Frustrated Lewis Pairs

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A Frustrated and Confused Lewis Pair

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Abstract: *We report a new class of frustrated Lewis pairs (FLPs) by the hydroboration of bulky isocyanates* $^{iPr2}ArNCO$ *(*$^{iPr2}Ar = 2,6\text{-}iPr_2C_6H_3$*) and* $^{Ph2tBu}ArNCO$ *(*$^{Ph2tBu}Ar = 2,6\text{-}Ph_2\text{-}4\text{-}tBuC_6H_2$*) with Piers' borane (*$HB(C_6F_5)_2$*). While hydroboration of smaller isocyanates such as* $^{iPr2}ArNCO$ *leads to isocyanate—N/B FLP adducts, hydroboration of the bulkier* $^{Ph2tBu}ArNCO$ *allows isolation of the substrate-free aminoborane with a short, covalent N—B bond. This confused FLP reversibly binds unsaturated substrates such as isocyanates and isocyanides, suggesting the intermediacy of a "normal" FLP along the reaction pathway, supported by high-level DFT studies and variable-temperature NMR spectroscopy. These results underscore the possibility of FLP behavior in systems that possess no obvious frustrated Lewis acid–base interaction.*

When enough steric bulk exists at both a Lewis acid and a Lewis base, the formation of a direct acid–base adduct is precluded leading to a "frustrated" interaction. Such frustrated Lewis pairs (FLPs) undergo cooperative reactivity with a wide variety of external substrates, displaying previously unprecedented metal-free pathways to small molecule capture and activation. The first example of small molecule activation by FLPs,[1] and perhaps the most widely studied, is the heterolytic splitting and activation of H_2,[2–4] which has resulted in the development of metal-free catalytic processes for the hydrogenation of imines, enamines, and silyl enol ethers.[5–8] FLPs have been developed that incorporate a wide variety of combinations of Lewis acids and bases, but the majority consist of sterically hindered phosphorus-, nitrogen-, and carbene-centered Lewis bases in conjunction with fluorinated aryl borane Lewis acids.[6,9] While the field was launched with phosphine/borane (P/B) based Lewis pairs,[10–12] N/B FLPs with pyridine-, amine-, and imine-based donors in conjunction with electron-deficient boranes also capture and activate CO_2, H_2, nitriles, aldehydes, and alkynes.[6,13,14] Some N/B FLPs are particularly potent metal-free reductants, capable of (hetero)arene reduction to saturated six-membered cycles[15] (Figure 1 a, R = Ph) and selective alkyne reduction to *cis* alkenes (Figure 1 b).[13] Moreover, N/B FLPs have found application in the metal-free borylation of pyrroles, furans, and thiophenes (Figure 1 c)[16] and have recently effected dehydrogenative oxidation of *N*-protected indolines through borane-induced hydride abstraction with subsequent deprotonation.[17]

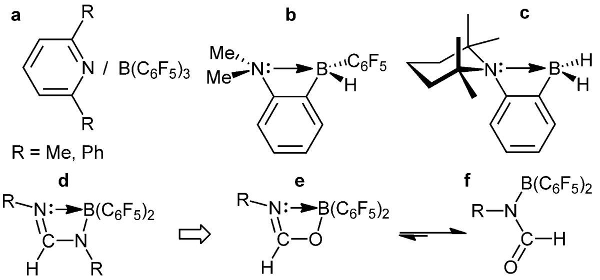

Figure 1. a–d) Selected inter- and intramolecular N/B FLPs e) with targeted isocyanate derived N/B FLP and f) its confused isomer.

Boron amidinates represent a family of intramolecular N/B FLPs reported by Stephan in 2010.[18] Hydroboration of bulky carbodiimides, RN=C=NR, with $HB(C_6F_5)_2$ generates strained four-membered chelates (Figure 1 d) that react with carbon monoxide (CO), carbon dioxide (CO_2), and *tert*-butylisocyanide (^tBuNC). Such N/B FLPs have a tight internal N/B interaction, leading to sluggish reactivity with substrates. These observations motivated us to develop new intramolecular N/B FLPs that would result from hydroboration of isocyanates, ArN=C=O, that feature a direct O—B linkage with a frustrated N—B interaction. We hypothesized that the electron-withdrawing oxygen atom could weaken the donor ability of the N lone pair (but perhaps also increase the Lewis acidity of the B center), modifying the N—B interaction and possibly enhancing overall reactivity (Figure 1 e). We herein report the synthesis of a new class of N/B FLPs that possess a "confused" aminoborane binding motif (Figure 1 f) but behave as a typical FLP through facile rearrangement.

