ARTICLE TYPE

Frustrated Lewis Pair Behavior of Monomeric (boryl)iminomethanes Accessed from Isocyanide 1,1-Hydroboration

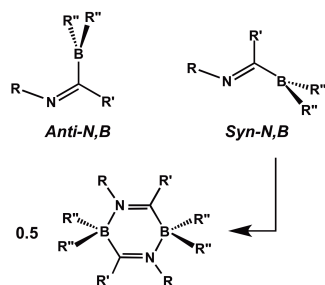**Brandon R. Barnett,**[a] **Curtis E. Moore,**[a] **Arnold L. Rheingold**[a] **, and Joshua S. Figueroa**[a]

The activation of carbon dioxide, organonitriles, and terminal acetylenes by (boryl)iminomethanes derived from isocyanide 1,1-hydroboration is described. Also detailed is the generality of hydroboration of *m*-terphenylisocyanides
10 **with hydroboranes of differing Lewis acidities.**

With the advent of phosphine/borane Frustrated Lewis Pairs (FLPs) by Stephan,[1] there has been significant interest in the development of transition-metal-free small-molecule activation
15 processes.[2-4] While a number of intra- and inter-molecular FLP platforms have been uncovered,[5,6] most feature strongly Lewis basic and acidic groups to enhance reactivity toward small molecule substrates. Recently however, computational investigations[7,8] have suggested that enhanced reactivity profiles
20 might be displayed by intramolecular FLP platforms that contain frontier orbitals mutually oriented in the direction of an incoming substrate.[9-15] Such "preorganized" FLPs should remain highly active, but decrease reliance on strongly Lewis acidic groups (*e.g.* perfluorinated arylboranes and alanes), which can inhibit
25 the imperative substrate release step in catalytic applications.[9] Accordingly, new, readily-prepared FLPs that feature a 'preorganized' architecture promise to be of broad interest.

Recently, we reported the synthesis of the platinum-(boryl)iminomethane complex, Pt(κ^2-*N,B*-^{Cy2}BIM)(CNAr^{Dipp2})
30 (^{Cy2}BIM = Cy$_2$BC(H)=NAr^{Dipp2}; Ar^{Dipp2} = 2,6-(2,6-(*i*-Pr)$_2$C$_6$H$_3$)$_2$C$_6$H$_3$) and demonstrated that the rigid, bidentate ^{Cy2}BIM ligand promoted a significant reverse-dative σ-interaction between the Pt and boron centers.[16] We also showed that the free (boryl)iminomethane ^{Cy2}BIM could be easily
35 prepared by 1,1-hydroboration of the *m*-terphenyl isocyanide[17] CNAr^{Dipp2} and that it readily activated both H$_2$ and H$_2$O in a manner consistent with FLP behavior. To our knowledge, this constituted the first report of (boryl)iminomethane formation by 1,1-hydroboration of an isocyanide. While both the ease of
40 synthesis and reactivity profile of ^{Cy2}BIM suggest that the

Fig. 1. Synthesis (left) and molecular structure (right) of **2a**.

(boryl)iminomethane (BIM) framework may be generally
50 competent for small-molecule activation processes, it is critical to note that kinetically persistent (boryl)iminomethane monomers are rare.[18-22] Indeed, when unencumbering substituents are present, (boryl)iminomethanes rapidly dimerize to heterocyclic 1,3-diaza-2,4-diboretidines (Scheme 1).[23-36]
55 Furthermore, of the few structurally-characterized (boryl)iminomethane monomers that have been reported,[19] all possess an *anti* relationship between the borane center and the imino nitrogen lone pair, thus precluding exploitation of their ambiphilic properties toward exogenous substrates. In an effort
60 to further detail the reaction profile available to monomeric (boryl)iminomethanes, we report here the reactivity of ^{Cy2}BIM toward unsaturated organic substrates and provide clear evidence for its "preorganized" intramolecular FLP-type behavior. Accordingly, despite the presence of a dicyclohexylboryl group
65 of moderate Lewis acidity, ^{Cy2}BIM readily activates carbon dioxide, organonitriles, and terminal acetylenes. In addition, we demonstrate that the formation of syn-*N,B* monomeric (boryl)iminomethanes is a general stereochemical outcome in the 1,1-hydroboration of *m*-terphenyl isocyanides.

