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Reactivity of a Frustrated Lewis Pair and Small-Molecule Activation by an Isolable Arduengo Carbene–B{3,5-$(CF_3)_2C_6H_3$}$_3$ Complex

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Dedicated to Professor Anthony J. Arduengo III on the occasion of his 60th birthday

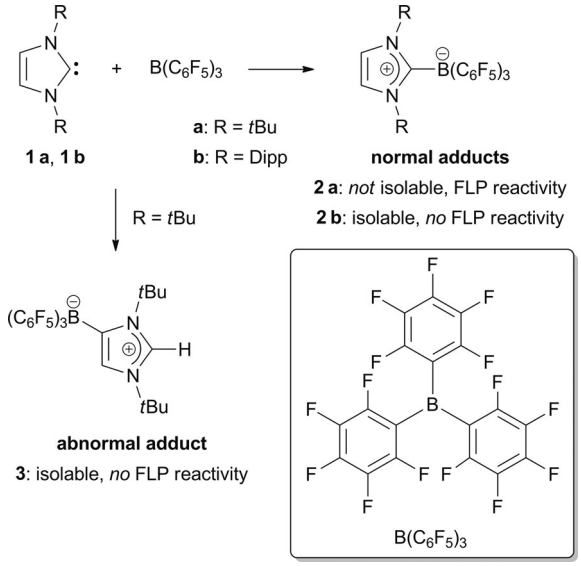
Abstract: Tris[3,5-bis(trifluoromethyl)-phenyl]borane reacts with the sterically demanding Arduengo carbenes 1,3-di-*tert*-butylimidazolin-2-ylidene and 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene to form isolable normal adducts. In the case of 1,3-di-*tert*-butylimidazolin-2-ylidene, the adduct exhibits dynamic behaviour in solution and frustrated-Lewis-pair (FLP) reactivity. Fast cleavage of dihydrogen and THF, the C–H activation of phenylacetylene, and carbon dioxide fixation were achieved by using solutions of this adduct in benzene. This adduct is stable at room temperature in the absence of suitable substrates; however, thermal rearrangement into an abnormal carbene–borane adduct can be observed. In contrast, the 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene adduct exhibits no evidence of FLP reactivity or of dissociation in solution. DFT calculations confirmed the experimental behaviour and stability of these carbene–borane adducts.

Keywords: boranes · carbenes · frustrated Lewis pairs · noncovalent interactions · small-molecule activation

Introduction

Since the first report of its preparation in 1963,[1] tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, has emerged from relative "obscurity to an industrially important commodity",[2] in particular because of its extensive use as a co-catalyst in homogeneous Ziegler–Natta olefin-polymerisation reactions.[3] Nowadays, $B(C_6F_5)_3$ has become firmly established as a "special boron Lewis acid for special reactions",[4] that is, as a catalyst or as a stoichiometric reagent for numerous organic and organometallic transformations.[2–5] More recently, this borane has found additional widespread application as the most prominent Lewis acid component in so-called frustrated Lewis pairs (FLPs), which are prevented from forming normal adducts by steric factors and, therefore, are capable of mutually activating small molecules, such as dihydrogen.[6,7]

Thus, the heterolytic cleavage of dihydrogen,[8,9] as well as the activation of other small molecules,[10,11] have been accomplished by a combination of $B(C_6F_5)_3$ with bulky N-heterocyclic carbene ("Arduengo carbene", NHC) **1a** (R = *t*Bu),[12] whereby the particularly strong propensity of this FLP to promote H_2 splitting can be ascribed to an enhanced cumulative acid–base strength.[13] However, in the absence of reactive substrates, self-deactivation and the irreversible formation of the abnormal carbene–borane adduct (**3**) were observed,[8] whereas the normal adduct (**2a**) could not be isolated (Scheme 1). In contrast, sterically less-demanding carbene **1b** (R = 2,6-diisopropylphenyl, Dipp)[14] gave the isolable normal adduct **2b** with no indication of FLP reactivity.[9] The different behaviour of these pairs, **1a**/$B(C_6F_5)_3$ and



Scheme 1. The formation of normal and abnormal carbene–borane adducts with $B(C_6F_5)_3$; Dipp = 2,6-diisopropylphenyl, *t*Bu = *tert*-butyl.

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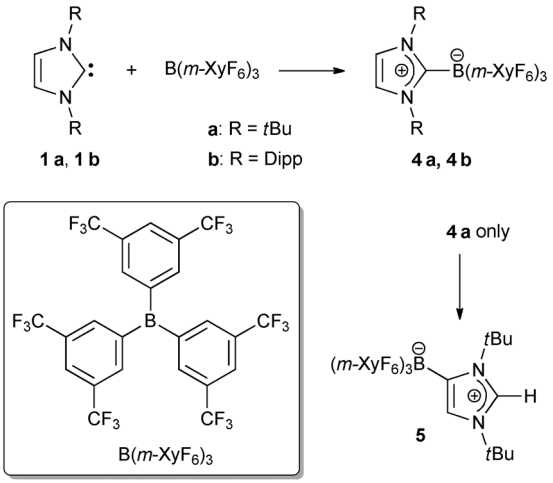
1b/$B(C_6F_5)_3$, can be conveniently rationalized by comparing the stability of their normal adducts, which indicated a much higher stability of the isolable **2b** ($\Delta E = -51.5$ kcal mol^{-1}) compared to elusive adduct **2a** ($\Delta E = -23.8$ kcal mol^{-1}; see Table 1 and discussion below).[15] Whereas the abnormal adduct (**3**) is significantly more stable ($\Delta E = -44.2$ kcal mol^{-1}),[8] we anticipated that adducts that are similar to structure **2a** should still become isolable if C–H activation at the 4,5-positions of the imidazole ring and rearrangement into an abnormal carbene–borane complex are blocked. Consequently, $B(C_6F_5)_3$ was treated with the 4,5-dimethyl and 4,5-dihydro congeners of compound **1a**, but the expected normal adducts avoided isolation through C–F activation or C–H activation, respectively.[15,16]

Table 1. Energies [kcal mol^{-1}] for the formation of normal and abnormal carbene–borane adducts.[a]

Compound (R)	Adduct type	Borane	ΔE_{M05-2X}	ΔE_{M06-2X}	ΔE_{B97-D}
2a (*t*Bu)	normal	$B(C_6F_5)_3$	−23.8[b]	−28.4	−24.8
2b (Dipp)	normal	$B(C_6F_5)_3$	−51.5[b]	−59.0	−56.7
3 (*t*Bu)	abnormal	$B(C_6F_5)_3$	−44.2[b]	−46.2	−43.8
4a (*t*Bu)	normal	$B(m\text{-}XyF_6)_3$	−25.1	−29.4	−36.7
4b (Dipp)	normal	$B(m\text{-}XyF_6)_3$	−52.1	−61.9	−69.4
5 (*t*Bu)	abnormal	$B(m\text{-}XyF_6)_3$	−41.6	−44.2	−47.6

[a] ΔE = uncorrected zero-point M05-2X, M06-2X, and B97-D/6-311G-(d,p) energies; for full thermodynamic data, including ΔE_{0K}, ΔH_{298K}, and ΔG_{298K}, see the Supporting Information. [b] These values have previously been reported in refs. [8] and [15].



Scheme 2. The formation of normal and abnormal carbene–borane adducts with $B(m\text{-}XyF_6)_3$; Dipp = 2,6-diisopropylphenyl, *t*Bu = *tert*-butyl.

