

Organopalladium-Functionalized Dendrimers: Insertion of Palladium(0) into Peripheral Carbon–Iodine Bonds of Carbosilane Dendrimers Derived from Polyols. Crystal Structure of $\text{Si}\{(\text{CH}_2)_3\text{O}_2\text{CC}_6\text{H}_4\text{I}-4\}_4$

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A carbosilane dendrimer with 12 peripheral iodoarene groups, $\text{Si}\{(\text{CH}_2)_3\{\text{Si}(\text{CH}_2)_3\text{O}_2\text{C}(\text{C}_6\text{H}_4\text{I}-4)\}_3\}_4$ ($G_1\text{-ArI}$, **5**), and the corresponding G_0 model compound, $\text{Si}\{(\text{CH}_2)_3\text{O}_2\text{CC}_6\text{H}_4\text{I}-4\}_4$ ($G_0\text{-ArI}$, **4**) have been prepared from polyol precursors. These compounds react with $\text{Pd}(\text{dba})_2/\text{tmeda}$ (dba = dibenzylideneacetone, tmeda = *N,N,N,N*-tetramethylethylenediamine) to yield periphery-palladated complexes, $\text{Si}\{(\text{CH}_2)_3\text{O}_2\text{C}(\text{C}_6\text{H}_4-4)\text{PdI}(\text{tmeda})\}_4$ ($G_0\text{-ArPdI}(\text{tmeda})$, **6**) and $\text{Si}\{(\text{CH}_2)_3\{\text{Si}(\text{CH}_2)_3\text{O}_2\text{C}(\text{C}_6\text{H}_4-4)\text{PdI}(\text{tmeda})\}_3\}_4$ ($G_1\text{-ArPdI}(\text{tmeda})$, **7**). Dendrimer **7** represents the first example of an exclusively σ -bonded completely periphery-palladated dendrimer. Reactions of the model palladium(II) complexes $\text{PdI}(\text{EtO}_2\text{C}(\text{C}_6\text{H}_4-4)(\text{tmeda}))$ (**2**) and $\text{PdI}(\text{EtO}_2\text{C}(\text{C}_6\text{H}_4-4)(\text{bpy}))$ (**3**) (bpy = 2,2'-bipyridyl) with the transmetalation reagents LiMe and SnMe_4 were not successful, while no reaction occurred with the related reagent $\text{Sn}(\text{C}\sim\text{N})\text{Me}_3$ [$\text{C}\sim\text{N}$ = 8-(dimethylamino)-1-naphthyl]. The molecular structure of $G_0\text{-ArI}$ (**5**) has been determined by X-ray crystallography and has C_{2v} symmetry in the solid state.

Introduction

Dendrimers are currently generating enormous interest in many diverse areas of science and technology, due to the range of applications and interesting materials properties arising from their nanoscale, precise molecular architecture, and the variation in branching and linking moieties incorporated into the structures.^{1–12} Various metals have also been incorporated into dendrimers, as part of the dendritic skeleton and/or as peripheral functionalization. For example, Cr ,¹³ W ,^{7c} Fe ,^{14–16a,17} Os/Ru ,^{16–21} Co ,^{14b,22} Rh ,²³ Ni ,²⁴ Pd/Pt ,^{8,23,25} Cu ,²⁶ Au ,^{7c,27} Zn ,^{17,28} and Ge ²⁹ have been incorporated,

with interesting luminescent,^{18d} redox,^{8,14d} and catalytic^{8,14d,24} properties resulting in some cases.

Periphery-functionalized dendrimers have considerable potential in homogeneous catalysis, since their chemical structure provides easily accessible and well-defined reactive sites for their precursors, and their

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macromolecular size should allow simple removal of catalyst residues from product streams. In contrast to coiled linear macromolecules, dendrimers possess higher overall shape persistence in solution. This allows their easy removal from the reaction solution by ultrafiltration since they cannot reptate through membranes as conventional polymers do. Recently, a carbosilane dendrimer containing 12 peripheral organonickel(II) groups was shown to be catalytically active in the Kharasch addition of polyhalogenoalkanes to carbon-carbon double bonds.²⁴ In view of the emerging importance of dendrimers as a new class of materials and the versatility of palladium in both stoichiometric and catalytic organic transformations, we have commenced an investigation into the periphery palladation of carbosilane dendrimers via the insertion of Pd(0) into the C-I bond of iodoarenes. This reaction type is a well-established route to arylpalladium systems.³⁰ To date, there have been no reports of dendrimers containing organopalladium moieties bonded directly to the periphery of the dendrimer exclusively via a Pd-C σ -bond.

We describe here the synthesis and characterization of a carbosilane dendrimer with peripheral iodoarene functionality, **5**; an X-ray crystallographic study of the G₀ model, Si{(CH₂)₃O₂CC₆H₄I-4}₄, **4**; and the synthesis of fully periphery-palladated G₀ (**6**) and G₁ (**7**). Mo-

noorganopalladium(II) complexes containing an ester function have been prepared as models for the palladated dendrimer system for an investigation of transmetalation.

Experimental Section

Unless stated otherwise, all syntheses were performed under an inert atmosphere using standard Schlenk techniques. Solvents were purified according to standard procedures and freshly distilled before use. The dendrimeric polyol precursors, Si{(CH₂)₃OH}₄ (G₀-OH), and Si{(CH₂)₃{Si(CH₂)₃OH}₃}₄ (G₁-OH),⁹ and the transmetalation reagent Sn(C~N)Me₃ [C~N = 8-(dimethylamino)-1-naphthyl]³¹ were prepared as described. Other reagents were commercial products used as received. NMR spectra were recorded with a Bruker AC300 spectrometer, with chemical shifts given in ppm relative to SiMe₄. Microanalyses were performed by Dornis und Kolbe Microanalytical Laboratories, Mulheim a.d. Ruhr, Germany, and the Central Science Laboratory, University of Tasmania. A combination of 10⁵, 10⁴, 10³, and 100 nm columns from Polymer Laboratories was used for GPC studies; chloroform was used as solvent, and data were referenced to narrow polystyrene standards. DSC traces were recorded using a Perkin-Elmer 7 Series thermal analysis system.

