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A frustrated-Lewis-pair approach to catalytic reduction of alkynes to *cis*-alkenes

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Frustrated Lewis pairs are compounds containing both Lewis acidic and Lewis basic moieties, where the formation of an adduct is prevented by steric hindrance. They are therefore highly reactive, and have been shown to be capable of heterolysis of molecular hydrogen, a property that has led to their use in hydrogenation reactions of polarized multiple bonds. Here, we describe a general approach to the hydrogenation of alkynes to *cis*-alkenes under mild conditions using the unique *ansa*-aminohydroborane as a catalyst. Our approach combines several reactions as the elementary steps of the catalytic cycle: hydroboration (substrate binding), heterolytic hydrogen splitting (typical frustrated-Lewis-pair reactivity) and facile intramolecular protodeborylation (product release). The mechanism is verified by experimental and computational studies.

Recently, a new approach to dihydrogen activation known as the frustrated Lewis pairs (FLPs) concept has been introduced[1–3]. A combination of highly Lewis-acidic boranes and sterically hindered bases can split hydrogen heterolytically to generate onium (for example, phosphonium, ammonium) borohydrides. These compounds demonstrate reduction activities resembling those of inorganic borohydrides such as $NaBH_4$; that is, they are suitable predominantly for the reduction of polarized multiple bonds. Imines, enamines, silyl ethers[4–6], α,β-enones[7], ynones[8] and *N*-alkylanilines[9] have been hydrogenated using stoichiometric or catalytic amounts of FLPs. Owing to the heterolytic nature of FLP–H_2 adducts, the hydrogenation of unactivated multiple C–C bonds using FLPs has some natural limitations, because during the relevant 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 in the hydrogenation of alkenes under ambient conditions, this method is predictably restricted to alkenes with high proton affinity[10].

Combining the FLP approach and previous knowledge about borane-catalysed hydrogenation of alkenes[11–14] and polyarenes[15–18], 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 the synthesis of natural and industrially relevant compounds[19–23]. Heterogeneous as well as homogeneous metal catalysts for this stereoselective hydrogenation are known[24–28]; however, metal-free catalytic hydrogenation of unactivated alkynes into alkenes has not been reported previously.

In contrast to classical FLP-catalysed reactions, the substrate is bound to catalyst **1** by hydroboration before hydrogen activation (Fig. 1b). The resulting borane **3**, together with a Lewis base co-catalyst, can activate hydrogen, producing adduct **4**. In this onium borohydride **4**, a proton transfer can occur, liberating the initial borane **1**, the Lewis base and 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, $(C_6F_5)_2BH$ (ref. 29), as a catalyst. $(C_6F_5)_2BH$ smoothly hydroborates different alkenes and alkynes[30,31]. Moreover, it has been 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 (Supplementary Section S47).

Recently, we have reported 2-[bis(pentafluorophenyl)boryl]-*N*,*N*-dialkylanilines, exemplifying a new class of bridged frustrated B/N Lewis pairs[34]. Interestingly, compound **6** exists as an intramolecular Lewis adduct, containing a strained four-membered C–N → B–C cycle. Owing to strain, the B–N bond in **6** is relatively weak, because at room temperature **6** reversibly reacts with hydrogen to give ammonium borohydride **7** (Fig. 2).

Results and discussion

New *ansa*-aminohydroborane as a catalyst. In this work we report that, upon heating of aminoborane **6** at 80 °C under 2 bar H_2, new signals (different from those of **6** or **7**) appear in the ^1H, ^{19}F and ^{10}B NMR spectra, together with the formation of C_6F_5H (**9**). The new species was isolated as a greenish oil and identified as hydroborane **8** (Fig. 2), producing in the ^1H NMR spectrum a characteristic partially relaxed quadruplet ($\delta = 4.35$ ppm, $J = 105$ Hz) attributed to B*H* signal. This reactivity is unprecedented, because neither inter- nor intramolecular FLPs have been reported to undergo B–C_6F_5 hydrogenolysis as a result of hydrogen activation[35–37].