Hydroboration of $^{iPr2}ArNCO$ ($^{iPr2}Ar = 2,6\text{-}iPr_2C_6H_3$) with Piers' borane,[19] $HB(C_6F_5)_2$ (HBCF), did not result in the desired four-membered cyclized product similar to the boron amidinate chemistry. Instead, addition of $^{iPr2}ArNCO$ to a fluorobenzene solution of HBCF resulted solely in the isocyanate adduct of the desired N/B FLP, $^{iPr2Ar}N/B\text{-}FLP(^{iPr2}ArNCO)$ (**1**) (Scheme 1). The structure of

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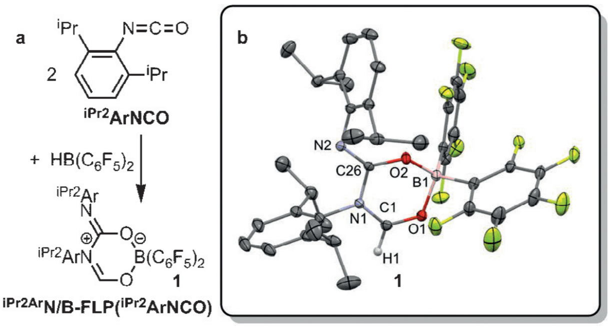
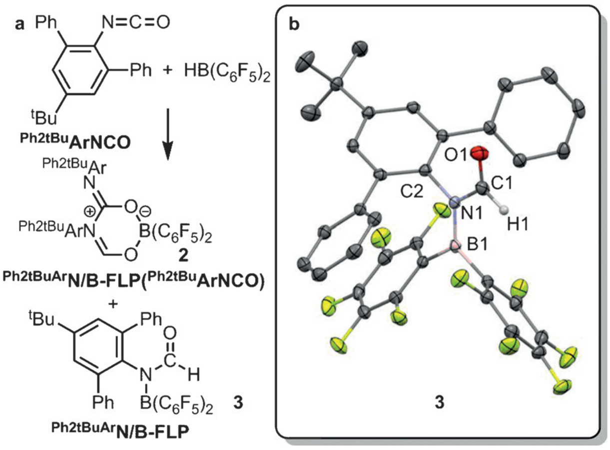


Scheme 1. a) Synthesis of $^{\text{iPr2Ar}}$N/B-FLP($^{\text{iPr2}}$ArNCO) (**1**). b) X-ray structure of **1**.

1 (Scheme 1) features a six-membered ring resulting from formal capture of the isocyanate by the anticipated N/B FLP and resembles that of Stephan's CO_2 adduct.[18] The N1–C26 bond distance (1.4387(12) Å) is expectedly slightly longer than the corresponding N−C bond of the CO_2 adduct (1.402(6) Å) due to sterics on the *N*-aryl ring while the O2–B1 distance (1.4825(15) Å) is quite similar to the corresponding O−B bond of the CO_2 adduct (1.493(5) Å).[18] The $^{\text{iPr2}}$ArNCO-adduct **1** displays a singlet at δ 7.18 ppm in the ^{1}H NMR spectrum ([D$_6$]benzene) corresponding to the formamidate C−H moiety while the ^{19}F NMR spectrum shows three signals at δ −136.4, −156.0, and −164.4 ppm corresponding to the *ortho*-, *para*-, and *meta*-F atoms, respectively.

With the goal of isolating a monomeric, boron formamidate-based N/B-FLP, we moved to a bulkier substituent at the 2,6-positions of the aryl isocyanate. Addition of HBCF to the especially crowded isocyanate $^{\text{Ph2tBu}}$ArNCO ($^{\text{Ph2tBu}}$Ar = 2,6-Ph$_2$-4-*t*BuC$_6$H$_2$), which possesses a *p*-*t*Bu and two *o*-Ph groups on the isocyanate *N*-aryl ring, resulted in a mixture of two predominant products by NMR spectroscopy (Scheme 2a). The first species, **2**, exhibits features in the ^{1}H and ^{19}F NMR spectra similar to those of isocyanate adduct **1**, with a downfield ^{1}H NMR C−H signal at δ 6.79 ppm and two *t*-butyl groups at δ 1.20 and 1.12 ppm, as well as equivalent C$_6$F$_5$ rings as judged by ^{19}F NMR spectroscopy. A second species, **3**, displays a more downfield ^{1}H NMR signal at δ 8.41 ppm, a single *t*-butyl group at δ 1.11 ppm, and two sets of ^{19}F resonances of equal intensity, indicating product **3** possesses two inequivalent C$_6$F$_5$ rings.



