Supplementary Information

1,4-Addition Reactions of Frustrated Lewis Pairs to 1,3-Dienes

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General Remarks

All manipulations were carried out under an atmosphere of dry, O₂-free N₂ employing an Innovative Technology glove box and a Schlenk vacuum-line. Solvents were purified either by employing a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Schlenk glass bombs equipped with Young-type teflon valve stopcocks (hexanes, toluene, CH₂Cl₂), or were dried over the appropriate agents and distilled into the same kind of Young bombs (C₆H₂Br). All solvents were thoroughly degassed after purification (repeated freeze-pump-thaw cycles). Deuterated solvents were dried over the appropriate agents, vacuum-transferred into Young bombs and degassed accordingly (C₆D₅Br, CD₂Cl₂). When intended to be used in the glove box, all solvents were transferred through the antechambers in bombs with evacuated headspaces, and refilled inside into brown glass bottles equipped with 4 Å molecular sieves (small pieces of silver foil were further added to CH₂Cl₂ and CD₂Cl₂). 1H, 11B, 13C, 19F and 31P NMR spectra were recorded at 25 °C on Varian 300 and 400 MHz spectrometers, and were referenced using (residual) solvent resonances relative to SiMe₄ (1H, 13C) or relative to an external standard [11B: (Et₂O)BF₃; 19F: CFCl₃; 31P: 85% H₃PO₄]. In some instances, signal and/or coupling assignment was derived from two-dimensional NMR experiments. Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer.
**Starting Materials**

$t\text{-Bu}_3\text{P}$ (10 wt.% solution in hexanes) was obtained from Strem Chemicals, Inc. (USA) and used as received. $\text{B(C}_6\text{F}_5)_3$ was a generous gift from NOVA Chemicals Corp. (Canada), and was doubly sublimed before use. Dienes were purchased from Aldrich or Alfa Aesar. 1,3-Butadiene was purified immediately prior to use by condensing a few mL from the reservoir lecture bottle into a thick-walled Young glass bomb cooled to $-196 \, ^{\circ}\text{C}$ that contained $\text{CaCl}_2$ pellets. After thorough evacuation at that temperature to remove trace gas impurities, the bomb was closed and left stirring for 1 h at $-20 \, ^{\circ}\text{C}$. It was then connected to the reaction glass bomb (cooled to $-196 \, ^{\circ}\text{C}$) and the dry 1,3-butadiene vacuum-transferred by immersing the drying glass bomb into a cold water bath. 2,3-Dimethyl-1,3-butadiene and 1,3-cyclohexadiene were purified by stirring over $\text{CaCl}_2$ pellets, followed by vacuum transfer and degassing (repeated freeze-pump-thaw cycles). 2,3-Diphenyl-1,3-butadiene was recrystallized from hexanes at $-35 \, ^{\circ}\text{C}$ and dried *in vacuo*.

**Syntheses**

In all cases, the FLP combination $[t\text{-Bu}_3\text{P}/\text{B(C}_6\text{F}_5)_3]$ was prepared in the glove box by adding $t\text{-Bu}_3\text{P}$ (0.60 mL or 408 mg of a 10 wt.% solution in hexanes; 40.8 mg, 202 $\mu$mol) to solid $\text{B(C}_6\text{F}_5)_3$ (102 mg, 200 $\mu$mol) in a glass vial. For use outside of the glove box, the resulting yellow mixture was transferred with toluene (2 ml) into a teflon-valve Young reaction bomb equipped with a stir bar.

