Frustrated Lewis Pairs

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Exploring the Reactivity of Carbon(0)/Borane-Based Frustrated Lewis Pairs**

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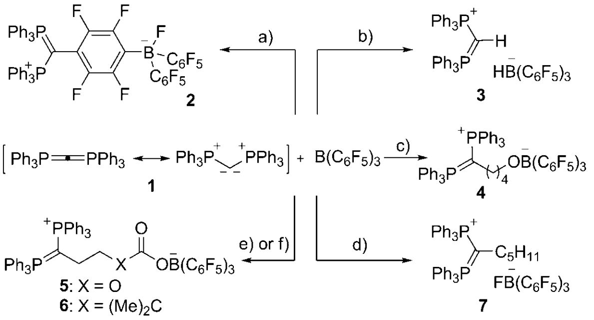
Dedicated to Professor Rosario Fernández

Since the unveiling of the concept of frustrated Lewis pairs (FLPs) by Stephan et al.,[1] the chemistry of these systems has flourished. Arguably their most attractive application has been the heterolytic activation of H_2,[2] and the subsequent development of metal-free hydrogenation catalysis directly employing dihydrogen[3] rather than a surrogate.[4] Although several other bonds such as C–O,[5] C–H,[6] B–H,[7] S–S,[8] and C–C,[9] have also been cleaved by using FLPs, these systems largely rely on P- or N-based Lewis bases combined with a polyfluorinated borane.[10] The sole exceptions are the sterically crowded carbene 1,3-di-*tert*-butyl-1,3-imidazol-2-ylidene (I*t*Bu) in combination with $B(C_6F_5)_3$, a pair that contains a C-derived base,[11] and the use of $Al(C_6F_5)_3$ instead of a borane as Lewis acid.[12] Clearly, extension of the FLP concept to include currently unexplored partners is desirable, as it may lead to the discovery of a range of interesting new applications.

In our research to broaden the range of bases that can be used in FLP chemistry, we were inspired by the computational investigations of Tonner and Frenking on the nature of carbodiphosphoranes.[13,14] They proposed that these compounds should be considered to comprise two phosphine ligands coordinated to a central zero-valent carbon atom that retains its four valence electrons. This view has been subsequently confirmed experimentally by the work of Bertrand et al., Fürstner et al., and others.[15]

The available information suggests that C^0 compounds must be exceptionally good nucleophiles. In fact, the calculated proton affinity for carbodiphosphoranes surpasses the values reported for amines, phosphines, and even N-heterocyclic carbenes. It can be envisaged therefore that, if sufficiently sterically hindered, C^0 compounds should be qualified to function as bases in the framework of FLP chemistry. Herein, in an attempt to address this issue, the pair hexaphenylcarbodiphosphorane (**1**)/$B(C_6F_5)_3$ is studied and its reactivity towards several small molecules evaluated.[17]

Initially, we carried out the reaction of **1** with $B(C_6F_5)_3$ in toluene at room temperature. The NMR spectroscopic data of the obtained product suggested formation of **2** by nucleophilic attack at the *para* position of the pentafluorophenyl ring and trapping of the generated fluoride anion by the boron atom. X-ray crystallographic analysis later confirmed the structure of **2** (see Supporting Information).[18] However, when the same reagents were mixed at −78 °C, NMR spectroscopy indicated no interaction between the partners, that is, "frustration". Purging this stoichiometric mixture with H_2 resulted in formation of a white precipitate which could be isolated in 91 % yield. The NMR data support the formulation for this product as $[(Ph_3P)_2CH][HB(C_6F_5)_3]$ (**3**; Scheme 1). The cation exhibits a ^1H signal at $\delta = 1.73$ ppm with $^2J(^1H,^{31}P)$ of 5.4 Hz and a $^{31}P\{^1H\}$ resonance at $\delta = 21.3$ ppm, while the anion gives the expected ^{11}B signal of a borohydride at $\delta = -25.5$ ppm with a $^1J(^1H,^{11}B)$ of 100 Hz. Single crystals were obtained by slow diffusion of pentane into a solution of **3** in CH_2Cl_2, and X-ray structure analysis confirmed not only the proposed structure (Figure 1), but also the ability of **1**/$B(C_6F_5)_3$ to function as an FLP.



