

Synthesis and Reactivity of the Pentacoordinate Organosilicon and -germanium Compounds Containing the C,P-Chelating *o*-Carboranylphosphino Ligand [*o*-C₂B₁₀H₁₀PPh₂-C,P](Cab^{C,P})

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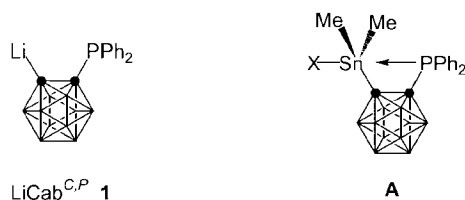
The synthesis of the intramolecular donor-stabilized silyl and germyl complexes of the type (Cab^{C,P})MMe₂X (**2a**: M = Si, X = Cl; **2b**: M = Ge, X = Cl; **2c**: M = Si, X = H) was achieved by the reaction of LiCab^{C,P} (**1**) with Me₂SiClX and Me₂GeCl₂, respectively. The intramolecular M ← P interaction in **2a-2c** is provided by ¹H, ¹³C, ³¹P, and ²⁹Si NMR spectroscopy. The salt elimination reactions of dichlorotetramethyldisilane and -digermene with **1** afforded the bis(*o*-carboranylphosphino)disilane and digermene [(Cab^{C,P})MMe₂]₂ (**4a**: M = Si; **4b**: M = Ge). The oxidative addition reaction of **4a-4b** with Pd₂(dba)₃·CHCl₃ afforded the bis(silyl)- and bis(germyl)-palladium complexes. The chloro-bridged dipalladium complexes were obtained by the reaction of **2a-2b** with Pd₂(dba)₃·CHCl₃. The crystal structures of **5a** and **7b** were determined by X-ray structural studies.

Keywords : Bis(germyl)palladium. Pentacoordinate organosilicon. *o*-Carboranylphosphino ligand.

Introduction

The structure and reactivity of pentacoordinate silicon compounds have been well documented.¹⁻³ Pentacoordination of silicon or germanium is achieved by coordinating anions to tetracoordinate silicon or germanium compounds or the intramolecular coordination of neutral donor group. The latter usually occurs *via* nitrogen.⁴⁻¹⁷ Pentacoordination of silicon or germanium is formed by a dative bond. However, organosilicon and -germanium compounds containing an intramolecular coordination of a C,P-chelating ligand have not been known, probably due to the difficulty of their preparation.

Recently, we¹⁸ reported the synthesis of organotin compounds of the type (Cab^{C,P})SnMe₂X (**A**), in which the tin center is pentacoordinate as a result of intramolecular Sn ← P coordination. Such an Sn ← P interaction in these compounds is favored by the presence of electronegative substituents on



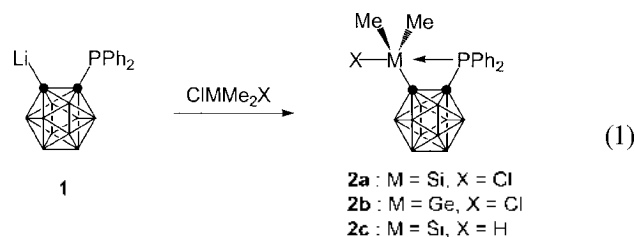
tin, such as a halogen and a carboranyl unit. With these results in mind, we turned our attention to the synthesis of analogous silicon and germanium compounds which a C,P-substituent (Cab^{C,P}) might stabilize the pentacoordinate silicon and germanium center.

In this paper, we describe (i) the synthesis of triorganosilicon and -germanium halides containing intramolecular coordination; (ii) the synthesis of the disilane and digermene

containing the carboranyl units; (iii) the synthesis of the bis(silyl)- and bis(germyl)palladium complexes; and (iv) the synthesis of the bridged dipalladium complexes and their cleavage reactions.

Results and Discussion

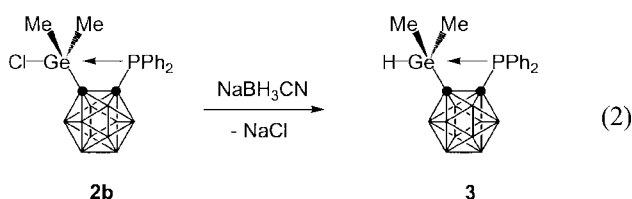
Synthesis and Characterization of the Triorganosilicon and -germanium Compounds (Cab^{C,P})MMe₂X (2a-2c**).** The silicon and germanium compounds **2a-2c** were synthesized *via* a route similar to the one to prepare the analogous tin compounds.¹⁸ The reaction of LiCab^{C,P} with 1.2 equiv. of CIMMe₂X (M = Si, Ge; X = H, Cl) afforded the corresponding organosilicon or germanium complexes according to eq. 1. These complexes are virtually insoluble in hexane but



