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Synthesis and Study of Cyclic π-Systems Containing Silicon and Germanium. The Question of Aromaticity in Cyclopentadienyl Analogues

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Abstract: Synthetic routes to the metallole species $C_4Me_4E(H)R$ (**9**, E = Si, R = $Si(SiMe_3)_3$; **10**, E = Si, R = Mes (mesityl); **11**, E = Ge, R = $Si(SiMe_3)_3$; **12**, E = Ge, R = Mes), $C_4R_4E(SiMe_3)_2$ (**13**, E = Si, R = Me; **14**, E = Ge, R = Me; **19**, E = Si, R = Et; **20**, E = Ge, R = Et), and $C_4Me_4E(R)E(R)Me_4C_4$ (**15**, E = Si, R = $SiMe_3$; **16**, E = Si, R = Me; **17**, E = Ge, R = $SiMe_3$; **18**, E = Ge, R = Me) are described. In the presence of 18-crown-6, dihalides **1** and **2** are reduced by potassium in tetrahydrofuran to give crystalline samples of the silole dianion $[K(18\text{-crown-}6)^+]_2[C_4Me_4Si^{2-}]$ (**21**) and the germole dianion $[K_4(18\text{-crown-}6)_3][C_4Me_4Ge]_2$ (**22**). Compound **21** adopts an inverse-sandwich geometry, while **22** is a dimer with a bridging $[K(18\text{-crown-}6)K]^{2+}$ group and η^5-binding modes for all of the potassium atoms. The metallole dianions in these structures appear to possess delocalized π-systems, as evidenced by nearly equivalent C−C bond lengths in the five-membered rings. Silolyl and germolyl anions have been obtained by various methods involving nucleophilic cleavage of bonds to germanium and silicon. Deprotonation of **11** and **12** in the presence of a crown ether gave the anions $[K(18\text{-crown-}6)][C_4Me_4GeR]$ (**23**, R = $Si(SiMe_3)_3$; **24**, R = Mes) and $[Li(12\text{-crown-}4)_2][C_4Me_4GeR]$ (**25**, R = $Si(SiMe_3)_3$; **26**, R = Mes). NMR parameters for these species, and X-ray structures for **25** and **26**, indicate that the anionic rings possess pyramidal germanium centers and bond localization in the diene portion of the ring. Spectroscopic and X-ray crystallographic data for $[Na(15\text{-crown-}5)][C_4Me_4GeMe]$ (**28**), prepared by reductive cleavage of the Ge−Ge bond in **18**, reveal a similar structure for the germolyl ring. The latter compound possesses a Na···Ge interaction in the solid state. Silolyl and germolyl anions $M[C_4Me_4E(SiMe_3)]$ (**30**, E = Si, M = Li; **31**, E = Si, M = K; **32**, E = Si, M = $Li(12\text{-crown-}4)_2$; **33**, E = Si, M = K(18-crown-6); **34**, E = Ge, M = K; **35**, E = Ge, M = K(18-crown-6)) have been prepared by nucleophilic cleavage of the $E-SiMe_3$ bond in $C_4Me_4E(SiMe_3)_2$ with MCH_2Ph (M = Li, K). By similar methods, the monoanionic species $[K(18\text{-crown-}6)][C_4Me_4E(SiMe_3)C_4Me_4E]$ (**36**, E = Si; **37**, E = Ge) were obtained. A crystal structure determination for **33** revealed a highly pyramidalized Si center (the angle between the C_4Si plane and the Si−Si bond is 99.6°) and pronounced double bond localization in the ring. Interaction between the $[K(18\text{-crown-}6)]^+$ cation and the anion is rather weak, as indicated by the K···Si distance (3.604(2) Å) and the atomic position for K. By variable-temperature ^1H NMR spectroscopy, inversion barriers for the compounds $[Li(12\text{-crown-}4)_2][C_4Et_4ESiMe_3]$ (**38**, E = Si; **40**, E = Ge) and $K[C_4Et_4ESiMe_3]$ (**39**, E = Si; **41**, E = Ge) were estimated. Barriers for the germolyl anions **40** and **41** (10.5(1) and 9.4(1) kcal mol^{-1}, respectively) are distinctly higher than those for the corresponding silolyl anions **38** and **39**, as might be expected from periodic trends. The silolyl anions exhibited coalescence temperatures below the freezing point of tetrahydrofuran (165 K), but upper limits to the inversion barriers were estimated from spectra recorded at the lowest temperatures (≤ 8.4 kcal mol^{-1} for **38** and <8.4 kcal mol^{-1} for **39**). The measured inversion barriers for compounds **38**−**41** provide energy differences between the pyramidal anions and their corresponding planar (possibly aromatic) structures, and their low values may be attributed to stability imparted to the transition state by delocalization of π-electron density in the ring.

There has been considerable recent interest in cyclic π-systems containing silicon and germanium.[1] Much of this interest concerns the possibility of aromatic character for such systems, which may arise via delocalization of p-orbitals on silicon or germanium with carbon-based π-systems. Theoretical calculations indicate that silabenzene is nearly as aromatic as benzene,[2] whereas the silolyl (or silacyclopentadienyl) anion $C_4H_4SiH^-$ is predicted to be only partially delocalized.[3,4] Early calculations indicated only a small degree of aromatic character for $C_4H_4SiH^-$,[3] but more recent studies predict significant delocalization despite the presence of a pyramidal silicon atom in the ground state.[4] Hong and Boudjouk have provided NMR parameters for the lithium and sodium salts of $C_4Ph_4Si^tBu^-$ which suggest some delocalization of negative charge in the ring.[5] Germolyl anions may also be generated in solution,[6] but an analysis of NMR data for $C_4Me_4GePh^-$ suggested that the negative charge was localized substantially on germanium.[7] We have reported the X-ray crystal structure for $[Li(12\text{-crown-}4)_2][C_4Me_4GeSi(SiMe_3)_3]$, which possesses a highly pyramidal Ge center and pronounced π-bond localization in the ring.[8] However, it is interesting to compare the properties for $(\eta^5\text{-}C_5Me_5)Ru\{\eta^5\text{-}C_4Me_4ESi(SiMe_3)_3\}$ (E = Si[9] and Ge[10]), which have significantly delocalized electron density in the C_4E rings, as shown by NMR spectroscopy and X-ray crystallography. It therefore seems that various substituent effects may greatly

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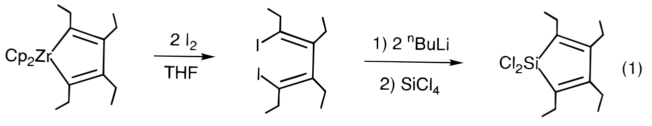
influence the degree of delocalization in silolyl and germolyl rings.

Related cyclic systems that have attracted more recent interest are silole and germole dianions $C_4R_4E^{2-}$. After the initial report by Joo and co-workers[11] on the generation of $C_4Ph_4Si^{2-}$, a number of investigations focused on the use of such species as synthetic intermediates.[12-16] Goldfuss and Schleyer published a theoretical study on the silole dianion $C_4H_4Si^{2-}$ which characterizes this cyclic system as highly aromatic,[17] and this view has been supported by recent crystallographic studies by West[15,18] and us.[16] Given the level of interest in anions of the types described above, and their potential to exhibit novel electronic properties, we have sought to characterize such systems in detail. Here we report a comprehensive study on the synthesis, structure, and electronic properties for related $C_4(alkyl)_4E{-}R^-$ and $C_4(alkyl)_4E^{2-}$ (E = Si, Ge) ring systems.

Results

Synthesis of Silole and Germole Precursors. A number of synthetic routes to siloles and germoles have been reported over the years.[19] For our investigations on stable η^5-silolyl and η^5-germolyl transition metal complexes,[9,10] we desired silole and germole starting materials that did not contain alternative binding sites for the metal (e.g., aryl groups). Therefore the compounds $C_4Me_4GeCl_2$ (**1**) and $C_4Me_4SiBr_2$ (**2**), reported by Fagan et al., seemed to offer ideal starting materials.[20] The synthesis of **1** was achieved by a modification of the Fagan procedure, involving the synthesis of $Cp_2ZrC_4Me_4$ and its conversion to **1** in a single reaction flask. The analogous ethyl derivative $C_4Et_4GeCl_2$ (**3**) was obtained similarly as a colorless oil in 70% yield, after distillation under vacuum. The reported synthesis of **2** gives impure material in relatively low yield. This method was modified by carrying out the reaction of $Cp_2ZrC_4Me_4$ and neat $SiBr_4$ at 135−140 °C over 12 h. In this way compound **2**, contaminated by 1−20% hexamethylbenzene, was obtained in 30% yield as light pink crystals after purification by short-path distillation, crystallization, and then sublimation. Attempts to obtain $C_4Et_4SiBr_2$ by the reaction of $Cp_2ZrC_4Et_4$ with $SiBr_4$ were unsuccessful. However, the analogous chloride derivative $C_4Et_4SiCl_2$ (**4**) was obtained by the sequence of reactions shown in eq 1, using methods previously described by Ashe[21] and West.[14]



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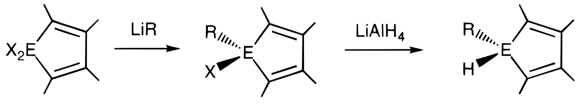
(1)

Desired precursors to silolyl and germolyl anions were the monosubstituted derivatives $C_4Me_4E(R)X$ and $C_4Me_4E(R)H$ (E = Si, Ge; R = alkyl, aryl, or silyl). Compounds of these types were obtained by the sequence of reactions shown in eq 2 (Mes = mesityl). In general, this method is successful only with sterically hindered R groups, as smaller nucleophiles lead to mixtures of mono- and disubstituted products. Silyl bromide **6** was not isolated, but was generated in situ for the preparation of **10**.



(2)

5, E = Si; X = Br; R = $Si(SiMe_3)_3$
6, E = Si; X = Br; R = Mes
7, E = Ge; X = Cl; R = $Si(SiMe_3)_3$
8, E = Ge; X = Cl; R = Mes

9, E = Si; R = $Si(SiMe_3)_3$
10, E = Si; R = Mes
11, E = Ge; R = $Si(SiMe_3)_3$
12, E = Ge; R = Mes

Routes to monoanions of interest were also based on the starting compounds **13**−**18** shown in Scheme 1. These metallole rings are obtained by the in situ alkylation or silylation of intermediate dianionic species obtained by the reduction of **1** and **2** with potassium metal. In a similar way, the silole $C_4Et_4Si(SiMe_3)_2$ (**19**) and the germole $C_4Et_4Ge(SiMe_3)_2$ (**20**) were prepared. This versatile method was pioneered by Joo and coworkers, who used it to obtain a number of tetraphenyl silole derivatives.[11]

Isolation and Structural Characterization of Silole and Germole Dianions. Given the strong interest in silole and germole dianions as synthetic intermediates and as potentially aromatic systems, we attempted to isolate and structurally characterize examples of this class of compounds. Addition of

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(1) (a) Colomer, E.; Corriu, R. J. P.; Lheureux, M. *Chem. Rev.* **1990**, *90*, 265−282. (b) Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 295−298. (c) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691−2692. (d) Heinemann, C.; Müller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023−2038. (e) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039−2046. (f) Blakeman, P.; Gehrhus, B.; Green, J. C.; Heinicke, J.; Lappert, M. F.; Kindermann, M.; Veszprémi, T. *J. Chem. Soc., Dalton Trans.* **1996**, 1475−1480. (g) Heinemann, C.; Herrmann, W. A.; Thiel, W. *J. Organomet. Chem.* **1994**, *475*, 73−84. (h) Barton, T. J.; Banasiak, D. *J. Am. Chem. Soc.* **1977**, *99*, 5199−5200. (i) Barton, T. J.; Burns, G. T. *J. Am. Chem. Soc.* **1978**, *100*, 5246. (j) Solouki, B.; Rosmus, P.; Bock, H.; Maier, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 51−52. (k) Märkl, G.; Schlosser, W. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 963−965. (l) Maier, G.; Mihm, G.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 52−53. (m) Nakadaira, Y.; Sato, R.; Sakurai, H. *Organometallics* **1991**, *10*, 435−442. (n) Rich, J. D.; West, R. *J. Am. Chem. Soc.* **1982**, *104*, 6884−6885. (o) Jutzi, P.; Meyer, M.; Dias, H. V. R.; Power, P. P. *J. Am. Chem. Soc.* **1990**, *112*, 4841−4846.

(2) (a) Schlegel, H. B.; Coleman, B.; Jones, M. *J. Am. Chem. Soc.* **1978**, *100*, 6499−6501. (b) Blustin, P. H. *J. Organomet. Chem.* **1979**, *166*, 21−24. (c) Baldrige, K. K.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 4204−4208.

(3) (a) Gordon, M. S.; Boudjouk, P.; Anwari, F. *J. Am. Chem. Soc.* **1983**, *105*, 4972−4976. (b) Damewood, J. R. *J. Org. Chem.* **1986**, *51*, 5028−5029.

(4) Goldfuss, B.; Schleyer, P. von R. *Organometallics* **1995**, *14*, 1553−1555.

(5) Hong, J.-H.; Boudjouk, P. *J. Am. Chem. Soc.* **1993**, *115*, 5883−5884.

(6) (a) Curtis, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 4241−4242. (b) Curtis, M. D. *J. Am. Chem. Soc.* **1969**, *91*, 6011−6018. (c) Jutzi, P.; Karl, A. *J. Organomet. Chem.* **1981**, *215*, 19−25.

(7) Dufour, P.; Dubac, J.; Dartiguenave, M.; Dartiguenave, Y. *Organometallic* **1990**, *9*, 3001−3003.

(8) Freeman, W. P.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L.; Gantzel, P. K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1887−1890.

(9) Freeman, W. P.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 8428−8429.

(10) Freeman, W. P.; Tilley, T. D.; Rheingold, A. L.; Ostrander, R. L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1744−1745.

(11) Joo, W.-C.; Hong, J.-H.; Choi, S.-B.; Son, H.-E.; Kim, C. H. *J. Organomet. Chem.* **1990**, *391*, 27−36.

(12) Hong, J.-H.; Boudjouk, P.; Castellino, S. *Organometallics* **1994**, *13*, 3387−3389.

