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Synthesis of a cyclopentadienyl(imino)stannylene and its direct conversion into halo(imino) stannylenes†

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The reaction of stannocene Cp_2Sn with iminolithium LiNIPr (NIPr = bis(2,6-diisopropylphenyl)imidazolin-2-iminato) afforded the dimeric cyclopentadienyl(imino)stannylene $[(\eta^1\text{-Cp})SnNIPr]_2$ (**1**). Compound **1** exhibits unexpected reactivity towards haloalkanes. The high-yield conversion of **1** into chlorostannylene $[ClSnNIPr]_2$ (**2**) and bromostannylene $[BrSnNIPr]_2$ (**3**) were accomplished by treatment with dichloromethane or 1,2-dibromoethane, respectively, through a Cp-substitution reaction.

Low-valent and low-coordinate group 14 compounds have been of great interest in main group chemistry and much attention has been paid to this compound class over the last several decades. Since the first monomeric diaminostannylene $[Sn(N(SiMe_3)_2)_2]$ **I** was published in 1974 (Fig. 1),[1] numerous compounds with a divalent tin center have been reported.[2] At the same time, the chemistry of stannocenes that are tin(II) analogues of metallocenes, has been intensively studied by the group of Jutzi, and others.[3] It is noteworthy that Cp_2Sn converted into cyclopentadienylchlorostannylene [CpSnCl] by disproportionation of stannocene with $SnCl_2$.[4] Chlorostannylene can be used as a starting material for a novel low-valent organotin compounds. Although transition metal complexes with cyclopentadienyl ligand(s) are the most studied organometallic compound class, the field of low-valent half sandwich Sn(II) species has not been fully developed so far.[5] For example, Wright and co-workers reported the synthesis and isolation of the Cp-substituted stannylene dimmer $([(\eta^3\text{-Cp})SnNC(NMe)_2]_2)$ **II** (Cp = C_5H_5) by the direct substitution of Cp_2Sn with $LiNC(NMe_3)_2$ (Fig. 1).[5a] Furthermore, Power and co-workers reported the Cp-substituted arylstannylene **III** by C–H activation of cycloalkene with distannyne (Fig. 1).[5h] Due to the π-electron donating nature of Cp ligand, Cp-substituted stannylenes possess an electron rich tin(II) center that may show unique reactivity towards organic molecules. Yet, remarkably little is known about the reactivity of Cp-substituted tin derivatives. The Cp ligand in **II** could be replaced with lithiated 1,3-dithianes as nucleophiles.[6] Development of a novel method for the facile access to halogenated stannylenes from a Cp-substituted stannylene would be of great importance because they could be suitable precursors for novel functionalized tin(II) compounds through nucleophilic substitutions.

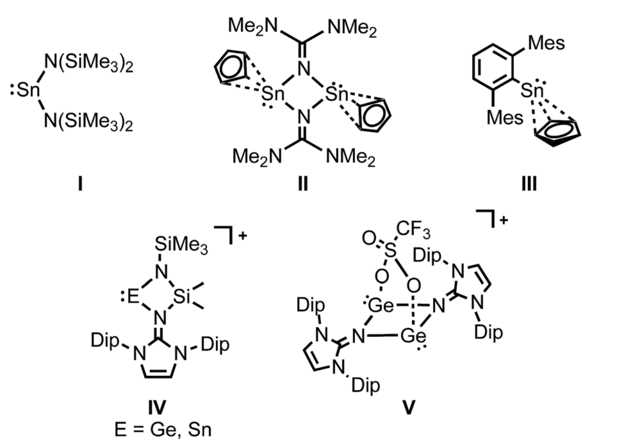

Fig. 1 Selected tin(II) compounds I–III (top) and metallyliumylidenes IV and V (bottom).

