Anionic Phosphane − A New Ligand with a Phosphane and a Weakly Coordinating Heteroborate Moiety

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Dedicated to Professor Ekkehard Lindner on the occasion of his 70th birthday

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Reaction of chloropropyl-substituted stanna-*closo*-dodecaborate $[Cl(CH_2)_3SnB_{11}H_{11}]^-$ with the nucleophile $Li[CH_2PPh_2]$ provided a straightforward synthesis of an anionic phosphane $[Ph_2PCH_2SnB_{11}H_{11}]^-$. Derivatization of the phosphane was carried out in reaction with sulfur and hydrochloric acid to give $[Bu_3MeN][Ph_2P(S)CH_2SnB_{11}H_{11}]$ and the zwitterion $[Ph_2P(H)CH_2SnB_{11}H_{11}]$. In reaction with various transition metal electrophiles, complexation reactions were accomplished resulting in the isolation of *trans*-substituted palladium and platinum complexes $[Bu_3MeN]_2[trans\text{-}(Ph_2PCH_2SnB_{11}H_{11})_2MCl_2]$ (M = Pd, Pt), a neutral silver adduct $[(acetone)Ag(Ph_2PCH_2SnB_{11}H_{11})]$, and a linearly coordinated bisphosphane of gold $[Bu_3MeN][Au(Ph_2PCH_2\text{-}SnB_{11}H_{11})_2]$. The solid state structures of the ligand salt, the palladium and gold coordination compounds were determined and discussed.

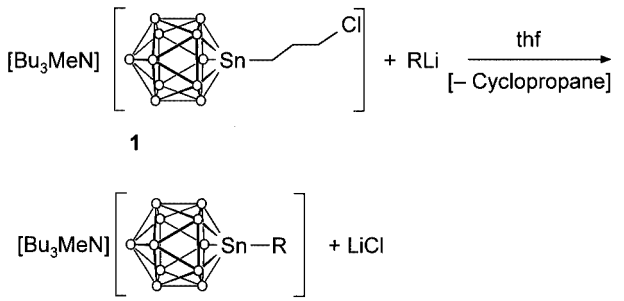
Introduction

In coordination chemistry phosphane ligands play a key role and are often used to control the properties of a certain transition metal complex. Phosphanes with an ionic moiety like sulfonate, carboxylate, ammonium or phosphonium are of interest for the synthesis of coordination compounds soluble in very polar solvents for two-phase catalysis purposes.[1] Recently Peters started to study systematically the coordination chemistry of monoanionic phosphane ligands provided with a tetracoordinated boron atom in the backbone of the ligand. Zwitterions with a cationic transition metal center have been isolated with chelating phosphides.[2−6] With the synthesis of the aluminate $Li[Al(CH_2PMe_2)_4]$ Karsch et al. found an anionic tetradentate phosphide.[7] Substitution reactions at the boron atom of borabenzene−trimethylphosphane with $K[PPh_2]$ resulted to give the phosphide $K[C_5H_5BPPh_2]$ in excellent yield.[8] Syntheses of monoboranephosphides $[R_2PBH_3]^-$ and examples for their coordination at Li, Al, Fe, Pd, and Pt can also be found in the literature.[9] Another class of anionic phosphanes, having a heteroborate as the anionic moiety, were presented by Teixidor.[10−11] Two diphenylphosphane groups are connected at the carbon atoms of the 7,8-dicarba-*nido*-undecaborate framework. This bis(diphenylphosphanyl)borate was shown to be a versatile ligand in transition metal chemistry.

Our group is interested in the coordination chemistry of ligands with a typical donor function and a weakly coordinating anionic moiety. Here we present a synthesis for a phosphane ligand connected at an anionic *closo*-heteroborate cluster.

Results and Discussion

Recently we found a method for the nucleophilic substitution at monoanionic alkylstanna-*closo*-dodecaborate.[12] Attack at the γ-chloropropyl-substituted cluster **1** with strong nucleophiles like RLi or RMgX resulted in the isolation of derivatives $[RSnB_{11}H_{11}]^-$ together with the formation of cyclopropane and the chloride anion as the leaving groups (Scheme 1).



Scheme 1. Nucleophilic substitution at the tin vertex with strong nucleophiles

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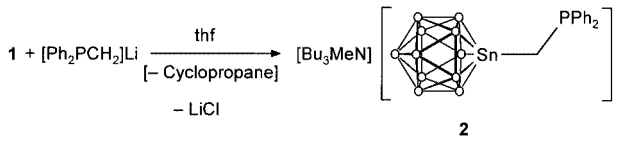
This method was transferred to the preparation of a new phosphane ligand by reacting the γ-chloropropyl-substituted heteroborate **1** with the anion $[Ph_2PCH_2]^-$ (Scheme 2).



Scheme 2. Syntheses of an anionic phosphane

The new phosphane **2** was characterized by NMR spectroscopy and X-ray structure analysis. In the ^{31}P NMR spectrum the resonance at $\delta = -15.5$ ppm showing tin satellites ($^2J_{P,Sn} = 71$ Hz) gives clear evidence for the successful coupling of the phosphane moiety at the anionic stannaborate cage. Single crystals suitable for X-ray structure analysis were prepared by slow diffusion of hexane into a dichloromethane solution of the coupling product **2**. The structure of the borate salt is depicted in Figure 1, and the data of the structure solution and refinement are listed in Table 1. This ligand is of interest to us since standard phosphane coordination chemistry can be combined with well-known B−H−M three-center-twoelectron bond coordination.[13] Anionic boron clusters show mono-, di- or trihapto coordination modes at transition metal centers. These agostic interactions can be detected either in the ^1H NMR spectrum from high-field proton resonances for the B−H−M unit or in the ^{11}B NMR spectrum exhibiting reduced $^1J_{BH}$ coupling constants.

