Transfer Hydrogenation

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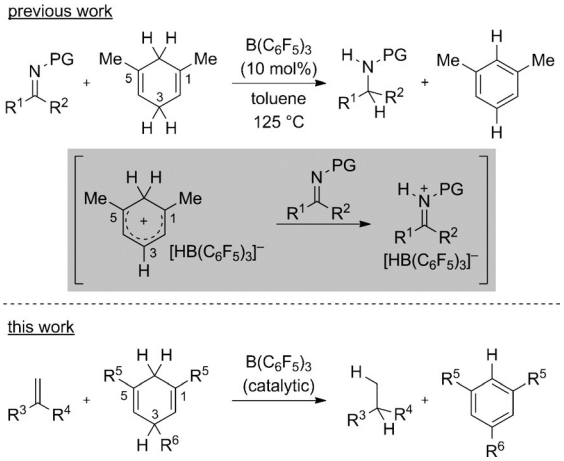
$B(C_6F_5)_3$-Catalyzed Transfer of Dihydrogen from One Unsaturated Hydrocarbon to Another

Indranil Chatterjee, Zheng-Wang Qu, Stefan Grimme, and Martin Oestreich**

Abstract: *A transition-metal-free transfer hydrogenation of 1,1-disubstituted alkenes with cyclohexa-1,4-dienes as the formal source of dihydrogen is reported. The process is initiated by $B(C_6F_5)_3$-mediated hydride abstraction from the dihydrogen surrogate, forming a Brønsted acidic Wheland complex and $[HB(C_6F_5)_3]^-$. A sequence of proton and hydride transfers onto the alkene substrate then yields the alkane. Although several carbenium ion intermediates are involved, competing reaction channels, such as dihydrogen release and cationic dimerization of reactants, are largely suppressed by the use of a cyclohexa-1,4-diene with methyl groups at the C1 and C5 as well as at the C3 position, the site of hydride abstraction. The alkene concentration is another crucial factor. The various reaction pathways were computationally analyzed, leading to a mechanistic picture that is in full agreement with the experimental observations.*

The heterolytic splitting of dihydrogen by the strong Lewis acid $B(C_6F_5)_3$ continues to attract ample attention.[1–3] The H–H bond activation usually leads to the formation of $[HB(C_6F_5)_3]^-$ and an onium ion that is derived either directly from the substrate or from an additional Lewis base, rendering it an FLP-type process (FLP = frustrated Lewis pair).[3] These systems are applicable to the reduction, namely the transition-metal-free hydrogenation, of a broad range of substrates.[4–9] We recently found that the same net result is achieved when cyclohexa-1,4-dienes are employed as dihydrogen surrogates (Scheme 1, top).[10] $B(C_6F_5)_3$ is able to abstract a hydride from adequately substituted cyclohexa-1,4-dienes,[10–12] and the resulting Wheland intermediate then acts as a Brønsted acid to fulfill the role of the aforementioned onium ion. We thus accomplished the transfer hydrogenation of imines (Scheme 1, top).[10,13]

The application of this approach to alkenes is a worthwhile goal as it would allow for the transfer of dihydrogen from one unsaturated hydrocarbon to another unsaturated hydrocarbon in a process that is catalyzed by a main-group Lewis acid (Scheme 1, bottom).[14,15] However, the involvement of carbenium ions at different stages of this process is likely to provoke cationic oligomerization of both reaction partners. It must be mentioned that Stephan and co-workers recently reported one example of a $B(C_6F_5)_3$-catalyzed alkene hydrogenation that required assistance by Et_2O as a Lewis basic component.[8,9,16,17] The same laboratory also elaborated a transfer hydrogenation of alkenes that is catalyzed by a Lewis acidic phosphonium ion $[(C_6F_5)_3PF]^+$, where hydride and proton were generated in a preceding cross-dehydrogenative Si–O or Si–N coupling.[18] Herein, we disclose the transfer hydrogenation of 1,1-disubstituted alkenes catalyzed by $B(C_6F_5)_3$ alone.[8,9] Undesired reactions of the formed carbenium ions were prevented by the use of a 1,3,5-trisubstituted cyclohexa-1,4-diene as the dihydrogen source.



