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Synthesis and Reactivity of 1,2-Bis(chlorodimethylgermyl)carborane and 1,2-Bis(bromodimethylstannyl)carborane

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The 1,2-bis(chlorogermyl)- (**1**) and 1,2-bis(bromostannyl)carborane (**2**) have been prepared by the reaction of dilithio-*o*-carborane with Me_2GeCl_2 and Me_2SnBr_2, respectively. Compounds **1** and **2** are found to be good precursors for the synthesis of a variety of cyclization compounds. The Wurtz-type coupling reaction of **1** and **2** using sodium metal afforded the four-membered digerma compound **3** and five-membered tristanna compound **4**, respectively. The salt elimination reactions of **1** and **2** using Li_2N^tBu and $Li_2PC_6H_5$ afforded the cyclic products $(Me_2)\overline{M(C_2B_{10}H_{10})\text{-}}$ $\overline{M(Me_2)E}$ (**5**, M = Ge, E = N^tBu; **6**, M = Sn, E = N^tBu; **7**, M = Ge, E = PC_6H_5; **8**, M = Sn, E = PC_6H_5). The 1,2-bis(dimethylgermyl)carborane **9** and 1,2-bis(dimethylstannyl)carborane **10** were prepared by the reaction of **1** and **2** with sodium cyanoborohydride. The reactions of **9** and **10** with $Pd(PPh_3)_4$ afforded the bis(germyl)palladium **12** and bis(stannyl)palladium **13** complexes, respectively.

Introduction

Organogermanium and organotin compounds have attracted considerable interest because of their potential applications such as electric conduction, nonlinear optics, and photoresists.[1] However, their chemistry is not well developed as compared with organosilicon chemistry due to the synthetic limitations available for these compounds. For example, the double-silylation reaction has been well documented.[2] On the other hand, the double-germylation and -stannylation reactions have sporadically appeared.[3] Recently, we[4] reported the double-silylation reactions of a P_2PtSi_2 complex using 1,2-bis(dimethylsilyl)carborane. Therefore, it was of interest to investigate the possibility of synthesizing the 1,2-bis(dimethylgermyl)carborane and 1,2-bis(dimethylstannyl)carborane for the double-germylation and -stannylation reactions. In fact, we could not prepare such compounds by a one-step reaction due to the inaccessibility of the starting materials. Previously, we[5] found that sodium cyanoborohydride was effective in the conversion of the tin bromide to the tin hydride. This fact prompted us to synthesize the 1,2-bis(halogermyl)- (**1**) and 1,2-bis(halostannyl)carborane (**2**) following the synthetic procedure of 1,2-bis(chlorosilyl)carboranes prepared by Heying et al.[6] Compounds **1** and **2** are also found to be good precursors for the synthesis of a variety of cyclization compounds. In this paper, we describe (i) the facile synthesis of 1,2-bis(chlorogermyl)- (**1**) and 1,2-bis(bromostannyl)carborane (**2**); (ii) the Wurtz-type coupling reaction of **1** and **2** with sodium metal; (iii) the isolation of the 1,2-bis(digermylazanyl)- (**5**) and 1,2-bis-

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(1) (a) Ban, H.; Deguchi, K.; Tanaka, A. *J. Appl. Polym. Sci*. **1989**, *37*, 1589. (b) Baumert, J. C.; Bjorklund, G. C.; Jundt, D. H.; Jurich, M. C.; Looser, H.; Miller, R. D.; Twieg, R. *J. Appl. Phys. Lett*. **1988**, *53*, 1147.

(2) (a) Beletskaya, I.; Moberg, C. *Chem. Rev*. **1999**, *99*, 3435. (b) Sharma, H. K.; Pannell, K. H. *Chem. Rev*. **1995**, *95*, 1351.

(3) (a) Herberhold, M.; Steffl, U.; Milius, W.; Wrackmeyer, B. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 1508. (b) Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem*. **1983**, *241*, C45. (c) Mitchell, T. N.; Schneider, U. *J. Organomet. Chem*. **1991**, *407*, 319. (d) Piers, E.; Skerlj, R. T. *J. Chem. Soc., Chem. Commun*. **1986**, 626. (e) Casson, S.; Kocienski, P.; Reid, G.; Smith, N.; Street, J. M.; Webster, M. *Synthesis* **1994**, 1301. (f) Tsuji, Y.; Kakehi, T.*; J. Chem. Soc., Chem. Commun*. **1992**, 1000. (g) Mitchell, T. N.; Killing, A. A. H.; Rutschow, D. *J. Organomet. Chem*. **1986**, *304*, 257. (h) Tsumuraya, T.; Ando, W. *Organometallics* **1989**, *8*, 2286. (i) Komoriya, H.; Kako, M.; Nakadaira, Y.; Mochida, K. *Organometallics* **1996**, *15*, 2014. (j) Hayashi, T.; Yamashita, H.; Sakakura, T.; Uchimaru, Y.; Tanaka, M. *Chem. Lett*. **1991**, 245. (k) Mochida, K.; Hodota, C.; Yamashita, H.; Tanaka, M. *Chem. Lett*. **1992**, 1635. (l) Komoriya, H.; Kako, M.; Nakadaira, Y.; Mochida, K. *J. Organomet. Chem*. **2000**, *611*, 420. (m) Barrau, J.; Rima, G.; Cassano, V.; Satgé, J. *Organometallics* **1995**, *14*, 5700.

(4) (a) Kang, Y.; Kang, S. O.; Ko, J. *Organometallics* **2000**, *19*, 1216 (b) Kang, Y.; Lee, J.; Kong, Y. K.; Kang, S. O.; Ko, J. *Chem. Commun*. **1998**, 2343.

(5) Lee, T.; Lee, S. W.; Jang, H. G.; Kang, S. O.; Ko, J. *Organometallics* **2001**, *20*, 741.

(6) Papetti, S.; Heying, T. L. *Inorg. Chem*. **1963**, *2*, 1405.

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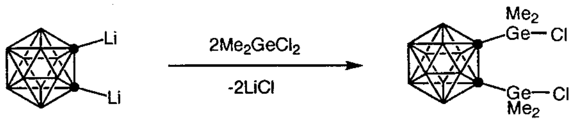
(distannazanyl)carborane (**6**) by the salt elimination reaction; (iv) the synthesis of 1,2-bis(2-phenyl-1,1,3,3-tetramethyldigermylphosphide)carborane (**7**) by the reaction of **1** and Li_2PPh; and (v) the synthesis of the bis(germyl)- (**12**) and bis(stannyl)palladium (**13**) complexes by the oxidative addition reaction of **9** and **10** with a zerovalent palladium compound.

