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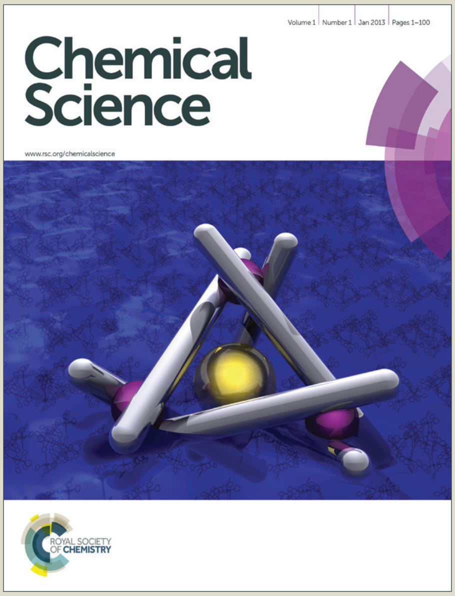

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ARTICLE TYPE

Hydrogen abstraction from organotin di- and trihydrides by *N*-heterocyclic carbenes: a new method for the preparation of NHC adducts to tin(II) species and observation of an isomer of a hexastannabenzene derivative [R_6Sn_6].”

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N-heterocyclic carbenes are shown to cleanly abstract dihydrogen from organotin di- and trihydrides to intermediately form the reactive stannylene species [R_2Sn] and [R`SnH], respectively, as well as the corresponding dihydro imidazole [R = Ph, trip: 2,4,6-triisopropylphenyl; R`= trip, Ar* : 2,6-bis(2’,4’,6’-triisopropylphenyl)phenyl]. Depending on the molar ratio of the carbene, these intermediates undergo follow reactions to form tetraorgano distannanes and carbene adducts in excellent yields. Since the side products can be removed as volatiles, the method offers a facile, clean and high yielding route to stannylene derivatives with strongly decreased sterical protection compared to previously known compounds. On stoichiometric reaction hydrogen was completely removed from an organotin trihydride and a novel tin cluster with overall composition R_6Sn_6 (R = trip) was structurally characterized.

Introduction

Organotin(IV) monohydrides have been proven to be valuable reagents in organic synthesis and their application as reducing agents has been studied intensely for decades.[1, 2] Their applicability in many reductions mainly goes back to the weak Sn–H bond (bond dissociation enthalpie ca. 320 kJ/mol)[2] and the easy homolytic cleavage of the respective bond to form radical hydrogen and tin intermediates. Much less attention has been paid to tin di- or trihydrides atom although in recent years tin dihydrides were found to be valuable precursors for dehydrogenating polymerization reactions forming polystannanes by various approaches.[3-5] Yet, the remarkably easy release of dihydrogen from diorgano tin dihydrides in the presence of amine bases such as pyridine has first been reported in the 1960s.[6-9] In the last ten years a few studies on the dehydrogenating dimerization of organotin dihydrides towards tetraorgano distannanes applying transition metal and lanthanide metal catalysts have been reported.[10-12] The reported studies on the reactivity of organotin trihydrides remained limited. When reacted with organo osmium complexes, the bulky substituted tin trihydride, (trip)SnH_3, has been shown to completely transfer hydrides onto the transition metal at elevated temperatures under formation of an osmyl stannylene.[13] In case of hydrogen derivatives of tin(II) only few studies can be found in the literature, including seminal works by Power, Roesky and Jones.[14-22] Jones even demonstrated the applicability of a tin(II) hydride as catalyst in hydroboration reactions of carbonyls.[23] Recently a tin(II) dihydride complex was reported by Rivard et al. in which the highly reactive parent tin(II) hydride is stabilized in a push/pull manner by an electron donating carbene and an electron accepting tungsten carbonyl moiety.[24] Rivard extended this concept to successfully stabilize $H_2Si{=}EH_2$ (E=Ge, Sn).[25]

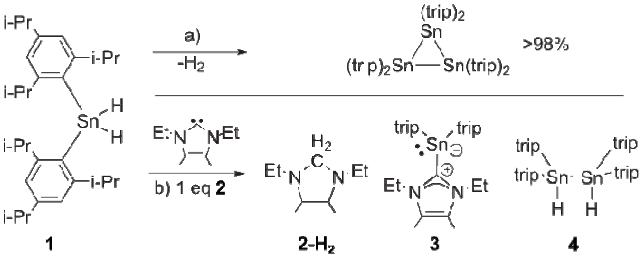
Results and Discussion

We started to investigate the dihydrogen abstraction from bulky substituted organotin di- and trihydrides by means of *N*-heterocyclic carbenes (NHC). Carbenes are known to reductively abstract, for example, hydrogen chloride from element organic group 14 compounds such as $RSiH_2Cl$ to form monoorgano silylenes that are usually stabilized by another equivalent of carbene.[26-32]
We expected the weak tin–hydrogen bond in organotin di- and trihydrides to easily react with carbenes in a similar manner to form a hydrogenated carbene-C and therefore achieve a transfer of the electronic sextet from carbon to the tin centre to generate diorgano stannylenes and organotin(II) hydrides, respectively. The latter have been prepared and studied by Power applying bulky terphenyl moieties.[14-18] These reported compounds were formed either by metathesis reactions of the organotin(II) chloride and complex inorganic hydrides such as $NaBH_4$ or by reacting tin analogues of acetylene with dihydrogen. The formation of hydrogenated carbenes as side products from mixtures with stabilized SnH_2 has been observed earlier by Rivard et al.[24]

Reactions of organotin dihydrides

In our first attempts to form a stannylene known to the literature we reacted bis(2,4,6-triisopropylphenyl)tin dihydride (trip$_2SnH_2$, **1**) with one equivalent of the small NHC 1,3-diethyl-4,5-dimethylimidazol-2-ylidene (**2**) at room temperature. We have been able to conveniently form Masamunes cyclotristannane

