

Synthesis and Reactivity of Organotin Compounds Containing the C,P-Chelating *o*-Carboranylphosphino Ligand [*o*-C₂B₁₀H₁₀PPh₂-C,P](Cab^{C,P}). X-ray Structures of (Cab^{C,CH₂P})SnMe₂Br, [(Cab^{C,P})SnMe₂]₂Pd, and [(Cab^{C,P})SnMe₂]Pd(PEt₃)Cl

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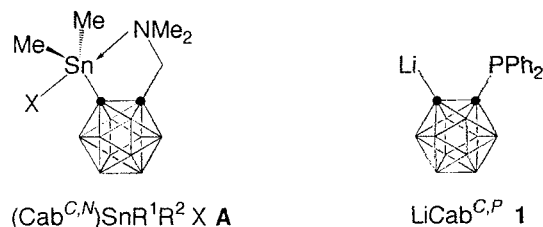
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The triorganotin halides (Cab^{C,P})SnMe₂X (**2a**, X = Cl; **2b**, X = Br) and a tetraorganotin compound (Cab^{C,P})SnMe₃ (**7**), containing the *o*-carboranylphosphino ligand (Cab^{C,P}), have been prepared by the reaction of LiCab^{C,P} (**1**) with Me₂SnX₂ and Me₃SnCl, respectively. ¹H, ¹³C, ³¹P, and ¹¹⁹Sn NMR spectroscopy indicate that the tin centers in **2a** and **2b** are pentacoordinate as a result of intramolecular Sn–P coordination, whereas the tin center in **7** is tetracoordinate. The substitution reactions of **2a** using NaI, NaN₃, NaCpFe(CO)₂, and NaB(CN)H₃ afforded the substituted products (Cab^{C,P})SnMe₂X (**3**, X = I; **4**, X = N₃; **5**, X = CpFe(CO)₂; **6**, X = H). The Wurtz-type coupling reaction of **2a** with sodium afforded the distannane. The reaction of the distannane **10** with Pd₂(dba)₃·CHCl₃ afforded the bis(stannyll)-palladium complex **11**. When compounds **2a** and **2b** were employed in the reaction with Pd₂(dba)₃, the halo-bridged metal complexes **12a** and **12b** were isolated. The crystal structures of **9b**, **11**, and **13** were determined by X-ray structural studies. As a result of the Sn–P interaction, the tin atom in **9b** exhibits a distorted trigonal-bipyramidal configuration.

Introduction

Although there is a variety of organotin halides with C,N-chelating ligands that are bonded to the tin atom by an Sn–C covalent bond and an Sn–N dative bond,¹ organotin compounds containing an intramolecular coordination of a C,P-chelating ligand have been quite limited, probably due to the difficulty of their preparation. Moreover, organotin compounds with phosphines which are soft bases are known only with strong acceptors such as monoorganotin trihalides² and diorganotin dihalides.³ Recently, Weichmann⁴ reported the

synthesis of phosphinoalkylchlorostannanes and Pt-[PPh₂(CH₂)_nSnMe₂]₂, which provided a mechanistic model for the double stannylation of unsaturated organic substrates. We⁵ have investigated the synthesis of organotin compounds of the type (Cab^{C,N})SnR¹R²X (**A**), in which the tin center is pentacoordinate as a result of intramolecular Sn–N coordination. Such an Sn–N interaction in these compounds is favored by the presence of electronegative substituents on tin, such as a halogen and a carboranyl unit.



We reasoned that intramolecularly coordinated organotin compounds containing a carboranyl unit and a C,P-substituent (Cab^{C,P}) might stabilize the pentacoordinate tin center and be useful starting compounds for further transformations. We have adopted a systematic approach to developing this system through the syn-

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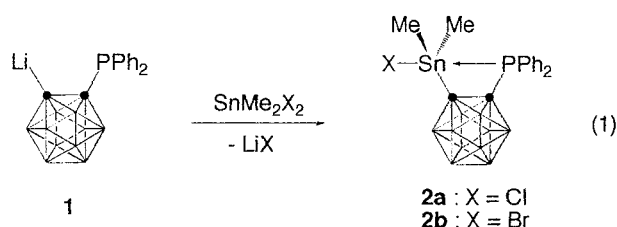
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thesis of analogues of $(\text{Cab}^{C,P})\text{SnMe}_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) functionalized at tin using the lithium derivative of the potentially bidentate C,P-chelating *o*-carboranylphosphino ligand system $\text{LiCab}^{C,P}$ (**1**). In this paper, we describe (i) the facile synthesis of triorganotin halides containing intramolecular Sn–P coordination; (ii) the isolation of the distannane by the Wurtz-type coupling reaction of $(\text{Cab}^{C,P})\text{SnMe}_2\text{Cl}$; (iii) the synthesis of a stable cyclic bis(*o*-carboranylstannyl)palladium complex; and (iv) the synthesis of bridged bimetallic complexes by the oxidative addition reaction of $(\text{Cab}^{C,P})\text{SnMe}_2\text{X}$ with a zerovalent palladium compound.

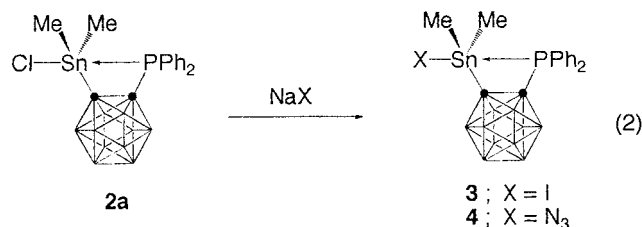
Results and Discussion

Synthesis of the Triorganotin Halides $(\text{Cab}^{C,P})\text{SnMe}_2\text{X}$ (2a** and **2b**).** Compounds **2a** and **2b** were prepared as colorless solids by the reaction of $\text{LiCab}^{C,P}$ (**1**) with a stoichiometric amount of Me_2SnX_2 according to eq 1. Compounds **2a** and **2b** are soluble in toluene



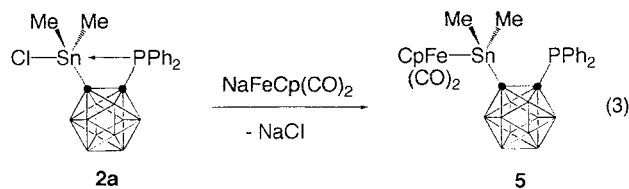
and THF. The ^1H , ^{13}C , and ^{31}P NMR spectra for **2a** and **2b** support the proposed structure. We observed indications of a weak intramolecular Sn–P interaction from the NMR spectra. The direct evidence for the existence of an intramolecular Sn–P coordination in **2a** is provided by (i) the distinctive splitting pattern in its ^1H NMR spectrum due to coupling of a P atom with the tin-methyl hydrogen ($^3J_{\text{H-P}} = 3.00$ Hz), (ii) the existence of a doublet at δ 3.40 ($^2J_{\text{C-P}} = 13.06$ Hz) in its ^{13}C NMR spectrum due to coupling of the tin-methyl carbon and a phosphorus atom, and (iii) the observation of a singlet with $^{117,119}\text{Sn}$ satellites, at δ 29.71 ($^1J_{^{31}\text{P}-^{119}\text{Sn}} = 74.3$ Hz) in its ^{31}P NMR spectrum, at δ 108.3 ($^1J_{^{119}\text{Sn}-^{31}\text{P}} = 72.6$ Hz) in its ^{119}Sn NMR spectrum by coupling of the ^{119}Sn and P atoms. The downfield shifts and the low values of the coupling constants of the ^1H , ^{13}C , and ^{31}P NMR spectra for **2a** and **2b** compared with those for the phosphinoalkylchlorostannanes of the type $\text{Me}_2\text{SnCl}(\text{CH}_2)_n\text{PR}^1\text{R}^2$ ($n = 2, 3$) indicate that the compounds **2a** and **2b** have weaker Sn–P interaction.⁴

Compound **2a** was found to be a good starting material for further transformations. When a colorless toluene-*d*₈ solution of **2a** was treated at ambient temperature with sodium iodide, a yellow color developed within 2 h. Analysis of this solution by ^1H NMR spectroscopy showed clean conversion to the product **3**, which was isolated and characterized (eq 2). The reac-



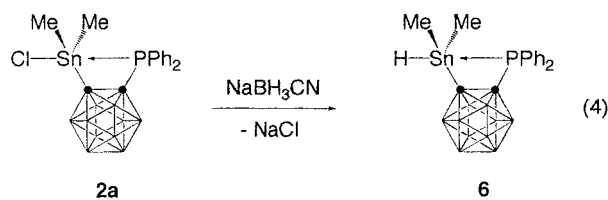
tion between **2a** and sodium azide proceeded cleanly to give compound **4** as colorless crystals. The ^1H , ^{13}C , and ^{31}P NMR spectral data of compounds **3** and **4** are consistent with the presence of the bidentate *o*-carboranylphosphino ligand.

