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Synthesis and Structure of the First Oxygen-Donor-Stabilized Organogermanium(II) Compounds†

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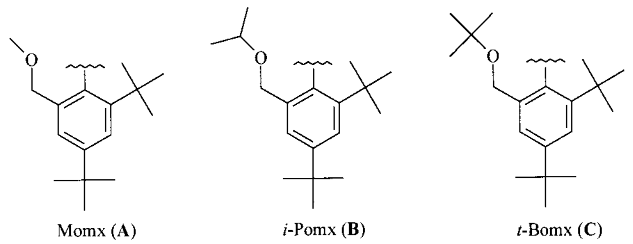
GeCl$_2$·dioxane reacts with 1 and 2 equiv of [2,4-di-*tert*-butyl-6-(*tert*-butoxymethyl)phenyl]lithium (*t*-BomxLi) to give the germanium(II) compounds *t*-BomxGeCl (1) and [*t*-Bomx]$_2$Ge (**2**), respectively. Reaction with 2 equiv of [2,4-di-*tert*-butyl-6-(*iso*-propoxymethyl)phenyl]lithium (*i*-PomxLi) affords [*i*-Pomx]$_2$Ge (**3**). Compounds **1**−**3** show intramolecular coordination of the alkoxy ligand to the germanium(II) center. The use of the 2,4-di-*tert*-butyl-6-(methoxymethyl)phenyl ligand (Momx) does not lead to the expected base-stabilized germanium(II) species Momx$_2$Ge but gives the germanium(IV) compound MomxGe[OCH$_2$-(2,4-di-*tert*-butylphenyl)](Me) (**4**) as the result of an intramolecular O−CH$_3$ bond oxidative addition process; X-ray crystal structure determinations are presented for **1**, **2**, and **4**.

The organometallic chemistry of donor-stabilized germanium(II) compounds has developed into an active area of research.[1] Whereas compounds with substituents bearing nitrogen[2] or phosphorus[3] donors are well established, systems stabilized with oxygen donors are unknown thus far. As demonstrated in the chemistry of donor-stabilized silicenium ions (R$_3$Si$^+$), variation of the donor element results in astonishing changes in structure, bonding, and reactivity;[4] comparable phenomena can be expected also in the chemistry of germanium(II) compounds. Here we report the synthesis and characterization of three oxygen-donor-stabilized germanium(II) species. Furthermore, we describe the formation of a germanium(IV) compound, which results from intramolecular oxidative addition to the corresponding germanium(II) center as a consequence of reduction of steric bulk and of the +I-effect of the alkyl group at the oxygen side-chain functionalized substituent.

Chart 1



We have used as substituents the 2,4-di-*tert*-butyl-6-(methoxymethyl)phenyl group (Momx = methoxymethyl-*m*-xylyl group) (**A**), published by Yoshifuji in 1993,[5] as well as the systems *i*-Pomx (*i*-propoxymethyl-*m*-xylyl group) (**B**) and *t*-Bomx (*t*-butoxymethyl-*m*-xylyl group) (**C**), which have been developed in our group (Chart 1). In **B** and **C** the abbreviations explained above are used in analogy to that of **A**, introduced by Yoshifuji. The "x" refers to the substitution pattern of *m*-xylene although *tert*-butyl groups are used instead of methyl substituents of the *m*-xylyl group.[5]

Reaction of GeCl$_2$·dioxane with *t*-BomxLi in THF in 1:1 ratio at −80 °C afforded [*t*-Bomx]GeCl (**1**) in 45% yield. Treatment with 2 equiv of *t*-BomxLi led to the formation of the homoleptic germanium(II) species [*t*-Bomx]$_2$Ge (**2**) (Scheme 1). Crystals of **1** and **2** suitable for X-ray structure analysis were obtained from *n*-hexane solution. The molecular structures are shown in Figures 1 and 2. Crystallographic data are given in Table 1; selected bond lengths and angles are presented in Tables 2 and 3.

In **1** the side-chain functionalized substituent coordinates in a bidentate fashion, leading to a remarkable

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† Dedicated to Professor Herbert Schumann on the occasion of his 65th birthday.

