Frustrated Lewis Pairs

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Functional-Group Tolerance in Frustrated Lewis Pairs: Hydrogenation of Nitroolefins and Acrylates**

*Lutz Greb, Constantin-Gabriel Daniliuc, Klaus Bergander, and Jan Paradies**

Apart from molecular hydrogen (H_2),[1] other small molecules, such as CO_2,[2] N_2O,[3] NO,[4] and SO_2,[5] were targeted by frustrated Lewis pairs (FLPs)[6] and resulted in the fixation or activation of these small molecules by Lewis acid interaction. Consequently, functionalized molecules, such as α,β-unsaturated esters, sulfoxides, or nitro compounds, are challenging substrates for FLP-catalyzed hydrogenations, and strategies toward higher functional-group tolerance are topic of current research. Soós et al. demonstrated that bulky mesityl-substituted boranes could attain a level of functional-group tolerance according to the size exclusion principle.[7] Other modifications of boranes to achieve stronger[8] and weaker[7c,8b,9] Lewis acidity in conjunction with FLP chemistry were reported. In particular, weaker Lewis acids appear to be favorable for the reduction of electron-deficient double bonds, such as α,β-unsaturated ketones, owing to the pronounced nucleophilicity of the corresponding hydridoborate anion.[10] However, reduced Lewis acidity might also suppress the H_2 activation, and a careful balance must be met. To date, there has been no report on the FLP-catalyzed hydrogenation of nitroolefins and acrylates. Only recently, $B(C_6F_5)_3$ (**1**) was applied for the reduction of strongly electrophilic malonates at elevated temperatures and pressure (80 °C, 60 bar H_2).[10a]

Herein we report the reactivity of $B(2,6\text{-}F_2\text{-}C_6F_3)_3$ (**2**) as Lewis acid in FLP-catalyzed hydrogenations and its unique structural features in solid state and solution. The unprecedented FLP-mediated hydrogenation of nitroolefins[11] and α,β-unsaturated esters under mild conditions (RT or 40 °C; 4 bar H_2) was established. In contrast to the size-exclusion concept, in this case functional-group tolerance was solely achieved by modification of the electronic nature of the Lewis acid and the Lewis base.

We initiated our studies with the synthesis of the borane $B(2,6\text{-}F_2\text{-}C_6H_3)_3$–THF adduct (**2**·THF) according to Naumann.[12] Surprisingly, **2**[13] has not been studied in FLP chemistry to date, even though it resembles an electronically modified $B(C_6F_5)_3$ with identical steric shielding. The solid-state structure of **2** was established and displays similar structural features to BPh_3 (Figure 1 a).[14]

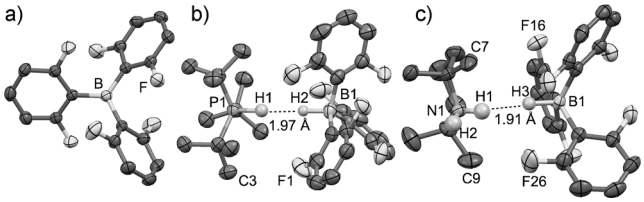

Figure 1. X-ray crystal structures of a) $B(2,6\text{-}F_2\text{-}C_6H_3)_3$ (**2**), b) [tBu$_3$P-H][H-$B(2,6\text{-}F_2\text{-}C_6H_3)_3$] ([**3**-H][H-**2**]), and c) [TMP-H][H-$B(2,6\text{-}F_2\text{-}C_6H_3)_3$] ([**4**-H][H-**2**]). Ellipsoids set at 50% probability; solvent molecules and selected hydrogen atoms omitted for clarity. Selected interatomic distances [Å]: [**3**-H][H-**2**]: H1–H2 1.97(4), H3–F1 2.84(5); [**4**-H][H-**2**]: H1–H3 1.91(1), H9–F26 2.54(8), H7–H16 2.48(0).

