Frustrated Lewis Pair

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Reductive Dehydrogenation of a Stannane via Multiple Sn-H Activation by Frustrated Lewis Pairs

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Abstract: A bulky substituted stannane Ar^*SnH_3 ($Ar^* = 2,6$ -(2',4',6'-triisopropylphenyl)phenyl) was treated with the wellknown frustrated Lewis pair (FLP) PtBu₃/B(C_6F_5)₃ in varying stoichiometries. To some degree, hydride abstraction and adduct formation is observed, leading to [$Ar^*SnH_2(PtBu_3)$]⁺ which is rather unreactive toward further dehydrogenation. In a competing process, the FLP proved to be capable of completely striping-off hydrogen and hydrides to generate the first cationic phosphonio-stannylene [$Ar^*Sn(PtBu_3)$]⁺. This behavior provides insight into the activation/abstraction mechanism processes involved in these Group 14 hydride derivatives.

The activation of small, non-polar molecules, such as hydrogen or silanes, via strong polarization stemming from the combination of sterically hindered Lewis acids and bases (so called "frustrated" Lewis pairs, FLP) has been a successful concept for a variety of synthetic chemical applications for the last decade.^[1]

It was strongly suggested, that the key step toward the activation of E–H moieties is the initial interaction with the strong Lewis acids (LA) leading to labile, hydride-bridged [R_n E–H····LA] complexes and generating a positively polarized E center activated for further nucleophilic attacks.^[2] It was only recently, that such elusive complexes have been isolated and studied in the solid state.^[3]

Since reports of borane-promoted carbonyl hydrosilylations by Piers and co-workers,^[4] the $B(C_6F_5)_3$ activation of R_3E -H (E = Si, Ge, Sn)^[5] toward additions to unsaturated functional groups has been intensely studied with a strong focus on silanes. For the reaction of $B(C_6F_5)_3$ with R_3SnH (R = alkyl), owing to the weaker Sn-H bond, complete hydride abstraction was reported.^[5d,6] We are particularly interested in the chemistry of organotin trihydrides RSnH₃ (R = bulky substituents) which may provide up to three hydrogen atoms. In the course of our interest in the reductive

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the author(s) of this article can be found under http://dx.doi.org/10. 1002/anie.201610254. dehydrogenation of organotin(IV) trihydrides we anticipated the abstraction of hydrogen in its ionic, charge separated form of H⁺/H⁻ from the rather non-polar stannane Ar*SnH₃ by an FLP. Successful dehydrogenation using N-heterocyclic carbenes (NHC),^[7] which can be seen as single-atom-based "frustrated" Lewis pairs, encouraged us to use the iconic P/B FLP PtBu₃/B(C₆F₅)₃.^[1c,8] Reductive dehydrogenation of a dihydrogermane with a NHC/B(C₆F₅)₃ FLP was previously described by Roesky.^[9]

We now exposed the sterically protected stannane $Ar*SnH_3$ to the FLP mixture and predicted the generation of dimeric Ar*SnH along with $[HPtBu_3]^+$ and $[HB(C_6F_5)_3]^-$



Scheme 1. Reductive dehydrogenations of Ar*SnH₃ using a frustrated Lewis pair under formation of mixtures including a phosphine-stabilized Sn^{IV} cation $[Ar*SnH_2(PtBu_3)]^+$ (1) and a phosphonio-stannylene $[Ar*Sn(PtBu_3)]^+$ (2).

(Scheme 1, top). However, if one equivalent of borane is added to an equimolar mixture of Ar^*SnH_3 and $PtBu_3$ in benzene, instead of forming a blue solution of $[Ar^*SnH]_2$,^[10] the colorless mixture immediately turned deep red-orange and slowly a deep red oily phase separated. On addition of the polar solvent (o-C₆H₄F₂) a homogeneous mixture is obtained. Neither phosphine nor borane individually revealed obvious reactions with Ar^*SnH_3 , also marking the distinguished lesshydridic nature of Ar^*SnH_3 compared to R_3SnH .^[5d, 6, 11]

The resulting solution was revealed to be a defined mixture of compounds including some residual Ar*SnH₃ (Scheme 1, below). All nuclei are NMR-active and (except for ¹¹B) feature spins of I = 1/2 allowing an almost unambiguous assignment of the molecular constitutions by means of heteronuclear NMR spectroscopy. Along with some free phosphine, the mixture contains the expected phosphonium cation [HPtBu₃]⁺ and the hydridoborate [HB(C₆F₅)₃]⁻. The

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sharp shape of ¹H- and ¹⁹F-NMR-signal sets for $[HB(C_6F_5)_3]^-$ are indicative of complete consumption of $B(C_6F_5)_3$ in these mixtures.