Results and Discussion

It has also been concluded that the reactivity and resulting self-destruction of carbene–borane Lewis pairs could not only be moderated by variation in the carbene,[15] but also by employing other Lewis acids.[17] In this regard, we identified tris[3,5-bis(trifluoromethyl)phenyl]borane, $B(m\text{-}XyF_6)_3$ (*m*-XyF_6 = hexafluoro-*meta*-xylyl, 3,5-$(CF_3)_2C_6H_3$), as an interesting candidate, even though, considering the prominence of the corresponding borate ion, $[B(m\text{-}XyF_6)_4]^-$ (BARF), as a weakly coordinating anion,[18] surprisingly little reference has been made to this borane, apart from in patent literature (Scheme 2).[19] Until very recently, the only reported preparation of $B(m\text{-}XyF_6)_3$ occurred accidentally by the degradation of the BARF ion in the presence of a cationic platinum(II) complex, whereby its molecular structure could be established by X-ray diffraction.[20] However, much to our surprise, Ashley and co-workers have now independently reported a preparative procedure for $B(m\text{-}XyF_6)_3$ and its use as an FLP component together with 2,2,6,6-tetramethyl-piperidine (TMP).[21] Following our first unsuccessful attempts to prepare $B(m\text{-}XyF_6)_3$ in analogy to $B(C_6F_5)_3$ from 3,5-bis(trifluoromethyl)phenyl bromide by reaction with *n*BuLi and BCl_3,[22] our final procedure, which was based on an early report on the synthesis of $B(C_6F_5)_3$ from C_6F_5MgBr and boron trifluoride etherate,[1c] turned out to be quite similar to that reported by Ashley and co-workers.[21] Hence, the Grignard reagent,[23] which was prepared according to the Knochel method from 3,5-bis(trifluoromethyl)phenyl bromide and *i*PrMgCl in THF,[24] was treated with $BF_3{\cdot}Et_2O$ in THF, thereby affording $B(m\text{-}XyF_6)_3$ as a white crystalline solid in 62–79% yield after evaporation, twofold sublimation, and recrystallization from hot toluene.[25] This procedure could be repeated several times, thus reliably producing 10–15 g of the product. At room temperature, $B(m\text{-}XyF_6)_3$ is insoluble in nonpolar hydrocarbon solvents and is only slightly soluble in aromatic and chlorinated solvents. Dissolution in donor solvents leads to the formation of solvate complexes, as evidenced by ^{11}B NMR spectroscopy ($\delta = 11.7$ ppm in [D_8]THF and $\delta = 10.9$ ppm in [D_6]acetone).

In contrast to the observed reactivity of compounds **1a** and **1b** towards $B(C_6F_5)_3$ (Scheme 1), the reactions of both carbenes with $B(m\text{-}XyF_6)_3$ in toluene afforded their normal adducts (**4a** and **4b**) in high yield. Their ^{11}B and ^{19}F NMR spectra (in C_6D_6) exhibit one resonance each, at $\delta = -5.9/-62.8$ ppm (**4a**) and at $\delta = -8.0/-62.2$ ppm (**4b**), thus indicating free rotation around the C–B bonds at room temperature on the NMR timescale.[26] The formation of normal carbene–borane adducts was unambiguously confirmed by X-ray diffraction analysis and their molecular structures (Figure 1) show B–C1 bond lengths of 1.675(4) Å (**4a**) and 1.662(3) Å (**4b**). These distances are similar to the corresponding B–C bond lengths that were established for compound **2b** in two different crystal modifications (1.663(5) and 1.684(2) Å).[9,15] However, these bond lengths are longer than that observed in the $B(C_6F_5)_3$ adduct of the sterically less encumbered NHC 1,3,4,5-tetramethylimidazolin-2-ylidene (1.641(2) Å).[27]

In contrast to this structure, steric congestion in compounds **4a** and **4b** is indicated by a significant tilting of the imidazole plane with respect to the B–C1 axis, whereby the

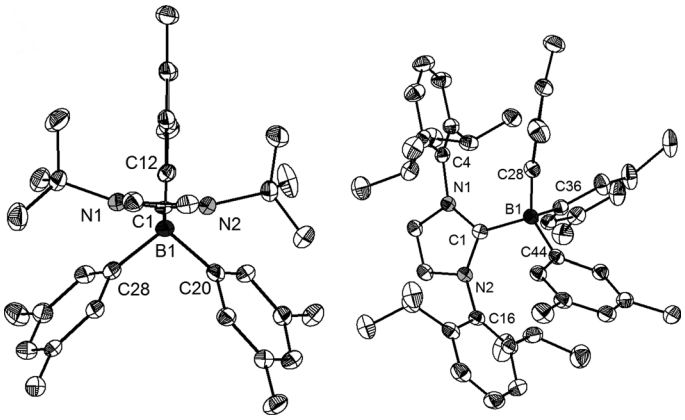


Figure 1. ORTEPs of compounds **4a** (left) and **4b** (right); thermal ellipsoids are set at 50% probability. Hydrogen and fluorine atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **4a**: B–C1 1.675(4), N1–C1 1.375(3), N2–C1 1.386(3); N1–C1–N2 104.9(2), C1–B–C12 107.80(18), C1–B–C20 109.0(2), C1–B–C28 111.9(2). **4b**: B–C1 1.662(3), N1–C1 1.368(3), N2–C1 1.387(3); N1–C1–N2 104.20(17), C1–B–C28 105.36(16), C1–B–C36 112.74(17), C1–B–C44 114.05(17).

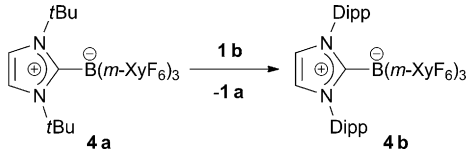
boron atoms lie 0.47 Å (**4a**) and 0.39 Å (**4b**) out of the C1–N1–C2–C3–N2 plane. In addition, the N-bonded substituents in both molecules are twisted towards one side and the CMe_3 carbon atoms in compound **4a** are significantly more strongly displaced (0.49/0.45 Å) with respect to the imidazole plane than the *ipso*-carbon atoms in compound **4b** (0.38/0.19 Å).

Based on their solid-state structures, compound **4a** is apparently more strongly distorted than compound **4b** and, therefore, might exhibit a higher degree of "frustration" and reactivity. As we have recently demonstrated, the thermodynamics of carbene–borane-adduct formation can be used as a good measure to rationalize and predict their FLP behaviour;[15] therefore, the energies for the formation of $B(C_6F_5)_3$ and $B(m\text{-}XyF_6)_3$ adducts **2a**/**2b** and **4a**/**4b** were calculated by using DFT methods. We employed the M05-2X, M06-2X, and B97-D functionals that were developed by Zhao and Truhlar[28] and by Grimme[29] to conveniently describe the noncovalent and long-term dispersion interactions that were expected to contribute significantly to the overall binding in adducts **2** and **4** (Table 1).[30] In agreement with the previously observed reactivity, FLP **2a** is significantly less stable than compound **2b** and the energy difference ($\Delta\Delta E \approx 30$ kcal mol^{-1}) is well-reproduced with all three functionals. The relative stabilities of compounds **4a** and **4b** are very similar ($\Delta\Delta E = 27.0$–32.7 kcal mol^{-1}) and the energies of formation decrease in the order M05-2X > M06-2X > B97-D. It is noteworthy that only the latter functional affords markedly different stabilities for $B(C_6F_5)_3$ adduct **2a** ($\Delta E_{B97-D} = -24.8$ kcal mol^{-1}) and its $B(m\text{-}XyF_6)_3$ congener (**4a**, $\Delta E_{B97-D} = -36.7$ kcal mol^{-1}), which accounts for the elusiveness of adduct **2a** in contrast to the successful isolation of compound **4a** (see above).