(13) Hong, J.-H.; Boudjouk, P. *Bull. Soc. Chim. Fr.* **1995**, *132*, 495−498.

(14) Bankwitz, U.; Sohn, H.; Powell, D. R.; West, R. *J. Organomet. Chem.* **1995**, *449*, C7−C9.

(15) West, R.; Sohn, H.; Powell, D. R.; Müller, T.; Apeloig, Y. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1002−1004.

(16) Freeman, W. P.; Tilley, T. D.; Yap, G. A. P.; Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 882−884.

(17) Goldfuss, B.; Schleyer, P. von R.; Hampel, F. *Organometallics* **1996**, *15*, 1755−1757.

(18) West, R.; Sohn, H.; Bankwitz, U.; Calabrese, J.; Apeloig, Y.; Mueller, T. *J. Am. Chem. Soc.* **1995**, *117*, 11608−11609.

(19) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215−263.

(20) (a) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880−1889. (b) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310−2312.

(21) Ashe, A. J.; Kampf, J. W.; Pilotek, S.; Rousseau, R. *Organometallics* **1994**, *13*, 4067−4071.

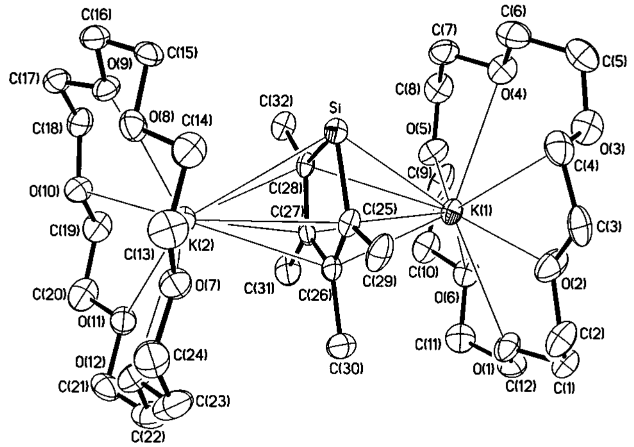
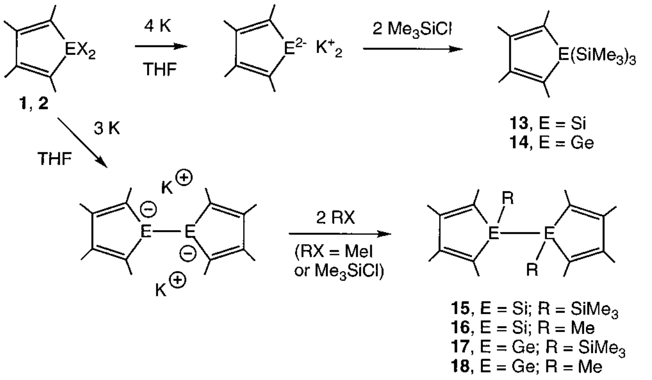


Figure 1. ORTEP diagram of the silole dianion $[K(18\text{-crown-6})^+]_2$-$[C_4Me_4Si^{2-}]$ (**21**).

Scheme 1



18-crown-6 (2 equiv) to reaction mixtures obtained by adding **1** or **2** to potassium in THF resulted in an increased rate for reduction to the dianions, as indicated by a more rapid development of the red colors associated with these species. Formation of the dianions from the dihalide starting materials is accompanied by a dramatic downfield shift in the ^1H NMR resonances, which is consistent with considerable aromatic character in the rings. For example, the ^1H NMR shifts for **2** (δ 1.38, 1.70) are replaced by shifts for the dianion **21** at δ 2.81 and 3.27.

Small quantities of crystalline samples were obtained by the slow (over 7−10 days), gas-phase diffusion of pentane into THF/18-crown-6 solutions of the dianions. In this way, we have isolated $[K(18\text{-crown-6})^+]_2[C_4Me_4Si^{2-}]$ (**21**), which adopts an "inverse sandwich" structure with both potassium atoms coordinated by the silole dianion in an η^5-fashion (Figure 1).[16] Nearly equivalent C−C distances in the five-membered ring suggest a high degree of delocalization, as predicted by theory. Unfortunately we were unable to obtain ^{13}C and ^{29}Si NMR data for this silole dianion due to its low solubility in unreactive solvents (e.g., benzene-d_6 and THF-d_8).

Crystals obtained by reduction of **1** contain the bis(germole dianion) complex $[K_4(18\text{-crown-6})_3][C_4Me_4Ge]_2$ (**22·**THF, Figure 2). Crystal and data collection parameters are given in Table 1, and selected bond distances and angles are listed in Table 2. The two germole dianions in the unit cell are related by a crystallographic point of inversion and are therefore identical. The slight differences in the C−C bond lengths of the C_4Ge ring (1.45(1), 1.43(1), and 1.42(1) Å) point toward considerable delocalization of π-electron density in the ring. The large difference in Ge−C bond distances results from the rather high

Table 1. Crystallographic data for Compounds **22·THF**, **26**, **28**, and **33**

compd	**22·THF**	**26**	**28**	**33**
(a) Crystal Parameters				
formula	$C_{56}H_{104}Ge_2K_4O_{19}$	$C_{33}H_{55}GeLiO_8$	$C_{19}H_{35}GeNaO_5$	$C_{23}H_{45}KO_6Si_2$
formula weight	1382.97	659.3	439.05	512.87
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	*C*2/*c*	*P*2$_1$/*c*	*P*2$_1$/*c*	$P\bar{1}$
a (Å)	20.681(3)	16.037(6)	10.101(1)	9.999(2)
b (Å)	19.347(2)	12.692(5)	14.270(1)	10.705(2)
c (Å)	20.887(2)	17.893(6)	16.422(3)	14.208(3)
α (deg)				94.08(2)
β (deg)	114.88(1)	103.25(3)	98.24(1)	92.79(2)
γ (deg)				102.58(2)
V (Å^3)	7582(2)	3545(2)	2342.6(5)	1477.2(4)
Z	4	4	4	2
cryst color	red-orange	yellow	yellow	yellow
D(calc), g cm^{-3}	1.212	1.235	1.245	1.153
μ(Mo Kα), cm^{-1}	10.70	9.10	13.49	2.92
temp, K	293	246	238	238
(b) Data Collection				
diffractometer	Siemens P4			
monochromator	graphite			
radiation	Mo Kα (λ = 0.71073 Å)			
2θ range, deg	4-50	4-42	4-45	4-50
rflns collected	6870	3913	4024	5923
indpt rflns	6670	3761	3056	4952
std rflns	3 std/197 rflns	3 std/197 rflns	3 std/197 rflns	3 std/197 rflns
(c) Refinement[a]				
R(*F*), %	7.10[b]	5.66	5.63[b]	5.13[b]
R(*wF*), %	16.23[c]	6.39	14.22[c]	12.54[c]
Δ/σ (max)	0.05	0.07	0.11	0.01
$\Delta(\rho)$, e Å^{-3}	0.62	0.42	0.46	0.29
N_o/N_v	17.5	5.5	12.9	17.1
GOF	0.89	1.14	0.88	0.70

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[a] Quantity minimized = $\sum w\Delta^2$; $R = \sum\Delta/\sum(F_o)$; $R(w) = \sum\Delta w^{1/2}/\sum(F_o w^{1/2})$, $\Delta = |(F_o - F_c)|$. [b] Quantity minimized = $R(wF^2) = \sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[(wF_o{}^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$. [c] $R(wF^2)$, %.

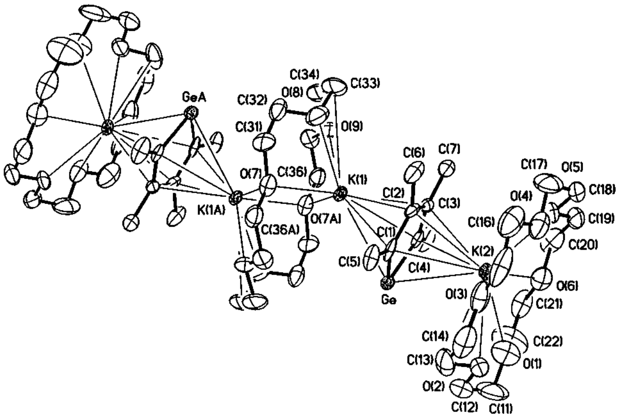


Figure 2. ORTEP diagram for the bis(germole dianion) complex $[K_4(18\text{-crown-}6)_3][C_4Me_4Ge]_2$ (**22**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[K_4(18\text{-crown-}6)_3][C_4Me_4Ge]_2\cdot THF$ (**22**·THF)

(a) Bond Distances			
Ge−C(1)	1.846(9)	K(1)−C(3)	2.881(7)
Ge−C(4)	1.959(8)	K(1)−C(4)	3.008(7)
C(1)−C(2)	1.451(11)	K(2)−Ge	3.348(2)
C(2)−C(3)	1.431(10)	K(2)−C(1)	3.098(7)
C(3)−C(4)	1.417(10)	K(2)−C(2)	3.007(7)
K(1)−Ge	3.302(2)	K(2)−C(3)	3.063(7)
K(1)−C(1)	3.049(6)	K(2)−C(4)	3.169(7)
K(1)−C(2)	2.885(7)		
(b) Bond Angles			
C(1)−Ge−C(4)	86.4(4)	C(5)−C(1)−C(2)	117.3(8)
Ge−C(1)−C(2)	113.0(5)	C(8)−C(4)−C(3)	123.2(8)
Ge−C(4)−C(3)	112.2(5)	C(1)−C(2)−C(6)	122.4(9)
C(1)−C(2)−C(3)	115.5(7)	C(4)−C(3)−C(7)	122.8(8)
C(4)−C(3)−C(2)	112.9(7)	C(6)−C(2)−C(3)	121.6(9)
Ge−C(1)−C(5)	129.7(7)	C(7)−C(3)−C(2)	124.1(8)
Ge−C(4)−C(8)	124.4(7)		

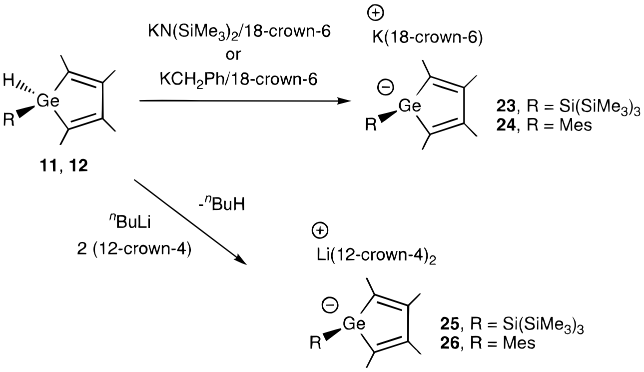
esd's associated with this structure, and is therefore not chemically meaningful.

Interestingly, silolyl and germolyl dianions were also produced (in only ca. 5% yield) when 3 equiv of potassium was used in the reduction. From the reduction of $C_4Me_4GeCl_2$ (**1**) by 3 equiv of potassium, a mixture of poorly formed crystals was obtained. This mixture reacts with Me_3SiCl in benzene-d_6 to give both **14** and **17** (3:1). Thus, it appears that the reactions with 3 equiv of potassium give mixtures of the dianions $C_4Me_4E(K)E(K)C_4Me_4$ and $C_4Me_4EK_2$. In preparative-scale reactions, however, compounds **15**−**18** are readily separated from the corresponding metalloles **13** and **14** by fractional crystallization. Similar observations on silole dianion systems have been described by Joo[11] and Boudjouk.[12]

Synthesis and Isolation of Silolyl and Germolyl Anions. We have employed three different methods for the synthesis of these monoanionic species. The first method, pioneered by Curtis in 1967,[6] involves abstraction of a proton from germanium. More recently, this method has been used to generate a solution of $[C_4Me_4GePh]^-$.[7] The second route, introduced by Boudjouk,[5] is based on reductive cleavage of an E−E bond. Finally, we have employed nucleophilic cleavage of E−E bonds[8,16] to produce both silolyl and germolyl anions.

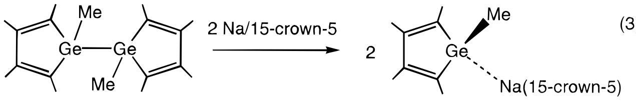
The proton abstraction route was successfully employed only for the hydrogermoles **11** and **12**. Anions **23**−**26** form cleanly in benzene-d_6 solution by ^1H NMR spectroscopy, and preparative scale reactions in toluene or diethyl ether allow isolation of these salts as crystalline solids (Scheme 2). In addition the base-free lithium germolyl $Li[C_4Me_4GeSi(SiMe_3)_3]$ (**27**) was isolated, as a yellow crystalline solid, from reaction of **11** with ^nBuLi. The NMR parameters for **23**−**27** indicate that the anions have very similar structures in solution. For example, the ^{13}C NMR shifts for the ring carbons (C_α and C_β) of compounds **23** and **25** are nearly equivalent (Table 3), and somewhat downfield shifted relative to analogous resonances for the corresponding germoles. Such shifts seem to be associated with bond localization in the rings, and considerable localization of negative charge onto the germanium atom.[7,8] Note that the analogous ^{13}C shifts for **27** are similar (Table 3), indicating that interaction of the lithium cation with the ring does not greatly perturb its electronic structure.

Scheme 2



X-ray quality crystals of **25** and **26** were obtained by slow diffusion of pentane into diethyl ether solutions of the compounds. The structure of **25** was communicated previously.[8] Both structures consist of discrete cations and anions. An ORTEP drawing of the anion in **26** is shown in Figure 3, and important bond distances and angles are listed in Table 4. The anion possesses a pyramidal germanium center, which results in an angle between the C_4Ge plane and the Ge−C(Mes) bond of 113.4°. For comparison the analogous angle in **25** is considerably smaller, at 100.1°. In addition the C_4Ge ring possesses pronounced bond localization, as indicated by the variation in C−C bond lengths. Table 5 compares germole ring C−C bond distances with related C−C distances in germolyl anions. As can be seen from these data, the germolyl anions **25** and **26** exhibit similar differences (Δd) between the $C_\alpha-C_\beta$ and $C_\beta-C_\beta$ bond distances, indicating that both compounds have considerable diene character.