First, a phosphine adduct to the Sn^{IV} dihydrostannyl cation $[Ar*SnH_2(PtBu_3)]^+$ (1) is formed. Only a few phosphine adducts to stannylium ions are known.^[12] The NMR spectra characteristically feature a doublet signal at $\delta_{\rm H} =$ 5.90 ppm for the two Sn-bonded hydrides. These split up to a doublet arising from a ${}^{2}J_{P-H}$ coupling of 40 Hz and further reveal ^{119/117}Sn satellites with a ${}^{1}J_{Sn-H}$ coupling constant of 2100/2008 Hz. This coupling constant is almost 180 Hz greater than that observed for the parent neutral Ar*SnH₃; an increase that may be rationalized by a higher Sn s-orbital share in the Sn–H bonding. The ¹H-coupled ¹¹⁹Sn NMR signal appears at $\delta_{Sn} = -340 \text{ ppm}$ as a triplet, corroborating the constitution of a Sn atom with two hydrogen atoms attached (further splitting from a small ${}^{1}J_{\text{Sn-P}}$ coupling is not resolved). The shift is in the range of tetra-substituted stannanes and the predicted ¹¹⁹Sn chemical shift for a computationally determined structure of this cation is in reasonable agreement $(\delta_{Sn,calcd} = -382 \text{ ppm})$. The ³¹P NMR signal for [Ar*SnH₂- $(PtBu_3)$]⁺ (1) is observed at $\delta_P = 72.1$ ppm with tin satellites revealing a very small ${}^{1}J_{\text{Sn-P}}$ coupling of only 32 Hz which is an order of magnitude smaller than in [Me₃PSnMe₃]⁺.^[12c] The formation process of 1 resembles Burford's approach to stannylphosphonium cations.[12c]

The second compound formed in the reaction is assigned to the phosphine adduct to the Sn^{II} cation $[Ar*Sn(PtBu_3)]^+$ (2). It reveals a ¹¹⁹Sn NMR resonance at $\delta_{Sn} = 1420$ ppm as a doublet due to strong ${}^{1}J_{\text{Sn-P}}$ coupling of about 1990 Hz, in the range known for P-Sn^{II} compounds.^[13] The downfield shift is indicative of dicoordinate Sn^{II} compounds and the computationally predicted ^{119}Sn NMR shift ($\delta_{\text{Sn,calcd}}\!=\!1387\,\text{ppm})$ is in excellent agreement with the experimental data. No further splitting of the signal is observed in ¹H-coupled spectra, confirming that all hydrogen atoms have been removed from the Sn. $^{31}\!P\,NMR$ spectroscopy reveals a signal at $\delta_P\!=\!$ 95.0 ppm with the respective tin satellites. The drastic increase of ${}^{1}J_{Sn-P}$ coupling constants upon reductive dehydrogenation from $[Ar*SnH_2(PtBu_3)]^+$ (1) to $[Ar*Sn(PtBu_3)]^+$ (2) by almost two orders of magnitude may mark the differing nature of the P-Sn bond in these species. The Sn-P coupling behaves invers to couplings of the Sn-H moiety where ${}^{1}J_{Sn^{IV}-H}$ is often one order of magnitude bigger than ${}^{1}J_{Sn^{II}-H}$. For neutral phosphinyl stannylenes a ${}^{1}J_{Sn-P}$ coupling of around 1450 Hz was reported.^[13a] A ³¹P-EXSY-NMR experiment only revealed chemical exchange of the free phosphine with $[Ar*Sn(PtBu_3)]^+$ (2), but not with $[Ar*SnH_2(PtBu_3)]^+$ (1) on the examined NMR time scale.

X-ray diffraction studies revealed the molecular structure of **2** with the phosphine being arranged almost symmetrically between the two flanking Trip-groups (Trip = 2,4,6-*i*Pr₃C₆H₂-; Figure 1). Compound **2** represents an example of the rare structural motif of cationic, dicoordinate tetrylenes.^[14] An example of phosphine adducts to cationic Sn^{II} transition metal complexes is known.^[15] The Sn–P bond of 2.7071(3) Å is fairly long compared to a neutral phosphino stannylene Ar*SnP-(SiMe₃)₂ (2.527(1) Å).^[13a] The tin atom strongly deviates (ca. 22°) from the central phenyl plane, which is an established



Figure 1. ORTEP of $[Ar*Sn(PtBu_3)]^+$ (2). Thermal ellipsoids are set at 50% probability and protons, the counteranion, and lattice benzene are omitted for clarity. Canonical frontier molecular orbitals at an isodensity value of. 0.05 are shown. Selected distances [Å] and angles [°]: Sn–P 2.7071(3), Sn–C1 2.1876(12); closest Sn-*ortho*-C_{Trip} of the two Trip groups 3.27/3.35; P-Sn-C1 113.38(3), C4-C1-Sn 158.0(1). HOMO–LUMO gap: 5.610 eV.