$(\text{Cab}^{C,P})\text{SnMe}_2\{\text{FeCp}(\text{CO})_2\}$ (**5**) was prepared as yellow crystals by the reaction of compound **2a** with a stoichiometric amount of $\text{NaFeCp}(\text{CO})_2$ (eq 3). Com-



pound **5** decomposes in air. The signal for Sn–CH₃ in the ^1H and ^{13}C NMR spectroscopic data is at a higher field than that of compounds **2**–**4**. The splitting pattern due to the coupling of ^{119}Sn and P in the ^{31}P NMR spectrum is absent. The NMR data suggest that compound **5** is tetracoordinated in solution. This is demonstrated clearly by the downfield shift of the ^{119}Sn NMR resonance at 196.5 ppm. It was known that, in the case of triorganotin halides, the acceptor strength of the tin atom is so weak that only a few stable adducts with phosphines were known.⁶ Accordingly, the presence of a strong metal nucleophile such as $\text{CpFe}(\text{CO})_2$ as a substituent will not allow adduct formation with the Lewis base, a phosphorus donor.

The triorganotin hydride $(\text{Cab}^{C,P})\text{SnMe}_2\text{H}$ (**6**) compound was prepared by the reaction of compound **2a** with sodium cyanoborohydride as a reducing agent (eq 4). Initially, we attempted the substitution reaction of



compound **2a** with LiAlH_4 at room temperature, but decomposition occurred. After many attempts, we found that sodium cyanoborohydride, a mild reducing agent, served well in the conversion of the tin chloride to the tin hydride without any cleavage of the Sn–C (carborane) bond. An ^1H NMR signal ascribable to the Sn–H bond was observed at 6.23 ($^2J_{\text{H-P}} = 10.2$ Hz, $^3J_{\text{H-H}} = 1.8$ Hz) ppm. The ^{31}P NMR spectrum of **6** shows the expected pattern of a singlet ($^1J_{^{31}\text{P}-^{119}\text{Sn}} = 71.6$ Hz) at 25.12 ppm. The infrared spectrum of **6** shows the stretching mode of $\nu(\text{SnH})$ at 1878 cm^{-1} .

Synthesis of the Tetraorganotin Complex $(\text{Cab}^{C,P})\text{SnMe}_3$ (7**).** $(\text{Cab}^{C,P})\text{SnMe}_3$ was prepared readily in high yield by the reaction between $\text{LiCab}^{C,P}$ and Me_3SnCl . The signal for $\text{Sn}(\text{CH}_3)_3$ in the ^1H NMR spectrum is at a higher field compared with that of the triorganotin halides $(\text{Cab}^{C,P})\text{SnMe}_2\text{X}$. However, the splitting pattern and coupling constants are comparable to those of $(\text{Cab}^{C,P})\text{SnMe}_2\text{X}$ (**2a** and **2b**). The ^{119}Sn NMR spectrum of **7** shows a resonance at 106.4 ppm. The chemical

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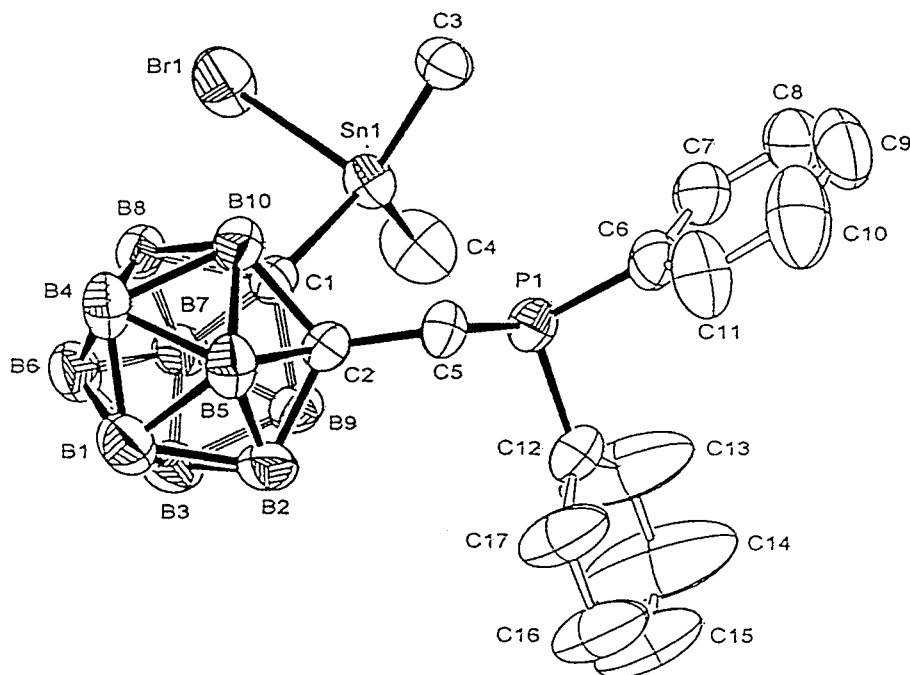
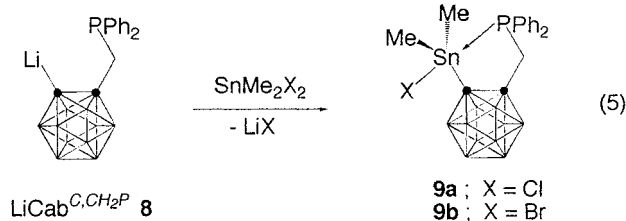


Figure 1. X-ray crystal structure of **9b** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Sn(1)–P(1) 3.188(1), Sn(1)–Br(1) 2.5568(7), Sn(1)–C(1) 2.204(4), C(1)–Sn(1)–Br(1) 96.49(9).

shift is consistent with prior observations of a five-coordinated Sn atom. The compound is unusual in that our previous study demonstrated that the tetraorganotin complex (Cab^{C,N})SnMe₃ has a tetrahedral ligand arrangement around the tin atom. Accordingly, this could involve a weak intramolecular interaction between the tin and phosphorus atoms.

Synthesis of the Five-Membered Triorganotin Halides (Cab^{C,CH₂P})SnMe₂X (9a and 9b). Although the triorganotin halides (Cab^{C,P})SnMe₂X with an intramolecular Sn←P coordination are well established, we believed that the compounds have a relatively weak Sn–P interaction due to the rigidity of the carborane backbone. A more suitable alternative ligand for a stronger Sn–P interaction is the five-membered bidentate phosphinomethylcarboranyl ligand. This proved to be the case. The reaction between LiCab^{C,CH₂P} (**8**) and Me₂SnX₂ (X = Cl, Br) proceeds cleanly to give (Cab^{C,CH₂P})SnMe₂X as colorless crystals (eq 5).



