Palladium Chemistry with Stanna-closo-dodecaborate and Isocyanides

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The substitution equilibrium between isocyanides and stanna-*closo*-dodecaborate with palladium(II) was investigated. The mixed substituted products of type $[(RNC)_2Pd-(SnB_{11}H_{11})_2]^{2-}$ and $[(RNC)Pd(SnB_{11}H_{11})_3]^{4-}$ were characterized by X-ray crystal structure analysis, elemental analysis

Introduction

Palladium isocyanide chemistry is of interest in catalysis with respect to a variety of bond formation reactions.^[1-8] For example palladium isocyanide complexes can act as efficient catalysts in the Suzuki-Miyaura reaction.^[8] Furthermore, element-carbon bonds like Sn-C are formed with isocyanide palladium complexes [(tBuNC)₂PdCl₂] as catalysts. In these cases bistannylation of alkynes or arynes was carried out under palladium catalysis. In the course of these reactions the formation of the intermediate [(RNC)₂Pd-(SnR'₃)₂] was proposed. Oxidative addition of hexaalkylditin [R'₃Sn-SnR'₃] at palladium complexes in formal oxidation state zero Pd⁰ or substitution at the dichloride [(RNC)₂PdCl₂] are the discussed reaction pathways for the formation of the possible intermediate.^[5-7] So far complexes of the discussed intermediate type have not been characterized by single-crystal structure solution. However complexes with the trichlorostannate ligand [SnCl₃]⁻ like $[(CNR)_2Pd(SnCl_3)_2]$ (R = Ph, Cy) were characterized by elemental analysis and IR spectroscopy.^[9,10] Besides coordinating at palladium atoms isocyanides can also insert into palladium-carbon bonds, palladium-platinum bonds or react catalytically with palladium complexes to insert into silicon-silicon or silicon-tin bonds.[11-20]

As part of our coordination chemistry project we are studying the ligand abilities of the germylene and stannylene type ligands $[GeB_{11}H_{11}]^{2-}$, $[SnB_{11}H_{11}]^{2-}$, $[SnCHB_{10}H_{10}]^{-}$, $[Ge_2B_{10}H_{10}]^{2-}$ and $[Sn_2B_{10}H_{10}]^{2-}$.^[21-33] In this publication we are presenting the results of our studies of the palladium coordination chemistry with stanna-*closo*-dodecaborate and isocyanide ligands. Substitution reactions and insertion reactions are discussed.

Results and Discussion

We have shown in recent publications that the dianionic tin ligands $[EB_{11}H_{11}]^{2-}$ (E = Ge, Sn) substitute halides in various transition metal complexes and furthermore are able to replace chelating diolefin ligands like 1,5-cyclooctadiene in [(COD)PtCl₂] and [(COD)PdCl₂] to give the tetrasubstituted hexaanionic complexes [M(EB₁₁H₁₁)₄]⁶⁻ (M = Pd, Pt; E = Ge, Sn).^[21,25] Thus it is not surprising, that a mixture of isocyanide palladium complex [(RNC)₂-PdCl₂] (RNC = benzyl, *tert*-butyl, cyclohexyl, 2,6-dimethylphenyl) with four equivalents of tin nucleophile reacts to give the known square-planar complex [Pd(SnB₁₁H₁₁)₄]^{6-,[22–30]} In the case of the salt [Et₃MeN]₆-[Pd(SnB₁₁H₁₁)₄] (1) we were able to solve the disorder problem of the cation in the crystal structure solution.^[25] In Fig-

and NMR spectroscopy. Isocyanide insertion into palladium-

carbon bonds was also found. The zwitterionic complexes

isolated from the reaction of $[(P'_2)Pd(Me)(SnB_{11}H_{11})]^ (P'_2 =$

dppe, dppp, dppf) with isocyanides were characterized.

ure 1 the square-planar-coordinated palladium complex is shown. Details of the crystal structure analysis are listed in Table 1.



Figure 1. Molecular structure of the anion of $[Et_3MeN]_6[Pd-(SnB_{11}H_{11})_4]$ (1), hydrogen atoms and cations have been omitted for clarity, ellipsoids with 50%. Interatomic distances [Å] and angles [°] Pd1–Sn1 2.5625(6), Pd1–Sn2 2.5629(6), Sn1–Pd1–Sn2 89.90(2).

From the reaction mixtures of four isocyanide palladium dichloride complexes [(RNC)₂PdCl₂] (RNC = benzyl, *tert*-butyl, cyclohexyl, 2,6-dimethylphenyl) with two equivalents of the tin nucleophile [SnB₁₁H₁₁]^{2–} (Scheme 1) we were able



