RESEARCH ARTICLE

N-Heterocyclic Imine-Stabilized Binuclear Tin(II) Cations: Synthesis, Reactivity, and Catalytic Application

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Dedicated to Professor Cameron Jones on the occasion of his 60th birthday

The reaction of Cp*Sn[OTf] (Cp*=C_5Me_5; OTf=O_3SCF_3) with one equivalent of IPrNLi (IPrN=bis(2,6-diisopropylphenyl)imidazolin-2-iminato) resulted in the binuclear [OTf]-bridged tin complex **1**. Similarly, the [BF_4]-bridged bimetallic complex **2** was synthesized by the reaction of Cp*Sn[BF_4] with IPrNLi (1 eq.). It was also possible to prepare **1** from **2** via an anion exchange reaction. The high-yield conversion of **2** into the binuclear iodostannylene [IPrNSnI]_2 **3** was accomplished by treatment with LiI. The catalytic potential of **1** and **2** was demonstrated in the hydroboration of carbonyls.

Introduction

Low-valent tin cations have attracted wide interest in inorganic and organometallic chemistry due to their intriguing electronic structure and their capability to activate small molecules akin to transition metals.[1] Monovalent tin(II) cations, featuring a lone pair of electrons and two vacant *p*-orbitals at the tin center (stannyliumylidenes [R–Sn:]+), combine the properties of stannylenes and stannylium ions, thereby exhibiting both electrophilic and nucleophilic character (Figure 1, top).[1a] Owing to their high reactivity, stannyliumylidenes have been utilized in the activation of small molecules,[1g] and have shown potential as Lewis acidic catalysts in the hydrosilylation of alkenes and alkynes.[1h]

Since the seminal reports of Jutzi and coworkers on half-sandwich stannocene cations (**A**, Figure 1),[2] only a handful of examples of monomeric tin cations stabilized by suitable donor ligands have been reported. For it to be possible to isolate stable Sn(II) cations several groups have utilized various mono-anionic bulky N-donor ligands, such as aminotroponiminato (**B**),[3] β-diketiminato (**C**),[4] diaminopyridine (**D**),[5] and monoami-

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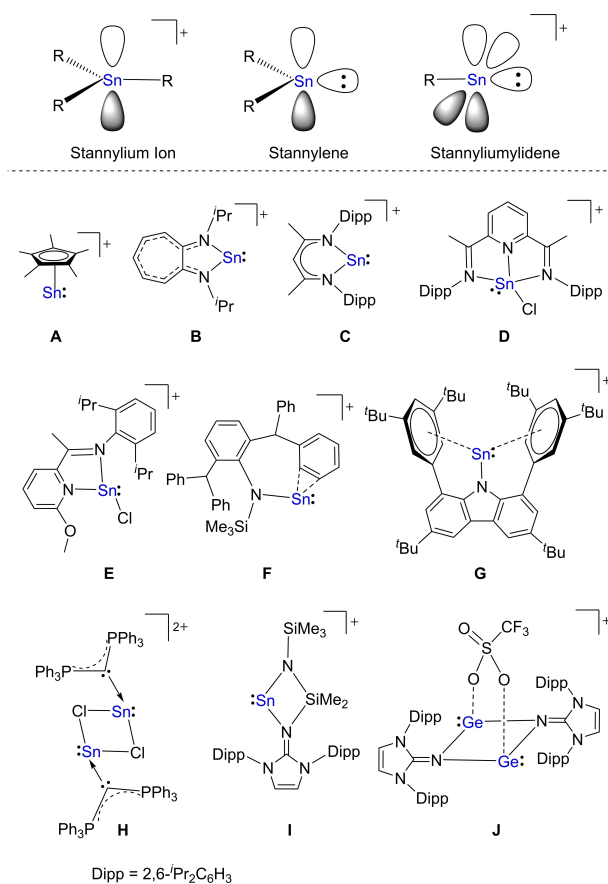Garching bei München (Germany)
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Figure 1. Low-valent tin compounds (top), and selected examples of low-valent tin cations, as well as the triflate-bridged germanium complex **J** (bottom).

nopyridine (**E**).[6] In 2012, the groups of Jones and Krossing reported the extremely bulky amido-tin(II) cation (**F**), which is intramolecularly stabilized by weak η^2-arene interactions.[7] More recently, the pseudo-one-coordinated Sn(II) cation (**G**) stabilized by a bulky carbazolyl moiety was reported by Hinz.[8]

The dimeric tin cation [LSnCl]$_2^+$ (**H**, L = hexaphenylcarbodiphosphorane) was isolated by Alcarazo and coworkers.[9] Compounds **F** and **H** readily react with 4-(dimethylamino)pyridine (DMAP) to afford the corresponding adducts, demonstrating their electrophilicity.

