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Synthesis of 2-(lutidinyl)organoboranes and their reactivities against dihydrogen and pinacol borane

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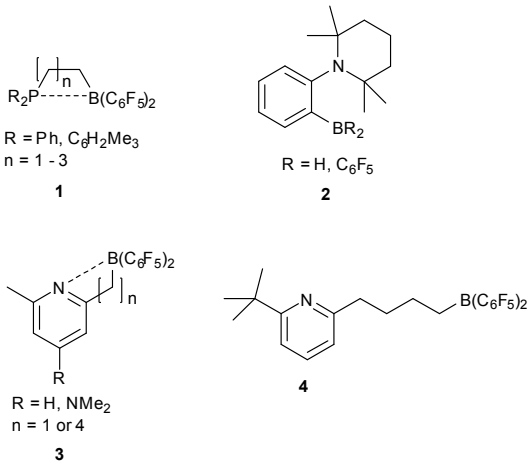
Two 2,4,6-tris(trifluoromethyl)phenyl-substituted 2-(lutidinyl)organoboranes (**5a** and **5b)** were prepared. These complexes can function as intramolecular vincinal B/N frustrated Lewis pairs to heterolytically activate dihydrogen. When these complexes were treated with HBpin, two different reaction pathways took place. Whereas the reaction between **5a** and HBpin affords a formal ligand-redistribution product, the reaction of **5b** with HBpin leads to a dearomative dehydroborylation product.

In recent years, the chemistry of "frustrated Lewis pair" (FLP) is receiving substantial attention.[1, 2] The unquenched Lewis acid and base centers in FLPs can cooperate in a synergistic manner to activate small molecules, such as H_2, CO_2 and alkenes. Intramolecular FLPs, exemplified by Erker's vicinal P/B FLPs (**1**)[3, 4] and Repo's "molecular tweezers" (**2**),[5] can substantially enhance the synergistic effects, thus leading to some remarkable reactivities (Scheme 1). Besides the phosphine and amine moieties, pyridine moieties were also introduced as the Lewis base components for intramolecular FLPs.[6-8] However, as pyridine can only provide limited steric protection for the Lewis base center, pyridine-based intramolecular FLPs often bears strong Lewis acid-base interaction. For example, very recently Mitzel et al. reported the synthesis of a series of intramolecular boron-pyridine Lewis pairs (**3** and **4**) (Scheme 1).[8] The complexes **3** contain strong B-N coordination and complex **4** shows no B-N interaction due to the large substitution at 2-position of pyridine. Although H/D-scrambling was observed when complex **4** was treated with H_2/D_2 mixture, none of these complexes showed reactivity against H_2, CO_2 and THF. We recently showed that the organoborane substituted with bulky Ar^F (Ar^F = 2,4,6-tris(trifluoromethyl)phenyl) ligands, Ar^F_2BMe, does not form Lewis adduct with pyridine.[9] We assumed that incorporation of Ar^F_2B moiety into the intramolecular pyridine-boron systems could lead to formation of vicinal N/B FLPs without strong B-N interactions. Such systems could show typical FLP reactivity against small molecules. Herein, we present the preparation of the Ar^F-substituted 2-(lutidinyl)organoboranes **5a** and **5b** and study of their reactivities against H_2 and HBpin.



Scheme 1

Results and discussion

Treating ((4-methyl-2-pyridyl)methyl)lithium with Ar^F_2BF can afford the target complex **5a** in 71% yield after recrystallization (Scheme 2). The ^{11}B NMR spectrum of **5a** displays a singlet at 3.57 ppm, within the range for a tetracoordinated boron, suggesting interaction between the boryl and pyridinyl moieties. Possible intermolecular B-N interaction in the solution of **5a** was excluded as addition a strong base DMAP into the solution of **5a** does not lead to any coordination of DMAP to **5a**. Single-crystal X-ray analysis revealed that the structure of **5a** contains a constrained four-membered ring (Figure 1). The distance between B and N atoms is 1.643 Å, shorter than that observed in 2,6-lutidine-$B(C_6F_5)_3$ adduct (1.661 Å), a intermolecular FLP which readily reacts with H_2 under ambient conditions.[10] The distance between the boron atom and the methylene carbon is 1.671 Å, comparable to the other two B-C bonds (1.657 and 1.671 Å). To increase the