The relative Lewis acidity of **2** compared to $B(C_6F_5)_3$ (set to 100 %)[15] was determined to be 58 % and 82 % according to the methods of Childs[16] and Gutmann-Beckett,[15b,17] respectively.[18] When the Lewis acid **2** was reacted with tBu$_3$P (**3**) or 2,2,6,6-tetramethylpiperidine (TMP; **4**) and molecular hydrogen at room temperature, the respective hydridoborate salts [**3**-H][H-**2**] and [**4**-H][H-**2**] were quantitatively formed. The H_2 activation products were fully characterized in the solid state (Figure 1 b,c)[19] and in solution by NMR spectroscopy. The most striking features are the short PH···HB and NH···HB distances of 1.97 Å and 1.91 Å, respectively[20] and indicate an intermolecular dihydrogen bond.[21]

To date, reported H_2 activation products employing $B(C_6F_5)_3$[22] or $B(4\text{-H-}C_6F_4)_3$[23] and PtBu$_3$ (**3**) or TMP (**4**) have longer H–H distances, suggesting majorly electrostatic interactions between the ions pairs rather than dihydrogen bonding. Careful inspection of the molecular structures revealed additional interactions of the ions in the solid state. For [**3**-H][H-**2**] six and for [**4**-H][H-**2**] four short H···F interactions were found (2.9 Å to 2.5 Å). Surprisingly this structure is also conserved in solution. The cross-peaks in the corresponding ^{1}H,^{1}H NOESY NMR spectra confirmed the vicinity of the PH and NH to the H–B moiety in the onium borate salts. Furthermore the orientation of the onium salts were verified by ^{1}H,^{19}F HOESY NMR experiments (see the Supporting Information). Polarization transfer from the tBu group in [**3**-H][H-**2**] and from the CH_3 and the 3,5-CH_2 groups in [**4**-H][H-**2**] to the *ortho*-F-atoms of the borate verified the facial arrangement as observed in solid state. To our knowl-

[*] Dipl.-Chem. L. Greb, Priv.-Doz. Dr. J. Paradies
Institute of Organic Chemistry
Karlsruhe Institute of Technology (KIT)
Fritz-Haber-Weg 6, 76131 Karlsruhe (Germany)
E-mail: jan.paradies@kit.edu
Homepage: http://paradies-group.de
Dr. C.-G. Daniliuc, Dr. K. Bergander
Institute of Organic Chemistry, University of Münster
Corrensstrasse 40, 48149 Münster (Germany)

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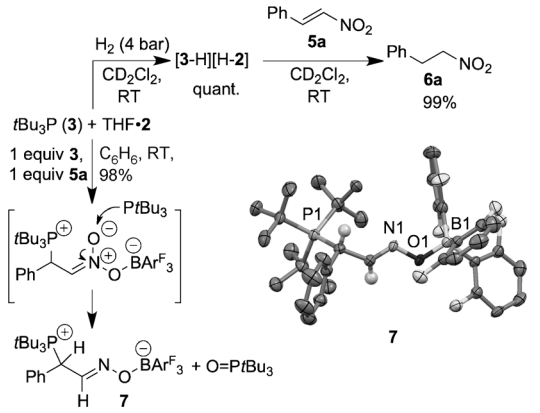
edge this is the first report of spectroscopic evidence of FLP-derived onium hydridoborate ion-pair structures in solution.

The reduced Lewis acidity of **2** suggests increased nucleophilic character of the hydride in the $[H\text{-}\mathbf{2}]^-$ ion,[24] so that the reduction of functionalized α,β-unsaturated substrates seems feasible. For this challenging task the reactivity of the onium hydridoborates (nucleophilicity, pK_a of the onium species), as well as the free FLP towards such substrates is of utmost importance, because multiple deactivation pathways are possible as for $B(C_6F_5)_3$ (**1**). In our hands the catalytic hydrogenation of nitroolefins or acrylates using the FLPs derived from **3**/**1** or **4**/**1** was unsuccessful owing to Lewis acid inhibition, in contrast to free borane **2** or the **2**·THF adduct.[25]

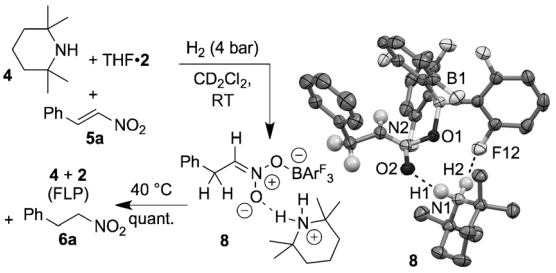
We investigated the stoichiometric reduction of (*E*)-β-nitrostyrene (**5a**) by [**3**-H][H-**2**] at ambient temperature. Indeed the complete reduction of the double bond was observed within a short time, providing the saturated product **6a** in excellent yield (Scheme 1, top). Surprisingly, when



Scheme 1. Reactivity of nitroolefin **5a** with FLP **3**/**2** ($Ar^F = 2,6\text{-}F_2\text{-}C_6H_3$). Ellipsoids set at 50% probability; selected hydrogen atoms omitted for clarity.

equimolar amounts of substrate **5a**, **2**, and two equiv P*t*Bu$_3$ (**3**) were mixed in CD_2Cl_2 in the absence of hydrogen, the clean conversion into the FLP-stabilized oxime **7** was observed (Scheme 1, bottom). The oxime **7** resulted from the conjugate addition of **3** to the β position in **5a** and reduction of the generated nitronate species by the second equiv of P*t*Bu$_3$. The NMR data are in accordance with the proposed zwitterionic structure **7**, which was also verified by X-ray crystal structure analysis (see the Supporting Information).