Synthesis of Model Compounds. Ethyl *p*-Iodobenzoate, CH₃CH₂O₂CC₆H₄I-4 (1**).** An ethanol solution of *p*-iodobenzoic acid containing 5% (wt) concentrated H₂SO₄ was refluxed overnight. The solvent was removed by rotary evaporation, and the residue was dissolved in dichloromethane. The dichloromethane solution was washed with aqueous NaOH and dried over Na₂SO₄. Removal of the solvent *in vacuo* yielded the product as a pale yellow oil. On the basis of its NMR spectra, purification was considered unnecessary. ¹H NMR (CDCl₃): δ 7.69 (AB, ³J = 8.9 Hz, 4, C₆H₄), 4.30 (q, ³J = 7.1 Hz, 2, CH₂), 1.33 (t, ³J = 7.1 Hz, 3, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 165.9 (OCO), 137.6 (C₆H₄, ortho to I), 131.0 (C₆H₄, ortho to OCO), 129.9 (C₆H₄, CCOOR), 100.7 (C₆H₄, CI), 61.2 (CH₂), 14.4 (CH₃).

PdI(CH₃CH₂O₂CC₆H₄-4)(tmeda) (2**).** To a solution of Pd(dba)₂ (0.59 g, 1.03 mmol) in benzene (100 mL) were added ethyl *p*-iodobenzoate (0.28 g, 1.03 mmol) in benzene (5 mL) and tmeda (0.2 mL, 1.3 mmol). The solution was stirred at room temperature for 2 h, during which time the color changed from deep purple to orange. The solution was filtered to remove traces of metallic palladium, the volume was reduced *in vacuo*, and pentane was added to precipitate the product as a yellow solid, which was washed with pentane/ether (1:1) and collected by centrifugation. Yield: 95%. Mp: 168 °C dec. Anal. Found: C, 36.14; H, 5.10; N, 5.58. Calcd for C₁₅H₂₅I-N₂O₂Pd (498.7): C, 36.13; H, 5.05; N, 5.62. ¹H NMR (CDCl₃): δ 7.58 (d, ³J = 8.3 Hz, 2, C₆H₄ ortho to COOR), 7.38 (d, ³J = 8.3 Hz, 2, C₆H₄ ortho to Pd), 4.30 (q, ³J = 7.1 Hz, 2, CH₂), 2.62 and 2.55 (m, 10, NMe₂ and NCH₂CH₂N overlapping), 2.32 (s, 6, NMe₂), 1.34 (t, J = 7.1 Hz, 3, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 167.8 (COOR), 156.1 (CPd), 136.5 (C₆H₄), 126.7 (C₆H₄), 125.3 (CCOOR), 62.2 (OCH₂), 60.3 (NMe₂), 58.4 (NMe₂), 50.0 and 49.7 (NCH₂CH₂N), 14.5 (CH₃).

PdI(CH₃CH₂O₂CC₆H₄-4)(bpy) (3**).** A benzene solution of **2** was stirred at room temperature with 1.1 equiv of 2,2'-bipyridine (bpy). The solvent was removed *in vacuo* and the residue was washed with (1:1 vol) pentane/diethyl ether. The yellow solid product was obtained in 100% yield. Anal. Found: C, 45.18; H, 3.68; N, 4.71. Calcd for C₁₉H₁₇N₂O₂Pd·0.5C₆H₆: C, 45.73; H, 3.50; N, 4.85. ¹H NMR (CDCl₃): δ 9.63 (d, ³J = 4.9 Hz, 1, bpy H⁶), 8.04 (m, 4, bpy), 7.71 (d, ³J = 8.3 Hz, 2, C₆H₄), 7.55 (m, 4, C₆H₄ and bpy overlapping), 7.35 ("t", 1, bpy), 4.35 (q, ³J = 7.1 Hz, 2, CH₂), 1.38 (t, ³J = 7.1 Hz, CH₃). ¹³C{¹H} NMR (CDCl₃) δ 153.5 (CPd), 150.5 (bpy), 139.4, 139.3,

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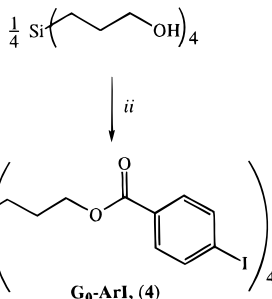
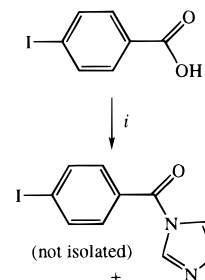
Table 1. Crystal Data and Details of the Structure Determination of G₀-ArI, Si{(CH₂)₃{Si(CH₂)₃O₂C(C₆H₄I-4)}₃}₄ (4)