Results and Discussion

Synthesis of 1,2-Bis(chlorogermyl)carborane (1) and 1,2-Bis(bromostannyl)carborane (2). Previously, the synthesis of 1,2-bis(chlorosilyl)carborane was carried out by salt elimination reaction of 1,2-$Li_2C_2B_{10}H_{10}$ and 2 equiv of Me_2SiCl_2 by Heying.[6] The utilization of the same preparative procedures has proven satisfactory for the preparation of 1,2-bis(chlorogermyl)carborane (**1**) and 1,2-bis(bromostannyl)carborane (**2**), which were found to be good precursors for the synthesis of cyclization compounds. Thus, compound **1** was prepared as a colorless solid by the reaction of 1,2-$Li_2C_2B_{10}H_{10}$ with 2 equiv of Me_2GeCl_2 according to eq 1. Compound **1** is soluble in toluene and THF. The ^{1}H and ^{13}C NMR, mass spectrometry, and elemental analysis for **1** support the proposed structure. The initial indication of the formulation for **1** stemmed from the observation of a parent ion in the mass spectrum at *m*/*z* 418. In the ^{1}H and ^{13}C NMR spectra of **1**, the methyl group on Ge gives rise to one signal at 0.55 and 6.44 ppm, respectively, which is significantly upfield shifted from that of Me_2GeCl_2 (1.22 and 15.34 ppm). A similar reaction of 1,2-$Li_2C_2B_{10}H_{10}$ with Me_2SnBr_2 gave the 1,2-bis(bromostannyl)carborane (**2**) (eq 2). The ^{1}H NMR signal of **2** ascribable to the $SnMe_2$ moiety was observed at 0.16 ppm. In particular, the ^{119}Sn NMR signal had clearly shifted from 70 ppm for Me_2SnBr_2 to 103 ppm for **2**.



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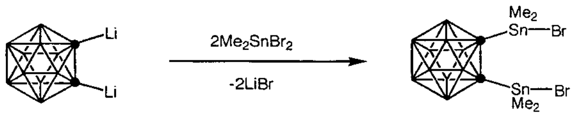
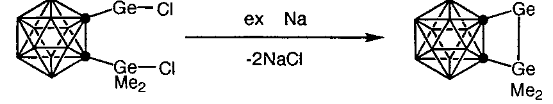
(1)



2

(2)

Synthesis of the 3,4-Carboranylene-1,1,2,2-tetramethyl-1,2-digermacyclobutane (3). The Wurtz-type coupling reaction of **1** using sodium metal afforded the strained four-membered digerma compound **3** (eq 3). Compound **3** is readily soluble in CH_2Cl_2 and toluene and is relatively stable in air. The identity of compound **3** was confirmed by its ^{1}H and ^{13}C NMR, mass spectrum, and elemental analysis. The structure of **3** was determined from its X-ray crystal structure. The ORTEP view of **3** is shown in Figure 1. The C(1)−C(1A) bond length (1.698(5) Å) is typical for *o*-carborane (1.63−1.72 Å).[7] The Ge−Ge bond distance (2.4416(6) Å) is within known values of Ge−Ge bond lengths in analogous compounds.[8] The small Ge(A)−Ge−C(1) bond angle (79.35(7)°) demonstrates that **3** is highly strained. Such a geometry was observed in a similar silicon compound.[9]



1 **3**

(3)

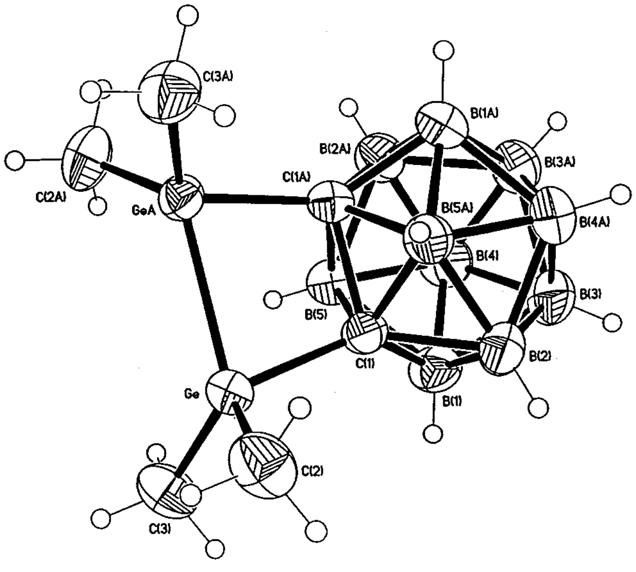
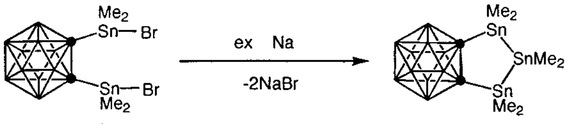


Figure 1. X-ray cystal structure of **3** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Ge−Ge(A) 2.4416(6), Ge−C(1) 2.012(3), C(1)−C(1A) 1.698(5), C(1)−Ge−Ge(A) 79.35(7), C(1A)−C(1)−Ge 100.65(7).

Synthesis of the 4,5-Carboranylene-1,1,2,2,3,3-hexamethyl-1,2,3-tristannacyclopentane (4). The Wurtz-type coupling reaction of **2** using sodium metal in refluxing toluene afforded the unexpected product, **4**, in 28% yield (eq 4). The structure of **4** is consistent with its ^{1}H, ^{13}C, and ^{119}Sn NMR spectra. ^{1}H NMR signals in **4** ascribable to the SnMe were observed at 0.59 (s, $^2J_{H-^{119}Sn} = 52.8$ Hz, $^2J_{H-^{117}Sn} = 50.4$ Hz, $^3J_{H-Sn} = 24.0$ Hz) and 0.49 (s, $^2J_{H-^{119}Sn} = 49.2$ Hz, $^2J_{H-^{117}Sn} = 46.8$ Hz, $^3J_{H-Sn} = 10.2$ Hz) ppm, which are indicative of two kinds of methyl groups on the Sn atoms in a 1:2 ratio. The ^{13}C NMR spectrum of **4** exhibits the expected two resonances at −5.2 and −12.5 ppm. Of particular interest is the ^{119}Sn NMR spectrum, which shows two resonances at −116.9 and −181.4 ppm with a typical ^{117}Sn satellite signal of $^1J_{^{119}Sn-^{117}Sn} = 3426.6$ Hz and $^2J_{^{119}Sn-^{117}Sn} = 670.8$ Hz. The



2 **4**

(4)

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(7) Yang, X.; Knobler, C. B.; Zheng, Z.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1994**, *116*, 7142.

(8) Mochida, K.; Shibayama, N.; Goto, M. *Chem. Lett.* **1998**, 339.

(9) de Rege, F. M.; Kasselbaum, J. D.; Scott, B. L.; Abney, K. D.; Balaich, G. J. *Inorg. Chem.* **1999**, *38*, 486.