Because **8** is a potentially hydroborating BH species and can be produced *in situ* from **6**, we attempted to use **8** as a catalyst in the 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 °C. After 15 h, no products of hex-1-ene and hex-1-yne hydrogenation were detected by NMR. In the case of **11a**, no evidence of starting alkyne was found; instead, a complex mixture of alkenes was observed, mostly comprising *cis*-hex-3-ene **11b**. Minor amounts of *trans*-hex-3-ene and other hexenes were attributed to

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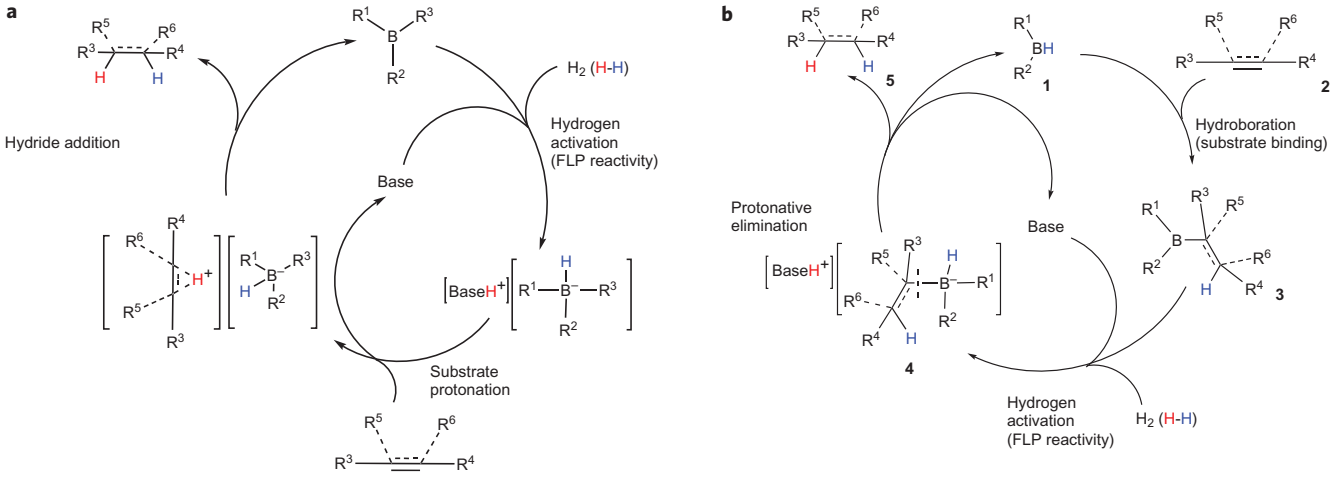


Figure 1 | FLP-catalysed hydrogenation of multiple C–C bonds. a, Traditional approach including heterolytic hydrogen splitting by the catalyst followed by protonation of the substrate as the key steps. **b**, In the novel approach, substrate activation via hydroboration precedes hydrogen activation. Reduced substrate is then released via protonation of the formed H_2 adduct.