Scheme 1. Some reactions of FLP **1**/$B(C_6F_5)_3$. Reagents and conditions (yields): a) toluene, −78 °C→RT (74 %); b) H_2 1 atm, toluene, −78 °C→RT (91 %); c) THF, −78 °C→RT (76 %); d) $nC_5H_{11}F$, toluene, −78 °C, quant.; e) ethylene carbonate, toluene, −78 °C→RT (84 %); f) 2,2-dimethyl-γ-butyrolactone, toluene, 78 °C→RT (71 %).

As expected for an FLP, **1**/$B(C_6F_5)_3$ in solution in THF resulted in ring opening of the ether to produce phosphonio borate **4**, also confirmed by X-ray analysis (see Supporting Information). This reactivity was extended to ethylene carbonate and the non-enolizable ester 3,3-dimethyl-γ-butyrolactone to produce zwitterionic species **5** and **6**, respectively. Moreover, addition of one equivalent of 1-fluoropentane to a suspension of **1**/$B(C_6F_5)_3$ at −78 °C generates $[(Ph_3P)_2C$-

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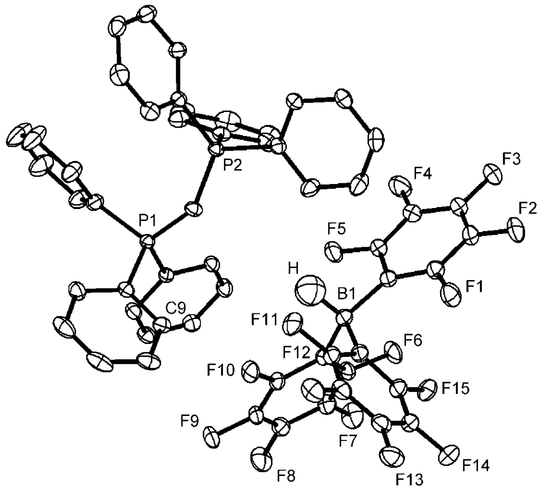


Figure 1. Molecular structure of **3** in the solid state (except for the hydrogen atom bonded to B, hydrogen atoms and solvent molecules were removed for clarity; ellipsoids set at 50% probability).[16]

$(C_5H_{11})][FB(C_6F_5)_3]$ in quantitative yield. This C–F bond activation of an alkyl fluoride is unprecedented in the scope of FLP chemistry and does not take place in the absence of borane, even at room temperature.[19]

The reactivity of terminal alkynes such as phenylacetylene in presence of several P/B- and P/Al-based FLPs has been studied by Stephan and co-workers.[6] Two possible reaction pathways, involving either deprotonation of the alkyne or Markovnikov addition of the FLP to the C–C triple bond, were observed. This divergent reactivity was explained in terms of the Brønsted basicity of the phosphines used. The very basic $t\mathrm{Bu}_3\mathrm{P}$ prompts deprotonation of the alkyne C–H, while aryl phosphines, which are less basic, prefer nucleophilic attack on the activated alkyne. Nonetheless, this rationale does not explain the fact that treatment of phenylacetylene with **1**/$B(C_6F_5)_3$, whereby **1** is a stronger base than $t\mathrm{Bu}_3\mathrm{P}$, resulted in formation of both possible products, that is, the expected **8** but also **9**. This points towards a concomitant, previously unconsidered, influence of steric factors. The X-ray structure of **9** is shown in Figure 2.