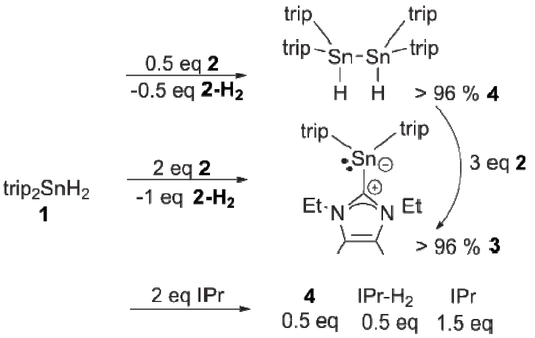
$[trip_2Sn]_3$ in perfect yield by treatment of $(trip)_2SnH_2$ with TMEDA following known procedures towards dihydrogen release from diorganotin dihydrides (see supporting information). Hence, we expected the analogous formation of $[trip_2Sn]_3$ by means of a stoichiometric dihydrogen abstractor.[5, 6, 33, 34] On addition of one equivalent of the carbene an indicative bright orange-pink colour was observed that rapidly faded into a pale yellow colour within seconds. Although the proton NMR revealed formation of the hydrogenated carbene (dihydro imidazole **2-H₂**) the expected brightly coloured hexaorgano cyclotristannane was not observed. Instead, a clean mixture of two tin containing compounds in a molar ratio of approximately 1:1 was identified by means of proton-coupled ^{119}Sn-NMR spectroscopy. One product (δ = –325.3 ppm) featured a doublet of doublet pattern ($^1J_{Sn–H}$ = 1539 Hz and $^2J_{Sn–H}$ 152 Hz) resulting from tin-hydrogen coupling whilst the other compound revealed a singlet at δ = –150.3 ppm.



Scheme 1 Dehydrogention reactions with $trip_2SnH_2$ **1.** a) THF/TMEDA, rt, 12-16h. b) benzene, rt, 10-15 min.

Scheme 1 depicts the observed behaviour for the reaction of diorgano tin dihydride with one equivalent of carbene **2.** The finding can be rationalized by the assumption of intermediately formed two thirds of an equivalent of the highly reactive stannylene $(trip)_2Sn$ that rapidly reacts with either the remaining third equivalent of free **2** to form the adduct **3** or undergoes the well known insertion into the Sn–H bond of still unreacted **1** to form the tetraorgano distannane **4**.

In order to prove the findings we reacted dihydride **1** with half an equivalent of carbene **2** to obtain pure distannane **4** along with hydrogenated carbene **2-H₂** as well as two equivalents of **2** to purely obtain the carbene aduct **3** (Scheme 2). Further treatment of isolated **4** with three equivalents **2** resulted in clean formation of **3**. The reactions were carried out at room temperature and were complete within seconds in benzene or toluene. According to NMR experiments performed rapidly after mixing the educts, the products were formed quantitatively in all cases. When the reaction was performed in hydrocarbon solvents such as hexane the decolourization of initially bright orange solutions took significantly longer and only 80-90% conversion was observed after 18h.



Scheme 2 Reaction behaviour of $trip_2SnH_2$ **1** with varying amounts of carbenes

The work up can be easily performed by removal of the solvent and **2-H₂** in vacuo offering a facile and high yielding route to both products, distannane and carbene adduct. Derivatives of both compounds are known to the literature.[35] So far, **4** represents the tetraorgano distannane with the largest steric bulk of the substituents. To the best of our knowledge, only few procedures are known to yield tetraorgano distannanes most of them involving transition metal or rare earth metal catalysts.[3, 10-12, 34, 36, 37]

The carbene adduct to the $(trip)_2Sn$ stannylene **3** is precedented by works of Weidenbruch who structurally characterized and reported the 1,3-diisopropyl-imidazol-2-ylidene ($^{i\text{-}Pr}$NHC) derivative which was differently accessed by the direct reaction of $[trip_2Sn]_3$ with the free carbene.[35] The number of carbene adducts to stannylenes and stannenes increased only recently.[38-42] The ^{119}Sn chemical shift for Weidenbruchs adduct was reported at δ = 710 ppm, whilst the herein reported compound **3** is found to resonate at δ = –150 ppm, meaning a highfield shift of 860 ppm caused by the change from an *N*-bond isopropyl residue to an ethyl moiety. ^{119}Sn NMR resonances in the range of –100 ppm are usually observed for tri- or tetracoordinate Sn(IV) derivatives whilst resonances shifted to lower fields are indicative for a decrease of the coordination number around the Sn centre.[43] In this case the resonance shift may be interpreted as an increased Sn–C interaction in solution between stannylene and carbene. It would represent an example for vast impact on the electronic situation at the Sn centre or on the strength of the C–Sn bond, respectively, due to potentially small changes in steric bulk (ethyl vs. isopropyl). Though the ^{119}Sn NMR data indicate different strength of the Sn–carbene interaction between the two similar species, the carbene ^{13}C NMR resonances are quite comparable (Et: 175.9 ppm, *i*Pr: 177.2 ppm).

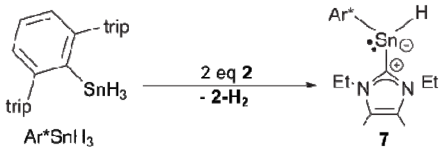
Reactivity studies of dihydride **1** with two equivalents of the bulkier carbenes such as 1,3-bis(2’,6’-diisopropylphenyl)-imidazol-2-ylidene (IPr) revealed no formation of the analogous stannylene-IPr adduct but proton NMR spectroscopy clearly showed the complete conversion of **1** to distannane **4** along with hydrogenation of 0.5 equivalents of IPr and 1.5 euivalents of unreacted free IPr. Solutions of these mixtures were stable at room temperature (under exclusion of light) for weeks (Scheme 2).

$$Ph_2SnH_2 \xrightarrow{2\ eq\ \mathbf{2}} \underset{\mathbf{5}}{Ph_2Sn(NHC)} + \mathbf{2\text{-}H_2} \qquad (1)$$

By treatment of diphenyltin dihydride with two equivalents of carbene **2** at room temperature and in situ generation of the respective stannylene a bright yellow mixture was obtained that revealed to be a clean 1:1 mixture of the carbene adduct $Ph_2Sn(NHC)$ (**5**) and **2-H$_2$** (Equation 1). The ^{119}Sn NMR spectrum reveals a sharp singlet at $\delta = -121$ ppm. Therefore, this approach offers a possibility to obtain the carbene adducts to stannylenes with small substituents such as diphenyl tin(II) which usually forms higher aggregates such as hexamers.[44]

Reactions of organotin trihydrides

In order to expand the scope of this remarkably clean hydrogen abstraction we applied varying stoichiometries of **2** on bulky substituted organotin trihydrides such as 2,6-bis(2',4',6'-triisopropylphenyl)phenyltin trihydride (Ar^*SnH_3) and (trip)tin trihydride (**6**). Reacting two equivalents of carbene **2** to Ar^*SnH_3 and subsequent removal of the solvent and **2-H$_2$** under reduced pressure quantitatively yielded the so far unknown adduct to Powers organo tin(II) monohydride [Ar*Sn(NHC)H] (**7**) as depicted in Scheme 3.[14] In the course of the reaction, which is finished within seconds, no change in colour was observed. This would have indicated the intermediate presence of known Ar*SnH.



