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Reviews

Stanna-*closo*-dodecaborate Chemistry

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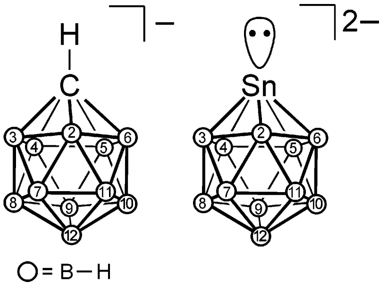
The chemistry of the stanna-*closo*-dodecaborate cluster is summarized in this account. This dianionic group 14 heteroborate is a versatile ligand in coordination chemistry and can employ various coordination modes. Our contributions to the field are described with regard to the different transition-metal centers, which also coincide roughly with the chronological order of the contributions.

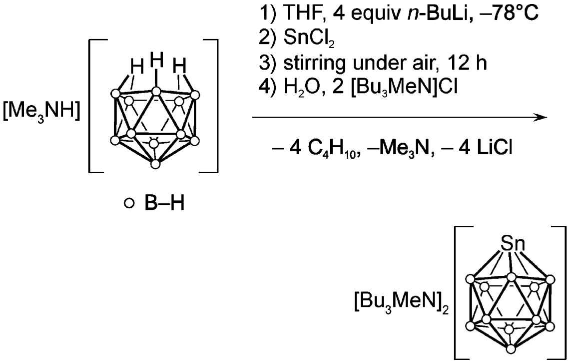
Introduction

The monocarbaborate anion $[1\text{-CB}_{11}\text{H}_{12}]^-$ (Chart 1) and its derivatives have received much attention, due to their excellent properties as weakly coordinating anions,[1−4] and their conjugate acids are the strongest isolable Brønsted acids presently known.[5−7] While the virtually "noncoordinating" properties of particular derivatives of $[1\text{-CB}_{11}\text{H}_{12}]^-$ are of central importance in this field of chemistry, a number of transition-metal coordination compounds of the monocarbaborate cluster as a ligand also have been described. The monocarbaborate and its derivatives typically are coordinated via B−X bonds (X = H, Cl, Br),[8−14] and only a few coordination compounds with an exo carbon−transition-metal bond have been described.[15,16]

Chart 1. Molecular Structure and Numbering Scheme of $[\text{CB}_{11}\text{H}_{12}]^-$ and $[\text{SnB}_{11}\text{H}_{11}]^{2-}$



In this review we focus on the coordination chemistry of the tin homologue $[\text{SnB}_{11}\text{H}_{11}]^{2-}$ of the monocarbaborate anion which was first reported, together with the germanium and lead homologues, by Todd and co-workers in 1992.[17] A few years later, we completed the series of the group 14 heteroborates with the synthesis of the silicon homologue $[1\text{-Me-1-SiB}_{11}\text{H}_{11}]^-$,[18] and we set out to investigate the chemistry of $[\text{SnB}_{11}\text{H}_{11}]^{2-}$. The original synthesis of $[\text{SnB}_{11}\text{H}_{11}]^{2-}$ as reported by Todd involved deprotonation of $[\text{Me}_3\text{NH}][\text{B}_{11}\text{H}_{14}]$ in THF with 4 equiv of *n*-butyllithium followed by the addition of 1 equiv of SnCl_2 in THF at −78 °C (eq 1). Workup under air and



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subsequent precipitation from an aqueous solution afforded a variety of different stanna-*closo*-dodecaborate salts depending on the countercation employed (e.g., Et_4N^+, Bu_3MeN^+, Bu_4N^+, Ph_4P^+, Cs^+).[19] The solubility of the salts can be modified by

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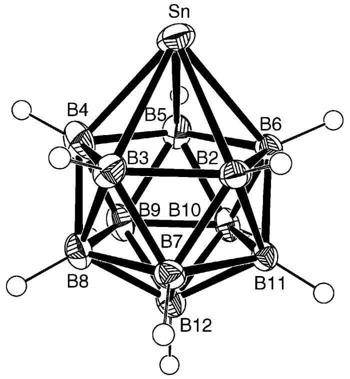
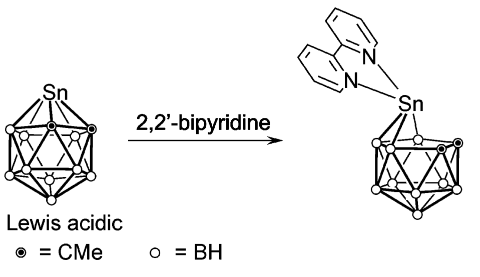


Figure 1. ORTEP plot of the molecular structure (50% probability level) of the dianionic stannaborate cluster, as obtained from the single-crystal structure of the lithium salt $[Li(THF)_3]_2[SnB_{11}H_{11}]$.[19] The lithium cations and the THF solvent molecules have been omitted for clarity.

changing the respective cation. For example, the alkali cations and the Me_4N^+ cation give water soluble stannaborate salts; the tetrabutylammonium salt is readily soluble in CH_2Cl_2, acetone, DMSO, DMF and acetonitrile, while the tetraphenylphosphonium salt exhibits poor solubility in CH_2Cl_2 and acetone. The resulting colorless solids are accessible on a multigram scale and are stable toward air for weeks. However, exposure to air for multiple months results in oxidation of the stannaborate dianion. In the absence of oxygen the stannaborate dianion exhibits remarkable thermal stability and the cesium salt decomposes at above 900 °C, which is comparable to the thermal stability of $Cs_2[B_{12}H_{12}]$.[19,20] The solid-state structure of the lithium salt of the stannaborate dianion was determined (Figure 1).[19] The tin vertex is positioned above the center of the pentagonal B_5 face, and the tin−boron distances range from 2.381(4) to 2.389(3) Å.