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	1	2	3	4
Empirical formula	C42H152B44N6PdSn4	C ₂₈ H ₆₈ B ₂₂ N ₄ PdSn ₂	$C_{36}H_{100}B_{22}Cl_4N_4PdSn_2$	C ₄₅ H ₁₃₃ B ₃₃ N ₈ Pd ₁ Sn ₃
M_r [gmol ⁻¹]	1798.65	1042.46	1312.71	1605.92
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Temperature [K]	173	173	173	173
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	PĪ	$P2_1/n$	$P2_1/n$
Ζ	2	1	2	4
a [Å]	10.7581(8)	8.2055(11)	16.1951(12)	33.953(2)
b [Å]	16.9313(10)	9.9410(12)	10.7196(5)	12.6386(7)
c [Å]	25.3051(14)	14.6716(18)	20.1237(15)	19.5441(12)
a [°]	90	89.822(10)	90	90
β [°]	99.430(5)	81.242(10)	110.959(6)	104.813(5)
γ [°]	90	85.592(10)	90	90
Volume [Å ³]	4547.0(5)	1179.3(3)	3262.4(4)	8108.0(8)
Density $\rho_{\text{calcd.}}$ [g/cm ³]	1.314	1.468	1.336	1.315
Absorption coefficient μ [mm ⁻¹]	1.310	1.456	1.226	1.168
F(000)	1824	520	1336	3280
Crystal size [mm ³]	$0.2 \times 0.2 \times 0.1$	$0.2 \times 0.2 \times 0.1$	$0.2 \times 0.2 \times 0.2$	$0.2 \times 0.2 \times 0.2$
Theta range [°]	5.67 to 25.35	5.67 to 25.35	5.68 to 25.35	5.67 to 25.35
Index range	$-12 \le h \le 12$	$-9 \le h \le 9$	$-19 \le h \le 19$	$-40 \le h \le 40$
	$-20 \le k \le 20$	$-11 \le k \le 11$	$-12 \le k \le 11$	$-14 \le k \le 15$
	$-29 \le l \le 30$	$-17 \le l \le 17$	$-22 \le l \le 24$	$-23 \le l \le 23$
Reflections collected	50472	14368	25093	96549
Independent reflections/ R_{int}	8219/0.0926	4252/0.0915	5666/0.0673	14674/0.0934
Completeness	98.8%	98.7%	94.8%	98.8%
Absorption correction	numerical	numerical	numerical	numerical
Max./min. transmission	0.8796/0.6934	0.8808/0.7337	0.8713/0.7686	0.4159/0.3287
Parameters/restraints	381/151	259/0	327/106	952/445
R_1/wR_2 indices $[I > 2\sigma(I)]$	0.0837/0.1977	0.0394/0.0783	0.0671/0.1592	0.0685/0.1427
R_1/wR_2 for all reflections	0.1054/0.2115	0.0548/0.0827	0.0890/0.1745	0.0890/0.1529
Goodness-of-fit on F^2	1.128	1.051	1.102	1.052
Largest diff. peak/hole [eA ⁻³]	1.769/-1.661	0.823/-1.158	1.542/-0.710	1.992/-1.692

Table 1. Crystal and structure refinement parameters of 1, 2, 3 and 4.

to isolate mixed substitution products (see Figures 2, 3, 4, and 5). Although after two days of reaction time the known tetrasubstituted complex 1 is the only reaction product with a tin ligand. Obviously the adjustment of the substitution equilibrium is slow enough to prepare mixed-substituted complexes only, and the homoleptically tetrasubstituted complexes have the highest stability in this mixture. The mixed isocyanide complexes $[Et_3NH]_2[trans-(C_6H_5CH_2-N\equiv C)_2-Pd(SnB_{11}H_{11})_2]$ (2), $[Bu_3NH]_2[trans-(Me_3C-N\equiv C)_2Pd-(SnB_{11}H_{11})_2]$ (3), $[Et_4N]_4[(C_6H_{11}-N\equiv C)Pd(SnB_{11}H_{11})_3]$ (4) and, $[Et_4N]_4[(2,6-Me_2C_6H_3-N\equiv C)Pd(SnB_{11}H_{11})_3]$ (5) were isolated after crystallization and characterized by NMR spectroscopy, single crystal structure analysis and elemental analysis (Scheme 1). The countercation was varied due to

crystallization purposes. In Figures 2–5 the anionic isocyanide palladium complexes are shown. Details of the crystal structure analysis are listed in Tables 1 and 2.

In isocyanide coordination chemistry the value of the stretching frequency $v(C \equiv N)$ together with the angle at nitrogen in $C \equiv N-C-R'$ are diagnostic tools for the interpretation of the bonding situation of the ligands and the metal centre. In complexes 2–5 the respective IR frequencies $v(C \equiv N)$ exhibit higher values (58–73 cm⁻¹) than the respective uncoordinated molecules.^[34] Furthermore, in the solid state the isocyanides show nearly linear coordination (angles at N M–C1–N–C2: 176.0–178.9°). Both features are significant for low π -back bonding in the isocyanide bond and indicate low electron density at the palladium atom.

$$2 [L_2PdCl_2] + 4 [R_4N]_2[SnB_{11}H_{11}] \longrightarrow 2 [R_4N][L_2PdCl(SnB_{11}H_{11})] + 2 [R_4N]_2[SnB_{11}H_{11}] \longrightarrow 2 [R_4N]_2[SnB_{11}H_{11}] + 2 [R_4N]_2[SnB_{11}H_{11}] + 4 [R_4N]Cl \longrightarrow 2 [R_4N]_4[LPd(SnB_{11}H_{11})_3] + [L_3Pd(SnB_{11}H_{11})] + 4 [R_4N]Cl \longrightarrow 2 [R_4N]Cl \longrightarrow 2 [R_4N]_4[LPd(SnB_{11}H_{11})_3] + (R_4N]Cl \longrightarrow 2 [R_4N]_4[R_4N]Cl \longrightarrow 2 [R_4N]_4[R_4N]_4[R_4N]Cl \longrightarrow 2 [R_4N]_4[R_4N]Cl \longrightarrow 2 [R_4N]_4[R_4N]_4[R_4N]Cl \longrightarrow 2 [R_4N]_4[R_4N]Cl \longrightarrow 2 [R_4N]_4[R_4N]Cl \longrightarrow 2 [R_4N]_4[R_4N]_4[R_4N]Cl \longrightarrow 2 [R_4N]_4[R_4N]_4[R_4N]_4[R_4N]Cl \longrightarrow 2 [R_4N]_4[R_4N]_4[R_4N]Cl \longrightarrow 2 [R_4N]_4[R_4N]_4[R_4N]_4[R_4N]Cl \longrightarrow 2 [R_4N]_4[R$$

