A Zwitterionic Platinum Complex with a Carbene Ligand

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A new stannaborate complex of platinum is prepared from the reaction of $[Bu_3MeN]_2$[*trans*-$(Et_3Pt)_2Pt(SnB_{11}H_{11})_2$] and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (dpdmiy). [*trans*-$(Et_3P)_2Pt(SnB_{11}H_{11})$(dpdmiy)] has been analyzed by X-ray crystallography and NMR spectroscopy.

Key words: Borane Cluster, Platinum, Carbene Ligand

Introduction

The development of new materials suitable for electrooptical studies has recently received a great deal of attention. One strategy deals with the preparation of zwitterionic molecules which are provided with a very high ground-state dipole moment [1, 2]. Michl and coworkers have presented in 1999 a tropylium ylide [12-C_7H_6-$CB_{11}H_{11}$] with a dipole moment of 11.25 D and a first hyperpolarizability of 236×10^{-30} esu at 1064 nm [3]. Spencers group has studied polyhedral-based nonlinear optical materials on the basis of carborane substituted betains like 1,12-[$(C_7H_7)C_2B_{10}H_{10}(C_5H_3Me_2)$] [4, 5].

Currently we are exploring the coordination chemistry of a new tin ligand, the stanna-*closo*-dodecaborate dianion. This heteroborate coordinates readily at transition metal centers and a variety of coordination compounds have been synthesized. In the square planar coordinated complexes of platinum(II) the heteroborate shows a strong *trans* influence [8]. Furthermore, stannaborate substituted phosphine complexes are selective catalysts in the hydroformylation of octene [9]. Since the stannaborate dianion $[SnB_{11}H_{11}]^{2-}$ is able to react as a monodentate ligand under replacement of a halide anion, this substitution results in the incorporation of a negative charge into the respective transition metal complex.

Therefore, in reaction with cationic transition metal halides $[L_nPtCl]^+$ zwitterionic molecules of the type $[(H_{11}B_{11}Sn)PtL_n]$ can be synthesized [6 – 8]. Several of these polar transition metal complexes have been synthesized so far and the structures in the solid state have been determined by single crystal structure analyses. Here we report on the synthesis and structural characterization of a new stannaborate based zwitterionic platinum complex.

Results and Discussion

During our investigations, we found that the *trans* coordinated platinum complex [*trans*-$(Et_3P)_2Pt(SnB_{11}H_{11})_2]^{2-}$ (anion of **1)** reacts with isonitrile (CN*t*Bu) under formation of a pentacoordinated adduct **2** (Scheme 1). Other Lewis bases such as CO, alkenes, pyridine, Et_3N, Ph_3P do not show this reaction [8].

In order to further elucidate the adduct formation we treated the bis(stannaborate)complex **1** with a cyclic carbene, 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (dpdmiy) [10], which is known to react with a variety of electrophiles under adduct formation [11, 12]. From this reaction mixture we were able to isolate the substitution product **3** as a zwitterionic complex (Scheme 2).

On the basis of the NMR spectroscopic findings the formation of the zwitterion is quantitative. Crystallization from a dichloromethane/methanol mixture resulted in the isolation of **3** as yellow crystals in the yield of 89%.

In the ^{11}B NMR spectrum resonances at -8.3 and -14.5 ppm are characteristic for the coordination of stanna-*closo*-dodecaborate at the platinum center. From the integration of the Sn satellites in the ^{31}P NMR spectrum the coordination of one tin ligand is evident. The Sn-P and Pt-P coupling constants are