Compounds **9a** and **9b** are moderately soluble in toluene and THF. The structure of **9b**, unambiguously established by single-crystal X-ray analysis, is shown in Figure 1. Crystallographic data and processing parameters are given in Table 1. Atoms C(1), C(3), and C(4) constitute a basal plane, while the coordination sphere of Sn(1) is completed by P(1) and Br(1) residing in the axial positions. Because the P(1)–Sn(1)–Br(1) bond angle is 168.4(3)^o and the sum of the bond angles surrounding the Sn atom on the basal plane is 358.2^o,

the coordination environment about Sn(1) may be described as slightly distorted trigonal bipyramidal. Such distorted geometry was found in other structural reports on {3-[*tert*-butyl(phenyl)phosphino]propyl}dimethyltin chloride.⁶ The Sn(1)–P(1) intramolecular interaction distance (3.188(1) Å) is comparable to that observed for Me₂SnCl[(CH₂)₃PR₂] (3.078 Å). On the basis of an average value of 2.52 Å for the few known Sn–P single bond lengths,⁷ the Sn–P distance of 3.188(1) Å in **9b** indicates that the Sn–P intramolecular coordination is weak. The Sn–Br bond distance (2.5568(7) Å) shows a slight lengthening, which falls in the range observed for other pentacoordinated adducts of triorganotin halides.⁸

The ¹H, ¹³C, ³¹P, and ¹¹⁹Sn NMR spectra of **9b** were consistent with the structure determined by X-ray crystallography. ¹H NMR signals ascribable to the SnMe₂ and CH₂ were observed at 1.19 (d, ³J_{H–P} = 4.2 Hz, ²J_{H–¹¹⁹Sn} = 67.5 Hz, ²J_{H–¹¹⁷Sn} = 63.6 Hz) and 3.25 (d, ²J_{H–P} = 2.1 Hz) ppm, respectively. The ³¹P NMR signal had shifted from 29.12 (s, ¹J_{P–¹¹⁹Sn} = 48.6 Hz) ppm for (Cab^{C,P})SnMe₂Br to 35.22 ppm with a big coupling constant of ¹J_{P–Sn} (55.2 Hz). The ¹¹⁹Sn NMR chemical shift of –30.2 ppm as a doublet strongly resembles the literature value for the intramolecular P-functional triorganotin halides.^{4b}

Synthesis of the Bis(*o*-carboranylphosphino)-distannane, [(Cab^{C,P})SnMe₂]₂ (10). The Wurtz-type coupling reaction of **2a** using sodium afforded the corresponding distannane containing pseudo-tetracoordinate tin centers (eq 6). The reaction of **2a** with 5 equiv

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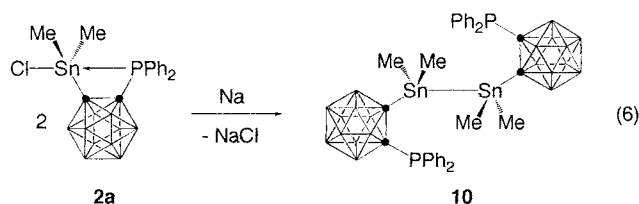
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Table 1. Crystal Data of **9b**, **11**, and **13**

	9b	11	13
empirical formula	C ₁₇ H ₂₈ B ₁₀ BrPSn	C ₃₂ H ₅₂ B ₂₀ P ₂ PdSn ₂	C ₂₂ H ₃₁ B ₁₀ ClP ₂ PdSn
molecular weight	570.06	1058.66	726.05
cryst syst	monoclinic	monoclinic	orthorhombic
space group	<i>C2/c</i>	<i>P2₁/c</i>	<i>P_{mma}</i>
<i>a</i> (Å)	27.071(4)	12.106(1)	12.840(1)
<i>b</i> (Å)	14.322(2)	16.056(2)	15.035(2)
<i>c</i> (Å)	14.151(3)	23.321(2)	17.247(1)
β (deg)	113.272(9)	95.077(7)	
<i>V</i> , Å ³	5040(1)	4515.2(8)	3329.4(5)
<i>Z</i> value	8	4	4
<i>D</i> (calcd) (g cm ⁻³)	1.503	1.557	1.448
cryst size, mm	0.80 × 0.60 × 0.28	0.62 × 0.60 × 0.24	0.28 × 0.20 × 0.20
<i>F</i> (000)	2240	1792	1424
μ (mm ⁻¹)	2.677	1.589	1.479
2θ range (deg)	4.06–50	3.5–50	3.5–50
scan type	ω	ω	ω
no. of reflns measd	4461	8097	3318
no. of obsd reflns (<i>I</i> > 2 σ (<i>I</i>))	4364	7698	3026
<i>R</i>	0.0358	0.0343	0.0462
<i>wR</i> ₂ ^a	0.0912	0.0836	0.1167
goodness of fit	1.038	1.099	1.061

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

of sodium in toluene at room temperature for 3 h gave the distannane [(Cab^{C,P})SnMe₂]₂ (**10**) in 46% yield.

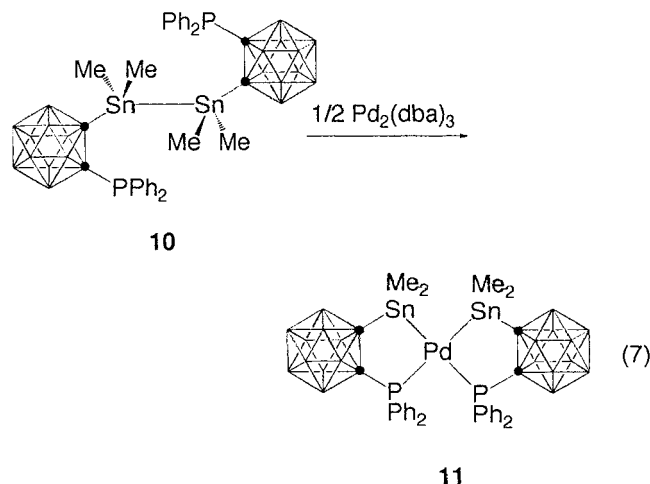


The composition of **10** was established by elemental analysis. The ¹H, ¹³C, and ³¹P NMR spectra of **10** also are consistent with its assigned structure. The signals for Sn(CH₃) in the ¹H NMR spectrum are at a higher field than for the intramolecular tin compounds (**2–4**). In particular, the ³¹P NMR signal had clearly shifted from 29.71 (d, ¹J_{31P–¹¹⁹Sn} = 74.3 Hz) ppm for (Cab^{C,P})-SnMe₂Cl to –12.78 ppm as a singlet. The NMR data suggest that compound **10** is tetracoordinated in solution and has no interaction between tin and phosphorus. This is demonstrated most clearly by the downfield shift of the ¹¹⁹Sn NMR resonance at 162.6 ppm.

Synthesis of the Bis(stannyll)palladium Complex (Cab^{C,P})₂Pd (11**).** Bis(stannyll)palladium complexes have been implicated as key intermediates in the double stannylation of alkynes,⁹ 1,3-dienes,¹⁰ and allenes.¹¹ However, only a few bis(stannyll)complexes have been fully characterized.¹¹ The complexes were found to be formed by the oxidative addition reaction of organodistannane with palladium compounds. Compound **10** was chosen as a good candidate for the oxidative addition reaction because the tin atom is anchored to the palladium atom through the chelating phosphine tethers.

Treatment of the distannane **10** with Pd₂(dba)₃·CHCl₃ (dba = dibenzylideneacetone) in toluene at room temperature resulted in the oxidative addition of the Sn–

Sn to the palladium to afford the bis(stannyll)palladium complex **11** as colorless crystals in 34% yield (eq 7). Complex **11** is stable in an inert-gas environment and shows slow decomposition when in contact with air. It is readily soluble in organic solvents such as aromatic hydrocarbons and THF.



The molecular structure of **11** has been determined by X-ray diffraction. The structure is given in Figure 2, and crystallographic data are given in Table 1. Complex **11** has a square-planar geometry with cis-arrangement of the two tin atoms. The Pd–Sn bond distance (2.5743(5)–2.5760(5) Å) of **11** is in agreement with the corresponding values observed in (d¹bpe)PdH(SnMe₃) (2.573(2) Å)¹² and Pd[η²-(SiMe₂CH₂CH₂PPh₂)] [η²-(SnMe₂CH₂CH₂PPh₂)] (2.573(2) Å).¹³ The distance between Sn(1) and Sn(2) (3.2612(5) Å) suggests the presence of considerable Sn–Sn interaction. The ¹H, ¹³C, and ³¹P NMR spectra of **11** were consistent with the structure determined by X-ray crystallography. In particular, the ³¹P NMR spectrum of **11** showed a resonance centered at 78.50 ppm with satellite peaks due to ²J_{P–Sn(transoid)} (2054.8 Hz with ¹¹⁹Sn and 1943.0 Hz with ¹¹⁷Sn), ²J_{P–¹¹⁹Sn(cisoid)} (207.7 Hz), and ²J_{P–¹¹⁷Sn(cisoid)} (194.2 Hz).

