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FLP-CO₂ adducts: convenient sources of frustrated Lewis pairs for stoichiometric and catalytic chemistry†Jordan Thomson,^a Marc-André Courtemanche,^b Rebecca C. Neu^a and Douglas W. Stephan^b *^a

The compounds [tBu₃PCO₂B(C₆F₅)₃] **1** and [TMPh][C₅H₆Me₄NCO₂B(C₆F₅)₃] **7** are easily handled synthons releasing CO₂ on warming generating the corresponding FLPs which can activate H₂, disulfides, alkynes, silanes and phenols. Compound **7** was also shown to be an effective FLP catalyst precursor for the hydrogenation and hydrosilylation of imines, electron deficient olefins, and ketones while less effective for electron-rich olefins. The advantages and limitations of this approach are considered.

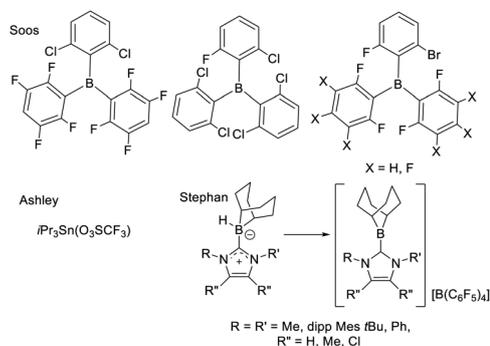
Although the Lewis acid B(C₆F₅)₃ first prepared by Stone *et al.*¹ in 1963 drew little attention at the time, it has become an iconic Lewis acid for a range of chemistry. It garnered attention in the 1990s with the organometallic community when Marks² exploited it to abstract alkyl groups from early metal system generating active polymerization catalysts. On the other hand, Piers³ showed that it was an effective Lewis acid catalyst for hydrosilylation catalysis, drawing attention from organic and polymer chemists. In the 2000s, the advent of frustrated Lewis pair (FLP) chemistry^{4–8} began with many systems derived from B(C₆F₅)₃, further broadening the interest in this Lewis acid across the discipline.

In the latter area of application, the discovery that combinations of sterically encumbered Lewis acids and bases could activate H₂⁹ led to the development of metal-free catalytic hydrogenations.¹⁰ This inspired studies probing variations in FLP catalysts, the organic substrates for reduction and even the utility of chiral catalysts for stereoselective reductions. These advances have been reviewed.^{11–13}

At the same time, the ability of FLPs to activate other small molecules led to a broad range of reactivity with alkynes, olefins, CO₂, CO, SO₂, and NO, among others.^{4–7,14} These efforts

have uncovered new avenues to C–C bond formations and their applications in organic synthesis,¹⁵ while reactivity of greenhouse gases have targeted issues around climate change.¹⁴

Despite these various applications, FLP chemistry is often challenged by moisture or oxygen sensitivity of the individual components. The propensity of Lewis acids to form adducts with water quenches Lewis acidity and can prompt a diversion of the reactivity to proton mediated processes, necessitating the use of anhydrous and anaerobic conditions. Several authors have targeted efforts to address such issues. For example, Soós and coworkers^{16–18} have cleverly developed a family of borane derivatives that are air and moisture stable for hydrogenation catalysis (Scheme 1), while Ashley¹⁹ has exploited iPr₃Sn(O₃SCF₃) (Scheme 1) as a readily accessible and easily handled Lewis acid for such reductions. In our own efforts, we^{20,21} prepared air stable carbene–borane adducts of the form (NHC)(9-BBN) which are readily activated to the corresponding boronium cation (Scheme 1). While such cations are air sensitive but highly effective hydrogenation catalysts, their use benefits from the convenience of bench stable precursors. More recently, a strategy for the stabilization of FLPs has been their inclusion into metal–organic frameworks (MOFs).^{22–25} This



Scheme 1 Molecular variants of Lewis acids as approaches to air-stable precursors.

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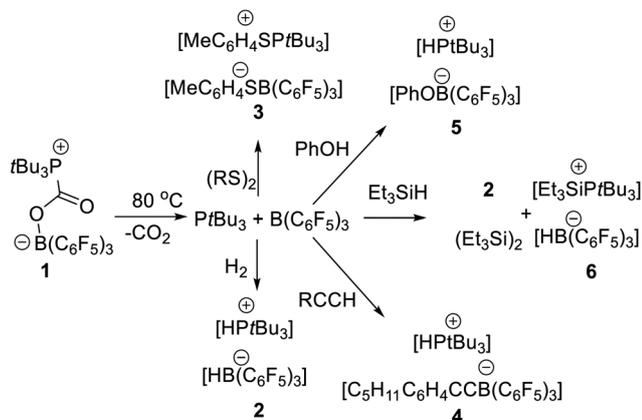
† Electronic supplementary information (ESI) available: Synthetic details, and spectral data are deposited, X-Ray data are deposited. CCDC 2441188 for **5**. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d5dt00942a>

approach has yielded catalysts that are recyclable, substrate size-selective and in some cases stereoselective.

