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# Synthesis of new asymmetric substituted boron amidines - Reactions with CO and transfer hydrogenations of phenylacetylene

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The syntheses of the new asymmetric subtituted boron amidines [N'-(2,6-diisopropylphenyl)-N-(pentafluorophenyl) acetimidamide]bis(pentafluorophenyl)borate (**2a**) and [N'-(2,6-diisopropylphenyl)-N-(4-cyanophenyl) acetimidamide] bis(pentafluorophenyl)borate (**2b**) were achieved by reaction of one equivalent of $HB(C_6F_5)_2$ and the respective amidine **1a** and **1b**. These adducts, bearing electron withdrawing groups, showed thermal induced $H_2$ elimination forming the four-membered cyclic diazaborate derivatives **3a** and **3b**. These new species were characterized by spectroscopic methods. X-ray diffraction studies have carried out on **2a**, **2b** and **3a**. To prevent undesired reactions at the nitrile group, one equivalent of $B(C_6F_5)_3$ was added to **2b** yielding the **2b**-$B(C_6F_5)_3$ nitrile adduct **4**. Compound **4** underwent thermal induced dehydrogenation to give the four-membered cyclic diazaborate derivative **5**. CO was inserted into the ring systems of **2a** and **2b** forming the five-membered diazaborolone derivatives **6a** and **6b.** Phenylacetylene reacted stoichiometrically with the asymmetric subtituted boron amidines **2a**, **2b** and **4** to give styrene by double H transfer.

## Introduction

The observation that strong bonds formation between Lewis pairs can be fully prevented and nevertheless these pairs retain intrinsic reactivity by staying at non-bonding distances of encounter complexes, has led to the development of the concept of Frustrated Lewis Pairs (FLPs). Their intrinsic reactivity can often be used for reactions with small molecules, which was first addressed by Stephan's and Erker's groups.[1] One respective strategy in the field consisted of intramolecular incorporation of the Lewis acid and the Lewis base function. These Lewis pairs require provisions to be made preventing strong intra- and intermolecular Lewis pair interactions. Usually this was accomplished by appropriate molecular geometries in conjunction with steric protection of the respective centers.

In the preparation of FLPs $RB(C_6F_5)_2$ derivatives (*e.g.* R: H, $C_6F_5$) are the most frequently employed Lewis acids. As an example the synthesis of the intramolecular FLP $(C_6H_2Me_3)_2P(C_6F_4)B(C_6F_5)_2$ in its hydrogenated form obtained by nucleophilic aromatic substitution of $B(C_6F_5)_3$ with the sterically demanding secondary phosphine $(C_6H_2Me_3)_2PH$ afforded the zwitterionic phosphonium borate $(C_6H_2Me_3)_2PH(C_6F_4)BF(C_6F_5)_2$, which can be reacted further with $Me_2SiHCl$ to induce H/F exchange, see Scheme 1, path (**a**).[2] The hydrogenated $(C_6H_2Me_3)_2PH(C_6F_4)BH(C_6F_5)_2$ species marked the starting point of FLP research and is still one of the most active FLPs on hydrogenation process.[1g,3]

On the other hand, the Erker's group has developed intramolecular FLPs on the basis of the hydroboration of unsaturated alkenyl compounds with "Piers' borane",[4] $HB(C_6F_5)_2$, reacting these components under mild conditions to furnish bifunctional phosphine-boranes (Scheme 1, path (**b**)).[5] In addition, structurally related amino-boranes can be accessed by related reaction routes (Scheme 1, path (**c**).[6] Since then, several other P---B or N---B systems were developed.[7] This strategy allowed to control the structure of the bridges between the Lewis acidic and basic functions of the FLPs[5a,8] and as one of the most important factors of such intramolecular arrangements the geometry on the bridges enabled control of the distance between the reaction centers.

Hydroboration with Piers' borane represents also a valuable direct method for the hydroboration of, for example, enamines[9] and amidines (Scheme 1, path (**d**))[10] displaying the generation of new types of FLPs with unusual reactivities capable of activating for instance CO, $CO_2$ and imines.[9] The synthesis and reactivity studies of FLP type adducts formed by addition of group 13 hydrides ($EH_3$, E = B, Al, etc.) onto amidinate and guanidine derivatives were recently studied to

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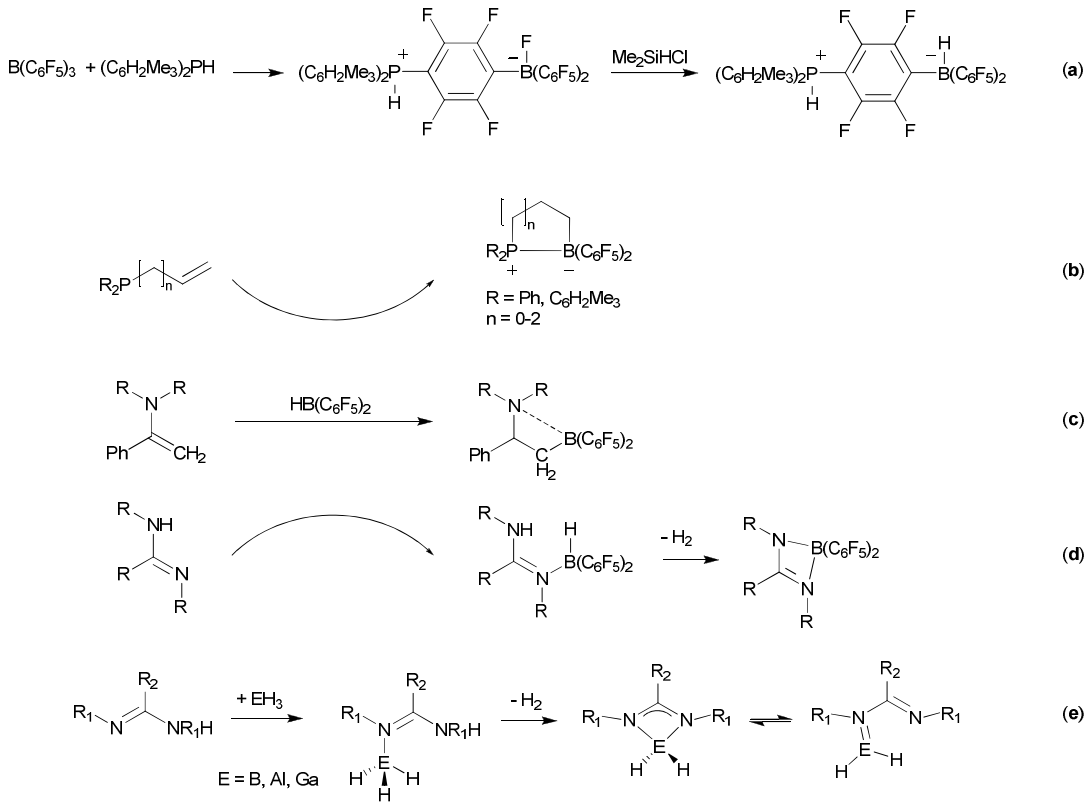



