Highly selective metal-free catalytic hydrogenation of unactivated alkynes to *cis*-alkenes

*Konstantin Chernichenko[1], Ádám Madarász[2], Imre Pápai[2], Martin Nieger[1], Markku Leskelä[1], and Timo Repo[1]**

[1] Department of Chemistry, Laboratory of Inorganic Chemistry, University of Helsinki

P.O. Box 55, FIN-00014, Finland. Fax: +358 (9)19150198; E-mail:timo.repo@helsinki.fi

[2] Institute of Organic Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences

P.O. Box 17, H-1525 Budapest, Hungary

Recently, a new approach to dihydrogen activation known as frustrated Lewis pairs (FLPs) concept has been introduced[1, 2, 3]. A combination of highly Lewis acidic boranes and sterically hindered bases can split hydrogen heterolytically generating onium (phosphonium, ammonium, etc.) borohydrides. These compounds show reduction activity resembling that of inorganic borohydrides like $NaBH_4$, i. e. they are suitable mostly for reduction of polarized multiple bonds. Imines, enamines, silyl ethers[4, 5, 6], α,β-enones[7], ynones[8], *N*-alkylanilines[9] were hydrogenated using stoichiometric or catalytic amounts of FLPs. Due to heterolytic nature of FLP-H_2 adducts, hydrogenation of *unactivated* multiple C–C bonds using FLPs has some natural limitations, since during the respective step of the catalytic cycle a proton transfer from catalyst to substrate should take place (Fig. 1a). Although Greb *et al.* have implemented this approach to hydrogenation of alkenes under ambient conditions, this method is predictably restricted to the alkenes with high proton affinity[10].

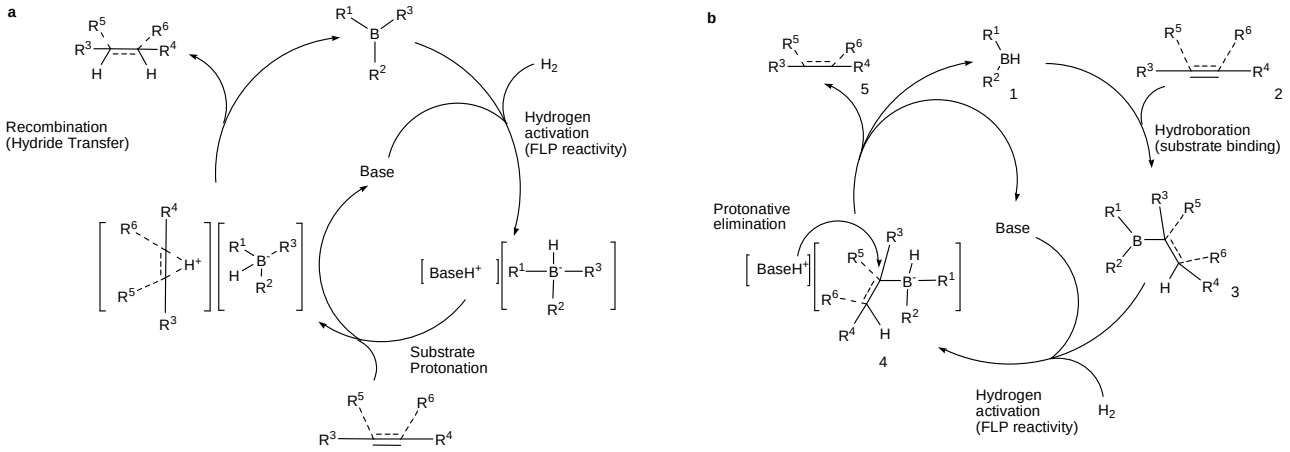


Figure 1. FLP-catalyzed hydrogenation of multiple C-C bonds. a, Traditional approach. **b**, Approach via hydroboration-hydrogen activation-protonation.

Combining the FLP approach and previous knowledge about borane-catalyzed hydrogenation of alkenes[11, 12, 13, 14] and polyarenes[15, 16, 17, 18], we propose herein a new general catalytic pathway to the hydrogenation of unsaturated hydrocarbons (Fig. 1b) and demonstrate its validity by the highly selective hydrogenation of alkynes into *cis*-alkenes. Stereoselective hydrogenation of alkynes is an important protocol in synthesis of natural and industrially relevant compounds.[19, 20, 21, 22, 23]. Heterogeneous as well as homogeneous metal catalysts for this purpose are known[24, 25, 26, 27, 28], however, *metal-free* catalytic hydrogenation of unactivated alkynes into alkenes has not been reported previously.