soluble in toluene, CH₂Cl₂, and THF. The complexes **2a-2c** have characterized by ¹H, ¹³C, ³¹P, and ²⁹Si NMR spectra, and elemental analyses. We observed indications of a weak intramolecular M ← P interaction from the NMR spectra. The evidence for the existence of an intramolecular M ← P interaction in **2a** is provided by (i) the distinctive splitting pattern in its ¹H NMR spectrum due to coupling of a P atom with the silicon-methyl hydrogen (³J_{H-P} = 1.80 Hz), (ii) the existence of a doublet at δ 5.18 (²J_{C-P} = 9.52 Hz) in its ¹³C NMR spectrum due to coupling of the silicon-methyl carbon

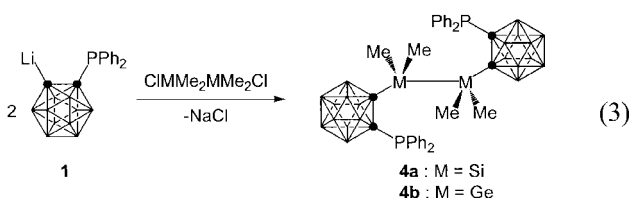
and a phosphorus atom, and (iii) the observation of a doublet at δ 23.86 ($^1J_{\text{Si-P}} = 5.00$ Hz) in its ^{29}Si NMR spectrum by coupling of the ^{29}Si and P atoms. The low values of the coupling constants of the ^1H , ^{13}C , and ^{29}Si NMR spectra for **2a-2c** compared with those for the triorganotin halides of the type $(\text{Cab}^{\text{C,P}})\text{SnMe}_2\text{X}$ indicate that the compounds **2a-2c** have weaker $\text{M} \leftarrow \text{P}$ interaction.

The triorganogermanium hydride $(\text{Cab}^{\text{C,P}})\text{GeMe}_2\text{H}$ (**3**) compound was prepared as a colorless solid by the reaction of $(\text{Cab}^{\text{C,P}})\text{GeMe}_2\text{Cl}$ (**2b**) with sodium cyanoborohydride according to eq. 2. The complex decomposes slowly in the presence of air, both in the solid state and in solution. It is readily soluble in benzene, toluene, and THF.



The composition of **3** was confirmed by ^1H , ^{13}C , and ^{31}P NMR spectra. The ^1H NMR data suggest that compound **3** is pentacoordinated in solution. An ^1H NMR signal ascribable to the Ge-H bond was observed at δ 4.87 ($^2J_{\text{H-P}} = 1.18$ Hz, $^3J_{\text{H-H}} = 3.92$ Hz) ppm. The ^{13}C NMR spectrum of **3** shows the expected pattern of a doublet ($^2J_{\text{C-P}} = 8.02$ Hz) at δ 2.08 due to coupling of the germanium-methyl carbon and a phosphorus atom.

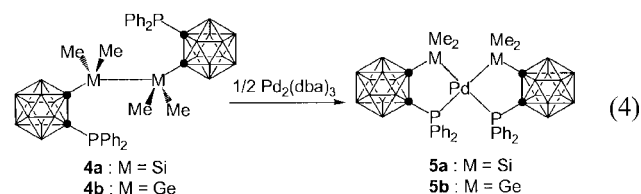
Synthesis of the Bis(*o*-carboranylphosphino)disilane and Digermane, $[(\text{Cab}^{\text{C,P}})\text{MMe}_2]_2$ ($\text{M} = \text{Si}, \text{Ge}$). Although the bis(*o*-carboranylphosphino)-distannane, $[(\text{Cab}^{\text{C,P}})\text{SnMe}_2]_2$ ¹⁸ was prepared through the Wurtz-type coupling reaction of $(\text{Cab}^{\text{C,P}})\text{SnMe}_2\text{Cl}$ using sodium, the Wurtz-type coupling reaction of **2a** and **2b** under the same reaction condition remained unchanged. As an alternative synthesis for **4a** and **4b**, we chose the ligands of dichlorotetramethyldisilane and -digermane for the incorporation of *o*-carboranylphosphino units. Thus, the reaction of dichlorotetramethyldisilane with two equivalents of $\text{LiCab}^{\text{C,P}}$ afforded the disilane complex (**4a**) according to eq. 3.



The initial indication of the disilane formulation for **4a** stemmed from the observation of a parent ion in the mass spectrum at m/z 771. The spectroscopic data (^1H , ^{13}C , and ^{31}P NMR) for **4a** also are consistent with its assigned structure. The signals for $\text{Si}(\text{CH}_3)$ in the ^1H and ^{13}C NMR spectra appear at a higher field than those for the intramolecular silicon compound (**2a**). In particular, the ^{29}Si NMR signal had clearly shifted from δ 23.86 for $(\text{Cab}^{\text{C,P}})\text{SiMe}_2\text{Cl}$

to δ -0.70. The absence of coupling constants of $J_{\text{H-P}}$ and $J_{\text{C-P}}$ in **4a** suggests that compound **4a** is tetracoordinated in solution and has no interaction between silicon and phosphorus.