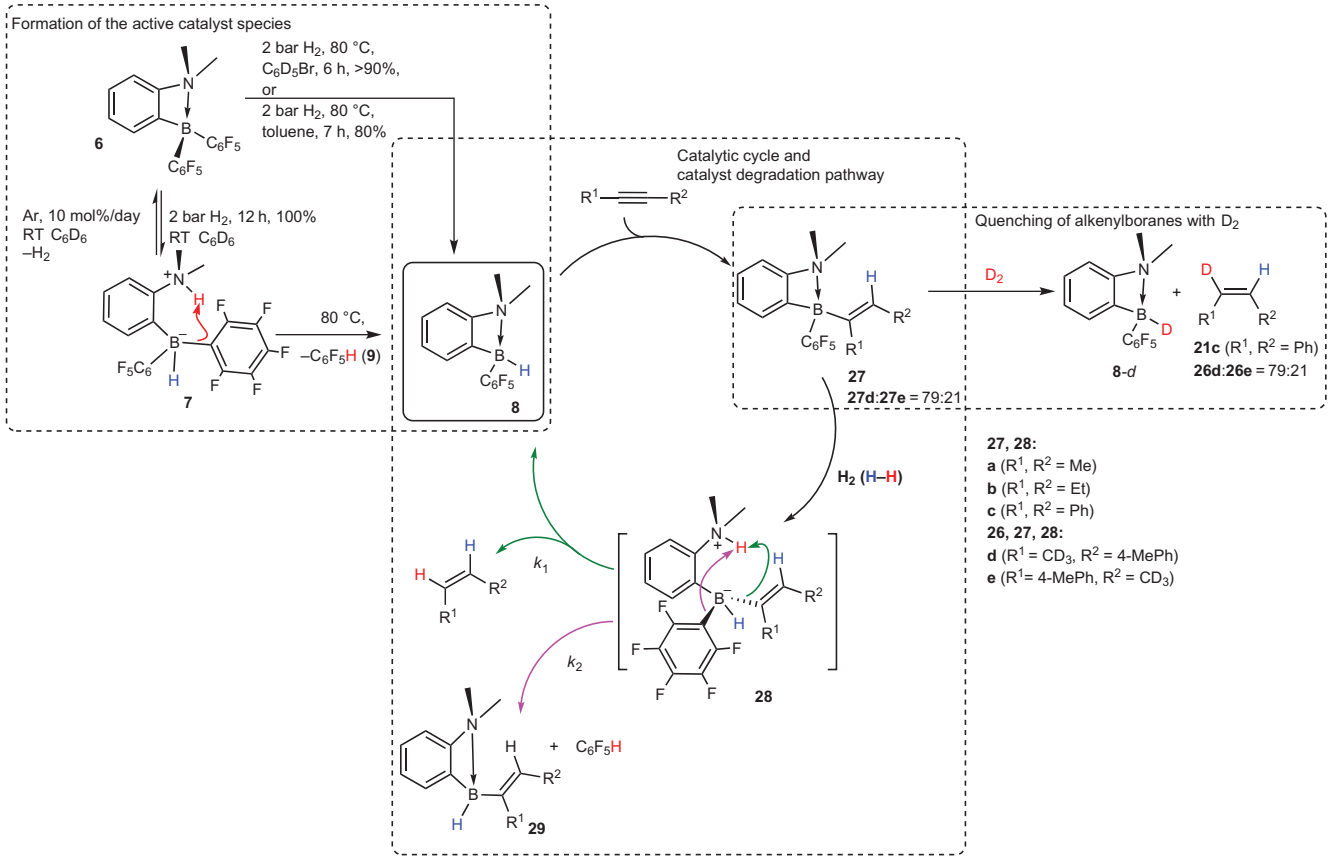
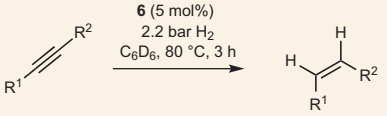