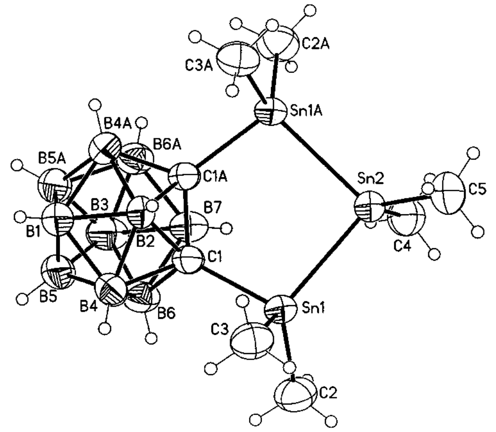
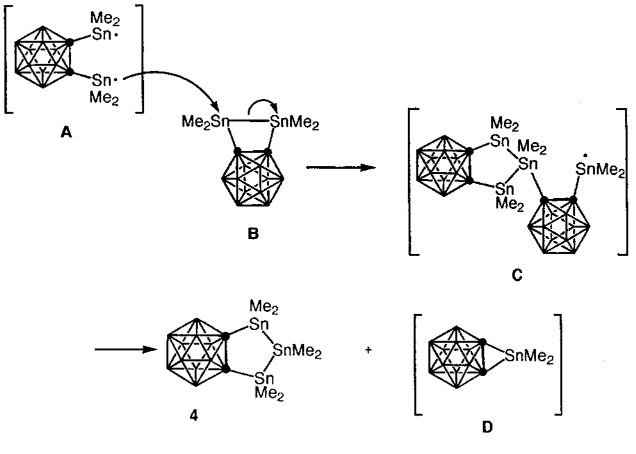


Figure 2. X-ray cystal structure of **4** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Sn(1)−C(1) 2.215(4), Sn(1)−Sn(2) 2.7571(4), C(1)−C(1a) 1.701(6), C(1)−Sn(1)−Sn(2) 98.89(9), Sn(1)−Sn(2)−Sn(1a) 93.187(16), C(1a)−C(1)−Sn(1) 121.36(9).

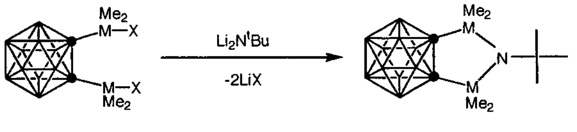
values strongly resemble the literature ones for 1,2,3-tristanna[3]ferrocenophane.[10]

The assignment of **4** was further confirmed by an X-ray diffraction study. The molecular structure of **4** is shown in Figure 2. The X-ray study revealed **4** to be a five-membered cyclization product. The five-membered ring of **4** is slightly puckered with the dihedral angle between Sn(1)−C(1)−C(1a)−Sn(1a) and Sn(1)−Sn(2)−Sn(1a) being 10.2(3)°. The Sn(1)−Sn(2) bond length of 2.7571(4) Å is comparable to that observed for distanna[2]ferrocenophane.[10]

A reasonable mechanism for the formation of **4** involves the initial insertion of the radical intermediate (A) into the Sn−Sn bond (B) formed during the Wurtz-type coupling reaction, followed by cyclization to **4**. In order to trap the intermediate D, we carried out the Wurtz-type reaction using dimethylphenylsilane and diphenylacetylene as trapping agents. While the expected stannylene trapped product was not obtained, product **4** was obtained in 34% yield. Similar results were observed in the thermolysis of the four-membered phenylene disilacycle[11] and digermacycle.[12]



Reaction of 1 and 2 with Dilithio-*tert*-butylamine. The compounds **5** and **6** can be prepared either by reacting **1** or **2** with *tert*-butylamine in the presence of NEt_3, as in the preparative method of 1,3-disilaisoindoline,[13] or by reacting **1** or **2** with dilithio-*tert*-butylamine as in the synthesis of hexa-*tert*-butyldistannaazane.[14] Because the former procedure may in some cases result in cleavage of the C(carborane)−M (M = Ge; Sn) bond, the latter procedure is preferred. Thus, 1,2-bis(digermylazanyl)carborane (**5**) was prepared as a colorless solid by the reaction of **1** with a stoichiometric amount of dilithio-*tert*-butylamine (eq 5). When 1,2-bis(bromodimethylstannyl)carborane was treated with dilithio-*tert*-butylamine, a similar reaction occurred to give the cyclic distannaazane **6**. Initially, we attempted the substitution reaction of 1,2-bis(chlorostannyl)carborane with dilithio-*tert*-butylamine, but no reaction occurred, probably due to the strong bond of Sn−Cl. After many attempts, we found that 1,2-bis(bromostannyl)carborane **2** served well for the conversion of Sn−Br to the cyclic distannaazane without any cleavage of the Sn−C(carborane) bond. Compounds **5** and **6** were purified by low-temperature recrystallization from toluene as colorless crystals. Satisfactory elemental analyses were obtained for both compounds, and the ^{1}H, ^{13}C, and ^{119}Sn NMR spectral data are consistent with the presence of the cyclic azanyl carborane. The signal at −0.15 ppm for $Sn-CH_3$ in the ^{1}H NMR spectrum for **6** locates at a higher field than that for **2**. The ^{119}Sn NMR chemical shift of 84.6 ppm resembles the literature value for distannylamine compounds.[15]



(5)

1 ; M= Ge: X= Cl
2 ; M= Sn: X= Br

5; M= Ge
6; M= Sn

Reaction of 1 and 2 with Dilithiophenylphosphine. Although the synthesis of the organogermylphosphine and organostannylphosphine[16] was well established by reaction of the corresponding halides and primary phosphine in the presence of NEt_3, Couret[17] and Schumann[18] reported that the digerma-2,5-phospholane and cyclic bis(triorganogermyl)-phosphine could be prepared by the reaction of dilithium alkylphosphide and alkylgermanium dihalide. 2,5-Distannaphospholane was also prepared from the reaction of distannachloride **2** and $RPLi_2$.[19] This preparative method is

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(10) Herberhold, M.; Steffl, U.; Milius, W.; Wrackmeyer, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1803.

(11) Naka, A.; Hayashi, M.; Okazaki, S.; Ishikawa, M. *Organometallics* **1994**, *13*, 4994.

(12) Komoriya, H.; Kako, M.; Nakadaira, Y. *Organometallics* **1996**, *15*, 2014.

(13) (a) Schröck, R.; Dreihäupl, K.-H.; Sladek, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **1996**, 4193. (b) Tamao, K.; Sun, G.-R.; Kawach, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2079.

(14) Puff, H.; Hänssgen, D.; Beckermann, N.; Roloff, A,; Schuh, W. *J. Organomet. Chem.* **1989**, *373*, 37.

(15) Diemer, S.; Nöth, H.; Polborn, K.; Storch, W. *Chem. Ber.* **1992**, *125*, 389.

(16) (a) Schumann, H.; Benda, H. *Chem. Ber.* **1971**, *104*, 333 (b) Schumann, H,; Benda, H. *Angew. Chem.* **1968**, *80*, 845.

(17) Couret, C,; Stagé, J.; Escudie, J.; Andriamizaka, J. D. *J. Organomet. Chem.* **1977**, *132*, C5.