Synthesis of the Bis(silyl)- and Bis(germyl)palladium Complexes (5a** and **5b**).** Addition of $[(\text{Cab}^{\text{C,P}})\text{SiMe}_2]_2$ to $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ in toluene leads to virtually quantitative yield of the colorless, crystalline bis-chelate $[(\text{Cab}^{\text{C,P}})\text{SiMe}_2]_2\text{Pd}$ (**5a**) (eq. 4). Complex **5a** is relatively stable in air and to



brief heating to 110–120 °C. Compound **5a** is moderately soluble in toluene, dichloromethane, and THF. The structure of **5a**, unambiguously established by single-crystal X-ray analysis, is shown in Figure 1. Crystallographic data and processing parameters are given in Table 1. Complex **5a** has a slightly distorted square-planar geometry with *cis*-arrangement of the two silicon atoms. The equatorial plane, defined by Pd1, P1, P2, Si1, and Si2 atoms, is relatively planar with the average atomic displacement of 0.0426 Å. The two 5-membered metalacycles (Pd1, C29, C30, Si1, P1; Pd1, C31, C32, Si2, P2) are twisted with each other with a dihedral angle of 8.81°. These metallacycles are also twisted with the equatorial plane with dihedral angles of 17.16(3)° and 8.52(4)°. The Pd-Si bond distance (2.3596(6)–2.3626(6) Å) of **5a** is in agreement with the corresponding values observed in $\text{Pd}(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ (2.367(1) Å),¹⁹ (dcpe) $\text{Pd}(\text{SiHMe}_2)_2$ (2.3561 Å),²⁰ and analogous complexes (2.34–2.41 Å).^{21–23}

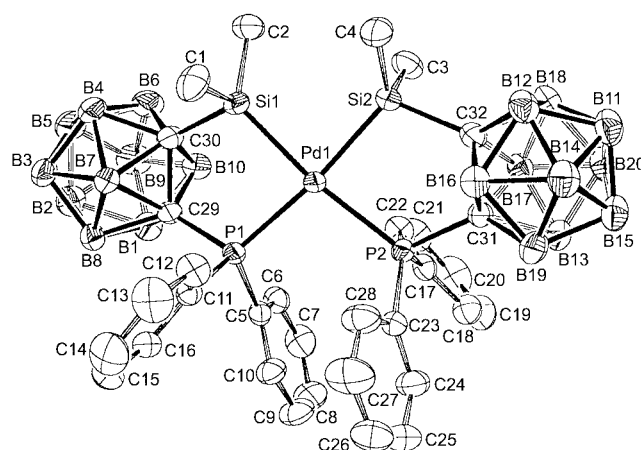


Figure 1. X-ray crystal structure of **5a** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Pd(1)-P(2) 2.3594(6), Pd(1)-Si(2) 2.3596(6), Pd(1)-Si(1) 2.3626(6), Pd(1)-P(1) 2.3663(5), P(1)-C(29) 1.885(2), P(2)-C(31) 1.877(2), P(1)-C(29) 1.885(2), Si(2)-C(4) 1.879(2), Si(2)-C(32) 1.961(2), P(2)-Pd(1)-Si(2) 88.11(2), P(2)-Pd(1)-Si(1) 172.77(2), Si(2)-Pd(1)-Si(1) 84.69(2), P(2)-Pd(1)-P(1) 99.09(2), Si(2)-Pd(1)-P(1) 171.33(2), Si(1)-Pd(1)-P(1) 88.04(2).

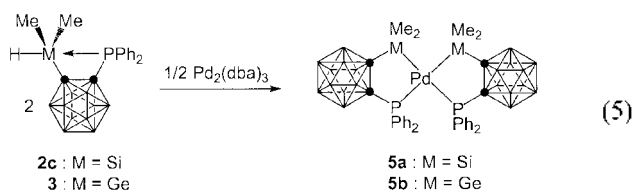
Table 1. Crystal Data of **5a** and **7b**