In contrast to classical FLP-catalyzed reactions, the substrate is bound to the catalyst **1** by hydroboration prior to hydrogen activation (Fig. 1b). The resulting borane **3**, together with a Lewis base cocatalyst can activate hydrogen, producing the adduct **4**. In this onium borohydride **4** a proton transfer can occur liberating the initial borane **1**, the Lewis base and the hydrogenated substrate **5**. To the best of our knowledge, this approach has not been studied experimentally or theoretically.

Initially, we attempted to use Piers' borane, $(C_6F_5)_2BH$[29], as a catalyst. $(C_6F_5)_2BH$ smoothly hydroborates different alkenes and alkynes[30, 31]. Moreover, it was shown that the resulting bis(pentafluorophenyl)alkylboranes as well as $(C_6F_5)_2BH$ itself[32] together with the properly chosen Lewis bases can split hydrogen heterolytically to give the respective onium borohydrides[33]. However, upon heating of these compounds only hydrogen release was observed, demonstrating the reversibility of H_2 uptake by these FLPs. Our numerous attempts to realize the approach depicted in Fig. 1b using $(C_6F_5)_2BH$ together with different bases and additives were unsuccessful[34].

Recently, we have reported 2-[bis(pentafluorophenyl)boryl]-*N*,*N*-dialkylanilines exemplifying a new class of bridged frustrated B/N Lewis pairs[35]. Interestingly, compound **6** exists as an intramolecular Lewis adduct,

containing a strained four-membered C–N→B–C cycle. Due to strain the B-N bond in **6** is relatively weak, since at room temperature **6** reversibly reacts with hydrogen to give ammonium borohydride **7** (Fig. 2a)

New ansa-aminohydroborane as a catalyst

In this work we report that upon heating of aminoborane **6** at 80 ℃ under 2 bar H_2 new signals different from those of **6** or **7** in the ^{1}H, ^{19}F and ^{10}B NMR spectra appear along with formation of C_6F_5H. The new species was isolated as a greenish oil and identified as the hydroborane **8** (Fig. 2a) containing in the ^{1}H NMR spectrum a characteristic partially relaxed quadruplet (δ = 4.35 ppm, J = 105 Hz) attributed to B*H* signal. This reactivity is unprecedented, since neither inter- no intramolecular FLPs have been reported to undergo B–C_6F_5 hydrogenolysis as a result of hydrogen activation[36, 37, 38].

Since **8** is a potentially hydroborating BH-species and can be produced *in situ* from **6**, we attempted to use **8** as a catalyst in hydrogenation of unactivated alkenes and alkynes following the strategy depicted in Fig. 1b. Hex-1-ene (**12b**), hex-1-yne (**12a**) and hex-3-yne (**11a**) were heated separately together with 10 mol. % of precatalyst **6** in C_6D_6 under 2 bar H_2 at 80 ℃. After 15 h, no products of hex-1-ene and hex-1-yne hydrogenation were detected by NMR. In case of **11a** no evidence of starting alkyne were found but a complex mixture of alkenes comprising mostly of *cis*-hex-3-ene **11b**. Minor amounts of *trans*-hex-3-ene and other hexenes were attributed to isomerization of initially produced *cis*-hex-3-ene via hydroboration/retrohydroboration sequence, catalyzed either by **8** or other hydroborane species. When hydrogenation of **11a** was repeated for 3 h with 5 mol. % of **6**, *cis*-hex-3-ene **11b** was produced almost exclusively according to NMR.