Scheme 1. Examples of the synthesis of various intramolecular FLPs

evaluate their potential as hydrogenating agents and also as models for applications in the field of molecular hydrogen storage requiring reversibility of the $H_2$ reactions (Scheme 1, path (**e**)).[11] Bulky amidines, like PhNC(H)N(H)Ph and PhNC(t-Bu)N(H)Ph, can form as Lewis pair adducts relatively strong intramolecular HE⋯NH contacts and weakening of the Lewis pair interaction was found to facilitate the liberation of $H_2$. Mononuclear amidinate complexes were found to be the first products of an intramolecular $H_2$ elimination. Factors that facilitate re-hydrogenation of the ENCN four-member cyclic moiety (Scheme 1, path (**e**)) define the reversibility of the $H_2$ reactions and at the same time the propensity for catalytic hydrogenation with such systems. In case of the adduct formation with Piers' borane (Scheme 1, path (**d**)), formation of four-coordinated, boron-centered cycles occurs, which rapidly proceeds at room temperature and furnishes good yields. Contrary to expectations, direct evidence could not be provided for the opening of the cycles even at high temperatures, despite the high ring strain and the high steric bulk of these compounds. However, various substrates, like $CO_2$, CO, acetonitrile and isocyanide, can be inserted into such ring systems.

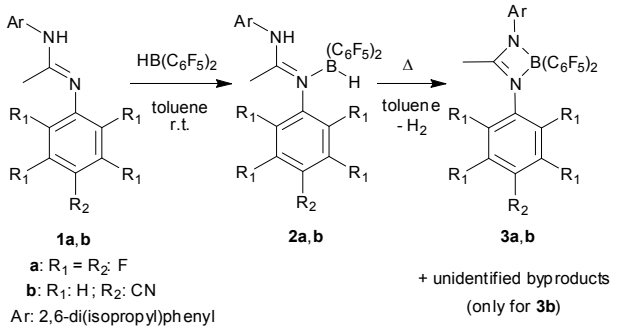
Attempting further exploration of these reaction modes, we approached a study of the influence of electron withdrawing groups on the principal propensity for formation of asymmetric subtituted boron amidine adducts and of their dehydrogenation and transfer hydrogenation behaviour. The reactivity of the dehydrogenated four-membered cyclic diazaborate compounds was intended to be tested by their capability of inserting CO.

## Results and discussion

### Synthesis and characterization of amidine-borane compounds

The reaction sequence to prepare the amidine-$BH(C_6F_5)_2$ adducts started with the synthesis of the amidine ligands N'-(2,6-diisopropylphenyl) - N - (2, 3, 4, 5, 6-pentafluorophenyl) acetimidamide) (**1a**) and N'-(2,6-diisopropylphenyl)-N-(4-cyano phenyl)acetimidamide (**1b**), which were accomplished using the addition reaction between equimolar amounts of the respective imidoyl chloride[12] and of 2,3,4,5,6-pentafluoro aniline or 4-aminobenzonitrile to give [N'-(2,6-diisopropyl phenyl)-N-(pentafluorophenyl) acetimidamide]bis (pentafluoro phenyl)borate (**2a**) and [N'-(2,6-diisopropylphenyl) -N-(4-cyano phenyl)acetimidamide]bis(pentafluorophenyl) borate (**2b**), respectively (Scheme 2). The preparation of **1a** was previously reported by our group.[13] By a similar procedure **1b** was isolated as a white solid in 70% yield and was characterized by elemental analysis, NMR spectroscopy and mass spectrometry. For further details see Table 1 and ESI, †. The $^1$H NMR spectrum showed resonances typical of the isopropyl fragment (double doublet at 1.18 and 1.15 ppm). In addition a septet at

2.94 ppm was observed corresponding to the $H_c$ proton of the *i*Pr moiety. At 1.31 ppm a singlet appeared belonging to the $CH_3$ group of the acetimidamide moiety. The $^{13}C$ NMR spectrum showed a singlet at 151.7 ppm attributed to the internal Ar-N*C*N-$C_6H_4$CN carbon atom. In the FT-IR spectrum a strong band appeared at 2225 $cm^{-1}$ assigned to a ν(CN) vibration.




Scheme 2. General scheme for the preparation of the asymmetric subtituted boron-amidine adducts **2a**,**b** and their dehydrogenation to the cyclic azaborate derivatives **3a**,**b**.

The adduct formation proceeded smoothly upon treatment of **1a** or **1b** with 1 equivalent of $HB(C_6F_5)_2$ at room temperature forming compounds [N'-(2,6-diisopropylphenyl)-N-(penta fluorophenyl) acetimidamide] bis (pentafluorophenyl) borate (**2a**) and [N'-(2,6-diisopropylphenyl)-N-(4-cyanophenyl)acet imidamide]bis(pentafluorophenyl)borate (**2b**), respectively (Scheme 2). Compound **2a** was isolated in 87% yield as a colorless crystalline solid. NMR scale experiments indicated that the adduct formation occurred instantaneously at ambient temperature after mixing the reagents. The X-ray crystal structure analysis of **2a** showed that the $HB(C_6F_5)_2$ function is coordinated to the amidine moiety by the imine nitrogen atom (Fig. 1).

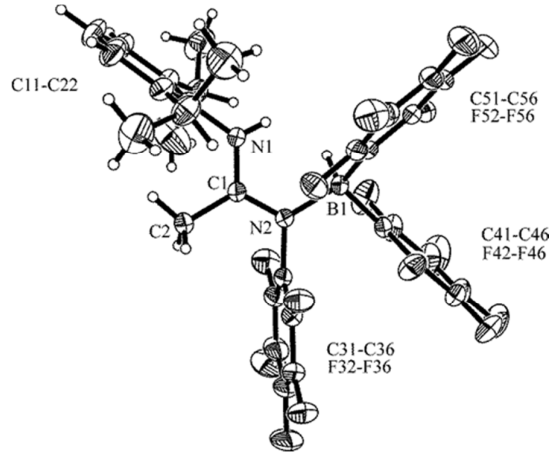



Fig. 1. Molecular structure of the adduct **2a**. Thermal ellipsoids are shown with 30% probability.

