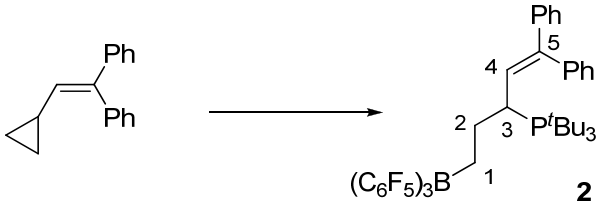
Supplementary Data for:

Ring-Opening of Cyclopropanes by "Frustrated Lewis Pairs"†

Jason G. M. Morton, Meghan A. Dureen and Douglas W. Stephan*

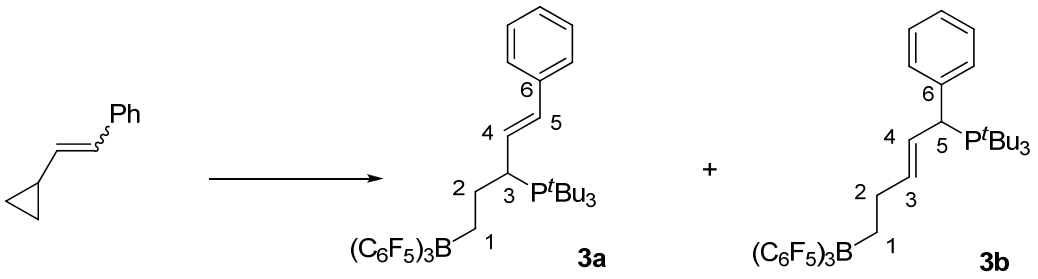
Synthesis of 1 To a solution of tris(pentafluorophenyl)borane (100 mg, 0.2 mmol) and tri-*tert*-butylphosphine (50 mg, 0.25 mmol) in toluene (5 mL), cyclopropylbenzene (0.5 mL, 4.0 mmol) was added in one portion. The reaction mixture was left undisturbed overnight, over which period large colourless crystals formed (113 mg, 69%). **^{1}H NMR** (CD_2Cl_2): δ 7.3 (d, 2H, $^{3}J_{H\text{-}H}$ = 7 Hz, *o*-Ph), 7.2-7.1 (m, 3H), 3.6 (at, 1H, $^{3}J_{H\text{-}P}$ = 11 Hz, $^{3}J_{H\text{-}H}$ = 11 Hz, PC(Ph)*H*CH_2), 2.1 (m, 1H, PC(Ph)HC*H*H'), 1.8 (m, 1H, PC(Ph)HCH*H'*), 1.4 (d, 27H, $^{3}J_{H\text{-}P}$ = 14 Hz, P^{t}*Bu*$_3$), 1.1 (t, br, 1H, , $^{3}J_{H\text{-}H}$ = 13 Hz, CH_2C*H*H'B), 0.8 (t, br, 1H, , $^{3}J_{H\text{-}H}$ = 13 Hz, CH_2CH*H'*B). **^{11}B NMR** (CD_2Cl_2): δ -13.5 (s). **^{13}C{^{1}H} NMR** (*d*$_8$-THF), partial: δ 148.2 (dm, $^{1}J_{C\text{-}F}$ = 246 Hz, *o*-C_6F_5), 138.0 (dm, $^{1}J_{C\text{-}F}$ = 243 Hz, *p*-C_6F_5), 136.8 (dm, $^{1}J_{C\text{-}F}$ = 249 Hz, *m*-C_6F_5), 133.6, 131.4, 128.2, 126.5, 125.9, 123.9, 37.7 (d, $^{1}J_{C\text{-}P}$ = 26 Hz, P*C*Me$_3$), 30.1 (s, PC*Me*$_3$). **^{19}F NMR** (376 MHz, CD_2Cl_2): δ -132.0 (d, 6F, $^{3}J_{F\text{-}F}$ = 24 Hz, *o*-C_6F_5), -165.4 (t, 3F, $^{3}J_{F\text{-}F}$ = 20 Hz, *p*-C_6F_5), -168.0 (t, 6F, $^{3}J_{F\text{-}F}$ = 21 Hz, *m*-C_6F_5). **^{31}P{^{1}H} NMR**(162 MHz, CD_2Cl_2): δ 54.1 (s). C, H analysis calc for $C_{39}H_{37}BF_{15}P$ (832.486): C, 56.27; H, 4.48. Found: C, 56.58; H, 4.19.



