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Platinum complexes of stanna-*closo*-dodecaborate

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Dedicated to Professor Sheldon Shore on the occasion of his 70th birthday.

Abstract

The platinum(II)chlorides *cis*-L_2PtCl_2 (L=PPh_3, PEt_3), (dppe)$PtCl_2$, *trans*–$(Ph_3P)_2Pt(Cl)Ph$, (dppe)Pt(Cl)Me and (dppe)Pt(Cl)Ph were treated with $[Bu_3MeN]_2[SnB_{11}H_{11}]$ (**1**) to give the air and moisture inert stannaborate substituted complexes $[Bu_3MeN]_2$-[*trans*-$L_2Pt(SnB_{11}H_{11})_2$] (**2**: L=PPh_3, **3**: L=PEt_3), $[Bu_3MeN]_2$[(dppe)$Pt(SnB_{11}H_{11})_2$] (**4**), $[Bu_3MeN]$[*trans*-$(Ph_3P)_2Pt(SnB_{11}H_{11})Ph$] (**8**), $[Bu_3MeN]$[(dppe)$Pt(SnB_{11}H_{11})Me$] (**9**) and $[Bu_3MeN]$[(dppe)$Pt(SnB_{11}H_{11})Ph$] (**10**). The nearly square planar coordination at the transition metal centre in the anion of **8** was confirmed by X-ray crystal structure analysis. (dppe)$PtCl_2$ reacts with one equivalent of **1** to give a 1:1 mixture of **4** and (dppe)$PtCl_2$. Reaction of **9** and **10** with one equivalent of HCl resulted not in the isolation of the monochloride $[(dppe)Pt(SnB_{11}H_{11})Cl]^-$ (**A**), instead the 1:1 mixture between was **4** and (dppe)$PtCl_2$ isolated. From the reaction of [(triphos)PtCl][BF_4] and **1** a zwitterionic platinum complex (triphos)$Pt(SnB_{11}H_{11})$ (**11**) was isolated. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Boron; Cluster; Tin; Nucleophilic substitution; Platinum complexes

1. Introduction

During the course of our investigations towards zwitterionic compounds of the stanna-*closo*-dodecaborate cluster we are studying the nucleophilicity of this cluster dianion in reaction with various electrophiles. The synthesis of this heteroborate was described in 1992 by Todd et al. together with the methylation carried out by reaction of the dianion $[MePh_3P]_2[SnB_{11}H_{11}]$ with methyliodide [1]. The chemistry of the homologue carba-*closo*-dodecaborate cluster has been investigated thoroughly especially with respect to the weakly coordinating properties of this anion [2]. Thus, the perhalogenated derivatives of this cluster have been used to crystallize reactive cations [3]. The reaction of the carbaborate with a copper electrophile was published as the first example for the formation of an exo carbon–transition metal bond [4].

Recently we have shown that the anionic stannaborate $[SnB_{11}H_{11}]^{2-}$ is a nucleophile in reaction with several transition metal halides resulting in the formation of a transition metal tin bond [5]. In this publication we present the first reactions of the stanna-*closo*-dodecaborate cluster with platinum chlorides.

2. Results and discussion

The platinum complexes *cis*–L_2PtCl_2 (L=PPh_3, PEt_3) and (dppe)$PtCl_2$ react with two equivalents of stanna-*closo*-dodecaborate under complete substitution (Scheme 1). During the reaction time of 48 h the colorless mixture turned yellow. The substitution products were isolated after crystallization by slow diffusion of hexane into a dichloromethane solution.

The crystalline substances **2, 3** and **4** are inert towards moisture and air and were completely characterized by elemental analyses and NMR-spectroscopy (Table 1). It is well established that the ^2J(SnP) coupling constants permit unambigous assignment of the stereochemistry in Pt(II) complexes [6]. Indirect coupling between ligand atoms is known to be much larger for *trans* than *cis* related ligands. Thus *trans* ^2J(SnP) coupling constants are around ten times larger than the

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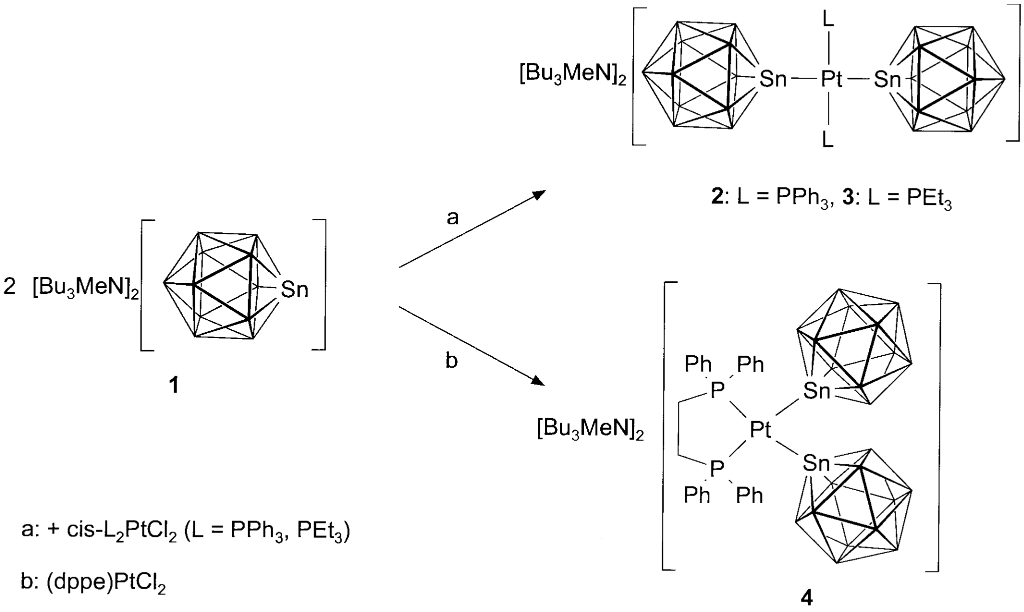


