Synthetic Methods

Ring-opening of Epoxides Mediated by Frustrated Lewis Pairs

Tetiana Krachko,[a] Emmanuel Nicolas,[a, b] Andreas W. Ehlers,[a, c] Martin Nieg[er][d] and J. Chris Slootweg*[a]

Abstract: Treatment of the preorganized frustrated Lewis pairs (FLPs) rBu₂PCH₂BPh₂ (1) and o-P₂H₂P(C₆H₄)₂Cat (Cat = catechol) (4) with 2-methylxirane, 2-phenylxirane and 2-(trifluoromethyl)xirane resulted in epoxide ring-opening to yield the six- and seven-membered heterocycles 2a–c and 5a–c, respectively. These zwitterionic products were characterized spectroscopically, and compounds 2a, 2b, 5a and 5c were structurally characterized by single-crystal X-ray structure analyses. Based on computational and kinetic studies, the mechanism of these reactions was found to proceed via activation of the epoxide by the Lewis acidic borane moiety followed by nucleophilic attack of the phosphine of a second FLP molecule. The resulting chain-like intermediates afford the final cyclic products by ring-closure and concurrent release of the second equivalent of FLP that behaves as catalyst in this reaction.

Introduction

Frustrated Lewis pairs (FLPs) are well-known metal-free compounds that can activate small molecules and this feature defines their intensive use in stoichiometric and catalytic main-group chemistry.[1] Accordingly, the combination of a Lewis acid and a Lewis base, which are sterically prevented from forming a classical Lewis acid–base adduct, allows the activation of a variety of small molecules,[2] including dihydrogen,[3,4] olefins,[5] alkynes,[6] N₂[7] NO,[8] CO,[9] N₂O[10] isocyanates, azides,[11] as well as singlet dioxygen.[12] Moreover, FLPs are also able to ring-open cyclic substrates. Stephan and co-workers showed that phosphine/borane[13] or amine/borane[14] combinations induce ring-opening of THF, while Tamm’s group demonstrated that N-heterocyclic carbenes (NHCs) as Lewis bases can cleave THF in the presence of the highly electron-deficient tris(pentafluorophenyl)borane (B(C₅F₅)₃) affording in all cases zwitterionic species of type A (Figure 1).[15] Analogous reactions of 1,4-dioxiane or 1,4-thioxiane with B(C₅F₅)₃ and an appropriate Lewis base result in C–O bond cleavage and the formation of ring-opened products of type B or C, respectively.[16] FLPs derived from P- or N-based Lewis bases and B(C₅F₅)₃ also induce ring-opening of δ-valerolactone to give zwitterionic species D, while the analogous reactions with rac-lactide result in ring contraction to give salts of type E.[17] Phosphine/borane FLPs also promote C–C bond scission of the three-membered cyclopropanes yielding the phosphonium borates F (Figure 1).[17] Commonly, these ring-opening reactions occur via nucleophilic attack by a base on a Lewis acid-activated cyclic molecule. Furthermore, a cationic aluminium phosphine complex was shown to ring-open propylene oxide.[18] Zhang, Darenbourg and co-workers extended this concept to catalytic ring-opening reactions, thereby developing the copolymerization of carboxyl sulfide and epoxides catalyzed by metal-free Lewis pairs.[19] To further advance this field, a better mechanistic un-

[a] Dr. T. Krachko, Dr. E. Nicolas, Dr. A. W. Ehlers, Assoc. Prof. J. C. Slootweg
Van ’t Hoff Institute for Molecular Sciences
University of Amsterdam
Science Park 904, P.O. Box 94157
1090 GD Amsterdam (The Netherlands)
E-mail: j.c.slootweg@uva.nl

[b] Dr. E. Nicolas
Current address: NIMBE, CEA, CNRS
Université Paris-Saclay, CEA Saclay
91191 Gif sur Yvette Cedex (France)

[c] Dr. A. W. Ehlers
Department of Chemistry, Science Faculty
University of Johannesburg
P.O. Box 254
Auckland Park, Johannesburg (South Africa)

[d] Dr. M. Nieg[er]
Department of Chemistry
University of Helsinki
A. I. Virtasen aukio 1, P.O. Box 55
Helsinki (Finland)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
https://doi.org/10.1002/chem.201801909.
derstanding of these ring-opening processes is desirable, which will aid in the development of more active and selective metal-free catalysts.