Scheme 3 Synthesis of carbene adduct **7**

Single crystals of **7** suitable for X-ray diffraction were obtained from concentrated solutions in toluene at –40°C. Figure 1 depicts the molecular structure of **7**. The Sn(1)–C(1) [2.232(2) Å] bond distance is essentially equal dimeric, parent $[Ar^*SnH]_2$ [2.210(2) Å] but shorter than the $_{ipso}C$–Sn distance in $[(trip)_2Sn(^{i\text{-}Pr}NHC)]$ [2.321(2), 2.308(2) Å].[14, 35] The C(37)–Sn(1) bond length amounts to 2.295(2) Å which is shorter than for $[(trip)_2Sn(^{i\text{-}Pr}NHC)]$ [2.379(5) Å] but equal to the C–Sn bond length of a reported $^{i\text{-}Pr}NHC$ adduct to $SnCl_2$ [2.290(5) Å].[45] The Sn(1)–H(600) [1.65(2) Å] bond length may be underestimated since it was found in the difference Fourier map and is shorter than the Sn–H distance for $[Ar^*SnH]_2$ [1.89(3), 1.95(3) Å][14], for which also neutron diffraction data are reported [20 K, 1.941(7), 1.943(7) Å][15]. The Sn(1)–C(37) bond deviates slightly from the NCN-plane by 14.3°. The dihedral angle between C(1)-Sn(1)-C(37) and Sn(1)-C(37)-N(1) amounts to 81.8(1)°. The C(37)–Sn(1) bond deviates by 11.6(2)° from 90° on the C(1)-Sn(1)-H(600) plane. The C(1)-Sn(1)-H(600) angle [96.3(8)°] is still close to 90° but slightly larger than in $[Ar^*SnH]_2$ [91.7(9)° and 93.6(9)°].[14] The sum of the interligand angles at tin amounts to 286.5° which furtherly underpins the pyramidalization at Sn(1) and the presence of a tin-centred lone pair. The observed geometries are consistent with the expected bonding situation of a σ-donation of the carbene into the vacant p-orbital of the Ar*SnH stannylene.

The structure is similar to the 1,3-dimethyl-imidazol-2-ylidene (^{Me}NHC) adduct to Ar*SiCl reported by Filippou et al. which was obtained by a dehydrochlorination approach. The structural similarity is retrieved in the observation of chemically inequivalent *ortho*- and *meta*-positions of the trip-moieties at Ar* caused by the stereogenic tin centre according to proton and ^{13}C NMR spectroscopy.[29] For **7** proton NMR shows a splitting of the methylene protons at the N-ethyl moiety into two broad sets of signals.

The proton-coupled ^{119}Sn NMR spectra of **7** revealed a sharp doublet at $\delta = -337$ ppm with a $^1J_{Sn\text{–}H}$ coupling constant of 237 Hz. This highfield shift for **7** of > 1000 ppm compared to the free, in solution monomeric hydride Ar*SnH ($\delta = +697.7$ ppm) is consistent with a strong bonding interaction of the carbene with the tin(II), maintained in solution.[14] The $^1J_{Sn\text{–}H}$ coupling constant as well decreases by >350 Hz from 592 Hz (Ar*SnH).[14] The proton NMR reveals the Sn–H to resonate at $\delta = 6.92$ ppm flanked by the respective $^{117/119}Sn$ satellites. The ^{13}C NMR revealed a coupling constant $^1J_{119Sn\text{–}C}$ for the sharp carbene C resonance of 598.7 Hz, which lies well in the range of the few reported values for Sn–C coupling constants for Sn=C systems.[46] Another rare example for a tin(II) hydride which includes a tri-coordinated Sn(II) center is a β-diketiminate complex developed by Roesky for which a ^{119}Sn NMR chemical shift of $\delta = -4.5$ ppm and a $^1J_{Sn\text{–}H}$ coupling constant of 64 Hz was reported.[19, 20] Under inert conditions, solutions of compound **7** were stable for weeks at room temperature and on exposure to daylight.

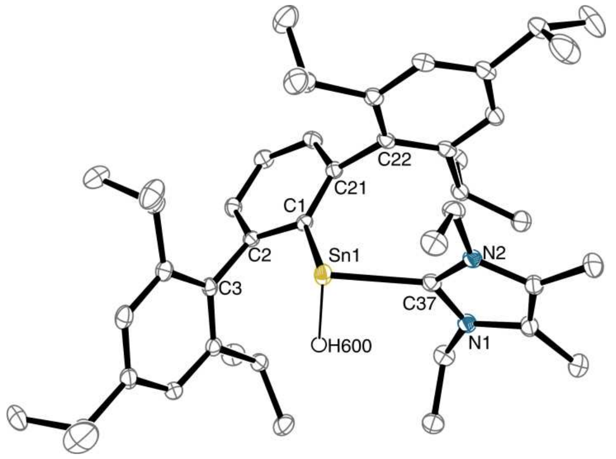


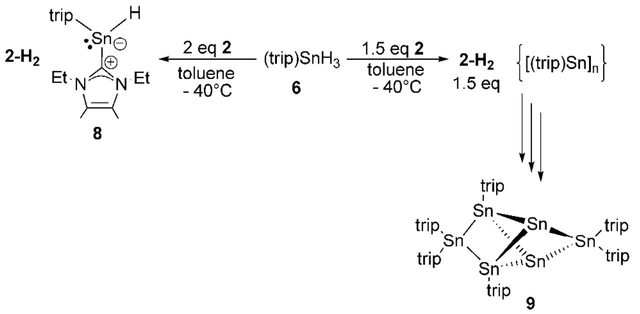
Fig. 1 ORTEP plot of the molecular structure of 7 · toluene. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms [except H(600)] and lattice toluene are omitted for clarity. Hydrogen atom H(600) was located in the difference Fourier map. Selected bond lengths [Å] and angles are given: C(37)−Sn(1) 2.295(2), C(1)−Sn(1) 2.232(2), Sn(1)−H(600) 1.65(2), C(1)−Sn(1)−H(600) 96.3(8)°, C(1)−Sn(1)−C(37) 101.62(5)°, C(37)−Sn(1)−H(600) 88.6(8)°, N(1)−C(37)−N(2) 104.44(13)°.