Reductive cleavage of the Ge−Ge bond in **18** with Na/15-crown-5 in toluene produced **28**, which is the germolyl anion analog of pentamethylcyclopentadienide ($C_5Me_5^-$) (eq 3). The



18 **28** (3)

^{13}C NMR data for **28** indicate that the anionic ring, like those in **25** and **26**, is bond-localized and nonaromatic (Table 3). This species was crystallized by simply cooling the reaction solution to −40 °C. The molecular structure is shown in Figure 4, and important bond distances and angles are listed in Table 6. This structure differs from those for **25** and **26**, in that there is a strong interaction between the cation and anion. This interaction brings the sodium atom in contact with only the germanium atom of the ring; there are no sodium−carbon bonding interactions in the structure. Thus, the germanium atom is in a distorted tetrahedral environment. Bond distances in the ring reflect a nonaromatic diene structure, and are very similar to the corresponding distances in **25** and **26**, despite the presence of the Na···Ge bonding interaction. The angle between the Ge−C(Me) bond and the C_4Ge plane, 110.0°, is very close to the corresponding value for the free anion **26** (113.4°).

Table 3. ^{13}C and ^{29}Si NMR Shifts for Ring Atoms of Selected Germoles, Siloles, Germolyl Anions, and Silolyl Anions

compd	$\delta(C_\alpha)$	$\delta(C_\beta)$	δ(ring Si)
(a) Germoles			
$C_4Me_4Ge(H)Si(SiMe_3)_3$ (**11**)[a]	132.89	146.45	
$C_4Me_4Ge(H)Mes$ (**12**)[b]	144.69	146.65	
$C_4Me_4Ge(SiMe_3)_2$ (**14**)[b]	134.86	145.67	
$C_4Me_4Ge(SiMe_3)Ge(SiMe_3)C_4Me_4$ (**17**)[b]	135.83	145.47	
$C_4Me_4Ge(Me)Ge(Me)C_4Me_4$ (**18**)[b]	133.79	145.22	
$C_4Et_4Ge(SiMe_3)_2$ (**20**)[b]	144.34	151.18	
(b) Siloles			
$C_4Me_4Si(H)Si(SiMe_3)_3$ (**9**)	129.53[b]	150.94[b]	−8.90[a]
$C_4Me_4Si(H)Mes$ (**10**)	129.28[b]	151.00[b]	−27.57[a]
$C_4Me_4Si(SiMe_3)_2$ (**13**)[b]	130.99	149.81	−34.26
$C_4Me_4Si(SiMe_3)Si(SiMe_3)C_4Me_4$ (**15**)[b]	131.83	150.11	−34.71
$C_4Me_4Si(Me)Si(Me)C_4Me_4$ (**16**)[b]	131.25	149.11	−13.95
$C_4Et_4Si(SiMe_3)_2$ (**19**)[b]	139.78	155.56	−37.50
(c) Germolyl Anions			
[K(18-crown-6)][$C_4Me_4GeSi(SiMe_3)_3$] (**23**)[b]	137.13	157.06	
[K(18-crown-6)][C_4Me_4GeMes] (**24**)[b]	145.94	156.40	
[Li(12-crown-4)$_2$][$C_4Me_4GeSi(SiMe_3)_3$] (**25**)[c]	136.95	157.03	
[Li(12-crown-4)$_2$][C_4Me_4GeMes] (**26**)[c]	145.49	155.21	
Li[$C_4Me_4GeSi(SiMe_3)_3$] (**27**)[d]	141.29	156.90	
Li[C_4Me_4GePh][7] [d]	138.7	151.5	
[Na(15-crown-5)][C_4Me_4GeMe] (**28**)[b]	136.10	156.89	
[K(18-crown-6)][C_4Me_4GeMe] (**29**)[b]	145.83	159.96	
K[$C_4Me_4GeSiMe_3$] (**34**)[d]	141.10	157.40	
[K(18-crown-6)][$C_4Me_4GeSiMe_3$] (**35**)[b]	136.72	158.56	
[K(18-crown-6)][$C_4Me_4Ge(SiMe_3)C_4Me_4Ge$] (**37**)[b]	140.63	156.43	
[Li(12-crown-4)$_2$][$C_4Et_4GeSiMe_3$] (**40**)[d]	142.45	166.84	
K[$C_4Et_4GeSiMe_3$] (**41**)[d]	141.05	168.62	
(d) Silolyl Anions			
Li[$C_4Me_4SiSiMe_3$] (**30**)[d]	138.66	146.38	−45.38
K[$C_4Me_4SiSiMe_3$] (**31**)[d]	136.23	148.97	−42.70
[Li(12-crown-4)$_2$][$C_4Me_4SiSiMe_3$] (**32**)[b]	135.78	148.62	−43.96
[K(18-crown-6)][$C_4Me_4SiSiMe_3$] (**33**)[b]	135.76	149.60	−41.52
[K(18-crown-6)][$C_4Me_4Si(SiMe_3)C_4Me_4Si$] (**36**)[b]	138.49	149.08	−53.43
[Li(12-crown-4)$_2$][$C_4Et_4SiSiMe_3$] (**38**)[d]	141.96	158.27	−53.12
K[$C_4Et_4SiSiMe_3$] (**39**)[d]	140.88	158.42	−47.38

[a] Dichloromethane-d_2. [b] Benzene-d_6. [c] Benzene-d_6−THF-d_8 (1:1). [d] THF-d_8.

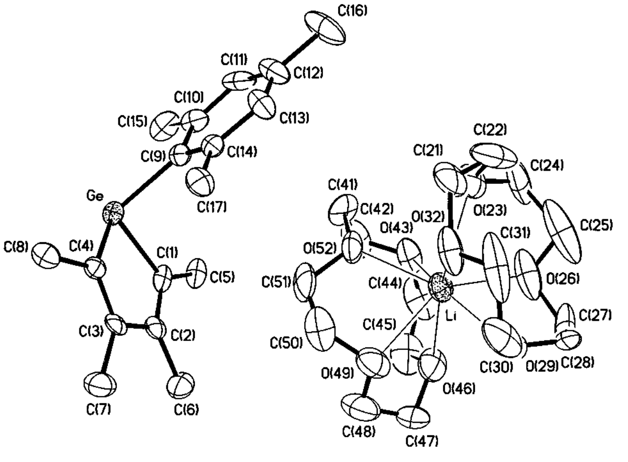


Figure 3. ORTEP diagram for [Li(12-crown-4)$_2$][C_4Me_4GeMes] (**26**).

Table 4. Selected Bond Distances (Å) and Angles (deg) for [Li(12-crown-4)$_2$][C_4Me_4GeMes] (**26**)

(a) Bond Distances			
Ge−C(1)	2.007(9)	Ge−C(9)	2.039(10)
Ge−C(4)	1.961(8)	C(1)−C(5)	1.500(12)
C(1)−C(2)	1.340(15)	C(2)−C(6)	1.497(15)
C(2)−C(3)	1.472(12)	C(3)−C(7)	1.511(14)
C(3)−C(4)	1.346(14)	C(4)−C(8)	1.521(11)
(b) Bond Angles			
C(1)−Ge−C(9)	98.5(4)	C(2)−C(3)−C(4)	116.9(9)
C(4)−Ge−C(9)	111.8(4)	C(3)−C(4)−C(8)	122.6(8)
C(1)−Ge−C(4)	84.8(4)	C(5)−C(1)−C(2)	125.7(8)
Ge−C(1)−C(5)	124.0(7)	C(4)−C(3)−C(7)	124.1(8)
Ge−C(4)−C(3)	110.6(6)	C(1)−C(2)−C(6)	124.7(8)
Ge−C(4)−C(8)	124.7(7)	C(2)−C(3)−C(7)	119.0(9)
Ge−C(1)−C(2)	110.2(6)	C(3)−C(2)−C(6)	119.1(9)
C(1)−C(2)−C(3)	116.2(9)		

Attempted reduction of the silicon analog, $C_4Me_4Si(Me)Si(Me)C_4Me_4$ (**16**), with potassium/18-crown-6 in THF, gave numerous products. However, reduction of **16** with sodium dispersion/15-crown-5 in benzene-d_6 produced a slightly impure product which displayed ^{1}H NMR shifts (at δ 2.30 and 2.65) that were similar to those observed for **28**.

The generation of silyl anion species via nucleophilic cleavage of a Si−Si bond is a well-established synthetic method.[22] Ishikawa et al. have previously described extension of this method to generation of the 1-methyldibenzosilacyclopentadieneide anion, by cleavage of a Si−Si bond with $Ph_2MeSiLi$ in THF.[23] We have extended this method to the synthesis of tetraalkyl-substituted silolyl and germolyl anions. For example, the Ge−Ge bond of $C_4Me_4Ge(Me)Ge(Me)C_4Me_4$ (**18**) is cleaved by KCH_2Ph/18-crown-6 to form [K(18-crown-6)][C_4Me_4GeMe] (**29**).

Nucleophilic cleavage of the E−$SiMe_3$ bonds in **13** and **14** with benzyl lithium or benzyl potassium proceeds cleanly in toluene, benzene-d_6, or tetrahydrofuran-d_8 (eq 4). Complexing agents for Li or K were readily incorporated by simply adding them to the reaction mixture. Compounds **33** and **35** were isolated in moderate yields by crystallization from toluene, as orange-yellow and yellow crystals, respectively. The remaining

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(22) Tamao, K.; Kawachi, A. *Adv. Organomet. Chem.* **1995**, *38*, 1−58.

(23) Ishikawa, M.; Tabohashi, T.; Okashi, H.; Kumada, M.; Iyoda, J. *Organometallics* **1983**, *2*, 351−352.

Table 5. Bond Length Data for Germoles and Germolyl and Silolyl Anions

compd	d[E−C$_\alpha$] (av) (Å)	d[C$_\alpha$−C$_\beta$] (av) (Å)	d[C$_\beta$−C$_\beta$] (Å)	Δd^a (Å)
$C_4Me_4Ge(H)Si(SiMe_3)_3$ (**11**)[8]	1.95	1.34	1.504(4)	0.16
$C_4Ph_4Ge(SiMe_3)_2$[b]	–	1.361(4)	1.494(4)	0.13
[Li(12-crown-4)$_2$][$C_4Me_4GeSi(SiMe_3)_3$] (**25**)	1.98	1.36	1.46(6)	0.10
[Li(12-crown-4)$_2$][C_4Me_4GeMes] (**26**)	1.98	1.34	1.47(1)	0.13
[Na(15-crown-5)][C_4Me_4GeMe] (**28**)	1.96	1.33	1.48(1)	0.15
[K(18-crown-6)][$C_4Me_4Si(SiMe_3)$] (**33**)	1.88	1.36	1.450(5)	0.09

[a] Δd is the difference between the C$_\beta$−C$_\beta$ and C$_\alpha$−C$_\beta$ bond lengths. [b] West, R., personal communication.

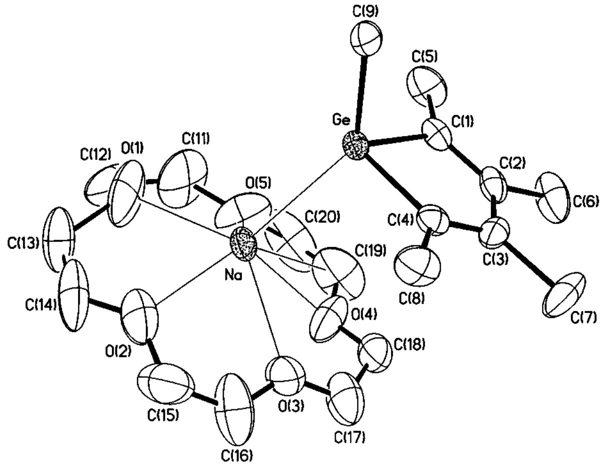


Figure 4. ORTEP diagram for [Na(15-crown-5)][C_4Me_4GeMe] (**28**).

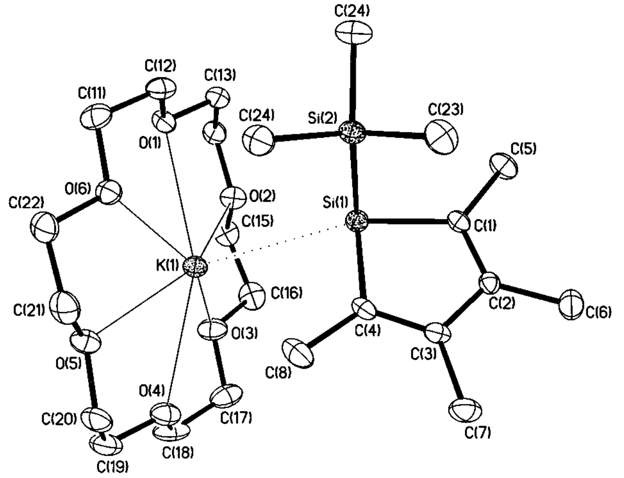
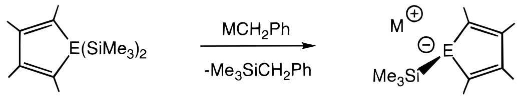


Figure 5. ORTEP diagram for [K(18-crown-6)][$C_4Me_4SiSiMe_3$] (**33**).

Table 6. Selected Bond Distances (Å) and Angles (deg) for [Na(15-crown-5)][C_4Me_4GeMe] (**28**)

(a) Bond Distances			
Ge−C(1)	1.957(7)	Ge−C(9)	2.006(6)
Ge−C(4)	1.967(7)	C(1)−C(5)	1.525(10)
Ge−Na	2.975(3)	C(2)−C(6)	1.522(10)
C(1)−C(2)	1.335(11)	C(3)−C(7)	1.536(10)
C(2)−C(3)	1.484(11)	C(4)−C(8)	1.493(9)
C(3)−C(4)	1.331(9)		
(b) Bond Angles			
C(1)−Ge−C(9)	103.0(3)	C(2)−C(3)−C(4)	116.9(7)
C(4)−Ge−C(9)	102.0(3)	C(3)−C(4)−C(8)	126.4(7)
C(1)−Ge−C(4)	85.7(3)	C(5)−C(1)−C(2)	124.8(7)
Ge−C(1)−C(5)	124.0(6)	C(4)−C(3)−C(7)	123.8(9)
Ge−C(4)−C(3)	109.9(5)	C(1)−C(2)−C(6)	123.8(9)
Ge−C(4)−C(8)	123.5(6)	C(2)−C(3)−C(7)	119.3(8)
Ge−C(1)−C(2)	110.5(6)	C(3)−C(2)−C(6)	120.4(9)
C(1)−C(2)−C(3)	115.9(6)	Na−Ge−C(9)	142.4(2)

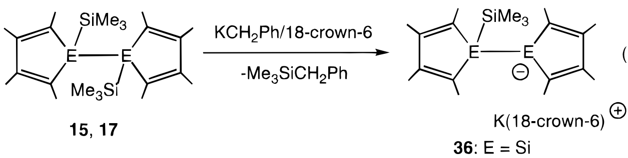
silolyl and germolyl anions were generated in solution and characterized by NMR spectroscopy. Similarly, **36** and **37** were formed by cleavage of an E−SiMe$_3$ bond in **15** and **17** (eq 5).



