

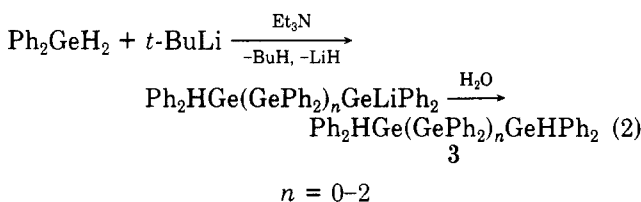
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Table I. IR and ^1H NMR Data for (Diarylgermyl)lithiums and the Starting Organogermanes

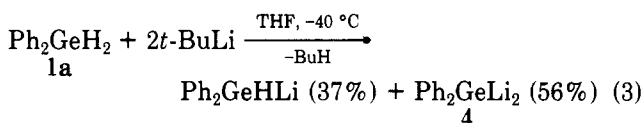
compd	$\nu(\text{Ge-H}),^a$ cm^{-1}	^1H NMR, b ppm	
		$\delta(\text{Ge-H})$	$\delta(\text{C}_6\text{H}_5)$ or $\delta(\text{C}_6\text{H}_2)$
Ph_2GeH_2 (1a)	2024	5.00	7.10–7.50
Ph_2GeHLi (2a)	2012	4.60	6.80–7.05, 7.45–7.60
Mes_2GeH_2 (1b)	2040	5.00	6.80
Mes_2GeHLi (2b)	2020	4.40	6.45
Mes_2GeH_2 (1b)	2060 ^c		
Mes_2GeHLi (2b)	2000 ^c		

^a Spectra were recorded in THF/pentane solution unless otherwise noted. ^b In THF- d_8 /pentane solution. ^c In Nujol mull.

These metalation reactions require the use of a slight excess of $t\text{-BuLi}$ (20–40%) and a low-temperature procedure to avoid competitive alkylation reactions. In the case of (organosilyl)lithium, Tilley and co-workers have recently isolated $\text{Mes}_2\text{HSiLi}(\text{THF})_2^8$ as off-white crystals. Compounds **2** are more difficult to crystallize from the solution but were completely characterized by ^1H and ^{13}C NMR spectroscopy and their reactivity. In solution, their stability depends on the solvent used and the nature of R. Compound **2b** is stable in such solvents as pentane, THF, and amines. Compound **2a** slowly decomposes in THF at 20 °C within 24 h. This decomposition is more effective in the presence of an amine (Et_3N or Et_2NMe) and gives di-, tri-, and tetragermyllithiums.^{6,9} The nature of these polygermanes depends mainly on the reaction time. The selective synthesis of di-, tri-, and tetragermanes can be achieved and monitored by GC analysis.



If a large excess of $t\text{-BuLi}$ (>100%) is used, diphenylgermane gives (diphenylgermyl)dilithium in good yield:



The yields were determined by alkylation of the Ge–Li bond with use of MeI.

The formation of **4** has been reported¹⁰ only in the reaction of Ph_2GeH_2 with Li in HMPA, with use of a procedure similar to that described for the preparation of Ph_2GeK_2 . Recently a new synthesis of Et_2GeLi_2 has been described in the literature.¹¹

IR, ^1H , and ^{13}C NMR parameters of (diarylgermyl)lithiums are summarized in Tables I and II, together with those of the starting materials.

The IR data show a $\nu(\text{Ge-H})$ displacement to high frequency due to the inductive effect (+I) of the alkali metal. However, the $\Delta\nu(\text{M}_{14}\text{-H})$ value observed between R_2GeH_2 and R_2HGeLi (Nujol mull) is about half of that observed for the silicon series.⁸ The chemical shifts of Ge–H and the aromatic protons in **2a** and **2b** in comparison with

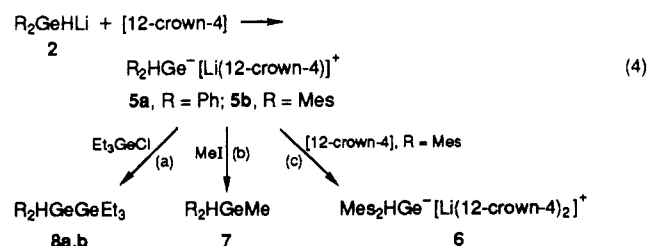
Table II. ^{13}C NMR Data for (Diarylgermyl)lithiums and Diarylgermanes

compd	solvent ^a	¹³ C NMR, ppm						
		C ₁	C ₂	C ₃	C ₄	<i>o</i> -CH ₃	<i>p</i> -CH ₃	
Ph ₂ GeH ₂	THF	135.0	136.1	129.4	130.1			
Ph ₂ GeHLi	THF	159.4	137.6	127.0	124.1			
Ph ₂ GeHLi	TDA-1	164.9	136.9	125.9	122.3			
Mes ₂ GeH ₂	THF	131.9	144.4	129.5	139.4	24.2		21.5
Mes ₂ GeHLi	THF	153.9	144.4	127.2	132.6	24.1		21.5
Mes ₂ GeHLi	TDA-1	159.3	143.9	125.9	130.3	25.7		21.1

^a TDA-1 is $\text{N}(\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$.

those of the corresponding diarylgermanes are shifted slightly to a lower field ($\Delta\delta \approx 0.4\text{--}0.6$ ppm). These observed shifts correlate with a negative charge at the germanium. The ^{13}C NMR values seem to confirm this result. The ipso ^{13}C resonance for **2a** and **2b** is shifted drastically to lower field while the para ^{13}C resonance is shifted slightly to lower field. The chemical shifts of the meta and para carbons are least affected by lithiation of the arylgermanes. These results are similar to those previously reported^{5,10,12} for other organometallic compounds; they can be attributed to a polarization of the phenyl ring resulting in decreased electron density at the ipso carbon. Such polarization can be caused by a localized negative charge residing on the germanium center, which is consistent with a predominant inductive effect and the absence of a mesomeric (resonance) effect in the germlyl anion. An additional feature is the influence of solvent on these chemical shifts (Table II). As previously noted, the chemical shift of the ipso carbon is the most sensitive to interaction with solvent. The dissociation of ion pairs is more effective in polar solvents, and so the negative charge at the germanium is increased.