When only one equivalent of carbene **2** is reacted with Ar^*SnH_3 a 1:1 mixture of adduct **7** and unreacted trihydride was obtained according to an NMR experiment and no change in product composition was found after several days. This indicates that an intermediately formed bulky-substituted species [Ar*SnH] much quicker reacts with every amount of free carbene before an insertion into another Sn–H bond of Ar^*SnH_3 under formation of diorgano distannane $Ar^*H_2Sn\text{-}SnH_2Ar^*$, occurs. The behaviour upon addition of a half equivalent of **2** accordingly yielded the carbene adduct **7** along with unreacted trihydride in a molar ratio of 1:3.

In order to test this dehydrogenation approach towards the generation of carbene-stabilized much more reactive organotin(II) hydride species with less bulkier substituted residues, $(trip)SnH_3$

(**6**) was reacted with varying stoichiometries of carbene. An X-ray structure of (trip)SnH_3 **6** is presented in the supporting information, augmenting the still small number of structurally characterized tin trihydrides.[47] On reacting cooled solutions of **6** and carbene **2** in a molar ratio of 1:2 NMR spectroscopy at lower temperatures revealed clean formation of dihydro-imidazole **2-H₂** along with the trip-analogue of adduct **7**: [(trip)Sn(NHC)H] (**8**). The Sn–H proton resonance is found at slightly lower field (δ = 7.59 ppm) with a furtherly reduced coupling constant of $^1J_{117,119\text{Sn–H}}$ = 160 Hz. Proton-coupled ^{119}Sn NMR revealed a clean doublet at δ = –368.8 ppm ($^1J_{119\text{Sn–H}}$ = 162 Hz). When kept at room temperature the sample slowly decomposes over a few hours to unassigned products indicated by proceeding darkening of the sample as well as a decrease of the Sn–H signal integral relative to solvent signal of the sample. In contrast, the integral of the ethyl-moiety protons in **2-H₂** increases which also suggests further hydrogenation of the yet unreacted carbene **2**. Possible side products include higher aggregates $[(\text{trip})\text{Sn}]_n$ as well as metal-rich organotin clusters like $[(\text{trip})_{1-x}\text{Sn}]_n$ (vide infra).[48-50] After several days dark red brown solutions but no precipitates such as elemental tin are observed. When kept at –40°C for several weeks no decomposition of [(trip)Sn(NHC)H] **8** was observed. Thermolability of **8** did not allow the usual work up and prevented the isolation for further analytical investigations, yet the formation and presence is clearly evidenced by means of NMR spectroscopy and comparison with the findings for [Ar*Sn(NHC)H] **7**. When (trip)SnH_3 **6** was treated with two equivalents of the sterically more encumbering IPr in order to form a potentially more thermally stable adduct the hydrogen transfer was observed to be much slower and after a few hours inseparable mixtures were obtained.

In case one equivalent of carbene **2** was added to cooled (–20 - –40°C) solutions of **6** in toluene-d_8 proton NMR control of the dark orange coloured mixtures revealed quantitative formation of **2-H₂** along with unreacted trihydride **6**. Yet, the proton coupled ^{119}Sn NMR revealed only the quartet of (trip)SnH_3 at δ = –416 ppm and even after screening on a largely extended field range and prolonged pulsing no further tin species (including the carbene adduct **8** or a potential diorgano distannane $[(\text{trip})\text{Sn}(H_2)]_2$) were found. Surprisingly, when **6** and **2** were reacted in an exact molar ratio of 2:3 at –40°C in toluene and the brightly orange solution was immediately transferred under maintained cooling, the proton NMR at –40°C solely revealed the pure signals of **2-H₂**. The expected signals in the aromatic region as well as the isopropyl moieties of derivatives bearing the 2,4,6-triisopropylphenyl group were broadened beyond recognition and no signal set for yet unreacted **2** was observable. Extended screening for a ^{119}Sn NMR resonance (at –80°C and room temperature) remained unsuccessful as well as a screening for a radical species by means of EPR spectroscopy. This remarkable finding indicates a complete stripping off of hydrogen from the tin. The solutions stayed bright orange in the cold and slowly turn dark red at room temperature but even after several days no formation of precipitating elemental tin was indicated.



Scheme 4 Reaction of tripSnH₃ with carbene **2** and formation of the adduct **8** as well as aggregate **9**