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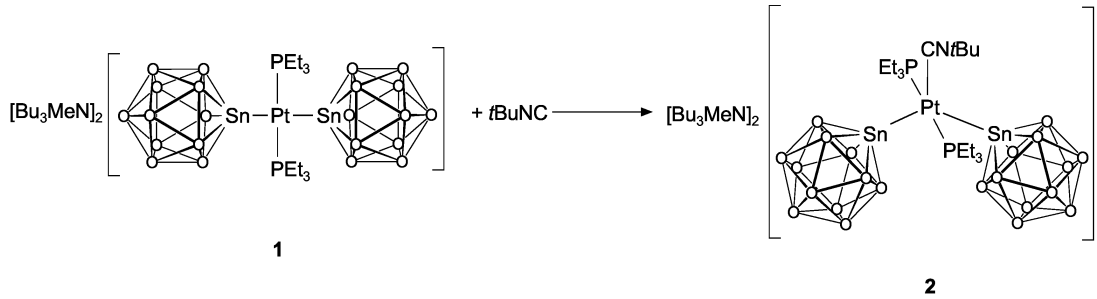
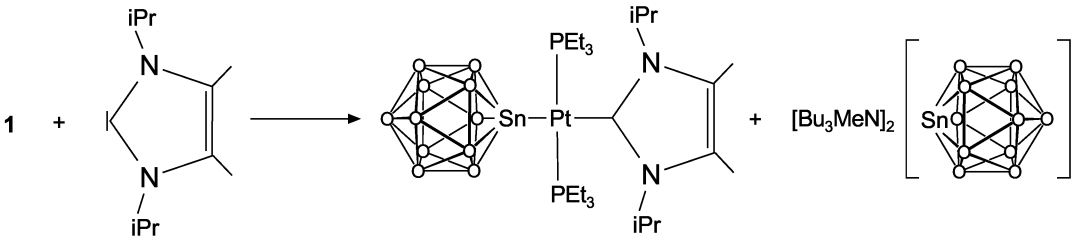


1 **2**

Scheme 1. Adduct formation of [*trans*-$(Et_3P)_2Pt(SnB_{11}H_{11})_2]^{2-}$.



3

Scheme 2. Substitution at [*trans*-$(Et_3P)_2Pt(SnB_{11}H_{11})_2]^{2-}$.

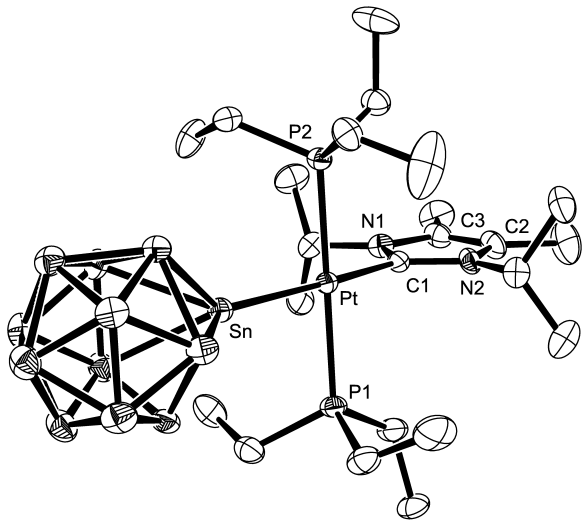


Fig. 1. Molecular structure of the zwitterion **3**. For the sake of clarity, hydrogen atoms have been omitted.

very close to the values of the starting material, and especially the $^2J_{Sn-P}$ coupling constant is diagnostic for a *cis* arrangement of the respective ligands.

The zwitterion crystallizes as yellow crystals under the inclusion of half an equivalent of methanol in the monoclinic space group $P2_1/n$. Details of the crystal structure determination are listed in Table 1, the geometry of the molecule in the solid state is depicted in Fig. 1, and selected interatomic distances and angles are listed in Table 2. The platinum center is nearly square planar coordinated with Pt-P [2.325(1), 2.329(1) Å] and Pt-Sn [2.605(1) Å] interatomic distances which are in the range of comparable complexes [*trans*-$(Et_3P)_2Pt(SnB_{11}H_{11})$(CN*t*Bu)], [$Bu_3MeN$][*trans*-$(Et_3P)_2Pt(SnB_{11}H_{11})_2$(CN*t*Bu)]. The Pt—C bond length of 2.062(4) Å is slightly longer than the respective distances found in the literature [13, 14].