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10.1021/om000679f CCC: $20.00

Table 1. Crystallographic Data for 1, 2, and 4

empirical formula	$C_{19}H_{31}ClGeO$, **1**	$C_{38}H_{62}GeO_2$, **2**	$C_{32}H_{50}GeO_2$, **4**
fw	383.48	623.47	539.31
cryst. color, habit	colorless, rhombic	yellow, irregular	colorless, irregular
cryst. size, mm^3	0.6 × 0.6 × 0.3	0.7 × 0.5 × 0.3	0.7 × 0.4 × 0.2
temp, K	173(2)	173(2)	173(2)
radiation (λ, Å)	Mo Kα (0.71073 Å), graphite monochromator		
space group	*P*21/c	*P*21/*n*	P-1
unit cell dimensions, Å	$a = 11.441(4)$	$a = 12.324(5)$	$a = 10.559(4)$
	$b = 12.158(3)$	$b = 19.887(9)$	$b = 11.866(4)$
	$c = 14.579(6)$	$c = 14.962(7)$	$c = 13.140(3)$
unit cell angles, deg	$\alpha = 90$	$\alpha = 90$	$\alpha = 75$
	$\beta = 96.57(3)$	$\beta = 92.28(3)$	$\beta = 77.72(2)$
	$\gamma = 90$	$\gamma = 90$	$\gamma = 74.45(3)$
V, Å^3	2014.6(12)	3664(3)	1513.8(8)
Z	4	4	2
density (calcd), Mg/m^3	1.264	1.130	1.183
θ range, data collection	2.19–30.00	2.02–30.03	2.17–28.50
reflns collected	6135	11132	8064
independent reflns (R_{int})	5869 (0.0418)	10 689 (0.0746)	7659 (0.0385)
absorption correction from ψ-scans	semiempirical	semiempirical	empirical
final R_F [$I > 2\sigma(I)$]	0.0515	0.0732	0.0562
final $R_F{}^2$ [$I > 2\sigma(I)$]	0.1047	0.1214	0.1234
no. of reflns used	4232	5718	5782
parameters	218	338	328
largest diff. peak/hole, e Å^3	0.630/0.532	0.495/0.612	0.726/0.508
diffractometer used	Siemens P2(1)	Siemens P2(1)	Siemens P2(1)
programs used	Siemens SHELXTL plus SHELXL-97		
structure refinement	full-matrix least squares on F^2		

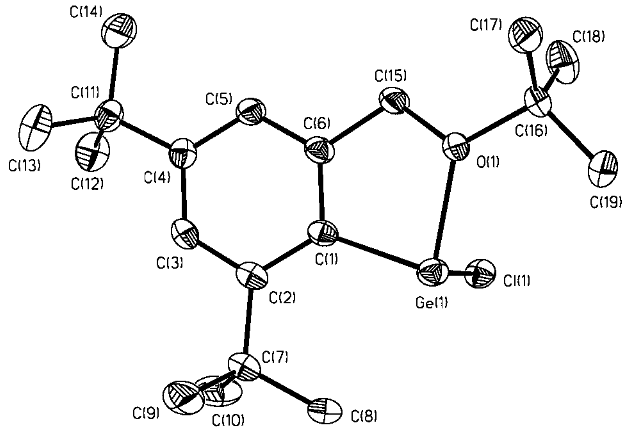


Figure 1. Molecular structure of **1** (50% probability).

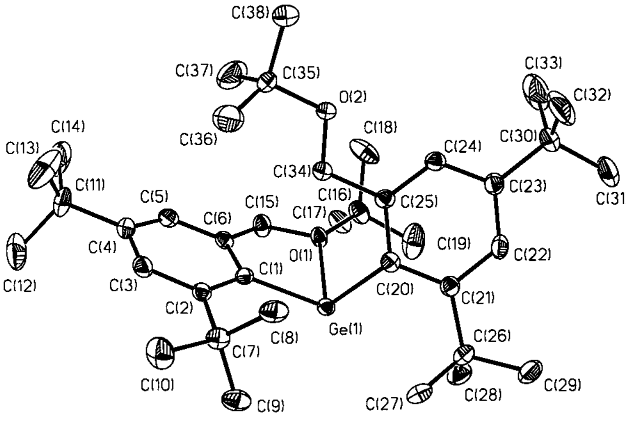
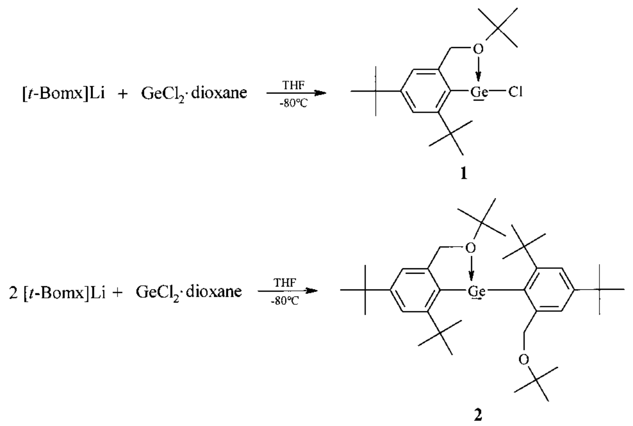