Scheme 1.

respective *cis* coupling constants. In the case of the triphenyl- and triethylphosphine substituted platinum complexes (anion of **2** and **3**) a *cis*/*trans* isomerization takes place during substitution. This isomerization is a well known phenomenon in Pt(II) substitutiton chemistry and was already mentioned in 1967 with the reaction of *cis*–$(PEt_3)_2PtCl_2$ and $(Me_3Ge)_2Hg$ to give *trans*–$(PEt_3)_2Pt(Cl)GeMe_3$ [7].

In order to synthesize zwitterionic platinum complexes we studied the monosubstitution between $(dppe)PtCl_2$ and the stanna-*closo*-dodecaborate nucleophile. So far we were not able to isolate a monosubstitution product from this reaction. Instead the reaction resulted in the formation of a one to one mixture between the double substituted complex **4** and starting material (Scheme 2).

In a plausible mechanistic sequence for the formation of the disubstituted product a stepwise replacement of the halogenides is most likely to occur (Scheme 3). However, we were not able to detect the monosubstituted platinumchloride **A**. Two explanations for this result were taken into consideration: the second substitution step takes place with a much higher reaction rate than the first step ($k_2 \gg k_1$) (Scheme 3a); or an equilibrium between the monosubstitution product and the disubstitution product and dihalogenide lies completely on the right side (Scheme 3b).

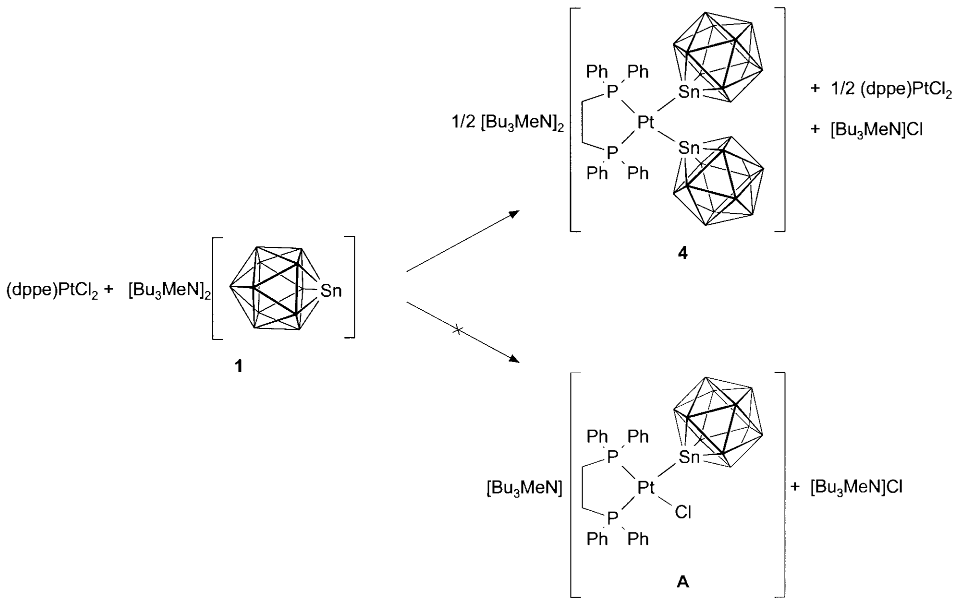
In order to find some indications for one of the two explanations we tried to synthesize a monohalogenide complex like **A** by another than the substitution procedure. The methyl and phenyl substituted monochloride complexes (**5**, **6**, and **7**) react straightforwardly with one equivalent of the cluster nucleophile. These tetraalkylammonium salts **8**, **9**, and **10** were isolated in high yield and completely characterized by elemental analyses and NMR spectroscopy. In the case of $[Bu_3MeN]$-[*trans*–$(Ph_3P)_2Pt(Ph)(SnB_{11}H_{11})$] (**8**) an X-ray crystal structure analysis was carried out. Following the reaction sequence in Scheme 4 the methyl or phenyl substituent at the platinum centre was replaced by a chlorine atom in reaction of **9** or **10** with stoichiometric amounts of acetylchloride and methanole. It is known from the literature that the HCl molecule reacts with the Pt(II)-complex under oxidative addition following a reductive elemination of the C–H unit [8]. With this method Me, Ph and benzyl substituents were straightforwardly replaced by a chlorine atom [9]. The ^{31}P-

Table 1
^{31}P-NMR parameters for the substitution products

	^{31}P-NMR shift (ppm)	$^{1}J(Pt–P)$ (Hz)	$^{2}J(^{117/119}Sn–Pt–P)$ (Hz)
2	12.9	2406	*cis*: 225
3	11.9	2041	*cis*: 214
4	57.4	2819	*cis*: 163 *trans*: ^{117}Sn 2171, ^{119}Sn 2075
8	21.1	2899	*cis*: 225
9	53.4 [a]	1777	*cis*: 182
	56.2 [a]	3243	*trans*: ^{117}Sn 2639, ^{119}Sn 2518
10	47.3	1708	*cis*: 180
	48.2	3231	*trans*: ^{117}Sn 2620, ^{119}Sn 2498
11	46.4(2P)	2323	*cis*: 194
	109.7	2433	*trans*: [b]

[a] Due to a relatively large half line width the $^{2}J(PP)$ coupling was not detected.

