

## 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<sub>5</sub>C<sub>2</sub>)<sub>3</sub>SnCH<sub>2</sub>P(tBu)<sub>2</sub> (**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<sub>5</sub>C<sub>2</sub>)<sub>2</sub>SnCH<sub>2</sub>PH(tBu)<sub>2</sub> (**3**). It was characterized by means of multinuclear NMR spectroscopy and single crystal X-ray diffraction. NMR experiments with the two isotopologues H<sub>2</sub> and D<sub>2</sub> showed it to be formed via an H<sub>2</sub> adduct (F<sub>5</sub>C<sub>2</sub>)<sub>3</sub>HSnCH<sub>2</sub>PH(tBu)<sub>2</sub> (**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<sub>2</sub>, [HP(tBu)<sub>2</sub>Me][Sn(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>] (**4**), in <sup>1</sup>H 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<sup>[6,7]</sup>) 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<sub>3</sub>Sn<sup>+</sup> (R = *i*Pr, 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<sub>5</sub>C<sub>2</sub>)<sub>3</sub>ECH<sub>2</sub>P(tBu)<sub>2</sub> (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<sub>2</sub>/D<sub>2</sub> mixtures of 1 bar total pressure. We now found that a reaction between dihydrogen H<sub>2</sub> and **1** is possible under harsher conditions.

The exposure of a solution of **1** in CD<sub>2</sub>Cl<sub>2</sub> to 10 bar of H<sub>2</sub> 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 <sup>1</sup>H NMR spectrum after 15 days showed a doublet of doublets (<sup>2</sup>J<sub>PH</sub> = 14 Hz, <sup>3</sup>J<sub>H,H</sub> = 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 (<sup>2</sup>J<sub>FH</sub> = 52 Hz, <sup>3</sup>J<sub>FH</sub> = 3 Hz) at 5.95 ppm is clearly assigned to pentafluoroethane,<sup>[11]</sup> the doublet of triplets (<sup>1</sup>J<sub>PH</sub> = 439 Hz, <sup>3</sup>J<sub>H,H</sub> = 7 Hz) at 5.25 ppm is characteristic for a methylene bound P-H moiety. Surprisingly, neither the <sup>1</sup>H nor the <sup>119</sup>Sn NMR spectrum gave signals of a corresponding Sn-H function, implying that the resulting species **3** may not be the expected H<sub>2</sub> 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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