Complexation of R_2GeHLi . The stabilization of **2** by a complexing reagent was examined with tris(3,6-dioxahexptyl)amine, abbreviated TDA-1, known to stabilize RMgX .¹³ We observed only the decomposition of **2** with nucleophilic assistance as described above for R_3N . Treatment of **2** in THF solution with an excess of 12-crown-4 gives a new insoluble complex with 1/1 stoichiometry. When 12-crown-4 is used as solvent, a new ^1H NMR signal shifted to low field appears, which is probably due to the formation of a complex with 1/2 stoichiometry¹⁴ (eq 4c).



Germyllithium complexes **5a,b** were isolated as powders sensitive toward hydrolysis. Compound **5b** seems less stable in solution than **5a**, which is probably due to steric

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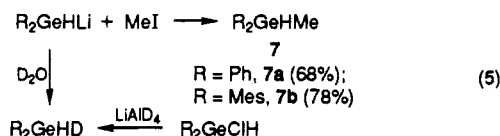
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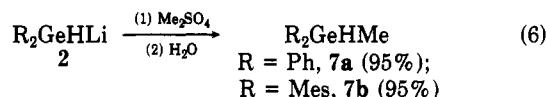
hindrance enhancing its lability. The characterization reactions (eq 4a and 4b) of **5a** occurred in high yields. When R = Mes (compound **5b**), the yields of reactions 4a and 4b were enhanced in comparison with the reactivity of **2** (eq 5).

Reactivity of (Diarylgermyl)lithium. Methyl iodide is a very effective alkylation reagent for the characterization of these organometallic compounds; the reactions proceed at room temperature and lead to the corresponding organogermenes (eq 5).

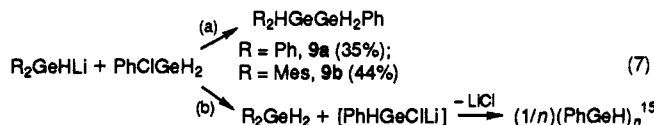


Deuterolysis of the germanium–lithium bond is effective but can be used only as a qualitative test since exchange reactions, Ge–H/Ge–D, occur.

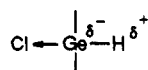
Compounds **2** react immediately and almost quantitatively at 20 °C with dimethyl sulfate (eq 6).



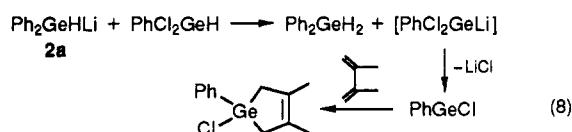
(Organogermyl)lithiums are also very useful intermediates in organometallic synthesis, particularly for the preparation of asymmetric hydropolygermanes, which are usually difficult to obtain (eq 7a).



However, in the case of arylchlorogermenes, the acidic character of the hydrogen atom

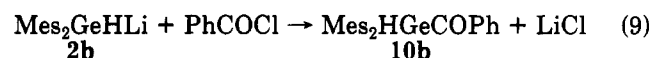


leads to a competitive lithiation reaction (eq 7b). The transient (arylchlorogermyl)lithium gives germylene and polygermane through an α -elimination process.¹⁵ This mechanism is supported by the characterization of stabilized phenylchlorogermylene in the reaction between **2a** and phenyldichlorogermene (eq 8).

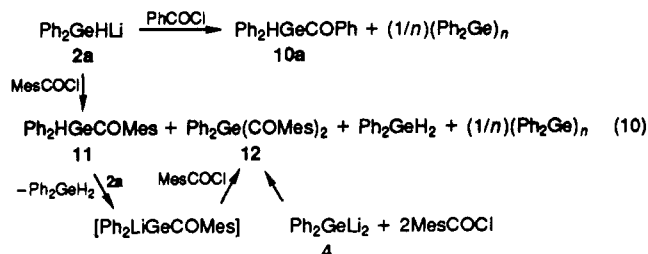


Phenylchlorogermylene was easily characterized by its 1,4-cycloaddition to 2,3-dimethylbuta-1,3-diene¹⁶ (eq 8).

The reactions of (triorganogermyl)lithium, R_3GeLi , with carboxylic acid chlorides have been used to prepare acylgermanes.¹⁷ The reaction of an excess of benzoyl chloride with **2a** at low temperature products the first-isolated diarylgermyl ketone **10b** (eq 9).

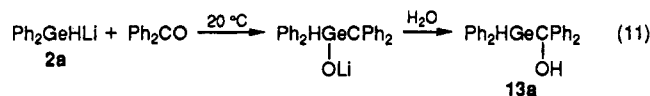


Within the phenyl series, the formation of $(\text{Ph}_2\text{Ge})_n$ polymers probably results from partial decomposition of the germyl ketone **10a** (eq 10).

