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Synthesis and Characterization of New Lithiated Organogermanium Compounds

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New (8-methoxy-1-naphthyl)arylgermanes **1a**−**c** are synthesized. The crystal structure of **1b** (aryl = mesityl), determined by X-ray diffraction, shows that an intramolecular interaction occurs between the oxygen and germanium atoms, the Ge- - -O distance being 2.75 Å. The corresponding (diarylgermyl)lithiums R$_2$HGeLi are prepared in high yield by hydrogermolysis of *tert*-butyllithium in THF and are susprisingly stable. Their characterization by ^{1}H, ^{13}C, and ^{7}Li NMR spectroscopy is reported. Dimetalation of the initial arylgermanes depends upon steric hindrance around the germanium atom and the nature of the organolithium compound RLi. The reaction of **1a** or **1c** with *n*-BuLi followed by MeI affords the expected dialkylation product, whereas **1b** gives the unexpected iodide **5b** due to steric hindrance around the germanium atom.

Introduction

In our studies of organogermyllithium compounds R$_2$HGeLi[1a] we have described the first compounds of this type[1b] and we have shown that they can be stabilized by steric effects. More recently, the (triorganogermyl)lithiums (Me$_3$Si)$_3$GeLi·2THF[2a] and Mes$_3$GeLi·2THF,[2b] as well as a germacyclopentadienide anion,[3a] have been isolated, suggesting the possibility of stabilization by steric crowding or by an electronic effect. In this paper, we consider the possibility of stabilization of (organogermyl)lithiums by intramolecular complexation. To this end, we have used chelating substituents having methoxy groups such as 2-methoxyphenyl and 1,8-methoxynaphthyl, because methoxy groups are well-known to undergo intramolecular coordination in organolithium systems.

Results and Discussion

The starting diorganogermanes were prepared by an organomagnesium route or directly by the reaction of the corresponding organolithiums. Their reduction by LiAlH$_4$ gave the expected diorganogermanes **1** (eqs 1 and 2).

The new compounds are stable in air at room temperature, but certain ones such as **1a** should be stored in the dark. In chlorinated solvents, the corresponding chlorohydrogen derivatives, Ar$_2$GeHCl, are formed rapidly.

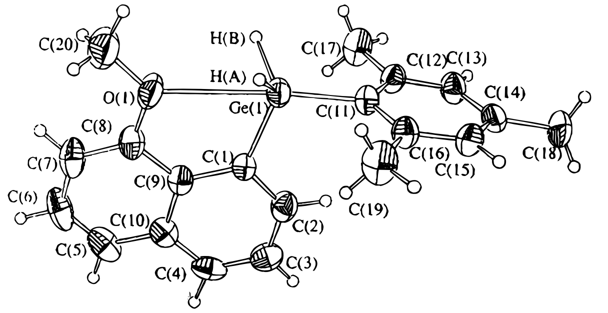
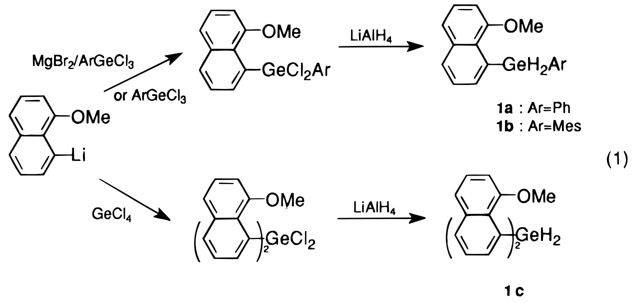


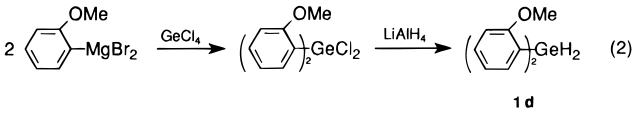
Figure 1. ORTEP drawing of **1b** with ellipsoids drawn at 50% probability.



1a : Ar=Ph
1b : Ar=Mes

1c

(1)



1d

(2)

The results of an X-ray crystal structure determination of compound **1b** are shown in Figure 1[4] Tables 1 and 2. Regarding crystal packing, there is no evidence of an intermolecular interaction between the methoxy oxygen atom of one molecule and the germanium atom of a neighboring molecule. A simple stacking of aromatic rings is observed. The Ge−O distance of 2.75 Å is longer than that of the Ge−O covalent bond (1.95 Å)[5] but appreciably less than the van der Waals radii sum (3.40 Å). This suggests a weak coordinative interaction between germanium and methoxy-oxygen atoms. Interestingly, a study of the structures of pentavalent germanium compounds[6] showed that Ge−O bond distances between 3.23 and 2.51 Å indicate weak interactions, whereas distances between 2.17 and 2.08 Å

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S0276-7333(96)00299-3 CCC: $12.00

Table 1. Crystallographic Data

chem formula	$C_{20}H_{22}GeO$
fw	350.98
cryst system	orthorhombic
space group	*Pbca*
Z	8
F(000)	1449.90
a (Å)	11.3208(13)
b (Å)	38.846(7)
c (Å)	8.1331(11)
V(Å^3)	3576.7(9)
d (g cm^{-3})	1.304
diffractometer	AFC6S
λ (Å) (graphite monochromator)	1.54056
data collcn (deg in 2θ)	4−120
hkl range	−12/12, −43/43, 0/9
cryst size (mm)	0.50 × 0.40 × 0.02
collcn temp (°C)	20
abs corr	ψ scans
μ (cm^{-1})	22.8
transm range	0.802−0.998
secondary extinctn	0.011(3)
R^a	0.059
$R_w{}^a$	0.056
S[a]	2.73
no. of reflcns measd	9745
no. of unique reflcns (R_{int})	2667
no. used in LS ($I > 3\sigma(I)$)	1801
no. of variables	228
no. of atoms	44
last ΔF map (e/Å^3)	−0.33 to 0.33