Hence, we envisioned to examine the reactions of metal-free FLPs with epoxides, and study these reactions mechanistically by employing intramolecular FLPs. For this study, we chose the preorganized, non-fluorinated phosphinoborane $\text{Bu}_2\text{PCH}_2\text{BPh}_3$ (1) developed in our group that exhibits typical FLP reactivity towards $\text{H}_2\text{CO}$ isocyanates,[20] terminal alkynes, nitriles, and nitritium salts.[2b, 21] In addition, the ortho-phenylene bridged phosphinoborane $\text{o-Ph}_2\text{P}[(\text{CH}_2)\text{Cat}=\text{catechol}][22]$ (4) bearing rather mild donor and acceptor sites was probed to study the influence of the FLP backbone and substituents on the reactivity. Herein, we describe the stoichiometric reactions of these two FLPs with mono-substituted epoxides and postulate the reaction mechanism based on DFT calculations and kinetic studies.

Results and Discussion

First, the reactivity of $\text{Bu}_2\text{PCH}_2\text{BPh}_3$ (1) towards epoxides was investigated. Addition of 2-methyloxirane (propylene oxide; 4 equiv), 2-phenyloxirane (styrene oxide; 2 equiv) or 2-(trifluoromethyl)oxirane (4 equiv) to a toluene solution of 1 at 0 °C and stirring for 16–24 hours at room temperature afforded 2a–c in 65%, 72% and 80% yield, respectively, after recrystallization (Scheme 1). The corresponding $^{11}\text{B}$ NMR spectra indicate the formation of tetracoordinate borate units displaying sharp singlets at $–1.5$ (2a), $–1.4$ (2b) and $–1.2$ ppm (2c). The $^{31}\text{P}[1^\text{H}]$ NMR signals at 46.0 (2a), 46.3 (2b) and 46.5 ppm (2c) are consistent with the formation of tetracoordinate phosphonium centers. The $^{19}\text{F}$ NMR resonance of 2c is shifted upfield from $–7.54$ to $–79.9$ ppm, which is indicative for 2-(trifluoromethyl)oxirane ring-opening.[23] The $^1\text{H}$ and $^1\text{H}[^{13}\text{P}]$ NMR spectra unambiguously confirm the methylene group of the 2-substituted oxiranes to be neighboring the P atom in the product ($\delta_{\text{HF}}=15.3$ (2a), 10.1 (2b), 11.5 (2c) Hz). In addition, the phenyl and tert-butyl groups as well as the protons of the methylene groups are all diastereotopic due to the presence of a stereogenic center in the molecule, and therefore provide distinct sets of signals in the $^1\text{H}$ NMR spectra.

The identification of 2a and 2b as cyclic zwitterionic phosphonium borates, resulting from a formal P/B FLP addition across the epoxide CH$_2$–O bond, was also confirmed crystallographically (Figure 2).[24] The molecular structures show six-membered heterocycles in a distorted boat (2a) or chair conformation (2b) with typical B1–O1 and P1–C22 bond lengths of 1.4909(14) (2a), 1.4838(15) (2b) and 1.8179(11) (2a), 1.8228(12) Å (2b), respectively. Both crystallize in the P2$_1$/n centrosymmetric space group, representing a racemic mixture of two enantiomers.

To elucidate the mechanism of the epoxide ring-opening reaction mediated by FLP 1, we performed $\text{eoB97X-D/6-31G(d,p)}[25, 26]$ calculations in the gas phase.[27] We verified our computational method by performing single point calculations at the $\text{eoB97X-D/6-311G(d,p)/eoB97X-D/6-31G(d,p)}$ level as well as included solvation effects (toluene), which in both cases gave similar relative Gibbs free energies (see Supporting Information). First, we focused on the ring-opening of 2-methyloxirane for which three possible pathways can be envisioned (Scheme 2).[28] Namely, the direct nucleophilic attack of a phosphorus nucleophile (A), activation of the epoxide by the Lewis acid followed by intramolecular nucleophilic attack by the Lewis base (B), and Lewis acid activation of the epoxide followed by intermolecular nucleophilic attack by the Lewis base of a second FLP moiety (C).

While strong anionic phosphorus nucleophiles, such as diphenylphosphide, have proven their effectiveness in epoxide ring-opening reactions,[28] reports on the employment of phosphines for this process are absent. Therefore, we were not surprised when our computations revealed that the direct C–O bond scission by P-nucleophilic attack of $\text{Bu}_2\text{PCH}_2\text{BPh}_3$ (1) is a high-energy process that requires an activation barrier of $\Delta G^* = 44.4$ kcal mol$^{-1}$, making route A unlikely (see the Supporting Information for further details).

Figure 2. Molecular structures of 2a and 2b (one enantiomer is shown; ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity). Selected bond lengths ($\AA$) and angles (°) for 2a: P1–C22 1.8179(11), C22–C23 1.5400(15), C23–O1 1.4068(13), C23–C24 1.5220(15), O1–B1 1.4909(14), B1–C1 1.7023(16), C1–P1 1.7934(11); P1–C1–C22 110.36(7), C22–C23–O1 107.76(9), C23–O1–B1 115.06(8), B1–P1–C22 1.8228(12), C22–C23 1.5479(15), C23–O1 1.4040(14), C23–C24 1.5223(16), O1–B1 1.4838(15), B1–C1 1.6924(17), C1–P1 1.7872(12); P1–C1–B1 115.77(8), P1–C22–C23 113.34(8), C22–C23–O1 110.02(9), C23–O1–B1 117.07(9).