Scheme 1. Regioisomers of monomeric (boryl)iminomethanes and dimerization of sterically unencumbered *syn-N,B* (boryl)iminomethanes
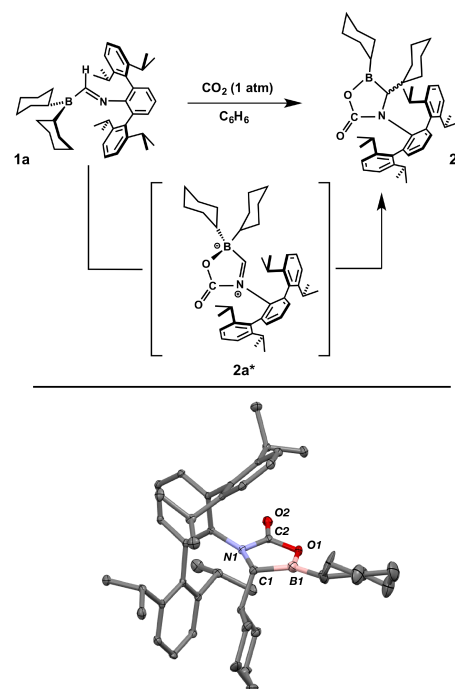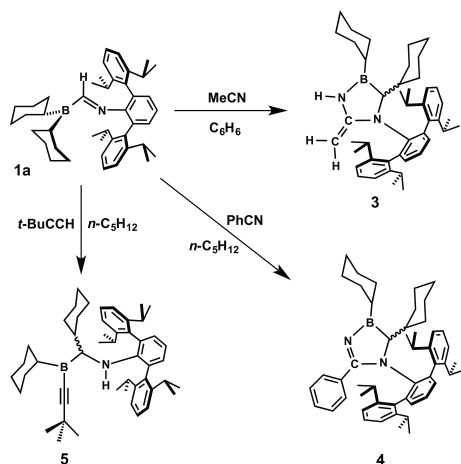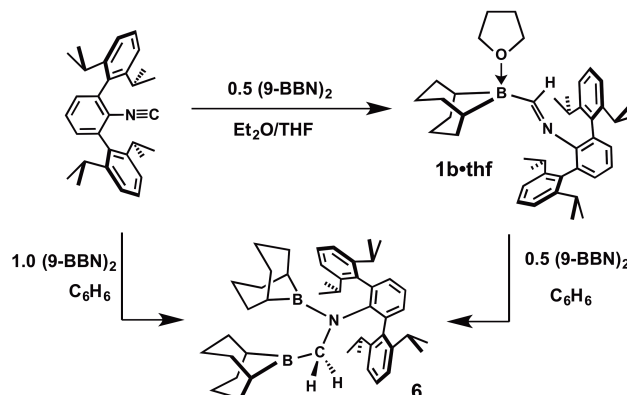45 to 1,3-diaza-2,4-diboretidines.

Scheme 2. Activation of acetonitrile, benzonitrile, and *t*-butylacetylene by [Cy2]BIM (**1a**).

Scheme 3. Single- and double-hydroboration of CNAr[Dipp2] with 9-borabicyclo[3.3.1]nonane (9-BBN).