	5a	7b
empirical formula	C ₃₂ H ₅₂ B ₂₀ P ₂ PdSi ₂	C ₂₂ H ₄₁ B ₁₀ ClGeP ₂ Pd
molecular weight	877.46	690.03
cryst syst	monoclinic	orthorhombic
space group	P2 ₁ /c	P ₂ 2 ₂ /a
a (Å)	11.8908(13)	12.761(2)
b (Å)	15.6583(17)	15.208(2)
c (Å)	23.431(3)	17.225(2)
β (deg)	93.551(8)	
V, Å ³	4354.2(8)	3342.9(8)
Z value	4	4
D(calcd), (g cm ⁻³)	1.503	1.371
cryst size, mm	0.62 × 0.60 × 0.24	0.68 × 0.40 × 0.36
F(000)	1792	1392
μ (mm ⁻¹)	0.582	1.625
2θ range, (deg)	2.14-24.99	3.5-50
scan type	ω	ω
no. of reflns measd	8037	3041
no. of obsd reflns (I > 2σ(I))	7644	2800
R	0.0285	0.0272
wR ₂ ^a	0.0744	0.0712
goodness of fit	1.037	1.043

$$^a wR_2 = \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]^{1/2}$$

The ¹H, ¹³C, and ³¹P NMR spectra of **5a** were consistent with the structure determined by X-ray crystallography. ¹H NMR signal ascribable to the Pd-SiMe₂ moiety was observed at 0.52 (d, ⁴J_{PH} = 1.50 Hz) ppm. The ³¹P NMR signal had clearly shifted from 17.48 ppm for [(Cab^{C,P})SiMe₂]₂ to 63.00 ppm.

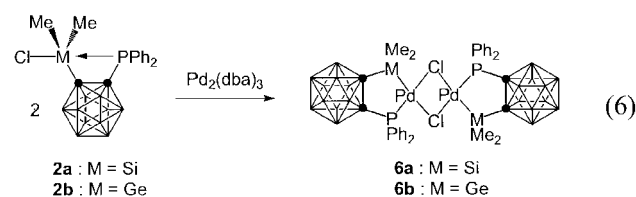
For an alternative synthesis of complex **5a**, the reaction of (Cab^{C,P})SiMe₂H (**2c**) with Pd₂(dba)₃·CHCl₃ afforded the same product, which was isolated as colorless crystal in 78 % yield (eq. 5). Analogous cyclic platinum complex *cis*-



(Cab^{Si,P})₂Pt has been previously prepared by the reaction of HMe₂SiC₂B₁₀H₁₀PPh₂ with (PPh₃)₂Pt(C₂H₄).²⁴ It was well established that hydrosilylation of low-valent metal complexes by the functional silane PPh₂CH₂CH₂SiMe₂H has provided access to a family of new bis-chelate derivatives of the silyl PPh₂CH₂CH₂SiMe₂- in which a silicon-transition metal bond is supported by simultaneous phosphine coordination to the metal. Such cyclic bis[(diphenylphosphino)ethyl]diorganosilyl]platinum complexes have been prepared by the reaction of Ph₂PCH₂CH₂SiHR¹R² with Pt(cod)₂.^{23,25}

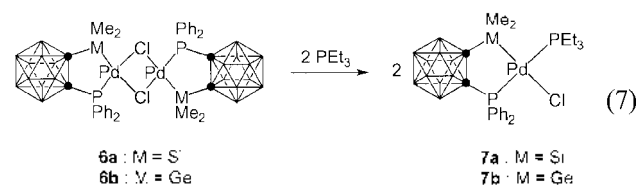
Synthesis of the Bridged Dipalladium Complexes [(Cab^{C,P})MMe₂Pd(μ-X)]₂ (6a, M = Si; 6b, M = Ge). Metathetical reactions of (Cab^{C,P})MMe₂Cl (**2a** and **2b**) with an

equivalent of Pd₂(dba)₃·CHCl₃ in toluene gave the new chloro bridged dipalladium complexes **6a** and **6b** in high yields (eq. 6). When spectroscopic and analytical data of **6a**-



6b are compared with those of the related Sn analogue [(Cab^{C,P})SnMe₂Pd(μ-X)]₂, compounds **6a-6b** have similar dinuclear structures, as shown in eq. 6. Elemental analyses gave satisfactory results for **6a** and **6b**. The dinuclear nature and the chloro bridged mode have been confirmed through single-crystal X-ray diffraction analyses, even though the quality of the crystal is not so good (R = 0.0993). The ¹H, ¹³C, and ³¹P NMR spectra are consistent with the proposed formulation. The ¹H NMR signal for SiMe₂ in **6a** appears at higher field (0.41 ppm) than that for compound **2a**. In particular, the ³¹P NMR signal had clearly shifted from 21.45 ppm for **2a** to 85.05 ppm.