Scheme 2. a) Synthesis of confused FLP **3** and its isocyanate adduct 2. b) X-ray structure of confused FLP **3**.

Careful crystallization of this mixture resulted in the isolation and structural characterization of both major products. While product **2** is confirmed to be the isocyanate adduct $^{\text{Ph2tBuAr}}$N/B-FLP($^{\text{Ph2tBu}}$ArNCO) of the bulky isocyanate/FLP pair (see Figure S9 in the Supporting Information), the unsymmetrical product **3** is the unanticipated, rearranged aminoborane isomer of the targeted $^{\text{Ph2tBuAr}}$N/B-FLP. The X-ray crystal structure of **3** (Scheme 2b) displays an alternative coordination motif for this FLP with a covalent B−N bond (N1–B1 = 1.4124(19) Å) and a free formamide moiety (C1–O1 = 1.2007(17) Å) that conceptually results from hydroboration of the hindered N=C bond of the isocyanate. This B−N bond is typical of borylamides R$_2$B-NR$_2$.[20–24] The B-N-C(H)=O atoms essentially lie in one plane (B1-N1-C1-O1 = 170.6°) consistent with a delocalized π system involving the carbonyl C=O double bond in conjugation with the N→B π interaction. The IR spectrum displays a band at 1647 cm^{-1} corresponding to the C=O stretch at a bit lower energy than in unconjugated formamides such as HC(O)NMe$_2$ (1675 cm^{-1}).[25] The diastereotopic B-C$_6$F$_5$ groups observed by ^{19}F NMR spectroscopy thus reflect hindered B−N bond rotation due to participation of the N lone pair in this conjugated π system.

While we were surprised at this "confused" isomer of our targeted intramolecular FLP that places the sterically demanding $^{\text{Ph2tBu}}$ArN moiety adjacent to the B(C$_6$F$_5$)$_2$ group, DFT calculations identify this experimental structure as the lowest energy isomer (Figure 2). At the PW6B95-D3/def2-QZVP (COSMO-RS, fluorobenzene)//PBEh-3c level of theory,[26] this "confused" FLP isomer **3** is predicted to be 1.8 kcal mol^{-1} lower in free energy in fluorobenzene than the anticipated "frustrated" species **3′** that possesses both O−B and N−B interactions. The O−B and N−B bond distances of the FLP-type isomer **3′** are 1.56 and 1.62 Å, respectively. This N−B bond length in frustrated **3′** is just outside the range of the N–B distances observed in Stephan's N/B boron amidinate FLPs (1.583(3) –1.606(2) Å).[18] On the other hand, the fully "open" isomer **3″** that does not benefit from any N–B interaction is significantly higher in free energy than **3** (+ 9.3 kcal mol^{-1}).

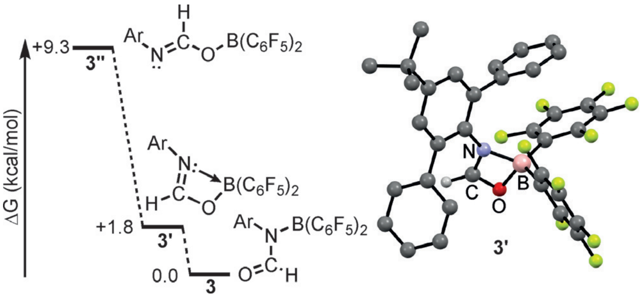
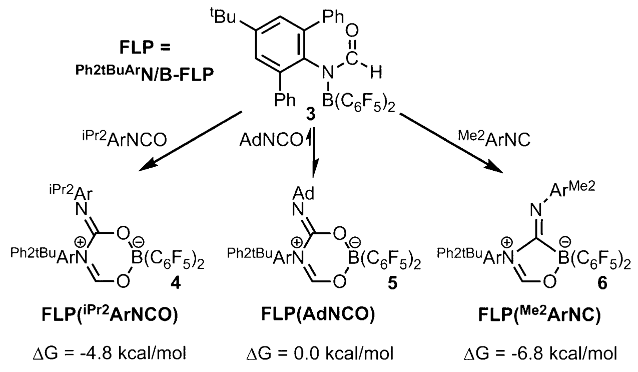


Figure 2. Relative free energies of FLP isomers **3** (confused), **3′** (frustrated), and **3″** (open) by DFT at 298 K in fluorobenzene.

