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Intramolecular pyridine-based frustrated Lewis-pairs

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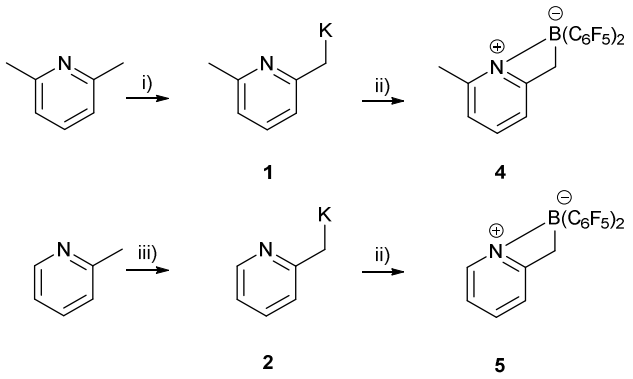
Deprotonation of the methylpyridines 2,6-lutidine, 2-picoline, 4-dimethylamino-2,6-dimethyl-pyridine as well as 2,6-dimethyl-4-(piperidine-1-yl)pyridine with *n*-butyllithium or *n*-butyl-lithium/KO-*t*-Bu at the methyl positions led to the corresponding organolithium or -potassium compounds. Treatment with $ClB(C_6F_5)_2$ resulted in formation of the 2-borylmethylpyridines py-CH_2-$B(C_6F_5)_2$. They are monomeric and form intramolecular B–N bonds and four-membered rings. A short intramolecular B–N distance was observed in the crystal structure of the dimethylamino-functionalized derivative and proposed to be responsible for the low reactivity of the products towards hydrogen, thf, acetonitrile and CO_2. Hydroboration of 6-*tert*-butyl-2-but-4'-enylpyridine with $HB(C_6F_5)_2$ led to the corresponding hydroboration product *t*-Bu-py-$(CH_2)_4$-$B(C_6F_5)_2$ which shows no intramolecular B–N bond formation due to steric crowding. H/D-scrambling experiments with a H_2/D_2 mixture revealed its reactivity towards hydrogen.

Introduction

Frustrated Lewis pairs (FLPs) are systems for which the conventional adduct formation between a Lewis acid and base is precluded by either steric demands or ring strain. This former textbook phenomenon began to attract enormous interest after Stephan and co-workers discovered the extraordinary reactivity of such systems. They have shown that combinations of sterically encumbered phosphanes and electron-poor boranes are able to activate hydrogen and other small molecules.[1,2] Furthermore, hydrogen can be cleaved reversibly, bound and liberated at elevated temperatures and used for catalytic reductions of sterically demanding imines.[3] Since then, a variety of frustrated Lewis pairs has been discovered. Besides the initially reported intra-[1,3,4] and intermolecular[2] boron-phosphorus frustrated Lewis pairs, such based on boron/NHC,[5] aluminium/phosphorus[6] and some zinc-based FLP systems (including combinations Zn/P, Zn/NHC, and $Zn/R_2P{=}C{=}PR_2$)[7] as well as silicenium-based ones[8] have been studied. Shortly after the discovery of frustrated Lewis pairs, the concept was applied to nitrogen Lewis bases and it has been shown that inter[9]- and intramolecular[10–12] boron-nitrogen FLPs are capable of hydrogen cleavage in a heterolytic manner and can be used in catalytic reductions of sterically less demanding imines and enamines. sp^2-Hybridised nitrogen has been used in intermolecular frustrated Lewis pairs in a combination of 2,6-lutidine and tris-(pentafluorophenyl)borane. This is capable of reversible hydrogen cleavage.[13] Bourissou and co-workers[14] as well as Son and Hoefelmeyer[15] have reported the synthesis of a series of 2-(picolyl)boranes, 2-(picolyl)-BR_2 [R = Cy, Et, Ph, BR_2 = 9-borafluorenyl, 9-borabicyclononane (9-BBN)]. The dimeric compounds show nucleophilic 1,2-addition (carboboration) to nitriles, aldehydes, ketones and amides. Son and Hoefelmeyer have proposed a Lewis base induced formation of a *N*-boronium stabilized 2-picolyl anion by a dissociation of the B–C(benzylic) bond as the initial step of the reaction. The reaction rate of the 1,2-addition has been calculated to be faster with less electron-withdrawing ability of the organic groups attached to boron. Strongly electron-withdrawing groups at the boron atom might therefore prevent the 1,2-addition reaction and make these systems bifunctional catalysts in the activation of polar unsaturated bonds. Hence, we synthesized intramolecular pyridine-boron Lewis pairs by deprotonating 2-methylpyridines followed by borylation with bis(pentafluorophenyl)chloroborane. Furthermore, the basicity and acidity of the reacting Lewis functions, as well as the common steric demand have a strong influence on the reactivity of frustrated Lewis pairs towards hydrogen and other small molecules.[2,11,16] For this reason, we studied the effect of a varied basicity of the pyridine nitrogen by introducing +M substituents in *para*-position of the aromatic backbone.

Results and discussion

Metallated lutidine **1** as well as metallated picoline **2** were prepared in 98% and 63% yield by deprotonation of 2,6-lutidine or 2-picoline with KO-*t*-Bu and *n*-butyllithium neat or in *n*-hexane (Scheme 1).[17]



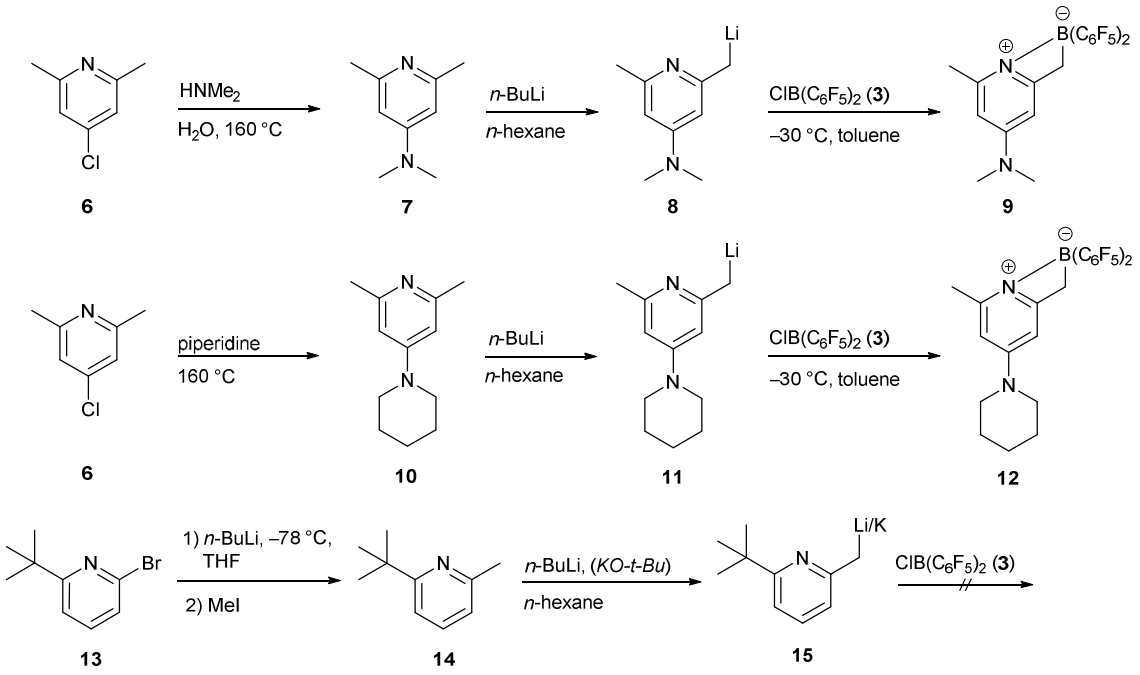
Scheme 1: Synthesis of four-membered ring boron-pyridine Lewis pairs. Deprotonation of methyl pyridines followed by the reaction with chloroborane **3** yields the Lewis pairs **4** and **5** selectively. Conditions: i) KO-*t*-Bu, *n*-BuLi, neat; ii) $ClB(C_6F_5)_2$, −30 °C, toluene; iii) KO-*t*-Bu, *n*-BuLi, *n*-hexane.

The resulting solids, yellow **1** and orange **2**, were characterized by solution NMR spectroscopy. The corresponding lithium compounds were synthesised as well and show different chemical shifts of the CH_2 groups attached to the alkali metal. Further, the absence of lithium was confirmed by the absence of resonances in the ^{7}Li NMR spectra of **1** and **2**. The reactions of potassium compounds **1** and **2** with bis(pentafluorophenyl)-chloroborane (**3**) in toluene at −30 °C yielded the Lewis pair **4** as a slightly yellow, as well as **5** as an orange solid. The products were identified by NMR spectroscopy, high resolution mass spectrometry as well as by CHN elemental analyses. The ^{11}B NMR spectra indicate four-coordinate boron atoms with a ^{11}B NMR chemical shift of −0.75 ppm for **4** and −0.77 ppm for **5**, respectively. The small difference between the ^{19}F NMR chemical shifts of the *para*- and *meta*-fluorine atoms confirms boron to be four-coordinate.[18] The ^{19}F NMR spectrum shows only one set of signals for the two C_6F_5 rings and the ^{1}H NMR spectrum contains one signal for the bridging CH_2 group, which indicates a monomeric structure in solution. Comparable 2-picolylboranes, with organic groups of comparable size attached to the boron, e.g. phenyl groups, are found to adopt a dimeric 8-membered ring structure in solution. This was demonstrated by the detection of diastereotopic protons of the bridging CH_2 groups as well as of the organic groups attached to boron.[15] An attempt to determine the crystal structure of **4** was hampered by structural disorder within the crystals. The limited quality of the resulting structure determination does not allow discussing structural parameters. Anyhow, **4** has a four-coordinated boron atom in the solid state, with intramolecular coordination of nitrogen to boron. The monomeric structures in the solid state as well as in solution are therefore in contrast to the dimeric structures observed.[15] To prevent disorder in the crystal, Lewis pair **5** was synthesized, but so far no suitable crystals for X-ray diffraction experiments were obtained.

