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# Reactions of phosphorus/boron frustrated Lewis pairs with $SO_2$†

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The frustrated Lewis pair $t$Bu$_3$P/B(C$_6$F$_5$)$_3$ (**1**) readily adds $SO_2$ to yield the zwitterionic adduct $t$Bu$_3$P$^+$–S(O)–OB$^-$(C$_6$F$_5$)$_3$ (**3**). A series of intramolecular vicinal P/B FLPs Mes$_2$P–(X)–B(C$_6$F$_5$)$_2$ [X = –CH$_2$–CH$_2$– (**2a**), –CHMe–CH$_2$– (**2b**), cyclo-C$_6$H$_{10}$ (**5**)] add $SO_2$ at −78 °C to yield the corresponding six-membered addition products **4a**, **4b**, **6**. The adducts contain a chiral sulfur center. The [B]–O–(O)S–[P] addition products **3**, **4b** and **6** were characterized by X-ray diffraction.

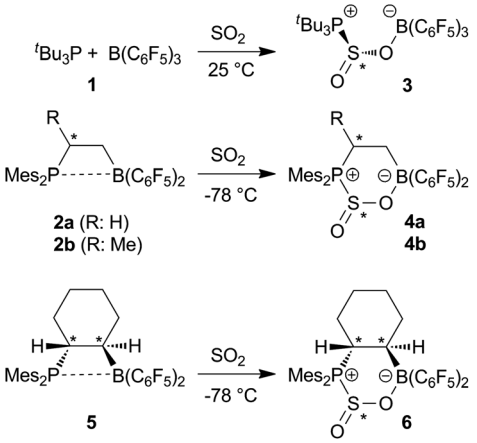


## Introduction

The advent of frustrated Lewis pair (FLP) chemistry has provided a new strategy for small molecule binding and/or activation.[1] Foremost in these efforts is the ability of FLPs to heterolytically split the dihydrogen molecule.[2] There is an increasing scope of substrates that can be employed in FLP-mediated hydrogenations.[3] In addition, this concept has been applied to effect the stoichiometric reduction of the aromatic rings of anilines to the corresponding cyclohexylamines.[4] Small molecule binding is another aspect of FLP chemistry that has garnered much attention.[5] FLP binding of alkenes, alkynes and unsaturated conjugated systems[6] as well as a variety of carbonyl compounds[7] have been explored. Perhaps most importantly, FLPs have been shown to bind to a number of greenhouse gases, such as carbon dioxide[8] or nitrogen oxides.[9] Sulfur dioxide is another environmentally problematic gas.[10] Herein, we describe the ability of a small series of inter- and intramolecular FLPs to capture the gas sulfur dioxide.[11] The dynamic and structural implications arising from the stereochemistry at sulfur are probed.

## Results and discussions

The intermolecular FLP **1** reacts with sulfur dioxide at room temperature in bromobenzene to give a new product **3** in 80% yield. This compound shows a $^{31}$P NMR resonance at $\delta = 67.8$ ppm, typical of a phosphonium center. The corresponding $^{11}$B NMR signal is seen at $\delta = 0.3$ ppm, suggestive of four-coordinate boron. Single crystals of compound **3** suitable for the X-ray crystal structure analysis were obtained by crystallization from $CH_2Cl_2$. It confirmed that the FLP **1** had undergone 1,2-addition to a S=O bond of sulfur dioxide to form the zwitterion $t$Bu$_3$-P(S(O)O)B(C$_6$F$_5$)$_3$ **3**. The lengths of the newly formed P1–S1 and O1–B1 bonds are found to be 2.2753(6) and 1.565(2) Å, respectively, while the S1–O1–B1 angle is 118.2(1)°. The corresponding S1–O1 bond length is 1.572(1) Å while the corresponding terminal S1–O2 bond distance is 1.465(1) Å. The angles about S sum to 314.58° (O2–S1–O1 110.07(8)°, O2–S1–P1 105.89(6)°,




**Scheme 1** Reactions of inter- and intramolecular FLPs with $SO_2$.

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† Electronic supplementary information (ESI) available: For additional experimental details, further structural information, additional data from the solid state NMR and theoretical studies. CCDC 895193–895195. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2sc21161k

‡ Computational chemistry.

§ Solid state NMR.

¶ X-ray crystal analyses.

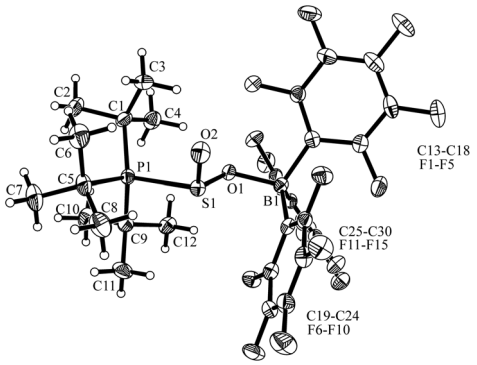



**Fig. 1** Molecular structure of compound **3** (thermal ellipsoids are shown with 50% probability).

O1–S1–P1 98.54(5)°) consistent with a distorted trigonal pyramidal geometry at sulfur (Scheme 1, Fig. 1).