(18) (a) Schumann, H.; Benda, H. *Angew. Chem.* **1968**, *80*, 846. (b) Schumann, H.; Benda, H. *Angew. Chem.* **1969**, *81*, 1049.

Table 1. Crystal Data of **3**, **4**, **8**, and **11**

	3	**4**	**8**	**11**
empirical formula	$C_6H_{22}B_{10}Ge_2$	$C_8H_{28}B_{10}Sn_3$	$C_{12}H_{27}B_{10}PSn_2$	$C_8H_{32}B_{20}Ge_2$
mol wt	347.52	588.47	547.79	489.72
cryst syst	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	*P*2/*n*	*Pnma*	*Pnma*	*P*2$_1$/*c*
a (Å)	7.0027(6)	15.5491(7)	16.2836(14)	9.8685(8)
b (Å)	8.7871(8)	11.7044(5)	10.9236(9)	9.6393(7)
c (Å)	13.0248(11)	11.4205(5)	12.3182(9)	13.1644(10)
β (deg)	94.267(2)	90	90	107.349(6)
V, Å^3	799.18(12)	2078.45(16)	2191.1(3)	1195.3(2)
Z value	2	4	4	2
D_{calcd}, (g cm^{-3})	1.444	1.881	1.661	1.361
cryst size, mm^3	0.20 × 0.30 × 0.40	0.16 × 0.30 × 0.30	0.42 × 0.10 × 0.12	0.32 × 0.24 × 0.10
F(000)	344	1104	1056	488
μ (mm^{-1})	3.731	3.561	2.346	2.511
2θ range (deg)	2.32−28.27	2.21−28.32	2.07−25.00	3.5−50
scan type	ω	ω	ω	ω
no. of reflns with $I > 2\sigma(I)$	1930	2705	2018	1782
R	0.0357	0.0331	0.0519	0.0313
wR2[a]	0.0893	0.0856	0.1201	0.0758
GOF	1.061	1.173	1.039	1.065

[a] $wR2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

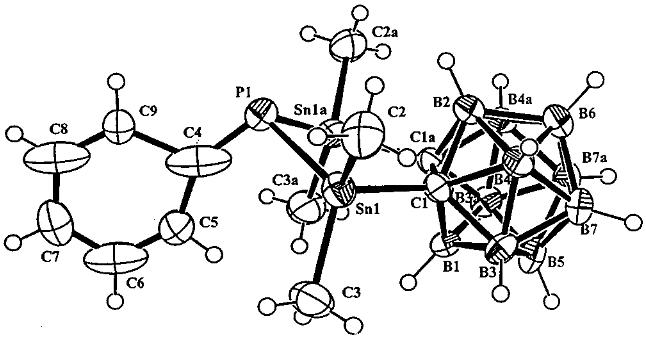
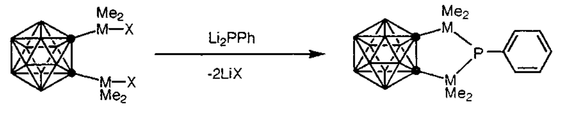


Figure 3. X-ray cystal structure of **8** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Sn(1)−C(2) 2.119(5), Sn(1)−C(3) 2.128(9), Sn(1)−C(1) 2.189(5), Sn(1)−P(1) 2.518(2), C(2)−Sn(1)−C(3) 115.0(3), C(2)−Sn(1)−C(1) 105.3(2), C(3)−Sn(1)−C(1) 105.4(3), C(1)−Sn(1)−P(1) 100.68(14), C(4)−P(1)−Sn(1) 100.8(4), C(4)−P(1)−Sn(1a) 95.58(11).

applicable for the synthesis of our compounds. Thus, 4,5-carboranylene-2-phenyl-1,1,3,3-tetramethyl-2-phospha-1,3-digermacyclopentane **7** was readily prepared in high yield by the reaction of dilithiophenylphosphine with **1** (eq 6). Compound **8** was also prepared using the same synthetic method as **7**. Compounds **7** and **8** are moderately soluble in



(6)

1 ; M= Ge: X= Cl
2 ; M= Sn: X= Br

7; M= Ge
8; M= Sn

toluene and THF. The structure of **8**, unambiguously established by the single-crystal X-ray analysis, is shown in Figure 3. The crystallographic data and processing parameters are given in Table 1. The plane of symmetry of the molecule coincides with the crystallographic plane of symmetry. This is why the compound has a *Z* value of 4 instead of 8. The plane of symmetry passes through the P1, B1, B2, B6, C4, C5, C7, C8,and C9 atoms. As the dihedral angle between the two planes (C1, C1^a, Sn1, Sn1^a and P1, Sn1, Sn1^a) is 137.27° and the bond angle of P1−Sn1−C1 is 100.68(14)°, the coordination environment about Sn(1) may be described as a distorted tetrahedral configuration. The Sn(1)−P(1) bond distance (2.518(2) Å) is comparable to that observed for a few known Sn−P bond lengths (2.52 Å).[20]

The ^{1}H, ^{13}C, ^{31}P, and ^{119}Sn NMR spectra of **8** were consistent with the structure determined by X-ray crystallography. The ^{1}H NMR signals ascribable to Sn−Me for **8** were observed as two doublets at 0.28 (d, $J_{H-P} = 3.0$ Hz, $J_{H-^{119}Sn} = 56.4$ Hz, $J_{H-^{117}Sn} = 54.6$ Hz, anti to the lone pair on phosphorus) and 0.08 (d, $J_{H-P} = 0.9$ Hz, $J_{H-^{119}Sn} = 54.6$ Hz, $J_{H-^{117}Sn} = 52.8$ Hz, syn to the lone pair on phosphorus). The ^{31}P NMR signal appeared at 77.2 ppm with high coupling constants of $J_{P-^{119}Sn} = 934.3$ Hz and $J_{P-^{117}Sn} = 892.8$ Hz. The chemical shift is very close to that of 2,5-distannaphospholane (77.2 ppm).[17]

Reaction of 1 and 2 with Sodium Cyanoborohydride. *o*-Bis(dimethylsilyl)carborane was found to be a good precursor for the double silylation reaction.[21] However, its congeners, the germanium and tin chemistry, are not developed because synthetic methods available for such compounds are not accessible. Recently, we[6] prepared the triorganotin hydride, (Cab^{C,P})SnMe$_2$H (Cab^{C,P} = 1-PPh$_2$-1,2-$C_2B_{10}H_{10}$), by the reaction of (Cab^{C,P})SnMe$_2$Br with sodium cyanoborohydride as a reducing agent. This preparative procedure was also effective for the synthesis of 1,2-bis(dimethylgermyl)carborane (**9**) and 1,2-bis(dimethylstannyl)carborane (**10**). Thus, compounds **9** and **10** were prepared by the reaction of compounds **1** and **2** with sodium cyanoborohydride (eq 7). Compounds **9** and **10** are crystalline solids that are relatively stable in air and to brief heating to

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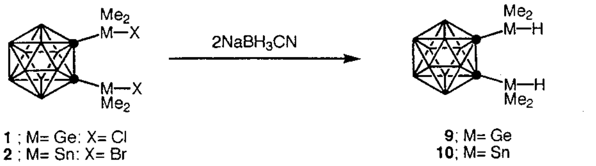
(19) Andriamizaka, J. D.; Couret, C.; Escudié, J.; Satgé, J. *Phosphorus Sulfur* **1982**, *12*, 265.