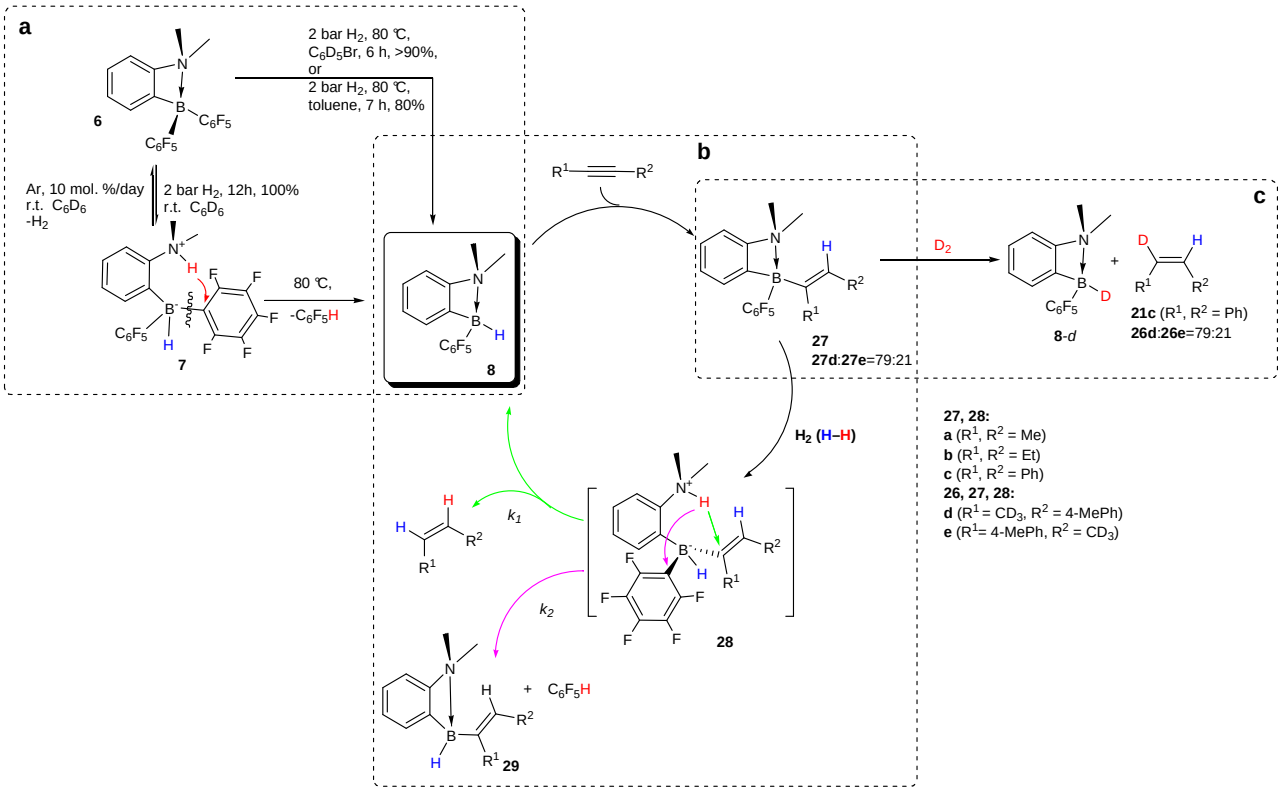
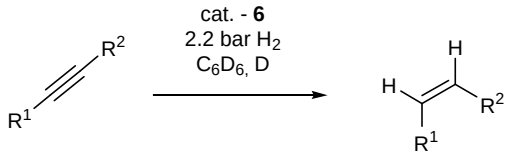


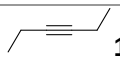
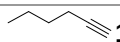
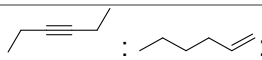
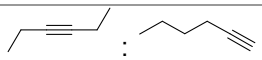
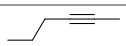
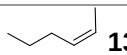
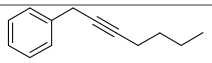
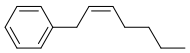
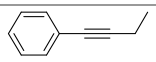
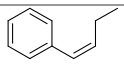
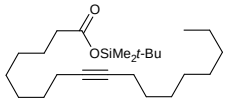
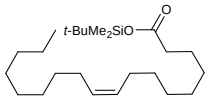
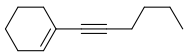
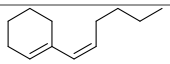
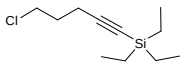
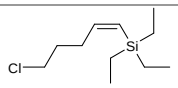
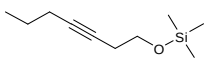
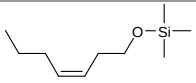
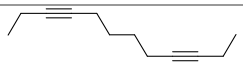
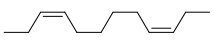
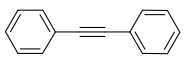
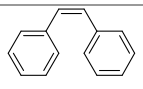
Figure 2. Catalytic hydrogenation of alkynes into *cis*-alkenes. a, Formation of the active catalyst species **8** via hydrogenolysis of precatalyst **6**. **b**, The catalytic cycle of alkynes hydrogenation. Intramolecular protonation of vinyl carbon in **28** causes cycle propagation, while C_6F_5 group cleavage leads to active catalyst degradation. **c**, Reaction of hydroboration intermediates **27** with D_2 results in selective formation of monodeuterated *cis*-alkenes **21c**, **26d-e** and catalyst **8**-*d.* Deuteration occurs selectively to the B–***C*** carbon.

