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Synthesis and Characterization of the Platinum(IV) Hydride $[PtH(SnB_{11}H_{11})_5]^{7-}$

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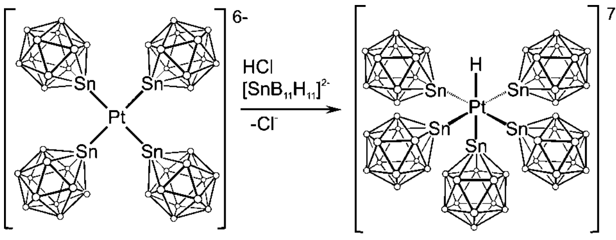
Summary: The square-planar platinum(II) compound $[Pt(SnB_{11}H_{11})_4]^{6-}$ *can be readily protonated in the presence of stanna-closo-dodecaborate, resulting in the formation of the octahedral platinum(IV) compound* $[PtH(SnB_{11}H_{11})_5]^{7-}$. *When this reaction is carried out with DCl, the corresponding deuteride derivative* $[PtD(SnB_{11}H_{11})_5]^{7-}$ *can be obtained.*

Introduction

The chemistry of platinum hydrides has been a field of active research for more than 50 years.[1,2] With the platinum atom in oxidation state II or IV, many examples with Pt−H bonds were characterized.[3] In particular, platinum(IV) hydrides were obtained by protonation[4−11] of platinum(II) complexes or oxidative addition of hydrogen halides or element hydrides such as Me_3SnH, GeH_3Cl, $PhSiH_3$, $o\text{-}C_6H_4(SiH_3)_2$, or Et_3SiH.[12−17] In recent decades, platinum hydrides have received much attention especially with regard to catalytic C−H activations.[18−26] Although organoplatinum(IV) hydrides are postulated as intermediates in these reactions, only few characterized examples of organoplatinum(IV) hydrides exist.[3,4,6,11,23]

It is well documented that $[SnB_{11}H_{11}]^{2-}$ has nucleophilic properties and is a versatile ligand in the coordination chemistry of transition metals. With platinum(II), the square-planar compound $[Pt(SnB_{11}H_{11})_4]^{6-}$ has been reported.[27,28] Recently, the octahedral coordination compounds $[M(SnB_{11}H_{11})_6]^{8-}$ (M = Ni, Pd, Pt) have been published, with the metals of the nickel triad in the formal oxidation state IV.[29] Herein, the octahedral platinum(IV) compound $[Bu_3NH]_7[PtH(SnB_{11}H_{11})_5]$ (**1**) is reported and characterized by means of heteronuclear NMR spectroscopy and elemental analysis.

Scheme 1. Synthesis of $[Bu_3NH]_7[PtH(SnB_{11}H_{11})_5]$ (1)



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Results and Discussion

The square planar platinum compound $[Bu_3NH]_6[Pt(SnB_{11}H_{11})_4]$ was readily obtained by the reaction of $[Pt(COD)Cl_2]$ with four equivalents of $[Bu_3NH]_2[SnB_{11}H_{11}]$. This compound was protonated with etheric HCl in the presence of one additional equivalent of stannaborate in dichloromethane. It should be mentioned that no reactivity was found if only HCl or additional stannaborate was present. Therefore, the simultaneous presence of both reagents yielded the octahedral Pt species $[Bu_3NH]_7[PtH(SnB_{11}H_{11})_5]$ (**1**) as a yellow solid in 76% yield (Scheme 1). Although crystallization attempts have been carried out with a large variety of countercations, no single crystalline material was obtained. The deuteride derivative $[Bu_3NMe]_7[PtD(SnB_{11}H_{11})_5]$ can be obtained under similar conditions with a mixture of DCl and $[Bu_3NMe]_2[SnB_{11}H_{11}]$. Interestingly, in this case the formation of $[PtH(SnB_{11}H_{11})_5]^{7-}$ can also be observed in the ^1H and the ^{195}Pt spectra. This can