The chloro bridged dipalladium complexes **6a** and **6b** are easily cleaved by triethylphosphine to give the mononuclear palladium complexes **7a** and **7b** (eq. 7). The ¹H, ¹³C, and ³¹P



NMR data for **7b** support the proposed structure. The ¹H NMR spectrum consists of a singlet at 0.72 ppm (*J*_{HP} = 1.20 Hz) due to the Ge-CH₃. In the ³¹P NMR spectrum, two resonances appear at 81.82 and 22.32 ppm for the inequivalent ³¹P nuclei. The large coupling (²J_{P,P} = 384.47 Hz) indicates that the two phosphorus atoms are *trans*. The structure of **7b** was unambiguously established by single-crystal X-ray analysis. The resulting ORTEP plot and selected bond distances and angles of **7b** are shown in Figure 2. Complex **7b** has a square planar geometry and the equatorial plane (Ge(1), Pd(1), P(1), P(2), and Cl(1)) of the Pd moiety is perfectly planar. The Pd-Ge distance (2.3676(5) Å) of **7b** is slightly shorter than that of analogous Pt-Ge complex.²⁶

In summary, we have prepared the first intramolecularly coordinated organosilicon and -germanium compounds of the type (Cab^{C,P})MMe₂X containing the C,P-substituent. The salt elimination reactions of dichloro-tetramethyldisilane and -digermane with **1** afforded the bis(*o*-carboranylphosphino)disilane and -digermane. Bis(silyl)- and (germyl)palladium complexes were prepared by the oxidative addition reaction of the disilane and digermane. Compounds **2a** and **2b** undergoes an oxidative addition reaction with zero valent

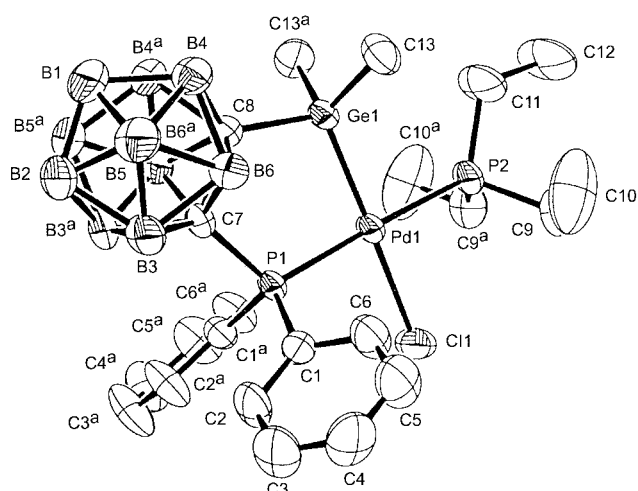


Figure 2. X-ray crystal structure of **7b** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Pd(1)-P(1) 2.3185(9), Pd(1)-P(2) 2.3400(9), Pd(1)-Ge(1) 2.3676(5), Pd(1)-Cl(1) 2.4230(10), Ge(1)-C(8) 2.034(3), P(1)-C(7) 1.893(3), C(7)-C(8) 1.682(4), P(1)-Pd(1)-P(2) 178.20(3), P(1)-Pd(1)-Ge(1) 89.45(2), P(2)-Pd(1)-Ge(1) 92.35(3), P(1)-Pd(1)-Cl(1) 89.44(3), P(2)-Pd(1)-Cl(1) 88.76(3), Ge(1)-Pd(1)-Cl(1) 178.89(3).

palladium compound to give the chloro-bridged dipalladium complexes, which are easily cleaved by triethylphosphine to give the mononuclear metal complexes.

Experimental Section

All experiments were performed under a dry nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques. Toluene and THF were freshly distilled from sodium benzophenone. Hexane was dried and distilled from CaH_2 . ^1H , ^{13}C , and ^{31}P , and ^{29}Si NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.00, 75.44, 121.44, and 59.60 MHz, respectively. Chemical shifts were referenced to TMS (^1H), benzene- d_6 (^1H , δ 7.156; ^{13}C { ^1H }, δ 128.00), and H_3PO_4 . 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 the Callery Chemical Co. and used without purification. The starting materials, $\text{Pd}_2(\text{dba})_3$, ClSiMe_2X (X = H, Cl), Me_2GeCl_2 , NaBH_3CN , $\text{ClSiMe}_2\text{SiMe}_2\text{Cl}$, and PEt_3 were purchased from Aldrich. 1- PPh_2 -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ ²⁷ and $\text{ClGeMe}_2\text{GeMe}_2\text{Cl}$ ²⁸ were prepared according to the literature.