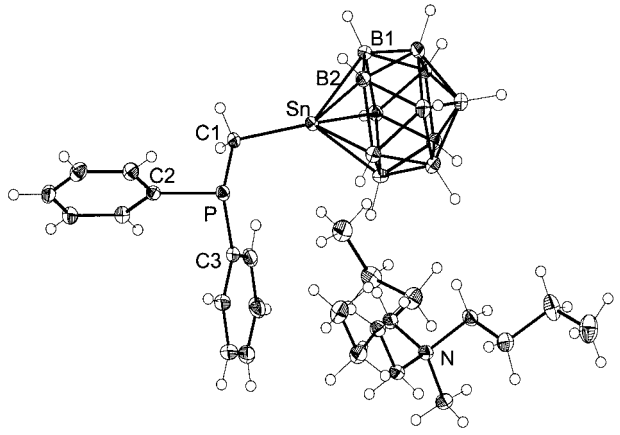
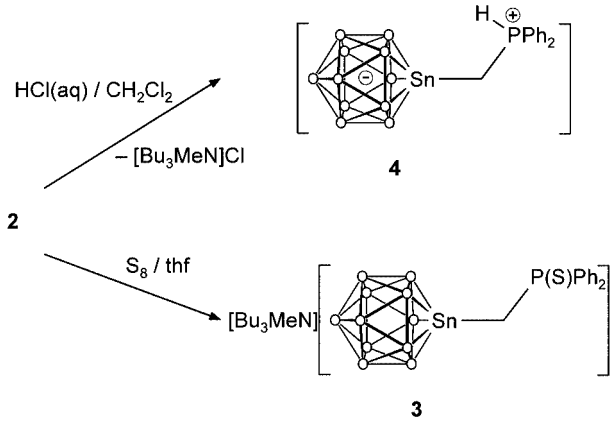


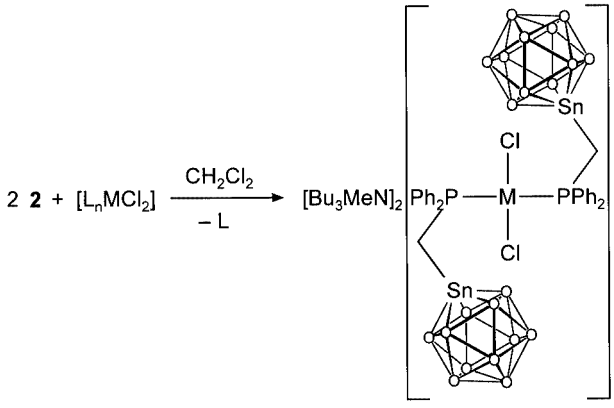
Figure 1. Molecular structure of the phosphane salt $[Bu_3MeN][Ph_2PCH_2SnB_{11}H_{11}]$ (**2**) in the solid state; interatomic distances in pm and angles in degrees (with estimated standard deviations in parentheses): Sn−C1 212.7 (2), Sn−B1 227.9(3), Sn−B2 228.1(3), Sn−B3 228.5(3), Sn−B4 228.9(3), Sn−B5 230.1(3), P−C1 182.9(2), P−C2 184.3(2), P−C3 184.7(2); P−C1−Sn 110.9, C1−Sn−B1 140.3(1), C1−Sn−B2 128.4(1), C1−Sn−B3 124.9(1), C1−Sn−B4 133.8(1), C1−Sn−B5 144.5(1)

In reaction with elemental sulfur and hydrochloric acid two derivatives of the phosphane were synthesized and characterized (Scheme 3). The sulfur compound exhibits in the ^1H NMR spectrum a doublet ($^2J_{H,P} = 4.5$ Hz) with tin satellites $^2J_{H,Sn} = 100$ Hz at $\delta = 3.08$ ppm for the PCH_2Sn moiety. A characteristic signal at $\delta = 6.85$ ppm for the proton connected at the phosphorus *H*P and a down-field shift of 1.2 ppm for the resonance of the PCH_2Sn unit [4.26 ppm ($^2J_{H,P} = 12$ Hz, $-P-CH_2-Sn$, $^2J_{H,Sn} = 98$ Hz)] was detected in the case of the zwitterionic phosphonium borate.