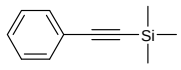
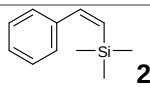
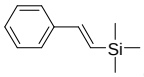
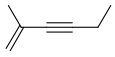
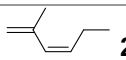
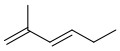
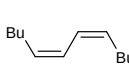
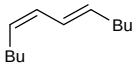
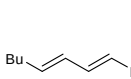
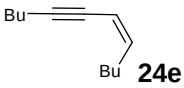
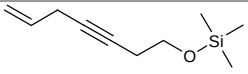
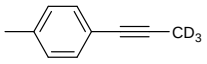
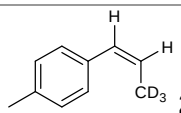
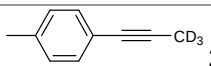
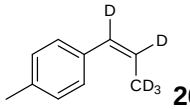
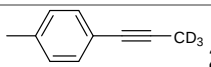
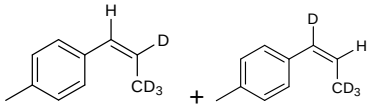
Various dialkyl-, diaryl-, arylalkylacetylenes were successfully hydrogenated under standard conditions: 5 mol % of **6** in C_6D_6, 2 bar of H_2, 80 ℃, 3 h (Table 1), demonstrating the generalit y of the approach and providing exceptional *cis*-stereoselectivity., Enynes, silyl-protected ynols diynes and silyl-protected esters (Table 1, entries 10, 19, 12, 13,) were successfully hydrogenated as well. The products were isolated in excellent yields in experiments scaled up to 10 mmol of substrate. Some of the substrates required prolonged reaction time or/and higher temperature and the catalyst loading, while some were not hydrogenated at all. There are essentially two substrate classes which are unreactive with the current method: terminal alkynes and alkynes comprising a terminal double bond. Nevertheless, terminal alkynes can be silylated using conventional methods and the obtained silylacetylenes were smoothly hydrogenated (Table 1, entries 11, 16). Catalytic activity up to 31.6 h^{-1} was estimated using **6** or **8** as the catalyst under standard conditions and **11a** or **15a** as substrates. Remarkably, the catalytic hydrogenation proceeds at room temperature, though 20 times slower than at 80 ℃. Conversely, high pressure of H_2 (30 bar) causes almost 10-fold acceleration of hydrogenation up to 296 h^{-1} (Supp. § 7).

No over-reduction to alkanes was detected. Under standard conditions *cis*-alkenes were produced exclusively, the traces of other products like *trans*-alkenes have been barely detected by ^{1}H NMR. The only exception found is 1-trimethylsilyl-2-phenylacetylene **22a**: the substantial amount of *trans*-alkene **22c** was produced (12 mol. %) independently on the conversion level (Table 1, entries 16, 17). **22c** is likely to be produced directly during hydrogenation. Accumulation of *trans*-alkenes as a result of *isomerization* was observed when prolonged heating and/or high temperature (120 ℃) was applied to force hydrogenation of poorly reactive substrates (Table 1, entries 19, 21).

Table 1. Catalytic hydrogenation of alkynes using **6** as a precatalyst.



Entry	Substrate(s)	Product(s)	Catalyst **6**, mol. %	Time, h	T, ℃	Conversion[a] (isolated yield)
1	**10a**	 **10b**	7	3	80	100
2	 **11a**	 **11b**	5	3	80	100
3	 **12a**	–	5	15	80	n.r.[b]
4	 **12b** 1:1	–	5	3	80	n.r.
5	 1:1	–	5	3	80	n.r.
6	 **13a**	 **13b**	7	3	80	100
7	 **14a**	 **14b**	10	3	80	100
8	 **15a**	 **15b**	5	3	80	100 (80)
9	 **16a**	 **16b**	5	3	80	100 (98)
10	 **17a**	 **17b**	5	3	80	100
11	 **18a**	 **18b**	5	3	80	100 (95)
12	 **19a**	 **19b**	5	3	80	100
13	 **20a**	 **20b**	5	3	80	100 (94)
14	 **21a**	 **21b**	5	3	80	52
15				9	80	100 (91)