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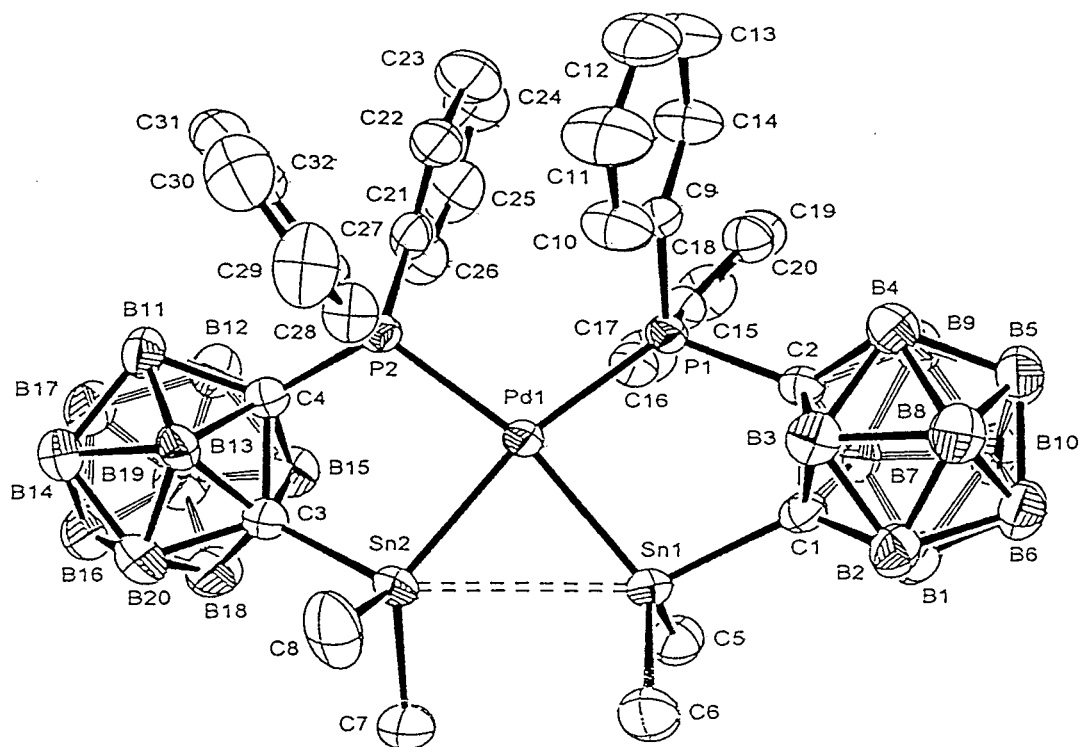
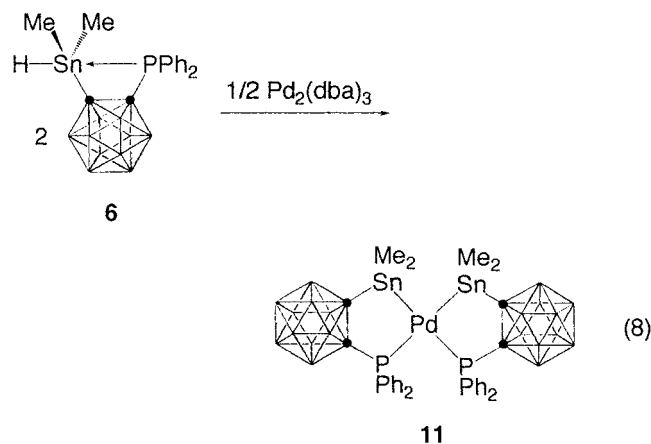


Figure 2. X-ray crystal structure of **11** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Sn(1)–C(1) 2.213(4), Sn(1)–Pd(1) 2.5760(5), Sn(1)–Sn(2) 3.2612(5), Sn(2)–C(3) 2.215(5), Sn(2)–Pd(1) 2.5743(5), Pd(1)–P(1) 2.345(1), Pd(1)–P(2) 2.349(1), P(1)–C(2) 1.896(4), P(2)–C(4) 1.908(4), C(1)–Sn(1)–Pd(1) 100.73(11), C(3)–Sn(2)–Pd(1) 99.27(12), P(1)–Pd(1)–P(2) 104.23(4), P(1)–Pd(1)–Sn(2) 166.87(3), P(2)–Pd(1)–Sn(2) 88.89(3), P(1)–Pd(1)–Sn(2) 88.44(3), P(2)–Pd(1)–Sn(1) 165.87(3), Sn(2)–Pd(1)–Sn(1) 78.573(14).

These values resemble the literature values for the *cis*-{Pt[PPh₂(CH₂)₂SnMe₂]₂}^{4a} and Pt(SnMe₃)₂(PR₃)₂¹⁴ complexes.

We have also carried out the reaction of 1-PPh₂-2-SnMe₂H-1,2-C₂B₁₀H₁₀ (**6**) with Pd₂(dba)₃ in toluene in an alternative synthesis of complex **11**, which was isolated as colorless crystals in 80% yield (eq 8). It was



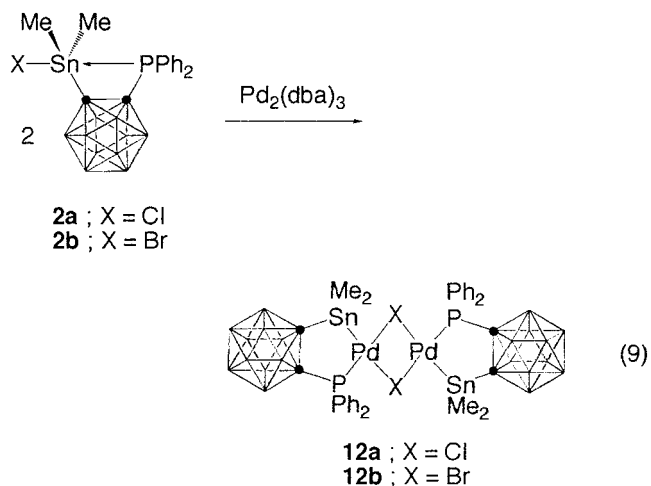
well established that hydrosilylation of low-valent metal complexes by the functional silane PPh₂CH₂CH₂SiMe₂H¹⁵ has provided access to a family of new bis-chelate derivatives of the silyl PPh₂CH₂CH₂SiMe₂– in which a silicon–transition metal bond is supported by simultaneous phosphine coordination to the metal atom. Such

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cyclic bis[(diphenylphosphinoethyl)diorganosilyl]platinum complexes have been prepared by the reaction of Ph₂PCH₂CH₂SiHR¹R² with Pt(cod)₂.¹⁶

Synthesis of the Bridged Dipalladium Complex [(Cab^{C,P})₂Pd(μ-X)]₂ (12a** and **12b**).** To determine how the five-coordinate tin complexes **2a** and **2b** would react with the low-valent metal complexes, the reaction of **2a** and **2b** with Pd₂(dba)₃ was investigated. Consequently, when compounds **2a** and **2b** were employed as starting compounds in the reaction with Pd₂(dba)₃, the halobridged dipalladium metal complexes **12a** and **12b** were isolated as yellow crystals in high yield (eq 9). The



yellow products **12a** and **12b** are moderately stable in air and decompose slowly on contact with moisture. Compounds **12a** and **12b** are soluble in toluene and