empirical formula	C ₄₀ H ₄₀ I ₄ O ₈ Si
fw	1184.46
cryst syst	monoclinic
space group	C2/c (No. 15)
a, b, c (Å)	33.165(2), 6.8714(3), 23.8827(17)
β (deg)	128.729(7)
V _{calcd} (Å ³)	4245.9(6)
Z	4
D _{calcd} (g/cm ³)	1.853
F(000) (electrons)	2280
μ(Mo Kα) (cm ⁻¹)	30.1
cryst size (mm)	0.05 × 0.20 × 0.30
temp (K)	150
radiation, Mo Kα (graphite monochromated) (Å)	0.710 73
θ _{min} , θ _{max} (deg)	1.6, 27.5
scan type	ω
scan (deg)	0.64 + 0.35 tan θ
no. of ref refln(s)	3, decay 1.8%
data set	-42: 38; 0: 8; -27: 30
total no. of unique data	8371, 4839
no. of obsd data (I > 2.0σ(I))	3616
N _{ref} , N _{par}	4839, 254
R, wR, S	0.0337, 0.0758, 1.01
weighting scheme	w ⁻¹ = σ ² (F _o ²) + 0.0325P ² + 6.2190P [P = (F _o ² + 2F _c ²)/3]
max and av shift/error	0.00, 0.00
min and max resd intensity (e/Å ³)	-0.90, 0.70

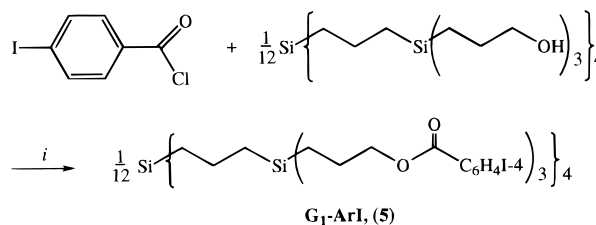
137.2, 137.0, 128.8, 128.0, 127.4, 127.2, 127.1, 126.3, 122.7, 122.2, 60.9 (CH₂), 15.0 (CH₃).

Synthesis of G₀-ArI and G₁-ArI. **G₀-ArI, Si{(CH₂)₃O₂-CC₆H₄I-4)}₄ (4).** *p*-Iodobenzoic acid (1.576 g, 6.354 mmol) and carbonyldiimidazole (CDI) (0.957 g, 5.902 mmol) were dissolved in dry *N,N*-dimethylformamide (DMF) (10 mL). The solution was stirred for 1.5 h at ambient temperature and subsequently heated at 60 °C for 12 h. Si(CH₂CH₂CH₂OH)₄ (G₀-OH) (0.3 g, 1.135 mmol) was dissolved in dry DMF (5 mL) and added to the solution of the acid imidazolide. The reaction mixture was kept at 80 °C for 44 h. The DMF was removed *in vacuo*, and the remaining solid was redissolved in CH₂Cl₂ and filtered. The filtrate was washed twice with saturated aqueous NaHCO₃ and twice with water. After drying over Na₂SO₄ and evaporation of the solvent the crude product was recrystallized from acetone/CHCl₃ (8:1) to yield the product as a crystalline white solid (0.82 g, 61%). Crystals suitable for X-ray analysis were obtained from acetone/CHCl₃ (5:1) at 4 °C. Anal. Found: C, 40.55; H, 3.36; I, 42.65. Calcd for C₄₀H₄₀I₄O₈Si (1184.5): C, 40.56; H, 3.40; I, 42.86. ¹H NMR (CDCl₃): δ 0.70 (m, 8, SiCH₂), 1.78 (m, 8, SiCH₂CH₂), 4.26 (t, ³J = 6.8 Hz, 8, CH₂O), 7.71 (d, ³J = 6.8 Hz, 8, C₆H₄), 7.77 (d, ³J = 6.8 Hz, 8, C₆H₄). ¹³C{¹H} NMR (CDCl₃): δ 8.0 (SiC), 23.2 (SiCH₂CH₂), 67.5 (SiCH₂CH₂CH₂), 100.8 (CI), 129.8 (OC(O)C), 131.0 (Ar, C meta to CI), 137.8 (Ar, C ortho to CI), 166.0 (OC(O)). Melting point: 129 °C.

G₁-ArI, Si{(CH₂)₃{Si(CH₂)₃O₂C(C₆H₄I-4)}₃}₄ (5). To a solution of G₁-OH (0.350 g, 0.344 mmol) in pyridine (8 mL) cooled in an ice/water bath was added dropwise a solution of 4-iodobenzoyl chloride (1.414 g, 5.306 mmol) in THF (12 mL). The reaction mixture was allowed to warm to ambient temperature, was stirred for 3 days, and then was poured into water (150 mL) containing concentrated HCl (9 mL). The resulting suspension was extracted with CH₂Cl₂ (300 mL), and the organic layer was washed with a saturated solution of NaHCO₃ and finally water. After drying over Na₂SO₄ and filtration, the solvent was removed and the residue was extracted several times with acetone. The remaining solid was dissolved in CHCl₃, and insoluble material was removed by filtration. The solvent was removed, and the residue was purified by chromatography on silica using CH₂Cl₂/diethyl

Scheme 1^a

^a (i) carbonyldiimidazole, -imidazole, -CO₂, DMF, 60 °C, 12 h; (ii) -imidazole, DMF, 80 °C, 44 h.

Scheme 2^a

^a (i) -HCl, pyridine/THF, 0 °C to room temperature, 3 days.

ether (100:1 vol) as eluent, yielding glassy G₁-ArI (0.52 g, 40%). Anal. Found: C, 41.97; H, 4.13. Calcd for C₁₃₂H₁₄₄I₁₂O₂₄Si₅ (3777.8): C, 41.97; H, 3.84. ¹H NMR (CDCl₃): δ 0.60 (m, 40, SiCH₂), 1.31 (m, 8, SiCH₂CH₂CH₂Si), 1.73 (m, 24, SiCH₂-CH₂CH₂O), 4.22 (t, ³J = 6.8 Hz, 24, RCH₂O), 7.72 (d, ³J = 6.4 Hz, 24, C₆H₄, ortho to COOR), 7.65 (d, J = 6.4 Hz, 24, C₆H₄ ortho to I). ¹³C{¹H} NMR (CDCl₃): δ 165.8 (COOR), 137.7 (C₆H₄, ortho to I), 130.8 (C₆H₄, meta to I), 129.6 (C₆H₄, para to I), 100.8 (CI), 67.5 (CH₂O), 23.2 (SiCH₂CH₂CH₂O), 18.5–17.2 (carbons of the inner core), 7.9 (SiCH₂CH₂CH₂O).

