Olefin Reduction

DOI: 10.1002/anie.201204007

Metal-free Catalytic Olefin Hydrogenation: Low-Temperature H_2 Activation by Frustrated Lewis Pairs**

Lutz Greb, Pascual Oña-Burgos, Birgitta Schirmer, Stefan Grimme, Douglas W. Stephan, and Jan Paradies**

The hydrogenation of double bonds is one of the most fundamental transformations[1] in organic chemistry, and has numerous applications in the commodity chemical, agrochemical, pharmaceutical, polymer, and food industries.[2] Despite significant advances in the last 100 years, efforts to improve metal-based technologies for hydrogenation are still the focus of current research.[3] In parallel to these continuing efforts, metal-free strategies for effecting reductions have also been pursued. While organic reagents such as Hantsch's esters[4] and silanes[5] have been used as stoichiometric reducing agents, it was not until 2006[6] that the first metal-free systems, the so-called frustrated Lewis pairs (FLPs),[7] were shown to reversibly activate dihydrogen. This discovery allowed the development of FLP-based catalysts for the reduction of polar unsaturated bonds such as imines,[8] nitriles,[8a,c] aziridines,[8a,c] enamines,[8b] silylenolethers,[9] and aromatic reductions of anilines.[10] Herein, we report the discovery of FLP systems which, while appearing unreactive at room temperature, in fact are capable of dihydrogen activation at temperatures as low as −80 °C. This finding was then exploited for the catalytic hydrogenation of olefins at temperatures between 25 and 70 °C. Experimental and computational data support a plausible mechanism involving protonation of the olefin with subsequent hydride transfer. These FLPs represent the first metal-free hydrogenation catalysts for the reduction of olefins bearing carbocation-stabilizing moieties.

It is well known that the reactions of olefins with Brønsted acids in the presence of a nucleophilic halide, leads to addition products according to a protonation/addition mechanism. In considering the potential of such a mechanism for FLP hydrogenation of C=C double bonds, it was recognized that while the generated borohydride would act as the nucleophile, this pathway would require the generation of a countercation which was sufficiently acidic to effect protonation of the olefin. While the majority of FLP activations of dihydrogen have been demonstrated for phosphine/borane combinations,[7b] a variety of other donors including amines,[8a,11] pyridines,[12] carbenes,[13] and phosphinimines[14] have been shown to be effective when paired with boron or aluminum Lewis acids. However, in all of these cases, the generated cations are only weak Brønsted acids and thus are incapable of protonation of olefinic double bonds.

Seeking to enhance the Brønsted acidity of the cation generated by the FLP activation of dihydrogen, we initiated investigations employing $(C_6F_5)_3B$ (**1**) in combination with the weakly basic phosphine $(C_6F_5)Ph_2P$ (**2**). An NMR spectroscopic examination of a 1:1 mixture of **1** and **2** at 25 °C resulted in spectra that did not differ from those of the individual components. Exposure of this FLP to hydrogen (5 bar) did not lead to significant changes in the NMR spectra at room temperature. However, the situation altered when the temperature was gradually lowered to −80 °C. The $^{31}P\{^1H\}$ NMR signal shifts to lower field upon cooling of the solution. At −66 °C a new resonance appeared at $\delta = -12.5$ ppm, whereas at −80 °C the resonance for free phosphine completely disappeared, and only one sharp ($\delta = -12.5$ ppm) and one broad signal ($\delta = -9$ to -15 ppm) remained (see the Supporting Information). The broad signal was attributed to the dynamic formation of the Lewis pair adduct. More importantly, the resonance at $\delta = -12.5$ ppm was assigned to the phosphonium species $[(C_6F_5)Ph_2PH]^+$ as a phosphorus to hydrogen coupling of $J = 531$ Hz is observed in the ^{31}P NMR spectrum. The corresponding ^{11}B and ^{19}F NMR spectra are consistent with the formation of the phosphonium borate salt $[(C_6F_5)Ph_2PH][(C_6F_5)_3BH]$ [Eq. (1)]. Upon heating the sample to −50 °C the system readily released dihydrogen and the initial FLP system was regenerated. These data clearly demonstrate the reversible activation of hydrogen in the temperature range between −60 °C and −80 °C.[15] While previous examples have been reported to effect reversible dihydrogen uptake and release at room temperature,[16] the present system

