Organic & Biomolecular Chemistry

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c5ob01602a

Enamine/butadienylborane cycloaddition in the frustrated Lewis pair regime†

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Received 31st July 2015,
Accepted 19th August 2015

DOI: 10.1039/c5ob01602a

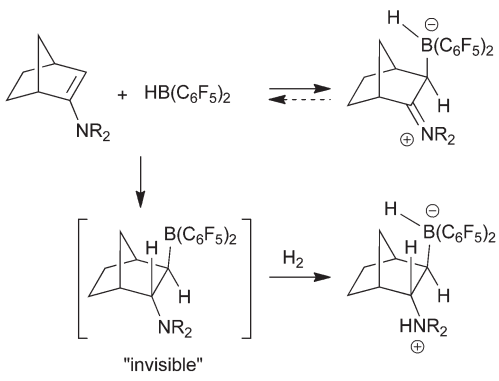
www.rsc.org/obc

The dienylborane **2a** was prepared by regioselective alkyne hydroboration of the conjugated enyne **1a** with Piers' borane [$HB(C_6F_5)_2$]. Its reaction with a series of acetophenone derived enamines **3** resulted in the formation of the strong enamine β-carbon adduct with the borane Lewis acid (**4**). In contrast B–C adduct formation between the dienylborane **2a** and a series of much more bulky cyclohexanone derived enamines (**6**) is rapidly reversible above *ca.* –30 °C and then leads to the formation of the [4 + 2]cycloaddition products **8**. A DFT study revealed that this reaction is probably taking a stepwise route, proceeding by means of enamine addition to the dienylborane terminus to generate a zwitterionic borata–alkene/iminium ion intermediate that undergoes rapid subsequent ring closure. Heating of the products **8** led to amidoborane elimination from the vicinal amino/borane pair at the product framework to give the respective hexahydronaphthalene product **10**. Subsequent treatment with TEMPO (2 equiv.) resulted in selective oxidation of the unsaturated ring to give the respective tetrahydronaphthalene derivative **12**.

Introduction

Hydroboration of enamines with $HB(C_6F_5)_2$ has provided a viable pathway for synthesizing vicinal N/B frustrated Lewis pairs (N/B FLPs).[1] Some of them have been used for small molecule binding and/or activation. Most notably this regarded the heterolytic splitting of dihydrogen to give the respective ammonium/hydrido-borate zwitterions, some of which provided a suitable basis for the development of active metal-free hydrogenation catalysts.[2] However, the use of the enamine/$HB(C_6F_5)_2$ entry was not completely unproblematic since these systems tend to show a few side reactions. At the stage of the actual N/B FLP, hydride abstraction from C–H units at the α-position to the amine by the adjacent borane represented the most serious interference *via* typical FLP reactivity,[1,3] but complications could also arise at the very beginning of the reaction sequence. The enamine β-carbon atom is a nucleophile and, consequently, in many cases adduct formation took place with the electrophilic borane. Fortunately, this turned out to become reversible in some cases in the presence of suitable trapping agents, such as dihydrogen.[4] In some examples we had observed effective H–H splitting directly taking place from the enamine/$HB(C_6F_5)_2$ adduct. This was thought to take place by means of an "invisible" intermediate FLP which was actually never directly observed along the reaction pathway. Scheme 1 shows a typical example.[4,5]

We have now found that enamines may show a related behavior towards strongly electrophilic dienylboranes. In some cases they just form stable adducts; in other cases this adduct formation is reversible, which opens up an interesting route to achieve a formal [4 + 2]cycloaddition reaction. On this account we report about some typical examples and discuss both the uncommon reaction mechanism of this six-membered ring



Scheme 1

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† Electronic supplementary information (ESI) available: Details of the DFT calculations and experimental details. CCDC 1411182–1411189. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ob01602a

‡ X-ray single crystal structure analyses.

§ Computational chemistry.

formation and the synthetically significant follow-up reactions of the resulting frameworks that contain vicinal amine/borane pairs of complementary functional groups.

Results and discussion

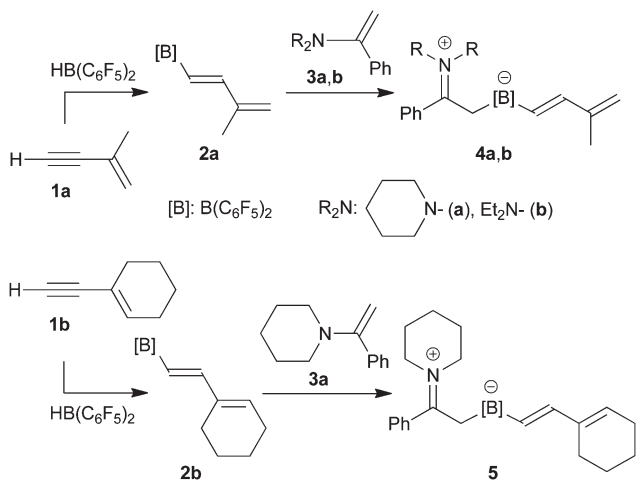
Enamine/dienylborane adduct formation

We generated the starting materials dienylboranes **2a,b** by $HB(C_6F_5)_2$ hydroboration of the conjugated enynes 3-methylbutenyne (**1a**) and 1-ethynylcyclohexene (**1b**).[6,7] The reactions were complete after 3 h at r.t. The hydroboration took place selectively at the terminal carbon–carbon triple bonds of these substrates and left the C=C double bond untouched.

