered (n = 1)[a]	disordered (n = 2)[b]
	Bond Distances	
Pd(n)−C(11n)	2.121(8)	2.01(3)[c]
Pd(n)−C(12n)	1.971(9)	1.996(8)
Pd(n)−N(1n)	2.111(7)	2.123(7)
Pd(n)−N(2n)	2.120(8)	2.122(7)
Pd(2)−Cl(1)		2.38(2)[c]
	Bond Angles	
C(11n)−Pd(n)−C(12n)	85.0(3)	87.3(10)
C(11n)−Pd(n)−N(1n)	178.4(3)	175.0(10)
C(11n)−Pd(n)−N(2n)	101.3(3)	98.2(10)
C(12n)−Pd(n)−N(1n)	96.3(3)	97.7(3)
C(12n)−Pd(n)−N(2n)	171.6(3)	174.2(3)
N(1n)−Pd−N(2n)	77.5(3)	76.9(3)
Pd(n)−C(12n)−C(13n)	118.0(6)	121.0(6)
Pd(n)−C(12n)−C(17n)	126.4(6)	124.0(6)
Pd(n)−N(1n)−C(1n)	125.8(6)	126.1(6)
Pd(n)−N(1n)−C(5n)	116.2(5)	115.9(5)
Pd(n)−N(2n)−C(6n)	115.5(5)	115.7(6)
Pd(n)−N(2n)−C(10n)	127.1(7)	126.7(6)
Cl(1)−Pd(2)−C(122)		88.5(6)
Cl(1)−Pd(2)−N(12)		173.2(6)
Cl(1)−Pd(2)−N(22)		96.8(6)

[a] Deviations from the "PdC_2N_2" mean plane (in Å; χ^2 = 254): Pd(1),-0.0404(7); C(111), 0.057(8); C(121), −0.060(8); N(11), 0.064(7); N(21), −0.059(7). The mean planes of pyridine rings containing N(11), N(21), and the phenyl ring bound to palladium form dihedral angles of 4.0(3), 10.8(4), and 76.2(4)° with the "PdC_2N_2" mean plane. The phenyl ring bonded to palladium forms dihedral angles of 1.6(8), 2.1(8), and 89.9(4)° with "C(151),O(11),C(181)", "O(11),C(181),C(191)", and the other phenyl ring plane. [b] Deviations from the "PdC_2N_2" mean plane (in Å; χ^2 = 9.4): Pd(2), 0.015(1); C(112), 0.03(3); C(122), −0.023(8); N(12), 0.028(7); N(22), −0.024(7). The mean planes of pyridine rings containing N(12), N(22), and the phenyl ring bound to palladium form dihedral angles of 3.5(6), 6.0(6), and 65.9(6)° with the "PdC_2N_2" mean plane. The phenyl ring bonded to palladium forms dihedral angles of 7.3(7), 9.0(8), and 67.9(4)° with "C(152),O(12),C(182)", "O(12),C(182),C(192)", and the other phenyl ring plane. [c] Occupancies for C(11n) and Cl(1) were refined as 0.71 and 0.29, respectively.

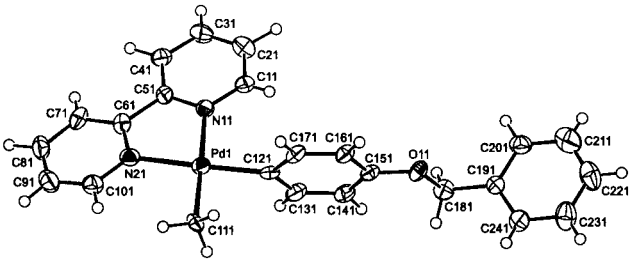
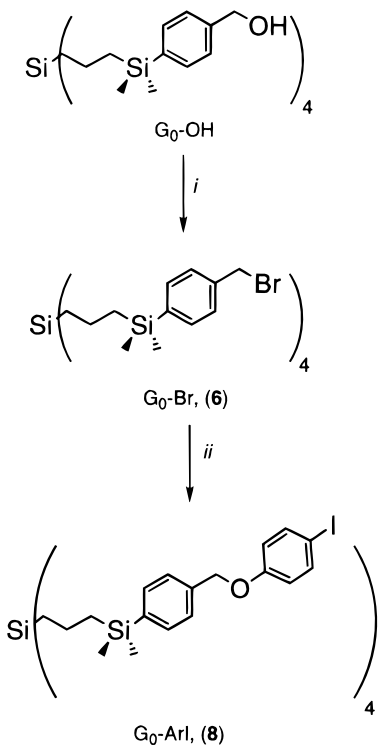


Figure 2. ORTEP drawing (50% probability level) of [PdMe(C_6H_4(OCH_2Ph)-4)(bpy)] (**4a**) (molecule 1).

carbons of G_1 are visible, and the third resonance occurs together with resonances of one of the outer methylene carbons. MALDI-TOF-MS spectra of G_0-Br and G_1-Br show signals at m/z 1127.8 and 3644.6 corresponding to $[G_0\text{-Br} + 1Na]^+$ (calcd 1127.1) and $[G_1\text{-Br} + 1Ag]^+$ (calcd 3644.4), respectively. A solution of sodium acetate in THF was added to the sample of G_0-Br, and a solution of silver(I) trifluoroacetate in THF was added to the sample of G_1-Br in order to improve the peak resolution.

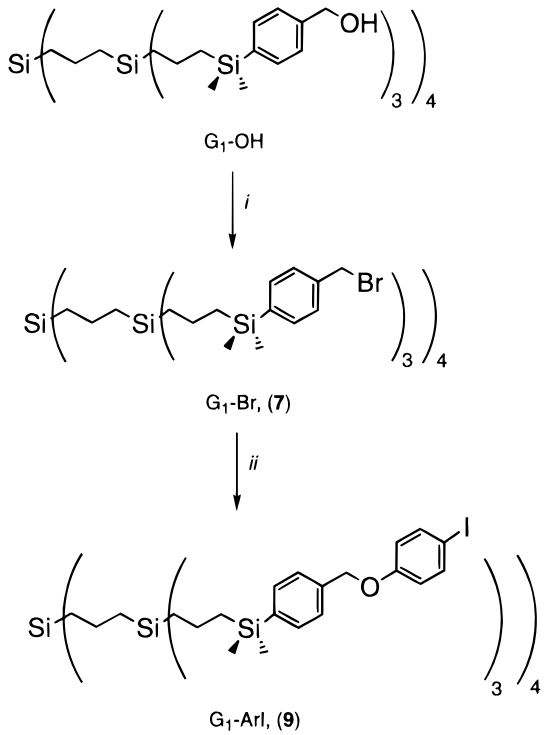
The iodides **8** and **9** were readily obtained from the bromides **6** and **7** and were synthesized in high overall yield (68% and 75%; Schemes 1 and 2). They exhibited NMR resonances with integrations as expected: two AA′BB′ patterns (aryl) and 24 G_0 and 72 G_1 "outer"

Scheme 1[a]



[a] Reagents and conditions: (*i*) 4.1 equiv of CBr_4, 4.1 equiv of PPh_3, THF, room temperature, 24 h; (*ii*) HOC_6H_4I-4, K_2CO_3, acetone, room temperature, 24 h.