Figure 2. Molecular structure of **2** (50% probability).

Scheme 1



geometry at the germanium center. The angle α (C_1–Ge–O) is 82.04°, the angle β (C_1–Ge–Cl) is 96°, and the angle γ (O–Ge–Cl) is nearly rectangular (~91°). The O→Ge donor bond is unexpectedly short [2.073(2) Å], much shorter than the Ge–O bond lengths in $GeCl_2$·dioxane (2.48 and 2.41 Å);[6] the observed distance approaches that in covalent O–Ge(II) bonds as present in [(t-Bu)$_3$CO]$_2$Ge [1.896(16) and 1.832(11) Å][7] and in Ge[O(2,6-(t-Bu)$_2$-4-Me-(C_6H_2))]$_2$ [1.802(8) and 1.812(7) Å].[8] Similar Ge–O bond lengths (1.99 and 1.84 Å) are present in the binuclear germanium calix[4]arene [*t*-Bu

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

Ge(1)–O(1)	2.073(2)
Ge(1)–Cl(1)	2.3331(11)
Ge(1)–C(1)	2.009(3)
C(1)–Ge(1)–O(1)	82.04(9)
C(1)–Ge(1)–Cl(1)	96.29(8)
O(1)–Ge(1)–Cl(1)	91.24(7)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2

Ge(1)–O(1)	2.189(3)
Ge(1)–C(1)	2.041(4)
Ge(1)–C(20)	2.058(4)
C(1)–Ge(1)–O(1)	80.32(12)
C(1)–Ge(1)–C(20)	109.13(14)
O(1)–Ge(1)–C(20)	91.52(12)

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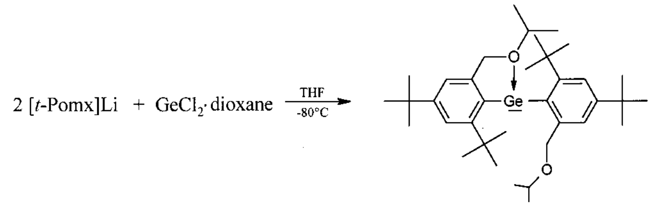
Scheme 2



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calix]Ge$_2$.[9] The Ge−Cl bond length is 2.3331(11) Å, comparable to that in the related amino-functionalized germanium(II) species [2,4-(*t*-Bu)$_2$-6-(CH$_2$NMe$_2$)-(C$_6$H$_2$)]-GeCl (MamxGeCl) [2.3283(4) Å] described in a previous work.[2f] In **2** the structural features of the [*t*-Bomx]Ge frame are quite similar to those found for **1**; the geometry at the germanium center and the Ge−C and Ge←O bond lengths are comparable. As shown in Figure 2, only one of the two ether groups coordinates to the germanium center. VT-NMR spectra show that the side chains exchange their positions in solution. This dynamic process is fast on the NMR time scale at 80 °C but slow at −40 °C. The Gibbs free energy of activation ($\Delta G^{\#}$) as estimated from the coalescence of the diastereotopic CH$_2$ groups is ~47 kJ/mol at 233 K.