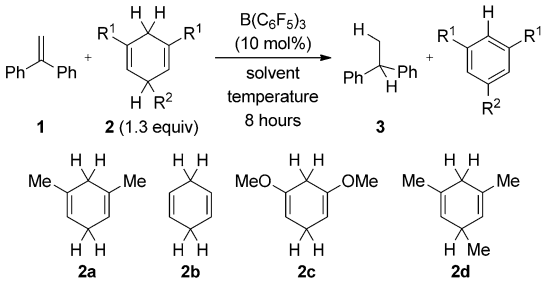
Scheme 1. $B(C_6F_5)_3$-catalyzed transfer hydrogenation of imines and 1,1-disubstituted alkenes using cyclohexa-1,4-dienes as the dihydrogen source. PG = protective group.

We chose 1,1-diphenylethylene (**1**) as the model substrate,[8] and 1,5-dimethylcyclohexa-1,4-diene (**2a**) was selected as the reductant as it had performed best in the transfer hydrogenation of imines (see Scheme 1, top).[10] However, the application of this procedure to **1** resulted in little conversion (Table 1, entry 1). The situation changed in halogenated solvents such as CH_2Cl_2 (Table 1, entry 2; for the solvent screen, see the Supporting Information). A gradual decrease in the temperature to room temperature and a change in concentration from 0.24 M to 0.4 M furnished alkane **3** with near-quantitative conversion; the use of 1,2-$F_2C_6H_4$ brought about further improvement (Table 1, entries 3–5). It is noteworthy that unsubstituted cyclohexa-

[*] Dr. I. Chatterjee, Prof. Dr. M. Oestreich
Institut für Chemie, Technische Universität Berlin
Strasse des 17. Juni 115, 10623 Berlin (Germany)
E-mail: martin.oestreich@tu-berlin.de
Homepage: http://www.organometallics.tu-berlin.de
Dr. Z.-W. Qu, Prof. Dr. S. Grimme
Mulliken Center for Theoretical Chemistry
Institut für Physikalische und Theoretische Chemie
Rheinische Friedrich-Wilhelms-Universität Bonn
Beringstrasse 4, 53115 Bonn (Germany)
E-mail: grimme@thch.uni-bonn.de
Homepage: http://www.thch.uni-bonn.de/tc

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/anie.201504941.

Table 1: Screening of cyclohexa-1,4-dienes as the dihydrogen source and identification/optimization of the reaction conditions.

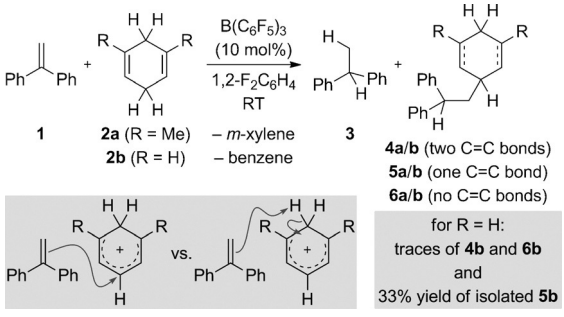


Entry	Cyclohexa-1,4-diene	Solvent	*T*	Conv. [%][a]	Yield [%][b]
1	**2a**	toluene[c]	125 °C	13	–
2	**2a**	CH_2Cl_2[c]	80 °C	54	–
3	**2a**	CH_2Cl_2[c]	RT	66	–
4	**2a**	CH_2Cl_2[d]	RT	88	61
5	**2a**	1,2-$F_2C_6H_4$[d]	RT	90	64
6	**2b**	1,2-$F_2C_6H_4$[d]	RT	100	38
7	**2c**	1,2-$F_2C_6H_4$[d]	RT	n.r.	–
8	**2d**	CH_2Cl_2[d]	RT	100	86
9	**2d**	1,2-$F_2C_6H_4$[d]	RT	100	97
10	**2d**	1,2-$F_2C_6H_4$[d,e,f]	RT	100	97