Scheme 2[a]



[a] Reagents and conditions: (*i*/*ii*) procedures similar to those used for the synthesis of **8** in Scheme 1.

methylene protons as three well-resolved resonances. Benzylic protons appear as singlets at 4.99 and 4.94 ppm, respectively. The $^{13}C\{^1H\}$ NMR spectra show characteristic signals for C−I at 83.4 and the benzylic carbon at 70.4 ppm for both **8** and **9**. The MALDI-TOF-MS spectra of G_0-ArI and G_1-ArI show signals at m/z

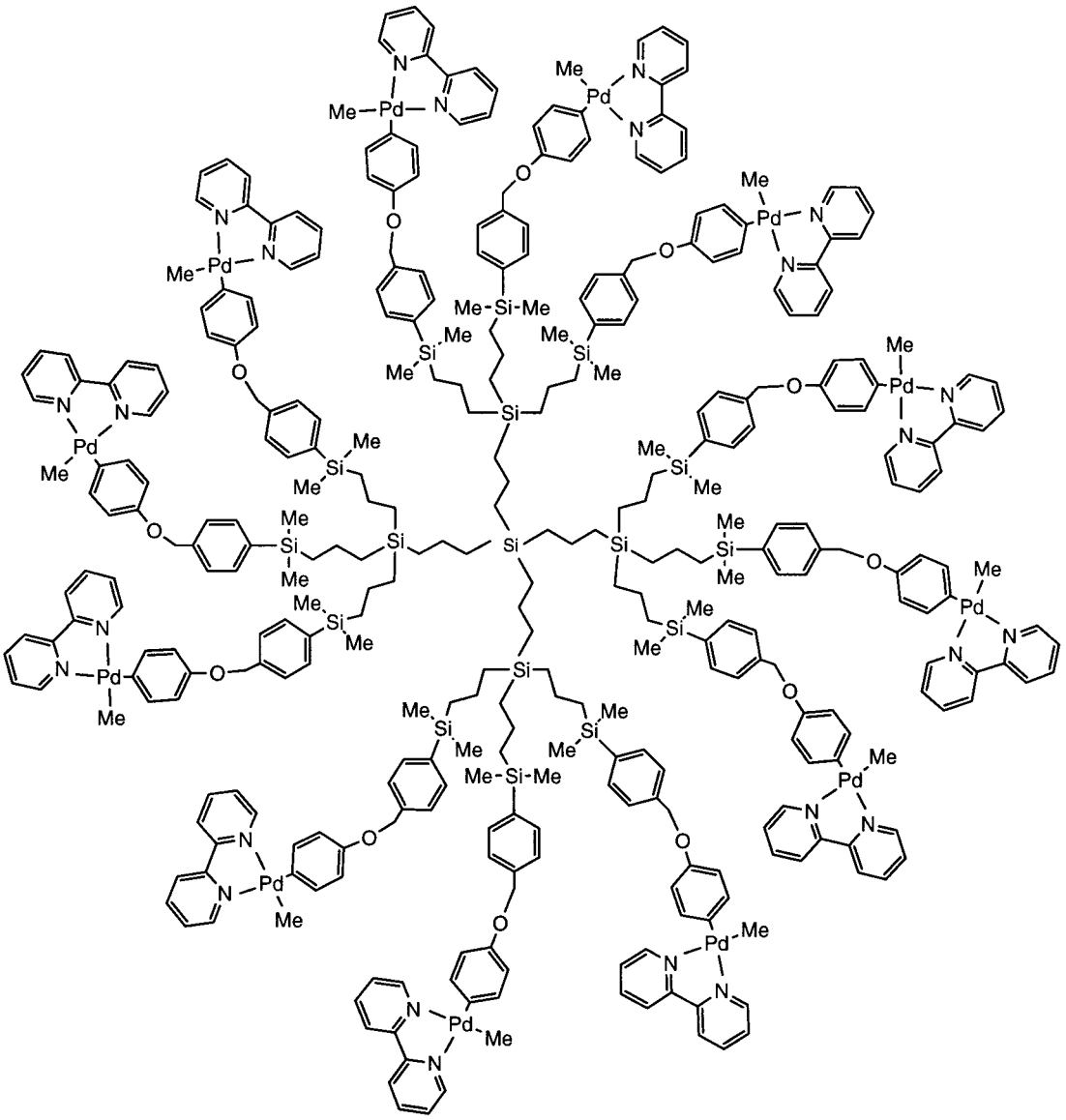


Figure 3. G_1-ArPdMe(bpy) (**13**).

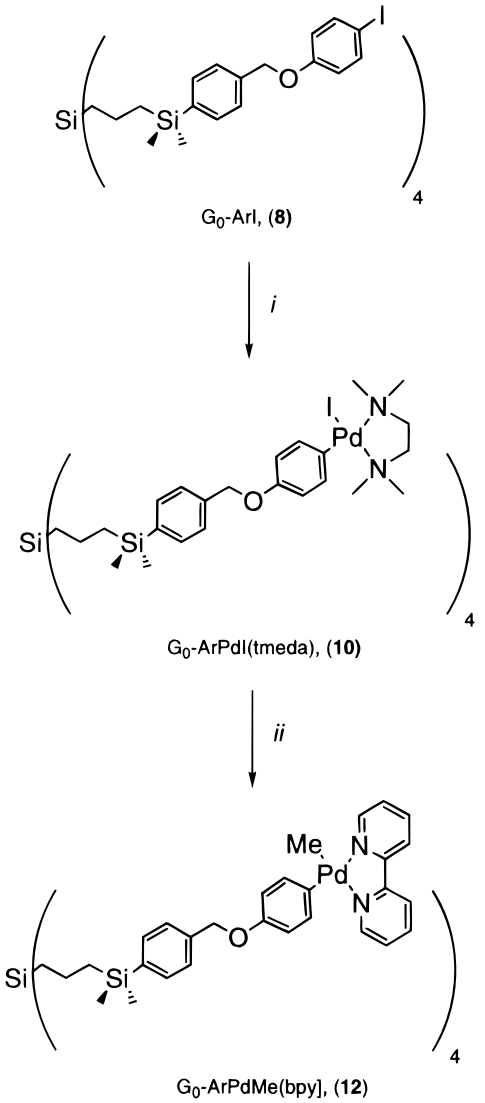
1772.9 and 5323.2, corresponding to [G_0-ArI + 1Ag] (calcd 1772.1) and [G_1-ArI + 1Ag] (calcd 5324.6), respectively.

Reactions of G_0-ArI and G_1-ArI with [$Pd_2(dba)_3$·dba/tmeda]: Synthesis and Characterization of Complexes. The oxidative addition of substituted dendritic iodoarenes to Pd(0) proceeded very well. These complexes were synthesized in 88% (**10**) and 33% (**11**) overall yield. The complexes exhibited NMR resonances with integrations as expected. The most characteristic feature of the $^{13}C\{^1H\}$ NMR spectra is the lack of a signal at approximately 100 ppm, arrising from C−I in G_0-ArI and G_1-ArI, indicating, in conjunction with the "clean" AA′BB′ pattern in the ^1H NMR spectra, complete palladation. The MALDI-TOF-MS spectra of [G_0-ArPdI(tmeda)] and [G_1-ArPdI(tmeda)] show signals at *m*/*z* 2582.1 and 7927.1, corresponding to [G_0-ArPdI(tmeda) + 1Na] (calcd 2583.3) and [G_1-ArPI(tmeda) + 1Na] (calcd 7928.1), respectively.

Reactions of [G_0-ArPdI(tmeda)] and [G_1-ArPdI(tmeda)] with LiMe and bpy: Synthesis and Characterization of Complexes. Reaction of excess LiMe with **10** and **11** gave the diorganopalladium complexes without formation of metallic palladium. However, due to their thermal instability in the solid state, the ligand exchange reactions were performed as soon as possible after drying and solvent exchange procedures. These complexes were synthesized in 63% (**12**) and 51% (**13**) overall yields (Figure 3 and Schemes 3 and 4). The Pd−Me resonance in ^1H NMR appear at 0.38 and 0.37 ppm, respectively, and appear in $^{13}C\{^1H\}$ NMR at −3.8 and −3.7 ppm, respectively**.** The MALDI-TOF-MS spectra of G_0-ArPdMe(bpy) and G_1-ArPdMe(tbpy) show signals at *m*/*z* 2379.8 and 7147.9, corresponding to [G_0-ArPdMe(bpy) + Ag] (calcd 2380.4) and [G_1-ArPdMe(bpy) + Ag] (calcd 7149.7), respectively.