It is important to note that the neutral *closo*-stannacarboboranes $Sn(CR)_2B_4H_4$,[21] $Sn(CMe)_2B_9H_9$,[22] and the 13-vertex species $Sn(CR_2)_2B_{10}H_{10}$[23,24] behave as Lewis acids and react with Lewis bases to form heteroborane cages with slipped tin vertices (eq 2), while the isolobal stannaborate $[SnB_{11}H_{11}]^{2-}$ shows no tendency to react with Lewis bases but can readily be methylated at the tin vertex with methyl iodide (eq 3). The methylated stannaborate monoanion $[1\text{-}MeSnB_{11}H_{11}]^-$ and the monocarbaborate monoanion $[CB_{11}H_{12}]^-$ are electronically isovalent heteroborate clusters and have in common the ability to coordinate to transition-metal fragments via B−H bonds.[25] What makes the stannaborate cluster unique is the stability of the dianion $[SnB_{11}H_{11}]^{2-}$ together with its pronounced nucleophilicity at the tin vertex. Accordingly, the stannaborate cluster can also be regarded as a special tin(II) ligand. As such, its metal complexes can be compared to the large number of transition-metal coordination compounds with a variety of tin(II) ligands which have been described in the literature.[26−28] These systems constitute structurally interesting compounds in their own right,[29−34] and some exhibit catalytic properties: for example, in hydrogenation reactions,[35−37] water-gas shift reactions,[38] or hydroformylation reactions.[39−42]



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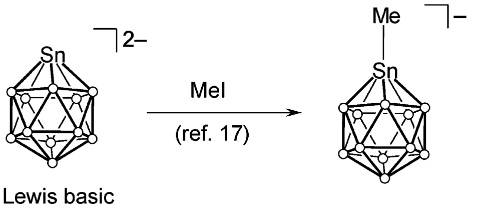

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The aim of this review is to provide a brief account of some of our contributions to the chemistry of the stanna-*closo*-dodecaborate dianion.

First Coordination Compounds with $[SnB_{11}H_{11}]^{2-}$

The first coordination compounds of the stanna-*closo*-dodecaborate ligand were reported in 1999.[43] We were interested in the coordinating abilities of the group 14 heteroborate anion and chose a series of transition-metal halogen derivatives as model electrophiles (Scheme 1). The reactions between these compounds and $[Bu_4N]_2[SnB_{11}H_{11}]$ proceeded smoothly at room temperature, and the halide was substituted by the stannaborate

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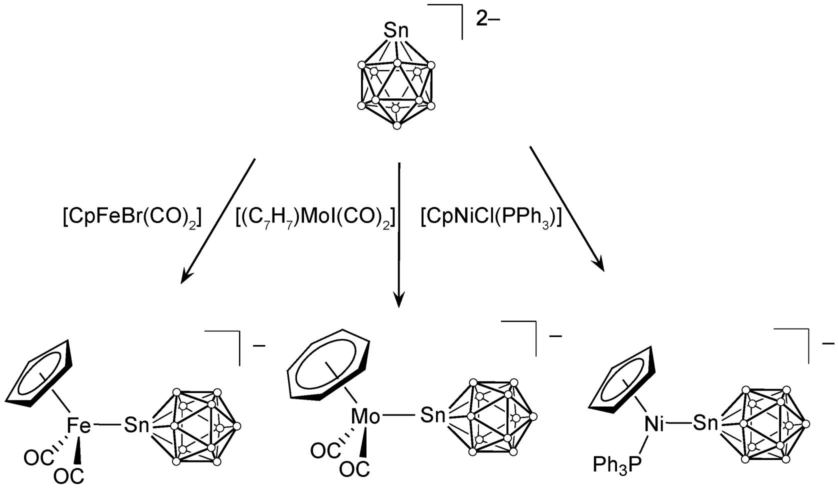
Scheme 1. Synthesis of the First Transition-Metal Coordination Compounds with the Stanna-*closo*-dodecaborate Ligand $[SnB_{11}H_{11}]^{2-}$ [43]

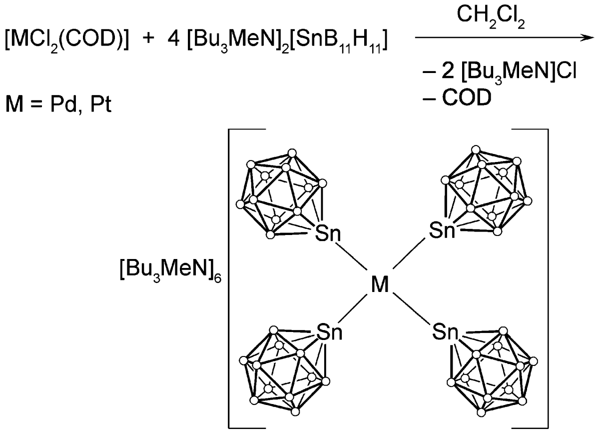


unit in all cases. The resulting monoanionic products with a stannaborate ligand could be crystallized using the $[Bu_4N]^+$ cation, and the structural data revealed that the tin−metal bonds have lengths similar to those of related tin(II) ligands such as $SnCl_3^-$. Boron-11 NMR spectroscopy is a valuable tool for monitoring substitution reactions of the tin−boron cluster. The free ligand exhibits three resonances in the $^{11}B\{^1H\}$ NMR spectrum at −6, −11, and −12 ppm with an integration ratio of 1:5:5, while the coordinated cluster typically shows a resonance around −11 ppm for the antipodal boron vertex B12 and another resonance at −15 ppm which is ascribed to the accidentally isochronous boron atoms B2−B11. This pattern is found for all stannaborate coordination compounds with a tin−metal bond between the borate and the transition-metal fragment.

Palladium and Platinum Coordination Compounds of the $[SnB_{11}H_{11}]^{2-}$ Anion

After the nucleophilicity of the stannaborate cluster anion toward transition-metal fragments had been established, we set out to develop the transition-metal chemistry of stanna-*closo*-dodecaborate in detail. The first metal center which was thoroughly investigated with regard to the ligand properties of $[SnB_{11}H_{11}]^{2-}$ was platinum.

