Olefin Hydrogenation

Deutsche Ausgabe: DOI: 10.1002/ange.201504109
Internationale Ausgabe: DOI: 10.1002/anie.201504109

Electrophilic Fluorophosphonium Cations in Frustrated Lewis Pair Hydrogen Activation and Catalytic Hydrogenation of Olefins[**]

Thorsten vom Stein, Manuel Peréz, Roman Dobrovetsky, Daniel Winkelhaus,
Christopher B. Caputo, and Douglas W. Stephan[*]

Abstract: *The combination of phosphorus(V)-based Lewis acids with diaryl amines and diaryl silylamines promotes reversible activation of dihydrogen and can be further exploited in metal-free catalytic olefin hydrogenation. Combined experimental and density functional theory (DFT) studies suggest a frustrated Lewis pair type activation mechanism.*

The catalytic hydrogenation of unsaturated functionalities is one of the most important fundamental tools in modern chemical synthesis.[1] While the field is still largely dominated by metal-based catalytic systems, the discovery of reversible hydrogen activation by frustrated Lewis pairs (FLPs) in 2006 has paved the way for metal-free catalytic hydrogenation.[2] Over the past nine years, a number of FLP catalysts have emerged for an increasing scope of substrates. To date, FLP hydrogenation has been used to reduce unsaturated functionalities, including imines,[3] aziridines,[3] enamines,[4] silyl enol ethers,[5] olefins,[6] alkynes,[7] polyaromatics,[8] and most recently ketones[9] and aldehydes.[10] The catalysts used for these reductions have involved boron-based Lewis acids. While the majority of studies employ highly electrophilic boranes such as $B(C_6F_5)_3$ or related derivatives,[11] a recent development has been the use of carbene-stabilized borenium-based catalysts.[12] Another innovation exploits hydroboration of chiral-derived olefins by Piers' borane $HB(C_6F_5)_2$,[13] affording a highly efficient catalyst for asymmetric hydrogenations.[14] In terms of the basic component of the FLP, a variety of sterically demanding phosphines or amine species are most common, although this has been extended to include electronic deficient phosphines, as well as ethers.[6b,9,15]

Despite the apparent limitation of FLP hydrogenations to largely boron-based Lewis acids, a growing range of Lewis acids including Al, C, Si as well as Ti and Zr derivatives have been investigated in FLP chemistry.[15,16] The Lewis acidity of phosphonium centers received lesser attention[17] although Gabbaï and co-workers have used phosphonium centers for enhanced fluoride ion sensing.[18] On the other hand, we have developed highly electrophilic phosphonium cations (EPCs). These latter compounds proved to be highly Lewis acidic. This arises from a low lying σ* orbital, whereas classical Group 13 Lewis acids derive their Lewis acidity from a vacant p orbital. In an initial study we showed that an electrophilic P center can be used in CO_2 capture,[19] in manner analogous to that seen for FLPs. Utilizing this acidity we have also shown that EPCs are more Lewis acidic than $B(C_6F_5)_3$ and effective catalysts for hydrodefluorination of fluoralkanes,[20] hydrosilylation of olefins, alkynes,[21] imines, and ketones[22] and dehydocoupling of silanes with carboxylic acids, alcohols, thiols, and amines.[23] Furthermore, concurrent catalytic hydrogenation was achieved upon addition of olefins to these dehydrocoupling reactions.[23] In these studies of catalysis by the EPC $[FP(C_6F_5)_3][B(C_6F_5)_4]$ **1**, DFT computations inferred intermediates including hydridophosphorane $[(C_6F_5)_3PFH]$ and $[Ph_2N(H)SiEt_3]^+$. We recognized that these intermediates could also be generated by the activation of hydrogen between **1** and Ph_2NSiEt_3. Herein, we demonstrate that Lewis acidity of EPCs in combination with sterically encumbered aryl-substituted amines can be exploited as FLPs for H_2 activation and hydrogenation catalysis.