We then treated the *in situ* generated conjugated dienyl bis(pentafluorophenyl)borane **2a** with the enamines **3a,b**. The reaction of **2a** and the enamine **3a** (see Scheme 2) was complete within 1 h at r.t. in dichloromethane and the workup gave the product **4a** as a colorless solid in 81% yield. The X-ray crystal structure analysis revealed that we had isolated the Lewis acid/base adduct.[8] The enamine had served as a carbon nucleophile and was added to the electrophilic boron atom. This resulted in a zwitterionic product containing an iminium ion having the $-B(dienyl)(C_6F_5)_2$ group at the β-carbon atom (see Fig. 1). In solution the iminium/borate betaine shows a typical borate ^{11}B NMR signal and a characteristic iminium ^{13}C NMR resonance (see Table 1). It shows three ^{19}F NMR signals of the $B(C_6F_5)_2$ moiety with a small $\Delta\delta^{19}F_{m,p}$ chemical shift separation as it is usually found for such a C_6F_5 substituent containing borate moiety.[9]

The reaction of the enamine **3b** with the dienylborane **2a** proceeded analogously to give the C–B adduct **4b** as a colorless solid in 70% yield. It shows typical NMR features similar to those of compound **4a** (see Table 1).

The enamine **3a** was also exposed to the dienylborane **2b** (*in situ* generated). Again we observed rapid Lewis base and Lewis acid addition product formation under our typical reaction conditions (r.t. dichloromethane, 1 h). The workup gave the product **5** in *ca.* 80% yield (see Table 1 for selected NMR data; additional data of compounds **4a,b** and **5** are provided in the ESI†).



Scheme 2

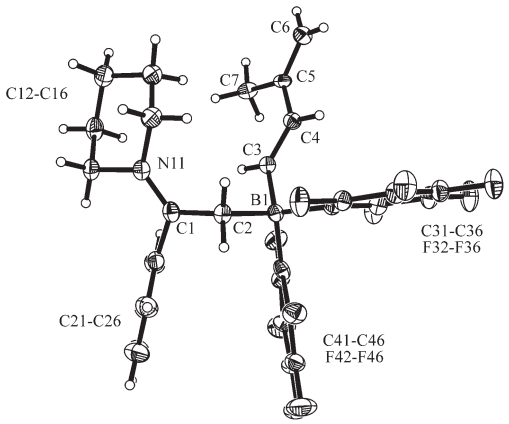


Fig. 1 Molecular structure of the adduct **4a** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (°): C1–N11, 1.304(3); C1–C2, 1.473(3); C2–B1, 1.697(3); C3–C4, 1.328(3); C4–C5, 1.474(5); C5–C6, 1.335(6); N11–C1–C21, 120.1(2); N11–C1–C2, 124.3(2); C1–C2–B1, 114.2(1); B1–C3–C4, 128.7(2); C3–C4–C5, 126.3(4); N11–C1–C2–B1, −104.2(2); C21–C1–C2–B1, 74.9(2); B1–C3–C4–C5, −179.1(6).

Table 1 Selected NMR features of the iminium/borate adducts **4** and **5**[a]

NR_2	**4a**[b] NC_5H_{10}	**4b**[c] NEt_2	**5**[d] NC_5H_{10}
$\delta^{11}B$	−10.9	−11.4	−11.1
$\delta^{13}C$:			
C1	194.9	196.4	194.4
C2	41.8	41.3	41.4
C3	143.7	142.8	138.3
C4	135.6	135.1	135.8
C5	144.5	144.3	137.4
C6	112.7	112.6	125.9
$\delta^{1}H$:			
3-H	6.50	6.46	6.32
4-H	5.73	5.74	5.54
^{3}J(3H,4H)	17.7	17.6	17.4
6-H	4.80/4.66	4.80/4.66	5.40

[a] Chemical shift in ppm (δ scale). [b] In CD_2Cl_2 at 273 K. [c] In CD_2Cl_2 at 263 K. [d] In CD_2Cl_2 at 253 K.

Formation of cycloaddition products

Since it appeared that the enamines **3a,b** were too basic and strongly favored nucleophilic attack at the electrophilic boron Lewis acid side of the dienylboranes **2a,b** we used considerably more bulky enamines pyrrolidino-, piperidino- and morpholinocyclohexene (**6a–c**) for reaction with the dienylborane system **2a**.[10]

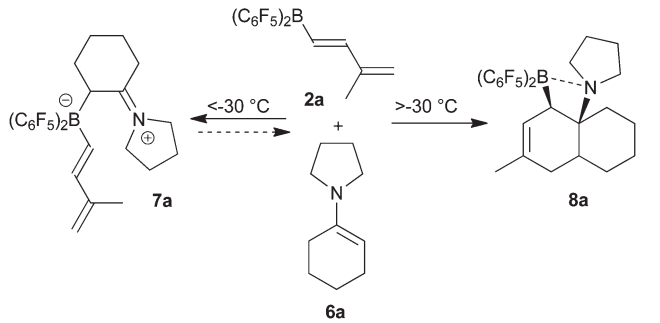
We first investigated the reaction of the dienylborane **2a** with pyrrolidinocyclohexene. The dienylborane was generated

in situ by hydroboration of the enyne **1a** with Piers' borane [$HB(C_6F_5)_2$] in CD_2Cl_2 as usual and then the enamine (1 molar equiv.) was added at −80 °C. Reaction control by ^{11}B NMR spectroscopy revealed that the Lewis acid/Lewis base adduct **7a** was formed instantaneously. The mixture was slowly warmed up with ^{11}B NMR control. The adduct turned out to be stable up to *ca.* −30 °C, but at −20 °C and above it rearranged rapidly and completely to a new species, which later was positively identified as the cycloaddition product **8a** (see Scheme 3).