 $[R_4N]_6[Pd(SnB_{11}H_{11})_4] + [PdL_4]Cl_2 + 2 [R_4N]Cl_4]$

Scheme 1. Possible substitution equilibrium showing the formation of the (with respect to the tin ligand) mono-, di-, tri- and tetrasubstituted palladium complexes (L = isocyanide).



Figure 2. Molecular structure of the anion of $[Et_3NH]_2[trans-(C_6H_5CH_2-N=C)_2Pd(SnB_{11}H_{11})_2]$ (2), hydrogen atoms and cations have been omitted for clarity, ellipsoids with 50%. Interatomic distances [Å] and angles [°]: Pd1–Sn1 2.5640(4); Pd1–C1 1.970(5); C1–N1 1.143(6); C1–Pd1–Sn1 90.1(1), C1–N1–C2 178.8(5).



Figure 3. Molecular structure of the anion of $[Bu_3NH]_2[trans-(Me_3C-N=C)_2Pd(SnB_{11}H_{11})_2]$ (3), hydrogen atoms and cations have been omitted for clarity, ellipsoids with 50%. Interatomic distances [Å] and angles [°]: Pd1–Sn1 2.5589(5), Pd1–C1 1.96(1), C1–N1 1.13(1), C1–Pd1–Sn1 89.0(2), C1–N1–C2 176.0(9).



Figure 4. Molecular structure of the anion of $[Et_4N]_4[(C_6H_{11}-N=C)Pd(SnB_{11}H_{11})_3]$ (4), hydrogen atoms and cations have been omitted for clarity, ellipsoids with 30%. Interatomic distances [Å] and angles [°]: Pd1–Sn1 2.5682(7), Pd1–Sn2 2.5290(7), Pd1–Sn3 2.5622(7), Pd1–C1 1.951(11), N1–C1 1.23(2), C1–Pd1–Sn2 177.5(4), C1–Pd1–Sn3 91.4(3), Sn2–Pd1–Sn3 90.54(2), C1–Pd1–Sn1 90.2(3), Sn2–Pd1–Sn1 87.78(2), Sn3–Pd1–Sn1 173.78(4), C1–N1–C2 164 (disorder).

The electronic situation in the stannaborate isocyanide complexes can be compared with isocyanide trichlorostannate compounds of palladium.^[9,10] The Pd–C bond lengths in complexes **2–5** are in the close range of 1.95–1.98 Å and lie in the area of known isocyanide palladium complexes.^[35] The Pd–Sn distances in compound **2–5** show an interesting



Figure 5. Molecular structure of the anion of $[Et_4N]_4[(2,6-Me_2C_6H_3-N\equiv C)Pd(SnB_{11}H_{11})_3]$ (5), hydrogen atoms and cations have been omitted for clarity, ellipsoids with 50%. Interatomic distances [Å] and angles [°]: Pd1–Sn1 2.5611(4), Pd1–Sn2 2.5351(4), Pd1–Sn3 2.5515(4), Pd1–C1 1.978(4), C1–N1 1.148(5), Sn2–Pd1–Sn1 86.82(1), C1–Pd1–Sn1 92.7(1), Sn2–Pd1–Sn3 89.77(1), C1–Pd1–Sn3 91.0(1), C1–Pd1–Sn2 176.5(1), Sn3–Pd1–Sn1 174.39(1), C1–N1–C2 178.9(4).

trend: *trans*-oriented tin ligands exhibit Pd–Sn bond lengths of 2.56 Å, whereas the tin ligands in **4** and **5** *trans* to the isocyanide show slightly shorter distances of 2.53 Å to palladium. This might be an indication of the slightly weaker *trans* influence of the isocyanide ligand.

NMR Spectroscopy in Solution

The reactions were monitored by ¹¹⁹Sn{¹H} NMR spectroscopy in solution. The uncoordinated heteroborate shows a resonance at $\delta = -540$ ppm, whereas the tin for coordinated stanna-closo-dodecaborate shows a signal at chemical shifts in an area from -300 to -350 ppm. The reaction mixture of [cis-(isocyanide)₂PdCl₂] with two equivalents of ligand [SnB₁₁H₁₁]²⁻ displays in the ¹¹⁹Sn NMR spectrum three broad signals in the range of $\delta = -305$ ppm -330 ppm at the beginning of the reaction, which probably indicates the formation of three products [trans-(isocyanide)2- $Pd(SnB_{11}H_{11})_2]^{2-}$, [(isocyanide) $Pd(SnB_{11}H_{11})_3]^{4-}$ and $[Pd(SnB_{11}H_{11})_4]^{6-}$. After 48 h the signal of [*trans*-(isocyanide)₂Pd(SnB₁₁H₁₁)₂]²⁻ almost disappeared and the signal of [Pd(SnB₁₁H₁₁)₄]⁶⁻ has increased. In the ¹¹B NMR spectrum the uncoordinated heteroborate shows resonances at $\delta = -6, -11$ and -13 ppm with an intensity ratio of 1:5:5, whereas for the coordination of the stanna-closo-dodecaborate to a transition metal shows only one peak at $\delta \approx$ -15 ppm for ten boron atoms. Compounds 1 und 2 exhibit two signals in the ${}^{11}B{}^{1}H{}$ NMR spectrum at -9.3 (B12), -14.8 (B2-B11) ppm and -9.4 (B12), -15.0 (B2-B11) ppm, indicating coordination of the stanna-closo-dodecaborate ligand.