Although it is in complete agreement with the experimental findings, this vast calculated difference in stability between the borane adducts that contain NHCs **1a** (R = *t*Bu) and **1b** (R = Dipp) is nonetheless somewhat puzzling, even in view of the fact that NHC **1a** is clearly a bigger ligand than compound **1b** when referring, for instance, to the "percent buried volume", as introduced by the groups of Nolan and Cavallo, to measure the steric bulk of a NHC.[31] Apart from bulkiness, the clear difference between the two carbenes is that compound **1a** contains *N*-alkyl groups, whereas compound **1b** represents an aromatic N-substituted NHC ligand. For transition-metal complexes of this latter class, it has recently been established that, in addition to the conventional picture of metal–NHC bonding,[32] a new mode of interaction occurs through π-face donation from the aromatic substituents, that involves, in particular, the *ipso*-carbon atoms.[33,34] Calculations revealed the operation of two different mechanisms: 1) direct donation to empty metal orbitals, and 2) donation to another arene moiety that is bound to the metal atom,[34] as evidenced, for instance, by π–π interactions between mesitylene and benzylidene groups in the solid-state structures of second-generation Grubbs-type catalysts.[35] Evaluation of compound **4b** for similar interactions reveals several very short intramolecular C···C distances that are well below the sum of their van der Waals radii ($r_{vdW}(C) = 1.70$ Å);[36] the shortest contacts involve the *ipso*-carbon atoms of the Dipp substituents and the *ipso*- and *ortho*-carbon atoms of the XyF_6 rings, namely C4–C28 3.23 Å, C4–C33 3.16 Å, C16–C44 3.16 Å, and C16–C45 3.20 Å. A re-inspection of the crystal structure of compound **2b** unveils even shorter distances of 2.97 and 3.01 Å for the Dipp–C_{ipso} atoms[15] and, therefore, we propose that π-face donation in compounds **2b** and **4b** contributes significantly to the overall stability of these adducts and to their resulting lack of FLP reactivity (see below).[37]

Because the DFT calculations indicate that adducts **4a** and **4b** have significantly different stabilities, we set out to probe their behaviour in solution further by using 2D exchange NMR spectroscopy (2D EXSY). At room temperature, ^{1}H,^{1}H EXSY spectra of mixtures of compounds **1a**/**4a** and **4a**/$B(m\text{-}XyF_6)_3$ in [D_8]toluene showed exchange peaks between the resonances that were assigned to compound **4a** and to the uncoordinated species (for a detailed representation of selected spectra, see the Supporting Information). These signals could be observed even after short mixing times, thus confirming a fast exchange between uncoordinated and coordinated carbene and borane species in solution. In contrast, mixtures of compounds **1b**/**4b** and **4b**/$B(m\text{-}XyF_6)_3$ did not afford spectra with any indication of exchange in solution at room temperature, which was in full agreement with the significantly higher calculated stability of compound **4b** compared to compound **4a** ($\Delta\Delta E \approx 30$ kcal mol^{-1}; Table 1). In line with these findings, the addition of one equivalent of compound **1b** to a solution of compound **4a** in C_6D_6 led to complete carbene exchange and to the quantitative formation of a mixture of compounds **1a**/**4b**, as indicated by NMR spectroscopy (Scheme 3).

In light of the dynamic behaviour of compound **4a** in solution, we set out to experimentally investigate this adduct for potential FLP reactivity. Compound **4a** is indefinitely



Scheme 3. Solution-phase behaviour of normal carbene–borane adduct **4a**.

stable in benzene at room temperature and also for at least one hour under reflux conditions ($T=80\,°C$), whereas heating in toluene at 110 °C resulted in fast rearrangement into abnormal adduct **5** within 15 min. On cooling a hot solution of compound **4a** in toluene, adduct **5** was isolated as a colourless crystalline solid in 92% yield. Single resonances are found in the ^{11}B and ^{19}F NMR spectra (in [D_6]acetone) at $\delta=-7.4$ and -62.3 ppm and the observation of two doublets at $\delta=9.10$ and 6.84 ppm for the imidazole CH hydrogen atoms and of two singlets at $\delta=1.62$ and 1.28 ppm for the *t*Bu methyl groups indicate the formation of adduct **5** with an asymmetrically bound abnormal NHC ligand. X-ray diffraction analysis revealed a B–C2 distance of 1.661(2) Å, which is very close to the values for compounds **4a** and **4b**. In contrast to the corresponding normal adduct **4a**, the absence of any unusual structural distortions indicates the presence of an unstrained adduct (Figure 2). DFT calcula-

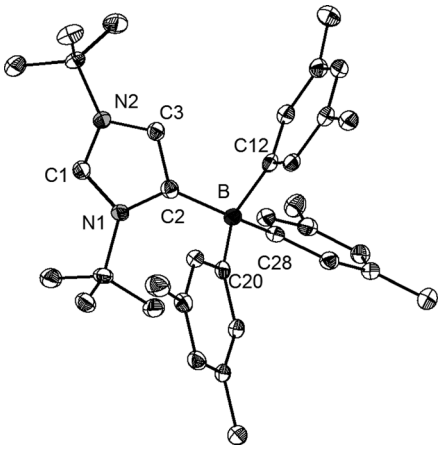
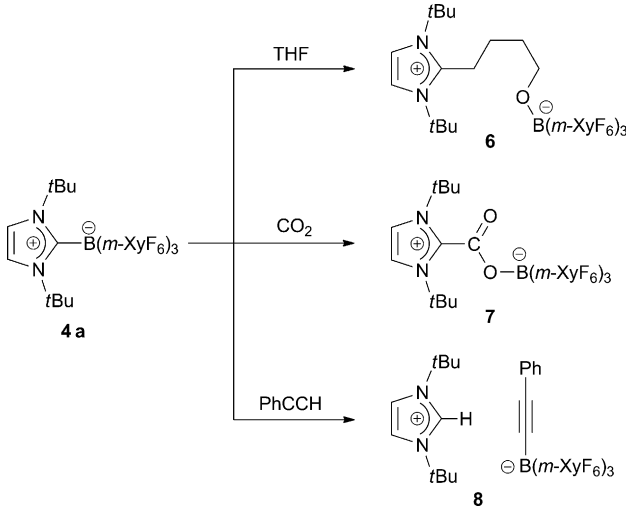


Figure 2. ORTEP of compound **5**; thermal ellipsoids are set at 50% probability. Hydrogen and fluorine atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–C1 1.338(2), N1–C2 1.428(2), N1–C4 1.521(2), N2–C1 1.324(2), N2–C3 1.383(2), B–C2 1.661(2), B–C12 1.663(2), B–C20 1.639(2), B–C28 1.639(2); N1–C1–N2 110.05(14), N1–C2 –B 133.21(13), C3–C2–B 123.43(14), C12–B–C2 106.50(12), C20–B–C2 110.77(13), C28–B–C2 113.19(13).

tions confirm the expected higher stability of adduct **5** relative to compound **4a**; comparison with the corresponding couple **3**/**2a** reveals a smaller difference in energy, which varies with the applied functionals (Table 1). Again, the B97-D functional affords the highest stabilities for compounds **4a** and **5**, whilst producing the smallest difference ($\Delta\Delta E=11.0$ kcal mol^{-1}).