(20) (a) Mathiasch, B. *J. Organomet. Chem.* **1979**, *165*, 295. (b) Dräger, M.; Mathiasch, B. *Angew. Chem.* **1981**, *93*, 1079.

(21) (a) Kang, Y.; Lee, J.; Kong, Y, K.; Kang, S. O.; Ko, J.*Organometallics* **2000**, *19*, 1722. (b) Kang, Y.; Kim, J.; Kong, Y. K.; Lee, J.; Lee, S. W.; Kang, S. O.; Ko, J. *Organometallics* **2000**, *19*, 5026.

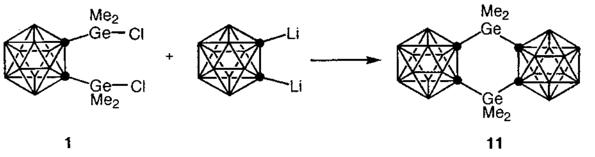


(7)

100−110 °C. Compounds **9** and **10** are moderately soluble in toluene and THF.

The ^{1}H and ^{13}C spectra of **10** were consistent with the proposed structure. The ^{1}H NMR signals ascribable to the $SnMe_2$ and SnH were observed at 0.07 (d, $J_{H-H} = 1.80$ Hz, $J_{H-^{119}Sn} = 60.6$ Hz, $J_{H-^{117}Sn} = 57.6$ Hz) and 5.57 (sept, $J_{H-Sn} = 2058.4$ Hz, $J_{H-H} = 1.80$ Hz) ppm, respectively. The infrared spectrum of **10** shows the stretching mode of ν(SnH) at 1913 cm^{-1}. The mass spectrum of **10** showed a molecular ion at m/z 441.

Reaction of 1 with 1,2-Dilithio-*o*-carborane. The reaction of **1** with 1,2-dilithio-*o*-carborane in ether affords the 2,3,5,6-dicarboranylene-1,1,4,4-tetramethyl-1,4-digermacyclohexane **11** (eq 8). The structure of **11** was determined by spectral data and confirmed by X-ray structural analysis. The structure is given in Figure 4 with selected bond lengths and angles. The central six-membered ring has a boat conformation, and the tricyclic framework has a butterfly conformation with a dihedral angle of 158°, which is comparable to that of 9,10-dihydro-9,10-digermylanthracene.[22] Since the ORTEP diagram of **11** shows that each germanium has pseudoaxial and pseudoequatorial methyl groups, its ^{1}H NMR spectrum is expected to show two signals for the nonequivalent methyl groups. However, a singlet at 0.65 ppm due to the methyl groups did not change in the temperature range from 25 to −50 °C. Therefore, it is reasonable to assume that a boat to boat inversion occurs in solution as observed in the 9,10-dihydro-9,10-distannaanthracene.[22] The tin analogue of **11** has been reported by Zakharkin et al.[23]



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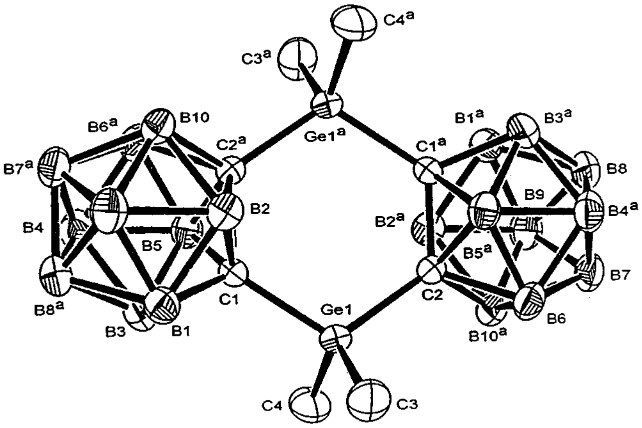
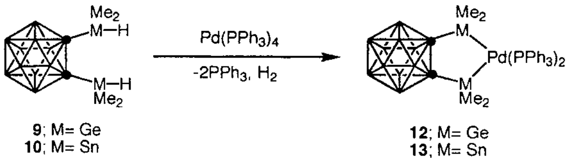


Figure 4. X-ray cystal structure of **11** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Ge(1)−C(3) 1.930(4), Ge(1)−C(4) 1.933(4), Ge(1)−C(1) 1.982(3), Ge(1)−C(2) 1.986(3), C(1)−Ge(1)−C(2) 110.90(12).

Synthesis of the Bis(germyl)palladium (12) and Bis(stannyl)palladium Complexes (13). Bis(germyl)palladium[24] and bis(stannyl)palladium[25] complexes have been implicated as key intermediates in the double germylation and stannylation of alkynes, 1,3-dienes, and allenes. However, only a few bis(germyl)- and bis(stannyl)palladium complexes have been characterized due to the synthetic limitation on organogermanium and tin compounds. We chose compounds **9** and **10** as good candidates for the bis(germyl)- and bis(stannyl)metal complexes because an analogous system, 1,2-bis(dimethylsilyl)carborane, was known to react with metal compounds to give the cyclic bis(silyl)metal complexes.[4] Moreover, Nakadaira and co-workers[26] reported that the reaction of 1,2-bis(diethylgermyl)benzene with $Pd(PPh_3)_4$ underwent dehydrocoupling to give the cyclic digermylapallada complex. Thus, treatment of compounds **9** and **10** with $Pd(PPh_3)_4$ in toluene resulted in the oxidative addition of M−H (M = Ge, Sn) to the palladium to afford the bis(germyl)palladium (**12**) and bis(stannyl)palladium complexes (**13**) as yellow crystals in high yield (eq 9).



(9)

Compounds **12** and **13** are stable in an inert-gas environment and showed slow decomposition when in contact with air. They are readily soluble in organic solvents such as toluene and THF.

The ^{1}H, ^{13}C, and ^{31}P NMR spectra of **13** were consistent with the proposed formulation. The ^{1}H NMR spectrum of **13** shows one peak at −0.16 ($J_{H-Sn} = 41.1$ Hz; peaks due to ^{117}Sn and ^{119}Sn were not resolved) ppm due to the hydrogen atoms of the Sn−Me groups. The $^{31}P\{^1H\}$ NMR spectrum of **13** showed a resonance centered at 24.0 ppm with satellite peaks due to $^2J_{P-Sn(transoid)}$ ($^2J_{P-^{119}Sn} = 1442.5$ Hz, $^2J_{P-^{117}Sn} = 1401.4$ Hz) and $^2J_{P-Sn(cisoid)}$ (154.8 Hz), which is consistent with the cis configuration of **13**.[25a,27]

In summary, we have prepared 1,2-bis(chlorogermyl)carborane (**1**) and 1,2-bis(bromostannyl)carborane (**2**). The two compounds were effective reactants in the cyclization reaction. The two starting compounds, **1** and **2**, readily

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(22) Saito, M.; Nitta, M.; Yoshioka, M. *Organometallics* **2001**, *20*, 749.