[b] Due to the low solubility of **11** the satellites were not observed.

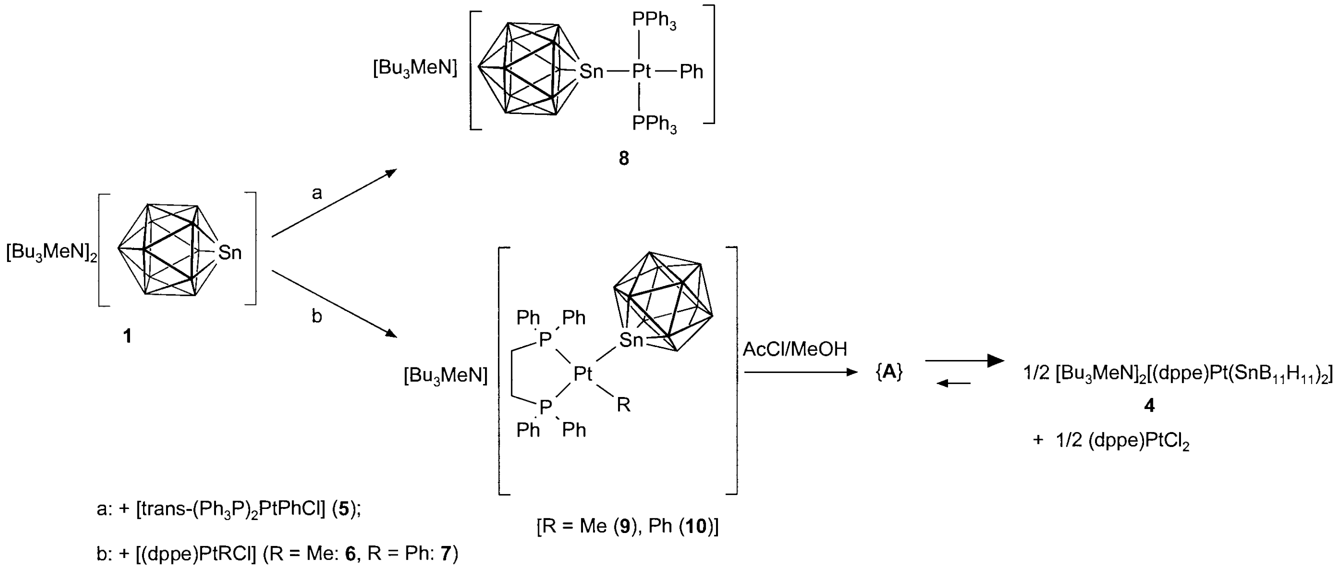


Scheme 2.

$$\text{3a: (dppe)PtCl}_2 \xrightarrow[k_1]{\mathbf{1}} \underset{\mathbf{A}}{\{[\text{Bu}_3\text{MeN}][(\text{dppe})\text{PtCl}(\text{SnB}_{11}\text{H}_{11})]\}} \xrightarrow[k_2]{\mathbf{1}} \underset{\mathbf{4}}{[\text{Bu}_3\text{MeN}]_2[(\text{dppe})\text{Pt}(\text{SnB}_{11}\text{H}_{11})_2]}$$

$$\text{3b: (dppe)PtCl}_2 + \mathbf{1} \longrightarrow \underset{\mathbf{A}}{\{[\text{Bu}_3\text{MeN}][(\text{dppe})\text{PtCl}(\text{SnB}_{11}\text{H}_{11})]\}} \rightleftharpoons 1/2\ \mathbf{4} + 1/2\ (\text{dppe})\text{PtCl}_2$$

Scheme 3.



[R = Me (**9**), Ph (**10**)]

a: + [trans-(Ph$_3$P)$_2$PtPhCl] (**5**);

b: + [(dppe)PtRCl] (R = Me: **6**, R = Ph: **7**)

Scheme 4.

NMR spectroscopical characterization of this reaction mixture gives clear indications for the dichloride and the bis(stannaborate)complex. We think that this result gives good evidence for the explanation, that the mono-substituted platinum complex **A** is thermodynamically unstable with respect to the dihalide and bis(stannaborate)complex. Interestingly the platinum tin bond in complex **4** is resistant towards hydrogenchloride as was

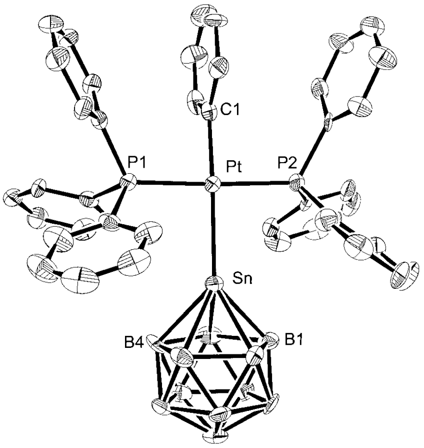


Fig. 1. ORTEP diagram of the anion of **8**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for the sake of clarity.