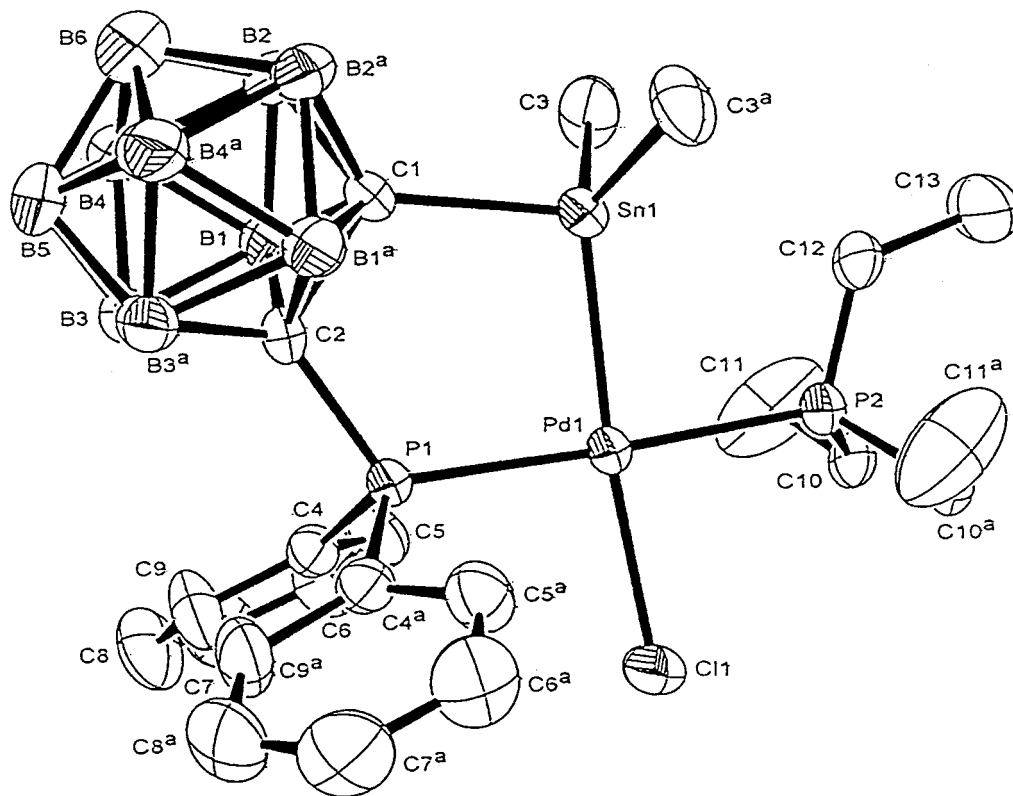
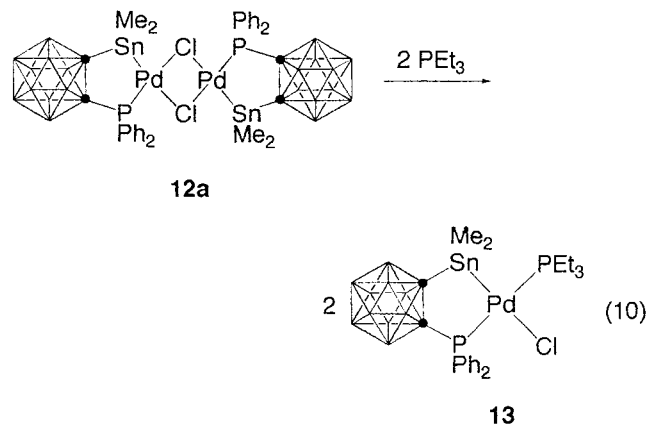


Figure 3. X-ray crystal structure of **13** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Sn(1)–C(1) 2.222(8), Sn(1)–Pd(1) 2.5169(8), Pd(1)–P(2) 2.281(2), Pd(1)–P(1) 2.338(2), Pd(1)–Cl(1) 2.417(2), P(1)–C(2) 1.883(8), C(1)–Sn(1)–Pd(1) 101.2(2), P(2)–Pd(1)–P(1) 176.86(8), P(2)–Pd(1)–Cl(1) 88.48(8), P(1)–Pd(1)–Cl(1) 94.66(8), P(2)–Pd(1)–Sn(1) 86.14(6), P(1)–Pd(1)–Sn(1) 90.73(5), Cl(1)–Pd(1)–Sn(1) 174.61(6).

THF and were characterized by ^1H , ^{13}C , and ^{31}P NMR and elemental analysis. The ^1H NMR signal for SnMe_2 in **12a** is at higher field (0.42 ppm) than that for compound **2a**. In particular, the ^{31}P NMR signals had clearly shifted from 29.71 ($^1J_{^{31}\text{P}-^{119}\text{Sn}} = 74.3$ Hz) ppm for $(\text{Cab}^{C,P})\text{SnMe}_2\text{Cl}$ to 91.37 ppm with a rather big coupling constant of $^2J_{\text{P}-\text{Sn}}$ (208.6 Hz). The ^{119}Sn spectrum of **12a** showed a resonance at -118.3 ppm.

Compound **12a** is easily cleaved by an external strong donor ligand such as triethylphosphine to give the mononuclear palladium compound **13** (eq 10). The



formulation of **13** was established by elemental analysis. Furthermore, the spectroscopic data (^1H , ^{13}C , and ^{31}P NMR) for **13** also are consistent with its assigned structure. The ^1H NMR spectrum consists of a singlet due to the SnMe at 0.59 ppm. In the ^{31}P NMR spectrum,

two signals are observed at 80.49 and -94.53 ppm for the inequivalent ^{31}P nuclei, for which the coupling $^2J_{\text{P}-\text{P}}$ is large. The large couplings ($^2J_{^{31}\text{P}-^{31}\text{P}} = 428.8$ Hz) indicate that the two phosphorus atoms are trans.

The structure of **13** was unambiguously established by single-crystal X-ray analysis. The molecular structure of **13** is shown in Figure 3. 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 Sn(1), Pd(1), Cl(1), P(1), P(2), B(5), C(1), C(2), C(12), and C(13) atoms. This symmetry clearly explains that seven atoms (Pd(1), Sn(1), P(1), P(2), Cl(1), C(1), and C(2)) are perfectly coplanar and also that the equatorial plane (Pd(1), Sn(1), P(1), P(2), and Cl(1)) of the Pd moiety is perfectly planar. The Pd–Sn distance (2.5169(8) Å) of **13** conforms to literature expectations (2.554–2.595 Å).¹⁷

In summary, we have isolated intramolecularly coordinated organotin compounds of the type $(\text{Cab}^{C,P})\text{SnMe}_2\text{X}$ containing the C,P-substituent. The compound $(\text{Cab}^{C,P})\text{SnMe}_2\text{Cl}$ readily undergoes a substitution reaction with NaI , NaN_3 , and $\text{NaFeCp}(\text{CO})_2$ to afford the substituted products. The compound **2a** also undergoes a Wurtz-type coupling reaction with Na to give the distannane compound. A bis(stannyll)palladium complex was prepared by the oxidative addition reaction of the distannane or by dehydrostannylation of the chelated

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tin hydride by $\text{Pd}_2(\text{dba})_3$. Compound **2a** undergoes an oxidative addition reaction with $\text{Pd}_2(\text{dba})_3$ to afford the bridged dipalladium complex, which is easily cleaved by a donor ligand to give the mononuclear metal compound. Compound **2a** was found to be a good starting material. 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. Toluene and THF were freshly distilled from sodium benzophenone. Hexane was dried and distilled from CaH_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; $^{13}\text{C}\{^1\text{H}\}$, 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, $\text{Pd}_2(\text{dba})_3$, $\{\text{CpFe}(\text{CO})_2\}_2$, and Me_2SnX_2 ($\text{X} = \text{Cl}, \text{Br}$), were purchased from Strem Chemical. 1- PPh_2 -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ ¹⁸ and 1- PPh_2 - CH_2 -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ ¹⁹ were prepared according to the literature.