[a] Determined by GLC analysis with respect to the substrate. [b] Yield of isolated product after flash column chromatography on silica gel. [c] Alkene (0.24 M) in the indicated solvent. [d] Alkene (0.4 M) in the indicated solvent. [e] Using 5.0 mol% of catalyst. [f] Reaction time: 1 h. n.r. = no reaction.

1,4-diene (**2b**), which had been completely unreactive in the imine hydrogenation,[10] afforded full conversion (Table 1, entry 6).

Although the conversions were high, the yields of isolated products were substantially lower (Table 1, entries 5 and 6). A closer look at these reactions revealed that significant amounts of both alkene **1** and reductant **2a**/**2b** are consumed in the formation of adducts **4**–**6** (Scheme 2). The high-energy Wheland complex is expected to protonate **1**, but instead of acting as a strong Brønsted acid, it is nucleophilically attacked by **1** (Scheme 2, bottom left). Reduction of the resulting carbenium ion with $[HB(C_6F_5)_3]^-$ yields **4** as the primary adduct. The double bonds in **4** are subject to further hydrogenation to afford **5** and **6**. An experiment on larger scale with **2b** showed that **4** and **6** were formed in trace amounts, while **5** was isolated in 33% yield and fully characterized. The undesired pathway is more pronounced with unsubstituted **2b**, which is devoid of methyl groups at the C1 and C5 positions, than with **2a**, which suggests that the more stabilized Wheland intermediate is less prone to attack by the alkene at the remaining electrophilic C3 position.

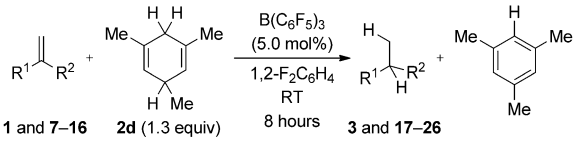


Scheme 2. Undesired pathways: the Wheland complex as an electrophile or a Brønsted acid.

We therefore tested **2c**, which features more strongly electron-donating methoxy groups in the C1 and C5 positions, but no reaction was seen[10] (Table 1, entry 7). The idea was then to suppress the nucleophilic attack of the alkene at the C3 carbon atom by installation of another methyl group in this position. $B(C_6F_5)_3$ was still able to abstract the hydride from that methine carbon atom in **2d**. With **2d**, we indeed achieved excellent yields of **3** at full conversion of **1** in either CH_2Cl_2 or 1,2-$F_2C_6H_4$ (Table 1, entries 8 and 9). None of the previously observed adducts were obtained. Lowering the catalyst loading to 5.0 mol% did not make a difference (Table 1, entry 10). The reactions were routinely maintained at room temperature for eight hours, but following the progress by ^{1}H NMR spectroscopy showed that full conversion was reached within less than one hour.

We decided to proceed with the optimized procedure (5.0 mol% $B(C_6F_5)_3$ and 1.3 equiv **2d** at RT) and tested various 1,1-disubstituted alkenes (Table 2). 1,1-Diarylalkenes **7**–**11** reacted smoothly, independent of the electronic properties of the arene, which could even be a sulfur-containing heterocycle (Table 2, entries 2–6). The situation changed when one of the aryl groups was replaced by an alkyl group (Table 2, entries 7–9). A small alkyl group as in α-methylstyrene (**12**) resulted in significant dimerization whereas isopropyl and cyclohexyl substituents as in **13** and **14** were not detrimental, furnishing the corresponding alkanes in excellent yields. The same trend was seen with the 1,1-dialkylalkenes **15** and **16** as dimerization was again observed for these alkene substrates with primary alkyl substituents (Table 2, entries 10 and 11). Monosubstituted, 1,2-disubstituted, trisubstituted as well as exocyclic alkenes did not participate.