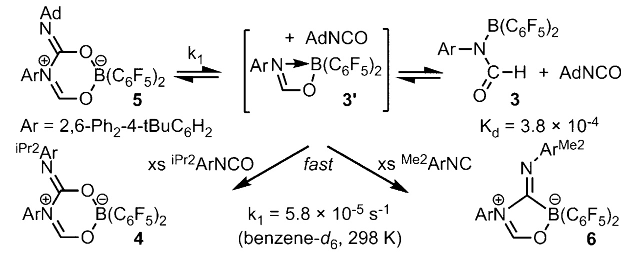


Scheme 3. Capture of unsaturated substrates by confused FLP **3** along with DFT-calculated energies at 298 K in fluorobenzene.

Importantly, addition of unsaturated substrates, such as isocyanates, to the rearranged FLP **3** reveals normal FLP reactivity to give the expected substrate adducts (Scheme 3). Addition of $^{\mathrm{iPr2}}$ArNCO or 1-adamantyl isocyanate (AdNCO) to **3** in fluorobenzene results in rapid conversion to the FLP adducts $^{\mathrm{Ph2tBuAr}}$N/B-FLP($^{\mathrm{iPr2}}$ArNCO) (**4**) and $^{\mathrm{Ph2tBuAr}}$N/B-FLP-(AdNCO) (**5**). X-ray crystallography of **4** and **5** reveals six-membered rings featuring coordination of the isocyanate C=O bond across the N⋯B interaction in frustrated FLP isomer **3′** (Figure 3). The N1–C36 (1.448(3) and 1.4571(19) Å) and B1–O2 (1.473(3) and 1.470(2) Å) distances in **4** and **5**, respectively, are quite similar to those found in **1** and **2**. Both **4** and **5** possess a slightly puckered six-membered ring as judged by the sum of the internal angles (709.01 and 707.87°, respectively), compared to 720° for a purely planar cycle. NMR spectra reveal that the adduct structures are maintained in solution with formamidate C–H ^{1}H resonances at δ 7.42 and 6.80 ppm, respectively. ^{19}F NMR spectra reveal that both isocyanate adducts **4** and **5** possess equivalent B(C_6F_5)$_2$ groups, as well.

Capture of an isocyanide by **3** leads to a five-membered cycle. NMR studies reveal that addition of 2,6-dimethylphenyl isocyanide ($^{\mathrm{Me2}}$ArNC) to **3** results in clean and immediate conversion to the isocyanide adduct $^{\mathrm{Ph2tBuAr}}$N/B-FLP($^{\mathrm{Me2}}$ArNC) (**6**) that also possesses equivalent B(C_6F_5)$_2$ groups. The X-ray structure of **6** (Figure 3) clearly reveals this adduct as a formal 1,1-addition product of the isocyanide to the frustrated FLP isomer **3′**.[27] This FLP adduct possesses N1–C36 and B1–C36 distances of 1.463(3) and 1.656(4) Å within a planar five-membered ring (sum of internal angles = 539.96°; ideal value = 540°).

Dissolution of pure crystals of $^{\mathrm{Ph2tBuAr}}$N/B-FLP(AdNCO) (**5**) in [D$_6$]benzene leads to a small amount of free AdNCO and confused FLP **3** observed by ^{1}H and ^{19}F NMR spectroscopies, which we propose proceeds via the short-lived intermediate **3′**. At RT (298 K), substrate-bound **5** is in equilibrium ($K_d = 3.8\times10^{-4}$ M) with confused FLP **3** and AdNCO (Scheme 4, top). Variable-temperature NMR studies in [D$_6$]benzene indicate increased dissociation at higher temperatures; van't Hoff analysis gives $\Delta H = 13.1(4)$ kcal mol^{-1} and $\Delta S = 28.6(1.2)$ cal mol^{-1} K^{-1} for dissociation of AdNCO from **5** to give **3**.



Scheme 4. Exchange of substrates at FLP **3** through dissociation of AdNCO from **5**.