The $^1H$ NMR spectrum of **2a** revealed significant changes compared with the spectrum of **1a**: for example, the NH proton is shifted from 4.92 to 8.33 ppm presumably due to the presence of the adjacent borane group. In addition a new broad signal appeared at 4.57 ppm, which was assigned to the BH hydrogen atom. The $^{13}C$ NMR spectrum revealed as a main feature of the adduct **2a** a shift of the Ar-N*C*N-$C_6F_5$ atom from 159.0 to 169.2 ppm. The $^{11}B$ NMR characterization showed a broad boron signal at -13.3 ppm with a line width of 230 Hz (for further details see ESI,†) typical for tetrahedral boron.[7g,10b]

Compound **2b** was isolated in 90% yield as a colorless crystalline solid. The X-ray diffraction study of **2b** showed that the $HB(C_6F_5)_2$ is coordinated to the amidine and not to the CN group of the molecule (see Fig. 2). In the FT-IR spectrum a strong ν(CN) band was observed at 2233 $cm^{-1}$, shifted by 8 $cm^{-1}$ to higher wavenumbers with respect to the free amidine ligand (2225 $cm^{-1}$), which is typical for the expected electronic effect exerted on the nitrile group by coordination of a Lewis acid to the ArN*C*$C_6H_4$CN atom. The $^1H$ NMR spectrum for the adduct structure of **2b** (see Table 1) display a shift of the NH hydrogen atom from 5.72 to 8.03 ppm and is furthermore corroborated by the presence of a new signal at 4.55 ppm assigned to the BH hydrogen atom. The $^{13}C$ NMR spectrum revealed a shift from 151.7 to 165.5 ppm of the signal assigned to the Ar-N*C*N-$C_6H_4$CN carbon atom, again interpreted in terms of the neighborhood effect caused by the borane coordination. In the $^{11}B$ NMR spectrum a broad signal was found at -14.6 ppm with a line width of 210 Hz, also consistent with the borane attachment and the tetrahedral coordination of the boron atom.

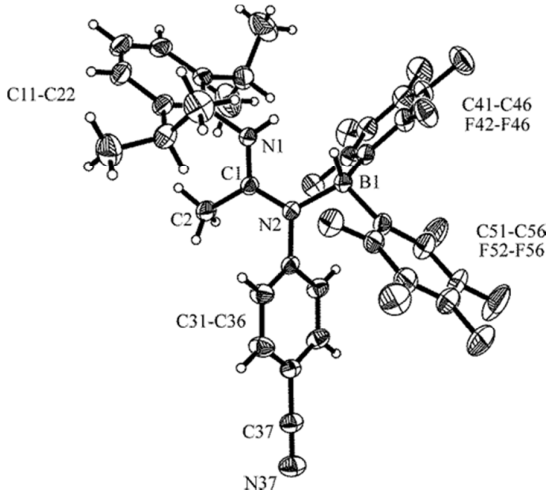



Fig. 2. Molecular structure of the adduct **2b**. Thermal ellipsoids are shown with 30% probability.

In order to explore the hydrogenation/dehydrogenation behaviour of **2a** and **2b**, thermolysis tests were performed at different temperatures and variation of the reaction times determining the optimum reaction conditions for the dehydrogenation process. For **2a** the best conditions for the release of $H_2$ were found to be 100°C and 4 h of reaction time

yielding compound **3a** as a colorless solid material in 95% yield. **3a** was characterized by an X-ray diffraction study (Fig. 3) and in addition by spectroscopic investigations. The $^{1}$H NMR spectrum indeed revealed the presence of a dehydrogenated species due to the disappearance of signals for the $H_N$ and $H_B$ atoms of **2a**, matching in addition with the appearance of a signal for the liberated dissolved $H_2$ at 4.52 ppm. Furthermore, the resonance at 1.27 ppm of the methyl group at the internal C atom of the imine moiety of **2a** shifted to 1.47 ppm for **3a**. The $^{13}$C NMR of **3a** displayed a large shift of the carbon atom of the Ar-N*C*N-$C_6F_5$ fragment from 169.2 to 177.3 ppm, in turn attributed to the neighborhood of the $N_{imine}$ attached boron moiety and to the ring effect of the four-membered system. The effect from the tetrahedral boron atom cyclization is also corroborated by the $^{11}$B NMR, which showed a signal 7.5 ppm with a line width of 210 Hz (further details see ESI,†).

Table 1 Selected spectroscopic properties of compounds **1**-**3**.[a]

| | **1a**[13] | **1b** | **2a** | **2b** | **3a** |
|---|---|---|---|---|---|
| | | $\delta^{13}$C | | | |
| $^{Ar\text{-}N}C^{N\text{-}Ph}$ | 159.0 | 151.7 | 169.2 | 165.5 | 177.3 |
| *C*≡N | - | 105.3 | - | 112.4 | - |
| H*C*$^{iPr}$ | 29.0 | 28.6 | 28.8 | 29.1 | 28.9 |
| *C*H$_3^{iPr}$ | 24.1 | 23.8 | 23.9 | 23.8 | 24.5 |
| | 24.0 | 23.0 | 22.6 | 22.5 | 23.6 |
| *C*H$_3^{C\text{-}N}$ | 17.1 | 18.3 | 16.8 | 16.9 | 13.9 |
| | | $\delta^{1}$H | | | |
| *H*$^{N}$ | 4.92 | 5.72 | 8.33 | 8.03 | - |
| *HC*$^{iPr}$ | 3.07 | 2.94 | 2.87 | 2.87 | 2.69 |
| C*H*$_3^{C\text{-}N}$ | 1.29 | 1.31 | 1.27 | 1.15 | 1.47 |
| C*H*$_3^{iPr}$ | 1.32 | 1.18 | 1.06 | 1.09 | 1.00 |
| | 1.21 | 1.15 | 0.91 | 0.94 | 0.72 |
| | | $\delta^{11}$B | | | |
| | - | - | -13.3 | -14.6 | 7.5 |
| | | FT-IR [cm$^{-1}$] | | | |
| ν(C≡N) | - | 2225 | - | 2233 | - |

[a] NMR spectra in toluene-$d_8$ solution.

Compound **2a** was subjected to deuterium exchange tests in presence of $D_2$ in toluene at 50 °C, 70 °C and 90 °C. $^{2}$D NMR spectra revealed no change in the spectra indicating that D-incorporation into **2a** did not take place.