Recently, our group has described a variety of *N*-heterocyclic carbene (NHC) or *N*-heterocyclic imine (NHI) stabilized tetryliumylidenes [R−E:]$^+$ (E = Si, Ge, Sn).[10] These low-valent cations exhibit reactivity towards various small molecules (*e.g.* CO_2, H_2O, chalcogens, and coinage metals *etc.*). Moreover, they can be used as versatile catalysts in the cyanosilylation and hydroboration of carbonyls, as well as the reductive *N*-functionalization of amines with CO_2 and silane. We have shown the synthesis of a cyclic tin(II) cation (**I**) from an amino(imino)stannylene (Figure 1).[11] In addition, the imino ligand can also be implemented in the isolation of triflate-bridged germanium complex (**J**),[12] which has significant bis(germyliumylidene) dication character. The non-coordinated counterion (OTf) can be replaced by anion exchange with Na[BAr$^F_4$] [Ar^F = 3,5−(CF$_3$)$_2$−C$_6$H$_3$] or Ag[Al(OR^F)$_4$] [R^F = C(CF$_3$)$_3$]. To expand this chemistry, we were interested in preparing the tin analogues of complex **J** and explore their potential applications in bond activation and catalysis.

Results and Discussion

The reaction of Cp*Sn[OTf] (Cp* = C$_5$Me$_5$; OTf = O$_3$SCF$_3$) with one equivalent of IPrNLi (IPrN = bis(2,6-diisopropylphenyl)imidazolin-2-iminato) in dry THF at −78 °C followed by warming to room temperature gave the binuclear tin complex [IPrNSnOTf]$_2$ **1** in moderate yield (61%; Scheme 1, path **a**). Compound **1** is soluble in CD$_3$CN, but the solubility decreases significantly in THF. Compound **1** was characterized by multinuclear NMR, LIFDI-MS measurements, and elemental analysis (see the Supporting Information for more details). The ^{119}Sn{^{1}H} NMR spectrum of **1** displays a signal at 146.0 ppm in CD$_3$CN, which is downfield shifted in comparison to **I** (33.5 ppm, CD$_3$CN), indicating a more electron-poor Sn(II) center. The NHI backbone signal in the ^{1}H NMR spectrum of **1** (6.88 ppm, CD$_3$CN) is more high-field shifted compared to that of **I** (7.02 ppm, CD$_3$CN). The signals of the Dipp groups are also shifted to higher field than those of **I**.

Single crystal X-ray diffraction (SC-XRD) analysis revealed that **1** contains a planar and rhombic N$_2$Sn$_2$ ring. The triflate group bridges the two tin centers with the formation of two coordinative interactions between the tin centers and two oxygen atoms (see Figure S31). The structural features are very similar to that seen in **J**. However, further structure discussion regarding bond lengths and angles is restricted, due to the poor quality of the obtained data.