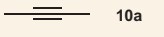
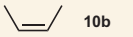
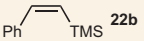
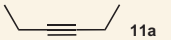
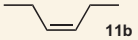
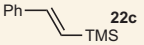
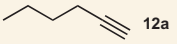
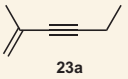
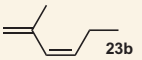
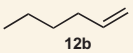
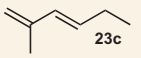
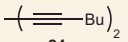
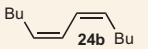
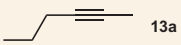
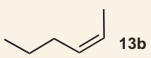
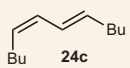
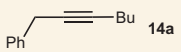
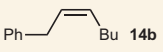
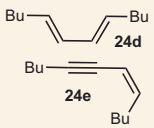
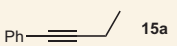
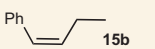
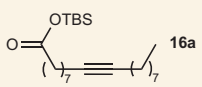
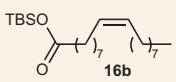
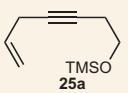
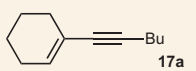
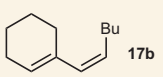
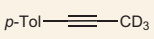
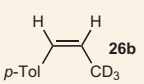
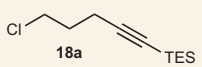
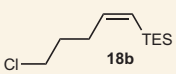
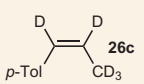
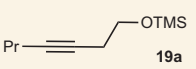
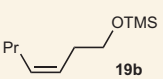
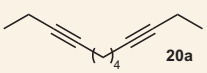
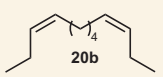
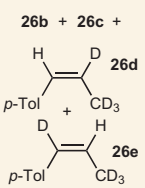
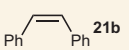
Figure 2 | Mechanism of catalytic hydrogenation of alkynes into *cis*-alkenes. Formation of the active catalyst species **8** proceeds through H_2 addition to the precatalyst **6**, followed by intramolecular protonative cleavage of the C_6F_5 ring. Produced catalyst **8** hydroborates alkyne (substrate binding), producing vinylborane **27**. The latter activates hydrogen by the FLP mechanism. Intramolecular protonation of vinyl carbon in **28** causes cycle propagation, while C_6F_5 group cleavage leads to active catalyst degradation. 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, giving solid support to the proposed mechanism.

isomerization of the initially produced *cis*-hex-3-ene via a hydroboration/retrohydroboration sequence, catalysed either by **8** or other hydroborane species. When hydrogenation of **11a** was repeated for 3 h with 5 mol% **6**, *cis*-hex-3-ene **11b** was produced almost exclusively (according to NMR).

Various dialkyl-, diaryl-, arylalkylacetylenes were successfully hydrogenated under standard conditions—5 mol% **6** in C_6D_6, 2 bar H_2, 80 °C, 3 h (Table 1)—demonstrating the generality of the approach and providing exceptional *cis*-stereoselectivity. Silyl-protected esters, enynes, silyl-protected ynols and diynes (Table 1, entries 9, 10, 19, 12, 13) were also successfully hydrogenated. The products were isolated in excellent yields in experiments scaled up to 10 mmol of substrate. Some of the substrates required prolonged reaction times and/or higher temperatures and catalyst

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



Entry	Substrate	Product	Conversion: isolated yield (%)	Entry	Substrate	Product(s)	Conversion: product (%)
1*	 10a	 10b	100	16	22a	 22b	88 (22b) 12 (22c)
2	 11a	 11b	100	17¶	22a	 22c	30.5 (22b) 4.3 (22c)
3†	 12a	–	n.r.‡	18	 23a	 23b	<20 (23b)
4	11a +  12b 1:1	–	n.r.	19**	23a	 23c	71 (23b) 9.5 (23c)
5	11a + 12a 1:1	–	n.r.	20††	 24a	 24b	44 (24b) 26 (other alkenes)
6*	 13a	 13b	100			 24c	
7§	 14a	 14b	100	21‡‡	24a	 24d, 24e	42 (24b) 10 (24c) 10.5 (24d) 10.2 (24e)
8	 15a	 15b	100 (80)				
9	 16a	 16b	100 (98)	22	 25a	–	n.r.
10	 17a	 17b	100	23	 26a	 26b	100
11	 18a	 18b	100 (95)	24§§	26a	 26c	100
12	 19a	 19b	100				
13	 20a	 20b	100 (94)	25¶¶	26a	 26b + 26c + 26d + 26e	14.4 (26b) 15.9 (26c) 18.7 (26d) 11 (26e)
14	21a	 21b	50				
15‖	21a	21b	100 (91)				