Homoleptic Square-Planar Complexes. Homoleptic square-planar stannaborate complexes of platinum and palladium were formed in a straightfoward reaction between $MCl_2(COD)$ (M = Pd, Pt; COD = 1,5-cyclooctadiene) and 4 equiv of $[SnB_{11}H_{11}]^{2-}$ (eq 4).[44] The resulting hexaanionic complexes are accessible in high yields on a multigram scale and are remarkably stable toward air and moisture. Their spectroscopic properties are characteristic for platinum−stannaborate complexes. The $^{11}B\{^1H\}$ NMR spectrum exhibits two signals at around −11 ppm (B12) and −13 ppm (B2−B11) due to accidental isochrony of both B_5 belts, and the ^{119}Sn NMR spectrum reveals a broad peak at −317 ppm ($^1J_{Pt,Sn}$ = 14 000 Hz). Furthermore, the Mössbauer data show that the tin atom in $[Pt(SnB_{11}H_{11})_4]^{6-}$ has an isomer shift of 1.66 mm s^{-1}, which lies between the isomer shift of the tin(IV) compound $[MeSnB_{11}H_{11}]^-$ (1.18 mm s^{-1}) and that of the tin(II) compound $[SnB_{11}H_{11}]^{2-}$ (2.46 mm s^{-1}). The Pt−Sn stretching vibration was found at 170 cm^{-1}, which is lower than the corresponding Pd−Sn stretching vibration at 190 cm^{-1}. Structural parameters could be obtained from X-ray diffraction and indicate that the interatomic platinum−tin separations Pt−Sn1 = 2.554(1) Å and Pt−Sn2 = 2.565(1) Å lie within the range of known tin−platinum distances.[17]



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Ligand Properties: Substitution. The fact that the stannaborate cluster anion easily substitutes halides at transition-metal centers prompted us to examine the substitution reaction in detail. A key question in this context is concerned with the fact that only one substitution product with a stannaborate ligand has been isolated which also carries a halide ligand—a Pt(IV) complex which was prepared by oxidative addition of benzyl bromide to $[Pt(Ph)(SnB_{11}H_{11})(4,4'\text{-}tert\text{-butyl-}2,2'\text{-bipyridine})]^-$.[45] Normally, the stannaborate ligand substitutes all coordinated halides. The square-planar platinum compound $[PtCl_2(dppe)]$ reacted with 1 equiv of $[SnB_{11}H_{11}]^{2-}$ to form the disubstitution product; i.e., only half of the platinum reactant was consumed during the reaction (eq 5).[46] To elucidate whether the absence of the monosubstitution product is due to kinetic or thermodynamic reasons, we reacted the monostannaborate complex $[Pt(Ph)(SnB_{11}H_{11})(dppe)]^-$ with a mixture of acetyl chloride and methanol which is known to cleave Pt−Ph bonds with formation of benzene and a Pt−Cl bond.[47,48] The fact that this reaction

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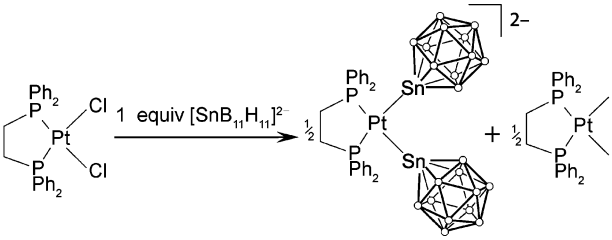

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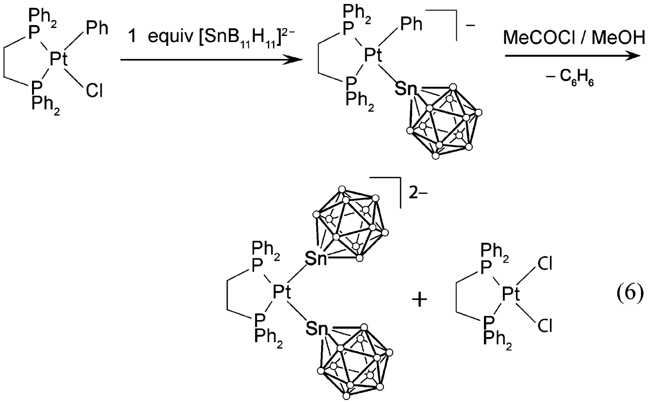
again yielded a mixture of the bis-stanna− and dichloro−platinum complexes (eq 6) strongly suggests a thermodynamic preference for these systems compared to the mixed platinum complex.



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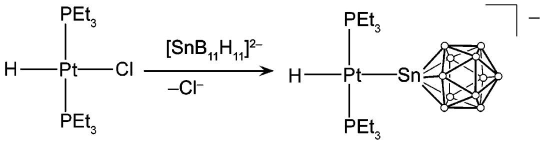
Ligand Properties: Trans Influence. Square-planar platinum complexes with a suitable ligand in a position trans to the stannaborate moiety constitute ideal systems to study the trans influence of the stannaborate ligand. The platinum compound $[PtH(SnB_{11}H_{11})(PEt_3)_2]^-$ (eq 7) exhibits a Pt−H stretching mode



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at 2061 cm^{-1}, which can be compared to the respective stretching modes in analogous $PtHL(PEt_3)_2$ systems: 2041 cm^{-1} ($L = CN^-$), 2090 cm^{-1} ($L = PEt_3$), 2105 cm^{-1} ($L = SnCl_3^-$), and 2129 cm^{-1} ($L = CO$).[49] This trend indicates that the stannaborate ligand exerts a stronger trans influence than $SnCl_3^-$ or CO.