The ring-opening of THF is another characteristic reaction of carbene–borane and phosphane–borane FLP systems.[8,15,16] Therefore, compound **4a** was dissolved in THF and stirred for 24 h. Evaporation of the solvent afforded a white solid, NMR characterisation of which indicated the presence of the expected $(CH_2)_4O$-bridged product (**6**) together with the abnormal adduct (**5**) in a 3:2 ratio (Scheme 4). This reaction was not optimised further, but the formation of both products indicated FLP behaviour.



Scheme 4. FLP reactivity of normal carbene–borane adduct **4a**.

Another important issue in FLP chemistry is CO_2 fixation;[38] consequently, the reactivity of compound **4a** towards carbon dioxide was studied. When CO_2 was bubbled through a clear solution of compound **4a** in hot benzene ($T=60\,°C$), a white precipitate formed instantaneously and the CO_2 adduct (**7**) could be isolated in 66% yield by filtration and crystallisation from CH_2Cl_2/*n*-hexane (Figure 3). Alternatively, the exposure of a suspension of compound **4a** in benzene to CO_2 at room temperature for 24 h afforded compound **7** in higher yield (86%) and purity. The ^1H and ^{19}F NMR spectra of compound **7** are very similar to those of compound **4a**, whilst its ^{13}C NMR spectrum exhibits an additional resonance at $\delta=157.7$ ppm for the CO_2 carbon atom; the ^{11}B NMR resonance is found at $\delta=4.7$ ppm. X-ray diffraction analysis confirmed the formation of a CO_2-bridged zwitterion with C1–C12 and B–O2 distances of 1.5289(19) and 1.5910(18) Å, respectively. The CO_2 fragment is planar (angular sum of 359.98°) and displays two distinctly different C–O bond lengths of 1.2141(18) Å (C12–O1) and 1.2930(18) Å (C12–O2).

The activation of phenylacetylene had previously been observed for the FLP **1a**/$B(C_6F_5)_3$;[11] similarly, the addition of phenylacetylene to a suspension of compound **4a** in benzene afforded a yellow oil, which was separated after stirring the reaction mixture for 20 min. Cooling a hot solution of this oil in C_6H_6/CH_2Cl_2 afforded colourless crystals of compound **8** in 91% yield. ^{11}B and ^{19}F NMR analysis of these

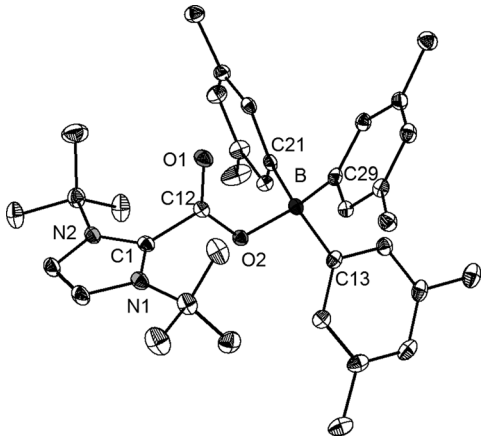


Figure 3. ORTEP of compound **7**; thermal ellipsoids are set at 50% probability. Hydrogen and fluorine atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–C1 1.3507(19), N2–C1 1.3812(19), C1–C12 1.5289(19), O1–C12 1.2141(18), O2–C12 1.2930(18), B–O2 1.5910(18), B–C1 1.675(4), B–C13 1.627(2), B–C21 1.634(2), B–C29 1.627(2); N1–C1–N2 108.42(12), N1–C1–C12 126.63(13), N2–C1–C12 124.17(13), O1–C12–C1 116.98(13), O2–C12–C1 115.09(12), O1–C12–O2 127.92(13), O2–B–C13 103.95(11), O2–B–C29 109.69(11), O2–B–C21 105.97(11).

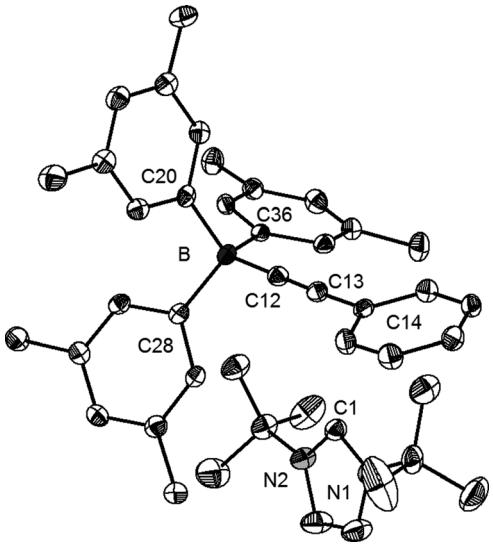
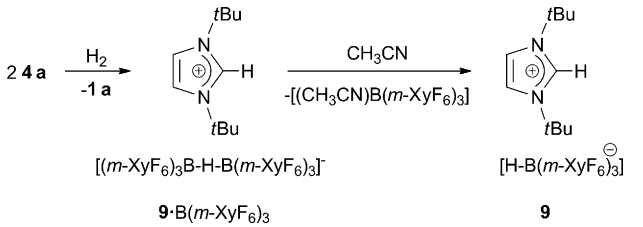


Figure 4. ORTEP of one independent ion pair of compound **8**; thermal ellipsoids are set at 50% probability. Hydrogen and fluorine atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: B–C12 1.593(3), B–C20 1.644(3), B–C28 1.647(3), B–C36 1.643(3), C12–C13 1.210(3), C13–C14 1.442(3); N1–C1–N2 110.1(2), C12–B–C20 107.21(18), C12–B–C28 110.07(18), C12–B–C36 110.70(18), C13–C12–B 179.3(2), C12–C13–C14 178.2(2).

crystals show signals at $\delta = -8.9$ and -62.3 ppm and the ^{1}H NMR spectrum exhibits a characteristic low-field triplet ($\delta = 7.35$ ppm) that can be assigned to an imidazolium NC(H)N hydrogen atom, thus indicating that heterolytic C–H bond cleavage and the formation of the imidazolium phenylalkynylborate (**8**) had occurred. Single crystals of **8**·C_6D_6 that were suitable for X-ray diffraction were obtained by the slow evaporation of CD_2Cl_2 from a solution of compound **8** in C_6D_6/CD_2Cl_2. The asymmetric unit contains two crystallographically independent cations and anions with similar structural parameters; Figure 4 shows one imidazolium phenylalkynylborate ion pair. The B–C12 and C12–C13 bond lengths, 1.593(3) and 1.210(3) Å, together with the C12–C13–C14 angle, 178.2(2)°, are similar to the reported values for the related $[PhC{\equiv}CB(C_6F_5)_3]^-$ ion.[11]