On reducing the steric bulk and the +I-effect of the alkyl group on the oxygen center by the use of *i*-Pomx (**B**) instead of *t*-Bomx (**C**), the corresponding monochlorogermanium(II) compound is too unstable to permit its characterization; only unidentifiable products were obtained. However, the stable homoleptic species [*i*-Pomx]$_2$Ge (**3**) was formed by reaction of GeCl$_2$·dioxane with *i*-PomxLi in THF at −80 °C in 1:2 ratio (Scheme 2). The solution NMR data of **3** are comparable to those collected for **2**. Dynamic behavior is observed at room temperature but can be frozen out at −80 °C. The Gibbs free energy of activation ($\Delta G^{\#}$) for the dynamic process as estimated from the coalescence of the (CH$_3$)$_2$C*H* groups is ~43 kJ/mol at 223 K.

Upon utilization of the Momx group (**A**), which is less bulky than **B** or **C** and which possesses a smaller +I-effect, neither a heteroleptic nor a homoleptic germanium(II) compound could be isolated. GeCl$_2$·dioxane reacted with MomxLi in 1:2 ratio at −80 °C to give the germanium(IV) compound MomxGe[OCH$_2$-(2,4-di-*tert*-butylphenyl)](Me) (**4**) (Scheme 3). **4** is the product of an intramolecular O−CH$_3$ oxidative addition at the germanium center of the assumed intermediate germanium(II) compounds MomxGeCl or Momx$_2$Ge, which could not be obtained even at low (−80 °C) temperature.

The solid-state structure of **4** was determined by X-ray diffraction studies. Crystallographic data are given in Table 1; selected bond lengths and angles are collected in Table 4. The molecular structure depicted in Figure 3 shows a distorted tetrahedral geometry at the germanium center. The angle α (C_1–Ge−O = 91.3°) is reduced as a consequence of the ring strain. Due to this fact and due to the steric requirements of the second alkoxy ligand, the angles β (C_1–Ge−C_{17}) and γ (C_{17}–Ge−C_{16}) are enlarged ($\beta = 119.74°$, $\gamma = 128.05°$); the angles δ (O−Ge−C_{17}) and ϵ (O−Ge−C_{16}) are ~103°.

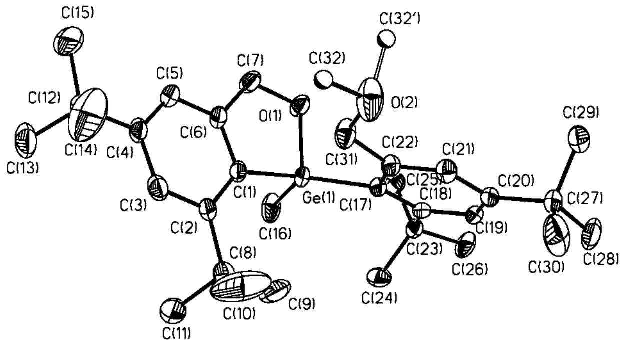
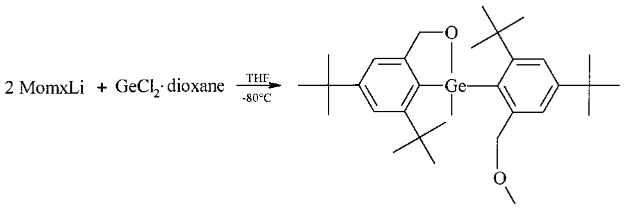


Figure 3. Molecular structure of **4** (50% probability).

Scheme 3



4

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 4

Ge(1)−O(1)	1.805(2)
Ge(1)−C(16)	1.959(3)
Ge(1)−C(1)	1.960(3
Ge(1)−C(17)	1.991(3)
C(1)−Ge(1)−O(1)	91.31(11)
O(1)−Ge(1)−C(16)	103.93(15)
C(16)−Ge(1)−C(1)	103.40(14)
O(1)−Ge(1)−C(17)	102.63(11)
C(16)−Ge(1)−C(17)	128.05(14)
C(1)−Ge(1)−C(17)	119.74(12)

In summary, we have prepared three novel oxygen-donor-stabilized germanium(II) species (**1**−**3**) belonging to a so far unknown class of compounds, by making use of various 2,4-di-*tert*-butyl-6-(alkoxymethyl)phenyl substituents. Additionally, we have demonstrated that some steric bulk and a pronounced +I-effect of the alkyl group at the oxygen center are necessary for the stabilization of such germanium(II) compounds.