(23) Zakharkin, L. I.; Bregadze, V. I.; Okhlobystin, O. Y. *J. Organomet. Chem.* **1965**, *4*, 211.

(24) (a) Barrau, J.; Rima, G.; Cassano, V.; Satge, J. *Inorg. Chim. Acta.* **1992**, *198*, 461. (b) Yamashita, H.; Kobayashi, T.; Tanaka, M.; Samuels, J. A.; Streib, W. E. *Organometallics* **1992**, *11*, 2330.

(25) (a) Tsuji, Y.; Nishiyama, K.; Hori, S.; Ebihara, M.; Kawamura, T. *Organometallics* **1998**, *17*, 507. (b) Müller, C.; Schubert, V. *Chem. Ber.* **1991**, *124*, 2181. (c) Obora, Y.; Tsuji, Y.; Nishiyama, K.; Ebihara, M.; Kawamura, T. *J. Am. Chem. Soc.* **1996**, *118*, 10922.

(26) (a) Komoriya, H.; Kako, M.; Nakadaira, Y.; Mochida, K. *Organometallics* **1996**, *15*, 2014. (b) Komoriya, H.; Kako, M.; Nakadaira, Y.; Mochida, K. *J. Organomet. Chem.* **2000**, *611*, 420.

(27) Ebsworth, E. A.; Maganian, V. M.; Reed, F. T. S.; Group, R. O. *J. Chem. Soc., Dalton Trans.* **1978**, 1167.

undergo a substitution reaction with Li_2N^tBu and Li_2PPh to afford new classes of heterocycles. Compounds **1** and **2** also react with sodium cyanoborohydride, generating a new class of hydride compounds. 1,2-Bis(dimethygermyl)carborane (**9**) and 1,2-bis(dimethylstannyl)carborane (**10**) were found to be good precursors for the synthesis of the bis(germyl)-palladium (**12**) and bis(stannyl)palladium complexes (**13**), which are implicated as important active catalyst species in a number of transition-metal-catalyzed germylation and stannylation reactions. This potential has been further exploited in a series of novel chemical transformations with this system.

Experimental Section

All experiments were performed under a dry nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques. Diethyl ether, toluene, and THF were freshly distilled from sodium benzophenone. Hexane was dried and distilled from CaH_2 and chloroform from $CaCl_2$. ^1H, ^{13}C, ^{31}P, and ^{119}Sn NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.00, 75.44, 121.44, and 111.82 MHz, respectively. Chemical shifts were referenced to TMS (^1H), benzene-d_6 (^1H, δ 7.156; $^{13}C\{^1H\}$, δ 128.00), H_3PO_4 (^{31}P), and Me_4Sn (^{119}Sn). IR spectra were recorded on a Biorad FTS-165 spectrometer. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer.

o-Carborane was purchased from KATCHEM Ltd. and used without purification. The starting materials Me_2GeCl_2, Me_2SnBr_2, $PhPH_2$, and Na_2PdCl_4 were purchased from Strem Chemical and $NaBH_3(CN)$ from Aldrich. $Pd(PPh_3)_4$[28] and Li_2PPh[29] were prepared according to the literature.

Synthesis of *o*-Bis(chlorodimethylgermyl)carbarane (1). *n*-BuLi (3.10 mmol, 1.6 M in hexane) was slowly added to a stirred solution of *o*-carborane (0.20 g, 1.40 mmol) in toluene (15 mL) at −78 °C. The solution was warmed to room temperature and stirred for 12 h. To that solution was added $GeMe_2Cl_2$ (0.60 g, 3.47 mmol) in toluene (15 mL) at −78 °C. The solution was warmed to room temperature and stirred for 12 h. The solution was evaporated under vacuum and washed with hexane (3 mL). The residue was recrystallized from toluene (20 mL) to yield colorless crystals in 82% yield. Mp: 108−110 °C. ^1H NMR (C_6D_6): δ 0.55 (s, 12H, Ge−C*H*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 73.6 (carborane *C*), 6.4 (Ge−*C*H$_3$). MS(EI): *m*/*z* 418 [M$^+$]. Anal. Calcd for $C_6H_{22}B_{10}Cl_2Ge_2$: C, 17.22; H, 5. 29. Found: C, 16.86; H, 5.04.

Synthesis of *o*-Bis(bromodimethylstannyl)carborane (2). *n*-BuLi (4.17 mmol, 1.6 M in hexane) was slowly added to a stirred solution of *o*-carborane (0.30 g, 2.08 mmol) in THF (20 mL) at −78 °C. The solution was warmed to room temperature and stirred for 12 h. This solution was added to $SnMe_2Br_2$ (1.20 g, 4.17 mmol) in THF (60 mL) at −78 °C and warmed to room temperature. The solution was stirred for 12 h at that temperature. The solution was evaporated under vacuum and washed with hexane (20 mL). The residue was recrystallized from toluene (30 mL) to yield colorless crystals in 55% yield. Mp: 355−360 °C. ^1H NMR (C_6D_6): δ 0.16 (s, 12H, $J_{H-^{119}Sn} = 61.2$ Hz, $J_{H-^{117}Sn} = 58.5$ Hz, Sn−C*H*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 66.4 (carborane *C*), −4.8 (Sn−*C*H$_3$). $^{119}Sn\{^1H\}$ NMR (C_6D_6): δ 103. MS(EI): *m*/*z* 599 [M$^+$]. Anal.Calcd for $C_6H_{22}B_{10}Br_2Sn_2$: C, 12.01; H, 3.69. Found: C, 11.82; H, 3.46.

Synthesis of 3,4-Carboranylene-1,1,2,2-tetramethyl-1,2-digermacyclobutane (3). Sodium (0.027 g, 1.18 mmol) was added to a solution of **1** (0.20 g, 0.48 mmol) in toluene. The mixture was heated under reflux for 72 h, and solvent was removed under reduced pressure. The residue was extracted with hexane (20 mL). Reduction of the volume (10 mL) and cooling of the solution afforded **3** as colorless crystals in 35% yield. Mp: 231−235 °C. ^1H NMR (C_6D_6): δ 0.21 (Ge−C*H*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ −0.2 (Ge−*C*H$_3$). MS(EI): *m*/*z* 348 [M$^+$]. Anal.Calcd for $C_6H_{22}B_{10}Ge_2$: C, 20.73; H, 6.33. Found: C, 20.31; H, 6.18.