From one reaction, after two weeks at –40°C a small quantity of needle-shaped crystals of dark burgundy color grew from toluene solutions of the reaction mixture. X-ray diffraction revealed the formation of a tin cluster **9** of the general composition $(\text{trip})_6\text{Sn}_6$. The found constitution $[(\text{trip})_2\text{Sn}[(\text{trip})\text{Sn}]_2\text{Sn}_2\text{Sn}(\text{trip})_2]$ is shown in Figure 2. The isostructural silicon analogue has been described by Scheschkewitz and the silicon arrangement was found to represent the likely global minimum for Si_6H_6.[51, 52] The mixed heavier homologues $E_2Si_4(\text{trip})_6$ (E = Ge, Sn) have most recently been reported as well.[53] In analogy, **9** can be seen as a structural modification of a hexastannabenzene derivative.[54] A compound with the total composition R_6Sn_6 already known to the literature features a prismane structure.[55] **9** resembles the structure of [1.1.1]stannapropellanes and closes the gap between the already structurally characterized R_6Sn_5 and R_6Sn_7 (R = 2,6-diethylphenyl).[56] These have so far been accessed by thermolysis of the cyclotristannane or alkali metal reduction of mixtures of cyclotristannanes and tin(II) chloride.[56-61] Structural deduction can be described by a double insertion of a formal Sn(0) atom into the R–Sn bonds of two bridging R_2Sn moieties of the parent [1.1.1]stannapropellanes. The Sn(1)–Sn(3) bond distance [3.3704(4) Å] of the naked bridging Sn atoms is significantly shorter than the distance between bridging [(trip)Sn] fragments Sn(2)–Sn(5) [3.5729(4) Å]. Yet, Sn(1)–Sn(2) lies well within the range of distances for comparable moieties in R_5Sn_6 [3.367 Å, R = 2,6-diethylphenyl; 3.42 Å, R = 2,6-di(isopropoxyl)phenyl] and R_7Sn_6 (3.348 Å, R = 2,6-diethylphenyl).[58, 62] Consistently the Sn–Sn–Sn angle around the R_2Sn fragments differ [Sn(4): 72.43(1)°, Sn(6): 78.796(9)°]. Due to the small quantities of obtained crystalline material no NMR spectroscopic data can be provided.

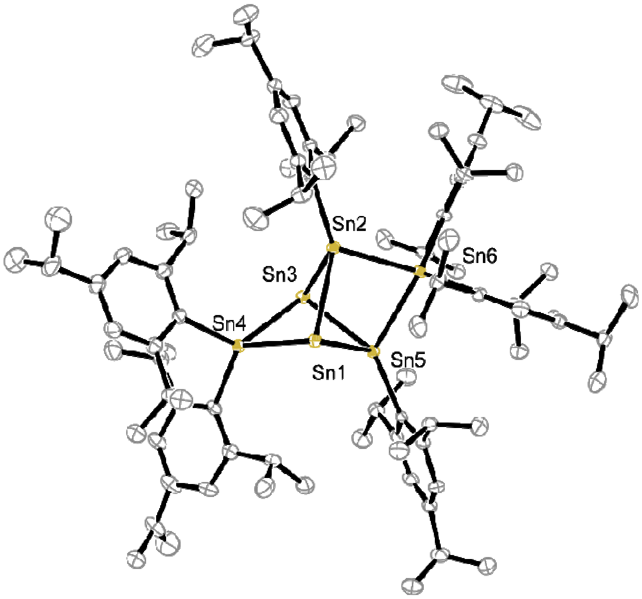


Fig. 2 ORTEP plot of the molecular structure of **9** (2 toluene). Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms and lattice toluene have been omitted for clarity. Selected bond lengths [Å] and angles are given: Sn(1)–Sn(4) 2.8560(4), Sn(3)–Sn(4) 2.8487(4), Sn(1)–Sn(2) 2.8255(4), Sn(1)–Sn(5) 2.8890(4), Sn(2)–Sn(3) 2.8799(4), Sn(3)–Sn(5) 2.8316(4), Sn(2)–Sn(6) 2.7992(4), Sn(5)–Sn(6) 2.8299(3), Sn(1)–Sn(3) 3.3704(4), Sn(2)–Sn(5) 3.5729(4). Sn(4)–Sn(1)–Sn(2) 93.721(10)°, Sn(4)–Sn(3)–Sn(2) 92.719(10)°, Sn(3)–Sn(4)–Sn(1) 72.43(1)°, Sn(4)–Sn(3)–Sn(5) 93.380(11)°, Sn(4)–Sn(1)–Sn(5) 94.775(11)°, Sn(2)–Sn(1)–Sn(5) 77.391(11)°, Sn(2)–Sn(3)–Sn(5) 77.44(1)°, Sn(1)–Sn(2)–Sn(3) 72.413(9)°, Sn(1)–Sn(2)–Sn(6) 91.052(11)°, Sn(3)–Sn(2)–Sn(6) 89.477(10)°, Sn(1)–Sn(5)–Sn(6) 89.14(1)°, Sn(3)–Sn5)–Sn(6) 89.842(10)°, Sn(5)–Sn(6)–Sn(2) 78.796(9)°.

The behaviour of the reaction mixture (vide supra) observed by NMR spectroscopy indicates a formation via intermediately generated [(trip)Sn] with subsequent aggregation and ligand disproportion, rather than slow decomposition of intermediately formed **8**. Nevertheless the latter cannot be ruled out as potential formation pathway. [RSn] species as intermediates in the formation of organotin compounds have been postulated earlier.[56] Examples for the formation of similar aggregates and metal-rich clusters have been prepared and described earlier by Power through thermolysis of [Ar*SnH] in hot toluene to yield [Ar*$_3$Sn$_9$].[49, 50] By application of the much less bulky trip-moiety according thermolysis conditions at room temperature would be reasonable. Although it was so far not possible to obtain further crystalline material sufficient for detailed analytical examinations from accordingly performed reactions, the finding is consistent with a stoichiometric abstraction of three hydrogens from the trihydride by carbenes. The hydrogen abstraction route by carbenes may offer a further route to [RSn(I)] building blocks for subvalent tin clusters with potentially less technical complexity as is given for the known and well-developed co-condensation techniques to generate sources of low-valent group 14 element halides as precursors applied by Schnepf.[63, 64]

Experiments to explore the ability of the carbene adduct for a potential transfer of the reactive (trip)SnH stannylene on transition metals similarly to the findings for a comparable [RSi(NHC)H][28] species as well as the assignability of the dihydrogen abstraction reaction on other maingroup element hydrides are under current investigation.

Conclusions

In summary we have developed a new, clean and most convenient method for the in situ preparation of highly reactive mono- and diorganotin(II) species. The approach offers a new access to both: bulky substituted distannanes as well as carbene adducts of sterically less encumbered stannylenes and is gate-opening for further studies on the reactivity of these scarcely investigated species. A new route towards organotin(II) hydride derivatives from a tetravalent tin source is established. The approach has also proven to provide a convenient access to reactive putative RSn(I) intermediates, indicated by the observation of higher aggregates [RSn]$_6$ (R = trip).