To conclude, the bis(stannaborate) complex [*trans*-$(Et_3P)_2Pt(SnB_{11}H_{11})_2]^{2-}$ reacts with the carbene 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene under stannaborate substitution, to give the new zwitterionic molecule [trans-$(Et_3P)_2Pt$(dpdmiy)$(SnB_{11}H_{11})$].

Experimental Section

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. $[Bu_3MeN]_2$[*trans*-$(Et_3P)_2Pt(SnB_{11}H_{11})_2$] [7] as well as 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (dpdmiy) [10] were synthesized according to literature procedures. – NMR Bruker AC 200 (^{1}H: 200.13 MHz, int. TMS; $^{13}C\{^1H\}$: 50.33 MHz, int. TMS; $^{31}P\{^1H\}$: 81.01 MHz, ext. H_3PO_4; $^{11}B\{^1H\}$:

Table 1. Crystal data and structure refinement parameters for **3**·1/2CH_3OH.

Empirical formula	$C_{23.5}H_{61}B_{11}N_2O_{0.5}P_2SnPt$
Crystal system	monoclinic
Space group	$P2_1/n$ (no. 14)
a [pm]	1324.70(8)
b [pm]	1890.05(12)
c [pm]	1487.26(10)
β [deg]	93.180(5)
Volume [nm^3]	3.7180(4)
Z	4
Formula mass [g mol^{-1}]	874.37
ρ_{calc} [g cm^{-3}]	1.562
μ [mm^{-1}]	4.536
Absorption correction	numerical
Transmission max / min	0.5660 / 0.3908
θ Range [deg]	1.74 – 27.31
Total data collected	62757
Index range	$-17 \le h \le 17$, $-24 \le k \le 24$, $-19 \le l \le 18$
Unique data	8277
Observed data	6208
Diffractometer	STOE **I**mage **P**late **D**iffraction **S**ystem
Radiation	Mo-K$_\alpha$ (Graphit-Monochromator, λ = 71.073 pm)
Temperature [K]	170(2)
R_{merg}	0.0873
R Indexes [$I > 2\sigma(I)$]	R_1 = 0.0338, wR_2 = 0.0614
R Indexes (all data)	R_1 = 0.0519, wR_2 = 0.0656
Goodness of fit (S_{obs})	0.993
Goodness of fit (S_{all})	0.911
No. of variables	381
F(000)	1732
Largest difference map hole / peak [e 10^{-6}pm^{-3}]	−1.211 / 1.198

$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^2)^2]^{1/2}$, $S_2 = [\sum w(|F_o|^2 - |F_c|^2)^2/(n-p)]^{1/2}$, with $w = 1 / [\sigma^2(F_o)^2 + (0{,}0339 \cdot P)^2]$, $P = (F_o^2 + 2F_c^2)/3$. $F_c^* = kF_c[1 + 0{,}001 \cdot |F_c|^2\lambda^3/\sin(2\theta)]^{-1/4}$.

64.17 MHz, ext. $BF_3 \cdot Et_2O$). – Elemental analysis: Institut für Anorganische Chemie der Universität zu Köln, Heraeus C,H,N,O-Rapid elemental analyser.

*[trans-(Et$_3$P)$_2$Pt(dpdmiy)(SnB$_{11}$H$_{11}$)] (**3**).* 80.1 mg of dpdmiy (M: 180.29, 0.444 mmol) were added at room temperature to 0.59 g of [Bu$_3$MeN]$_2$[*trans*-(Et$_3$P)$_2$Pt(SnB$_{11}$H$_{11}$)$_2$] (**1**) (M: 1329.6 gmol^{-1}, 0.444 mmol) dissolved in 30 ml of CH_2Cl_2. After 30 min stirring crystallization of the product was achieved by slow diffusion of 20 ml of CH_3OH into the dichloromethane solution to give pale yellow crystals suitable for single crystal X-ray crystallography. Yield of **3**: 0.346 g, M = 876.413 g/mol, 89%.