Scheme 1. Reaction of FLP 1 with 2-methyloxirane (a), 2-phenyloxirane (b) and 2-(trifluoromethyl)oxirane (c).

Scheme 2. Three epoxide ring-opening pathways. [P] = P$\text{Bu}_2$; [B] = B$\text{Ph}_3$. 
Next, we evaluated routes B and C which involve the initial activation of the epoxide by the Lewis acidic boron moiety of 1. We found that activation can be achieved by the formation of Lewis adduct Ia (ΔG = 4.3 kcal mol⁻¹, ΔG⁰ = 7.3 kcal mol⁻¹; Scheme 3) that displays a slightly elongated C22−O1 bond of 1.44 Å (vs. 1.42 Å in 2-methyloxirane). The next step is a nucleophilic attack of the phosphine on the least hindered epoxide C atom followed by ring opening. The activation energy required for C−O bond scission by intramolecular nucleophilic attack (Path B, see the Supporting Information) is high (TS₂a; ΔG⁰ = 33.1 kcal mol⁻¹), this is the result of hampered orbital overlap of the σ*(C−O) and the lone pair on the P atom. In contrast, the intermolecular nucleophilic attack of an additional FLP molecule has a substantially lower barrier (TS₂a; ΔG⁰ = 16.1 kcal mol⁻¹; Scheme 3), and is, therefore, the preferred reaction pathway for this process. The nucleophilic attack of the second FLP moiety occurs from the backside of the epoxide, maximizing overlap with the σ* orbital of the C−O bond, resulting in the formation of the chain-like intermediate IIa (ΔG = −16.4 kcal mol⁻¹; Scheme 3), which rearranges by rotation along the B2−O1 and B1−C1 bond to the more stable conformer IIIa (ΔG⁰ = 16.1 kcal mol⁻¹) and the magnitude of these barriers is fully consistent with the mild reaction conditions observed experimentally (room temperature, 16 hours). Note that the nucleophilic attack by the phosphine on the more hindered, tertiary carbon of the epoxide is disfavored (ΔG° = 26.7 kcal mol⁻¹, see the Supporting Information), which is in line with the isolation of only one regioisomer. Overall, FLP tBu₂PCH₂BPh₂ (1) acts in this reaction both as stoichiometric reagent and catalyst at the same time.

To support the notion that epoxide ring-opening is induced by the action of a Lewis acidic borane and a Lewis basic phosphine from two separated FLP molecules, we performed the same reaction but now with a bimolecular FLP that mimics tBu₂PCH₂BPh₂ (1). Thus, treatment of a toluene solution of triphenylborane with 2-methyloxirane, followed by the addition of di-tert-butylmethylphosphine afforded after 20 minutes at room temperature the zwitterionic phosphonium borate 3a in 82% isolated yield (δ¹¹B = −44.8 ppm, δ³¹P = −1.0 ppm; Figure 3). The molecular structure of 3a is unambiguously established by single-crystal X-ray diffraction analysis (Figure 3, bottom) and shows that the ring-opened 2-methyloxirane gives rise to...
slightly elongated B1–O1 (1.519(2) Å) and P1–C22 bonds (1.8192(17) Å) compared to the ones of 2a (1.4909(14) and 1.8179(11) Å, respectively). The formation of 3a supports our proposed mechanism for the formation of 2a (Scheme 3), and it is interesting to note that the structure of 3a is similar to the ones of the proposed intermediates IIa and IIIa.

Next, we investigated the mechanism of the reaction of 2-phenyloxirane with FLP 1. Calculations at ωB97X-D/6-31G(dp) revealed that 2-phenyloxirane also forms Lewis adduct 1b (ΔG = 4.9 kcal mol⁻¹, ΔG* = 7.1 kcal mol⁻¹; Scheme 3), which after epoxide ring-opening directly affords intermediate IIIb (ΔG = −21.3 kcal mol⁻¹, ΔG* = 13.5 kcal mol⁻¹). Subsequent cyclization with concomitant release of the second FLP moiety affords the final product 2b (ΔG = −33.6 kcal mol⁻¹, ΔG* = 21.2 kcal mol⁻¹). Compared to 2-methyloxirane, the activation barrier for the ring-opening step (TS₂b) of 2-phenyloxirane is slightly lower (ΔΔG = −2.6 kcal mol⁻¹), likely due to the higher basicity of 2-phenyloxirane, while TS₂b for product formation is higher (ΔΔG = +4.9 kcal mol⁻¹) and becomes the rate-determining step.