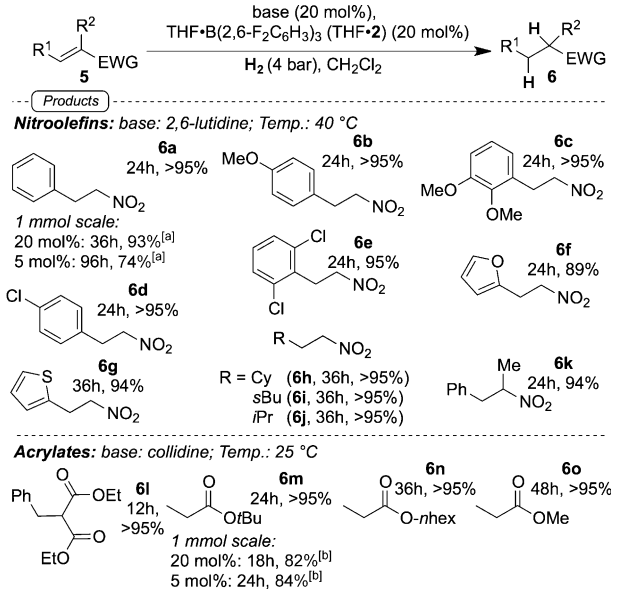
The reduction of the nitro group to an oxime functionality shows new reactivity of FLPs in reduction processes of functional groups, although not in a catalytic fashion. In contrast, when TMP (**4**) was used as Lewis base, no nitro group reduction was observed. Subsequent pressurization of an equimolar mixture of TMP (**4**), $B(2,6\text{-}F_2\text{-}C_6H_3)_3$ (**2**), and nitroolefin **5a** with hydrogen led to the clean formation of the hydride addition intermediate **8**, which was unambiguously identified by NMR spectroscopy and X-ray crystallography (Scheme 2). This finding provides important evidence for the



Scheme 2. Hydrogenation of β-nitrostyrene by FLP **4**/**2** ($Ar^F = 2,6\text{-}F_2\text{-}C_6H_3$). Ellipsoids set at 50% probability; solvent molecules and selected hydrogen atoms omitted for clarity. Selected interatomic distances [Å] for **8**: H2–F12 2.14, H1–O2 1.85.

initial hydride attack mechanism.[10a,b] Heating a solution of **8** to 40 °C resulted in the protodeboronation to liberate the saturated nitro compound **6a** and the FLP. However, the hydrogenation of **5a** could not be achieved in a catalytic fashion, because **4** served as potent base for Henry-type additions of the produced nitro alkane **6a** to **5a**. This side-reaction was prevented by the application of weaker bases according to our transient hydrogen-activation concept.[26]

The combination of **2** with 2,6-lutidine (**9**) or collidine (**10**; pK_a(2,6-lutidine) = 6.6 or pK_a(collidine) = 7.4 versus pK_a (TMP) = 11.1)[27] under an atmosphere of H_2 showed no change of the individual NMR resonances of the components. However, we have demonstrated that the H_2 activation is a fast equilibrium that is determined by the pK_a of the generated Brønsted acids.[26] Accordingly, the FLP system derived from **9**[28] efficiently hydrogenated the nitroolefins **5a**–**k** under mild conditions (Scheme 3).[29] Electron-rich (**5b**,**c**) and electron-deficient (**5d**,**e**) aromatic nitroolefins proved to be viable substrates for the FLP-catalyzed hydrogenation. Heteroaromatic substrates bearing strong Lewis-basic donor functionalities (furyl **6f** and thiophenyl **6g**) were hydrogenated in high to excellent yield. Aliphatic substitution on the nitroolefin fragment was also well tolerated, and the saturated compounds **6h–j** were obtained in excellent yield. Even α-methyl-β-nitrostyrene (**5k**), a challenging substrate for Hantzsch's ester reductions,[30] was hydrogenated in 94% yield. Furthermore, the catalyst system showed high reactivity for the reduction of α,β-unsaturated esters. Collidine (**10**) proved to be the best base for the hydrogenation of malonate **5l** under mild conditions (4 bar H_2, RT; compared to 60 bar H_2 and 80 °C).[10a] Identical conditions allowed the hydrogenation of acrylates, which have not been viable substrates to date for FLP-catalyzed hydrogenations. Irrespective of the nature of the ester, excellent yields (**6m–o**) were obtained, and even the quantitative reduction of the smallest acrylate **5o** was observed. This finding clearly underlines that the functional-group tolerance is achieved by electronic and not by steric modifications. Reactions on a 1 mmol scale with various catalyst loadings (20 mol% and 5 mol%) were investigated for selected examples (**5a** and **5m**). Prolonged reaction times were necessary for the reduction of **5a**, but the product was provided in good to excellent yields (74–93%) with catalyst loadings as low as 5 mol%. The acrylate **5m** was rapidly hydrogenated within 24 h with only 5 mol% catalyst