We became intrigued by the possibility of substrate exchange that could proceed through the "frustrated" intermediate **3′** immediately formed upon loss of AdNCO from $^{\mathrm{Ph2tBuAr}}$N/B-FLP(AdNCO) (**5**). Indeed addition of both $^{\mathrm{iPr2}}$ArNCO and $^{\mathrm{Me2}}$ArNC to **5** results in the corresponding FLP adducts **4** and **6**, respectively (Scheme 4). Addition of 1 equiv $^{\mathrm{Me2}}$ArNC to a solution of **5** in [D$_6$]benzene results in complete conversion to $^{\mathrm{Ph2tBuAr}}$N/B-FLP($^{\mathrm{Me2}}$ArNC) (**6**) within 15 h. Addition of excess $^{\mathrm{Me2}}$ArNC (10 or 20 equiv) to **5** gives the same first-order rate constant $k = 5.8(1)\times10^{-5}$ s^{-1}, indicating a dissociative mechanism for the substitution of AdNCO in **5** with $^{\mathrm{Me2}}$ArNC to give **6**. On the other hand, replacement of AdNCO with 1 equiv $^{\mathrm{iPr2}}$ArNCO was incomplete after 20 h. Addition of excess $^{\mathrm{iPr2}}$ArNCO (20 or 30 equiv) to **5**, however, drives the equilibrium to afford complete conversion to $^{\mathrm{Ph2tBuAr}}$N/B-FLP($^{\mathrm{iPr2}}$ArNCO) (**4**) in 20 h with the same first-order rate constant $k = 5.7(2)\times10^{-5}$ s^{-1}. Notably, these two rate constants for reaction with

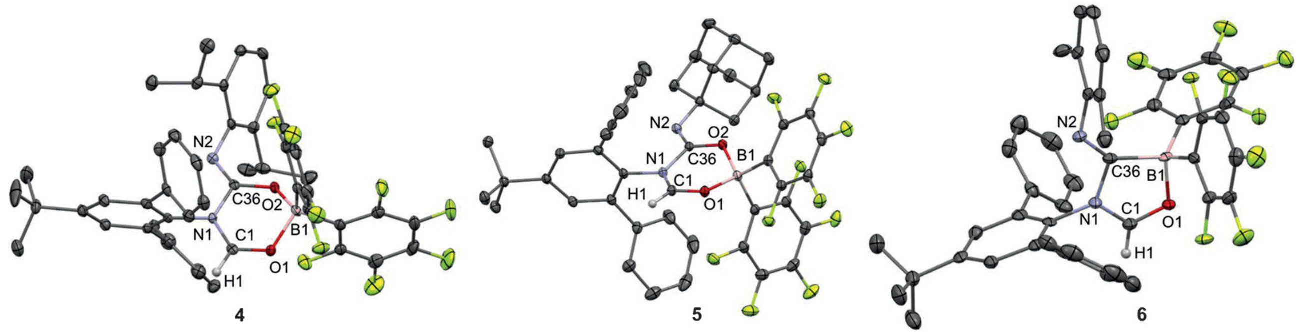

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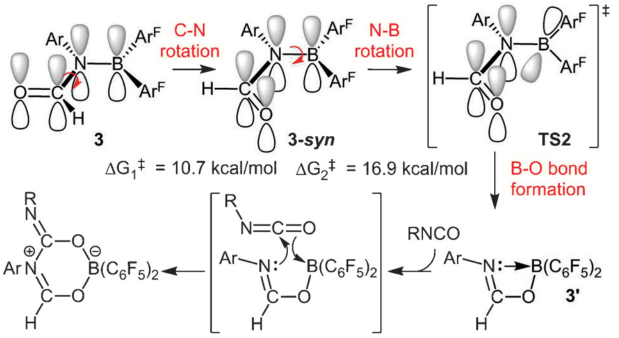
Figure 3. X-ray structures of isocyanate and isocyanide adducts **4**–**6** through substrate capture by confused FLP **3**.

excess ^{iPr2}ArNCO or ^{Me2}ArNC are experimentally indistinguishable, indicating rate limiting loss of AdNCO from **5**. Moreover, the conditions required to achieve complete conversion to **4** or **6** are consistent with the thermodynamic preferences revealed by DFT in Scheme 3. Substitution of ^{Me2}ArNC for ^{iPr2}ArNCO in **4** was similarly observed but was also incomplete, further consistent with the calculated ΔG values in Scheme 3.