1-Diphenylphosphino-2-chlorodimethylsilyl-1,2-carborane (2a). To a stirred toluene solution (15 mL) of 1- PPh_2 -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (0.2 g, 0.61 mmol) was added a solution of *n*-butyllithium in hexane (0.46 mL, 1.6 M, 0.73 mmol) at 0 °C. The reaction mixture was allowed to ambient temperature and was stirred for 12 h. The reaction mixture was cooled to -78 °C, and a solution of Me_2SiCl_2 (0.16 mL, 0.73 mmol) was added to the reaction mixture at that temperature. The reaction mixture was warmed to ambient temperature and stirred for 3 h, followed by filtration on a celite pad. All

volatiles were removed under reduced pressure and washed with hexane (10 mL) to give **2a** in 56% yield. ^1H NMR (CDCl_3): δ 7.75-7.26 (m, 10H, PPh_2), 0.84 (d, 6H, $^3J_{\text{H-P}} = 1.80$ Hz, Si- CH_3). ^{13}C { ^1H } NMR (CDCl_3): δ 135.15, 134.82, 133.02, 132.86, 130.84, 128.96, 128.66 (*Ph*), 5.18 (d, $^2J_{\text{C-P}} = 9.52$ Hz, Si-C). ^{31}P NMR (CDCl_3): δ 19.11. ^{29}Si NMR (CDCl_3): δ 23.86 (d, $^1J_{\text{Si-P}} = 5.00$ Hz). Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{B}_{10}\text{ClPSi}$: C, 46.65; H, 6.21. Found: C, 45.28; H, 6.04.

1-Diphenylphosphino-2-chlorodimethylgermyl-1,2-carborane (2b). The same procedure was used as described for **2a** except dimethylgermanium dichloride was used instead of dichlorodimethylsilane. yield: 78%. mp: 127 °C. ^1H NMR (CDCl_3): δ 7.75-7.26 (m, 10H, PPh_2), 1.11 (d, 6H, $^3J_{\text{H-P}} = 2.40$ Hz, Ge- CH_3). ^{13}C { ^1H } NMR (CDCl_3): δ 133.58, 133.10, 132.64, 129.46, 127.33, 127.14 (*Ph*), 5.92 (d, $^2J_{\text{C-P}} = 10.66$ Hz, Ge-C). ^{31}P NMR (CDCl_3): δ 21.45. Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{B}_{10}\text{ClPGe}$: C, 41.28; H, 5.62. Found: C, 40.84; H, 5.44.

1-Diphenylphosphino-2-hydridodimethylsilyl-1,2-carborane (2c). The same procedure was used as described for **2a** except chlorodimethylsilane was used instead of dichlorodimethylsilane. yield: 62%. ^1H NMR (CDCl_3): δ 7.81-7.26 (m, 10H, PPh_2), 4.49 (dh, 1H, $^3J_{\text{H-H}} = 4.80$ Hz, $^3J_{\text{H-P}} = 1.24$ Hz, SiH), 0.42 (dd, 6H, $^3J_{\text{H-H}} = 4.80$ Hz, $^3J_{\text{H-P}} = 1.24$ Hz, Si- CH_3). ^{13}C { ^1H } NMR (CDCl_3): δ 135.27, 135.21, 135.07, 132.24, 131.37, 129.03, 128.96 (*Ph*), -2.13 (d, $^2J_{\text{C-P}} = 5.68$ Hz, Si-C). ^{31}P NMR (CDCl_3): δ 17.09. ^{29}Si NMR (CDCl_3): δ -4.50 (d, $^1J_{\text{Si-P}} = 5.84$ Hz). Anal. Calcd for $\text{C}_{16}\text{H}_{27}\text{B}_{10}\text{PSi}$: C, 49.71; H, 7.03. Found: C, 49.34; H, 6.76.

1-Diphenylphosphino-2-hydridodimethylgermyl-1,2-carborane (3). To a stirred toluene solution (15 mL) of **2b** (0.12 g, 0.26 mmol) was added NaBH_3CN (0.033 g, 0.52 mmol, 1 M in THF) at room temperature. After filtering through celite, all volatiles were removed *in vacuo* and washed with hexane. yield: 88%, mp: 102 °C. ^1H NMR (CDCl_3): δ 7.82-7.26 (m, 10H, PPh_2), 4.87 (dh, 1H, $^3J_{\text{H-H}} = 3.92$ Hz, $^3J_{\text{H-P}} = 1.18$ Hz, GeH), 0.58 (dd, 6H, $^3J_{\text{H-H}} = 3.92$ Hz, $^3J_{\text{H-P}} = 1.18$ Hz, Ge- CH_3). ^{13}C { ^1H } NMR (CDCl_3): δ 136.44, 133.85, 132.04, 129.75, 128.64, 127.92 (*Ph*), 2.08 (d, $^2J_{\text{C-P}} = 8.02$ Hz, Ge-C). ^{31}P NMR (CDCl_3): δ 18.30. MS: m/z 431 [M^-]. Anal. Calcd for $\text{C}_{16}\text{H}_{27}\text{B}_{10}\text{PGe}$: C, 44.58; H, 6.30. Found: C, 44.94; H, 6.48.