It has been shown that imidazolin-2-imino ligands, namely N-heterocyclic imines (NHIs), can be employed as ligands for a variety of transition-metal complexes.[7] Also, by the use of this ligand system, a number of fascinating main group element complexes[8] (boron,[9] aluminium,[10] silicon,[11] germanium,[12] tin,[13] and phosphorus[14]) have been reported. For instance, our group recently developed a new straightforward method for synthesizing Ge(II)[12b] and Sn(II)[13a] cations **IV** (Fig. 1). Furthermore, this ligand can also be implemented for the isolation of new triflate-coordinate bis(germyliumylidene) **V** (Fig. 1),[12c] ascribed to a combination of a strong electron-donating effect and

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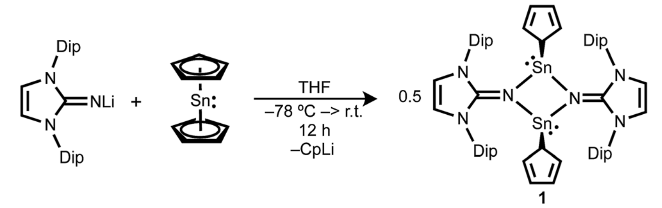


Scheme 1 Synthesis of **1** $[CpSnNIPr]_2$ (Dip = 2,6-diisopropylphenyl).

a delocalization of a positive charge. Herein we describe the synthesis and structure of the Cp-substituted iminostannylene **1** as well as its unusual reactivity toward haloalkanes.

The reaction of Cp_2Sn with one equivalent of LiNIPr (NIPr = bis(2,6-diisopropylphenyl)imidazolin-2-iminato) in THF affords the dimeric cyclopentadienyl(imino)stannylene $[(\eta^1\text{-Cp})SnNIPr]_2$ (**1**) (Scheme 1). The formation of **1** was confirmed by multinuclear NMR spectroscopy, high resolution mass spectrometry and single-crystal X-ray diffraction data (Fig. 2).

The molecular structure of **1** consists of a nearly centrosymmetric dimer arrangement with a nearly planar Sn_2N_2 core (the sum of internal tetragonal angles = 358.2°) protected by two bulky IPr groups. The imino groups bridge the two Sn centers almost symmetrically in the Sn_2N_2 ring (Sn(1)–N(1) 2.227(7) Å, Sn(1)–N(4) 2.220(7) Å, Sn(2)–N(1) 2.193(7) Å, Sn(2)–N(1) 2.222(7) Å), which defines the presence of strong N → Sn interaction. These values are slightly elongated in comparison to the corresponding values of azido- (av. 2.186(3) Å), and chlorostannylene (av. 2.198(5) Å) analogues,[13b] probably owing to the more sterically crowded environment on the Sn atoms in **1**. Unlike other imino-substituted tin(II) dimers ($[XSnNIPr]_2$, X = N_3, Cl),[13] the terminal η^1-Cp ligands have a *cis* orientation with respect to the Sn_2N_2 ring for **1**. The C–N distances in the imidazoline fragment (1.287(12), 1.297(12) Å) are typical for a carbon–nitrogen double bond.[15]