In order to prove whether the isocyanide tin complexes react under transfer of the tin ligand on an unsaturated substrate we studied the chemical behaviour of the complex $[Bu_3NH]_2[trans-(Me_3C-N\equiv C)_2Pd(SnB_{11}H_{11})_2]$ (3) towards

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	Table 2. Crystal and	structure refinement	parameters of	f 5, 6,	7, 8	3 and 9.
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	5	6	7	8	9
Empirical formula	C31H99B33N8PdSn3	C46H70B11ClN4P2PdSn	C ₃₉ H ₅₉ B ₁₁ N ₄ P ₂ PdSn	C41H54B11Cl2FeNP2PdSn	C42H52B11Cl2FeNP2PdSn
$M_{\rm p}/{\rm g}{\rm mol}^{-1}$	1403.38	1120.45	989.84	1093.54	1103.54
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Temperature [K]	173	173	173	173	173
Crystal system	monoclinic	triclinic	triclinic	triclinic	monoclinic
Space group	$P2_{1}/c$	PĪ	ΡĪ	PĪ	$P2_{1}/c$
Z	4	2	2	2	4
a [Å]	16.4056(6)	12.0401(9)	10.6699(12)	10.6095(12)	13.9436(8)
<i>b</i> [Å]	16.2748(7)	13.8578(13)	14.2068(16)	14.1845(16)	18.5741(8)
c [Å]	25.5053(10)	17.2027(16)	16.8443(17)	17.7287(19)	18.5784(13)
a [°]	90	100.667(7)	73.907(8)	103.898(9)	90
β [°]	93.013(3)	104.834(7)	80.096(9)	96.639(9)	100.319(5)
γ [°]	90	93.599(7)	87.601(9)	93.210(9)	90
Volume [Å ³]	6800.4(5)	2708.3(4)	2416.7(5)	2562.8(5)	4733.8(5)
Density $\rho_{\text{calcd.}}$ [g/cm ³]	1.371	1.374	1.360	1.417	1.548
Absorption coefficient μ	1.381	0.937	0.987	1.306	1.415
[mm ⁻¹]					
F(000)	2808	1144	1004	1096	2208
Crystal size [mm ³]	$0.2 \times 0.2 \times 0.2$	$0.3 \times 0.2 \times 0.1$	$0.3 \times 0.2 \times 0.2$	$0.2 \times 0.2 \times 0.2$	$0.2 \times 0.2 \times 0.1$
Theta range [°]	5.67-25.35	5.67-25.35	5.67-25.35	5.67-25.35	5.67-25.35
Limiting indices $\pm h$, $\pm k$, $\pm l$	19, 19, 30	14, 16, 20	12, 17, 20	12, 17, 21	16, 22, 22
Reflections collected	80448	31028	23401	29399	51229
Independent reflections/R _{int}	12309/0.0693	9654/0.0655	8529/0.1282	9255/0.1148	8562/0.0808
Completeness	98.8%	97.2%	96.4%	98.6%	98.7%
Absorption correction	numerical	numerical	numerical	numerical	numerical
Max./min. transmission	0.8675/0.7781	0.9291/0.8009	0.8862/0.7227	0.8777/0.7542	0.9999/0.4899
Parameters/restraints	695/6	581/355	526/69	526/3	520/0
R_1/wR_2 indices $[I > 2\sigma(I)]$	0.0385/0.0770	0.0443/0.0931	0.0923/0.1753	0.0776/0.1561	0.0539/0.1008
R_1/wR_2 for all reflections	0.0497/0.0806	0.0581/0.1009	0.1358/0.1927	0.1209/0.1737	0.0683/0.1056
Goodness-of-fit on F^2	1.104	1.029	1.170	1.107	1.178
Largest diff. peak/hole [e A-3]	0.911/-0.768	1.158/-1.204	2.804/-1.584	1.638/-1.019	1.690/-1.502

(trimethylsilyl)acetylene at room temperature. However, from this mixture we could not detect any reaction products.

Insertion Reactions

In platinum stanna-closo-dodecaborate chemistry we found activation of a Pt-C bond towards an isocyanide insertion.^[23] Tin ligands like SnCl₃ for example are known for activation of metal organic complexes in catalysis.^[36] We are interested in the behaviour of our coordinated tin ligand in palladium chemistry. Here we present isocyanide insertion, which was carried out starting with the palladium methyl complex $[(P'_2)Pd(CH_3)Cl]$ carrying three different chelating phosphanes like P'2: dppe, dppp and dppf. In a simple one pot procedure we reacted the chloride complexes of type $[(P'_2)Pd(CH_3)Cl]$ with the tin nucleophile $[SnB_{11}H_{11}]^{2-}$. (These reaction products were also isolated and characterized for the ligands dppp and dppf.) After a period of stirring for 1 h for in acetonitrile the respective isocyanide was added. Isocyanide insertion into Pd-C bonds of $[(P'_2)Pd(CH_3)(SnB_{11}H_{11})]^-$ was conducted at room temperature and the insertion products were isolated as zwitterionic molecules with a protonated nitrogen atom (Scheme 2). The trialkylammonium salt of the stanna-closododecaborate [R₃NH]₂[SnB₁₁H₁₁] cluster serves as the source of the protons. In these neutral molecules the coordinated heteroborate carries the negative charge and the protonated nitrogen atom the positive charge. In one case we isolated a substitution and not the insertion product: instead of the methyl substituent a cyclohexyl isocyanide is coordinated to palladium in complex 9. This compound is also a zwitterionic complex consisting of the dicationic $[(dppf)Pd(C \equiv N-C_6H_{11})]$ moiety and the dianionic heteroborate ligand.