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $S = [\Sigma w(|F_o| - |F_c|)^2/(N - V)]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) in Compound 1b[a]

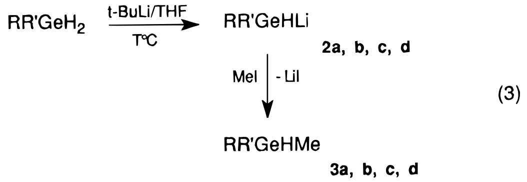
Ge(1)−O(1)	2.746(5)	Ge(1)−C(11)	1.954(7)
Ge(1)−H_A	1.47(5)	O(1)−C(8)	1.354(11)
Ge(1)−H_B	1.54(6)	O(1)−C(20)	1.420(11)
Ge(1)−C(1)	1.966(6)		
C(1)-Ge(1)-C(11)	105.6(3)	C(11)-Ge(1)-H_B	110.5(21)
C(1)-Ge(1)-H_A	113.3(17)	H_A-Ge(1)-H_B	104.0(3)
C(1)-Ge(1)-H_B	110.9(21)	O(1)-Ge(1)-C(11)	175.20(23)
C(11)-Ge(1)-H_A	112.0(17)		

[a] Standard uncertainties are in parentheses.

indicate strong interactions. The germanium atom retains its tetrahedral geometry though slightly deformed (cf. Table 2) as has already been observed in silicon analogs,[7] and the two hydrogen atoms occupy equatorial positions.

In the ^1H NMR spectra, complexation is indicated by a change in the chemical shift displacement, $\Delta\delta = -0.22$ ppm, of the δ(OMe) signal relative to the starting 1-methoxynaphthalene. Such a shift is not observed in **1d** for which a Ge···O interaction appears difficult or impossible.

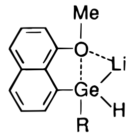
These organogermanes easily undergo metalation on reaction with *t*-BuLi giving (organohydrogermyl)lithiums in high yield (eq 3).



(3)

Compound **1c** gives only a moderate (∼50%) yield of lithiation product with *t*-BuLi. The presence of two methoxynaphthyl groups probably decreases the reactivity of the Ge−H bond due to steric hindrance. The (organogermyl)lithiums **2a**,**c**,**d** are very stable at ambient temperature; **2b** should be prepared and stored at low temperature.

The proton NMR spectra show high-field chemical shift displacements characteristic of δ(GeH).[1b] In the ^{13}C NMR spectra, displacements of ipso aromatic carbon atoms (mesityl, phenyl, and naphthyl) are near those of the methoxynaphthyl group; they can be unambiguously assigned by HMBC ($^1H/^{13}C-^3J$) and COSY ($^1H/^1H$) correlations (Figure 2).[2] Chemical shift variations of ipso aromatic carbon atoms (cf. Table 3) toward low field suggest a localization of negative charge on the germanium atom.[1b,8] At the methoxy group, shifts to lower field are also observed, in the ^1H NMR as in the ^{13}C NMR spectra. The same phenomenon has already been reported for the reaction of 1-methoxynaphthalene with *n*-BuLi, and this has been attributed to an oxygen−lithium complexation.[9] In our case, strengthening of the oxygen−germanium interaction in (organogermyl)lithiums appears less probable because the germanium atom already has a negative charge due to the presence of the lithium. Therefore, we suggest an intramolecular OCH_3/Li interaction in a structure of the following type:



Our ^7Li NMR spectra of (organohydrogermyl)lithiums were measured in THF relative to an external reference consisting of 1 M LiCl in D_2O (cf. Table 4). In a comparison of the $\delta(^7Li)$ signal of our germyllithiums with those of *n*-BuLi and *t*-BuLi,[10ab] it appears that germyllithiums exhibit a lower ionic character than *t*-BuLi but a higher ionic character than *n*-BuLi. Thus, as Lambert et al.[10c] have previously observed, the ionicities of our germyllithiums are about midrange on the scale for lithium−carbon systems.

The UV spectrum of the (arylgermyl)lithium **2a,** compared to that of the starting compound **1a**, exhibits a new absorption band ($\lambda_{max} = 348$ nm) in a wavelength range similar to those observed in the case of (trimethylgermyl)alkali metals. This absorption can be considered as characteristic of a transition from the nonbonding orbital of the germyl anions (HOMO) to the more accessible LUMO in the conjugated (arylgermyl)lithium compound.[11]

All new (organogermyl)lithiums were characterized mainly by alkylation with MeI which proved to be the best trapping agent.