Experimental Section

General Information

All manipulations were carried out under argon atmosphere using standard Schlenk techniques or an MBraun Glovebox. Toluene, diethylether and benzene were distilled from sodium/benzophenone, toluene from sodium and hexane from potassium. Pentane was obtained from an MBRAUN solvent purification system. Solvents were degassed by several freeze-pump-thaw cycles. Benzene-d$_6$ toluene-d$_8$ were distilled from sodium and stored over potassium.

Hydrides Ph$_2$SnH$_2$,[8] (trip)SnH$_3$,[13] Ar*SnH$_3$[65] as well as the NHC (**2**[66] ad IPr[67]) were prepared according to modified literature procedures. Educt compounds were purchased commercially (Aldrich) and used without further purification.

Elemental analysis was performed by the Institut für Anorganische Chemie, Universität Tübingen using a Vario MICRO EL analyzer. Attempts to obtain analytical data by mass spectrometry (EI/ESI) of compounds **3** and **5** revealed only fragments assignable to ligand fragments. Crystallographic details as well as synthesis of some precursors can be found in the supporting information.

NMR spectroscopy

NMR spectra were recorded with either a Bruker DRX-250 NMR spectrometer equipped with a 5 mm ATM probe head and operating at 250.13 (^{1}H), 62.90 (^{13}C) 93.3 MHz (^{119}Sn), a Bruker AvanceII+400 NMR spectrometer equipped with a 5 mm QNP (quad nucleus probe) head and operating at 400.13 (^{1}H), 100.62 (^{13}C) or a Bruker AVII+ 500 NMR spectrometer with a 5 mm ATM probe head and operating at 500.13 (^{1}H), 125.76 (^{13}C), 186.5 MHz (^{119}Sn) and a low-temperature set-up. Chemical shifts are reported in δ values in ppm referenced on the solvent ^{2}H resonance frequency. The proton and carbon signals were assigned where possible via a detailed analysis of ^{1}H, ^{13}C, ^{13}C-UDEFT, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC spectra. 1D-NMR spectra of the compounds can be found in the supporting information.

Synthesis

[(trip)$_2$Sn×NHC] (3): To a solution of **2** (57.7 mg, 0.379 mmol, 2 eq) in toluene (0.6 mL) at room temperature a solution of **1** (100.0 mg, 0.190 mmol, 1 eq) in toluene (0.6 mL) was added at once via syringe and the initially bright orange solution was stirred for 10 min. Volatiles were completely removed from the yellow solution under reduced pressure for 6 h to yield **3** as a yellow powder (121 mg, 0.180 mmol, 94%). Analytical data: ^{1}H (400.13 MHz, tol-d_8) δ 7.16 (s, 4H, H$_{ar}$), 3.94 (quart, 4H, $^3J_{H-H}$ = 7.19 Hz, ethyl-C*H*$_2$), 3.88 (sept., 4H, $^3J_{H-H}$ = 6.74 Hz, *o*- C*H*Me$_2$), 2.90 (sept., 2H, $^3J_{H-H}$ = 6.94 Hz, *p*-C*H*Me$_2$), 1.45 (s, 6H, NHC-C*H*$_3$), 1.34 (d, 24H, $^3J_{H-H}$ = 6.93 Hz, *o*-CH*Me*$_2$), 1.25 (d, 12H, $^3J_{H-H}$ = 6.76 Hz, *p*-CH*Me*$_2$), 0.84 (br t, 6H, $^3J_{H-H}$ = 7.06 Hz, ethyl-C*H*$_3$); ^{13}C (100.62 MHz, tol-d_8) δ 175.9 (s, NHC-*C*-Sn), 158.9 (s, *ipso*-*C*$_{ar}$), 156.3 (s, *o*-*C*$_{ar}$), 146.9(s, *p*-*C*$_{ar}$), 125.1 (s, overlaying with strong solvent signals, NHC-*C*-Me), 120.8 (s, *m*-*C*$_{ar}$), 43.6 (s. ethyl-*C*H$_2$), 37.4 (s, *o*-*C*HMe$_2$), 34.7 (s, *p*-*C*HMe$_2$), 25.9 (s, *o*-CH*Me*$_2$), 25.3 (s, *p*-CH*Me*$_2$), 24.6 (s, *o*-CH*Me*$_2$), 15.0 (s, ethyl-*C*H$_3$), 8.2 (s, NHC-*C*H$_3$); ^{119}Sn{^{1}H} (93.28 MHz, C_6D_6) δ –150.7. Anal. Calcd for $C_{39}H_{62}N_2Sn$: C 69.13, H 9.22, N 4.13. Found: C 69.22, H 9.37, N 5.77.

[(trip)$_4$Sn$_2$H$_2$] (4): To a stirred solution of **1** (100.0 mg, 0.190 mmol, 1 eq) in toluene (1.2 mL) at room temperature a solution of **2** (14.4 mg, 0.095 mmol, 0.5 eq) in toluene (1.5 mL) was added dropwise over 1 min. After complete addition the brightly orange-red solution was stirred for 30 min until a clear yellow solution remains. Volatiles were removed in vacuo to yield **4** (96 mg, 0.091 mmol, 96%) as a pale yellow powder. Analytical data: ^{1}H (400.13 MHz, C_6D_6) δ 7.18 (s, 8H, *m*-H$_{ar,}$ $^4J_{117/119Sn-H}$ = 18.7 Hz), 6.57 (s, 2H, Sn–H, $^3J_{H-H}$ = 14.47 Hz, $^1J_{119Sn-H}$ = 1544 Hz, $^1J_{117Sn-H}$ = 1474 Hz, $^2J_{119Sn-H}$ = 152.4 Hz, $^2J_{119Sn-H}$ = 152.4 Hz, $^2J_{117Sn-H}$ = 146.1 Hz), 3.46 (sept, 8H, $^3J_{H-H}$ = 6.65 Hz, *o*-C*H*Me$_2$), 2.84 (sept., 4H, $^3J_{H-H}$ = 6.89 Hz, *p*-C*H*Me$_2$), 1.34 (d, 24H, $^3J_{H-H}$ = 6.70 Hz, *o*-CH*Me*$_2$), 1.28 (d, 24H, $^3J_{H-H}$ = 6.92 Hz, *p*-CH*Me*$_2$), 1.18 (d, 24H, $^3J_{H-H}$ = 6.63Hz, *o*-CH*Me*$_2$); ^{13}C{^{1}H} (100.64 MHz, C_6D_6) δ 155.3 (s, *m*-C$_{ar}$, $^2J_{119Sn-C}$ = 36.4 Hz), 149.6 (s, *p*-*C*$_{ar}$), 138.4 (s, $^1J_{119Sn-C}$ = 454 Hz/$^1J_{117Sn-C}$ = 429 Hz, $^2J_{119/117Sn-C}$ = 52 Hz, *ipso*-*C*$_{ar}$), 121.8 (s, $^3J_{119/117Sn-C}$ = 40.3 Hz, *m*-*C*$_{ar}$), 38.8 (s, *o*-*C*HMe$_2$), 34.3 (s, *p*-*C*HMe$_2$), 24.8 (s. *o*-CH*Me*$_2$), 24.3 (s, *o*-CH*Me*$_2$), 24.0 (s, *p*-CH*Me*$_2$), 23.9 (s, *p*-CH*Me*$_2$); ^{119}Sn ^{1}H-coupled (93.28 MHz, C_6D_6) δ –325.3 (ABX spin system, $^1J_{119Sn-117Sn}$ = 4995 Hz); Anal. Calcd for $C_{60}H_{94}Sn_2$: C 68.45, H 9.00. Found: C 68.17, H 9.10.