To test whether compound **4a** was capable of promoting the heterolytic cleavage of dihydrogen with the concomitant formation of the imidazolium hydroborate (**9**, Scheme 5), a suspension of compound **4a** in benzene was stirred overnight under a H_2 atmosphere (1 atm), thereby affording a white precipitate. The solid was isolated by filtration and washed with CH_2Cl_2; it was appreciably soluble only in THF. Its ^{1}H NMR spectrum in [D$_8$]THF exhibits a triplet and a doublet at $\delta = 8.78$ and 7.90 ppm, respectively, in line with the formation of an imidazolium salt. In addition, broad resonances at $\delta = 7.87$ and 7.68 ppm correspond to the *ortho*- and *para*-hydrogen atoms of the XyF_6 groups. However, their integrals indicate the presence of two borane moieties and thus suggest the formation of **9**·B(*m*-XyF_6)$_3$, which contains the $[(m\text{-}XyF_6)_3B{-}H{-}B(m\text{-}XyF_6)_3]^-$ anion, as was also observed for the TMP/B(*m*-XyF_6)$_3$ pair (see above).[21] Moreover, this anion gives rise to a broad ^{1}H NMR resonance at $\delta = 3.75$ ppm for the BHB moiety and



Scheme 5. Heterolytic cleavage of dihydrogen by carbene–borane adduct **4a**.

to another broad ^{11}B NMR signal at $\delta = -10.0$ ppm. Elemental analysis also confirmed the composition of **9**·B(*m*-XyF_6)$_3$. Evidently, the reaction of compound **4a** with H_2 only consumed half the amount of carbene **1a** that was present in adduct **4a** and, consequently, the other half could be isolated and spectroscopically characterized from the benzene filtrate. Optimisation of the H_2-activation procedure was achieved by exposing a 1:1 mixture of compound **4a** and B(*m*-XyF_6)$_3$ to dihydrogen gas in benzene, which afforded **9**·B(*m*-XyF_6)$_3$ in 84% yield.

For the TMP/B(*m*-XyF_6)$_3$ system,[21] the addition of pyridine (py) to the $[(m\text{-}XyF_6)_3B{-}H{-}B(m\text{-}XyF_6)_3]^-$ salt afforded pyridine adduct [(py)B(*m*-XyF_6)$_3$] and hydroborate ion $[H{-}B(m\text{-}XyF_6)_3]^-$. In our hands, the addition of a few drops of MeCN to a suspension of **9**·B(*m*-XyF_6)$_3$ in CD_2Cl_2 gave a clear solution that contained compound **9**; the presence of the $[H{-}B(m\text{-}XyF_6)_3]^-$ ion was unambiguously confirmed by the observation of a quadruplet at $\delta = 3.63$ ppm in the ^{1}H NMR spectrum and a doublet at $\delta = -8.7$ ppm in the ^{11}B NMR spectrum with ^1J(B,H) = 83 Hz (Scheme 4). Additional broad signals can be assigned to the acetonitrile

adduct, [$(CH_3CN)B(m\text{-}XyF_6)_3$]. Clearly, $B(m\text{-}XyF_6)_3$ displays a significantly higher tendency than $B(C_6F_5)_3$ to form a hydrogen-bonded hydrodiborate,[39] which could be ascribed to its high Lewis acidity along with its lower steric demand.

Finally, it should be emphasized that complexes **2b** and **4b**, which both contained Dipp-substituted carbene **1b**, displayed no FLP-type reactivity; they were stable in THF and solutions of these complexes in toluene did not react with dihydrogen, even after long periods of time (2 weeks) or at elevated temperatures. Compound **2b** has been reported to be unstable in solution and, indeed, it slowly decomposed in refluxing toluene to afford a mixture of products.[9,15] In contrast, compound **4b** remained stable under these conditions and its NMR spectra in such solutions showed no signs of decomposition, which, again, was in agreement with the higher calculated stability of compound **4b** compared to those of compounds **2b** and **4a** (Table 1, see above).

Conclusion

In this contribution, we have introduced a procedure for the bulk preparation of the new fluorinated borane $B(m\text{-}XyF_6)_3$ and have studied its use for the design of frustrated carbene–borane Lewis pairs. In combination with 1,3-di-*tert*-butylimidazolin-2-ylidene (**1a**), the isolable Lewis acid–base adduct **4a** "at the boundary of classical and frustrated-Lewis-pair reactivity" was obtained;[40] this adduct partially dissociated in solution and, therefore, was able to exhibit FLP-type reactivity, such as CO_2 fixation, C–H activation, and even dihydrogen splitting. This observed reactivity can be interpreted in terms of the concept of "thermally induced frustration",[41] with the "reactive frustrated Lewis form" of compound **4a** being sufficiently populated at room temperature, whereas similar reactivity cannot be thermally induced for the more stable adduct **4b** in the studied temperature range. However, in the absence of substrates, the rearrangement of compound **4a** into abnormal carbene–borane adduct **5** can be achieved under comparatively forcing conditions. Whilst this stable adduct has lost its FLP potential, it can serve as a source of a new members of the recently established class of anionic N-heterocyclic carbenes that contain weakly coordinating borate moieties (WCA-NHC).[42]

Experimental Section

Materials and methods: All operations with air- and moisture-sensitive compounds were performed in a glove box under a dry argon atmosphere (MBraun 200B) or on a high-vacuum line by using Schlenk techniques. The ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were recorded on Bruker DPX 200 (200 MHz), Bruker AVII 300 (300 MHz), and Bruker DRX 400 (400 MHz) devices. The chemical shifts are expressed in parts per million (ppm) with tetramethylsilane (TMS) or the residual solvent signal as an internal standard. Coupling constants (J) are reported in Hertz (Hz) and splitting patterns are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), sept (septet), and br (broad). Elemental analysis was carried out on a Vario Micro Cube System. A Bruker Vertex 70 spectrometer was used to record the IR spectra. Mass spectra were recorded on Finnigan MAT 95 (EI) and Finnigan MAT 95 XL (ESI) systems, respectively. All solvents were purified by a solvent purification system (MBraun) and stored over molecular sieves (4 Å) prior to use. In addition, benzene and THF were purified by distillation over sodium/benzophenone. Unless otherwise indicated, all of the starting materials were obtained from Aldrich or Acros and were used without further purification. Gaseous dihydrogen (99.999%) and carbon dioxide (99.5%) were purchased from Westfalen AG and passed through a P_2O_5 column prior to use. 1,3-Di-*tert*-butylimidazolin-2-ylidene (**1a**)[12] and 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (**1b**)[14] were prepared according to literature procedures.

X-ray crystallography: Crystallographic data are given in Table 2. *Data collection and reduction*: Single crystals were mounted in inert oil and transferred into a stream of cold gas in an Oxford Diffraction Xcalibur E diffractometer. Intensities were recorded by using monochromated $Mo_{K\alpha}$ radiation. Absorption corrections were based on multiple scans. *Refinement*: Structures were refined anisotropically on F^2 by using the program SHELXL-97.[43] Hydrogen atoms were either 1) included as idealized methyl groups that were allowed to rotate but not tip or 2) placed geometrically and allowed to ride on their attached carbon atoms. *Special features*: Except for compounds **5** and **7**, the large number of trifluoromethyl groups led to problems with disorder (or at least high U values). Disordered groups were treated by using appropriate systems of restraints to improve the stability of the refinement; details are given in the CIF files. In addition, compound **4b** contained disordered toluene molecules that could not be refined satisfactorily; for this reason, the program SQUEEZE[44] was used to mathematically remove the effects of the solvent. Compound **8** crystallized with two independent molecules of compound **8** and three independent molecules of deuterated benzene (two with inversion symmetry) in the asymmetric unit. *Short hydrogen bonds*: Compound **7** displayed a short intermolecular interaction, H2···O1 2.20 Å.