1-Diphenylphosphino-2-chlorodimethyltin-1,2-carborane (2a). To a stirred toluene solution (15 mL) of 1- PPh_2 -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (0.3 g, 0.91 mmol) was added a solution of *n*-butyllithium in hexane (0.7 mL, 1.6 M, 1.12 mmol) at 0 °C. The reaction mixture was allowed to warm to ambient temperature and was stirred for 12 h. The reaction mixture was cooled to -78 °C, and a solution of Me_2SnCl_2 (0.2 g, 0.91 mmol) was added to the reaction mixture at that temperature. The reaction mixture was warmed to ambient temperature and stirred for 8 h, followed by filtration on a Celite pad. All volatiles were removed under reduced pressure and washed with hexane (15 mL \times 3). Recrystallization from toluene gave the title compound (0.35 g, 74%) as colorless crystals, mp 188–190 °C. ^1H NMR (CDCl_3): δ 7.70–7.42 (m, 10H, *PPh}_2*), 1.06 (d, 6H, $^3J_{\text{H-P}} = 3.00$ Hz, $^2J_{\text{H-}^{119}\text{Sn}} = 68.4$ Hz, $^2J_{\text{H-}^{117}\text{Sn}} = 62.4$ Hz, Sn-CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 134.72, 134.43, 131.56, 129.13, 129.06, 129.00 (*Ph*), 3.40 (d, $^2J_{\text{C-P}} = 13.06$ Hz, Sn-C). ^{31}P NMR (CDCl_3): δ 29.71 (s, $^1J_{^{31}\text{P-}^{119}\text{Sn}} = 74.3$ Hz, *PPh}_2*). ^{119}Sn NMR (CDCl_3): δ 108.3 (d, $^1J_{^{119}\text{Sn-}^{31}\text{P}} = 72.6$ Hz). Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{B}_{10}\text{ClPSn}$: C, 37.55; H, 5.08. Found: C, 37.24; H, 4.98.

1-Diphenylphosphino-2-bromodimethyltin-1,2-carborane (2b). The same procedure was used as described for **2a** except dibromodimethyltin was used instead of dichlorodimethyltin. Yield: 67%, mp 188–190 °C. ^1H NMR (CDCl_3): δ 7.72–7.39 (m, 10H, *PPh}_2*), 1.14 (d, 6H, $^3J_{\text{H-P}} = 4.5$ Hz, $^2J_{\text{H-}^{119}\text{Sn}} = 101.1$ Hz, $^2J_{\text{H-}^{117}\text{Sn}} = 92.4$ Hz, Sn-CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 134.85, 134.40, 132.04, 131.52, 129.18, 128.99 (*Ph*), 4.08 (d, $^2J_{\text{C-P}} = 21.04$ Hz, Sn-C). ^{31}P NMR (CDCl_3): δ 29.12 (s, $^1J_{^{31}\text{P-}^{119}\text{Sn}} = 48.6$ Hz, *PPh}_2*). ^{119}Sn NMR (CDCl_3): δ 96.4 (d, $^1J_{^{119}\text{Sn-}^{31}\text{P}} = 118.8$ Hz). Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{B}_{10}\text{BrPSn}$: C, 34.57; H, 4.68. Found: C, 34.74; H, 4.76.

1-Diphenylphosphino-2-iododimethyltin-1,2-carborane (3). To a stirred toluene solution (10 mL) of **2a** (0.1 g, 0.2 mmol) was added NaI (0.03 g, 0.2 mmol) at room temperature, and the mixture was stirred for 8 h at that temperature. The reaction mixture was filtered. The colorless solution was reduced to incipient crystallization and stored in a ca. -10 °C freezer to give **3**. Yield: 78%, mp 172 °C. ^1H NMR (CDCl_3): δ

7.71–7.43 (m, 10H, *PPh}_2*), 1.25 (d, 6H, $^3J_{\text{H-P}} = 3.0$ Hz, $^2J_{\text{H-}^{119}\text{Sn}} = 65.7$ Hz, $^2J_{\text{H-}^{117}\text{Sn}} = 44.7$ Hz, Sn-CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 134.64, 134.38, 132.22, 131.67, 129.32, 128.96 (*Ph*), 4.21 (d, $^2J_{\text{C-P}} = 17.62$ Hz, Sn-C). ^{31}P NMR (CDCl_3): δ 28.32 (s, $^1J_{^{31}\text{P-}^{119}\text{Sn}} = 56.2$ Hz, *PPh}_2*). Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{B}_{10}\text{IPSn}$: C, 31.88; H, 4.31. Found: C, 31.42; H, 4.18.

1-Diphenylphosphino-2-azidodimethyltin-1,2-carborane (4). To a stirred toluene solution (15 mL) of **2a** (0.07 g, 0.137 mmol) was added NaN_3 (0.044 g, 0.685 mmol) at room temperature, and the mixture was refluxed for 48 h. After filtering through Celite, the solution was concentrated under reduced pressure to incipient crystallization and stored in a ca. -10 °C freezer to give **4** as colorless crystals. Yield: 67%, mp 198 °C. ^1H NMR (CDCl_3): δ 7.68–7.26 (m, 10H, *PPh}_2*), 0.93 (d, 6H, $^3J_{\text{H-P}} = 2.1$ Hz, $^2J_{\text{H-}^{119}\text{Sn}} = 66.2$ Hz, $^2J_{\text{H-}^{117}\text{Sn}} = 62.8$ Hz, Sn-CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 135.06, 134.72, 134.13, 131.06, 129.68, 128.43 (*Ph*), 8.06 (d, $^2J_{\text{C-P}} = 14.72$ Hz, Sn-C). ^{31}P NMR (CDCl_3): δ 31.06 (s, $^1J_{^{31}\text{P-}^{119}\text{Sn}} = 58.1$ Hz, *PPh}_2*). IR (KBr pellet, cm^{-1}): ν 2084 (N_3). Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{B}_{10}\text{N}_3\text{PSn}$: C, 37.11; H, 5.02. Found: C, 36.84; H, 4.93.

1- PPh_2 -2- $\text{SnMe}_2\{\text{FeCp}(\text{CO})_2\}$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (5). To a stirred toluene solution (15 mL) of **2a** (0.07 g, 0.137 mmol) was added $\text{NaCpFe}(\text{CO})_2$ (0.03 g, 0.150 mmol) at room temperature, and the mixture was stirred for 8 h. After filtering through Celite, the solution was concentrated under reduced pressure to incipient crystallization and stored in a ca. -15 °C freezer to give **5** as yellow crystals. Yield: 77%, mp 168–171 °C. ^1H NMR (CDCl_3): δ 7.67–7.26 (m, 10H, *PPh}_2*), 4.87 (s, 5H, C_5H_5), 0.55 (s, 6H, $^2J_{\text{H-Sn}} = 42.9$ Hz, Sn-CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 213.53 (*CO*), 134.61, 134.41, 131.54, 130.22, 128.66, 128.60 (*Ph*), 82.11 (C_5H_5), -9.23 (Sn-C). ^{31}P NMR (CDCl_3): δ 24.37 (*PPh}_2*). ^{119}Sn NMR (CDCl_3): δ 196.5. IR (KBr pellet, cm^{-1}) ν 2201, 1944 ($\text{C}\equiv\text{O}$). Anal. Calcd for $\text{C}_{23}\text{H}_{31}\text{O}_2\text{B}_{10}\text{PFeSn}$: C, 42.31; H, 4.75. Found: C, 41.96; H, 4.58.