[*] L. Greb, Dr. J. Paradies
Karlsruhe Institute of Technology (KIT), Institute of Organic Chemistry, Fritz-Haber Weg 6, 76131 Karlsruhe (Germany)
E-mail: jan.paradies@kit.edu
Dr. P. Oña-Burgos
Karlsruhe Institute of Technology (KIT), Institute of Inorganic Chemistry, Karlsruhe (Germany)
B. Schirmer
Organisch-Chemisches Institut, Universität Münster
Münster (Germany)
Prof. Dr. S. Grimme
Mulliken Center for Theoretical Chemistry, Institut für Physikalische und Theoretische Chemie, Universität Bonn
Beringstr. 4, 53115 Bonn (Germany)
E-mail: grimme@thch.uni-bonn.de
L. Greb, Prof. Dr. D. W. Stephan
Department of Chemistry, University of Toronto
Ontario (Canada)

[**] The LGF, FCI, and AvH are gratefully acknowledged by L.G., J.P., and P.O.B. for financial support. J.P. thanks S. Bräse and F. Breher for kind support and fruitful discussions. B.S., S.G., and D.W.S. gratefully acknowledge the financial support from the DFG-SNF 1175 and NSERC of Canada for the award of a Canada Research Chair.

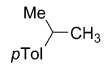
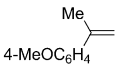
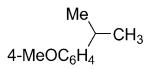
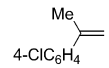
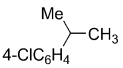
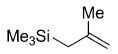
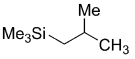
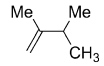
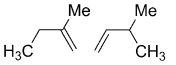
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201204007.

provides, to the best of our knowledge, the lowest barrier for reversible metal-free hydrogen activation reported to date.

$$\underset{\mathbf{2}}{(C_6F_5)Ph_2P} + \underset{\mathbf{1}}{B(C_6F_5)_3} \overset{H_2}{\rightleftharpoons} [(C_6F_5)Ph_2PH][HB(C_6F_5)_3] \quad (1)$$

The extremely low temperature for loss of H_2 from $[(C_6F_5)Ph_2PH][HB(C_6F_5)_3]$ is consistent with the increased Brønsted acidity of the cation. Thus, this prompted efforts to exploit this feature for the hydrogenation of olefins. Consequently, a 20 mol% mixture of **1** and **2** were exposed to 1,1-diphenylethene (**3a**) under 5 bar of dihydrogen. Hydrogenation of the olefin proceeded smoothly at room temperature and the saturated product 1,1-diphenylethane (**4a**) was provided in quantitative yield (Table 1, entry 1).[17] Other electron-deficient yet sterically demanding phosphines were also evaluated in the hydrogenation of 1,1-diphenylethene. For example, when 20 mol% of the FLP consisting of $(C_6F_5)_2PhP$ (**5**) and **1** was applied, the catalysis was completely ineffective (Table 1, entry 2). This was attributed to the low nucleophilicity of **5** induced by the two C_6F_5 substiutents.[18,19] In marked contrast, when the substituted tris(aryl)phosphines $(2,6\text{-}C_6H_3Cl_2)_3P$ (**6**) and tris(1-naphthyl)phosphine $(C_{10}H_7)_3P$ (**7**) were used in combination with **1** to generate catalysts (20 mol%), the hydrogenation of **3a** proceeded in quantitative yield at either room temperature or 50°C (Table 1, entries 3 and 4). The substrate scope of this unprecedented metal-free olefin hydrogenation was explored utilizing substrates capable of generating stabilized carbenium ions (entries 5–14). It was found that not all Lewis bases are compatible with the substrates. The Brønsted acid catalyzed dimerization was observed as a competing side reaction, presumably because of the inefficient hydride transfer. Hence, the balance between the protonation and efficient nucleophilic attack is critical. This key requirement was met by the phosphine **7**, which displayed the highest substrate compatibility. For example, 2-phenylpropene (**3b**) and 2-tolylpropene (**3c**) were hydrogenated in 99 and 85% yields, respectively (Table 1, entries 5 and 6). The more electron-rich 4-methoxy-substituted styrene derivative **3d** was hydrogenated in 30% yield and was accompanied by significant amounts of the dimerization products (entry 7). However, the less acidic bisphosphine **8** (GemPhos)[9a,20] proved to be an efficient Lewis base for the hydrogenation of **3d** and provided the saturated product **4d** in quantitative yield within 48 hours. The reaction of the electron-deficient substrate **3e** did not go to completion even after 100 hours at an elevated temperature (70°C) when **7** was employed as Lewis base (entry 8). These results lead to the conclusion that the reactivity of the unsaturated compounds is dominated by their propensity for protonation, thus generating a stabilized carbenium ion. Consequently, it is conceivable to target specifically selected substrates based on their nucleophilicity parameter *N*. Accordingly, when examining the table of nucleophilicity parameters from Mayr and co-workers[21] we identified **3f–i** as potential substrates ($N = 1.10$ to 4.41). Accordingly, 2-neosilylpropene (**3f**; $N = 4.41$)[22] was quantitatively reduced at room temperature within 12 hours by all catalyst systems (entries 9 and 10). Cyclopentadiene (**3g**; $N = 2.30$)[23] was quantitatively reduced with a catalyst loading of 40 mol% within 24 hours (entry 11), and the reduction of 2,3-dimethyl-