phenomenon for ArSnX and usually rationalized by steric effects.^[16] The P-Sn-C angle amounts to 113.38(3)°. From the combination of a large R-E-(L) angle for a cationic $[RE(L)]^+$ species we anticipate further interesting reactivity.^[14a,17] The flanking Trip groups mildly tilt over towards the cationic tin center indicating weak arene interactions. The Sn–arene distances are comparable to those computationally predicted for $[Ar'Sn(^{Me}NHC)]^+$ $(Ar' = 2,6-Mes_2C_6H_3-, Mes = 2,4,6-Mes_3C_6H_2-).^{[18]}$ However, computational probing reveals a significant impact on the ¹¹⁹Sn NMR shift (Figure 2) and there-



Figure 2. Computational examination of the arene interaction on the ¹¹⁹Sn NMR shift on hypothetical [ArSn(PtBu₃)]⁺ derivatives. Structural modifications have been made to the optimized [Ar*Sn(PtBu₃)]⁺ structure and the shifts were directly computed on the basis of these structures without further re-optimization. Shifts δ_{Sn} are given in parts per million, relative to tetramethylstannane.

fore strongly indicates an electronic interaction.^[18] Flanking arene interactions in Group 14 cations have been observed previously.^[19] Attempts to obtain crystals of $[Ar*SnH_2-(PtBu_3)]^+$ (1) from the reaction mixtures only yielded colorless needles of phosphonium hydridoborate $[HP(tBu)_3][HB-(C_6F_5)_3]$.^[1c]

According to ³¹P NMR spectroscopy, the initial integration ratio of $2/1/PtBu_3/[HPtBu_3]^+$ is (roughly) 1.3:2:1:2.^[20] These mixtures were formed within a couple of minutes and only slowly showed some further conversions and partial decomposition over several days. Small amounts of dehydrocoupling product Ar*H₂SnSnH₂Ar* were formed under

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consumption of residual Ar^*SnH_3 . After two weeks, the ³¹P-NMR spectrum revealed integration ratios of approximately 1.7:1.3:1:4 indicating further consumption of the PtBu₃ and $[Ar^*SnH_2(PtBu_3)]^+$ (1) in favor of $[HPtBu_3]^+$ and distannane $Ar^*H_2SnSnH_2Ar^*$.

However, we found no indication for the formation of the phosphine adduct to the neutral hydrostannylene Ar*SnH-(PtBu₃) which is considered to be the intermediate after deprotonation of $[Ar*SnH_2(PtBu_3)]^+$ (1) by the phosphine (Scheme 2). Ar*SnH(PtBu₃) is not stable and expected to readily dissociate to Ar*SnH. The formation of Ar*H₂SnSnH₂Ar* is traced back to Ar*SnH reacting with Ar*SnH₃.^[22] The dimeric hydrostannylene $[Ar*SnH]_2$ could not be detected during the reaction.^[10]

Considering that $[Ar*SnH_2(PtBu_3)]^+$ (1) is the formal product of the reaction with one equivalent of FLP and $[Ar*Sn(PtBu_3)]^+$ (2) the respective product of the reaction with two equivalents of FLP, we reasoned that selective formation of [Ar*Sn(PtBu₃)]⁺ (2) should occur if Ar*SnH₃ was treated with two equivalents of the FLP. Under these conditions, the initial ¹H NMR spectrum confirms complete consumption of Ar*SnH₃ and formation of a mixture exclusively containing $[Ar*SnH_2(PtBu_3)]^+$ (1), $[Ar*Sn(PtBu_3)]^+$ (2), $PtBu_3$, and $[HPtBu_3]^+$ along with $[HB(C_6F_5)_3]^-$. Unlike in the 1:1 mixture, the hydride signal for $[HB(C_6F_5)_3]^-$ appears as a broad singlet rather than a broad quartet, which indicates the presence of residual free $B(C_6F_5)_3$ interacting with the hydridoborate. This assumption is further supported by ¹⁹F NMR spectroscopy which reveals broad resonances, rather than sharp signal sets for pure $[HB(C_6F_5)_3]^-$. ³¹P NMR spectroscopy provides a rough approximation of the relative ratios of phosphine derivatives (Table 1), differing from the reaction with only one equivalent of FLP. The

Table 1: Composition of the reaction mixture from the reaction of
Ar*SnH ₃ + 2 equiv FLP in C ₆ D ₆ / o -C ₆ H ₄ F ₂ over time according to ³¹ P NMR
spectra integrals (in %). ^[20]

Time	[Ar*Sn(PtBu ₃)] ⁺	[Ar*SnH ₂ (PtBu ₃)] ⁺	PtBu ₃	[HPtBu ₃] ⁺
25 min	20	28	22	30
7 days	30	13.6	9.1	47.3
14 days ^[a]	32.1	6.4	4.3	57.3

[a] ¹H NMR spectroscopy also reveals formation of a minor amount of new unassigned products without a corresponding $^{31}\mathsf{P}$ signal.

fact, that the expected product $[Ar*Sn(PtBu_3)]^+$ (2) is not formed quantitatively in these reaction mixtures that still contain both unreacted $B(C_6F_5)_3$ and $PtBu_3$, was surprising.

