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To Rearrange or not to Rearrange: Reactivity of NHCs towards Chloro- and Hydrostannanes R_2SnCl_2 (R = Me, Ph) and Ph_3SnH

Heidi Schneider,[a] Mirjam J. Krahfuß,[a] and Udo Radius*[a]

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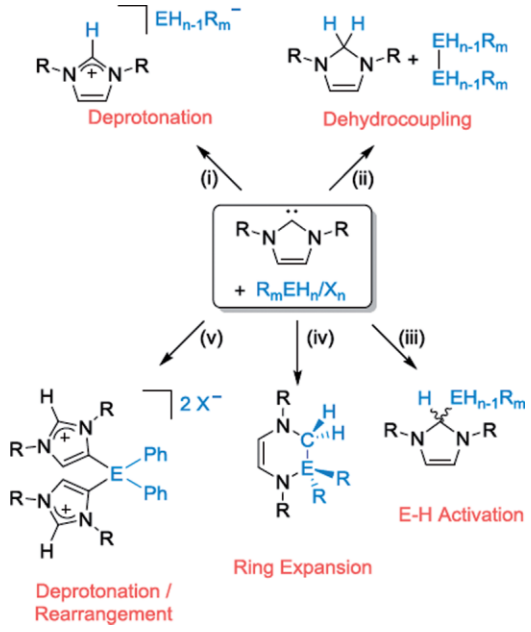
Abstract. The reaction of 1,3-di*iso*propylimidazolin-2-ylidene (iPr$_2$Im) with diphenyldichlorostannane and dimethyldichlorostannane, respectively, leads to the formation of the adducts (iPr$_2$Im)·SnPh$_2$Cl$_2$ (**1**) and (iPr$_2$Im)·SnMe$_2$Cl$_2$ (**2**). These compounds are stable in solution to temperatures up to 80 °C for several days and rearrangement to backbone-tethered bis(imidazolium) salts or ring expansion reaction to six membered heterocyclic rings was not observed. The reaction of iPr$_2$Im with triphenylstannane Ph$_3$SnH leads to reductive dehydrocoupling of the stannane to yield distannane Sn$_2$Ph$_6$ and iPr$_2$ImH$_2$. Thus, the reactivity of these tin compounds is completely different compared to those of the lighter congener silicon, for which rearrangement (chlorides) and NHC ring expansion (hydrides) was reported earlier.

Introduction

The application of *N*-heterocyclic carbenes (NHCs) and related molecules[1] is not restricted to their use as spectator ligands in transition-metal chemistry, as has been shown over the last two decades. The importance of this class of compounds, for example, in main-group element chemistry is constantly growing.[2] Reactions of carbenes even with simple main-group element compounds reveal an enormous richness and lead into a variety of reaction pathways.[3] In dependence on the nature of the main-group element compound, and on the electronic and steric properties of the carbene used, different reactivity may be observed. This can be exemplified for the reactions of singlet carbenes with main-group element hydrides (Scheme 1). Because of the basic character of carbenes, the reaction with (even rather weak) Brønsted acids like alcohols or hydrogen halides leads to deprotonation of the substrate with formation of the corresponding imidazolium salt [Scheme 1 (i)].[4] In contrast, the reaction of NHCs with less acidic and more basic element hydrides leads to a completely different reaction pattern. We have shown for group 15 element hydrides, for example, that secondary and primary phosphines may be converted with NHCs into diphosphines or cyclooligophosphines by reductive dehydrocoupling, using the carbenes as *E*–H activator and hydrogen acceptor [Scheme 1 (ii)].[5] Furthermore, we and others have shown that NHCs and related molecules such as CAACs and diamidocarbenes can activate element hydrogen bonds, for example in boranes (B–H), silanes (Si–H), and phosphines (P–H) [Scheme 1 (iii)].[6] Singlet ground state carbenes possess an energetically high lying occupied donor orbital and an accessible unoccupied acceptor orbital located at the carbene carbon atom, which makes them – similar to most of the transition metal complexes – to *Lewis* acids and *Lewis* bases in one molecule.[1] Thus, they are capable to undergo oxidative addition reactions of non-polar element hydride bonds.



Scheme 1. NHC-mediated reactions of main-group element hydrogen compounds.

In addition, ring expansion reactions (RER) of NHCs have been established for certain group 2, 13, and 14 hydrides over the last few years [Scheme 1 (iv)]. It has been demonstrated that these RERs follow *E*–H bond activation reactions at higher temperatures, for example for element hydrides of beryllium, boron, and silicon.[7] Computational [8] and experimental studies on the mechanism of RERs have shown that the

* Prof. Dr. U. Radius
E-Mail: u.radius@uni-wuerzburg.de
[a] Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland
97074 Würzburg, Germany