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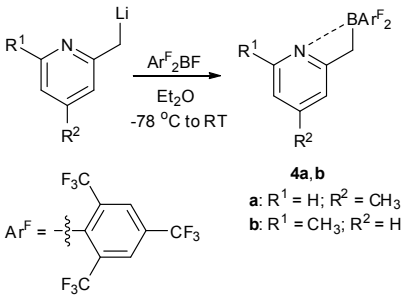
steric bulk around the N atom, we synthesized (6-methyl-2-pyridyl)methyl-substituted orgaoborane **5b** with a similar strategy and it can be isolated in 63% yield (Scheme 2). The ^{11}B NMR spectrum of **5b** reveals a singlet at 19.78 ppm which is in a lower field compared to **5a**, indicating weakened pyridine-borane coordination. This is corroborated by structure analysis (Figure 2). In the solid state of **5b,** the B-N distance of 1.661 Å is substantially longer than that of **5a**, suggesting a weakened B-N dative bond due to larger steric congestion. The distance between the boron atom and the methylene carbon of **5b** is 1.678 Å, comparable to that observed in **5a**.



Scheme 2

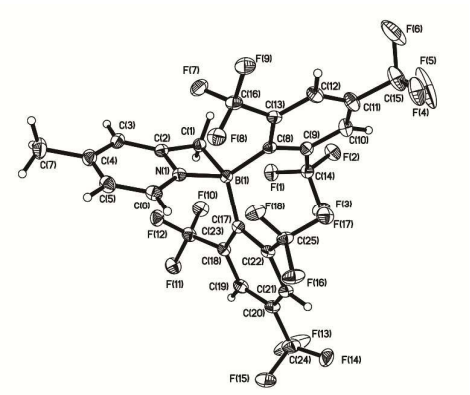


Fig. 1 Molecular structure of **5a** (thermal ellipsoids are shown with 30% probability). Selected bond length [Å] and angles [°]: N(1)–B(1) 1.643(3), N(1)–C(2) 1.346(3), C(2)–C(1) 1.490(3), C(1)–B(1) 1.671(3), N(1)–C(2)–C(1) 99.75(17), N(1)–B(1)–C(1) 81.81(14),C(2)–N(1)–B(1) 92.15(16), C(2)–C(1)–B(1) 86.13(16).

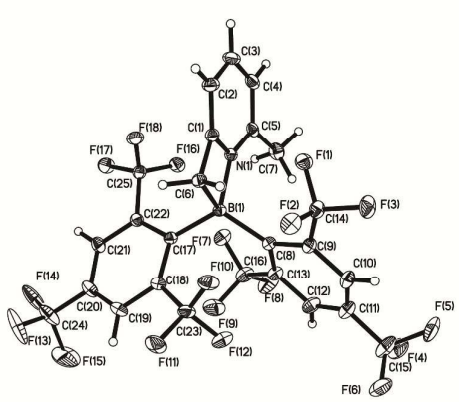
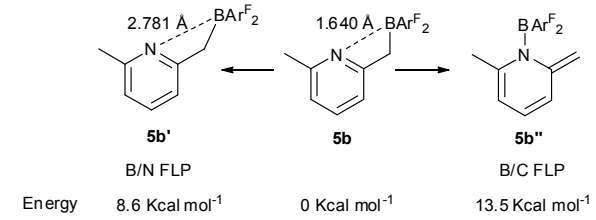


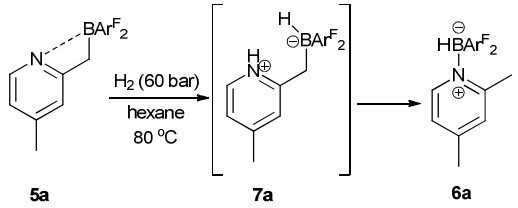
Fig. 2 Molecular structures of **5b** (thermal ellipsoids are shown with 30% probability). Selected bond length [Å] and angles [°]: N(1)–B(1) 1.661(2), N(1)–C(1) 1.353(2), C(6)–C(1) 1.487(2), C(6)–B(1) 1.678(2), N(1)–C(1)–C(6) 100.56(13), N(1)–B(1)–C(6) 81.79(11),C(1)–N(1)–B(1) 91.34(12), C(1)–C(6)–B(1) 86.19(12).

As both complexes **5a** and **5b** contain a highly strained 4-member ring, there are two ways to open this 4-member ring, which can lead to a B/N or B/C FLP. To examine which way is favoured, we carried out DFT (M06-2X) calculations to optimize the structure of **5b**, its B/N "open" isomer **5b'** and B/C "open" isomer **5b'** (Scheme 3). The optimized geometry of **5b** is close to that of determined by single crystal analysis. The B-N distance in the calculated structure of **5b** is 1.640 Å. In the B/N "open" isomer **5b'**, the B-N distance is increased to 2.781 Å and it is calculated to be 8.6 Kcal mol^{-1} less stable than **5b**. Similar values were also reported for Erker's vicinal P/B FLPs.[4a] On the other hand, the B/C "open" isomer **5b''** is 13.5 Kcal mol^{-1} less stable than **5b**, thus suggesting that complexes **5a** and **5b** are likely to function as B/N instead of B/C FLPs.