(4)

13, **14**

30: E = Si, M = Li
31: E = Si, M = K
32: E = Si, M = Li(12-crown-4)$_2$
33: E = Si, M = K(18-crown-6)
34: E = Ge, M = K
35: E = Ge, M = K(18-crown-6)



(5)

15, **17**

36: E = Si
37: E = Ge

The ^{13}C NMR shift data for the ring carbons of these anions are listed in Table 3. The germolyl anions **34**, **35**, and **37** exhibit shifts that are very similar to those observed for the related germanium-centered anions described above. Generally, formation of the silolyl anions results in a downfield shift of the ring carbons with respect to the parent silole compounds, especially for the C$_\alpha$ carbon atoms. Note also that the silolyl anions possess ^{29}Si NMR shifts for the ring silicon atoms that are quite upfield, and shifted considerably upfield with respect to analogous neutral silole compounds. These data are entirely consistent with silyl anion character for these species,[24] and significant charge localization on silicon. Not that the NMR shift parameters for **30** and **31** (in tetrahydrofuran-d_8), which may have significant metal−ring interactions in solution, are very similar to the shifts observed for the anion in **32**, which should have no coordinated metal atom.

Given the complete lack of structural data for silolyl anions, and reported suggestions that they might be delocalized,[3−5] we determined the structure of compound **33**. A view of the structure is given in Figure 5, and important metrical data are listed in Table 7. The [$C_4Me_4SiSiMe_3$]$^-$ anion in this structure is clearly nonaromatic, as indicated by the pronounced bond localization which is reflected in a difference between the C$_\alpha$−C$_\beta$ and C$_\beta$−C$_\beta$ distances of almost 0.1 Å. In particular, the sharp angle of 99.6° between the C$_4$Si plane and the Si−Si bond indicates a high degree of pyramidalization at silicon. The [K(18-crown-6)]$^+$ cation interacts with the anion, but only via contact with the ring silicon atom, at a long distance of 3.604(2) Å. For comparison, the K−Si bond distances in **21** are 3.387(3) and 3.364(3) Å.[16] Further evidence for a relatively weak K···Si interaction is seen in the atomic position for K, which is far removed from the remaining tetrahedral position about Si(1). This can be seen for example in the inequivalent K(1)−Si(1)−C(1) and K(1)−Si(1)−C(4) bond angles of 146.8(1) and 95.9(1)°, respectively. The Si−C$_\alpha$ distances (1.890(4)

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(24) (a) Scholl, R. L.; Maciel, G. E.; Musker, W. K. *J. Am. Chem. Soc.* **1972**, *94*, 6376−6385. (b) Stanislawski, D. A.; West, R. *J. Organomet. Chem.* **1981**, *204*, 295−305. (c) Sharp, K. G.; Sutor, P. A.; Williams, E. A.; Cargioli, J. D.; Farrar, T. C.; Ishibitsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 1977−1979. (d) Sekiguchi, A.; Nanjo, M.; Kabuto, C.; Sakurai, H. *Organometallics* **1995**, *14*, 2630−2632.

Table 7. Selected Bond Distances (Å) and Angles (deg) for $[K(18\text{-crown-}6)][C_4Me_4Si(SiMe_3)]$ (**33**)

(a) Bond Distances

Si(1)−C(1)	1.880(3)	Si(1)−Si(2)	2.334(2)
Si(1)−C(4)	1.890(4)	C(1)−C(5)	1.515(5)
Si(1)−K(1)	3.604(2)	C(2)−C(6)	1.525(5)
C(1)−C(2)	1.360(5)	C(3)−C(7)	1.527(5)
C(2)−C(3)	1.450(5)	C(4)−C(8)	1.507(5)
C(3)−C(4)	1.354(5)		

(b) Bond Angles

C(1)−Si(1)−Si(2)	95.2(1)	C(2)−C(3)−C(4)	115.6(3)
C(4)−Si(1)−Si(2)	96.2(1)	C(3)−C(4)−C(8)	123.9(3)
C(1)−Si(1)−C(4)	87.9(2)	C(5)−C(1)−C(2)	122.4(3)
Si(1)−C(1)−C(5)	127.0(3)	C(4)−C(3)−C(7)	123.8(4)
Si(1)−C(4)−C(3)	110.3(3)	C(1)−C(2)−C(6)	124.4(3)
Si(1)−C(4)−C(8)	125.7(3)	C(2)−C(3)−C(7)	120.6(3)
Si(1)−C(1)−C(2)	110.5(2)	C(3)−C(2)−C(6)	120.2(3)
C(1)−C(2)−C(3)	115.3(3)	K(1)−Si(1)−Si(2)	117.01(5)
K(1)−Si(1)−C(1)	146.8(1)	K(1)−Si(1)−C(4)	95.9(1)

Table 8. Inversion Barriers for **38**−**41**

compd	T_c, K[a]	barrier, kcal mol^{-1}
$[Li(12\text{-crown-}4)_2][C_4Et_4SiSiMe_3]$ (**38**)[b]	≤170	≤8.4
$K[C_4Et_4SiSiMe_3]$ (**39**)[c]	<170	<8.4
$[Li(12\text{-crown-}4)_2][C_4Et_4GeSiMe_3]$ (**40**)	210	10.5(1)
$K[C_4Et_4GeSiMe_3]$ (**41**)	190	9.4(1)

[a] Coalescence temperature. Data were obtained at 300 MHz in THF-d_8. [b] The chemical shift difference between the coalescing peaks was estimated to be the same as for the germanium analog **40** ($\Delta\nu_c = 26.2$ Hz). [c] $\Delta\nu_c$ estimated to be the same as for the germanium analog **41** (24.8 Hz).

and 1.880(3) Å) and the Si−Si distance (2.334(2) Å) represent typical single bond lengths.

Inversion Barriers in Silolyl and Germolyl Anions. The structural and spectroscopic data described above clearly characterize germolyl and silolyl anions as metallole-like species, with minimal delocalization of π-electron density in the five-membered rings. To probe the stability of these pyramidal structures, we sought to measure their inversion barriers. For this purpose we synthesized ion pairs **38**−**41** (Table 8), using the methods described above. These species possess diastereotopic methylene hydrogens which are interconverted by inversion at silicon or germanium. Thus, the measured inversion barriers provide energy differences between the ground state pyramidal and planar (possibly delocalized) structures.

Inversion barriers were determined by variable-temperature ^1H NMR spectroscopy, which allowed analysis of the coalescence behavior for the diastereotopic hydrogens of the methylene groups bonded to the C_α carbons (Figure 6). Barriers for the germolyl anions **40** and **41** are distinctly higher than those for the corresponding silolyl anions **38** and **39**, as might be expected from periodic trends.[25] The silolyl anions exhibited coalescence temperatures below the freezing point of tetrahydrofuran (165 K), but upper limits to the inversion barriers were estimated from spectra recorded at the lowest temperatures. Spectra recorded at 170 K indicated that compound **38** was very close to coalescence, and closer than **39**. Note that the inversion barriers are slightly higher for the "free anion" species **38** and **40**.

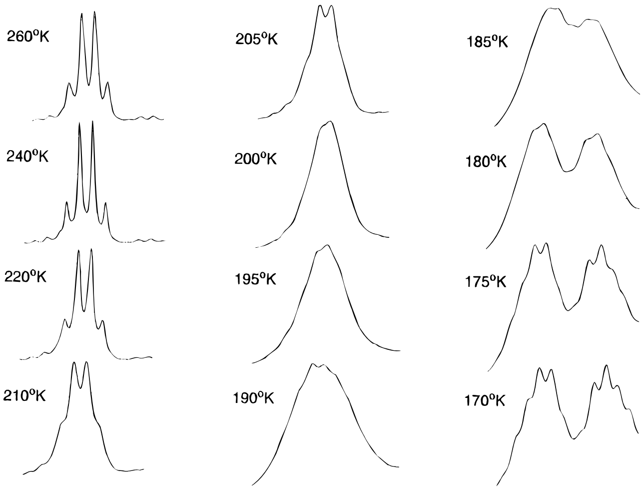

Figure 6. Coalescence behavior for the diastereotopic α-methylene hydrogens in $K[C_4Et_4GeSiMe_3]$ (**41**) in ^1H NMR spectra.

Discussion

We describe here a general approach to the synthesis of silole and germole derivatives, based on Fagan's zirconocene-mediated route to the dihalides **1** and **2**.[20] This approach has proven to be useful in the synthesis of a number of cyclic main group compounds,[20,21,26] and in this work we show that it provides a convenient synthetic pathway to silolyl and germolyl anions, and silole and germole dianions.

Via alkali metal reduction of dihalide starting materials **1**−**4**, solutions of the dianions $[R_4C_4E]^{2-}$ may be conveniently generated in solution. This synthetic method, pioneered by Joo and co-workers,[11] has proven to be a valuable synthetic method for the synthesis of various silole and germole derivatives. The long reaction times associated with dianion formation may be reduced with the use of ultrasound,[13] or by addition of a crown ether. The dianions are formed cleanly, as demonstrated by derivatization reactions carried out in situ, such as those represented in Scheme 1. In the presence of 18-crown-6, crystalline samples of the dianion complexes **21** and **22** may be obtained in low yield. The structural analyses of these compounds reveal the presence of delocalized π-systems, as indicated by roughly equivalent C−C distances in the ring. This was also observed for the dianion rings in $[Li(THF)_2][Li(THF)_3][\eta^5,\eta^1\text{-}C_4Ph_4Si]$,[18] $[Li(dioxane)_2]_2[\eta^5\text{-}C_4Ph_4Ge]$, and $[Li(dioxane)_2]_2[\eta^5,\eta^1\text{-}C_4Ph_4Ge]$.[15] In addition, Hong and Boudjouk have recently reported NMR data for the dianions $[Ph_4C_4Ge]^{2-}$ and $[Ph_4C_4Si]^{2-}$ which is consistent with delocalized π-electron density in the rings.[13] Aromaticity in silole dianions has recently been investigated theoretically by Goldfuss et al. via *ab initio* calculations.[17] These calculations indicate that $C_4H_4Si^{2-}$ would be even more aromatic than isoelectronic phosphole and thiophene systems, and about as aromatic as $C_5H_5^-$. This aromaticity apparently reflects the absence of a pyramidal silicon atom in the dianion. Consistent with aromatic character in $C_4H_4Si^{2-}$, the calculations indicate that the dilithium, disodium, and dipotassium salts would adopt "inverse-sandwich" structures with simultaneous η^5-binding of the silole dianion to both metal atoms. This bonding mode is in fact observed for three of the five structurally characterized silole and germole dianions.

Various methods were employed for the synthesis of silolyl and germolyl anions. Of particular note is the utility of benzyl potassium as a nucleophilic reagent which generally gives short reaction times and clean conversions. The most general routes

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(25) (a) Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271−276. (b) Pyykkö, P.; Desclaux, J.-P. *Acc. Chem. Res.* **1979**, *12*, 276−281.

(26) (a) Fagan, P. J.; Burns, E. G.; Calabrese, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 2979−2981. (b) Buchwald, S. L.; Fisher, R. A.; Foxman, B. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 771−772. (c) Spence, R. E. v. H.; Hsu, D. P.; Davis, W. M.; Buchwald, S. L.; Richardson, J. F. *Organometallics* **1992**, *11*, 3492−3493. (d) Hsu, D. P.; Warner, B. P.; Fisher, R. A.; Davis, W. M.; Buchwald, S. L. *Organometallics* **1994**, *13*, 5160−5162. (e) Kanji, A.; Meunier, P.; Gautheron, B.; Dubac, J.; Daran, J.-C. *J. Organomet. Chem.* **1993**, *454*, 51−58. (f) Cowley, A. H.; Gabbaï, F. P.; Decken, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1370−1372.

involve nucleophilic cleavage of E−E bonds. This method was pioneered by Hong and Boudjouk, who generated THF solutions of $M[C_4Ph_4Si^tBu]^-$ (M = Li, Na) by reductive cleavage of the Si−Si bond in $C_4Ph_4(^tBu)SiSi(^tBu)C_4Ph_4$.[5] In general, we have introduced crown ethers as metal-complexing agents that (1) accelerate formation of the anions by solubilizing and/or activating the nucleophilic reagent, (2) render the final products more crystalline and therefore more amenable to structural analysis, and (3) serve to weaken or cancel metal···anion interactions, so that the inherent electronic properties of the anions may be probed directly.