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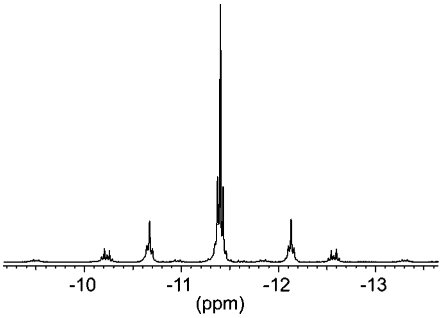

Figure 1. Hydride region of the ^{1}H NMR spectrum of $[Bu_3NH]_7[PtH(SnB_{11}H_{11})_5]$ (**1**) recorded at RT.

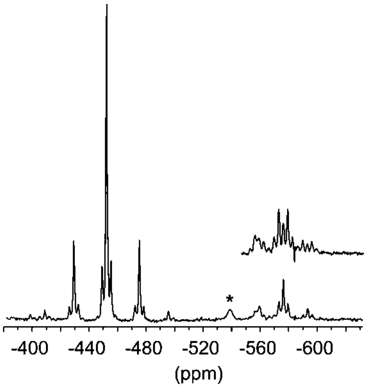

Figure 2. $^{119}Sn\{^{1}H\}$ NMR spectrum of **1** recorded at RT (accumulation of 119000 scans). The ^{119}Sn spectrum without ^{1}H decoupling is shown above (accumulation of 300000 scans). The asterisk marks a small amount of unreacted stannaborate.

be attributed to an H/D exchange of the BH units, which can also be observed for uncoordinated $[SnB_{11}H_{11}]^{2-}$ with DCl in the presence of a catalytic amount of $AlCl_3$ resulting in the formation of $[SnB_{11}D_{11}]^{2-}$.[30]

The platinum coordinated hydride in **1** gives rise to one signal at −11.4 ppm in the hydride region of the ^{1}H NMR spectrum with an interesting coupling pattern (Figure 1). At first, the coupling with ^{195}Pt resulted in a 34% splitting of the resonance with $^{1}J(^{195}Pt-^{1}H) = 731$ Hz. This coupling constant compares well with $^{1}J(^{195}Pt-^{1}H) = 715$ Hz in $[Pt(CO)(PPh_3)_2H(SnCl_3)]$.[31] In addition, good agreement was found with $^{1}J(^{195}Pt-^{1}H)$ couplings in $[PtH_2X(CN)(PEt_3)_2]$ (X = Cl, Br, I) ranging between 669 and 706 Hz with the cyanide ligand in *trans* position to the hydride.[32] Further coupling with the tin atom in *trans* position to the hydride leads to satellites with $^{2}J(^{119}Sn-^{1}H) = 1080$ Hz and $^{2}J(^{117}Sn-^{1}H) = 1040$ Hz, whereas coupling with the four tin atoms in *cis* position to the hydride gives rise to tin satellites with $^{2}J(^{119/117}Sn-^{1}H) = 28$ Hz. In the $^{11}B\{^{1}H\}$ NMR spectrum of **1**, the η^{1}(Sn)-coordination of $[SnB_{11}H_{11}]^{2-}$ is indicated by one broad signal at −15.4 ppm. More information can be obtained from the $^{119}Sn\{^{1}H\}$ NMR spectrum of **1**, which contains two signals at −452 pm and −577 ppm with an integration ratio of 4:1 (Figure 2). This integration ratio allows the assignment of the signal at −452 ppm to the four tin atoms in *cis* position to the hydride, whereas the remaining resonance at −577 ppm can be ascribed to the signal in *trans* position to the hydride. Both resonances exhibit ^{195}Pt couplings with $^{1}J(^{195}Pt-^{119}Sn) = 8540$ Hz (signal at −452 ppm) and $^{1}J(^{195}Pt-^{119}Sn) = 6500$ Hz (signal at −577 ppm). In addition, $^{2}J(^{119}Sn-^{117}Sn)$ couplings can be observed for both signals with *cis*-$^{2}J(^{119}Sn-^{117}Sn) = 1250$ Hz and *trans*-$^{2}J(^{119}Sn-^{117}Sn) = 16000$ Hz. The examination of the ^{1}H coupled ^{119}Sn spectrum reveals the *trans*-$^{2}J(^{119}Sn-^{1}H)$ coupling of 1080 Hz (signal at −577 ppm), which was already observed in the ^{1}H NMR spectrum. In the ^{195}Pt NMR spectrum, one doublet can be detected at −7520 ppm (Figure 3), which exhibits the already observed $^{1}J(^{195}Pt-^{1}H)$ coupling of 731 Hz and the $^{1}J(^{195}Pt-^{119}Sn)$ and $^{1}J(^{195}Pt-^{117}Sn)$ couplings of 8540 and 8200 Hz, respectively. The apparent deviation from the expected 1:1 intensity ratio is caused by different line widths (230 Hz, 200 Hz) and is indicative of differential relaxation.[33] Additionally, the $^{1}J(^{195}Pt-^{119/117}Sn)$ coupling with the tin heteroborate in *trans* position to the hydride can be observed at 6500 Hz. Compared to the ^{195}Pt chemical shift of $[Pt(SnB_{11}H_{11})_6]^{8-}$ (−7724 ppm), the resonance of **1** is shifted toward lower field.[29] However, this ^{195}Pt chemical shift is another example of the extreme highfield shift of stannaborate coordinated platinum compounds. The deuteride derivative $[PtD(SnB_{11}H_{11})_5]^{7-}$ exhibits a resonance at −7528 ppm. The highfield shift of −8 ppm with respect to the hydride derivative **1** arises from the isotopic effect, which is in good agreement with the isotopic shift of −9 ppm for each deuteride in $K_2[PtD_6]$.[34] The resonance shows a $^{1}J(^{195}Pt-^{2}H)$ coupling of 80 Hz as well as a $^{1}J(^{195}Pt-^{119/117}Sn)$ coupling of 8510 Hz.