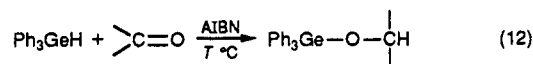


With the more sterically hindered 2,4,6-trimethylbenzoyl chloride, the expected reaction occurs in low yield. We also observed the formation of an unexpected germylated β -diketone, which was formed by diarylation of (diphenylgermyl)dilithium (eq 10) and may be due to the enhancement of the acidic character of the hydrogen attached to germanium in **11**. This results from an attractive effect of the acyl group, allowing a transmetalation reaction (eq 10).

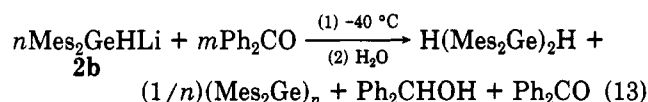
Compound **2a** also adds to the carbonyl group of aromatic ketones, leading to the corresponding germylated alcohols (eq 11).



We have not observed any interaction reaction between the germanium–hydrogen bond and the carbonyl group to form alkoxygermanes, which usually occurs through radical initiation or in thermolysis¹⁸ (eq 12).

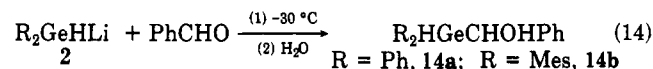


In the case of (dimesitylgermyl)lithium (**2b**), steric hindrance inhibits this addition reaction:

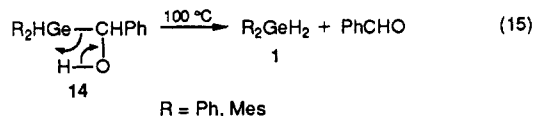


Formation of a germylated alcohol is not observed in eq 13, but instead, the unexpected diphenylcarbinol is obtained and also a small quantity of 1,1,2,2-tetramesityldigermene. The formation of these compounds can be explained by a mechanism involving radicals formed by a monoelectronic transfer from the germyllithium **2b** to the ketone as the first step.⁴

With benzaldehyde compounds **2** react at low temperature to form the corresponding germyl alcohols in good yield (eq 14).



Compounds **14** are thermally unstable.¹⁹ They decompose partially above 100 °C to give benzaldehyde and diorganogermenes **1**, according to eq 15.



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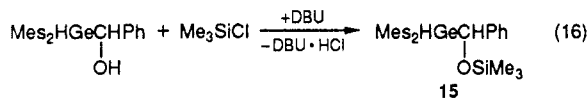
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Table III

time	polygermane	yield, %
5 min	H(GePh ₂) ₂ H ²³	26
9.5 h	H(GePh ₂) ₃ H	46
14 h	H(GePh ₂) ₄ H	69

The proposed mechanism (eq 15) is confirmed by the *O*-silylation of the OH group, which gives the stable distillable compound 15 (eq 16).



Concluding Remarks

The presence of two functional sites in compounds 2 (germanium-lithium and germanium-hydrogen bonds) makes them very useful reagents in the synthesis of new organohydropolygermanes and functional organogermanes. Their germylation reactions produce intermediates with low-coordinate germanium, as we will describe in a future paper.²⁰

Experimental Section

All manipulations were performed under an inert atmosphere of nitrogen or argon by using standard Schlenk and high-vacuum-line techniques. NMR spectra were recorded on a Varian EM 360 A spectrometer at 60 MHz (¹H) and on a Bruker WP 90 spectrometer at 36.4 MHz (¹³C). Infrared spectra were recorded on a Perkin-Elmer 457 infrared spectrometer. Mass spectra recorded on a Ribermag R 1010 or a Varian Mat 311 A spectrometer operating in the electron-impact mode at 70 eV. Gas-phase chromatography was done with a Varian Aerograph 1400 (SE 30) instrument, and yields were calculated by using an internal reference (Bu₄Ge). Elemental analyses were done by the "Service Central de Microanalyse du CNRS" (France). The compounds Ph₂GeH₂²¹ and Mes₂GeH₂²² were prepared according to literature procedures.

Ph₂GeHLi (2a). A solution of 4.8 mmol of *t*-BuLi (1.7 M) in pentane was added to a solution of Ph₂GeH₂ (0.92 g, 4 mmol) in THF (4 mL) at -40 °C. The mixture was stirred for 15 min at -20 °C. Analysis by ¹H and ¹³C NMR spectroscopy showed that 2a had formed exclusively (~95%) (cf. Tables I and II).

Mes₂GeHLi (2b). A solution of 1.4 mmol of *t*-BuLi (1.7 M) in pentane was added to a solution of Mes₂GeH₂ (0.31 g, 1.0 mmol) in THF (4 mL) at -20 °C. The mixture was stirred for 40 min at -20 °C. Analysis by ¹H and ¹³C NMR spectroscopy showed that 2b had formed in high yield (~84%) (cf. Tables I and II). Removal of the solvents under vacuum gave a yellow powder, which was washed three times with pentane (5 mL). Attempts to isolate pure 2b in a solid state were not successful. Compound 2b hydrolyzed rapidly to give 1b.

In all manipulations, freshly prepared solutions of 2 were used.

