

## ■ Frustrated Lewis Pairs

# A Zwitterionic Phosphonium Stannate(II) via Hydrogen Splitting by a Sn/P Frustrated Lewis-Pair and Reductive Elimination

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**Abstract:** The reactivity of the frustrated Lewis pair (FLP)  $(F_5C_2)_3SnCH_2P(tBu)_2$  (**1**) was investigated with respect to the activation of elemental hydrogen. The reaction of **1** at elevated hydrogen pressure afforded the intramolecular phosphonium stannate(II)  $(F_5C_2)_2SnCH_2PH(tBu)_2$  (**3**). It was characterized by means of multinuclear NMR spectroscopy and single crystal X-ray diffraction. NMR experiments with the two isotopologues  $H_2$  and  $D_2$  showed it to be formed via an  $H_2$  adduct  $(F_5C_2)_3HSnCH_2PH(tBu)_2$  (**2**) and the subsequent formal reductive elimination of pentafluoroethane; this is supported by DFT calculations. Parahydrogen-induced polarization experiments revealed the formation of a second product of the reaction of **1** with  $H_2$ ,  $[HP(tBu)_2Me][Sn(C_2F_5)_3]$  (**4**), in  $^1H$  NMR spectra, whereas **2** was not detected due to its transient nature.

With the concept of frustrated Lewis pairs (FLP) and their subsequent applications, molecular main group chemistry has gained an undeniable momentum in recent years.<sup>[1]</sup> As a leading example, in 2006 Stephan et al. discovered metal-free, reversible, heterolytic hydrogen cleavage, which later enabled FLP-catalyzed reductions of unsaturated substrates.<sup>[2]</sup> The majority of developed FLP systems consist of inter- and intramolecular combinations of boron- or aluminum-based Lewis acids and nitrogen- or phosphorus-based Lewis bases.<sup>[1]</sup> Rare-earth metals,<sup>[3]</sup> transition metals<sup>[4]</sup> and group 14 elements (Si,<sup>[5]</sup> Ge,<sup>[6]</sup>

$Sn^{[6,7]}$ ) have later been incorporated as Lewis acids into FLP systems. The tetrel elements were mainly introduced as electron deficient moieties in the form of silylium<sup>[5]</sup>/stannylum<sup>[7d,e]</sup> cations or stannylenes.<sup>[7a-c]</sup> Wesemann et al. succeeded in using intramolecular Sn<sup>II</sup>/P Lewis pairs for binding alkynes and alkenes.<sup>[7a-c]</sup> Intermolecular combinations of triflate salts of  $R_3Sn^+$  ( $R = iPr, Bn$ ) synthons and nitrogen Lewis bases enabled the reversible binding of elemental hydrogen and usage for catalytic hydrogenation of C=O, C=N and C=C double bonds.<sup>[7d,e]</sup> Recently, Power and Ashley showed that reversible hydrogen binding using distannynes and stannylenes is also possible without base or with catalytic amounts of base.<sup>[8]</sup> The introduction of strongly electron-withdrawing pentafluoroethyl groups<sup>[9]</sup> enabled us to increase the Lewis acidity of tetrel-based Lewis acids sufficiently to apply them in neutral methylene-bridged E/P ( $E = Si, Ge, Sn$ ) FLPs.<sup>[10]</sup> According to the HSAB concept, the reactivity of these FLP systems can be fine-tuned regarding the hardness or softness of the corresponding Lewis acid group. Among the previously presented tetrel-based E/P FLPs,  $(F_5C_2)_3ECH_2P(tBu)_2$  ( $E = Si, Ge, Sn$  (**1**)), the geminal Sn/P FLP **1** proved to have the widest range of FLP applications.<sup>[10]</sup> Contrary to its versatility, **1**, unlike the corresponding Si derivative, showed no reactivity in H/D scrambling experiments with  $H_2/D_2$  mixtures of 1 bar total pressure. We now found that a reaction between dihydrogen  $H_2$  and **1** is possible under harsher conditions.

The exposure of a solution of **1** in  $CD_2Cl_2$  to 10 bar of  $H_2$  led to the formation of new signals in all NMR spectra after one day (Figure 1). Integration of suitable signals resulted in a ratio of **1** to the newly formed species **3** of 87:13. After 15 days, the ratio was almost reversed and the emerging species **3** dominated with about 74% (Scheme 1).

