Ring-opening of cyclopropanes by "frustrated Lewis pairs"†

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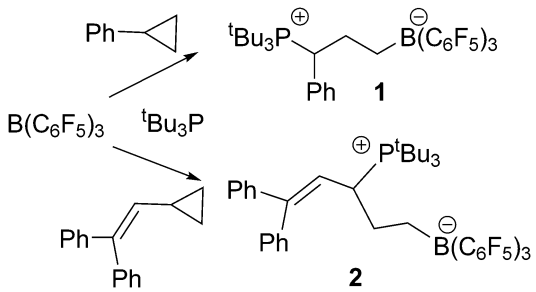
Reactions of phosphine/borane frustrated Lewis pairs with cyclopropanes result in the ring opening, yielding phosphonium borate products.

Frustrated Lewis pairs (FLPs) have been shown to react with a variety of reagents other than H_2.[1–5] These include terminal olefins,[6] alkynes,[7] B–H bonds,[8] disulfides,[9] the C–O bonds of cyclic ethers,[10] CO_2[11] and N_2O.[12–15] But for the heterolytic cleavage of disulfides,[9] these reactions of FLPs generally involve molecules with either a multiple bond and/or markedly polar character. In the activation of molecules with heteroatoms or π bonds, intuitively one can imagine electron donation to the Lewis acid of the FLP polarizes the substrate and prompts attack by the nucleophilic base. In the case of the heterolytic cleavage of H_2, computational studies[16–21] of this intriguing reaction infer that the field generated by the sterically restricted approach of an electron donor to the electron deficient Lewis acid is sufficient to polarize the otherwise non-polar H_2 molecule and thus induce heterolytic cleavage.

The above observations prompt questions about the ability of FLPs to effect the heterolytic cleavage of other bonds. In this regard our attention turned to C–C bonds. A number of studies have exploited transition metal catalyzed or Lewis acid activators to effect the ring-opening of functionalized cyclopropanes such as donor-acceptor cyclopropanes[22] and vinylidene cyclopropanes.[23–26] In contrast, alkyl or aryl substituted cyclopropanes are much less studied as such systems are less activated as they do not possess a "handle" for activation by a metal or a Lewis acid. Herein, we demonstrate that FLPs effect the heterolytic ring-opening of such cyclopropanes, affording zwitterionic products derived from C–C bond scission.

The cyclopropane PhC_3H_5 was added to a toluene solution of tBu$_3$P and $B(C_6F_5)_3$. On standing overnight this reaction afforded colorless crystals of a new species **1** which were subsequently isolated in 69% yield. The ^{11}B NMR spectrum of **1** gave a sharp singlet at −13.5 ppm. This together with the ^{19}F NMR data were consistent with the formation of a borate unit. The corresponding ^{31}P{^{1}H} NMR signal was observed at 54.1 ppm consistent with a phosphonium center. Among the ^{1}H NMR signals are signals at 3.6, 2.1, 1.8, 1.1 and 0.8 ppm with the appropriate couplings indicative of an alkyl chain. These data lead to the formulation of **1** as tBu$_3$PCH(Ph)CH$_2$CH$_2$B(C$_6$F$_5$)$_3$ (Scheme 1). While this was subsequently confirmed crystallographically (Fig. 1),‡ the metric parameters were unexceptional.



Scheme 1 Synthesis of **1** and **2**.

The analogous reaction of $B(C_6F_5)_3$ and tBu$_3$P with the cyclopropane $Ph_2C{=}CCHC_3H_5$ resulted in the formation of the zwitterionic phosphonium borate tBu$_3$PCH(CH=CPh$_2$)-CH$_2$CH$_2$B(C$_6$F$_5$)$_3$ **2** in 64% yield. This species results from a similar ring-opening of the cyclopropane, with P–C bond formation at the substituted carbon atom (Fig. 2).‡

It is clear that the formation of products **1** and **2** occurs *via* regio-specific cyclopropane ring opening, with formation of the B–C bond at the unsubstituted methylene carbon and the P–C bond to the phenyl-substituted carbon. The regiochemistry is consistent with attack of P at the substituted carbon which stabilizes the developing cationic charge.

To probe substituent effects on such reactions, the cyclopropanes $PhHC{=}CHC_3H_5$ and $H_2C{=}CHC_3H_3Ph_2$ were also reacted with $B(C_6F_5)_3$ and tBu$_3$P (Scheme 2). In the former case, an approximately 1 : 1.3 mixture of two phosphonium borate products **3a** and **3b** was obtained. The spectroscopic

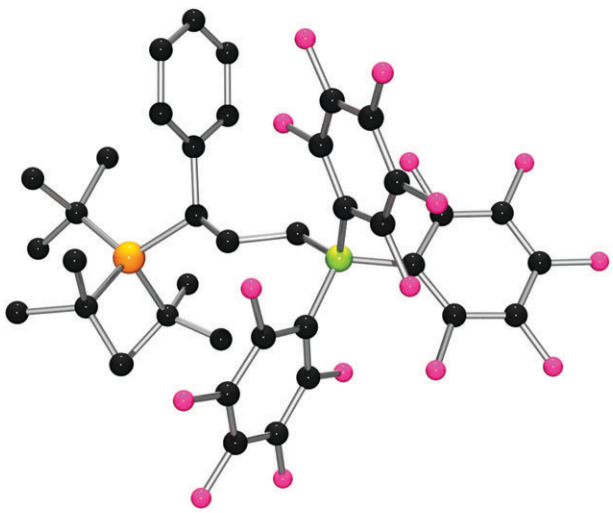


Fig. 1 POV-ray depictions of **1**, H-atoms have been deleted for clarity, C: black, F: pink, B: yellow-green, P: orange.