We were able to characterize the adduct **7a** by X-ray diffraction (see Fig. 2). For this purpose we performed the reaction of the enamine **6a** with the dienylborane **2a** in dichloromethane at low temperature (−45 °C). A layer of pentane was carefully added on top and the mixture was left at −45 °C for several days to give single crystals suitable for X-ray crystal structure analysis of compound **7a**. It showed that even the bulky enamine **6a** had added to the Lewis acidic boron center through its nucleophilic β-carbon atom. The product **7a** contains an exocyclic iminium ion moiety at the central six-membered ring and the borate substituent at its α-position [θ N1–C7–C6–B1 96.4(2)]. The intact conjugated dienyl unit is attached to the boron atom. The alkenylborane subunit is *E*-configured and the dienyl moiety is found in a planar s-*trans* conformation.

Since we had seen in the *in situ* NMR-experiment that in this case the adduct formation was apparently reversible and the compounds eventually reacted to give the product **8a** we performed the reaction between **6a** and **2a** under conditions of thermodynamic control.

The *in situ* generated dienylborane **2a** reacted with the enamine **6a** in dichloromethane solution at r.t. Workup after 1 h reaction time gave the product **8a** in 76% yield. It was characterized by spectroscopy and X-ray diffraction. Single crystals for the X-ray crystal structure analysis were obtained from dichloromethane/pentane by the diffusion method. The structure features the newly formed bicyclo[4.4.0]decene framework with a C=C double bond between carbon atoms C3 and C4 (see Table 2 and Fig. 3). Carbon atom C4 also bears the methyl



Scheme 3

Table 2 Selected structural parameters of the cycloaddition products **8**[a]

NR_2	**8a** NC_4H_8	**8b** NC_5H_{10}	**8c** NC_4H_8O
B1–N1	1.687(2)	1.733(5)	1.758(3)
C1–N1	1.589(2)	1.588(4)	1.586(3)
B1–C2	1.640(2)	1.643(5)	1.641(3)
C1–C2	1.541(2)	1.525(5)	1.532(3)
C3–C4	1.329(3)	1.329(5)	1.318(3)
C1–C2–B1	90.2(1)	91.6(3)	92.1(1)
C2–B1–N1	84.2(1)	83.1(2)	82.5(1)
B1–N1–C1	86.9(1)	86.2(2)	86.0(1)
N1–C1–C2	90.9(1)	92.0(2)	92.1(1)
B1–C2–C1–N1	−21.8(1)	−21.2(3)	22.0(1)
B1–C2–C1–C6	91.7(1)	94.4(3)	−93.4(2)

[a] Bond lengths in Å and bond angles in deg.

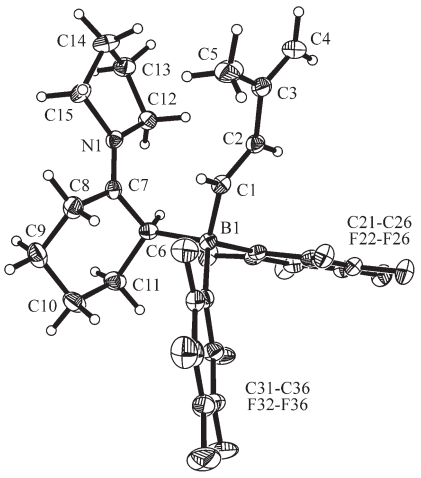


Fig. 2 A view of the molecular structure of the enamine/dienylborane adduct **7a** (thermal ellipsoids are shown with 50% probability). Selected bond lengths (Å) and angles (°): N1–C7, 1.295(2); C6–C7, 1.478(2); B1–C6, 1.715(2); B1–C1, 1.616(2); C1–C2, 1.335(2); C2–C3, 1.472(2); C3–C4, 1.337(3); N1–C7–C6, 121.7(1); C1–B1–C6, 106.3(1); C1–C2–C3, 126.4(2); B1–C6–C7–N1, 96.4(2); C1–C2–C3–C4, –174.8(2).

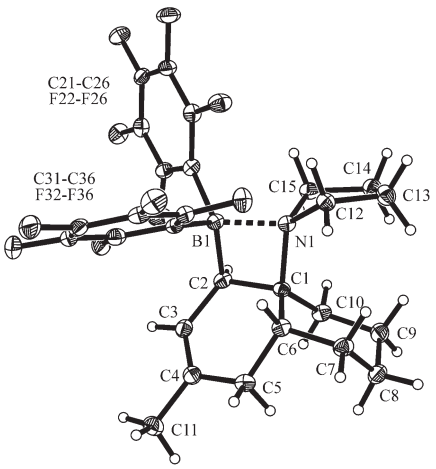


Fig. 3 A view of the molecular structure of the cycloaddition product **8a** (thermal ellipsoids are shown with 50% probability).

substituent. There is a vicinal pair of pyrrolidino and $B(C_6F_5)_2$ substituents attached at the bridgehead carbon atom C1 and the adjacent carbon center C2. The boron Lewis acid and the amine Lewis base make a rather strong contact.[1] This pair of substituents is found to be *cis*-attached at the bicyclic carbon framework.

