Stanna-*closo*-dodecaborate: A Nucleophile in Transition Metal Chemistry

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Keywords: Stannaborate cluster / Transition metal complexes / Tin / Coordination modes / Clusters / Boron

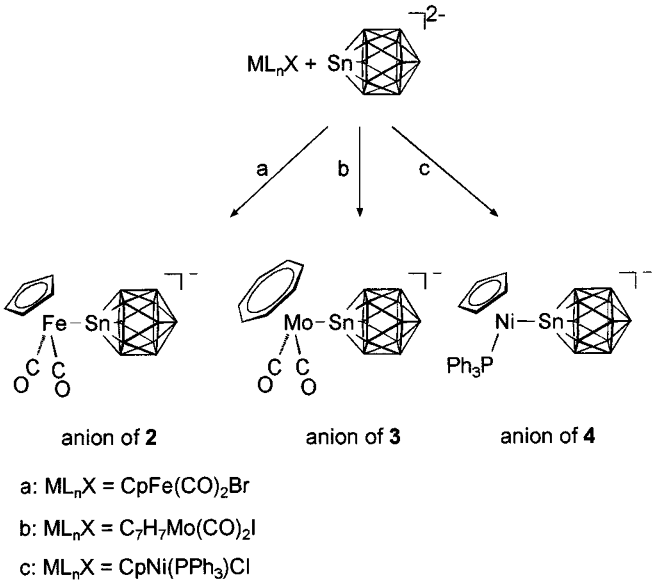
Reactions of the stannaborate salt $[NBu_4]_2[SnB_{11}H_{11}]$ (**1**) with the organometallic electrophiles $[CpFe(CO)_2Br]$, $[(C_7H_7)Mo(CO)_2I]$, and $[CpNi(PPh_3)Cl]$ resulted in substitution of the halide to give the stannaborate coordination products $[NBu_4][CpFe(CO)_2(SnB_{11}H_{11})]$ (**2**), $[NBu_4][(C_7H_7)Mo(CO)_2(SnB_{11}H_{11})]$ (**3**), and $[NBu_4][CpNi(PPh_3)(SnB_{11}H_{11})]$ (**4**) in high yields. Single crystals of the air- and moisture-stable products have been characterized by X-ray crystal structure analyses.

The incorporation of transition metals into the skeletons of boranes and heteroboranes has been extensively studied.[1] However, the direct coordination of a *closo* cluster at a transition metal centre has been realized in only a few cases.[2]

Recently, as part of a study on the chemistry of weakly coordinating anions, Strauss reported on the first structurally characterized example of a *closo*-monocarborane with an *exo* carbon−transition metal bond $\{[NBu_4]_2[CuCl(CB_{11}F_{11})]\}$.[3] The dianion $[CB_{11}F_{11}]^{2-}$ can be regarded as a new ligand in transition metal chemistry, offering the possibility of synthesizing complexes with zwitterionic structures incorporating weakly coordinating anions.

In our approach to this field, we set out to explore the synthetic potential of the *closo*-stannaborate dianion $[NBu_4]_2[SnB_{11}H_{11}]$ (**1**). This stannaborate was first synthesized by Todd starting from the readily accessible undecaborate cluster $[Me_3NH][B_{11}H_{14}]$.[4] Deprotonation with *n*-butyllithium and treatment with tin dichloride resulted in the formation of the *closo* cluster dianion **1**.