Table 2
Selected interatomic distances (Å) and angles (°) for the anion of **8** [*trans*-$(Ph_3P)_2Pt(Ph)(SnB_{11}H_{11})]^-$

Interatomic distances		Bond angles	
Sn–B1	2.320(6)	P1–Pt–P2	176.05(4)
Sn–B2	2.330(6)	Sn–Pt–C1	167.98(13)
Sn–B3	2.336(6)	P1–Pt–Sn	91.13(3)
Sn–B4	2.319(6)	P2–Pt–Sn	91.24(3)
Sn–B5	2.312(6)	P1–Pt–C1	88.47(13)
Pt–P1	2.306(1)	P2–Pt–C1	89.87(13)
Pt–P2	2.298(1)		
Pt–C1	2.062(5)		
Pt–Sn	2.651(1)		

proved by the reaction of compound **9** and **10** with an excess of acid. This result is in contrast to the observations in trimethylstannyl complexes of platinum(II) [10]. Complexes of type $(dppe)Pt(SnMe_3)_2$ react with HCl under stepwise substitution of a trimethylstannyl group against a chlorine atom and formation of Me_3SnH.

The crystal structure analysis of **8** was determined by X-ray diffraction on a single crystal. Fig. 1 shows an ORTEP plot of the anion and Table 2 summarizes selected interatomic distances and angles. The geometry around the transition metal can be described as nearly square planar. The interatomic distances are in the range of values known from the literature: *trans*–$(Ph_3P)_2Pt(H)SnCl_3$ Pt–Sn 2.601(1) [11]; $(bipy)(Me)_2Pt(SnMe_3)I$ Pt–Sn 2.547(5) [12]; *trans*–$(Ph_3P)_2Pt(Cl)(2–(Me_2N)C_6H_4)$ Pt–P 2.310(4), 2.319(3), Pt–C 2.030(12) [13a]; *trans*–$(Ph_3P)_2Pt(Cl)Ph$ Pt–P 2.302(6), 2.297(6), Pt–C 200(2) [13b].

Zwitterionic complexes are of certain interest since they are known to be single-component catalysts in the field of metallocene Ziegler catalysts systems [14]. Ion pairing can be prevented in these polar molecules since the anion and cation are linked together via a suitable ligand environment. We are interested in the intermolecular linkage of an anionic heteroborate with a cationic transition metal complex. So far zwitterionic transition metal complexes of *closo*-borates are not present in the literature. Michl has published an example for a cluster zwitterion with the combination of the tropylium cation and the carba-*closo*-dodecaborate anion [15]. We have synthesized a zwitterion of a cationic platinum(II) complex and the stanna-*closo*-dodecaborate anion (Scheme 5).

The zwitterion **11** was completely characterized by elemental analysis, NMR-spectroscopy and mass spectrometry. However due to the very low solubility we did not study the chemistry of this complex, which is the first example for a zwitterionic heteroborate transition metal complex.

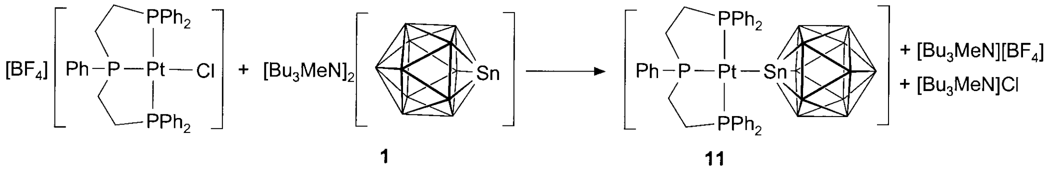
3. Conclusion

Platinum(II) chlorides react readily under substitution with the stannaborate **1**. The monosubstitution in $(dppe)PtCl_2$ is not possible resulting in a mixture of disubstituted complex and dichloride. Regarding the *trans* ^1J(Pt–P) coupling constants in $[(dppe)PtR(SnB_{11}H_{11})]^-$ is tempting to classify the stannaborate substituent as a ligand with a weak *trans* effect. To our surprise the stannaborate linkage is resistant towards HCl.

4. Experimental

4.1. General methods

All manipulations were carried out under dry N_2 in Schlenk glassware. Solvents were dried and purified by standard methods and were stored under N_2. —NMR



Scheme 5.

Bruker AC 200 (^{1}H: 200 MHz, int. TMS; ^{13}C{^{1}H}: 50 MHz, int. TMS; ^{31}P{^{1}H}: 81 MHz, ext. H_3PO_4; ^{11}B{^{1}H}: 64 MHz, ext. BF_3?Et_2O). —Elemental analysis: Institut fuer Anorganische Chemie der Universitaet zu Koeln, Heraeus C,H,N,O-Rapid elemental analyser. MS: Finnigan MAT 95. *cis*–$(PPh_3)_2PtCl_2$ [16], (dppe)Pt(Cl)Me [17] were prepared by the methods published in literature. (dppe)$PtCl_2$ [18] was synthesized by a modified version of Jensen‘s method described in the literature.