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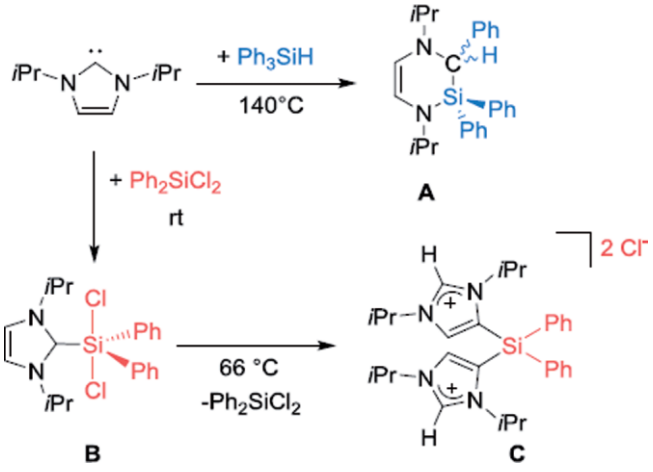
reaction progress can be divided into four steps that include (i) adduct formation between the *Lewis* basic NHC and the *Lewis* acidic element hydride, (ii) hydride migration from the element hydride to the NHC carbene carbon atom (= oxidative addition of *E*–H), (iii) C–N bond cleavage and ring expansion of the NHC with insertion of the main-group element moiety into the NHC ring, and (iv) stabilization of the ring expanded NHC, for example via migration of another hydrogen atom to the (former) NHC carbene carbon atom. For the reaction of iPr$_2$Im (iPr$_2$Im = 1,3-di*iso*propylimidazolin-2-ylidene) with Ph_3SiH, for example, we have isolated and (also structurally) characterized the ring expansion product **A** (Scheme 2).[7c] In contrast to that, we have also shown that the reaction of the NHC iPr$_2$Im with diphenyldichlorosilane Ph_2SiCl_2 enters a completely different pathway and leads to the adduct (iPr$_2$Im)·$SiPh_2Cl_2$ (Scheme 2 **B**), which rearranges to the backbone tethered bis(imidazolium) salt $[(^aHiPr_2Im)_2SiPh_2]^{2+}2Cl^-$ ["a" denotes "abnormal" coordination of the NHC; Scheme 1 (v); Scheme 2 **C**].[9] Although the mechanism of this reaction is not clear yet, we currently assume that the rearrangement from the "normal" to the "abnormal" coordination mode is triggered by protonation/deprotonation steps in (iPr$_2$Im)·$SiPh_2Cl_2$ with concomitant dissociation of a chloride substituent and coordination of a second NHC, which rearranges in turn.

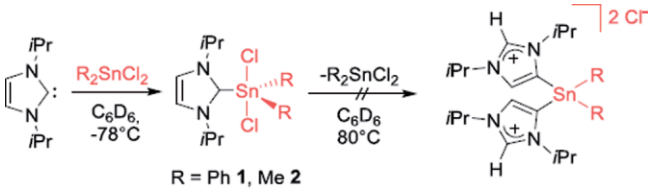


Scheme 2. The reactivity the NHC iPr$_2$Im towards chloro- and hydrosilanes.

Since the investigations in our group have clearly established significant differences in the reactivity of NHCs with silicon hydrides and chlorides, which ended in both cases in novel pathways, we were interested to explore the reactivity of NHCs such as iPr$_2$Im with stannanes and tin chlorides. Some NHC adducts of tin organyl halides are already known,[10] but none of them was tested on their behavior at higher temperatures. It is currently unknown if these molecules rearrange or not. For tin hydrides, *Wesemann* et al. reported the NHC-mediated dehydrocoupling of organotin dihydride (trip)$_2SnH_2$ and trihydride tripSnH_3 with the sterically demanding trip (trip = 2,4,6-tri*iso*propylphenyl) substituent using 1,3-diethyl-4,5-dimethylimidazolin-2-ylidene (Et_2Me_2Im) as the carbene.[11] These reactions led to compounds with Sn–Sn bonds such as trip$_2$(H)Sn–Sn(H)trip$_2$ and Sn_6trip$_6$. We were thus interested in the reactivity of NHCs toward tin hydrides equipped with simple substituents such as methyl or phenyl. Herein, we wish to report first investigations on the reactivity of iPr$_2$Im or iPr$_2$Me$_2$Im with Ph_2SnCl_2, Me_2SnCl_2, and Ph_3SnH.

Results and Discussion

The reactivity of the *N*-heterocyclic carbene iPr$_2$Im with Ph_2SnCl_2 and Me_2SnCl_2 is summarized in Scheme 3. The NHC iPr$_2$Im reacts cleanly at –78 °C in thf or toluene with diphenyldichlorostannane and dimethyldichlorostannane to afford the NHC adducts (iPr$_2$Im)·$SnPh_2Cl_2$ (**1**) and (iPr$_2$Im)·$SnMe_2Cl_2$ (**2**) in form of white solids. Compounds **1** and **2** were isolated in good yield (70 % for **1**, 67 % for **2**) and characterized using multinuclear NMR spectroscopy, elemental analysis and X-ray diffraction. In the ^{13}C NMR spectra of **1** and **2** the resonances of the NHC carbene carbon atoms are significantly high field shifted to 163.7 ppm for (iPr$_2$Im)·$SnPh_2Cl_2$ and to 161.3 ppm for (iPr$_2$Im)·$SnMe_2Cl_2$ compared to iPr$_2$Im (δ = 211.6 ppm). The ^{119}Sn{^{1}H} NMR spectrum of **1** shows in accordance with literature known (iPr$_2$Me$_2$Im)·$SnPh_2Cl_2$ (–314.4 ppm in $CDCl_3$)[10] a resonance at –317.7 ppm (**1**) in deuterobenzene, significantly shifted from the resonance of Ph_2SnCl_2 at –26.4 ppm. The ^{119}Sn NMR spectrum of compound **2** gives rise to a resonance at –227.0 ppm, also shifted from the signal of Me_2SnCl_2 (δ = 139.8 ppm). Signal pattern and the integration of the resonances in the proton NMR account for the coordination of one NHC to the central tin atom via the carbene carbon atom.