Although Todd has shown previously that the stannaborate reacts as a nucleophile with methyl iodide, the nucleophilic power of the dianion towards transition metal electrophiles has remained unexplored. In order to investigate the nucleophilicity of the cluster $[SnB_{11}H_{11}]^{2-}$, we studied its reaction with several transition metal halides. The stannaborate salt **1** was treated with $[CpFe(CO)_2Br]$, $[(C_7H_7)Mo(CO)_2I]$, and $[CpNi(PPh_3)Cl]$ in CH_2Cl_2. In all three cases the substitution product was straightforwardly obtained, in almost quantitative yield on the basis of ^{11}B-NMR spectroscopy. Besides the cluster coordination product, one equivalent of $[NBu_4]$[halide] was formed, which could be separated by extraction with water. The air- and moisture-stable transition metal complexes were crystallized by slow diffusion of hexane into a dichloromethane solution of the respective salt. Each transition metal complex was characterized by elemental analysis, NMR spectroscopy, and X-ray diffraction analysis of single crystals. In the ^{11}B-NMR spectrum of the cluster dianion **1** in solution, three signals in an intensity ratio of 1:5:5 for the eleven boron atoms indicate C_{5v} symmetry. The ^{11}B-NMR signals of the substitution products **2**, **3**, and **4** appear at higher field and the signals for the two B_5 groups are isochronic (Scheme 1). Thus, ^{11}B-NMR spectroscopy is an appropriate tool for monitoring the progress of the reactions. ^{119}Sn-NMR spectra were recorded in all three cases, although for the nickel derivative no resonance was observed. The ^{119}Sn-NMR spectra of **2** and **3** feature a single resonance at $\delta = -208$ ($W_{1/2} = 112$ Hz) and $\delta = -257$ ($W_{1/2} = 124$ Hz), respectively. The ^{119}Sn chemical shift depends on the oxidation state, the coordination number, and the solvent.[5] For the two oxidation states, the chemical shift ranges overlap markedly, thereby making impossible any assessment of the oxidation state on the basis of the observed chemical shifts. The measured chemical shifts can be compared with that of the methyl-substituted derivative $[MeSnB_{11}H_{11}]^-$ ($\delta = -196.5$).[4]



Scheme 1. Syntheses of the organometallic stannaborate complexes

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In each case, crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a dichloromethane solution of the respective salt. Views of the cluster anions of **2**, **3**, and **4** are depicted in Figures 1, 2, and 3, respectively. Selected interatomic lengths are listed in Table 1. In all three cases, the interatomic lengths between the cluster atoms indicate a close resemblance to the structure of $[MePPh_3][MeSnB_{11}H_{11}]$. The observed bond lengths between the tin atoms and the transition metal atoms [Fe−Sn 2.479(1) Å, Mo−Sn 2.711(1) Å, Ni−Sn 2.412(1) Å] fall within the ranges of known M−Sn lengths in related organometallic compounds [$CpFe(CO)_2SnBr_3$: Fe−Sn 2.462(2) Å, $CpFe(CO)_2SnCl_3$: Fe−Sn 2.467(2) Å, $CpFe(CO)_2SnPh_3$: Fe−Sn 2.536(2) Å],[6] [$(C_7H_7)Mo(CO)_2SnCl_3$: Mo−Sn 2.720(1) Å, $Cp_2Mo(Br)(SnBr_3)$: Mo−Sn 2.691(4) Å],[7] [$[(CpNiPEt_3)_2SnCl_2]$: Ni−Sn 2.468(1) Å, $(CpNiPEt_3)_3SnCl$: Ni−Sn 2.531(1) Å].[8]

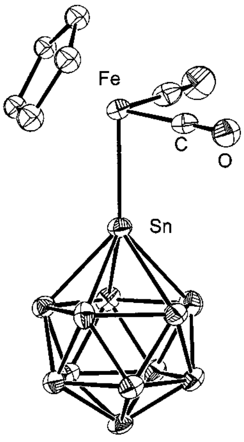

Figure 1. Molecular structure of the anion of **2**

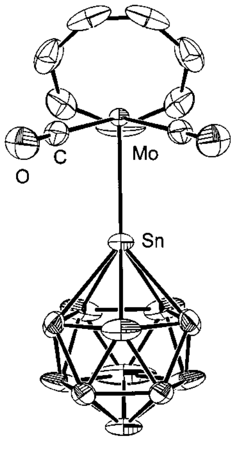

Figure 2. Molecular structure of the anion of **3**

The salts **2** and **4** crystallize in lattices built up of $[NBu_4]^+$ cations and $[L_nM(SnB_{11}H_{11})]^-$ anions. In the anion lattice, the charge-bearing stannaborates are directed towards the cation lattice.

In summary, the stannaborate cluster reacts as a nucleophile towards organometallic electrophiles and installs a negative charge in the complex, which is localized on the cluster atoms. The substitution products show remarkable stability towards air and moisture.