While the above advances facilitate FLP chemistry, we sought to uncover a general and convenient approach to the use $B(C_6F_5)_3$ in a range of stoichiometric FLP chemistry and catalysis. To this end, we noted that Piers and coworkers^{26,27} have prepared a series of triphenylsulfonium carbamates from the lithiation of an amine, reaction with CO_2 and then reaction with $B(C_6F_5)_3$ and $[Ph_3S]Cl$. Photolysis of the resulting salts provided an effective route to liberate $B(C_6F_5)_3$ for applications in the reaction between silanes and alkoxy silanes. We recognized that a closely related approach could be employed to access FLP chemistry as FLPs are known to readily capture of CO_2 to form air stable zwitterions or salts. Moreover, such capture of CO_2 is thermally reversible.^{28–30} In this manuscript, we demonstrate that such species are readily handled, bench stable precursors that can be employed to provide precisely stoichiometric combinations of Lewis acids and bases for FLP reactions and catalysis.

The capture of CO_2 by the FLP $tBu_3P/B(C_6F_5)_3$ is known to afford the zwitterion $tBu_3PCO_2B(C_6F_5)_3$ ²⁸ while using the N-base $C_5H_6Me_4NH$ (TMP), the salt $[TMPH][C_5H_6Me_4NCO_2B(C_6F_5)_3]$ ³⁰ is obtained. These products are relatively robust in air, exhibiting minimal degradation with humidity. At the same time these compounds, thermally release CO_2 to regenerate the corresponding FLP. We hypothesized that these species could act as convenient synthons for FLPs.

To probe this idea, $tBu_3PCO_2B(C_6F_5)_3$ **1** was dissolved in *ortho*-difluorobenzene (*o*DFB) solution and heated to 80 °C for 20 minutes under an H_2 atmosphere. Monitoring by NMR spectroscopy revealed the formation of a mixture of products. This was attributed to the known reactions of CO_2 with products of H_2 activation by an FLP.³⁰ However, repeating the generation of the FLP under N_2 followed by subsequent evacuation and replacement of the atmosphere with H_2 resulted in a clean and immediate reaction affording a ³¹P resonance at 63.2 ppm, a ¹¹B signal at –22.7 ppm and three ¹⁹F resonances at –132.4, –164.5, and –167.0 ppm. These data are consistent with the formation of the known salt $[tBu_3PH][HB(C_6F_5)_3]$ **2**³¹ (Scheme 2).



Scheme 2 Thermal liberation of the FLP, tBu_3P and $B(C_6F_5)_3$ and subsequent stoichiometric FLP chemistry.

In a similar fashion the generation of the FLP from **1** in the presence of $(MeC_6H_4S)_2$ gave the clean formation of species $[tBu_3PSC_6H_4Me][MeC_6H_4SB(C_6F_5)_3]$ **3**³² (Scheme 2) as evidenced by the ³¹P, ¹¹B and ¹⁹F resonances at 84.2 ppm, –9.5 ppm, and –130.7, –164.1, –167.7 ppm, respectively.

The corresponding generation of the FLP from **1** in the presence of the alkyne, 1-ethynyl-4-pentyl-benzene, resulted in the known reaction of the FLP with alkynes,³³ as evidenced by the ³¹P signal at 59.9 ppm, a ¹¹B signal at –20.9 ppm and ¹⁹F resonances at 132.0, –163.4 and –166.8 ppm, respectively, consistent with the formation of $[tBu_3PH][C_5H_{11}C_6H_4CCB(C_6F_5)_3]$ **4** (Scheme 2).

Heating **1** in the presence of PhOH afforded the species **5**. Based on the ³¹P, ¹¹B and ¹⁹F resonances at 63.2, –1.0, and 132.4, –162.6, –166.6 ppm, respectively, this species was formulated as $[tBu_3PH][PhOB(C_6F_5)_3]$ **5** (Scheme 2). The nature of **5** was confirmed unambiguously by an independent synthesis from the reaction of the FLP $tBu_3P/B(C_6F_5)_3$ with phenol and a subsequent X-ray diffraction study (Fig. 1). The B–O bond length was found to be 1.510(4) Å while the remaining metric parameters were unexceptional.