^{1}H NMR(200.13 MHz, CD_2Cl_2): δ = 5.10 (m, 2H, N—C*H*(CH$_3$)$_2$), 2.39 (m, 12H, PCH$_2$), 2.16 (m, 12H, N—CH(C*H*$_3$)$_2$), 1.57 (m, 6H, C═CC*H*$_3$), 1.17 (m, 18H, PCH$_2$C*H*$_3$). – ^{11}B{^{1}H} NMR (64.17 MHz, CD_2Cl_2): δ = −8.3 (s, B12), −14.5 (s, B2 / B3 / B4 / B5 / B6, B7 / B8 / B9 / B10 / B11). – ^{13}C{^{1}H} NMR (50.33 MHz, CD_2Cl_2): δ = 128.49 (s, C4,5), 62.37 (s, N—*C*H(CH$_3$)$_2$), 23.04 (s, N—CH(*C*H$_3$)$_2$), 19.66 (m, P*C*H$_2$CH$_3$), 11.20 (s, C═C*C*H$_3$), 9.17 (m, PCH$_2$*C*H$_3$). – ^{31}P{^{1}H} NMR (81.01 MHz, CD_2Cl_2): δ = 8.56 ($^1J_{Pt-P}$ = 2126 Hz, $^2J_{Sn-P}$ = 248 Hz). – $C_{23}H_{61}B_{11}N_2P_2PtSn \cdot 1/2CH_3OH$(876.413): calcd. C 32.21, H 7.25, N 3.20; found: C 31.19, H 7.11, N 3.08.

Table 2. Selected interatomic distances [Å] and bond angles [°] for **3**.

Pt-P1	2.329(1)	Sn-Pt-C1	175.7(1)
Pt-P2	2.325(1)	Sn-Pt-P1	87.6(1)
Pt-C1	2.062(4)	Sn-Pt-P2	87.9(1)
Pt-Sn	2.605(1)	P1-Pt-C1	92.8(1)
C1-N1	1.354(6)	P2-Pt-C1	91.9(1)
C1-N2	1.362(5)	N1-C1-N2	106.3(4)
N1-C3	1.397(6)		
N2-C2	1.413(6)		
C2-C3	1.350(7)		

X-ray Crystallography

A suitable single crystal was carefully selected under a polarizing microscope and mounted in a glass fiber. The scattering intensities were collected by an imaging plate diffractometer IPDS II (STOE & CIE) equipped with a normal focus, 1.75 kW, sealed tube X-ray source (Mo-K$_\alpha$, λ = 71.073 pm) operating at 50 kV and 40 mA. Intensity data were collected at 170 K in 198 frames with ω-scans ($0 \le \omega \le 180°$, $\varphi = 0°$; $0 \le \omega \le 180°$, $\varphi = 90°$; $0 \le \omega \le 36°$, $\varphi = 135°$; $\Delta\omega = 2°$, exposure time of 3 min) in the 2Θ range of 1.9 to 54.8°. The structure was solved by direct methods SHELXS-97 [15] and difference Fourier syntheses. Full matrix least squares structure refinements against $|F^2|$ were carried out using SHELXL-93 [16].

3 crystallizes under the inclusion of 0.5 molecules of methanol which is located around the special site 2c (0, 0, 1/2) of the space group $P2_1/n$. The methanol molecule occupies two positions. The hydrogen atoms for **3** were placed geometrically and held in the riding mode. The methanol molecule was refined without hydrogen atoms. The last cycles of refinement included atomic positions for all atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms [17]. A numerical absorption correction was applied after optimization of the crystal shape (X-RED [18] and X-SHAPE [19]). Details of the refinement are given in Table 1.

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