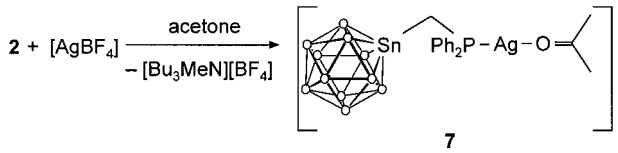


Scheme 3. Reaction with sulfur and protonation of the anionic phosphane

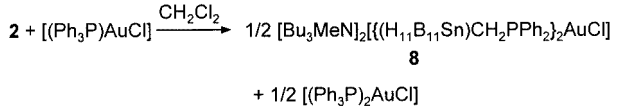
First complexation reactions of the new ligand **2** were carried out with the following transition metal complexes: [*cis*-$(Ph_3P)_2PdCl_2$], [$(cod)PtCl_2$], [$AgBF_4$], and [$(Ph_3P)AuCl$] (Scheme 4, Scheme 5, Scheme 6). *trans*-Substituted coordination compounds **5** and **6** have been isolated and characterized with platinum and palladium chlorides. In the case of the platinum derivative the $^1J_{Pt,P}$ coupling constant of 1850 Hz allows unambiguous assignment for *trans*-coordination.[14] Obviously the anionic part of the ligand is not of the nucleophilicity to substitute the chloride atoms and form M−H−B bonds. The products **5** and **6** are stable towards moisture, and air and crystallization from CH_2Cl_2/hexane resulted in the isolation of single crystals in the case of the palladium complex.

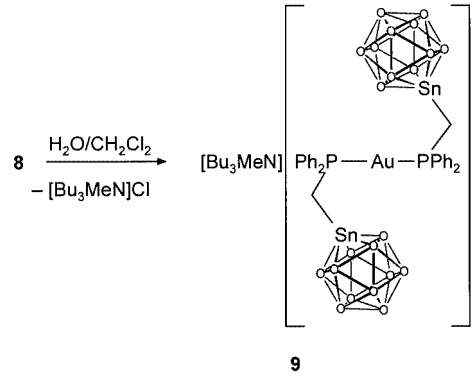


Scheme 4. Complexation reaction with palladium and platinum coordination compounds (L_nMCl_2 = [*cis*-$(Ph_3P)_2PdCl_2$], M = Pd for **5**; L_nMCl_2 = [$(cod)PtCl_2$], M = Pt for **6**)



Scheme 5. Complexation with a silver electrophile, formation of a zwitterion





Scheme 6. Formation of a triply coordinated gold complex; loss of the chloride substituent under the contact with water

The salt **5** crystallizes under the inclusion of two equivalents of CH_2Cl_2 in the monoclinic space group $P2_1/n$, with the dianion lying on the twofold rotation axis. In Figure 2 the structure of the anion in the solid state is shown, and the data of the structure solution and refinement are listed in Table 1. The coordination at the palladium center is in close relation to the structure of [*trans*-$(Ph_2MeP)_2PdCl_2$] crystallizing in the same space group with almost identical Pd–P 233.06(12) pm and Pd–Cl 230.45(9) pm interatomic distances.[15]

A neutral silver complex was synthesized from the reaction of the phosphane **2** with $AgBF_4$ (Scheme 5). This zwitterionic molecule was characterized by NMR spectroscopy and elemental analysis and should be a versatile starting material for further complexation reactions. With respect to the phosphane ligand, the monosubstituted product was the only isolated silver complex, whereas in the case of [(Ph_3P)AuCl] two anionic phosphanes coordinate at the gold center (Scheme 6) to give a diphosphanyl chloride complex **8**.[16]

The primarily formed reaction product **8** was stirred with water to give the linearly coordinated complex **9** in high yield. The salt **9** was crystallized and the structure in the solid state was determined by X-ray diffraction. The molecular structure of the anion of **9** is shown in Figure 3, and the data of the structure solution and refinement are listed in Table 1.

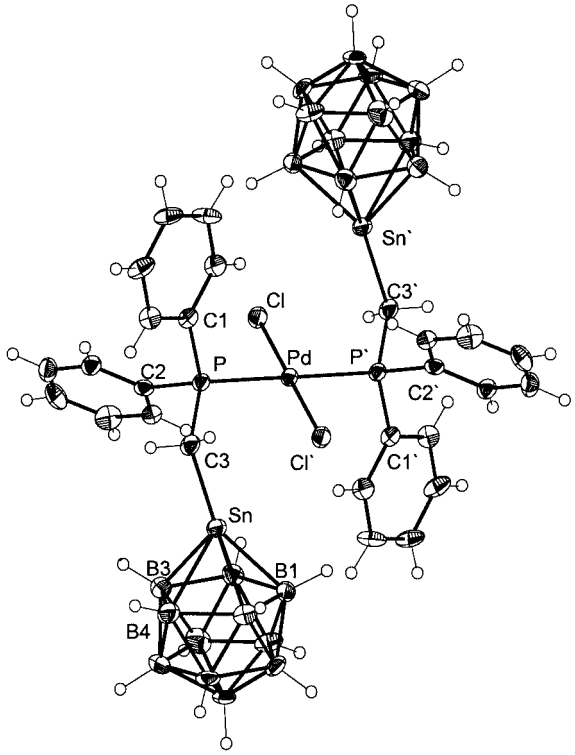


Figure 2. Molecular structure of the anion of $[Bu_3MeN]_2$-$[PdCl_2(PPh_2CH_2SnB_{11}H_{11})_2]$ (**5**) in the solid state; interatomic distances in pm and angles in degrees (with estimated standard deviations in parentheses): Pd–Cl 229.6(2), Pd–P 233.2(2), P–C3, 184.0(8), Sn–C3 211.7(7), Sn–B1 228.7(8), Sn–B2 228.9(9), Sn–B3 227.9(10), Sn–B4 228.8(10), Sn–B5 227.8(8), C3–Sn–B1 150.4(3), C3–Sn–B2 140.6(3), C3–Sn–B3 122.9(3), C3–Sn–B4 121.1(3), C3–Sn–B5 134.4(3), Cl–Pd–P 91.0(1), Cl′–Pd–P 89.0(1)