1-Diphenylphosphino-2-hydridodimethyltin-1,2-carborane (6). To a stirred toluene solution (15 mL) of **2a** (0.25 g, 0.49 mmol) was added NaBH_3CN (0.063 g, 1.00 mmol, 1 M in THF) at room temperature, and the mixture was stirred for 1 day at that temperature. After filtering through Celite, all volatiles were removed in vacuo. Then **6** was yielded as sticky white powder. Yield: 92%, mp 123–126 °C. ^1H NMR (CDCl_3): δ 7.81–7.26 (m, 10H, *PPh}_2*), 6.23 (dsep, 1H, $^1J_{\text{H-}^{119}\text{Sn}} = 2055.6$ Hz, $^2J_{\text{H-P}} = 10.2$ Hz, $^3J_{\text{H-H}} = 1.8$ Hz, Sn-H). 0.54 (dd, 6H, $^3J_{\text{H-H}} = 1.8$ Hz, $^3J_{\text{H-P}} = 1.2$ Hz, $^2J_{\text{H-}^{119}\text{Sn}} = 61.2$ Hz, $^2J_{\text{H-}^{117}\text{Sn}} = 56.7$ Hz, Sn-CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 136.42, 135.25, 132.75, 130.22, 127.97 (*Ph*), -6.44 (d, $^2J_{\text{C-P}} = 15.76$ Hz, Sn-C). ^{31}P NMR (CDCl_3): δ 25.12 (s, $^1J_{^{31}\text{P-}^{119}\text{Sn}} = 71.6$ Hz, *PPh}_2*). ^{119}Sn NMR (CDCl_3): δ -52.8 (d, $^1J_{\text{H-}^{119}\text{Sn}} = 2055.6$ Hz, $^1J_{^{119}\text{Sn-}^{31}\text{P}} = 68.4$ Hz). IR (KBr pellet, cm^{-1}): ν 1878 (Sn-H). Anal. Calcd for $\text{C}_{16}\text{H}_{27}\text{B}_{10}\text{PSn}$: C, 40.29; H, 5.66. Found: C, 40.03; H, 5.47.

1-Diphenylphosphino-2-trimethyltin-1,2-carborane (7). The same procedure was used as described for **2a** except trimethyltin chloride (0.2 g, 1.00 mmol) was used instead of dichlorodimethyltin. In this case, cold hexane (5 mL) was used for washing. Yield: 62%, mp 228 °C. ^1H NMR (CDCl_3): δ 7.71–7.41 (m, 10H, *PPh}_2*), 0.43 (d, 9H, $^3J_{\text{H-P}} = 15.0$ Hz, $^2J_{\text{H-}^{119}\text{Sn}} = 57.2$ Hz, $^2J_{\text{H-}^{117}\text{Sn}} = 54.3$ Hz, Sn-CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 136.22, 133.55, 132.06, 129.97, 129.51, 127.91 (*Ph*), -4.27 (d, $^2J_{\text{C-P}} = 9.13$ Hz, Sn-C). ^{31}P NMR (CDCl_3): δ 23.38 (s, $^1J_{^{31}\text{P-}^{119}\text{Sn}} = 62.2$ Hz, *PPh}_2*). ^{119}Sn NMR (CDCl_3): δ 106.4 (d, $^1J_{^{119}\text{Sn-}^{31}\text{P}} = 108.3$ Hz). Anal. Calcd for $\text{C}_{17}\text{H}_{29}\text{B}_{10}\text{PSn}$: C, 41.59; H, 5.91. Found: C, 41.24; H, 5.72.

1- PPh_2 - CH_2 -2- ClSnMe_2 -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (9a). To a stirred hexane solution (20 mL) of 1- PPh_2CH_2 -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (0.25 g, 0.73 mmol) was added a solution of *n*-butyllithium in hexane (0.55 mL, 1.6 M, 0.88 mmol) at 0 °C. The reaction mixture was allowed to warm to ambient temperature and was stirred for 8 h. The solvent was removed in vacuo and dissolved in toluene (15 mL). The reaction mixture was cooled to -78 °C, and a toluene solution (10 mL) of Me_2SnCl_2 (0.19 g, 0.876

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mmol) at $-78\text{ }^{\circ}\text{C}$ was added to the reaction mixture and stirred for 5 h. After filtering through Celite, the solution was concentrated under reduced pressure to incipient crystallization and stored in a ca. $-15\text{ }^{\circ}\text{C}$ freezer to give **9a** as colorless crystals. Yield: 75%, mp $201\text{--}203\text{ }^{\circ}\text{C}$. ^1H NMR (CDCl_3 , $25\text{ }^{\circ}\text{C}$): δ 7.71–7.35 (m, 10H, PPh_2), 3.27 (d, 2H, $^2J_{\text{H-P}} = 2.7\text{ Hz}$, CH_2), 1.10 (d, 6H, $^3J_{\text{H-P}} = 4.2\text{ Hz}$, $^2J_{\text{H-}^{119}\text{Sn}} = 73.8\text{ Hz}$, $^2J_{\text{H-}^{117}\text{Sn}} = 65.1\text{ Hz}$, Sn-CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 132.87, 132.35, 131.26, 130.11, 129.84, 128.81 (Ph), 35.09 (d, $^2J_{\text{C-P}} = 12.27\text{ Hz}$, CH_2), 5.22 (d, $^2J_{\text{C-P}} = 26.55\text{ Hz}$, Sn-C). ^{31}P NMR (CDCl_3): δ 34.18 (s, $^1J_{^{31}\text{P-}^{119}\text{Sn}} = 54.0\text{ Hz}$, PPh_2). Anal. Calcd for $\text{C}_{17}\text{H}_{28}\text{B}_{10}\text{ClP}_2\text{Sn}$: C, 38.85; H, 5.33. Found: C, 38.96; H, 5.44.

1-PPh₂CH₂-2-BrSnMe₂-1,2-C₂B₁₀H₁₀ (9b). The same procedure was used as described for **9a** except dibromodimethyltin was used instead of dichlorodimethyltin. Yield: 79%, mp $204\text{--}207\text{ }^{\circ}\text{C}$. ^1H NMR (CDCl_3 , $25\text{ }^{\circ}\text{C}$): δ 7.42–7.16 (m, 10H, PPh_2), 3.25 (d, 2H, $^2J_{\text{H-P}} = 2.1\text{ Hz}$, CH_2), 1.19 (d, 6H, $^3J_{\text{H-P}} = 4.2\text{ Hz}$, $^2J_{\text{H-}^{119}\text{Sn}} = 67.5\text{ Hz}$, $^2J_{\text{H-}^{117}\text{Sn}} = 63.6\text{ Hz}$, Sn-CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 133.04, 132.24, 132.02, 131.44, 130.26, 128.64 (Ph), 36.22 (d, $^2J_{\text{C-P}} = 12.84\text{ Hz}$, CH_2), 5.42 (d, $^2J_{\text{C-P}} = 26.82\text{ Hz}$, Sn-C). ^{31}P NMR (CDCl_3): δ 35.22 (s, $^1J_{^{31}\text{P-}^{119}\text{Sn}} = 55.2\text{ Hz}$, PPh_2). ^{119}Sn NMR (CDCl_3): δ -30.2 (d, $^1J_{^{119}\text{Sn-}^{31}\text{P}} = 320.3\text{ Hz}$). Anal. Calcd for $\text{C}_{17}\text{H}_{28}\text{B}_{10}\text{BrP}_2\text{Sn}$: C, 35.83; H, 4.91. Found: C, 35.48; H, 4.78.

1,2-Bis(1-diphenylphosphino-1,2-carborane)tetramethyldistannane (10). To a stirred toluene solution (20 mL) of **2a** (0.15 g, 0.27 mmol) was added an excess of sodium (0.031 g, 1.35 mmol) at room temperature, and the mixture was stirred for 3 h. After filtering through Celite, the solution was concentrated under reduced pressure to incipient crystallization and stored in a freezer at ca. -10 to $-15\text{ }^{\circ}\text{C}$ to give **10** as colorless crystals. Yield: 46%, mp $290\text{ }^{\circ}\text{C}$. ^1H NMR (CDCl_3 , $25\text{ }^{\circ}\text{C}$): δ 7.66–7.25 (m, 20H, PPh_2), 0.67 (s, 12H, $^2J_{\text{H-}^{119}\text{Sn}} = 121.5\text{ Hz}$, $^2J_{\text{H-}^{117}\text{Sn}} = 74.7\text{ Hz}$, $^3J_{\text{H-}^{119}\text{Sn}} = 26.4\text{ Hz}$, $^3J_{\text{H-}^{117}\text{Sn}} = 18.3\text{ Hz}$, Sn-CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 135.59, 135.06, 134.00, 134.55, 131.29, 129.08, 128.89, 128.54, 128.06, 127.58 (Ph), 3.13 (s, Sn-C). ^{31}P NMR (CDCl_3): δ -12.78 (s, PPh_2). ^{119}Sn NMR (CDCl_3): δ 162.6. Anal. Calcd for $\text{C}_{32}\text{H}_{52}\text{B}_{20}\text{P}_2\text{Sn}_2$: C, 40.37; H, 5.46. Found: C, 39.96; H, 5.24.