Ligand Properties: Lability. During reactivity studies of the aforementioned platinum−hydride complex, we found that the reaction with *tert*-butyl isocyanide at room temperature resulted in the formation of a trigonal-bipyramidal platinum complex with two stannaborate ligands in 37% yield (eq 8).[49]

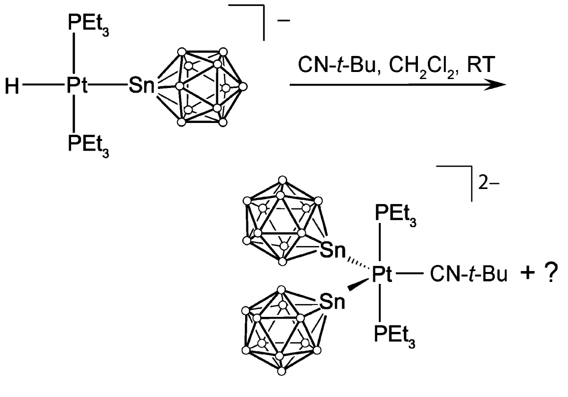

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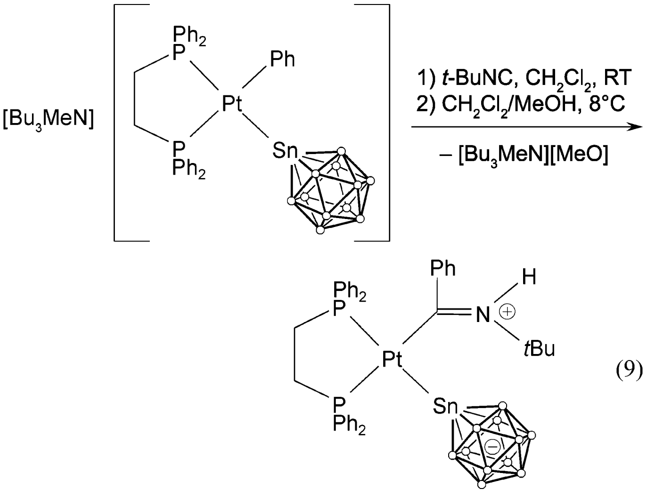
Table 1. Comparison of Hydroformylation Results Using Platinum Catalysts with the $[SnB_{11}H_{11}]^{2-}$ Ligand and the $SnCl_3^-$ Ligand[56]

	100 °C		140 °C	
cat.	TOF	n/iso	TOF	n/iso
$[Pt(Ph)(SnB_{11}H_{11})(dppp)]^-$	11.0	7.8	72.8	8.2
$[Pt(SnB_{11}H_{11})_2(dppp)]^{2-}$	19.3	8.8	73.9	9.2
$[Pt(Ph)(SnCl_3)(dppp)]$	50.5	1.7	dec	dec
$[Pt(SnCl_3)_2(dppp)]$	31.6	1.4	dec	dec

Although the nature of the byproducts of this reaction could not be determined, the formation of a platinum complex with two heteroborate ligands clearly must involve the transfer of one $[SnB_{11}H_{11}]^{2-}$ group between two platinum centers. This finding can tentatively be ascribed to the ligand's lability.

Another aspect of the platinum stannaborate chemistry which is best interpreted on the basis of the lability of the heteroborate is the insertion of *tert*-butyl isocyanide into the Pt−Ph bond of $[Pt(Ph)(SnB_{11}H_{11})(dppe)]^-$ (eq 9).[50] This insertion occurred at



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room temperature, and thus the stannaborate platinum compound undergoes insertion of isonitriles into its Pt−Ph bond more readily than the related compounds $[PtR_2(PPh_3)_2]$ and $[PtRX(PPh_3)_2]$ (R = Me, Ph; X = Br, I), which were studied by Treichel.[51,52]

Reactivity: Hydroformylation. It is known that platinum complexes of the type L_2PtCl_2 are suitable catalysts for the hydroformylation reaction if they are treated with $SnCl_2$, which inserts into a Pt−Cl bond to give the respective platinum trichlorostannate complex.[53−55] This motivated us to examine the catalytic properties of Pt complexes with the stannaborate ligand. In fact, we prepared analogous $Pt-[SnB_{11}H_{11}]^{2-}$ and $-SnCl_3^-$ complexes in order to compare their catalytic activities in the hydroformylation reaction (eq 10 and Table 1).[56] The

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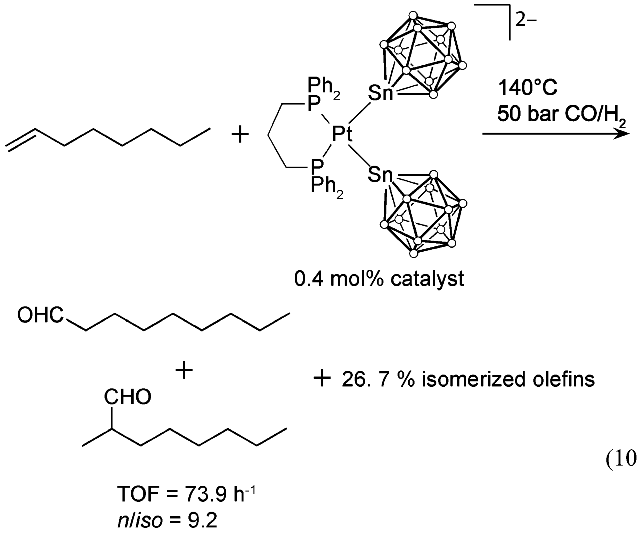

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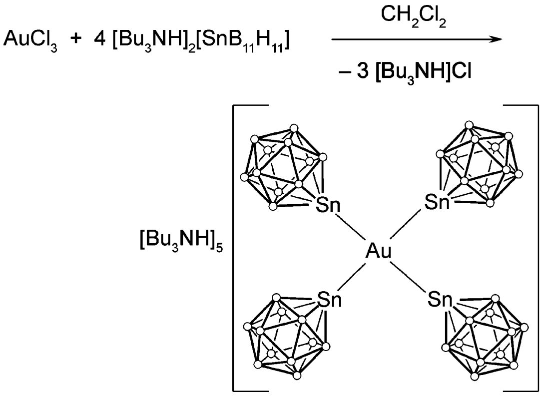
examined stannaborate complexes are thermally more stable than their $SnCl_3^-$ analogues and give significantly higher n/iso ratios of the formed aldehydes.