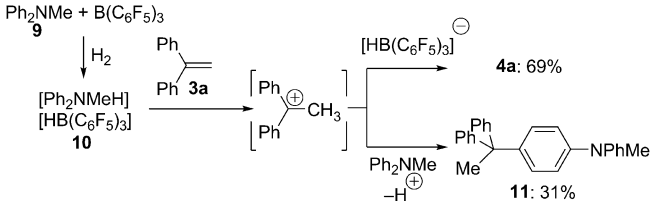
Table 1: Catalytic olefin hydrogenation by FLPs.[a]

Entry	Olefin	Lewis Base	*t* [h]	Product	Yield [%]
					
1	**3a**	**2**	24	**4a**	99
2	**3a**	**5**	100	**4a**	0
3	**3a**	**6**	24	**4a**	99
4[b]	**3a**	**7**	12	**4a**	95
					
5[b]	**3b**	**7**	240	**4b**	96
					
6	**3c**	**7**	96	**4c**	85
					
7[c]	**3d**	**7**	24	**4d**	30
	3d	**8**	48	**4d**	99
					
8[d]	**3e**	**7**	100	**4e**	10
					
9	**3f**	**2**	12	**4f**	95
10	**3f**	**7**	12	**4f**	95
					
11[b]	**3g**	**7** (40 mol%)	24	**4g**	99
					
12[b]	**3h**	**7**	240	**4h**	99
					
13[b]	**3i**	**7**	240	**4ia** **4ib**	82 + 8
14	**3a**	**9**	40	**4a**	80
15	**3a**	**12** (10 mol%)	40	**4a**	95
16	**3a**	**12** (5 mol%)	40	**4a**	87
17	**3e**	**12** (20 mol%)	48	**4e**	95
18	**3f**	**12** (5 mol%)	12	**4f**	99

[a] Reactions were performed on a 0.1 mmol scale in CD_2Cl_2 (0.5 mL, 0.2 M) using 20 mol% of the Lewis base and $(C_6F_5)_3B$ (**1**). Yields were determined by ^1H NMR spectroscopy with the residual solvent signal as an internal standard. [b] Reactions were performed at 50°C. [c] Significant amounts of dimerization product were observed (60%). [d] Reaction was performed at 70°C.

butadiene (**3h**; $N = 1.17$)[23] required heating to 50 °C to achieve 99 % yield of 2,3-dimethyl-butene (entry 12). Interestingly, reduction of 2-methyl-butadiene (**3i**; $N = 1.10$)[24] was accomplished in 90 % yield, and a mixture of the products, 3-methyl-butene (**4ia**) and 2-methyl-butene (**4ib**) in a ratio of 10:1 was observed, thus showing that the more easily accessed double bond is preferably hydrogenated (entry 13). Substrates featuring an exocyclic double bond, such as methylenecyclopentane ($N = 2.82$)[24] or methylenecyclohexane ($N = 1.66$)[23] are efficiently isomerized to the thermodynamically more stable endocyclic double bond, which was unreactive towards hydrogenation. Thus, these data clearly demonstrate that efficient hydrogenation is dependent on two factors: the nucleophilicity of the double bond that forms the carbocations and the efficiency of hydride transfer from the hydridoborate $[HB(C_6F_5)_3]$.