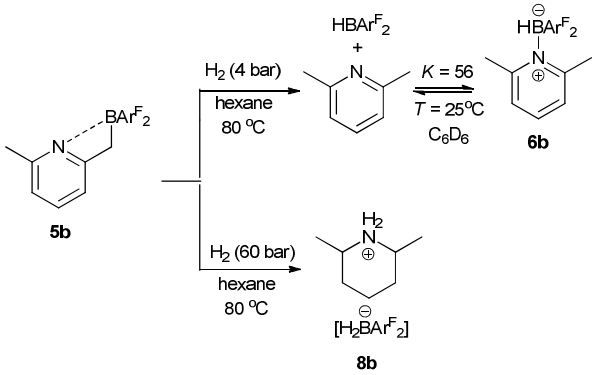
Scheme 3

Treatment of complex **5a** with H_2 (ca. 4 bar) in hexane at 25°C or 80°C led to no reaction. When the pressure of H_2 was increased to 60 bar, complex **5a** was quantitatively converted to 2,4-lutidine-HBAr$^F_2$ adduct **6a**, which can be subsequently isolated in 89% yield after workup (Scheme 4). Although we were not able to observe any intermediate during the formation of **6a**, we assume that complex **5a** activates H_2 to afford a zwitterionic complex **7a**, which then undergoes a proton transfer reaction to generate the protodeboronation product **6a**. In the solid state of **6a**, we observed a short B-N bond (1.617 Å), which could be the cause of the lack of reactivity of **6a** against H_2 even under harsh conditions.



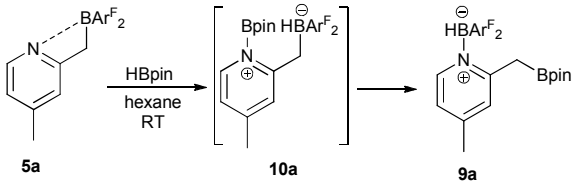
Scheme 4

When complex **5b** was exposed to H_2 (ca. 4 bar) in C_6D_6 at 80°C, quantitative conversion to an equilibrium mixture of $HBAr^F_2$ and 2,6-lutidine was observed (Scheme 5). The equilibrium constant between free $HBAr^F_2$/2,6-lutidine and their adduct **6b** in C_6D_6 is 56 at 298 K as determined by ^{1}H NMR analysis. In a larger scale reaction carried out in hexane, **6b** can be obtained in 81% yield. The increased reactivity of **5b** compared to **5a** is possibly due to the larger steric demand around the nitrogen atom in **5b**. The molecular structure of **6b** was determined and the B-N distance (1.643 Å) is longer than the one in **6a**. At higher pressure of H_2 (60 bar), complex **5b** was completely transformed to piperidinium dihydridoborate salt **8b** after stirring at 80 °C for 24 hours (Scheme 5). We believe that the original formed adduct **6b** undergoes further H_2 activation to yield the hydrogenation product **8b**. Similar $B(C_6F_5)_3$ mediated hydrogenation of pyridine derivatives was also observed by the groups of Stephan[11] and Du.[12] It is noteworthy that the related intermolecular FLPs comprised of Ar^F_2BMe and 2,4-lutidine or 2,6-lutidine showed no reactivity against H_2 (60 bar) at 80°C, highlighting the advantage of vincinal N/B pairs in H_2 activation.[14]