In an initial experiment, an equimolar mixture of *p*-Tol_2NH and **1** was heated under an HD atmosphere. After 24 h at 100 °C the formation of H_2 was observed, indicating reversible hydrogen activation. HD scrambling was subsequently shown to proceed at lower temperatures (60 °C) albeit at lower rates of reaction (see the Supporting Information, Section S3). These observations suggest that the combination of **1** and *p*-Tol_2NH acts as an FLP to effect the heterolytic activation of H_2.

To probe the interactions of **1** and *p*-Tol_2NH, stoichiometric combination of the Lewis acid and base were monitored by ^1H NMR spectroscopy. The normally sharp resonances for the amine are broadened dramatically. A very broad resonance is observed at 7.10 ppm while the resonances attributable to the *p*-Me fragment is not seen. A low-temperature NMR study was also undertaken, however $[FP(C_6F_5)_2Ph][B(C_6F_5)_4]$ **2** was used for solubility reasons. At −90 °C the peaks arising from the *p*-Tol_2NH began to resolve (Supporting Information, Section S3), although a limiting spectrum was observed. These experimental data support the postulate of the generation of an encounter complex analogous to that computed for the Lewis acid–base combination of tBu_3P and $B(C_6F_5)_3$.[24]

---

[*] Dr. T. vom Stein,[+] Dr. M. Peréz,[+] Dr. R. Dobrovetsky,
Dr. D. Winkelhaus, Dr. C. B. Caputo, Prof. Dr. D. W. Stephan
Department of Chemistry, University of Toronto
80 St. George St, Toronto Ontario M5S3H6 (Canada)
E-mail: dstephan@chem.utoronto.ca

[+] These authors contributed equally to this work.

[**] The authors acknowledge NSERC of Canada for continuing support of this research and D.W.S. is grateful for the award of a Canada Research Chair. T.v.S. thanks the Alexander von Humboldt Foundation for a Feodor von Lynen Research Fellowship. C.B.C. gratefully acknowledges the receipt of an NSERC of Canada CGS-D Award.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201504109.

In further probing the FLP character of the present system, DFT calculations at WB97XD/def2TZV level of theory[25] were performed on the Lewis acidic cation $[FP(C_6F_5)_3]^+$ and the Lewis base Ph_2NH. Interestingly, the optimized structure shows an approach of the donor to the acceptor but no direct covalent interaction between P and N centers. The resulting P···N distance is 3.52 Å. π-Stacking interactions[26] between two of the electron poor C_6F_5 rings of the fluorophosphonium with the electron-rich phenyl rings of the amine is observed with ring separations of approximately 3.20 Å (Figure 1). The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of this encounter complex were mainly concentrated on the nitrogen atom and the phosphorus atom respectively. While these orbitals are oriented towards each other, the steric conflicts and π-stacking preclude a dative interaction. The formation of the π-stacking-stabilized encounter complex is exergonic ($\Delta G = -6.3$ kcal mol^{-1}) and exothermic ($\Delta H = -23.4$ kcal mol^{-1}; Figure 2).

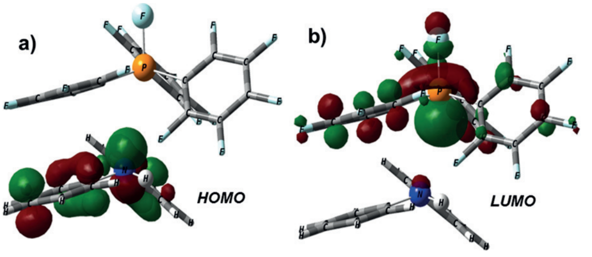


Figure 1. a) HOMO and b) LUMO of the $[(C_6F_5)_3P]^+/Ph_2NH$ encounter complex (isovalue = 0.05).