Palladium(IV)−Dendrimer Chemistry. The model Pd(IV) complexes **5a**,**b** have low stability, and it was considered unlikely that it would be possible to isolate Pd(IV) complexes with the G_0 and G_1 skeletons. Thus, the reactions of [G_0-ArPdMe(bpy)] (**12**) and [G_1-ArPdMe(bpy)] (**13**) with benzyl bromide were examined initially by ^1H NMR spectroscopy, and as a result of this examination the isolation of complexes was not attempted. Complexes **12** and **13** are slightly soluble in $(CD_3)_2CO$ and $CDCl_3$. The latter solvent was used to

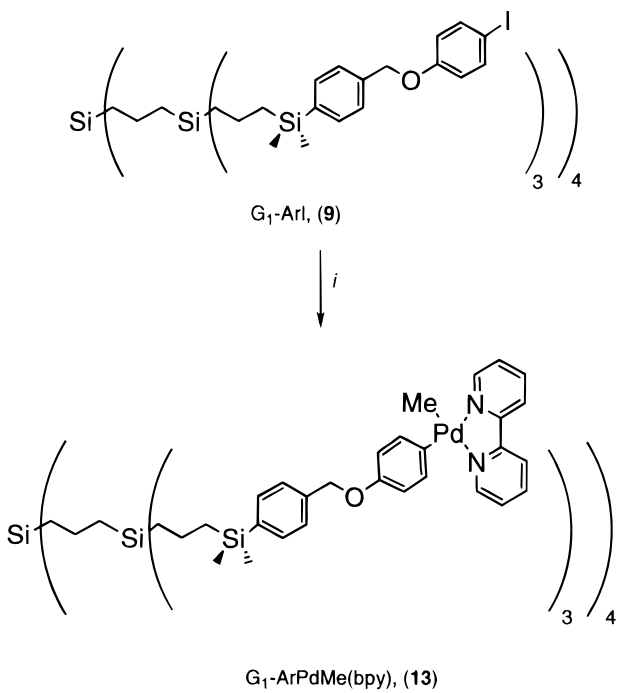
Scheme 3[a]



[a] Reagents and conditions: (*i*) 4 $Pd(dba)_2$, 4 tmeda, benzene, 0 °C, 1 h; (*ii*) 4 LiMe, Et_2O/THF; 4 bpy, benzene, room temperature.

characterize Pd(IV) model complexes formed in the reaction with benzyl bromide and to study their decomposition. When solutions of **12** and **13** with excess benzyl bromide were warmed from −20 °C, reaction was detected at −10 °C. Complex spectra were obtained, containing broad resonances for the cloudy solutions, which become more yellow with time. Resonances could be attributed to $Pd^{IV}CH_2Ph$ groups (H_a, H_b for the benzylic group at 3.60 and 3.89 ppm and $H^{3,5}$, $H^{2,6}$ for the phenyl group at 6.70 and 6.48 ppm) on comparison with spectra of the model complexes **5a**,**b** in the same solvent. The $Pd^{IV}CH_2Ph$ resonances decreased as the reaction was monitored, and a broad resonance at 2.38 ppm, which appeared soon after reaction commenced, continued to increase in intensity and could be readily attributed to "4-MeC_6H_4". GC-MS analysis revealed the presence of $Me-CH_2Ph$ and $PhCH_2-CH_2Ph$. Bibenzyl formation is consistent with the observation (see above) that reaction of the model Pd(II) complex **5a** with excess benzyl bromide results in the formation of 7% $PhCH_2-CH_2Ph$. Thus, although the stoichiometry of reductive elimination from Pd(IV) centers generated on reaction

Scheme 4[a]



[a] Reagents and conditions: (*i*) procedures similar to those used for the synthesis of **12** in Scheme 3.

of benzyl bromide with **12** and **13** could not be determined, Pd(IV) centers *were* detected and the occurrence of $Me-Ar$ and $Me-CH_2Ph$ coupling is consistent with formation of Pd(IV) centers.

Discussion

The organoiodides **1a**,**b** may be successfully converted into organopalladium(II) and -(IV) complexes, and the methyl(aryl)benzylpalladium(IV) complexes so obtained have a *fac*-PdC_3 configuration. The decomposition behavior of the Pd(IV) complexes [PdBrMe(C_6H_4(O-$CH_2C_6H_4$R-4′)-4)(CH_2Ph)(bpy)] **5a** (R = H) and **5b** (R = $SiMe_3$) differs from that of related complexes reported earlier. Thus, in contrast to the reaction of eq 3, [PdBrMe(C_6H_4R-4)(CH_2Ph)(bpy)] (R = H, OMe) give exclusively [PdBr(CH_2Ph)(bpy)] and Me−Ph.[54] The decrease in selectivity in reductive elimination for **5a** (see eq 3) compared with that of other [PdBrMeAr(CH_2Ph)-(bpy)] complexes is not as large as that observed for analogous complexes where the bidentate nitrogen donor ligand is 1,10-phenanthroline (phen), where up to 20% of the observed reductive elimination products arise from $Ar-CH_2Ph$ coupling.[54] Thermodynamic factors have been suggested as the main determinants in selectivity in C−C bond formation during reductive elimination from [PdBrMe_2(CH_2Ph)(L_2)] (L_2 = bpy, phen),[45] and the selectivity observed for structurally simple [PdBrMe(Ar)(CH_2Ph)(bpy)] complexes is consistent with this proposal, since the Ar−Me bond has higher energy than those of $Ar-CH_2Ph$ and $Me-CH_2$-Ph. The difference in selectivity exhibited by the phen complexes has been ascribed to kinetic factors, predominantly the expected requirement for axial/equatorial orientation of the ligands to be coupled,[61] which requires

(61) Byers, P. K.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D. *Organometallics* **1988**, *7*, 1363.

isomerization from configuration **5a,b** to allow Me−Ar coupling. The increased difficulty in achieving this orientation from the (assumed) cationic intermediate formed on dissociation of bromide when phen is present, compared with more flexible bpy, is believed to account for the lowering in selectivity.[54] In the present case, where the more flexible bpy ligand is present, it is likely that the decrease in selectivity results from more hindered motion around an (assumed) intermediate cationic Pd(IV) center due to the dramatic increase in steric bulk of the Ar group.

For complex **5b** (R = $SiMe_3$), which decomposes differently from **5a** (R = H), to give Me−Ar (92%), Me−CH_2Ph (3%), $PhCH_2$−Br (3%), and $PhCH_2$−CH_2Ph (2%), other processes appear to be occurring together with reductive elimination. The formation of $PhCH_2$−Br implies that the oxidative addition of $PhCH_2$−Br to Pd(II) may be reversible. There are few examples of reversible oxidative addition in similar systems, and they appear to be limited to $[PdIMe_3(L_2)]$ (L_2 = bis(*p*-tolylimino)acenaphthene)[53] and $[PtIMe_3(dppe)]$.[62] The formation of $PhCH_2$−CH_2Ph indicates the occurrence of complex decomposition mechanism(s), and similar observations have been reported for the reaction of $PhCH_2$-Br with $[PdMe_2(PPh_3)_2]$, where a Pd(IV) intermediate was not detected spectroscopically.[63]

Although Pd(IV) centers could be generated at the periphery of [G_0-ArPdMe(bpy)] and of the dendrimer [G_1-ArPdMe(bpy)], decomposition at the temperature required for synthesis indicated that it is most unlikely that a fully palladated Pd(IV) dendrimer could be isolated.

Concluding Remarks

Procedures for all steps in the preparation of the methyl(aryl)palladium(II) and methyl(aryl)benzylpalladium(IV) model complexes for periphery palladated carbosilane dendrimers have been optimized, and structural studies provide potential configurations for the aryl benzyl ether fragment of a dendrimer arm bonded to 'Pd^{II}Me(bpy)'. The wide variation in the conformations of the'[$Pd(C_6H_4OCH_2Ph)$]' group in molecules 1 and 2 in the crystal obtained on partial decomposition of **4a**, illustrated by torsion and dihedral angles, indicate that there may considerable flexibility in these parameters in dendrimers containing palladated fragments of this type.

Although Pd(IV) complexes of bpy are thermally unstable, they have been isolated here in high yield, and in situ studies show that the oxidative addition of model organohalides to palladium(II) is quantitative and that decomposition of the unstable complexes can be studied by NMR and GC-MS. Application of this approach to [G_0-ArPdMe(bpy)] (**12**) and the palladated dendrimer [G_1-ArPdMe(bpy)] (**13**) shows that the Pd(IV) centers can be generated at the periphery of dendrimers, that the complexes decompose at the same temperature as those required for their formation, rendering isolation extremely difficult, and that (at least) both Me−Ar and Me−CH_2Ph coupling occurs from the Pd(IV) centers.