16	 **22a**	 **22b**  **22c**	5	3	80	88 – **22b** 12 – **22c**
17				1.5	80	30.5 – **22b** 4.3 – **22c**
18	 **23a**	 **23b**  **23c**	5	3	80	<20
19			10	15	120	71 – **23b** *9.5* – **23c**
20	 **24a**	 **24b**  **24c**  **24d**  **24e**	20	18	80	44 – **24b** *26 – other alkenes*[c]
21			15	10	120	42 – **24b** 10 – **24c** 10.5 – **24d** 10.2 – **24e**
22	 **25a**	–	5	3	80	n.r.
23	 **26a**	 **26b**	5	3	80	100
24[d]	 **26a**	 **26c**	10	5	80	100
25[e]	 **26a**	**26b** + **26c** +  **26d** **26e**	5	3	80	14.4 – **26b** 15.9 – **26c** 18.7 – **26d** 11 – **26e** **26b**:**26c**:**26d**:**26e**= 24:26.5:31.1:18.4[f]

[a] *Cis*-alkene if not otherwise stated. Defined by a crude sample analysis with $^{1}H/^{13}C$ NMR. [b] No reaction. [c] Including bound to the catalyst. [d] D_2 was used instead of H_2. [e] HD gas was used instead of H_2. Low conversion (60%) is due to insufficient pressure of available HD (1.2 bar). [f] Isotopes scrambling in ca. 1:1:1:1 ratio.

Mechanistic insight into the catalytic cycle

The reaction mechanism of the catalytic hydrogenation of alkynes was investigated in a combined experimental/theoretical study. The basic steps of the envisioned catalytic cycle are depicted in Fig. 2b, and they are consistent with the new concept outlined in Fig. 1b.

The initial step of the catalytic cycle, i.e. the hydroboration of alkynes with **8**, is verified by the isolation of respective intermediates **27b-e**. Additionally, relative rates of hydroboration of different alkynes and alkenes by **8** were measured in competitive experiments. The relative rate is descending in the row: hex-3-yne : hex-1-yne : but-2-yne : hex-1-ene : *cis*-hex-3-ene : prop-1-yn-1-ylbenzene (α+β-positions) : prop-1-yn-1-ylbenzene (β-position) : prop-1-yn-1-ylbenzene (α-position) : diphenylacetylene : *cis*-but-1-en-1-ylbenzene = 136 : 109 : 57 : 44 : 5.5 : 5 : 4 : 1 : no reaction (25 °C) : no reaction (80 °C) (Supp. § 31). These rates are in agreement with common rules of hydroboration[39]. Hydroboration of **10a** appears instantly at room temperature. Replacement of a methyl group with a phenyl substituent leads to 14-fold retardation of

hydroboration to sterically less hindered site of prop-1-yn-1-ylbenzene and 57-fold to the more hindered site. Eventually, diphenylacetylene **21a** remains intact with **8** at room temperature and requires heating at 80 ℃ making the hydroboration, apparently, the rate-limiting step in the overall slow hydrogenation of this substrate.

DFT calculations (Supp. § 49) carried out for the reaction of catalyst **8** with but-2-yne (**10a**) predict relatively small activation barrier (16.2 kcal/mol) for the hydroboration process, and point to high exergonicity of this step (see Fig. 3). These results suggest that alkyne hydroboration is irreversible, so compound **8** can be recovered only upon completion of the catalytic cycle. The irreversibilty was demonstrated experimentally as well (Supp. § 32).

