Reactivity of Platinum Stanna-*closo*-dodecaborate Complexes: First Hydroformylation Studies

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Dedicated to Professor Dieter Naumann on the occasion of his 60th birthday

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The synthesis and characterization of two (dppp)Pt complexes with the stannaborate ligand $SnB_{11}H_{11}$ is described. In the case of the salt $[Bu_3MeN]_2[(dppp)Pt(SnB_{11}H_{11})_2]$ the structure in the solid state was determined by X-ray crystal structure analysis. As a result of comparative catalysis studies between $SnCl_3$ and $[SnB_{11}H_{11}]^-$-substituted platinum complexes we found selective hydroformylation of 1-octene catalysed by the $[(dppp)PtPh(SnB_{11}H_{11})]^-$ and $[(dppp)Pt(SnB_{11}H_{11})_2]^{2-}$ complexes.

Introduction

We are interested in the coordination abilities of the hetero-*closo*-dodecaborate clusters $[EB_{11}H_{11}]^{2-}$ of the group 14 elements.[1,2] The first example of the complexation of these *closo*-borates at a transition metal centre was the copper compound $\{[Bu_4N]_2[ClCu(CB_{11}F_{11})]\}$ reported by Strauss et al.[3] For E = Sn we have synthesised coordination compounds of the type $L_nM\text{-}(SnB_{11}H_{11})$ for a wide variety of transition metals (Fe, Mo, Rh, Ir, Ni, Pd, Pt).[4−7] Characterization of the hydride complex $[Bu_3MeN][trans\text{-}(Et_3P)_2PtH(SnB_{11}H_{11})]$ led us to the conclusion that the stannaborate ligand has a higher *trans* influence than the trichlorostannyl ligand ($SnCl_3$).[7] Furthermore, we found that the tin ligand $[SnB_{11}H_{11}]^-$ activates Pt−C bonds towards isocyanide insertion.[8] In the field of carbonylation hydroformylation is one of the most important reactions catalysed homogeneously by transition metal complexes, with cobalt and rhodium complexes being amongst the most important.[9] The mechanistic aspects of platinum-catalysed hydroformylation have been studied extensively.[10] In particular, the insertion of the carbon monoxide molecule and the effect of the bite angle of the chelating phosphane have been investigated.

Asymmetric hydroformylation using chiral phosphanes has been carried out successfully with platinum complexes.[11] Most of the platinum complexes studied so far in hydroformylation experiments are of the type L_2PtCl_2 and have to be reacted with $SnCl_2$ to provide hydroformylation activity;[12,13] tin(II) chloride inserts into the Pt−Cl bond and forms the trichlorostannyl ligand.[14] The role of this ligand is the subject of many studies and it appears that the lability of the $SnCl_3$ group is one reason for the activation of platinum complexes.[15] Besides these trichlorostannyl complexes several very interesting alternative platinum catalysts have been developed ($[Pt(C_2H_4)$(chelating phosphane)$]/CH_3SO_3H$;[16] platinum-diphenylphosphinous acid complex catalyst).[17] The easily accessible stanna-*closo*-dodecaborate cluster is resistant towards moisture and air and reacts with most of the transition metal electrophiles studied so far by complexation and formation of a metal-tin bond. Since (phosphane)Pt-$(R)SnCl_3$ complexes are well known for their catalytic activity in hydroformylation reactions we started a comparative study on the hydroformylation activity of $SnCl_3$ and $SnB_{11}H_{11}$ complexes of platinum.

Results and Discussion

At the beginning of our stannaborate complex synthesis we decided to use the 1,3-bis(diphenylphosphanyl)propane (dppp) as the chelating ligand. Following our standard procedure two stannaborate complexes were synthesised in high yield by nucleophilic substitution of the chloride anion with the stannaborate dianion (Scheme 1 and 2).