Comparing the results of the chemistry of alkoxymethyl side-chain functionalized germanium(II) species with those for related aminomethyl side-chain functionalized compounds of the type MamxGeR (Mamx = methylaminomethyl-*m*-xylyl derivative),[2f,h] similarities as well as differences are observed. Common to all compounds is a very strong D→Ge donor−acceptor interaction, leading to an ammonium or oxonium character at the donor atom. The average D→Ge bond lengths (2.09−2.19 Å for N→Ge systems and 2.073−2.189 Å for the O→Ge systems) are more in the range of covalent than in the range of coordinative bonds; the latter are typical of other base-stabilized germanium(II) compounds.[1,2]

The consequences of the strong D→Ge bond are quite different. In the case of the Momx substituent, the pronounced oxonium character in an intermediate coordination compound (MomxGeCl or [Momx]$_2$Ge) leads via methyl-group transfer to the final oxidation product **4**. In contrast, alkyl-group transfer is not observed in compounds with the Mamx or with the *i*-Pomx or *t*-Bomx substituent.

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Investigations concerning the chemistry of **1**−**3** in comparison to related aminomethyl-functionalized species are in progress.

Experimental Section

General Data. All manipulations were carried out under a purified argon atmosphere by standard vacuum techniques. The solvents were commercially available and were purified by conventional means and distilled immediately prior to use. KO*t*-Bu and *n*-BuLi (1.6 M solution in *n*-hexane) were commercially available. Momx, 2-Bromo-3,5-di-*tert*-butylbenzylbromide, and NaO*i*-Pr were prepared according to the literature. Elemental analyses were performed by the Microanalytical Laboratory of the Univeristät Bielefeld. The NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer (^{1}H 500.1 MHz; ^{13}C{^{1}H}125.8 MHz). Chemical shifts are reported in parts per million (ppm) and are referenced to the solvent as an internal standard. Mass spectrometry was performed on a VG Autospec spectrometer. Only characteristic fragments and isotopes of the highest abundance are listed.

General Procedure for the Preparation of 2,4-Di-*tert*-butyl-6-(*iso*-propoxymethyl)phenyl Bromide and 2,4-Di-*tert*-butyl-6-(*tert*-butoxymethyl)phenyl Bromide. A solution of 19.29 g (53.3 mmol) of 2-bromo-3,5-di-*tert*-butylbenzyl bromide in 80 mL of THF was added dropwise to a suspension of 160.00 mmol of the alkoxide (2 = NaO*i*-Pr, 3 = KO*t*-Bu) in 40 mL of THF at 0 °C. The reaction mixture was allowed to warm to room temperature and then stirred for another 12 h. The resulting suspension was hydrolyzed with 350 mL of water and extracted with diethyl ether (1 × 200 mL; 2 × 150 mL). The combined organic layers were dried over Na_2SO_4. After removal of the solvent, the residue was distilled in vacuo to give 2,4-di-*tert*-butyl-6-(*iso*-propoxymethyl)phenyl bromide or 2,4-di-*tert*-butyl-6-(*tert*-butoxymethyl)phenyl bromide.

2,4-Di-*tert*-butyl-6-(*iso*-propoxymethyl)phenyl Bromide. Bp 90 °C, 0.01 mbar. Yield 14.74 g (43.17 mmol, 81%). ^{1}H NMR (C_6D_6): δ 1.12 (d, 6H, CH(CH_3)$_2$, ^3J = 6 Hz), 1.27, 1.57 (2s, 9H, *t*-Bu), 3.48 (septet, 1H, C*H*(CH$_3$)$_2$, ^3J = 6 Hz), 4.64 (s, 2H, -CH$_2$-), 7.51, 7.73 (2d, 1H, aryl, ^4J = 2 Hz). ^{13}C NMR (C_6D_6): δ 22.3 (CH(*C*H$_3$)$_2$), 30.3, 31.4 (C(*C*H$_3$)$_3$), 34.9, 37.4 (*C*(CH$_3$)$_3$), 71.4 (-*C*H$_2$-), 71.8 (*C*H(CH$_3$)$_2$), 120.3 (quaternary aryl C), 124.0, 142.1 (tertiary aryl C), 140.6, 147.1, 149.6 (quaternary aryl C). MS [CI; *m*/*z* (I_{rel})] 360 (59, M + NH$_4^+$), 298 [100, M$^+$ + H − (*i*-Pr)], 283 [42, M$^+$-(*t*-Bu)]. Anal. Calcd for $C_{18}H_{29}OBr$ (M_r = 341.34): C, 63.33; H, 8.56. Found: C, 62.90; H, 8.43.