Treatment of Lewis pair **4** with hydrogen, acetonitrile as well as carbon dioxide resulted in no observable reactions. Furthermore Lewis pair **4** did also not show reactivity in H/D-scrambling experiments when exposing a solution in CD_2Cl_2 to a H_2/D_2 mixture revealing the absence of typical FLP activity.[19] A 1,2-carboboration reaction, as it was found for the less electron-poor picolyl-boranes, was also not observed; this agrees with earlier theoretical descripttions.[15]

In order to achieve FLP activity, we tried to enhance the reactivity of the system by introducing +M substituents in *para*-position of the aromatic ring to afford a higher basicity of the pyridine nitrogen site. Repo and co-workers showed that the introduction of a more basic dimethylamino group in the system R_2N-C_6H_4-$B(C_6F_5)_2$ leads to FLP activity.[11] By contrast, the less basic diphenylamino derivative is not capable of heterolytic hydrogen splitting.[20] Moreover, the steric demand at the pyridine nitrogen atom was enhanced by introducing *tert*-butyl groups in *ortho*-position. The required aminolutidines **7** and **10** were synthesized by nucleophilic substitution of the chlorine functions of 4-chloro-2,6-dimethylpyridine (**6**) with aqueous dimethyl amine solution or, alternatively, in a solvent-free transformation with piperidine at 160 °C (Scheme 2).

Compounds **7** and **10** were characterized by NMR spectroscopy, high resolution mass spectrometry as well as CHN elemental analyses. Deprotonation with *n*-butyllithium in *n*-hexane afforded organolithium compounds **8** and **11** in 72% and 87% yield, respectively. Their reactions with chloroborane **3** in toluene at −30 °C proceeded with high selectivity. The previously described deprotonation of the methyl pyridines **7** and **10** with KO-*t*-Bu and *n*-butyllithium was also tried, but the obtained organopotassium compounds turned out to be less selective in the reaction with chloroborane **3**. The lithium compounds where characterized by multinuclear NMR spectroscopy, the Lewis pairs **9** and **12** by NMR spectroscopy as well as high resolution mass spectrometry. The NMR spectra again reveal a fourfold-coordinate boron atom. The ^{11}B NMR chemical shifts of **9** (−2.27 ppm) and **12** (−2.43 ppm) indicate stronger boron-nitrogen bonds due to higher Lewis basicity of the nitrogen atom caused by the amino +M substituents in *para*-position of the aromatic ring. The crystal structure of Lewis pair **9** was determined and is depicted in Figure 1. The structure reveals a strong and thereby short boron-nitrogen bond [1.607(2) Å]. This strong bond causes small angles about the aromatic carbon atom C(1) with ∢[N(1)–C(1)–C(7)] = 98.6(1)° and about the methylene group C(7) ∢[C(1)–C(7)–B(1)] = 85.2(1)°. Compared to the literature-known intramolecular frustrated Lewis pairs with aromatic[11] and aliphatic[12] backbones with B–N distances of 1.719(3) Å and 1.771(3) Å, respectively, Lewis pair **9** shows an extremely short boron-nitrogen bond (Figure 1, right). The B–N distance in Lewis pair **9** is as long as that in the adduct of 4-(dimethylamino)pyridine with tris(pentafluorophenyl)borane. In contrast to **9**, the latter contains the stronger Lewis acid and does not have to overcome ring strain during formation. Intramolecular bonding is obviously favoured over



Scheme 2: Synthesis of the four-membered ring boron-pyridine Lewis pairs with +M-substituent in *para*-position.

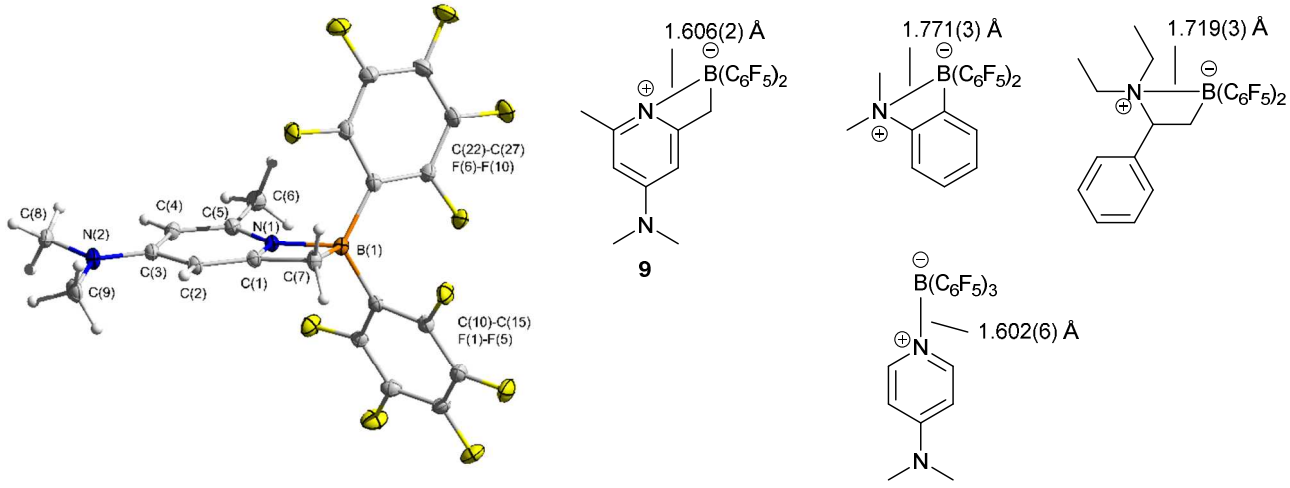


Figure 1: Left: Crystal structure of dimethylamino substituted Lewis pairs **9** (displacement ellipsoids drawn at 50% probability level). Right: Comparison of the boron-nitrogen distances in the crystal structures of literature-known active frustrated Lewis pairs[11,12,21] and Lewis pair **9**. Selected bond length [Å] and angles [°]: N(1)–B(1) 1.607(2), N(1)–C(1) 1.360(2), C(1)–C(7) 1.507(2), C(7)–B(1) 1.679(2), N(1)–C(1)–C(7) 98.6(1), C(1)–C(7)–B(1) 85.2(1), C(7)–B(1)–N(1) 82.9(1), B(1)–N(1)–C(1) 93.1(1).

an intermolecular B–N bonding, e.g. with either the terminal dimethylamino group or in a possible dimeric or polymeric form, all without necessity to overcome ring strain. The introduction of a sterically more demanding *t*-butyl group in *ortho*-position did not yield the desired product. Deprotonation of 2-*tert*-butyl-6-methylpyridine (**14**) either with *n*-butyllithium in *n*-hexane or in combination with KO-*t*-Bu and the following reaction of the organolithium and -potassium compounds with chloroborane **3** afforded product mixtures that could not be separated (Scheme 2).

Treatment of Lewis pairs **9** and **12** with an atmosphere of hydrogen as well as that of **12** with acetonitrile, tetrahydrofuran and carbon dioxide did not result in reactions typical for frustrated Lewis pairs. Furthermore Lewis pair **9** did also not show reactivity in H/D-scrambling experiments.[19] This characteristic is attributed to the short and consequently strong boron-nitrogen bond found in the crystal structure of the dimethylamino functionalized Lewis pairs **9**. The typical reactivity of frustrated Lewis pairs would require a weaker coordination between the acid and the base.

Table 1: Calculated relative energies ΔE (open – closed) in kcal mol^{-1} and B–N distances (in Å) of the closed form of several pyridines with spacer-bound $B(C_6F_5)_2$ groups in position 2 and further substituents in positions 6 and 4.

pyridine substituents		ΔE	r_e(B–N)
2-CH_2-$B(C_6F_5)_2$	6-Me	15.0	1.623
	6-Me-4-NMe_2	17.8	1.610
	6-Me-4-Pip	17.3	1.611
2-$(CH_2)_2$-$B(C_6F_5)_2$	6-Me	32.5	1.622
	6-Me-4-NMe_2	36.7	1.608
	6-*t*-Bu	19.9	1.665
2-$(CH_2)_3$-$B(C_6F_5)_2$	6-Me	23.1	1.635
	6-*t*-Bu	10.9	1.674
2-$(CH_2)_4$-$B(C_6F_5)_2$	6-Me	11.4	1.654
	6-*t*-Bu	–2.8	1.694

Considering what is necessary to weaken the strong bond of the pyridine nitrogen to the Lewis acid we undertook DFT calculations [PBE0-D3/6-31G(d,p)]. The elongation of the alkyl spacer in Py-$(CH_2)_n$-$B(C_6F_5)_2$ (Py = 6-R,4-R'-pyridin-2-yl, with R = Me, *t*-Bu, R' = H, NMe_2, Pip) in combination with the introduction of a sterically demanding group in pyridine-position 6 next to the Lewis base site was expected to result in a frustrated Lewis pair. Starting from n = 1 in the substituent $(CH_2)_n$-$B(C_6F_5)_2$ both conformers, B–N bonded (closed form) and B–N non-bonded (open form) were found and optimised. In most cases the closed form was predicted to be more stable than the open form. First, from n = 1 to n = 2, the relative stability of the closed form reaches a maximum (see Table 1). With further increasing n the relative stability of the closed form became lower while the B–N bond lengthened. Introduction of a *t*-Bu instead of a Me group in position 6 significantly decreases the stability of the closed form and forces further elongation of the B–N bond. In comparison to this effect the influence of substituents in position 4 is negligible. Finally, at n = 4 and with a *t*-Bu group in position 6 the open form becomes 2.8 kcal mol^{-1} more stable than the closed one. Taking entropy into account makes it even more stable with $\Delta G°_{298.15}$ = 8.3 kcal mol^{-1}. An additional stabilising effect in this open form arises probably from π-π stacking, which was geometrically identified in the optimised structure (Figure 2).