By NMR spectroscopy, it seems that the nature of the countercation has little effect on the electronic structure of the silolyl and germolyl anions (e.g., compare data for compounds **30**−**33** in Table 3). The ^{13}C chemical shifts for the ring carbons in these anions are very similar to the corresponding shifts for related siloles and germoles (Table 3). The ^{29}Si NMR shifts for the silolyl anions reported here are displaced upfield with respect to values for the corresponding neutral starting materials, and appear in the region expected for classical silyl anions of the type $RR'R''Si^-$.[24] Thus, the NMR data are consistent with significant localization of charge on the heavy group 14 element (Si or Ge) and a nonaromatic, bond-localized structure. Similar results for related anions have been reported for $Li[C_4Me_4GePh]$[7] and 1-lithio-1-methyl-1-silafluorenide.[27] This picture is supported by X-ray crystal structures that have been determined for three germolyl anions (**25**, **26**, and **28**) and the silolyl anion **33**, which reveal highly pyramidalized Ge and Si centers and π-bond localization that rivals that found in isolated dienes. Boudjouk and co-workers have recently determined the structure of a novel trisgermole dianion, $[Li(THF)(tmed)][C_4Et_4Ge(GeEt_4C_4)_2Li]$, which also displays pyramidal Ge centers and bond localization.[28]

Theoretical studies have also concluded that silolyl and germolyl anions should be pyramidal and nonaromatic.[3,4,8] We have reported RHF-level calculations on isolated $[C_4H_4ESiH_3]^-$ ions, which predict a high degree of localization in the π-systems for E = Si, Ge, and Sn, and give good agreement with the bond parameters for **25**. This is consistent with a high degree of p-character in the bonding orbitals for E, as might be expected.[25] Earlier theoretical studies have described the silolyl anion $[C_4H_4SiH]^-$ as being pyramidal at silicon, but delocalized in the ring to some degree.[3] Most recently, Goldfuss and Schleyer have come to the interesting conclusion that although $[C_4H_4SiH]^-$ would be pyramidal, it should possess roughly half of the aromaticity associated with $C_5H_5^-$. The planar $[C_4H_4SiH]^-$ ion was calculated to be destabilized relative to the ground state by only 3.8 kcal mol^{-1}, which corresponds to the inversion barrier for the silolyl anion. These calculations also indicate that Li^+ would coordinate to $[C_4H_4SiH]^-$ in an η^5 fashion, to give a structure that would be significantly more aromatic than the free ion.[4]

In light of the above results, it is somewhat surprising that the silolyl anions $M[C_4Ph_4Si^tBu]$ (M = Li, Na)[5] exhibit NMR parameters that are consistent with significant delocalization in the ring. Perhaps most significantly, the downfield ^{29}Si NMR shifts suggest delocalization of the negative charge throughout the ring. These results therefore stand in sharp contrast to what we observe for the silolyl anions prepared in our laboratory, which exhibit upfield shifts for the silicon atoms. The only silolyl anion to be structurally characterized, compound **33**, possesses a strongly pyramidalized silicon center. An important question that remains, therefore, is whether or not the ground state properties of silolyl and germolyl anions can be greatly influenced by the nature of substituents on the five-membered ring.

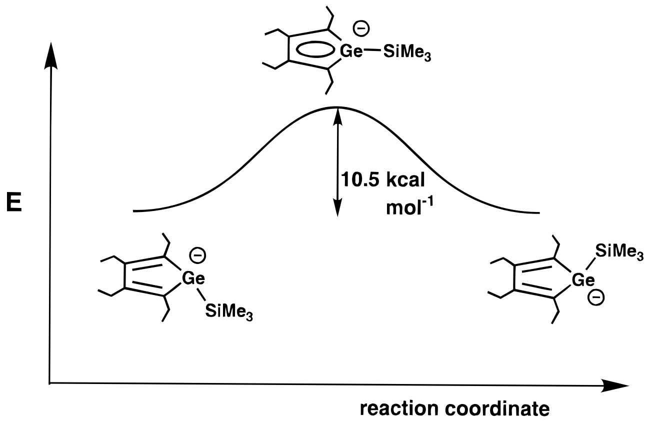

Figure 7. Reaction coordinate diagram for inversion in the complex $[Li(12\text{-}crown\text{-}4)_2][C_4Et_4GeSiMe_3]$ (**40**).

It is interesting to compare the results obtained for the free anions with those observed for the metal complexes $(\eta^5\text{-}C_5Me_5)Ru\{\eta^5\text{-}C_4Me_4ESi(SiMe_3)_3\}$ (E = Si[9] and Ge[10]). For the germolyl complex, the C_4Ge ring appears to be highly delocalized, as indicated by the summation of bond angles at Ge (358.1°) and the equivalent C−C distances of 1.42 Å. In addition, the germolyl ring carbons in this molecule have similar chemical shifts, at $\delta = 80.23$ and 87.32. Also, NMR parameters for the silolyl complex indicate significant delocalization in the C_4Si ring. Therefore coordination of a transition metal fragment induces considerable π-delocalization and apparent aromatic character for silolyl and germolyl rings.

The measured inversion barriers for compounds **38**−**41** provide energy differences between the pyramidal anions and their corresponding planar (possibly aromatic) structures (Figure 7). For the germolyl anions investigated, this barrier is approximately 10 kcal mol^{-1}, and the corresponding silolyl anions have inversion barriers that we estimate to be on the order of 7−8 kcal mol^{-1}. Thus, the observed barriers are significantly higher than the value of 4 kcal mol^{-1} predicted for $[C_4H_4SiH]^-$.[4] However, they are much lower than the estimated inversion barrier for SiH_3^- (26 kcal mol^{-1}),[29] and Lambert and Urdaneta-Perez have concluded that inversion barriers for $LiSiR_3$ and $LiGeR_3$ anions are greater than 24 kcal mol^{-1}.[30] Therefore the low barriers observed for **38**−**41** may be attributed to stability imparted to the transition state by delocalization of π-electron density in the ring. It should be noted, however, that the $-SiMe_3$ substituents in these anions may also play a role in lowering the barrier to inversion.[31] This possibility will be addressed in future experiments intended to broaden the database for such inversion barriers.

The difference in barriers between analogous silolyl and germolyl anions apparently reflects a slightly greater degree of delocalization in the silicon compounds. The barriers also seem to be influenced slightly by the nature of the countercation. Although the structures of the $K[C_4Et_4ESiMe_3]$ species in tetrahydrofuran solution are unknown, it seems possible that these derivatives possess some kind of potassium−anion interaction, as was observed in **28** and **33**. It is therefore tempting to speculate that a weak interaction of this kind may stabilize a delocalized transition state, as predicted by Goldfuss

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[27] Hong, J.-H.; Boudjouk, P.; Stoenescu, I. *Organometallics* **1996**, *15*, 2179−2181.

[28] Hong, J. H.; Pan, Y. L.; Boudjouk, P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 186−188.

[29] Eades, R. A.; Dixon, D. A. *J. Chem. Phys.* **1980**, *72*, 3309−3313.

[30] Lambert, J. B.; Urdaneta-Pérez, M. *J. Am. Chem. Soc.* **1978**, *100*, 157−162.

[31] (a) Apeloig, Y.; Godleski, S. A.; Heacock, D. J.; McKelvey, J. M. *Tetrahedron Lett.* **1981**, *22*, 3297−3300. (b) Godleski, S. A.; Heacock, D. J.; McKelvey, J. M. *Tetrahedron Lett.* **1981**, *23*, 4453−4456.

and Schleyer.[4] Clearly there is much more to be learned about the electronic structures of this type of anion, and how their electronic properties may be manipulated via changes in ring substituents and the nature of the cation. Future investigations will address these issues.

Experimental Section

All manipulations were conducted under an atmosphere of nitrogen or argon using standard Schlenk techniques or a Vacuum Atmospheres glovebox. Dry, deoxygenated solvents were employed for all manipulations (except chromatography). Olefin impurities were removed from pentanes by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, saturated $NaHCO_3$, and then $MgSO_4$. Removal of residual thiophenes from benzene and toluene was accomplished by washing each with concentrated H_2SO_4, saturated $NaHCO_3$, and then $MgSO_4$. Solvents were distilled from sodium benzophenone ketyl. The NMR solvents benzene-d_6 and toluene-d_8 were purified by vacuum distillation from Na/K alloy. Dichloromethane-d_2 was stirred over CaH_2 for 2 days, transferred by vacuum distillation onto P_2O_5, stirred for 2 h, and then vacuum-distilled for purification. The compounds LiMes,[32] $(THF)_3LiSi(SiMe_3)_3$,[33] KCH_2Ph,[34] and $(Et_2O)LiCH_2Ph$[34] were synthesized by literature methods. The reagents *n*-butyllithium (1.6 M in hexanes) and Cp_2ZrCl_2 were used as received. $GeCl_4$, $SiBr_4$, $ClSiMe_3$, and MeI were distilled before use, and $LiAlH_4$ was purified by extraction into diethyl ether, followed by removal of the ether by vacuum transfer. 12-Crown-4 and 15-crown-5 were distilled from P_2O_5, and 18-crown-6 was sublimed twice. Elemental analyses were performed by Desert Analytics or the College of Chemistry Microanalytical Laboratory at UC Berkeley. NMR spectra were recorded on GE QE-300 or Bruker AMX-300 instruments at 300 MHz (^{1}H), 75.5 MHz (^{13}C), 59.6 MHz (^{29}Si), or on a Bruker AMX-400 instrument at 400 MHz (^{1}H) and 100 MHz (^{13}C). Infrared spectra were recorded with a Perkin-Elmer 1330 spectrometer.

$C_4Me_4GeCl_2$ (1). A modification of the literature procedure[20] was followed. Cp_2ZrCl_2 (30.0 g, 102 mmol) in 250 mL of THF was cooled to −80 °C, and then 2-butyne (16.1 mL, 205 mmol) was added. A hexane solution of *n*-butyllithium (1.6 M, 128 mL, 205 mmol) was then added dropwise to the reaction flask over 90 min, and the solution was stirred for 15 min at −80 °C. The cold bath was removed, and stirring of the solution was continued for 3 h. The reaction mixture was then cooled to 0 °C, and $GeCl_4$ (19.3 mL, 195 mmol) was added over 2 min by syringe. After the reaction mixture was stirred for 12 h at room temperature, the volatiles were removed by vacuum transfer, and the resulting residue was extracted with pentane (4 × 50 mL). The combined pentane extracts were concentrated to 100 mL and cooled to −80 °C to yield the oily crystalline product which was pure by ^{1}H NMR spectroscopy. Sublimation gave colorless, non-oily crystals of the product in 60% yield. ^{1}H NMR (300 MHz, benzene-d_6): δ 1.31, 1.70 (s, 6 H, $C_4\mathit{Me}_4Ge$). ^{13}C{^{1}H} NMR (75.5 MHz, benzene-d_6): δ 12.49, 13.69 (s, $C_4\mathit{Me}_4Ge$), 124.58, 145.81 (s, C_4Me_4Ge).

$C_4Me_4SiBr_2$ (2). The literature procedure was followed.[20] The product was distilled (40−70 °C; 0.001 Torr), dissolved in 3 times its volume of pentane, and crystallized at −40 °C. The product was then sublimed (35 °C; 0.001 Torr) and isolated as light pink transparent crystals that contain 1−20% hexamethylbenzene. The yield was typically ca. 30%. ^{1}H NMR (400 MHz, benzene-d_6): δ 1.38, 1.70 (s, 6 H, $C_4\mathit{Me}_4Si$).

$C_4Et_4GeCl_2$ (3). The method described for **1** was followed. ^{1}H NMR (400 MHz, benzene-d_6): δ 0.70, 1.18 (t, 6 H, $CH_2\mathit{CH}_3$), 1.92, 2.22 (q, 4 H, CH_2CH_3). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 14.11, 14.76, 20.97, 21.97 (s, CH_2CH_3), 132.61, 149.81 (s, C_4Et_4Ge).

$Cp_2ZrC_4Et_4$. This compound was obtained in 70% yield by the method reported by Fagan for $Cp_2ZrC_4Me_4$.[20] Anal. Calcd for $C_{22}H_{30}Zr$: C, 68.50; H, 7.86. Found: C, 68.25; H, 7.80. ^{1}H NMR (400 MHz, benzene-d_6): δ 0.88, 1.00 (t, 6 H, $CH_2\mathit{CH}_3$), 2.21, 2.32 (q, 4 H, CH_2CH_3), 5.92 (s, 10 H, C_5H_5). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 14.52, 16.15, 21.54, 29.50 (s, CH_2CH_3), 109.84 (s, C_5H_5), 134.00, 191.02 (s, C_4Et_4Si).

$C_4Et_4I_2$. A modification of the literature procedure for $C_4Me_4I_2$ was followed,[21] using crystalline $Cp_2ZrC_4Et_4$. The product was purified by column chromatography on silica gel (200−400 mesh) with petroleum ether. The product was isolated as a slightly impure, light-sensitive, colorless oil in 70% yield. ^{1}H NMR (400 Mz, benzene-d_6): δ 1.00, 1.06 (t, 6 H, $CH_2\mathit{CH}_3$), 2.01, 2.19, 2.37, 2.46 (m, 2 H, CH_2CH_3). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 13.49, 13.99, 25.70, 34.81 (s, CH_2CH_3), 108.99, 149.39 (s, C_4Et_4Si).

$C_4Et_4SiCl_2$ (4). This procedure is a modification of the one used by West et al. to prepare $C_4Me_4SiCl_2$.[14] To a cold (−80 °C) diethyl ether (100 mL) solution of $C_4Et_4I_2$ (7.41 g, 14.4 mmol) was added a hexane solution of *n*-butyllithium (1.6 M, 18.9 mL, 30.3 mmol) which had been diluted with 100 mL of diethyl ether. The latter reagent was added slowly over 1 h. The reaction mixture was allowed to warm to room temperature (over 1 h), and was then stirred for an additional 20 min. After the reaction mixture was cooled to −110 °C with a liquid nitrogen/pentanes slurry, $SiCl_4$ (16.5 mL, 144 mmol) was added. The resulting mixture was stirred for 15 min before the cold bath was removed, and stirring was continued for 12 h. The volatiles were removed by vacuum transfer and then the product was extracted with pentane (4 × 50 mL). The pentane was evaporated from the combined extracts to give the product as a yellow oil. Distillation (45 °C; 0.001 Torr) gave a 75% yield of somewhat impure material. Anal. Calcd for $C_{12}H_{20}Cl_2Si$: C, 54.73; H, 7.67. Found: C, 51.08; H, 7.69. ^{1}H NMR (400 MHz, benzene-d_6): δ 0.75, 1.18 (t, 6 H, $CH_2\mathit{CH}_3$), 1.97, 2.21 (q, 4 H, CH_2CH_3). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 14.06, 14.64, 20.90, 20.92, (s, CH_2CH_3), 131.15, 155,76 (s, C_4Et_4Si).