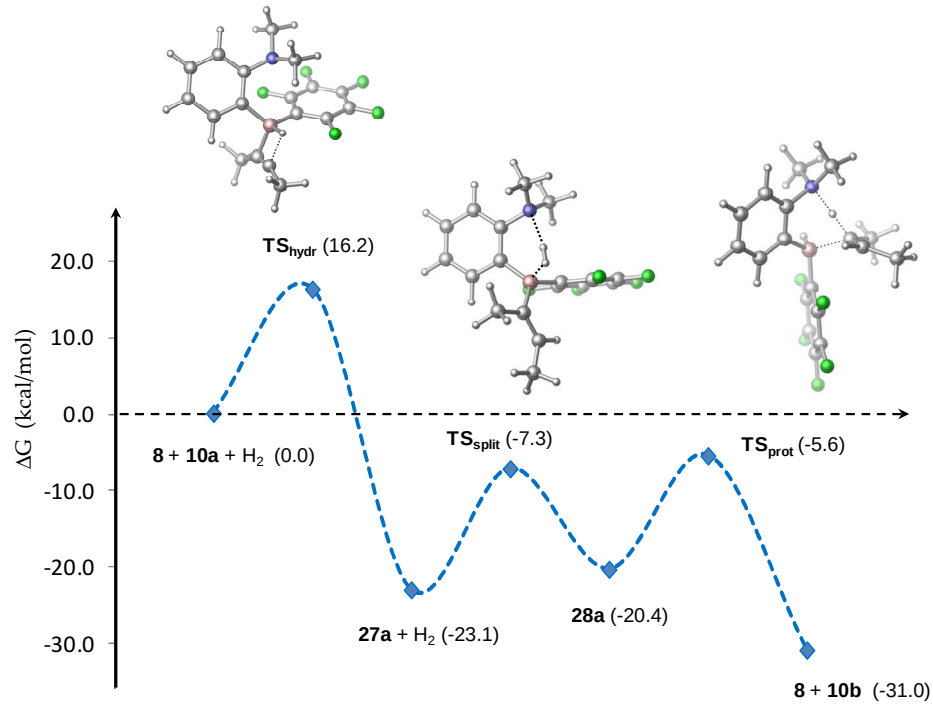


Figure 3. Solution-phase Gibbs free energy diagram computed for the hydrogenation of but-2-yne (10a). Optimized structures of transition states identified for hydroboration (**TS$_{hydr}$**), heterolytic hydrogen splitting (**TS$_{split}$**) and protonation (**TS$_{prot}$**) steps are shown in the upper part of the figure. A detailed description of the structure and energetics of species involved in the catalytic cycle is given in the Supplementary Information.

The zwitterionic reaction intermediates **28b-e** formed in the hydrogen activation step were not detectable, which can be rationalized in light of the computed energetics. Although the formation of **28a** takes place via low barrier (**TS$_{split}$** lies only15.8 kcal/mol above **27a** + H_2 in free energy), this step is found to be slightly endergonic. Notably, heterolytic H_2 splitting with B/N FLPs containing only one electron withdrawing C_6F_5 group on the Lewis acceptor site is unprecedented due to reduced acidity of the resulting borane. However,

as pointed out previously, the *ortho*-phenylene linker between the B/N centers provides significant electrostatic stabilization in the zwitterionic species formed upon the H_2 cleavage[40].

The calculations predict facile intramolecular protonation of the vinyl substituent in **28a**, which proceeds as direct protodeborylation leading to the elimination of *cis*-alkene **10b** and the regeneration of the catalyst. The barrier of product elimination is rather low (14.8 kcal/mol relative to **28a**), and it is thermodynamically favored. The mutual position of B/N sites of the catalyst core plays a crucial role in this process because it determines the feasibility of the proton shift. In this particular case, a low-lying isomer of **28a** could be identified computationally with the NH bond oriented towards the alpha carbon atom of the vinyl group (Supp. § 55).

Protodeborylation of **28** resulting in B–C_6F_5 cleavage and degradation of the active catalyst into inactive vinylborane **29** and C_6F_5H is an alternative reaction pathway in this phase of the catalytic cycle (Fig. 2b), which has been explored computationally as well. The calculated barrier of aryl elimination is notably higher than that of the alkene formation (19.1 kcal/mol relative to **28a**), but this process is still feasible at the applied reaction conditions. The protodeborylation of **28a** is analogous to that taking place in the generation of **8** from precatalyst **6**, for which computations predict even higher barrier (23.0 kcal/mol; Supp. § 48). Assuming the C_6F_5H elimination to be the only catalyst degradation pathway, the ratio of reaction rates of these two intramolecular protonation pathways corresponds to maximum turnover number, which was found to be 91 for hydrogenation of hex-3-yne (Supp. § 9). Eventually, the exceptional *cis*-selectivity observed in the hydrogenation reactions results from exclusive *syn*-hydroboration and the configuration is retained during subsequent elementary steps, particularly protodeborylation[39].

Additional experimental support for the proposed mechanism was collected in isotope-labelling experiments. 1-Methyl-4-prop-1-ynylbenzene-d_3 **26a**, a model substrate, was hydrogenated with HD resulting in all four possible isotopomeric *cis*-styrenes **26b**-**26e** in nearly equal ratio (Table 1, entry 25). Isotope scrambling is in full accordance with the proposed mechanism, since BH(D) hydrogen in **8** originates from a preceding catalytic cycle (Fig. 2b). In addition, when **26a** was treated with equimolar amount of **8**, products of hydroboration were isolated as 79:21 mixture of regioisomers **27d** and **27e**. Upon treatment with D_2 a mixture of **26d** and **26e** in a ratio 79:21 was produced together with equimolar amount of deuterated **8**-*d* (see Fig. 2c). Thus, deuteration of alkynes appears exclusively at the carbon being adjacent to the boron atom in the alkenyl borane intermediate **27**. Similar experiment performed with diphenylacetylene led to exclusive formation of monodeuterated *cis*-stilbene-*d* **21c** (Fig. 2c).