Base-Catalyzed Decomposition of 2a. Synthesis of Polygermanes. A solution of 4.8 mmol of *t*-BuLi (1.7 M) in pentane was added to a solution of Ph₂GeH₂ (0.92 g, 4 mmol) in Et₂NMe (4 mL) at -40 °C. After 5 min the solution was heated to 20 °C. The mixture was stirred for the times indicated in Table III. After hydrolysis, extraction, and concentration, the polygermanes were recovered by recrystallization from ether/methanol (4/1) (cf. Table III). H(GePh₂)₃H: mp 90–92 °C; ¹H NMR (C₆D₆) δ 5.65 (s, 2 H, GeH), 6.90–7.75 (m, 30 H, C₆H₅); mass spectrum *m/z* 682 (M⁺); IR (Nujol, KBr) 2034 cm⁻¹ (Ge-H). Anal. Calcd for C₃₆H₃₂Ge₃: C, 63.38; H, 4.69. Found: C, 63.15; H, 4.74. H(GePh₂)₄H: mp 130–135 °C; ¹H NMR (C₆D₆) δ 5.67 (s, 2 H, GeH), 6.85–7.75 (m, 40 H, C₆H₅); mass spectrum *m/z* 910 (M⁺). IR (Nujol, KBr) 2000

cm⁻¹ (Ge-H). This tetragermane was contaminated by small amounts of di- and trigermanes. Attempts to further purify H(GePh₂)₄H were not successful.

Confirmation of the Formation of LiH. A solution of 4.8 mmol of *t*-BuLi (1.7 M) in pentane was added to a solution of Ph₂GeH₂ (0.92 g, 4 mmol) in Et₃N (4 mL) at -40 °C. After 15 min at -40 °C and then 2 h at 20 °C, the mixture was concentrated under vacuum. The residue was washed with pentane (10 mL) and dried in vacuo. It was then treated with 3 mL of THF and a solution of Et₃GeCl (0.39 g, 2 mmol) in THF (2 mL). The reaction mixture was heated in a Carius tube for 15 h at 60 °C. Analysis of the solution by GC showed the quantitative formation of Et₃GeH.

Ph₂GeLi₂ (4). A solution of 4.8 mmol of *t*-BuLi (1.7 M) in pentane was added to a solution of Ph₂GeH₂ (0.46 g, 2 mmol) in THF (2 mL) at -40 °C. The mixture was stirred 40 min at -40 °C and then treated with an excess of MeI. After 15 min, the solution was allowed to warm to ambient temperature. After 1 h at 20 °C and hydrolysis, extraction, and concentration under vacuum, analysis of the residue showed the formation of Ph₂GeMe₂²⁴ (56%) and Ph₂GeHMe²⁵ (37%).

Solvation of 2a by 12-crown-4. 12-crown-4 (0.53 g, 3 mmol) was added to a solution of 2a (3 mmol) in THF at -20 °C, giving an yellow oil. Analysis by NMR and GC methods showed the formation of crude 5a (~90%): ¹H NMR (pure) δ 4.70 (s, 1 H, GeH), 3.35 (s, 16 H, OCH₂), 6.70–6.95 and 7.40–7.60 (m, 10 H, C₆H₅); ¹³C NMR (pure) δ 163.2 (C₁), 137.1 (C₂), 126.5 (C₃), 123.1 (C₄); IR (Nujol, KBr, 1993 cm⁻¹) (Ge-H). The product was washed several times with pentane and dried under vacuum, giving the pale yellow solid 5a, which hydrolyzed rapidly in air to give 1a.

Reaction of 5a with Et₃GeCl. A solution of Et₃GeCl (0.20 g, 1 mmol) in THF (1.5 mL) was added to a suspension of 5a (1 mmol) in pentane (0.5 mL) at 20 °C. The mixture was stirred 30 min at 20 °C. After hydrolysis, extraction, and concentration under vacuum, analysis of the residue by GC and ¹H NMR spectroscopy showed the formation of Ph₂HGeGeEt₃ (68%) and Ph₂GeH₂ (8%). The pure digermane 8a was recovered by distillation: bp 70 °C (5 × 10⁻² mmHg); yield 0.22 g (56%); ¹H NMR δ 1.00 (s, 15 H, C₂H₅), 5.17 (s, 1 H, GeH), 6.90–7.15 and 7.30–7.60 (m, 10 H, C₆H₅); IR (pure, KBr) 2000 cm⁻¹ (Ge-H). Anal. Calcd for C₁₈H₂₆Ge₂: C, 55.77; H, 6.77. Found: C, 55.25; H, 6.92.

Reaction of 5a with MeI. 5a (1.5 mmol) was treated with an excess of MeI at 20 °C. After hydrolysis, extraction, and concentration, nearly pure 7a²⁵ (identified by ¹H NMR) was obtained in 82% yield (0.43 g).

Solvation of 2b by 12-crown-4. 12-crown-4 (0.49 g, 2.8 mmol) was added dropwise to a solution of 2b (2 mmol) in THF (5 mL). The solution was stirred 1 h at 20 °C and then reduced in volume to 4 mL. Addition of 5 mL of pentane gave a precipitate, which was washed with pentane (10 mL) and dried in vacuo. 5b was so obtained in 17% yield (0.23 g): mp 145–147 °C dec; ¹H NMR (THF-*d*₈) δ 2.05 (s, 6 H, *p*-CH₃), 2.25 (s, 12 H, *o*-CH₃), 3.50 (s, 16 H, OCH₂), 4.39 (s, 1 H, GeH), 6.38 (s, 4 H, C₆H₂); IR (THF, KBr) 1980 cm⁻¹ (Ge-H). 5b was very sensitive to moisture and always contained traces of Mes₂GeH₂. The same reaction was performed with an excess of 12-crown-4: a solution of 2b (1 mmol) was added to a solution of 12-crown-4 (0.49 g, 2.8 mmol) in pentane (0.5 mL). With use of the same procedure, the precipitate so obtained was dissolved in 2 mL of THF and analyzed by ¹³C NMR spectroscopy: δ(C₁), 157.9 and 159.4; δ(C₂), 144.3; δ(C₃), 126.5; δ(C₄), 131.4; δ(*o*-CH₃), 23.3; δ(*p*-CH₃), 21.2.