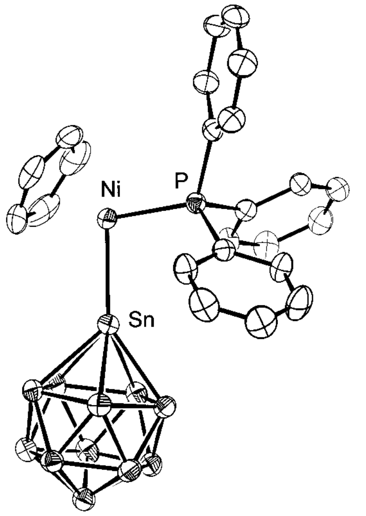

Figure 3. Molecular structure of the anion of **4** (the ellipsoids represent 50% probability)

Table 1. Selected interatomic distances [Å] in **2**, **3**, and **4**

	Fe	Mo	Ni
M−Sn	2.479(1)	2.711(1)	2.412(1)
Sn−B2	2.311(7)	2.266(9)	2.301(3)
Sn−B3	2.342(7)	2.266(9)	2.295(3)
Sn−B4	2.308(7)	2.30(1)	2.305(3)
Sn−B5	2.289(7)	2.30(1)	2.318(3)
Sn−B6	2.298(7)	2.32(1)	2.309(3)

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: Varian Unity 500 (^1H: 500 MHz, int. TMS; $^{13}C\{^1H\}$: 126 MHz, int. TMS; ^{31}P: 202 MHz, ext. H_3PO_4; ^{11}B: 160 MHz, ext. $BF_3 \cdot OEt_2$; ^{119}Sn: 186 MHz, ext. Me_4Sn). − MS: Finnigan MAT 95. − Elemental analysis: Institut für Anorganische Chemie RWTH Aachen, Carlo−Erba model 1106 elemental analyser.

$[NBu_4][CpFe(CO)_2SnB_{11}H_{11}]$ (2): A solution of 230 mg (257.1 g/mol, 0.89 mmol) of $CpFe(CO)_2Br$ in 10 mL CH_2Cl_2 was added at room temperature to a solution of 600 mg (733.8 g/mol, 0.82 mmol) of $[NBu_4]_2[SnB_{11}H_{11}]$ in 20 mL CH_2Cl_2. After stirring for 30 min, the solvent was evaporated in vacuo and the resulting brown waxy residue was stirred in 80 mL H_2O for 4 h. The remaining solid was filtered off, dried in vacuo, and crystallized from 20 mL CH_2Cl_2 by slow diffusion of hexane at +8 °C to give 370 mg (67% yield) of **2** as orange-brown crystals. − $^1H\{^{11}B\}$ NMR (CD_2Cl_2): $\delta = 1.02$ (t, 12 H, $^3J = 7.3$ Hz, CH_2CH_3), 1.44 (m, 8 H, $^3J = 7.3$ Hz, $CH_2CH_2CH_3$), 1.63 (m, 8 H, $CH_2CH_2CH_2$), 3.14 (m, 8 H, NCH_2CH_2), 5.32 (m, 5 H, C_5H_5). − $^{11}B\{^1H\}$ NMR (CD_2Cl_2): $\delta = -10.8$ (s, B12), −15.1 (s, B2−6 and B7−11). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 12.7$ (CH_2CH_3), 19.0 ($CH_2CH_2CH_3$), 23.2 ($CH_2CH_2CH_2$), 58.2 (NCH_2CH_2), 82.3 (C_5H_5), 210.4 (M−CO). − ^{119}Sn NMR (CD_2Cl_2): $\delta = -208.4$. − MS (70 eV) SIMS; *m/z* (%):

248.0 (100) [M$^-$ − CpFe(CO)$_2$]. − $C_{23}H_{52}B_{11}FeNO_2Sn$ (668.1): calcd. C 41.35, H 7.84, N 2.10; found C 41.11, H 7.93, N 1.93.