The  $^1H$  NMR spectrum after 15 days showed a doublet of doublets ( $^2J_{PH} = 14$  Hz,  $^3J_{HH} = 7$  Hz) at 1.07 ppm for the methylene protons, while the resonance of the protons of the *tert*-butyl group was found at 1.43 ppm. In addition to the signal of unconverted hydrogen, two distinct signals were detected at lower field. While the triplet of quartets ( $^2J_{FH} = 52$  Hz,  $^3J_{FH} = 3$  Hz) at 5.95 ppm is clearly assigned to pentafluoroethane,<sup>[11]</sup> the doublet of triplets ( $^1J_{PH} = 439$  Hz,  $^3J_{HH} = 7$  Hz) at 5.25 ppm is characteristic for a methylene bound P-H moiety. Surprisingly, neither the  $^1H$  nor the  $^{119}Sn$  NMR spectrum gave signals of a corresponding Sn-H function, implying that the resulting species **3** may not be the expected  $H_2$  addition product **2**.

In order to ensure that pentafluoroethane formation is not due to hydrolysis, but rather due to preceding hydrogen acti-

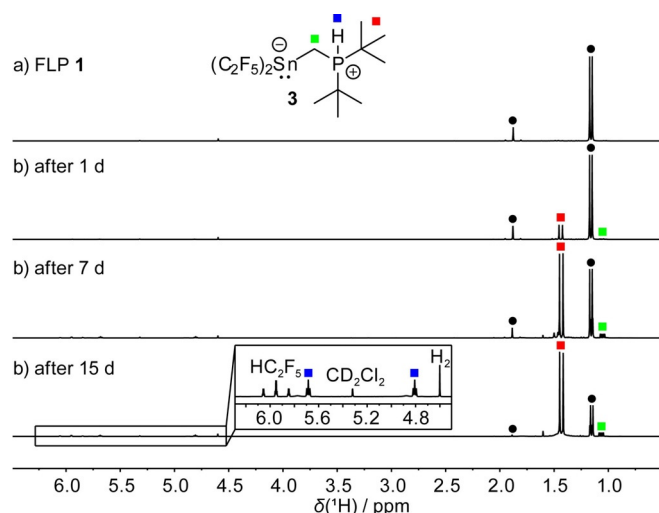
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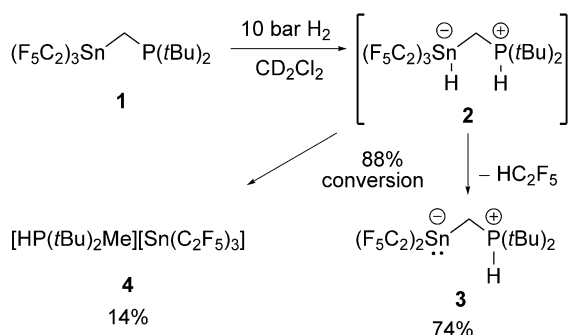
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**Figure 1.**  $^1\text{H}$  NMR spectra at 11.7 T of a) a sample of **1** (●) in  $\text{CD}_2\text{Cl}_2$  and b) a sample of **1** in  $\text{CD}_2\text{Cl}_2$ , exposed to 10 bar of  $\text{H}_2$  after different times of reaction.



**Scheme 1.** Reaction of FLP **1** with  $\text{H}_2$  on an NMR scale. Conversions were determined using  $^1\text{H}$  NMR integrals.

vation, the high-pressure NMR experiment was repeated with 10 bar of the heavier isotopologue deuterium,  $\text{D}_2$ . As in the corresponding experiment with hydrogen, new signals could be detected in all NMR spectra after one day.

Of particular significance is the triplet ( $^2J_{\text{FD}}=8$  Hz) at 5.95 ppm in the  $^2\text{H}$  NMR spectrum assigned to deuteriopentafluoroethane  $\text{CF}_3\text{CF}_2\text{D}$ . The same coupling constant was observed in the  $^{19}\text{F}$  NMR spectrum for the  $\text{CF}_2$  resonance, a 1:1:1 triplet of quartets ( $^2J_{\text{FD}}=8$  Hz,  $^3J_{\text{FF}}=3$  Hz) with a chemical shift of  $-139.2$  ppm; a coupling of the  $\text{CF}_3$  fluorine atoms to deuterium could not be resolved in this spectrum. The  $\text{CF}_3$  signal is detected as a triplet ( $^3J_{\text{FF}}=3$  Hz) at a chemical shift of  $-86.2$  ppm. Similarly, the formation of the deuterated species **3D** is confirmed by a 1:1:1 triplet with tin satellites ( $^1J_{\text{PD}}=67$  Hz,  $^2J_{\text{Sn,P}}=101$  Hz) at 57.1 ppm in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum and a doublet ( $^1J_{\text{PD}}=67$  Hz) at 5.28 ppm in the  $^2\text{H}$  NMR spectrum. At the same time, these results provide strong evidence for the initial step of formation of **3** to be the activation and splitting of  $\text{H}_2$  as postulated in Scheme 1.