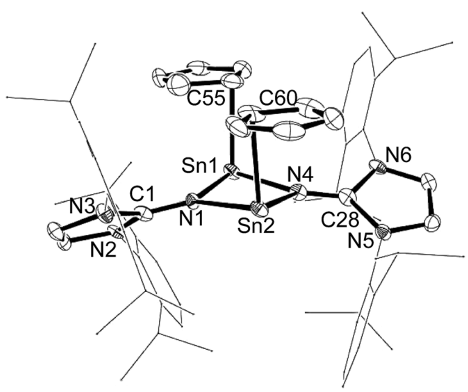


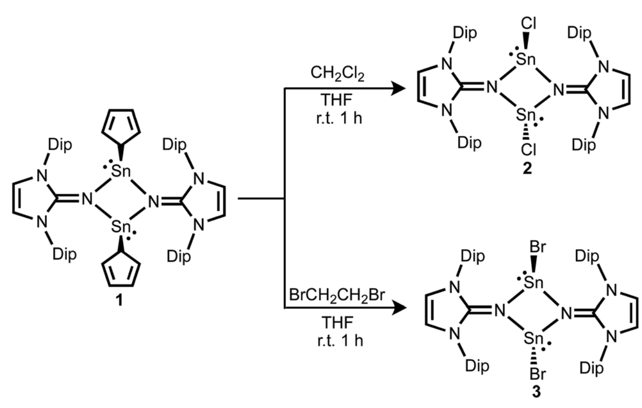
Fig. 2 ORTEP representation of the molecular structure of **1** in the solid state. Thermal ellipsoids are at the 40% probability level. Hydrogen atoms are omitted for clarity. Dip groups are depicted as wireframes. Selected bond lengths (Å) and bond angles (deg): Sn1–N4 2.220(7), Sn1–N1 2.227(7), Sn2–N1 2.193(7), Sn2–N4 2.222(7), Sn1–C55 2.442(10), Sn2–C60 2.438(10), N1–C1 1.287(12), N2–C1 1.414(11), N3–C1 1.398(12), N4–C28 1.297(12), N5–C28 1.392(12), N6–C28 1.412(12); N4–Sn1–N1 76.9(3), N1–Sn2–N4 77.6(3), Sn2–N1–Sn1 102.2(3), Sn1–N4–Sn2 101.5(8), N4–Sn1–C55 96.3(3), N1–Sn1–C55 99.0(4), N1–Sn2–C60 93.7(3), N4–Sn2–C60 97.9(4).

The asymmetric coordination mode of Cp ligands found in the solid structure of **1** is not reflected by the solution-state ^{1}H NMR measurements, where a single resonance for the Cp ring is observed at 5.66 ppm. This data clearly shows that **1** exhibits fluxional behaviour of a Cp ligand in a solution. In sharp contrast to **II**, compound **1** does not exist in equilibrium between the *cis* and *trans* Cp isomers in the solution. The ^{119}Sn NMR spectrum displays a singlet at −232 ppm. This resonance is low field shifted compared to that of stannocene (δ = −2199 ppm),[16] but is high field shifted than that of the stannylene **III** (δ = 94 ppm)[5h] probably due to the dimeric form of **1**.

To take a closer look at the overall electronic nature of **1**, DFT calculations for **1** were carried out using the B3LYP theory level with the def2-SVP basis set. The optimized structure closely reproduced the experimentally observed structure of **1**. The frontier molecular orbitals of **1** show that the HOMO corresponds to the Sn lone-pair electrons, while the LUMO is the π*-orbital of the Dip groups in the imidazoline ligands (Fig. S13†).

The reactivity of bis(amino)stannylene $[Sn(N(SiMe_3)_2)_2]$ **I** towards halogenated substrates has been thoroughly investigated by Lappert and co-workers.[17] The oxidative addition of **I** with haloalkanes was found to proceed *via* an electron transfer reaction between the stannylene and the substrate, followed by abstraction of the halide to leave the tin and alkyl radicals, which act as the propagating species in a radical chain reaction.[17] In sharp contrast, the study of half-sandwich stannylenes has been limited so far. This motivated us to explore the reactivity of **1** bearing both Cp as well as imino ligand.

The stannylene **1** readily reacts with CH_2Cl_2 or $BrCH_2CH_2Br$, producing the halogenated compounds $[ClSnNIPr]_2$ **2** and $[BrSnNIPr]_2$ **3**, respectively (Scheme 2). This reaction is thought to be the substitution of Cp ligand by halide of the substrates. While the arene elimination at the tin(II) center of stannylene instigated by hydrogen or ammonia was investigated both experimentally and theoretically,[18] the observed reaction is a rare example of a direct transformation of metallylenes to halometallylenes using haloalkanes.[19] This is in sharp contrast to that of $[Sn(N(SiMe_3)_2)_2]$ **I**, which undergoes oxidative addition.[17] The identity of the chlorostannylene dimer **2** was



Scheme 2 Synthesis of **2** and **3**.