CCDC-883184 (**4a**), CCDC-883185 (**4b·0.5**C_7H_8), CCDC-88318 (**5**), CCDC-883187 (**7**), and CCDC-883188 (**8·**C_6D_6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

B(m-XyF$_6$)$_3$: To a mixture of m-$(CF_3)_2C_6H_3Br$ (0.08 mol, 23.44 g) and THF (150 mL) in a 250 mL Schlenk flask under an argon atmosphere at 4°C (ice bath) was added a 2.0 M solution of *i*PrMgCl in THF (40 mL). The reaction mixture was allowed to warm to RT and stirred for 4 h. The mixture was cooled to −20°C and a solution of freshly distilled $Et_2O{\cdot}BF_3$ (3.79 g) in THF (40 mL) was added dropwise. The mixture was warmed to RT and then heated at reflux for 2 h. The solvent was evaporated and the remaining oil was dried in vacuo. The resulting solid was sublimed twice at 160°C under in vacuum (0.3 mbar). During the first sublimation, it was necessary to increase the temperature of the sublimation device slowly to prevent contamination of the product by magnesium salts. The product was further purified by recrystallisation from hot toluene. Yield: 10.69–13.63 g (62–79%); white crystalline powder; m.p. 217–219°C (slow sublimation was observed at >170°C); b.p. 316–320°C; ^{1}H NMR (400 MHz, CD_2Cl_2, 25°C): $\delta = 8.23$ (br s, 3H; p-$C_6H_3(CF_3)_2$), 8.02 ppm (br s, 6H; o-$C_6H_3(CF_3)_2$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): $\delta = 8.23$ (br s, 3H; p-$C_6H_3(CF_3)_2$), 8.00 ppm (br s, 6H; o-$C_6H_3(CF_3)_2$); ^{1}H NMR (300 MHz, C_6D_6, 25°C): $\delta = 7.87$ (sept, ^4J(H,F) = 0.6 Hz, 3H; p-$C_6H_3(CF_3)_2$), 7.68 ppm (m, ^4J(H,F) = 0.6 Hz, 6H; o-$C_6H_3(CF_3)_2$); ^{13}C NMR (100 MHz, CD_2Cl_2, 25°C): $\delta = 142.8$ (br s; *ipso*-$C_6H_3(CF_3)_2$), 138.5 (br s; o-$C_6H_3(CF_3)_2$), 132.2 (q, ^2J(C,F) = 33.7 Hz; m-$C_6H_3(CF_3)_2$), 127.1 (sept, ^3J(C,F) = 3.6 Hz; p-$C_6H_3(CF_3)_2$), 124.0 ppm (q, ^1J(C,F) = 273.9 Hz; CF_3); ^{19}F NMR (376 MHz, CD_2Cl_2, 25°C): $\delta = -63.3$ ppm; MS (EI): m/z (%): 650.05 (100); IR (Neat): $\tilde{\nu}$ = 1606, 1382, 1275, 1224, 1166, 1119, 984, 943, 907, 844, 731, 718, 707, 694, 681, 656 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_9BF_{18}$: C 44.34, H 1.40, N 0.00; found: C 44.55, H 1.52, N 0.00.

B(m-XyF$_6$)$_3$·THF adduct: ^{1}H NMR (300 MHz, [D$_8$]THF, 25°C): $\delta = 8.03$ (dt, ^4J(H,H) = 1.1 Hz, ^4J(H,F) = 0.6 Hz, 6H; o-$C_6H_3(CF_3)_2$), 7.91 ppm (sept, ^4J(H,F) = 0.8 Hz, 3H; p-$C_6H_3(CF_3)_2$); ^{13}C NMR (75 MHz, [D$_8$]THF, 25°C): $\delta = 150.4$ (br; *ipso*-$C_6H_3(CF_3)_2$), 134.4 (q, ^3J(C,F) = 2.1 Hz; o-$C_6H_3(CF_3)_2$), 131.6 (q, ^2J(C,F) = 32.2 Hz; m-$C_6H_3(CF_3)_2$), 125.0 (q, ^1J(C,F) =

Table 2. Crystallographic data.

	4a	**4b**·0.5 C_7H_8	**5**	**7**	**8**·C_6D_6
empirical formula	$C_{35}H_{29}BF_{18}N_2$	$C_{54.5}H_{49}BF_{18}N_2$	$C_{35}H_{29}BF_{18}N_2$	$C_{36}H_{29}BF_{18}N_2O_2$	$C_{49}H_{35}D_6BF_{18}N_2$
M_r	830.41	1084.77	830.41	874.42	1016.69
T [K]	100	100	100	100	100
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a [Å]	10.811(2)	13.9953(2)	9.7033(3)	14.0690(3)	18.4322(5)
b [Å]	10.936(2)	25.6426(4)	11.0871(3)	21.2587(5)	18.4691(5)
c [Å]	17.160(3)	15.4957(3)	18.6065(6)	12.6289(3)	28.2520(7)
α [°]	92.861(16)	90	77.753(3)	90	90
β [°]	107.395(18)	103.218(2)	84.421(3)	100.913(2)	95.376(3)
γ [°]	110.29(2)	90	70.698(3)	90	90
V [Å^3]	1788.9	5413.7	1845.40	3708.8	9575.4
Z	2	4	2	4	8
total reflns/$2\theta_{max}$	57140/50	186263/52.6	60680/56.4	149444/52.6	240670/50
unique reflns	6308	11062	8375	7577	16892
	(R_{int} = 0.155)	(R_{int} = 0.072)	(R_{int} = 0.034)	(R_{int} = 0.046)	(R_{int} = 0.077)
ρ_{calcd} [g cm^{-3}]	1.542	1.331	1.494	1.566	1.410
μ [mm^{-1}]	0.16	0.12	0.15	0.16	0.13
parameters/restraints	511/0	715/134	511/0	538/0	1355/96
$R(Fo)$, [$I > 2\sigma(I)$]	0.062	0.068	0.043	0.037	0.053
$R_w(Fo^2)$	0.173	0.167	0.099	0.087	0.140
GOF on F^2	1.08	1.11	1.03	1.02	1.03
$\Delta\rho$ [e Å^{-3}]	0.67/−0.50	0.49/−0.34	0.44/−0.36	0.51/−0.43	0.48/−0.47

272.5 Hz; CF_3), 121.6 ppm (sept, ^3J(C,F) = 3.8 Hz; *p*-$C_6H_3(CF_3)_2$); ^{11}B NMR (96 MHz, [D$_8$]THF, 25 °C): δ = 11.7 ppm.

B(*m*-XyF$_6$)$_3$·acetone adduct: ^{11}B NMR (96 MHz, [D$_6$]acetone, 25 °C): δ = 10.9 ppm (decomposition of the solution was observed within a few days).