Scheme 3. The reactivity of the *N*-heterocyclic carbene iPr$_2$Im with Ph_2SnCl_2 and Me_2SnCl_2.

The molecular structures of compounds **1** and **2** were determined by X-ray diffraction and are presented in Figure 1 and Figure 2. Single crystals of **1** were grown from a saturated *n*-hexane solution of this compound at –30 °C. (iPr$_2$Im)·$SnPh_2Cl_2$ (**1**) crystallizes in the orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit. The central tin atom is distorted trigonal bipyramidal coordinated with two phenyl groups, two chloride substituents, and one NHC ligand. The two chloride atoms occupy the axial positions of the bipyramid, whereas the two phenyl groups and iPr$_2$Im occupy the equatorial positions. The distance between the NHC carbene carbon atom C(1) and the tin atom of 2.1773(19) Å is in perfect agreement with the distance found for (iPr$_2$Me$_2$Im)·$SnPh_2Cl_2$ (2.179(3) Å),[10] the tin aryl and Sn–Cl bond lengths show no significant deviations as well. Both chloride substituents are bend towards the NHC ligand with an angle Cl1–Sn–Cl2 of 163.037(18)°, significantly smaller than 180°.

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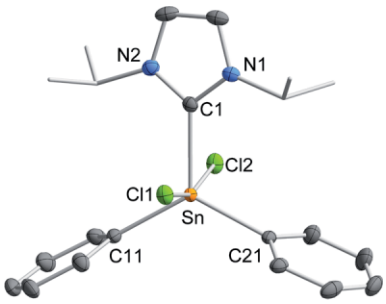


Figure 1. Molecular structure of (iPr$_2$Im)·SnPh$_2$Cl$_2$ (**1**) in the solid state (ellipsoids set at 50 % probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and bond angles /°: Sn–C1 2.1773(19), Sn–C11 2.1454(19), Sn–C21 2.1465(19), Sn–Cl1 2.5479(5), Sn–Cl2 2.5381(5); C1–Sn–C11 119.45(7), C1–Sn–C21 116.47(7), C1–Sn–Cl1 81.50(5), C1–Sn–Cl2 81.54(5), C11–Sn–C21 124.08(7), C11–Sn–Cl1 93.74(8), C11–Sn–Cl2 94.12(8), C21–Sn–Cl1 93.54(8), C21–Sn–Cl2 94.46(8), Cl1–Sn–Cl2 163.034(18).

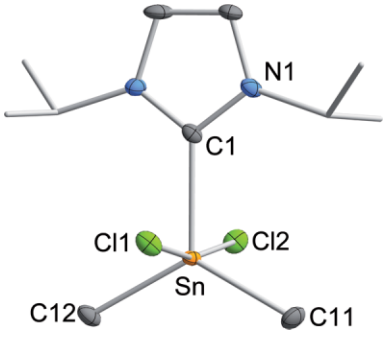
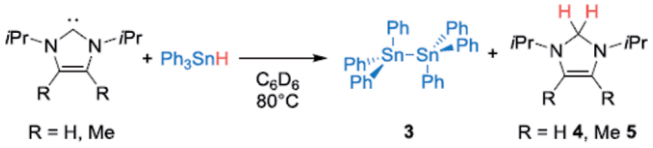


Figure 2. Molecular structure of (iPr$_2$Im)·SnMe$_2$Cl$_2$ **2** in the solid state (ellipsoids set at 50 % probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and bond angles /°: Sn–C1 2.1908(55), Sn–C11 2.1246(62), Sn–C12 2.1293(60), Sn–Cl1 2.5689(16), Sn–Cl2 2.5820(16); C1–Sn–C11 119.424(231), C1–Sn–C12 118.701(213), C1–Sn–Cl1 84.304(157), C1–Sn–Cl2 83.552(145), C11–Sn–C12 121.866(239), C11–Sn–Cl1 94.306(176), C11–Sn–Cl2 91.359(178), C12–Sn–Cl1 92.148(166), C12–Sn–Cl2 93.973(168), Cl1–Sn–Cl2 167.851(45).