*7 mol% of 6; †Reaction time, 15 h; ‡No reaction; §10 mol% of 6; ‖Reaction time, 9 h; ¶Reaction time, 1.5 h; **10 mol% of 6, 120 °C, 15 h; ††20 mol% of 6, 18 h; ‡‡15 mol% of 6, 120 °C, 10 h; §§D_2 was used instead of H_2, 10 mol% of 6, 5 h; ¶¶HD gas was used instead of H_2. Low conversion (60%) is due to insufficient pressure of available HD (1.2 bar). Isotopes scrambling in ~1:1:1:1 ratio. Bu, butyl; Ph, phenyl; Pr, propyl; *p*-Tol, 4-methylphenyl; TBS, *tert*-butyldimethylsilyl; TES, triethylsilyl; TMS, trimethylsilyl.

loading, and some were not hydrogenated at all. There are essentially two substrate classes that are unreactive using 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

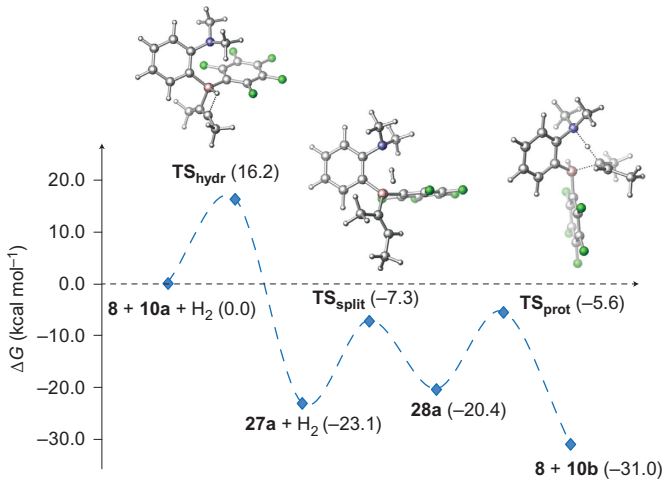


Figure 3 | Solution-phase Gibbs free energy diagram computed for the hydrogenation of but-2-yne (10a). Optimized structures of transition states identified for hydroboration (**TS$_{hydr}$**), heterolytic hydrogen splitting (**TS$_{split}$**) and protonation (**TS$_{prot}$**) steps are shown in the upper part of the figure. The energetics of the elementary steps identified computationally is consistent with the proposed reaction mechanism. A detailed description of the structure and energetics of species involved in the catalytic cycle is given in Supplementary Section S49.

catalytic hydrogenation proceeds at room temperature, although 20 times slower than at 80 °C. Meanwhile, high-pressure H_2 (30 bar) causes almost tenfold acceleration of hydrogenation up to 296 h^{-1} (Supplementary Section S7).

No over-reduction to alkanes was detected. Under standard conditions *cis*-alkenes were produced exclusively, with traces of other products such as *trans*-alkenes barely detected by ^{1}H NMR. The only exception was 1-trimethylsilyl-2-phenylacetylene **22a**, where a substantial amount of *trans*-alkene **22c** was produced (12 mol%), independently of the conversion level (Table 1, entries 16, 17). Product **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 °C) was applied to force hydrogenation of poorly reactive substrates (Table 1, entries 19, 21).

Mechanistic insight into the catalytic cycle. The reaction mechanism for 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. 2, and are consistent with the new concept outlined in Fig. 1b.

The initial step of the catalytic cycle, that is, the hydroboration of alkynes with **8**, was 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 order 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-yl benzene = 136 : 109 : 57 : 44 : 5.5 : 5 : 4 : 1 : no reaction (25 °C) : no reaction (80 °C) (Supplementary Section S31). These rates are in agreement with common rules of hydroboration[38]. 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 the 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 °C, apparently making the hydroboration the rate-limiting step in the overall slow hydrogenation of this substrate.