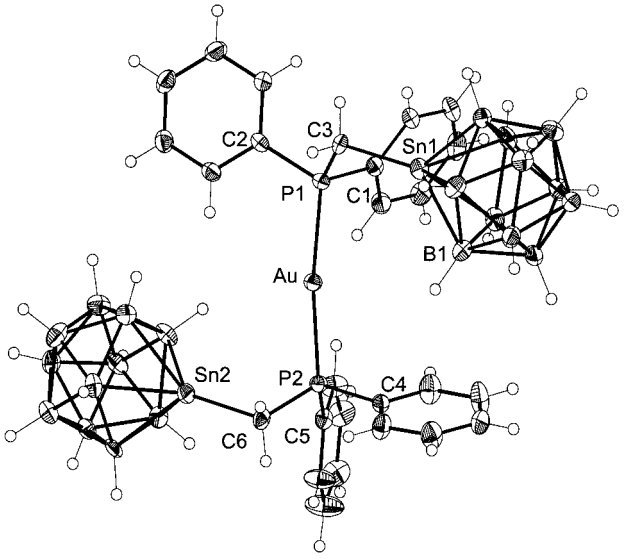


Figure 3. Molecular structure of the anion of $[Bu_3MeN]$-$[Au(PPh_2CH_2SnB_{11}H_{11})_2]$ (**9**) in the solid state. Interatomic distances in pm and angles in degrees (with estimated standard deviations in parentheses): P1–Au 231.0(2), P2–Au 231.4(2), C3–P1 181.6(7), Sn1–C3 213.7(6), C6–P2 187.8(8), Sn2–C6 214.6(7), P1–Au–P2 171.1(1), Au–P1–C3 113.5(3), P1–C3–Sn1, 113.9(3), Au–P2–C6 114.8(3), P2–C6–Sn2 109.1(4)

Nearly linearly coordinated gold(I) cations $[Au(PR_3)_2]^+$ are well-known in the literature and the metal−ligand bonding has been studied with respect to relativistic and non relativistic structure calculations.[17,18] In the crystal structure a very weak interaction (H−Au 268.0 pm) between a BH unit and the gold center, which results in the formation of dimer, can be detected (Figure 4). Stone et al. have found much shorter BH−Au interatomic distances in the range of 190−210 pm.[19] Nevertheless, we interpret this contact as a weak electrostatic interaction of the cationic gold fragment with the anionic borate moiety.

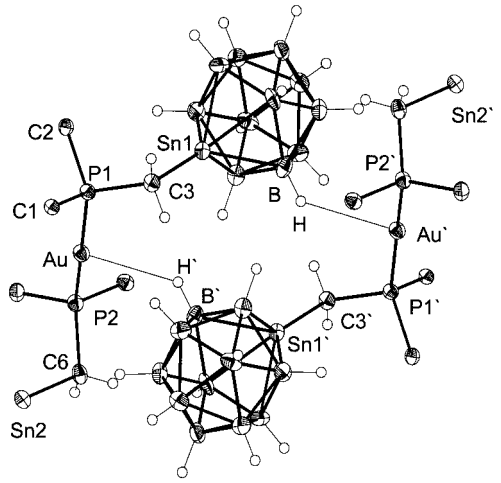


Figure 4. Weak interaction between a stannaborate cluster and gold center in compound **9**; H−Au 268.0 pm (all hydrogen atoms at calculated positions); phenyl substituents and boron cluster cages at Sn2 and Sn2′ have been omitted for the sake of clarity

To conclude, a synthesis for an anionic phosphane with two different coordination sites is presented: a diarylalkylphosphane nucleophile and an anionic borate where common B−H−M coordination can take place.

Experimental Section

General Procedures: All manipulations were carried out using Schlenk techniques under an atmosphere of dry N_2. All solvents were dried and purified by standard methods and were stored under dry N_2. $[Bu_3MeN]_2[SnB_{11}H_{11}]$ was synthesized following a modification of Todd's procedure.[25] The compounds $[Bu_3MeN][H_{11}B_{11}Sn-(CH_2)_3-Cl]$, [*cis*-$(PPh_3)_2PdCl_2$],[26] [$PPh_3$-CuCl],[27] and $Li[CH_2PPh_2]$[28] were synthesized by literature procedures. All other chemicals were purchased from Aldrich and were used without further purification. ^1H, ^{11}B, and ^{31}P NMR spectra were recorded on a Bruker AC 200 instrument and referenced to the deuterated solvent. Elemental analyses were carried out on a Hekatech EuroEA C,H,N,S,O elemental analyzer at Institut für Anorganische Chemie der Universität zu Köln.