Scheme 2. Formation of the zwitterionic complexes **6–8**. a: reaction with one equivalent of $[R_3NH]_2[SnB_{11}H_{11}]$ in acetonitrile; b: reaction of the mixture with one equivalent of the respected isocyanide. **6**: dppe, 2,6-dimethylphenyl isocyanide; **7**: dppp, *tert*-butyl isocyanide; **8**: dppf, *tert*-butyl isocyanide.

Due to the high polarity the molecules, 6-9 are only very slightly soluble in common solvents and were therefore only characterized by elemental analysis and X-ray structure analysis. In Figures 6, 7, 8, and 9 the structures of the molecules in the solid state are shown and relevant interatomic distances and angles are listed. In Table 2 the details of the crystal structure analysis are listed. The palladium atoms are nearly square-planar-coordinated by the tin, phosphane and iminoacyl ligands. The Pd–C distance in complex 6-8

is 2.04–2.05 Å long and lies in the range of other iminoacyl complexes.^[14] The Pd–Sn bond length of nearly 2.57 Å in **6–9** is known for other Pd–SnB₁₁H₁₁ complexes.^[25]

Figure 6. Molecular structure of [(dppe)Pd(SnB₁₁H₁₁)-{C(Me)=NH-2,6-Me₂C₆H₃}] (6), H atoms have been omitted for clarity, ellipsoids with 50%. Interatomic distances [Å] and angles [°]: Sn1-Pd1 2.5819(4), Pd1-P1 2.316(1), Pd1-P2 2.322(1), C2-Pd1 2.052(5), C2-N1 1.277(6), C2-Pd1-P1 96.7(1), P1-Pd1-P2 84.09(4), P2-Pd1-Sn1 93.10(3), C2-Pd1-Sn1 85.7(1), N1-C2-Pd1 121.3(4).



Figure 7. Molecular structure of $[(dppp)Pd(SnB_{11}H_{11})-{C(Me)=NH-CMe_3}]$ (7), H atoms have been omitted for clarity, ellipsoids with 50%. Interatomic distances (Å) and angles [°]: Sn1-Pd1 2.570(1), Pd1-P1 2.333(3), Pd1-P2 2.330(3), C2-Pd1 2.04(1), C2-N1 1.27(1), C2-Pd1-P1 91.3(3), P1-Pd1-P2 95.4(1), P2-Pd1-Sn1 89.83(7), C2-Pd1-Sn1 83.1(3), N1-C2-Pd1 129.7(8).



Figure 8. Molecular structure of $[(dppf)Pd(SnB_{11}H_{11})-{C(Me)=NH-CMe_3}]$ (8), H atoms have been omitted for clarity, ellipsoids with 50%. Interatomic distances [Å] and angles [°]: Sn1-Pd1 2.575(1), Pd1-P1 2.352(3), Pd1-P2 2.359(2), C2-Pd1 2.042(8), C2-N1 1.28(1), C2-Pd1-P1 90.0(2), P1-Pd1-P2 99.46(8), P2-Pd1-Sn1 87.51(6), C2-Pd1-Sn1 82.5(2), N1-C2-Pd1 131.2(6).



Figure 9. Molecular structure of $[(dppf)Pd(SnB_{11}H_{11})(C\equiv N-C_6H_{11})]$ (9), H atoms and cations have been omitted for clarity, ellipsoids with 50%. Interatomic distances [Å] and angles [°]: Sn1–Pd1 2.5790(5), Pd1–P1 2.342(1), Pd1–P2 2.361(1), C1–Pd1 1.997(6), C1–N1 1.141(8), C1–Pd1–Sn1 81.3(1), C1–Pd1–P2 91.4(1), P1–Pd1–P2 98.47(5), P1–Pd1–Sn1 89.62(4), C1–Pd1–P1 168.3(1), P2–Pd1–Sn1 169.70(4).

Conclusions

From the reaction of isocyanide complexes of type [cis- $(R-N\equiv C)_2PdCl_2$] with two equivalents of the tin nucleophile [SnB₁₁H₁₁]^{2–} different reaction products depending on the substituents at the isocyanide were isolated. *trans*-Coordinated palladium complexes with isocyanides and tin ligands were structurally characterized for the first time. Furthermore isocyanide insertion into the Pd–C bond was carried out with complexes [(P'_2)Pd(CH_3)(SnB_{11}H_{11})][–] (P'_2 = dppe, dppp, dppf) resulting to give zwitterionic molecules [(P'_2)Pd(SnB_{11}H_{11}){C(Me)=NH-R}] (R = 2,6-C_6H_3Me_2, CMe_3).