Single crystals of **2** suitable for X-ray diffraction were grown by recrystallization from toluene. The adduct (iPr$_2$Im)·SnMe$_2$Cl$_2$ (**2**) crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. Similar to (iPr$_2$Im)·SnPh$_2$Cl$_2$ (**1**), the central tin atom is trigonal bipyramidally surrounded by two methyl groups, two chloride substituents, and the NHC ligand. The NHC–C(1)–Sn distance of 2.1908(55) Å is slightly longer than that of compound **1**, whereas the tin methyl bond lengths as well as the tin chloride bond distances are almost identical to those found for compound **1**. The axially coordinated chloride substituents are also strongly bend towards the NHC ligand with an angle Cl1–Sn–Cl2 of 167.851(46)°. However, the trigonal plane is ideally arranged with a sum of the angles between the equatorial ligands (NHC, and the two methyl groups) of 359.99°.

Compounds **1** and **2** are in contrast to the silicon analogue (iPr$_2$Im)·SiPh$_2$Cl$_2$ readily soluble in solvents like benzene or toluene and are stable even after prolonged heating to the boiling point of these solvents. Continuous heating of solutions of both tin adducts (iPr$_2$Im)·SnPh$_2$Cl$_2$ (**1**) and (iPr$_2$Im)·SnMe$_2$Cl$_2$ (**2**) in thf or benzene for several days to 80 °C did not result in any change of the NMR spectra or formation of any insoluble precipitate. However, small amounts of imidazolium salt [iPr$_2$ImH]$^+$ Cl$^-$ were detected after several days. For (iPr$_2$Im)·SiPh$_2$Cl$_2$ it was observed that [(^{a}HiPr$_2$Im)$_2$SiPh$_2$]$^{2+}$2Cl$^-$ precipitated in form of a white solid at similar conditions.[9] These findings account for a much larger stability of the NHC adducts **1** and **2** of the more *Lewis*-acidic tin compounds R_2SnCl$_2$ compared to the corresponding silicon compound Ph$_2$SiCl$_2$, and thus no transformation of the carbene from its "normal" coordination mode to an "abnormal" coordination mode was detected.

The reaction of triphenylstannane Ph$_3$SnH with iPr$_2$Im or iPr$_2$Me$_2$Im in the stoichiometric ratio of 2:1 for 18 h at 80 °C in benzene or toluene leads with formation of iPr$_2$ImH$_2$ (**4**) or iPr$_2$Me$_2$ImH$_2$ (**5**) to the dehydrocoupling product Ph$_6$Sn$_2$ (**3**) in good yield of 60 % and 69 %, respectively (see Scheme 4). To prove that the reaction pathway is independent on substituents on the backbone, we tested for this reaction both with backbone methylated iPr$_2$Me$_2$Im, as the *Wesemann* group did, and backbone unsubstituted iPr$_2$Im. However, in both cases dehydrocoupling of Ph$_3$SnH to the distannane **3** was observed in quantitative yield, if performed on NMR scale. The distannane **3** was characterized by ^{1}H and ^{119}Sn NMR spectroscopy (resonance at –141.3 ppm for Ph$_6$Sn$_2$ [12]) and elemental analysis. The hydrogenated carbenes, e.g. iPr$_2$ImH$_2$ (**4**) can be easily detected in the proton NMR spectrum. Compound **4** reveals a sharp singlet at δ = 3.98 ppm for the two hydrogen atoms at the former carbene carbon atom. The corresponding septet of the methine protons was detected at δ = 2.48 ppm, resonances for the protons of the backbone of the NHC and the methyl groups of the *iso*propyl arms are observed as a singlet at 5.51 and as a doublet at δ = 0.96 ppm. Similarly, the ^{13}C NMR spectrum reveals a resonance for the methylene unit of iPr$_2$ImH$_2$ (**4**) at δ = 73.9 ppm, significantly shifted from the resonance of the NHC carbene carbon atom of iPr$_2$Im at δ = 211.9 ppm.



Scheme 4. NHC-mediated reductive dehydrocoupling of Ph$_3$SnH to Ph$_6$Sn$_2$ with the NHC as hydrogen acceptor.

No formation of an adduct of the type (iPr$_2$Im)·SnPh$_3$H was observed spectroscopically, neither at room temperature, nor if a stoichiometric ratio Ph$_3$SnH:NHC of 1:1 was used. Also, no ring expanded product was detected for the reaction of iPr$_2$Im with Ph$_3$SnH, which is in significant contrast to the reactivity we have found for the lighter homologue Ph$_3$SiH. Instead, dehydrocoupling of the stannane prevails, which confirms the findings of *Wesemann* et al. on the reactivity of NHC with aryl stannanes with bulky aryl substituents.[11] In dependence on the ratio of carbene to stannane used, *Wesemann's* group detected adduct formation and subsequent dehydrocoupling to

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yield distannane $Sn_2H_2trip_4$ (starting from $trip_2SnH_2$) or tin cluster compounds such as Sn_6trip_6 (starting from $tripSnH_3$). As observed here or for the dehydrocoupling of primary or secondary phosphines the NHC acts simultaneously as Sn–H activator and hydrogen acceptor to form hydrogenated NHC·H_2.