$[Bu_3MeN][H_{11}B_{11}Sn-CH_2-P(C_6H_5)_2]$ (2): A solution of $[Bu_3MeN][H_{11}B_{11}Sn-(CH_2)_3-Cl]$ (6.17 g, 11.72 mmol) in THF (60 mL) was added to a solution of $Li[CH_2PPh_2]$ (3.14 g, 15.23 mmol) in THF (60 mL) dropwise at room temperature. After stirring overnight at room temperature all volatiles were removed. The residue was dissolved in CH_2Cl_2 (60 mL) and treated with water (3 × 30 mL). The organic phase was separated and stirred over anhydrous Na_2SO_4. After the solvent was removed, the yellow, semifluid raw product was dissolved in a little CH_2Cl_2 and washed with *n*-hexane and Et_2O. Removing the solvent resulted in isolation of the yellow, semifluid but translucent product. Yield: 77%, 5.85 g, 9.02 mmol. ^1H NMR (200 MHz, 25 °C, CD_2Cl_2): δ = 1.01 (t, 9 H, ^3J = 7.1 Hz, $-CH_2-CH_3$), 1.42 (m, 6 H, ^3J = 7.2 Hz, $-CH_2-CH_3$), 1.65 (m, 6 H, ^3J = 7.3 Hz, $-CH_2-CH_2-CH_3$), 2.98 (s, 3 H, $N-CH_3$), 3.06 (d, 2 H, $^2J_{H,P}$ = 4.5 Hz, $P-CH_2-Sn$), 3.16 (m, 6 H, ^3J = 7.3 Hz, $N-CH_2-CH_2-$), 7.39−7.54 ppm [m, 10 H, $-P-(C_6H_5)_2$]. $^{11}B\{^1H\}$ NMR (64 MHz, 25 °C, CD_2Cl_2): δ = −12.3 (s, B12), −17.0 (s, B2−6 and B7−11) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, 25 °C, C_3D_6O): δ = 13.8 (d, $^1J_{C,P}$ = 35 Hz, $-P-CH_2-Sn$), 16.8 (s, $-CH_2-CH_3$), 23.2 (s, $-CH_2-CH_3$), 27.6 (s, $N-CH_2-CH_2-$), 51.8 (s, $N-CH_3$), 65.2 (s, $N-CH_2-CH_2-$), 132.4 (d, $^3J_{C,P}$ = 7 Hz, C_{meta}, $-P-(C_6H_5)_2$], 132.8 (s, C_{para}, $-P-(C_6H_5)_2$], 136.0 (d, $^2J_{C,P}$ = 20 Hz, C_{ortho}, $-P-(C_6H_5)_2$], 143.3 ppm [d, $^1J_{C,P}$ = 14 Hz, C_{ipso}, $-P-(C_6H_5)_2$]. $^{31}P\{^1H\}$ NMR (81 MHz, 25 °C, C_3D_6O): δ = −15.5 ppm (s, $^2J_{P,Sn}$ = 71 Hz, $-P-(C_6H_5)_2$]. $C_{26}H_{53}B_{11}NPSn$ (648.32): calcd. C 48.17, H 8.24, N 2.16; found C 46.77, H 8.76, N 1.50.

$[Bu_3MeN][H_{11}B_{11}Sn-CH_2-P(S)-(C_6H_5)_2]$ (3): A solution of $[Bu_3MeN][H_{11}B_{11}Sn-CH_2-P(C_6H_5)_2]$ (**1**, 0.82 g, 1.26 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a suspension of sulfur (0.04 g, 1.26 mmol) in CH_2Cl_2 (20 mL). After stirring for 4 h at room temperature, the sulfur had dissolved by then, all volatiles were removed, and **2** was isolated as a yellow, hygroscopic solid. Yield: 89%, 0.76 g, 1.12 mmol. ^1H NMR (200 MHz, 25 °C, CD_2Cl_2): δ = 3.80 (d, 2 H, $^2J_{H,P}$ = 11, $^2J_{H,Sn}$ = 100 Hz, $-P-CH_2-Sn$), 7.51−7.95 ppm (m, 10 H, $-P-(C_6H_5)_2$]. $^{11}B\{^1H\}$ NMR (64 MHz, 25 °C, CD_2Cl_2): δ (ppm) = −11.8 (s, B12), −17.1 (s, B2−6 and B7−11). $^{31}P\{^1H\}$ NMR (81 MHz, 25 °C, CD_2Cl_2): δ = 40.98 ppm (s, $^2J_{P,Sn}$ = 46 Hz, $-P-(C_6H_5)_2$]. $C_{26}H_{53}B_{11}NPSSn$ (680.38): calcd. C 45.90, H 7.85, N 2.06, S 4.71; found C 44.17, H 7.88, N 2.02, S 4.65.

$[H_{11}B_{11}Sn-CH_2-P(H)-(C_6H_5)_2]$ (4): A solution of $[Bu_3MeN][H_{11}B_{11}Sn-CH_2-P(C_6H_5)_2]$ (**1**, 1.00 g, 1.54 mmol) in CH_2Cl_2 (20 mL) was stirred rapidly under a layer of diluted hydrochloric acid (25 mL) overnight. The resulting colorless solid was separated, washed with water and dried in vacuo. Yield: 94%, 0.65 g, 1.45 mmol. ^1H NMR (200 MHz, 25 °C, C_3D_6O): δ = 4.26 (d, 2 H, $^2J_{H,P}$ = 12 Hz, $-P-CH_2-Sn$, $^2J_{H,Sn}$ = 98 Hz), 6.85 (d, 1 H, $^1J_{H,P}$ = 12 Hz, $-P-H$), 7.78−7.94 (m, 10 H, $-P-(C_6H_5)_2$] ppm. $^{11}B\{^1H\}$ NMR (64 MHz, 25 °C, C_3D_6O): δ = −12.5 (s, B12), −17.3 ppm (s, B2−6 and B7−11). $^{31}P\{^1H\}$ NMR (81 MHz, 25 °C, C_3D_6O): δ = 33.27 ppm (s, $^2J_{P,Sn}$ = 59 Hz, $-P(H)-(C_6H_5)_2$]. $C_{13}H_{24}B_{11}PSn$ (448.94): calcd. C 34.78, H 5.39; found C 35.36, H 5.82.