Experimental Section

General: All manipulations were carried out under argon in Schlenk glassware. Solvents were dried and purified by standard methods and stored under argon. NMR spectra were recorded with a Bruker DRX-250 NMR spectrometer equipped with a 5 mm ATM probe head and operating at 250.13 (¹H), 80.25 (¹¹B), 62.90 (¹³C), 101.25 (³¹P) and 93.25 MHz (¹¹⁹Sn) and a Bruker DRX-400 NMR spectrometer equipped with a 5 mm QNP (quad nucleus probe) head and operating at 400.13 (¹H) and 100.13 MHz (¹³C). Chemical shifts are reported in δ values in ppm relative to external TMS (¹H, ¹³C), BF₃·Et₂O (¹¹B), or SnMe₄ (¹¹⁹Sn) using the chemical shift of the solvent ²H resonance frequency. Elemental analyses were performed at the Institut für Anorganische Chemie Universität of Tübingen using a Vario EL analyzer. The infrared spectra were measured on a Bruker Vertex 70 spectrometer equipped with an ATR unit (attenuated total reflection).

Crystallography: X-ray data for compounds **1–9** were collected with a Stoe IPDS 2T diffractometer and corrected for Lorentz and polarization effects and absorption by air. In the case of compound **4** two orientations (68 and 32%) of the cyclohexyl isocyanide ligand were found in the crystal structure solution. In Figure 4 the orientation with 68% is shown.

The programs used in this work were Stoe's X-Area and WinGX suite of programs including SHELXS and SHELXL for structure

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solution and refinement. Numerical absorption correction based on crystal-shape optimization was applied for **1–9** with Stoe's X-Red and X-Shape.^[37–43] Crystal data are listed in Tables 1 and 2.

[*cis*-($R-N\equiv C$)₂PdCl₂] [R = Me₃C, C₆H₁₁, 2,6-Me₂C₆H₃, C₆H₅CH₂]: A suspension of PdCl₂ and 2 equiv. of isocyanide in CH₃CN were stirred for 24 h. The solvent was removed in vacuo to give a solid. The products were characterized by IR spectroscopy.

 $[Et_3MeN]_6[Pd(SnB_{11}H_{11})_4]$ (1): 28.6 mg (0.10 mmol) of [(COD)-PdCl₂] and 192.2 mg (0.40 mmol) [Et₃MeN]₂[SnB₁₁H₁₁] were allowed to react in 10 mL of CH₃CN. Crystals were obtained by slow diffusion of ethyl ether into the acetonitrile solution: 137.2 mg of 1, 76% yield.

 $[Et_3NH]_2[trans-(C_6H_5CH_2-N=C)_2Pd(SnB_{11}H_{11})_2]$ (2): [cis- $(C_6H_5CH_2-N\equiv C)_2PdCl_2$] (41.2 mg, 0.10 mmol) and $[Et_3NH]_2-$ [SnB₁₁H₁₁] (90.5 mg, 0.20 mmol) were dissolved in acetonitrile. Red crystals were obtained by slow diffusion of ethyl ether into the acetonitrile solution (63.1 mg, 60.5% yield). C₂₈H₆₈B₂₂N₄PdSn₂ (1042.56): calcd. C 32.26, H 6.57, N 5.37; found C 32.52, H 6.62, N 5.53. IR (ATR): $\tilde{v} = 2217$ [s, $v(C \equiv N)$] cm⁻¹. NMR spectroscopy: $[Bu_3NH]_2[trans-(C_6H_5CH_2-N=C)_2Pd(SnB_{11}H_{11})_2]:$ ¹H NMR CH2-CH2-), 1.64 (m, 12 H, -CH2-CH2-CH2-), 1.31 (m, 12 H, -CH₂-CH₂-CH₃), 0.88 (m, 18 H, -CH₂-CH₃) ppm. ¹¹B{¹H} NMR (CD₂Cl₂): δ = -9.3 (B12), -14.8 (B2-B11) ppm. ¹³C{¹H} NMR (CD₂Cl₂): δ = 205.7 (Pd–C=N–), 128.5, 126.5 (br., –C₆H₅), 52.1 (-N-CH2-CH2-), 29.8 (N-CH2-C6H5), 24.7 (-CH2-CH2-CH₂-), 19.3 (-CH₂-CH₂-CH₃), 12.7 (-CH₂-CH₃) ppm. ¹¹⁹Sn{¹H} NMR (CD₂Cl₂): $\delta = -307$ ppm.

[Bu₃NH]₂[trans-(Me₃C–N≡C)₂Pd(SnB₁₁H₁₁)₂] (3): The complex was prepared in the same way as **2**. Instead of acetonitrile dichloromethane was used (73.3 mg, 64.1% yield). C₃₄H₉₆B₂₂N₄PdSn₂ (1142.85): calcd. C 35.73, H 8.47, N 4.90; found C 35.88, H 8.47, N 4.81. IR (ATR): $\tilde{v} = 2201$ [s, v(C≡N)] cm⁻¹. ¹H NMR (CD₂Cl₂): $\delta = 3.03$ (m, 12 H, −N–CH₂–CH₂–), 1.73 (m, 12 H, −CH₂–CH₂–CH₂–), 1.55 (m, −C–(CH₃)₃), 1.39 (m, 12 H, −CH₂–CH₂–CH₃), 0.94 (m, 18 H, −CH₂–CH₃) ppm. ¹¹B{¹H} NMR (CD₂Cl₂): $\delta = -9.4$ (B12), −15.0 (B2–B11) ppm. ¹³C{¹H} NMR (CD₂Cl₂): $\delta = 125.5$ (Pd–C≡N–), 60.8 [–N–C(CH₃)], 53.3 (–N–CH₂–CH₂–), 30.1 [–C(CH₃)], 25.9 (–CH₂–CH₂–CH₂–), 20.4 (–CH₂–CH₂–CH₃), 13.9 (–CH₂–CH₃) ppm. ¹¹⁹Sn{¹H} NMR (CD₂Cl₂): $\delta = -305$ [d, ²*J*(¹¹⁹Sn-¹¹⁷Sn) = 17106 Hz] ppm.