Reaction of 5b with Et₃GeCl. A solution of Et₃GeCl (0.20 g, 1 mmol) and 5b (0.49 g, 1 mmol) in pentane (1 mL) was stirred at ambient temperature for 30 min. After hydrolysis, extraction, and concentration under vacuum, analysis of the residue by ¹H NMR spectroscopy showed that Mes₂HGeGeEt₃ (8b) had been formed in 98% yield. 8b was then recovered by distillation: yield 0.30 g (64%); bp 198–200 °C (7 × 10⁻² mmHg); ¹H NMR (C₆D₆) δ 1.07 (s, 15 H, C₂H₅), 2.10 (s, 6 H, *p*-CH₃), 2.40 (s, 12 H, *o*-CH₃), 5.40 (s, 1 H, GeH), 6.70 (s, 4 H, C₆H₂); IR (pure, KBr) 2010 cm⁻¹ (Ge-H). Anal. Calcd for C₂₄H₃₈Ge₂: C, 61.09; H, 8.13. Found: C, 61.69; H, 8.15.

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Reaction of 5b with MeI. With use of the same procedure, a solution of **5b** (1 mmol) in pentane (0.5 mL) and MeI (excess) gave **7b** in 98% yield.

Reaction of 2a with MeI. An excess of MeI (100%) was added to a solution of **2a** (4 mmol) in THF at -40°C . The mixture was heated to 20°C . After 1 h and hydrolysis, extraction, and concentration, the residue was analyzed by ^1H NMR spectroscopy and showed that **7a**²⁶ had been formed in 68% yield.

Reaction of 2b with MeI. An excess of MeI (100%) was added to a solution of **2b** (1 mmol) in THF at -10°C . The mixture was heated to ambient temperature. After 2 h at 20°C and hydrolysis, extraction, and concentration under vacuum, a white solid identified as **7b** was obtained: yield 0.25 g (78%); mp $90-94^{\circ}\text{C}$; ^1H NMR (C_6D_6) δ 0.80 (d, 3 H, CH_3), 2.10 (s, 6 H, $p\text{-CH}_3$), 2.30 (s, 12 H, $o\text{-CH}_3$), 5.50 (q, 1 H, GeH), 6.70 (s, 4 H, C_6H_2), $J(\text{HC-GeH}) = 4$ Hz; IR (Nujol, KBr) 2040 cm^{-1} (Ge-H); mass spectrum m/z 328 (M^{+}). Anal. Calcd for $\text{C}_{19}\text{H}_{26}\text{Ge}$: C, 69.77; H, 8.03. Found: C, 69.94; H, 8.07.

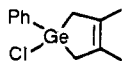
Reaction of 2a with D_2O . A solution of **2a** (1 mmol) in THF was hydrolyzed by D_2O at -40°C and then extracted and concentrated under vacuum. Analysis of the residue by ^1H NMR spectroscopy showed the formation of Ph_2GeHD (C_6D_6): δ 5.10 (t, 1 H, GeH), 6.90–7.20 and 7.20–7.49 (m, 10 H, C_6H_5), $J(\text{H-Ge-D}) = 0.9$ Hz.

Ph_2GeHD was prepared by reduction, with use of LiAlD_4 (0.03 g, excess), of a solution of Ph_2GeHCl (0.26 g, 1 mmol) in ether (0.5 mL) at 0°C . In solution, Ph_2GeHD slowly formed Ph_2GeH_2 over several days at 20°C .

Reaction of 2 with Me_2SO_4 . A solution of R_2GeHLi (1 mmol) in THF was added to an excess of Me_2SO_4 ($\text{R} = \text{Ph}$, 20%; $\text{R} = \text{Mes}$, 40%) in THF (0.5 mL) at 20°C . An exothermic reaction was observed. After 3 h at 20°C , the mixture was hydrolyzed, extracted, and concentrated under vacuum. Analysis of the residue by ^1H NMR spectroscopy showed the formation of **7a** in 95% yield and **7b** in 95% yield.

Reaction of 2 with PhClGeH_2 . A solution of R_2GeHLi (2 mmol) in THF was added to a solution of PhClGeH_2 (0.37 g, 2 mmol) in THF (1 mL) at -20°C . After 20 min at -20°C , the mixture was heated to ambient temperature and stirred (2 h for **2a**, 14 h for **2b**) at 20°C . After hydrolysis, extraction, and concentration under vacuum, analysis of the residue showed the formation of the following compounds: for **2a**, **1a** (20%), **9a** (35%), $\text{H}(\text{Ph}_2\text{Ge})_2\text{H}^{23}$ (5%), $(\text{PhHGe})_n^{15}$ (40%); for **2b**, **1a** (41%), **9b** (44%), $(\text{PhHGe})_n^{15}$ (60%). **9a** and **9b** were identified by comparison with other samples prepared by a different route.²⁰ **9a**: bp 150°C (0.2 mmHg); ^1H NMR (C_6D_6) δ 4.60 (d, 2 H, GeH_2), 5.50 (t, 1 H, GeH), $J(\text{HC-GeH}) = 4$ Hz, 6.90–7.60 (m, 15 H, C_6H_5); IR (pure, KBr) 2050 cm^{-1} (Ge-H); mass spectrum m/z 380 (M^{+}). **9b**: mp $85-86^{\circ}\text{C}$; ^1H NMR (C_6D_6) δ 2.10 (s, 6 H, $p\text{-CH}_3$), 2.30 (s, 12 H, $o\text{-CH}_3$), 4.75 (d, 2 H, GeH_2), 5.50 (t, 1 H, GeH), $J(\text{HC-GeH}) = 4$ Hz, 6.65 (s, 4 H, C_6H_2), 6.85–7.40 (m, 5 H, C_6H_5); IR (Nujol, KBr) $2050-2060\text{ cm}^{-1}$ (Ge-H); mass spectrum m/z 464 (M^{+}). Anal. Calcd for $\text{C}_{24}\text{H}_{30}\text{Ge}_2$: C, 62.18; H, 6.48. Found: C, 61.99; H, 6.62.