In order for the confused FLP **3** to undergo reactivity with substrates, a rearrangement must occur to form the O–B bond observed in all FLP–substrate adducts **4**–**6**. On the way to rearrangement, the N–B interaction must be weakened; specifically, the N–B bond must rotate so that the N and B substituents are no longer in the same plane. To gain experimental insight into these dynamic processes, we carefully examined variable temperature ^{19}F NMR spectra of **3** in [D$_8$]toluene. At RT, **3** displays a pair of diastereotopic B-C$_6$F$_5$ groups characteristic of the restricted rotation about the N–B bond due to the dative π interaction between the N lone pair and the B empty p orbital (Scheme 5). Warming the solution results in broadened resonances, and at 105 °C, the *para*-F signals coalesce to give $\Delta G^{\ddagger}(378\ \mathrm{K}) = 17.6(3)\ \mathrm{kcal\,mol^{-1}}$ for N–B bond rotation. Lineshape analysis gives $\Delta H^{\ddagger} = 11.0\ \mathrm{kcal\,mol^{-1}}$ with $\Delta S^{\ddagger} = -17.4\ \mathrm{cal\,mol^{-1}{\cdot}K}$ corresponding to $\Delta G^{\ddagger}(378\ \mathrm{K}) = 17.6\ \mathrm{kcal\,mol^{-1}}$. The N–B rotational barrier in **3** is considerably lower than alkyl or arylsubstituted borylamines (ca. 25 kcal mol^{-1})[21,28] due to competition with the formyl group for the N lone pair. Rather, it is similar to the decreased N–B rotational barriers observed in early transition metal borylamides ($\Delta G^{\ddagger} = 15.2$–$17.4\ \mathrm{kcal\,mol^{-1}}$) in which vacant metal d orbitals can compete with B for acceptance of the N lone pair.[23–24]



Scheme 5. Mechanism for isomerization from confused FLP **3** to open FLP **3′** and subsequent capture of isocyanate substrate. Energies determined by DFT at 298 K and in fluorobenzene.

DFT calculations indicate the presence of two transition states along the reaction pathway that connects confused **3** with frustrated **3′** ready for substrate capture (Scheme 5 and Figure S14). The C–N bond first rotates to bring the O atom of the formamide to the same side of the C–N bond as the B atom with a low barrier ($\Delta G_1^{\ddagger} = 10.7\ \mathrm{kcal\,mol^{-1}}$) to generate ***3-syn***. Next, the B–N bond rotates (**TS2**) to prime the empty p orbital of the B atom to accept a pair of electrons from the formamide C=O double bond ($\Delta G_2^{\ddagger} = 16.9\ \mathrm{kcal\,mol^{-1}}$), forming the O–B bond present in frustrated **3′**. Since the calculated barrier for N–B rotation is higher than that of formamide isomerization determined from VT NMR, N–B rotation is the key step required to interconvert confused **3** with frustrated **3′**.

A new class of nitrogen/boron frustrated and confused Lewis pairs results from the hydroboration of bulky arylisocyanates. While hydroboration of smaller isocyanates with HB(C$_6$F$_5$)$_2$ directly leads to N/B FLP(isocyanate) adducts, significantly increasing the isocyanate steric bulk with ^{Ph2tBu}ArNCO allows for the isolation of the substrate-free FLP **3**. Surprisingly, this confused FLP **3** possesses a covalent N–B bond without any direct O–B interaction, despite considerable steric crowding about the N–B bond with bulky N–Ar and B(C$_6$F$_5$)$_2$ groups. Nonetheless, high-level DFT calculations predict this confused isomer **3** to be most stable. Isomerization of confused **3** to the frustrated, O–B bonded isomer **3′** allows for typical N/B FLP-type reactivity with isocyanates and isocyanides. Unfortunately, exposure of **3** to common FLP substrates such as H$_2$ or CO$_2$ does not lead to clean, facile reactions. In part, this may reflect the kinetic and thermodynamic barriers associated with the isomerization of confused **3** to frustrated **3′** required to capture substrates, which leaves room for development of the isocyanate component to lower these barriers. Nonetheless, these studies make clear that FLP-like reactivity may be observed from structural motifs without any obvious frustrated Lewis acid–base interaction.

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[29] Section 5 in the Supporting Information contain crystallographic data for complexes **1**–**6**. CCDC 1504054, 1504055, 1504056, 1504057, 1504058 and 1504059 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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