Therefore, the calculations predicted the hydroboration of a 6-but-3'-enyl-2-*tert*-butylpyridine (**18**) to yield the frustrated Lewis pair **21**, where the steric repulsion between the $B(C_6F_5)_2$ groups and the *t*-butyl group in **21** inhibits the coordination of the Lewis base to boron. The corresponding methyl pyridines, with less steric crowding next to the pyridine nitrogen atom, were predicted to form the closed seven-membered ring structures and were synthesised for comparison (Scheme 3).

Deprotonation of 2,6-lutidine as well as methyl pyridines **7** and **14** with *n*-butyllithium in diethyl ether and treatment with allyl bromide yielded the but-4'-enylpyridines **16**, **17** and **18**. The products were purified by either distillation or column chromatography and characterized by NMR spectroscopy, high resolution mass spectrometry and CHN elemental analyses. Hydroboration of the terminal olefin functions with Piers' borane **3** in toluene at 120 °C selectively yielded the hydroboration products **19**, **20** and **21**. The products where characterized by multinuclear NMR spectroscopy, high resolution mass spectrometry as well as CHN elemental analyses. Both compounds **19** and **20** show a small separation of the ^{19}F resonances of *para*- and *meta*-fluorine atoms. This and ^{11}B resonances at 0.11 and −2.16 ppm indicate the boron atoms to be four-coordinate. The molecular structure of **19** in the crystal was determined and is depicted in Figure 3. It shows a structural disorder of N(1) and C(1) to C(10) over two positions in a ratio of 55:45. Structure **19a** (Figure 3, ellipsoid model) shows a chair conformation of the seven-membered ring, structure **19b** (Figure 3, wire-model) shows a twist conformation. The B–N distances (**19a**: 1.66(1) Å, **19b**: 1.65(2) Å) are within the range of pyridine perfluoroarylboron adducts with comparable steric demand.[13,22]

The reaction of the *t*-butyl substituted pyridine **18** with Piers' borane yielded the hydroboration product **21** as colourless oil (Scheme 3). Its ^{11}B NMR spectrum shows a typical resonance for a threefold-coordinate boron atom at 74.8 ppm, in agreement with the quantum-chemical calculations discussed above. Therefore, the B–N bond formation could be precluded by the combination of more steric demand of the *t*-butyl group and the elongation of the alkyl spacer. The frustrated Lewis pair **21** was again treated with an atmosphere of hydrogen and carbon dioxide, but under these conditions showed no reaction. In order to test the reactivity against molecular hydrogen, degassed solutions of Lewis pairs **19** and **20** as well as of FLP **21** in CD_2Cl_2 were exposed to an atmosphere of a 1:1 mixture of hydrogen and deuterium. For compound **19** and **20**, with fourfold coordinate boron, no reaction was observed. However, for FLP **21** the formation of deuterium hydride, HD, was observed by the characteristic 1:1:1 triplet at 4.57 ppm with a $^1J_{D,H}$ = 42.6 Hz coupling constant in the ^{1}H NMR spectrum. Due to steric demand of the *tert*-Butyl group the B-N bond formation was precluded successfully and FLP-reactivity was achieved by rational design.

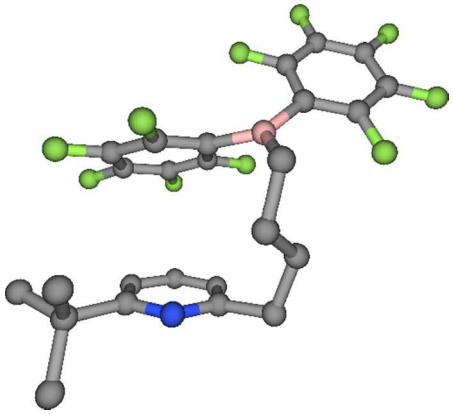
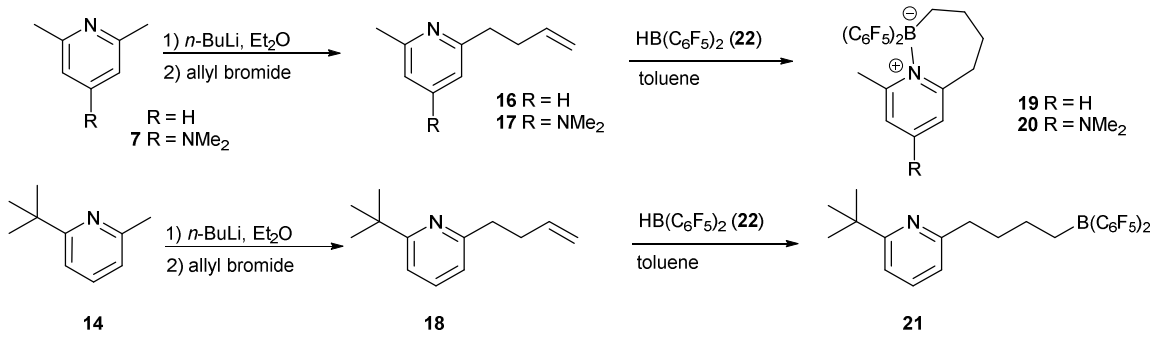


Figure 2: Optimized structure [PBE0-D3/6-31G(d,p)] of the open form of **21** [2-$(CH_2)_4$-$B(C_6F_5)_2$,6-*t*Bu-pyridine]. Hydrogen atoms are omitted for clarity.



Scheme 3: Syntheses of intramolecular Lewis pairs **19** and **20** as well as the frustrated Lewis pair **21** by hydroboration of the respective olefins **16**, **17** and **18**.

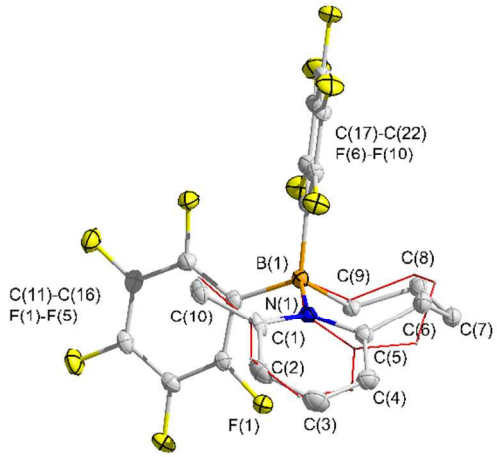


Figure 3: Molecular structure of Lewis pair **19** in the crystal. Hydrogen atoms are omitted for clarity. Due to structural disorder two different conformers where found in a ratio of 55:45. The structure presented as an ellipsoid model (drawn at 50% probability level) for the majority chair conformation **19a** (site occupation 55%), the part represented as a wire-model the minority twist conformation **19b** (site occupation 45%). Selected bond length [Å] and angles [°] for the majority chair conformation **19a**: N(1)–B(1) 1.66(1), N(1)–C(5) 1.38(1), N(1)–C(1) 1.363(8), C(5)–C(6) 1.517(5), C(9)–B(1) 1.68(2), B(1)–N(1)–C(1) 122.2(8), B(1)–N(1)–C(5) 121.4(7), N(1)–C(5)–C(6) 120.5(9), C(9)–B(1)–N(1) 108.7(8).

Conclusion

Reactions of metallated methylpyridines (**1**, **2**, **8** and **11**) with bis(pentafluorophenyl)chloroborane afforded intramolecular four-membered ring B/N Lewis pairs (**4**, **5**, **9** and **12**). ^{19}F and ^{11}B NMR confirm the presence of monomeric structures in solution, and a crystal structure determination of **9** (*p*-Me_2N-*o*-Me-*o*-[$CH_2B(C_6F_5)_2$]-C_6H_2N) reveals a monomeric structure in the solid state. This is in contrast to previously observed dimeric boryl-2-methylpyridines with boron-substituents of comparable size (solution and solid). Despite the obvious presence of ring strain the new compounds form strong intramolecular B–N bonds (the B–N bond length in **9** is 1.602 Å). These are the likely reason for the absence of typical frustrated Lewis-pair-type reactivity: Lewis pairs **4**, **9** and **12** proofed to be unreactive towards hydrogen and **4** and **12** towards carbon dioxide, acetonitrile as well as towards H_2/D_2 mixtures in scrambling experiments.

Attempts to weaken the B–N coordination by placing sterically demanding *tert*-butyl groups next to the pyridine nitrogen were unsuccessful; reactions of the corresponding metallated pyridines with $ClB(C_6F_5)_2$ were unselective. Quantum-chemical calculations predicted longer alkyl-spacers between pyridine and boron function to afford frustrated Lewis pairs with no B–N bond if such bulky pyridine-substituents in *ortho*-position were present. Indeed, the *o*-methyl **18** and *p*-dimethylamino functionalized derivatives **19** show intramolecular B–N bonds, whereas the *o*-*tert*-butyl derivative **21** does not. The obtained frustrated Lewis-pair **21** showed no quantitative addition of hydrogen or carbon dioxide, however H/D-scrambling was observed upon treatment with an atmosphere of a 1:1 mixture of H_2 and D_2 (formation of HD)

In essence, this demonstrates the complex interplay of steric, ring strain and electronic factors in the formation of intramolecular Lewis acid-base adducts – one of the aspects needed for the rational design of new frustrated Lewis-pairs.