(E)-$\lfloor t\text{-Bu}_3\text{P}\rfloor \text{CH}_2\text{CH}=\text{CHCH}_2\lfloor \text{B(C}_6\text{F}_5)_3\rfloor$ (1). A Young reaction bomb charged with $[t\text{-Bu}_3\text{P}/\text{B(C}_6\text{F}_5)_3]$ (200 $\mu$mol) in toluene/hexanes (6 mL/0.6 mL) was cooled to $-196 \, ^{\circ}\text{C}$. A second, closed (!) Young bomb (cooled to $-20 \, ^{\circ}\text{C}$) containing dry 1,3-butadiene (~ 2 mL) was connected via a vacuum transfer bridge having a Schlenk gas adapter. As all liquid in the first bomb was frozen, its Teflon valve was opened and the FLP solution degassed for 15 min. The gas adapter was closed, the $-20 \, ^{\circ}\text{C}$ cooling bath of the second bomb replaced by a cold water bath, and its Teflon valve opened carefully to transfer the 1,3-butadiene. The first bomb was then closed and its liquid $\text{N}_2$ cooling bath removed. While the reaction mixture was melting, its yellow color discharged instantly, and a colorless solid started forming. Stirring was continued for 5 min at room temperature,
then the solvents and excess diene were removed in vacuo, leaving an off-white residue. The Young reaction bomb was taken back into the glove box, and the solid transferred with CH₂Cl₂ (2 ml) into a glass vial. The solution was concentrated in vacuo to ~ 2 mL, and hexanes (5 mL) was added dropwise with stirring to yield a colorless precipitate. The supernatant was removed with a pipette, the powdery solid swirled up in hexanes (1 mL) and allowed to settle at −35 °C for 1 h, the supernatant carefully removed and the solid dried in vacuo. Yield 94 mg (122 µmol, 61%). ¹H NMR (CD₂Cl₂): δ 6.03 (dm, 1 H, 3J_HC=CH-trans = 15.2, PCH₂CH=CH₂B), 5.92 (dm, 1 H, 3J_HC=CH-trans = 15.2, PCH₂CH=CH₂B), 2.99 (dq, 2 H, 2J_HP § 2J_HH § 4, 4J_HH-allyl = 1.6, PC₂H₂CH=CH₂B), 2.99 (dq, 2 H, 2J_HP = 6.7, 3J_HH = 1.2, PCH₂CH=CHCH₂B), 1.59 [d, 27 H, 3J_HP = 14.0, C(CH₃)₃]. ¹H NMR (C₆D₅Br): δ 5.74 (dm, 1 H, 3J_HC=CH-trans = 15.0, PCH₂CH=CHCH₂B), 5.49 (dm, 1 H, 3J_HC=CH-trans = 15.0, PCH₂CH=CHCH₂B), 4.28 (br s, 2 H, PC₂H₂CH=CH₂B), 2.24 (br q, 2 H, 2J_HP = 6.7, PCH₂CH=CHCH₂B), 0.95 [d, 27 H, 3J_HP = 14.0, C(CH₃)₃]. ¹¹B{¹H} NMR (CD₂Cl₂): −2.0. ¹³C NMR (CD₂Cl₂, partial): 148.5 (br dm, 1J_CF ≈ 240, o-CF), 138.9 (br dm, 1J_CF ≈ 245, p-CF), 138.6 (br dd, 1J_CH ≈ 160, 2J_CP = 11, PCH₂CH=CHCH₂B), 137.0 (br dm, 1J_CF ≈ 245, m-CF), 123.6 (very br, ipso-C), 118.4 (br dd, 1J_CH ≈ 160, 3J_CP = 8, PCH₂CH=CHCH₂B), 40.1 [d, 1J_CP = 28, C(CH₃)₃], 30.0 [qm, 1J_CH = 129, C(CH₃)₃]. ¹⁹F NMR (CD₂Cl₂): −130.2 (d, 3J_FF = 18.0, o-CF), −163.6 (t, 3J_FF = 20.0, p-CF), −167.7 (dd, 3J_FF ≈ 3J_FF = 19.0, m-CF). ³¹P{¹H} NMR (CD₂Cl₂): 47.6. Elemental anal. calcd. for C₃₄H₃₃BF₁₅P: C 53.15, H 4.33; found C 52.91, H 4.41.