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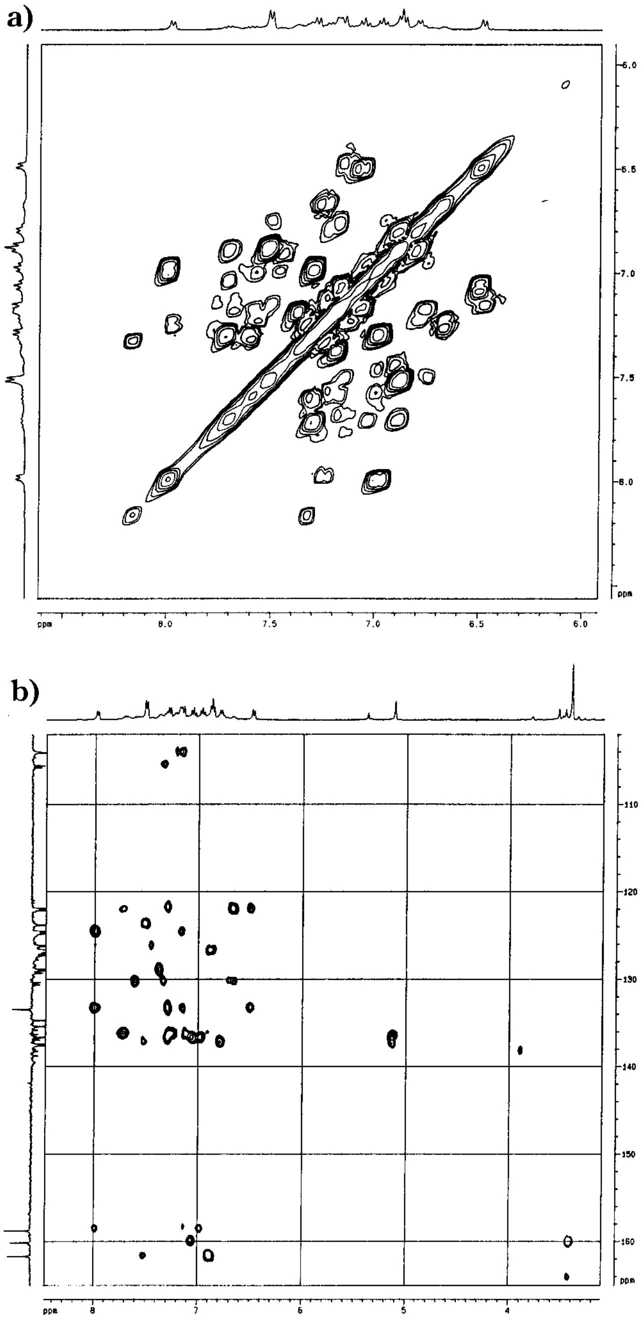


Figure 2. (a) 2D ^{1}H,^{1}H COSY homonuclear shift correlation using 45° read pulse of **1b**. (b) 2D ^{1}H/^{13}C correlation of **1b** via heteronuclear zero and double-quantum coherence optimized on long coupling with a low-pass, *J*-filter to suppress one-bond correlations and no decoupling during acquisition.

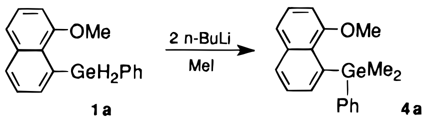
Table 3. Variation of δ (ppm) of the (Diarylgermyl)lithums Compared to Starting Compounds

	NMR ^{1}H (THF-d_8)		NMR ^{13}C (THF-d_8)		
	Δδ(OCH$_3$)	Δδ(GeH)	Δδ(OCH$_3$)	Δδ(C$_{1'}$)	Δδ(C$_1$)
2a/1a	−0.19	−0.25	+0.52	+23.53	+28.68
2b/1b	−0.22	−0.36	+0.40	+25.09	+27.16
2c/1c	−0.08	−0.23	+1.18		+26.83
2d/1d	−0.01	−0.61	−0.18	+25.47	

We tried to prepare (organogermyl)dilithiums by the same method. At present, little is known about germyldilithiums. The formation of (diphenylgermyl)dilithium has been noted, without comment, in the reaction of lithium with diphenylgermane in HMPA using a method analogous to that described for Ph$_2$GeK$_2$.[8b] More recently, the preparation of Et$_2$GeLi$_2$ by a very difficult route has been described.[12] Also, transitory germyl anions [Me$_4$C$_4$Ge]$^-$·2M$^+$ have been characterized by a silylation reaction.[3a,b] The reaction of 2 equiv of *n*-BuLi with **1a** followed by alkylation with MeI gave the expected dimethyl derivative **4a** almost quantitatively (eq 4).

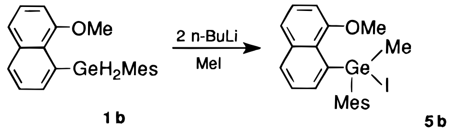
Table 4. ^{7}Li NMR Data (δ; in THF-d_8) for (Diarylgermyl)lithiums

1b	2b	2c	2d
0.67 (s)	0.86 (s)	0.98 (s)	0.81 (s)

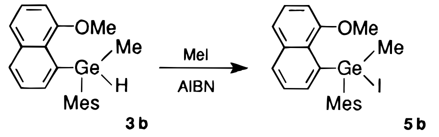


(4)

Dialkylation using MeI[1b,13] or disilylation using Me$_3$SiCl,[3a,b] through direct nucleophilic substitution, is thought to involve the transient formation of a germanium-centered dianion. However, the reaction mechanism might be more complex than expected, as we observed that steric hindrance around the germanium atom in **1b** induces a different pathway which results in the formation of the unexpected iodide **5b** (eq 5). In this case, a radical mechanism (eq 6) is proposed, as it was recently shown that a reaction mixture of RI/RLi can generate radical species R$^\bullet$ by SET.[14]

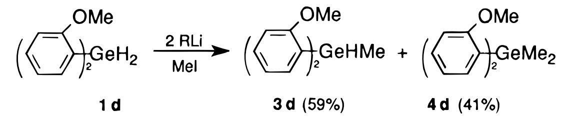


(5)



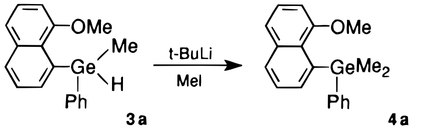
(6)

In contrast, regardless of the organolithium used, *n*-BuLi or *t*-BuLi, **1d** gives only partial dialkylation (eq 7).