X-ray Crystallographic Study of 2: $C_{23}H_{52}B_{11}NO_2FeSn$; formula mass 668.13 g/mol; triclinic, space group $P\bar{1}$ (no. 2); a = 11.493(4), b = 11.852(6), c = 14.39(1) Å, α = 95.62(6), β = 90.55(6), γ = 120.44(3)°, V = 1678(2) Å^3, Z = 2, $d_{\text{calcd.}}$ = 1.322 g cm^{-3}, $\mu_{\text{lin.}}$ = 1.20 mm^{-1}. Enraf−Nonius CAD4 diffractometer; Mo-K_α radiation (λ = 0.71073 Å); graphite monochromator. Data collection at 203 K on a crystal of dimensions ca. 0.35 × 0.35 × 0.2 mm using ω scans in the range 2° ≤ θ ≤ 27° yielded 7197 reflections. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on azimuthal scans[9] was applied. After merging symmetry equivalent data, 4856 unique observations with $I > 1.0\ \sigma(I)$ remained for structure solution[10] by Patterson and subsequent Fourier difference syntheses. Orientational disorder of the Cp ring was encountered. Least-squares refinement on structure factors[10] was performed with isotropic displacement parameters for the Cp carbon atoms, anisotropic displacement parameters for all other nonhydrogen atoms, and hydrogen atoms placed in calculated positions (C−H = 0.98 Å, B−H = 1.1 Å). Convergence was obtained for 349 variables, 4856 data, and R = 0.078, R_w = 0.068, GoF = 1.523. A final difference Fourier map showed fluctuations of less than 1.5 eÅ^{-3} close to the Sn atom.[11]

[NBu$_4$][(C$_7$H$_7$)Mo(CO)$_2$SnB$_{11}$H$_{11}$] (3): A solution of 352 mg (371.0 g/mol, 0.95 mmol) of $(C_7H_7)Mo(CO)_2I$ in 10 mL CH_2Cl_2 was added to a solution of 696 mg (733.8 g/mol, 0.95 mmol) of $[NBu_4]_2[SnB_{11}H_{11}]$ in 20 mL CH_2Cl_2 at room temperature. After stirring for 30 min, the solvent was removed in vacuo and then the red waxy residue was treated with 80 mL H_2O for 4 h. The remaining dark-red solid was separated by filtration, dried in vacuo, and recrystallized from 20 mL CH_2Cl_2 by slow diffusion of hexane at +8 °C to give 455 mg (65% yield) of **3** as dark-red needles. − $^1H\{^{11}B\}$ NMR (CD_2Cl_2): δ = 1.00 (t, 12 H, ^3J = 7.3 Hz, CH_2CH_3), 1.45 (m, 8 H, ^3J = 7.3 Hz, $CH_2CH_2CH_3$), 1.61 (m, 8 H, $CH_2CH_2CH_2$), 3.15 (m, 8 H, NCH_2CH_2), 5.73 (m, 7 H, C_7H_7). − $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = −9.2 (s, B12), −14.4 (s, B2−6 and B7−11). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 13.8 (CH_2CH_3), 20.1 ($CH_2CH_2CH_3$), 24.3 ($CH_2CH_2CH_2$), 59.3 (NCH_2CH_2), 93.4 (C_7H_7), 215.1 (M−CO). − ^{119}Sn NMR (CD_2Cl_2): δ = −257.2. − $C_{25}H_{54}B_{11}MoNO_2Sn$ (735.3): calcd. C 40.89, H 7.41, N 1.91; found C 39.58, H 7.45, N 1.78.

X-ray Crystallographic Study of 3: $C_{25}H_{54}B_{11}MoNO_2Sn$; formula mass 734.27 g/mol; orthorhombic, space group $Pnma$ (no. 62); a = 28.941(3), b = 10.684(4), c = 11.703(3) Å, V = 3619(2) Å^3, Z = 4, $d_{\text{calcd.}}$ = 1.348 g cm^{-3}, $\mu_{\text{lin.}}$ = 1.05 mm^{-1}. Enraf−Nonius CAD4 diffractometer; Mo-K_α radiation (λ = 0.71073 Å); graphite monochromator. Data collection at 293 K on a crystal of dimensions ca. 0.3 × 0.3 × 0.2 mm using ω-2θ scans in the diffraction range 3° < θ < 25° resulted in 13384 reflections. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on azimuthal scans[9] was applied. After merging symmetry equivalent data, 3133 unique reflections remained for structure solution by direct methods.[12] The structure model was completed by Fourier difference synthesis: the cation was found to be disordered with respect to the crystallographic mirror plane. Tentative refinements in the noncentrosymmetric subgroup did not give satisfactory results and no Bijvoet differences could be detected, even though this subgroup should exhibit polarity. Least-squares refinement on structure factors[10] was performed with anisotropic displacement parameters for all nonhydrogen atoms except for the nitrogen atom in the cation close to the symmetry element. Hydrogen atoms were placed in calculated positions (C−H = 0.98 Å; B−H = 1.05 Å). Convergence was obtained for 266 variables, 2513 observed data with $I > 1.0\ \sigma(I)$ and R = 0.055, R_w = 0.055, GoF = 1.225. A final difference Fourier map showed fluctuations of less than 0.9 eÅ^{-3} close (0.8 Å) to B9.[11]