$C_4Me_4Si(Br)Si(SiMe_3)$ (5). A solution of $(THF)_3LiSi(SiMe_3)_3$ (6.57 g, 15.5 mmol) in 50 mL of toluene was added to **2** (4.17 g, 15.5 mmol) in cold (0 °C) toluene (50 mL). The cold bath was removed after 5 min and the reaction solution was stirred for 90 min at room temperature. The volatiles were then removed by vacuum transfer, and the residue was extracted with pentane (3 × 40 mL). The combined pentane extracts were reduced to 60 mL and cooled (−80 °C) to give light pink crystals in 50% yield. Anal. Calcd for $C_{17}H_{39}BrSi_5$: C, 44.01; H, 8.49. Found: C, 42.20; H, 8.68. ^{1}H NMR (300 MHz, benzene-d_6): δ 0.32 (s, 27 H, $SiMe_3$), 1.61, 1.98 (s, 6 H, $C_4\mathit{Me}_4Si$). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 2.75 (s, $SiMe_3$), 14.04, 14.35 (s, $C_4\mathit{Me}_4Si$), 130.57, 149.61 (s, C_4Me_4Si). ^{29}Si{^{1}H} NMR (59.6 MHz, benzene-d_6): δ −130.82 (s, $\mathit{Si}(SiMe_3)_3$), −8.72 (s, $SiMe_3$), 8.21 (s, $C_4Me_4\mathit{Si}$).

$C_4Me_4Ge(Cl)Si(SiMe_3)_3$ (7). The method for **5** was followed, using **1** (0.998 g, 3.97 mmol) and $(THF)_3LiSi(SiMe_3)_3$ (1.68 g, 3.97 mmol), to give colorless crystalline product in 70% yield. Anal. Calcd for $C_{17}H_{39}ClGeSi_4$: C, 44.01; H, 8.49. Found: C, 44.26; H, 8.66. ^{1}H NMR (300 MHz, benzene-d_6): δ 0.32 (s, 27 H, $SiMe_3$), 1.59, 2.07 (s, 6 H, C_4Me_4Ge). ^{13}C{H} NMR (75.5 MHz, benzene-d_6): δ 2.42 (s, $SiMe_3$), 14.53, 15.47 (s, $C_4\mathit{Me}_4Ge$), 133.63, 146.02 (s, C_4Me_4Ge). Mp 159−161 °C.

$C_4Me_4Ge(Cl)Mes$ (8). A pressure bottle containing **1** (6.01 g, 23.88 mmol), LiMes (3.01 g, 23.88 mmol), and toluene (75 mL) was heated at 70 °C for 6 h, and then the volatile materials were removed by vacuum transfer. The white residue was extracted with pentane (4 × 40 mL), and the combined extracts were concentrated and cooled (−80 °C) to give the product as a colorless powder in 56% yield. Anal. Calcd for $C_{17}H_{23}ClGe$: C, 60.87; H, 6.92. Found: C, 56.15; H, 6.44. ^{1}H NMR (300 MHz, benzene-d_6): δ 1.57, 1.96 (s, 6 H, C_4Me_4Ge), 2.05 (s, 3 H, *p*-Me), 2.53 (s, 6 H, *o*-Me), 6.69 (s, 2 H, *m*-H). ^{13}C{H} NMR (100 MHz, benzene-d_6): δ 14.24, 14.80 (s, $C_4\mathit{Me}_4Ge$), 24.21 (s, *o*-Me), 20.94 (s, *p*-Me), 129.42, 130.61, 130.85, 140.04 (s, Ph), 143.77, 146.33 (s, C_4Me_4Ge).

$C_4Me_4Si(H)Si(SiMe_3)_3$ (9). A solution of **5** (4.58 g, 9.87 mmol) in 50 mL of THF was added to $LiAlH_4$ (0.370 g, 9.87 mmol) in 50 mL of cold (0 °C) THF. After stirring at 0 °C for 10 min, the cold bath was removed and the reaction solution was then stirred for an additional 90 min before the volatiles were removed by vacuum transfer. The product was extracted with pentane (4 × 40 mL) and the combined extracts were concentrated and cooled (−80 °C) to give the product as a colorless powder in 85% yield. Anal. Calcd for $C_{17}H_{40}Si_5$: C, 53.03; H, 10.49. Found: C, 52.87; H, 10.65. ^{1}H NMR (300 MHz; benzene-d_6): δ 0.30 (s, 27 H, $SiMe_3$), 1.75, 2.04 (s, 6 H, $C_4\mathit{Me}_4Si$), 4.79 (s, 1

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[32] Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1984**, *3*, 793−800.

[33] Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1−3.

[34] Schlosser, M.; Hartmann, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 508−509.

H, SiH). $^{13}C\{^1H\}$ NMR (75.5 MHz; benzene-d_6): δ 2.86 (s, $SiMe_3$), 14.77, 15.69 (s, C_4*Me*$_4$Si), 129.53, 150.94 (s, *C*$_4Me_4Si$). $^{29}Si\{^1H\}$ NMR (59.6 MHz; dichloromethane-d_2): δ −138.64 (s, *Si*$(SiMe_3)_3$), −32.68 (s, C_4Me_4*Si*), −8.90 (s, $SiMe_3$).

$C_4Me_4Si(H)Mes$ (10). A solution of **6** was generated from the reaction of **2** (1.60 g, 5.93 mmol) and MesLi (0.735 g, 5.93 mmol) in toluene (40 mL). After reaction at 65 °C for 14 h, the volatile materials were removed, and the resulting residue was dissolved in 50 mL of THF. This solution was then added to a cold (0 °C) solution of $LiAlH_4$ (0.225 g, 5.93 mmol) in 30 mL of THF. The reaction mixture was stirred at room temperature for 60 min, the volatiles were removed by vacuum transfer, and then the residue was extracted with pentane (3 × 40 mL). Evaporation of the pentane gave an oil which was purified by column chromatography on silica gel (200−400 mesh) with hexanes. The hexanes were removed by vacuum transfer and the product was dried under vacuum for 12 h. The silane was then crystallized from pentane at −80 °C as colorless crystals in 45% yield. Anal. Calcd for $C_{17}H_{24}Si$: C, 79.60; H, 9.45. Found: C, 79.71; H, 9.55. ^1H NMR (300 MHz, benzene-d_6): δ 1.75, 1.88 (s, 6 H, C_4*Me*$_4$Si), 2.10 (s, 3 H, *p*-Me), 2.44 (s, 6 H, *o*-Me), 5.29 (s, 1 H, SiH), 6.76 (s, 2 H, *m*-H). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6): δ 14.03, 14.44 (s, C_4*Me*$_4$Si), 21.16, 23.16 (s, *o*- and *p*-Me), 128.59, 128.92, 139.67, 146.07 (s, Ph), 129.28, 151.00 (s, *C*$_4Me_4Si$). $^{29}Si\{^1H\}$ NMR (59.6 MHz, dichloromethane-d_2): δ −27.57 (s, C_4Me_4*Si*).

$C_4Me_4Ge(H)Si(SiMe_3)_3$ (11). The method for **9** was followed, using **7** (3.68 g, 7.73 mmol) and $LiAlH_4$ (0.293 g, 7.73 mmol), to give the product as colorless crystals in 80% yield. Anal. Calcd for $C_{17}H_{40}GeSi_4$: C, 47.55; H, 9.41. Found: C, 46.95; H, 9.70. ^1H NMR (300 MHz, benzene-d_6): δ 0.29 (s, 27 H, $SiMe_3$), 1.77, 2.13 (s, 6 H, C_4Me_4Ge), 4.96 (s, 1 H, GeH). $^{13}C\{H\}$ NMR (75.5 MHz, dichloromethane-d_2): δ 2.46 (s, $SiMe_3$), 14.80, 17.36 (s, C_4*Me*$_4$Ge), 132.89, 146.45 (s, *C*$_4Me_4Ge$). $^{29}Si\{H\}$ NMR (59.6 MHz, dichloromethane-d_2): δ −127.62 (s, *Si*$(SiMe_3)_3$), −8.83 (s, $SiMe_3$).

$C_4Me_4Ge(H)Mes$ (12). The method for **9** was followed, with **8** (3.98 g, 11.9 mmol) and $LiAlH_4$ (0.450 g, 11.9 mmol), to give the product as a colorless powder in 73% yield. Anal. Calcd for $C_{17}H_{24}Ge$: C, 67.83; H, 8.05. Found: C, 68.04; H, 8.15. ^1H NMR (300 MHz, benzene-d_6): δ 1.76, 1.95 (s, 6 H, C_4Me_4Ge), 2.11 (s, 3 H, *p*-Me), 2.39 (s, 6 H, *o*-Me), 5.62 (s, 1 H, GeH), 6.76 (s, 2 H, *m*-Me). $^{13}C\{H\}$ NMR (75.5 MHz, benzene-d_6): δ 14.51, 15.90 (s, C_4*Me*$_4$Ge), 21.10 (s, *p*-Me), 23.41 (s, *o*-Me), 128.81, 129.92, 130.95, 138.76 (s, Ph), 144.69, 146.65 (s, *C*$_4Me_4Ge$).

$C_4Me_4Si(SiMe_3)_2$ (13). Compound **2** (0.533 g, 1.98 mmol) in 100 mL of THF was added to chunks of potassium (0.310 g, 7.92 mmol), and the resulting reaction solution was stirred for 10 days at room temperature. The initially clear, colorless solution slowly turned white and then ruby red as the potassium was consumed. The reaction solution was cooled to −80 °C and $ClSiMe_3$ (1.50 mL, 11.8 mmol) was added. The volatiles were removed and the product was extracted with pentane (4 × 30 mL). The pentane was removed from the combined extracts and the product was isolated as a slightly yellow oil in 75% yield. ^1H NMR (400 MHz, benzene-d_6): δ 0.19 (s, 18 H, $SiMe_3$), 1.84, 2.01 (s, 6 H, C_4*Me*$_4$Si). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ −0.34 (s, $SiMe_3$), 14.65, 15.38 (s, C_4*Me*$_4$Si), 130.99, 149.81 (s, *C*$_4Me_4Si$). $^{29}Si\{^1H\}$ NMR (59.6 MHz, benzene-d_6): δ −34.26 (s, C_4Me_4*Si*), −14.83 (s, $SiMe_3$).

$C_4Me_4Ge(SiMe_3)_2$ (14). The method for **13** was followed, using **1** (1.27 g, 5.04 mmol), potassium (0.808 g, 20.7 mmol) and $ClSiMe_3$ (9.00 mL, 70.8 mmol), to give the product as a slightly yellow oil in 75% yield. Anal. Calcd for $C_{14}H_{30}GeSi_2$: C, 51.39; H, 9.26. Found: C, 50.40; H, 8.98. ^1H NMR (400 MHz, benzene-d_6): δ 0.23 (s, 18 H, $SiMe_3$), 1.86, 2.11 (s, 6 H, C_4*Me*$_4$Ge). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 0.51 (s, $SiMe_3$), 14.71, 17.53 (s, C_4*Me*$_4$Ge), 134.86, 145.67 (s, *C*$_4Me_4Ge$). $^{29}Si\{^1H\}$ NMR (59.6 MHz, benzene-d_6): δ −7.55 (s, $SiMe_3$).

$C_4Me_4Si(SiMe_3)Si(SiMe_3)C_4Me_4$ (15). **2** (0.620 g, 2.30 mmol) in 50 mL of THF was added to chunks of potassium (0.270 g, 6.90 mmol), and the reaction solution was stirred for 10 days at room temperature. The initially clear colorless solution slowly turned white and then bright red as the potassium was consumed. Then the reaction solution was cooled to −80 °C and $ClSiMe_3$ (1.50 mL, 11.8 mmol) was added, and after 5 min the cold bath was removed and the reaction solution was stirred for 60 min longer. After removal of the volatiles, the residue was extracted with pentane (3 × 40 mL) and the combined pentane extracts were concentrated and cooled to −40 °C. The product was isolated as colorless crystals in 60% yield. Anal. Calcd for $C_{22}H_{42}Si_4$: C, 63.06; H, 10.12. Found: C, 62.89; H, 10.24. ^1H NMR (400 MHz, benzene-d_6): δ 0.13 (s, 18 H, $SiMe_3$), 1.87, 2.12 (s, 12 H, C_4*Me*$_4$Si). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ −0.61 (s, $SiMe_3$), 14.81, 15.74 (s, C_4*Me*$_4$Si), 131.83, 150.11 (s, *C*$_4Me_4Si$). $^{29}Si\{^1H\}$ NMR (59.6 MHz, benzene-d_6): δ −34.71 (s, C_4Me_4*Si*), −13.24 (s, $SiMe_3$).

$C_4Me_4Si(Me)Si(Me)C_4Me_4$ (16). The procedure for **15** was followed, using **2** (1.28 g, 4.76 mmol), potassium (0.558 g, 14.3 mmol), and MeI (1.50 mL, 24.0 mmol), to give the product as colorless crystals in 15% yield. Anal. Calcd for $C_{18}H_{30}Si_2$: C, 71.43; H, 10.01. Found: C, 69.78; H, 10.10. ^1H NMR (400 MHz, benzene-d_6): δ 0.28 (s, 6 H, SiMe), 1.78, 1.92 (s, 12 H, C_4*Me*$_4$Si). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ −8.06 (s, SiMe), 14.14, 14.24 (s, C_4*Me*$_4$Si), 131.25, 149.11 (s, *C*$_4Me_4Si$). $^{29}Si\{^1H\}$ NMR (59.6 MHz, benzene-d_6): δ −13.95 (s, C_4Me_4*Si*).

$C_4Me_4Ge(SiMe_3)Ge(SiMe_3)C_4Me_4$ (17). The procedure for **15** was followed, with **1** (1.21 g, 4.83 mmol), potassium (0.585 g, 14.9 mmol), and $ClSiMe_3$ (8.20 mL, 64.5 mmol), to give the product as colorless crystals in 33% yield. Anal. Calcd for $C_{22}H_{38}Ge_2Si_2$: C, 52.02; H, 8.35. Found: C, 51.69; H, 8.47. ^1H NMR (300 MHz, benzene-d_6): δ 0.19 (s, 9 H, $SiMe_3$), 1.87, 2.20 (s, 6 H, C_4Me_4Ge). $^{13}C\{H\}$ NMR (100 MHz, benzene-d_6): δ 0.12 (s, $SiMe_3$), 14.80, 17.58 (s, C_4*Me*$_4$Ge), 135.83, 145.47 (s, *C*$_4Me_4Ge$). $^{29}Si\{^1H\}$ NMR (59.6 MHz, benzene-d_6): δ −4.93 (s, $SiMe_3$).