The ability of [Cy2]BIM (**1a**) to act as a competent Frustrated Lewis Pair allows it to effect the facile C=O bond reduction of carbon dioxide. Placing a frozen benzene solution of [Cy2]BIM (**1a**) under 1 atm of CO_2 causes an immediate color change from bright yellow to colorless upon thawing. Analysis of the solution by ^{1}H and ^{11}B NMR spectroscopy indicates complete conversion to a single new product. The absence of any ^{1}H NMR signals diagnostic for an aldimine functionality hints at reduction of the C=N double bond of [Cy2]BIM (**1a**), while the appearance of a strong infrared absorbance at 1772 cm^{-1} suggests the presence of an ester group. The solid-state structure as determined by X-ray diffraction reveals this product to be the boralactone (**2a**; Fig. 1) derived from nucleophilic attack of the imime nitrogen at the CO_2 carbon atom and coordination of one oxygen atom to boron. As opposed to the vast majority of FLP-activated CO_2 adducts which are zwitterionic,[4,27] the endocyclic C2-O1 distance in **2a** (1.391(9) Å) is consistent with that of a carbon-oxygen single bond, suggesting a larger degree of activation than is typically seen in such species. Formation of the five-membered ring is accompanied by a 1,2-cyclohexyl shift, as observed previously for [Cy2]BIM (**1a**) in the heterolytic H-O bond cleavage of water.[16] This boron-to-carbon cyclohexyl migration,[28] reminiscent of a Wagner-Meerwein rearrangement,[29] has been observed with other (boryl)iminomethanes following their head-to-tail dimerization.[24,26] Relevantly, this 1,2-cyclohexyl shift may be at least partially responsible for the irreversibility of CO_2 reduction by [Cy2]BIM (**1a**), as heating solutions of **2a** to 80 °C under an N_2 atmosphere (or, alternatively, heating solid samples to 150 °C under vacuum) produces no evidence of reversion to [Cy2]BIM (**1a**) and free CO_2. This supposition is supported by Density Functional Theory calculations, which indicate that **2a** is stabilized by 18.2 kcal/mol with respect to its zwitterionic constitutional isomer **2a*** (Fig. 1 and ESI†). In the absence of cyclohexyl migration, the formation of **2a*** from [Cy2]BIM (**1a**) and CO_2 is computed to be enthalpically favored by 12.7 kcal/mol, indicating that the cyclohexyl migration event provides significant stabilization to the resulting adduct, and as such represents a substantial portion of the driving force toward irreversible CO_2 capture.

Despite the widespread progress that has been made in recent years toward the FLP-mediated activation of unsaturated organic molecules,[5,6] examples of nitrile C≡N bond reduction remain extremely limited.[30] As most FLP systems utilize strongly Lewis acidic fluorinated aryl-borane or alane moieties, there is likely a thermodynamic preference toward formation of a Lewis adduct with the nitrile *in lieu* of addition to its triple bond. It is therefore remarkable that treatment of [Cy2]BIM (**1a**) with acetonitrile results in formation of the eneamine **3** (Scheme 2), which undoubtedly is derived from 1,2-addition to the nitrile functionality accompanied by tautomerization of the resultant imine. Pursuant to this is the observation that benzonitrile, which lacks hydrogen atoms at the carbon *alpha* to the nitrile group, is similarly activated by [Cy2]BIM (**1a**) to give the 1,2-addition product imine (**4**, Scheme 2). Both transformations are essentially complete upon mixing as evidenced by an immediate decoloration of the reaction solutions upon nitrile addition. We suggest that the observed activity of [Cy2]BIM (**1a**) toward nitriles is largely due the presence of a relatively weakly Lewis acidic – BCy_2 fragment that decreases the stabilization associated with formation of a nitrile-borane adduct. As is the case with CO_2 activation, the cyclohexyl migration event in the formation of **3** and **4** likely provides further driving force toward 1,2-addition to the nitrile.

[Cy2]BIM (**1a**) is also reactive toward *t*-butylacetylene, effecting deprotonation of the acetylenic proton to give an alkynylborane (**5**, Scheme 2). No evidence of products derived from 1,2-addition to the alkyne triple bond is seen. Both 1,2-addition and deprotonation reactions of terminal alkynes effected by FLPs have been reported,[31-36] although *t*-butylacetylene appears to typically undergo preferential deprotonation, likely due to the steric encumbrance that the *t*-butyl group imposes at the internal *sp* carbon atom.