The analogous treatment of a solution of **1** with Et_3SiH generated a mixture of products containing **2** as well as $[tBu_3PSiEt_3][HB(C_6F_5)_3]$ **6** as evidenced by the ³¹P NMR signal at 38.2 ppm. While the species **6** is formed by FLP activation of silane, the cation can react with additional silane transiently generating the cation $[Et_3Si(HSiEt_3)]^+$ which protonates the phosphine affording the phosphonium cation of **2** and releasing $(Et_3Si)_2$. The ability of $B(C_6F_5)_3$ to effect such dehydrogenative coupling of silanes has been patented.³⁴ The formation of these products was also supported by ²⁹Si/¹H HMBC experiment as signals at –33.8 and 10.9 ppm were similar to literature data for $[tBu_3PSiEt_3]^+$ ³⁵ and $(Et_3Si)_2$,³⁶ respectively (see ESI†).

In a further extension, the FLP reactions products were accessed using $[TMPH][TMPCO_2B(C_6F_5)_3]$ **7** as the FLP precursor. Reactions with H_2 , alkyne, and phenol afforded the species, $[(TMP)H][HB(C_6F_5)_3]$ **8**,³⁷ $[(TMP)H][C_5H_{11}C_6H_4CCB(C_6F_5)_3]$ **9**,³⁸ and $[(TMP)H][PhOB(C_6F_5)_3]$ **10**, respectively (Scheme 3). Spectral data confirmed these products and were analogous to published data and that described above.

The above chemistry demonstrated the ability of **1** and **7** to access the corresponding FLPs. As FLP reactivity is often air

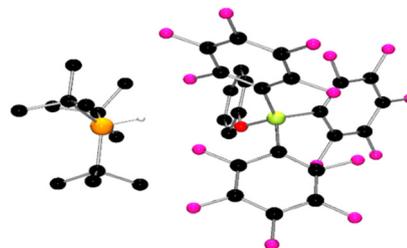
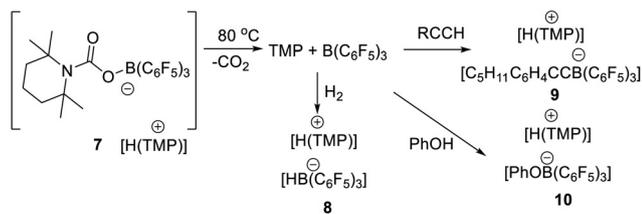


Fig. 1 POV-ray depiction of the crystallographic structure of the salt **5**, hydrogen atoms except for the PH unit are omitted for clarity. C: black, P: orange, O: red, B: yellow-green, F: pink, H: white.





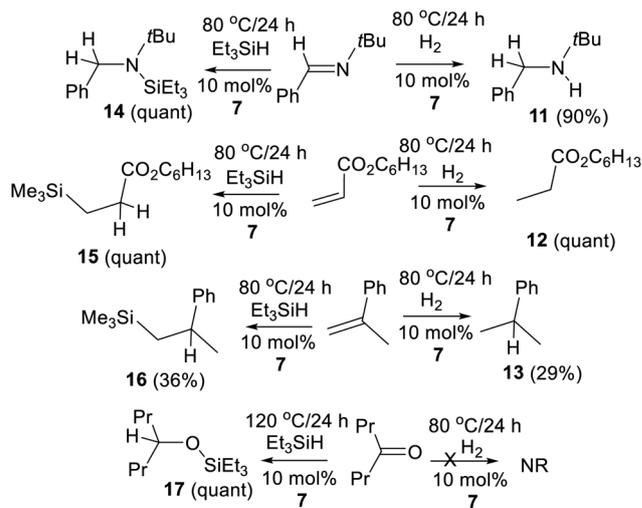
Scheme 3 Thermal liberation of the FLP, TMP and $B(C_6F_5)_3$ and subsequent stoichiometric FLP chemistry.

and moisture sensitive, we next examined the tolerance of **1** for manipulation on the bench. To that end, **1** was weighed on the bench and left in an open vial for 24 h. This sample of **1** was then used in the reaction with $(MeC_6H_4S)_2$. While the reaction mixture was subsequently heated under an N_2 atmosphere, this aerobic manipulation of **1** had no impact and the expected product **3** was formed with only a trace of the product of the reaction of the FLP with water.