Table 2: Transfer hydrogenation of 1,1-disubstituted alkenes.

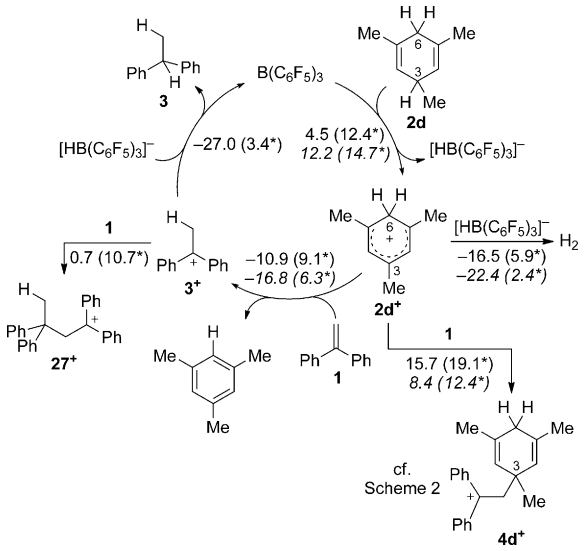


Entry	Alkene	R^1	R^2	Alkane	Yield [%][a]
1	**1**	Ph	Ph	**3**	97
2	**7**	Ph	4-$OMeC_6H_4$	**17**	94
3	**8**	Ph	4-BrC_6H_4	**18**	87
4	**9**	4-FC_6H_4	4-FC_6H_4	**19**	80
5	**10**	4-MeC_6H_4	4-MeC_6H_4	**20**	99
6	**11**	Ph	thien-2-yl	**21**	88
7	**12**	Ph	Me	**22**	33[b]
8	**13**	Ph	*i*Pr	**23**	99[b]
9	**14**	Ph	Cy	**24**	95
10	**15**	Me	*n*Hept	**25**	53[b]
11	**16**	Cy	Cy	**26**	92[b]

[a] Yield of isolated product after flash column chromatography on silica gel. [b] Determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as the internal standard, which was added after the reaction.

Monitoring the transfer hydrogenation by ^{1}H NMR spectroscopy using a slight excess of **2d** (1.3 equiv) revealed that the reaction was finished within one hour. Importantly, dihydrogen is present from the beginning of the reaction. Treatment of 1,3,5-trimethylcyclohexa-1,4-diene (**2d**) with $B(C_6F_5)_3$ at room temperature in the absence of an alkene quantitatively yielded mesitylene and dihydrogen within the same time. However, any released dihydrogen will not contribute to the transfer hydrogenation as $B(C_6F_5)_3$ alone cannot catalyze this alkene hydrogenation,[8] even under a high pressure of dihydrogen (100 bar), at room temperature in 1,2-$F_2C_6H_4$. Furthermore, reactions with equimolar amounts of **1** and **2d** did not reach full conversion of alkene **1**, which clearly indicates that the dihydrogen release is a minor pathway.