4.2. Preparation of [*trans*–$(PPh_3)_2Pt(SnB_{11}H_{11})_2$][$Bu_3NMe$]$_2$ (**2**)

0.79 g (790.54 g/mol, 1.00 mmol) *cis*–$(PPh_3)_2PtCl_2$ was disolved in 20 ml CH_2Cl_2 and added to a solution of 1.30 g (649.48 g/mol, 2.00 mmol) $[Bu_3NMe]_2$-$[SnB_{11}H_{11}]$ in 20 ml CH_2Cl_2. After a reaction time of 48 h, the solvent was evaporated in vacuo and the orange residue was washed with water in order to remove [Bu_3NMe]Cl. The remaining solid was dried in vacuo and subsequently crystallized from methylenchloride by diffusion of hexane at +8°C to give 0.98 g (61% yield) of **2**. —^{1}H-NMR (D_6-Aceton): $\delta = 0.97$ (t, 18H, $^3J = 7.3$ Hz, –CH_2–CH_3), $\delta = 1.41$ (m, 12H, $^3J =$ 7.3 Hz, –CH_2–CH_2–CH_3), $\delta = 1.80$ (m, 12H, –CH_2–CH_2–CH_2–), $\delta = 3.11$ (s, 6H, –N–CH_3), $\delta = 3.39$ (m, 12H, –N–CH_2–CH_2–), $\delta = 7.12$–7.42 (m, 18H, P–C_6H_5), $\delta = 8.15$–8.25 (m, 12H, P–C_6H_5). —^{11}B{^{1}H} NMR (D_6-Aceton): $\delta = -10.9$ (s, B12), $\delta = -14.1$ (s, B2/B3/B4/B5/B6), $\delta = -15.7$ (s, B7/B8/B9/B10/B11). —^{13}C{^{1}H} NMR (D_6-Aceton): $\delta = 13.9$ (s, –CH_2–CH_3), $\delta = 20.4$ (s, –CH_2–CH_2–CH_3), $\delta = 24.8$ (s, –CH_2–CH_2–CH_2–), $\delta = 49.0$ (s, N–CH_3), $\delta = 62.4$ (s, N–CH_2–CH_2–), $\delta = 129.2$ (m, C–H (P–C_6H_5)), $\delta =$ 131.1 (m, C–H (P–C_6H_5)), $\delta = 135.4$ (m, C–H (P–C_6H_5)).-^{31}P{^{1}H}-NMR (D_6-Aceton): $\delta = 12.9$ (s, $^1J_{P-Pt} = 2406$ Hz, $^2J_{P-Sn} = 225$ Hz, PPh_3). —$C_{62}H_{112}B_{22}N_2P_2PtSn_2$ (1617.9): calc. C 46.03, H 6.98, N 1.73; Found C 47.02, H 6.90, N 1.67%.

4.3. Preparation of [*trans*–$(PEt_3)_2Pt(SnB_{11}H_{11})_2$][$Bu_3NMe$]$_2$ (**3**)

1.32 g (649.48 g/mol, 2.03 mmol) $[Bu_3NMe]_2$-$[SnB_{11}H_{11}]$ was dissolved in 20 ml CH_2Cl_2 and added to a solution of 0.51 g (502.47 g/mol, 1.01 mmol) *cis*–$(PPh_3)_2PtCl_2$ in 20 ml CH_2Cl_2. After a reaction time of 2 h the white precipitate was isolated by filtration and washed with a little amount of CH_2Cl_2. The remaining white powder was dried in vacuo and subsequently crystallized from acetone by diffusion of hexane at +8°C to give 1.18 g (89% yield) of **3**. —^{1}H-NMR (D_6-DMSO): $\delta = 0.92$ (t, 18H, $^3J = 7.3$ Hz, –CH_2–CH_3), $\delta = 1.11$ (t, 18H, $^3J = 8.5$ Hz, P–CH_2–CH_3), $\delta = 1.29$ (m, 12H, $^3J = 7.3$ Hz, –CH_2–CH_2–CH_3), $\delta = 1.59$ (m, 12H, –CH_2–CH_2–CH_2–), $\delta = 2.20$–2.70 (m, br, 12H, P–CH_2–CH_3), $\delta =$ 3.03 (s, 6H, –N–CH_3), $\delta = 3.18$ (m, 12H, –N–CH_2–CH_2–). —^{11}B{^{1}H} NMR (D_6-DMSO): $\delta = -9.28$ (s, B12), R = –14.2 (s, B2/B3/B4/B5/B6, B7/B8/B9/B10/B11). —^{13}C{^{1}H} NMR (D_6-DMSO): $\delta = 9.6$ (t, $^2J_{C-P} = 12.9$ Hz, P–CH_2–CH_3), $\delta = 13.5$ (s, –CH_2–CH_3), $\delta = 19.2$ (s, –CH_2–CH_2–CH_3), $\delta = 21.9$ (t, $^1J_{C-P} = 17.1$ Hz, P–CH_2–CH_3), $\delta = 23.4$ (s, –CH_2–CH_2–CH_2–), $\delta =$ 47.5 (s, N–CH_3), $\delta = 60.4$ (s, N–CH_2–CH_2–). —^{31}P{^{1}H} NMR (D_6-DMSO): $\delta = 11.9$ (s, $^1J_{P-Pt} = 2041$ Hz, $^2J_{P-Sn} = 214$ Hz, PEt_3). —$C_{38}H_{112}B_{22}N_2P_2PtSn_2$ (1329.6): calc. C 32.78, H 7.81, N 1.53; Found C 33.58, H 8.28, N 2.06%.