(7)

The dimethyl derivatives **4a,d** have also been synthesized (eqs 8 and 9).



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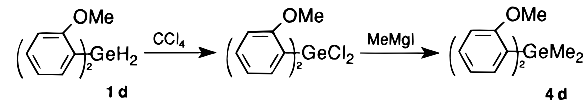

(9)

These results show that the presence of methoxyphenyl and methoxynaphthyl groups stabilizes (organohy-

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drogermyl)lithiums. By contrast, dimetalations are more difficult since they depend upon the substituent on germanium and on the organolithium used. At present, we are trying to stabilizes (organogermyl)dilithiums with strongly complexing bidentates with the object of determining their true structures.

Experimental Section

All of the reactions were performed under a dry argon atmosphere using standard Schlenk techniques. The compounds were characterized by the usual analytical techniques: ^{1}H NMR, AC 80 Bruker; ^{13}C NMR, AC 200 and ARX 400 Bruker; ^{7}Li NMR, AC 200 Bruker (external reference: 1 M LiCl in D_2O); IR, Perkin-Elmer 1600 FT; mass spectra, Ribermag R 10 10 (DCI, CH_4) and HP 5989 A (CG/MS); UV, Hewlett Packard 8452 A diode array spectrophotometer (solutions in THF). Elemental analyses were done by the Centre de Microanalyse de l'Ecole Nationale Supérieure de Chimie de Toulouse.

Synthesis of (8-methoxy-1-naphthyl)phenylgermane, 1a. A solution of 17.9 mmol of (8-methoxynaphthyl)lithium[15] in 50 mL of THF was added dropwise at 20 °C to a suspension of 18.8 mmol of $MgBr_2$ in 20 mL of THF. The mixture was refluxed 2 h and then added to a solution of $PhGeCl_3$ (5.58 g, 17.9 mmol) in 14 mL of THF. The mixture was stirred at room temperature overnight and then reduced by $LiAlH_4$ (1.71 g, 44.9 mmol) in 30 mL of ether. After 1 h at 40 °C, hydrolysis, extraction, drying with Na_2SO_4, and concentration, the residue was distilled resulting in **1a** (4.08 g, 74%): Bp 120 °C/0.05 mmHg; mp 34 °C; ^{1}H NMR ($CDCl_3$) δ 3.74 (s, 3H, OCH_3), 5.46 (s, 2H, GeH_2), 6.80 (dd, $J = 6.2$ Hz, $J = 2.5$ Hz, 1H, $C_{10}H_6$), 7.24−7.59 (m, 8H, C_6H_5, $C_{10}H_6$), 7.72 (dd, $J = 6.9$ Hz, $J = 1.6$ Hz, 1H, $C_{10}H_6$), 7.85 (dd, $J = 7.9$ Hz, $J = 1.6$ Hz, 1H, $C_{10}H_6$); ^{13}C NMR (50.32 MHz, $CDCl_3$, {1H}) δ 53.78 (OCH_3), 128.22, 128.47, 134.74, 137.72 (C_6H_5), 104.84, 121.38, 126.01, 126.23, 129.41, 129.45, 129.68, 135.10, 136.36, 155.98 ($C_{10}H_6$); IR (neat) 2014.9, 2061.4 (GeH); MS (EI, 70eV) *m/z* 310 ((M^+), 63%), 309 ((M − H), 82%), ((M − H − CH_3), 43%), 233 ((M − Ph), 23%). Anal. Calcd for $C_{17}H_{16}GeO$: C, 66.10; H, 5.22. Found: C, 66.35; H, 4.89.

Synthesis of Mesityl(8-methoxynaphthyl)germane, 1b. A solution of 22.8 mmol of (8-methoxynaphthyl)lithium[15] in 50 mL of THF was added dropwise at −78 °C to a solution of 6.79 g (22.79 mmol) of $MesGeCl_3$ in 50 mL of THF. The mixture was warmed to room temperature and stirred at 20 °C overnight. It was then reduced with $LiAlH_4$ as described above. The residue so obtained was recrystallized from methanol leading to pure white crystals of **1b**: 5.27 g (66%); mp 83 °C; ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3H, p-CH_3), 2.35 (s, 6H, o-CH_3), 3.89 (s, 3H, OCH_3) 5.46 (s, 2H, GeH_2), 6.85 (dd, $J = 5.9$ Hz, $J = 2.7$ Hz, 1H, $C_{10}H_6$), 6.91 (s, 2H, C_6H_2), 7.20−7.44 (m, 4H, $C_{10}H_6$), 7.82 (dd, $J = 6.8$ Hz, $J = 2.5$ Hz, 1H, $C_{10}H_6$); ^{13}C NMR (50.32 MHz, $CDCl_3$, {1H}) δ 21.28 (p-CH_3), 23.87 (o-CH_3), 128.26, 129.94, 138.54, 144.24 (C_6H_2), 104.90, 121.37, 125.85, 126.27, 129.22, 129.56, 132.67, 134.17, 135.17, 156.52 ($C_{10}H_6$); IR (Nujol) 2125.6, 2076.9 (GeH); MS (EI, 70 eV) *m/z* 352 ((M^+), 81%), 351 ((M − H), 76%), 233 ((M − C_9H_{11}), 29%), 336 ((M − H − CH_3), 38%). Anal. Calcd for $C_{20}H_{22}GeO$: C, 68.44; H, 6.31. Found: C, 68.46; H, 6.30.