Experimental

All operations with air and moisture sensitive compounds were performed under conventional Schlenk technique or in a glovebox. Volatile compounds were handled in a vacuum line. Toluene and tetrahydrofuran were dried over potassium, *n*-hexane, *n*-pentane and diethyl ether over $LiAlH_4$ and distilled prior to use. C_6D_6 and thf-d8 were dried over Na/K alloy, $CDCl_3$ and CD_2Cl_2 over CaH_2. Workup and column chromatography were performed with technical grade solvents. 2,6-Lutidine was purchased from Merck, 2-picoline from Sigma-Aldrich, allyl bromide from Acros Organics, piperidine from Sigma-Aldrich and dimethylamine solution from BASF. Chlorobis(pentafluorophenyl)borane (**3**),[23] bis(pentafluorophenyl)borane (**22**),[24] 4-chloro-2,6-dimethylpyridine (**6**)[25] and 2-bromo-6-*tert*-butylpyridine (**13**)[26] were prepared as described in literature. Column chromatography was performed on silica gel 60 (0.04 – 0.063 mm mesh). NMR spectra were recorded using BRUKER AV 300, BRUKER DRX 500, BRUKER Avance III 500 and BRUKER AV 600 spectrometers at ambient temperature. NMR spectroscopic chemical shifts were referenced to the residual peaks of the

protons of the used solvents[27] (^{1}H, ^{13}C) or externally (^{7}Li: LiCl in D_2O; ^{11}B: $BF_3{\cdot}OEt_2$; ^{19}F: $CFCl_3$). Elemental analyses were carried out using a EuroEA Elemental Analyser. ESI mass spectra were recorded using an Esquire 3000 ion trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a standard ESI source. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as the nebulizer gas and the dry gas. EI mass spectra were recorded using an Autospec X magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. Samples were introduced by push rod in aluminium crucibles. Ions were accelerated by 8 kV in EI mode.

[(6-Methylpyridin-2-yl)methyl]potassium (1)

To a suspension of KO-*t*-Bu (2.24 g, 20.0 mmol) in 2,6-lutidine (21.4 g, 0.20 mol), purified by distillation over CaH_2, was added *n*-butyllithium solution in *n*-hexane (12.5 mL, 1.6 M, 20 mmol) within 20 min and the orange suspension was stirred for 2 h at ambient temperature. The yellow precipitate **1** was filtered off, washed with *n*-pentane (10 mL) and dried in *vacuo* (2.83 g, 98%). ^{1}H NMR (500 MHz, thf-d_8): δ [ppm] = 5.99 (dd, $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 6.2 Hz, 1H, H^4), 5.43 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, H^3), 4.68 (d, $^3J_{H,H}$ = 6.3 Hz, 1H, H^5), 2.58 (d, $^2J_{H,H}$ = 1.8 Hz, 1H, CH_2), 2.53 (d, $^3J_{H,H}$ = 1.8 Hz, 1H, CH_2), 1.76 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (126 MHz, thf-d_8): δ [ppm] = 163.5 (C^2), 156.6 (C^6), 132.4 (C^4), 121.3 (C^3), 94.7 (C^5), 58.9 (CH_2), 25.1 (CH_3).

(Pyridin-2-yl-methyl)potassium (2)

To a suspension of 2-picoline (2.8 g, 20 mmol) and KO-*t*-Bu (3.41 g, 30.4 mmol) in *n*-hexane (15 mL) was added *n*-butyllithium solution in *n*-hexane (19.0 mL, 1.6 M, 30 mmol) dropwise at ambient temperature and the orange suspension was stirred for 1 h. The orange solid was filtered off, washed with *n*-hexane (15 mL) and dried in *vacuo* to yield **2** (2.53 g, 63%). ^{1}H NMR (500 MHz, thf-d_8): δ [ppm] = 6.96 (d, $^3J_{H,H}$ = 4.4 Hz, 1H, H^5), 5.98 (m, 1H, H^6), 5.53 (d, $^3J_{H,H}$ = 9.0 Hz, 1H, H^3), 4.73 (t, $^3J_{H,H}$ = 5.9 Hz, 1H, H^4), 2.51 (s, 2H, CH_2). ^{13}C{^{1}H} NMR (126 MHz, thf-d_8): δ [ppm] = 162.1 (C^2), 148.9 (C^5), 130.6 (C^6), 113.0 (C^3), 94.5 (C^4), 57.9 (CH_2).

2-{[Bis(pentafluorophenyl)boryl]methyl}-6-methylpyridine (4)

To a solution of chlorobis(pentafluorophenyl)borane (**3**) (0.570 g, 1.50 mmol) in toluene (10 mL) was added organopotassium compound **1** (0.220 g, 1.52 mmol) at −30 °C. The orange suspension was slowly warmed to ambient temperature and stirred at ambient temperature for 1 h. The yellow suspension was filtered, the toluene was evaporated to dryness and the resulting oil was washed three times with *n*-pentane (5 mL) to yield **4** as a yellowish solid (0.45 g, 66%). Analytically pure crystals were obtained from a concentrated toluene solution at −80 °C. ^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 6.76 (t, $^3J_{H,H}$ = 7.9 Hz, 1H, H^4), 6.33 (d, $^3J_{H,H}$ = 7.8 Hz, 1H, H^3), 6.11 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, H^5), 2.43 (s, 2H, CH_2), 1.78 (s, 3H, CH_3). ^{11}B NMR (160 MHz, C_6D_6): δ [ppm] = −0.75 (s, $\tau_{1/2}$ = 109 Hz). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ [ppm] = 166.9 (C^2), 154.2 (C^6), 148.2 (dm, $^1J_{F,C}$ = 238 Hz, *o*-C-F), 141.3 (C^4), 140.3 (dm, $^1J_{F,C}$ = 252 Hz, *p*-C-F), 137.6 (dm, $^1J_{F,C}$ = 248 Hz, *m*-C-F), 122.9 (C^5), 121.2 (C^3), 117.8 (broad, *i*-C), 24.3 (broad, CH_2), 17.9 (CH_3). ^{19}F NMR (470 MHz, C_6D_6): δ [ppm] = −135.1 (m, 4F, *o*-F), −157.4 (m, 2F, *p*-F), −163.6 (m, 4F, *m*-F). ESI-MS (positive ions, acetonitrile): *m/z* = 452.0 ([M + H]$^+$). HR-MS (ESI, positive ions, acetonitrile): calcd for $C_{19}H_8BF_{10}N^+$ 452.06521, found 452.06629. Analysis: calcd for $C_{19}H_9BF_{10}N$ C 50.7, H 1.8, N 3.1%; found C 51.0, H 2.0, N 3.0%.

2-{[Bis(pentafluorophenyl)boryl]methyl}pyridine (5)

To a solution of chlorobis(pentafluorophenyl)borane (**3**) (0.581 g, 1.53 mmol) in toluene (7 mL) was added organopotassium compound **2** at −30 °C and the orange suspension was slowly warmed to ambient temperature and stirred for three days at ambient temperature. The resulting lithium salts were filtered off and the solvent was removed in *vacuo*. The resulting solid was suspended in *n*-hexane (20 mL) and a main part of the product was dissolved at boiling heat. The clear supernatant liquid was transferred to another flask via a syringe and the product was precipitated at −30 °C. The supernatant liquid was removed by a syringe and the yellowish solid dried in *vacuo* to yield **5** (0.20 g, 29%). ^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 8.08 (m, 1H, H^4), 6.75 (m, 1H, H^3), 6.30 (m, 2H, H$^{5/6}$), 2.50 (s, 2H, CH_2). ^{11}B NMR (160 MHz, C_6D_6): δ [ppm] = −0.77 (s, $\tau_{1/2}$ = 120 Hz). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ [ppm] = 167.5 (C^2), 147.7 (dm, $^1J_{F,C}$ = 240 Hz, *o*-C-F), 143.6 (C^4), 140.3 (dm, $^1J_{F,C}$ = 250 Hz, *p*-C-F), 137.6 (dm, $^1J_{F,C}$ = 247 Hz, *m*-C-F), 123.8 and 122.2 (C$^{5/6}$), 117.8 (br., *i*-C), 23.1 (br., CH_2). ^{19}F NMR (470 MHz, C_6D_6): δ [ppm] = −133.7 (m, 4F, *o*-F), −157.5 (m, 2F, *p*-F), −163.5 (m, 4F, *m*-F). ESI-MS (positive ions, acetonitrile): *m/z* = 438.1 ([M + H]$^+$). HR-MS (ESI, positive ions, acetonitrile): calcd for $C_{18}H_6BF_{10}N^+$ 438.05064, found 438.04841.

2,6-Dimethyl-4-dimethylaminopyridine (7)

A glass ampoule was filled with 4-chloro-2,6-dimethylpyridine (**6**) (1.00 g, 7.98 mmol) and aqueous dimethylamine solution (10 mL, 79 mmol, 40 wt%) and the colourless suspension was stirred at 160 °C for 3 days. Water (30 mL) was added at room temperature and the aqueous phase extracted three times with dichloromethane (30 mL). The combined organic extracts were washed with brine (30 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure to yield **7** as a colourless solid (1.04 g, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 6.22 (s, 2H, Ar-H), 2.97 (m, 6H, NC*H*$_3$), 2.43 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (76 MHz, $CDCl_3$): δ [ppm] = 157.6 (C^2), 155.5 (C^4), 103.4 (C^3), 39.3 (N–*C*H$_3$), 24.9 (CH_3). EI-MS (70 eV): *m/z* = 150.0 ([M]$^{+\cdot}$, 100%), 149.0 ([M − H]$^+$, 99%), 135.0 ([M − CH_3]$^+$, 30%). HR-MS (EI, 70 eV): calcd for $C_9H_{14}N_2^{+\cdot}$ 150.11515, found: 150.11517. Analysis: calcd for $C_9H_{14}N_2$ C 72.0, H 9.4, N 18.7%; found C 71.5, H 9.7, N 18.4%.