In solution compound **8a** features a ^{11}B NMR resonance in the typical tetracoordinated borate range (see Table 3).[9] There is a single set of ^{1}H and ^{13}C NMR signals. The pairs of the methylene hydrogens at the ring carbon atoms C5, C7–C10 and also of the pyrrolidino-CH_2 groups are all pairwise diastereotopic. Due to the chirality of the compound the pair of C_6F_5 substituents at the tetracoordinated boron center is diastereotopic. There is hindered rotation around the B-C_6F_5 vectors at low temperature and we monitored a total of 10 ^{19}F NMR signals of the compound **8a** in d_2-dichloromethane below 263 K.[11]

The reaction of piperidinocyclohexene **6b** with the dienylborane **2a** was performed analogously. It gave the cycloaddition product **8b** after workup in 64% yield. The product was characterized by C,H-elemental analysis, X-ray diffraction and variable temperature NMR spectroscopy. It shows similar structural features of the framework as derivative **8a**. However, the more bulky piperidino substituent has a considerably weaker N1···B1 amine/borane interaction (see Table 2). The piperidino substituent is found in the usual chair conformation. At the tetracoordinated ammonium center in compound **8b** it is the borane moiety that in the solid state structure is orientated axially and the carbon substituent (C1) is arranged equatorially (see Fig. 4).

In solution compound **8b** shows the typical NMR features. Due to the molecular chirality the C_6F_5 groups at the tetravalent borate are diastereotopic and give rise to a pair of *p*-C_6F_5 ^{19}F NMR signals. Lowering the temperature resulted in the observation of several decoalescence processes. First of all we see that the rotation around the B-C_6F_5 vectors becomes hindered and eventually "frozen" in the ^{19}F NMR time scale. Then

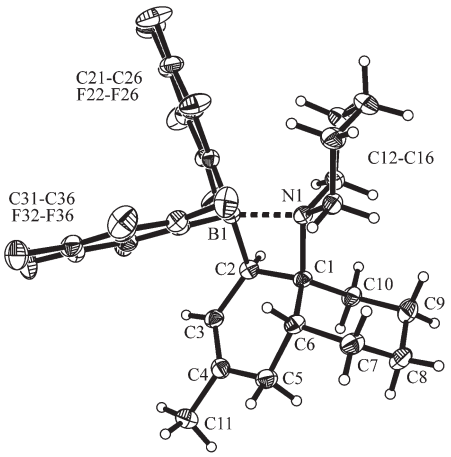


Fig. 4 Molecular structure of the cycloadduct **8b** (thermal ellipsoids are shown with 30% probability).

we observe a decoalescence phenomenon that eventually leads to the observation of a second isomer (**8b′**). Each of the isomers then gave rise to the observation of 10 ^{19}F NMR resonances. At 213 K in CD_2Cl_2 the isomer ratio was *ca.* 2 : 1.

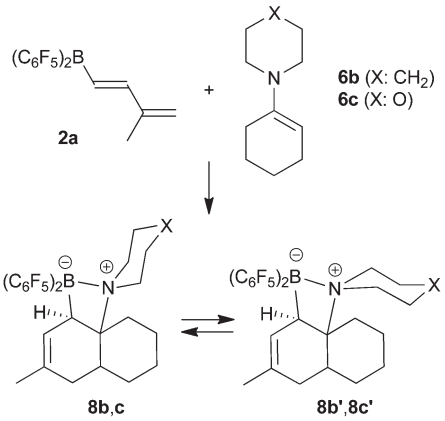
We assume that we have observed slowing down of the conformational piperidine chair interconversion on the ^{19}F NMR time scale, which gives rise to the observation of one isomer having the boron atom attached axially at the ammonium nitrogen (as it was found in the crystal), whereas the other isomer has the boron atom equatorially attached (see Scheme 4, for further details see the ESI†).

The reaction of morpholinocyclohexene (**6c**) with the dienylborane **2a** took a similar course. In this case the product **8c** was isolated in 83% yield. The X-ray crystal structure analysis again showed a conformational arrangement at the ammonium nitrogen center that shows the N–B vector orientated axially. In solution we again detected a pair of conformational isomers at low temperature (193 K) in a ratio of

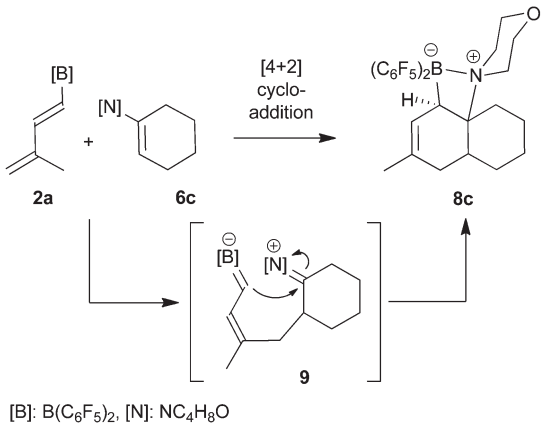
Table 3 Selected NMR spectroscopic features of the cycloaddition products **8**[a]