To gain further insight into the formation of 2b, we performed kinetic studies and monitored the FLP concentration for a stoichiometric mixture of 1 and 2-phenyloxirane in toluene at 30°C using ³¹P{(1)H} NMR spectroscopy. We found that the FLP concentration decay is following first-order kinetics (Figure 4) with a rate constant of 6.01 × 10⁻³ s⁻¹ that, by using the Eyring equation, provides an activation barrier of ΔG* = 20.8 kcal mol⁻¹. These findings are consistent with our DFT calculations that also predicted a unimolecular process to be the rate-determining step (TS₁b; ΔG* = 21.2 kcal mol⁻¹).

Similar to 2a, the reaction pathway for the formation of 2c from 2-(trifluoromethyl)oxirane and 1 features activation barriers of comparable Gibbs free energy, TS₂c (ΔG* = 16.4 kcal mol⁻¹) and TS₂c (ΔG* = 15.7 kcal mol⁻¹). Consistently, kinetic data on this system show that the FLP concentration decrease corresponds neither to a first nor second order reaction type, indicating a more complicated reaction rate.[30]

To assess the influence of the FLP backbone and substituents on the reaction, α-phenylene-bridged FLP α-P₃(C₅H₃)BCat (4) was treated with 2-methyloxirane, 2-phenyloxirane and 2-(trifluoromethyl)oxirane. As expected, the reduced Lewis acidity and basicity of 4 compared to 1 led to longer reaction times. The reactions with 2-methyl- and 2-phenyloxirane were completed after 72 and 24 hours at room temperature, respectively, whereas 2-(trifluoromethyl)oxirane required 72 hours at 70°C for full conversion. The corresponding ring-opened products 5a and 5c were isolated in 90% and 85% yield (Scheme 4), respectively, while 5b was obtained in 20% yield, likely due to the formation of oligomeric chains as side product.[31] The ¹¹B NMR signals at 10.0 (5a, 5c) and 10.5 ppm (5b) and the ³¹P NMR resonances at 25.8 (5a), 32.0 (5b) and 25.6 (5c) ppm are in agreement with the formation of phosphonium borates akin to 2. X-ray diffraction analysis of suitable crystals of 5a and 5c confirms the formation of zwitterionic seven-membered heterocycles (Figure 5),[34] which display typical B1–O1(3) (1.4573(3) Å) and 1.4762(2) Å, respectively and P1–C25 bonds (1.8092(2) Å and 1.8154(15) Å, resp) and show that the PCCB plane of the FLP moiety (P1–C2–C1–B1 –3.2(2)° (5a) and 1.3(2)° (5c) is orthogonal to the C25-C26-O1(3) plane of the ring-opened epoxide.

ωB97X-D/6-31G(dp) calculations for the formation of 5a revealed some interesting differences compared to the formation of 2a (see the Supporting Information). First, the activation barrier for ring-opening is increased (TS₃; ΔG* = 20.4 kcal mol⁻¹ (5a) vs. 16.1 kcal mol⁻¹ (2a)), due to the reduced P-nucleophilicity of 4. Second, product formation by cyclization of intermediate III and elimination of the second FLP moiety in this case a much more facile process (TS₅; ΔG* = 5.1 kcal mol⁻¹ (5a) vs. 16.3 kcal mol⁻¹ (2a)), likely due to the reduced electrophilic-
ity of 4 that promotes its release from the reaction site. As a result, epoxide ring-opening by the second equivalent of FLP becomes the rate-limiting step (see the Supporting Information). This is supported by kinetic data which shows that the FLP concentration decay follows second-order kinetics (Figure 6) with a rate constant of $8.41 \times 10^{-4}$ s$^{-1}$ ($\Delta G^* = 24.3$ kcal mol$^{-1}$), which is consistent with a rate-limiting bimolecular process.

![Figure 6](image)

**Figure 6.** Plot of inverse FLP (4) concentration (1/FLP) versus time determined by $^1$H NMR spectroscopy for the reaction of 4 (1 equiv) with 2-methyloxirane (1 equiv). Slope ($k$) = $8.41 \times 10^{-4}$ s$^{-1}$, $R = 0.99869$.

After observing these facile FLP-mediated epoxide ring-opening reactions, we were keen to learn whether this mode of action is also operational for the higher homologues of the substrate. We found that the P/B-based FLP tBu$_2$PCH$_2$BP$_2$ (1) is also reactive towards the sulfur analogues of epoxides (episulfides) that are applied in industrial copolymerization processes,[32] but that the reaction follows a different course.[33] Namely, treatment of a toluene solution of 1 with propylene sulfide (2.8 equiv) afforded after 2 hours at room temperature and work-up zwitterionic product 6 ($\delta^{13}$P = 79.4 ppm, $\delta^{13}$B = 8.2 ppm; Figure 7) in 94% isolated yield. The molecular structure of 6 obtained by an X-ray crystal structure determination (Figure 7, right)[34] unequivocally established the formation of a planar four-membered heterocycle (S1-P1-C1-B1 0.921(1)) with the sulfur atom in the bridging position between the P and B atoms, which points out that the FLP-mediated ring-opening of heterocyclopropanes is tunable and can be converted into a heteroatom transfer reaction.