4.4. Preparation of [(dppe)$Pt(SnB_{11}H_{11})_2$][Bu_3NMe]$_2$ (**4**)

A solution of 0.34 g (664.46 g/mol, 0.51 mmol) (dppe)$PtCl_2$ in 40 ml 1,2-dichloromethane was treated with a solution of 0.67 g (M = 649.48 g/mol, 1.03 mmol) $[Bu_3NMe]_2[SnB_{11}H_{11}]$ in 20 ml 1,2-dichloromethane. After stirring for 48 h the resulting yellow solution was evaporated in vacuo and the residue was washed with water to remove [Bu_3NMe]Cl. For furher purification the formed light brown powder was recrystallized from CH_2Cl_2/Hexane at +8°C to give 0.69 g (90% yield) of **4**. —^{1}H-NMR (D_6-Aceton): $\delta = 0.96$ (t, 18H, $^3J = 7.2$ Hz, –CH_2–CH_3), $\delta = 1.41$ (m, 12H, –CH_2–CH_2–CH_3), $\delta = 1.78$ (m, 12H, –CH_2–CH_2–CH_2–), $\delta = 2.30$–2.80 (m, br, 4H, P–CH_2–CH_2–P), $\delta = 3.18$ (s, 6H, –N–CH_3), $\delta = 3.44$ (m, 12H, –N–CH_2–CH_2–), $\delta = 7.35$–7.65 (m, 12H, P–C_6H_5), $\delta =$ 7.80–8.10 (m, 8H, P–C_6H_5). —^{11}B{^{1}H} NMR (D_6-Aceton): $\delta = -8.5$ (s, B12), $\delta = -15.4$ (s, B2/B3/B4/B5/B6), B7/B8/B9/B10/B11). —^{13}C{^{1}H} NMR (D_6-Aceton): $\delta = 14.0$ (s, –CH_2–CH_3), $\delta = 20.4$ (s, –CH_2–CH_2–CH_3), $\delta = 24.8$ (s, –CH_2–CH_2–CH_2–), $\delta =$ 49.1 (s, N–CH_3), $\delta = 62.1$ (s, N–CH_2–CH_2–), $\delta =$ 129.0–130.5 (m, br, C–H (P–C_6H_5)), $\delta = 132.0$–133.5 (m, br, C–H (P–C_6H_5)), $\delta = 134.0$–136.5 (m, br, C–H (P–C_6H_5)). —^{31}P{^{1}H} NMR (81 MHz, D_6-Aceton): $\delta = 57.4$ (s, PPh_3, $^1J_{P-Pt} = 2819$ Hz, $^2J_{P-Sn} = 163$ Hz). —$C_{52}H_{106}B_{22}N_2P_2PtSn_2$ (1491.7): calc. C 41.87, H 7.16, N 1.88; Found C 41.82, H 7.60, N 1.89%.

4.5. Preparation of [*trans*-$(Ph_3P)_2Pt(Ph)(SnB_{11}H_{11})$][$Bu_3NMe$] (**8**)

A solution of 0.41 g (M = 649.48 g/mol, 0.63 mmol) $[Bu_3NMe]_2[SnB_{11}H_{11}]$ in 20 ml CH_2Cl_2 was added under stirring to a solution of 0.53 g (M = 832.28 g/mol, 0.64 mmol) *cis*–$(PPh_3)_2Pt(Cl)Ph$ in 20 ml CH_2Cl_2. After stirring for 3 h all volatiles were removed in vacuo and the remaining solid was washed several times with water. The resulting colourless powder was dried in vacuo and afterwards crystallized from a mixture of dichloromethane and hexane. Yield: 0.72 g (90%) **8**. —^{1}H-NMR (CD_2Cl_2): $\delta = 0.98$ (t, 9H, $^3J = 7.2$ Hz, $-CH_2-CH_3$), $\delta = 1.37$ (m, 6H, $-CH_2-CH_2-CH_3$), $\delta = 1.59$ (m, 6H, $-CH_2-CH_2-CH_2-$), $\delta = 2.94$ (s, 3H, $-N-CH_3$), $\delta = 3.13$ (m, 6H, $-N-CH_2-CH_2-$), $\delta = 6.00$–6.30 (m, 3H, C–H, C–H (Pt–C_6H_5)), $\delta = 6.66$ (d, 2H, C–H (Pt–C_6H_5)), $\delta = 7.22$–7.34 (m, 18H, C–H, C–H (P–C_6H_5)), $\delta = 7.50$–7.70 (m, 12H, C–H (P–C_6H_5)). —$^{11}B\{^1H\}$ NMR (CD_2Cl_2): $\delta = -10.1$ (s, B12), $\delta = -15.6$ (s, B2/B3/B4/B5/B6), B7/B8/B9/B10/B11). —$^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 13.8$ (s, $-CH_2-CH_3$), $\delta = 20.0$ (s, $-CH_2-CH_2-CH_3$), $\delta = 24.6$ (s, $-CH_2-CH_2-CH_2-$), $\delta = 49.5$ (s, $N-CH_3$), $\delta = 62.1$ (s, $N-CH_2-CH_2-$), $\delta = 121.6$ (s, C–H (Pt–C_6H_5)), $\delta = 128.3$ (m, C–H (P–C_6H_5), C–H (Pt–C_6H_5)), $\delta = 130.5$ (s, C–H (P–C_6H_5)), $\delta = 132.2$ (s, $^1J_{C-P} = 58.3$ Hz, C_{ipso} (Pt–C_6H_5)), $\delta = 135.3$ (m, C–H (P–C_6H_5)), $\delta = 136.5$ (m, C–H (Pt–C_6H_5)), $\delta = 155.7$ (d, $^1J_{C-P} = 8.5$ Hz, C_{ipso} (P–C_6H_5)). —$^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 21.1$ (s, $^1J_{P-Pt} = 2899$ Hz, $^2J_{P-Sn} = 225$ Hz, PPh_3). —$C_{55}H_{76}B_{11}NP_2PtSn$: calc. C 53.02, H 6.15, N 1.12; Found C 52.69, H 6.30, N 1.23%.