[NBu$_4$][CpNi(PPh$_3$)SnB$_{11}$H$_{11}$] (4): A solution of 383 mg (421.6 g/mol, 0.91 mmol) of $CpNi(PPh_3)Cl$ in 10 mL CH_2Cl_2 was added at room temperature to a solution of 666 mg (733.8 g/mol, 0.91 mmol) of $[NBu_4]_2[SnB_{11}H_{11}]$ in 20 mL CH_2Cl_2. The reaction mixture was stirred for 30 min and then the solvent was evaporated in vacuo. The brown waxy residue was stirred in 80 mL H_2O. After filtration, the collected solid was dried and then recrystallized from 20 mL CH_2Cl_2 by slow diffusion of hexane at +8 °C to give 574 mg (72% yield) of **4** as small golden-brown crystals. − $^1H\{^{11}B\}$ NMR (CD_2Cl_2): δ = 0.98 (t, 12 H, ^3J = 7.3 Hz, CH_2CH_3), 1.41 (m, 8 H, ^3J = 7.3 Hz, $CH_2CH_2CH_3$), 1.62 (m, 8 H, $CH_2CH_2CH_2$), 3.22 (m, 8 H, NCH_2CH_2), 5.32 (m, 5 H, C_5H_5), 7.50 (m, 5 H, C_6H_5). − $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = −10.7 (s, B12), −15.2 (s, B2−6 and B7−11). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 14.0 (CH_2CH_3), 20.1 ($CH_2CH_2CH_3$), 24.3 ($CH_2CH_2CH_2$), 59.3 (NCH_2CH_2), 92.3 (C_5H_5), 128.7 (C_{meta}, C_{para}), 130.8 (C_{ortho}), δ = 134.2 (P−C). − ^{31}P NMR (CD_2Cl_2): δ = 42.3 (s, PPh_3). − $C_{40}H_{69}B_{11}Cl_2NNiPSn$ (877.3 + CH_2Cl_2): calcd. C 49.93, H 7.23, N 1.46, found C 48.55, H 7.26, N 1.35.

X-ray Crystallographic Study of 4: $C_{40}H_{69}B_{11}Cl_2NNiPSn$; formula mass 877.3 g/mol + CH_2Cl_2; monoclinic space group $P2_1/c$ (no. 14); a = 16.192(6), b = 15.000(8), c = 19.689(9) Å, α = 96.21(3)°, V = 4754(4) Å^3, Z = 4, $d_{\text{calcd.}}$ = 1.344 g cm^{-3}, $\mu_{\text{lin.}}$ = 1.10 mm^{-1}. Siemens/Stoe AED2 diffractometer; Mo-K_α radiation (λ = 0.71073 Å); graphite monochromator; data collection at 200(2) K on a single crystal of dimensions 0.2 × 0.3 × 0.6 mm, 1.5° ≤ θ ≤ 25°; 8106 independent reflections measured, 6634 "observed" [$I > 2\ \sigma(I)$]; Lorentz and polarization factors; structure solution by direct methods and difference Fourier synthesis,[13] F^2 refinement; anisotropic parameters for nonhydrogen atoms, CH_2Cl_2 disordered, hydrogen atoms placed in calculated positions (C−H = 0.98 Å; B−H = 1.12 Å). Convergence was obtained for 516 variables with wR_2 = 0.057, R_1 = 0.028, GoF = 1.031. Max./min residual density +1.12/−0.52 eÅ^{-3}.[14]

Acknowledgments

We wish to acknowledge the Deutsche Forschungsgemeinschaft and the Institut für Anorganische Chemie der TH Aachen for financial support.

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[11] Crystallographic data (excluding structure factors) for the structures of **2** and **3** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-116068 (**2**) and -116069 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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[14] Crystallographic data (excluding structure factors) for the structure **4** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-115869. Copies of the data can be obtained free of charge from the address given in ref.[11]

Received March 18, 1999
[I99089]