R_2N	**8a**[b] Pyrrolidino	**8b**[c] Piperidino	**8c**[d] Morpholino
$\delta^{11}B$	3.2	2.7 [2.7]	2.2 [2.2]
$\delta^{13}C$:			
C1	75.5	75.9 [78.2]	75.8 [79.1]
C2	36.8	34.3 [25.8]	33.7 [25.4]
C3	122.1	121.0 [124.8]	120.2 [125.0]
C4	126.5	126.1 [125.7]	126.1 [125.1]
CH_3	22.8	22.4 [24.1]	22.2 [23.8]
C6	32.8	31.0 [38.0]	30.4 [38.7]
$\delta^{1}H$:			
2-H	2.72	2.89 [2.91]	2.88 [2.94]
3-H	5.45	5.30 [5.38]	5.28 [5.39]
5-H	2.09/1.62	2.08/1.50 [2.45/1.61]	2.06/1.51 [2.08/1.66]
6-H	2.48	2.31 [2.22]	2.27 [2.33]
$\Delta\delta^{19}F_{mp}$	5.0, 5.9	7.1, 6.6, 5.4, 4.7 [6.5, 4.9, 4.6, 4.0]	7.5, 7.1, 5.7, 5.0 [6.7, 5.3, 4.7, 4.2]

[a] Chemical shift in ppm (δ scale). [b] In CD_2Cl_2 at 299 K. [c] In CD_2Cl_2 at 213 K; major [minor] isomer. [d] In CD_2Cl_2 at 193 K; major [minor] isomer.



Scheme 4



Scheme 5

ca. 5 : 1, each of them showing a total of 10 ^{19}F NMR signals due to hindered rotation around the B-C_6F_5 vectors (for details see the ESI†).

DFT (Density Functional Theory) analysis of the dienylborane/enamine cycloaddition reaction

There are two principal mechanistic alternatives to be taken into account for the dienylborane **2a** plus enamine conversions to the cycloaddition products **8**. This could be a concerted [4 + 2]cycloaddition reaction. In this case it would correspond to a Diels–Alder reaction with inverse electron demand since the enamines **6** are certainly quite electron rich dienophiles.[12] Then the question remains whether the attachment of the single $(C_6F_5)_2B$ substituent at the diene terminus would make this component electron poor enough to bring the overall reaction into a reaction rate regime as it was experimentally observed.

A stepwise reaction pathway would be an attractive alternative, because it had been observed (and recently quantified) that boranes enable carbanion formation thermodynamically and markedly favored at their α-position.[13] The resulting α-borylcarbanions must rather be regarded as borata–alkenes due to the substantial delocalization of the negative charge with the adjacent borane Lewis acid.[14–16] We had recently shown that this stabilizing effect is especially pronounced for the $[(C_6F_5)_2B{=}CHR]^-$ borata–alkene situation.[13] A recent DFT study has shown that $(C_6F_5)_2B$-CH_3 is as CH acidic as cyclopentadiene ($pK_a \approx 18$ in DMSO solution). Therefore, addition of the enamine to the terminal dienylborane position giving the zwitterionic intermediate **9** must be considered as an alternative to the concerted [4 + 2]cycloaddition reaction. Subsequent nucleophilic attack of the borata–alkene carbon atom at the adjacent iminium ion functionality of the intermediate **9** would directly lead to the observed product **8** (see Scheme 5).

We were able to distinguish and decide between these alternatives by a computational analysis of the system **2a** + **6c** → **8c** employing dispersion-corrected DFT methods.[17–22] For single-point energies, we used the PW6B95 hybrid *meta* functional with the large def2-QZVP basis set and the atom-pairwise D3(BJ) dispersion correction.[17–19] A modified rigid-rotor harmonic-oscillator treatment was used to account for rotational–vibrational contributions to the free energy using harmonic frequencies from a corrected minimal basis Hartree–Fock method (HF-3c),[18,21–23] while solvation contributions were included by means of the COSMO-RS(2012) approach.[24,25]

Our results are shown in Fig. 5. Our DFT results strongly disfavour that this reaction proceeds *via* a concerted [4 + 2]cycloaddition since the resulting transition state is predicted to be more than 50 kcal mol^{-1} in Gibbs free energy ($\Delta G^{\ddagger}$) above the reactants (for details see the ESI†). A two-step procedure is, however, reasonable. The highest barrier was found for the first step (*i.e.*, the formation of the intermediate **9**) and has a $\Delta G^{\ddagger}$ of about 15 kcal mol^{-1}. The zwitterionic compound **9** is slightly

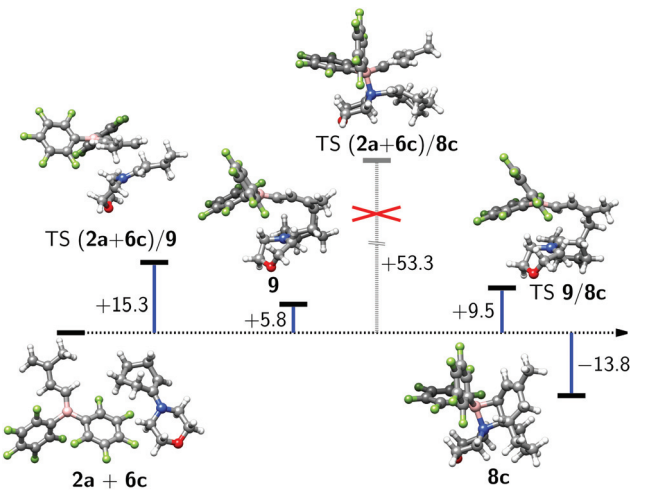


Fig. 5 Energy diagram for the conversion of the dienylborane **2a** and the enamine **6c** to the product **8c**. The values given are computed Gibbs free energies ($\Delta G/\Delta G^{\ddagger}$) in kcal mol^{-1} (for details see the ESI†). Electronic energies are obtained at the PW6B95-D3(BJ)/def2-QZVP level.