The mechanism of the FLP-catalyzed reduction of **3a** was probed. The similar activities of the catalysts derived from **2**, **6**, and **7** are consistent with similar degrees of steric congestion about the P atom and the analogous pK_a values of the corresponding phosphonium cations. These findings infer a mechanism involving the protonation of the double bond to generate an transient aryl-stabilized carbocation prior to hydride attack. Although the interaction of double bonds with Lewis acids[25] has been described, our control experiments do not support such an activation in the present process.[26] To gather further insight into the mechanism we considered a competition experiment to trap the proposed transient carbocationic species with a π nucleophile, for example, an arylamine. Erker, Stephan, and co-workers have recently demonstrated that aniline derivatives can effect H_2 activation, thus generating $[PhNMe_2H][HB(C_6F_5)_3]$.[27] Following a similar strategy Ph_2NMe (**9**) was subjected as a Lewis base to the hydrogenation reaction with the intention to produce the more acidic ammonium cation $[Ph_2NMeH][HB(C_6F_5)_3]$ (**10**; Scheme 1). Generation of this strong Brønsted acid in the presence of olefin **3a** results in a transient aryl-stabilized carbocation, which can then react in two ways: 1) by addition of the hydride to give the hydrogenation product **4a**, or 2) by electrophilic aromatic substitution, thus furnishing $Ph_2MeC(C_6H_4)NMePh$ (**11**). Indeed, combination of 1,1-diphenylethene and 1.2 equivalents of Ph_2NMe with 20 mol % **1** resulted in a 69 % yield of the saturated product, and 31 % yield of **11**. The interception of the carbocation strongly supports that the FLP-catalyzed hydrogenation of the olefin proceeds by protonation followed by hydride attack. Interestingly, use of 20 mol % Ph_2NMe led to an increase of the hydrogenation product, thus affording **4a** in 80 % yield together with 20 % of **11** (Table 1, entry 14). However, by blocking of the *para* position to inhibit the undesired electrophilic substitution, the even more active catalyst $pTol_2NMe$ (**12**) was obtained for the hydrogenation of **3a** (entries 15 and 16). The catalyst loading could even be reduced to 5 mol % with only a marginal loss in yield. As expected from the low pK_a value, **12** was not compatible with substrates prone to Brønsted acid catalyzed dimerization. Nevertheless, the electron-deficient styrene derivative **3e** was reduced in quantitative yield even at room temperature (Table 1, entry 17) and the allylsilane **3d** was hydrogenated in quantitative yield within 12 hours (entry 18).



Scheme 1. Reaction of Ph_2NMe (**9**; 1.2 equiv), $B(C_6F_5)_3$ (**1**; 20 mol %), $Ph_2C{=}CH_2$ (**3a**; 1 equiv) and H_2 (5 bar) for 12 h.

With these mechanistic indications, quantum chemical studies were initiated which fully support the experimental findings. Single-point calculations with the highly accurate double-hybrid density functional B2PLYP[28] and the D3[29] dispersion correction were carried out for the first four entries from Table 1. Thermal and entropic corrections at 298.15 K and 213.15 K and solvent effects (by COSMO-RS for CH_2Cl_2) were taken into account, which led to the free reaction enthalpies given in Table 2[30] (see the Supporting Information for details).

Table 2: Calculated (B2PLYP-D3) free energy reaction enthalpies (Δ*G*) in CH_2Cl_2 (kcal mol^{-1}).[a]

Reaction	**2**	**5**	**6**	**7**
1 + PR_3 → [**1**][PR_3]	5.8 (−0.9)	1.4 (−1.6)	5.2 (1.8)	3.3 (0.1)
1 + PR_3 + H_2 → [**1**H][HPR_3]	2.7 (−0.5)	7.4 (4.9)	3.1 (−0.1)	−7.7 (−10.6)
[**1**H][HPR_3] + **3a** → **1** + PR_3 + **4a**	−26.9 (−23.6)	−31.6 (−29.3)	−27.2 (−24.3)	−16.9 (−13.9)

[a] Values in parentheses are Δ*G* values in CH_2Cl_2 at −60 °C.