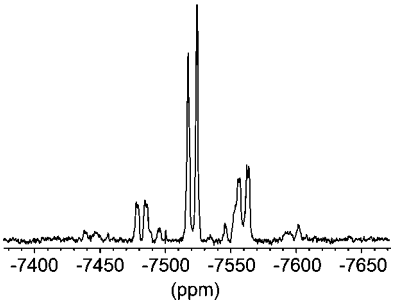

Figure 3. ^{195}Pt NMR spectrum of **1** recorded at 15 °C (accumulation of 225000 scans). The line widths of the main resonances are 230 Hz (left resonance) and 200 Hz (right resonance), respectively.

In the IR spectrum of **1**, the Pt−H stretching mode can be detected at 2043 cm^{-1}, which is in good agreement with the stretching vibration of 2061 cm^{-1} in *trans*-$[Pt(PEt_3)_2(H)(SnB_{11}H_{11})]$.[35] Despite the fact that the metal centers exhibit different formal oxidation states in the latter compound and compound **1**, this is additional evidence for the strong *trans* influence of stannaborate. It should be noted that the Pt−H stretching mode of 2165 cm^{-1} in *trans*-$[Pt(PPh_3)_2H(SnCl_3)]$ is significantly shifted to higher wavenumbers,[36] whereas the Pt−H stretching mode of *trans*-$[Pt(PEt_3)_2(H)(CN)]$ can be found at 2041 cm^{-1}.[37] The Pt-D stretching mode can be found at 1490 cm^{-1}, which agrees well with the Pt-D stretching mode in $K_2[PtD_6]$.[32]

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Conclusions

To conclude, $[Bu_3NH]_6[Pt(SnB_{11}H_{11})_4]$ can be readily protonated in the presence of additional stannaborate. As in $[Pt(SnB_{11}H_{11})_6]^{8-}$, the ^{195}Pt NMR spectrum exhibits an extremely highfield shifted resonance, which indicates strong shielding properties of stannaborate. In addition, the deuteride derivative $[PtD(SnB_{11}H_{11})_5]^{7-}$ was synthesized and characterized by NMR spectroscopy.