In a similar fashion to **1**, the reaction of Cp*Sn[BF$_4$] with IPrNLi (1 eq.) resulted in the [BF$_4$]-bridged binuclear tin complex **2** in 53% yield (Scheme 1, path **b**), which was characterized by multinuclear NMR and elemental analysis (see the Supporting Information for more details). Compound **2** is soluble in polar solvents such as THF and acetonitrile, but dissolves poorly in
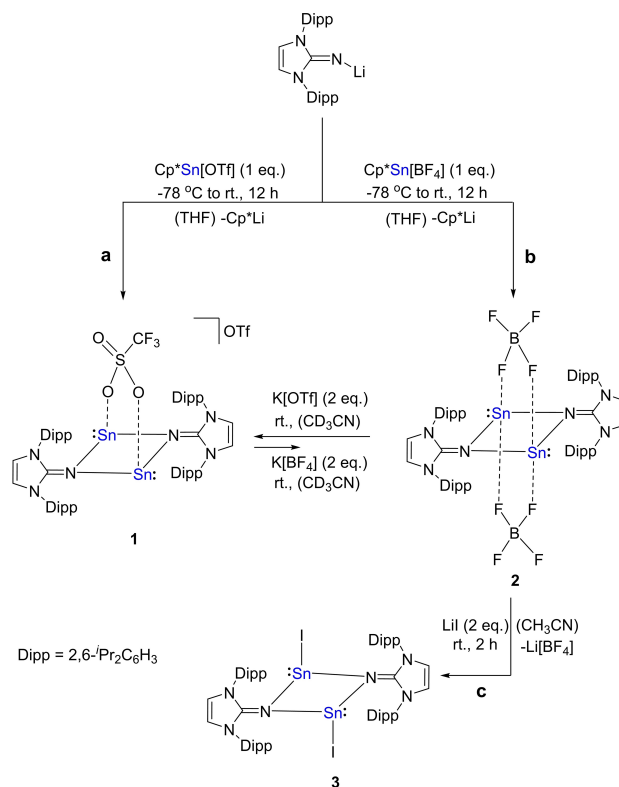
Scheme 1. Synthesis of [OTf]-bridged tin complex **1** and [BF$_4$]-bridged tin complex **2**, as well as anion exchange reactions.

nonpolar hydrocarbons. The ^{119}Sn{^{1}H} NMR spectrum shows a doublet at 81.9 ppm with a $J(^{119}$Sn,^{19}F) value of 610 Hz, which is shifted upfield in comparison to **1** [146.0 ppm, CD$_3$CN], presumably because the electron-donating capacity of the two [BF$_4$] moieties is higher than that of the triflate anion. The low number of signals for the Dipp groups in the ^{1}H NMR spectrum of **2** reflects a more symmetric structure compared to that of **1** in solution (CD$_3$CN). The $J($Sn,F$)$ value is significantly smaller than those for neutral covalently bonded fluorostannanes (2286–2893 Hz),[13] indicating the absence of Sn−F covalent bonding in **2**.

Colorless crystals of **2** were obtained by slow diffusion of Et$_2$O into a saturated THF solution at −30 °C for several days. It crystallizes in the space group $P2_1/n$. SC-XRD analysis of **2** revealed that the molecular structure in the solid state comprises a centrosymmetric dimer, with a planar and rhombic N$_2$Sn$_2$ ring (sum of internal tetragonal angles: 360°, Figure 2). A related structure was observed in the cyclic bis(triflate)dibismadiazane [ArNBiOTf]$_2$ [Ar = 2,6-bis(2,4,6-trimethylphenyl)phenyl], with a planar N$_2$Bi$_2$ ring and two bridging triflate anions.[14] The Sn−N bond lengths (Sn1−N1 2.155(3) Å; Sn1−N1# 2.166(3) Å) are comparable to that in complex **I** (Sn−N$_{imino}$ 2.197(2) Å),[11] in which a high dative bond character between the tin(II) center and the imino-nitrogen atom was reported. The Sn⋯F distance (Sn1⋯F1 2.461(2) Å; Sn1⋯F2# 2.501(2) Å) is significantly longer than those in monomeric fluorostannanes such as Mes$_3$SnF (1.961 Å; Mes =
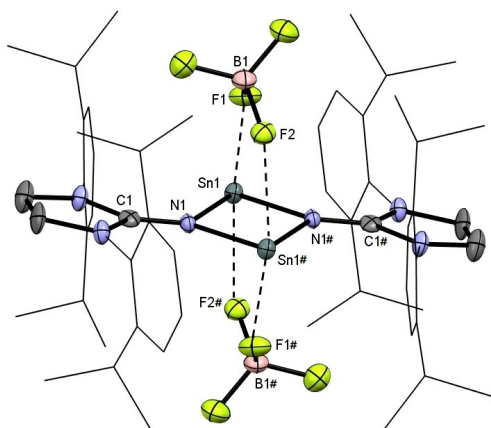
Figure 2. Molecular structure of 2.[17] Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1—N1 2.155(3), Sn1—N1# 2.166(3), Sn1···F1 2.461(2), Sn1···F2# 2.501(2), N1—C1 1.296(4), Sn1—N1—C1 129.1(2), Sn1—N1#—C1# 128.1(2), Sn1—N1—Sn1# 102.1(1), N1—Sn1—N1# 77.9(1).
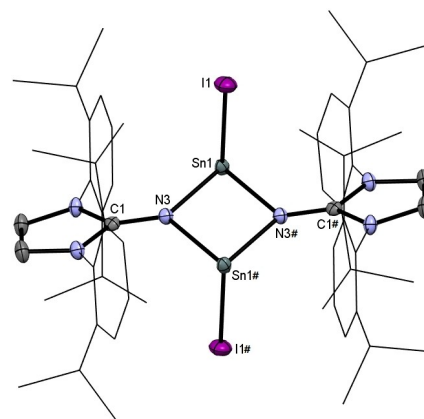