### Conclusions

In this study, the reactivity of intramolecular P/B-based FLPs towards mono-substituted epoxides has been explored, which resulted in the formation of zwitterionic six- and seven-membered heterocycles that are obtained regioselectively upon epoxide ring-opening. The mechanism of this reaction has been assessed computationally and is supported by kinetic studies, showing that the rate-determining step of the reaction is strongly dependent on the Lewis acidity and basicity of the FLP as well as the basicity of the epoxide, which shows these are important design principles, while the nature of the heterocyclopropanes can also determine the reaction outcome. These findings will stimulate the advancement of (co)polymerization of epoxides mediated by metal-free (frustrated) Lewis pairs knowing that these systems can be readily tuned by varying the strength of the available Lewis acidic and basic sites.

### Experimental Section

**General methods and materials:** All syntheses were carried out under an atmosphere of dry nitrogen employing standard Schlenkline and glovebox techniques. Solvents were purified, dried and degassed according to standard procedures. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance 500 or Bruker Avance 400 and internally referenced to the residual solvent resonances (CDCl$_3$: $^1$H $\delta = 7.26$ ppm, $^{13}$C $\delta = 77.16$ ppm; CD$_2$Cl$_2$: $^1$H $\delta = 5.32$ ppm, $^{13}$C $\delta = 53.84$ ppm). $^3$P($^1$H), $^1$B($^1$H) spectra were recorded on a Bruker Avance 400 and externally referenced (85% H$_2$PO$_4$ and BF$_3$OEt$_2$, respectively). $^{19}$F NMR spectra were recorded on a Bruker Avance 250 and externally referenced (CFCl$_3$). The $^1$H and $^{13}$C resonance signals were attributed by means of 2D HSQC and HMBC experiments. Melting points were measured on samples in sealed capillaries on a Stuart Scientific SMP3 melting point apparatus and are uncorrected. High resolution mass spectra (HRMS) were recorded on a Bruker Daltonics microTOF spectrometer using electrospray ionization (ESI).

$^3$P$_2$CH$_2$BP$_2$ (1)[22] and o-Ph$_2$P(C$_6$H$_4$)BCat (4)[22] were prepared according to literature procedures. All epoxides as racemic mixtures were purchased from commercial resources and stored over activated 3 Å molecular sieves.

**Synthesis of 2a:** A solution of 2-methyloxirane (0.345 mL, 4.93 mmol, 1.0 equiv) in toluene (5 mL) was added dropwise to a solution of 1 (0.400 g, 1.23 mmol, 1.0 equiv) in toluene (5 mL) at 0°C. Then the reaction mixture was allowed to warm to room temperature. After subsequent stirring overnight at room temperature, the excess of 2-methyloxirane and half of toluene were removed under reduced pressure. Cooling to −20°C resulted in the deposition of white crystals which were collected by filtration, washed with cold toluene (2×5 mL) and n-pentane (2×5 mL) to give 2a as a white solid in 65% yield (0.306 g, 0.800 mmol). Crystals suitable for single X-ray diffraction were grown by vapor diffusion of pentane into a concentrated solution of 2a in DCM. M.p.: 199–203°C.

$^1$H NMR (500.2 MHz, CDCl$_3$, 293 K): $\delta = 7.55$ (d, $J_{CH} = 7.5$ Hz, 2H; o-C$_6$H$_4$H$_2$), 7.46 (d, $J_{CH} = 7.5$ Hz, 2H; o-C$_6$H$_4$H$_2$), 7.18 (t, $J_{CH} = 7.4$ Hz, 2H; o-C$_6$H$_4$H$_2$).
Synthesis of 2b: A solution of 2-phenoxylirine (0.280 mL, 2.46 mmol, 2.0 equiv) in toluene (5 mL) was added dropwise to a solution of 1 (0.400 g, 1.23 mmol, 1.0 equiv) in toluene (5 mL) at 0 °C. Then the reaction mixture was allowed to warm to room temperature. After subsequent stirring overnight at room temperature, the reaction mixture was concentrated to half of its original volume. Cooling to −20 °C resulted in the deposition of colorless crystals which were collected by filtration, washed with cold toluene (2 × 5 mL) and n-pentane (2 × 5 mL) at −20 °C to give 2b in 72% yield (0.393 g, 0.884 mmol). Crystallization from toluene at room temperature afforded X-ray quality crystals. M.p.: 198–199 °C.