$[Bu_3MeN]_2$[*trans*-$\{H_{11}B_{11}Sn-CH_2-P(C_6H_5)_2\}_2PdCl_2$] (5): A solution of $[Bu_3MeN][H_{11}B_{11}Sn-CH_2-P(C_6H_5)_2]$ (1.43 g, 2.20 mmol) in CH_2Cl_2 (25 mL) was added dropwise to a stirred solution of $(PPh_3)_2PdCl_2$ (0.77 g, 1.10 mmol) in CH_2Cl_2 (20 mL). After the mixture was stirred for 16 h at room temperature, the solvent was removed under reduced pressure, and the yellow residue was washed with benzene, toluene, and *n*-hexane (3 × 20 mL). The yellow product was isolated by filtration and dried in vacuo. Yield: 64%, 1.04 g, 0.70 mmol. ^1H NMR (200 MHz, 25 °C, CD_2Cl_2): δ (ppm) = 0.99 (t, 18 H, ^3J = 7.1 Hz, $-CH_2-CH_3$), 1.37 (m, 12 H, ^3J = 6.9 Hz, $-CH_2-CH_3$), 1.64 (m, 12 H, ^3J = 7.0 Hz, $-CH_2-CH_2-CH_3$), 2.99 (s, 6 H, $N-CH_3$), 3.17 (m, 12 H, ^3J = 8.3 Hz, $N-CH_2-CH_2-$), 3.43 (d, 4 H, $^2J_{H,P}$ = 7 Hz, $-P-CH_2-Sn$), 7.26−7.90 (m, 20 H, $-P-(C_6H_5)_2$]. $^{11}B\{^1H\}$ NMR (64 MHz, 25 °C, CD_2Cl_2): δ = −12.2 (s, B12), −16.8 ppm

Table 1. Crystal data and structure refinement parameters for $[Bu_3MeN][Ph_2PCH_2SnB_{11}H_{11}]$ (**2**), $[Bu_3MeN][PdCl_2(PPh_2CH_2SnB_{11}H_{11})_2]\cdot 2CH_2Cl_2$ (**5**) and $[Bu_3MeN][Au(PPh_2CH_2SnB_{11}H_{11})_2]$ (**9**)

	2	**5**	**9**
Empirical formula	$C_{26}H_{53}B_{11}NPSn$	$C_{54}H_{110}B_{22}Cl_6N_2P_2PdSn_2$	$C_{39}H_{76}AuB_{22}NP_2Sn_2$
Formula mass	648.26	1643.68	1293.11
Data collection			
Diffractometer	STOE IPDS II		
Radiation	Mo-K_α (graphite-monochromated, λ = 71.073 pm)		
Temperature [K]	130(2)	120(2)	150(2)
Index range	$-15 \le h \le 15$	$-22 \le h \le 21$	$-16 \le h \le 14$
	$-16 \le k \le 18$	$-13 \le k \le 13$	$-20 \le k \le 20$
	$-18 \le l \le 18$	$-24 \le l \le 24$	$-20 \le l \le 20$
Rotation angle range	$0° \le \omega \le 180°$; $\psi = 0°$	$0° \le \omega \le 180°$; $\psi = 0°$	$0° \le \omega \le 180°$; $\psi = 0°$
	$0° \le \omega \le 180°$; $\psi = 90°$	$0° \le \omega \le 60°$; $\psi = 90°$	$0° \le \omega \le 150°$; $\psi = 90°$
Increment	$\Delta\omega = 2°$	$\Delta\omega = 2°$	$\Delta\omega = 2°$
No. of images	180	120	165
Exposure time [min]	3	15	12
Detector distance (mm)	100	120	120
2θ range (°)	2.2−59.5	1.9−54.8	1.9−54.8
Total data collected	34041	31861	40319
Unique data	9653	6910	12307
Observed data	7697	2840	6403
R_{merg}	0.0463	0.1879	0.1003
Absorption correction	numerical, after crystal shape optimization[20,21]		
Transmission min./max.	0.7858/0.9442	0.7470/0.9277	0.4312/0.7568
Crystallographic data[22]			
Crystal size (mm)	0.3×0.3×0.2	0.2×0.2×0.1	0.2×0.2×0.1
Color, habit	colorless, polyhedron	yellow, plate	colourless, plate
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a [pm]	1138.1(1)	1885.1(3)	1282.0(2)
b [pm]	1311.5(1)	1111.1(2)	1579.1(2)
c [pm]	1304.1(1)	2072.1(2)	1612.2(2)
α (°)	76.07(1)		65.52(1)
β (°)	88.77(1)	115.23(1)	79.28(1)
γ (°)	67.04(1)		68.83(1)
Volume [nm^3]	1.7338(3)	3.9261(9)	2.7674
Z	2	2	2
$\rho_{calcd.}$ [g cm^{-3}]	1.242	1.390	1.552
μ [mm^{-1}]	0.801	1.138	3.628
F(000)	672	1672	1272
Structure analysis and refinement			
Refinement method	Full-matrix least-squares on F^2		
Structure determination	SHELXS-97[23] and SHELXL-93[24]		
No. of variables	574	407	608
R indexes [$I > 2\sigma(I)$]	R_1 = 0.0350	R_1 = 0.0495	R_1 = 0.0431
	wR_2 = 0.0809	wR_2 = 0.0682	wR_2 = 0.0764
R indexes (all data)	R_1 = 0.0488	R_1 = 0.1508	R_1 = 0.1062
	wR_2 = 0.0859	wR_2 = 0.0860	wR_2 = 0.0911
Goodness of fit (S_{obs})	1.004	0.707	0.823
Goodness of fit (S_{all})	1.004	0.707	0.823
Largest difference map hole/peak [e·10^{-6}pm^{-3}]	−1.096/0.789	−0.675/0.738	−2.881/1.151