4.6. Preparation of $[(dppe)Pt(Me)(SnB_{11}H_{11})][Bu_3NMe]$ (9)

To a solution of 1.27 g (644.04 g/mol, 1.97 mmol) (dppe)Pt(Cl)Me in 30 ml CH_2Cl_2 was added 1.28 g (649.48 g/mol, 1.97 mmol) $[Bu_3NMe]_2[SnB_{11}H_{11}]$ solved in 20 ml CH_2Cl_2. After stirring for 3 h the solvent was evaporated in vacuo and the white solid was washed with water. The resulting powder was dried in vacuo and recrystallized from methylenchloride by diffusion of hexane at +8°C to give 1.79 g (86% yield) of **9**. —^{1}H-NMR (CD_2Cl_2): $\delta = 0.98$ (t, 9H, $^3J = 7.2$ Hz, $-CH_2-CH_3$), $\delta = 1.26$ (s, 3H, $Pt-CH_3$), $\delta = 1.41$ (m, 6H, $-CH_2-CH_2-CH_3$), $\delta = 1.63$ (m, 6H, $-CH_2-CH_2-CH_2-$), $\delta = 2.37$ (m, 4H, $P-CH_2-CH_2-P$), $\delta = 3.06$ (s, 3H, $-N-CH_3$), $\delta = 3.23$ (m, 6H, $-N-CH_2-CH_2-$), $\delta = 7.30$–7.58 (m, 12H, C–H (P–C_6H_5)), $\delta = 7.60$–7.82 (m, 8H, C–H (P–C_6H_5)). —$^{11}B\{^1H\}$ NMR (CD_2Cl_2): $\delta = -10.6$ (s, B12), $\delta = -15.4$ (s, B2/B3/B4/B5/B6), B7 /B8/B9/B10/B11). —$^{13}C\{^1H\}$ NMR (D_6-DMSO): $\delta = -17.9$ (s, $Pt-CH_3$), $\delta = 13.8$ (s, $-CH_2-CH_3$), $\delta = 20.0$ (s, $-CH_2-CH_2-CH_3$), $\delta = 24.1$ (s, $-CH_2-CH_2-CH_2-$), $\delta = 27.4$–30.4 (m, $P-CH_2-CH_2-P$), $\delta = 49.4$ (s, $N-CH_3$), $\delta = 62.0$ (s, $N-CH_2-CH_2-$), $\delta = 128.0$–130.5 (m, C–H (P–C_6H_5)), $\delta = 133.1$ (m, C–H (P–C_6H_5)). —$^{31}P\{^1H\}$ NMR (D_6-DMSO): $\delta = 53.4$ (s, $^1J_{Pt-P} = 1777$ Hz, $^2J_{P-Sn} = 182$ Hz, Ph_2P-CH_2- (*trans* $-CH_3$)), $\delta = 56.2$ (s, $^1J_{Pt-P} = 3243$ Hz, Ph_2P-CH_2- (*trans* $-SnB_{11}H_{11}$)). —$C_{40}H_{68}B_{11}NP_2PtSn$ (1057.6): calc. C 45.43, H 6.48, N 1.32; Found C 45.96, H 6.62, N 1.43%.

4.7. Preparation of $[(dppe)Pt(Ph)(SnB_{11}H_{11})][Bu_3NMe]$ (10)

A solution of 0.62 g (M = 649.48 g/mol, 0.95 mmol) $[Bu_3NMe]_2[SnB_{11}H_{11}]$ in 20 ml CH_2Cl_2 was added to a dichloromethane solution of 0.67 g (M = 706.11 g/mol, 0.95 mmol) (dppe)Pt(Cl)Ph. After stirring for 3 h all volatiles were removed in vaccuo and remaining waxy solid was several times washed with water. After drying in high vaccuo the resulting colourless powder was crystallized from a mixture of CH_2Cl_2/Hexan to give 0.94 g (88%) of **10**. —^{1}H-NMR (MHz, CD_2Cl_2): $\delta = 0.97$ (t, 9H, $^3J = 7.2$ Hz, $-CH_2-CH_3$), $\delta = 1.41$ (m, 6H, $-CH_2-CH_2-CH_3$), $\delta = 1.59$ (m, 6H, $-CH_2-CH_2-CH_2-$), $\delta = 2.43$ (m, 4H, $P-CH_2-CH_2-P$), $\delta = 2.92$ (s, 3H, $-N-CH_3$), $\delta = 3.18$ (m, 6H, $-N-CH_2-CH_2-$), $\delta = 6.61$ (m, 1H, C–H (Pt–C_6H_5)), $\delta = 6.77$ (m, 2H, C–H (Pt–C_6H_5)), $\delta = 7.08$ (m, 2H, C–H (Pt–C_6H_5)), $\delta = 7.30$–7.60 (m, 12H, C–H (P–C_6H_5)), $\delta = 7.80$–8.10 (m, 8H, C–H (P–C_6H_5)). —$^{11}B\{^1H\}$ NMR (CD_2Cl_2): $\delta = -10.6$ (s, B12), $\delta = -15.9$ (s, B2/B3/B4/B5/B6), B7/ B8/B9/B10/B11). —$^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 13.9$ (s, $-CH_2-CH_3$), $\delta = 20.0$ (s, $-CH_2-CH_2-CH_3$), $\delta = 24.6$ (s, $-CH_2-CH_2-CH_2-$), $\delta = 27.5$–30.6 (m, $P-CH_2-CH_2-P$), $\delta = 49.3$ (s, $N-CH_3$), $\delta = 62.1$ (s, $N-CH_2-CH_2-$), $\delta = 122.1$ (s, C–H (Pt–C_6H_5)), $\delta = 127.0$–128.5 (m, C–H (Pt–C_6H_5)), $\delta = 128.5$–130.5 (m, C–H (P–C_6H_5)), $\delta = 130.5$–133.0 (m, C–H, C_{ipso} (Pt–C_6H_5)), $\delta = 133.0$–135.0 (m, C–H (P–C_6H_5)), $\delta = 139.4$ (m, C–H (Pt–C_6H_5)), $\delta = 146.4$ (d, $^1J_{C-P} = 6.5$ Hz, C_{ipso} (P–C_6H_5)), $\delta = 148.3$ (d, $^1J_{C-P} = 6.1$ Hz, C_{ipso} (P–C_6H_5)).– $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 47.3$ (s, $^1J_{Pt-P} = 1708$ Hz, $^2J_{P-Sn} = 179$ Hz, Ph_2P-CH_2- (*trans* $-CH_3$)), $\delta = 48.2$ (s, $^1J_{Pt-P} = 3231$ Hz, $^2J_{P-Sn} = 324$ Hz, Ph_2P-CH_2- (*trans* $-SnB_{11}H_{11}$)). —$C_{45}H_{70}B_{11}NP_2PtSn$: calc. C 48.27, H 6.30, N 1.25; Found C 48.34, H 6.07, N 1.25%.