The experiment of dehydrogenation of **2b** was carried out at 100 °C to form **3b**. However, the dehydrogenation of **2b** did not occur cleanly obtaining several species, which could only partially be identified. The $^{1}$H NMR spectrum indicated that among other reactions reduction of the CN group to an imine had taken place as recognize from resonance at 2.51, 1.67 and 0.58 ppm. In order to prevent reactions at the nitrile group, we anticipated that $B(C_6F_5)_3$ could protect this function by adduct formation.[14] Treatment of **2b** with one equivalent of $B(C_6F_5)_3$ gave in toluene-$d_8$ at ambient temperature and in almost quantitative yield the respective **2b**-$B(C_6F_5)_3$ adduct **4** (determined by $^{1}$H NMR), with $B(C_6F_5)_3$ coordinated at the nitrile group (Scheme 3). After workup **4** was isolated in 84 % yield. The $^{19}$F NMR spectrum of **4** revealed two groups of signals appearing for the chemically non-equivalent pairs of $C_6F_5$ rings. The $^{1}$H NMR spectrum of **4** showed a typical $H_N$ signal for the boron-substituted imine unit appearing at δ 8.03 ppm. Furthermore, the elemental analysis of **4** confirmed the composition of this compound (for further information see the Experimental Section and the ESI,†).

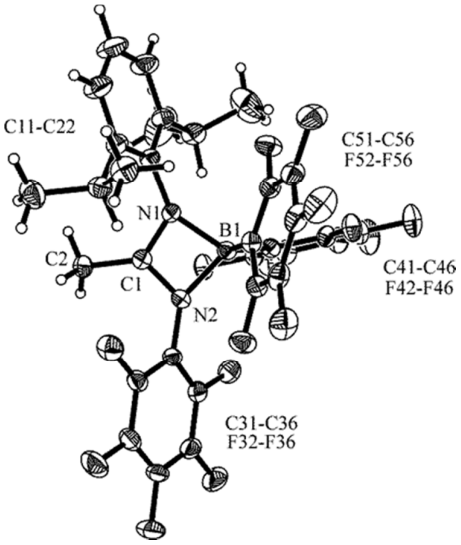
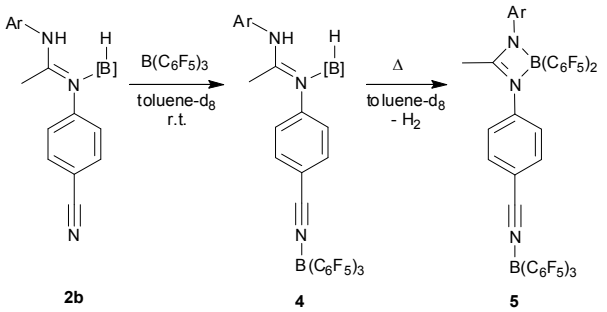



Fig. 3. Molecular structure of the boron amidate **3a**. Thermal ellipsoids are shown with 30% probability.

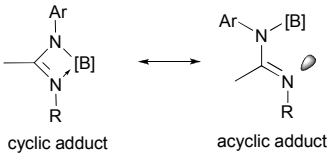
The dehydrogenation of **4** was carried out in an in situ fashion mixing equimolar amounts of **2b** and $B(C_6F_5)_3$ followed by heating to 130 °C for 22 h in toluene-$d_8$. The $^{1}$H NMR spectrum revealed the presence of $H_2$ at 4.44 ppm and the formation of **5**. In accord with the given structure of **5** in Scheme 3, $^{19}$F NMR spectroscopy revealed 3 signals for a $B(C_6F_5)_2$ subunit and also 3 signals for a $B(C_6F_5)_3$ subunit confirming its formation along the lines of the formation of **3a**. Besides the signals for **5**, there were resonances in the NMR spectra for products, which structures could not be assigned, as yet. Attempts to isolate **5** failed as results of decomposition reactions during the purification process. This was indicated by the presence of free $B(C_6F_5)_3$ observed in the $^{19}$F NMR.




Scheme 3. $B(C_6F_5)_3$ adduct formation to give **4** and dehydrogenation to **5**.

**Reactions of 2a and 2b with CO**

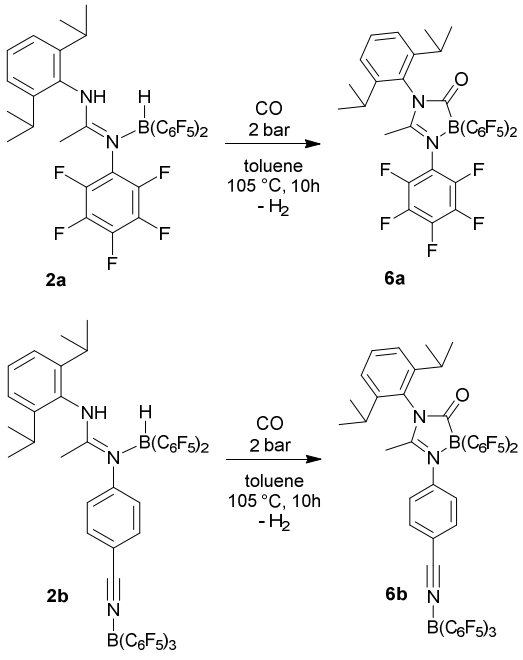
Stephan and Erker[10b,15] have emphasized that the uptake of CO into FLPs is an issue of great general interest, first of all from the point of view of CO activation, and furthermore because of potential applications in catalysis and in organic synthesis. In case that compounds of type **3** can exist as acyclic adduct (see Scheme 4) they are expected to undergo CO insertions similar to the heterocyclic $HC(RN)_2B(C_6F_5)_2$ [R = *i*Pr or *t*Bu] compounds with tetrahedral boron centers.[10b,c]




Ar: 2,6-di(isopropyl)phenyl, R: Aryl, [B]: $B(C_6F_5)_2$

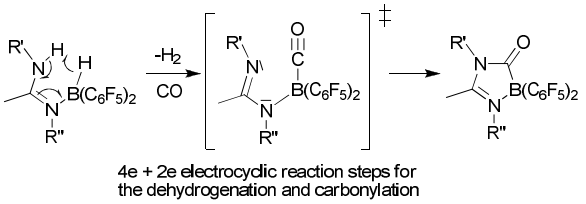
Scheme 4. Illustrative sketch of type **3** boron-amidine adducts.

Therefore thermal dehydrogenation of **2a** and **2b** was attempted forming in situ **3a** and **3b** or their open forms and concomitant carbonylation was to take place in presence of 2 bar of CO at 105 °C and 120 °C for 10 h (see Scheme 5). The cyclic five-membered diazaborolone products **6a** and **6b** were formed, where insertion of the CO molecule into Lewis pair bonds of open **3a** or **3b** had occurred in a presumed 4e + 2e electrocyclic fashion (Scheme 6). **6a** and **6b** were isolated as colorless and light green powders in 95 and 87% yields, respectively.




Scheme 5. Dehydrogenation of **2a**,**b** and carbonylation reactions to the five-membered ring compounds **6a** and **6b**.