Alkenes under hydrogenation conditions

In an attempt to apply the new synthetic approach (Fig. 1b) to alkene hydrogenation, the reactivity of various terminal and *cis*-disubstituted alkenes with **6**, **8** and H_2 was examined, however, no alkane products were detected (Suppl. § 8). In stoichiometric reactions, terminal alkene **12b** is hydroborated rapidly and irreversibly by catalyst **8**, *cis*-di(*n*-alkyl)ethenes (**10b**, **11b**) react at slower rate and reversibly, whereas **8** remains intact with more sterically hindered *cis*-alkenes (Fig. 4a). Alkylboranes **30a-c** can be produced directly via hydrogenolysis of **6** in the presence of **12b** or alkynes **10a**, **11a** (Fig. 4b) and found to be particularly stable to further hydrogenolysis: **30c** is the major boron-containing component of the reaction mixture after 15 h at 2 bar H_2. As a result, alkynes that contain terminal double bond cause partial or complete deactivation of the catalyst via formation of alk-1-ylboranes, which are unable to propagate the catalytic cycle (Compare: Table 1, entry 2 *versus* 4, 10 *versus* 18, 12 *versus* 22, Supp. § 24-25). Although at the end of **11a** hydrogenation the catalyst is present as alkylborane **30c**, the latter can easily dissociate to give active catalyst species **8** pointing again to the reversibility of hydroboration in the reactions with *cis*-di(*n*-alkyl)ethenes (Supp. § 33).

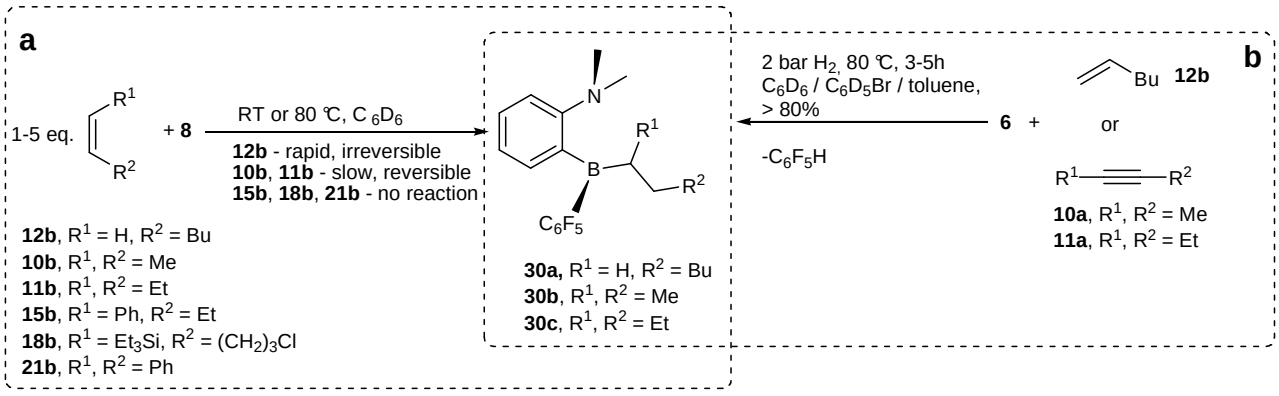


Figure 4. Reaction of 6 and 8 with alkenes. a, Alkenes hydroboration outcome depends on steric crowdness of the double bond: rapid and irreversible for terminal alkenes (**12b**); slow and reversible for *cis*-di(n-alkyl)ethenes (**10b**, **11b**), no reaction for **15b**, **18b**, **21b**. **b**, Alkylboranes **30** are produced from alkenes or alkynes and **6** under hydrogenation conditions.

These results can be readily interpreted in terms of the free energy profiles computed for the hydrogenation of *cis*-but-2-ene and ethylene as model substrates for internal and terminal alkenes (Supp. §§ 50-51). Calculations predict rather different exergonicities for these substrates (-11.9 and -20.5 kcal/mol for *cis*-but-2-ene and ethylene, respectively), which is in qualitative agreement with the observed reactivity. The subsequent heterolytic hydrogen cleavage is kinetically and thermodynamically allowed elementary step, however, the intramolecular protonation of the alkyl substituent in alkylborohydride intermediate is hindered by a large activation barrier. Actually, this step represents the only limiting factor towards the hydrogenation

of alkenes using the present approach, and it is associated with the lack of π-system in the zwitterionic intermediate formed in the H_2 activation step.