(E/Z)-[t-Bu₃P][CH₂C(CH₃)=C(CH₃)CH₂][B(C₆F₅)₃] (2). In the glove box, [t-Bu₃P/B(C₆F₅)₃] (200 µmol) in hexanes (0.6 mL), pre-mixed in a glass vial, was diluted with toluene (5 mL) to give a light yellow solution, which was then stored at −35 °C for 15 min. In the meantime, a solution of 2,3-dimethyl-1,3-butadiene (~ 0.2 mL, ~ 160 mg, ~ 10 eq.) in toluene (1 mL) was prepared. The FLP solution was taken out of the freezer and treated dropwise with the diene solution with stirring, whereby the yellow color vanished quickly and an off-white precipitate started forming. Stirring was continued for 2 h, then the reaction mixture was cooled to −35 °C overnight. The supernatant was removed with a pipette, the remaining solid washed with cold hexanes (2 ml) and then dried in vacuo. The solid was redissolved in CH₂Cl₂ (3 mL), and hexanes (5 mL) was added dropwise with stirring, yielding a colorless precipitate. The supernatant was removed
with a pipette and the solid dried in vacuo. Yield 108 mg (136 \mu mol, 68\%). Crystals suitable for XRD measurements were grown from cooling a saturated CH$_2$Cl$_2$ solution layered with hexanes to $-35$ °C for several days. $^1$H NMR (CD$_2$Cl$_2$): 3.04 [br, 2 H, PCH$_2$C(CH$_3$)=C(CH$_3$)CH$_2$B], 2.49 [br, 2 H, PCH$_2$C(CH$_3$)=C(CH$_3$)CH$_2$B], 1.69 [br, 3 H, CH$_3$], 1.59 [d, 27 H, $^3$J$_{HP}$ = 14, C(CH$_3$)$_3$, minor isomer], 1.56 [d, 27 H, $^3$J$_{HP}$ = 14, C(CH$_3$)$_3$, major isomer], 1.49 [br, 3 H, CH$_3$]. $^{11}$B ($^1$H) NMR (CD$_2$Cl$_2$): $-13.2$. $^{13}$C ($^1$H) NMR (CD$_2$Cl$_2$, partial): 148.8 (br dm, $^1$J$_{CF}$ = 238, o-CF), 148.6 [d, $^2$J$_{CP}$ = 12.0, PCH$_2$C(CH$_3$)=C(CH$_3$)CH$_2$B, major isomer], 148.3 [d, $^2$J$_{CP}$ = 11.2, PCH$_2$C(CH$_3$)=C(CH$_3$)CH$_2$B, minor isomer], 148.0 (br dm, $^1$J$_{CP}$ = 244, p-CF), 138.2 (d, $^3$J$_{CF}$ = 20.0, o-CF, major isomer), 138.0 (d, $^3$J$_{CF}$ = 18.0, o-CF, minor isomer), $-164.3$ (t, $^3$J$_{FF}$ = 20.5, p-CF, major), $-164.7$ (t, $^3$J$_{FF}$ = 20.5, p-CF, minor), $-167.6$ (t, $^3$J$_{FF}$ = 19.0, m-CF, major), $-168.0$ (t, $^3$J$_{FF}$ = 19.5, m-CF, minor). $^{31}$P ($^1$H) NMR (CD$_2$Cl$_2$): 51.9 (major isomer), 51.7 (minor isomer). Elemental anal. calcd. for C$_{36}$H$_{37}$BF$_{15}$P: C 54.29, H 4.68; found C 54.01, H 4.33.