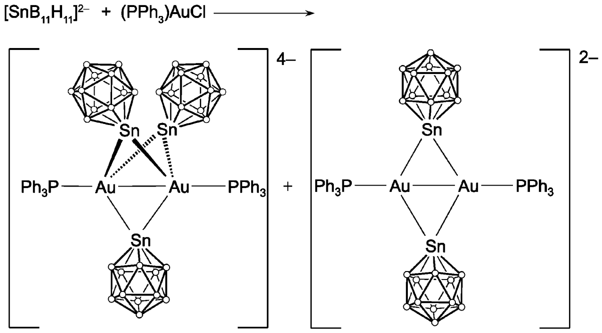
Gold−Stannaborate Compounds: Clusters with Very Short Au−Au Distances

After we had explored the properties of the stannaborate ligand at platinum centers, we began to elaborate the gold chemistry of $[SnB_{11}H_{11}]^{2-}$. As it turned out, this chemistry led to remarkable gold−stannaborate clusters. However, the first isolated gold compound with a $[SnB_{11}H_{11}]^{2-}$ ligand was the homoleptic square-planar Au(III) complex $[Au(SnB_{11}H_{11})_4]^{5-}$ (eq 11).[44] The gold−tin distances are 2.589(1) and 2.601(1) Å.



(11)

To our surprise, the reaction of [(PPh$_3$)AuCl] with 1 equiv of $[SnB_{11}H_{11}]^{2-}$ yielded a reaction mixture which contained three species (as determined by ^{31}P NMR spectroscopy): namely $[Au_2(SnB_{11}H_{11})_2(PPh_3)_2]^{2-}$ as well as the tetraanionic $[Au_2(SnB_{11}H_{11})_3(PPh_3)_2]^{4-}$ (eq 12) and unreacted [(PPh$_3$)AuCl].[57]

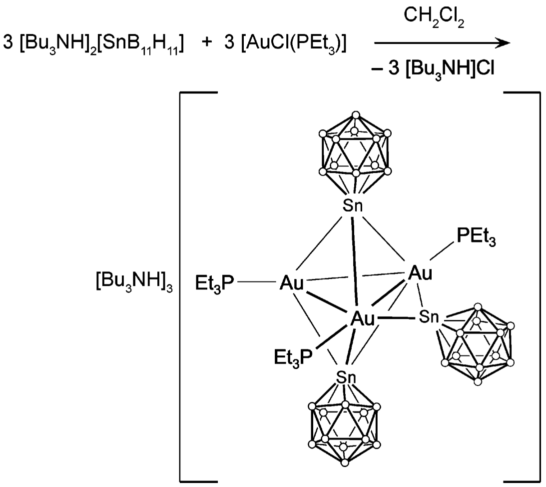


(12)

Samples for solid-state structure determinations of both gold−stannaborate clusters could be obtained by selective crystallization employing different ammonium cations. While the structure motif is not unprecedented, the Au−Au interatomic distances are very short: 2.625(1) Å in $[Au_2(SnB_{11}H_{11})_2(PPh_3)_2]^{2-}$ and 2.590(1) Å in $[Au_2(SnB_{11}H_{11})_3(PPh_3)_2]^{4-}$. The usual bond distances for Au(I)−Au(I) interactions lie in the range of 2.75−3.25 Å.[58] The Au−Sn distances in $[Au_2(SnB_{11}H_{11})_2(PPh_3)_2]^{2-}$ are similar to distances described earlier,[59,60] while those in $[Au_2(SnB_{11}H_{11})_3(PPh_3)_2]^{4-}$ are unsymmetrical and exhibit three rather long Au−Sn distances and three that are normal.

The bonding situation was studied in detail by DFT and HF+MP2 calculations, and it was concluded that the stability of the dimeric species over the respective monomers is predominantly due to dispersive interactions between the valence electrons of tin and gold.

The stannaborate's ability to form larger gold clusters was subsequently demonstrated. A trinuclear gold cluster was obtained by reaction of [AuCl(PEt$_3$)] with 1 equiv of $[Bu_3NH]_2[SnB_{11}H_{11}]$ (eq 13).[61] Two stannaborate units μ_3-cap the triangular gold core, and the third heteroborate μ_2-bridges an Au−Au edge, which forms an almost linear arrangement with two triethylphosphine ligands and contains the shortest Au−Au distance of 2.606(1) Å. The whole structure motif can be derived from $[Au_2(SnB_{11}H_{11})_3(PPh_3)_2]^{4-}$ by coordinating a $(R_3P)Au^+$ unit to the Au−Au bond, which results in significantly longer Au−Au distances of 2.894(1) and 2.793(1) Å compared to the short linear P−Au−Au−P edge.