1H NMR (500.2 MHz, CDCl₃, 293 K): δ = 7.66 (d, J_HH = 7.5 Hz, 2H; o-C₃H₅), 7.65 (d, J_HH = 7.2 Hz, 2H; o-C₃H₅), 7.48 (d, J_HH = 7.0 Hz, 2H; o-C₃H₅), 7.37 (t, J_HH = 7.6 Hz, 2H; m-CH(C₆H₅)), 7.31 (t, J_HH = 7.3 Hz, 1H; p-C₃H₅), 7.14 (t, J_HH = 7.4 Hz, 2H; m-CH(C₆H₅)), 7.10 (t, J_HH = 7.4 Hz, 2H; m-CH(C₆H₅)), 6.96 (t, J_HH = 7.2 Hz, 1H; o-C₃H₅), 6.97 (t, J_HH = 7.2 Hz, 1H; p-C₃H₅), 4.78 (ddd, J_HH = 11.0 Hz, J_HH = 2.5 Hz, J_HH = 1.5 Hz, 1H; CH₃), 1.97 (m, 2H; CH₂), 1.45 (ddd, J_HH = 15.0 Hz, 1H; CH₃), 1.26 (dd, J_HH = 15.3 Hz, 1H; CH₃); P(31P) NMR (128.4 MHz, CDCl₃, 293 K): δ = −1.14 ppm (s, 31P(CH₃)).

Synthesis of 3a: A solution of 2-Methyloxirane (0.12 mL, 1.65 mmol, 2.0 equiv) was added dropwise to a solution of triphenylborane (200 mg, 0.826 mmol, 1.0 equiv) in toluene (4 mL) at −60 °C, followed by the addition of a solution of di-tert-butylmethylphosphate (0.16 mL, 0.823 mmol, 1.0 equiv) in toluene (6 mL) at the same temperature. The resulting mixture was stirred for 10 min at −60 °C, after which it was allowed to warm to room temperature. After subsequent stirring for 20 min at room temperature, a white precipitate had formed. The suspension was cooled down to −60 °C, and then all white crystals were collected by filtration and washed with toluene (3 × 5 mL) and n-pentane (2 × 5 mL) to give 3a in 82% yield (0.312 g, 0.678 mmol). To increase the purity even further, the residue can also be recrystallized from a saturated DCM solution of 3a with n-pentane. Suitable crystals for single X-ray diffraction were grown by vapor diffusion of pentane into a concentrated solution of 3a in DCM. M.p.: > 173 °C (decomposition).

1H NMR (400.0 MHz, CDCl₃, 293 K): δ = 7.49 (d, J_HH = 7.3 Hz, 6H; o-C₃H₅), 7.08 (t, J_HH = 7.3 Hz, 6H; m-CH₅), 6.95 (t, J_HH = 7.2 Hz, 3H; p-C₃H₅), 3.69–3.54 (m, 1H; CH₂), 2.37 (ddd, J_HH = 15.3 Hz, J_HH = 5.3 Hz, J_HH = 2.5 Hz, 1H; CH₃), 1.88 (d, J_HH = 15.3 Hz, J_HH = 5.3 Hz, J_HH = 2.5 Hz, 2H; CH₂), 1.34 (d, J_HH = 3.6 Hz, 3H; CH₃), 3.34 (d, J_HH = 3.6 Hz, 3H; CH₃), 2.95 (d, J_HH = 9.5 Hz, 3H; CH₃), 2.33 (s, J_HH = 4.5 Hz, CH₃), 0.74 (ppm; br. s; PCH₂). Carbon atoms directly attached to boron (iso-PrCH₂) and PCH₂ are not observed in direct 1H NMR spectra, but are seen in HMBC and HSQC experiments. 31P NMR (128.5 MHz, CDCl₃, 293 K): δ = 161.0 ppm. 31P NMR (126.0 MHz, CDCl₃, 293 K): δ = −46.3 ppm (s). HRS-ESI-MS: calculated for C₅H₅B(O)PH₂⁺ (M+H)⁺ 219.1878, found 219.1889. m/z (%): 243.1 (100) [M+H⁺]⁺, 175.2 (10) [P(31P)CH₂(CH₃)].
solution of 4 (0.300 g, 0.789 mmol, 1.0 equiv) in toluene (17 mL) at room temperature. After the addition was completed, the reaction was allowed to stir at room temperature for 72 hours, at which time the slurry was concentrated to half of its original volume and filtered over a glass frit. The collected solid was washed with cold toluene (3 x 10 mL) and pentane (3 x 5 mL) to give 5a as a colorless powder in 90% yield (0.310 g, 0.870 mmol). Crystallization from dichloromethane/pentane at room temperature afforded X-ray quality crystals. M.p.: 233 °C. 1H NMR (500.0 MHz, CDCl3, 293 K): δ = 7.99 (dd, J1,H = 7.2 Hz, J4,H = 4.4 Hz, 1H; Hf), 7.73 (td, J1,H = 7.5 Hz, J3,H = 1.1 Hz, 1H; p-C6H4), 7.71–7.64 (m, 1H; p-C6H4), 7.64–7.53 (m, 7H; o-C6H4, m-C6H4, Hf), 7.45 (dd, J1,3 = 7.7 Hz, J3,H = 11.7 Hz; o-C6H4), 7.20 (td, J2,H = 7.6 Hz, J4,H = 3.8 Hz, 1H; Hf), 6.77 (dd, J3,H = 1.7 Hz, J4,H = 14.2 Hz, 1H; Hf), 6.66 (br. s, 2H; Hf), 6.61–6.54 (m, 2H; Hf), 4.58 (sep, J6,H = 6.8 Hz, 1H; CH(CH3)), 3.47 (dd, J2,H = 7.9 Hz, J3,H = 12.3 Hz, 2H; CH2), 1.31 ppm (dd, J2,H = 6.2 Hz, J3,H = 1.6 Hz, 3H; CH3). 13C{1H} NMR (128.4 MHz, CDCl3, 293 K): δ = 114.9 ppm (s). HR ESI-MS: calcld for C29H23BFOP (M + H)+ 510.1791, found 510.1787, m/z (%): 501.2 (2) [M+H]+, 409.2 (100) [M+OC6H5]+. 3 H2 (6.61–6.54 ppm). 2 H3 (6.66–6.54 ppm). 3 H (4.58 ppm). 4 CH2 (3.47 ppm). 6 H (1.31 ppm). 5 CH3 (1.31 ppm).