Calculation of the subsequent barrier for H_2 activation found to be relatively low ($\Delta G^{\neq} = 12.9$ kcal mol^{-1} and $\Delta H^{\neq} = 6.1$ kcal mol^{-1}) while the overall process of the heterolytic H_2 cleavage is energetically favorable ($\Delta G = -22.6$ kcal mol^{-1} and $\Delta H = -31.8$ kcal mol^{-1}; Figure 2). This generates an activation barrier of 29.2 kcal mol^{-1} for the reverse reaction, which is consistent with the requirement of heating to 100 °C for HD scrambling to be observed. The transition state for the activation of H_2 was computed and shows the H_2 molecule oriented between the N and P such that one H atom is 2.46 Å from N and the other is 2.83 Å from P, with an H−H distance of 0.74 Å and N-H-H and P-H-H angles of 119.3° and 102.3°, respectively. This geometry gives rise to a P···N separation of 5.42 Å. This dissymmetric geometry suggests the polarization of the H_2 molecule and is reminiscent of the non-linear transition state computed for the interaction of the FLP $tBu_3P/B(C_6F_5)_3$ with H_2.[24]

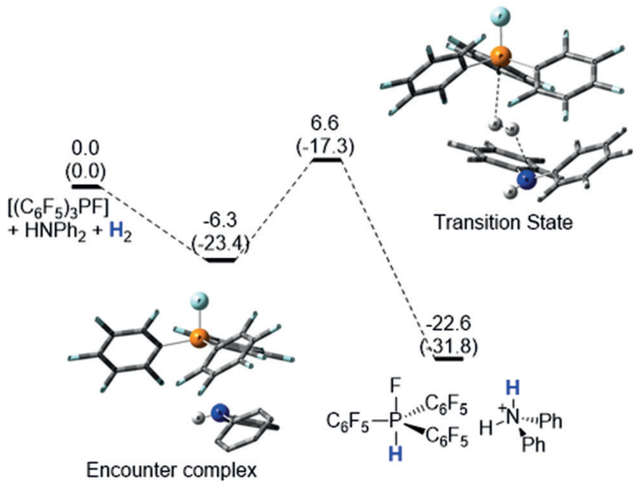
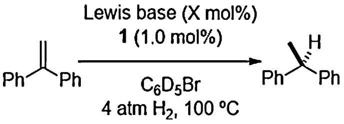


Figure 2. Reaction coordinate of the H_2 activation by $[(C_6F_5)_3P]^+/Ph_2NH$. Gibbs free energy (enthalpy) in kcal mol^{-1} are given relative to starting materials.

The ability to activate H_2 suggests the potential for catalytic hydrogenation. To avoid Lewis acid mediated Friedel–Crafts reactions $Ph_2C{=}CH_2$ was combined with 1 mol % **1** and 20 mol % p-Tol_2NH in C_6D_5Br. This mixture was pressurized under 4 atm of H_2 and heated to 100 °C. This resulted in less than 5 % conversion to Ph_2CHCH_3 (Table 1, entry 1). In contrast, employing 1 mol % **1** and 20 mol % p-Tol_2NSiEt_3 to generate the FLP catalyst resulted in the efficient hydrogenation of $Ph_2C{=}CH_2$, affording Ph_2CHCH_3 after 24 h (Table 1, entry 2). Lowering the catalyst loading gave the correspondingly lower conversion (Table 1, entries 3, 4). Employing 20 mol % of the amino silanes p-$Tol_2NSi(iPr)_3$, p-$Tol_2NSiMe_2(tBu)$, and p-Tol_2NSiPh_3 also promoted the catalytic hydrogenation of $Ph_2C{=}CH_2$, yielding Ph_2CHCH_3 after 24 h in yields ranging from 51–56 % (Table 1, entries 5–7). The reduced conversions of these latter catalyst systems in comparison to that generated from **1**/p-Tol_2NSiEt_3 suggest that increased steric encumbrance of the N-base lowers the catalytic efficiency, presumably by impeding formation of the appropriate encounter complex geometry.

Table 1: Catalytic hydrogenation of $Ph_2C{=}CH_2$.[a]



	Lewis base	[mol %]	T [°C]	t [h]	Conv. [%]
1	p-Tol_2NH	20	100	24	< 5 %
2	p-Tol_2NSiEt_3	20	100	24	98
3	p-Tol_2NSiEt_3	10	100	24	86
4	p-Tol_2NSiEt_3	5	100	24	43
5	p-$Tol_2NSi(iPr)_3$	20	100	24	56
6	p-$Tol_2NSiMe_2(tBu)$	20	100	24	54
7	p-Tol_2NSiPh_3	20	100	24	51
8[b]	Et_3SiH/p-Tol_2NH	20	100	24	15
9	Et_3SiH/p-Tol_2NH	20	100	24	99 (92)[c]
10	Et_3SiH/p-Tol_2NH	20	100	4	43
11	Et_3SiH/p-Tol_2NH	20	100	8	85
12	Et_3SiH/p-Tol_2NH	20	75	24	51
13	Et_3SiH/p-Tol_2NH	20	50	24	23