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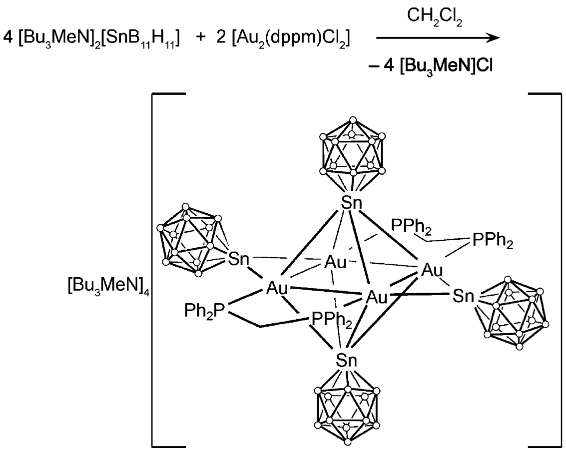
Furthermore, it was possible to synthesize a tetranuclear gold cluster by reacting the dinuclear gold electrophile [Au$_2$Cl$_2$(dppm)] with the tin−borate (eq 14). The Au$_4$ core is best



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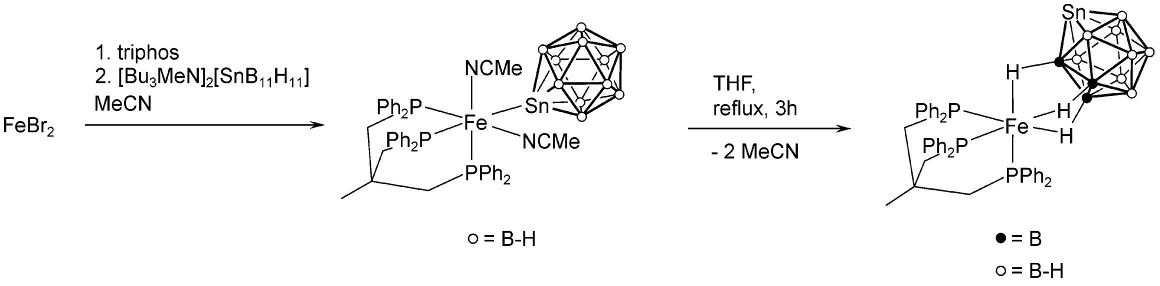
Scheme 2. Two-Step Synthesis Including a η^1(Sn) to η^3(B−H) Rearrangement of the Zwitterionic Iron Complex [Fe($SnB_{11}H_{11}$)(triphos)]

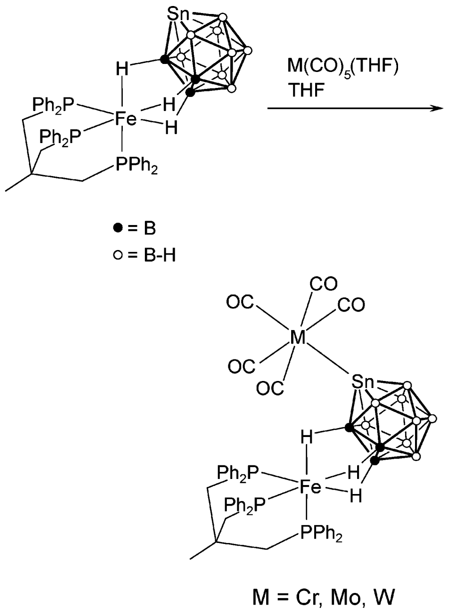


described as a rectangle with short linear P−Au−Au−P edges, d(Au−Au) = 2.622(1) Å, which are μ_2-bridged by stannaborate ligands and longer Au−Au edges (2.848(1) Å) which are bridged by the chelating phospine ligands. Moreover, the Au_4 rectangle is μ_4-capped by two $[SnB_{11}H_{11}]^{2-}$ ligands.

Iron Complexes: η^3(B−H) and Ambidentate Stannaborate Coordination

The stannaborate cluster predominantly forms tin−metal bonds with late-transition-metal fragments. With iron and ruthenium fragments, however, coordination of the dianionic cluster via a triangular cluster face becomes competitive. In fact, the zwitterionic complex [Fe($SnB_{11}H_{11}$)(triphos)], which contains an η^3(B−H) coordinated heteroborate can easily be prepared on a multigram scale in a two-step synthesis starting from $FeBr_2$ (Scheme 2).[62] This procedure includes a η^1(Sn) to η^3(B−H) rearrangement reaction of the stannaborate ligand which occurs with the loss of two acetonitrile ligands when the insoluble initial product [Fe($SnB_{11}H_{11}$)$(MeCN)_2$(triphos)] is heated at reflux in THF.

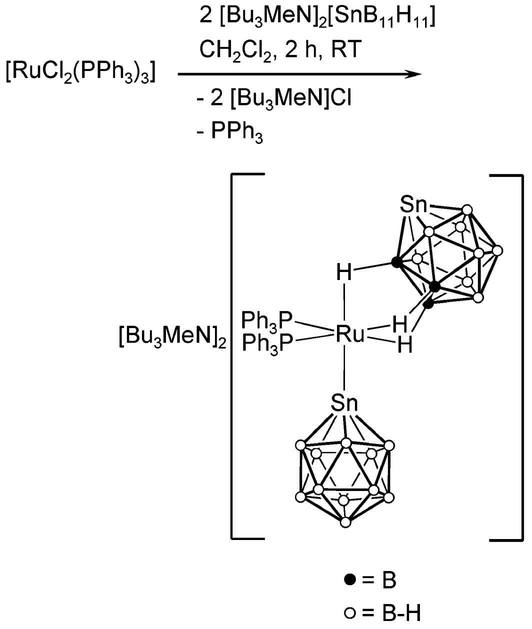
The nucleophilicity of the tin vertex in the zwitterionic complex [Fe($SnB_{11}H_{11}$)(triphos)] is significantly reduced compared to that of the dianionic $[SnB_{11}H_{11}]^{2-}$. Methylation of the tin atom using MeI, for example, is a straightfoward reaction with $[SnB_{11}H_{11}]^{2-}$ which takes place at room temperature. This reaction is not feasible with the iron coordination compound, even at elevated temperatures and with an excess of MeI. The tin vertex can still function as a nucleophile nonetheless if reactive transition-metal electrophiles such as $[M(CO)_5(THF)]$ (M = Cr, Mo, W) are introduced (eq 15).[62] The resulting bimetallic coordination compounds feature an ambidentate stannaborate moiety which employs both η^1(Sn) and η^3(B−H) coordination.