According to these data, both the formation of the Lewis pair adduct [**1**][PR_3] and of the zwitterionic hydrogen activation product [**1**H][HPR_3] are endergonic for phosphines **2**, **5**, and **6** at room temperature. This qualitatively agrees with the experimental observation that these products are not detected but the Δ*G* values are small enough that the species can be present in significant amounts under equilibrium conditions. Decreasing the temperature in the calculations to −60 °C leads to even smaller values, for example, for **2**, Δ*G* is computed to be 2.7 kcal mol^{-1} at 298 K and −0.5 kcal mol^{-1} at 213 K. This data supports the findings that H_2-activation products and starting materials are detectable by NMR spectroscopy only at low temperatures. Furthermore, the reduction of the olefinic double bond as observed experimentally is computed to be highly exergonic as required for an efficient catalytic cycle. The reaction of phosphine **7** with **1** and H_2 yields a negative Δ*G* value even at 298 K and should therefore be observable. Indeed a 1:1 mixture of **7** and **1** reacted cleanly with H_2 to give the activation product $[(C_{10}H_7)_3PH][HB(C_6F_5)_3]$. The hydrogen uptake by **7**/**1** was experimentally found to be reversible at 40 °C in solution.

Collectively, these experimental and theoretical data support a mechanism which proceeds by protonation of the olefin, followed by hydride delivery. These fundamental steps are analogous to those originally envisioned for the hydrosilylation of imines[5b,31] and for the hydrogenation by FLPs.[8a,c,32] However, the present result demonstrates that even poorly basic donors are suitable to activate H_2 in combination with a Lewis acid, thus, providing an onium salt which is sufficiently acidic to protonate the olefin.

In summary, a metal-free catalytic route to the hydrogenation of olefins has been demonstrated employing an FLP strategy. This development evolved from the recognition that the inability to observe the activation of H_2 by an FLP at room temperature does not necessarily imply the absence of reactivity. This rather misleading situation results from a remarkably facile hydrogen evolution or back reaction. Such fast equilibriums also explain that selected FLPs have not been experimentally observed to split dihydrogen although the activation was computed to be energetically favored.[33] Nonetheless, in the presence of substrate, the transient dihydrogen-activation product is intercepted by an olefin, thus effecting hydrogenation. The optimization of the present catalysts as well as the potential and utility of other FLP systems in olefin hydrogenation and catalysis continues to be the focus of our efforts.

Received: May 23, 2012
Revised: June 27, 2012
Published online: August 31, 2012

Keywords: alkenes · frustrated Lewis pairs · hydrogenation · olefin · phosphanes

[1] a) P. Sabatier, M. J. Nye, *Chem. World* **2004**, *1*, 46 – 49; b) P. Sabatier, La Catalyse en chimie organique, Paris, Branger, **1913**; c) G. Wilkinson, *Bull. Soc. Chim. Fr.* **1968**, *12*, 5055 – 5058.

[2] *Handbook of Homogeneous Hydrogenation* (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2006**.

[3] a) R. Noyori, *Angew. Chem.* **2002**, *114*, 2108 – 2123; *Angew. Chem. Int. Ed.* **2002**, *41*, 2008 – 2022; b) W. S. Knowles, *Angew. Chem.* **2002**, *114*, 2096 – 2107; *Angew. Chem. Int. Ed.* **2002**, *41*, 1998 – 2007.

[4] for reviews see: a) C. Zheng, S. L. You, *Chem. Soc. Rev.* **2012**, *41*, 2498 – 2518; b) S. G. Ouellet, A. M. Walji, D. W. C. MacMillan, *Acc. Chem. Res.* **2007**, *40*, 1327 – 1339; for recent examples see: c) J. Paradies, J. F. Schneider, M. B. Lauber, V. Muhr, D. Kratzer, *Org. Biomol. Chem.* **2011**, *9*, 4323 – 4327; d) N. J. A. Martin, X. Cheng, B. List, *J. Am. Chem. Soc.* **2008**, *130*, 13862 – 13863; e) M. Rueping, A. P. Antonchick, T. Theissmann, *Angew. Chem.* **2006**, *118*, 6903 – 6907; *Angew. Chem. Int. Ed.* **2006**, *45*, 6751 – 6755; f) S. G. Ouellet, J. B. Tuttle, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2005**, *127*, 32 – 33; g) M. Rueping, E. Sugiono, C. Azap, T. Theissmann, M. Bolte, *Org. Lett.* **2005**, *7*, 3781 – 3783.