Conclusions

To summarize, we have shown that the reactivity of aryl tin hydrides and aryl tin chlorides with *N*-heterocyclic carbenes such as *i*Pr_2Im differs significantly from the situation we have found for the corresponding silicon compounds.[7c,9] The reaction of Ph_2SiCl_2 with *i*Pr_2Im leads to formation of an adduct (*i*Pr_2Im)·$SiPh_2Cl_2$, which is thermally unstable and rearranges at elevated temperatures to a backbone-silicon-tethered bis(imidazolium) salt. In contrast to this, the novel NHC adducts (*i*Pr_2Im)·SnR_2Cl_2 [*R* = Ph (**1**) Me (**2**)] remain intact upon prolonged heating to higher temperatures over several days, which accounts for a much higher stability of these adducts compared to their silicon analogues. For the reaction of *i*Pr_2Im with the silicon compound Ph_3SiH we have observed ring expansion with incorporation of Ph_2Si into the five membered ring of the NHC before. In sharp contrast to this we report here dehydrocoupling of the tin hydride Ph_3SnH with Sn–Sn bond formation using *i*Pr_2Im as hydrogen acceptor. This interesting reaction seems to be rather general for tin hydrides and has to be exploited in the future.

Experimental Section

General Procedure: All reactions and subsequent manipulations were performed in an argon atmosphere using standard Schlenk techniques.[13] Elemental analysis were performed in the microanalytical laboratory at the department of the University Würzburg with an Elementar vario micro cube. NMR spectra were recorded with a Bruker Avance 400 (^{1}H, 400.4 MHz; ^{13}C, 100.7 MHz; ^{119}Sn, 149.3 MHz), using C_6D_6 as the solvent and referenced to the internal C_6D_5H signal (^{1}H, δ = 7.16, ^{13}C, δ = 128.1 ppm). The NHCs *i*Pr_2Im (1,3-di*iso*propylimidazolin-2-ylidene)[14] and *i*Pr_2Me_2Im (1,3-di*iso*propyl-4,5-dimethylimidazolin-2-ylidene)[15] were prepared according to published procedures. Ph_3SnH was prepared by reduction of Ph_3SnCl with $LiAlH_4$ and purified by fractionated distillation. Ph_2SnCl_2 and Me_2SnCl_2 were purchased from ABCR and used as received.

(*i*Pr_2Im)·$SnPh_2Cl_2$ (1): *i*Pr_2Im (133 mg, 873 µmol) was added at –78 °C to a solution of diphenyldichlorostannane (300 mg, 873 µmol) in thf (20 mL)and allowed to warm up to room temperature overnight. All volatiles were removed in vacuo and the residue was suspended in *n*-hexane (20 mL). The precipitate was filtered off and dried in vacuo to afford 302 mg (609 µmol, yield: 70 %) of a colorless powder. $C_{21}H_{26}Cl_2N_2Sn$ [496.06 g·mol^{-1}]: calcd. (found): C: 50.85 (51.18), H: 5.28 (5.34), N: 5.65 (5.18) %. **^{1}H NMR** (400.4 MHz, C_6D_6, 298 K): δ = 1.32 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, *i*Pr–CH_3), 4.90 (sept, 2 H, $^3J_{HH}$ = 6.7 Hz, *i*Pr–C*H*), 7.31 – 7.40 (m, 6 H, aryl-C*H*), 7.53 (s, 2 H, NC*HCH*N), 8.48 – 8.53 (m, 4 H, aryl-C*H*). **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 22.6 (*i*Pr-*C*H_3), 53.3 (*i*Pr-*C*H), 118.6 (N*CHCH*N), 128.7, 130.0, 137.58 143.0 (aryl-*C*), 163.7 (N*C*N); **^{119}Sn{^{1}H} NMR** (149.3 MHz, C_6D_6, 298 K): δ = –316.7 ppm.

(*i*Pr_2Im)·$SnMe_2Cl_2$ (2): *i*Pr_2Im (209 mg, 1.37 mmol) was added at –78 °C to a solution of dimethyldichlorostannane (300 mg, 1.37 mmol) in thf (20 mL) and allowed to warm up to room temperature overnight. All volatiles were removed in vacuo and the residue was suspended in *n*-hexane (20 mL). The precipitate was filtered off and dried in vacuo to afford 339 mg (911 µmol, yield: 67 %) of a colorless powder. $C_{11}H_{22}Cl_2N_2Sn$ [371.92 g·mol^{-1}]: calcd. (found): C: 35.52 (33.59), H: 5.96 (5.80), N: 7.53 (6.87) %. **^{1}H NMR** (400.4 MHz, C_6D_6, 298 K): δ = 1.16 (s, 6 H, Sn-CH_3), 1.54 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, *i*Pr–CH_3), 5.13 (sept, 2 H, $^3J_{HH}$ = 6.7 Hz, *i*Pr–C*H*), 7.60 (s, 2 H, NC*HCH*N). **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 11.7 (Sn–CH_3), 23.0 (*i*Pr–CH_3), 32.8 (*i*Pr–*C*H), 119.0 (N*CHCH*N), 161.5 (N*C*N). **^{119}Sn{^{1}H}** (149.3 MHz, C_6D_6, 298 K): δ = –227.0 ppm.