Table 2 shows selected $^1$H and $^{13}$C NMR data of **6a** and **6b**. The $^1$H NMR spectra turned out not to be much different in chemical shifts from the spectra of the dehydrogenated compounds **3a** and **3b**. However, the $^{13}$C NMR data were distinguished showing a characteristic signals for the *C*=O atoms at 193.0 for **6a** and at 193.9 ppm for **6b**, respectively. These signals revealed partially relaxed coupling to the neighboring $^{11}$B nuclei indicated by signal broadening. The $^{11}$B NMR spectra of **6a** and **6b** revealed signals at -10.0 and -10.2 ppm, respectively, clearly distinguished from the signals of **2a** and **2b** (-13.3 and -14.6 ppm). The $^{11}$B NMR spectrum of **3a** (7.5 ppm) showed in comparison to **6a** an even very large shift of the resonance of almost 18 ppm to high field, which may point to an electron-withdrawing influence of the carbonyl group on the boron center, confirming that via the CO insertion reactions new species was generated.




Scheme 6. Mechanistic sketch of the 4e + 2e electrocyclic reaction steps for dehydrogenation and carbonylation.

For **6a** $^{19}$F NMR resonances of the $B(C_6F_5)_2$ fragment were observed at -132.4, -155.4 and -163.0 ppm and at -145.4, -151.3 and -159.8 for the *o*-, *p*- and *m*-flourine atoms of the pentafluorophenyl ring located at the N atom. **6b** exhibited $^{19}$F NMR chemical shifts for the fluorine atoms of the $B(C_6F_5)_2$ fragment (-133.0, -155.3 and -162.6 ppm), which were found to be comparable in chemical shift to those of **6a**.

Table 2 Selected spectroscopic parameters of compounds **6a** and **6b**.[a]

| | **6a** | **6b** |
|---|---|---|
| | $\delta^{13}$C | |
| *C*=O | 193.0 | 193.9 |
| $^{Ar\text{-}N}C^{N\text{-}Ph}$ | 176.5 | 172.2 |
| *C*≡N | - | 112.8 |
| $CH_3^{C\text{-}N}$ | 15.7 | 15.3 |
| | $\delta^{1}$H | |
| $HC^{iPr}$ | 2.80 | 2.72 |
| $CH_3^{C\text{-}N}$ | 1.53 | 1.48 |
| $CH_3^{iPr}$ | 1.11 | 1.11 |
| | 1.07 | 1.01 |
| | $\delta^{11}$B | |
| | -10.0 | -10.2 |
| | FT-IR [cm$^{-1}$] | |
| ν(C≡N) | - | 2232 |
| ν(C=O) | 1752 | 1758 |

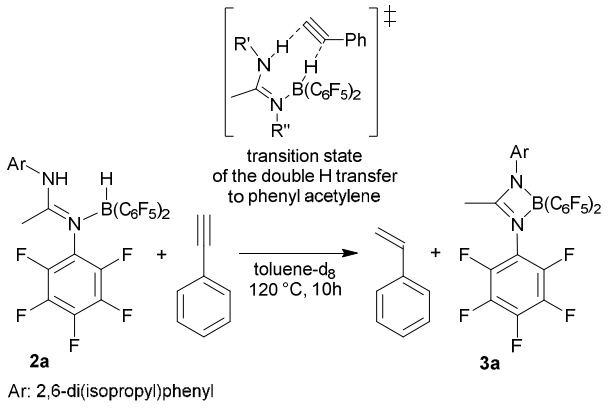
[a] NMR spectra in toluene-$d_8$ solution.

In the IR spectra of **6a** and **6b** absorptions were found at 1752 and 1758 $cm^{-1}$, respectively, attributable to the ν(CO) vibrations of electron deficient C=O groups and for **6b** a band at 2232 $cm^{-1}$ was attributed to the ν(C≡N) vibration. The elemental analyses and the MS analyses confirmed the compositions of **6a** and **6b** (see ESI,† and Table 2).

#### Stoichiometric transfer hydrogenations of phenylacetylene applying 2a, 2b and 4 as hydrogen donors

Based on the reactivity of the C-H bond of a terminal alkyne with the boron amidine compounds (four membered heterocycle) reported by Stephan,[10b] we applied the amidine–$BH(C_6F_5)_2$ adducts **2a**, **2b** and **4** to hydrogenate phenylacetylene by transfer hydrogenation at 120 °C, which yielded styrene quantitatively. Ethyl benzene potentially produced by two consecutive transfer hydrogenation steps was not observed. Mechanistically these processes are supposed to be double H transfer reactions, which might occur stepwise or simultaneously.[16]

**2a** required 10 h to accomplish styrene formation and generation of **3a** (Scheme 7). **2b** completed the reaction to styrene in 8 h under otherwise the same conditions. Finally when the adduct **4** (**2b** + $B(C_6F_5)_3$) was used as the hydrogen donor a significantly shorter reaction time of 1 h was observed. This was attributed to the presence of an activated reactive center of the boron-amidine adduct of **4** via enhanced electrophilicity of the molecule originating from the Lewis acid coordinated CN group (for further details see ESI,†). **2b** and **4** apparently promoted the hydrogenation process more efficiently than **2a**. Nonetheless, for the reaction of **4** by-products were detected, which were apparently originating from the thermal dehydrogenation processes of **2a** and **2b** described above (Scheme 2 and 3).




Scheme 7. Transfer hydrogenation of phenylacetylene using compound **2a** with a supposed transition state of double H transfer.

## Conclusions

The amidine **1b** and the asymmetric subtituted boron amidine compounds **2** - **6** were newly prepared and fully characterized. It could be demonstrated that the amidine–$BH(C_6F_5)_2$ adducts **2a** and **2b** underwent thermal $H_2$ loss forming the four-membered cyclic diazaborate derivatives of type **3**. Two small molecule activation reactions were tested with the **2** and **3** type compounds. The **3** type compounds inserted, probably by means of equilibration with the ring-opened isomer, CO leading to formation of cyclic diazaborolone derivatives of type **6**. Using compounds of type **2** and **4** as hydrogen donors stoichiometric transfer hydrogenation of phenylacetylene could be achieved. The $B(C_6F_5)_3$ addition compound **4** was the most active hydrogenation species. At present, optimizations of the amidine-borane systems are underway for reversible uptake and release of $H_2$ and CO in order to generate compounds being more suited for efficient metal-free catalytic hydrogenations and related CO reactions.