1,2-Bis(1-diphenylphosphino-1,2-carborane)tetramethyldisilane (4a). The same procedure was used as described for **2a** except 0.5 equiv. of dichlorotetramethyldisilane was used instead of dichlorodimethylsilane. yield: 68%. mp: 248 °C. ^1H NMR (CDCl_3): δ 7.92-7.26 (m, 20H, PPh_2), 0.67 (s, 12H, Si- CH_3). ^{13}C { ^1H } NMR (CDCl_3): δ 135.11, 134.62, 134.22, 133.95, 130.85, 129.13, 128.94, 128.06, 127.57 (*Ph*), 2.98 (s, Si-C). ^{31}P NMR (CDCl_3): δ 17.48. ^{29}Si NMR (CDCl_3): δ -0.70. MS: m/e 771 [M^-]. Anal. Calcd for $\text{C}_{32}\text{H}_{52}\text{B}_{20}\text{P}_2\text{Si}_2$: C, 49.84; H, 6.79. Found: C, 49.52; H, 6.44.

1,2-Bis(1-diphenylphosphino-1,2-carborane)tetramethylgermane (4b). The same procedure was used as described for **2a** except 0.5 equiv. of dichlorotetramethyldigermane was used instead of dichlorodimethylsilane. yield: 72%. mp: 251 °C. ^1H NMR (CDCl_3): δ 7.86-7.26 (m, 20H, PPh_2), 0.84 (s, 12H, Ge- CH_3). ^{13}C { ^1H } NMR (CDCl_3): δ 135.10, 134.62,

130.87, 129.12, 128.94, 128.06, 127.57 (*Ph*), 4.68 (s, Ge-C). ^{31}P NMR (CDCl_3): δ 18.42. Anal. Calcd for $\text{C}_{32}\text{H}_{52}\text{B}_{20}\text{P}_2\text{Ge}_2$: C, 44.68; H, 6.08. Found: C, 44.34; H, 5.84.

Preparation of Pd(1-PPh₂-2-SiMe₂-1,2-C₂B₁₀H₁₀)₂ (5a). To a stirred toluene solution (10 mL) of **4a** (0.10 g, 0.13 mmol) was added Pd₂(dba)₃ (0.09 g, 0.098 mmol) dissolved in toluene (10 mL) at room temperature, and the mixture was stirred for 3 h. The solvent was removed *in vacuo* and chromatographed using CH₂Cl₂ and hexane (15 : 1) as eluent (*R_f* = 0.62). The first band was crystallized from CH₂Cl₂/hexane at -10 °C to give **5a** as white crystals in 88% yield. mp: 270 °C. ^1H NMR (CDCl_3): δ 7.84-7.12 (m, 20H, *PPh*₂), 0.52 (d, 12H, *J_{H-P}* = 1.50 Hz, Si-CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 134.92, 134.76, 134.57, 131.65, 131.24, 128.27 (*Ph*), 6.20 (s, Si-C). ^{31}P NMR (CDCl_3): δ 63.00. Anal. Calcd for $\text{C}_{32}\text{H}_{52}\text{B}_{20}\text{P}_2\text{Si}_2\text{Pd}$: C, 43.80; H, 5.96. Found: C, 43.48; H, 5.68.

Preparation of Pd(1-PPh₂-2-GeMe₂-1,2-C₂B₁₀H₁₀)₂ (5b). The same procedure was used as described for **5a** except **4b** was used instead of **4a**. yield: 82%. mp: 275 °C. ^1H NMR (CDCl_3): δ 7.64-7.12 (m, 20H, *PPh*₂), 0.64 (s, 12H, Ge-CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 134.87, 134.62, 131.96, 131.70, 128.40, 128.28 (*Ph*), 3.62 (s, Ge-C). ^{31}P NMR (CDCl_3): δ 71.04. Anal. Calcd for $\text{C}_{32}\text{H}_{52}\text{B}_{20}\text{P}_2\text{Ge}_2\text{Pd}$: C, 39.76; H, 5.41. Found: C, 39.41; H, 5.26.

Preparation of [(1-PPh₂-2-SiMe₂-1,2-C₂B₁₀H₁₀)Pd(μ -Cl)]₂ (6a). To a stirred toluene solution (15 mL) of **2a** (0.34 g, 0.81 mmol) was added Pd₂(dba)₃ (0.37 g, 0.40 mmol) dissolved in toluene (10 mL) at room temperature, and the mixture was stirred for 5 h at that temperature. All volatiles were removed *in vacuo*. Recrystallization from toluene (10 mL) at -15 °C afforded **6a** as colorless crystals in 78% yield. mp: 165 °C. ^1H NMR (CDCl_3): δ 8.20-7.19 (m, 20H, *PPh*₂), 0.41 (s, 12H, Si-CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 136.29, 136.10, 132.93, 132.59, 128.31, 128.10 (*Ph*), 4.52 (d, *J_{C-P}* = 72.90 Hz, Si-C). ^{31}P NMR (CDCl_3): δ 85.05. Anal. Calcd for $\text{C}_{32}\text{H}_{52}\text{B}_{20}\text{Cl}_2\text{P}_2\text{Si}_2\text{Pd}_2$: C, 36.64; H, 4.96. Found: C, 36.64; H, 4.78.