$R_1 = \Sigma| |F_o| - |F_c| |/\Sigma|F_o|$, $wR_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2/\Sigma w (|F_o|^2)^2]^{1/2}$, $S_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2/(n-p)]^{1/2}$, with $w = 1/[\sigma^2 (F_o)^2 + (0.0533\ P)^2]$ for **2**, $w = 1/[\sigma^2 (F_o)^2 + (0.0131\ P)^2]$ for **5** and $w = 1/[\sigma^2 (F_o)^2 + (0.0307\ P)^2]$ for **9**, were $P = (F_o^2 + 2F_c^2)/3$. $F_c^* = k\ F_c\ [1 + 0.001\ |F_c|^2\ \lambda^3/\sin(2\theta)]^{-1/4}$. The H atoms for **2** were derived from the difference Fourier map. Hydrogen atoms for (**5**) and (**9**) were generated geometrically and allowed to ride on their parent carbon/boron atoms.

(s, B2−6 and B7−11). $^{31}P\{^1H\}$ NMR (81 MHz, 25 °C, CD_2Cl_2): δ = 30.3 ppm (s, $-P-(C_6H_5)_2$]. $C_{52}H_{106}B_{22}Cl_2N_2P_2PdSn_2$ (1473.96): calcd. C 42.37, H 7.25, N 1.90; found C 43.57, H 7.25, N 1.82.

$[Bu_3MeN]_2$[*trans*-{$H_{11}B_{11}Sn-CH_2-P(C_6H_5)_2$}$_2$$PtCl_2$] (6): A solution of $[Bu_3MeN][H_{11}B_{11}Sn-CH_2-P(C_6H_5)_2]$ (1.28 g, 1.98 mmol) in CH_2Cl_2 (25 mL) was added dropwise to a stirred solution of $(cod)PtCl_2$ (0.37 g, 0.99 mmol) in CH_2Cl_2 (25 mL). After the mix-

ture was stirred at room temperature overnight, all volatiles were removed under reduced pressure and the residue was washed with *n*-hexane and diethyl ether (3 × 20 mL). The light brown product was isolated by filtration and dried in vacuo. Yield: 56%, 0.86 g, 0.55 mmol. ^{1}H NMR (200 MHz, 25 °C, CD_2Cl_2): δ = 0.99 (t, 18 H, ^3J = 6.8 Hz, $-CH_2-CH_3$), 1.41 (m, 12 H, ^3J = 6.7 Hz, $-CH_2-CH_3$), 1.65 (m, 12 H, ^3J = 7.0 Hz, $-CH_2-CH_2-CH_3$), 3.02 (s, 6 H, $N-CH_3$), 3.17 (m, 12 H, ^3J = 8.3 Hz, $N-CH_2-CH_2-$), 3.58 (d, 4 H, $^2J_{H,P}$ = 8 Hz, $-P-CH_2-Sn$), 7.23−7.62 ppm (m, 20 H, $-P-(C_6H_5)_2$]. ^{11}B{^{1}H} NMR (64 MHz, 25 °C, CD_2Cl_2): δ = −11.9 (s, B12), −17.0 ppm (s, B2−6 and B7−11). ^{31}P{^{1}H} NMR (81 MHz, 25 °C, CD_2Cl_2): δ = 8.67 ppm (s, $^1J_{P,Pt}$ = 1850 Hz, $-P-(C_6H_5)_2$]. $C_{52}H_{106}B_{22}Cl_2N_2P_2PtSn_2$ (1562.62): calcd. C 39.97, H 6.84, N 1.79; found C 40.00, H 7.54, N 1.51.