Reaction of 2a with PhCl_2GeH . A solution of **2a** (4 mmol) in THF was added to a solution of PhCl_2GeH (0.89 g, 4 mmol) in ether (2 mL) at -70°C . After 1 h at -70°C , the mixture was concentrated under vacuum. The oily residue was washed twice with pentane (4 mL). The pentane solution was evaporated, and the residue, analyzed by ^1H NMR spectroscopy, showed the presence of **1a** (43%), $\text{H}(\text{GePh}_2)_2\text{H}^{23}$ (33%), and PhCl_2GeH (30%). The viscous oil was treated with an excess of 2,3-dimethylbuta-1,3-diene in benzene (1 mL). The reaction mixture was heated in a Carius tube for 2 h at 80°C . After concentration, analysis by GC and ^1H NMR methods showed the formation of



in 30% yield.¹⁶

Reaction of 2b with PhCOCl . A solution of **2b** (2 mmol) in THF was added dropwise to a solution of PhCOCl (0.39 g, 2.8 mmol) in ether (1 mL) at -78°C . After 30 min at -78°C , the solution was heated to ambient temperature. The reaction was monitored by GC. After 30 min at 20°C , the mixture was hydrolyzed ($\text{NaHCO}_3/\text{H}_2\text{O}$), extracted, dried over anhydrous sodium

sulfate, and concentrated under vacuum. The residue was crystallized from a mixture of methanol (2 mL) and ether (3 mL) at -30°C . A yellow solid precipitated, was isolated after decantation, and dried in vacuo, giving **10b**: yield 0.48 g (58%); mp $148-154^{\circ}\text{C}$; ^1H NMR (C_6D_6) δ 2.10 (s, 6 H, $p\text{-CH}_3$), 2.40 (s, 12 H, $o\text{-CH}_3$), 6.50 (s, 1 H, GeH), 6.70 (s, 4 H, C_6H_2), 6.90–7.20 and 7.90–8.20 (m, 5 H, C_6H_5); IR (Nujol, KBr) 2048 (Ge-H), 1643 cm^{-1} (CO); mass spectrum m/z 418 (M^{+}). Anal. Calcd for $\text{C}_{25}\text{H}_{28}\text{OGe}$: C, 71.98; H, 6.78. Found: C, 71.53; H, 6.79.

Reaction of 2a with PhCOCl . A solution of **2a** (3 mmol) in THF was added dropwise to a solution of PhCOCl (0.51 g, 3.6 mmol) in ether (1 mL) at -78°C . After 30 min at -78°C , the mixture was heated to ambient temperature. After 1 h at 20°C , hydrolysis with an aqueous solution of NaHCO_3 , extraction, drying, and concentration in vacuo, analysis of the residue by ^1H NMR spectroscopy confirmed the formation of **10a** (55%) and $(\text{Ph}_2\text{Ge})_n$ ($\sim 40\%$). **10a**: ^1H NMR (C_6D_6) δ 5.90 (s, 1 H, GeH), 7.00–7.10, 7.25–7.65, and 7.65–7.90 (m, 15 H, C_6H_5); IR (pure, KBr) 2052 (Ge-H), 1686 cm^{-1} (CO).

Reaction of 2a with MesCOCl . A solution of **2a** (2 mmol) in THF was added dropwise to a solution of MesCOCl ²⁶ (0.44 g, 2.4 mmol) in ether (2 mL) at -78°C . After 40 min at -78°C , the mixture was heated to ambient temperature. After 3 h of stirring at 20°C , it was hydrolyzed ($\text{NaHCO}_3/\text{H}_2\text{O}$), extracted, dried, over anhydrous sodium sulfate, and concentrated in vacuo. Analysis of the residue by ^1H NMR and GC/MS methods showed the presence of **11** (15%), **1a** (15%), **12** (19%), and $(\text{Ph}_2\text{Ge})_n$ ($\sim 50\%$). **11**: ^1H NMR (C_6D_6) δ 2.00 (s, 6 H, $p\text{-CH}_3$), 2.10 (s, 12 H, $o\text{-CH}_3$), 5.75 (s, 1 H, GeH), 6.48 (s, 2 H, C_6H_2), 6.90–7.60 (m, 10 H, C_6H_5); IR (pure, KBr) 2048 (Ge-H), 1637 cm^{-1} (CO); mass spectrum m/z 376 (M^{+}). **12** was identified by comparison with a sample prepared by a different route (see below).