[a] Reaction conditions: 0.5 mmol $Ph_2C{=}CH_2$, 0.005 mmol **1**, 1 mL C_6D_5Br, 4 atm H_2, 100 °C. Conversion determined by ^1H NMR spectroscopy. [b] Reaction done in absence of H_2. [c] Yield of isolated product.

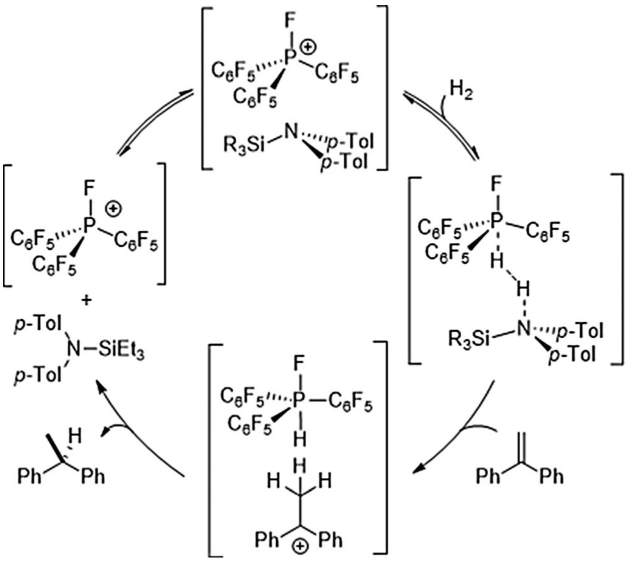
The above experiments demonstrate that p-Tol_2NSiEt_3 is the best of the bases tested. We have previously reported the synthesis of this species by catalyzing the dehydrocoupling of *p*-Tol$_2$NH and HSiEt$_3$ using **1** as the catalyst.[23] Thus, treatment of Ph$_2$C=CH$_2$ with 20 mol % of *p*-Tol$_2$NH and HSiEt$_3$ using **1** as the catalyst but in absence of hydrogen gave only 15 % reduction via the reported transfer hydrogenation pathway (Table 1, entry 8).[23] However, this process did show that the silylamine *p*-Tol$_2$NSiEt$_3$ could be conveniently generated in situ (Supporting Information, Figure S82). Thus, 20 mol % of Et$_3$SiH and *p*-Tol$_2$NH was added to a solution of **1** in the presence of Ph$_2$C=CH$_2$ under H$_2$ (4 atm). Heating to 100 °C for 24 h afforded near quantitative conversion to the hydrogenated olefin which was isolated in 92 % yield (Table 1, entry 9). Reduction of the time to 4 or 8 h, or reduction of the temperature to 50 or 75 °C lead to diminished reduction conversion (Table 1, entries 10–13). The observed difference in reactivity of *p*-Tol$_2$NH (Table 1, entry 1) and *p*-Tol$_2$NSiEt$_3$ (Table 1, entry 4) suggests a beneficial effect of silyl moiety on the catalytic hydrogenation (see mechanistic discussion below).

Table 2: Catalytic hydrogenation of olefins.[a]