Experimental Section

General Comments. All syntheses were performed under an inert atmosphere using standard Schlenk techniques. Solvents were purified according to standard procedures and freshly distilled before use. Model compounds $IC_6H_4(OCH_2$-Ph)-4 (**1a**)[64] and $Me_3SiC_6H_4(CH_2Br)$-4[65] were prepared by a literature procedure, and the dendrimeric silane polyolic precursors $[Si\{(CH_2)_3SiMe_2(C_6H_4CH_2OH\text{-}4)\}_4]$ (G_0-OH) and $[Si\{(CH_2)_3Si((CH_2)_3SiMe_2(C_6H_4CH_2OH))_3\}_4]$ (G_1-OH) were prepared as previously reported.[60] Melting points were determined using a Büchi melting point apparatus and are uncorrected. $[Pd_2(dba)_3{\cdot}dba]$ was prepared as reported.[66] All other reagents were obtained from Acros, unless otherwise indicated. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 200 and 50 MHz, respectively, using a Bruker AC200 spectometer, or at 300 and 75 MHz, respectively, using a Bruker AC300 spectrometer, at room temperature unless otherwise indicated. Chemical shifts are reported relative to Me_4Si. GC-MS analyses were performed on a Unicam Automass instrument, using electron impact (EI, 70 eV). Microanalyses were performed by Dornis und Kolbe Microanalytical Laboratories, Mulheim a.d. Ruhr, Germany, and the Central Science Laboratory, University of Tasmania. MALDI-TOF-MS spectra were acquired using a Voyager-DE BioSpectrometry Workstation (PerSeptive Biosystems Inc., Framingham, MA) mass spectrometer equipped with a nitrogen laser emitting at 337 nm. The instrument was operated in the linear mode at an accelerating voltage in the range 23 000−25 000 V. External calibration was performed using insulin (bovine), and detection was done by means of a linear detector and a digitizing oscilloscope operating at 500 MHz. Sample solutions with ~30 mg/mL in THF were used, and the matrix was 3,5-dihydroxybenzoic acid in THF (36 mg/mL). A solution of sodium acetate in THF or a solution of silver(I) trifluoroacetate in THF was added to the sample in order to improve the peak resolution. The sample solution (0.2 μL) and the matrix solution (0.2 μL) were combined and placed on a gold MALDI target and analyzed after evaporation of the solvents.

Synthesis of the Model Compound. $Me_3SiC_6H_4(CH_2O$-$(C_6H_4I\text{-}4')$-4) (1b). To a solution of $Me_3SiC_6H_4(CH_2Br)$-4 (2.17 g, 8.88 mmol) in 50 mL of acetone were added 4-iodophenol (1.95 g, 8.88 mmol) and K_2CO_3 (3 g). The resulting mixture was stirred at reflux temperature overnight, following which the volatiles were removed in vacuo and the product partioned between CH_2Cl_2 and water. The aqueous layer was washed (3 × 20 mL) with CH_2Cl_2, and the combined organic extracts were dried over Na_2SO_4. Removal of the solvent in vacuo gave a brown oil which solidified upon standing and which was purified by column chromatography (silica gel, 25 × 2 cm, eluent CH_2Cl_2) to give a white waxy solid in 52% yield. Melting point: 71 °C. Anal. Calcd for $C_{16}H_{19}IOSi$ (MW = 382.3): C, 50.27; H, 5.01. Found: C, 50.34; H, 4.96. ^1H NMR ($CDCl_3$): δ 7.59 m (4H, Si-C_6H_4, 2H, and O−C_6H_4−I, 2H, *ortho* to I, overlapping), 7.40 (d, J = 7.9 Hz, 2H, Si-C_6H_4, 2H), 6.76 d (2H, J = 7.2 Hz, O-C_6H_4-I, 2H, *ortho* to O), 5.03 s (2H, CH_2), 0.29 s (9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 158.7 (O-C_6H_4-I, O−C_{ipso}), 140.5 ((SiMe$_3$)-$C_6H_4CH_2$, SiMe$_3$-C_{ipso}), 138.3 (O-C_6H_4-I, *ortho* to I), 137.0 ((SiMe$_3$)-$C_6H_4CH_2$, CH_2-C_{ipso}), 133.7 ((SiMe$_3$)-C_6H_4-CH_2, *ortho* to SiMe$_3$), 126.8 ((SiMe$_3$)-C_6H_4-CH_2, *ortho* to CH_2), 117.3 (O-C_6H_4-I, *ortho* to O), 83.1 (O-C_6H_4-I, I-C_{ipso}), 70.1 (Ph-CH_2), −1.07 ($SiMe_3$).

Synthesis of the Model Organopalladium Complexes. $[PdI(C_6H_4(OCH_2Ph)\text{-}4)(tmeda)]$ (2a). To a stirred solution of $[Pd_2(dba)_3{\cdot}dba]$ (0.67 g, 1.2 mmol) in benzene (100 mL) was added tmeda (0.22 mL, 1.4 mmol) and **1a** (0.36 g, 1.2 mmol). The resulting solution was stirred at room temperature for 1

(62) Goldberg, K. I.; Yan, J. Y.; Breitung, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 6889.
(63) de Graaf, W.; Boersma, J.; van Koten, G. *Organometallics* **1990**, *9*, 1479.
(64) Cativiela, C.; Serrano, J. L.; Zurbano, M. *J. Org. Chem.* **1995**, *60*, 3074.
(65) Jacob, L. A.; Chen, B.-L.; Stec, D. *Synthesis* **1993**, *6*, 611.
(66) Rettig, M. F.; Maitlis, P. M. *Inorg. Synth.* **1971**, 134.

h, during which time the color changed from deep purple to yellow. The solution was filtered and the solvent removed in vacuo to give a yellow residue, which was washed with 3 × 10 mL of diethyl ether/pentane (1:1). The remaining yellow solid was collected by centriguation and dried in vacuo. Yield: 100%. The complex is stable in air and was recrystallized from CH_2Cl_2/pentane at −20 °C to give orange cubes. Melting point: 131 °C dec. Anal. Calcd for $C_{19}H_{27}IN_2OPd$ (MW = 532.8): C, 42.84; H, 5.11; N, 5.26. Found: C, 42.77; H, 5.17; N, 5.19. ^{1}H NMR ($CDCl_3$): δ 7.36 m (5H, CH_2Ph aromatic protons), 7.11 (d, J = 8.4 Hz, 2H, C_6H_4 *o* to Pd), 6.70 d (2H, J = 8.4 Hz, C_6H_4 *o* to O), 4.95 s (2H, CH_2Ph), 2.70 m (2H, tmeda, CH_2), 2.68 s (6H, NMe_2), 2.58 m (2H, tmeda, CH_2), 2.33 s (6H, NMe_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.93, 137.78, 136.12, 132.22, 128.46, 127.71, 127.63, 113.69 (aromatics), 70.04 (CH_2Ph), 62.11 (N(CH_3)$_2$), 58.30 (N(CH_3)$_2$), 49.90 and 49.76 (tmeda CH_2).

[PdI(C_6H_4($OCH_2C_6H_4SiMe_3$-4′)-4)(tmeda)] (2b). This compound was prepared in the same manner as **2a**, except that the benzene solution of [Pd_2(dba)$_3$·dba] was cooled in an ice/water bath before addition of **1b** and tmeda. The complex was isolated as an air- and temperature-stable orange crystalline solid in 95% yield. The complex may be recrystallized from CH_2Cl_2/pentane at −20 °C. Melting point: 140 °C dec. Anal. Calcd for $C_{22}H_{35}IN_2OSiPd$ (MW = 605.0): C. 43.68; H. 5.83; N. 4.63. Found: C, 43.42; H, 5.73; N, 4.71. ^{1}H NMR ($CDCl_3$): δ 7.52 d (2H, J = 7.8 Hz, $SiMe_3$-C_6H_4), 7.39 d (2H, J = 7.8 Hz, $SiMe_3$-C_6H_4), 7.11 d (2H, J = 8.5 Hz, C_6H_4Pd *o* to Pd), 6.71 d (2H, J = 8.4 Hz, C_6H_4O, *o* to O), 4.94 s (2H, OCH_2), 2.76−2.54 m and 2.68 s (10H, tmeda CH_2 and NMe_2), 2.34 s (6H, NMe_2), 0.26 s (9H, SiMe_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.1 (C_6H_4O, C_{ipso}), 139.8 (C_6H_4Pd, C_{ipso}), 138.3 ($C_6H_4CH_2$, C_{ipso}), 136.1 (C_6H_4-Pd, *o* to Pd), 133.5 ($C_6H_4CH_2$), 132.1 (C_6H_4Si, C_{ipso}), 127.0 (C_6H_4-CH_2), 113.9 (C_6H_4O, *o* to O), 70.0 (CH_2), 62.1 (NMe_2), 58.3 (NMe_2), 49.9 & 49.8 (tmeda CH_2), −1.1 (SiMe_3).