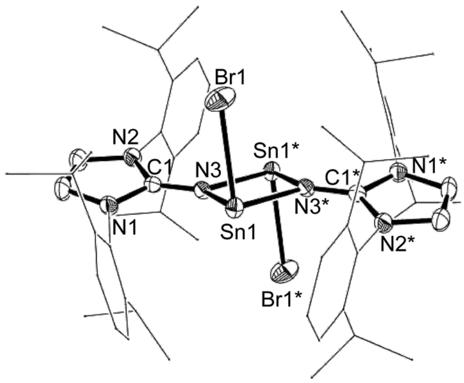


Fig. 3 ORTEP representation of the molecular structure of the cation of **3** in the solid state. Thermal ellipsoids are at the 40% probability level. Dip groups are depicted as wireframes. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Sn1–N3 2.185(3), Sn1–N3* 2.161(3), Sn1–Br1 2.6933(6), C1–N1 1.378(5), C1–N2 1.410(5), C1–N3 1.302(5); N3–Sn1–N3* 77.53(12), Sn1–N3–Sn1* 102.47(11), N3–Sn1–Br1 86.93(7), N3*–Sn1–Br1 89.65(8).

confirmed by comparison of the NMR spectra to literature data.[13b] The bromostannylene **3** has been characterized by high-resolution mass spectrum, NMR spectroscopy and X-ray structure analysis. The ^{119}Sn NMR spectrum of **3** exhibits a singlet resonance at −88 ppm, which is low-field shifted by the chloride analogue **2** (−125 ppm) owing to the lower electronegativity of Br than Cl. The X-ray single-crystal structure of **3** revealed a four-membered Sn_2N_2 ring with two additional terminal bromine atoms. The bromine and tin atoms in **3** are disordered and only one component is shown in Fig. 3. The internal ring angle at the tin is 77.53(12)°, and that at nitrogen average 102.47(11)°. The average Sn–N bond length (2.173(3) Å) is shorter than those in **1** (2.216(7) Å) and **2** (2.198(5) Å). Akin to **2**, the halide moieties of **3** adopt a *trans* configuration with respect to the Sn_2N_2 ring after substitution of the Cp ligands. The Sn–Br bond in **3** is oriented nearly perpendicular to both Sn–N bonds, with Br1–Sn1–N1 and Br1–Sn1–N2 bond angles of 89.65(8)° and 86.93(7)°, respectively, which are comparable to those in **2** (average 87.72(15)°).

The relative energy calculations for the *cis*/*trans* isomers of $[(\eta^1\text{-Cp})SnNIPr]_2$ **1** and $[ClSnNIPr]_2$ **2** were carried out. The *cis* isomer of **1** is thermodynamically more stable than the *trans* isomer by 1.2 kcal mol^{-1} calculated at the B3LYP/def2-SVP level of theory. In contrast, the calculation shows that *trans*-$[ClSnNIPr]_2$ is more stable compared to *cis*-$[ClSnNIPr]_2$ in **2** by 6.2 kcal mol^{-1}. Although energy differences for these isomers were not large, this theoretical study is consistent with the experimental observations, demonstrating that the *cis*/*trans* conformation of the dimeric iminostannylenes deeply depends on the steric factors of the substituents.

Conclusions

In summary, we report the synthesis and characterization of a Cp-substituted iminostannylene **1**. In addition, we have shown its reactivity toward haloalkanes, resulting in the C–E (E = Cl, Br) bond cleavage reaction as well as substitution reaction of the Cp group by the halides. This methathesis reaction afforded the dimeric organotin(II) halides **2** and **3** in high yield. We are currently investigating other small molecules activation such as O_2, CO_2 and N_2O by using dimeric tin(II) compounds **1–3** and preparing novel four-membered stannylenes by nuclephiric addition or halide abstraction reaction of halogen-substituted stannylens **2** and **3**.

Acknowledgements

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