[Et₄N]₄[(C₆H₁₁−N≡C)Pd(SnB₁₁H₁₁)₃] (4): The complex was prepared in the same way as 2 (85.4 mg, 57.6% yield). C₃₉H₁₂₄B₃₃N₅PdSn₃ (1482.76): calcd. C 31.59, H 8.43, N 4.72; found C 31.32, H 8.46, N 4.57. IR (ATR): $\tilde{v} = 2198$ [s, v(C≡N)] cm⁻¹.

$$\label{eq:meansatz} \begin{split} & [Me_4N]_4[(2,6-Me_2C_6H_3-N=C)Pd(SnB_{11}H_{11})_3] \ \ (5): \ \ The \ \ complex \\ & was prepared in the same way as 2 (74.6 mg, 59.0 \% yield). [Et_4N]_4- \\ & [(2,6-Me_2C_6H_3-N=C)Pd(SnB_{11}H_{11})_3]\cdot Et_2O. \ C_{45}H_{132}B_{33}N_5OPdSn_3 \\ & (1578.89): \ calcd. \ C \ 34.23, \ H \ 8.43, \ N \ 4.44; \ found \ C \ 34.60, \ H \ 8.11, \\ & N \ 4.52. \ IR \ (ATR): \ \tilde{\nu} = 2193 \ [s, \ \nu(C=N)] \ cm^{-1}. \end{split}$$

[(dppe)Pd(SnB₁₁H₁₁){C(Me)=NH-2,6-C₆H₃Me₂}] (6): [(dppe)Pd-(Me)Cl] (55.5 mg, 0.10 mmol) and [Et₃NH]₂[SnB₁₁H₁₁] (45.3 mg, 0.10 mmol) were dissolved in acetonitrile, stirred for 1 h and 2,6-dimethylphenyl isocyanide (13.1 mg, 0.10 mmol) was added. Crystals were obtained by slow diffusion of ethyl ether into the acetonitrile solution (54.5 mg, 60.5%). C₃₆H₄₈B₁₁NP₂PdSn (900.78): calcd. C 48.00, H 5.37, N 1.55; found C 48.61, H 4.94, N 0.48. IR (ATR): $\tilde{v} = 1585$ [s, $v(C \equiv N)$] cm⁻¹.

[(dppp)Pd(SnB₁₁H₁₁){C(Me)=NH-CMe₃}] (7): [(dppp)Pd(Me)Cl] (56.9 mg, 0.10 mmol) and [Et₃NH]₂[SnB₁₁H₁₁] (45.3 mg, 0.10 mmol) were dissolved in acetonitrile, stirred for 1 h and *tert*-butyl isocyanide (11 μ L, 0.10 mmol) was added. Crystals were obtained by slow diffusion of ethyl ether into the acetonitrile solution (58.6 mg, 67.6%). C₃₃H₅₀B₁₁NP₂PdSn (866.77): calcd. C 45.73, H 5.81, N 1.62; found C 45.52, H 5.37, N 1.64. IR (ATR): $\tilde{v} = 1574$ [s, v(C=N)] cm⁻¹.

[(dppf)Pd(SnB₁₁H₁₁){**C(Me)=NH–CMe**₃}] (8): [(dppf)Pd(Me)Cl] (55.5 mg, 0.10 mmol) and [Bu₃NH]₂[SnB₁₁H₁₁] (62.1 mg, 0.10 mmol) were dissolved in dichloromethane, stirred for 1 h and *tert*-butyl isocyanide (11 µL, 0.10 mmol) was added. Crystals were obtained by slow diffusion of ethyl ether into the dichloromethane solution (63.6 mg, 63.1%). $C_{40}H_{52}B_{11}FeNP_2PdSn$ (1008.71): calcd. C 47.63, H 5.20, N 1.39; found C 47.15, H 5.04, N 1.18. IR (ATR): $\tilde{v} = 1580$ [s, v(C=N)] cm⁻¹.