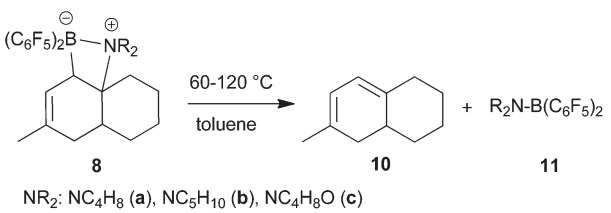
higher in free energy compared with the separate reactants **2a** and **6c** ($\Delta G \sim 6$ kcal mol^{-1}). The second addition proceeds with a small barrier of about 4 kcal mol^{-1} (w.r.t. the zwitterion **9**) and the respective transition state is roughly 10 kcal mol^{-1} higher in free energy than the initial reactants. A significant difference between both reaction pathways is the existence/absence of the B–N Lewis adduct. It is present in the geometry of the concerted transition state, thus weakening the electron-withdrawing effect of the borane as well as the electron-donating effect of the amine. In the two-step mechanism no Lewis adduct is formed until the very end and therefore, the formation of the zwitterionic intermediate **9** (see Scheme 5) is not hindered.

In this case we have also calculated the relative energy (ΔG) of the enamine/borane (C/B) adduct **7c**. It is energetically roughly as stable as the separate species **2a** and **6c** ($\Delta G \sim +1$ kcal) at room temperature. This means that it is slightly more stable than the alleged intermediate **9** but much less as compared to the final product **8c**. The relative stability computed here for compounds **7c**, **8c** and intermediate **9** is therefore in qualitative agreement with the experimental observation made for the homologues **7a** and **8a**.

Subsequent reactions

Although the N···B contact in compound **8c** seems to be rather loose, the system shows a tendency towards R_2N-B$(C_6F_5)_2$ elimination.[26,27] On a preparative scale this was cleanly achieved by maintaining the cycloaddition product **8c** in toluene solution at 120 °C for 3 h. Workup involving filtration through silica eventually gave the bicyclic cyclohexadiene derivative **10** as a colorless oil in 82% yield (Scheme 6). The compound shows ^{13}C NMR signals of the conjugated diene subunit at δ 138.9 (C1), 117.4 (C2), 118.6 (C3) and 132.7 (C4), respectively, with the corresponding ^{1}H NMR resonances at δ 5.47 and 5.46 (each m, each 1H, 3,2-H). The ^{1}H NMR resonances of the bridgehead C6-H unit occurs at δ 2.29 (^{13}C: 36.7). Compound **10** shows a methyl ^{1}H NMR resonance at δ 1.71 (for further details see the ESI†). The amidoborane elimination product **11c** was also isolated and it was characterized by X-ray diffraction (see Fig. 6).

The pyrrolidino and piperidino substituted cycloaddition products **8a** and **8b** underwent the analogous reaction under comparable conditions. We isolated the product **10** in these cases as colorless oils in 54% and 79% yields, respectively (for details see the ESI†).



Scheme 6

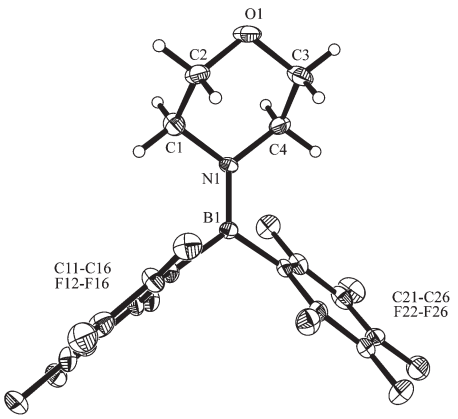
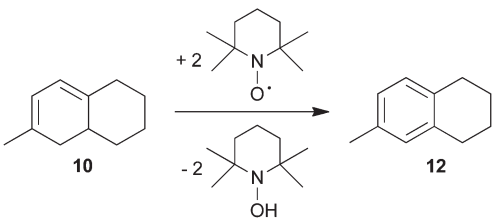


Fig. 6 Molecular structure of the amidoborane elimination product **11c** (thermal ellipsoids are shown with 15% probability). Selected bond lengths (Å) and angles (°) from molecule A: B1–N1, 1.369(8); N1–C4, 1.464(1); N1–C1, 1.482(2); B1–N1–C1, 123.7(1); B1–N1–C4, 126.4(1); B1–N1–C1–C2, 123.1(1); C11–B1–N1–C4, 179.2(1); C21–B1–N1–C1, 174.8(1).



Scheme 7

The bicyclic conjugated 1,3-diene system **10** was converted to the aromatic methyl tetrahydroindenyl derivative **12**. Heating of the starting material **10** with two molar equivalents of TEMPO[28–30] for 4 days at 95 °C in benzene solution resulted in a slow conversion to the arene derivative **12** by means of a sequential hydrogen atom abstraction reaction by the persistent nitroxyl radical with formation of the diamagnetic reaction product TEMPOH (see Scheme 7).

Compound **12** was isolated in 51% yield. It shows three separate ^{1}H NMR signals of the hydrogen atoms at the aromatic nucleus [δ^1H: 6.91, 6.88, and 6.79; ^{13}C: δ 129.3, 126.6, 130.0]. The ^{1}H NMR signal of the 3-CH_3 group occurs at δ 2.16 (for further details see the ESI†).