To gain deeper mechanistic insight, the 1,1-disubstituted alkene **1** and two cyclohexa-1,4-dienes, **2a** and **2d**, were chosen as the model systems for our detailed theoretical study. State-of-the-art dispersion-corrected DFT calculations[19] at the PW6B95-D3/def2-QZVP + COSMO-RS-(CH_2Cl_2) level of theory using the TPSS-D3/def2-TZVP + COSMO(CH_2Cl_2) optimized geometries and thermal corrections were performed to explore the Gibbs free energies (ΔG) of the various reaction paths (Scheme 3). As shown for 1,3,5-trimethylcyclohexa-1,4-diene (**2d**), the catalyst $B(C_6F_5)_3$ selectively abstracts a hydride from the C3 position [italicized numbers for 1,5-dimethylcyclohexa-1,4-diene (**2a**)].[11c] Hydride transfer from the C6 carbon atom is kinetically negligible owing to a ≥ 10 kcal mol^{-1} higher Gibbs free energy barrier. The initial hydride transfers to $B(C_6F_5)_3$ are endergonic by 4.5 and *12.2* kcal mol^{-1}, respectively, over moderate barriers ($\Delta G^{\neq}$) of 12.4 and *14.7* kcal mol^{-1} for **2d** and **2a**, respectively. These numbers confirm that the additional methyl group at the C3 position renders **2d** a better hydride donor than **2a**. Furthermore, this endergonic step will keep the concentrations of the separated ion pair intermediates consisting of Wheland complex $\mathbf{2d}^+$ or $\mathbf{2a}^+$ and the borate anion $[HB(C_6F_5)_3]^-$ relatively low. When no alkene substrate is present, intermolecular proton/hydride recombination between $\mathbf{2d}^+$ or $\mathbf{2a}^+$ and $[HB(C_6F_5)_3]^-$ easily occurs with a low Gibbs free energy barrier of 5.9 or *2.4* kcal mol^{-1} and is highly exergonic by 16.5 or *22.4* kcal mol^{-1} to release dihydrogen along with the arene (mesitylene or *meta*-xylene).[20] Hence, the initial hydride transfer of this dehydrogenation is rate-limiting.



Scheme 3. Catalytic cycle of the $B(C_6F_5)_3$-catalyzed transfer hydrogenation of alkenes with competing pathways (see the Supporting Information for calculated structures of relevant intermediates and transition states). For each reaction step, the Gibbs free reaction energies and barriers (labeled with an asterisk in parentheses) were computed at the PW6B95-D3 level of theory for 1,3,5-trimethylcyclohexa-1,4-diene (**2d**) as the dihydrogen source, $B(C_6F_5)_3$ as the catalyst, and 1,1-diphenylethylene (**1**) as the alkene substrate. For comparison, the corresponding Gibbs free energies are also given for the reaction with 1,5-dimethylcyclohexa-1,4-diene (**2a**) as the dihydrogen source (italicized values).

When alkene substrate **1** is present at relatively high concentration,[20] the Wheland complexes $\mathbf{2d}^+$ and $\mathbf{2a}^+$ are also able to react competitively with **1** at the less hindered alkene terminus in an undesired or a desired way: either as an electrophile at the C3 position ($\mathbf{2}^+ \rightarrow \mathbf{4}^+$) or as a Brønsted acid, releasing a proton from the C6 position[21] ($\mathbf{2}^+ \rightarrow \mathbf{3}^+$). The former pathway is endergonic by 15.7 or *8.4* kcal mol^{-1} and proceeds over sizable barriers of 19.1 and *12.4* kcal mol^{-1} to form the carbenium ions $\mathbf{4d}^+$ and $\mathbf{4a}^+$, respectively. These intermediates are eventually transformed into the experimentally observed adducts **4**–**6** after hydride transfer and further hydrogenation (see Scheme 2). The Wheland complex $\mathbf{2d}^+$ with a methyl group at the C3 position is less electrophilic than $\mathbf{2a}^+$, with a 6.7 kcal mol^{-1} higher Gibbs free energy barrier for the addition to **1**. This is mainly a result of increased steric congestion at the electrophilic site in $\mathbf{2d}^+$. Conversely, the intermolecular proton transfer from $\mathbf{2d}^+$ or $\mathbf{2a}^+$ to **1** is exergonic by 10.9 or *16.8* kcal mol^{-1} and proceeds over 10.0 or *6.1* kcal mol^{-1} lower Gibbs free energy barriers to yield intermediate $\mathbf{3}^+$ along with mesitylene or *meta*-xylene.[21] The electron-donating methyl group at the C3 position in $\mathbf{2d}^+$ reduces its reactivity relative to that of $\mathbf{2a}^+$ as reflected by a 2.8 kcal mol^{-1} higher barrier for the proton transfer to **1**. The desired pathway ($\mathbf{2}^+ \rightarrow \mathbf{3}^+$) is not only kinetically favored over the undesired C–C bond formation ($\mathbf{2}^+ \rightarrow \mathbf{4}^+$), but the barrier for alkene protonation by $\mathbf{2d}^+$ or $\mathbf{2a}^+$ is also 3.3 or *8.4* kcal mol^{-1} lower than that for the preceding hydride transfer and thus not rate-limiting.[20,22]