	Substrate	1 [mol %]	Base [mol %]	*t* [h]	Conv.[b] [%]
1	Ph(3,4-Me$_2$(C$_6$H$_3$)C=CH$_2$	1.5	Et$_3$SiH/*p*-Tol$_2$NH (20)	24	99 (91)
2	Ph(2-MeC$_6$H$_4$)C=CH$_2$	2	Et$_3$SiH/*p*-Tol$_2$NH (20)	24	14
3	Ph(2-MeC$_6$H$_4$)C=CH$_2$	2	*p*-Tol$_2$NSiEt$_3$ (20)	96	18
4	Ph(4-F-C$_6$H$_4$)C=CH$_2$	2	Et$_3$SiH/*p*-Tol$_2$NH (20)	24	85
5	Ph(4-Et$_3$SiO-C$_6$H$_4$)C=CH$_2$	1	*p*-Tol$_2$NSiEt$_3$ (20)	24	99 (90)
6	Ph(4-Br-C$_6$H$_4$)C=CH$_2$	2	Et$_3$SiH/*p*-Tol$_2$NH (20)	24	50
7[c]	Ph(3-Br-C$_6$H$_4$)C=CH$_2$	5	*p*-Tol$_2$NSiEt$_3$ (20)	24	22
8[c]	C$_{14}$H$_{10}$	5	*p*-Tol$_2$NSi(*i*Pr)$_3$ (20)	72	65
9[c]	MeC$_{14}$H$_9$	5	*p*-Tol$_2$NSi(*i*Pr)$_3$ (20)	72	43
10[c]	Ph(Me)C=CHPh	10	*p*-Tol$_2$NSi(*i*Pr)$_3$ (40)	96	45
11[c]	Ph$_2$C=CHPh	10	*p*-Tol$_2$NSi(*i*Pr)$_3$ (40)	240	8
12[c]	Ph(Me)C=CH$_2$	1	*p*-Tol$_2$NSiEt$_3$ (40)	24	99[d]

[a] Reactions conditions: 0.5 mmol olefin, 1 mL C$_6$D$_5$Br, 4 atm H$_2$ pressure. Conversions determined by ^{1}H NMR integration. [b] Yields of isolated product in brackets. [c] 0.1 mmol olefin, 0.75 mL C$_6$D$_5$Br. [d] 1,3-dimethyl-1-phenyl-2,3-dihydro-1*H*-indene is the major product.

With these optimized conditions, the scope of substrates for these reductions were assessed. Thus, treatment of Ph(3,4-Me$_2$(C$_6$H$_3$)C=CH$_2$ with 20 mol % of *p*-Tol$_2$NH and HSiEt$_3$ using **1** as the catalyst for 24 h at 100 °C and 4 atm of H$_2$ resulted in full hydrogenation in 99 % and 92 % yield (Table 2, entry 1). The corresponding reaction of Ph(2-MeC$_6$H$_4$)C=CH$_2$ was quite sluggish, ultimately requiring 96 h to achieve 18 % conversion (Table 2, entries 2, 3). This retarded reaction is attributable to the steric congestion about the olefinic bond. In contrast, Ph(4-Br-C$_6$H$_4$)C=CH$_2$, Ph(4-F-C$_6$H$_4$)C=CH$_2$, and Ph(4-Me$_3$SiO-C$_6$H$_4$)C=CH$_2$ were hydrogenated efficiently (Table 2, entries 4–6). On the other hand the *meta* substitution in Ph(3-Br-C$_6$H$_4$)C=CH$_2$ reduced the susceptibility to hydrogenation (Table 2, entry 7). Anthracene derivatives were reduced with increased catalyst loadings and reaction times (Table 2, entries 8 and 9). While methyl stilbene Ph(Me)C=CPh could be reduced in 45 % yield, phenyl-substituted Ph$_2$C=CHPh was essentially unreactive (Table 2, entries 10 and 11). This further supports the previous observation that bulky olefins represent challenging substrates. On the other hand, styrene derivative Ph(Me)C=CH$_2$ gave mostly the dimerized olefin (Table 2, entry 12).



Scheme 1. Proposed mechanism for hydrogenation of olefins by **1**/*p*-Tol$_2$NSiEt$_3$ ([B(C$_6$F$_5$)$_4$]$^-$ anions are not shown).