Preparation of Pd(1-PPh₂-2-SnMe₂-1,2-C₂B₁₀H₁₀)₂ (11). To a stirred toluene solution (15 mL) of **10** (0.1 g, 0.105 mmol) was added $\text{Pd}_2(\text{dba})_3$ (0.08 g, 0.087 mmol) dissolved in toluene (5 mL) at room temperature, and the mixture was stirred for 3 h at that temperature. The solvent was removed in vacuo and chromatographed using CH_2Cl_2 and hexane (1:1) as eluent ($R_f = 0.58$). The first band was crystallized from CH_2Cl_2 /hexane at $-15\text{ }^{\circ}\text{C}$ to give **11** as white crystals in 34% yield, mp $198\text{--}201\text{ }^{\circ}\text{C}$. ^1H NMR (CDCl_3 , $25\text{ }^{\circ}\text{C}$): δ 7.38–7.06 (m, 20H, PPh_2), 0.48 (s, 12H, $^2J_{\text{H-Sn}} = 64.3\text{ Hz}$, Sn-CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 134.81, 134.64, 134.05, 131.61, 131.24, 129.62, 128.86, 128.34, 128.06, 127.45 (Ph), 2.85 (s, Sn-C). ^{31}P NMR (CDCl_3): δ 78.60 (d, $^2J_{\text{P-}^{119}\text{Sn}(\text{trans})} = 2054.8\text{ Hz}$, $^2J_{\text{P-}^{117}\text{Sn}(\text{trans})} = 1943.0\text{ Hz}$, $^2J_{\text{P-}^{119}\text{Sn}(\text{cis})} = 207.7\text{ Hz}$, $^2J_{\text{P-}^{117}\text{Sn}(\text{cis})} = 194.2\text{ Hz}$, PPh_2). ^{119}Sn NMR (CDCl_3): δ 166.1 (d, $^1J_{^{119}\text{Sn-}^{31}\text{P}} = 1284.2\text{ Hz}$, $^2J_{^{117}\text{Sn-}^{31}\text{P}} = 144.2\text{ Hz}$). Anal. Calcd for $\text{C}_{32}\text{H}_{52}\text{B}_{20}\text{P}_2\text{PdSn}_2$: C, 36.31; H, 4.91. Found: C, 36.02; H, 4.71.

Preparation of [(1-PPh₂-2-SnMe₂-1,2-C₂B₁₀H₁₀)Pd(μ -Cl)]₂ (12a). To a stirred toluene solution (20 mL) of **2a** (0.15 g, 0.207 mmol) was added $\text{Pd}_2(\text{dba})_3$ (0.095 g, 0.104 mmol) at room temperature, and the mixture was stirred for 2 h. After filtering through Celite, the solvent was removed in vacuo. The reaction mixture was washed with hexane (15 mL \times 3). The residue was extracted with 25 mL of toluene. The volume of

the solution was reduced to 5 mL, and it was cooled to $-15\text{ }^{\circ}\text{C}$ for 48 h. Complex **12a** was obtained as yellow crystals in 88% yield, mp $196\text{ }^{\circ}\text{C}$. ^1H NMR (CDCl_3 , $25\text{ }^{\circ}\text{C}$): δ 8.18–7.56 (m, 20H, PPh_2), 0.42 (s, 12H, $^2J_{\text{H-Sn}} = 56.4\text{ Hz}$, Sn-CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 136.02, 135.82, 132.69, 129.44, 128.65, 128.50, (Ph), -1.53 (s, Sn-C). ^{31}P NMR (CDCl_3): δ 91.37 (s, $^2J_{^{31}\text{P-}^{119}\text{Sn}} = 208.6\text{ Hz}$, PPh_2). ^{119}Sn NMR (CDCl_3): δ -118.3 (d, $^2J_{^{119}\text{Sn-}^{31}\text{P}} = 189.8\text{ Hz}$). Anal. Calcd for $\text{C}_{32}\text{H}_{52}\text{B}_{20}\text{Cl}_2\text{P}_2\text{Pd}_2\text{Sn}_2$: C, 31.10; H, 4.21. Found: C, 30.84; H, 4.08.

Preparation of [(1-PPh₂-2-SnMe₂-1,2-C₂B₁₀H₁₀)Pd(μ -Br)]₂ (12b). The same procedure was used as described for **12a** except **2b** was used instead of **2a**. Yield: 85%, mp $200\text{ }^{\circ}\text{C}$. ^1H NMR (CDCl_3 , $25\text{ }^{\circ}\text{C}$): δ 8.16–7.56 (m, 20H, PPh_2), 0.44 (s, 12H, $^2J_{\text{H-Sn}} = 56.1\text{ Hz}$, Sn-CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 136.00, 135.80, 132.70, 129.54, 128.60, 128.44, (Ph), -0.39 (s, Sn-C). ^{31}P NMR (CDCl_3): δ 93.67 (s, $^2J_{^{31}\text{P-}^{119}\text{Sn}} = 215.5\text{ Hz}$, PPh_2). ^{119}Sn NMR (CDCl_3): δ -132.5 (d, $^2J_{^{119}\text{Sn-}^{31}\text{P}} = 217.4\text{ Hz}$). Anal. Calcd for $\text{C}_{32}\text{H}_{52}\text{B}_{20}\text{Br}_2\text{P}_2\text{Pd}_2\text{Sn}_2$: C, 29.02; H, 3.93. Found: C, 28.85; H, 3.82.

Preparation of (1-PPh₂-2-SnMe₂-1,2-C₂B₁₀H₁₀)Pd(PEt₃-Cl) (13). To a stirred toluene solution (15 mL) of **12a** (0.1 g, 0.81 mmol) was added PEt_3 (0.25 mL, 1 M, 0.25 mmol) at room temperature, and the mixture 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 **13** as a colorless crystalline solid (88% yield), mp $176\text{--}179\text{ }^{\circ}\text{C}$. ^1H NMR (CDCl_3 , $25\text{ }^{\circ}\text{C}$): δ 8.07–7.44 (m, 10H, PPh_2), 3.76 (m, 6H, CH_2), 1.25–1.36 (m, 9H, CH_3). 0.59 (s, 6H, $^2J_{\text{H-}^{119}\text{Sn}} = 51.6\text{ Hz}$, Sn-CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 136.39, 136.19, 132.10, 129.22, 128.28, 128.13, (Ph), 16.86 (s, CH_2), 9.18 (s, CH_3), -1.33 (s, Sn-C). ^{31}P NMR (CDCl_3): δ 80.49 (d, $^2J_{\text{P-P}} = 428.8\text{ Hz}$, PPh_2), -94.53 (d, $^2J_{\text{P-P}} = 428.8\text{ Hz}$, PEt_3). Anal. Calcd for $\text{C}_{22}\text{H}_{41}\text{B}_{10}\text{ClP}_2\text{PdSn}$: C, 35.91; H, 5.51. Found: C, 36.14; H, 5.62.

X-ray Crystallography. Details of the crystal data and a summary of intensity data collection parameters for **9b**, **11**, and **13** are given in Table 1. Crystals of **9b** and **11** were grown from toluene, and a crystal of **13** was grown from toluene/hexane stored at -10 to $-20\text{ }^{\circ}\text{C}$. Crystals of **9b**, **11**, and **13** were mounted in thin-walled glass capillaries and sealed under argon. The data sets for the three crystals were collected on an Enraf CAD 4 automated diffractometer. Mo $\text{K}\alpha$ radiation ($\lambda = 0.7107\text{ \AA}$) 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 **9b**, **11**, and **13** were refined anisotropically. All other hydrogen atoms were included in the calculated positions.

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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 **9b**, **11** and **13**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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