Synthesis of 4,5-Carboranylene-1,1,2,2,3,3-hexamethyl-1,2,3-tristannacyclopentane (4). This complex was prepared as described for the synthesis of **3** and was crystallized from toluene at −10 °C to give **4** in 28% yield. Mp: 205−210 °C. ^1H NMR (C_6D_6): δ 0.59 (s, 6H, $^2J_{H-^{119}Sn} = 52.8$ Hz, $^2J_{H-^{117}Sn} = 50.4$ Hz, $^3J_{H-Sn} = 24.0$ Hz, SnSn*Me*$_2$Sn), 0.49 (s, 12H, $^2J_{H-^{119}Sn} = 49.2$ Hz, $^2J_{H-^{117}Sn} = 46.8$ Hz, $^3J_{H-Sn} = 10.2$ Hz, Sn*Me*$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ −5.2 ($^1J_{^{13}C-^{119}Sn} = 286.3$ Hz, $^2J_{^{13}C-^{119}Sn} = 64.8$ Hz), −12.5 ($^1J_{^{13}C-^{119}Sn} = 208.6$ Hz, $^2J_{^{13}C-^{119}Sn} = 42.6$ Hz). $^{119}Sn\{^1H\}$ NMR (C_6D_6): δ −116.9 ($^1J_{^{119}Sn-^{117}Sn} = 3426.6$ Hz, $^2J_{^{119}Sn-^{117}Sn} = 670.8$ Hz), −181.4 ($J = 3428.4$ Hz). Anal.Calcd for $C_8H_{28}B_{10}Sn_3$: C, 16.32; H, 4.75. Found: C, 16.69; H, 4.52.

Synthesis of 4,5-Carboranylene-2-*tert*-butyl-1,1,3,3-tetramethyl-2-aza-1,3-digermacyclopentane (5). *n*-BuLi (4.76 mmol, 1.6 M in hexane) was slowly added to a stirred solution of *tert*-butylamine (0.2 mL, 1.90 mmol) dissolved in triethylamine (1 mL) and ethyl ether (8 mL) at −78 °C. The solution was warmed to room temperature and stirred for 12 h. The precipitated product was filtered and dried. $Li_2N^tC_4H_9$ (0.014 g, 0.167 mmol) in THF (10 mL) was added to a THF (10 mL) solution of **1** (0.07 g, 0.167 mmol) at −78 °C. The solution was refluxed for 6 h and evaporated to dryness under vacuum. The residue was recrystallized from toluene (30 mL) to yield colorless crystals in 70% yield. Mp: 145−150 °C. ^1H NMR (C_6D_6): δ 1.22 (s, 9H, ^{t}*Bu*), 0.60 (s, 12H, Ge−C*H*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 71.4, 35.0 (*C*−CH$_3$), 4.7 (C−*C*H$_3$), 1.3 (Ge−*C*H$_3$). MS(EI): *m*/*z* 418 [M$^+$]. Anal. Calcd for $C_{10}H_{31}B_{10}NGe_2$: C, 28.68; H, 7.45. Found: C, 28.34; H, 7.21.

Synthesis of 4,5-Carboranylene-2-*tert*-butyl-1,1,3,3-tetramethyl-2-aza-1,3-distannacyclopentane (6). Compound **6** was prepared using the same procedure as described for **5**. Yield: 75%. Mp: 160−164 °C. ^1H NMR (C_6D_6): δ 0.98 (s, 9H, ^{t}*Bu*), −0.15 (s, 12H, $J_{H-^{119}Sn} = 56.7$ Hz, $J_{H-^{117}Sn} = 54.6$ Hz, Sn−C*H*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 30.5 (*C*−CH$_3$), 5.2 (C−*C*H$_3$), 0.6 (Sn−*C*H$_3$). $^{119}Sn\{^1H\}$ NMR(C_6D_6): δ 84.6. MS(EI): *m*/*z* 510 [M$^+$]. Anal. Calcd for $C_{10}H_{31}B_{10}NSn_2$: C, 23.51; H, 6.11. Found: C, 23.24; H, 5.98.

Synthesis of 4,5-Carboranylene-2-phenyl-1,1,3,3-tetramethyl-2-phospha-1,3-digermacyclopentane (7). *n*-BuLi (1.13 mmol, 1.6 M in hexane) was slowly added to a stirred solution of phenylphosphide (0.50 g, 0.45 mmol) in Et_2O (15 mL) at −78 °C. The solution was warmed to room temperature and stirred for 12 h. The yellow precipitate (Li_2PPh) was filtered and dried. Li_2PPh (0.02 g, 0.167 mmol) in THF (10 mL) was added to a THF (10 mL) solution of **1** (0.07 g, 0.167 mmol) at −78 °C. The solution was stirred for 8 h at room temperature and evaporated to dryness under vacuum. The residue was recrystallized from hexane (30 mL) to yield colorless crystals in 85% yield. Mp: 170−173 °C. ^1H NMR (C_6D_6): δ 7.32−6.95 (m, 5H, *Ph*), 0.42 (d, 6H, $J_{H-P} = 6.6$ Hz, Ge−C*H$_3$* anti to the lone pair on phosphorus), 0.18 (d, 6H, $J_{H-P} = 1.2$ Hz, Ge−C*H$_3$* syn to the lone pair on phosphorus). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 137.0, 136.8, 128.8, 128.7, 128.5 (*Ph*), 2.7 ($J_{C-P} = 28.9$ Hz, Ge−*C*H$_3$, anti to the lone pair on phosphorus), 0.8

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(28) Brauer, G. *Handbuch der Präparativen Anorganischen Chemie*; Ferdinand Enke Verlag: Stuttgart, 1981; p 2013.

(29) Petrie, M. A.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 1309.

(J_{C-P} = 4.2 Hz, Ge−CH_3, syn to the lone pair on phosphorus). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 119.99. MS(EI): *m/z* 455 [M^+]. Anal. Calcd for $C_{12}H_{27}B_{10}PGe_2$: C, 31.63; H, 5.96. Found: C, 31.28; H, 5.78.

Synthesis of 4,5-Carboranylene-2-phenyl-1,1,3,3-tetramethyl-2-phospha-1,3-distannacyclopentane (8). Compound **8** was prepared using the same procedure as described for **7**. Yield: 85%. Mp: 201−205 °C. ^1H NMR (C_6D_6): δ 7.32−6.92 (m, 5H, *Ph*), 0.28 (d, 6H, J_{H-P} = 3.0 Hz, $J_{H-^{119}Sn}$ = 56.4 Hz, $J_{H-^{117}Sn}$ = 54.6 Hz, Sn−CH_3, anti to the lone pair on phosphorus), 0.08 (d, 6H, J_{H-P} = 0.9 Hz, $J_{H-^{119}Sn}$ = 54.6 Hz, $J_{H-^{117}Sn}$ = 52.8 Hz, Sn−CH_3, syn to the lone pair on phosphorus). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 138.5, 136.6, 129.1, 127.7, 127.1 (*Ph*), 73.7, −3.4, −5.0. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 77.2 ($J_{P-^{119}Sn}$ = 934.3 Hz, $J_{P-^{117}Sn}$ = 892.8 Hz, Sn−*P*). $^{119}Sn\{^1H\}$ NMR (C_6D_6): δ 52 (J_{Sn-P} = 892.1 Hz) MS(EI): *m/z* 547 [M^+]. Anal. Calcd for $C_{12}H_{27}B_{10}PSn_2$: C, 26.30; H, 4.96. Found: C, 26.72; H, 5.06.