Figure 3. Molecular structure of 3.[17] Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1—I1 2.9176(4), Sn1—N3 2.168(1), Sn1—N3# 2.182(1), N3—C1 1.295(2), I1—Sn1—N3 85.90(4), I1—Sn1—N3# 87.87(4), N3—Sn1—N3# 77.72(5), Sn1—N3—C1 126.4(1), Sn1—N3#—C1# 130.3(1), Sn1—N3—Sn1# 102.28(5).

2,4,6-trimethylphenyl),[13b] TpsiSnMe$_2$F (1.965(2) Å; Tpsi = (PhMe$_2$Si)$_3$C),[13a] and polymeric Me$_2$SnF$_2$ (2.12(1) Å).[13d]

It was also possible to form **1** by the reaction of **2** with K[OTf] (2 eq.) in CD$_3$CN at room temperature, albeit in a product ratio of 73:27 (**1**:**2**), as confirmed by ^{1}H NMR spectroscopy (Scheme 1). In addition, the yields of **1** and **2** did not significantly change when **1** was reacted with two equivalents of K[BF$_4$]. Interestingly, we did not observe the expected BF$_4$/OTf-mixed intermediate in the ^{1}H NMR spectrum.

With compound **2** in hand, we investigated its reactivity towards the nucleophiles Cp*Li, Na$_2$Fe(CO)$_4$, and LiI. No reaction was observed between **2** and Cp*Li (2 eq.) or Na$_2$Fe(CO)$_4$ (1 eq. or 2 eq.) in CD$_3$CN, even at elevated temperatures. The reaction of **2** towards LiI (2 eq.) in CD$_3$CN at room temperature was also performed and the selective formation of the dimeric imino(iodo)stannylene **3** was obtained (Scheme 1, path **c**). Due to its poor solubility in common organic solvents, it was not possible to observe any signals in the ^{119}Sn{^{1}H} NMR spectrum. The NHI backbone signal in the ^{1}H NMR spectrum of **3** (6.34 ppm, CDCl$_3$) is high-field shifted compared to that of **1** (6.88 ppm, CD$_3$CN) and **2** (6.83, CD$_3$CN). It should be noted that the reaction of **1** and LiI (2 eq.) in CD$_3$CN at room temperature led to an undefined product mixture.

Colorless crystals of **3** were obtained from a saturated dichloromethane solution stored at −30°C. Compound **3** crystallizes in the $P2_1/n$ space group. SC-XRD analysis revealed that **3** consists of a centrosymmetric dimer, with a planar and rhombic N$_2$Sn$_2$ ring with two additional terminal iodine atoms (sum of internal tetragonal angles: 360°, Figure 3). The two iodine atoms adopt a *trans* configuration with respect to the N$_2$Sn$_2$ ring. The structural features are very similar to those of iminostannylenes [IPrNSnX] (X = Cl, Br, N$_3$),[11,15] but differ from the dimeric cyclopentadienyl(imino)stannylene [IPrNSn(η^1-Cp)]$_2$ in which the two η^1-Cp ligands have a *cis* orientation with respect to the N$_2$Sn$_2$ ring.[15b] The Sn—N distances of 2.168(1) Å

and 2.182(1) Å are in the range of Sn—N bond lengths reported for halo(imino)stannylenes [IPrNSnX] (X = Cl, Br) [2.161(3)–2.216(4)]. The Sn—I bond in **3** is oriented perpendicularly to both Sn—N bonds, with I1—Sn1—N3 and I1—Sn1—N3# bond angles of 85.90(4)° and 87.87(4)°, respectively.