Synthesis of 12. A solution of MesCOCl (0.73 g, 4 mmol) in ether (2 mL) was added rapidly to a solution of **4** (2 mmol) in THF at -40°C . After 15 min at -40°C , the mixture was heated to ambient temperature. The reaction was monitored by GC. After 3 h of stirring at 20°C , the reaction mixture was hydrolyzed ($\text{NaHCO}_3/\text{H}_2\text{O}$), extracted, dried, and concentrated under vacuum. The residue was analyzed by ^1H NMR spectroscopy, which showed the presence of **12** (58%), **1a** (13%), and Ph_2GeHCl (14%). Pure compound **12** was recovered by distillation: yield 0.17 g (33%); bp 170°C (0.2 mmHg); ^1H NMR (C_6D_6) δ 1.90 (s, 6 H, $p\text{-CH}_3$), 2.10 (s, 12 H, $o\text{-CH}_3$), 6.30 (s, 4 H, C_6H_2), 6.75–7.60 (m, 10 H, C_6H_5); IR (pure, KBr) 1637 cm^{-1} (CO); mass spectrum m/z 522 (M^{+}). Anal. Calcd for $\text{C}_{32}\text{H}_{32}\text{O}_2\text{Ge}$: C, 73.73; H, 6.20. Found: C, 73.32; H, 6.27.

Reaction of 2a with Ph_2CO . A solution of **2a** (2 mmol) in THF was added to a solution of Ph_2CO (0.44 g, 2.4 mmol) in ether (2 mL) at ambient temperature. The mixture was stirred for 4 h and then hydrolyzed, extracted, dried, and concentrated in vacuo. Addition of pentane (4 mL) gave a precipitate, which was isolated after eliminating pentane and drying in vacuo. The product was pure **13a**: yield 0.66 g (80%); ^1H NMR (C_6D_6) δ 5.70 (s, 1 H, GeH), 2.15 (s, 1 H, OH), 6.80–7.15 and 7.25–7.50 (m, 20 H, C_6H_5); IR (Nujol, KBr) 2033 (Ge-H), 3362 cm^{-1} (OH); mass spectrum m/z 412 (M^{+}). Anal. Calcd for $\text{C}_{25}\text{H}_{22}\text{GeO}$: C, 73.08; H, 5.35. Found: C, 72.70; H, 5.30.

Reaction of 2b with Ph_2CO . A solution of **2b** (1 mmol) in THF was added dropwise to a solution of Ph_2CO (0.25 g, 1.4 mmol) in THF (1 mL), and the mixture was refluxed for 2 h. After hydrolysis, extraction, drying, and concentration in vacuo, analysis of the residue by ^1H NMR, IR, and GC methods showed the presence of $(\text{Mes}_2\text{HGe})_2^{27}$ (40%), $(\text{Mes}_2\text{Ge})_n$ ($\sim 60\%$), Ph_2CHOH ($\sim 50\%$), and the remaining Ph_2CO .

Reaction of 2a with PhCHO . A solution of **2a** (3 mmol) in THF was added dropwise to a solution of PhCHO (0.38 g, 3 mmol) in ether (1 mL) at -30°C . The mixture was stirred for 30 min at -30°C and then heated to ambient temperature. After 1 h at 20°C , it was hydrolyzed, extracted, dried, and concentrated in vacuo. Analyses by ^1H NMR spectroscopy showed that **14a**¹⁹ had formed in good yield (87%). The presence of **1a** (traces) and PhCH_2OH (13%) was also confirmed.

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Reaction of 2b with PhCHO. A solution of **2b** (1 mmol) in THF was added dropwise to a solution of PhCHO (0.15 g, 1.4 mmol) in ether (1 mL) at -20°C , and the reaction was monitored by ^1H NMR spectroscopy. The mixture was stirred for 30 min at -20°C and then hydrolyzed, extracted, dried, and concentrated in vacuo. The residue was treated with pentane (2 mL) at -20°C . After decantation and drying in vacuo, the resulting white powder was identified as pure **14b**: yield 0.26 g (62%); mp $78-80^{\circ}\text{C}$; ^1H NMR (C_6D_6) δ 2.10 (s, 6 H, $p\text{-CH}_3$), 2.23 and 2.25 (s, 12 H, $o\text{-CH}_3$), 5.20 (d, 1 H, CH), 5.30 (d, 1 H, GeH), $J(\text{HC-GeH}) = 3$ Hz, 6.60 and 6.63 (s, 4 H, C_6H_2), 6.95 (s, 5 H, C_6H_5); IR (Nujol, KBr) 2060 (Ge-H), 3300 cm^{-1} (OH); mass spectrum m/z 420 (M^{+}). Anal. Calcd for $\text{C}_{25}\text{H}_{30}\text{GeO}$: C, 71.69; H, 7.16. Found: C, 71.76; H, 7.58.

The thermal decomposition of **14b** was monitored by ^1H NMR spectroscopy with use of a solution of **14b** in C_6D_6 that had been

heated in a sealed tube for 4 h at 160°C . The presence of **1b** (25%), PhCHO (25%), and **14b** (73%) was thereby confirmed.