Conclusions

The reaction between the dienylboranes **2** and enamines seems to be sensitive to steric bulk of the reagents. The dienylboranes **2** can apparently serve as strong boron Lewis acids as well as carbon electrophiles. The enamines used in this study all behaved as typical carbon nucleophiles or carbon Lewis bases, respectively. The sterically non-encumbered acetophenone

based enamines **3** all formed strong boron–carbon Lewis acid/base adducts. So far we have not found any indication of their transformation to cycloaddition products under equilibrium conditions.

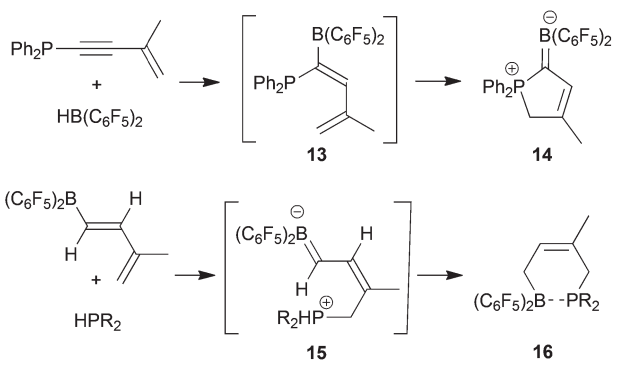
The more bulky cyclohexanone derived enamines **6** behave differently. The reaction between pyrrolidinocyclohexene **6a** and the dienylborane **2a** was shown to actually give the B–C Lewis acid/base adduct at low temperature, but this is a weak adduct that rapidly dissociates upon warming. This seems to be a typical situation under frustrated Lewis pair control, namely weak reversible Lewis acid/base contact formation followed by another reaction pathway under equilibrium conditions.[31,32] Consequently, at temperatures above −30 °C we have observed the formal [4 + 2]cycloaddition product formation between **6a** and **2a** to give compound **8a** for this specific example.

The formation of the products **8** from the dienylboranes **2** and the enamines **6** can formally be regarded as [4 + 2]cycloaddition products. The result of our DFT study is not crucial for the synthetic outcome of the reaction, but is essential for understanding its mechanistic course. It points out that in this case the concerted Diels–Alder reaction is characterized by a very high activation barrier, despite the actually favorable fact that the diene/ene orientation is prefixed by the prevailing B–N contact. But it might actually be that the electronic consequences of that contact may have rendered the overall energetic situation rather unfavorable by converting an energetically unfavorable Diels–Alder situation of inverse electron demand into an equally unfavorable Diels–Alder situation of usual electron demand but with only weakly inductively interacting substituents at both the diene and the dienophile.[5] It may actually be that the preferred favorable B–N contact makes the electronics of the [4 + 2]cycloaddition transition state unfavorable [$\Delta G^{\ddagger}_{calc} \geq 50$ kcal mol^{-1}].[23,24]

On the other hand the favored stepwise pathway according to the DFT study might be substantially profiting from the high electronic stabilization of the resulting borata–alkene functional group.[13] We had previously shown that the addition of the internal phosphane nucleophile to the adjacent dienylborane in **13** (see Scheme 8) yields a stable zwitterionic borata–alkene/phosphonium product **14**, which was isolated and structurally characterized by X-ray diffraction.[15,16] It seems that this reaction as well as the recently reported uncatalyzed hydrophosphination of the dienylborane **2a** to give the frustrated Lewis pair **16** represent a situation quite similar to the here proposed nucleophilic enamine addition reaction to the dienylborane terminus (see Schemes 5 and 8).[13,33,34]

In a way the borata–alkenes themselves resemble enolate anions as they add to carbonyl groups and analogues and may subsequently proceed on to a condensation step (see the formation of **11**).[35] Since the borata–alkenes contain one carbon atom less than the enolate anions their reactions eventually lead to "Umpolungs"-products, such as the formally 1,6-disubstituted amino/boryl substituted products **8**. But as already pointed out we do not want to drive this notion too far since the products **10** eventually could not be structurally distinguished from normal Diels–Alder products, were it not for the very high calculated activation barrier of the concerted dienylborane plus enamine [4 + 2]cycloaddition reaction.

The products **8** each feature a vicinal pair of enamine/borane substituents at the newly formed framework. In the examples looked at in our study this led to a favorable R_2N-B-$(C_6F_5)_2$ elimination reaction upon heating to give the respective hexahydronaphthalene derivatives **10** that contain a newly formed conjugated diene unit inside the framework. Subsequent treatment with TEMPO as a hydrogen atom abstracting oxidant selectively converted **10** to the aromatic tetrahydronaphthalene derivative **12**. This sequence indicates that the dienylborane plus enamine cycloadduct forming reaction may have some synthetic relevance, and it will be useful to explore the scope and application potential of this reaction in some detail.



Scheme 8

Experimental section

For general information and details of the characterization of the compounds, see the ESI.†

Preparation of compound 4a

A solution of the enyne **1a** (21.0 mg, 0.32 mmol, 1 eq.) in dichloromethane (1 mL) was added to a stirred suspension of bis(pentafluorophenyl)borane (110 mg, 0.32 mmol, 1 eq.) and dichloromethane (1 mL). After stirring the reaction mixture for 3 h at room temperature, a solution of the enamine **3a** (59.0 mg, 0.32 mmol, 1 eq.) in dichloromethane (1 mL) was added to the yellow suspension. Before removal of the volatiles *in vacuo*, the reaction mixture was stirred for 1 h at room temperature. Then the obtained residue was washed with *n*-pentane (2 × 1 mL) twice. Drying of the obtained solid *in vacuo* gave compound **4a** as a colorless powder (154 mg, 0.26 mmol, 81%). Crystals suitable for X-ray crystal structure analysis were obtained at room temperature from a solution of compound **4a** in dichloromethane covered with *n*-pentane. Anal. Calc. for $C_{30}H_{24}BF_{10}N$: C, 60.12; H, 4.04, N, 2.34. Found: C, 60.35; H, 4.26; N, 2.23.