Experimental Section

General. All manipulations were carried out under argon atmosphere in Schlenk glassware. Solvents were dried and purified by standard methods and were stored under argon. NMR spectra were recorded on Bruker DRX-250 (^{11}B) and Bruker Avance II+ 500 (^{1}H, ^{119}Sn, ^{195}Pt) NMR spectrometers, equipped with a 5 mm ATM and a 5 mm TBI triple resonance probe head, respectively. The chemical shifts are reported in δ values in ppm relative to external $BF_3 \bullet Et_2O$ (^{11}B), $SnMe_4$ (^{119}Sn) or $Na_2[PtCl_6]$ (^{195}Pt) using the chemical shift of the solvent ^{2}H resonance frequency in combination with the unified frequency scale according to paragraph 3.6 of the IUPAC 2001 recommendations.[38] Elemental analysis was performed by the Institut für Anorganische Chemie, Universität Tübingen using a Vario EL analyzer. $[Bu_3NH]_2[SnB_{11}H_{11}]$ was synthesized using a modified protocol of the original work of Todd's group.[39] $[Bu_3NH]_6[Pt(SnB_{11}H_{11})_4]$ was synthesized following the procedure described in the literature.[28]

$[Bu_3NH]_7[PtH(SnB_{11}H_{11})_5]$ (1). To an orange solution of 100 mg (0.043 mmol) of $[Bu_3NH]_6[Pt(SnB_{11}H_{11})_4]$ in 10 mL of dichloromethane was added 27 mg (0.043 mmol) of $[Bu_3NH]_2[SnB_{11}H_{11}]$. Afterward, 43 μL of 1 M etheric HCl was added, and the color of the solution changed from orange to yellow. After evaporation of the solvent and washing of the residue with water, 89 mg (76%) of **1** was obtained as light yellow material. IR (KBr): 2480 cm^{-1} (BH), 2043 cm^{-1} (Pt−H). ^{1}H NMR (500.13 MHz, CD_2Cl_2): δ −11.4 [1H, $^{1}J(^{195}Pt-^{1}H) = 731$ Hz, *cis*-$^{2}J(^{119}Sn-^{1}H) = 28$ Hz, *trans*-$^{2}J(^{117}Sn-^{1}H) = 1080$ Hz]. $^{11}B\{^{1}H\}$ NMR (80.25 MHz, CD_2Cl_2): −15.4 (11B, B2−B12). $^{119}Sn\{^{1}H\}$ NMR (186.50 MHz, CD_2Cl_2): δ −452 [4Sn, $^{1}J(^{195}Pt-^{119}Sn) = 8540$ Hz, *cis*-$^{2}J(^{119}Sn-^{117}Sn) = 1250$ Hz, *trans*-$^{2}J(^{119}Sn-^{117}Sn) = 16000$ Hz], −565 [1Sn, $^{1}J(^{195}Pt-^{119}Sn) = 6500$ Hz, *cis*-$^{2}J(^{119}Sn-^{117}Sn) = 1250$ Hz, *trans*-$^{2}J(^{119}Sn-^{117}Sn) = 16000$ Hz]. ^{195}Pt NMR (106.70 MHz, CD_2Cl_2): −7520 [$^{1}J(^{195}Pt-^{1}H) = 731$ Hz, $^{1}J(^{195}Pt-^{119}Sn) = 8540$ Hz, $^{1}J(^{195}Pt-^{117}Sn) = 8200$ Hz, $^{1}J(^{195}Pt\text{-}^{119/117}Sn) = 6500$ Hz]. Anal. Calcd. (%) for $C_{84}H_{252}B_{55}N_7PtSn_5$: C, 36.77; H, 9.26; N, 3.57; found: C, 37.16; H, 8.82; N, 3.69.

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