$C_4Me_4Ge(Me)Ge(Me)C_4Me_4$ (18). The procedure for **15** was followed, with **1** (1.59 g, 6.32 mmol), potassium (0.741 g, 18.9 mmol), and MeI (1.50 mL, 24.0 mmol), to give the product as colorless crystals in 35% yield. Anal. Calcd for $C_{18}H_{30}Ge_2$: C, 55.20; H, 7.74. Found: C, 55.07; H, 7.80. ^1H NMR (400 MHz, benzene-d_6): δ 0.50 (s, 6 H, GeMe), 1.78, 2.03 (s, 12 H, C_4*Me*$_4$Ge). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ −6.27 (s, GeMe), 14.37, 15.89 (s, C_4*Me*$_4$Ge), 133.79, 145.22 (s, *C*$_4Me_4Ge$).

$C_4Et_4Si(SiMe_3)_2$ (19). The procedure for **13** was followed, using **4** (2.87 g, 10.9 mmol), potassium (1.73 g, 44.3 mmol), and $ClSiMe_3$ (6.93 mL, 54.7 mmol), to give the product as a yellow oil in 45% yield. Anal. Calcd for $C_{18}H_{38}Si_3$: C, 63.80; H, 11.33. Found: C, 64.04; H, 11.38. ^1H NMR (400 MHz, benzene-d_6): δ 0.22 (s, 18 H, $SiMe_3$), 1.00, 1.12 (t, 6 H, CH_2*CH*$_3$), 2.33, 2.42 (q, 4 H, *CH*$_2CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 0.10 (s, $SiMe_3$), 15.50, 17.21, 21.79, 23.29 (s, CH_2CH_3), 139.78, 155.56 (s, *C*$_4Et_4Si$). $^{29}Si\{^1H\}$ NMR (59.6 MHz, benzene-d_6): δ −37.50 (s, C_4Et_4*Si*), −14.78 (s, $SiMe_3$).

$C_4Et_4Ge(SiMe_3)_2$ (20). The procedure for **13** was followed, using **3** (1.52 g, 4.98 mmol), potassium (0.792 g, 20.2 mmol), and $ClSiMe_3$ (6.00 mL, 47.2 mmol), to give the product as a slightly yellow oil in 85% yield. Anal. Calcd for $C_{18}H_{38}GeSi_2$: C, 56.39; H, 10.01. Found: C, 56.38; H, 10.11. ^1H NMR (400 MHz, benzene-d_6): δ 0.26 (s, 18 H, $SiMe_3$), 1.03, 1.14 (t, 6 H, CH_2*CH*$_3$), 2.35, 2.49 (q, 4 H, *CH*$_2CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 0.77 (s, $SiMe_3$), 15.66, 17.59, 21.87, 25.06 (s, CH_2CH_3), 144.34, 151.18 (s, *C*$_4Et_4Ge$). $^{29}Si\{^1H\}$ NMR (59.6 MHz, benzene-d_6): δ −7.74 (s, $SiMe_3$).

[K(18-crown-6)]$_2$[C_4Me_4Si] (21). **2** (0.404 g, 1.50 mmol), 18-crown-6 (0.793 g, 3.00 mmol), small potassium chunks (0.240 g, 6.15 mmol), and 70 mL of THF were combined, and the reaction solution was stirred for 3 days. The product was crystallized from the red solution by pentane diffusion as red crystals in 5% yield. Anal. Calcd for $C_{32}H_{60}K_2O_{12}Si$: C, 51.71; H, 8.15. Found: C, 49.12; H, 7.94. ^1H NMR (400 MHz, benzene-d_6): δ 2.81, 3.27 (s, 6 H, C_4*Me*$_4$Si), 3.47 (br s, 24 H, 18-crown-6). Attempts to obtain acceptable elemental analysis data for this compound failed, perhaps due to its extreme air-sensitivity.

[K_4(18-crown-6)$_3$][C_4Me_4Ge]$_2$·THF (22·THF). **1** (0.748 g, 2.97 mmol), 18-crown-6 (1.57 g, 5.94 mmol), small potassium chunks (0.476 g, 12.2 mmol), and 80 mL of THF were stirred together for 3 days. The product was crystallized from the red solution by pentane diffusion as orange crystals in 5% yield. Anal. Calcd for $C_{56}H_{104}Ge_2K_4O_{19}$: C, 48.62; H, 7.59. Found: C, 45.20; H, 7.08. ^1H NMR (400 MHz, benzene-d_6): δ 2.80, 3.56 (s, 6 H, C_4*Me*$_4$Ge), 3.44 (br s, 24 H, 18-crown-6). Attempts to obtain acceptable elemental analysis data for this compound failed, perhaps due to its extreme air-sensitivity.

[K(18-crown-6)][$C_4Me_4GeSi(SiMe_3)_3$] (23). To **11** (0.202 g, 0.470 mmol), 18-crown-6 (0.124 g, 0.470 mmol), and $KN(SiMe_3)_2$ (0.094 g, 0.47 mmol) were added 50 mL of toluene, and the resulting reaction solution was stirred for 30 min at room temperature. The product was crystallized at −40 °C as yellow crystals in 45% yield. Anal. Calcd for $C_{29}H_{63}GeKO_6Si_4$: C, 47.59; H, 8.68. Found: C, 47.44; H, 8.57. ^{1}H NMR (300 MHz, benzene-d_6): δ 0.59 (s, 27 H, $SiMe_3$), 2.22, 2.62 (s, 6 H, $C_4\textit{Me}_4Ge$), 3.09 (s, 24 H, 18-crown-6). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, benzene-d_6): δ 3.98 (s, $SiMe_3$), 15.96, 20.46 (s, $C_4\textit{Me}_4Ge$), 69.91 (s, 18-crown-6), 137.13, 157.06 (s, $\textit{C}_4Me_4Ge$). $^{29}Si\{^{1}H\}$ NMR (59.6 MHz, benzene-d_6): δ −125.03 (s, $\textit{Si}(SiMe_3)_3$), −8.22 (s, $SiMe_3$).

[K(18-crown-6)][C_4Me_4GeMes] (24). To an NMR tube containing **12** (0.018 g, 0.061 mmol), 18-crown-6 (0.016 g, 0.061 mmol), and 0.35 mL of benzene-d_6 was added KCH_2Ph (0.0079 g, 0.061 mmol), then the NMR tube was shaken for 20 min. ^{1}H NMR (400 MHz, benzene-d_6): δ 2.27, 2.61 (s, 6 H, $C_4\textit{Me}_4Ge$), 2.33 (s, 3 H, *p*-Me), 2.96 (s, 6 H, *o*-Me), 3.15 (s, 24 H, 12-crown-4), 7.03 (s, 2 H, *m*-H). $^{13}C\{^{1}H\}$ NMR (100 MHz, benzene-d_6): δ 15.56, 19.23 (s, $C_4\textit{Me}_4Ge$), 21.39, 26.04 (s, *o*- and *p*-Me), 70.00 (s, 18-crown-6), 127.15, 133.00, 134.09, 152.05 (s, Mes), 145.94, 156.40 (s, $\textit{C}_4Me_4Ge$).

[Li(12-crown-4)$_2$][$C_4Me_4GeSi(SiMe_3)_3$] (25). To **11** (0.258 g, 0.602 mmol) and 12-crown-4 (0.194 mL, 1.20 mmol) in 25 mL of Et_2O was added a hexane solution of *n*-butyllithium (1.6 M, 0.396 mL, 0.632 mmol). Diffusion of pentane into the reaction solution yielded the product as yellow crystals in 42% yield. Anal. Calcd for $C_{33}H_{71}GeLiO_8Si_4$: C, 50.30; H, 9.10. Found: C, 50.22; H, 9.10. ^{1}H NMR (300 MHz, benzene-d_6): δ 0.62 (s, 27 H, $SiMe_3$), 2.26, 2.69 (s, 6 H, $C_4\textit{Me}_4Ge$), 3.18 (s, 32 H, 12-crown-4). $^{13}C\{^{1}H\}$ NMR (100 MHz, benzene-d_6; THF-d_0): δ 3.77 (s, $SiMe_3$), 15.59, 20.30 (s, $C_4\textit{Me}_4Ge$), 69.19 (s, 12-crown-4), 136.95, 157.03 (s, $\textit{C}_4Me_4Ge$). $^{29}Si\{^{1}H\}$ NMR (59.6 MHz, benzene-d_6): δ −125.57 (s, $\textit{Si}(SiMe_3)_3$), −8.43 (s, $SiMe_3$).

[Li(12-crown-4)$_2$][C_4Me_4GeMes] (26). The procedure for **25** was followed, with **12** (0.204 g, 0.677 mmol), 12-crown-4 (0.219 mL, 1.35 mmol), and *n*-butyllithium (1.6 M, 0.440 mL, 0.712 mmol), to yield the product as yellow crystals in 35% yield. Anal. Calcd for $C_{33}H_{55}GeLiO_8$: C, 60.10; H, 8.42. Found: C, 60.01; H, 8.47. ^{1}H NMR (300 MHz, benzene-d_6): δ 2.29, 2.60 (s, 6 H, $C_4\textit{Me}_4Ge$), 2.31 (s, 3 H, *p*-Me), 2.92 (s, 6 H, *o*-Me), 3.20 (s, 32 H, 12-crown-4), 7.04 (s, 2 H, *m*-H). $^{13}C\{^{1}H\}$ NMR (100 MHz, benzene-d_6, THF-d_0): δ 15.12, 18.83 (s, $C_4\textit{Me}_4Ge$), 21.14, 25.67 (s, *o*- and *p*-Me), 69.44 (s, 12-crown-4), 126.71, 132.60, 133.84, 152.13 (s, Mes), 145.49, 155.21 (s, $\textit{C}_4Me_4Ge$).

Li[$C_4Me_4GeSi(SiMe_3)_3$] (27). The procedure for **25** was followed, with **11** (0.35 g, 0.81 mmol) and *n*-butyllithium (1.6 M in hexanes, 0.53 mL, 0.85 mmol), to yield the product as yellow crystals in 20% yield. Anal. Calcd for $C_{17}H_{39}GeLiSi_4$: C, 46.89; H, 9.04. Found: C, 47.22; H, 9.51. ^{1}H NMR (400 MHz, THF-d_8): δ 0.09 (s, 27 H, $SiMe_3$), 1.77, 2.16 (s, 6 H, $C_4\textit{Me}_4Ge$). $^{13}C\{^{1}H\}$ NMR (100 MHz, THF-d_8): δ 6.50 (s, $SiMe_3$), 18.11, 22.78 (s, $C_4\textit{Me}_4Ge$), 141.29, 156.90 (s, $\textit{C}_4Me_4Ge$).

[Na(15-crown-5)][C_4Me_4GeMe] (28). A solution of **18** (0.212 g, 0.540 mmol) and 15-crown-5 (0.238 g, 1.08 mmol) in 10 mL of toluene was added to a sodium dispersion (0.038 g, 1.62 mmol) in 5 mL of toluene. The reaction solution was stirred for 4 days at room temperature, and then the product was extracted with toluene (5 × 15 mL) and the extracts were combined, concentrated, and cooled to −40 °C. The product formed as yellow crystals in 40% yield. Anal. Calcd for $C_{19}H_{35}GeNaO_5$: C, 51.97; H, 8.05. Found: C, 51.62; H, 7.82. ^{1}H NMR (400 MHz, benzene-d_6): δ 0.95 (s, 3 H, SiMe), 2.27, 2.67 (s, 6 H, $C_4\textit{Me}_4Si$), 3.17 (s, 20 H, 15-crown-5). $^{13}C\{^{1}H\}$ NMR (100 MHz, benzene-d_6): δ 0.36 (s, GeMe), 15.30, 18.64 (s, $C_4\textit{Me}_4Ge$), 69.82 (s, 15-crown-5), 136.10, 156.89 (s, $\textit{C}_4Me_4Ge$).

[K(18-crown-6)][C_4Me_4GeMe] (29). To an NMR tube containing **18** (0.021 g, 0.053 mmol), 18-crown-6 (0.014 g, 0.058 mmol), and 0.35 mL of benzene-d_6 was added KCH_2Ph (0.069 g, 0.058 mmol), then the NMR tube was shaken for 20 min. For **29**: ^{1}H NMR (400 MHz, benzene-d_6): δ 1.01 (s, 3 H, GeMe), 2.25, 2.69 (s, 6 H, $C_4\textit{Me}_4Ge$), 3.16 (s, 24 H, 18-crown-6). $^{13}C\{^{1}H\}$ NMR (100 MHz, benzene-d_6): δ 0.96 (s, GeMe), 15.36, 18.92 (s, $C_4\textit{Me}_4Ge$), 69.99 (s, 18-crown-6), 145.83, 159.96 (s, $\textit{C}_4Me_4Ge$). For $C_4Me_4Ge(Me)CH_2Ph$: ^{1}H NMR (400 MHz, benzene-d_6): δ 0.25 (s, 3 H, GeMe), 1.71, 1.82 (s, 6 H, $C_4\textit{Me}_4Ge$), 2.32 (s, 2 H, $\textit{CH}_2Ph$), 6.98−7.11 (m, 5 H, Ph). $^{13}C\{^{1}H\}$ NMR (100 MHz, benzene-d_6): δ −7.21 (s, GeMe), 14.07, 15.57 (s, $C_4\textit{Me}_4Ge$), 23.35 (s, $\textit{CH}_2Ph$), 124.44, 128.06, 128.46, 140.87 (s, Ph), 131.31, 135.26 (s, $\textit{C}_4Me_4Ge$).