[Ph$_2$Sn×NHC] (5): To a solution of **2** (110.7 mg, 0.728 mmol, 2 eq) in toluene (0.8 mL) at room temperature a solution of Ph$_2$SnH$_2$ (100.0 mg, 0.364 mmol, 1 eq) in toluene (1.5 mL) was added at once to immediately form a cloudy yellow mixture with some initially bright orange precipitate. After 10 min the mixture was filtered through a syringe filter and volatiles were completely removed from the yellow solution under reduced pressure for 6 h to yield **5** as a yellow powder (149 mg, 0.350 mmol, 96%). Analytical data: ^{1}H (400.13 MHz, C_6D_6) δ 8.13 (m, 4H, *o*-H$_{ar}$), 7.46 (m, 4H, *m*-H$_{ar}$), 7.33 (m, 2H, *p*-H$_{ar}$), 3.84 (quart, 4H, $^3J_{H-H}$ = 7.22 Hz, ethyl-C*H*$_2$), 1.37 (s, 6H, NHC-C*H*$_3$), 0.82 (br t, 6H, $^3J_{H-H}$ = 7.22 Hz, ethyl-C*H*$_3$); ^{13}C{^{1}H} (62.90 MHz, tol-d_8) δ 172.8 (br s, NHC-*C*-Sn), 161.5 (s, $^1J_{119Sn-C}$ = 303.4 Hz/$^1J_{117Sn-C}$ = 289.4 Hz, *ipso*-*C*$_{ar}$), 139.0 (s, $^2J_{117/119Sn-C}$ = 55.7 Hz, *o*-*C*$_{ar}$), 128.3 (s, overlaying with strong solvent signals, *m*-*C*$_{ar}$), 126.4 (s, *p*-*C*$_{ar}$), 125.3 (s, NHC-*C*-Me), 43.1 (s, ethyl-*C*H$_2$), 16.3 (s, ethyl-*C*H$_3$), 8.4 (s, NHC-*C*H$_3$); ^{119}Sn{^{1}H} (93.28 MHz, C_6D_6) δ –121.0. Anal. Calcd for $C_{21}H_{26}N_2Sn$: C 59.33, H 6.16, N 6.59. Found: C 59.68, H 5.61, N 6.74.

[(Ar*Sn(NHC)(H)] (7): To a stirred solution of Ar*SnH$_3$ (40 mg, 0.066 mmol, 1 eq) in toluene (0.6 mL) at room temperature a solution of **2** (20.2 mg, 0.133 mmol, 2 eq) in toluene (0.5 mL) was added at once at room temperature and the colorless solution was kept at room temperature for 20 min. Volatiles were removed in vacuo to yield **7** (48 mg, 0.064 mmol, 96%) as a colorless solid. Crystals with two co-crystallizing molecules toluene per formula unit suitable for X-ray diffraction were obtained from concentrated solutions in toluene at –40°C over a period of days. Analytical data: ^{1}H (500.13 MHz, C_6D_6) δ 7.41 (m, 2H, *m*-H$_{trip}$), 7.31 (m, 1H, *p*-H$_{Ph}$), 7.23 (m, 2H, *m*-H$_{Ph}$), 7.19 (m, 2H, *m*-H$_{trip}$) 6.93 (s, 1H, $^1J_{119Sn-H}$ = 237.5 Hz, $^1J_{117Sn-H}$ = 227.6 Hz, Sn–H), 3.88 (two overlapping quart, 2H, ethyl-C*H*$_2$), 3.65 (sept., 2H, $^3J_{H-H}$ = 6.86 Hz, *o*-C*H*Me$_2$) overlaying with 3.57 (br quart., 2H, ethyl-C*H*$_2$), 3.17 (sept., 2H, $^3J_{H-H}$ = 6.82 Hz, *p*-C*H*Me$_2$), 3.01 (sept., 2H, $^3J_{H-H}$ = 6.92 Hz, *o*-C*H*Me$_2$), 1.79 (d, 6H, $^3J_{H-H}$ = 6.87 Hz, *o*-CH*Me*$_2$), 1.53 (s, 6H, NHC-C*H*$_3$), 1.43 (d, 6H, $^3J_{H-H}$ = 6.95 Hz, *o*-CH*Me*$_2$), 1.42 (d, 6H, $^3J_{H-H}$ = 6.95 Hz, *o*-CH*Me*$_2$), 1.41 (d, 6H, $^3J_{H-H}$ = 6.95 Hz, *o*-CH*Me*$_2$), 1.31 (d, 6H, $^3J_{H-H}$ = 6.78 Hz, *p*-CH*Me*$_2$), 1.23 (d, 6H, $^3J_{H-H}$ = 6.86 Hz, *p*-CH*Me*$_2$), 1.03 (t, 6H, $^3J_{H-H}$ = 7.22 Hz, ethyl-C*H*$_3$); ^{13}C{^{1}H}-udeft (125.76 MHz, C_6D_6) δ 172.3 (s, NHC-*C*-Sn, $^1J_{119Sn-C}$ = 598.7 Hz, $^2J_{119Sn-C}$ = 573.1 Hz), 161.5 (s, *ipso*-*C*$_{Ph}$), 148.5 (s, *o*-*C*$_{Ph}$), 147.0 (s, *p*-*C*$_{trip}$), 146.9 (s, *o*-*C*$_{trip}$), 146.8 (s, *o*-*C*$_{trip}$), 142.4 (s, *ipso*-*C*$_{trip}$), 128.6 (s, *m*-*C*$_{Ph}$), 124.1 (s, *p*-*C*$_{Ph}$), 124.0 (s, NHC-*C*-Me), 120.8 (s, *m*-*C*$_{trip}$), 120.1 (s, *m*-*C*$_{trip}$), 43.2 (s, ethyl-*C*H$_2$), 34.5 (s, *p*-*C*HMe$_2$), 30.9 (s, *o*-*C*HMe$_2$), 30.5 (s, *o*-*C*HMe$_2$), 26.5 (s, *o*-CH*Me*$_2$), 26.0 (s, *o*-CH*Me*$_2$), 24.4 (s, *p*-CH*Me*$_2$), 24.3 (s, *p*-CH*Me*$_2$), 23.9 (s, *o*-CH*Me*$_2$), 23.1 (s, *o*-CH*Me*$_2$), 15.4 (ethyl-*C*H$_3$), 8.1 (NHC-*C*H$_3$); ^{119}Sn ^{1}H-coupled (186.50 MHz, C_6D_6) δ –337.9 (d, $^1J_{119Sn-H}$ = 237.5 Hz). Anal. Calcd for $C_{45}H_{66}SnN_2$: C 71.71, H 8.83 N 3.72. Found: C 71.84, H 8.40, N 3.24; [IR, ATR,solid, cm^{-1}] Sn–H 1759 (br, w).