Next, we examined the reactivity of **2** towards small molecules. Exposure of a CD$_3$CN solution of **2** to an atmosphere of H$_2$ or N$_2$O showed no conversion, even at elevated temperatures. Treatment of **2** with CO$_2$ (1 bar) at room temperature formed an unidentified product mixture. The reaction of **2** with Na[BAr$^F_4$] (1 eq.) in CD$_3$CN at ambient temperature resulted in decomposition containing a large amount of free ligand IPrNH, and other undefined species.

The application of heavy Group 14 compounds in catalytic transformations have garnered much attention in the last decades, with many examples of tetrylenes and tetryliumylidenes being effective as catalysts.[10d,16] Our preliminary study on the catalytic application of complexes **1** and **2** revealed that both complexes catalyze the hydroboration of aldehydes and ketones with pinacolborane (HBpin) (Table 1), with complex **2** having a higher activity. Because of its poor solubility in common organic solvents the catalytic activity of **3** was not examined.

Various aldehydes and ketones were screened for the hydroboration reaction catalyzed by **1** or **2** (Table 1). The reduction of benzaldehyde in the presence of 0.5 mol% of **1** was completed within 5 hours, whereas a shorter reaction time of only 0.5 h was observed when using the same loading of **2**. The reaction proceeds with a lower catalyst loading than those previously reported for neutral bis-amido tin catalysts in which 2 mol% catalyst loading in toluene at room temperature gave a conversion of 80~87% within 4–6 h.[16f] However, the catalytic activity is less efficient than other tin examples.[16a] It should be noted that both **1** and **2** are much more effective in the hydroboration of benzaldehyde compared to Na[BF$_4$] and K[OTf]

Table 1. Hydroboration of aldehydes and ketones with pinacol-borane (HBpin), catalyzed by **1** or **2**.[a]

Entry	Substrate	Cat.	Loading, mol %	Conv.,[b] %	Time, h
1	PhCHO	**1**	0.5	99	5
2	PhCHO	**2**	0.5	95	0.5
3	isobutyraldehyde	**2**	0.5	99	2
4	4-MeO-C6H4CHO	**2**	0.5	84	120
5	mesitaldehyde	**2**	0.5	99	36
6	acetophenone	**2**	5	83	19
7	benzophenone	**2**	5	99	156
8	PhCHO	Na[BF4]	0.5	63	24
9	PhCHO	K[OTf]	0.5	36	24

[a] All reactions were carried out with 1.0 mmol of carbonyl compounds, 1.0 mmol of HBpin, in CD_3CN (0.4 mL) at room temperature. [b] NMR yield.

(Table 1, entries 8 and 9). When isobutyraldehyde was used as the substrate, full conversion was observed after 2 h when using compound **2** (Table 1, entry 3). Substituted aromatic aldehydes with electron-donating groups (Table 1, entries 4 and 5) resulted in high yields, however longer reaction times were needed. The hydroboration of aromatic ketones was also possible utilizing **2** (Table 1, entries 6 and 7). In these cases, higher catalyst concentration was necessary to obtain satisfactory yields, compared to the reduction of aldehydes. Reduction of acetophenone in the presence of 5 mol % of **2** was completed within 19 h whereas for benzophenone, a longer reaction time was needed (Table 1, entry 7).

Conclusions

In summary, we have reported on the synthesis of the [OTf]- and [BF4]-bridged binuclear tin complexes **1** and **2**, with a planar and rhombic N_2Sn_2 ring. Complex **2** reacts with LiI to afford the dimeric iodostannylene [IPrNSnI]2 **3**. Notably, complex **2** showed higher catalytic activity in the hydroboration of aldehydes and ketones than that of the complex **1**. The further

reactivity and catalytic applications of these low-valent tin cations are currently under investigation.