Crystal and Experimental Data for 1b. Crystallographic information is given in Table 1. An ORTEP[4] diagram of **1b** is shown in Figure 1. Selected bond lengths and angles are in Table 2. The structure was solved by the Patterson heavy atom method; the first difference map afforded positions for all atoms except hydrogen. Hydrogen atoms on Ge and in methyl groups were located in difference maps, the remainder were introduced in calculated positions, all C−H distances were normalized to 0.95 Å, and thermal parameters were refined anisotripically. Refinement was on $|F|$ with weights based on counting statistics. Final agreement factors were $R = 0.059$, $R_w = 0.056$, and $S = 2.73$. Calculations were done with NRCVAX,[16] and scattering factors are from usual sources.[17] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, U.K. CB2/EW.

Synthesis of Bis(8-methoxynaphthyl)germane, 1c. A solution of 35.4 mmol of (8-methoxynaphthyl)lithium in 100 mL of THF was added dropwise to a solution at −78 °C of 3.8 g (17.7 mmol) of $GeCl_4$ freshly distilled in 25 mL of THF. The mixture was warmed to room temperature and stirred overnight. The mixture was reduced with $LiAlH_4$ as described above. The residue so obtained was analyzed by ^{1}H NMR and showed the formation of three compounds. Several treatments with a mixture of methanol/ether allowed isolation of pure **1c** as white crystals: 2.29 g (33%); mp 131 °C; ^{1}H NMR ($CDCl_3$) δ 3.68 (s, 6H, OCH_3), 5.81 (s, 2H, GeH_2), 6.81 (dd, $J = 6.2$ Hz, $J = 2.5$ Hz, 2H, $C_{10}H_6$), 7.24−7.46 (m, 6H, $C_{10}H_6$), 7.59 (dd, $J = 6.8$ Hz, $J = 1.6$ Hz, 2H, $C_{10}H_6$), 7.81 (dd, $J = 7.8$ Hz, $J = 1.6$ Hz, 2H, $C_{10}H_6$); ^{13}C NMR (50.32 MHz, $CDCl_3$, {1H}) δ 54.31 (OCH_3), 104.68, 121.21, 125.63, 126.19, 128.76, 129.61, 133.30, 134.94, 135.41, 156.52 ($C_{10}H_6$); IR (Nujol) 2077.2, 2028.8 (GeH); MS (EI, 70 eV) *m/z* 390 ((M^+), 18%); 389 ((M − H), 22%), 374 ((M − H − CH_3), 8%), 233 ((M − $C_{11}H_9O$), 14%). Anal. Calcd for $C_{22}H_{20}GeO_2$: C, 67.93; H, 5.18. Found: C, 67.76; H, 5.24.

Synthesis of Bis(2-methoxyphenyl)germane, 1d. A solution of 100 mmol of (2-methoxyphenyl)magnesium (prepared from 5 g (206 mmol) of Mg and 18.94 g (100 mmol) of 1-bromoanisole) was added dropwise to a solution of $GeCl_4$ (10.82 g, 50 mmol) in 200 mL of ether. The mixture was stirred overnight and then hydrolyzed (6 N HCl), extracted, dried, and concentrated. The residue was dissolved into 40 mL of THF and reduced with $LiAlH_4$ as above. After concentration, the reaction mixture was crystallized by adding 30 mL of pentane. Pure white crystals of **1d** were obtained after a second recrystallization from pentane: 4.88 g (34%); mp 85−86 °C; ^{1}H NMR ($CDCl_3$) δ 3.78 (s, 3H, OCH_3), 5.01 (s, 2H, GeH_2), 6.91 and 7.34 (m, 4H, C_6H_4); ^{13}C NMR (50.32 MHz, $CDCl_3$, {1H}) δ 55.51 (OCH_3), 109.84, 121.01, 122.90, 136.96, 163.20 (C_6H_4;. IR (Nujol) 2077 (GeH); MS (EI, 70 eV) *m/z* 290 ((M^+), 31%); 182 ((M − H − ($MeOC_6H_4$), 32%). Anal. Calcd for $C_{14}H_{16}GeO_2$: C, 58.20; H, 5.58. Found: C, 57.94; H, 5.46.

Reaction of 1a−d with *t*-BuLi. General Procedure. A solution of 1.4 mmol of *t*-BuLi (1.7 M in pentane) was added to a solution of the organogermane (1 mmol) in 4 mL of THF (**1a,** 20 °C; **1b**−**d**, −40 °C). The mixture was stirred for 40 min at the indicated temperature. Analysis by ^{1}H, ^{13}C, and ^{7}Li NMR showed that the corresponding (organogermyl)lithiums were formed in high yield.