[PdMe(C_6H_4(OCH_2Ph)-4)(tmeda)] (3a). The white complex (MW = 420.9) was obtained in 93% yield using the reported procedure for MePhPd^{II} complexes.[48] The complex is insufficiently stable for microanalysis. However, it was sufficiently characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, and afterward it was converted to complex **4a** by ligand exchange. ^{1}H NMR ($CDCl_3$, 253 K): δ 7.39 m (7H, *Ph* and C_6H_4 Pd *o* to Pd, overlapping), 6.75 d (2H, J = 8.1 Hz, C_6H_4O *o* to O), 4.96 s (2H, CH_2), 2.59 m (4H, tmeda, CH_2), 2.52 s, (6H, NMe_2), 2.30 s (6H, NMe_2), −0.08 s (3H, Pd-*Me*). ^{13}C{^{1}H} NMR ($CDCl_3$, 253 K): δ 154.6 (C_6H_4O, C_{ipso}), 150.6 (C_6H_4Pd, C_{ipso}), 137.9 ($PhCH_2$, C_{ipso}), 137.4 (C_6H_4Pd, *o* to Pd), 128.6 ($PhCH_2$), 128.0 ($PhCH_2$), 127.8 ($PhCH_2$), 113.0 (C_6H_4O, *o* to O), 69.5 (CH_2), 59.9 (NMe_2), 59.3 (NMe_2), 48.6 (tmeda, CH_2), −8.2 (Pd-*Me*).

[PdMe(C_6H_4($OCH_2C_6H_4$($SiMe_3$)-4′)-4)(tmeda)] (3b). This complex was synthesized as described for **3a**, in 97% yield, and is a white, thermally unstable compound (MW = 493.1). ^{1}H NMR ($CDCl_3$, 253 K): δ 7.56 d (2H, AA′BB′, J = 7.8 Hz, C_6H_4Si), 7.46 d (2H, AA′BB′, J = 7.7 Hz, C_6H_4Si), 7.36 d (2H, AA′BB′, J = 8.2 Hz, C_6H_4Pd, *o* to Pd), 6.77 d (2H, AA′BB′, J = 8.1 Hz, C_6H_4O *o*- to O), 4.96 s (2H, CH_2), 2.57 m (4H, tmeda, CH_2), 2.52 s, (6H, NMe_2), 2.31 s (6H, NMe_2), 0.27 s (9H, SiMe_3), −0.08 s (3H, Pd*Me*). ^{13}C{^{1}H} NMR ($CDCl_3$, 253 K): δ 154.6 (C_6H_4O, C_{ipso}), 150.6 (C_6H_4Pd, C_{ipso}), 139.9 (C_6H_4Si, C_{ipso}), 138.4 ($C_6H_4CH_2$, C_{ipso}), 137.4 (C_6H_4Pd, *o* to Pd), 133.7 (C_6H_4Si, *o* to Si), 127.3 ($C_6H_4CH_2$, *o* to CH_2), 112.9 (C_6H_4O, *o*-to O), 69.4 (CH_2), 59.9 (NMe_2), 59.3 (NMe_2), 48.6 (tmeda, CH_2), −0.94 (SiMe_3), −8.2 (Pd*Me*).

[PdMe(C_6H_4(OCH_2Ph)-4)(bpy)] (4a). The bright yellow air- and temperature-stable complex was obtained in quantitative yield using the reported procedure for MePhPd^{II} complexes.[54] This complex is light-sensitive, decomposing to metallic palladium after approximately 2 days when stored in the light. Anal. Calcd for $C_{24}H_{22}N_2OPd$ (MW = 460.9): C, 62.55; H, 4.81; N, 6.08. Found: C, 62.38; H, 4.80; N, 5.94. ^{1}H NMR ($CDCl_3$): δ 8.88 d (1H, J = 5.12 Hz, bpy H^6), 8.38 d (1H, J = 4.37 Hz, bpy $H^{6'}$), 7.96 m (4H, bpy), 7.55 m and 7.39 m (9H, overlapping bpy, *Ph* and C_6H_4), 6.90 d (2H, J = 8.48 Hz, C_6H_4 *o*- to O), 5.07 s (2H, CH_2), 0.60 s (3H, Pd*Me*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.3 (bpy), 155.2 (bpy), 154.1 (C_6H_4O, C_{ipso}), 150.7 (C_6H_4Pd, C_{ipso}), 150.3 (bpy), 148.4 (bpy), 138.13, 138.08, 137.6, 128.5, 128.4, 127.7, 127.6, 126.1, 125.8, 121.6, 121.2 (aromatics), 113.9 (C_6H_4O, *o* to O), 69.9 (CH_2), −4.0 (Pd*Me*).

[PdMe(C_6H_4($OCH_2C_6H_4SiMe_3$-4′)-4)(bpy)] (4b). This compound was prepared as described for **4a**. Anal. Calcd for $C_{27}H_{30}N_2OPdSi·H_2O$ (MW = 551.1): C, 58.85; H, 5.85; N, 5.08. Found: C, 58.94; H, 5.38; N, 5.35. ^{1}H NMR ($CDCl_3$): δ 8.87 d (1H, J = 5.3 Hz, bpy H^6), 8.37 d (1H, J = 4.7 Hz, bpy $H^{6'}$), 7.94 m, 7.49 m, 7.30 m and 6.86 d (14H, bpy, C_6H_4O & C_6H_4Si overlapping), 5.05 s (2H, CH_2), 0.59 s (3H, Pd*Me*), 0.28 s (9H, SiMe_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.3, 155.2, 154.2, 150.7, 150.3, 148.4, 139.7, 138.7, 138.1, 137.6, 136.4, 133.5, 127.0, 126.1, 125.9, 121.6, 121.2, 113.9 (aromatics), 69.9 (CH_2), −1.1 (SiMe_3), −4.0 (Pd*Me*). The presence of water in the sample is apparent in the ^{1}H NMR spectrum and arises from the rapid synthesis of this compound from **3b** (vide supra).

[PdBrMe(C_6H_4(OCH_2Ph)-4)(CH_2Ph)(bpy)] (5a). To an acetone solution of **4a** (60.8 mg, 0.13 mmol) at 0 °C was added 10 equiv of $PhCH_2Br$, and the resulting solution was stirred for 30 min and then cooled to −30 °C for 5 h, during which time a white precipitate had formed. The solid was collected by filtration at ∼−40 °C and washed with cold (−30 °C) ether until $PhCH_2Br$ was not detected in the washings by GC-MS. The compound was dried in vacuo at 0 °C. Yield: 89%. ^{1}H NMR (263 K, $CDCl_3$): δ 8.68 d (1H, J = 5.9 Hz, bpy H^6), 8.32 d (1H, J = 5.0 Hz, bpy H$^{6'}$), 8.05 d (1H, J = 8.1 Hz, bpy), 7.94 d (1H, J = 8.1 Hz, bpy), 7.84 t (1H, J = 7.6 Hz, bpy), 7.78 b (2H, bpy), 7.68 t (1H, J = 7.5 Hz, bpy), 7.46 m (6H, $PhCH_2O$, $H^{2,3,5,6}$ and C_6H_4Pd *o* to Pd overlapping), 7.22 t (1H, J = 6.8 Hz, $PhCH_2O$, H^4), 6.99 d (2H, J = 8.5 Hz, C_6H_4O *o* to O), 6.77 t (1H, J = 7.3 Hz, PdCH_2Ph, H^4), 6.59 t (2H, J = 7.2 Hz, PdCH_2Ph, $H^{3,5}$), 6.39 b (2H, PdCH_2Ph, $H^{2,6}$), 5.10 s (2H, OCH_2-Ph), 3.83 d (1H, J = 7.2 Hz, PdC$H_a$$H_b$Ph), 3.69 d (1H, J = 7.2 Hz, PdC$H_a$$H_b$Ph), 2.35 s (3H, Pd*Me*).