2,4-Di-*tert*-butyl-6-(*tert*-butoxymethyl)phenyl Bromide. Bp 95 °C, 0.01 mbar. Yield 14.96 g (42.11 mmol, 79%). ^{1}H NMR (C_6D_6): δ 1.17, 1.29, 1.58 (3s, 9H, *t*-Bu), 4.66 (s, 2H, -CH$_2$-), 7.51, 7.83 (2d, 1H, aryl, ^4J = 2 Hz). ^{13}C NMR (C_6D_6): δ 27.7, 30.3, 31.4 (C(*C*H$_3$)$_3$), 34.9, 37.5, 73.4 (*C*(CH$_3$)$_3$), 65.4 (-*C*H$_2$-), 120.3 (quaternary aryl C), 123.9, 124.3 (tertiary aryl C), 141.1, 147.1, 149.6 (quaternary aryl C). MS [CI; *m*/*z* (I_{rel})]: 372 (15, M + NH$_4^+$), 356 (14, M$^+$), 298 [100, M$^+$ + H − (*t*-Bu)], 219 [54, M$^+$ + H − (*t*-Bu) − Br]. Anal. Calcd for $C_{19}H_{31}OBr$ (M_r = 355.36): C, 64.21; H, 8.79. Found: C, 64.26, H, 8.93.

Preparation of [2,4-di-*tert*-butyl-6-(*tert*-butoxymethyl)phenyl]germanium(II) Chloride (1). During 3 min, 2.3 mL (3.69 mmol) of a 1.6 M solution of *n*-BuLi in *n*-hexane was added to a stirred solution of 2,4-di-*tert*-butyl-6-(*tert*-butoxymethyl)phenyl bromide (1.31 g, 3.69 mmol) in 15 mL of THF at −80 °C. The reaction mixture was stirred at that temperature for 2 h and then slowly added to a cooled solution (−80 °C) of 0.85 g (3.69 mmol) of GeCl$_2$·dioxane in 20 mL of THF. The yellow solution was warmed to room temperature during 1 h. The solvent was removed in vacuo, and the residue was extracted with *n*-hexane. Cooling the solution to −30 °C after filtration and concentration yielded 0.64 g (1.66 mmol, 45%) of **1** as colorless crystals. ^{1}H NMR (C_6D_6): δ 1.18, 1.33, 1.51 (3s, 9H, C(C*H*$_3$)$_3$), 4.41, 5.11 (2d, 1H, -C*H*$_2$-, ^2J = 11 Hz), 6.97, 7.47 (s, 2H, aryl). ^{13}C NMR (C_6D_6): δ 28.2, 31.5, 33.8 (C(*C*H$_3$)$_3$), 34.9, 38.1 (*C*(CH$_3$)$_3$), 71.6 (-*C*H$_2$-), 85.3 (O*C*(CH$_3$)$_3$), 116.8, 121.7, 143.0, 150.6, 154.5, 155.9 (aryl C). MS [CI; *m*/*z* (I_{rel})]: 383 (7, M$^+$ − H), 347 (2, [*t*-BomxGe]$^+$ − 2H), 203 [100, [*t*-Bomx]$^+$ − (O*t*-Bu)]. Anal. Calcd for $C_{19}H_{31}OGeCl$ (M_r = 383.55): C, 59.49; H, 8.14. Found: C, 59.12, H, 8.46.