[5] a) M. Rubin, T. Schwier, V. Gevorgyan, *J. Org. Chem.* **2002**, *67*, 1936 – 1940; b) J. M. Blackwell, E. R. Sonmor, T. Scoccitti, W. E. Piers, *Org. Lett.* **2000**, *2*, 3921 – 3923; c) A. Berkefeld, W. E. Piers, M. Parvez, *J. Am. Chem. Soc.* **2010**, *132*, 10660 – 10661; d) W. E. Piers, T. Chivers, *Chem. Soc. Rev.* **1997**, *26*, 345 – 354; e) W. E. Piers, A. J. V. Marwitz, L. G. Mercier, *Inorg. Chem.* **2011**, *50*, 12252 – 12262.

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

[7] a) D. W. Stephan, S. Greenberg, T. W. Graham, P. Chase, J. J. Hastie, S. J. Geier, J. M. Farrell, C. C. Brown, Z. M. Heiden, G. C. Welch, M. Ullrich, *Inorg. Chem.* **2011**, *50*, 12338 – 12348; b) D. W. Stephan, G. Erker, *Angew. Chem.* **2010**, *122*, 50 – 81; *Angew. Chem. Int. Ed.* **2010**, *49*, 46 – 76; c) D. W. Stephan, *Dalton Trans.* **2009**, 3129 – 3136; d) D. W. Stephan, *Org. Biomol. Chem.* **2008**, *6*, 1535 – 1539.

[8] a) P. A. Chase, T. Jurca, D. W. Stephan, *Chem. Commun.* **2008**, 1701 – 1703; b) P. Spies, S. Schwendemann, S. Lange, G. Kehr, R. Fröhlich, G. Erker, *Angew. Chem.* **2008**, *120*, 7654 – 7657; *Angew. Chem. Int. Ed.* **2008**, *47*, 7543 – 7546; c) P. A. Chase, G. C. Welch, T. Jurca, D. W. Stephan, *Angew. Chem.* **2007**, *119*, 8196 – 8199; *Angew. Chem. Int. Ed.* **2007**, *46*, 8050 – 8053.

[9] a) L. Greb, P. Oña-Burgos, A. Kubas, F. C. Falk, F. Breher, K. Fink, J. Paradies, *Dalton Trans.* **2012**, *41*, 9056 – 9060; b) H. D. Wang, R. Fröhlich, G. Kehr, G. Erker, *Chem. Commun.* **2008**, 5966 – 5968.

[10] T. Mahdi, Z. M. Heiden, S. Grimme, D. W. Stephan, *J. Am. Chem. Soc.* **2012**, *134*, 4088 – 4091.

[11] a) V. Sumerin, K. Chernichenko, M. Nieger, M. Leskela, B. Rieger, T. Repo, *Adv. Synth. Catal.* **2011**, *353*, 2093 – 2110; b) V. Sumerin, F. Schulz, M. Nieger, M. Leskela, T. Repo, B. Rieger, *Angew. Chem.* **2008**, *120*, 6090 – 6092; *Angew. Chem. Int. Ed.* **2008**, *47*, 6001 – 6003; c) V. Sumerin, F. Schulz, M. Atsumi, C. Wang, M. Nieger, M. Leskela, T. Repo, P. Pyykko, B. Rieger, *J. Am. Chem. Soc.* **2008**, *130*, 14117 – 14118.

[12] a) C. B. Caputo, S. J. Geier, D. Winkelhaus, N. W. Mitzel, V. N. Vukotic, S. J. Loeb, D. W. Stephan, *Dalton Trans.* **2012**, *41*, 2131 – 2139; b) S. J. Geier, P. A. Chase, D. W. Stephan, *Chem. Commun.* **2010**, *46*, 4884 – 4886; c) S. J. Geier, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 3476 – 3477.

[13] a) P. A. Chase, A. L. Gille, T. M. Gilbert, D. W. Stephan, *Dalton Trans.* **2009**, 7179 – 7188; b) D. Holschumacher, C. Taouss, T. Bannenberg, C. G. Hrib, C. G. Daniliuc, P. G. Jones, M. Tamm, *Dalton Trans.* **2009**, 6927 – 6929; c) P. A. Chase, D. W. Stephan, *Angew. Chem.* **2008**, *120*, 7543 – 7547; *Angew. Chem. Int. Ed.* **2008**, *47*, 7433 – 7437; d) D. Holschumacher, T. Bannenberg, C. G. Hrib, P. G. Jones, M. Tamm, *Angew. Chem.* **2008**, *120*, 7538 – 7542; *Angew. Chem. Int. Ed.* **2008**, *47*, 7428 – 7432.