[PdBrMe{C_6H_4($OCH_2C_6H_4$($SiMe_3$)-4′)-4)(CH_2Ph)(bpy)] (5b). This compound was prepared as for **5a** above. Yield: 87%. ^{1}H NMR (263 K, $CDCl_3$): δ 8.71 d (1H, J = 5.3 Hz, bpy H^6), 8.35 d (1H, J = 5.0 Hz, bpy H$^{6'}$), 8.07 d (1H, J = 8.0 Hz, bpy), 7.92 m (2H, bpy), 7.76 m (3H, bpy & C_6H_4Pd *o* to Pd overlapping), 7.60 d (2H, J = 7.8 Hz, C_6H_4Si), 7.49 d (2H, J = 7.5 Hz, C_6H_4Si), 7.45 t (1H, J = 6.5 Hz, bpy), 7.26 t (1H, J = 6.7 Hz, bpy), 6.98 d (2H, J = 8.6 Hz, C_6H_4O *o* to O), 6.79 t (1H, J = 7.5 Hz, PdCH_2Ph, H^4), 6.61 t (2H, J = 7.3 Hz, PdCH_2Ph, $H^{3,5}$), 6.43 b (2H, PdCH_2Ph, $H^{2,6}$), 5.10 s (2H, OCH_2-Ph), 3.84 d (1H, J = 7.2 Hz, PdC$H_a$$H_b$Ph), 3.69 d (1H, J = 7.2 Hz, PdC$H_a$$H_b$Ph), 2.36 s (3H, Pd*Me*), 0.28 s (9H, SiMe_3).

Synthesis of G_0-Br and G_1-Br. G_0-Br Si{$(CH_2)_3SiMe_2$-(C_6H_4-4)CH_2Br}$_4$ (6). To a solution of G_0-OH (0.84 g, 0.98 mmol) in THF (20 mL) were added PPh_3 (1.61 g, 6.15 mmol) and, in small portions, CBr_4 (2.04 g, 6.15 mmol). The mixture was stirred at room temperature for 17 h and filtered, and the solvent was removed in vacuo. The residue was dissolved in DCM and the solution chromatographed on silica gel (DCM eluent). The product was obtained as a pale yellow oil in 80% yield. Anal. Calcd for $C_{48}H_{72}Br_4Si_5$ (MW = 1109.2): C, 51.98; H, 6.54; Si, 12.66. Found: C, 52.13; H, 6.63; Si, 12.61. ^{1}H NMR ($CDCl_3$): δ 7.48 (d, J = 8.1 Hz, 8H, Ar*H*, 7.37 (d, J = 8.1 Hz, 8H, Ar*H*), 4.49 (s, 8H, ArCH_2), 1.30 (m, 8H, $SiCH_2CH_2$), 0.78 (t, J = 8.1 Hz, 8H, CH_2SiAr), 0.50 (t, J = 8.1 Hz, 8H, CH_2-SiCH_2), 0.24 (s, 24H, Si(CH_3)$_2$Ar). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 140.9 (4C, Ar, *C*-Si), 138.6 (4C, Ar, *C*-CH_2), 134.5 (8C, Ar, *C o* to Si), 128.7 (8C, Ar, *C o* to CH_2), 34.1 (4C, ArCH_2), 21.0 (4C, CH_2SiAr), 19.0 (4C, CH_2CH_2SiAr), 17.9 (4C, $SiCH_2CH_2CH_2$), −2.4 (SiCH_3)$_2$Ar). MALDI-TOF-MS: *m*/*z* 1127.8 [G_0-ArCH_2-Br + 1Na]$^+$ (calcd 1127.1).

G_1-Br, Si{$(CH_2)_3$Si($(CH_2)_3SiMe_2$($C_6H_4CH_2$Br-4))$_3$}$_4$ (7). The synthetic procedure is identical with that described for **6**,

starting from G_1-OH (1.22 g, 0.44 mmol) in tetrahydrofuran (20 mL) and PPh_3 (2.12 g, 8.12 mmol) and in small portions CBr_4 (2.68 g, 8.08 mmol). A pale yellow oil was obtained. Yield: 0.85 g, 0.24 mmol, 55%. Anal. Calcd for $C_{156}H_{240}Br_{12}Si_{17}$ (3552.0): C, 52.75; H, 6.81; Si, 13.44. Found: C, 52.96; H, 6.79; Si, 13.59. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.44 (d, J = 7.8 Hz, 24H, Ar*H*), 7.29 (d, J = 7.6 Hz, 24H, Ar*H*), 4.44 (s, 24H, ArCH_2), 1.32 (m, 24H CH_2CH$_2$SiAr), 1.27 (m, 8H, CH$_2$-SiCH$_2$CH_2CH$_2$SiCH$_2$), 0.79 (t, J = 7.7 Hz, 24H, CH_2SiAr), 0.53 (m, 40H, CH_2SiCH_2), 0.21 (s, 72H, Si(CH_3)$_2$Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 140.9 (12C, Ar, *C*-Si), 138.8 (12C, Ar, *C*-CH$_2$), 134.6 (24C, Ar, *C o* to Si), 128.5 (24C, Ar *C o* to CH$_2$), 34.9 (24C, ArCH$_2$), 20.8 (12C, *C*H$_2$SiAr), 18.9 (16C, *C*H$_2$CH$_2$SiAr and CH$_2$SiCH$_2$*C*H$_2$CH$_2$SiCH$_2$), 18.4 (4C, CH$_2$SiCH$_2$CH$_2$*C*H$_2$-SiCH$_2$), 18.1 (4C, CH$_2$Si*C*H$_2$CH$_2$CH$_2$SiCH$_2$), 17.7 (12C, CH$_2$-Si*C*H$_2$CH$_2$CH$_2$SiAr), −2.7 (24C, Si(*C*H$_3$)$_2$Ar). MALDI-TOF-MS: *m*/*z* 3644.6 [G_1-Br + 1Ag]$^+$ (calcd 3644.4).

Synthesis of G_0-ArI and G_1-ArI. G_0-ArI, Si{(CH²)$_3$SiMe$_2$-(C$_6$H$_4$CH$_2$OC$_6$H$_4$I-4)}$_4$ (8). To a solution of G_0-Br (**6**; 0.56 g, 0.51 mmol) in acetone (50 mL) were added 4-iodophenol (0.45 g, 2.05 mmol) and K_2CO_3 (0.35 g, 2.53 mmol), and the mixture was stirred at reflux for 17 h. After removal of the solvent in vacuo, the residue was extracted with DCM/water. The organic layer was washed with water and dried over Na_2SO_4. The volume was reduced, and the sample was chromatographed on silica gel (DCM eluent). The product was obtained as a very viscous, colorless oil, in 68% yield. Anal. Calcd for $C_{72}H_{88}I_4O_4Si_5$ (1665.5): C, 51.92; H, 5.33; Si, 8.43. Found: C, 52.05; H, 5.41; Si, 8.52. ^{1}H NMR ($CDCl_3$): δ 7.55 (d, J = 8.9 Hz, 8H, Ar*H o* to I), 7.50 (d, J = 8.2 Hz, 8H, Ar*H*), 7.37 (d, J = 7.6 Hz, 8H, Ar*H*), 6.74 (d, J = 8.7 Hz, 8H, *Ph, o* to O), 4.99 (s, 8H, ArCH_2), 1.31 (m, 8H, SiCH$_2$CH_2), 0.78 (t, J = 8.1 Hz, 8H, CH_2-SiAr), 0.50 (t, J = 8.2 Hz, 8H, CH_2SiCH_2), 0.24 (s, 24H, Si-(CH_3)$_2$Ar. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 159.1 (4C, Ar, *C*-O), 140.3 (4C, Ar, *C*-CH$_2$), 138.7 (8C, Ar, *C o* to I), 137.4 (4C, Ar, *C*-Si), 134.3 (8C, Ar, *C o* to Si), 127.3 (8C, Ar, *C o* to CH$_2$), 117.7 (8C, Ar, *C o* to O), 83.5 (4C, Ar, *C*-I), 70.5 (4C, ArCH$_2$), 21.0 (4C, *C*H$_2$SiAr), 19.0 (4C, *C*H$_2$CH$_2$SiAr), 17.9 (4C, Si*C*H$_2$CH$_2$CH$_2$), −2.4 (Si(*C*H$_3$)$_2$). MALDI-TOF-MS: *m*/*z* 1772.9 [G_0-ArI + 1Ag]$^+$ (calcd 1772.1).