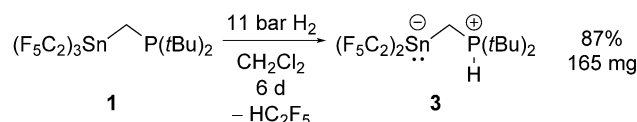
This tempted us to investigate the reaction on a preparative scale. Reacting **1** with 11 bar of  $\text{H}_2$  in a stainless steel autoclave

for six days afforded compound **3** as a colorless solid in 87% (165 mg) yield (Scheme 2).

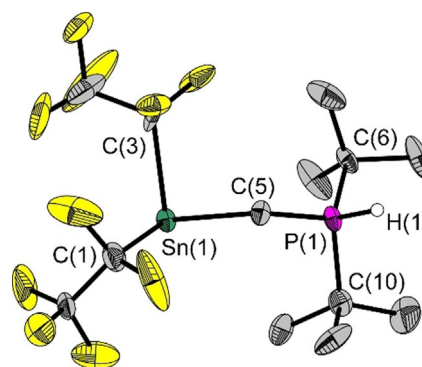
The molecular structure of **3**, revealed by single crystal X-ray diffraction (Figure 2), displays a trisubstituted tin atom linked by a methylene unit to a quaternary protonated phosphorus atom. Accordingly, **3** represents an intramolecular phosphonium stannate(II), formed after formal reductive elimination of  $\text{HC}_2\text{F}_5$ . Pentafluoroethylated stannates(II) are known from recent work by Hoge et al.<sup>[12]</sup> In accordance with a slightly widened  $\text{Sn}(1)\text{-C}(5)\text{-P}(1)$  angle of  $118.6(4)^\circ$ , the  $\text{Sn}(1)\cdots\text{P}(1)$  distance at  $3.512(1)$  Å is about  $0.16$  Å longer than in **1** (cf. ( $\text{Sn-C-P}$ )  $113.9(1)^\circ$ ,  $d(\text{Sn}\cdots\text{P})$   $3.349(1)$  Å).<sup>[10c]</sup> The C-Sn-C angles range from  $84.4(9)^\circ$  to  $93.9(7)^\circ$ , indicating a trigonal pyramidal coordinated tin atom; this is consistent with a localized lone pair at the tin atom. In analogy, the protonation of the phosphorus atom is accompanied by a slightly larger sum of C-P-C angles of  $342.1(31)^\circ$  compared to FLP **1** ( $\Sigma(\text{C-P-C})$ :  $312.0(17)^\circ$ ).<sup>[10c]</sup>

The solid state structure contains the conformer, where proton and tin atom at the  $\text{P}(1)\text{-C}(5)$  bond are *trans*-oriented. Surprisingly, the corresponding *cis*-conformer is quantum-chemically predicted to be energetically slightly more favorable by only  $1$   $\text{kJ mol}^{-1}$  (PBE0(D3BJ)/def2-TZVPP)—a hint that it is not the polarity of this zwitterionic structure stabilizing this form in the solid state.

To our surprise, the zwitterionic structure **3** is more stable than the tautomeric structure with the proton being located at the tin atom, the phosphinomethyl-stannane(IV) ( $\text{F}_5\text{C}_2)_2\text{HSnCH}_2\text{P}(\text{tBu})_2$  (**5**, Scheme 3). **5** is predicted to be  $18$   $\text{kJ mol}^{-1}$  higher in energy than the *cis*-conformer of **3**,



**Scheme 2.** Synthesis of **3** from FLP **1** and  $\text{H}_2$ .



**Figure 2.** Molecular structure of compound **3** in the solid state. Ellipsoids are set at 50% probability; hydrogen atoms, apart from the P-H moiety, are omitted for clarity. Selected bond lengths [Å] and angles [ $^\circ$ ]:  $\text{P}(1)\text{-C}(5)$   $1.800(10)$ ,  $\text{P}(1)\text{-C}(6)$   $1.830(8)$ ,  $\text{P}(1)\text{-C}(10)$   $1.831(9)$ ,  $\text{Sn}(1)\text{-C}(1)$   $2.238(13)$ ,  $\text{Sn}(1)\text{-C}(3)$   $2.347(17)$ ,  $\text{Sn}(1)\text{-C}(5)$   $2.275(5)$ ;  $\text{P}(1)\text{-C}(5)\text{-Sn}(1)$   $118.6(4)$ ,  $\text{C}(5)\text{-P}(1)\text{-C}(6)$   $118.5(12)$ ,  $\text{C}(5)\text{-P}(1)\text{-P}(10)$   $105.5(13)$ ,  $\text{C}(6)\text{-P}(1)\text{-P}(10)$   $118.1(4)$ ,  $\text{C}(1)\text{-Sn}(1)\text{-C}(3)$   $92.3(3)$ ,  $\text{C}(1)\text{-Sn}(1)\text{-C}(5)$   $93.9(7)$ ,  $\text{C}(3)\text{-Sn}(1)\text{-C}(5)$   $84.4(9)$ .