Ph_6Sn_2 (3): Synthesis via reaction of Ph_3SnH with *i*Pr_2Im: Triphenylstannane (779 mg, 2.22 mmol) was added at room temperature to a solution of *i*Pr_2Im (169 mg, 1.11 mmol) in toluene (10 mL) and heated to 100 °C for 1 d. During this time a colorless precipitate was formed, which was filtered off, washed with *n*-hexane (5 mL) twice and dried in vacuo to afford 465 mg (664 µmol, yield: 60 %) Ph_6Sn_2 as colorless powder. Synthesis via reaction of Ph_3SnH with *i*Pr_2Me_2Im: Triphenylstannane (779 mg, 2.22 mmol) was added at room temperature to a solution of *i*Pr_2Me_2Im (200 mg, 1.11 mmol) in toluene (10 mL) and heated to 100 °C for 1 d. During this time a colorless precipitate was formed, which was filtered off, washed with *n*-hexane (5 mL) twice and dried in vacuo to afford 537 mg (767 µmol, yield: 69 %) Ph_6Sn_2 in form of a colorless powder. $C_{21}H_{26}Cl_2N_2Sn$ [700.06 g·mol^{-1}]: calcd. (found): C: 61.77 (61.32), H: 4.32 (4.49) %. **^{1}H NMR** (400.4 MHz, C_6D_6, 298 K): δ = 7.08–7.10 (m, 18 H, aryl-C*H*), 7.60–7.74 (m, 12 H, aryl-C*H*). **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 129.2, 137.9, 139.5 (aryl-*C*); **^{119}Sn{^{1}H} NMR** (149.3 MHz, C_6D_6, 298 K): δ = –141.3 ppm.

NMR Spectroscopic Experiments: Conversion of 1 equiv. of *i*Pr_2Im and 2 equiv. of Ph_3SnH in C_6D_6: Triphenylstannane (103 mg, 293 µmol) was added at room temperature to a solution of *i*Pr_2Im (22.0 mg, 145 µmol) in C_6D_6 (700 µL) and heated to 80 °C for 18 h. Identified products: ***i*Pr_2ImH$_2$ (4):** **^{1}H NMR** (400.4 MHz, C_6D_6, 298 K): δ = 0.96 (d, 12 H, $^3J_{HH}$ = 6.4 Hz, *i*Pr-CH_3), 2.48 (sept, 2 H, $^3J_{HH}$ = 6.4 Hz, *i*Pr-C*H*), 3.98 (s, 2 H, NCH_2N), 5.51 (s, 2 H, NC*HCH*N). **^{13}C NMR** (100.7 MHz, C_6D_6, 298 K): δ = 21.1 (*i*Pr-*C*H_3), 52.6 (*i*Pr-*C*H), 73.8 (NCH_2N), 118.5 (N*CHCH*N). **Ph_6Sn_2 (3): ^{1}H NMR** (400.4 MHz, C_6D_6, 298 K): δ = 7.08–7.11 (m, 18 H, aryl-C*H*), 7.60–7.75 (m, 12 H, aryl-C*H*). **^{13}C NMR** (100.7 MHz, C_6D_6, 298 K): δ = 129.2 (aryl-*C*), 137.9 (aryl-*C*), 139.5 (aryl-C_{ipso}). **^{119}Sn{^{1}H} NMR** (149.3 MHz, C_6D_6, 298 K): δ = –141.4. Conversion of 1 equiv. of *i*Pr_2Me_2Im and 2 equiv. of Ph_3SnH in C_6D_6: Triphenylstannane (62.2 mg, 177 µmol) was added at room temperature to a solution of *i*Pr_2Me_2Im (16.0 mg, 88.7 µmol) in C_6D_6 (700 µL) and heated to 80 °C for 18 h. Identified products: ***i*Pr_2Me_2ImH$_2$ (5):** **^{1}H NMR** (400.4 MHz, C_6D_6, 298 K): δ = 0.98 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, *i*Pr–CH_3), 1.61 [s, 6 H, NC(CH_3)C(CH_3)N], 3.32 (sept, 2 H, $^3J_{HH}$ = 6.7 Hz, *i*Pr–C*H*), 4.21 (s, 2 H, NCH_2N). **^{13}C NMR** (100.7 MHz, C_6D_6, 298 K): δ = 18.4 (*i*Pr–*C*H_3), 10.5 [NC(*C*H_3)C(*C*H_3)N], 47.1 (*i*Pr–*C*H), 61.6 (N*C*N), 121.2 (N*CC*N). Ph_6Sn_2 (**3**): vide supra.

Single Crystal X-ray Diffraction: Crystal data of **1** and **2** were collected with a Bruker X8 Apex-II diffractometer with a CCD area detector and graphite- or mirror-monochromated Mo-K_α radiation at 100 K. The structures were solved by intrinsic phasing method (SHELXT) and refined with the SHELXL program.[16] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were assigned to idealized geometric positions.