{[4-(Dimethylamino)-6-methylpyridine-2-yl]methyl}lithium (8)

To a solution of aminolutidine **7** (0.64 g, 4.3 mmol) in *n*-hexane (10 mL) was added *n*-butyllithium solution in *n*-hexane (2.8 mL, 1.6 M, 4.5 mmol) within 15 minutes at 0 °C and the resulting yellow suspension was stirred at ambient temperature for 3 h. The yellow solid was filtered off, washed with *n*-hexane (5 mL) and dried in *vacuo* to yield **8** (0.48 g, 72%). ^{1}H NMR (500 MHz, thf-d_8): δ [ppm] = 5.02 (s, 1H, H^3), 4.88 (s, 1H, H^5), 2.67 (m, 6H, N-CH_3), 2.26 (s, 2H, CH_2Li), 1.81 (s, 3H, CH_3). ^{7}Li NMR (194 MHz, thf-d_8): δ [ppm] = 0.40. ^{13}C{^{1}H} NMR (126 MHz, thf-d_8): δ [ppm] = 168.5 (C^4), 155.9 (C^6), 154.8 (C^2), 91.4 (C^3), 90.2 (C^5), 50.0 (CH_2Li), 39.8 (N-CH_3), 25.1 (C^1).

2-{[Bis(pentafluorophenyl)boryl]methyl}-4-dimethylamino-6-methylpyridine (9)

To a solution of chlorobis(pentafluorophenyl)borane (**3**) (0.731 g, 1.92 mmol) in toluene (8 mL) was added organolithium compound **8** (0.300 g, 1.92 mmol) at −30 °C. The yellow solution was slowly warmed to ambient temperature and stirred overnight. The brown suspension was filtered, the solvent was evaporated and the brown residue washed with *n*-pentane (5 mL). The brown solid was suspended in *n*-hexane (20 mL), a main part of the product was dissolved and the supernatant solution transferred to a separate flask by syringe. The product **9** was crystallized at −30 °C, the supernatant was removed by syringe and the slightly yellow solid dried in *vacuo* (0.16 g, 17%). Crystals suitable for X-ray diffraction were obtained from a concentrated solution in benzene at r.t. ^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 5.69 (s, 1H, H^3), 5.52 (s. 1H, H^5), 2.53 (s, 2H CH_2), 2.00 (s, 6H, N-CH_3), 1.93 (s, 3H, CH_3). ^{11}B NMR (160 MHz, C_6D_6): δ [ppm] = −2.27 (s, $\tau_{1/2}$ = 172 Hz). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ [ppm] = 164.7 (C^2), 157.0 (C^4), 152.0 (C^6), 148.1 (dm, $^{1}J_{F,C}$ = 239 Hz, *o*-C-F), 139.7 (dm, $^{1}J_{F,C}$ = 249 Hz, *p-C*-F), 137.3 (dm, $^{1}J_{F,C}$ = 252 Hz, *m*-C-F), 119.7 (br., *i*-C), 104.7 (C^3), 102.1 (C^5), 38.3 (NCH_3), 23.3 (br., CH_2B), 17.9 (CH_3). ^{19}F NMR (470 MHz, C_6D_6): δ [ppm] = −135.0 (m, 4F, *o*-F), −158.5 (m, 2F, *p*-F), −164.1 (m, 4F, *m*-F). ESI-MS (positive ions, acetonitrile): *m/z* = 495.2 ([M + H]$^{+\cdot}$). HR-MS (ESI, positive ions, acetonitrile): calcd for $C_{21}H_{14}BF_{10}N_2^+$ 495.10849, found 495.10693.

2,6-Dimethyl-4-(piperidine-1-yl)pyridine (10)

A glass ampoule was filled with 4-chloro-2,6-dimethylpyridine (**6**) (2.14 g, 7.63 mmol) and piperidine (12.9 g, 151 mmol), sealed and stirred for 3 days at 160 °C. The colourless precipitate was filtered off, washed two times with *n*-hexane (5 mL). The solvent and the residual piperidine were removed in *vacuo* and 2,6-dimethyl-4-(piperidin-1'-yl)pyridine (**10**) was obtained as a colourless solid (2.51 g, 93%). ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 6.38 (s, 2H, Ar-H), 3.30 (m, 4H, N–CH_2), 2.41 (s, 6H, CH_3), 1.63 (m, 6H, N–CH_2–CH_2–CH_2). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ [ppm] = 158.1 ($C^{2,6}$), 156.3 (C^4), 105.2 ($C^{3,5}$), 47.6 (N–CH_2), 25.3 and 25.0 (s, N–CH_2–CH_2–CH_2), 24.6 (CH_3). EI-MS (70 eV): *m/z* = 190.2 ([M]$^{+\cdot}$, 67%), 189.2 ([M − H]$^+$, 100%), 175.2 ([M − CH_3]$^+$, 6%), 161.1 (8%), 149.1 (14%), 134.1 (24%). ESI-MS (positive ions, acetonitrile): *m/z* = 191.1 ([M + H]$^{+\cdot}$). HR-MS (EI, 70 eV): calcd for $C_{12}H_{18}N_2^{+\cdot}$: 190.14645, found: 190.14694. Analysis: calcd for $C_{12}H_{18}N_2$ C 75.7, H 9.5, N 14.7%; found C 75.5, H 10.0, N 14.8%.

{[6-Methyl-4(piperidin-1'-yl)pyridine-2-yl]methyl}lithium (11)

To a solution of aminolutidine **10** (2.51 g, 13.2 mmol) in *n*-hexane (30 mL) was added *n*-butyllithium solution in *n*-hexane (9.0 mL, 1.6 M, 14 mmol) within 10 min at 0 °C and the resulting yellow suspension was stirred at ambient temperature for 2 h. The yellow solid was filtered off, washed with *n*-hexane (10 mL) and dried in *vacuo* to yield **11** (2.25 g, 87%). ^{1}H NMR (500 MHz, thf-d_8): δ [ppm] = 5.12 (s, 1H, H^3), 4.83 (s. 1H, H^5), 2.91 (m, 4H, $H^{2'}$), 2.32 (s, 2H, CH_2Li), 1.79 (s, 3H, CH_3), 1.52 (m, 6H, $H^{3'/4'}$). ^{7}Li NMR (194 MHz, thf-d_8): δ [ppm] = 0.33. ^{13}C{^{1}H} NMR (126 MHz, thf-d_8): δ [ppm] = 167.8 (C^4), 155.8 (C^6), 155.5 (C^2), 94.1 (C^3), 91.8 (C^5), 52.0 (CH_2–Li), 49.9 ($C^{2'}$), 27.0 ($C^{3'}$), 25.0 ($C^{4'}$).

2-{[Bis(pentafluorphenyl)boryl]methyl}-6-methyl-4-(piperidin-1'-yl)pyridine (12)

To a solution of chlorobis(pentafluorophenyl)borane (**3**) (0.612 g, 1.60 mmol) in toluene (8 mL) was added organolithium compound **11** (0.299 g, 1.60 mmol) at −30 °C. The yellow suspension was slowly warmed to ambient temperature and stirred for three days. The brown suspension was filtered, the solvent was evaporated and the resulting residue washed with *n*-pentane (5 mL) three times and dried in *vacuo*. The resulting brown solid was suspended in *n*-hexane (50 mL) and most of the product was dissolved. The supernatant liquid was transferred to a separate flask, concentrated and **12** precipitated at −30 °C. The supernatant liquid was removed by a syringe and the remaining solid dried in *vacuo* to yield **12** (0.28 g, 32%). ^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 5.84 (s, 1H, H^3), 5.70 (s, 1H, H^5), 2.55 (m, 6H, N–CH_2 and CH_2–B), 1.93 (s, 3H, CH_3), 1.10 (m, 2H, $C^{4'}$), 0.99 (m, 4H, $C^{3'}$). ^{11}B NMR (160 MHz, C_6D_6): δ [ppm] = −2.43 (s, $\tau_{1/2}$ = 197 Hz). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ [ppm] = 165.5 (C^2), 157.4 (C^4), 152.9 (C^6), 148.1 (dm, $^{1}J_{F,C}$ = 227 Hz, *o*-C-F), 140.0 (dm, $^{1}J_{F,C}$ = 249 Hz, *p-C*-F), 137.6 (dm, $^{1}J_{F,C}$ = 252 Hz, *m*-C-F), 119.9 (broad, *i*-C), 105.9 (C^3), 103.3 (C^5), 46.8 (N–CH_2), 25.1 ($C^{3'}$), 24.0 ($C^{4'}$), 23.7 (br., CH_2-B), 18.3 (CH_3). ^{19}F NMR (470 MHz, C_6D_6): δ [ppm] = −135.0 (m, 4F, *o*-F), −158.4 (m, 2F, *p*-F), −164.1 (m, 4F, *m*-F). ESI-MS (pos., acetonitrile): *m/z* = 535.2 ([M + H]$^+$). HR-MS (ESI, pos. acetonitrile): calcd for $C_{23}H_{18}BF_{10}N_2^+$ 535.13979, found 535.13851.