Scheme 3. Theoretical equilibrium between the tautomers **3** and **5**.

which means the neutral phosphane function is more basic than the anionic stannate(II) function.

The solid state structure in *trans*-conformation, the small energy difference between *cis*- and *trans*-conformations and the absence of a minimum structure with a proton bridging the phosphane and stannate(II) sites in the sense of a proton-sponge-like motif demonstrate the clear location of the proton at phosphorus. This is further proven by the  $^{31}\text{P}$  NMR spectrum of **3** containing a doublet of multiplets ( $^1J_{\text{P,H}} = 439$  Hz) at 57.4 ppm.  $^1\text{H}$  decoupling results in a  $^{31}\text{P}$  singlet resonance with tin satellites ( $^2J_{\text{Sn,P}} = 114$  Hz). The  $^{119}\text{Sn}$  NMR resonance ( $-99.7$  ppm) is significantly downfield-shifted compared to **1** ( $\delta(^{119}\text{Sn}) = -176.6$  ppm).<sup>[10c]</sup> The  $^{19}\text{F}$  NMR spectrum features three signals at chemical shifts of  $-82.3$ ,  $-118.0$  and  $-119.5$  ppm. The high-field shifted resonances represent AB spin systems ( $^2J_{\text{F,F}} = 331$  Hz) with  $^2J_{\text{Sn,F}}$  coupling constants of 146 and 53 Hz, respectively, indicating chemically inequivalent  $\text{CF}_2$  fluorine atoms. In comparison, the  $\text{CF}_3$  resonance at lower field is detected as a singlet with characteristic tin satellites ( $^3J_{\text{Sn,F}} = 55$  Hz). This coupling is typically not resolved in pentafluoroethyltin(IV) compounds and therefore provides diagnostic evidence for pentafluoroethylated tin(II) species.<sup>[12]</sup>

The formation of intramolecular phosphonium stannate(II) **3** has prompted us to examine the reaction of **1** with parahydrogen, the spin-0 nuclear-spin isomer of  $\text{H}_2$ . This experiment could enable observation of the intermediate **2** in  $^1\text{H}$  NMR spectra, since breaking the symmetry of parahydrogen molecules upon addition to **1** should enable strong NMR signal enhancements of the parahydrogen originating spins of **2**.<sup>[13]</sup> So far, parahydrogen-induced polarization (PHIP) was used to study reactive metal complex intermediates,<sup>[14]</sup> metal-free catalysts<sup>[15]</sup> and reaction mechanisms.<sup>[16]</sup> In our study, applying 5 bar of parahydrogen to a solution of **1** at room temperature did not result in any hyperpolarization effects. It was clear that the reaction is slow under these experimental conditions. Heating the sample to  $60^\circ\text{C}$  led, i.e., to the immediate observation of two enhanced antiphase quartet signals corresponding to the doublet of quartets of P-H proton signal of **4** at 5.35 ppm ( $^1J_{\text{P,H}} = 450$  Hz,  $^3J_{\text{H,H}} = 6$  Hz; Figure 3a).

The intermediate **2** was not detected in these experiments, most likely due to its transient nature, that is, very short lifetime. However, the observed PHIP signals of **4** provided an evidence of a competitive decomposition of **2** in addition to the one that leads to the formation of **3**. Both **3** and **4** are formed by the formal reductive elimination from **2** (Figure 3, top). Hyperpolarization effects were also observed for the methyl group of **4** ( $^2J_{\text{P,H}} = 13$  Hz,  $^3J_{\text{H,H}} = 6$  Hz) at 1.85 ppm indicating the other hyperpolarized proton that stems from parahydrogen (Figure S29 in the Supporting Information). Product **3** did not show any hyperpolarization effects, since the reaction leads to