Preparation of compound 4b

Following the procedure described for the generation of compound **4a**, the enamine **3b** (78.0 mg, 0.44 mmol) in dichloromethane (1 mL) reacted with compound **2a** [0.44 mmol, *in situ* prepared by the reaction of bis(pentafluorophenyl)borane (153 mg) with the enyne **1a** (29.0 mg)]. Compound **4b** was isolated as a colorless powder (128 mg, 70%). Crystals suitable for X-ray crystal structure analysis were obtained from a solution of compound **4b** in dichloromethane at room temperature. Anal. Calc. for $C_{29}H_{24}BF_{10}N$: C, 59.31; H, 4.12; N, 2.38. Found: C, 58.92; H, 3.75; N; 2.33.

Preparation of compound 5

Following the procedure described for the generation of compound **4a**, the enamine **3a** (54.0 mg, 0.29 mmol) in dichloromethane (1 mL) reacted with compound **2a** [0.44 mmol, *in situ* prepared by the reaction of bis(pentafluorophenyl)borane (100 mg) with enyne **1b** (31.0 mg)]. Compound **5** was isolated as a colorless powder (116 mg, 81%). Anal. Calc. for $C_{33}H_{28}BF_{10}N$: C, 61.99; H, 4.41; N, 1.69. Found: C, 60.6; H, 4.21; N, 1.69.

Preparation of compound 8a

The enyne **1a** (33.0 mg, 0.5 mmol) and bis(pentafluorophenyl)-borane (173 mg, 0.5 mmol) were dissolved in dichloromethane (5 mL). The solution was stirred at r.t. for 3 h. Then the pyrrolidinocyclohexene **6a** (75.6 mg, 0.5 mmol) was added and the reaction mixture was stirred at r.t. for 1 h. After removal of the volatiles *in vacuo*, pentane (2 mL) was added. The solid of the resulting suspension was collected and washed with pentane (2 × 1 mL) to give compound **8a** in 76% yield (214 mg, 0.38 mmol). Crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **8a** in dichloromethane at −35 °C. Anal. Calc. for $C_{27}H_{24}BF_{10}N$: C 57.57; H 4.29; N 2.49. Found: C, 56.98; H, 3.93; N, 2.72.

Preparation of compound 8b

Compound **2a** [0.88 mmol, *in situ* prepared by the reaction of bis(pentafluorophenyl)borane (304 mg) with the enyne **1a** (54.0 mg)], reacted with piperidinocyclohexene (146 mg, 0.88 mmol) in dichloromethane (1 mL). Before removal of the volatiles *in vacuo*, the reaction mixture was stirred for 1 h at room temperature. The resulting yellow residue was suspended in dichloromethane (2 mL) and *n*-pentane (4 mL) and then stored at −35 °C for 2 h. Subsequently the supernatant solution was removed by decantation. Drying of the residue *in vacuo* gave a yellow powder, which was dissolved in *n*-pentane (2 mL). After 30 min at room temperature crystalline material of compound **8b** was formed (325 mg, 0.56 mmol, 64%). Crystals suitable for X-ray crystal structure analysis were obtained from a concentrated *n*-pentane solution of compound **8b** at room temperature. Anal. Calc. for $C_{28}H_{26}BF_{10}N$: C, 58.25; H, 4.54; N, 2.43. Found: C, 58.68; H, 4.47; N, 2.70.

Preparation of compound 8c

Following the procedure described for the generation of compound **8b**, compound **2a** [0.36 mmol, *in situ* prepared by the reaction of bis(pentafluorophenyl)borane (123 mg) with the enyne **1a** (24.0 mg)], reacted with morpholinocyclohexene (59.0 mg, 0.36 mmol) in dichloromethane (1 mL) to give colorless crystals of compound **8c** (171 mg, 83%) which were suitable for X-ray crystal structure analysis. Anal. Calc. for $C_{27}H_{24}BF_{10}NO$: C, 55.98; H, 4.18; N, 2.24. Found: C, 55.28; H, 4.01; N, 2.35.

Generation of compound 10

For example: after heating a solution of compound **8b** (320 mg, 0.55 mmol, 1 eq.) in toluene (2 mL) at 120 °C for 3 h, the reaction mixture was filtered twice through a column (SiO_2). Removal of the volatiles of the filtrate *in vacuo* gave compound **10** as a colourless oil (65 mg, 0.44 mmol, 79%).

Preparation of compound 12

A solution of compound **10** (205 mg, 1.38 mmol, 1 eq.) in benzene-d_6 (0.5 mL) was added to a solution of TEMPO (432 mg, 2.77 mmol, 1 eq.) in benzene-d_6 (1 mL). The reaction-mixture was stirred for 4 days at 95 °C. After filtration (four times) through a short silica column all volatiles were removed *in vacuo* to give compound **12** as a yellow oil (103 mg, 0.70 mmol, 51%).

Acknowledgements

Financial support from the European Research Council (ERC) and the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

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