Synthesis of Palladated G₀ and G₁. **G₀-ArPdI(tmeda), Si{(CH₂)₃O₂C(C₆H₄-4)PdI(tmeda)}₄ (6).** To a solution of Pd(dba)₂ (0.19 g, 0.33 mmol) in THF (50 mL) were added G₀-ArI (4; 95.5 mg, 0.081 mmol) in THF (5 mL) and tmeda (0.1 mL, 0.66 mmol). The solution was stirred at room temperature for 1 h and filtered, and the solvent was removed *in vacuo*. The residue was washed with pentane/diethyl ether (1:1) and dried *in vacuo* to give the yellow solid product in 95% yield. Anal. Found: C, 37.13; H, 4.72; N, 5.00. Calcd for C₆₄H₁₀₄I₄N₈O₈Pd₄Si (2075.0): C, 37.05; H, 5.05; N, 5.40. ¹H NMR (CDCl₃): δ 7.57 (d, ³J = 8.3 Hz, 8, C₆H₄ H_{2,6}), 7.42 (d, ³J = 8.2 Hz, 8, C₆H₄ H_{3,5}), 4.20 (t, ³J = 6.5 Hz, 8, CH₂O), 2.71–2.55 and 2.68 (m, 32, NMe₂ and NCH₂ overlapping), 2.55 (m, 8, NCH₂), 2.26 (s, 24, NMe₂), 1.74 (m, 8, SiCH₂CH₂), 0.71 (m, 8, SiCH₂). ¹³C{¹H} NMR (CDCl₃): δ 167.7 (COOR), 156.6 (CPd), 136.6 (Ar), 126.6 (Ar), 125.1 (CCOOR), 66.8 (CH₂O), 62.2 (NMe₂), 58.4 (NMe₂), 50.0 and 49.9 (NCH₂CH₂N), 23.3 (SiCH₂CH₂), 8.1 (SiCH₂).

G₁-ArPdI(tmeda), Si{(CH₂)₃{Si(CH₂)₃O₂C(C₆H₄-4)PdI(tmeda)}₃}₄ (7). To a solution of G₁-ArI (0.162 g, 0.043 mmol) in THF (25 mL) were added tmeda (15 μL, 0.099 mmol) and Pd(dba)₂ (0.050 g, 0.087 mmol). The resulting purple solution was stirred at room temperature for 30 min, during which time

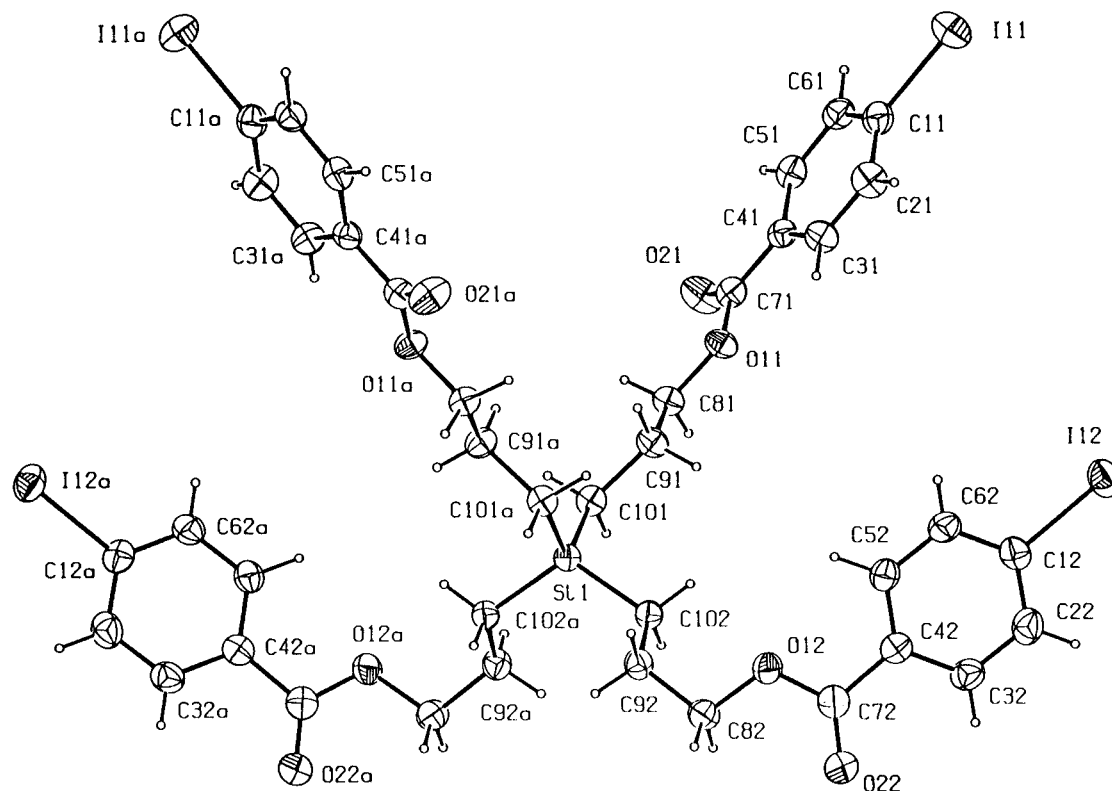


Figure 1. ORTEP drawing (50% probability level) of $\text{Si}\{(\text{CH}_2)_3\text{O}_2\text{CC}_6\text{H}_4\text{I}-4\}_4$ (**4**).