2-*tert*-Butyl-6-methylpyridine (14)

To a solution of 2-bromo-6-*tert*-butylpyridine (**13**) (6.46 g, 30.2 mmol) in thf (150 mL) was added *n*-butyllithium solution in *n*-hexane (19.0 mL, 1.6 M, 30 mmol) within 20 min at −78 °C and the yellow solution stirred at this temperature for another 40 min. Methyl iodide (4.40 g, 31.0 mmol) was added and the solution warmed to ambient temperature and stirred overnight. An excess of methyl iodide was quenched with aque-

ous ammonia (5 mL, 25 wt%), water was added (200 mL) and the aqueous phase was extracted three times with dichloromethane (200 mL). The combined organic extracts were washed with brine (50 mL), dried over Na_2SO_4 and the solvents removed under reduced pressure. Pyridine derivative **14** was obtained after vacuum distillation (b.p. 80 °C, 3 Torr) as a colourless liquid (2.75 g, 61%). ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.47 (t, $^3J_{H,H}$ = 7.8 Hz, 1H, H^4), 7.12 (d, $^3J_{H,H}$ = 7.9 Hz, 1H, H^3), 6.92 (d, $^3J_{H,H}$ = 7.6 Hz, 1H, H^5), 2.53 (s, 3H, CH_3), 1.36 (s, 9H, *t*-Bu). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ [ppm] = 168.7 (C^2), 157.1 (C^6), 136.2 (C^4), 120.0 (C^5), 115.7 (C^3), 37.4 [$C(CH_3)_3$], 30.4 [$C(CH_3)_3$], 24.9 (CH_3). EI-MS (70 eV): *m/z* = 149.1 (([M]$^{+\cdot}$, 17%), 148.1 ([M − H]$^+$, 28%), 134.0 ([M − CH_3]$^+$, 100%), 107.0 (43%).

{[6-(*tert*-Butyl)pyridine-2-yl]methyl}lithium (15)

To a solution of methyl pyridine **14** (1.34 g, 8.98 mmol) in *n*-hexane (6 mL) was added *n*-butyllithium solution in *n*-hexane (7.0 mL, 1.6 M, 11 mmol) at 0 °C within 10 min and stirred at ambient temperature for 3 h. The precipitated yellow solid was filtered off, washed with *n*-hexane (3 mL), dried in *vacuo* and **15** was obtained as a yellow solid (0.77 g, 55%). ^{1}H NMR (300 MHz, thf-d_8): δ [ppm] = 6.21 (dd, $^3J_{H,H}$ = 6.7 Hz, $^3J_{H,H}$ = 8.6 Hz, 1H, H^4), 5.62 (d, $^3J_{H,H}$ = 8.7 Hz, 1H, H^3), 5.11 (d, $^3J_{H,H}$ = 6.7 Hz, 1H, H^5), 2.25 (s, 2H, CH_2), 1.10 (s, 9H, *t*-Bu). ^{13}C{^{1}H}-NMR (76 MHz, thf-d_8): δ [ppm] = 166.1 (C^6), 163.7 (C^2), 132.0 (C^4), 111.9 (C^3), 92.2 (C^5), 50.3 (CH_2–Li), 35.7 [$C(CH_3)$], 29.6 [$C(CH_3)$].

2-But-3'-enyl-6-methylpyridine (16)

To a solution of 2,6-lutidine (5.69 g, 53.1 mmol) in diethyl ether (100 mL) was added *n*-butyllithium solution in *n*-hexane (34 mL, 1.6 M, 54.4 mmol) within 15 min and the deep red solution was stirred at ambient temperature for 1.5 h. A solution of allyl bromide (7.18 g, 59.3 mmol) in diethyl ether (15 mL) was added dropwise and the resulting yellow solution stirred at ambient temperature overnight. Water (100 mL) was added, the phases separated and the aqueous phase extracted three times with dichloromethane (50 mL). The combined organic extracts were dried over Na_2SO_4 and the solvents removed under reduced pressure to yield **16** after vacuum distillation (b.p. 60 °C, 4 torr) as a colourless liquid (3.15 g, 40%). The NMR data are in good agreement with the literature.[28] ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.45 (t, $^3J_{H,H}$ = 7.6 Hz, 1H, H^4), 6.93 (t, $^3J_{H,H}$ = 7.6 Hz, 2H, $H^{3/5}$), 5.86 (m, 1H, *C*H=CH_2), 5.03 (d, $^3J_{H,H}$ = 17.0 Hz, 1H, CH=C$H_{2,trans}$), 4.95 (d, $^3J_{H,H}$ = 10.4 Hz, 1H, CH=C$H_{2,cis}$) 2.83 (t, $^3J_{H,H}$ = 7.6 Hz, 2H, CH_2–CH_2–CH=CH_2), 2.50 (s, 3H, CH_3), 2.45 (q, $^3J_{H,H}$ = 7.5 Hz, 2H, CH_2–CH_2–CH=CH_2). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ [ppm] = 160.9 (C^2), 157.8 (C^6), 138.0 (CH_2–CH_2–*C*H=CH_2), 136.4 (C^4), 120.6 and 119.6 ($C^{3/5}$), 115.0 (CH_2–CH_2–CH=*C*H_2), 37.9 (*C*H_2–CH_2–CH=CH_2), 34.1 (CH_2–*C*H_2–CH=CH_2), 24.6 (CH_3).

2-But-3'-enyl-4-dimethylamino-6-methyl-pyridine (17)

To a solution of aminolutidine **7** (1.45 g, 9.65 mmol) in diethyl ether (30 mL) was added *n*-butyllithium solution in *n*-hexane (6.25 mL, 1.6 M, 10 mmol) within 10 min and the yellow suspension was stirred at ambient temperature for 2 h. Allyl bromide (1.46 g, 12.2 mmol) in diethyl ether (10 mL) was added dropwise and the resulting colourless suspension stirred at ambient temperature overnight. Water (20 mL) was added, the aqueous phase was extracted three times with dichloromethane (20 mL) and the combined organic extracts were washed with brine (20 mL). After drying over Na_2SO_4, all volatile compounds were removed in *vacuo*. *n*-Pentane (20 mL) was added and the pyridine acidified with 2 mL conc. HCl in water (20 mL). The aqueous phase was separated, basified with NaOH and extracted three times with dichloromethane (30 mL). The combined organic extracts were dried over Na_2SO_4 and all volatile compounds removed in *vacuo*. After column chromatography (*n*-pentane/dichloromethane 5:1 + 1.5% Et_3N) **17** was obtained as a slightly yellow liquid (0.79 g, 45%). ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 6.23 (s, 2H, $H^{3/5}$), 5.89 (m, 1H, *CH*=CH_2), 5.07 (d, $^3J_{H,H}$ = 17.2 Hz, 1H, CH=C$H_{2,trans}$), 4.97 (d, $^3J_{H,H}$ = 10.2 Hz, 1H, CH=C$H_{2,cis}$), 2.97 (s, 6H, $N(CH_3)_2$), 2.74 (t, $^3J_{H,H}$ = 7.8 Hz, 2H, CH_2–CH_2–CH=CH_2), 2.43 (m, 5H, CH_2–CH_2–CH=CH_2 and Ar-CH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ [ppm] = 161.1 (C^2), 157.9 (C^6), 155.5 (C^4), 138.6 (CH_2–CH_2–*C*H=CH_2), 114.7 (CH_2–CH_2–CH=*C*H_2), 103.7 (C^5), 102.9 (C^3), 37.3 ($N(CH_3)_2$), 38.4 (*C*H_2–CH_2–CH=CH_2), 34.4 (CH_2–*C*H_2–CH=CH_2), 25.2 (Ar-CH_3). EI-MS (70 eV): *m/z* = 190.2 ([M]$^{+\cdot}$, 82%), 189.1 ([M − H]$^+$, 100%), 176.0 ([M − CH_3]$^+$, 30%), 163.1 (30%), 150.1 (M − allyl). HR-MS (EI, 70eV): calcd for $C_{12}H_{18}N_2^{+\cdot}$ 190.14645, found: 190.14682. Analysis: calcd for $C_{12}H_{18}N_2$ C 75.7, H 9.5, N 14.7%; found C 75.2, H 9.7, N 14.2%.

6-But-3'-enyl-2-*tert*-butylpyridine (18)

To a solution of methyl pyridine **17** (1.22 g, 8.18 mmol) in diethyl ether (20 mL) was added *n*-butyllithium solution in *n*-hexane (5.6 mL, 1.6 M, 9.0 mmol) dropwise and the orange solution stirred at ambient temperature for 3 h. Allyl bromide (1.21 g, 10.0 mmol) in diethyl ether (10 mL) was added within 20 min and the mixture stirred overnight. Water (40 mL) was added and the aqueous phase extracted three times with dichloromethane (30 mL). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4 and all volatile compounds were removed in *vacuo*. The product **18** was obtained after column chromatography (dichloromethane/*n*-hexane 1:3) as a colourless liquid (0.96 g, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.48 (t, $^3J_{H,H}$ = 7.8 Hz, 1H, H^4), 7.11 (d, $^3J_{H,H}$ = 7.8 Hz, 1H, H^3), 6.90 (d, $^3J_{H,H}$ = 7.8 Hz, 1H, H^5), 5.89 (m, 1H, C*H*=CH_2), 5.05 (d, $^3J_{H,H}$ = 17.3 Hz, 1H, CH=C$H_{2,trans}$), 4.95 (d, $^3J_{H,H}$ = 10.3 Hz, 1H, CH=C$H_{2,cis}$), 2.86 (t, $^3J_{H,H}$ = 7.0 Hz, 2H, CH_2–CH_2–CH=CH_2), 2.51 (q, $^3J_{H,H}$ = 7.0 Hz, 2H, CH_2–CH_2–CH=CH_2), 1.34 (s, 9H, *t*-Bu). ^{13}C{^{1}H} NMR (76 MHz, $CDCl_3$): δ [ppm] = 168.5 (C^2), 159.9 (C^6), 138.5 (CH_2-CH_2-*C*H=CH_2), 136.0 (C^4), 119.4 (C^5), 115.8 (C^3), 114.6 (CH_2-CH_2-CH=*C*H_2), 37.8 (*C*H_2–CH_2–CH=CH_2), 37.4 (*C*$(CH_3)_3$), 33.4 (CH_2–*C*H_2–CH=CH_2), 30.2 (C(CH_3)$_3$). EI-MS (70 eV): *m/z* = 189.1 ([M]$^{+\cdot}$, 21%), 188.1 ([M − H]$^+$, 49%), 174.1 ([M − CH_3]$^+$,100%), 147.1 (M – H − C_3H_5), 133.1. HR-

MS (EI, 70eV): calcd for $C_{13}H_{19}N^{+\cdot}$ 189.15120, found 189.15158. Analysis: calcd for $C_{13}H_{19}N$ C 82.5; H 10.1; N 7.4%; found C 82.2; H 10; N 7.4%.