[14] C. Jiang, D. W. Stephan, *Dalton Trans.* **2012**, DOI: 10.1039/C1032DT30720K.

[15] The formation of the phosphonium borate salt is additionally facilitated by the increased dielectric constant of the solvent at this temperature. See: I. Fernández, E. Martínez-Viviente, F. Breher, P. S. Pregosin, *Chem. Eur. J.* **2005**, *11*, 1495 – 1506.

[16] M. Ullrich, A. J. Lough, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 52 – 53.

[17] No reaction was observed when **3a** was reacted with either **1** or **2** and **1/2** in the absence of hydrogen.

[18] This notion is also consistent with the inability to observe the activation of hydrogen in solution by **1/5** even at −90 °C by NMR spectroscopy.

[19] a) A. Stute, G. Kehr, R. Fröhlich, G. Erker, *Chem. Commun.* **2011**, *47*, 4288 – 4290; b) C. Rosorius, G. Kehr, R. Fröhlich, S. Grimme, G. Erker, *Organometallics* **2011**, *30*, 4211 – 4219.

[20] F. C. Falk, R. Fröhlich, J. Paradies, *Chem. Commun.* **2011**, *47*, 11095 – 11097.

[21] a) H. Mayr, A. R. Ofial, *J. Phys. Org. Chem.* **2008**, *21*, 584 – 595; b) T. B. Phan, M. Breugst, H. Mayr, *Angew. Chem.* **2006**, *118*, 3954 – 3959; *Angew. Chem. Int. Ed.* **2006**, *45*, 3869 – 3874; c) H. Mayr, M. Patz, *Angew. Chem.* **1994**, *106*, 990 – 1010; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 938 – 957.

[22] H. A. Laub, H. Yamamoto, H. Mayr, *Org. Lett.* **2010**, *12*, 5206 – 5209.

[23] H. Mayr, B. Kempf, A. R. Ofial, *Acc. Chem. Res.* **2003**, *36*, 66 – 77.

[24] H. Mayr, T. Bug, M. F. Gotta, N. Hering, B. Irrgang, B. Janker, B. Kempf, R. Loos, A. R. Ofial, G. Remennikov, H. Schimmel, *J. Am. Chem. Soc.* **2001**, *123*, 9500 – 9512.
[25] a) G. Ménard, D. W. Stephan, *Angew. Chem.* **2012**, *124*, 8397 – 8400; *Angew. Chem. Int. Ed.* **2012**, *51*, 8272 – 8275; b) X. Zhao, D. W. Stephan, *Chem. Sci.* **2012**, *3*, 2123 – 2132; c) X. Zhao, D. W. Stephan, *J. Am. Chem. Soc.* **2011**, *133*, 12448 – 12450.
[26] No reaction was observed when **3a** was reacted with $PhNMe_2$ or Ph_2NMe (**7**) and **1** in the absence of H_2.
[27] T. Voss, T. Mahdi, E. Otten, G. Kehr, R. Fröhlich, D. W. Stephan, G. Erker, *Organometallics* **2012**, *31*, 2367 – 2378.
[28] S. Grimme, *J. Chem. Phys.* **2006**, *124*, 034108.
[29] a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456 – 1465.
[30] a) F. Eckert, A. Klamt; COSMOtherm, Version C2.1, Release 01.11; COSMOlogic GmbH & Co. KG, Leverkusen, Germany, **2010**; b) J. J. P. Stewart, *J. Mol. Model.* **2007**, *13*, 1173 – 1213; c) F. Eckert, A. Klamt, *Aiche J.* **2002**, *48*, 369 – 385; d) A. Klamt, *J. Phys. Chem.* **1995**, *99*, 2224 – 2235; e) A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans. 2* **1993**, 799 – 805.
[31] J. B. Lambert, Y. Zhao, H. W. Wu, *J. Org. Chem.* **1999**, *64*, 2729 – 2736.
[32] B. H. Xu, G. Kehr, R. Fröhlich, B. Wibbeling, B. Schirmer, S. Grimme, G. Erker, *Angew. Chem.* **2011**, *123*, 7321 – 7324; *Angew. Chem. Int. Ed.* **2011**, *50*, 7183 – 7186.
[33] T. A. Rokob, A. Hamza, I. Papai, *J. Am. Chem. Soc.* **2009**, *131*, 10701 – 10710.