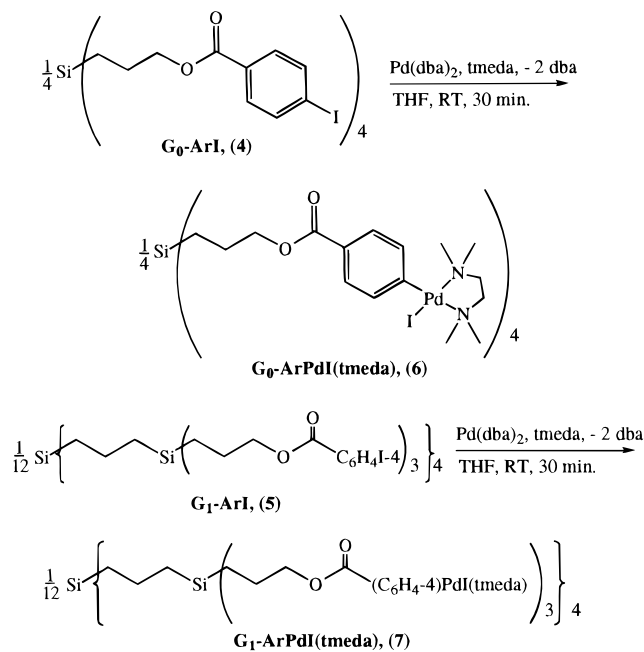
the color changed to bright orange. The THF was removed *in vacuo*, and the orange residue was extracted with CH_2Cl_2 and filtered. The solvent was removed and the residue washed with diethyl ether (4×5 mL) and then stirred in diethyl ether for 3 days, during which time the oily residue became a powdery solid, which was collected by centrifugation and dried *in vacuo* (0.22 g, 81%). Anal. Found: C, 38.09; H, 5.25; N, 5.23. Calcd for $\text{C}_{204}\text{H}_{336}\text{I}_{12}\text{N}_{24}\text{O}_{24}\text{Si}_5\text{Pd}_{12}$ (6449): C, 37.99; H, 5.25; N, 5.21. ^1H NMR (CD_2Cl_2): δ 7.52 (d, $^3J = 8.2$ Hz, 24, C_6H_4 $H_{2,6}$), 7.37 (d, $^3J = 8.2$ Hz, 24, C_6H_4 $H_{3,5}$), 4.15 (t, $^3J = 6.0$ Hz, 24, CH_2O), 2.63 (s, 72, NMe_2), 2.55 (s, 48, NCH_2), 2.21 (s, 72, NMe_2), 1.69 (m, 24, SiCH_2CH_2), 1.34 (m, 8, $\text{SiCH}_2\text{CH}_2\text{-CH}_2\text{Si}$), 0.65 (m, 40, SiCH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 167.6 (COOR), 157.6 (CPd), 137.0 (Ar), 126.6 (Ar), 125.4 (CCOOR), 67.3 (CH_2O), 62.4 (NMe_2), 58.6 (NMe_2), 50.2 and 50.0 ($\text{NCH}_2\text{-CH}_2\text{N}$), 23.7 (SiCH_2CH_2), 8.4 (SiCH_2), 18.8–15.4 (carbons of the inner core).

Attempts To Transmetalate Pd(II) Model Complexes 2 and 3. With MeLi. $\text{PdI}(\text{EtO}_2\text{CC}_6\text{H}_4-4)(\text{tmeda})$ was stirred in ether at -40 °C with 1 equiv of MeLi. Decomposition occurred before and during workup at 0 °C.

With SnMe_4 . $\text{PdI}(\text{EtO}_2\text{CC}_6\text{H}_4-4)(\text{tmeda})$ was stirred in THF at room temperature with 1 equiv of SnMe_4 for 2 days. After removal of solvent *in vacuo* and washing of the residue with diethyl ether, NMR analysis (CDCl_3) showed no conversion to a diorganopalladium(II) species. $\text{PdI}(\text{EtO}_2\text{CC}_6\text{H}_4-4)(\text{bpy})$ was stirred in THF with 1 equiv of SnMe_4 overnight at room temperature and then at reflux for 2 h. After removal of the solvent and washing of the residue with diethyl ether, NMR analysis (CDCl_3) showed no conversion to a diorganopalladium(II) species.

With (8-(Dimethylamino)-1-naphthyl)trimethyltin, $\text{Sn}(\text{C}\sim\text{N})\text{Me}_3$. $\text{PdI}(\text{EtO}_2\text{CC}_6\text{H}_4-4)(\text{tmeda})$ was stirred overnight in THF at room temperature with 1 equiv of $\text{Sn}(\text{C}\sim\text{N})\text{Me}_3$. After removal of the solvent, NMR analysis (toluene- d_6) showed no conversion to $\text{Sn}(\text{C}\sim\text{N})\text{Me}_2\text{I}$. $\text{PdI}(\text{EtO}_2\text{CC}_6\text{H}_4-4)(\text{bpy})$ was stirred with 1 equiv of $\text{Sn}(\text{C}\sim\text{N})\text{Me}_3$ in THF at room temperature for 3 days. After removal of the solvent, NMR analysis (toluene- d_6) showed no conversion to $\text{Sn}(\text{C}\sim\text{N})\text{Me}_2\text{I}$. The residue was washed with toluene, and NMR

Scheme 3



analysis (CDCl_3) showed no conversion to a diorganopalladium(II) species.