Scheme 3. FLP-catalyzed hydrogenation of α,β-unsaturated compounds. Reactions were performed on 0.1 mmol scale unless indicated otherwise; yields were determined by NMR spectroscopy (see the Supporting Information). [a] Yields of isolated product. [b] Reduced yield of isolated product owing to the high volatility of the product (yield from crude reaction mixture determined by NMR > 95%). Cy = cyclohexyl.

loading, rendering the FLP-catalyzed hydrogenation of nitroolefins and acrylates a synthetically valuable method.

In conclusion, we have achieved functional-group tolerance by electronic modification of the Lewis pairs. We have demonstrated that the electronic modulation of both the Lewis acid and the Lewis base in FLP chemistry provides functional-group tolerance towards nitro, furyl, or thiophene groups. This approach was exemplified by the hydrogenation of nitroolefins and acrylates, which have been incompatible with FLP-chemistry to date. The weak Lewis acid $B(2,6\text{-}F_2\text{-}C_6H_3)_3$ in combination with $t\text{Bu}_3\text{P}$ and TMP activated hydrogen at room temperature reversibly, providing the corresponding onium hydridoborate salts, which were characterized in solid state and in solution. Solid-state and solution structure analysis support the unprecedented interaction of the H_2-activation product through a dihydrogen bond. Pyridine-derived bases in combination with $B(2,6\text{-}F_2\text{-}C_6H_3)_3$ provided highly active catalysts for the reduction of nitroolefins and acrylates. The reversible coordination of the borane to polar functional groups and the adjustment of the Lewis base provided the basis for the FLP-catalyzed hydrogenations. The electronically adjusted FLP system is another example for the transient hydrogen-activation concept in catalysis, and the application of weaker Lewis pairs is in focus of current research.

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[1] a) G. Erker, *Pure Appl. Chem.* **2012**, *84*, 2203 – 2217; b) D. W. Stephan, G. Erker, *Angew. Chem.* **2010**, *122*, 50 – 81; *Angew. Chem. Int. Ed.* **2010**, *49*, 46 – 76; c) 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.

[2] a) E. Theuergarten, J. Schlosser, D. Schluns, M. Freytag, C. G. Daniliuc, P. G. Jones, M. Tamm, *Dalton Trans.* **2012**, *41*, 9101 – 9110; b) I. Peuser, R. C. Neu, X. X. Zhao, M. Ulrich, B. Schirmer, J. A. Tannert, G. Kehr, R. Fröhlich, S. Grimme, G. Erker, D. W. Stephan, *Chem. Eur. J.* **2011**, *17*, 9640 – 9650; c) X. X. Zhao, D. W. Stephan, *Chem. Commun.* **2011**, *47*, 1833 – 1835; d) A. Berkefeld, W. E. Piers, M. Parvez, *J. Am. Chem. Soc.* **2010**, *132*, 10660 – 10661; e) C. M. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan, G. Erker, *Angew. Chem.* **2009**, *121*, 6770 – 6773; *Angew. Chem. Int. Ed.* **2009**, *48*, 6643 – 6646.

[3] a) R. C. Neu, E. Otten, A. Lough, D. W. Stephan, *Chem. Sci.* **2011**, *2*, 170 – 176; b) E. Otten, R. C. Neu, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 9918 – 9919.