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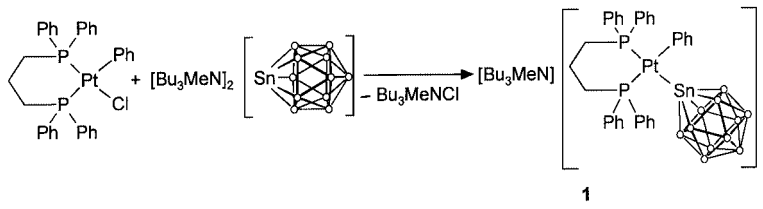
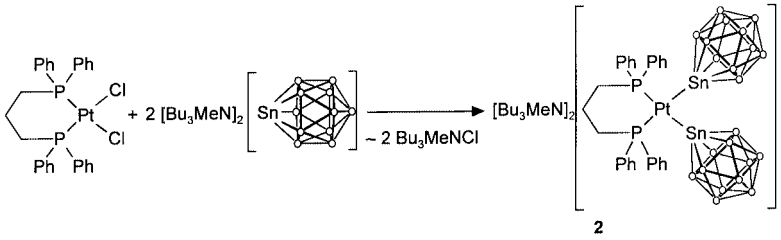


Scheme 1



Scheme 2

The salts **1** and **2** were characterised by elemental analysis, NMR spectroscopy and in the case of **2** by a single-crystal structure analysis. It is well established that the $^2J_{SnP}$ coupling constant permits unambiguous assignment of the stereochemistry in Pt^{II} complexes. Indirect coupling between ligand atoms is known to be much larger for *trans* than for *cis* related ligands.[18] Here the $^2J_{SnP}$ of the signal at $\delta = 2.40$ ppm (*trans* to Sn) is around 10 times larger than the respective coupling of the signal at $\delta = -5.40$ ppm (*cis* to Sn).

Single crystals of complex **2** were obtained at room temperature from acetone and methanol solution. The salt crystallises as yellow-green octahedra in the orthorhombic space group *Pbcn* with the dianion $[(dppp)Pt(SnB_{11}H_{11})]^{2-}$ lying on a twofold rotation axis.[19] Figure 1 shows the molecular structure of the dianion of **2**.

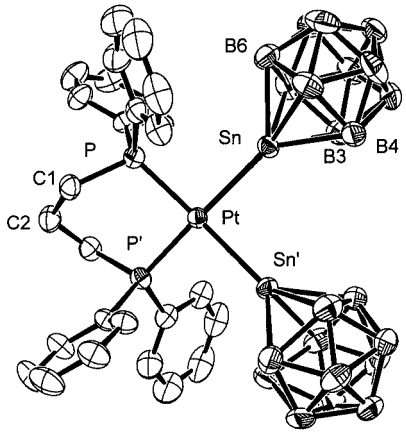
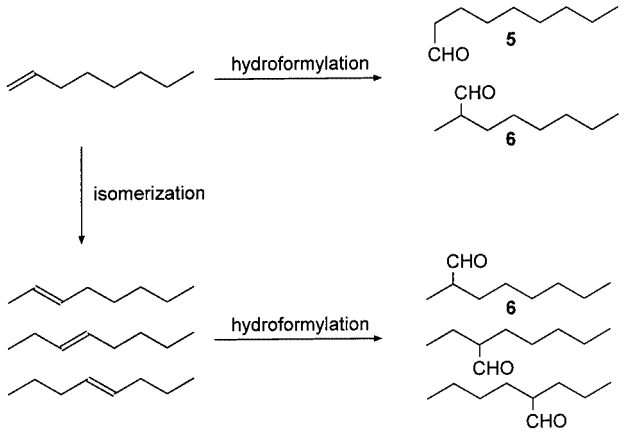


Figure 1. Molecular structure of the $[(dppp)Pt(SnB_{11}H_{11})_2]^{2-}$ dianion in the crystal structure of **2**; bond lengths [Å] and angles [°] (with estimated standard deviations in parentheses): Pt−Sn 2.596(1), Pt−P 2.279(2), Sn−B2 2.288(8), Sn−B3 2.322(8), Sn−B4 2.285(8), Sn−B5 2.308(9), Sn−B6 2.299(9), P−C1 1.821(7), P−Pt−P′ 91.07(8), Sn−Pt−Sn′ 88.87(2), P−Pt−Sn 91.32(4)

Due to steric crowding around the platinum centre the square-planar coordination is slightly distorted towards a tetrahedral arrangement with a torsion angle (P−P′−Sn−Sn′) of 17°. The interatomic distances are similar to those in other stannaborate complexes.