Experimental Section

General Considerations

All experiments and manipulations were carried out under a dry oxygen-free argon atmosphere using standard Schlenk techniques or in a glovebox. All glass junctions were coated with PTFE-based grease, Merkel Triboflon III. All the solvents were dried and freshly distilled under Ar atmosphere prior to use by standard techniques. The ^1H, ^{19}F, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$ and $^{119}Sn\{^1H\}$ NMR spectra were recorded on Bruker 400 MHz spectrometer. Chemical shifts are referenced to (residual) solvent signals (CD_3CN: $\delta(^1H) = 1.94$ ppm and $\delta(^{13}C) = 1.32$ ppm; $CDCl_3$: $\delta(^1H) = 7.26$ ppm and $\delta(^{13}C) = 77.16$ ppm). Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet. Elemental analysis (EA) was conducted with a EURO EA (HEKA tech) instrument equipped with a CHNS combustion analyzer. Liquid Injection Field Desorption Ionization Mass Spectrometry (LIFDI-MS) was measured directly from an inert atmosphere glovebox with a Thermo Fisher Scientific Exactive Plus Orbitrap equipped with an ion source from Linden CMS. Unless otherwise stated, all commercially available chemicals were purchased from *abcr GmbH*, *Sigma-Aldrich Chemie GmbH* or *Tokyo Chemical Industry Co., Ltd.*, and used without further purification. The starting materials IPrNLi (IPrN = bis(2,6-diisopropylphenyl)imidazolin-2-imino),[18] Cp*Sn[BF4],[2b] and Cp*Sn[OTf],[2c] were prepared according to the literature procedures, respectively.

Synthesis of [IPrNSnOTf]2, (1)

IPrNLi (203 mg, 496 μmol) dissolved in THF (6 mL) was added dropwise to a solution of Cp*Sn[OTf] (200 mg, 496 μmol, 1.0 eq.) in THF (4 mL) at −78°C. The reaction mixture was stirred for 12 h followed by warming to room temperature. The solvent was removed *in vacuo* and the solid residue was washed with toluene (5 mL×3) and dried *in vacuo* to give pure **1** (180 mg, 61%) as a white powder. Colorless crystals of **1** suitable for single crystal X-ray analysis were obtained from a saturated solution in CD_3CN at −30°C for several days.

^1H NMR (400 MHz, CD_3CN) $\delta = 7.42$ (t, $J = 7.7$ Hz, 4H, Ar$\underline{H}$), 7.29 (d, $J = 7.7$ Hz, 8H, Ar$\underline{H}$), 6.88 (s, 4H, NC$\underline{H}$), 2.67–2.56 (m, 8H, C$\underline{H}$(CH3)2), 1.21 (d, $J = 6.8$ Hz, 24H, CH(C$\underline{H}$3)2), 1.09 (d, $J = 6.8$ Hz, 24H, CH(C$\underline{H}$3)2).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN) $\delta = 153.3$ (N$\underline{C}$N), 148.5 (N$\underline{C}$Ar), 133.4 (Ar$\underline{C}$), 132.9 (Ar$\underline{C}$), 129.9 (Ar$\underline{C}$), 129.2 (Ar$\underline{C}$), 127.5 (Ar$\underline{C}$), 126.3 (Ar$\underline{C}$), 118.3 (N$\underline{C}$H), 68.3 (SO3$\underline{C}$F3), 29.4 ($\underline{C}$H(CH3)2), 26.2 (CH($\underline{C}$H3)2), 25.7 (CH($\underline{C}$H3)2), 23.1 (CH($\underline{C}$H3)2), 21.5 (CH($\underline{C}$H3)2).

$^{119}Sn\{^1H\}$ NMR (149 MHz, CD_3CN) $\delta = 146.0$.

^{19}F NMR (376 MHz, CD_3CN) $\delta = -79.4$.

Anal. Calcd. [%] for $C_{56}H_{72}F_6N_6O_6S_2Sn_2$: C, 50.17; H, 5.41; N, 6.27. Found [%]: C, 50.10; H, 5.48; N, 6.35.