## Experimental

All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques. All reagents were used as received from Aldrich, unless otherwise specified. Toluene and pentane were distilled from benzophenone ketyl. Bis(pentafluorophenyl)borane ($HB(C_6F_5)_2$) and **1a** were prepared as described in literature.[4a,13] NMR spectra were recorded on NMR *Varian Inova* 500 MHz, *Bruker Unity Plus* 600 MHz and Bruker AV 400. Chemical shifts are given in parts per million relative to TMS [$^1H$ and $^{13}C$, $\delta(SiMe_4)$ = 0] or an external standard [$\delta(BF_3OEt_2)$ = 0 for $^{11}B$ NMR, $\delta(CFCl_3)$ = 0 for $^{19}F$ NMR]. Most NMR assignments were supported by additional 2D experiments. Elemental analysis data were recorded on a Foss-Heraeus CHNO-Rapid analyzer. For ESI mass spectra characterization Bruker Daltonics Micro TOF was used. FT-IR spectra were recorded on a Bruker Vector-22 Spectrophotometer using KBr pellets. For X-ray crystal structure analysis, data sets were collected with a Nonius Kappa CCD diffractometer by Dr. Constantin G. Daniliuc; full details can be found in the independently deposited crystallography information files (cif).

#### Synthesis of compound 1b

N-(2,6-diisopropylphenyl)acetimidoylchloride[12] (1.11 g; 4.7 mmol) and $NEt_3$ (0.7 ml) was added to a solution of 4-aminobenzonitrile (0.55 g; 4.7 mmol) in anhydrous toluene (40 ml). The mixture was refluxed for 3 h with vigorous stirring. The white precipitate ($[Et_3NH]Cl$) formed was removed by filtration and the yellow solution was evaporated in vacuo to dryness. The crude product was washed with cold toluene and recrystallized from methanol. **1b** was isolated as white solid in 70% yield (1.04 g; 3.3 mmol). $^1H$ NMR (400 MHz, $C_7D_8$, 298 K): δ/ppm = 7.48 (d, *J* = 8.6Hz, 2H, *m*-$C_6H_4CN$), 7.12 (d, *J* = 6.9Hz , 2H, *m*-Ar), 7.09 (m, 1H, *p*-Ar), 7.05 (d, *J* = 8.6Hz, 2H, *o*- $C_6H_4CN$), 5.83 (br., 1H, *NH*), 2.95 (hept, *J* = 6.9Hz, 2H, HC(*i*Pr)), 1.33 (s, 3H, Me(C)), 1.18 (d, *J* = 6.9 Hz, 6H, Me(*i*Pr)), 1.15 (d, *J* = 6.9 Hz, 6H, Me(*i*Pr')). $^{13}C\{^1H\}$ NMR (100 MHz, $C_7D_8$, 298 K): δ/ppm = 151.7 ($^{Ar\text{-}N}C^{N\text{-}C6H4CN}$), 145.1 (*i*-Ar), 144.8 (*i*-$C_6H_4CN$), 138.1 (*o*-Ar), 133.0 (*o*-$C_6H_4CN$), 123.8 (*p*-Ar), 123.4 (*m*-Ar), 119.3 (*p*-$C_6H_4CN$), 118.7 (*m*-$C_6H_4CN$), 105.3 (C≡N)), 28.6 (HC(*i*Pr)), 23.8 (Me(*i*Pr')), 23.0 (Me(*i*Pr)), 18.3 (Me(C)). FT-IR (KBr): ν/$cm^{-1}$ = 2225 (ν(C≡N), s). Elemental analysis (%): $C_{21}H_{25}N_3$ (M = 319.44

g/mol): calculated C 78.96, H 7.89, N 13.15; found C 79.04, H 7.84, N 13.17. MS (ESI, Exact mass): Calc: 342.195; Found: 342.194 [$C_{21}H_{25}N_3Na^+$]. Calc: 320.213; Found: 320.212 [$C_{21}H_{25}N_3H^+$].

**Synthesis of compound 2a**

Bis(pentafluorophenyl)borane [$HB(C_6F_5)_2$] (180 mg, 0.52 mmol) in toluene was added to a solution of **1a** (200 mg, 0.52 mmol) in toluene. The reaction mixture was stirred for 2 h at room temperature. Then, the volatiles were removed in vacuo, and the solid washed with pentane. Finally the white solid is recrystallized from cold toluene given **2a** as a white crystalline material in 87% yield (331 mg, 0.45 mmol). Single crystals for X-ray crystallography were grown by layering pentane onto a toluene solution of compound **2a** at -30°C. $^1$H NMR (600 MHz, $C_7D_8$, 298 K): δ/ppm = 8.33 (s, 1H, NH), 7.05 (m, 1H, *p*-Ar), 6.88 (d, *J* = 6.9Hz, 2H, *m*-Ar), 4.57 (br, 1H, *BH*), 2.87 (hept, *J* = 6.9Hz, 2H, HC(*i*Pr)), 1.27 (s, 3H, Me(C)), 1.06 (d, *J* = 6.9 Hz, 6H, Me(*i*Pr)), 0.91 (d, *J* = 6.9 Hz, 6H, Me(*i*Pr')). $^{13}$C{$^1$H} NMR (151 MHz, $C_7D_8$, 298 K): δ/ppm = 169.2 ($^{Ar\text{-}N}C^{N\text{-}C6F5}$), 146.3 (*o*-Ar), 131.0 (*p*-Ar), 130.6 (*i*-Ar), 124.8 (*m*-Ar), 28.8 (HC(*i*Pr)), 23.9 (Me(*i*Pr')), 22.6 (Me(*i*Pr)), 16.8 (Me(C)). $^{11}$B{1H} NMR (192 MHz, C7D8, 298 K): δ/ppm = -13.3 (ν1/2 ~ 230 Hz). Elemental analysis (%) $C_{32}H_{22}BF_{15}N_2$ (M = 730.32 g/mol): calculated C 52.63, H 3.04, N 3.84; found C 54.30, H 3.27, N 3.80.