Limitation of the current approach to non-terminal alkynes required additional studies as well. It is known from previous publications that FLPs react with terminal alkynes via deprotonative borylation pathway, producing the respective onium alkynylborates[41, 42, 43, 44, 45, 46]. Indeed, **6** reacts with hex-1-yne giving the respective adduct **31** (Scheme 6). Upon heating **6** with excess of hex-1-yne at 80 ℃ under 2 bar H_2, **31** remains the major product after 1 h. However, after 3 h three new aminoborane species were formed in the ratio 3:3:2, each containing the hex-1-ynyl group, as evident by ^{1}H and ^{11}B NMR. ^{19}F NMR spectrum revealed complete cleavage of the C_6F_5-group into C_6F_5H. Evidently, the inability to hydrogenate terminal alkynes is a result of the catalysts degradation into species inert to hydrogen due to complete elimination of the perfluorophenyl groups.

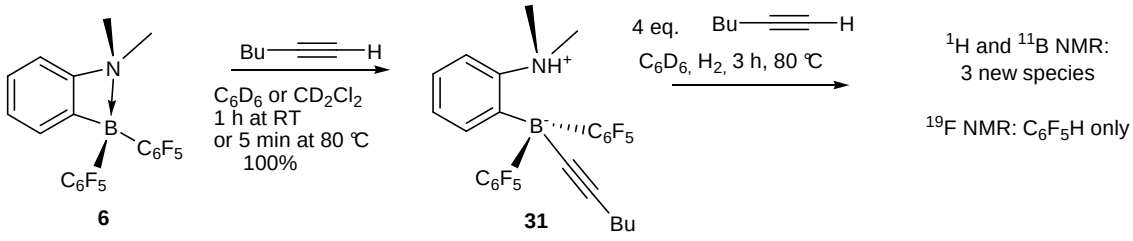


Figure 5. Reaction of aminoborane **6** with hex-1-yne and H_2.

Summary

In conclusion, we have developed a new strategy to catalytic metal-free hydrogenation of unactivated multiple C-C bonds using frustrated Lewis pairs. Using catalyst **8**, formed in situ from aminoborane **6**, the approach was implemented as highly chemo- and stereoselective hydrogenation of internal alkynes into the respective *cis*-alkenes under mild conditions: 2 bar H_2, 80 ℃. The catalytic pathway includes three steps: hydroboration of alkyne (substrate binding), heterolytic H_2 cleavage with formed vinylborane followed by intramolecular protodeborylation of vinyl substituent, recovering **8** and releasing *cis*-alkene. High *cis*-selectivity is a result of exclusive *syn*-hydroboration, and is retained during subsequent steps, particularly, the intramolecular protonation. Mutual *ansa*-B/N geometry plays a key role in all elementary steps, especially during protodeborylation, which proceeds in a single step, rather than including carbocation intermediates. The mechanism was supported by isolation of some intermediates, including the active catalyst species **8**, isotope-labelling studies and quantum-chemical calculations. Substrate restrictions associated with the

presence of the terminal double and triple bonds were studied and rationalized. The computational analysis provides solid support for the proposed mechanism as all elementary steps could be identified and the obtained energetics is in full accordance with experimental findings. In principle, alkenes could be hydrogenated using the current approach, however, at the final stage of the catalytic cycle the C_6F_5 group is cleaved easier than the alkyls, causing catalyst degradation rather than alkane release.

Methods

Standard protocol: 0.2–0.5 mmol of an alkyne were placed into a 25 ml Schlenk tube, followed by 5 mol % of **6** and 0.7 ml of C_6D_6. The tube was filled with 2–2.2 bar of hydrogen by two freeze-pump-thaw cycles and vigorously stirred at 80 ℃ for 3 h or longer if ne eded. The reaction mixture was transferred into an NMR tube and analyzed.

Computational details. Density functional theory with the dispersion-corrected, range-separated hybrid *ω*B97X-D exchange-correlation functional[47] was employed to examine possible reaction pathways relevant to the title reaction. For geometry optimizations, vibrational analysis, and the estimation of solvent effects, the 6-311G(d,p) polarized triple-ζ basis set was used, and additional single-point energy calculations were carried out for each located stationary point with the larger 6-311++G(3df,3pd) basis set. The energy values reported in the paper correspond to solution phase Gibbs free energies. Additional computational details are provided in Supplementary.

Acknowledgements

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