LIFDI-MS (positive ion mode): calculated for $[M-OTf]^+$: 1193.33826. Found: 1193.32344.

Synthesis of [IPrNSnBF4]2, (2)

IPrNLi (223 mg, 543 μmol) dissolved in THF (6 mL) was added dropwise to a solution of Cp*Sn[BF4] (185 mg, 543 μmol, 1.0 eq.) in THF (4 mL) at −78°C. The reaction mixture was stirred for 12 h

followed by warming to room temperature. The solvent was removed *in vacuo* and the solid residue was washed with toluene (5 mL×3) and dried *in vacuo* to give pure **2** (174 mg, 53%) as a white powder. Colorless crystals of **2** suitable for single crystal X-ray analysis were obtained by slow diffusion of Et$_2$O into a saturated THF solution at −30°C for several days.

^{1}H NMR (400 MHz, CD$_3$CN) δ = 7.43 (t, *J* = 7.7 Hz, 4H, Ar*H*), 7.26 (d, *J* = 7.7 Hz, 8H, Ar*H*), 6.83 (s, 4H, NC*H*), 2.60 (septet, *J* = 6.8 Hz, 8H, C*H*(CH$_3$)$_2$), 1.12 (d, *J* = 6.8 Hz, 48H, CH(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, CD$_3$CN) δ = 152.4 (N*C*N), 148.3 (N*C*Ar), 133.0 (Ar*C*), 132.4 (Ar*C*), 130.0 (Ar*C*), 129.3 (Ar*C*), 127.0 (Ar*C*), 126.3 (Ar*C*), 125.5 (Ar*C*), 117.4 (N*C*H), 29.8 (*C*H(CH$_3$)$_2$), 25.0 (CH(*C*H$_3$)$_2$), 23.4 (CH(*C*H$_3$)$_2$).

^{119}Sn{^{1}H} NMR (149 MHz, CD$_3$CN) δ = 81.9 (d, *J* = 609.9 Hz).

^{11}B{^{1}H} NMR (128 MHz, CD$_3$CN) δ = −1.2.

^{19}F NMR (376 MHz, CD$_3$CN) δ = −41.2 (Sn*F*), −152.5.

Anal. Calcd. [%] for C$_{54}$H$_{72}$B$_2$F$_8$N$_6$Sn$_2$: C, 53.33; H, 5.97; N, 6.91. Found [%]: C, 53.26; H, 6.05; N, 7.00.

Synthesis of [IPrNSnI]$_2$, (3)

LiI (11 mg, 82 μmol, 2.0 eq.) dissolved in CH$_3$CN (2 mL) was added dropwise to a solution of **2** (50 mg, 41 μmol, 1.0 eq.) in CH$_3$CN (4 mL) at room temperature. The reaction mixture was stirred for 2 h. The volatiles were removed *in vacuo* and the solid residue was dissolved in dichloromethane (DCM) and the solution was concentrated by slow evaporation of the solvent until formation of the crystalline product commenced. The crystals were separated from the liquid phase to afford colorless **3** after drying *in vacuo* (41 mg, 76%).

^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.27 (t, *J* = 7.7 Hz, 4H, Ar*H*), 7.12 (d, *J* = 7.7 Hz, 8H, Ar*H*), 6.34 (s, 4H, NC*H*), 3.22–3.17 (m, 8H, C*H*(CH$_3$)$_2$), 1.39 (d, *J* = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.04 (d, *J* = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ = 148.3 (N*C*N), 133.1 (Ar*C*), 130.6 (Ar*C*), 124.9 (Ar*C*), 116.6 (N*C*H), 28.3 (*C*H(CH$_3$)$_2$), 26.1 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$).

Anal. Calcd. [%] for C$_{54}$H$_{72}$I$_2$N$_6$Sn$_2$: C, 50.03; H, 5.60; N, 6.48. Found [%]: C, 49.96; H, 5.68; N, 6.56.

Electronic Supporting Information available: NMR spectra, crystallographic details including ORTEP representations, and catalysis studies details.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: anion exchange · catalysis · hydroboration · stannylene · stannyliumylidene

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