Normal adduct 4a: To a mixture of B(*m*-XyF$_6$)$_3$ (2.350 g, 3.61 mmol, 1 equiv) and compound **1a** (0.651 g, 3.61 mmol, 1 equiv) was added toluene (30 mL) and the reaction was stirred for 24 h. *n*-Hexane (30 mL) was added to the reaction mixture and the precipitate was filtered off, washed with toluene/*n*-hexane (1:1), and dried in vacuo (2.410 g). A second crop of the product was obtained by keeping the combined filtrate in a freezer at −30 °C for a few days to afford complete precipitation of the product, which was filtered off, washed with toluene/*n*-hexane (1:1), and dried in vacuo (0.433 g). Yield: 2.841 g (95 %); white crystalline powder; ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ = 7.77 (br s, 6H; *o*-$C_6H_3(CF_3)_2$), 7.67 (sept, ^4J(H,F) = 0.8 Hz, 3H; *p*-$C_6H_3(CF_3)_2$), 1.60 ppm (s, 18H; *t*Bu; CH=CH protons were not observed because of fast deuteration by CD_3CN); ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 8.04 (br s, 6H; *o*-$C_6H_3(CF_3)_2$), 7.63 (br s, 3H; *p*-$C_6H_3(CF_3)_2$), 6.42 (s, 1H; CH=CH), 0.62 ppm (s, 18H; *t*Bu); ^{13}C NMR (75 MHz, CD_3CN, 25 °C): δ = 165.1 (NCN), 160.0 (br; *ipso*-$C_6H_3(CF_3)_2$), 134.6 (br s; *o*-$C_6H_3(CF_3)_2$), 130.0 (q, ^2J(C,F) = 31.6 Hz; *m*-$C_6H_3(CF_3)_2$), 125.7 (q, ^1J(C,F) = 271.7 Hz; CF_3), 120.9 (t, ^1J(D,C) = 30.0 Hz; CD=CD), 119.3 (sept, ^3J(C,F) = 3.9 Hz; *p*-$C_6H_3(CF_3)_2$), 61.2 ($C(CH_3)_3$), 29.8 ppm (CH_3); ^{11}B NMR (96 MHz, CD_3CN, 25 °C): δ = −4.8 ppm; ^{11}B NMR (96 MHz, C_6D_6, 25 °C): δ = −5.9 ppm; ^{19}F (188 MHz, C_6D_6, 25 °C): δ = −62.8 ppm; elemental analysis calcd (%) for $C_{35}H_{29}BF_{18}N_2$: C 50.62, H 3.52, N 3.37; found: C 50.29, H 3.68, N 3.36.

Normal adduct 4b: To a mixture of B(*m*-XyF$_6$)$_3$ (0.325 g, 0.5 mmol, 1 equiv) and compound **1b** (0.194 g, 0.5 mmol, 1 equiv) was added toluene (20 mL) and the reaction was stirred for 2 h. The mixture was concentrated to approximately 5 mL in vacuo and *n*-hexane (30 mL) was added. The resulting precipitate was filtered off, washed with toluene/*n*-hexane (1:10), and dried in vacuo. Yield: 0.461 g (89 %); white powder; ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.54 (br s, 3H; *p*-$C_6H_3(CF_3)_2$), 7.47 (br s, 6H; *o*-$C_6H_3(CF_3)_2$), 6.89 (t, ^3J(H,H) = 7.8 Hz, 2H; *p*Dipp), 6.60 (d, ^3J(H,H) = 8.0 Hz, 4H; *m*Dipp), 6.38 (s, 2H; CH=CH), 2.55 (br s, 4H; C*H*(CH$_3$)$_2$), 0.85 (d, ^3J(H,H) = 5.5 Hz, 12H; CH$_3$), 0.79 ppm (d, ^3J(H,H) = 6.6 Hz, 12H; CH$_3$); ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 145.0 (*ipso*-Dipp), 136.3 (br; *o*-$C_6H_3(CF_3)_2$), 135.2 (Dipp), 132.1 (Dipp), 129.7 (q, ^2J(C,F) = 32.2 Hz; *m*-$C_6H_3(CF_3)_2$), 126.6 (Dipp), 125.0 (CH=CH), 124.9 (q, ^1J(C,F) = 272.6 Hz; CF_3), 120.0 (sept, ^3J(C,F) = 4.2 Hz; *p*-$C_6H_3(CF_3)_2$), 29.4 (*i*Pr), 26.8(*i*Pr), 21.4 ppm (*i*Pr), the resonances for the *ipso*-$C_6H_3(CF_3)_2$ and NCN moieties were not detected; ^{11}B NMR (96 MHz, C_6D_6, 25 °C): δ = −8.0 ppm; ^{19}F (188 MHz, C_6D_6, 25 °C): δ = −62.2 ppm; elemental analysis calcd (%) for $C_{51}H_{45}BF_{18}N_2$: C 58.97, H 4.37, N 2.70; found: C 56.96, H 4.12, N 2.57.

Abnormal adduct 5: Compound **4a** (0.150 g, 0.18 mmol) was heated at reflux in toluene (5 mL) for 15 min and then slowly cooled to RT. The resulting large crystals of compound **5** were filtered off, washed with cold toluene, and dried in vacuo. Yield: 0.138 g (92 %); colourless crystals; ^{1}H NMR (300 MHz, [D$_6$]acetone, 25 °C): δ = 9.10 (d, ^4J(H,H) = 2.1 Hz, 1H; NCHN), 7.82 (br s, 6H; *o*-$C_6H_3(CF_3)_2$), 7.71 (sept, ^4J(H,F) = 0.8 Hz, 3H; *p*-$C_6H_3(CF_3)_2$), 6.84 (d, ^4J(H,H) = 1.9 Hz, 1H; CH=CH), 1.62 (s, 9H; *t*Bu), 1.28 ppm (s, 9H; *t*Bu); ^{13}C NMR (75 MHz, [D$_6$]acetone, 25 °C): δ = 160.5 (br; *ipso*-$C_6H_3(CF_3)_2$), 136.3 (br; *o*-$C_6H_3(CF_3)_2$), 130.2 (q, ^2J(C,F) = 31.6 Hz; *m*-$C_6H_3(CF_3)_2$), 126.9 (s; BC=*C*H), 125.4 (q, ^1J(C,F) = 272.0 Hz; *C*F$_3$), 119.0 (quin, ^3J(C,F) = 4.2 Hz; *p*-$C_6H_3(CF_3)_2$), 62.9 ($C(CH_3)_3$), 59.6 ($C(CH_3)_3$), 31.7 (CH_3), 29.6 ppm (CH_3), the resonance for the NCN moiety was not detected; ^{11}B NMR (96 MHz, [D$_6$]acetone, 25 °C): δ = −7.4 ppm; ^{19}F (188 MHz, [D$_6$]acetone, 25 °C): δ = −62.3 ppm; elemental analysis calcd (%) for $C_{35}H_{29}BF_{18}N_2$: C 50.62, H 3.52, N 3.37; found: C 50.37, H 3.41, N 3.43.

CO_2-activation product (7): A suspension of compound **4a** (0.100 g, 0.120 mmol) in benzene (10 mL) was stirred under CO_2 (1 atm) overnight. The resulting precipitate was filtered off and dried in vacuo. Yield 0.081 g (86 %); white powder; ^{1}H NMR (200 MHz, CD_2Cl_2, 25 °C): δ = 7.90 (br s, 6H; *o*-$C_6H_3(CF_3)_2$), 7.70 (br s, 3H; *p*-$C_6H_3(CF_3)_2$), 7.23 (s, 1H; CH=CH), 1.49 ppm (s, 18H; *t*Bu); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C): δ = 157.7 (CO_2), 154.3 (br; *ipso*-$C_6H_3(CF_3)_2$), 140.8 (NCN), 134.6 (br; *o*-$C_6H_3(CF_3)_2$), 130.0 (q, ^2J(C,F) = 31.9 Hz; *m*-$C_6H_3(CF_3)_2$), 125.1 (q, ^1J(C,F) = 272.6 Hz; CF_3), 120.0 (sept, ^3J(C,F) = 3.9 Hz; *p*-$C_6H_3(CF_3)_2$), 118.3 (CH=CH), 64.3 ($C(CH_3)_3$), 30.1 ppm (CH_3); ^{11}B NMR (96 MHz, CD_2Cl_2, 25 °C): δ = 4.7 ppm (br s); ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ = −62.9 ppm; elemental analysis calcd (%) for $C_{36}H_{30}BF_{18}N_2O_2$: C 49.39, H 3.45, N 3.20; found: C 50.14, H 3.48, N 3.06.