(E)-[t-Bu$_3$P][CH$_2$C(C$_6$H$_5$)$_3$]=C(C$_6$H$_5$)CH$_2$][B(C$_6$F$_5$)$_3$] (3). In the glove box, [t-Bu$_3$P/ B(C$_6$F$_5$)$_3$] (200 \mu mol) in hexanes (0.6 mL), pre-mixed in a glass vial, was diluted with toluene (5 mL) to give a light yellow solution, which was then stored at $-35$ °C for 15 min. In the meantime, a solution of 2,3-diphenyl-1,3-butadiene (42 mg, 204 \mu mol) in toluene (2 mL) was prepared. The FLP solution was taken out of the freezer and treated dropwise with the diene solution with stirring. After stirring overnight, all volatiles were removed in vacuo, leaving a light yellow gum. The residue was redisolved in CH$_2$Cl$_2$ (3 mL), and hexanes (5 mL) was added dropwise with stirring to yield an off-white precipitate. The supernatant was removed with a pipette, and the solid washed repeatedly by swirling it up in hexanes (1 mL), allowing it to settle at $-35$ °C for 1 h, and removing the supernatant with a pipette. The powdery white solid was finally dried in vacuo. Yield 94 mg (102 \mu mol, 51\%). $^1$H NMR (CD$_2$Cl$_2$): 6.98 - 7.07 [m, 3 H, ...
 cis-/trans-{
[(-Bu3P)[(-H2C)CHCH=CHCH(CH2-)B, C6F5]3]} (4). In the glove box, 
[(-Bu3P)/B(C6F5)3] (200 μmol) in hexanes (0.6 mL), pre-mixed in a glass vial, was diluted with 
toluene (5 mL) to give a light yellow solution, which was 
stored at –35 °C for 15 min. In the meantime, a solution of 
1,3-cyclohexadiene (~0.2 mL, ~160 mg, ~10 eq.) in toluene 
(1 mL) was prepared. The FLP solution was taken out of the 
freezer and treated dropwise with the diene solution with stirring, whereby the yellow color 
vanished quickly. Stirring was continued for 2 h, during which the reaction mixture turned 
slightly cloudy. Storage at –35 °C overnight yielded a colorless, polycrystalline precipitate. 
The supernatant was removed with a pipette, the residue washed with hexanes (2 mL) and 
dried in vacuo. The solid was redissolved in CH2Cl2 (2 mL), and hexanes (5 mL) was 
added dropwise with stirring, yielding a colorless precipitate. The supernatant was removed 
with a pipette and the solid dried in vacuo. Yield 105 mg (132 μmol, 66%). Crystals suitable 
for XRD measurements were grown from slow evaporation of a saturated C6H5Br solution. 