2a (red solution) (90%): ^{1}H NMR (400.13 MHz, THF-d_8) δ 3.41 (s, 3H, OCH_3), 5.11 (s, 1H, GeH), 6.48 (d, $J = 7.5$ Hz, 1H, H_7 naphthyl), 6.78 (t, $J = 7.1$ Hz, 1H, H_4 phenyl), 6.87 (dd, $J = 7.1$ Hz, $J = 6.8$ Hz, 2H, H_3 phenyl), 6.96 (dd, $J = 7.6$ Hz, $J = 6.8$ Hz, 1H, H_3 naphthyl), 7.05 (dd, $J = 7.5$ Hz, $J = 7.9$ Hz, 1H, H_6 naphthyl), 7.15 (d, $J = 7.9$ Hz, 1H, H_5 naphthyl), 7.28 (d, $J = 7.6$ Hz, 1H, H_4 naphthyl), 7.50 (d, $J = 6.8$ Hz, 2H, H_2 phenyl), 7.97 (d, $J = 6.6$ Hz, 1H, H_2 naphthyl); ^{13}C NMR (100.62 MHz, THF-d_8, {1H}) δ 54.90 (OCH_3), 123.77 (C_4), 126.65 (C_3), 137.43 (C_2), 161.71 (C_1) (C_6H_5), 104.05 (C_7), 121.87 (C_5), 124.50 (C_4), 124.72 (C_6 and C_3), 133.42 (C_9), 136.38 (C_{10}), 136.62 (C_2), 158.76 (C_1), 160.15 (C_8) ($C_{10}H_6$); ^{7}Li NMR (77.77 MHz, THF-d_8) δ 0.67 (s).

2b (red solution) (90%): ^{1}H NMR (200.13 MHz, THF-d_8) δ 2.13 (s, 3H, p-CH_3), 2.36 (s, 3H, o-CH_3), 3.57 (s, 3H, OCH_3), 5.07 (s, 1H, GeH), 6.54 (d, $J = 8$ Hz, 1H, $C_{10}H_6$), 6.59 (s, 2H, C_6H_2), 6.77−7.24 (m, 4H, $C_{10}H_6$), 7.57 (d, $J = 7$ Hz, 1H, $C_{10}H_6$); ^{13}C NMR (50.32 MHz, THF-d_8, {1H}) δ 21.53 (p-CH_3), 26.70 (o-CH_3), 54.86 (OCH_3), 127.05, 132.40, 144.55, 155.57 (C_6H_2),

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103.83, 121.59, 123.58, 124.25, 125.66, 133.00, 133.74, 136.32, 158.73, 160.20 ($C_{10}H_6$); ^{7}Li NMR (77.77 MHz, THF-d_8) δ 0.86 (s) ppm.

2c (red solution) (55%): ^{1}H NMR (200.13 MHz, THF-d_8) δ 3.50 (s, 6H, OCH_3), 5.58 (s, 1H, GeH), 6.61 (d, $J = 7.3$ Hz, 2H, $C_{10}H_6$), 6.95 (d of d, $J = 7.8$ Hz, $J = 7.1$ Hz, 2H, $C_{10}H_6$), 7.12 (d of d, $J = 7.6$ Hz, $J = 8$ Hz, 2H, $C_{10}H_6$), 7.24−7.43 (m, 4H, $C_{10}H_6$), 7.92 (d, $J = 6.7$ Hz, 2H, $C_{10}H_6$); ^{13}C NMR (50.32 MHz, THF-d_8, {1H}) δ 55.59 (OCH_3), 105.00, 122.20, 123.99, 126.01, 133.52, 135.13, 136.30, 160.40, 160.76 ($C_{10}H_6$); ^{7}Li NMR (77.77 MHz, THF-d_8) δ 0.98 (s) ppm.

2d (yellow solution) (90%): ^{1}H NMR (200.13 MHz, THF-d_8) δ 3.88 (s, 3H, OCH_3), 4.60 (s, 1H, GeH), 6.80−8.00 (m, 6H, C_6H_4); ^{13}C NMR (50.32 MHz, THF-d_8, {1H}) δ 55.33 (OCH_3), 109.08, 120.67, 125.59, 139.78, 146.82, 164.26 (C_6H_4).

Reaction of 2a−d with MeI. An excess of MeI (100%) was added to a solution of (organohydrogermyl)lithium at the temperature used for their preparation (**2a**, 20 °C; **2b**−**2d** −40 °C). The mixture was allowed to warm to ambient temperature for 1 h. After hydrolysis, extraction, and concentration, the residue yielded the following.

3a (51%): viscous oil which slowly precipitated white crystals at 20 °C; mp 51−53 °C; ^{1}H NMR ($CDCl_3$) δ 0.79 (d, $J = 3.1$ Hz, 3H, $GeCH_3$), 3.67 (s, 3H, OCH_3), 5.42 (q, $J = 3.1$ Hz, 1H, GeH), 6.77 (dd, $J = 6.1$ Hz, $J = 2.2$ Hz, 1H, $C_{10}H_6$), 7.24−7.52 (m, 8H, C_6H_5, $C_{10}H_6$), 7.68 (dd, $J = 6.9$ Hz, $J = 1.5$ Hz, 1H, $C_{10}H_6$), 7.83 (dd, $J = 7.9$ Hz, $J = 1.6$ Hz, 1H, $C_{10}H_6$); ^{13}C NMR (50.32 MHz, $CDCl_3$, {1H}) δ −2.21 (CH_3Ge), 54.07 (OCH_3), 127.98, 128.12, 133.98, 141.02 (C_6H_5), 104.49, 121.31, 125.77, 126.01, 129.36, 131.01, 132.49, 135.13, 135.55, 155.96 ($C_{10}H_6$); IR (pure) 2043.9, 1991.4 (GeH); MS (EI, 70 eV) m/z = 324 ((M^+), 26%), 309 ((M − CH_3), 100%), 231 ((M − CH_3 − C_6H_6), 40%), 200 ((M − CH_3 − C_6H_6 − OCH_3, 11%). Anal. Calcd for $C_{18}H_{18}GeO$: C, 66.94; H, 5.62. Found: C, 66.70; H, 5.68.