The mechanism of these hydrogenations is thought to proceed via initial H$_2$ activation analogous to that described above between **1** and *p*-Tol$_2$NH. In the present case, the generation of the transient hydridophosphorane [FP(C$_6$F$_5$)$_3$H] and ammonium salt [*p*-Tol$_2$N(H)SiEt$_3$]$^+$ is postulated (Scheme 1). This view is also supported by experimental H$_2$ and HD activation studies (Supporting Information, Sections S5 and S3.2)[27] as well as DFT calculations at WB97XD/def2TZV[25] level of theory (Supporting Information, Section S6), in which the activation of H$_2$ by [FP(C$_6$F$_5$)$_3$]$^+$/Ph$_2$NSiMe$_3$ was shown to proceed via an encounter complex, similar to that computed for **1** and *p*-Tol$_2$NH. However, in the present case only one C$_6$F$_5$ ring and one phenyl ring participate in π stacking, probably a result of steric congestion. This gives rise to a weaker stabilization of the encounter complex ($\Delta G = -1.8$ kcal mol^{-1}, $\Delta H = -17.1$ kcal mol^{-1}). The ensuing reaction with H$_2$ forming (C$_6$F$_5$)$_3$P(F)H and [Ph$_2$N(H)SiMe$_3$]$^+$ is exergonic ($\Delta G = -32.3$ kcal mol^{-1}) and exothermic ($\Delta H = -26.4$ kcal mol^{-1}), which is 17.9 kcal mol^{-1} more exothermic and 16.0 kcal mol^{-1} more exergonic than the activation of H$_2$ using Ph$_2$NH (Supporting Information, Schemes S17 and S18). The effective energy barrier for H$_2$ activation is $\Delta G^{\neq} = 6.0$ kcal mol^{-1}, which is less than half of the corresponding barrier calculated for *p*-Tol$_2$NH ($\Delta G^{\neq} = 12.9$ kcal mol^{-1}, see Figure 1). This difference in activation energy accounts for the differing reactivity of the two Lewis bases in catalytic hydrogenations (see Table 1). Reductive cleavage of the N−Si bond of p-Tol_2NSiEt_3 with hydrogen is excluded as the FLP p-$Tol_2NSi(iPr)_3$/**1** catalyzes hydrogenation, but iPr_3SiH and p-Tol_2NH does not liberate H_2 to give p-$Tol_2NSi(iPr)_3$ in the presence of **1**, even after 3 days at 100 °C (Supporting Information, Section S4.2.7). Likewise, hydrogen activation and transfer promoted by the generated $[p\text{-}Tol_2N(H)SiEt_3][B(C_6F_5)_4]$ could be excluded in control reactions (Supporting Information, Section S4.2.2).[28] Once H_2 is heterolytically split, protonation of the olefin and subsequent hydride delivery from the transient hydridophosphorane follows. In line with this hypothesis, it could be shown that the protonated amino silane $[p\text{-}Tol_2N(H)SiEt_3][B(C_6F_5)_4]$ is able to protonate 1,1-diphenylethylene at room temperature, leading to catalytic dimerization of the olefin.[29] Furthermore, an alternative pathway of H_2 activation by the transient Lewis acidic carbocation[30] has been excluded by control experiments (Supporting Information, Section S4.2.2). Moreover, it is noteworthy that hydridic phosphoranes have recently been described.[17g,h,31] These observations suggest that in contrast to p-Tol_2NH, the steric demands of p-Tol_2NSiEt_3 appear to strike the right balance allowing the heterolytic cleavage to proceed and favoring subsequent protonation of olefin, thus permitting catalytic hydrogenation to proceed.

In summary, the present work reports the use of electrophilic phosphonium cations in combination with bulky amines in the frustrated Lewis pair activation of H_2 and in the catalytic hydrogenation of olefins. These findings extend the scope of reactivity of EPCs and broaden the range of FLP systems. Future efforts are targeting specifically designed EPCs for FLP hydrogenations, which will provide improved reactivity. Furthermore, the breadth of Lewis acids and bases that are viable for FLP chemistry continues to be of interest to us.

Keywords: frustrated Lewis pairs · hydrogenation · Lewis acids · alkenes · phosphorus

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 10178–10182
Angew. Chem. **2015**, *127*, 10316–10320

---

[1] a) J. G. de Vries, C. J. Elsevier, *The Handbook of Homogeneous Hydrogenation*, Wiley-VCH, Weinheim, **2007**; b) S. Nishimura, *Handbook of Heterogeneous Catalytic Hydrogenation of Organic Synthesis*, Wiley, New York, **2001**.

[2] G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126.

[3] 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.