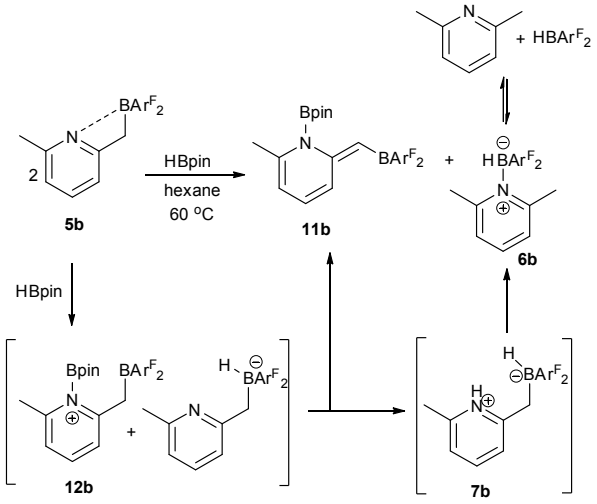
Scheme 5

Besides cleavage of H-H bond, B-H bond activation by FLPs has also attracted some attention. The groups of Stephan[15] and Crudden[16] reported HBcat or HBpin can be activated by phosphine/borane or amine/borane pairs, which has been successfully applied in borenium catalyzed imine hydroboration. Recently our group discovered that the FLP comprised of Ar^F_2BMe and pyridine can effectively activate HBpin which led to Ar^F_2BMe catalyzed pyridine 1,4-hydroboration.[9] We are interested to know if similar reaction mode can be observed for intramolecular B/N Lewis pairs **5a**,**b**. Addition of HBpin to the solution of **5a** in hexane resulted in the formation of **9a**, which can be obtained in 90% yield (Scheme 6). Complex **9a** was fully characterized by NMR spectroscopy, elemental analysis and single crystal X-ray analysis. We consider that the reaction of HBpin and **5b** could first produce intermediate **10a**. Then the highly-electrophilic borenium moiety of **10a** attacks the methylene group to afford 2-(borylmethyl)-4-methylpyridine and $HBAr^F_2$, which subsequently bind together to form **9a**.



Scheme 6

When 1 equiv of HBpin was added to the C_6D_6 solution of **5b**, surprisingly, we noticed slowly formation of a new complex **11b** with the concomitant formation of $HBAr^F_2$ and 2,6-lutidine. When the reaction temperature was increased to 60°C, complete consumption of **5b** was observed. Meanwhile, only o.5 equiv of HBpin was consumed. The molar ratio of formed $HBAr^F_2$ (both free and coordinated) and **11b** is around 1:1. In a larger scale carried out in hexane solution, we were able to isolate **11b** as an orange solid in 68% yield (Scheme 7). The ^{11}B NMR spectrum of **11b** displays two singlets at 22.6 and 44.5 ppm, indicating both the Ar^F_2B and Bpin moieties are likely three-coordinated. In the ^{1}H NMR of **11b**, no methylene signal was observed. Instead we found a singlet at 5.58 ppm which was assigned to a methine fragment. Furthermore, the signals from pyridine ring are upfield shifted to 6.11, 5.98 and 5.20 ppm, suggesting the pyridine ring has lost its aromaticity. The molecular structure of **11b** was determined by single-crystal X-ray analysis (Figure 3). Complex **11b** contains a deraomatizated pyridine ring. The distances of C2-C3 (1.401 Å) and C4-C5 (1.424 Å) are close to the value for a single bond. On the other hand, the bond lengths for C1-C2 (1.355 Å) and C3-C4 (1.354 Å) are in the range of a standard double bond. Interestingly, the exo-ring double bond C5-C6 (1.409 Å) is substantially longer than a typical double bond. This might be caused by electron charge transfer from the double bond to the adjacent boron atom. Indeed, we noticed that the bond of C6-B2 (1.463 Å) is significantly shorter than a typical C(sp^2)-B bond. The Ar^F_2B moiety is *anti* to the nitrogen atom of the lutidine moiety and the C5-C6-B2 angle is deviated from the ideal 120° due to the steric congestion. Right now the mechanism of formation of **11b** still remains elusive. We tentatively suggest that the initial coordination of **5b** to HBpin and a following intermolecular hydride abstraction by another **5b** could result in formation of a borenium species **12b**. With a more acidic methylene moiety,[17] **12b** can be deprotonated to form **11b** with the concomitant formation of **7b**, which can go though rearrangement to afford $HBAr^F_2$ and 2,6-lutidine.



Scheme 7

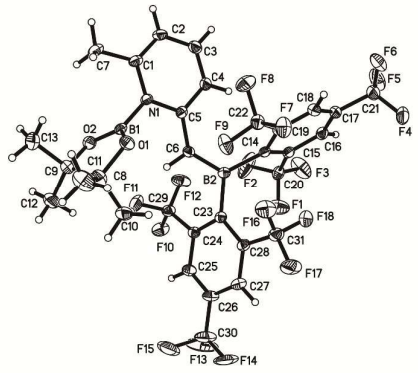


Fig. 3 Molecular structure of **11b** (thermal ellipsoids are shown with 30% probability).