Over two weeks, along with some minor decomposition (only apparent in the ¹H NMR spectrum), $[Ar*Sn(PtBu_3)]^+$ (2) slowly becomes the predominant Sn-containing species while $[Ar*SnH_2(PtBu_3)]^+$ (1) and FLP are consumed. The NMR signals of the hydridoborate in the late-stage mixture are sharp, indicating that $B(C_6F_5)_3$ has fully been converted into the hydridoborate.

The initially fast, then strongly decelerated formation rate of $[Ar*Sn(PtBu_3)]^+$ (2) as the product of the reaction of $Ar*SnH_3$ with two equivalents of the FLP, is puzzling. To rationalize this, we propose the initial step to be a reversible formation of a weakly associated borane–stannane complex (I, Scheme 2) of $Ar*SnH_3$ and $B(C_6F_5)_3$. Similar structurally characterized silane-borole/silane-alane complexes have been isolated by the groups of Piers and Chen.^[3] Although no obvious change in NMR spectroscopic features becomes apparent on mixing $Ar*SnH_3$ and $B(C_6F_5)_3$ in benzene solutions at room temperature, we observed a significantly increased H–D scrambling rate in mixtures of $Ar*SnH_3$ and



Scheme 2. Suggested rationalization of the hydride/proton/hydride abstraction sequences for the formation of $[Ar*Sn(PtBu_3)]^+$ (2).^[21]

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Ar*SnD₃ when the borane is present. This is an indication for activation involving the putative borane stannane complex (Scheme 2).^[23] The stannane–borane complex can now react with the phosphine in two distinct pathways (Scheme 2, **Ha/IIb**). Since the borane does apparently not react with Ar*SnH₃ to fully abstract a hydride forming [Ar*SnH₂][HB-(C₆F₅)], the involvement of the phosphine is crucial to successful heterolytic cleavage of Sn–H bonds. We propose the target of the nucleophilic phosphine attack to be criterion for determining the final composition of products.

According to step IIa (Scheme 2) the phosphine reacts, as originally anticipated, as a Brønsted base attacking the positively polarized, protic Sn-H moiety and abstracting a proton. The elusive Ar*SnH then further reacts with a second equivalent of FLP forming the neutral basestabilized stannylene (step IIIa, Scheme 2) and hydride abstraction (step IV).^[24] In the second pathway, IIb, the phosphine attacks at the Sn atom forming the dihydrostannyl cation $[Ar*SnH_2(PtBu_3)]^+$ (1) in a substitution reaction similar to the formation of Burford's [Me₃SnPMe₃]⁺.^[12c] According to ³¹P EXSY-NMR spectra, this adduct formation is irreversible. For steric reasons, a proton abstraction from $[Ar*SnH_2(PtBu_3)]^+$ (1) by PtBu₃ is not favorable and thus slow, preventing rapid further conversion. To explain the experimentally observed formation of product mixtures, step II is considered to be unselective with proton abstraction IIa and adduct formation IIb being competing mechanistic routes of similar reaction rates. On the way to [Ar*Sn- $(PtBu_3)^{\dagger}$ (2), substantial amounts of tin hydride species are therefore trapped by formation of the rather unreactive Sn^{IV} species $[Ar*SnH_2(PtBu_3)]^+$ (1). Even after prolonged reaction times we have not observed substantial (i.e. greater than 3-5%) decomposition of the cationic phosphonium compounds via the deprotonation/isobutene elimination sequence that would either lead to phosphinyl stannane Ar*SnH₂PtBu₂ or phosphinyl stannylene Ar*SnPtBu₂.

Herein we showed that stannanes can be reductively dehydrogenated by FLP and that the FLP is able to completely strip off all the hydrogen atoms from a monoorgano stannane to form a cationic phosphonio-stannylene via reductive dehydrogenation. Observation of a dihydrostannyl phosphonium cation provided valuable and unprecedented insight into the competing processes involved in the stannane–FLP interaction. This may be fruitful for further studies of FLP-activated Group 14 hydrides R_nEH_{4-n} —especially with $n \leq 2$. We are currently exploring further reactivities of the cationic species created and trying to shed light on the influence of the organic substituent at Sn.

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Conflict of interest

The authors declare no conflict of interest.

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