Synthesis of *o*-Bis(dimethylgermyl)carborane (9). $NaBH_3CN$ (0.15 g, 2.4 mmol) was added to a stirred solution of **1** (0.10 g, 0.24 mmol) in THF (20 mL) at −78 °C. The solution was warmed to room temperature and stirred for 12 h at room temperature. The solution was evaporated to dryness and extracted with hexane (20 mL). Yield: 92%. Mp: 184−188 °C. ^1H NMR (C_6D_6): δ 4.23 (sept, 2H, J_{H-H} = 3.0 Hz, Ge−*H*), 0.13 (d, 12H, J_{H-H} = 3.0 Hz, Ge−CH_3). $^{31}C\{^1H\}$ NMR (C_6D_6): −2.5 (Ge−*C*H_3). MS(EI): *m/z* 349 [M^+]. Anal. Calcd for $C_6H_{24}B_{10}Ge_2$: C, 20.61; H, 6.91. Found: C, 20.34; H, 6.72.

Synthesis of *o*-Bis(dimethylstannyl)carborane (10). $NaBH_3CN$ (1.0 mL, 1 M in THF) was added to a stirred solution of **2** (0.10 g, 0.17 mmol) in toluene (30 mL) at 0 °C. The solution was stirred for 6 h at 90 °C and then refluxed for 1 h. The solution was evaporated to dryness and extracted with hexane (30 mL). Yield: 32%. Mp: 185−192 °C. ^1H NMR (C_6D_6): δ 5.57 (sept, 2H, J_{H-Sn} = 2058.4 Hz, J_{H-H} = 1.80 Hz, Sn−*H*), 0.07 (d, 12H, J_{H-H} = 1.80 Hz, $J_{H-^{119}Sn}$ = 60.6 Hz, $J_{H-^{117}Sn}$ = 57.6 Hz, Sn−CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 67.0, −7.1 (Sn−*C*H_3). $^{119}Sn\{^1H\}$ NMR (C_6D_6): δ −12. MS(EI): *m/z* 441 [M^+]. Anal. Calcd for $C_6H_{24}B_{10}Sn_2$: C, 16.31; H, 5.47. Found: C, 16.04; H, 5.32.

Synthesis of 2,3,5,6-Dicarboranylene-1,1,4,4-tetramethyl-1,4-digermacyclohexa-2,5-diene (11). *o*-Bis(chlorodimethylgermyl)-carborane (0.10 g, 0.24 mmol) in ether (10 mL) was slowly added to a stirred solution of 1,2-dilithio-*o*-carborane (0.04 g, 0.24 mmol) dissolved in ether (20 mL) at −78 °C. The solution was warmed to room temperature and stirred for 6 h. The solution was filtered and evaporated under vacuum. The residue was recrystallized from toluene (5 mL) to yield colorless crystals in 65% yield. Mp: 160−162 °C. ^1H NMR ($CDCl_3$): δ 0.65 (Ge−CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 1.3. MS(EI): *m/z* 490 [M^+]. Anal. Calcd for $C_8H_{32}B_{10}Ge_2$: C, 19.61; H, 6.58. Found: C, 19.22; H, 6.78.

Synthesis of $(Me_2)\overline{Ge(1,2\text{-}C_2B_{10}H_{10})Ge(Me_2)}Pd(PPh_3)_2$ (12). To a stirred toluene (20 mL) solution of $Pd(PPh_3)_4$ (0.30 g, 0.26 mmol) was added compound **9** (0.10 g, 0.28 mmol) in toluene (10 mL) at −78 °C. The solution was warmed to room temperature and stirred for 3 h. Purification was achieved by column chromatography (eluent 1:1 benzene/hexane). The second yellow fraction (R_f = 0.32) was collected. The resulting yellow powder was dried in vacuo to give 0.28 g of **12**. Yield: 80%. Mp: 130−135 °C. ^1H NMR (C_6D_6): δ 7.36−7.04 (m, 30H, *Ph*), 0.02 (t, 12H, J_{H-P} = 2.40 Hz, Ge−CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 134.4, 134.3, 134.2, 133.2, 132.7, 130.1 (*Ph*). 7.0 (Ge−*C*H_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 21.6. Anal. Calcd for $C_{42}H_{52}B_{10}P_2Ge_2Pd$: C, 51.55; H, 5.35. Found: C, 51.28; H, 5.22.

Synthesis of $(Me_2)\overline{Sn(1,2\text{-}C_2B_{10}H_{10})Sn(Me_2)}Pd(PPh_3)_2$ (13). Compound **13** was prepared using the same procedure as described for **12** in 92% yield. Mp: 105−110 °C. ^1H NMR (C_6D_6): δ 7.42−7.04 (m, 30H, *Ph*), −0.16 (d, 12H, J_{H-Sn} = 41.1 Hz, Sn−CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 139.1, 134.7, 134.6, 132.3, 132.1, 132.0 (*Ph*), 4.8 (Sn−*C*H_3). $^{31}P\{^1H\}$ NMR(C_6D_6): δ 24.0 ($J_{P-^{119}Sn}$ = 1442.5 Hz, $J_{P-^{117}Sn}$ = 1401.4 Hz, $J_{P-Sn(cisoid)}$ = 154.8 Hz). Anal. Calcd for $C_{42}H_{52}B_{10}P_2Sn_2Pd$: C, 47.11; H, 4.89. Found: C, 46.94; H, 4.96.

X-ray Crystallography. Details of the crystal data and a summary of the intensity data collection parameters for **3**, **4**, **8**, and **11** are given in Table 1. Crystals **3**, **4**, **8**, and **11** were grown from hexane and toluene, respectively. Crystals **3**, **4**, **8**, and **11** were mounted in thin-walled glass capillaries and sealed under argon. The data sets for the four crystals **3**, **4**, **8**, and **11** were collected on an Enraf CAD-4 and a Siemens P4 diffractometer. Mo Kα radiation (λ = 0.7107 Å) was used for all structures. Each structure was solved by the application of direct methods using the SHELX-96 program and least-squares refinement using SHELXL-97. All non-hydrogen atoms in compounds **3**, **4**, **8**, and **11** were anisotropically refined. All other hydrogen atoms were included in the calculated positions.

Acknowledgment. We are grateful to the Brain Korea 21 program for the generous financial support.

Supporting Information Available: Tables listing crystallographic information, atomic coordinates and B_{eq} values, anisotropic thermal parameters, and intramolecular bond distances, angles, and torsion angles for **3**, **4**, **8**, and **11**. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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