Synthesis of 5c: A solution of 2-(trifluoromethyl)oxirane (0.280 mL, 3.0 mmol, 4.0 equiv) in toluene (3 mL) was added dropwise to a solution of 4 (0.300 g, 0.789 mmol, 1.0 equiv) in toluene (17 mL) at room temperature. After the addition was completed, the reaction was left to stir in a closed vessel at 70 °C for 72 hours, at which time the slurry was concentrated to half of its original volume and filtered over a glass frit. The collected solid was washed with cold toluene (3 x 10 mL) and pentane (3 x 5 mL) to give 5c as a white powder in 85% yield (0.330 g, 0.671 mmol). Crystallization from chloroform at room temperature afforded X-ray quality crystals. M.p.: 245 °C. 1H NMR (400.0 MHz, CDCl3, 293 K): δ = 8.01 (dd, J1,H = 6.8 Hz, J4,H = 4.7 Hz, 1H; Hf), 7.78 (td, J1,H = 7.4 Hz, J4,H = 1.3 Hz, 1H; p-C6H4), 7.75–7.69 (m, 1H; p-C6H4), 7.68–7.55 (m, 7H; o-C6H4, m-C6H4, Hf), 7.45 (dd, J1,3 = 7.4 Hz, J4,H = 11.9, 2H; o-C6H4), 7.26 (td, J2,H = 7.7 Hz, J4,H = 1.3 Hz, J3,H = 3.8 Hz, 1H; Hf), 6.81 (dd, J3,H = 7.8 Hz, J4,H = 14.4 Hz, 1H; Hf), 6.72 (d, J1,H = 7.1 Hz, J3,H = 1.8 Hz, Hf), 6.64–6.54 (m, 4H; Hf), 4.95 (m, 1H; CH(CH3)), 3.76 (dd, J1,3 = 16.2 Hz, J3,H = 3.7 Hz, J14,H = 9.0 Hz; CH2), 3.49 ppm (d, J1,3 = 15.4 Hz, J3,H = 11.2 Hz, J14,H = 5.9 Hz, 1H; CH). 13C{1H} NMR (101.0 MHz, CDCl3, 293 K): δ = 159.2 (br. s, C2), 152.8 (s, C2), 152.6 (s, C2), 137.1 (d, J2,4 = 16.4 Hz, C1), 134.6 (d, J2,4 = 3.5 Hz, p-C6H4), 134.5 (d, J2,4 = 2.8 Hz, p-C6H4), 134.0 (s, C2), 134.0 (d, J2,4 = 11.3 Hz, o-C6H4), 133.6 (d, J2,4 = 16.1 Hz, C1), 132.7 (d, J2,4 = 10.6 Hz, m-C6H4), 130.2 (d, J2,4 = 11.6 Hz, m-C6H4), 129.9 (d, J2,4 = 13.5 Hz, o-C6H4), 127.8 (d, J2,4 = 14.0 Hz, C1), 125.0 (qd, J2,4 = 282.1 Hz, J2,14 = 12.8 Hz; CF3), 122.2 (d, J2,4 = 88.3 Hz; ipso-C6H4), 122.1 (d, J2,4 = 89.3 Hz; ipso-C6H4), 118.1 (s, C2), 118.0 (s, C2), 116.9 (d, J2,4 = 87.6 Hz, C2), 109.7 (s, C2), 108.9 (s, C2), 64.3 (q, J2,4 = 33.9 Hz, J14,H = 6.1 Hz; CH(CH3), 32.7 ppm (d, J1,3 = 64.3 Hz, CH2); C1 is not observed in direct 13C NMR spectra, but is seen in HMBC at 159.2 ppm. 1H NMR (162.0 MHz, CDCl3, 293 K): δ = 25.6 ppm (s). 13C{1H} NMR (253.5 MHz, CDCl3, 293 K): δ = −78.9 (d, J2,4 = 6.8 Hz, 10.0 Hz). HR ESI-MS: calcld for C29H24BF2O3P (M + H)+ 493.3151, found 493.3159, m/z (%): 801.2 (100) [2M+2OC6H5]+; 493.1 (3) [M+H]+, 401.3 (34) [M+OC6H5]+. Synthesis of 6: A solution of propylene sulfide (0.200 mL, 2.55 mmol, 2.8 equiv) in pentane (5 mL) was added dropwise to a solution of 1 (0.300 g, 0.925 mmol, 1.0 equiv) in pentane (5 mL) at −78 °C. Then the reaction mixture was allowed to warm to room temperature. After subsequent stirring for 2 hours at room temperature, the reaction solution was filtered over a glass frit and washed with pentane (3 x 5 mL) to give 6 as a white powder in 94% yield (0.310 g, 0.870 mmol). Suitable crystals for single X-ray diffraction were grown by vapor diffusion of pentane into a con-
were independent ($R_{w} = 0.044$), 290 parameters, $R_{1} = 0.053$ (for 4134 $I > 2\sigma(I)$), $wR_{2} = 0.133$ (all data), $S = 1.07$, largest diff. peak/ hole = 0.50/0.345 eÅ⁻³.