There are also two competing reaction channels for the carbenium ion intermediate $\mathbf{3}^+$: either reduction by $[HB(C_6F_5)_3]^-$ ($\mathbf{3}^+ \rightarrow \mathbf{3}$) or nucleophilic attack by another molecule of **1** ($\mathbf{3}^+ \rightarrow \mathbf{27}^+$). The hydride transfer from $[HB(C_6F_5)_3]^-$ to $\mathbf{3}^+$ is highly exergonic by 27.0 kcal mol^{-1}, with a low Gibbs free energy barrier of 3.4 kcal mol^{-1}, and furnishes the desired alkane **3** together with the regenerated $B(C_6F_5)_3$ catalyst. On the other hand, dimerization through nucleophilic attack by the alkene terminus of **1** is almost thermoneutral with a 7.3 kcal mol^{-1} higher Gibbs free energy barrier. The formation of $\mathbf{27}^+$ is therefore kinetically less competitive mainly owing to severe steric hindrance around the carbenium carbon atom in $\mathbf{3}^+$. However, for alkenes with smaller substituents at the internal carbon atom, such as **12** and **15**, this pathway becomes prevalent (see Table 2, entries 7 and 10).

We have herein disclosed a rare case of an alkene transfer hydrogenation catalyzed by a main-group element.[14] The present approach relies on hydride abstraction from cyclohexa-1,4-dienes by the boron Lewis acid $B(C_6F_5)_3$, and the whole process passes through cationic intermediates until terminated by hydride transfer from $[HB(C_6F_5)_3]^-$. Problems arising from cationic hetero- and homodimerization of the reactants were solved by using a cyclohexa-1,4-diene with substitution at the site of hydride abstraction and by adjusting the alkene concentration. The mechanism, including the experimentally observed competing reaction pathways, was analyzed by state-of-the-art quantum-chemical calculations.

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[1] For general reviews, see: a) M. Oestreich, J. Hermeke, J. Mohr, *Chem. Soc. Rev.* **2015**, *44*, 2202–2220; b) W. E. Piers, A. J. V. Marwitz, L. G. Mercier, *Inorg. Chem.* **2011**, *50*, 12252–12262.

[2] For reviews on mainly FLP-, but also $B(C_6F_5)_3$-catalyzed hydrogenation, see: a) L. J. Hounjet, D. W. Stephan, *Org. Process Res. Dev.* **2014**, *18*, 385–391; b) J. Paradies, *Angew. Chem. Int. Ed.* **2014**, *53*, 3552–3557; *Angew. Chem.* **2014**, *126*, 3624–3629; c) J. Paradies, *Synlett* **2013**, 777–780; d) D. W. Stephan, *Org. Biomol. Chem.* **2012**, *10*, 5740–5746.

[3] For authoritative reviews, see: a) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400–6441; *Angew. Chem.* **2015**, *127*, 6498–6541; b) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76; *Angew. Chem.* **2010**, *122*, 50–81.