Hydroformylation experiments were carried out with 1-octene in CH_2Cl_2 with four different (dppp)Pt complexes: **1**, **2**, [(dppp)Pt(Ph)$SnCl_3$] (**3**) and [(dppp)Pt($SnCl_3$)$_2$] (**4**). Due to isomerization of 1-octene during the catalysis four different aldehydes are the expected products of this conversion (Scheme 3).



Scheme 3. Products of the hydroformylation of 1-octene and the olefins 2-, 3- and 4-octene, which result from preceding isomerization (isomerized olefins were drawn without considering the stereochemistry).

Besides other criteria the importance of olefin hydroformylation arises, of course, from the selectivity of the aldehyde formation. The *n*/*iso* ratio, which is always an important parameter in hydroformylation catalysis, refers to the amount of *n*-nonanal (**5**) and *iso*-nonanal (**6**), which is usually determined by gas chromatography. Table 1−4 show the results of the catalysis experiments with complexes

1−**4**. From comparative catalysis studies between $SnCl_3$- and $[SnB_{11}H_{11}]^-$-substituted platinum complexes we found the highest activity at 100 °C for the $SnCl_3$-substituted derivative. However, at 120 °C the activity of the stannaborate complex **1** is the highest and rises upon increasing the temperature. Thus, complexes **1** and **2** are thermally stable at 140 °C whereas their $SnCl_3$ counterparts decompose at this temperatures. In the range of temperature studied the *n*/*iso* selectivity is much higher with the borate complex, although upon increasing the temperature the amount of isomerized olefins also increases. Only a slight pressure dependence of the *n*/*iso* ratio in the case of the reactions with complex **2** was observed (Table 4). In our opinion it is very interesting that the isomerized olefins (Table 3) which were formed during catalysis were not hydroformylated by the stannaborate complexes. Instead 1-octene is selectively transformed into the aldehydes **5** and **6**. The olefin selectivity observed is presumably due to the higher steric crowding in the cluster compounds **1** and **2**. Furthermore, no reaction products from aldol condensation of the produced aldehydes were detected in the experiments with **1** and **2**.

Table 1. Initial TOF[a] [h^{-1}] for the hydroformylation of 1-octene with (dppp)Pt complexes **1**−**4** at different temperatures[b]

Pt compound	100 °C	120 °C	140 °C	160 °C
1	11.0	62.1	72.8	23.6[c]
2	19.3	34.1	73.9	52.7
3	50.5	46.6[c]	[c]	[c]
4	31.6	10.2	[c]	[c]

[a] Turnover frequencies were calculated as mol of aldehyde per mol of Pt per hour. [b] Reactions were carried out in 10 mL of CH_2Cl_2 under 50 bar of CO/H_2 with an octene/Pt catalyst ratio of 250 (0.02 mmol cat.) and reaction times of 2 h. [c] Decomposition of the catalyst.

Table 2. Influence of the temperature of the hydroformylation experiments on the *n*/*iso* ratio of nonanal[a]

Pt compound	100 °C	120 °C	140 °C	160 °C
1	7.8	8.4	8.2	6.0[b]
2	8.8	9.1	9.2	7.8
3	1.7	1.6[b]	[b]	[b]
4	1.4	1.6	[b]	[b]

[a] Reactions were carried out in 10 mL of CH_2Cl_2 under 50 bar of CO/H_2 with an octene/Pt catalyst ratio of 250 (0.02 mmol cat.) and reaction times of 2 h. [b] Decomposition of the catalyst.

Table 3. Degree of isomerization of 1-octene in hydroformylation reaction with complex **1** and **2**[a][b]

Pt compound	100 °C	120 °C	140 °C	160 °C
1	2.5%	13.7%	27.5%	55.3%
2	3.9%	8.5%	26.7%	46.1%

[a] Reactions were carried out in 10 mL of CH_2Cl_2 under 50 bar of CO/H_2 with an octene/Pt catalyst ratio of 250 (0.02 mmol cat.) and reaction times of 2 h. [b] In the case of complexes **3** and **4** the isomerized olefins were partially hydroformylated.