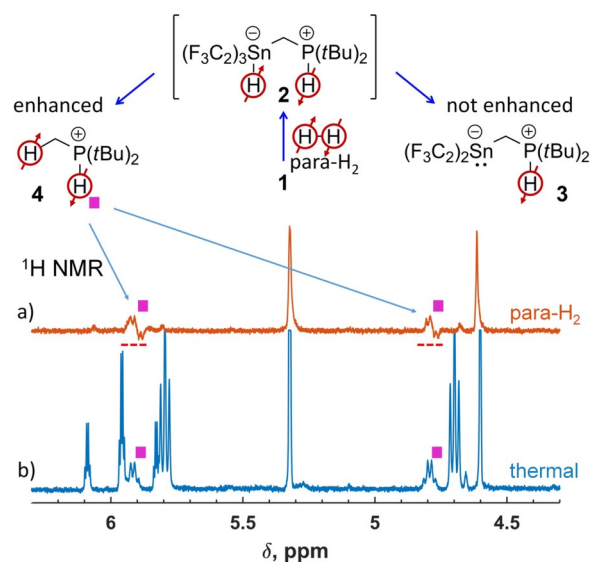


Figure 3. (a)  $^1\text{H}$  NMR spectrum measured after addition of parahydrogen (5 bar) into a solution of **1** in  $\text{CD}_2\text{Cl}_2$  at  $60^\circ\text{C}$  and 9.4 T. Antiphase quartet signals of the P-H proton are shown with blue arrows and underlined with a red dashed line. (b) A reference  $^1\text{H}$  NMR thermal spectrum of the same sample measured after 24 hours. The signals other than those of the P-H group belong to  $\text{HC}_2\text{F}_5$ , **3**,  $\text{CHDCl}_2$  and  $\text{H}_2$  (see Figure 1). The high-intensity signals corresponding to thermally polarized protons are off-scale and are cut in (b) for a better visibility of other signals.

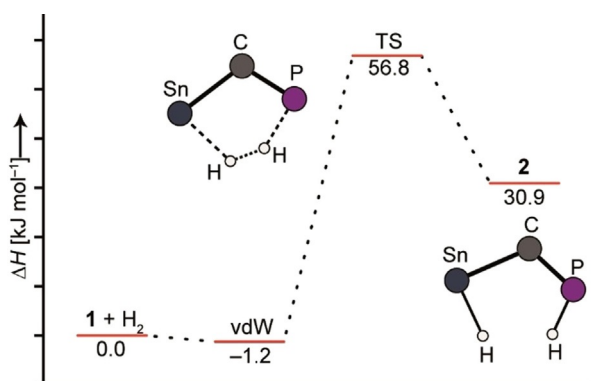
separation of the H atoms pair of parahydrogen, which prevents observation of hyperpolarization.

Without signal enhancement provided by PHIP, it was essentially impossible to detect **4** at the beginning. No less than 24 hours were required to accumulate this product and to observe it with thermal polarization (Figure 3b). Surprisingly, the signal intensity and thus the concentration of **4** does neither increase nor decrease significantly within one week after that. Instead, all NMR signals of **4** show signal broadening, most likely caused by a dynamic equilibrium in the form of a proton exchange reaction.

In contrast, the concentration of **3** increases over time, as was observed via NMR spectroscopy. This is consistent with the above described favored formation of intramolecular phosphonium stannate(II) **3** under preparative conditions. Upon closer examination, the same broadened signals of compound **4** can be observed as traces in the NMR spectra of the high pressure NMR experiments of **1** with  $\text{H}_2$  discussed above (Scheme 1, Figure 1).

For a closer investigation of the activation of molecular hydrogen, a reaction profile was constructed based on quantum-chemical calculations (Figure 4, computational details see Supporting Information). Upon formation of a van der Waals (vdW) complex of **1** with  $\text{H}_2$  the energy is lowered by  $1\text{ kJ mol}^{-1}$  compared to the separated FLP molecule and molecular dihydrogen. No significant structural changes, neither in the FLP **1** nor in the  $\text{H}_2$  molecule, are observed in this complex.

The transition state for hydrogen-splitting (TS) is located  $58\text{ kJ mol}^{-1}$  in energy above the vdW complex. Lower activation energies for hydrogen splitting have been calculated for geminal nitrogen/triell systems.<sup>[17]</sup> In this late transition state,



**Figure 4.** Computed reaction profile for the  $\text{H}_2$ -splitting reaction of **1**. All data have been computed at the PBE0(D3BJ)/def2-TZVPP level of theory. The substituents at tin and phosphorus have been omitted for the sake of clarity.