2

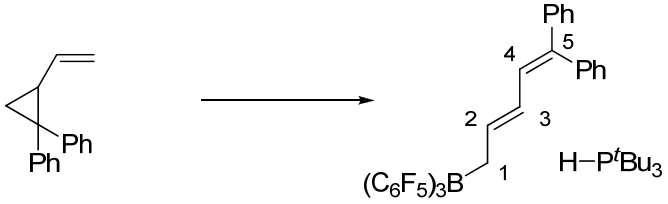
Synthesis of 2: (2-Cyclopropylethene-1,1-diyl)dibenzene (**1**) contaminated with diphenylmethane (1:0.2; 18.3 mg cyclopropane, 83.1 μmol) was added to a reaction vial. A solution of tri-*t*-butylphosphine (20 mg, 99.7μmol, 1.2 eq.) in 0.5 ml CD_2Cl_2 was added and the mixture magnetically stirred. A solution of tris(pentafluorophenyl)borane (47 mg, 91.4μ□mol, 1.1 eq.) in 0.5 ml CD_2Cl_2 was subsequently added, causing the reaction mixture to take on a yellow hue. The reaction was stirred overnight, after which time it had become white with precipitates. The solvent was removed *in vacuo* and the residue washed three times with hexanes, leaving 50 mg (64% yield) of the zwitterions **2** as a white solid. Crystals suitable for X-ray diffraction were obtained through slow evaporation of a toluene/THF solution. **^{1}H-NMR** (400 MHz, d_8-THF): δ 7.53-7.48 (m, 2H), 7.42-7.24 (m, 8H), 6.08 (dd, $J_{H\text{-}P}$ 11.5 Hz, $J_{H\text{-}P}$ = 4.5 Hz, 1H, *H4*), 3.73 (dd, $J_{H\text{-}H}$ = 10.9 Hz, $J_{H\text{-}P}$ = 21.3 Hz, 1H, *H3*), 2.07 (m, 2H, *H1 & H2*) 1.82 (m, 1H, *H2'*), 1.53 (d, $J_{H\text{-}P}$ = 13.6 Hz, 27H, *CH*$_3$) 1.02 (m, 1H, *H1*'). **^{13}C-NMR** (100 MHz, d_8-THF): δ150.5 (br,

C$_6$*F*$_5$), 148.1 (br, *C*$_6$*F*$_5$), 147.0 (d, $J_{C\text{-}P}$ = 12.1 Hz, *C5*), 144.4 (d, $J_{C\text{-}P}$ = 1.9 Hz), 140.0 (br, *C*$_6$*F*$_5$), 139.6 (d, $J_{C\text{-}P}$ = 2.1 Hz), 138.7 (br), 137.5 (br, *C*$_6$*F*$_5$), 136.2 (br, *C*$_6$*F*$_5$), 130.8 (d, $J_{C\text{-}P}$ = 0.9 Hz), 129.2 (d, $J_{C\text{-}P}$ = 1.5 Hz), 129.0, 128.6, 128.57 (d, $J_{C\text{-}P}$ = 1.5 Hz), 125.1 (d, $J_{C\text{-}P}$ = 6.1 Hz, *C4*), 42.2 (d, $J_{C\text{-}P}$ = 23.7 Hz, *C*(CH$_3$)$_3$), 41.2 (d, $J_{C\text{-}P}$ = 21.7 Hz, *C3*), 33.9 (br d, $J_{C\text{-}P}$ = 3.3 Hz, *C2*), 31.0 (s, *CH*$_3$), *C1* not observed in direct ^{13}C-NMR, but is seen in HSQC at 23.4 ppm. ^{1}H and ^{13}C assignments were confirmed using gCOSY, HSQC, and HMBC correlations. **^{11}B-NMR** (128 MHz, d$_8$-THF): δ -15.3 (s). **^{19}F-NMR** (376 MHz, d$_8$-THF): δ -133.9, (d, $J_{F\text{-}F}$ = 21.5 Hz, 6F, *o*-C$_6$F$_5$), -167.1 (t, $J_{F\text{-}F}$ = 20.3 Hz, 3F, *p*-C$_6$F$_5$), -169.7-169.9 (m, 6F, *m*-C$_6$F$_5$). **^{31}P{^{1}H}-NMR** (162 MHz, d$_8$-THF): δ 52.5 (s). C,H analysis calc. for $C_{47}H_{43}BF_{15}P$: C 60.40, H 4.64; found: C 59.95, H 5.17.