Conclusions

In summary, we have prepared and characterized two 2-(lutidinyl)organoboranes **5a** and **5b**. Although interaction between the nitrogen of lutidine fragment and the boron atom was observed in both solution and sold state, these complexes can function as intramolecular FLP to heterolytically activate dihydrogen. Their reactivity against H_2 is strongly dependent on the steric bulk around the nitrogen atom. For less congested **5a**, hash condition (60 bar of H_2, 80°C) is required for efficient H_2 activation. For more congested **5b**, H_2 can be activated under much milder conditions (4 bar of H_2, 80°C). When complexes **5a** and **5b** were treated with HBpin, two different reaction pathways took place. Whereas the reaction between **5a** and HBpin affords a formal ligand-redistribution product **9a**, the reaction of **5b** with HBpin leads to a dearomative dehydroborylation product **11b**. Although dehydroborylation has been very well studied as a way of C-H functionalization,[18] such dearomative dehydroborylation, to the best of our knowledge, has not been reported before. This observation could potentially provide a new method for the dearomatization of pyridine derivatives. Efforts to elucidate the mechanism of this reaction are currently underway.

Experimental

Synthesis of complex 5a. A solution of ((4-methyl-2-pyridyl)methyl)lithium (0.569 g, 5.04 mmol) in Et_2O (15 mL) was added to the solution of Ar^F_2BF (2.69 g, 4.55 mmol) in Et_2O (20mL) at -70°C. The reaction mixture was warmed up to room temperature and stirred for 16h. Then the volatile was removed under vacuum. The resulting oil was extracted with hexane (55 mL). The hexane solution was concentrated to ~3 mL and stored at -40°C, affording a brown solid which was filtered and dried under vacuum to give complex **5a** (2.20 g, 71%). X-ray quality crystals were grown from hexane at -20°C. ^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 8.01 (s, 4H, C_6H_2), 7.66 (d, 1H, $^3J_{H-H}$ = 5.8 Hz, *H*6(py)), 6.42(s, 1H, *H*3(py)), 6.26 (d, 1H, $^3J_{H-H}$ = 5.8 Hz, *H*5(py)), 2.79 (s, 2H, CH_2), 1.64 (s, 3H, CH_3). ^{19}F NMR (376 MHz, C_6D_6): δ [ppm] = -55.34 (s, 12F, *ortho*-CF_3-C_6H_2), -63.33 (s, 6F, *para*- CF_3-C_6H_2). ^{13}C NMR (125 MHz, C_6D_6): δ [ppm] = 169.39 (*C*2(py)), 154.65 (*C*4(py)), 142.20 (*C*6(py)), 135.95 (q, $^2J_{C-F}$ = 34 Hz, *ortho*-C_6H_2), 129.50 (q, $^2J_{C-F}$ = 34 Hz, *para*-C_6H_2), 127.15 (*meta*-C_6H_2), 124.46 (q, $^1J_{C-F}$ = 275, *ortho*-CF_3), 124.11 (*C*3(py)), 123.72 (q, $^1J_{C-F}$ = 275 Hz, *para*-CF_3), 122.72 (*C*5(py)), 27.21 (br s, CH_2), 21.35 (CH_3), *ipso*-C_6H_2 not observed. ^{11}B NMR (160 MHz, C_6D_6): δ [ppm] = 3.57(s). Element analysis: calcd for $C_{25}H_{12}BF_{18}N$: C 44.21, H 1.78, N 2.06%; found C 44.36, H 1.91, N 2.04%.

Synthesis of complex 5b. A solution of ((6-methyl-2-pyridyl)methyl)lithium (0.391 g, 3.46 mmol) in Et_2O (20 mL) was added to the solution of Ar^F_2BF (1.70 g, 2.87 mmol) in Et_2O (15 mL) at -70°C. The reaction mixture was stirred at room temperature for 12 h. Then the volatile was removed under vacuum. The resulting oil was extracted with hexane (40 mL). The hexane solution was concentrated to ~5 mL and stored at -40°C, affording an orange solid which was filtered and dried under vacuum to give complex **5b** (1.22 g, 63%). X-ray quality crystals were grown from hexane at -20°C. ^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 8.04 (s, 4H, *meta*-C_6H_2), 6.89 (t, 1H, $^3J_{H-H}$ = 7.8 Hz, *H*4(py)), 6.47 (d, 1H, $^3J_{H-H}$ = 7.8 Hz, *H*3(py)), 6.20 (d, 1H, $^3J_{H-H}$ = 7.8 Hz, *H*5(py)), 2.84 (s, 2H, CH_2), 1.78 (s, 3H, CH_3). ^{19}F NMR (376 MHz, C_6D_6): δ [ppm] = -54.67 (s, 12F, *ortho*-CF_3-C_6H_2), -63.39 (s, 6F, *para*-CF_3-C_6H_2). ^{13}C NMR (125 MHz, C_6D_6): δ [ppm] = 167.19 (*C*2(py)), 156.04 (*C*6(py)), 151.74 (br, *ipso*-C_6H_2), 140.20 (*C*4(py)), 135.76 (q, $^2J_{C-F}$ = 34 Hz, *ortho*-C_6H_2), 130.29 (q, $^2J_{C-F}$ = 34 Hz, *para*-C_6H_2), 127.29 (*meta*-C_6H_2), 124.37 (q, $^1J_{C-F}$ = 275 Hz, *ortho*-CF_3), 123.52 (q, $^1J_{C-F}$ = 275 Hz, *para*-CF_3), 122.52 (*C*3(py)), 120.89 (*C*5(py)), 32.17 (br, CH_2), 20.14 (CH_3). ^{11}B NMR (160 MHz, C_6D_6): δ [ppm] = 19.78(s). Element analysis: calcd for $C_{25}H_{12}BF_{18}N$: C 44.21, H 1.78, N 2.06%; found C 44.40, H 1.98, N 1.98%.