[$H_{11}B_{11}Sn-CH_2-P(C_6H_5)_2Ag(OC_3H_6)$] (7): Because of the sensitivity of the silver compounds, this synthesis was carried out in darkness. A solution of [Bu_3MeN][$H_{11}B_{11}Sn-CH_2-P(C_6H_5)_2$] (0.15 g, 0.23 mmol) in C_3H_6O (25 mL) was added dropwise to a stirred suspension of $AgBF_4$ (0.05 g, 0.23 mmol) in C_3H_6O (25 mL). After being stirred at room temperature overnight, the mixture was filtered, and the solvent of the filtrate was removed under reduced pressure. The product was isolated as light-brown powder. Yield: 65%, 0.08 g, 0.15 mmol. ^{1}H NMR (200 MHz, 25 °C, CD_3CN): δ = 2.08 (s, 6 H, Ag-OC_3H_6), δ = 3.46 (d, 2 H, $^2J_{H,P}$ = 6 Hz, $-P-CH_2-Sn$, $^2J_{H,Sn}$ = 98 Hz), 7.50−7.75 ppm (m, 10 H, $-P-(C_6H_5)_2$]. ^{11}B{^{1}H} NMR (64 MHz, 25 °C, CD_3CN): δ = −12.3 (s, B12), −17.1 ppm (s, B2−6 and B7−11). ^{31}P{^{1}H} NMR (81 MHz, 25 °C, C_3D_6O): δ = 3.69 ppm (s, $-P-(C_6H_5)_2$]. $C_{16}H_{29}AgB_{11}OPSn$ (613.88): calcd. C 31.31, H 4.76; found C 32.14, H 4.81.

[Bu_3MeN]$_2$[{$H_{11}B_{11}Sn-CH_2-P(C_6H_5)_2$}$_2$AuCl] (8): A solution of [Bu_3MeN][$H_{11}B_{11}Sn-CH_2-P(C_6H_5)_2$] (0.40 g, 0.62 mmol) in CH_2Cl_2 (25 mL) was added dropwise to a stirred solution of (PPh_3)AuCl (0.31 g, 0.62 mmol) in CH_2Cl_2 (25 mL). After the mixture was stirred for 16 h at room temperature, the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (10 mL) and reprecipitated by addition of toluene (40 mL). This procedure was repeated three times. Finally, the solid was separated by filtration and washed with toluene and diethyl ether (3 × 10 mL). The colorless product was isolated by filtration and dried in vacuo. Yield: 31%, 0.29 g, 0.19 mmol. ^{1}H NMR (200 MHz, 25 °C, CD_2Cl_2): δ = 1.00 (t, 18 H, ^3J = 7.3 Hz, $-CH_2-CH_3$), 1.41 (m, 12 H, ^3J = 7.2 Hz, $-CH_2-CH_3$), 1.66 (m, 12 H, ^3J = 7.3 Hz, $-CH_2-CH_2-CH_3$), 3.04 (s, 6 H, $N-CH_3$), 3.21 (m, 12 H, ^3J = 7.7 Hz, $N-CH_2-CH_2-$), 3.48 (d, 4 H, $^2J_{H,P}$ = 8 Hz, $-P-CH_2-Sn$), 7.54−7.86 ppm (m, 20 H, $-P-(C_6H_5)_2$]. ^{11}B{^{1}H} NMR (64 MHz, 25 °C, CD_2Cl_2): δ = −13.4 (s, B12), −17.2 ppm (s, B2−6 and B7−11). ^{31}P{^{1}H} NMR (81 MHz, 25 °C, CD_2Cl_2): δ = 34.36 ppm (s, $-P-(C_6H_5)_2$]. $C_{52}H_{106}AuB_{11}ClN_2P_2Sn_2$ (1529.06): calcd. C 40.85, H 6.99, N 1.83; found C 41.36, H 7.30, N 1.41.

[Bu_3MeN][{$H_{11}B_{11}Sn-CH_2-P(C_6H_5)_2$}$_2$Au] (9): A solution of [$Bu_3MeN$]$_2$[{$H_{11}B_{11}Sn-CH_2-P(C_6H_5)_2$}$_2$AuCl] (**9**, 0.15 g, 0.10 mmol) in CH_2Cl_2 (25 mL) was stirred rapidly under a layer of water (25 mL) overnight. The organic phase was separated and dried over Na_2SO_4. After being separated from the desiccant, the solvent was removed under reduced pressure, and **9** was isolated as a colorless solid. Yield: 89%, 0.11 g, 0.09 mmol. ^{1}H NMR (200 MHz, 25 °C, CD_2Cl_2): δ = 1.00 (t, 9 H, ^3J = 7.2 Hz, $-CH_2-CH_3$), 1.41 (m, 6 H, ^3J = 7.3 Hz, $-CH_2-CH_3$), 1.64 (m, 6 H, ^3J = 7.4 Hz, $-CH_2-CH_2-CH_3$), 3.04 (s, 3 H, $N-CH_3$), 3.14 (m, 6 H, ^3J = 7.5 Hz, $N-CH_2-CH_2-$), 3.53 (s, 4 H, $^2J_{H,Sn}$ = 93 Hz, $-P-CH_2-Sn$), 7.56−7.95 ppm (m, 20 H, $-P-(C_6H_5)_2$]. ^{11}B{^{1}H} NMR (64 MHz, 25 °C, CD_2Cl_2): δ (ppm) = −11.7 (s, B12), −17.0 (s, B2−6 and B7−11). ^{31}P{^{1}H} NMR (81 MHz, 25 °C, CD_2Cl_2, 213 K): δ = 40.79 ppm (s, $-P-(C_6H_5)_2$]. $C_{39}H_{76}AuB_{22}NP_2Sn_2$ (1293.22): calcd. C 36.22, H 5.92, N 1.08; found C 36.21, H 6.11, N 0.88.

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contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc. cam. ac. uk].

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