3b (47%): viscous oil; bp 80 °C/0.01 mmHg (with partial decomposition); ^{1}H NMR ($CDCl_3$) δ 0.76 (d, $J = 3.4$ Hz, 3H, $GeCH_3$), 2.29 (s, 9H, o-CH_3 and p-CH_3), 3.67 (s, 3H, OCH_3), 5.66 (q, $J = 3.4$ Hz, 1H, GeH), 6.78 (dd, $J = 6.1$ Hz, $J = 2.7$ Hz, 1H, $C_{10}H_6$), 6.84 (s, 2H, C_6H_2), 7.24−7.53 (m, 3H, $C_{10}H_6$), 7.61 (dd, $J = 6.9$ Hz, $J = 1.6$ Hz, 1H, $C_{10}H_6$), 7.78 (dd, $J = 7.9$ Hz, $J = 1.7$ Hz, 1H, $C_{10}H_6$); ^{13}C NMR (50.32 MHz, $CDCl_3$, {1H}) δ −0.43 ($GeCH_3$), 21.14 (p-CH_3), 24.32 (o-CH_3), 54.22 (OCH_3), 128.45, 134.55, 137.87, 143.41 (C_6H_2), 104.57, 121.32, 125.69, 126.11, 128.98, 131.12, 133.56, 135.24, 135.95, 156.51 ($C_{10}H_6$); IR (pure) 2062.0, 1980.5 (GeH); MS (EI, 70 eV) m/z 366 ((M^+), 6%), 351 ((M − CH_3), 100%), 336 ((M − 2CH_3), 29%), 247 ((M − C_9H_{11}), 26%), 232 ((M − CH_3 − C_9H_{11}), 38%).

3c formed as a white powder. ^{1}H NMR analysis showed the presence of **3c** (70%). Further recrystallizations did not allow us to isolate pure **3c**. ^{1}H NMR ($CDCl_3$): δ 0.80 (d, $J = 2.8$ Hz, 3H, $GeCH_3$), 3.58 (s, 6H, OCH_3), 5.76 (q, $J = 2.8$ Hz, 1H, GeH), 6.76 (dd, $J = 2.4$ Hz, $J = 6.3$ Hz, 2H, $C_{10}H_6$), 7.24−7.51 (m, 6H, $C_{10}H_6$), 7.62 (dd, $J = 1.5$ Hz, $J = 6.8$ Hz, 2H, $C_{10}H_6$), 7.78 (dd, $J = 1.5$ Hz, $J = 7.8$ Hz, 2H, $C_{10}H_6$). ^{13}C NMR (50.32 MHz, $CDCl_3$, {1H}): δ 0.88 ($GeCH_3$), 54.11 (OCH_3), 104.30, 121.21, 125.47, 125.99, 128.52, 134.75, 135.05, 136.47, 156.29 ($C_{10}H_6$). IR (Nujol): 2071.5, 2009.5 (GeH). MS (GC-MS, EI, 30 eV): m/z 404 ((M^+), 6%), 389 ((M − CH_3), 100%), 374 ((M − 2CH_3), 33%).

3d (64%) was obtained after crystallization from pentane: Mp 45−46 °C; ^{1}H NMR ($CDCl_3$) δ 0.78 (d, $J = 3$ Hz, 3H, CH_3), 3.81 (s, 3H, OCH_3), 5.17 (q, $J = 3$ Hz, 1H, GeH), 6.84−7.44 (m, 4H, C_6H_4); ^{13}C NMR (50.32 MHz, $CDCl_3$, {1H}) δ −4.27 (CH_3), 55.40 (OCH_3), 109.94, 120.85, 126.04, 130.58, 136.08, 163.32 (C_6H_4); IR (Nujol) 2073 (GeH); MS (EI, 70 eV) m/z = 304 ((M^+), 10%), 289 ((M − CH_3), 30%). Anal. Calcd for $C_{15}H_{18}GeO_2$: C, 59.43; H, 5.99. Found: C, 58.63; H, 6.14.

Reaction of 1a with 2 *n*-BuLi. A solution of 2.5 mmol of *n*-BuLi (1.6 M in hexane) was added to a solution of **1a** (0.25 g, 0.8 mmol) in 1 mL of ether at −40 °C. The mixture was stirring at −40 °C for 1 h, and an excess of MeI (0.2 mL) was then added. The mixture was allowed to warm for 2 h. After hydrolysis, extraction and concentration, analysis of the residue by ^{1}H NMR confirmed the formation of **4a** (86%) and **3a** (16%).