**Synthesis of compound 2b**

Bis(pentafluorophenyl)borane [$HB(C_6F_5)_2$] (217 mg, 0.63 mmol) in toluene was added to a solution of **1b** (200 mg, 0.63 mmol) in toluene. The reaction mixture was stirred for 2 h at room temperature. Then, the volatiles were removed in vacuo and the solid was washed with pentane and the residue recrystallized from cold toluene giving **2b** as a white crystalline material in 90% yield (375 mg, 0.56 mmol). Single crystals for X-ray crystallography were grown by layering pentane onto a toluene solution of **2b** at -30°C. $^1$H NMR (600 MHz, $C_7D_8$, 298 K): δ/ppm = 8.03 (s, 1H, NH), 7.06 (t, *J* = 7.7Hz, 1H, *p*-Ar), 6.89 (d, *J* = 7.7Hz, 2H, *m*-Ar), 6.81 (d, *J* = 8.5Hz, 2H, *m*-$C_6H_4CN$), 6.67 (d, *J* = 8.5Hz, 2H, *o*-$C_6H_4CN$), 4.55 (br, 1H, *BH*), 2.87 (hept, *J* = 6.9Hz, 2H, HC(*i*Pr)), 1.15 (s, 3H, Me(C)), 1.08 (d, *J* = 6.9 Hz, 6H, Me(*i*Pr)), 0.94 (d, *J* = 6.9 Hz, 6H, Me(*i*Pr')). $^{13}$C{$^1$H} NMR (151 MHz, $C_7D_8$, 298 K): δ/ppm = 165.5 ($^{Ar\text{-}N}C^{N\text{-}C6H4CN}$), 147.1 (*i*-$C_6H_4CN$), 146.3 (*o*-Ar), 133.1 (*o*-$C_6H_4CN$), 131.0 (*i*-Ar), 130.6 (*p*-Ar), 127.2 (*m*-$C_6H_4CN$), 124.7 (*m*-Ar),117.4 (*p*-$C_6H_4CN$), 112.4 (C≡N), 29.1 (HC(*i*Pr)), 23.8 (Me(*i*Pr')), 22.5 (Me(*i*Pr)), 16.9 (Me(C)). $^{11}$B{1H} NMR (192 MHz, $C_7D_8$, 298 K): δ/ppm = -14.6 ($\nu_{1/2}$ ~ 210 Hz). FT-IR (KBr): ν/cm$^{-1}$ = 2233 (ν(C≡N), s). Elemental analysis (%) $C_{33}H_{26}BF_{10}N_3$ (M = 665.37 g/mol): calculated C 59.57, H 3.94, N 6.32; found C 60.50, H 4.12, N 6.29.

**Synthesis of compound 3a**

A solution of **2a** (200 mg; 0.27mmol) in toluene was heated to 100 °C for 4 h. Then, the volatiles were removed in vacuo, and the solid washed with pentane. The white solid was recrystallized from cold toluene giving **3a** as a white crystalline material in 95% yield (189 mg; 0.26 mmol). Single crystals for X-ray crystallography were grown by layering pentane onto a toluene solution of **3a** at -30°C. $^1$H NMR (600 MHz, $C_7D_8$, 298 K): δ/ppm = 7.02 (m, 1H, *p*-Ar), 6.89 (d, *J* = 6.9Hz, 2H, *m*-Ar), 2.69 (hept, *J* = 6.9Hz, 2H, HC(*i*Pr)), 1.47 (s, 3H, Me(C)), 1.00 (d, *J* = 6.9 Hz, 6H, Me(*i*Pr)), 0.72 (d, *J* = 6.9 Hz, 6H, Me(*i*Pr')). $^{13}$C{$^1$H} NMR (151 MHz, $C_7D_8$, 298 K): δ/ppm = 177.3 ($^{Ar\text{-}N}C^{N\text{-}C6F5}$), 146.1 (*o*-Ar), 133.4 (*i*-Ar), 129.1 (*p*-Ar), 124.7 (*m*-Ar), 28.9 (HC(*i*Pr)), 24.5 (Me(*i*Pr)), 23.6 (Me(*i*Pr')), 13.9 (Me(C)). $^{11}$B{1H} NMR (192 MHz, $C_7D_8$, 298 K): δ/ppm = 7.52 ($\nu_{1/2}$ ~ 210 Hz). Elemental analysis (%) $C_{32}H_{20}BF_{15}N_2$ (M = 730.32 g/mol): calculated C 52.77, H 2.77, N 3.85; found C 51.14, H 2.47, N 4.32. MS (ESI, Exact mass): Calc: 727.1; Found: 727.1 [$C_{32}H_{19}BF_{15}N_2^+$]. Calc: 709.145; Found: 709.149 [$C_{32}H_{20}BF_{14}N_2^+$].

**Synthesis of compound 4**

To a stirred solution of **2b** (5.0 mg, 0.009 mmol) in toluene $d_8$ (0.6 ml) was added $B(C_6F_5)_3$ (4.7 mg, 0.08 mmol). After 15 min the solution was subjected to NMR spectroscopy showing virtually quantitative spectroscopic yield of **4** based on the $^{19}$F-NMR spectrum. The volatiles were removed in vacuo and the residue was recrystallized from toluene to afford compound **4** as a colourless solid (7.4 mg, 83.6 %). $^1$H NMR (300 MHz, 295 K, $C_7D_8$, ppm): 8.03 (s, 1H, NH), 7.02 – 6.75 (m, 8H, Ar-H), 2.74 (m, 2H, HC(*i*Pr)), 1.05 (d, *J* = 6.9 Hz, 12H, Me(*i*Pr)), 0.86 (d, *J* = 6.6 Hz, 6H, Me(*i*Pr')). $^{19}$F NMR (282 MHz, 295 K, $C_7D_8$, ppm): -134.77 (6F), -136.07 (4F), -156.37 (3F), -157.70 (2F), -164.08 - -164.47 (10 F). Elemental analysis (%) $C_{51}H_{26}B_2F_{25}N_3$ (M = 1177.35 g/mol): calculated C 52.03, H 2.23, N 3.57; found C 52.34, H 2.40, N 3.50.

**Synthesis of compound 5**

To a solution of **2b** (5.0 mg, 0.008 mmol) in toluene $d_8$ (0.6 ml) was added $B(C_6F_5)_3$ (4.7 mg, 0.009 mmol) and the mixture was heated to 120 °C for 22 h. The $^1$H NMR spectrum (Tol-$d_8$) indicated the presence of $H_2$ (δ 4.44 ppm) and a newly formed product, which from the main resonances of the NMR spectra is assumed to be **5**. Attempts to isolate **5** failed as decomposition reactions took place during the workup process showing free $B(C_6F_5)_3$ in the $^{19}$F NMR spectra. $^1$H NMR (400 MHz, $C_7D_8$, 295 K): δ/ppm = 7.18 – 6.90 (m, 8H, Ar), 2.54 (m, 2H, HC(*i*Pr)), 0.99 (d, *J* = 6.8 Hz, 6H, Me(*i*Pr)), 0.63 (d, *J* = 4.4 Hz, 6H, Me(*i*Pr')). $^{13}$C{$^1$H} NMR (125 MHz, $C_7D_8$, 310 K): δ/ppm = 174.7 ($^{Ar\text{-}N}C^{N\text{-}C6H4CN}$), 145.5 (*o*-Ar), 135.2 (*i*-Ar), 129.7 (*p*-Ar), 124.0 (*m*-Ar), 29.3 (HC*i*Pr), 24.6 (Me(*i*Pr)), 23.3 (Me(*i*Pr')), 16.5 (MeC). $^{19}$F NMR (282 MHz, $C_7D_8$, 295 K): δ/ppm = -134.55 (m, 4F, *o*-$C_6F_5$, -$B(C_6F_5)_2$), -135.86 (m, 6F,*o*-$C_6F_5$, $B(C_6F_5)_3$), -154.12 (t, *J* = 20.6 Hz, 2F, *p*-$C_6F_5$, -$B(C_6F_5)_2$), -156.73 (t, *J* = 19.7 Hz, 3F, *p*-$C_6F_5$, $B(C_6F_5)_3$), -163.14 (m, 4F, *m*-$C_6F_5$, -$B(C_6F_5)_2$), -164.27 (m, 6F, *m*-$C_6F_5$, $B(C_6F_5)_3$). $^{11}$B{1H} NMR (128 MHz, $C_7D_8$, 295 K): δ/ppm = -5.64 ($\nu_{1/2}$ ~ 128 Hz, -$B(C_6F_5)_2$), -0.88 ($\nu_{1/2}$ ~ 128 Hz, $B(C_6F_5)_3$).