$\text{PdI}(\text{EtO}_2\text{CC}_6\text{H}_4-4)(\text{bpy})$ was stirred in THF with $\text{Sn}(\text{C}\sim\text{N})\text{Me}_3$ in THF at reflux for 2 h, during which time decomposition to metallic palladium occurred. After workup, NMR analysis (toluene- d_6) showed no conversion to $\text{Sn}(\text{C}\sim\text{N})\text{Me}_2\text{I}$.

X-ray Structure Determination. A transparent colorless plate-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).^{32a} Crystal data and details of the structure determination are presented in Table 1. An empirical correction for absorption

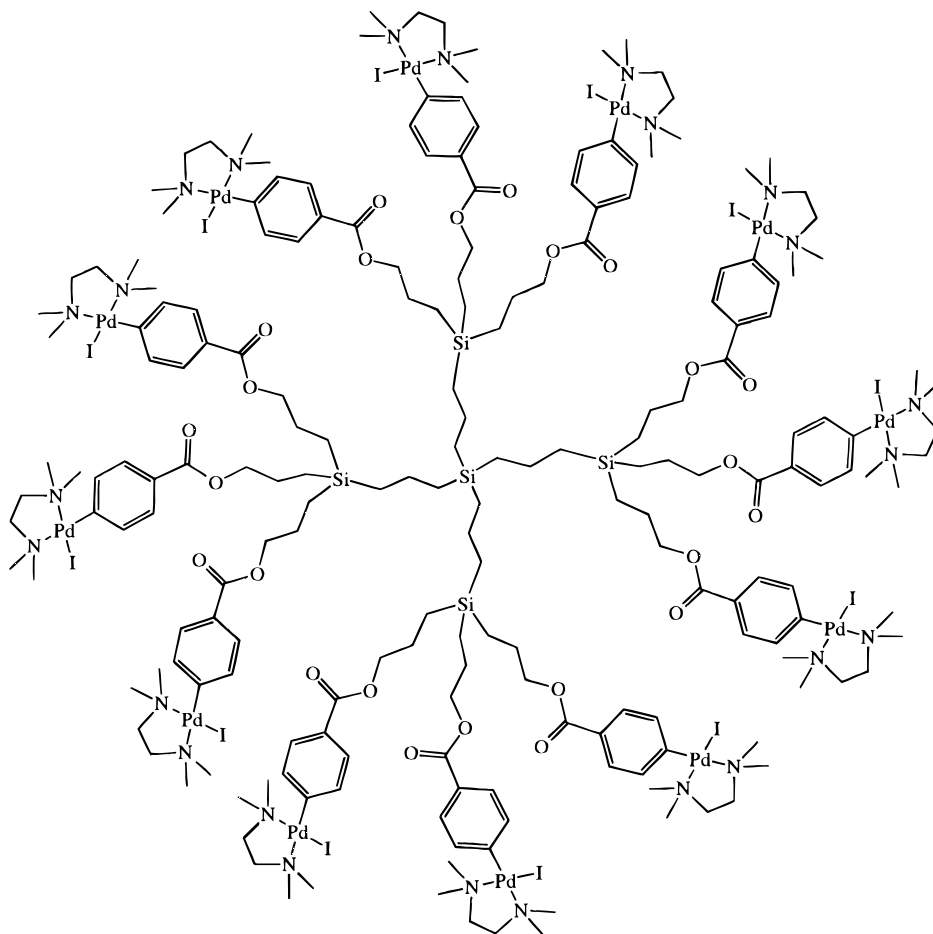


Figure 2. G_1 -ArPdI(tmeda) (7).

was done with the DIFABS technique^{32b} as implemented in PLATON^{32c} (correction range 0.614–1.374). The structure was solved with automated Patterson techniques using DIRDIF^{32d} and refined on F^2 by full matrix least-squares (SHELXL-96).^{32e} 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 the International Tables for Crystallography.^{32f} Geometrical calculations and the ORTEP illustration were done with PLATON.^{32c}

Results and Discussion

Synthesis and Characterization of G_0 -ArI and G_1 -ArI. Initial attempts to generate G_0 and G_1 with peripheral iodoarene groups focused on the generation of the imidazolidine-activated derivative of 4-iodobenzoic acid, followed by esterification with the polyol starting material, and the synthesis of G_0 -ArI was successfully achieved in good yield using this method (Scheme 1).

Other products of this reaction (CO_2 , imidazole) and excess carboxylic acid were easily removed by washing with acetone, in which the dendrimeric ester is insoluble. This method was also used to synthesize G_1 -

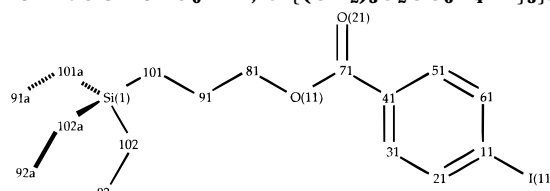
Table 2. Selected Bond Distances (Å) and Angles (deg) and Other Data for G_0 -ArI, $\text{Si}\{(\text{CH}_2)_3\text{O}_2\text{CC}_6\text{H}_4\text{-I}\}_3$ (4)