[Bu₃MeN][(dppp)Pd(Me)(SnB₁₁H₁₁)]: [(dppp)PdCl(Me)] (56.9 mg, 0.10 mmol) and $[Bu_3MeN]_2[SnB_{11}H_{11}]$ (64.9 mg, 0.10 mmol) were dissolved in dichloromethane and stirred for 1 h. The solution was removed and the yellow residue was washed with water. The powder was dried in vacuo. (69.3 mg, 70.5%). [Bu₃MeN][(dppp)-Pd(Me)(SnB₁₁H₁₁)]·H₂O. C₄₁H₇₂B₁₁NOP₂PdSn (1001.03): calcd. C 49.19, H 7.25, N 1.40; found C 48.87, H 7.09, N 1.81. NMR spectroscopy $[Bu_3NH][Pd(dppp)(Me)(SnB_{11}H_{11})]$: ¹H NMR (CD₂Cl₂): $\delta = 7.16-7.72$ (m, 20 H, P-C₆H₅), 3.01 (m, 6 H, -N-CH₂-CH₂-), 2.65 (m, 2 H, P-CH₂-CH₂), 2.45 (m, 2 H, P-CH₂-CH₂) 2.02 (m, 2 H, P-CH₂-CH₂-CH₂-P), 1.73 (m, 6 H, -CH₂-CH₂-CH₂-), 1.40 (m, 6 H, -CH₂-CH₂-CH₃), 0.89 (m, 9 H, -CH₂-CH₃), 0.58 [t, ${}^{3}J({}^{31}P^{1}H) = 7 \text{ Hz}, \text{ Pd-CH}_{3} \text{ ppm. } {}^{11}B\{{}^{1}H\} \text{ NMR (CD}_{2}Cl_{2}): \delta =$ -11.0 (B12), -15.2 (B2–B11) ppm. ¹³C{¹H} NMR (CD₂Cl₂): δ = 125.6-134.7 (m, P-C₆H₅), 53.2 (-N-CH₂-CH₂-), 28.9 (d, P-CH₂- CH_2), 28.0 (d, P- CH_2 - CH_2), 25.9 (- CH_2 - CH_2 - CH_2 -), 20.5 (-CH₂-CH₂-CH₃), 19.9 (s, P-CH₂-CH₂-CH₂-P), 13.8 (-CH₂-CH₃), -1.8 [d, ${}^{2}J({}^{31}P{}^{13}C) = 88$ Hz, Pd–CH₃] ppm. ${}^{31}P{}^{1}H{}$ NMR $(CD_2Cl_2): \delta = 14.2 \text{ [d, } {}^2J({}^{31}P{}^{31}P, cis) = 53, {}^2J({}^{119}Sn{}^{-31}P, trans) =$ 2584, ${}^{2}J({}^{117}Sn-{}^{31}P, trans) = 2474 Hz], -0.3 [d, {}^{2}J({}^{31}P^{31}P, cis) = 53,$ ${}^{2}J({}^{119}Sn-{}^{31}P, cis) = 343, {}^{2}J({}^{117}Sn-{}^{31}P, cis) = 330 \text{ Hz}] \text{ ppm. } {}^{119}Sn \{{}^{1}H\}$ NMR (CD₂Cl₂): $\delta = -281$ [d, ²*J*(¹¹⁹Sn-³¹P, *trans*) = 2673 Hz] ppm.

[Bu₃MeN][(dppf)Pd(Me)(SnB₁₁H₁₁)]: [(dppf)PdCl(Me)] (65.6 mg, 0.10 mmol) and $[Bu_{3}MeN]_{2}[SnB_{11}H_{11}]$ (64.9 mg, 0.10 mmol) were dissolved in dichloromethane and stirred for 1 h. The solution was removed and the yellow residue was washed with water. The powder was dried in vacuo. (82.1 mg, 73.0%). [Bu₃MeN][(dppf)- $Pd(Me)(SnB_{11}H_{11})]$ ·2H₂O. $C_{48}H_{76}B_{11}FeNO_2P_2PdSn$ (1160.98): calcd. C 49.66, H 6.60, N 1.21; found C 49.90, H 6.59, N 1.71. NMR spectroscopy [Bu₃NH][(dppf)Pd(Me)(SnB₁₁H₁₁)]: ¹H NMR $(CD_2Cl_2): \delta = 7.16-7.52 \text{ (m, 20 H, P-C_6H_5), } 3.72-4.63 \text{ (m, 8 H, P-}$ C₅H₄), 2.94 (m, 6 H, -N-CH₂-CH₂-), 1.70 (m, 6 H, -CH₂-CH₂-CH2-), 1.40 (m, 6 H, -CH2-CH2-CH3), 0.98 (m, 9 H, -CH2-CH3), 0.67 (m, Pd–CH₃) ppm. ¹¹B{¹H} NMR (CD₂Cl₂): $\delta = -15.4$ (B2– B11) ppm. ¹³C{¹H} NMR (CD₂Cl₂): δ = 125.6–134.3 (m, P–C₆H₅), 72.5-76.5 (m, P-C₅H₄), 53.5 (-N-CH₂-CH₂-), 26.5 (-CH₂-CH₂-CH₂-), 20.5 (-CH₂-CH₂-CH₃), 13.9 (-CH₂-CH₃), 0.7 [d, ${}^{2}J({}^{31}P{}^{13}C) = 84 \text{ Hz}, \text{ Pd-CH}_{3} \text{ ppm. } {}^{31}P\{{}^{1}H\} \text{ NMR } (CD_{2}Cl_{2}): \delta =$ 31.5 [d, ${}^{2}J({}^{31}P{}^{31}P, cis) = 34$, ${}^{2}J({}^{119}Sn{}^{-31}P, trans) = 2719$, ${}^{2}J({}^{117}Sn{}^{-1}P, cis) = 2719$, ${}^{2}J({}^{117$

³¹P, *trans*) = 2597 Hz], 16.5 [d, ${}^{2}J({}^{31}P-{}^{31}P, cis) = 34, {}^{2}J({}^{119}Sn-{}^{31}P, cis) = 372, {}^{2}J({}^{117}Sn-{}^{31}P, cis) = 356$ Hz] ppm. ${}^{119}Sn\{{}^{1}H\}$ NMR (CD₂Cl₂): $\delta = -275$ (d, ${}^{2}J({}^{119}Sn-{}^{31}P, trans) = 2751$ Hz) ppm.

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