5c: colorless crystals, C₁₂H₂₂BO₃P. CHCl₃, Mᵡ = 611.58, crystal size 0.40 x 0.22 x 0.16 mm, triclinic, space group P-1 (No. 2), a = 9.617007 (Å), b = 10.646607 (Å), c = 14.254410 (Å), $\alpha = 105.4142(2)$, $\beta = 96.6492(2)$, $\gamma = 122.3102(2)$, V = 1361.92(16) Å³, $Z = 2$, $\rho = 1.502$ Mg m⁻³, $\mu$(CuKα) = 4.080 mm⁻¹, 40985 reflections, of which 5320 were independent ($R_{int} = 0.028$), 353 parameters, $R_{1} = 0.031$ (for 5091 $I > 2\sigma(I)$), $wR_{2} = 0.078$ (all data), $S = 1.03$, largest diff. peak/ hole = 0.637/0.619 eÅ⁻³.

6: colorless crystals, C₁₀H₁₈PS₅, Mᵡ = 356.29, crystal size 0.32 x 0.08 x 0.04 mm, orthorhombic, space group P2₁2₁2₁ (No. 19), a = 9.7345(5) Å, b = 11.9393(6) Å, c = 17.1612(8) Å, $V = 194.53(17)$ Å³, $Z = 4$, $\rho = 1.187$ Mgm⁻³, $\mu$(CuKα) = 2.166 mm⁻¹, $F(000) = 768$, $2\theta_{max} = 144.2°$, 24944 reflections, of which 3918 were independent ($R_{int} = 0.026$), 218 parameters, $R_{1} = 0.023$ (for 3892 $I > 2\sigma(I)$), $wR_{2} = 0.062$ (all data), $S = 1.07$, largest diff. peak/ hole = 0.211/ -0.284 eÅ⁻³, inversion twin, $x = 0.489(16)$.

CCDC 1827770 (2a), 1827771 (2b), 1827772 (3a), 1827773 (5a), 1827775 (5c), and 1827776 (6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Acknowledgements

This work was supported financially by the European Union (Marie Curie ITN SusPhos, Grant Agreement No. 317404) and the Council for Chemical Sciences of The Netherlands Organization for Scientific Research (NWO/CW) by a VIDI grant (J.C.S.). We thank Kinga Kaniewska for her contribution to the synthesis of FLP 4.

Conflict of interest

The authors declare no conflict of interest.

Keywords: density functional calculations · epoxides · frustrated Lewis pairs · kinetic studies · ring-opening reactions


[24] CCDC 1827770 (a), 1827771 (b), 1827772 (c), 1827773 (d), 1827774 (e) and 1827775 (f) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.


[27] DFT calculations were carried out with Gaussian 09 (Revision D.01); see the Supporting Information for further details.


[30] See the Supporting Information for further details.

[31] Confirmed by mass-spectrometry analyses of the reaction mixture.