(15)

Ruthenium Complexes: η^1(Sn) and η^3(B−H) Coordination

The ruthenium coordination chemistry of the stannaborate ligand is similar to its iron chemistry. Reaction of the ruthenium(II) electrophile $[RuCl_2(PPh_3)_3]$ with 2 equiv of $[SnB_{11}H_{11}]^{2-}$ yields a dianionic compound which contains two stannaborate ligands, one of which is coordinated via a tin−ruthenium bond and the other via a triangular cluster face (eq 16).[63] Furthermore, the η^3(B−H)-coordinated stannaborate undergoes a rotational twisting around the respective triangular cluster face. The activation parameters could be determined using $^{31}P\{^1H\}$ selective inversion transfer experiments at different tempera-



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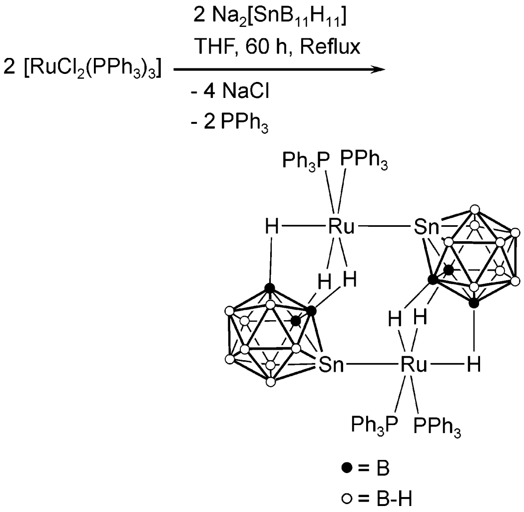
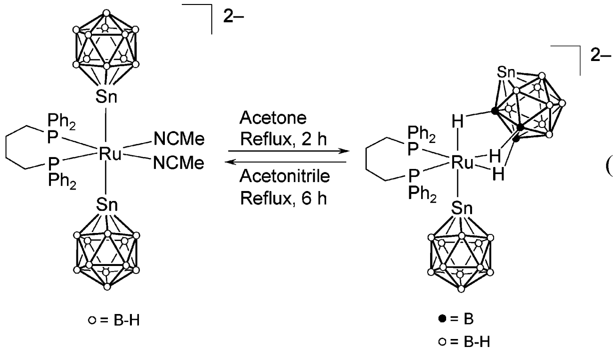
tures: $\Delta G^{\ddagger} = 70.8$ kJ mol^{-1}, $\Delta H^{\ddagger} = 62.7$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -27.1$ J mol^{-1} K^{-1}.[63]

Additionally, we succeeded in preparing a dimeric ruthenium complex with a bridging stannaborate ligand (eq 17). The heteroborate plays the role of an ambidentate ligand which employs both coordination modes (η^1(Sn) and η^3(B−H)) such that the tin vertex and the triangular B−H cluster face are coordinated to the respective ruthenium fragments.[63] The resulting compound can be regarded as a dimeric zwitterion and is insoluble in common solvents due to its high dipole moment.



(17)

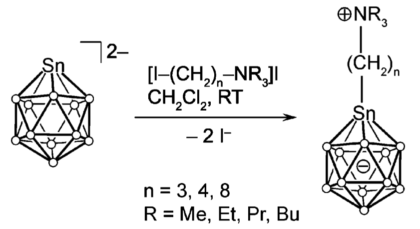
In light of the remarkable flexibility of the stannaborate ligand with regard to different coordination modes, it is not very surprising that rearrangement reactions have been described for a number of compounds.[64] Moreover, a reversible rearrangement reaction has also been reported. The bis(acetonitrile) adduct [Ru(SnB$_{11}$H$_{11}$)$_2$(dppb)(MeCN)$_2$]$^{2-}$ can be interconverted to [Ru(SnB$_{11}$H$_{11}$)$_2$(dppb)]$^{2-}$ by heating the former complex in refluxing acetone (eq 18). Heating the latter compound in acetonitrile led to the formation of the starting material, which constitutes the first example of a reversible η^3(B−H) to η^1(Sn) rearrangement reaction.[65]



(18)

Alkyl Derivatives of [SnB$_{11}$H$_{11}$]$^{2-}$

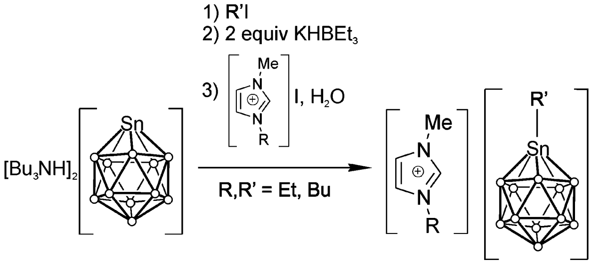
It already had been reported by Todd and co-workers that stanna-*closo*-dodecaborate can be easily methylated at the tin vertex. Using Todd's approach (viz. treatment of the stannaborate dianion with organic halides), we could synthesize a number of different organic derivatives such as [CH$_2$(SnB$_{11}$H$_{11}$)$_2$]$^{2-}$, [CH$_2$=CHCH$_2$−SnB$_{11}$H$_{11}$]$^-$ and [CH≡CCH$_2$−SnB$_{11}$H$_{11}$]$^-$.[66] Additionally, we prepared a series of ω-(stannadodecaborato)-1-(trialkylammonio)alkane zwitterions by reacting [SnB$_{11}$H$_{11}$]$^{2-}$ with different (ω-iodoalkyl)trialkylammonium iodides (eq 19).[67]



(19)

These easily accessible model systems were investigated with regard to their crystallographic properties. To find out about the influence of the electric field, we attempted crystallization of the zwitterionic systems in an external electric field. We speculated that the high dipole moment of the zwitterions might lead to different packing motifs in the crystal structure due to the presence of the external electric field. However, no such effect was observed.