[4] P. Spies, S. Schwendemann, S. Lange, G. Kehr, R. Fröhlich, G. Erker, *Angew. Chem. Int. Ed.* **2008**, *47*, 7543–7546; *Angew. Chem.* **2008**, *120*, 7654–7657.

[5] H. D. Wang, R. Fröhlich, G. Kehr, G. Erker, *Chem. Commun.* **2008**, 5966–5968.

[6] a) L. Greb, C. G. Daniliuc, K. Bergander, J. Paradies, *Angew. Chem. Int. Ed.* **2013**, *52*, 5876–5879; *Angew. Chem.* **2013**, *125*, 5989–5992; b) L. Greb, P. Oña-Burgos, B. Schirmer, S. Grimme, D. W. Stephan, J. Paradies, *Angew. Chem. Int. Ed.* **2012**, *51*, 10164–10168; *Angew. Chem.* **2012**, *124*, 10311–10315; c) L. Greb, S. Tussing, B. Schirmer, P. Oña-Burgos, K. Kaupmees, M. Lõkov, I. Leito, S. Grimme, J. Paradies, *Chem. Sci.* **2013**, *4*, 2788–2796; d) L. J. Hounjet, C. Bannwarth, C. N. Garon, C. B. Caputo, S. Grimme, D. W. Stephan, *Angew. Chem. Int. Ed.* **2013**, *52*, 7492–7495; *Angew. Chem.* **2013**, *125*, 7640–7643.

[7] K. Chernichenko, Á. Madarász, I. Pápai, M. Nieger, M. Leskelä, T. Repo, *Nat. Chem.* **2013**, *5*, 718–723.

[8] Y. Segawa, D. W. Stephan, *Chem. Commun.* **2012**, *48*, 11963–11965.

[9] T. Mahdi, D. W. Stephan, *J. Am. Chem. Soc.* **2014**, *136*, 15809–15812.

[10] D. J. Scott, M. J. Fuchter, A. E. Ashley, *J. Am. Chem. Soc.* **2014**, *136*, 15813–15816.

[11] a) D. W. Stephan, *Org. Biomol. Chem.* **2012**, *10*, 5740–5746; b) D. W. Stephan, G. Erker, *Top. Curr. Chem.* **2013**, *332*, 85–110; c) D. W. Stephan, *Chem. Commun.* **2010**, *46*, 8526–8533; d) J. Paradies, *Synlett* **2013**, *24*, 777–780; e) J. Paradies, *Angew. Chem. Int. Ed.* **2014**, *53*, 3552–3557; *Angew. Chem.* **2014**, *126*, 3624–3629; f) L. Shi, Y.-G. Zhou, *ChemCatChem* **2015**, *7*, 54–56.

[12] a) J. M. Farrell, J. A. Hatnean, D. W. Stephan, *J. Am. Chem. Soc.* **2012**, *134*, 15728–15731; b) J. M. Farrell, R. T. Posaratnanathan, D. W. Stephan, *Chem. Sci.* **2015**, DOI: 10.1039/C1034SC03675A.

[13] a) D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics* **1998**, *17*, 5492–5503; b) D. J. Parks, R. E. v. H. Spence, W. E. Piers, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 809–811; *Angew. Chem.* **1995**, *107*, 895–897.

[14] a) Y. Liu, H. Du, *J. Am. Chem. Soc.* **2013**, *135*, 6810–6813; b) S. Wei, H. Du, *J. Am. Chem. Soc.* **2014**, *136*, 12261–12264.

[15] a) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76; *Angew. Chem.* **2010**, *122*, 50–81; b) "Frustrated Lewis Pairs I" *Top. Curr. Chem. Vol. 332* (Eds.: D. W. Stephan, G. Erker), Springer, Berlin, **2013**; c) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, DOI: 10.1002/anie.201409800; *Angew. Chem.* **2015**, DOI: 10.1002/ange.201409800.

[16] D. F. Wass, A. M. Chapman, *Top. Curr. Chem.* **2013**, *334*, 261–280.