Synthesis of complex 6a. A solution of complex **5a** (186 mg, 0.275 mmol) in hexane (2 mL) was placed in a Parr autoclave and subjected to 60 atm H_2. After stirred at 80°C for 18h, the

reaction mixture was taken out of the autoclave and dried under vacuum. The residue was redissolved in hexane (1 mL) and stored at -20°C, affording a brown solid which was filtered and dried under vacuum to give complex **6a** (162mg, 89%). X-ray quality crystals were grown from CH_2Cl_2 at -20°C. ^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 8.20 (br s, 4H, *meta*-C_6H_2), 7.47 (d, 1H, $^3J_{H-H}$ = 6.2 Hz, *H*6(py)), 6.20 (s, 1H, *H*3(py)), 5.99 (d, 1H, $^3J_{H-H}$ = 6.2 Hz, *H*5(py)), 5.24 (br s, 1H, B*H*), 2.11 (s, 3H, C2(py)-CH_3), 1.49 (s, 3H, C4(py)-CH_3). ^{19}F NMR (376 MHz, C_6D_6): δ [ppm] = -55.52 (br s, 3F, *ortho*-CF_3-C_6H_2), -56.58 (br s, 3F, *ortho*-CF_3-C_6H_2), -58.30, (br s, 3F, *ortho*-CF_3-C_6H_2), -58.74 (br s, 3F, *ortho*-CF_3-C_6H_2), -63.09 (s, 6F, *para*-CF_3-C_6H_2). ^{13}C NMR (125 MHz, C_6D_6): δ [ppm] = 159.34 (*C*6(py)), 155.61 (br, *ipso*-C_6H_2), 154.08 (*C*2(py)), 148.77 (*C*4(py)), 136.87 (br, *ortho*-C_6H_2), 129.54 (q, $^2J_{C-F}$ = 34 Hz, *para*-C_6H_2), 128.19 (*C*3(py)), 126.88 (meta-C_6H_2), 124.52 (q, $^1J_{C-F}$ = 275 Hz, ortho-*C*F_3), 123.82 (q, $^1J_{C-F}$ = 275 Hz, para-*C*F_3), 122.72 (*C*5(py)), 22.66 (C2(py)-*C*H_3), 20.42 (C4(py)-*C*H_3). ^{11}B NMR (160 MHz, C_6D_6): δ [ppm] = -7.01(s). Element analysis: calcd for $C_{25}H_{14}BF_{18}N$: C 44.08, H 2.07, N 2.06%; found C 44.04, H 2.45, N 1.79%.

Synthesis of complex 6b. A solution of complex **5b** (220 mg, 0.324 mmol) in hexane (3 mL) was degassed twice and backfilled with 4 atm H_2. After stirred at 80°C for 20 h, the reaction mixture was concentrated to ~1 mL and stored at -40°C overnight, affording a white solid which was filtered and dried under vacuum to give pure complex **6b** (176 mg, 81%). X-ray quality crystals were grown from hexane at -20°C. ^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 8.26(s, 1H, *meta*-C_6H_2), 8.17(s, 2H, *meta*-C_6H_2), 8.07(s, 1H, *meta*-C_6H_2), 6.66 (t, 1H, $^3J_{H-H}$ = 7.5 Hz, *H4*(py)), 6.24 (d, 1H, $^3J_{H-H}$ = 7.5 Hz, *H*3(py)), 6.13 (d, 1H, $^3J_{H-H}$ = 8 Hz,*H*5(py)), 5.27 (br s, 1H, B*H*), 2.08 (s, 3H, CH_3), 1.61 (s, 3H, CH_3). ^{19}F NMR (376 MHz, C_6D_6): δ [ppm] = -55.60 (q, J_{H-F} = 12Hz, 3F, *ortho*-CF_3-C_6H_2), -56.91 (q, 3F, J_{H-F} = 12Hz, *ortho*-CF_3-C_6H_2), -58.30(s, 3F, *ortho*-CF_3-C_6H_2), -58.95 (s, 3F, *ortho*-CF_3-C_6H_2), -63.02 (s, 3F, *para*-CF_3-C_6H_2), -63.09 (s, 3F, *para*-CF_3-C_6H_2). ^{11}B NMR (160 MHz, C_6D_6): δ [ppm] = -6.33(s). Element analysis: calcd for $C_{25}H_{14}BF_{18}N$: C 44.08, H 2.07, N 2.06%; found C 44.19, H 2.13, N 1.89%.