Synthesis of 3a&b: A mixture of (2-cyclopropylvinyl)benzene (1 : 2.8 *cis/trans*, 19 mg, 0.132 mmol) was added to a reaction vial. A solution of tri-*t*-butylphosphine (26.7 mg, 0.132 mmol, 1.0 eq.) in 0.6 ml CD_2Cl_2 was added and the mixture magnetically stirred. A solution of tris(pentafluorophenyl)borane (67.5 mg, 0.132 mmol, 1.0 eq.) in 0.7 ml CD_2Cl_2 was subsequently added, causing the reaction mixture to take on a yellow hue. The reaction was stirred overnight, whereupon the solvent was removed *in vacuo*. The residue was washed three times with 4:1 pentane/diethyl ether, then trace solvent was removed *in vacuo* overnight to provide 104 mg of **3a** and **3b** (1 : 1.3, 92% yield) with small amounts (< 5%) of what may be the *cis* isomer of **3a** . **^{1}H-NMR** (400 MHz, d$_8$-THF): δ **3a:** 7.45 (d, *J* = 7.6 Hz, 2H, *Ph*), 7.40-7.22 (m, 3H, *Ph*), 6.73 (dd, *J* = 15.6, 2.9 Hz, 1H, *H5*), 6.19-6.08 (m, 1H, *H4*), 3.36 (app q, *J* = 10.3 Hz, 1H, *H3*), 2.12-1.96 (m, 1H, *H2*), 1.93 (br t, *J* = 13.0 Hz, 1H, *H1*), 1.61 (d, *J* = 13.5 Hz, 27H, *CH*$_3$), 1.58 (m, 1H, *H2'*), 1.00 (br t, *J* = 12.6 Hz, 1H, *H1'*), **3b:** 7.58 (d, *J* = 7.1 Hz, 2H, *Ph*), 7.40-7.22 (m, 5H, *Ph*), 6.15-6.03 (m, 1H, *H4*), 5.91-5.80 (m, 1H, *H3*), 4.90 (dd, *J* = 9.2, 13.8 Hz, 1H, *H5*), 1.74-1.64 (m, 1H, *H2*), 1.63-1.50 (m, 1H, *H2'*), 1.41-1.31 (m, 1H, *H1*), 1.31-1.21 (m, 1H, *H1'*). **^{13}C-NMR** (100 MHz, d$_8$-THF): δ 150.4 (br, *C*$_6$*F*$_5$), 148.0 (br, *C*$_6$*F*$_5$), 145.3 (d, $J_{C\text{-}P}$ = 10.7 Hz, **3b:***C3*), 139.7 (br, *C*$_6$*F*$_5$), 138.8 (d, $J_{C\text{-}P}$ = 12.6 Hz, **3a:***C5*), 138.5 (br, *C*$_6$*F*$_5$), 138.3 (d, $J_{C\text{-}P}$ = 3.9 Hz, **3b:***C6*), 173.3 (br, *C*$_6$*F*$_5$), 137.1 (s, **3b:** *C6*), 136.0 (br, *C*$_6$*F*$_5$), 131.5 (br), 130.2 (s), 129.5 (s), 129.3(s), 129.0 (s), 127.3 (s), 125.1 (d, $J_{C\text{-}P}$ = 6.6 Hz, **3a:***C4*), 123.1 (d, $J_{C\text{-}P}$ = 4.1 Hz, **3b:***C4*), 49.2 (d, $J_{C\text{-}P}$ = 25.4 Hz, **3b:***C5*), 45.5 (d, $J_{C\text{-}P}$ = 23.1 Hz, **3a:***C3*), 43.1 (d, $J_{C\text{-}P}$ = 23.0 Hz, **3b:***C*Me$_3$) 42.0 (d, $J_{C\text{-}P}$ = 25.2 Hz, **3a:***C*CH$_3$), 32.3 (d, $J_{C\text{-}P}$ = 3.6 Hz, **3a:***C2*), 31.3 (s, **3b:***CH*$_3$), 30.7 (s, **3a:***CH*$_3$), 29.0 (d, $J_{C\text{-}P}$ = 8.4 Hz,