Phenylacetylene-activation product (8): Compound **4a** (0.150 g, 0.180 mmol, 1 equiv) was mixed with benzene (2 mL) and a solution of

phenylacetylene (0.019 g, 0.180 mmol, 1 equiv) in benzene (0.5 mL) was added. After stirring for 20 min, a yellow oil separated out and was recrystallized from hot benzene/CH_2Cl_2. The resulting large crystals were ground into a fine powder and dried in vacuo. Yield: 0.154 g (91%); white powder; ^{1}H NMR (300 MHz, C_6D_6+5% CD_2Cl_2, 25°C): δ = 8.29 (br s, 6H; *o*-$C_6H_3(CF_3)_2$), 7.62 (br s, 3H; *p*-$C_6H_3(CF_3)_2$), 7.46–7.39 (m, 2H; Ph), 7.35 (t, ^4J(H,H) = 1.9 Hz, 1H; NCHN), 7.08–6.94 (m, 3H; Ph), 6.37 (d, ^4J(H,H) = 1.8 Hz, 2H; CH=CH), 0.82 ppm (s, 18H; *t*Bu); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 7.95 (br s, 6H; *o*-$C_6H_3(CF_3)_2$), 7.87 (t, ^4J(H,H) = 1.7 Hz, 1H; NCHN), 7.54 (br s, 3H; *p*-$C_6H_3(CF_3)_2$), 7.47–7.43 (m, 2H; Ph), 7.28–7.18 (m, 3H; Ph), 7.00 (d, ^4J(H,H) = 1.7 Hz; CH=CH), 1.35 ppm (s, 18H; *t*Bu); ^{13}C NMR (75 MHz, C_6D_6+5% CD_2Cl_2, 25°C): δ = 135.0 (br; *o*-$C_6H_3(CF_3)_2$), 132.0 (NCN), 129.9 (q, ^2J(C,F) = 30.5 Hz; *m*-$C_6H_3(CF_3)_2$), 128.7(Ph), 127.0 (Ph), 124.9 (q, *J* = 271.9 Hz; CF_3), 120.5 (CH=CH), 118.5 (sept, ^3J(C,F) = 4.2 Hz; *p*-$C_6H_3(CF_3)_2$), 60.8 ($C(CH_3)_3$), 29.1 ppm (CH_3), the resonances for the *ipso*-$C_6H_3(CF_3)_2$ and C≡C moieties were not detected; ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 161.0 (br; *ipso*-$C_6H_3(CF_3)_2$), 134.0 (br; *o*-$C_6H_3(CF_3)_2$), 131.3 (NCN), 128.9 (q, ^2J(C,F) = 31.6 Hz; *m*-$C_6H_3(CF_3)_2$), 128.3(Ph), 128.2 (Ph), 127.8 (Ph), 127.6 (Ph), 124.7 (q, ^1J(C,F) = 272.6 Hz; CF_3), 120.4 (CH=CH), 117.8 (sept, ^3J(C,F) = 3.9 Hz; *p*-$C_6H_3(CF_3)_2$), 60.7 ($C(CH_3)_3$), 29.2 ppm (CH_3), the resonances for the C≡C moiety were not detected; ^{11}B NMR (96 MHz, C_6D_6+5% CD_2Cl_2, 25°C): δ = −8.9 ppm; ^{11}B NMR (96 MHz, $CDCl_3$, 25°C): δ = −11.9 ppm; ^{19}F (188 MHz, C_6D_6+5% CD_2Cl_2, 25°C): δ = −62.3 ppm; elemental analysis calcd (%) for $C_{43}H_{35}BF_{18}N_2$: C 55.38, H 3.78, N 3.00; found: C 56.24, H 3.98, N 2.69.

H_2-activation product 9·B(*m*-XyF_6)$_3$: A suspension of compound **4a** (0.100 g, 0.120 mmol) and B(*m*-XyF_6)$_3$ (0.078 g, 0.120 mmol, 1 equiv) in benzene (10 mL) was stirred under H_2 (1 atm) overnight. The resulting precipitate was filtered off, washed with CH_2Cl_2, and dried in vacuo. Yield 0.150 g (84%); white powder; ^{1}H NMR (300 MHz, [D$_8$]THF, 25°C): δ = 8.78 (t, ^4J(H,H) = 1.8 Hz, 1H; NCHN), 7.90 (d, ^4J(H,H) = 1.7 Hz, 2H; CH=CH), 7.87 (br s, 12H; *o*-$C_6H_3(CF_3)_2$), 7.68 (br s, 6H; *p*-$C_6H_3(CF_3)_2$), 3.75 (br m, 1H; B–H–B), 1.65 (s, 18H; *t*Bu); ^{13}C NMR (100 MHz, [D$_8$]THF, 25°C): δ = 135.0 (br; *o*-$C_6H_3(CF_3)_2$), 132.4 (NCN), 130.5 (q, ^2J(C,F) = 32.1 Hz; *m*-$C_6H_3(CF_3)_2$), 128.2 (br q, ^1J(C,F) = 272.7 Hz; CF_3), 127.9 (q, ^1J(C,F) = 272.7 Hz; CF_3), 121.7 (CH=CH), 120.2 (br s; *p*-$C_6H_3(CF_3)_2$) 61.4 ($C(CH_3)_3$), 29.7 ppm (CH_3), the resonance for the *ipso*-$C_6H_3(CF_3)_2$ moiety was not detected; ^{11}B NMR (96 MHz, [D$_8$]THF, 25°C): δ = −10.0 ppm (br; B–H–B); ^{19}F (188 MHz, [D$_8$]THF, 25°C): δ = −64.3 (br s), −64.6 ppm (s); MS (ESI(+), MeOH): *m*/*z* (%): 181.17 (100) I*t*BuH; MS (ESI(−), MeOH): *m*/*z* (%): 651.17 (100) H–B(*m*-XyF_6)$_3$, 681.17 (30) MeO–B(*m*-XyF_6)$_3$; elemental analysis calcd (%) for $C_{59}H_{40}B_2F_{36}N_2$: C 47.80, H 2.72, N 1.89; found: C 48.32, H 2.39, N 1.65.

9+[CH_3CN·B(*m*-XyF_6)$_3$]: ^{1}H NMR (300 MHz, CD_2Cl_2+1% MeCN, 25°C): δ = 8.28 (t, ^4J(H,H) = 1.8 Hz, 1H; NCHN), 7.74, 7.71, 7.69, 7.67, 7.89, 7.63, 7.57, 7.50 (8×br s, 18H; *o*-$C_6H_3(CF_3)_2$+*p*-$C_6H_3(CF_3)_2$), 7.42 (d, ^4J(H,H) = 1.7 Hz, 2H; CH=CH), 3.63 (q, ^1J(H,B) = 82.3 Hz, 1H; B–H), 1.97 (s, CH_3CN), 1.65 ppm (s, 18H; *t*Bu); ^{11}B NMR (96 MHz, CD_2Cl_2+1% MeCN, 25°C): δ = −4.8 (br; CH_3CN·B(*m*-XyF_6)$_3$), −8.7 ppm (d, ^1J(H,B) = 83.3 Hz; B–H).

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