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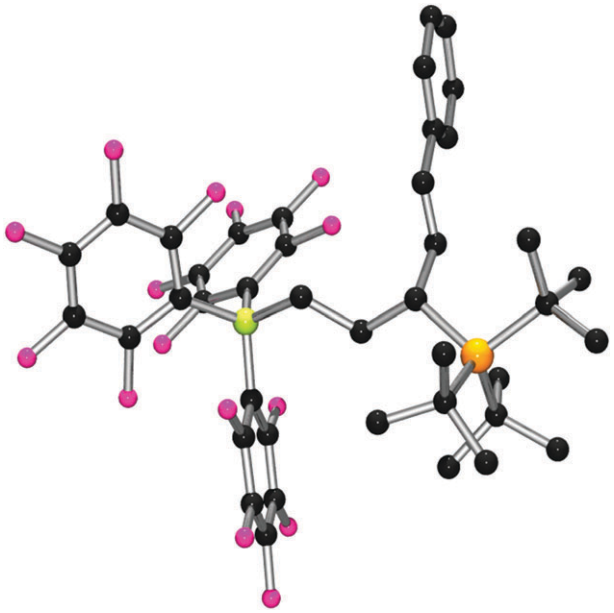
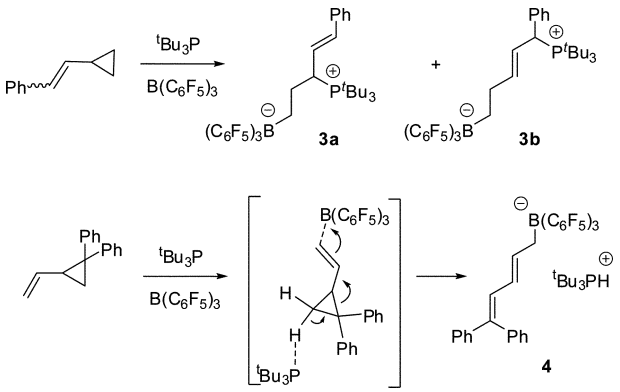


Fig. 2 POV-ray depictions of **2**, H-atoms have been deleted for clarity, C: black, F: pink, B: yellow-green, P: orange.



Scheme 2 Synthesis of **3** and **4**.

data for **3a** are consistent with the ring opening of the cyclopropane ring, akin to that seen for **1** and **2**. The species **3b** results from attack of the olefinic carbon with subsequent migration of the double bond and ring opening of the cyclopropane to give the borate fragment. These two products are thus consistent with S_N2 and S_N2' processes.

The product of the reaction of $B(C_6F_5)_3$, tBu_3P and $H_2C{=}CHC_3H_3Ph_2$ was isolated in 69% yield and spectroscopically identified as $[tBu_3PH][Ph_2C{=}CHCH{=}CHCH_2B(C_6F_5)_3]$ **4**. The formation of this species suggests a modified mechanism where steric demands about the cyclopropane shut down direct attack at this site. Rather, Lewis acid interaction with the exocyclic olefin results in enhanced acidity of the methylene protons of the cyclopropane, prompting deprotonation by phosphine and the cascade rearrangement to the butadiene-borate anion.

In considering the mechanism of interaction of the FLP with cyclopropane, it is important to note that it has been previously reported that no evidence of a discrete molecular interaction between cyclopropane and boron-based Lewis acids was observed *via* low temperature matrix-isolation spectroscopy.[27] Nonetheless, reactions of methylenecyclopropanes with nucleophiles such as alcohols in the presence of Lewis acids are thought to proceed *via* initial protonation of the cyclopropane species.[28] Conversely, while nucleophilic ring opening of activated cyclopropanes have been described,[23,28–32] no reaction is observed for the combination of the cyclopropanes and tBu_3P. It is noteworthy that prior theoretical work,[16–21] examining the reactions of FLPs with H_2 and olefins, suggests polarization of the substrate upon interaction with the "encounter complex" formed by the approach of the Lewis base with $B(C_6F_5)_3$. In the case of cyclopropanes, it is suspected that the process may involve initial Lewis acid interaction with the cyclopropane prompting a cooperative nucleophilic interaction with the Lewis base. While this notion would account for the formation of the products **1**, **2** and **3a**, the precise details of the mechanism await a thorough theoretical examination. In contrast, the formation of **4** suggests that sterically accessible olefinic fragments are more susceptible to reaction with FLPs than cyclopropanes.

Herein, the reactions of FLPs with cyclopropanes have been shown to result in ring opening. For sterically accessible cyclopropanes, P and B add across one of the C–C bond to afford three carbon linked phosphonium–borate zwitterions. The utility of these products and the further reactivity of FLPs continues to be the focus of efforts in our laboratories.

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Notes and references

‡ Crystallographic data. **1**: $P2_1/n$, a = 10.2236(5) Å, b = 16.6138(7) Å, c = 21.9968(9) Å, β = 100.4010(10)°, V = 3674.8(3) Å^3, data = 8462, var = 568, R ($>3\sigma$): 0.0712, R_w(all) = 0.2410, GOF = 1.030. **2**(1.5 CH_2Cl_2): $Pbca$, a = 19.5216(6) Å, b = 21.1148(6) Å, c = 21.3064(7) Å, V = 8782.4(5) Å^3, data = 9905, var = 602, R ($>3\sigma$): 0.0601, R_w (all) = 0.1590, GOF = 1.036.

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