2-{4'-[(Bis(perfluorophenyl)boranyl]butyl}-6-methylpyridine (19)

A reaction flask was filled with bis(pentafluorophenyl)borane (**22**) (471 mg, 1.36 mmol) and toluene (10 mL) and olefin **16** was added to the colourless suspension by syringe. The flask was closed and the colourless solution heated to 100 °C overnight. The solvent was condensed off, the remaining solid washed two times with *n*-pentane (2 mL) and dried in *vacuo*. Toluene (4 mL) was added and **19** was precipitated at −80 °C as a colourless solid (290 mg, 43%). ^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 6.59 (t, $^3J_{H,H}$ = 7.7 Hz, 1H, H^4), 6.23 (d. $^3J_{H,H}$ = 7.8 Hz, 1H, H^5), 6.05 (d, $^3J_{H,H}$ = 7.7 Hz, 1H, H^3), 2.54 (s, 2H, CH_2–B), 1.78 (s, 3H, CH_3), 1.48 and 1.43 (m, 6H, Ar–CH_2–CH_2–CH_2–CH_2–B). ^{11}B-NMR (160 MHz, C_6D_6): δ [ppm] = 0.11 (s, $\tau_{1/2}$ = 140 Hz). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ [ppm] = 165.3 (C^2), 160.4 (C^6), 148.2 (dm, $^1J_{F,C}$ = 240 Hz, *o*-C-F), 139.6 (dm, $^1J_{F,C}$ = 250 Hz, *p*-*C*-F), 139.2 (C^4), 137.6 (dm, $^1J_{F,C}$ = 243 Hz, *m*-C-F), 125.7 (C^5), 125.6 (C^3), 123.4 (br., *i*-C), 36.2 (*C*H$_2$–B), 25.6 (*C*H$_2$–CH$_2$–CH$_2$–CH$_2$–B), 24.2 (CH_3 and CH_2–*C*H$_2$–*C*H$_2$–CH$_2$–B). ^{19}F NMR (470 MHz, C_6D_6): δ [ppm] = −130 – −135 (very broad, *o*-F), −158.3 (broad, 2F, *p*-F), −163.9 (broad, 4F, *m*-F). ESI-MS (positive ions, acetonitrile): *m/z* = 494.1 ([M + H]$^+$). HR-MS (ESI, positive ions, acetonitrile): calcd for $(C_{22}H_{14}BF_{10}N)_2H^+$: 987.21920, found: 987.21676. Analysis: calcd for $C_{22}H_{14}BF_{10}N$ C 53.6, H 2.9, N 2.8%; found C 53.2, H 3.1, N 2.8%.

2-{4'-[Bis(perfluorophenyl)boranyl]butyl}-4-dimethylamino-6-methyl-pyridine (20)

Bis(pentafluorophenyl)borane (**22**) (183 mg, 0.96 mmol) was filled in a glass ampoule and toluene (5 mL) was condensed onto it. Olefine **17** (100 mg, 0.53 mmol) was added via syringe at ambient temperature and the colourless solution was heated to 120 °C overnight. Toluene was evaporated to dryness, the remaining colourless solid was washed with *n*-pentane (1.5 mL), dried in high vacuum and the hydroboration product **20** was obtained (0.28 g, 98%). ^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 5.65 (d, $^4J_{H,H}$ = 3.1 Hz, 1H, H^3), 5.53 (d, $^4J_{H,H}$ = 3.1 Hz, 1H, H^5), 2.62 (broad, 1H, Ar–CH$_2$–CH$_2$–CH$_2$–C*H*$_2$-B), 1.93 (s, 6H, N(CH$_3$)$_2$), 1.90 (s, 3H, CH_3), 1.62 (m, 6H, Ar–C*H*$_2$–C*H*$_2$–C*H*$_2$–CH$_2$–B). ^{11}B-NMR (160 MHz, C_6D_6): δ [ppm] = −2.16 (s, $\tau_{1/2}$ = 210 Hz). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ [ppm] = 163.1 (C^2), 158.0 (C^6), 154.0 (C^4), 148.1 (dm, $^1J_{F,C}$ = 238 Hz, *o*-C-F), 139.1 (dm, $^1J_{F,C}$ = 225 Hz, *p*-*C*-F), 137.2 (dm, $^1J_{F,C}$ = 235 Hz, *m*-C-F), 125.1 (br., *i*-C), 106.9 (C$^{3/5}$), 37.6 (N(CH$_3$)$_2$), 36.2 (Ar-CH$_2$–CH$_2$–CH$_2$–C*H*$_2$–B), 26.8 and 24.8 and 23.0 (Ar–*C*H$_2$–*C*H$_2$-*C*H$_2$–CH$_2$–B), 24.1 (CH_3). ^{19}F NMR (470 MHz, C_6D_6): δ [ppm] = −130 – −135 (very broad, *o*-F), −159.5 (br., 2F, *p*-F), −164.3 (br., 4F, *m*-F). ESI-MS (positive ions, acetonitrile): *m/z* = 537.3 ([M + H]$^+$). HR-MS (ESI, positive ions, acetonitrile): calcd for $C_{25}H_{21}BF_{10}N_2^+$: 537.15544, found: 537.15633. Analysis: calcd for $C_{24}H_{19}BF_{10}N_2$ C 53.8, H 3.6, N 5.2%; found C 53.8, H not detectable due to HF formation, N 4.9%.

6-{4'-[Bis(perfluorophenyl)boranyl]butyl}-2-*tert*-butylpyridine (21)

Bis(pentafluorophenyl)borane (**22**) (365 mg, 1.05 mmol) was filled into a glass ampoule and toluene (5 mL) was condensed onto it. Olefine **18** (200 mg, 1.05 mmol) was added via syringe at ambient temperature and the colourless solution was heated to 120 °C for 3 d. Toluene was evaporated to dryness, the remaining colourless solid was washed with *n*-pentane (5 mL), dried in high vacuum and the hydroboration product **21** was obtained (0.54 g, 96%). ^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 7.15 (overlap with C_6D_5H, H^3), 6.90 (d. $^3J_{H,H}$ = 7.9 Hz, 1H, H^3), 6.65 (d, $^3J_{H,H}$ = 7.7 Hz, 1H, H^5), 2.75 (t, $^3J_{H,H}$ = 7.4 Hz, 2H, Ar–C*H*$_2$–CH$_2$–CH$_2$–CH$_2$-B), 1.92 (t, $^3J_{H,H}$ = 7.7 Hz, 2H, Ar–CH$_2$-CH$_2$–CH$_2$–C*H*$_2$–B), 1.86 (quin, $^3J_{H,H}$ = 7.5 Hz, 2H, Ar–CH$_2$–C*H*$_2$–CH$_2$–CH$_2$–B), 1.56 (quin, $^3J_{H,H}$ = 7.5 Hz, 2H, Ar–CH$_2$–CH$_2$–C*H*$_2$–CH$_2$–B). ^{11}B NMR (160 MHz, C_6D_6): δ [ppm] = 74.8 (s, $\tau_{1/2}$ = ~1100 Hz). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ [ppm] = 168.9 (C^2), 160.5 (C^6), 147.0 (dm, $^1J_{F,C}$ = 248 Hz, *o*-C-F), 143.5 (dm, $^1J_{F,C}$ = 258 Hz, *p*-*C*-F), 139.2 (C^4), 137.6 (dm, $^1J_{F,C}$ = 251 Hz, *m*-C-F), 136.4 (C^4), 119.6 (C^5), 116.2 (C^3), 114.3 (br., *i*-C), 38.2 (*C*(CH$_3$)$_3$), 37.6 (*C*H$_2$–CH$_2$–CH$_2$–CH$_2$–B), 32.8 (CH$_2$–*C*H$_2$–CH$_2$–CH$_2$–B), 32.4 (CH$_2$–*C*H$_2$–CH$_2$–CH$_2$–B), 32.2 (br, *C*H$_2$–B) 30.3 (C(*C*H$_3$)$_3$), 24.8 (CH$_2$–*C*H$_2$–*C*H$_2$–CH$_2$–B).^{19}F NMR (470 MHz, C_6D_6): δ [ppm] = −130.4 (m, 4F, *o*-F), −147.3 (m, 2F, *p*-F), −160.8 (m, 4F, *m*-F). ESI-MS (positive ions, acetonitrile): *m/z* = 536.3 ([M + H]$^+$). HR-MS (ESI, positive ions, acetonitrile): calcd for $C_{25}H_{21}BF_{10}N^+$ 536.16019, found: 536.16088. Analysis: calcd for $C_{25}H_{20}BF_{10}N$ C 56.1, H 3.8, N 2.6%; found C 55.9, H 4.1, N 2.7%.