Preparation of 4a. A solution of 8.7 mmol of *t*-BuLi (1.7 M in pentane) was added to **3a** (2 g, 6.2 mmol) in 10 mL of THF at −40 °C. The mixture was stirred at −40 °C for 40 min and treated with an excess of MeI (see above). Analysis of the residue by ^{1}H NMR showed the presence of **4a** (96%). **4a** was then distilled: Bp 68 °C/0.003 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.76 (s, 6H, CH_3), 3.61 (s, 3H, OCH_3), 6.74 (dd, $J = 6.3$ Hz, $J = 2.5$ Hz, 1H, $C_{10}H_6$), 7.24−7.51 (m, 8H, C_6H_5, $C_{10}H_6$), 7.62 (dd, $J = 6.9$ Hz, $J = 1.7$ Hz, 1H, $C_{10}H_6$), 7.81 (dd, $J = 7.8$ Hz, $J = 1.8$ Hz, 1H, $C_{10}H_6$); ^{13}C NMR (50.32 MHz, $CDCl_3$, {1H}) δ 0.58 (CH_3), 53.88 (OCH_3), 127.77, 127.84, 133.30, 144.27 (C_6H_5), 104.27, 121.36, 125.68, 125.82, 129.21, 134.36, 134.55, 135.30, 156.00 ($C_{10}H_6$); MS (EI, 70eV) m/z = 338 ((M^+), 12%), 323 ((M − CH_3), 85%), 308 ((M − 2 CH_3), 48%), 261 ((M − C_6H_5), 12%), 293 ((M − 3CH_3), 31%). Anal. Calcd for $C_{19}H_{20}GeO$: C, 67.72; H, 5.98. Found: C, 68.23; H, 6.38.

Reaction of 1b with 2 *n*-BuLi. A solution of 1.7 mmol of *n*-BuLi (1.6 M in hexane) was added to **1b** in 2 mL of ether at −20 °C. After 8 min at this temperature, an excess of MeI was added. The mixture was allowed to warm to ambient temperature during 1 h and then concentrated. The residue was treated with 10 mL of CH_2Cl_2. After decantation from LiI, the solution was evaporated leading to a white powder identified as **5b**: 0.11 g (28%); mp 155−165 °C; ^{1}H NMR ($CDCl_3$) δ 1.54 (s, 3H, CH_3), 2.25 (s, 9H, p-CH_3 and o-CH_3), 3.38 (s, 3H, OCH_3), 6.75 (dd, $J = 1.8$ Hz, $J = 6.9$ Hz, 1H, $C_{10}H_6$), 6.76 (s, 2H, C_6H_2), 7.24−7.66 (m, 3H, $C_{10}H_6$), 7.87 (dd, $J = 1.4$ Hz, $J = 8.2$ Hz, 1H, $C_{10}H_6$), 8.18 (dd, $J = 1.4$ Hz, $J = 6.9$ Hz, 1H, $C_{10}H_6$); ^{13}C NMR (50.32 MHz, $CDCl_3$, {1H}) δ 16.35 (CH_3), 21.02 (p-CH_3), 23.80 (o-CH_3), 54.07 (OCH_3), 129.35, 134.87, 138.88, 141.08 (C_6H_2), 104.33, 121.79, 125.69, 127.04, 129.49, 134.17, 136.36, 137.68, 154.21 ($C_{10}H_6$); MS (DCI, CH_4) m/z = 493 (($MH)^+$, 2%), 477 ((M − CH_4), 3%), 461 ((M − CH_3OH), 2%), 365 ((M − HI), 100%). Anal. Calcd for $C_{21}H_{23}GeIO$: C, 51.38; H, 4.72. Found: C, 50.82; H, 4.80.

Reaction of 3b with MeI. The mixture of **3b** (0.064 g (0.13 mmol), 5 mL of MeI, and a catalytic quantity of AIBN (2,2′-azobis(2-methylpropionitrile)) was heated at 80 °C for 48 h. After concentration under vacuum, the analysis of the transparent residue showed the formation of **5b** (50%) with decomposition.

Reaction of 1d with 2 *n*-BuLi. A solution of 1.8 mmol of *n*-BuLi (1.6 M in hexane) was added to a solution of **1d** (0.22 g, 0.75 mmol) in 2 mL of ether at −40 °C. After 1 h, an excess of MeI was added and the mixture was treated using the same conditions as those described above. Analysis of the residue by ^{1}H NMR showed the formation of **3d** (51%) and **4d** (49%).

Reaction of 1d with 2 *t*-BuLi. The same reaction was realized with *t*-BuLi and led, after treatment with MeI, to a mixture of **3d** (41%) and **4d** (59%).

Preparation of 4d. A solution of **1d** (0.54 g, 2 mmol) in 5 mL of CCl_4 with a catalytic quantity of AIBN was warmed at reflux for 1 h. After concentration, a white powder identified as $(MeOC_6H_4)_2GeCl_2$ (0.54 g, 75%) was obtained. This compound was alkylated by MeMgI (20 mmol). After hydrolysis, extraction, and concentration, 0.20 g (32%) of **4d** was obtained: Mp 68−72 °C; ^{1}H NMR ($CDCl_3$) δ 0.65 (s, 6H, CH_3), 3.75 (s, 3H, OCH_3), 6.79−7.31 (m, 4H, C_6H_4); ^{13}C NMR (50.32 MHz, $CDCl_3$, {1H}) δ −1.66 (CH_3), 55.22 (OCH_3), 109.75, 120.60, 128.46, 130.13, 135.25, 163.41 (C_6H_4); MS (EI, 70 eV) m/z 318 ((M^+), 8%), 303 ((M − CH_3), 100%). Anal. Calcd for $C_{16}H_{20}GeO_2$: C, 60.64; H, 6.36. Found: C, 59.99; H, 6.26.

Supporting Information Available: Tables of crystal data, atom coordinates, thermal parameters, and bond distances and angles and ORTEP diagrams (11 pages). Ordering information is given on any current masthead page.

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