[4] For $B(C_6F_5)_3$-catalyzed imine hydrogenation, see: a) P. A. Chase, T. Jurca, D. W. Stephan, *Chem. Commun.* **2008**, 1701–1703; b) D. Chen, J. Klankermayer, *Chem. Commun.* **2008**, 2130–2131; c) C. Jiang, O. Blacque, H. Berke, *Chem. Commun.* **2009**, 5518–5520; d) Z. Heiden, D. W. Stephan, *Chem. Commun.* **2011**, *47*, 5729–5731.

[5] For $B(C_6F_5)_3$-catalyzed oxime ether hydrogenation, see: J. Mohr, M. Oestreich, *Angew. Chem. Int. Ed.* **2014**, *53*, 13278–13281; *Angew. Chem.* **2014**, *126*, 13494–13497.

[6] For $B(C_6F_5)_3$-catalyzed partial hydrogenation of nitrogen-containing heterocycles, see: a) S. J. Geier, P. A. Chase, D. W. Stephan, *Chem. Commun.* **2010**, *46*, 4884–4886; b) 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; c) G. Erős, K. Nagy, H. Mehdi, I. Pápai, P. Nagy, P. Király, G. Tárkányi, T. Soós, *Chem. Eur. J.* **2012**, *18*, 574–585; d) T. Mahdi, J. N. del Castillo, D. W. Stephan, *Organometallics* **2013**, *32*, 1971–1978.

[7] For $B(C_6F_5)_3$-catalyzed ketone and aldehyde hydrogenation, see: a) T. Mahdi, D. W. Stephan, *J. Am. Chem. Soc.* **2014**, *136*, 15809–15812; b) D. J. Scott, M. J. Fuchter, A. E. Ashley, *J. Am. Chem. Soc.* **2014**, *136*, 15813–15816.

[8] For $B(C_6F_5)_3$-catalyzed, ether-assisted alkene hydrogenation, see: a) 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 (Et_2O; 1,1-diphenylethylene); b) D. J. Scott, M. J. Fuchter, A. E. Ashley, *Angew. Chem. Int. Ed.* **2014**, *53*, 10218–10222; *Angew. Chem.* **2014**, *126*, 10382–10386 (THF; 1,2,3,4,5-pentamethylcyclopenta-1,3-diene).

[9] For seminal work on FLP-type alkene hydrogenation, see: a) 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; b) 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.

[10] I. Chatterjee, M. Oestreich, *Angew. Chem. Int. Ed.* **2015**, *54*, 1965–1968; *Angew. Chem.* **2015**, *127*, 1988–1991.

[11] For $B(C_6F_5)_3$-mediated hydride abstraction from cyclohexa-2,5-dienyl-substituted silanes as an entry into the related transfer hydrosilylation, see: a) A. Simonneau, M. Oestreich, *Angew. Chem. Int. Ed.* **2013**, *52*, 11905–11907; *Angew. Chem.* **2013**, *125*, 12121–12124; b) S. Keess, A. Simonneau, M. Oestreich, *Organometallics* **2015**, *34*, 790–799; for a computational analysis of its reaction mechanism, see: c) K. Sakata, H. Fujimoto, *Organometallics* **2015**, *34*, 236–241.

[12] $B(C_6F_5)_3$ also mediates hydride abstraction from 1,4-dihydropyridines; see: a) J. D. Webb, V. S. Laberge, S. J. Geier, D. W. Stephan, C. M. Crudden, *Chem. Eur. J.* **2010**, *16*, 4895–4902; b) D. V. Gutsulyak, A. van der Est, G. I. Nikonov, *Angew. Chem. Int. Ed.* **2011**, *50*, 1384–1387; *Angew. Chem.* **2011**, *123*, 1420–1423.

[13] $B(C_6F_5)_3$ is also able to abstract hydrides from amines, and a Meerwein–Pondorf–Verley-type reduction of imines was developed on this basis; see: J. M. Farrell, Z. M. Heiden, D. W. Stephan, *Organometallics* **2011**, *30*, 4497–4500.