Synthesis of complex 8b. A solution of complex **5b** (232 mg, 0.343 mmol) in hexane (3 mL) placed in a Parr autoclave was subjected to 60 atm H_2. The reaction was stirred at 80°C for 24 h. The resulting hexane solution was concentrated to ~2 mL, affording a white solid which was filtered and dried under vacuum to give pure complex **8b** (163 mg, 71%). X-ray quality crystals were grown from CH_2Cl_2 at -20°C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ [ppm] = 7.95 (s, 4H, *meta*-C_6H_2), 4.27 (br s, 2H, NH_2), 3.32 (m, 2H, CH_2), 2.82 (q, 2H, $^1J_{B-H}$ = 78 Hz, BH_2), 2.00 (m, 2H, CH_2CH), 1.92 (m, 1H, C*H*), 1.59 (m, 1H, C*H*), 1.36 (m, 2H, CH_2CH), 1.30 (d, 6H, J_{H-H}=6.4 Hz, CH_3). ^{19}F NMR (376 MHz, CD_2Cl_2): δ [ppm] = -57.83 (s, 12F, *ortho*-CF_3-C_6H_2), -63.01 (s, 6F, *para*-CF_3-C_6H_2). ^{13}C NMR (125 MHz, CD_2Cl_2): δ [ppm] = 164.85 (br, *ipso*-C_6H_2), 136.53 (q, $^2J_{C-F}$ = 34 Hz, *ortho*-C_6H_2), 126.21 (q, $^2J_{C-F}$ = 34 Hz, *para*-C_6H_2), 125.50 (*meta*-C_6H_2), 125.45 (q, $^1J_{C-F}$ = 275 Hz, *ortho*-CF_3), 124.50 (q, $^1J_{C-F}$ = 275 Hz, *para*-CF_3), 56.57 ($CH_2CH_2CH_2$), 31.52 ($CH_2CH_2CH_2$), 22.60 (*C*HCH_3), 19.64 (CH*C*H_3). ^{11}B NMR (160 MHz, CD_2Cl_2) δ = -21.37 (t, $^1J_{B-H}$ = 83 Hz). Element analysis: calcd for $C_{25}H_{22}BF_{18}N$: C 43.57, H 3.22, N 2.03%; found C 43.57, H 3.30, N 2.09%.

Synthesis of complex 9a. Complex **5a** (154 mg, 0.228 mmol) was mixed with HBpin (32 mg, 0.25 mmol) in hexane (2 mL). A white precipitation appeared and the reaction mixture was stirred at room temperature for 4h. The resulting slurry was dried under vacuum, affording complex **9a** (166 mg, 90%) as a white solid. X-ray quality crystals were grown from hexane at -20°C. ^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 8.22 (br s, 4H, *meta*-C_6H_2), 7.47 (d, 1H, $^3J_{H-H}$ = 6.1 Hz, *H*6(py)), 6.87 (s, 1H, *H*3(py)), 6.00 (d, 1H, $^3J_{H-H}$ = 6.1 Hz, *H*5(py)), 5.27 (br s, 1H, B*H*), 2.68 (br s, 1H, CH_2), 2.29 (br s, 1H, CH_2), 1.53 (s, 3H, CH_3), 1.06 (s, 12H, CH_3). ^{19}F NMR (376 MHz, C_6D_6): δ [ppm] = -55.10 (br s, 3F, *ortho*-CF_3-C_6H_2), -56.42 (br s, 3F, *ortho*-CF_3-C_6H_2), -57.80, (br s, 3F, *ortho*-CF_3-C_6H_2), -58.12 (br s, 3F, *ortho*-CF_3-C_6H_2), -63.10 (s, 6F, *para*-CF_3-C_6H_2). ^{13}C NMR (125 MHz, C_6D_6): δ [ppm] = 161.56 (*C*2(py)), 155.74 (br, *ipso*-C_6H_2), 153.13 (*C*4(py)), 148.13 (*C*6(py)), 137.93 (q, $^2J_{C-F}$ = 34 Hz, *ortho*-C_6H_2), 129.44 (q, $^2J_{C-F}$ = 34 Hz, *para*-C_6H_2), 128.55 (*C*3(py)), 127.00 (*meta*-C_6H_2), 124.71 (q, $^1J_{C-F}$ = 275 Hz, *ortho*-CF_3), 123.89 (q, $^1J_{C-F}$ = 275 Hz, *para*-CF_3), 121.97 (*C*5(py)), 84.26 (*C*$(CH_3)_2$), 24.81(C(*C*$H_3)_2$), 21.88 (br s, *C*H_2), 20.49 (*C*H_3). ^{11}B NMR (160 MHz, C_6D_6): δ [ppm] = 32.16 (s, *B*pin), -6.50 (s, *B*Ar^F). Element analysis: calcd for $C_{31}H_{25}B_2F_{18}NO_2$: C 46.13, H 3.12, N 1.74%; found C 46.44, H 3.45, N 1.67%.

