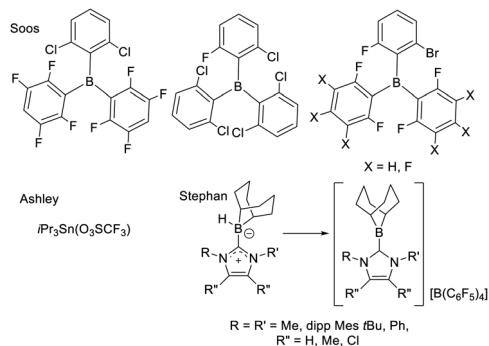




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At the same time, the ability of FLPs to activate other small molecules led to a broad range of reactivity with alkynes, olefins, CO<sub>2</sub>, CO, SO<sub>2</sub>, and NO, among others.<sup>4-7,14</sup> These efforts

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<sup>16–18</sup> have cleverly developed a family of borane derivatives that are air and moisture stable for hydrogenation catalysis (Scheme 1), while Ashley<sup>19</sup> has exploited  $\text{iPr}_3\text{Sn}(\text{O}_3\text{SCF}_3)$  (Scheme 1) as a readily accessible and easily handled Lewis acid for such reductions. In our own efforts, we<sup>20,21</sup> prepared air stable carbene–borane adducts of the form  $(\text{NHC})(9\text{-BBN})$  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).<sup>22–25</sup> This



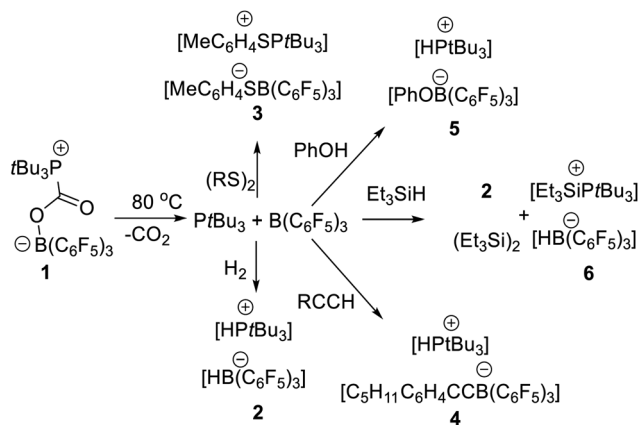
† Electronic supplementary information (ESI) available: Synthetic details, and spectral data are deposited, X-Ray data are deposited. CCDC 2441188 for 5. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d5dt00942a>

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<sup>26,27</sup> 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.<sup>28–30</sup> 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  $tBu_3PCO_2B(C_6F_5)_3$ <sup>28</sup> while using the N-base  $C_5H_6Me_4NH$  (TMP), the salt  $[TMPH][C_5H_6Me_4NCO_2B(C_6F_5)_3]$ <sup>30</sup> 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.<sup>30</sup> 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  $^{31}P$  resonance at 63.2 ppm, a  $^{11}B$  signal at –22.7 ppm and three  $^{19}F$  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**<sup>31</sup> (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**<sup>32</sup> (Scheme 2) as evidenced by the  $^{31}P$ ,  $^{11}B$  and  $^{19}F$  resonances at 84.2 ppm, –9.5 ppm, and –130.7, –164.1, –167.7 ppm, respectively.

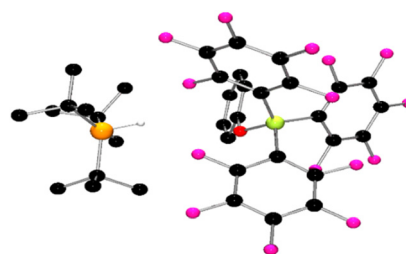
The corresponding generation of the FLP from **1** in the presence of the alkyne, 1-ethynyl-4-pentyl-benzene, resulted in the known reaction of the FLP with alkynes,<sup>33</sup> as evidenced by the  $^{31}P$  signal at 59.9 ppm, a  $^{11}B$  signal at –20.9 ppm and  $^{19}F$  resonances at 132.0, –163.4 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  $^{31}P$ ,  $^{11}B$  and  $^{19}F$  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  $^{31}P$  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.<sup>34</sup> The formation of these products was also supported by  $^{29}Si/^1H$  HMBC experiment as signals at –33.8 and 10.9 ppm were similar to literature data for  $[tBu_3PSiEt_3]^+$ <sup>35</sup> and  $(Et_3Si)_2$ ,<sup>36</sup> respectively (see ESI†).

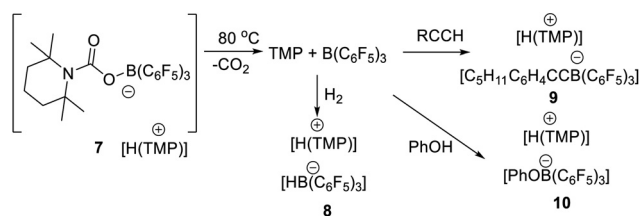
In a further extension, the FLP reactions products were accessed using  $[TMPH][TMPCO_2B(C_6F_5)_3]$  **7** as the FLP precursor. Reactions with  $H_2$ , alkyne, and phenol afforded the species,  $[(TMP)H][HB(C_6F_5)_3]$  **8**,<sup>37</sup>  $[(TMP)H][C_5H_{11}C_6H_4CCB(C_6F_5)_3]$  **9**,<sup>38</sup> 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.





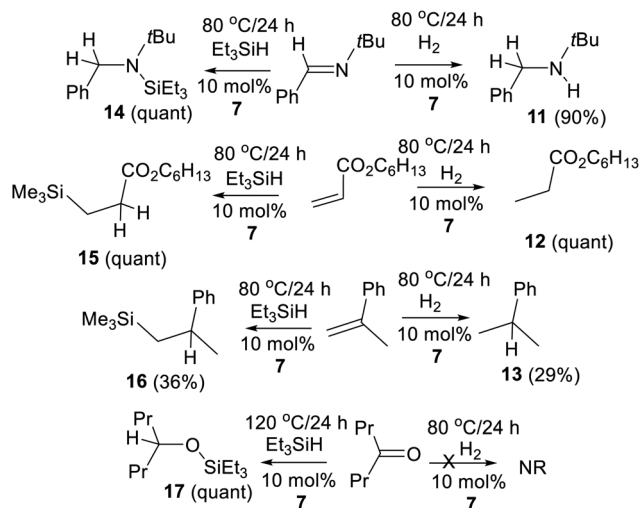
**Scheme 3** Thermal liberation of the FLP, TMP and  $B(C_6F_5)_3$  and subsequent stoichiometric FLP chemistry.

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**<sup>39</sup> in accord with the previous literature reports of FLP hydrogenations.<sup>10,40</sup> 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.<sup>41,42</sup> 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.<sup>43</sup>

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.<sup>44</sup>



**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**.<sup>45</sup> 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**<sup>46</sup> in 36% yield. Finally, the ketone,  $Pr_2CO$  was hydrosilylated quantitatively to  $Pr_2CHOSiEt_3$  **17**<sup>47</sup> (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.<sup>41,42</sup> 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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