4.8. Preparation of $[(triphos)Pt(SnB_{11}H_{11})]$ (11)

A solution of 0.25 g (M = 851.98, 0.29 mmol) $[(triphos)PtCl][BF_4]$ in 30 ml dichloromethane was added to a solution of 0.19 g (M = 649.48, 0.29 mmol) $[Bu_3NMe]_2[SnB_{11}H_{11}]$ in 20 ml of the same solvent. Immediately the colour of the reaction mixture turned yellow and after 18 h stirring at room temperature a white solid started to precipitate. After 48 h stirring the precipitate was collected by filtration and washed with small amounts of dichloromethane. Recrystallization from a mixture of dimethylsulfoxide and water resulted in the isolation of 0.24 g (85%) of **11**. —^{1}H-NMR (D_6-DMSO): $\delta = 2.09$–2.33 (m, br, 4H, $P-CH_2-CH_2P$), $\delta = 2.76$–3.09 (m, br, 4H, $P-CH_2-CH_2P$), $\delta = 7.38$–7.65 (m, 15H, C–H (P–C_6H_5), $P(C_6H_5)_2$), $\delta = 7.65$–7.79

(m, 2H, C–H (P–C_6H_5)), $\delta = 7.79–8.04$ (m, 8H, C–H ($P(C_6H_5)_2$)). —$^{11}B\{^1H\}$ NMR (MHz, D_6-DMSO): $\delta = -14.0$ (s). —$^{13}C\{^1H\}$ NMR (D_6-DMSO): $\delta = 23.2–35.6$ (m, br, P–CH_2–CH_2–P), $\delta = 128.5–130.2$ (m, C–H (P–C_6H_5), C–H ($P(C_6H_5)_2$)), $\delta = 131.7–132.7$ (m, C–H ($P(C_6H_5)_2$)), $\delta = 132.7–134.5$ (m, C–H (P–C_6H_5), ($P(C_6H_5)_2$)). —$^{31}P\{^1H\}$ NMR (D_6-DMSO): $\delta = 46.4$ (s, $^1J_{Pt-P} = 2323$ Hz, $^2J_{P-Sn} = 194$ Hz, Ph_2P–CH_2–), $\delta = 109.7$ (s, $^1J_{Pt-P} = 2433$ Hz, Ph–P– (*trans* –$SnB_{11}H_{11}$)). —$C_{34}H_{44}B_{11}P_3PtSn$: calc. C 41.74, H 4.53; Found C 40.97, H 4.78%. – MS (70eV) SIMS; m/z (%): 977.1 (40) [M^+–H], 729.4 (100) [M^+–($SnB_{11}H_{11}$)].

4.9. X-ray crystal structure analysis of **8**

$C_{55}H_{76}B_{11}NP_2PtSn$; formula mass 1245,80 g/mol; monoclinic space group $P2_1/c$ (no. 14); $a = 25.623(4)$Å, $b = 10.533(1)$Å, $c = 21.786(3)$Å, $\beta = 101.76(2)°$, $V = 5756$ (1) Å^3, $Z = 4$, $d_{calc.} = 1.437$ g cm^{-3}, μ(Mo–K_α) 2.953 mm^{-1}. Image plate diffractometer (IPDS, Stoe); Mo–K_α radiation (graphite monochromator, $\lambda = 71.07$ pm); data collection at 200 K on a single crystal of dimensions $0.4 \times 0.3 \times 0.5$ mm, $1.9 \leq \theta \leq 24.2°$; 9042 independent reflections measured, 7056 'observed' [$I > 2\sigma(I)$]; data corrections: Lorentz and polarization factors, numerical absorption with programs X-RED and X-Shape (Stoe Darmstadt, 1994) [19]; structure solution by direct methods and difference Fourier synthesis, F^2 refinement [20]; anisotropic parameters for non-hydrogen atoms. With the exception of one hydrogen atom the hydrogen atoms of the anion were found. Other hydrogen atoms were placed in calculated positions (C–H = 0.978Å). All hydrogens were refined with isotropic thermal parameters. Convergence was obtained for 775 variables with $wR_2 = 0.071$, $R_1 = 0.042$, GoF = 0.963. Max. min residual density $+0.63$ (1.51Å from Pt)/ -0.64 (0.84 Å from Pt) e Å^{-3}.

5. Supplementary material

Further details on the crystal structure determination are avaible on request from the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 142229. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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