In an effort to explore the generality of (boryl)iminomethane formation via isocyanide hydroboration, we targeted the synthesis of a BIM derived from 9-borabicyclo[3.3.1]nonane (9-BBN), due to both its commercial availability and the presence of a tethered carbon backbone. The latter trait was particularly attractive, as we envisioned that it might discourage 1,2-alkyl migration in the corresponding BIM.[37] Carrying out the reaction of CNAr[Dipp2] with 0.5 equivalents of 9-BBN dimer in the presence of THF allows for the hydroboration reaction to proceed smoothly to the THF-complexed (boryl)iminomethane [9-BBN]BIM·THF (**1b**·THF, Scheme 3), which has been structurally characterized (Fig. 2). The boron atom is oriented *syn* to the nitrogen lone pair across the imine double bond, as is seen with [Cy2]BIM (**1a**). The ^{11}B NMR spectrum of **1b**·THF features a singlet at 7.5 ppm, suggesting that the dative THF-borane interaction remains intact in solution. Indeed, successive *n*-pentane washes and exposure to high vacuum fail to liberate THF from **1b**·THF. Attempts to synthesize **1b** in the absence of THF resulted in the formation of several products. Although complete separation of these mixtures has proven unsuccessful, one of these species (**6**) was
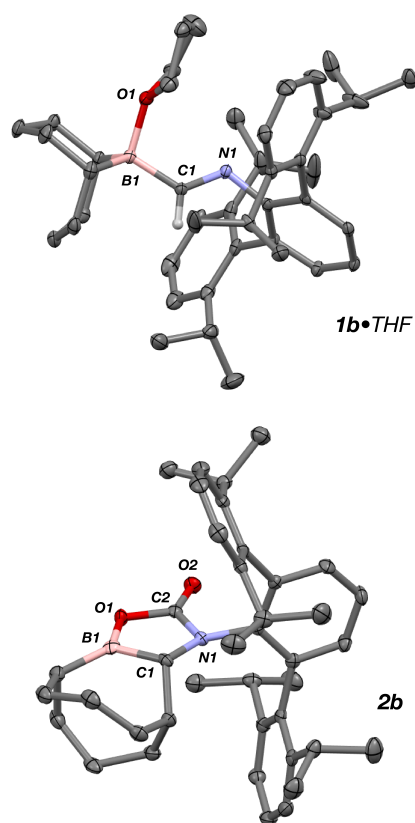
Fig. 2. Molecular structures of $^{9\text{-BBN}}$BIM·THF (**1b**·THF) and its CO_2 adduct **2b**.

Scheme 4. CO_2 activation and heterolytic H-O cleavage of water by **1b**·THF.

5 identified as the product of formal 1,1 and 1,2-double hydroboration of CNAr^{Dipp2} by an independent synthesis (Scheme 3). Presumably, this reaction proceeds via initial hydroboration of CNAr^{Dipp2} to give the (boryl)iminomethane $^{9\text{-}}$ ^{BBN}BIM (**1b**) which, in the presence of additional 9-BBN, 10 undergoes hydroboration of its imine functionality to furnish **6**. Indeed, addition of 9-BBN dimer to **1b**·THF in benzene solution results in conversion to **6** with release of THF (Scheme 3), lending credence to this proposed synthetic pathway.

Despite the THF-complexed nature of the borane unit in $^{9\text{-}}$ 15 ^{BBN}BIM·THF (**1b**·THF), frustrated Lewis pair reactivity is still accessible. Addition of CO_2 to a benzene solution of **1b**·THF results in immediate and irreversible conversion to a new product (**2b**, racemic mixture, Scheme 4) with liberation of one equivalent of THF as assayed by ^{1}H NMR. This product displays 20 a ^{11}B NMR resonance at 55.7 ppm indicating the presence of a three-coordinate boron center.[38] Crystallographic characterization of **2b** (Fig. 2) revealed the formation of a boralactone where the bicycloalkyl has undergone a ring expansion to produce a substituted 9-borabicyclo[3.3.2]decane 25 structure. Concomitant with this process is the eradication of the imine C=N double bond. The ring expansion process of the bicycloalkyl group, which has been observed in other systems containing the 9-BBN framework,[39-43] amounts to a 1,2-alkyl shift that is analogous to the cyclohexyl migration seen in 30 reactions of ^{Cy2}BIM (**1a**). Likewise, this process appears to be general to the $^{9\text{-BBN}}$BIM framework, as ring expansion also occurs upon the heterolytic H-O bond cleavage of water by$^{9\text{-}}$ ^{BBN}BIM·THF (**1b**·THF) to give the borinic acid **7** (racemic mixture, Scheme 4). These results indicate that a more judicious 35
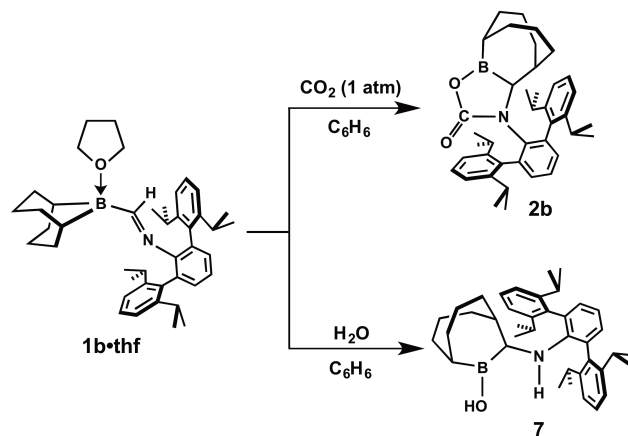
choice of borane substituents will be required if alkyl migration 40 is to be circumvented in the reaction chemistry of (boryl)iminomethanes.