Activation of Si–H bonds with the FLP **1**/$B(C_6F_5)_3$ was also attempted. Upon stirring an equimolar mixture of Ph_2SiH_2, **1** and $B(C_6F_5)_3$ at −78 °C in toluene, the yellow color of the suspension slowly vanished and an immiscible colorless oil separated from the toluene phase. Purification by column chromatography afforded a pure compound that showed ^{1}H signals at $\delta = 5.12$ ppm with $^3J(^1\mathrm{H},^{31}\mathrm{P})$ of 16 Hz and at $\delta = 3.54$ ppm with $^1J(^1\mathrm{H},^{11}\mathrm{B})$ of 92.6 Hz, which can be assigned to a silane proton and a borohydride proton respectively. A $^{31}\mathrm{P}\{^1\mathrm{H}\}$ resonance at $\delta = 26.7$ ppm and a $^{11}\mathrm{B}\{^1\mathrm{H}\}$ signal at $\delta = -23.8$ ppm, together with high-resolution mass spectra of both the anion and the cation, unambiguously confirmed the proposed structure for **10** (Scheme 2).[20] Activation of the Si–H bond in $EtMe_2SiH$ was also achieved under the same reaction conditions to give **11**. Formation of a free silylium cation by direct interaction of the silane with $B(C_6F_5)_3$ has been ruled out by the work of Oestreich and Render on the enantioselective reduction of acetophenone with a chiral silane.[21] Likewise, an equimolar solution of **1** and Ph_2SiH_2 in benzene does not show any reactivity even after a day at room temperature. These results confirmed that the synergic effect of the base and the acid of our FLP is responsible for activation of the Si–H bonds. To the best of our knowledge, the achieved activation of Si–H bonds also has no precedent in FLP chemistry.

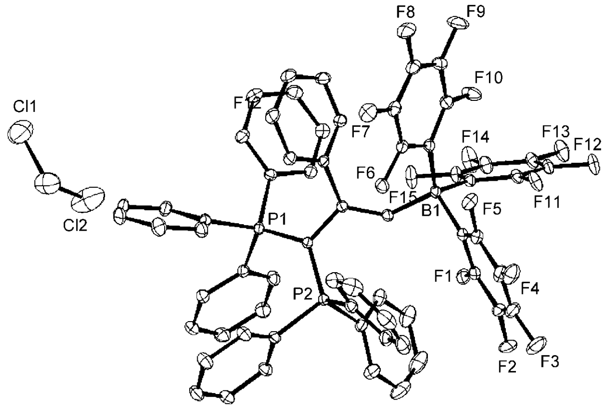
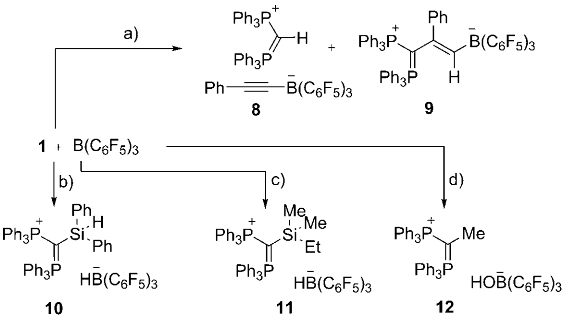


Figure 2. Molecular structure of **9**·CH_2Cl_2 in the solid state (hydrogen atoms removed for clarity; ellipsoids set at 50% probability).[16]

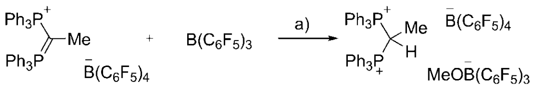


Scheme 2. Reactivity of the pair **1**/$B(C_6F_5)_3$ towards terminal alkynes. Reagents and conditions (yields): a) phenylacetylene, toluene −78 °C→RT, **8** (78%), **9** (12%); b) Ph_2SiH_2, toluene, −78 °C→RT (87%); c) Me_2EtSiH, toluene, −78 °C→RT (93%); d) Me_3SiOMe, toluene, −78 °C→RT, hydrolysis (88%).