Synthesis of complex 11b. Complex **5b** (358 mg, 0.530 mmol) was mixed with HBpin (38 mg, 0.30 mmol) in hexane (5 mL). After stirred at 60°C for 10 h, the reaction mixture was dried under vacuum. The residue was sublimated at 80°C under vacuum to remove Ar$^F{}_2$BH. The remaining solid was dissolved in hexane (1 mL) and stored at -20°C overnight, affording an orange solid which was filtered and dried under vacuum to give pure complex **11b** (146 mg, 68%). X-ray quality crystals were grown from the mixture of hexane and toluene at -20°C. ^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 8.35(s, 1H, *meta*-C_6H_2), 8.17(s, 2H, *meta*-C_6H_2), 7.98(s, 1H, *meta*-C_6H_2), 6.11 (d, 1H, $^3J_{H-H}$= 6.9 Hz, C*H*CCH), 5.98 (t, 1H, $^3J_{H-H}$ = 6.9 Hz, CHC*H*CH), 5.58 (s, 1H, BC*H*), 5.20 (d, 1H, $^3J_{H-H}$ = 6.9 Hz, C*H*CCH_3), 1.58 (s, 3H, CH_3), 0.86 (s, 12H, C(C$H_3)_2$). ^{19}F NMR (376 MHz, C_6D_6): δ [ppm] = -50.23 (br s, 3F, *ortho*-CF_3-C_6H_2), -53.69 (br s, 3F, *ortho*-CF_3-C_6H_2), -56.08, (br s, 3F, *ortho*-CF_3-C_6H_2), -59.24 (br s, 3F, *ortho*-CF_3-C_6H_2), -62.98 (s, 3F, *para*-CF_3-C_6H_2), -63.20 (s, 3F, *para*-CF_3-C_6H_2). ^{13}C NMR (125 MHz, C_6D_6): δ [ppm] = 164.17 (CH*C*CH), 146.77 (CH*C*CH$_3$), 137.65 (CH*C*HCH),130.73 (q, $^2J_{C-F}$ = 34 Hz, *ortho*-C_6H_2), 129.94 (q, $^2J_{C-F}$ = 34 Hz, *para*-C_6H_2), 125.37 (*meta*-C_6H_2), 125.28 (q, $^1J_{C-F}$ = 275 Hz, *ortho*-CF_3), 122.42 (*C*HCCH), 112.20 (*C*HCCH$_3$), 110.21 (B*C*H), 86.49 (*C*$(CH_3)_2$), 24.27 (C(*C*$H_3)_2$), 19.91 (*C*H_3). ^{11}B NMR (160 MHz, C_6D_6): δ [ppm] = 26.59 (s, *B*pin), 44.53 (s, *B*Ar^F). Element analysis: calcd for $C_{31}H_{23}B_2F_{18}NO_2$: C 46.25, H 2.88, N 1.74%; found C 46.13, H 2.96, N 1.51%.

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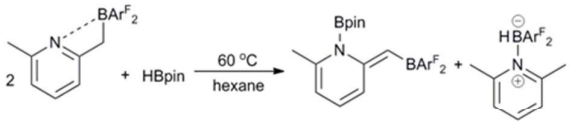

Dearomative dehydroborylation

Ar^F = 2,4,6-tris(trifluoromethyl)phenyl

The reactivity of two 2,4,6-tris(trifluoromethyl)phenyl-substituted 2-(lutidinyl)organoboranes as intramolecular frustrated Lewis pairs was investigated.