[4] a) M. Sajid, A. Stute, A. J. P. Cardenas, B. J. Culotta, J. A. M. Hepperle, T. H. Warren, B. Schirmer, S. Grimme, A. Studer, C. G. Daniliuc, R. Fröhlich, J. L. Petersen, G. Kehr, G. Erker, *J. Am. Chem. Soc.* **2012**, *134*, 10156 – 10168; b) A. J. P. Cardenas, B. J. Culotta, T. H. Warren, S. Grimme, A. Stute, R. Fröhlich, G. Kehr, G. Erker, *Angew. Chem.* **2011**, *123*, 7709 – 7713; *Angew. Chem. Int. Ed.* **2011**, *50*, 7567 – 7571.

[5] M. Sajida, A. Klose, B. Birkmann, L. Liang, B. Schirmer, T. Wiegand, H. Eckert, A. J. Lough, R. Fröhlich, C. G. Daniliuc, S. Grimme, D. W. Stephan, G. Kehr, G. Erker, *Chem. Sci.* **2013**, *4*, 213 – 219.

[6] a) D. W. Stephan, *Org. Biomol. Chem.* **2008**, *6*, 1535 – 1539; b) 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; c) G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124 – 1126.

[7] a) G. Eros, K. Nagy, H. Mehdi, I. Papai, P. Nagy, P. Kiraly, G. Tarkanyi, T. Soós, *Chem. Eur. J.* **2012**, *18*, 574 – 585; b) T. Soós, *Pure Appl. Chem.* **2011**, *83*, 667 – 675; c) G. Eros, H. Mehdi, I. Papai, T. A. Rokob, P. Kiraly, G. Tarkanyi, T. Soós, *Angew. Chem.* **2010**, *122*, 6709 – 6713; *Angew. Chem. Int. Ed.* **2010**, *49*, 6559 – 6563.

[8] a) T. J. Herrington, A. J. W. Thom, A. J. P. White, A. E. Ashley, *Dalton Trans.* **2012**, *41*, 9019 – 9022; b) A. L. Travis, S. C. Binding, H. Zaher, T. A. Q. Arnold, J.-C. Buffet, D. O'Hare, *Dalton Trans.* **2013**, *42*, 2431 – 2437; c) S. C. Binding, H. Zaher, F. M. Chadwick, D. O'Hare, *Dalton Trans.* **2012**, *41*, 9061 – 9066; d) A. E. Ashley, T. J. Herrington, G. G. Wildgoose, H. Zaher, A. L. Thompson, N. H. Rees, T. Krämer, D. O'Hare, *J. Am. Chem. Soc.* **2011**, *133*, 14727 – 14740; e) Z. Lu, Z. Cheng, Z. Chen, L. Weng, Z. H. Li, H. Wang, *Angew. Chem.* **2011**, *123*, 12435 – 12439; *Angew. Chem. Int. Ed.* **2011**, *50*, 12227 – 12231; f) J. M. Farrell, J. A. Hatnean, D. W. Stephan, *J. Am. Chem. Soc.* **2012**, *134*, 15728 – 15731.

[9] a) G. C. Welch, L. Cabrera, P. A. Chase, E. Hollink, J. D. Masuda, P. Wei, D. W. Stephan, *Dalton Trans.* **2007**, 3407 – 3414; b) M. Ullrich, A. J. Lough, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 52 – 53.

[10] a) B. Inés, D. Palomas, S. Holle, S. Steinberg, J. A. Nicasio, M. Alcarazo, *Angew. Chem.* **2012**, *124*, 12533 – 12536; *Angew. Chem. Int. Ed.* **2012**, *51*, 12367 – 12369; b) J. S. Reddy, B.-H. Xu, T. Mahdi, R. Fröhlich, G. Kehr, D. W. Stephan, G. Erker, *Organometallics* **2012**, *31*, 5638 – 5649; c) 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.

[11] a) J. Paradies, J. F. Schneider, M. B. Lauber, V. Muhr, D. Kratzer, *Org. Biomol. Chem.* **2011**, *9*, 4323 – 4327; b) Z. G. Zhang, P. R. Schreiner, *Synthesis* **2007**, 2559 – 2564; c) N. J. A. Martin, X. Cheng, B. List, *J. Am. Chem. Soc.* **2008**, *130*, 13862 – 13863; d) N. J. A. Martin, L. Ozores, B. List, *J. Am. Chem. Soc.* **2007**, *129*, 8976 – 8977; e) Z. G. Liu, Q. Liu, W. Zhang, R. Z. Mu, L. Yang, Z. L. Liu, W. Yu, *Synthesis* **2006**, 771 – 774; f) S. Yasui, M. Fujii, K. Nakamura, A. Ohno, *Bull. Chem. Soc. Jpn.* **1987**, *60*, 963 – 968.