\[ \text{cis} \rightarrow \text{trans} \]
trans}, 3.20 \{\text{br m}, 1 \text{H}, \text{P}[-\text{CH}_2]\text{CHCH=CHCH(CH}_3\text{H}_2\text{Heq-}]\text{B}, \text{cis}\}, 3.09 \{\text{br ddm}, 1 \text{H}, 3J_{HH} \approx 12, 3J_{HB} \approx 2, \text{P}[-\text{CH}_2]\text{CHCH=CHCH(CH}_3\text{H}_2\text{Heq-}]\text{B}, \text{trans}\}, 2.39 \{\text{ddm}, 1 \text{H}, 3J_{HH} \approx 12, 3J_{HB} \approx 2, \text{P}[-\text{CH}_2]\text{CHCH=CHCH(CH}_3\text{H}_2\text{Heq-}]\text{B}, \text{trans}\}, 2.36 \{\text{m}, 1 \text{H}, \text{P}[-\text{CH}_2]\text{CHCH=CHCH(CH}_3\text{H}_2\text{Heq-}]\text{B}, \text{cis}\}, 2.19 \{\text{tq 1111d}, 1 \text{H}, 3J_{HH} = 12.0, 2J_{CP} = 6.0, 3J_{HH} = 2.5, \text{P}[-\text{CH}_2]\text{CHCH=CHCH(CH}_3\text{H}_2\text{Heq-}]\text{B}, \text{trans}\}, 2.14 \{\text{m}, 1 \text{H}, \text{P}[-\text{CH}_2]\text{CHCH=CHCH(CH}_3\text{H}_2\text{Heq-}]\text{B}, \text{cis}\}, 2.01 \{\text{br dm}, 1 \text{H}, 3J_{HB} \approx 9.5, \text{P}[-\text{CH}_2]\text{CHCH=CHCH(CH}_3\text{H}_2\text{Heq-}]\text{B}, \text{trans}\}, 1.93 \{\text{br dm}, 1 \text{H}, 3J_{HH} \approx 12, \text{P}[-\text{CH}_2]\text{CHCH=CHCH(CH}_3\text{H}_2\text{Heq-}]\text{B}, \text{cis}\}, 1.55 \{\text{d}, 27 \text{H}, 3J_{CP} = 14, \text{C(CH}_3\text{)}_3, \text{trans}\}, 1.52 \{\text{d}, 27 \text{H}, 3J_{CP} = 14, \text{C(CH}_3\text{)}_3, \text{cis}\}, 1.02 \{\text{dt}, 1 \text{H}, 3J_{HH} \approx 3J_{HH} \approx 12, \text{P}[-\text{CH}_2]\text{CHCH=CHCH(CH}_3\text{H}_2\text{Heq-}]\text{B}, \text{trans}\}, 0.82 \{\text{dt}, 1 \text{H}, 3J_{HH} \approx 3J_{HH} \approx 12, \text{P}[-\text{CH}_2]\text{CHCH=CHCH(CH}_3\text{H}_2\text{Heq-}]\text{B}, \text{cis}\}, 11\text{B}\{1\text{H}\} \text{NMR (CD}_2\text{Cl}_2\}: -11.5. 13\text{C NMR (CD}_2\text{Cl}_2, \text{partial}): 148.9 \{\text{br dm}, 1J_{CF} \approx 240, \text{o-CF}\}, 146.9 \{\text{br dd}, 1J_{CH} = 165, 2J_{CP} = 8.5, \text{P}[-\text{CH}_2]\text{CHCH=CHCH(CH}_3\text{H}_2\text{Heq-}]\text{B}, \text{trans-isomer}\}, 145.2 \{\text{weak m}, 2J_{CP} = 8.5, \text{P}[-\text{CH}_2]\text{CHCH=CHCH(CH}_3\text{H}_2\text{Heq-}]\text{B}, \text{cis-isomer}\}, 138.3 \{\text{br dm}, 1J_{CF} \approx 245, \text{p-CF}\}, 137.1 \{\text{br dm}, 1J_{CF} \approx 245, \text{m-CF}\}, 125.7 \{\text{very br, ipso-C}\}, 115.5 \{\text{br dd}, 1J_{CH} = 165, 2J_{CP} = 6.0, \text{P}[-\text{CH}_2]\text{CHCH=CHCH(CH}_3\text{H}_2\text{Heq-}]\text{B}, \text{cis}\}, 115.2 \{\text{br dd}, 1J_{CH} = 165, 3J_{CP} = 6.0, \text{P}[-\text{CH}_2]\text{CHCH=CHCH(CH}_3\text{H}_2\text{Heq-}]\text{B}, \text{trans}\}, 41.6 \{\text{d}, 1J_{CP} = 25.4, \text{C(CH}_3\text{)}_3, \text{trans}\}, 41.2 \{\text{d}, 1J_{CP} = 25.4, \text{C(CH}_3\text{)}_3, \text{cis}\}, 36.1 \{\text{d}, 1J_{CP} = 30.5, \text{P}[-\text{CH}_2]\text{CHCH=CHCH(CH}_3\text{H}_2\text{Heq-}]\text{B}, \text{trans}\}, 35.2 \{\text{d}, 1J_{CP} = 31.0, \text{P}[-\text{CH}_2]\text{CHCH=CHCH(CH}_3\text{H}_2\text{Heq-}]\text{B}, \text{cis}\}, 31.3 \{\text{qm}, 1J_{CH} = 129, \text{C(CH}_3\text{)}_3, \text{trans}\}, 31.0 \{\text{qm}, 1J_{CH} = 129, \text{C(CH}_3\text{)}_3, \text{cis}\}. 19\text{F NMR (CD}_2\text{Cl}_2\): -128.8 \{\text{very br, o-CF, cis-isomer}\}, -136.6 \{\text{d}, 3J_{FF} = 20, \text{o-CF, trans-isomer}\}, -160.8 \{\text{very br, p-CF, cis}\}, -164.3 \{\text{t}, 3J_{FF} = 17, \text{p-CF, trans}\}, -166.1 \{\text{br, m-CF, cis}\}, -167.4 \{\text{br, m-CF, trans}\}. 31\text{P}\{1\text{H}\} \text{NMR (CD}_2\text{Cl}_2\): 51.0 \{\text{cis-isomer}\}, 50.9 \{\text{trans-isomer}\}.  
Elemental anal. calcd. for C_{36}H_{35}BF_{15}P: C 54.43, H 4.44; found C 54.74, H 4.39.