[(trip)Sn(NHC)(H)] (8): To a pre-cooled solution of **2** (56.2 mg, 0.369 mmol, 2 eq) in toluene-d_8 (–40°C, 0.4 mL) a pre-cooled solution of (trip)SnH$_3$ **6** (60.0 mg, 0.185 mmol, 1 eq) in toluene-d_8 (–40°C, 0.3 mL) was added at once at room temperature and the bright red-orange solution was immediately transferred into an NMR tube and cooled to –40°C. Under inert conditions and exclusion of light the clean 1:1 mixture of **8** and **2-H$_2$** is stable at –40°C for more than four weeks. At room temperature decomposition of **8** is complete within 7h. The reported NMR shifts correspond to the 1:1 mixture solution (see supporting information). Analytical data: ^{1}H (500.13 MHz, tol-d_8, –40°C) δ 7.59 (s, 1H, Sn–H, $^1J_{Sn–H}$ = 162 Hz), 7.27 (s, 2H, H$_{ar}$), 3.93 (sept., 2H, $^3J_{H–H}$= 6.65 Hz, *o*-C*H*Me$_2$), 3.77 (br, 4H, ethyl-C*H*$_2$), 2.98 (sept., 1H, $^3J_{H–H}$= 6.86 Hz, *p*-C*H*Me$_2$), 1.44 (d, 6H, $^3J_{H–H}$= 6.86 Hz, *p*-CH*Me*$_2$), 1.38 (br, 12H, *o*-CH*Me*$_2$), 1.34 (s, 6H, NHC-C*H*$_3$), 0.92 (t, 6H, $^3J_{H–H}$= 7.16 Hz, ethyl-C*H*$_3$); ^{13}C{^{1}H} (125.76 MHz, tol-d_8, –40°C) δ 173.3 (s, *C*$_{carbene}$–Sn), 155.9 (s, *o*-*C*$_{trip}$), 154.0 (s, *ipso*-*C*$_{trip}$), 146.4 (s, *p*-*C*$_{trip}$), 124.2 (s, NHC-*C*-Me), 120.1 (s, *m*-*C*$_{trip}$), 43.3 (s, ethyl-*C*H$_2$), 38.4 (s, *o*-*C*HMe$_2$), 34.8 (s, *p*-*C*HMe$_2$), 24.9 (s, *o*-CH*Me*$_2$), 24.8 (s, *m*-CH*Me*$_2$), 15.4 (s, ethyl-*C*H$_3$), 7.9 (s, NHC-*C*H$_3$).

[(trip)$_2$Sn{(trip)Sn}$_2$Sn$_2$Sn(trip)$_2$] (9): Exact conditions for the isolation of **9** are reported, nevertheless the results have not been successfully reproduced to yield larger amounts of **9**. Under the continuous total exclusion of light, to a solution of **6** (40 mg, 0.123 mmol, 1 eq) in toluene (–40°C, 0.3 mL) a solution of **2** (28.1 mg, 0.185 mmol, 1.5 eq) in toluene (–40°C, 0.5 mL) was added at once via syringe and the bright orange solution was kept at room temperature for 2 h until it was cooled to –78°C and allowed to slowly warm to room temperature over 12h. The deep dark red solution was then kept at –40°C for 10 days until a small amount of small burgundy needle-shape crystals (approx. 6 mg, 3.10 μmol, 15%) could be isolated. Anal. Calcd for $C_{90}H_{137}Sn_6$: C 55.94, H 7.20. Found: C 56.02, H 6.29

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental details on the synthesis and properties of **1** as well as crystallographic details and the 1D NMR spectra (^{1}H, ^{13}C, ^{119}Sn) of the compounds and reaction mixtures reported in this article]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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ARTICLE TYPE

Table of contents entry

Hydrogen abstraction from organotin di- and trihydrides by *N*-heterocyclic carbenes: a new method for the preparation NHC adducts to tin(II) species and observation of an isomer of a hexastannabenzene derivative [R_6Sn_6]

Christian P. Sindlinger[a] and Lars Wesemann*[a]

N-heterocyclic carbenes are shown to cleanly abstract dihydrogen from organotin di- and trihydrides to intermediately form the reactive stannylene species [R_2Sn] and [R`SnH], respectively.