A solution of **14b** (0.21 g, 0.5 mmol) in C_6H_6 (2 mL), Mes_3SiCl (0.06 g, 0.55 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.10 g, excess) was stirred for 15 h at 20°C . After removal of DBU-HCl by filtration, the solution was concentrated in vacuo. **15** was then recovered by distillation: yield 0.11 g (44%); bp 95°C (4×10^{-2} mmHg); ^1H NMR (C_6D_6) δ 0.05 (s, 9 H, SiMe_3), 2.05 (s, 6 H, $p\text{-CH}_3$), 2.30 (s, 12 H, $o\text{-CH}_3$), 5.50 (s, 2 H, GeH, CH),²⁸ 6.65 (s, 4 H, C_6H_2), 6.90-7.15 (m, 5 H, C_6H_5); IR (pure, KBr) 2050 cm^{-1} (Ge-H). Anal. Calcd for $\text{C}_{28}\text{H}_{38}\text{OSiGe}$: C, 68.50; H, 7.74. Found: C, 67.83; H, 7.96.

(28) Using CDCl_3 as solvent, we observed the expected $\delta(\text{CH})$ and $\delta(\text{GeH})$ signals and their coupling: δ 5.20 (d, 1 H, CH) and 5.35 (d, 1 H, GeH), $J(\text{HC-GeH}) = 3$ Hz.

Synthetic Routes to Methylpalladium(II) and Dimethylpalladium(II) Chemistry and the Synthesis of New Nitrogen Donor Ligand Systems

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Convenient and widely applicable synthetic routes to methylhalogenopalladium(II), $\text{PdXMe}(\text{L}_2)$, and dimethylpalladium(II) complexes, $\text{PdMe}_2(\text{L}_2)$, have been developed, including complexes of triphenylphosphine and a wide range of bidentate nitrogen donor ligands. These routes involve either the generation of $\text{Pd}^{\text{II}}\text{Me}_n$ species at low temperature from methylolithium reagents and $\text{trans-PdCl}_2(\text{SMe}_2)_2$ followed by addition of ligand, $\text{Pd}(\text{Ime})(2,2'\text{-bipyridyl})$ being synthesized through the oxidative-addition reactivity of $\text{Pd}_2(\text{dba})_3(\text{CHCl}_3)$, or the facile synthesis of complexes with the reagents $[\text{Pd}(\text{Ime})(\text{SMe}_2)]_2$ and $[\text{PdMe}_2(\text{pyridazine})]_n$ in organic solvents at ambient temperature. These reagents are particularly suitable for ligands sensitive to MeLi reagents, and $[\text{Pd}(\text{Ime})(\text{SMe}_2)]_2$ is also a suitable substrate for the synthesis of chloro and bromo complexes, $\text{PdXMe}(\text{L}_2)$, including PPh_3 complexes. Several new nitrogen donor bidentate ligands are described, containing 1-methylimidazol-2-yl (mim) and pyridin-2-yl (py) groups in $(\text{mim})_2\text{C}=\text{CH}_2$ and $(\text{py})(\text{mim})\text{C}=\text{CH}_2$ as relatives of planar ligands such as 2,2'-bipyridyl and mim, py, and pyrazol-1-yl (pz) groups in $(\text{py})(\text{mim})\text{CH}_2$, $(\text{py})(\text{mim})\text{CHMe}$, $(\text{mim})_2\text{CH}_2$, $(\text{mim})_2\text{CHMe}$, and $(\text{pz})(\text{mim})\text{CH}_2$ as relatives of ligands such as $(\text{py})_2\text{CH}_2$ and $(\text{pz})_2\text{CH}_2$. Methylpalladium(II) complexes of unsymmetrical bidentate ligands exhibit isomerism; e.g., isomers of $\text{Pd}(\text{Ime})(\text{py})(\text{mim})\text{C}=\text{O}$ occur in the ratio 9:1, where the dominant isomer has the pyridine ring trans to methyl. The ligands with methane bridges, e.g. $(\text{pz})(\text{py})\text{CH}_2$, ethane bridges, e.g. $(\text{pz})_2\text{CHMe}$, and propane bridges, e.g. $(\text{py})_2\text{CMe}_2$, form complexes $\text{PdMe}_2(\text{L}_2)$ and $\text{Pd}(\text{Ime})(\text{L}_2)$ that exhibit variable-temperature NMR spectra indicating boat-to-boat inversion of the chelate ring, but complexes of $(\text{mim})_2\text{CHMe}$ and $(\text{py})(\text{mim})\text{CHMe}$ appear to adopt only the conformation with the methyl group axial and adjacent to palladium.

Introduction

Palladium and its compounds are widely used in catalysis and organic synthesis,¹⁻⁵ and the organometallic chemistry of palladium involving Pd-C σ bonds has been focused primarily on the divalent oxidation state with phosphine-based ligands.^{1,6-8} Nitrogen donor complexes involve predominantly studies of cyclometalation and in-

tramolecular coordination systems,^{5,9} which also have applications for organic synthesis.^{5,10} The intramolecular coordination systems usually involve $\text{Pd}^{\text{II}}\text{-C}(\text{sp}^2)$ bonds,^{5,9} although some Pd-C(sp^3) systems are known, e.g. four- and five-membered palladacycle rings in $[\text{Pd}(\text{CHMeCHMeNMe}_2)(\text{NHMe}_2)_2]^+{}^{11}$ and $[\text{Pd}(\text{CH}_2(\text{C}(\text{CO}_2\text{Et})_2)\text{-CHCH}_2\text{NMe}_2)(\mu\text{-Cl})]_2$,¹² respectively. Palladacyclopentadiene complexes, e.g. $\text{Pd}[\text{C}(\text{CO}_2\text{Me})]_5(\text{bpy})$,¹³ 2,2'-biphenyldiyl complexes, e.g. $\text{PdC}_{12}\text{H}_8(\text{bpy})$,¹⁴ and some

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