As described above, a variety of alkylated stannaborate derivatives are accessible on a multigram scale using straightforward reactions. We thus decided to study the monoanionic clusters with regard to the properties of their imidazolium salts.[68] These salts can be obtained in a simple one-pot reaction sequence (eq 20). First, the tributylammonium salt of stanna-*closo*-dodecaborate was alkylated using an iodoalkane such as iodoethane, and in a second step KHBEt$_3$ was used to deprotonate the tributylammonium cation. Workup in water and precipitation with the respective imidazolium salt afforded the desired imidazolium alkyl−stannaborate salt. The obtained salts are not hygroscopic and exhibit melting points as low as 55 °C (for *N*-butyl-*N*′-methylimidazolium butyl-*closo*-stannadodecaborate).



(20)

During our alkylation studies, we discovered that the (γ-chloropropyl)stannaborate [Cl(CH$_2$)$_3$−SnB$_{11}$H$_{11}$]$^-$, which can be prepared by reaction of stannadodecaborate with 1-chloro-3-iodopropane, undergoes a nucleophilically induced elimination of the γ-chloropropyl group when treated with alkyllithium or aryllithium reagents (Scheme 3).[69] The phenylated stannaborate [C$_6$H$_5$SnB$_{11}$H$_{11}$]$^-$ could be prepared using this protocol. Furthermore, nucleophilic displacement of the γ-chloropropyl group also was possible with NaH, which generated the unsubstituted stannaborate [SnB$_{11}$H$_{11}$]$^{2-}$.

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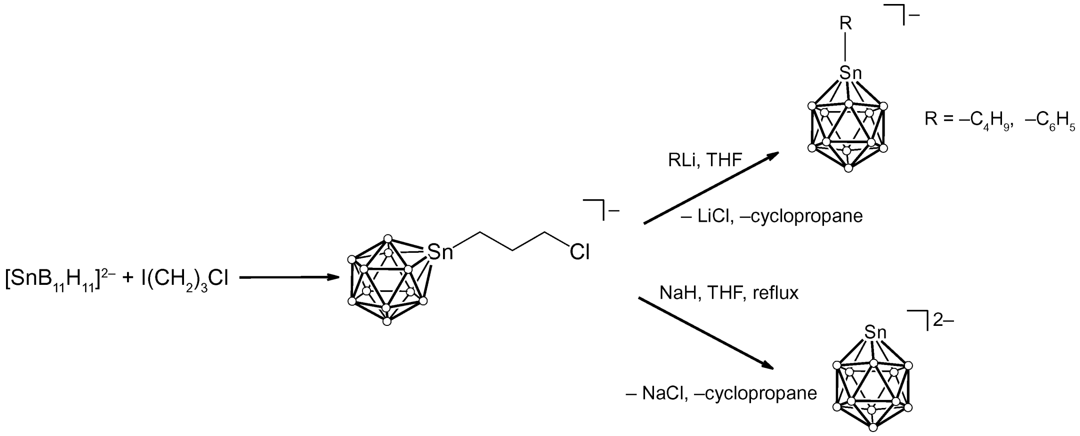
Scheme 3. Nucleophilic Substitution of a γ-Chloropropyl Residue Using Alkyl- and Aryllithium Reagents



Conclusions and Outlook

The plethora of isolated transition-metal complexes containing the stanna-*closo*-dodecaborate ligand beautifully demonstrates the variability of the heteroborate ligand. The stannaborate leads to gold−tin cluster formation with Au(I) fragments, to homoleptic complexes with metal−tin bonds (Pd, Pt, Au), and to ambidentate coordination with iron and ruthenium fragments. To sum up key aspects of transition metal stannaborate chemistry, the following can be concluded.

(1) Most complexes containing the stannaborate ligand are stable toward air.

(2) The stannaborate ligand can use different coordination modes depending on the transition-metal-element substrate.

(3) The formation of gold clusters is promoted by the tin−heteroborate.

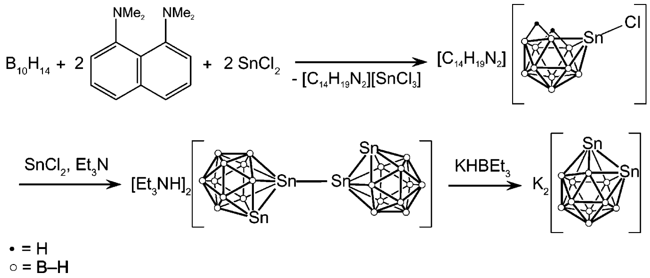
(4) Platinum stannaborate compounds display catalytic activity for the hydroformylation reaction.

(5) $[SnB_{11}H_{11}]^{2-}$ is a ligand with considerable trans influence.

We are currently investigating the stannaborate chemistry of other transition metals, and preliminary results indicate that the fascinating chemistry of $[SnB_{11}H_{11}]^{2-}$ (Figure 1) continues to provide new compounds with surprising structures.

Furthermore, new stannaborate chemistry also evolves from the recently prepared tin homolgue of *o*-dicarbaborane. The distanna-*closo*-dodecaborate $[Sn_2B_{10}H_{10}]^{2-}$ was synthesized in our laboratory, starting from decaborane, in three steps (Scheme 4).[70] Treating decaborane with 2 equiv of 1,8-bis(dimethylamino)naphthalene (Proton Sponge) and $SnCl_2$ yielded a chlorostanna-*nido*-undecaborate whose bromine analogue had been described earlier by Gaines.[71] Incorporation of a second tin vertex into the boron scaffold was achieved by reacting the chlorostanna-*nido*-undecaborate with another 1 equiv of $SnCl_2$ and triethylamine, which led to the formation of the distannaborate $[\{Sn_2B_{10}H_{10}\}_2]^{2-}$, which was reduced with $KHBEt_3$ to give the *o*-distannadodecaborate $[Sn_2B_{10}H_{10}]^{2-}$. It will be fascinating to study the coordination chemistry of this new stannaborate cluster.

Scheme 4. Synthesis of $[Sn_2B_{10}H_{10}]^{2-}$ Starting from $B_{10}H_{14}$



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