[17] a) D. Gudat, *Acc. Chem. Res.* **2010**, *43*, 1307–1316; b) N. Burford, P. J. Ragogna, *J. Chem. Soc. Dalton Trans.* **2002**, 4307–4315; c) M. Yoshifuji, *Sci. Synth.* **2009**, *42*, 63–69; d) G. Wittig, U. Schöllkopf, *Chem. Ber.* **1954**, *87*, 1318–1330; e) M. Terada, M. Kouchi, *Tetrahedron* **2006**, *62*, 401–409; f) O. Sereda, S. Tabassum, R. Wilhelm, *Top. Curr. Chem.* **2010**, *291*, 349–393; g) N. Dunn, M. Ha, A. Radosevich, *J. Am. Chem. Soc.* **2012**, *134*, 11330–11333; h) W. Zhao, S. M. McCarthy, T. Y. Lai, H. P. Yennawar, A. T. Radosevich, *J. Am. Chem. Soc.* **2014**, *136*, 17634–17644.

[18] T. W. Hudnall, Y. M. Kim, M. W. P. Bebbington, D. Bourissou, F. P. Gabbaï, *J. Am. Chem. Soc.* **2008**, *130*, 10890–10891.

[19] L. J. Hounjet, C. B. Caputo, D. W. Stephan, *Angew. Chem. Int. Ed.* **2012**, *51*, 4714–4717; *Angew. Chem.* **2012**, *124*, 4792–4795.

[20] C. B. Caputo, L. J. Hounjet, R. Dobrovetsky, D. W. Stephan, *Science* **2013**, *341*, 1374–1377.

[21] M. Perez, L. J. Hounjet, C. B. Caputo, R. Dobrovetsky, D. W. Stephan, *J. Am. Chem. Soc.* **2013**, *135*, 18308–18310.

[22] M. Pérez, Z.-W. Qu, C. B. Caputo, V. Podgorny, L. J. Hounjet, A. Hansen, S. Grimme, D. W. Stephan, *Chem. Eur. J.* **2015**, accepted.

[23] M. Perez, C. B. Caputo, R. Dobrovetsky, D. W. Stephan, *Proc. Natl. Acad. Sci. USA* **2014**, *111*, 10917–10921.

[24] a) S. Grimme, H. Kruse, L. Goerigk, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 1402–1405; *Angew. Chem.* **2010**, *122*, 1444–1447; b) T. A. Rokob, A. Hamza, A. Stirling, T. Soós, I. Pápai, *Angew. Chem. Int. Ed.* **2008**, *47*, 2435–2438; *Angew. Chem.* **2008**, *120*, 2469–2472.

[25] a) S. Grimme, *J. Comput. Chem.* **2006**, *27*, 1787–1799; b) J. D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.

[26] C. A. Hunter, J. K. M. Sanders, *J. Am. Chem. Soc.* **1990**, *112*, 5525 – 5534.

[27] In the absence of olefin, the hydrido fluorophosphorane and the silylammonium cation degrade to Et_3SiF, $P(C_6F_5)_3$, and $[(p\text{-}Tol)_2NH_2][B(C_6F_5)_4]$ (see the Supporting Information).

[28] Hydrogen activation by silylium phosphine adducts has recently been reported. See: 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.

[29] While the corresponding ammonium salt $[p\text{-}Tol_2NH_2][B(C_6F_5)_4]$ also promotes said dimerization, it is slightly less potent than $[p\text{-}Tol_2N(H)SiEt_3][B(C_6F_5)_4]$. This could be another factor why $p\text{-}Tol_2NH$ is not suitable as Lewis base component for the catalytic hydrogenation of olefines.

[30] a) E. R. Clark, M. J. Ingleson, *Angew. Chem. Int. Ed.* **2014**, *53*, 11306 – 11309; *Angew. Chem.* **2014**, *126*, 11488 – 11491; b) K. F. Kalz, A. Brinkmeir, S. Dechert, R. A. Mata, F. Meyer, *J. Am. Chem. Soc.* **2014**, *136*, 16626 – 16634.

[31] G. Zeng, S. Maeda, T. Taketsugu, S. Sakaki, *Angew. Chem. Int. Ed.* **2014**, *53*, 4633 – 4637; *Angew. Chem.* **2014**, *126*, 4721 – 4725.

Received: May 5, 2015
Revised: June 13, 2015