[12] D. Naumann, H. Butler, R. Gnann, *Z. Anorg. Allg. Chem.* **1992**, *618*, 74 – 76.

[13] The free borane was obtained by reaction of **2**·THF with Me_2SiHCl; see the Supporting Information.

[14] F. Zettler, H. D. Hausen, H. Hess, *J. Organomet. Chem.* **1974**, *72*, 157 – 162.

[15] a) M. M. Morgan, A. J. V. Marwitz, W. E. Piers, M. Parvez, *Organometallics* **2013**, *32*, 317 – 322; b) M. A. Beckett, D. S. Brassington, S. J. Coles, M. B. Hursthouse, *Inorg. Chem. Commun.* **2000**, *3*, 530 – 533.

[16] R. F. Childs, D. L. Mulholland, A. Nixon, *Can. J. Chem.* **1982**, *60*, 801 – 808.

[17] a) M. A. Beckett, G. C. Strickland, J. R. Holland, K. Sukumar Varma, *Polymer* **1996**, *37*, 4629 – 4631; b) V. Gutmann, *Coord. Chem. Rev.* **1976**, *18*, 225 – 255; c) U. Mayer, V. Gutmann, W. Gerger, *Monatsh. Chem.* **1975**, *106*, 1235 – 1257.

[18] For discussion, see Refs. [8a,d,16a] and: G. J. P. Britovsek, J. Ugolotti, A. J. P. White, *Organometallics* **2005**, *24*, 1685 – 1691; L. Luo, T. Marks, *Topics in Catalysis* **1999**, *7*, 97 – 106; D. J. Morrison, W. E. Piers, *Org. Lett.* **2003**, *5*, 2857 – 2860.

[19] a) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112 – 122; b) A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7 – 13; c) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467 – 473. CCDC 921110 – 921114 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[20] The N–H, P–H, and B–H hydrogen atoms were located by residual electron density; see the Supporting Information.

[21] R. Custelcean, J. E. Jackson, *Chem. Rev.* **2001**, *101*, 1963 – 1980.

[22] a) 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; b) G. C. Welch, D. W. Stephan, *J. Am. Chem. Soc.* **2007**, *129*, 1880 – 1881.

[23] M. Ullrich, A. J. Lough, D. W. Stephan, *Organometallics* **2010**, *29*, 3647 – 3654.

[24] a) M. Horn, L. H. Schappele, G. Lang-Wittkowski, H. Mayr, A. R. Ofial, *Chem. Eur. J.* **2013**, *19*, 249 – 263; b) D. Richter, Y. Tan, A. Antipova, X. Q. Zhu, H. Mayr, *Chem. Asian J.* **2009**, *4*, 1824 – 1829; c) D. Richter, H. Mayr, *Angew. Chem.* **2009**, *121*, 1992 – 1995; *Angew. Chem. Int. Ed.* **2009**, *48*, 1958 – 1961.

[25] **2** and **2**·THF showed identical reactivity, and therefore the adduct was used in the reactions.

[26] L. Greb, P. Oña-Burgos, B. Schirmer, S. Grimme, D. W. Stephan, J. Paradies, *Angew. Chem.* **2012**, *124*, 10311 – 10315; *Angew. Chem. Int. Ed.* **2012**, *51*, 10164 – 10168.

[27] Z. Rappoport, *Handbook of Tables for Organic Compound Identification*, *3rd ed.*, CRC, Boca Raton, **1967**.

[28] Different rates were achieved depending on the Lewis base. This was accounted to the accumulation of the intermediately formed borane-stabilized nitronate species **8**, which were found in 10% for **10** and in 5% for **9** in the reaction mixtures.

[29] The observation of a hydrogen-activated form is no requisite for a successful catalysis, as demonstrated recently. Furthermore, this reactivity is purely ascribed to the diminished Lewis acidity of **2**. By reacting nitroolefin **5a** with $B(C_6F_5)_3$ (**1**) and TMP (**4**) or 2,6-lutidine (**9**) under 4 bar of hydrogen, the adduct of the borane with the nitro group is the only observed transformation. Thus the reversible coordination of the modified Lewis acid **2** to the functional group is required for the successful reduction of this class of substrates.

[30] P. B. N. Quynh, J. N. Kim, T. H. Kim, *Tetrahedron* **2012**, *68*, 6513 – 6516.