The dialkylboryl substituents in the (boryl)iminomethanes **1a** and **1b** are among the most weakly 45 Lewis acidic components of a frustrated Lewis pair reported to date.[44,45] The competency of **1a** and **1b** to effect FLP-type reactivity is undoubtedly tied to the geminal relationship of the acidic and basic sites, as well as the rigid geometry enforced by the imine double bond, the same structural traits that allow 50 (boryl)iminomethanes to foster reverse-dative σ-interactions between a Lewis-basic metal center and the borane unit.[16] In order to test the limits of this approach, we synthesized the pinacolboryl-substituted ^{Pin}BIM (**1c**; Fig. 3), which contains a boron center of even further attenuated Lewis acidity. Unlike the 55 syntheses of **1a** and **1b**, the use of excess borane and prolonged heating are required to drive the formation of **1c** to completion. Fractional crystallization from *n*-pentane/hexamethyldisiloxane mixtures allows for isolation of analytically pure samples of ^{Pin}BIM (**1c**) in modest yields. Examination of the crystal 60 structure of **1c** reveals a *syn* orientation of the imine lone pair and boron atom, as well as a nearly planar orientation of the C(H)N-BO$_2$ units (dihedral angle = 5.8(2)°). Interestingly, the presence of the more weakly Lewis acidic pinacolboryl group inhibits the reactivity of the (boryl)iminomethane framework 65 with CO_2, as ^{Pin}BIM (**1c**) and CO_2 fail to react under the conditions utilized in the syntheses of **2a** and **2b**. Furthermore, a broadening of signals suggestive of reversible formation of a CO_2 adduct is not observed by ^{1}H NMR spectroscopy. These observations suggest that more strongly Lewis acidic groups are 70 necessary for stoichiometric FLP-type reactivity to occur between (boryl)iminomethanes and CO_2, while also illustrating the limits of a preorganized FLP architecture.[46]

In conclusion, we have synthesized a series of ambiphilic and monomeric (boryl)iminomethanes (BIMs) via the 1,1- 75 hydroboration of an *m*-terphenyl isocyanide. The same structural and electronic properties that allow (boryl)iminomethanes to behave as LZ-type chelating ligands toward electron-rich transition metal centers also promote the activation of unsaturated and protic substrates in an FLP manner. While this 80 reactivity is accessible when a BIM bears a moderately Lewis acidic dialkylboryl group, switching to the more weakly Lewis acidic pinacolboryl substituent inhibits reactivity with carbon dioxide. Further explorations of such weakly Lewis acidic (boryl)iminomethanes are currently being pursued, with an eye
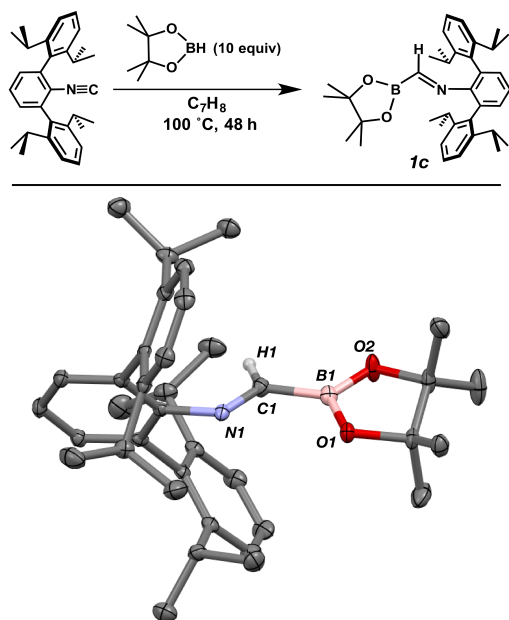
Fig. 3. Synthesis (top) and molecular structure (bottom) of ^{Pin}BIM (**1c**).

toward tailoring them to effect catalytic transformations of small molecules.

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† Electronic supplementary information (ESI) available: Synthetic details, results of computational studies and X-ray crystallographic data (CCDC 1028214 – 1028222). See DOI: 10.1039/b000000x

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