Preparation of [(1-PPh₂-2-GeMe₂-1,2-C₂B₁₀H₁₀)Pd(μ -Cl)]₂ (6b). The same procedure was used as described for **6a** except **2b** was used instead of **2a**. yield: 88% mp: 201 °C. ^1H NMR (CDCl_3): δ 8.19-7.54 (m, 20H, *PPh*₂), 0.54 (s, 12H, Ge-CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 135.99, 135.77, 132.67, 132.14, 128.55, 128.39 (*Ph*), 5.48 (s, Ge-C). ^{31}P NMR (CDCl_3): δ 89.41. Anal. Calcd for $\text{C}_{32}\text{H}_{52}\text{B}_{20}\text{Cl}_2\text{P}_2\text{Ge}_2\text{Pd}_2$: C, 33.60; H, 4.57. Found: C, 33.04; H, 4.38.

Preparation of [(1-PPh₂-2-SiMe₂-1,2-C₂B₁₀H₁₀)Pd(PEt₃)Cl] (7a). To a stirred toluene solution (15 mL) of **6a** (0.2 g, 0.189 mmol) was added PEt₃ (0.38 mL, 1 M, 0.378 mmol) at room temperature, and the solution was stirred for 8 h. After filtering through celite, the solvent was removed *in vacuo* and the residue was recrystallized from toluene/hexane to afford complex **7a** as colorless crystals in 93% yield. mp: 110 °C. ^1H NMR (CDCl_3): δ 8.10-7.26 (m, 10H, *PPh*₂), 2.04 (dq, 6H, *J_{H-H}* = 7.20 Hz, *J_{H-P}* = 1.20 Hz, CH₂), 1.18 (t, 9H, *J_{H-H}* = 7.20 Hz, CH₃), 0.60 (d, 6H, *J_{H-P}* = 2.10 Hz, Si-CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 136.42, 136.24, 132.21, 129.32,

128.29, 128.14 (*Ph*), 15.74 (d, *J_{C-P}* = 23.46 Hz, P-CH₂), 8.80, 6.01 (d, *J_{C-P}* = 5.50 Hz, Ge-CH₃). ^{31}P NMR (CDCl_3): δ 78.19 (d, *J_{P-P}* = 357.03 Hz, *PPh*₂), 21.30 (d, *J_{P-P}* = 357.03 Hz, PEt₃). Anal. Calcd for $\text{C}_{22}\text{H}_{41}\text{B}_{10}\text{ClP}_2\text{SiPd}$: C, 40.89; H, 6.54. Found: C, 40.52; H, 6.24.

Preparation of [(1-PPh₂-2-GeMe₂-1,2-C₂B₁₀H₁₀)Pd(PEt₃)Cl] (7b). The same procedure was used as described for **7a** except **6b** was used instead of **6a**. yield: 92%. mp: 273 °C. ^1H NMR (CDCl_3): δ 8.06-7.14 (m, 10H, *PPh*₂), 2.01 (dq, 6H, *J_{H-H}* = 8.08 Hz, *J_{H-P}* = 2.70 Hz, CH₂), 1.18 (t, 9H, *J_{H-H}* = 8.08 Hz, CH₃), 0.72 (d, 6H, *J_{H-P}* = 1.20 Hz, Ge-CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 136.41, 136.22, 132.44, 129.32, 128.26, 128.12 (*Ph*), 15.72 (d, *J_{C-P}* = 25.95 Hz, P-CH₂), 8.77 (CH₂CH₃), 6.84 (d, *J_{C-P}* = 3.92 Hz, Ge-CH₃). ^{31}P NMR (CDCl_3): δ 81.82 (d, *J_{P-P}* = 384.47 Hz, *PPh*₂), 22.32 (d, *J_{P-P}* = 384.47 Hz, PEt₃). Anal. Calcd for $\text{C}_{22}\text{H}_{41}\text{B}_{10}\text{ClP}_2\text{GePd}$: C, 38.23; H, 5.98. Found: C, 37.94; H, 5.92.

X-ray Crystallography. Details of the crystal data and a summary of intensity data collection parameters for **5a** and **7b** are given in Table 1. Crystals of **5a** was grown from CH₂Cl₂/Hexane at -10 °C, and crystal of **7b** was grown from toluene at -15 °C. Crystals of **5a** and **7b** were mounted in thin-walled glass capillaries and sealed under argon. The data sets for the two crystals were collected on an Enraf CAD 4 automated diffractometer. Mo K α 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 **5a** and **7b** were refined anisotropically. All other hydrogen atoms were included in the calculated positions.

Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition Nos. CCDC-183910 (**5a**) and CCDC-183911 (**7b**)). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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