[14] Gandon and co-workers reported a gallium(III)-assisted transfer hydrogenation of alkenes with cyclohexa-1,4-diene as the dihydrogen source. The mechanism and the role of the main-group metal remain to be clarified; see: B. Michelet, C. Bour, V. Gandon, *Chem. Eur. J.* **2014**, *20*, 14488–14492.

[15] For the use of a Hantzsch 1,4-dihydropyridine in the Pd/C-catalyzed transfer hydrogenation of unactivated alkenes, see: Q. Liu, J. Li, X.-X. Shen, R.-G. Xing, J. Yang, Z. Liu, B. Zhou, *Tetrahedron Lett.* **2009**, *50*, 1026–1028.

[16] For an alternative, mechanistically different approach to alkene hydrogenation catalyzed by $HB(C_6F_5)_2$, see: Y. Wang, W. Chen, Z. Lu, Z. H. Li, H. Wang, *Angew. Chem. Int. Ed.* **2013**, *52*, 7496–7499; *Angew. Chem.* **2013**, *125*, 7644–7647.

[17] For selected examples of FLP-type hydrogenations of electron-deficient alkenes, see: a) J. S. Reddy, B.-H. Xu, T. Mahdi, R. Fröhlich, G. Kehr, D. W. Stephan, G. Erker, *Organometallics* **2012**, *31*, 5638–5649; b) B. Inés, D. Palomas, S. Holle, S. Steinberg, J. A. Nicasio, M. Alcarazo, *Angew. Chem. Int. Ed.* **2012**, *51*, 12367–12369; *Angew. Chem.* **2012**, *124*, 12533–12536; c) L. Greb, C.-G. Daniliuc, K. Bergander, J. Paradies, *Angew. Chem. Int. Ed.* **2013**, *52*, 5876–5879; *Angew. Chem.* **2013**, *125*, 5989–5992.

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

[19] a) J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* **2003**, *91*, 146401; b) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104–154119; c) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465; d) S. Grimme, *J. Chem. Phys.* **2006**, *124*, 034108–034116; e) F. Eckert, A. Klamt in *COSMOtherm*, *Version C3.0*, *Release 14.01*, COSMOlogic GmbH & Co. KG, Leverkusen, Germany, **2013**; f) A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans. 2* **1993**, 799–805; g) F. Weigend, F. Furche, R.

Ahlrichs, *J. Chem. Phys.* **2003**, *119*, 12753 – 12762; h) A. Schaefer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829 – 5835; i) TURBOMOLE V6.4 **2012**, a development of the University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989 – 2007, TURBOMOLE GmbH, since 2007; available from www.turbomole.com.

[20] In practice, a higher alkene concentration enhances the proton transfer from the common Wheland intermediate onto the alkene substrate, thereby helping to suppress the undesired dihydrogen release.

[21] The possible proton transfer from the methyl groups of Wheland complexes $\mathbf{2d}^+$ and $\mathbf{2a}^+$ to **1** was also considered computationally. At the highest PW6B95-D3 level of theory, such proton-transfer reactions leading to non-aromatic intermediates (not shown) are highly endergonic: 15.8 kcal mol^{-1} for the methyl group at the C3 position of $\mathbf{2d}^+$ as well as 14.9 and 19.8 kcal mol^{-1} for the methyl groups at the C1/C5 positions of $\mathbf{2a}^+$ and $\mathbf{2d}^+$, respectively. These cannot compete with the desired exergonic proton transfer to **1** from the C6 carbon atom, which directly reestablishes aromaticity.

[22] However, the introduction of more strongly electron-donating substituents at the C1 and C5 (as well as C3) positions lent that much stabilization to the Wheland complex that the proton transfer eventually became rate-limiting or was even thwarted. This situation was experimentally observed with the 1,5-dimethoxy-substituted cyclohexa-1,4-diene **2c** (see Table 1, entry 7).

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