Preparation of Bis[2,4-di-*tert*-butyl-6-(*tert*-butoxymethyl)phenyl]germanium(II) (2). To a stirred solution of 1.15 g (3.24 mmol) of 2,4-di-*tert*-butyl-6-(*tert*-butoxymethyl)phenyl bromide in 10 mL of THF was added 2.02 mL of *n*-BuLi (1.6 M in hexane) at −80 °C. After stirring for 2 h, a solution of 0.37 g (1.62 mmol) of GeCl$_2$·dioxane in 5 mL of THF was added at that temperature. The reaction mixture was allowed to warm to room temperature within 1.5 h, and the solvent was removed in vacuo. The residue was extracted with *n*-hexane. Cooling the extracts to −30 °C afforded **2** as yellow crystals (0.62 g, 1.00 mmol, 62%). ^{1}H NMR (C_6D_6): δ 0.95, 1.39 (2s, 18H, C(C*H*$_3$)$_3$), 1.71 (br s, 18H, OC(C*H*$_3$)$_3$), 4.50, 4.57 (2d, 2H, -C*H*$_2$-, ^2J = 12 Hz), 7.35−7.55 (only integral, 2H, aryl), 7.58 (s, 2H, aryl). ^{13}C NMR (C_6D_6): δ 27.6, 31.6, 33.8 (C(*C*H$_3$)$_3$), 34.8, 38.3 (*C*(CH$_3$)$_3$), 68.0 (-*C*H$_2$-), 77.7 (O*C*(CH$_3$)$_3$), 119.1, 121.9, 142.9, 149.2, 155.3, 155.4 (aryl C). ^{1}H NMR (toluene-d_8, −80 °C): δ 0.83, 1.05, 1.38, 1.44, 1.48, 2.09 (6s, 9H, C(C*H*$_3$)$_3$), 4.38, 4.51 (2d, 1H, -CH$_2$- (noncoordinating), ^2J = 11 Hz), 4.43, 4.56 (2d, 1H, −CH$_2$- (coordinating), ^2J = 14 Hz), 7.02, 7.50,7.50, 8.11 (4s, 1H, aryl). ^{13}C NMR (toluene-d_8, −80 °C): δ 26.6, 27.7, 31.3, 35.0, 37.3, 39.0 (C(*C*H$_3$)$_3$), 24.2, 27.2, 31.0, 34.6, 65.9, 69.4 (*C*(CH$_3$)$_3$), 72.1, 82.2 (-*C*H$_2$-), 111.3, 117.6, 119.7, 121.0, 138.5, 146.5, 147.6, 149.4, 152.4, 154.3, 154.9, 157.5 (aryl C). MS [CI; *m*/*z* (I_{rel})]: 625 (1, M$^+$ + H), 569 [21, M$^+$ − HC(CH$_3$)$_3$], 511 [82, M$^+$ − 2C(CH$_3$)$_3$], 495 [13, M$^+$ − 2C(CH$_3$)$_3$-CH$_3$]. Anal. Calcd for $C_{38}H_{62}O_2Ge$ (M_r = 623.55): C, 73.19; H, 10.02. Found: C, 73.13, H, 10.06.

Preparation of Bis[2,4-di-*tert*-butyl-6-(*iso*-propoxymethyl)phenyl]germanium(II) (3). Within 5 min, 3.75 mL (6.0 mmol) of a 1.6 M solution of *n*-BuLi in *n*-hexane was added to a stirred solution of 2,4-di-*tert*-butyl-6-(*iso*-propoxymethyl)phenyl bromide (2.05 g, 6.00 mmol) in 20 mL of THF at −80 °C. The reaction mixture was stirred at that temperature for 2 h and then slowly added to a stirred solution of 0.69 g (3.00 mmol) of GeCl$_2$·dioxane in 20 mL of THF at −80 °C. The yellow solution was warmed to room temperature within 1.5 h. The solvent was removed in vacuo, and the residue was extracted with *n*-hexane. Cooling the extracts to −30 °C after filtration and concentration yielded 0.73 g (1.23 mmol, 41%) of **3** as a yellow solid. ^{1}H NMR (C_6D_6): δ 0.83, 0.88 (2d, 6H, CH(C*H*$_3$)$_2$, ^3J = 6 Hz), 1.38, 1.72 (2s, 18H, C(C*H*$_3$)$_3$), 3.48 (septet, 2H, C*H*(CH$_3$)$_2$, ^3J = 6 Hz), 4.48, 4.52 (2d, 1H, -C*H*$_2$-, ^2J = 12 Hz), 7.44 (br s, 2H, aryl), 7.60 (d, 2H, aryl, ^4J = 1 Hz). ^{13}C NMR (C_6D_6): δ 21.2 (CH(*C*H$_3$)$_2$), 31.6, 33.7 (C(*C*H$_3$)$_3$), 34.8, 38.3 (*C*(CH$_3$)$_3$), 71.3 (-*C*H$_2$-), 73.3 (*C*H(CH$_3$)$_2$), 119.2, 122.0 (tertiary aryl C), 142.6 149.4, 154.6, 155.9 (quaternary aryl C). ^{1}H NMR (−80 °C, toluene-d_8): δ 0.61, 0.79, 0.92, 1.12 (4m, 3H, CH-(C*H*$_3$)$_2$), 1.40, 1.42, 1.49, 2.19 (4s, 9H, C(C*H*$_3$)$_3$), 3.42, 3.58 (2m, 1H, C*H*(CH$_3$)$_2$), 4.15 (m, 2H, -C*H*$_2$-), 4.58, 4.81 (2d, 1H, -C*H*$_2$-, ^2J = 14 Hz), 6.94, 7.52, 7.84, 8.18 (4s, 1H, aryl). ^{13}C NMR (−80 °C, toluene-d_8): δ 19.3, 20.6, 20.7, 22.2 (CH(*C*H$_3$)$_2$), 31.4, 31.5, 31.7, 34.9 (C(*C*H$_3$)$_3$), 34.5, 35.0, 37.2, 40.0 (*C*(CH$_3$)$_3$), 70.0, 70.9 (*C*H(CH$_3$)$_2$), 70.3, 75.3 (-*C*H$_2$-), 117.2, 120.1, 121.5, 121.8 (tertiary aryl C), 137.6, 147.2, 147.8, 149.5, 151.0, 154.0, 156.2, 153.3 (quaternary aryl C). MS [CI; *m*/*z* (I_{rel})]: 613 (16, M$^+$ + NH$_3$), 597 (77, M$^+$ + H), 555 [46, M$^+$ − CH(CH$_3$)$_2$ + 2H], 335 (66, *i*-PomxGe$^+$ + H). Anal. Calcd for $C_{36}H_{58}O_2Ge$ (M_r = 595.50): C, 72.61; H, 9.81. Found: C, 72.45; H, 9.71.