Li[$C_4Me_4SiSiMe_3$] (30). To an NMR tube containing **13** (0.0408 g, 0.144 mmol) in 0.35 mL of THF-d_8 was added $(Et_2O)LiCH_2Ph$ (0.0260 g, 0.151 mmol), then the tube was shaken for 2 min. ^{1}H NMR (300 MHz, THF-d_8): δ −0.29 (s, 9 H, $SiMe_3$), 1.83, 2.02 (s, 6 H, C_4Me_4Si). $^{13}C\{^{1}H\}$ NMR (100 MHz, THF-d_8): δ 1.55 (s, $SiMe_3$), 14.78, 16.91 (s, $C_4\textit{Me}_4Si$), 138.66, 146.38 (s, $\textit{C}_4Me_4Si$). $^{29}Si\{^{1}H\}$ NMR (59.6 MHz, THF-d_8): δ −45.38 ($C_4Me_4\textit{Si}$), −12.47 ($SiMe_3$).

K[$C_4Me_4SiSiMe_3$] (31). To an NMR tube containing **13** (0.026 g, 0.094 mmol) in 0.35 mL of THF-d_8 was added KCH_2Ph (0.013 g, 0.098 mmol), then the tube was shaken for 2 min. ^{1}H NMR (400 MHz, THF-d_8): δ −0.03 (s, 9 H, $SiMe_3$), 1.81, 2.09 (s, 6 H, C_4Me_4Si). $^{13}C\{^{1}H\}$ NMR (100 MHz, THF-d_8): δ 1.90 (s, $SiMe_3$), 14.84, 17.72 (s, $C_4\textit{Me}_4Si$), 136.23, 148.97 (s, $\textit{C}_4Me_4Si$). $^{29}Si\{^{1}H\}$ NMR (59.6 MHz, THF-d_8): δ −42.70 ($C_4Me_4\textit{Si}$), −12.44 ($SiMe_3$).

[Li(12-crown-4)$_2$][$C_4Me_4SiSiMe_3$] (32). To an NMR tube containing **13** (0.0291 g, 0.103 mmol) and 12-crown-4 (33.3 μL, 0.206 mmol) in 0.35 mL of benzene-d_6 was added $(Et_2O)LiCH_2Ph$ (0.0177 g, 0.103 mmol), then the tube was shaken for 2 min. ^{1}H NMR (400 MHz, benzene-d_6): δ −0.49 (s, 9 H, $SiMe_3$), 2.30, 2.63 (s, 6 H, C_4Me_4Si), 3.37 (s, 32 H, 12-crown-4). $^{13}C\{^{1}H\}$ NMR (100 MHz, benzene-d_6): δ 2.74 (s, $SiMe_3$), 14.42, 18.35 (s, $C_4\textit{Me}_4Si$), 68.82 (s, 12-crown-4), 135.78, 148.62 (s, $\textit{C}_4Me_4Si$). $^{29}Si\{^{1}H\}$ NMR (59.6 MHz, benzene-d_6): δ −43.96 ($C_4Me_4\textit{Si}$), −11.68 ($SiMe_3$).

[K(18-crown-6)][$C_4Me_4SiSiMe_3$] (33). A toluene (10 mL) solution of **13** (0.465 g, 1.64 mmol) and 18-crown-6 (0.435 g, 1.64 mmol) was added to KCH_2Ph (0.224 g, 1.72 mmol) in 5 mL of toluene, and the resulting solution was stirred for 30 min at room temperature. Cooling to −40 °C produced orange-yellow crystals of the product in 20% yield. Anal. Calcd for $C_{23}H_{45}KO_6Si_2$: C, 53.85; H, 8.86. Found: C, 54.13; H, 8.94. ^{1}H NMR (400 MHz, benzene-d_6): δ 0.57 (s, 9 H, $SiMe_3$), 2.34, 2.67 (s, 6 H, $C_4\textit{Me}_4Si$), 3.20 (s, 24 H, 18-crown-6). $^{13}C\{^{1}H\}$ NMR (100 MHz, benzene-d_6): δ 2.50 (s, $SiMe_3$), 15.55, 18.34 (s, $C_4\textit{Me}_4Si$), 70.05 (s, 18-crown-6), 135.76, 149.60 (s, $\textit{C}_4Me_4Si$). $^{29}Si\{^{1}H\}$ NMR (59.6 MHz, benzene-d_6): δ −41.52 (s, $C_4Me_4\textit{Si}$), −11.00 (s, $SiMe_3$).

K[$C_4Me_4GeSiMe_3$] (34). To an NMR tube containing **14** (0.029 g, 0.090 mmol) in 0.35 mL of THF-d_8 was added KCH_2Ph (0.012 g, 0.095 mmol), then the tube was shaken for 1 min. ^{1}H NMR (400 MHz, THF-d_8): δ −0.02 (s, 9 H, $SiMe_3$), 1.87, 2.06 (s, 6 H, $C_4\textit{Me}_4Ge$). $^{13}C\{^{1}H\}$ NMR (100 MHz, THF-d_8): δ 2.03 (s, $SiMe_3$), 15.16, 19.42 (s, $C_4\textit{Me}_4Ge$), 141.10, 157.40 (s, $\textit{C}_4Me_4Ge$).

[K(18-crown-6)][$C_4Me_4GeSiMe_3$] (35). A mixture of compound **14** (0.203 g, 0.620 mmol) and 18-crown-6 (0.164 g, 0.620 mmol) in 10 mL of toluene was added to KCH_2Ph (0.085 g, 0.65 mmol) in 5 mL of toluene, and the reaction solution was stirred for 30 min at room temperature. The reaction solution was cooled to −40 °C to obtain the product as yellow crystals in 30% yield. Anal. Calcd for $C_{23}H_{45}GeKO_6Si$: C, 49.55; H, 8.15. Found: C, 49.55; H, 8.01. ^{1}H NMR (400 MHz, benzene-d_6): δ 0.54 (s, 9 H, $SiMe_3$), 2.26, 2.67 (s, 6 H, $C_4\textit{Me}_4Ge$), 3.19 (s, 24 H, 18-crown-6). $^{13}C\{^{1}H\}$ NMR (100 MHz, benzene-d_6): δ 2.49 (s, $SiMe_3$), 15.86, 20.06 (s, $C_4\textit{Me}_4Ge$), 70.07 (s, 18-crown-6), 136.72, 158.56 (s, $\textit{C}_4Me_4Ge$). $^{29}Si\{^{1}H\}$ NMR (59.6 MHz, benzene-d_6): δ −3.86 (s, $SiMe_3$).

[K(18-crown-6)][$C_4Me_4Si(SiMe_3)C_4MeSi$] (36). To an NMR tube containing **15** (0.0202 g, 0.048 mmol), 18-crown-6 (0.0127 g, 0.048 mmol), and 0.35 mL of benzene-d_6 was added KCH_2Ph (0.0063 g, 0.048 mmol), then the tube was shaken for 20 min. ^{1}H NMR (400 MHz, benzene-d_6): δ 0.44 (s, 9H, $SiMe_3$), 2.08, 2.39 (s, 6 H, $C_4\textit{Me}_4SiSiMe_3$), 2.33, 2.65 (s, 6 H, $C_4\textit{Me}_4Si^{-}K^{+}$), 3.24 (s, 24 H, 18-crown-6). $^{13}C\{^{1}H\}$ NMR (100 MHz, benzene-d_6): δ 0.60 (s, $SiMe_3$), 14.60, 16.45 (s, $C_4\textit{Me}_4SiSiMe_3$), 15.71, 18.43 (s, $C_4\textit{Me}_4Si^{-}K^{+}$), 69.95 (s, 18-crown-6), 137.23, 143.80 (s, $\textit{C}_4Me_4SiSiMe_3$), 138.49, 149.08 (s, $\textit{C}_4Me_4Si^{-}K^{+}$). $^{29}Si\{^{1}H\}$ NMR (59.6 MHz, benzene-d_6): δ −53.43 (s, $C_4Me_4\textit{Si}^{-}K^{+}$), −25.47 (s, $C_4Me_4\textit{Si}SiMe_3$), −13.49 (s, $SiMe_3$).

[K(18-crown-6)][$C_4Me_4Ge(SiMe_3)C_4Me_4Ge$] (37). A mixture of **17** (0.206 g, 0.405 mmol) and 18-crown-6 (0.107 g, 0.405 mmol) in 10 mL of toluene was added to KCH_2Ph (0.555 g, 0.426 mmol) in 5 mL of toluene, and the reaction solution was stirred at room temperature for 30 min. The solution was then cooled to −40 °C to obtain the product as yellow crystals in 20% yield. Anal. Calcd for $C_{31}H_{57}Ge_2KO_6Si$: C, 50.43; H, 7.80. Found: C, 50.59; H, 7.49. ^{1}H NMR (400 MHz, benzene-d_6): δ 0.38 (s, 9 H, $SiMe_3$), 2.04, 2.45 (s, 6 H, $C_4\textit{Me}_4GeSiMe_3$), 2.25, 2.69 (s, 6 H, $C_4\textit{Me}_4Ge^{-}K^{+}$), 3.16 (s, 24 H, 18-crown-

6). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 1.08 (s, $SiMe_3$), 14.82, 18.41 (s, $C_4\mathit{Me}_4GeSiMe_3$), 15.96, 20.01 (s, $C_4\mathit{Me}_4Ge^-K^+$), 70.16 (s, 18-crown-6), 138.46, 143.92 (s, $\mathit{C}_4Me_4GeSiMe_3$), 140.63, 156.43 (s, $\mathit{C}_4Me_4Ge^-K^+$). $^{29}Si\{^1H\}$ NMR (59.6 MHz, benzene-d_6): δ −5.99 (s, $SiMe_3$).

[Li(12-crown-4)$_2$][C$_4$Et$_4$SiSiMe$_3$] (38). To an NMR tube containing **19** (0.0407 g, 0.120 mmol) and 12-crown-4 (38.8 μL, 0.240 mmol) in 0.35 mL of THF-d_8 was added $(Et_2O)LiCH_2Ph$ (0.0217 g, 0.126 mmol), then the tube was shaken for 2 min. ^1H NMR (400 MHz, THF-d_8): δ −0.02 (s, 9 H, $SiMe_3$), 0.99, 1.12 (t, 6 H, $CH_2\mathit{CH}_3$), 2.36, 2.52 (q, 4 H, CH_2CH_3), 3.63 (s, 32 H, 12-crown-4). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8): δ 2.73 (s, $SiMe_3$), 17.20, 20.03, 22.47, 26.20 (s, $C_4\mathit{Et}_4Si$), 70.70 (s, 12-crown-4), 141.96, 158.27 (s, C_4Et_4Si). $^{29}Si\{^1H\}$ NMR (59.6 MHz, THF-d_8): δ −53.12 ($C_4Me_4\mathit{Si}$), −14.27 ($SiMe_3$).

K[C$_4$Et$_4$SiSiMe$_3$] (39). To an NMR tube containing **19** (0.026 g, 0.076 mmol) in 0.35 mL of THF-d_8 was added KCH_2Ph (0.010 g, 0.079 mmol), then the tube was shaken for 2 min. ^1H NMR (400 MHz, THF-d_8): δ −0.02 (s, 9 H, $SiMe_3$), 0.98, 1.14 (t, 6 H, $CH_2\mathit{CH}_3$), 2.40, 2.55 (q, 4 H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8): δ 2.56 (s, $SiMe_3$), 16.99, 20.56, 22.26, 25.90 (s, $C_4\mathit{Et}_4Si$), 140.88, 158.42 (s, C_4Et_4Si). $^{29}Si\{^1H\}$ NMR (59.6 MHz, THF-d_8): δ −47.38 ($C_4Me_4\mathit{Si}$), −14.22 ($SiMe_3$).

[Li(12-crown-4)$_2$][C$_4$Et$_4$GeSiMe$_3$] (40). To an NMR tube containing **20** (0.0517 g, 0.135 mmol) and 12-crown-4 (43.7 μL, 0.270 mmol) in 0.35 mL of THF-d_8 was added $(Et_2O)LiCH_2Ph$ (0.0244 g, 0.142 mmol), then the tube was shaken for 2 min. ^1H NMR (400 MHz, THF-d_8): δ −0.02 (s, 9 H, $SiMe_3$), 0.97, 1.11 (t, 6 H, $CH_2\mathit{CH}_3$), 2.31, 2.54 (q, 4 H, CH_2CH_3), 3.68 (s, 32 H, 12-crown-4). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8): δ 2.97 (s, $SiMe_3$), 16.96, 19.84, 22.59, 27.74 (s, CH_2CH_3), 69.64 (s, 12-crown-4), 142.45, 166.84 (C_4Et_4Ge).

K[C$_4$Et$_4$GeSiMe$_3$] (41). To an NMR tube containing **20** (0.0543 g, 0.142 mmol) in 0.35 mL of THF-d_8 was added KCH_2Ph (0.0194 g, 0.149 mmol), then the tube was shaken for 2 min. ^1H NMR (400 MHz, THF-d_8): δ −0.03 (s, 9 H, $SiMe_3$), 0.97, 1.14 (t, 6 H, $CH_2\mathit{CH}_3$), 2.34, 2.55 (q, 4 H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8): δ 2.52 (s, $SiMe_3$), 16.79, 20.06, 22.42, 27.54 (s, CH_2CH_3), 141.05, 168.62 (s, C_4Et_4Ge).

Crystallographic Structure Determinations. Crystallographic data are collected in Table 1. All data crystals were sealed in Lindemann capillary tubes under nitrogen. The Laue symmetry of each was photographically determined and the space groups assigned unambiguously for **26** and **28** from systematic absences. For **22**·THF and **33** the centrosymmetric alternatives were chosen initially based on the *E* statistics; the results of subsequent refinement supported these choses. ψ-scan data indicated that no corrections for absorption were required. All structures were solved by direct methods, refined with anisotropic thermal parameters (except as noted), and include idealized hydrogen-atom contributions. In **22**·THF, a partially occupied, multiply positioned molecule of disordered THF was found to accompany the asymmetric unit. The disorder was modeled as two concentric orientations in different planes with one atom in common with a combined occupancy of 0.5. The atoms of the solvent molecule were isotropically refined and hydrogen atoms were ignored. All computations used SHELXTL software (version 4.2 for **26**, and version 5.1 for the others; G. Sheldrick, Siemens XRD, Madison, WI.).

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Supporting Information Available: Tables of crystal, data collection, and refinement parameters, bond distances and angles, and anisotropic displacement parameters (29 pages). See any current masthead page for ordering and Internet access instructions.

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