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Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1496678 (**1**) and CCDC-1496679 (**2**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Crystal Data of (*i*Pr$_2$Im)·SnPh$_2$Cl$_2$ (1): $C_{28}H_{34}N_2Sn$, M_r = 588.16, colorless block, 0.29 × 0.23 × 0.20 mm, orthorhombic space group $P2_12_12_1$, a = 11.5079(6) Å, b = 13.7960(7) Å, c = 17.5383(9) Å, $\alpha = \beta = \gamma = 90°$, V = 2784.4(2) Å^3, T = 100 K, Z = 4, $\rho_{calcd.}$ = 1.403 g·cm^{-3}, μ = 1.127 mm^{-1}, $F(000)$ = 1200, 36338 reflections in h(–14/14), k(–17/17), l(–21/21) measured in the range $1.878° < \theta < 26.073°$, completeness 99.9 %, 5503 independent reflections, 5323 observed reflections [$I > 2\sigma(I)$], 304 parameters, 0 restraints; all data: R_1 = 0.0169 and wR_2 = 0.0419, $I > 2\sigma(I)$: R_1 = 0.0159 and wR_2 = 0.0408, *Goof* 1.048, largest difference peak/hole 0.427/–0.205 e·Å^{-3}.

Crystal Data of (*i*Pr$_2$Im)·SnMe$_2$Cl$_2$ (2): $C_{11}H_{22}N_2Sn$, M_r = 371.89, colorless block, 0.12 × 0.05 × 0.04 mm, monoclinic space group $P2_1/c$, a = 6.5815(13) Å, b = 15.339(3) Å, c = 15.895(3) Å, β = 95.74(3) $\alpha = \gamma = 90°$, V = 1596.6(6) Å^3, T = 100 K, Z = 4, $\rho_{calcd.}$ = 1.547 g·cm^{-3}, μ = 1.915 mm^{-1}, $F(000)$ = 744, 4493 reflections in h(–8/8), k(0/18), l(0/19) measured in the range $1.849° < \theta < 26.019°$, completeness 99.9 %, 4493 independent reflections, 4189 observed reflections [$I > 2\sigma(I)$], 152 parameters, 0 restraints; all data: R_1 = 0.0399 and wR_2 = 0.0767, $I > 2\sigma(I)$: R_1 = 0.0348 and wR_2 = 0.0743, *Goof* 0.839, largest difference peak/hole 0.680/–0.839 e·Å^{-3}.

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References

[1] a) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166–3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; b) O. Schuster, L. Yang, H. G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445–3478; c) J. Vignolle, X. Cattoën, D. Bourissou, *Chem. Rev.* **2009**, *109*, 3333–3384; d) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem.* **2012**, *124*, 8992–9032; *Angew. Chem. Int. Ed.* **2010**, *49*, 8810–8849; e) M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111*, 354–396.

[2] a) Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2007**, *129*, 12412–12413; b) Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer, P. v. R. Schleyer, G. H. Robinson, *Science* **2008**, *321*, 1069–1071; c) A. Sidiropoulos, C. Jones, A. Stasch, S. Klein, G. Frenking, *Angew. Chem.* **2009**, *121*, 9881–9884; *Angew. Chem. Int. Ed.* **2009**, *48*, 9701–9704; d) Y. Wang, G. H. Robinson, *Chem. Commun.* **2009**, 5201–5213; e) Y. Wang, G. H. Robinson, *Inorg. Chem.* **2011**, *50*, 12326–12337; f) H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki, A. Vargas, *Science* **2012**, *336*, 1420–1422; g) Y. Wang, G. H. Robinson, *Dalton Trans.* **2012**, *41*, 337–345; h) H. Braunschweig, R. D. Dewhurst, *Organometallics* **2014**, *33*, 6271–6277.

[3] S. Wurtemberger-Pietsch, U. Radius, T. B. Marder, *Dalton Trans.* **2016**, *45*, 5880–5895.

[4] a) A. C. Filippou, O. Chernov, B. Blom, K. W. Stumpf, G. Schnakenburg, *Chem. Eur. J.* **2010**, *16*, 2866–2872; b) S. Inoue, C. Eisenhut, *J. Am. Chem. Soc.* **2013**, *135*, 18315–18318; c) A. Jana, I. Objartel, H. W. Roesky, D. Stalke, *Inorg. Chem.* **2009**, *48*, 798–800; d) V. Jancik, L. W. Pineda, J. Pinkas, H. W. Roesky, D. Neculai, A. M. Neculai, R. Herbst-Irmer, *Angew. Chem.* **2004**, *116*, 2194–2197; *Angew. Chem. Int. Ed.* **2004**, *43*, 2142–2145; e) L. W. Pineda, V. Jancik, H. W. Roesky, D. Neculai, A. M. Neculai, *Angew. Chem.* **2004**, *116*, 1443–1445; *Angew. Chem. Int. Ed.* **2004**, *43*, 1419–1421.

[5] H. Schneider, D. Schmidt, U. Radius, *Chem. Commun.* **2015**, *51*, 10138–10141.