In contrast, heterolytic cleavage of Si–F and Si–O bonds in $PhMe_2SiF$ and Me_3SiOPh was not successful under the same reaction conditions, and only **2** was obtained after allowing the reaction mixture to reach room temperature. When Me_3SiOMe was tested, product **12** was isolated. This compound presumably results from activation of the C–O bond of the silyl ether and hydrolysis of the trimethylsilyl borate during chromatographic purification.

Frenking estimated the second proton affinity of **1** to be −193.4 kcal mol^{-1}. This basicity is considered a hallmark of carbon(0)-containing compounds and suggests that even protonated or alkylated derivatives of **1** may still have an appreciable degree of frustration when confronted with $B(C_6F_5)_3$. To explore this possibility, salt **13** consisting of the methylated cation $[\mathbf{1}\cdot\mathrm{Me}]^+$ and a noninterfering $[B(C_6F_5)_4]^-$ anion was synthesized.[17] Although the pair **13**/$B(C_6F_5)_3$ was not able to activate H_2 or N–H of amines, it still cleaves the

O–H bond of methanol, something that **13** alone is not able to do (Scheme 3). In fact, **13** can be crystallized from MeOH without generating any protonated product.



13 **14**

Scheme 3. Cleavage of the O–H bond of methanol with the pair **13**/$B(C_6F_5)_3$. Reagents and conditions (yields): a) MeOH (1 equiv), toluene, RT, **14** (86%).

This reveals a degree of frustration that, albeit clearly diminished in comparison to the **1**/$B(C_6F_5)_3$ pair, is still remarkable considering the cationic nature of the employed base. Cationic Lewis acids like $[CPh_3]^+$ have been studied in the context of FLPs;[12] however, this is the first example of the counterintuitive use of a cationic base in this field. The formulation of compound **14** is supported by a ^{1}H NMR signal at $\delta = 1.95$ ppm for the Me group with $^3J(^1\text{H},^{31}\text{P})$ of 16.0 Hz and a $^3J(^1\text{H},^1\text{H})$ of 7.6 Hz, a $^{31}\text{P}\{^1\text{H}\}$ resonance at $\delta = 28.6$ ppm and two $^{11}\text{B}\{^1\text{H}\}$ signals at $\delta = -2.3$ and -15.2 ppm. In addition, during attempts to crystallize **14**, crystals of **14**$[B(C_6F_5)_4]_2$ were obtained and its structure confirmed by X-ray analysis (Figure 3).

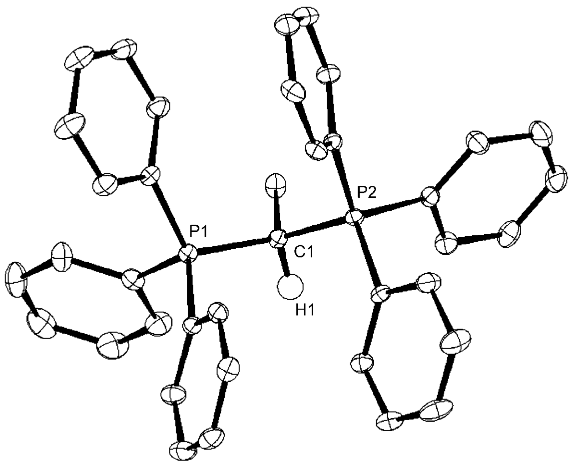


Figure 3. Molecular structure of **14**$[B(C_6F_5)_4]_2$ in the solid state. $(B(C_6F_5)_4$ anions and hydrogen atoms, except that bonded to C1, were removed for clarity; ellipsoids set at 50% probability).[16]

In conclusion, this study demonstrates that the combination of hexaphenylcarbodiphosphorane as carbon-based Lewis base and $B(C_6F_5)_3$ forms a novel frustrated Lewis pair. The system is not only able to achieve the classical H–H, C–O, and C–H bond cleavages, but also unprecedented activation of Si–H bonds and alkyl fluorides. The peculiar electronic situation of the C^0 base makes the system unique: after the first protonation or alkylation, some degree of frustration persists. The application of these FLPs in homogeneous catalysis is currently under investigation.

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