Density functional theory (DFT) calculations (Supplementary Section S49) carried out for the reaction of catalyst **8** with but-2-yne (**10a**) predict a relatively small activation barrier (16.2 kcal mol^{-1}) for the hydroboration process, and point to the high exergonicity of this step (Fig. 3). These results suggest that alkyne hydroboration is irreversible, so compound **8** can be recovered only upon completion of the catalytic cycle. This irreversibility has also been demonstrated experimentally (Supplementary Section S32).

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 a low barrier (**TS$_{split}$** lies only15.8 kcal mol^{-1} 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 the reduced acidity of the resulting borane. However, as pointed out previously, the *ortho*-phenylene linker between the B/N centres provides significant electrostatic stabilization in the zwitterionic species formed upon H_2 cleavage[39].

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 regeneration of the catalyst. The barrier to product elimination is rather low (14.8 kcal mol^{-1} relative to **28a**) and is thermodynamically favoured. The mutual position of the 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 (Supplementary Section S49).

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. 2), which has also been explored computationally. The calculated barrier of aryl elimination is notably higher than that of alkene formation (19.1 kcal mol^{-1} 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 an

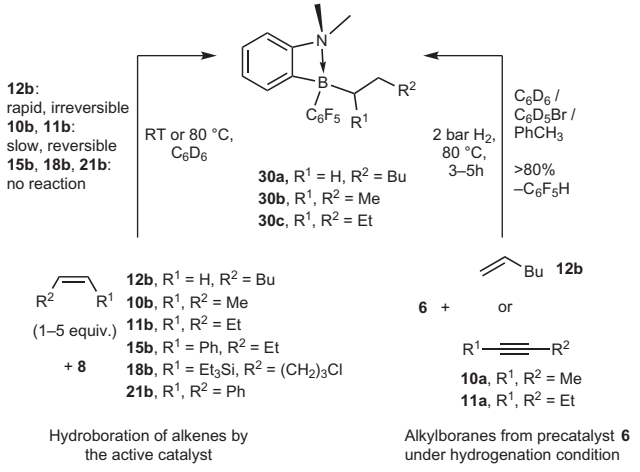


Figure 4 | Reaction of 6 and 8 with alkenes. Alkenes hydroboration outcome depends on the level of steric crowding of the double bond: rapid and irreversible for terminal alkenes (**12b**); slow and reversible for *cis*-di(*n*-alkyl)ethenes (**10b**, **11b**), no reaction for **15b**, **18b**, **21b**. Alternatively, alkylboranes **30** are produced from alkenes or alkynes and **6** under hydrogenation conditions. The one-pot reaction includes formation of **8** *in situ*, followed by hydroboration of the alkene loaded as is or produced *in situ* from the respective alkyne.

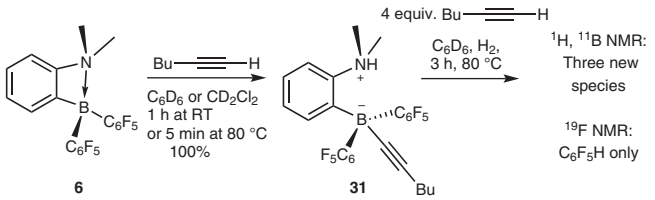


Figure 5 | Reaction of aminoborane 6 with hex-1-yne and H_2. Initially, adduct **31** is formed upon addition of hex-1-yne to precatalyst **6**. Upon heating **6** or **31** with excess hex-1-yne under H_2 pressure, three new boron-containing species are formed together with full cleavage of C_6F_5 groups. Without C_6F_5 groups the catalyst core cannot activate H_2.

even higher barrier (23.0 kcal mol^{-1}; Supplementary Section S48). Assuming the C_6F_5H elimination to be the only catalyst degradation pathway, the ratio of the reaction rates of these two intramolecular protonation pathways corresponds to the maximum turnover number, which was found to be 91 for hydrogenation of hex-3-yne (Supplementary Section S9). 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[38].