G_1ArI, Si{(CH$_2$)$_3$Si((CH$_2$)$_3$SiMe$_2$(C$_6$H$_4$CH$_2$OC$_6$H$_4$I-4))$_3$}$_4$ (9). The synthetic procedure is identical with that described for **8**, starting from G_1-Br (**7**; 80.0 mg, 23 μmol), 4-iodophenol (60.0 mg, 0.27 mmol), and K_2CO_3 (45.0 mg, 0.32 mmol) in acetone (15 mL). A pale yellow oil was obtained. Yield: 80 mg, 16 μmol, 75%. Anal. Calcd for $C_{228}H_{288}I_{12}O_{12}Si_{17}$ (MW = 5221.1): C, 52.45; H, 5.56; Si, 9.14. Found: C, 52.63; H, 5.54; Si, 9.26. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.52 (d, J = 9.0 Hz, 24H, Ar*H o* to I), 7.48 (d, J = 8.5 Hz, 24H, Ar*H*), 7.33 (d, J = 7.4 Hz, 24H, Ar*H*), 6.70 (d, J = 7.7 Hz, 8H, *Ph, o* to O), 4.94 (s, 24H, ArCH_2), 1.29 (m, 24H CH_2CH$_2$SiAr), 1.27 (m, 8H, CH$_2$-SiCH$_2$CH_2CH$_2$SiCH$_2$), 0.79 (m, 24H, CH_2SiAr), 0.53 (m, 40H, CH_2SiCH_2), 0.21 (s, 72H, Si(CH_3)$_2$Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 159.1 (12C, Ar, *C*-O), 140.2 (12C, Ar, *C*-CH$_2$), 138.7 (24C, Ar, *C o* to I), 137.4 (12C, Ar, *C*-Si), 134.3 (24C, Ar, *C o* to Si), 127.3 (24C, Ar, *C o* to CH$_2$), 117.7 (24C, Ar, *C o* to O), 83.5 (12C, Ar, *C*-I), 70.4 (24C, ArCH$_2$), 20.9 (12C, *C*H$_2$SiAr), 18.9 (16C, *C*H$_2$CH$_2$SiAr and CH$_2$SiCH$_2$*C*H$_2$CH$_2$SiCH$_2$), 18.5 (4C, CH$_2$SiCH$_2$CH$_2$*C*H$_2$SiCH$_2$), 18.2 (4C, CH$_2$Si*C*H$_2$CH$_2$CH$_2$-SiCH$_2$), 17.8 (12C, CH$_2$Si*C*H$_2$CH$_2$CH$_2$SiAr), −2.3 (24C, Si-(*C*H$_3$)$_2$Ar). MALDI-TOF-MS: *m*/*z* 5323.2 [G_1-ArI + 1Ag]$^+$ (calcd 5324.6).

Synthesis of Palladated G_0 and G_1. [G_0-ArPdI(tmeda)], [Si{(CH$_2$)$_3$SiMe$_2$(C$_6$H$_4$CH$_2$O(C$_6$H$_4$-4)PdI(tmeda))}$_4$] (10). This compound was prepared in the same manner as **2a**, starting from [Pd$_2$(dba)$_3$·dba] (0.43 g, 0.75 mmol), tmeda (0.14 mL, 0.93 mmol), and G_0-ArI (**8**; 0.31 g, 0.19 mmol) in benzene (70 mL), except that the benzene solution of Pd$_2$(dba)$_3$·dba was cooled to 8 °C by an ice/water bath before addition of **8** and tmeda. The compound was isolated as an air- and temperature-stable beige crystalline solid in 88% yield. Melting point: 162 °C dec. Anal. Calcd for $C_{96}H_{152}I_4N_8O_4Pd_4Si_5$ (MW = 2556.1): C, 45.11; H, 5.99; N, 4.38. Found: C, 45.05; H, 5.94; N, 4.28. ^{1}H NMR ($CDCl_3$): δ 7.55 (d, J = 7.6 Hz, 8H, Ar*H*), 7.37 (d, J = 8.0 Hz, 8H, Ar*H*), 7.11 (d, J = 8.5 Hz, 8H, Ar*H*, *o* to Pd)), 6.70 (d, J = 8.3 Hz, 8H, *Ph*, *o* to O), 4.90 (s, 8H, ArCH_2), 2.76−2.57 m and 2.67 s (10H, tmeda CH_2 and N(CH_3)$_2$), 2.29 s (6H, N(CH_3)$_2$)), 1.29 (m, 8H, SiCH$_2$CH_2), 0.76 (t, J = 7.8 Hz, 8H, CH_2SiAr), 0.49 (t, J = 7.6 Hz, 8H, CH_2SiCH_2), 0.22 (s, 24H, Si(CH_3)$_2$Ar. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.5 (4C, Ar, *C*-O), 139.7 (4C, Ar, *C*-Pd), 138.6 (4C, Ar, *C*-CH$_2$), 136.6 (8C, Ar, *C o* to Pd), 134.2 (8C, Ar, *C o* to Si), 132.7 (4C, Ar, *C*-Si), 127.5 (8C, Ar, *C o* to CH$_2$), 114.3 (8C, Ar, *C o* to O), 70.4 (4C, ArCH$_2$), 62.6 (N(*C*H$_3$)$_2$), 58.8 (N(*C*H$_3$)$_2$), 50.4 and 50.3 (tmeda *C*H$_2$), 21.0 (4C, *C*H$_2$SiAr), 19.0 (4C, *C*H$_2$CH$_2$SiAr), 17.9 (4C, Si*C*H$_2$CH$_2$-CH$_2$), −2.3 (Si(CH$_3$)$_2$). MALDI-TOF-MS: *m*/*z* 2582.1 [G_0-ArPdI-(tmeda) + 1Na]]$^+$ (calcd 2583.3).

[G_1-ArPdI(tmeda)], [Si{(CH$_2$)$_3$Si((CH$_2$)$_3$SiMe$_2$C$_6$H$_4$CH$_2$O-(C$_6$H$_4$-4)PdI−(tmeda))$_3$}$_4$] (11). This compound was prepared in the same manner as **2a**, starting from [Pd$_2$(dba)$_3$·dba] (79.4 mg, 0.14 mmol), tmeda (26 μL, 0.17 mmol), and G_1-ArI (**9**; 60.0 mg, 0.012 mmol) in benzene (50 mL), except that the benzene solution of [Pd$_2$(dba)$_3$·dba] was cooled to 8 °C by an ice/water bath before addition of **9** and tmeda. The compound was isolated as an air- and temperature-stable beige crystalline solid in 33% yield. Melting point: 181 °C dec. Anal. Calcd for $C_{300}H_{480}I_{12}N_{24}O_{12}Pd_{12}Si_{17}$ (MW = 7892.66): C, 45.65; H, 6.13; N, 4.26. Found: C, 45.72; H, 6.08; N, 4.31. ^{1}H NMR ($CDCl_3$): δ 7.55 (d, J = 7.6 Hz, 8H, Ar*H*), 7.37 (d, J = 8.0 Hz, 8H, Ar*H*), 7.11 (d, J = 8.5 Hz, 8H, Ar*H*, *o* to Pd)), 6.70 (d, J = 8.3 Hz, 8H, *Ph, o* to O), 4.90 (s, 8H, ArCH_2), 2.76−2.57 m and 2.67 s (10H, tmeda CH_2 and N(CH_3)$_2$), 2.29 s (6H, N(CH_3)$_2$)), 1.29 (m, 8H, SiCH$_2$CH_2), 0.76 (t, J = 7.8 Hz, 8H, CH_2SiAr), 0.49 (t, J = 7.6 Hz, 8H, CH_2SiCH_2), 0.22 (s, 24H, Si(CH_3)$_2$Ar. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.5 (4C, Ar, *C*-O), 139.7 (4C, Ar, *C*-Pd), 138.6 (4C, Ar, *C*-CH$_2$), 136.6 (8C, Ar, *C o* to Pd), 134.2 (8C, Ar, *C o* to Si), 132.7 (4C, Ar, *C*-Si), 127.5 (8C, Ar, *C o* to CH$_2$), 114.3 (8C, Ar, *C o* to O), 70.4 (4C, ArCH$_2$), 62.6 (N(*C*H$_3$)$_2$), 58.8 (N(*C*H$_3$)$_2$), 50.4 & 50.3 (tmeda *C*H$_2$), 20.8 (12C, *C*H$_2$SiAr), 18.9 (16C, *C*H$_2$CH$_2$SiAr and CH$_2$SiCH$_2$*C*H$_2$CH$_2$SiCH$_2$), 18.4 (4C, CH$_2$SiCH$_2$CH$_2$*C*H$_2$SiCH$_2$), 18.1 (4C, CH$_2$Si*C*H$_2$CH$_2$CH$_2$SiCH$_2$), 17.7 (12C, CH$_2$Si*C*H$_2$CH$_2$CH$_2$SiAr), −2.3 (Si(*C*H$_3$)$_2$). MALDI-TOF-MS: *m*/*z* 7927.1 [G_1-ArPdI(tmeda) + 1Na]]$^+$ (calcd 7928.1).