H/D-scrambling experiments

A Young valve NMR tube was filled with 15–25 mg of the sample and 0.4 mL CD_2Cl_2. The solution was degassed by two freeze pump thaw cycles and backfilled with one atmosphere of a 50:50 mixture of hydrogen and deuterium, premixed in a 60 mL glass tube. The formation of HD by compound **21** was detectable by NMR spectroscopy within 5 hours. HD: ^{1}H NMR (300 MHz, CD_2Cl_2): δ [ppm] = 4.57 (t 1:1:1, $^1J_{D,H}$ = 42.6 Hz).

Crystallographic data

Crystal structures were determined by X-ray diffraction on a *SuperNova*, single source at offset, *Eos* diffractometer. Using Olex2,[29] the structure was solved with the ShelXS[30] structure solution program using Direct Methods and refined with the ShelXL[30] refinement package using Least Squares minimisation. Data are listed in Table 2.

Quantum-chemical calculations

Density functional theory[31] calculations with the PBE0[32] functional with D3 correction[33] for dispersion interactions paired with built-in 6-31G(d,p) basis set were carried out using the Gaussian 09 program package.[34] Frequencies calculations were done for all optimized structures to prove their equilibrium nature.

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Table 2: Crystallographic data of compounds **9** and **19**.

	9	**19**
Empirical formula	$C_{21}H_{13}BF_{10}N_2$	$C_{22}H_{14}BF_{10}N$
M_r	494.14	493.15
λ [Å]	0.71073	0.71073
T [K]	94.98(13)	99.99(10)
$F(000)$	992	992
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a [Å]	12.0013(3)	11.2973(2)
b [Å]	11.1213(2)	13.7505(2)
c [Å]	14.8617(3)	12.6885(2)
β [°]	93.860(2)	96.5752(17)
V [Å^3]	1979.09(8)	1958.11(6)
Z	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.658	1.673
μ [mm^{-1}]	0.164	0.164
$2\theta_{max}$ [°]	60.06	59.99
Index range h	$-16 \le h \le 16$	$-15 \le h \le 14$
Index range k	$-15 \le k \le 15$	$-19 \le k \le 19$
Index range l	$-20 \le l \le 20$	$-17 \le l \le 17$
Refl. collect.	61610	55604
Indep. refl.	5765	5687
R_{int}	0.0325	0.0257
Observed refl., $I>2\sigma(I)$	5034	4928
Parameters	359	343
R_1, $I>2\sigma(I)$	0.0392	0.0387
wR_2, $I>2\sigma(I)$	0.1036	0.0920
R_1 (all data)	0.0459	0.0468
wR_2 (all data)	0.1084	0.0960
GoF	1.061	1.084
$\rho_{max/min}$ [e Å^{-3}]	0.50/–0.22	0.35/–0.23
CCDC-No.	1042619	1042620

Notes and references

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1 G. C. Welch, Juan, R. R. San, J. D. Masuda, and D. W. Stephan, *Science* 2006, **314**, 1124–1126.

2 G. C. Welch and D. W. Stephan, *J. Am. Chem. Soc*. 2007, **129**, 1880–1881.

3 P. A. Chase, G. C. Welch, T. Jurca and D. W. Stephan, *Angew. Chem. Int. Ed.* 2007, **46**, 8050–8053.

4 a) P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme and D. W. Stephan, *Chem. Commun*. 2007, 5072–5074; b) P. Spies, G. Kehr, K. Bergander, B. Wibbeling, R. Fröhlich and G. Erker, *Dalton Trans*. 2009, 1534–1541.

5 P. A. Chase and D. W. Stephan, *Angew. Chem. Int. Ed*. 2008, **47**, 7433–7437.

6 a) G. Ménard, J. A. Hatnean, H. J. Cowley, A. J. Lough, J. M. Rawson and D. W. Stephan, *J. Am. Chem. Soc*. 2013, **135**, 6446–6449; b) C. Appelt, J. C. Slootweg, K. Lammertsma and W. Uhl, *Angew. Chem. Int. Ed*. 2013, **52**, 4256–4259.

7 a) P. Jochmann and D. W. Stephan, *Angew. Chem. Int. Ed.* **2013**, *52*, 9831–9835; b) R. Dobrovetsky and D. W. Stephan, *Angew. Chem. Int. Ed.* **2013**, *52*, 2516–2519; c) R. Dobrovetsky and D. W. Stephan, *Israel J. Chem.* **2015**, *55*, 206–209.

8 M. Reißmann, A. Schäfer, S. Jung and T. Müller, *Organometallics* 2013, **32**, 6736−6744; b) A. Schäfer, M. Reißmann, A. Schäfer, M. Schmidtmann and T. Müller, *Chem. Eur. J.* 2014, **20**, 9381–9386.

9 V. Sumerin, F. Schulz, M. Nieger, M. Leskelä, T. Repo and B. Rieger, *Angew. Chem. Int. Ed.* 2008, **47** , 6001–6003.

10 V. Sumerin, F. Schulz, M. Atsumi, C. Wang, M. Nieger, M. Leskelä, T. Repo, P. Pyykkö and B. Rieger, *J. Am. Chem. Soc*. 2008, **130**, 14117–14119.

11 K. Chernichenko, M. Nieger, M. Leskelä and T. Repo, *Dalton Trans*. 2012, **41**, 9029–9032.

12 S. Schwendemann, R. Fröhlich, G. Kehr and G. Erker, *Chem. Sci*. 2011, **2**, 1842.

13 S. J. Geier and D. W. Stephan, *J. Am. Chem. Soc*. 2009, **131**, 3476–3477.

14 J. Vergnaud, T. Ayed, K. Hussein, L. Vendier, M. Grellier, G. Bouhadir, J.-C. Barthelat, S. Sabo-Etienne and D. Bourissou, *Dalton Trans*. 2007, 2370.

15 J.-H. Son and J. D. Hoefelmeyer, *Org. Biomol. Chem*. 2012, **10**, 6656.

16 T. A. Rokob, A. Hamza, I. Pápai, *J. Am. Chem. Soc*. 2009, **131**, 10701–10710.

17 Y. H. Kim, T. H. Kim, N. Y. Kim, E. S. Cho, B. Y. Lee, D. M. Shin and Y. K. Chung, *Organometallics* 2003**, 22**, 1503.

18 a) T. Beringhelli, D. Donghi, D. Maggioni and G. D'Alfonso, *Coord. Chem. Rev.* 2008, **252**, 2292–2313; b) H. Nöth and B. Wrackmeyer, *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*, Springer, Berlin, 1978, vol. 14; c) W. E. Piers, *Adv. Orgmet. Chem*, 2004, **52**, 1–76;

19 L. J. Hounjet, C. Bannwarth, C. N. Garon, C. B. Caputo, S. Grimme and D. W. Stephan, *Angew. Chem. Int. Ed.* 2013, **52**, 7492–7495.

20 R. Roesler, W. E. Piers and M. Parvez, *Organomet. Chem.* 2003, **680**, 218-222.

21 M. J. G. Lesley, A. Woodward, N. J. Taylor, T. B. Marder, I. Cazenobe, I. Ledoux, J. Zyss, A. Thornton, D. W. Bruce and A. K. Kakkar, *Chem. Mater.* 1998, **10**, 1355–1365.

22 S. J. Geier, A. L. Gille, T. M. Gilbert and D. W. Stephan, *Inorg. Chem.* 2009, **48**, 10466–10474.

23 D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492–5503.

24 D. J. Parks, R. E. von H. Spence and W. E. Piers, *Angew. Chem. Int. Ed.* 1995, **34**, 809–811.

25 B. Singh, G. Y. Lesher and P. O. Pennock, *J. Heterocycl. Chem.* 1990, **27**, 1841–1842.

26 Z. Zheng, M. K. Elmkaddem, C. Fischmeister, T. Roisnel, C. M. Thomas, J.-F. Carpentier and J.-L. Renaud, *New J. Chem.* 2008, **32**, 2150.

27 P. A van der Schaaf, R. Kolly, H.-J. Kirner, F. Rime, A. Mühlebach and A. Hafner, *J. Organomet. Chem.* 2000, **606**, 65–74.

27 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics* 2010, **29**, 2176–2179.
28 P. A van der Schaaf, R. Kolly, H.-J. Kirner, F. Rime, A. Mühlebach and A. Hafner, *J. Organomet. Chem.* 2000, **606**, 65–74.
29 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl Crystallogr.* 2009, **42**, 339–341.
30 G. M. Sheldrick, *Acta Crystallogr. A, Found. Crystallogr*. 2008, **64**, 112–122.
31 R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, USA, International Series of Monographs on Chemistry, 1989.
32 John P. Perdew, Kieron Burke and Matthias Ernzerhof, *Phys. Rev. Lett.* 1996, 77, 3865–3868.
33 S. Grimme, J. Anthony, S. Ehrlich and H. Krieg, *J. Chem. Phys.* 2010, **132**, 154104.
34 Gaussian 09, Revision D.01, M. J. Frisch et al., Gaussian, Inc., Wallingford CT, 2009.

TOC entry

Intramolecular pyridine-based frustrated Lewis-pairs

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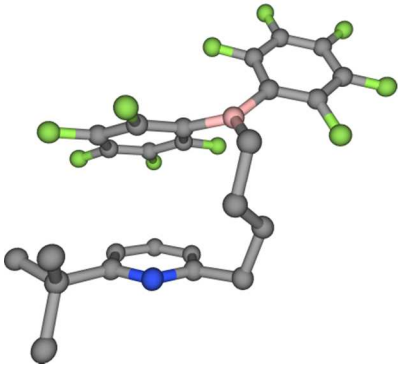
Besides a series of pyridine-based Lewis pairs with $B(C_6F_5)_2$ groups with varying electronic and steric situations and strong intramolecular B–N bonds, 2-[$(CH_2)_4B(C_6F_5)_2$]-6-*t*Bu-pyridine was found to behave as a frustrated Lewis pair.



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