the H–H bond length rises to 1.05 Å, comparable to the respective distance of 0.99 Å in the transition state of hydrogen activation by the geminal FLP  $\text{Ph}_2\text{BCH}_2\text{P}(\text{tBu})_2$ .<sup>[18]</sup> Additionally, the Sn...P distance in the transition state decreases to 3.30 Å (1: 3.39 Å) along with the Sn–C–P angle (110.2°, 1: 116.3°). In contrast, widening of the angle and enlargement of the donor/acceptor distance has been observed for nitrogen/boron FLPs.<sup>[19]</sup> Significant interactions between the hydrogen unit and the P or Sn atoms become manifest in distances far below the corresponding sum of the vdW radii [ $d(\text{Sn}\cdots\text{H}) = 2.00$  Å,  $\Sigma r_{\text{vdW}} = 3.62$  Å;  $d(\text{P}\cdots\text{H}) = 1.66$  Å,  $\Sigma r_{\text{vdW}} = 3.10$  Å].<sup>[20]</sup> Accordingly, this mechanism can be described as concerted. Note, that the activated hydrogen molecule and the P and Sn atoms are almost in plane ( $(\text{Sn}-\text{H}-\text{H}-\text{P}) = 3.3^\circ$ ).

The  $\text{H}_2$  activation product **2** is found to be 26  $\text{kJ mol}^{-1}$  lower in energy than the transition state. The H...H distance is enlarged to 2.10 Å accompanied by a widening of the Sn–H–H–P dihedral angle to 21.6°. Figure 4 shows the endothermic character of this reaction; the product **2** is about 30  $\text{kJ mol}^{-1}$  higher in energy than the educts. However, the system relaxes regarding the energy by a formal reductive elimination to either the linked phosphorus/tin pair **3** or the phosphonium stannate(II) ion pair **4**. The latter one is about 58  $\text{kJ mol}^{-1}$  more stable than the educts **1** and  $\text{H}_2$ , while the former one, **3**, together with pentafluoroethane is even 121  $\text{kJ mol}^{-1}$  more stable than the educts. The energetic preference of **3** over **4** is in conformity with the higher concentration of **3** observed by NMR spectroscopy and on a preparative scale.

The very slow formation of **3** led to the question whether the combination of FLP **1** and  $\text{H}_2$  could be used for catalytic hydrogenation of unsaturated substrates in a competitive pathway to the reductive elimination reactions. However, no catalytic hydrogenation was observed, when reacting *N*-benzylidene-*tert*-butylamine and ( $\beta$ -styryloxy)trimethylsilane with 10 bar  $\text{H}_2$  and 6 mol% of **1** for 19 h at ambient temperature. In order to demonstrate the use of FLP **1** for hydrogenation, that is, the catalytic transfer of  $\text{H}_2$ , experiments with other substrates besides these two benchmark systems are subject of current investigations.

Herein we have illuminated the reactivity of the neutral intramolecular Sn/P FLP **1** towards elemental hydrogen. While experiments with **1** and  $\text{H}_2/\text{D}_2$  mixtures of 1 bar total pressure show no evidence of H/D scrambling reactions, the reaction of **1** with 10 bar of hydrogen yields the unusual neutral and zwitterionic phosphonium stannate(II) **3**. High pressure NMR experiments with both isotopologues  $\text{H}_2$  and  $\text{D}_2$  prove that formation of **3** clearly proceeds via initial hydrogen activation and subsequent reductive elimination of pentafluoroethane. This illustrates the limits of stability of pentafluoroethyl substituents at elements like tin versus the hydrogenating power of FLP-split hydrogen. Attempts to detect and characterize such a hydrogen-activated intermediate (**2**) via PHIP NMR experiments failed, but instead revealed the presence of further hydrogenolysis mechanisms at tin by the detection of another product **4**, being formed in traces compared to **3**. Quantum-chemical calculations fully confirm these results, since **3** is energetically more stable by 152 and 63  $\text{kJ mol}^{-1}$  than the  $\text{H}_2$  adduct **2** or the by-product **4**, respectively. These results encourage us to further investigate the obtained species in future applications regarding the catalytic reduction of suitable unsaturated substrates, but also to test other electronegative substituents for an increased stability towards hydrogenolysis.

Deposition Number 2025485 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

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## Conflict of interest

The authors declare no conflict of interest.