	Bond Distances				
	$n = 1$	$n = 2$	$n = 1$	$n = 2$	
Si(1)–C(10 n)	1.868(4)	1.869(5)	C(4 n)–C(7 n)	1.475(6)	1.495(7)
C(1 n)–I(1 n)	2.095(5)	2.097(5)	C(5 n)–C(6 n)	1.382(6)	1.387(7)
C(1 n)–C(2 n)	1.388(6)	1.378(8)	C(7 n)–O(1 n)	1.336(5)	1.332(6)
C(1 n)–C(6 n)	1.379(6)	1.380(6)	C(7 n)–O(2 n)	1.210(5)	1.207(5)
C(2 n)–C(3 n)	1.380(7)	1.393(7)	C(8 n)–C(9 n)	1.505(5)	1.506(7)
C(3 n)–C(4 n)	1.391(5)	1.377(6)	C(8 n)–O(1 n)	1.448(5)	1.448(6)
C(4 n)–C(5 n)	1.389(5)	1.387(7)	C(9 n)–C(10 n)	1.527(7)	1.531(5)
Bond Angles at Silicon					
C(101)–Si(1)–C(102)	109.0(2)	C(101a)–Si(1)–C(102)	107.6(2)		
C(101)–Si(1)–C(101a)	112.7(2)	C(102)–Si(1)–C(102a)	111.1(2)		
C(101)–Si(1)–C(102a)	107.6(2)	C(101a)–Si(1)–C(102a)	109.0(2)		
Other Bond Angles					
	$n = 1$	$n = 2$			
Si(1)–C(10 n)–C(9 n)	116.5(2)	115.4(4)			
C(9 n)–C(8 n)–O(1 n)	107.5(3)	107.3(3)			
C(7 n)–O(1 n)–C(8 n)	116.2(3)	116.0(3)			
O(1 n)–C(7 n)–O(2 n)	122.4(4)	123.3(5)			
C(4 n)–C(7 n)–O(1 n)	112.8(3)	112.2(4)			
C(4 n)–C(7 n)–O(2 n)	124.8(4)	124.5(5)			

^a Deviations from the aryl mean plane ($\chi^2 = 5.4(1)$, 35.6(2)): C(1 n) 0.003(5), 0.017(4); C(2 n) 0.000(5), –0.009(4); C(3 n) –0.004(5), –0.007(4); C(4 n) –0.001(5), 0.014(3); C(5 n) 0.003(5), –0.006(4); C(6 n) –0.008(5), –0.010(4); C(7 n) 0.004(5), 0.076(4); I(1 n) 0.033(1), 0.160(1) Å.

ArI. However, as well as the desired product, a byproduct which is probably a carbonate-bridged "didendrimer" species, on the basis of its GPC(SEC) trace (which shows

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Table 3. Torsion Angles (deg) and Other Data Describing the Configuration at Silicon and the Conformation of G_0 -ArI, $Si\{(CH_2)_3O_2CC_6H_4I-4\}_3$ (4**)^a**

Torsion Angles at Silicon				
C(102)–Si(1)–C(101)–C(91)	–64.9(4)	C(101a)–Si(1)–C(101)–C(91)	54.4(4)	
C(102a)–Si(1)–C(101)–C(91)	174.6(3)	C(101)–Si(1)–C(102)–C(92)	179.0(3)	
C(101a)–Si(1)–C(102)–C(92)	56.5(3)	C(102a)–Si(1)–C(102)–C(92)	–62.7(3)	
C(81)–C(91)–C(101)–Si(1)	178.5(3)	C(82)–C(92)–C(102)–Si(1)	175.0(3)	
Other Torsion Angles				
	<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 1	<i>n</i> = 2
C(10 <i>n</i>)–C(9 <i>n</i>)–C(8 <i>n</i>)–O(1 <i>n</i>)	174.8(4)	61.0(4)	C(3 <i>n</i>)–C(4 <i>n</i>)–C(7 <i>n</i>)–O(1 <i>n</i>)	7.2(7)
C(9 <i>n</i>)–C(8 <i>n</i>)–O(1 <i>n</i>)–C(7 <i>n</i>)	–167.7(4)	–163.7(3)	C(3 <i>n</i>)–C(4 <i>n</i>)–C(7 <i>n</i>)–O(2 <i>n</i>)	–173.3(5)
C(8 <i>n</i>)–O(1 <i>n</i>)–C(7 <i>n</i>)–C(4 <i>n</i>)	176.3(4)	172.5(3)	C(5 <i>n</i>)–C(4 <i>n</i>)–C(7 <i>n</i>)–O(1 <i>n</i>)	–173.1(4)
C(8 <i>n</i>)–O(1 <i>n</i>)–C(7 <i>n</i>)–O(2 <i>n</i>)	–3.2(6)	–6.2(5)	C(5 <i>n</i>)–C(4 <i>n</i>)–C(7 <i>n</i>)–O(2 <i>n</i>)	6.4(7)

^a The aryl ring mean planes form angles of 7.0(6)° and 6.3(4)° with the “C(7*n*)O(1*n*)O(2*n*)” mean planes, respectively.

a rather broad molecular weight distribution with a tail into the higher molecular weight region), was also formed, as a result of incomplete consumption of carbonyldiimidazole (CDI) during the preparation of the acid imidazolid. Remaining CDI imidazolid leads inevitably to the formation of carbonate bridges between dendrimers bearing OH groups because in this respect it reacts as a phosgene equivalent.³³ This prompted the use of 4-iodobenzoyl chloride as the activated acid derivative, and under the conditions used, a moderate-yield, high-purity synthesis of G_1 -ArI was achieved (Scheme 2).