Table 4. Hydroformylation results of 1-octene with complex **2**[a] and their dependence on the CO/H_2 pressure at 140 °C

Pressure [bar]	*n*/*iso*	TOF [h^{-1}]	iso. Olefins[b]
20	8.9	25.4	43.0%
30	10.1	41.4	24.8%
40	9.7	63.7	27.6%
50	9.2	73.9	26.7%

[a] Reactions were carried out in 10 mL of CH_2Cl_2 under 50 bar of CO/H_2 with an octene/Pt catalyst ratio of 250 (0.02 mmol cat.) and reaction times of 2 h. [b] The isomerized olefins were detected by GC analysis.

In order to study the olefin selectivity, in a separate experiment the hydroformylation of *trans*-4-octene at 140 and 160 °C was investigated with complex **2**. Here the formation of 3-propyl-1-hexanal was not detected; olefin isomerization took place. The internal olefins thus formed did not undergo hydroformylation, and the only aldehydes obtained were *n*-nonanal (1-nonanal, **5**) and *iso*-nonanal (2-methyl-1-octanal, **6**).

Conclusion

To conclude, with the stanna-*closo*-dodecaborate dianion we have found a new ligand for the activation of platinum complexes for hydroformylation. The $Pt(SnB_{11}H_{11})$ derivatives studied here have a higher thermal stability and are more selective in hydroformylation experiments than their $SnCl_3$ analogues. *n*- and *iso*-nonanal (**5**, **6**) are the only aldehydes formed during the catalysis.

Experimental Section

General: 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 Bruker AC 200 (^1H: 200 MHz, int. TMS. $^{31}P\{^1H\}$: 81 MHz, ext. H_3PO_4. $^{11}B\{^1H\}$: 64 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.

$[Bu_3MeN][(dppp)PtPh(SnB_{11}H_{11})]$ (1): At room temperature (dppp)Pt(Ph)Cl (360 mg, 0.50 mmol) was dissolved in 10 mL of CH_2Cl_2 and reacted with a CH_2Cl_2 solution of $[Bu_3MeN]_2[SnB_{11}H_{11}]$ (341 mg, 0.53 mmol). The solution turned yellow immediately and was stirred for 24 h. The solvent was then evaporated and the remaining solid was washed with water to give **1** (493 mg, 87%). Since we were not able to recrystallise this salt, an elemental analysis of the crude product was carried out. ^1H NMR (CD_2Cl_2, 200 MHz, TMS, without the signals for $[Bu_3MeN]^+$): δ = 2.00 (m, 2 H, dppp), 2.50 (m, 4 H, dppp), 6.40 (m, 1 H, Pt-Ph), 6.53 (m, 2 H, Pt-Ph), 6.92 (m, 2 H, Pt-Ph), 7.2−7.4 (m, 12 H, P-Ph), 7.8−7.9 (m, 8 H, P-Ph) ppm. $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 64 MHz, ext. BF_3Et_2O): δ = −16.1 (s, B2−B11), −10.9 (s, B12) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 81 MHz, ext. H_3PO_4): δ = −5.4 (d, $^2J_{P\text{-}P}$ = 26.2, $^1J_{P\text{-}Pt}$ = 1733.0, $^2J_{P\text{-}Sn}$ = 204.9 Hz), 2.4 (d, $^2J_{P\text{-}P}$ = 26.2, $^1J_{P\text{-}Pt}$ = 3167.3, $^2J_{P\text{-}Sn}$ = 2419.5 Hz) ppm. $C_{46}H_{72}B_{11}NP_2PtSn$

(1133.7): calcd. C 48.73, H 6.40, N 1.24; found C 49.51, H 6.01, N 1.59.