**Synthesis of compound 6a**

A solution of **2a** (100 mg; 0.14mmol) in toluene was pressurized with 2 bar of CO and heated to 105°C for 10 h. Then, the volatiles were removed in vacuo. Finally the white solid was recrystallized from cold toluene/pentane giving **6a** as

a white crystalline material in 95% yield (98 mg; 0.13 mmol). $^{1}$H NMR (600 MHz, $C_7D_8$, 298 K): δ/ppm = 7.16 (t, *J* = 7.8 Hz, 1H, *p*-Ar), 7.00 (d, *J* = 7.8Hz, 2H, *m*-Ar), 2.80 (hept, *J* = 6.8Hz, 2H, HC(*i*Pr)), 1.53 (s, 3H, Me(C)), 1.11 (d, *J* = 6.9 Hz, 6H, Me(*i*Pr)), 1.07 (d, *J* = 6.8 Hz, 6H, Me(*i*Pr')). $^{13}$C{$^{1}$H} NMR (151 MHz, $C_7D_8$, 298 K): δ/ppm = 193 (br., C=O), 176.5 ($^{Ar\text{-}N}C^{N\text{-}C6F5}$), 147.1 (*o*-Ar), 131.5 (*p*-Ar), 127.6 (*i*-Ar), 125.0 (*m*-Ar), 28.9 (HC(*i*Pr)), 24.6 (Me(*i*Pr')), 23.4 (Me(*i*Pr)), 15.7 (Me(C)). $^{11}$B{1H} NMR (192 MHz, $C_7D_8$, 298 K): δ/ppm = -10.01 ($\nu_{1/2}$ ~ 210 Hz). FT-IR (KBr): ν/cm$^{-1}$ = 1752 (ν(C=O), s). Elemental analysis (%) $C_{33}H_{20}BF_{15}N_2O$ (M = 756.31 g/mol): calculated C 52.41, H 2.67, N 3.70; found C 53.04, H 3.01, N 3.33.

#### Synthesis of compound 6b

A solution of **2b** (180 mg; 0.27 mmol) in toluene was pressurized with 2 bar of CO and heated to 120°C for 10 h. Then, the volatiles were removed in vacuo. Finally the greenish yellow solid was recrystallized from cold toluene/pentane, giving **6b** as a green yellow crystalline material in 87% yield (163 mg, 0.24 mmol). $^{1}$H NMR (600 MHz, $C_7D_8$, 298 K): δ/ppm = 7.15 (t, *J* = 7.9Hz, 1H, *p*-Ar), 6.98 (d, *J* = 7.8Hz, 2H, *m*-Ar), 6.74 (d, *J* = 8.6Hz, 2H, *o*-$C_6H_4CN$), 6.71 (d, *J* = 8.7Hz, 2H, *m*-$C_6H_4CN$), 2.72 (hept, *J* = 6.73Hz, 2H, HC(*i*Pr)), 1.48 (s, 3H, Me(C)), 1.11 (d, *J* = 6.9 Hz, 6H, Me(*i*Pr)), 1.01 (d, *J* = 6.7 Hz, 6H, Me(*i*Pr')). $^{13}$C{$^{1}$H} NMR (151 MHz, $C_7D_8$, 298 K): δ/ppm = 193.9 (br., C=O), 172.2 ($^{Ar\text{-}N}C^{N\text{-}C6H4CN}$), 146.9 (*o*-Ar), 142.2 (*i*-$C_6H_4CN$), 133.5 (*o*-$C_6H_4CN$), 131.4 (*p*-Ar), 125.7 (*m*-$C_6H_4CN$), 124.9 (*m*-Ar), 124.8 (*i*-Ar), 117.2 (*p*-$C_6H_4CN$), 112.8 (C≡N), 29.0 (HC(*i*Pr)), 24.5 (Me(*i*Pr')), 23.3 (Me(*i*Pr)), 15.3 (Me(C)). $^{11}$B{1H} NMR (192 MHz, $C_7D_8$, 298 K): δ/ppm = -10.2 ($\nu_{1/2}$ ~ 180 Hz). FT-IR (KBr): ν/cm$^{-1}$ = 2232 (ν(C≡N), s), 1758 (ν(C=O), s). Elemental analysis (%) $C_{34}H_{24}BF_{10}N_3O$ (M = 691.37 g/mol): calculated C 59.07, H 3.50, N 6.08; found C 62.02, H 4.29, N 6.37. MS (ESI, Exact mass): Calc: 714.175; Found: 714.172 [$C_{34}H_{24}BF_{10}N_3ONa^+$]. Calc: 692.193; Found: 692.191 [$C_{34}H_{24}BF_{10}N_3OH^+$].

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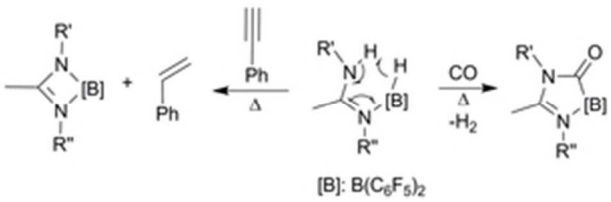


Formation of amidine-BH(C6F5)2 adducts and their dehydrogenation and transfer hydrogenation behaviour. These compounds were found to act as hydrogen donors in stoichiometric transfer hydrogenations of phenylacetylene to styrene. Additionally CO uptake of the dehydrogenated four-membered cyclic diazaborate compound could be established.
25x8mm (300 x 300 DPI)