[G_0-ArPdMe(bpy)], [Si{(CH$_2$)$_3$SiMe$_2$(C$_6$H$_4$CH$_2$O(C$_6$H$_4$-4)-PdMe-(bpy))}$_4$] (12). This compound was prepared in the same manner as **4a**, starting from [G_0-ArPdI(tmeda)] (**10**; 130 mg, 5.1 × 10^{-5} mol), LiMe (0.3 mL, 0.48 mmol, 1.6 M solution in Et$_2$O), and bpy (40 mg, 0.26 mmol) in Et$_2$O/thf (50 mL). The compound was isolated as an air- and temperature-stable yellow crystalline solid in 63% yield. Melting point: 112 °C dec. ^{1}H NMR ($CDCl_3$): δ 8.89 bs (1H, bpy *H*^{6}), 8.36 bs (1H, bpy *H*$^{6'}$), 8.02 m, 7.52 m, 7.30 m (14H, bpy, C$_6$*H*$_4$Si overlapping), 6.89 d (2H, J = 7.8 Hz, C$_6$*H*$_4$O), 5.03 s (2H, CH_2), 1.30 (m, 8H, SiCH$_2$CH_2), 0.80 (t, J = 7.8 Hz, 8H, CH_2SiAr), 0.59 s (12H, Pd*Me*), 0.49 (m, 8H, CH_2SiCH_2), 0.26 (s, 24H, Si(CH_3)$_2$-Ar). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.5, 155.3, 154.0, 150.9, 150.3, 148.4, 139.7, 138.7, 138.2, 137.6, 136.4, 133.9, 127.2, 126.4, 126.0, 121.7, 121.3, 112.1 (aromatics), 70.1 (*C*H$_2$), 20.8 (4C, *C*H$_2$SiAr), 18.8 (4C, *C*H$_2$CH$_2$SiAr), 17.7 (4C, Si*C*H$_2$CH$_2$CH$_2$), −2.5 (Si(*C*H$_3$)$_2$). −3.8 (Pd*Me*). MALDI-TOF-MS: *m*/*z* 2379.8 [G_0-ArPdMe(bpy) + Ag]$^+$ (calcd 2380.4).

[G_1-ArPdMe(bpy)], [Si{(CH$_2$)$_3$Si((CH$_2$)$_3$SiMe$_2$(C$_6$H$_4$CH$_2$O-(C$_6$H$_4$-4)Pd-Me(bpy)))$_3$}$_4$] (13). This compound was prepared in the same manner as **12**, starting from [G_1-ArPdI(tmeda)] (**11**; 90 mg, 1.3 × 10^{-5} mol), LiMe (0.2 mL, 0.32 mmol, 1.6 M solution in Et$_2$O), and bpy (50 mg, 0.32 mmol) in Et$_2$O/thf (50 mL). The compound was isolated as an air- and temperature-stable yellow crystalline solid in 51% yield. Melting point: 128 °C dec. ^{1}H NMR ($CDCl_3$): δ 8.89 bs (1H, bpy *H*^{6}), 8.36 bs (1H, bpy *H*$^{6'}$), 8.02 m, 7.52 m, 7.30 m (14H, bpy, C$_6$*H*$_4$Si overlapping), 6.89 d (2H, J = 7.8 Hz, C$_6$*H*$_4$O), 5.05 s (2H, CH_2), 1.29 (m, 24H, CH_2CH$_2$SiAr), 1.27 (m, 8H, CH$_2$SiCH$_2$CH_2CH$_2$SiCH$_2$), 0.79 (m, 24H, CH_2SiAr), 0.59 s (36H, Pd*Me*), 0.53 (m, 40H,

CH_2SiCH_2), 0.21 (s, 72H, $Si(CH_3)_2Ar$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.5, 155.1, 154.4, 150.2, 150.0, 148.3, 139.5, 138.6, 138.0, 137.8, 136.4, 133.5, 126.8, 126.0, 125.5, 121.3, 121.2, 113.7 (aromatics), 69.5 (CH_2), 20.9 (12C, CH_2SiAr), 19.0 (12C, CH_2CH_2SiAr) ($CH_2SiCH_2CH_2CH_2SiCH_2$, $CH_2SiCH_2CH_2CH_2SiCH_2$, and $CH_2SiCH_2CH_2CH_2SiCH_2$ not visible), 17.7 (12C, $CH_2SiCH_2CH_2CH_2SiAr$), −2.3 (24C, $Si(CH_3)_2Ar$), −3.7 (Pd*Me*). MALDI-TOF-MS: *m*/*z* 7147.9 $[G_1\text{-ArPdMe(bpy)} + Ag]^+$ (calcd 7149.7).

Reductive Elimination from Pd(IV) Model Complexes. The Pd(IV) complexes were dissolved in $CDCl_3$ at −10 °C, and their ^1H NMR spectra were recorded. As the solutions were warmed to 25 °C, decomposition was monitored by ^1H NMR spectroscopy. When resonances due to the Pd(IV) complex had disappeared entirely, the samples were chromatographed on silica gel in a Pasteur pipet column and eluted with diethyl ether. The eluent was analyzed by GC-MS. ^1H NMR spectra were analyzed by comparison with reference spectra, as previously reported.[52,54]

Reductive Elimination from in situ Prepared Dendritic Pd(IV) Complexes. The dendritic palladium complexes **12** and **13** were dissolved in $CDCl_3$ at −20 °C, followed by addition of excess benzyl bromide. The temperature was then slowly increased until reductive elimination was observed. The organic layer from the NMR tube was analyzed by GC-MS.

X-ray Data Collection, Structure Determination, and Refinement for 4a. A transparent yellow needle-shaped crystal was glued to the tip of a Lindemann glass capillary (inert oil technique) and transferred into the cold nitrogen stream of an Enraf-Nonius CAD4T diffractometer on a rotating anode. Accurate unit-cell parameters were derived from the setting angles of 25 reflections (SET4 method).[67] Crystal data and details of the structure determination are presented in Table 1. An empirical correction for absorption was done with the DIFABS technique[68] as implemented in PLATON[69] (correction range 0.738−1.264). The structure was solved with automated Patterson techniques using DIRDIF[70] and refined on F^2 by full-matrix least squares (SHELXL-96).[71] Both crystallographically independent molecules show partial substitution by chlorine on the Pd-bonded methyl site. One of them was refined with a disorder model that was refined to a Cl to CH_3 ratio of 0.29:0.71. The second disorder form was only minor and was ignored. Hydrogen atoms were taken into account at calculated positions riding on their carrier atoms. The highest residual features in the final difference map were near Pd. Neutral atom scattering factors were taken from ref 72. Geometrical calculations and the ORTEP illustration were done with PLATON.[69]

Acknowledgment. This work was supported by the Council for Chemical Sciences of The Netherlands Organization for Scientific Research (CW-NWO) and the Dutch Technology Foundation (STW) with financial aid from Gist-brocades. Dr. J. Verweij (Gist-brocades) and Prof. dr. J. G. de Vries (DSM) are kindly acknowledged for their stimulating discussions. Financial support for visits by J.L.H. (University of Tasmania, Utrecht University) and A.J.C. (Netherlands Institute for Catalysis, NIOK) is gratefully acknowledged.

Supporting Information Available: Listings of atom coordinates, thermal parameters, hydrogen atom parameters, and ligand geometry for the complexes (14 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

OM9901269

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