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- [1] a) D. W. Stephan, *Science* **2016**, *354*, aaf7229; b) D. W. Stephan, *Acc. Chem. Res.* **2015**, *48*, 306–316; c) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400–6441; *Angew. Chem.* **2015**, *127*, 6498–6541; d) D. W. Stephan, G. Erker, *Chem. Sci.* **2014**, *5*, 2625–2641; e) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76; *Angew. Chem.* **2010**, *122*, 50–81; f) D. W. Stephan, *Dalton Trans.* **2009**, 3129–3136.  
 [2] a) G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126; b) P. A. Chase, G. C. Welch, T. Jurca, D. W. Stephan, *Angew. Chem. Int. Ed.* **2007**, *46*, 8050–8053; *Angew. Chem.* **2007**, *119*, 8196–8199; c) K. Chernichenko, M. Nieger, M. Leskelä, T. Repo, *Dalton*

- Trans.* **2012**, *41*, 9029–9032; d) H. Wang, R. Fröhlich, G. Kehr, G. Erker, *Chem. Commun.* **2008**, 5966–5968.
- [3] M. Pieper, J.-H. Lamm, B. Neumann, H.-G. Stammler, N. W. Mitzel, *Dalton Trans.* **2017**, *46*, 5326–5336.
- [4] a) M. Pieper, P. Auer, S. Schwarzbach, F. Kühn, B. Neumann, H.-G. Stammler, N. W. Mitzel, *Z. Anorg. Chem.* **2017**, *643*, 909–915; b) X. Xu, G. Kehr, C. G. Daniliuc, G. Erker, *J. Am. Chem. Soc.* **2013**, *135*, 6465–6476; c) A. M. Chapman, M. F. Haddow, D. F. Wass, *J. Am. Chem. Soc.* **2011**, *133*, 8826–8829; d) A. M. Chapman, M. F. Haddow, D. F. Wass, *J. Am. Chem. Soc.* **2011**, *133*, 18463–18478; e) R. Dobrovetsky, D. W. Stephan, *Isr. J. Chem.* **2015**, *55*, 206–209; f) R. Dobrovetsky, D. W. Stephan, *Angew. Chem. Int. Ed.* **2013**, *52*, 2516–2519; *Angew. Chem.* **2013**, *125*, 2576–2579; g) P. Jochmann, D. W. Stephan, *Angew. Chem. Int. Ed.* **2013**, *52*, 9831–9835; *Angew. Chem.* **2013**, *125*, 10014–10018; h) K. Chang, X. Wang, Z. Fan, X. Xu, *Inorg. Chem.* **2018**, *57*, 8568–8580.
- [5] a) S. A. Weicker, D. W. Stephan, *Chem. Eur. J.* **2015**, *21*, 13027–13034; b) A. Schäfer, M. Reißmann, A. Schäfer, W. Saak, D. Haase, T. Müller, *Angew. Chem. Int. Ed.* **2011**, *50*, 12636–12638; *Angew. Chem.* **2011**, *123*, 12845–12848; c) T. J. Herrington, B. J. Ward, L. R. Doyle, J. McDermott, A. J. P. White, P. A. Hunt, A. E. Ashley, *Chem. Commun.* **2014**, *50*, 12753–12756.
- [6] Y. Yu, J. Li, W. Liu, Q. Ye, H. Zhu, *Dalton Trans.* **2016**, *45*, 6259–6268.
- [7] a) K. M. Krebs, S. Freitag, H. Schubert, B. Gerke, R. Pöttgen, L. Wesemann, *Chem. Eur. J.* **2015**, *21*, 4628–4638; b) S. Freitag, J. Henning, H. Schubert, L. Wesemann, *Angew. Chem. Int. Ed.* **2013**, *52*, 5640–5643; *Angew. Chem.* **2013**, *125*, 5750–5754; c) S. Freitag, K. M. Krebs, J. Henning, J. Hirdler, H. Schubert, L. Wesemann, *Organometallics* **2013**, *32*, 6785–6791; d) D. J. Scott, N. A. Phillips, J. S. Sapsford, A. C. Deacy, M. J. Fuchter, A. E. Ashley, *Angew. Chem. Int. Ed.* **2016**, *55*, 14738–14742; *Angew. Chem.* **2016**, *128*, 14958–14962; e) R. T. Cooper, J. S. Sapsford, R. C. Turnell-Ritson, D.-H. Hyon, A. J. P. White, A. E. Ashley, *Phil. Trans. R Soc. A* **2017**, *375*, 20170008.
- [8] a) S. Wang, T. J. Sherbow, L. A. Berben, P. P. Power, *J. Am. Chem. Soc.* **2018**, *140*, 590–593; b) R. C. Turnell-Ritson, J. S. Sapsford, R. T. Cooper, S. S. Lee, T. Földes, P. A. Hunt, I. Pápai, A. E. Ashley, *Chem. Sci.* **2018**, *9*, 8716–8722.