$[Bu_3MeN]_2[(dppp)Pt(SnB_{11}H_{11})_2]$ (2): At room temperature a solution of $[(dppp)PtCl_2]$ (250 mg, 0.37 mmol) in 20 mL of CH_2Cl_2 was added to a solution of $[Bu_3MeN]_2[SnB_{11}H_{11}]$ (479 mg, 0.74 mmol) also in 20 mL of CH_2Cl_2. The colour of the reaction mixture turned orange immediately and after 14 h stirring the solvent was evaporated. The resulting solid was washed with water (two times with 30 mL). Crystallization from acetone/methanol at room temperature yielded yellow-green crystals of **2** (498 mg, 90%). ^1H NMR (CD_2Cl_2, 200 MHz, TMS, without the signals for $[Bu_3MeN]^+$): δ = 2.08 (m, 2 H, dppp), 2.42 (m, 4 H, dppp), 7.48 (m, 12 H, Ph), 7.85 (m, 8 H, Ph) ppm. $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 64 MHz, ext. BF_3Et_2O): δ = −15.8 (s, B2−B11), −9.5 (s, B12) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 81 MHz, ext. H_3PO_4): δ = −1.1 (s, $^1J_{Pt\text{-}P}$ = 2820.7, $^2J_{P\text{-}Sn}$ = 2127.5 Hz)] ppm. $C_{53}H_{108}B_{22}N_2P_2PtSn$ (1387.0): calcd. C 42.28, H 7.23, N 1.86; found C 42.11, H 7.32, N 2.12.

Experimental Setup: All hydroformylations were carried out in a 75 mL steel autoclave which was built in the workshop of the Institut für Makromolekulare und Technische Chemie der Technischen Hochschule Aachen. The autoclave possesses a 25 mL dropping funnel equipped with a pressure release, a valve connected to a steel capillary with a diameter of 1 mm to take samples, a manometer and two other valves. The reaction mixture was stirred by a cross magnetic stirrer.

Experimental Procedure for Hydroformylations: The reactor was evacuated and filled with argon three times. The catalyst solution, prepared previously in a Schlenk vessel, was then introduced (the exact amount was determined by a syringe). The exact amounts of 1-octene and of GC standard (di-*n*-butyl ether) were transferred to the dropping funnel. The autoclave was pressurized with synthesis gas (CO/H_2) and was heated to reaction temperature by placing it in an oil bath. The reaction mixture was stirred at 750 rpm and kept for 30 minutes at the reaction temperature in order to ensure the preformation of the active catalyst species before the mixture of 1-octene and GC standard was added. Finally the autoclave was cooled in an ice bath, slowly vented and the mixture was analysed by GC.

Analytical Methods for Hydroformylations: The GC chromatograms were recorded on a Sichromat 2 apparatus (Siemens) equipped with a FID detector and an HP-LAS 3359 integrator. Column: 50m Pona-HP-FS; temperature program: 5 min isotherm at 80 °C; 8 °C per minute to 25 °C; temperature of the evaporator: 250 °C; He, 1.5bar; volume of the sample: 0.2 to 1.0 μL.

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[19] X-ray crystal structure analysis of **2**: $C_{53}H_{108}B_{22}N_2P_2PtSn_2$; M_r = 1505.64; orthorhombic space group *Pbcn* (no. 60); *a* = 20.2352(6), *b* = 19.5630(7), *c* = 17.9094(7) Å, *V* = 7089.6(4) Å^3, *Z* = 4, $\rho_{calcd.}$ = 1.411 g cm^{-3}; $\mu_{lin.}$ = 2.748 mm^{-1}; Stoe IPDS II diffractometer; Mo-K_α (λ = 0.71073 Å); graphite monochromator, data collection at 170 K in 323 frames with ω-scans (0 ≤ ω ≤ 180°, φ = 0°; 0 ≤ ω ≤ 180°, φ = 60°; 0 ≤ ω ≤ 180°, φ = 90°; 0 ≤ ω ≤ 106°, φ = 180°; Δω = 2°, exposition time of 1 min) in the 2θ range of 2.3 to 59.5° on a single crystal 0.7 × 0.4 × 0.5 mm; 233603 reflections measured, 9587 independent, 7492 observed with $I > 2\sigma(I)$; corrections for Lorentz and polarisation factors; numerical absorption correction, max./min. transmission 0.3371/0.1674; structure solution with direct methods[20] and difference Fourier synthesis, F^2 refinement;[21−23] anisotropic parameters for non-hydrogen atoms, and hydrogen atoms placed in calculated positions (C−H = 0.98 Å, B−H = 1.1 Å). Due to partial disorder the Bu_3MeN cations were refined using an isotropic structure model without hydrogen positions. Convergence obtained for 374 variables with *R*1(all) = 0.076 *wR*2(all) = 0.169, GooF = 1.176; max./min. residual electron density +2.31/−1.78 e Å^{-3}. CCDC-177990 contains 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,

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