[6] a) G. D. Frey, V. Lavallo, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Science* **2007**, *316*, 439–441; b) T. W. Hudnall, C. W. Bielawski, *J. Am. Chem. Soc.* **2009**, *131*, 16039–16041; c) G. D. Frey, J. D. Masuda, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2010**, *122*, 9634–9637; *Angew. Chem. Int. Ed.* **2010**, *49*, 9444–9447; d) M. J. Fuchter, *Chem. Eur. J.* **2010**, *16*, 12286–12294; e) T. W. Hudnall, J. P. Moerdyk, C. W. Bielawski, *Chem. Commun.* **2010**, *46*, 4288–4290; f) D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* **2011**, *2*, 389–399; g) D. N. Lastovickova, J. P. Moerdyk, A. R. Kelley, C. W. Bielawski, *J. Phys. Org. Chem.* **2015**, *28*, 75–78; h) D. N. Lastovickova, C. W. Bielawski, *Organometallics* **2016**, *35*, 706–712.

[7] a) S. M. I. Al-Rafia, R. McDonald, M. J. Ferguson, E. Rivard, *Chem. Eur. J.* **2012**, *18*, 13810–13820; b) M. Arrowsmith, M. S. Hill, G. Kociok-Köhn, D. J. MacDougall, M. F. Mahon, *Angew. Chem.* **2012**, *124*, 2140–2142; *Angew. Chem. Int. Ed.* **2012**, *51*, 2098–2100; c) D. Schmidt, J. H. J. Berthel, S. Pietsch, U. Radius, *Angew. Chem.* **2012**, *124*, 9011–9015; *Angew. Chem. Int. Ed.* **2012**, *51*, 8881–8885; d) P. Hemberger, A. Bodi, T. Gerber, M. Würtemberger, U. Radius, *Chem. Eur. J.* **2013**, *19*, 7090–7099; e) D. Franz, S. Inoue, *Chem. Asian J.* **2014**, *9*, 2083–2087; f) T. Wang, D. W. Stephan, *Chem. Eur. J.* **2014**, *20*, 3036–3039; g) P. Hemberger, A. Bodi, J. H. J. Berthel, U. Radius, *Chem. Eur. J.* **2015**, *21*, 1434–1438; h) M. Arrowsmith, M. S. Hill, G. Kociok-Köhn, *Organometallics* **2015**, *34*, 653–662; i) S. Pietsch, U. Paul, I. A. Cade, M. J. Ingleson, U. Radius, T. B. Marder, *Chem. Eur. J.* **2015**, *21*, 9018–9021; j) S. Würtemberger-Pietsch, H. Schneider, T. B. Marder, U. Radius, *Chem. Eur. J.* **2016**, DOI: 10.1002/chem.201603328.

[8] a) K. J. Iversen, D. J. D. Wilson, J. L. Dutton, *Dalton Trans.* **2013**, *42*, 11035–11038; b) K. J. Iversen, D. J. D. Wilson, J. L. Dutton, *Organometallics* **2013**, *32*, 6209–6217; c) M. R. Momeni, E. Rivard, A. Brown, *Organometallics* **2013**, *32*, 6201–6208; d) R. Fang, L. Yang, Q. Wang, *Organometallics* **2014**, *33*, 53–60; e) K. J. Iversen, D. J. D. Wilson, J. L. Dutton, *Dalton Trans.* **2014**, *43*, 12820–12823; f) M.-D. Su, *Inorg. Chem.* **2014**, *53*, 5080–5087; g) K. J. Iversen, D. J. D. Wilson, J. L. Dutton, *Dalton Trans.* **2015**, *44*, 3318–3325.

[9] H. Schneider, D. Schmidt, U. Radius, *Chem. Eur. J.* **2015**, *21*, 2793–2797.

[10] N. Kuhn, T. Kratz, D. Bläser, R. Boese, *Chem. Ber.* **1995**, *128*, 245–250.

[11] a) C. P. Sindlinger, L. Wesemann, *Chem. Sci.* **2014**, *5*, 2739–2746; b) C. P. Sindlinger, W. Grahneis, F. S. W. Aicher, L. Wesemann, *Chem. Eur. J.* **2016**, *22*, 7554–7566.

[12] B. M. Wile, R. McDonald, M. J. Ferguson, M. Stradiotto, *Organometallics* **2005**, *24*, 1959–1965.

[13] J. Attner, U. Radius, *Chem. Eur. J.* **2001**, *7*, 783–790.

[14] a) T. Schaub, U. Radius, A. Brucks, M. P. Choules, M. T. Olsen, T. B. Rauchfuss, *Inorg. Synth.* **2010**, *35*, 5; b) T. Schaub, M. Backes, U. Radius, *Organometallics* **2006**, *25*, 4196–4206.

[15] N. Kuhn, T. Kratz, *Synthesis* **1993**, 561–562.

[16] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2015**, *71*, 5.

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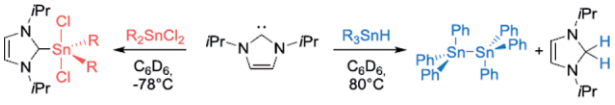

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