Preparation of [2,4-di-*tert*-butyl-6-(methoxymethyl)phenyl](methyl)[2,4-di-*tert*-butylphenyl-6-oxymethyl)germanium(IV) (4). During 5 min 3.75 mL (6.0 mmol) of a 1.6 M solution of *n*-BuLi in *n*-hexane was added to a stirred solution of 2,4-di-*tert*-butyl-6-(methoxymethyl)phenyl bromide (1.88 g, 6.00 mmol) in 20 mL of THF at −80 °C. The reaction mixture was stirred at that temperature for 2 h and then slowly added to a solution of 0.69 g (3.00 mmol) $GeCl_2$•dioxane in 20 mL of THF at −80 °C. The yellow solution was warmed to room temperature within 1.5 h. The solvent was removed in vacuo, and the residue was extracted with *n*-hexane. Cooling the extracts to −30 °C after filtration and concentration yielded 0.87 g (1.62 mmol, 54%) of **4** as colorless crystals. ^{1}H NMR (C_6D_6): δ 1.22 (s, 3H, $GeCH_3$), 1.26, 1.27, 1.28, 1.55 (4s, 9H, $C(CH_3)_3$), 2.67 (s, 3H, OCH_3), 4.33, 4.51 (2d, 1H, -CH_2-, ^2J = 12 Hz), 5.44, 5.51 (2d, 1H, -CH_2-, ^2J = 14 Hz), 7.11, 7.50, 7.66, 7.72 (4s, 1H, aryl). ^{13}C NMR (C_6D_6): δ 15.1 ($GeCH_3$), 31.2, 31.5, 32.6, 33.9 ($C(CH_3)_3$), 34.8, 34.9, 36.8, 37.1 ($C(CH_3)_3$), 57.4 (OCH_3), 71.9, 74.6 (-CH_2-), 122.6, 123.0, 125.4, 133.3, 135.8, 146.4, 148.5, 151.9, 153.3, 155.4, 158.0 (aryl C). MS [CI; *m*/*z* (I_{rel})]: 541 (30, M^+ + H), 525 (37, $M^+ - CH_3$), 509 (33, M^+ + H − OCH_3), 307 (100, M^+ + H − Momx). Anal. Calcd for $C_{32}H_{50}O_2Ge$ (M_r = 539.39): C, 71.60; H, 9.34. Found: C, 71.31, H, 9.46.

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Supporting Information Available: Tables of crystal data, positional and thermal parameters, and selected bond lengths and angles (28 pages). Ordering information is given on any current masthead page.

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