Having established the utility of **1** and **7** in stoichiometric FLP reactions, trials of catalytic reactions were undertaken. To this end, 10 mol% of **1** combined with the imine $PhCH=NtBu$ in an *o*DFB solution and heated to 80 °C for 24 h under 4 atm of H_2 . While this led to the formation of **2**, no catalytic reduction was observed consistent with the inability of $[tBu_3PH]^+$ to protonate the imine substrate.

In contrast, the corresponding reaction using **7** as the catalyst for the hydrogenation of the imine $PhCH=NtBu$ was monitored by NMR spectroscopy. This revealed 90% reduction of the substrate to the amine $PhCH_2NHtBu$ **11**³⁹ in accord with the previous literature reports of FLP hydrogenations.^{10,40} Under identical conditions hydrogenation of the acrylate $CH_2=CH(CO_2C_6H_{13})$ was performed. This gave quantitative reduction of the olefinic fragment affording $CH_3CH_2(CO_2C_6H_{13})$ **12**. Efforts to similarly reduce the olefin $CH_2=C(Me)Ph$ gave only 29% yield of the reduced product Me_2CHPh **13**. The contrasting reactivity for these two olefinic species is consistent with the established and differing mechanisms for electron deficient and electron rich olefins.^{41,42} In the former case, initial hydride delivery generates a transient but highly basic carbanion that can accept a proton from the ammonium cation $[TMPH]^+$ and thus the catalysis proceeds. In contrast, the reduction of the electron-rich olefin is initiated by protonation of the olefin. Proton transfer from $[TMPH]^+$ to the olefin is ineffective and thus reduction is slow. In a similar sense, attempts to hydrogenate the ketone Pr_2CO were completely unsuccessful. Again, the inability to initiate reduction *via* protonation of the ketone by $[TMPH]^+$ accounts for the absence of latter reactivity.⁴³

Similar experiments were also performed to probe hydrosilylation catalysis. Using 10 mol% of **1** or **7**, in the presence of 1.5 equivalents of Et_3SiH with heating to 80 °C for 24 h, the imine $PhCH=NtBu$ was quantitatively hydrosilylated to the product $PhCH_2NtBu(SiEt_3)$ **14** as evidenced by NMR spectroscopy.⁴⁴



Scheme 4 Hydrogenation and hydrosilylation catalysis using **7** as catalyst precursor.

In a similar fashion the catalytic hydrosilylation of $CH_2=CH(CO_2C_6H_{13})$ was also achieved affording the quantitative formation of the product $Et_3SiCH_2CH_2(CO_2C_6H_{13})$ **15**.⁴⁵ The electron rich olefin $CH_2=C(Me)Ph$ was partially hydrosilylated using **7** as the catalyst, affording the product $Et_3SiCH_2CH(Me)Ph$ **16**⁴⁶ in 36% yield. Finally, the ketone, Pr_2CO was hydrosilylated quantitatively to $Pr_2CHOSiEt_3$ **17**⁴⁷ (Scheme 4). The formulations of these products were confirmed by 1H NMR spectroscopy and all were in accord with the previous literature data.

The above results again point to the differing mechanism for the reduction of the electron deficient and electron-rich olefins.^{41,42} In the case of hydrosilylation of an electron rich olefin, reduction is initiated by interaction with the silylium cation, which is slowed by the base TMP. On the other hand, hydride delivery to the electron-poor olefin generates a carbanion that is a more effective nucleophile for silylium capture.

The above results demonstrate that compound **7** can act as useful pre-catalyst for the hydrogenation of imines and electron deficient olefins as well as the hydrosilylation of imines, electron deficient olefins, and ketones. It was less effective for the hydrogenation and hydrosilylation of electron-rich olefins and the hydrogenation of ketones. These successes and limitations can be understood upon consideration of the differing mechanisms of these reductions.

Conclusions

These findings serve as a proof-of-concept, demonstrating that these air stable FLP derivatives can be used to provide facile access to precisely stoichiometric combinations of a Lewis acid and base and that such mixtures are active FLPs for subsequent stoichiometric or catalytic FLP chemistry. While these precursors provide increased ease of precursor manipulation, the mechanism of the application targeted must be con-



sidered. We are continuing to explore this concept, targeting other FLP derivatives that might offer access to a broader range of Lewis acid/base combinations. In addition, we are exploring the applications of such derivatives in a wider range of catalysis.

Data availability

The data supporting this article have been included as part of the ESI.†

Crystallographic data for **5** has been deposited at the CCDC under 2441188† and can be obtained from Deposit- The Cambridge Crystallographic Data Centre (CCDC).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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