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–e** in nearly equal ratio (Table 1, entry 25). Isotope scrambling is in full accordance with the proposed mechanism, because the BH(D) hydrogen in **8** originates from a preceding catalytic cycle (Fig. 2). In addition, when **26a** was treated with an equimolar amount of **8**, products of hydroboration were isolated as a 79:21 mixture of regioisomers **27d** and **27e**. Upon treatment with D_2, a mixture of **26d** and **26e** in the ratio 79:21 was produced, together with an equimolar amount of deuterated **8**-*d* (Fig. 2). Thus, deuteration of alkynes appears exclusively at the carbon adjacent to the boron atom in the alkenyl borane intermediate **27**. A similar experiment performed with diphenylacetylene led to exclusive formation of monodeuterated *cis*-stilbene-*d* **21c** (Fig. 2).

Alkenes under hydrogenation conditions. In an attempt to apply the new synthetic approach (Fig. 1b) to alkene hydrogenation, the reactivities of various terminal and *cis*-disubstituted alkenes with **6**, **8** and H_2 were examined; however, no alkane products were detected (Supplementary Section S8). In stoichiometric reactions, terminal alkene **12b** is hydroborated rapidly and irreversibly by catalyst **8**, *cis*-di(*n*-alkyl)ethenes (**10b**, **11b**) react at a slower rate and reversibly, whereas **8** remains intact with more sterically hindered *cis*-alkenes (Fig. 4). Alkylboranes **30a–c** can be produced directly via hydrogenolysis of **6** in the presence of **12b** or alkynes **10a**, **11a** (Fig. 4) 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 a 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 (in Table 1 compare entry 2 and 4, 10 and 18, 12 and 22; Supplementary Sections S24,25). 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 (Supplementary Section S33).

These results can be interpreted readily 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 (Supplementary Sections S50,51). Calculations predict rather different exergonicities for these substrates (−11.9 and −20.5 kcal mol^{-1} for *cis*-but-2-ene and ethylene, respectively), which is in qualitative agreement with the observed reactivity. The subsequent heterolytic hydrogen cleavage is a 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 a π-system in the zwitterionic intermediate formed in the H_2 activation step.

The limitation of the current approach to non-terminal alkynes also required additional studies. It is known from previous publications that FLPs react with terminal alkynes via deprotonative borylation pathway, producing the respective onium alkynylborates[40–45]. Indeed, **6** reacts with hex-1-yne giving the respective adduct **31** (Fig. 5). Upon heating **6** with excess hex-1-yne at 80 °C 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 from ^1H and ^{11}B NMR. The ^{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 catalyst degradation into species inert to hydrogen due to complete elimination of the perfluorophenyl groups.

Conclusion

In conclusion, we have developed a new strategy for the 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 °C). 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 more easily than an alkyl group, causing catalyst degradation rather than alkane release. Some early examples of the catalytic hydrogenation of unactivated alkynes were reported by us as part of a review[46] (and are included again as entries 2, 6–8 and 11–15 in Table 1). Compared to other *ansa*-aminoboranes discussed there, **8** is unique enabling the catalytic hydrogenation of unactivated alkynes.

Methods

Standard protocol. A quantity of 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 °C for 3 h, or longer if needed. The reaction mixture was transferred into an NMR tube and analysed.

Computational details. DFT, with the dispersion-corrected, range-separated hybrid ωB97X-D exchange-correlation functional[47], was used 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 the Supplementary Information (Computational Protocol).

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Author contributions

K.C. and T.R. conceived and K.C. carried out the experiments. A.M. and I.P. designed and performed the DFT studies. All authors discussed and co-wrote the paper.

Additional information

Supplementary information and chemical compound information are available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to T.R. and those related to computational studies to I.P.

Competing financial interests

The authors declare no competing financial interests.