- [9] M. Wiesemann, B. Hoge, *Chem. Eur. J.* **2018**, *24*, 16457–16471.
- [10] a) B. Waerder, M. Pieper, L. A. Körte, T. A. Kinder, A. Mix, B. Neumann, H.-G. Stammler, N. W. Mitzel, *Angew. Chem. Int. Ed.* **2015**, *54*, 13416–13419; *Angew. Chem.* **2015**, *127*, 13614–13617; b) T. A. Kinder, R. Pior, S. Blomeyer, B. Neumann, H.-G. Stammler, N. W. Mitzel, *Chem. Eur. J.* **2019**, *25*, 5899–5903; c) P. Holtkamp, F. Friedrich, E. Stratmann, A. Mix, B. Neumann, H.-G. Stammler, N. W. Mitzel, *Angew. Chem. Int. Ed.* **2019**, *58*, 5114–5118; *Angew. Chem.* **2019**, *131*, 5168–5172; d) P. Holtkamp, T. Glodde, D. Poier, B. Neumann, H.-G. Stammler, N. W. Mitzel, *Angew. Chem. Int. Ed.* **2020**, *59*, 17388–17392; *Angew. Chem.* **2020**, *132*, 17541–17545.
- [11] a) M. D. Bartberger, W. R. Dolbier, J. Luszytyk, K. U. Ingold, *Tetrahedron* **1997**, *53*, 9857–9880; b) N. Ignatev, A. Kucherina, P. Sartori, *Acta Chem. Scand.* **1999**, *53*, 1110–1116.
- [12] a) M. Wiesemann, J. Klösener, M. Niemann, B. Neumann, H.-G. Stammler, B. Hoge, *Chem. Eur. J.* **2017**, *23*, 14476–14484; b) J. Klösener, M. Wiesemann, B. Neumann, H.-G. Stammler, B. Hoge, *Eur. J. Inorg. Chem.* **2018**, 3971–3977.
- [13] a) C. R. Bowers, D. P. Weitekamp, *Phys. Rev. Lett.* **1986**, *57*, 2645–2648; b) C. R. Bowers, *Sensitivity Enhancement Utilizing Parahydrogen* (Eds.: D. M. Grant, R. K. Harris), *Encyclopedia of Nuclear Magnetic Resonance*, Wiley, Chichester, **2002**, 750–769.
- [14] S. B. Duckett, S. A. Colebrooke, *Parahydrogen Enhanced NMR Spectroscopic Methods: a Chemical Perspective* (Eds.: D. M. Grant, R. K. Harris), *Encyclopedia of Nuclear Magnetic Resonance*, Wiley, Chichester, **2002**, 598–620.
- [15] a) V. V. Zhivonitko, K. Sorochkina, K. Chernichenko, B. Kótai, T. Földes, I. Pápai, V.-V. Telkki, T. Repo, I. Koptuyug, *Phys. Chem. Chem. Phys.* **2016**, *18*, 27784–27795; b) K. Sorochkina, V. V. Zhivonitko, K. Chernichenko, V.-V. Telkki, T. Repo, I. V. Koptuyug, *J. Phys. Chem. Lett.* **2018**, *9*, 903–907; c) V. V. Zhivonitko, J. Bresien, A. Schulz, I. V. Koptuyug, *Phys. Chem. Chem. Phys.* **2019**, *21*, 5890–5893.
- [16] a) V. V. Zhivonitko, K. V. Kovtunov, I. V. Skovpin, D. A. Barskiy, O. G. Salnikov, I. V. Koptuyug, *Catalytically Enhanced NMR of Heterogeneously Catalyzed Hydrogenations* (Ed.: V. P. Ananikov), *Understanding Organometallic Reaction Mechanisms and Catalysis*, Wiley-VCH, Weinheim, **2014**, 145–186; b) S. B. Duckett, N. J. Wood, *Coord. Chem. Rev.* **2008**, *252*, 2278–2291.
- [17] J. J. Cabrera-Trujillo, I. Fernández, *Chem. Eur. J.* **2018**, *24*, 17823–17831.
- [18] a) T. A. Rokob, I. Bakó, A. Stirling, A. Hamza, I. Pápai, *J. Am. Chem. Soc.* **2013**, *135*, 4425–4437; b) F. Bertini, V. Lyaskovskyy, B. J. J. Timmer, F. J. J. de Kanter, M. Lutz, A. W. Ehlers, J. C. Slootweg, K. Lammertsma, *J. Am. Chem. Soc.* **2012**, *134*, 201–204.
- [19] D. Yepes, P. Jaque, I. Fernández, *Chem. Eur. J.* **2016**, *22*, 18801–18809.
- [20] S. Alvarez, *Dalton Trans.* **2013**, *42*, 8617–8636.

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