G_0 -ArI and G_1 -ArI were characterized by NMR (¹H, ¹³C) spectroscopy, exhibiting resonances with integration as expected: an AB pattern (aryl), 24 (G_0) or 72 (G_1) “outer” methylene protons as three well-resolved resonances. The GPC(SEC) trace of G_1 -ArI shows a narrow molecular weight distribution, with $M_w/M_n = 1.02$. Differential scanning calorimetry (DSC) studies of G_1 -ArI show that it does not tend to crystallize with cooling, nor does it show any interesting phase behavior. However, its glass transition temperature, T_g , increased markedly to 17 °C, compared with the polyol precursor ($T_g = -40$ °C).⁹ It is the inner, flexible segments of the dendrimeric molecules which largely contribute to T_g ,³⁴ and it is likely that the terminal iodoarene groups exert a substantially increased ordering effect on these inner segments compared to terminal hydroxyl groups. G_0 -ArI and G_1 -ArI were characterized by elemental analysis, and G_0 -ArI was further characterized by X-ray crystallography (Figure 1, *vide infra*).

Reactions of G_0 -ArI and G_1 -ArI with Pd(dba)₂: Synthesis and Characterization of Complexes. The oxidative addition of substituted iodoarenes to Pd(0) precursors is well understood³⁰ and is shown here to be applicable to the high-yield and high-purity synthesis of dendrimeric materials (Scheme 3).

It is possible that this reaction system may present difficulties with increasing generation number, due to

decreasing solubility of partially palladated high molecular mass dendrimer molecules. ¹H NMR spectra of the complexes show the expected AB pattern for the phenyl ring protons, two signals for the NMe₂ groups, and three well-resolved signals for “outer” methylene groups (G_0 and G_1). The most characteristic feature of the ¹³C NMR spectra is the lack of a signal at approximately 100 ppm, arising from C–I in G_0 - and G_1 -ArI, indicating, in conjunction with the “clean” AB pattern in the ¹H NMR spectra, complete palladation. G_1 -ArPdI(tmeda) (Figure 2) displayed poor solubility in CDCl₃, precipitating as an oil during spectroscopic measurements; thus the spectra of this complex were recorded in CD₂Cl₂. Elemental analyses of palladated G_0 and G_1 are in excellent agreement with calculated values, although for complexes of high molecular weight, very close agreement between calculated and observed values is expected even in the presence of minor amounts of impurities. Despite the crystalline nature of G_0 -ArI, repeated attempts to grow crystals of G_0 -ArPdI(tmeda) suitable for X-ray crystallography have failed; the material generally precipitates from solution as an oil.

Reactions of Model Palladium Complexes: Attempts at Transmetalation. Model complexes **2** and **3** were synthesized in order to attempt the development of transmetalation procedures suitable for the palladated dendrimers. Methylation of PdIAr(tmeda) complexes with LiMe is generally straightforward, although it is not successful for aryl groups containing electron-withdrawing groups (NO₂, acetyl) at the 4-position.^{30c} In this study also, LiMe was an unsuitable reagent for the transmetalation of the model complexes, and studies of methylation have been extended to include SnMe₄ and Sn(C~N)Me₃ [C~N] = (8-(dimethylamino)-1-naphthyl).³¹ The latter tetraorganotin complex contains an intramolecularly coordinated C~N moiety, and in the triphenyl analogue, X-ray crystallographic studies have shown that the axial Sn–C bond *trans* to the nitrogen donor atom is significantly longer than the equatorial Sn–C bonds. Thus, this reagent is expected to have potential as a methylating reagent, via transfer of the axial methyl group, and in preliminary studies, this

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complex has been shown to transmetallate dihalide complexes of palladium and platinum and to undergo very rapid redistribution reactions with triorganotin halides.³¹ The tmeda complex was reacted with all three reagents, although not at reflux temperatures, since diorgano(tmeda)palladium(II) complexes containing substituted aryl groups are thermally unstable.³⁵ None of the transmetalation reactions were successful.

The complex of bpy (**3**) was reacted with SnMe₄ and Sn(C~N)Me₃ at room temperature and reflux in tetrahydrofuran, but not at all with LiMe, since previous attempts to transmetallate monoorganopalladium(II) halide complexes of bpy have not been successful. The inability to generate a diorganopalladium(II) complex using the model complexes precluded attempts at the functionalization of the ester-containing dendrimer, and model complexes, reported herein.

X-ray Crystallography. Molecules of compound **4** in the solid state have a crystallographic 2-fold axis through the silicon atom (Figure 1) with tetrahedral geometry at silicon [107.6(2)–112.7(2)°, Si–C = 1.868(4), 1.869(5) Å] (Table 2). The two crystallographically independent arms “(CH₂)₃O₂CC₆H₄I-4” have similar conformations except near the silicon atom (Table 3), exhibiting corresponding torsion angles within 4° except for C(10*n*)–C(9*n*)–C(8*n*)–O(1*n*) [174.8(4) and 61.0(4)°]. The crystal structure shows no special packing features, and there are no solvent accessible voids. The shortest intermolecular I···I interaction is 4.1440(6) Å.

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Concluding Remarks

The results reported here indicate that dendrimeric polyols are useful precursors for the synthesis of iodoarene-functionalized dendrimers. Oxidative addition reactions of Pd(dba)₂/tmeda with model reagents proceed in high yield, and this reaction chemistry also allows the synthesis of the fully palladated dendrimer **7** (Figure 2) in 81% yield. Dendrimer **7** is air stable at ambient temperature in CH₂Cl₂ solution and in the solid state. The crystal structure of G₀-ArI (Figure 1) provides a model for the structure of the core and chain geometry for iodoarene-functionalized carbosilane dendrimers. The chain conformations in the solid state for this molecule are probably dictated by packing requirements.

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Supporting Information Available: Listings of atom coordinates, thermal parameters, hydrogen atom parameters, and ligand geometry for the complexes (15 pages). Ordering information is given on any current masthead page.

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