3b:*C2*). **3a&b:***C1* not observed in direct ^{13}C-NMR, but are observed in HSQC at 22.5 and 21.8 ppm, respectively. ^{1}H and ^{13}C assignments were confirmed using gCOSY, HSQC, and HMBC correlations **^{11}B-NMR** (128 MHz, d_8-THF): δ **3a&b:** -13.5 (s). **^{19}F-NMR** (376 MHz, d_8-THF): δ **3a:** -131.9 (d, $J_{F\text{-}F}$ = 22.3 Hz, 6F, *o*-C_6F_5), -165.4 (t, $J_{F\text{-}F}$ = 20.6 Hz, 3F, *p*-C_6F_5), -168.0 (t, *J* = 20.4 Hz, 6F, *m*-C_6F_5) **3b:** -132.5 (d, $J_{F\text{-}F}$ = 22.1 Hz, 6F, *o*-C_6F_5), -166.0 (t, $J_{F\text{-}F}$ = 20.5 Hz, 3F, *p*-C_6F_5), -168.4 (t, *J* = 20.4 Hz, 6F, *m*-C_6F_5). **^{31}P{^{1}H}-NMR** (162 MHz, d_8-THF): δ **3a:** 51.8 (s), **3b:** 51.9 (s). C,H analysis calc. for $C_{41}H_{39}BF_{15}P \cdot ½\ CH_2Cl_2$: C 55.02, H 4.50; found C 55.42, 4.75.



4

Synthesis of 4: (2-Vinylcyclopropane-1,1-diyl)dibenzene (**3**) (22.0 mg, 100 mmol) was added to a reaction vial. A solution of tri-*t*-butylphosphine (22.2 mg, 110 mmol, 1.1 eq.) in 0.5 ml CD_2Cl_2 was added and the mixture magnetically stirred at -35 ^{o}C. A solution of tris(pentafluorophenyl)borane (51.1 mg, 100 mmol, 1.0 eq.) in 0.5 ml CD_2Cl_2 was subsequently added, causing the reaction mixture to take on a yellow hue. The reaction mixture was allowed to stir to room temperature and overnight. The next day, the solution was colorless. The solvent was removed *in vacuo* and the residue taken up into diethyl ether. Approximately twice this volume of pentane was then added, causing the solution to become opaque with a white precipitate. The precipitate was allowed to settle, whereupon it became oil-like at the bottom of the vial. The solvent was decanted off, and this procedure repeated. Removal of trace solvent *in vacuo* overnight afforded 64 mg of **4** (69% yield) as a white foam. **^{1}H-NMR** (400 MHz, CD_2Cl_2): δ 7.40-7.09 (m, 8H), 7.00-6.95 (m, 2H), 6.51 (d, $J_{H\text{-}H}$ = 11.0 Hz, 1H, *H2*), 6.15 (dt, $J_{H\text{-}H}$ = 14.9, 8.3 Hz, 1H, *H2*), 5.43 (dd, $J_{H\text{-}H}$ = 15.1, 11.1 Hz, 1H, *H3*), 5.16 (d, $J_{H\text{-}P}$ = 432 Hz, 1H, P-H), 2.15 (br d, $J_{H\text{-}H}$ = 6.9 Hz, 2H, *H1*), 1.59 (d, $J_{H\text{-}P}$ = 15.7 Hz, 27H, *CH_3*). **^{13}C-NMR** (100 MHz, CD_2Cl_2): δ 149.4 (br, *C_6F_5*), 147.6 (br, *C_6F_5*), 146.4 (*C2*), 143.7, 141.2, 139.4 (br, *C_6F_5*), 138.2 (br, *C_6F_5*), 136.9 (br, *C_6F_5*), 136.0 (*C5)*, 135.8 (br, *C_6F_5*), 130.94 (*C4*), 130.91, 128.5, 127.4, 127.1, 126.7, 125.3 (*C3*), 38.0 (d, $J_{C\text{-}P}$ = 27.1 Hz, *C*$(CH_3)_3$), 30.5 (*CH_3*). *C1* not observed in direct ^{13}C-NMR, but is seen in HSQC at 31.0 ppm. ^{1}H and ^{13}C assignments were confirmed using gCOSY, HSQC, and HMBC correlations. **^{11}B-NMR** (128 MHz, CD_2Cl_2): δ -13.3 (s). **^{19}F-NMR** (375 MHz, CD_2Cl_2): δ -132.2, (d, $J_{F\text{-}F}$ = 21.8 Hz, 6F, *o*-C_6F_5), -164.5 (t, $J_{F\text{-}F}$ = 20.6 Hz, 3F, *p*-C_6F_5), -167.4-167.6 (m, 6F, *m*-C_6F_5). **^{31}P-NMR** (162 MHz, CD_2Cl_2): δ 60.1 (d of *n*-plex *J* = 15.8, 443 Hz). **^{31}P{^{1}H}-NMR** (162 MHz, CD_2Cl_2): δ 60.1 (s).). C,H analysis calc. for $C_{47}H_{47}BF_{15}P$: C 60.14, H 5.07; found C 59.95, 5.01.