The intramolecular FLP **2a**[2b] also cleanly adds sulfur dioxide in a rapid reaction in pentane solution at −78 °C to yield the product **4a**. This was assigned the structure of the cyclic adduct $(C_6H_2Me_3)_2PCH_2CH_2B(C_6F_5)_2(S(O)O)$ (Scheme 1). The new compound shows typical heteronuclear NMR resonances at $\delta =$ 33.3 ppm ($^{31}$P) and $\delta = 1.2$ ppm ($^{11}$B), respectively. Compound **4a** is chiral due to the presence of the stereogenic sulfur atom. Consequently, NMR signals for the diastereotopic pair of $C_6F_5$ substituents on boron and a pair of diastereotopic mesityl groups at phosphorus are observed. In addition, the hydrogen atoms of the ethylene linker are also pairwise diastereotopic.

The overall structural features of this type of compounds were revealed by the X-ray crystal structure analysis of the methyl substituted derivative **4b** that was formed from **2b** and $SO_2$ at −78 °C (for details see the ESI†). It features the *rac*-(*R*,$^{S}$*S*)–**4b** diastereoisomer as different conformers (see Fig. 2), that shows B1A–O1A 1.574(3) Å [B1B–O1B 1.560(3) Å] and P1A–S1A 2.336(1) Å [P1B–S1B 2.347(1) Å] bond lengths inside the respective six-membered heterocyclic distorted half-chair conformations.

Compound **4a** shows temperature dependent dynamic NMR spectra. Coalescence of the pairs of *o*-, *p*- and *m*-$^{19}$F NMR resonances of the $B(C_6F_5)_2$ moiety was observed in the temperature range between 298 K and 339 K, indicating a rapid enantiomerization of the stereogenic sulfur atom on the NMR time scale (Scheme 2). From the dynamic $^{19}$F NMR spectra a Gibbs activation barrier of $\Delta G^{\neq}_{enant}$ (333 K) = 15.4 ± 0.1 kcal mol$^{-1}$ was calculated for this process.

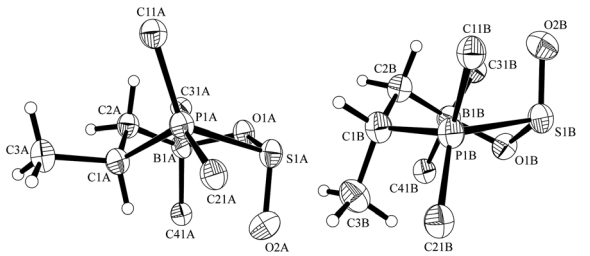
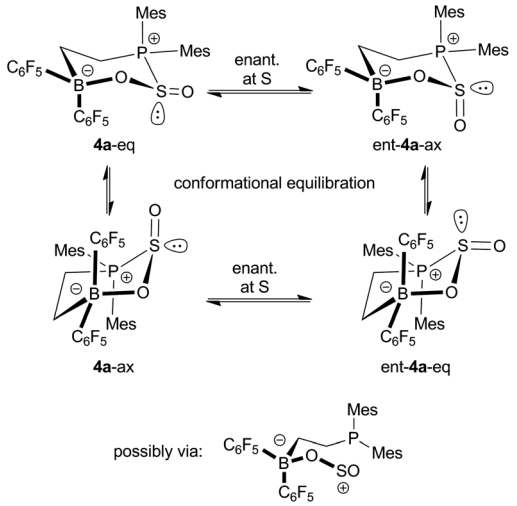



**Fig. 2** Molecular structure of the two conformers of the *rac*-(1*R*,$^{S}$*S*)-**4b** enantiomers found in the single crystal (thermal ellipsoids are shown with 30% probability; for clarity only the ipso-carbons of aryl ring at B and P are shown).




**Scheme 2** Enantiomerization and fluxional behavior of **4a**.

In addition a second distinct dynamic process of **4a** was observed by monitoring the temperature dependent $^{31}$P NMR spectra. These spectra revealed the presence of a *ca.* 1 : 4 mixture of two isomers at 183 K, giving rise to resonances at $\delta =$ 38.0 ppm and $\delta = 26.8$ ppm. Warming the sample rapidly resulted in coalescence of the signals at 243 K. In view of the results of a theoretical study of this system (*vide infra*) it is likely that these spectral changes arise from the occurrence of two ring conformers, featuring the S=O oxygen in the axial or equatorial position (Scheme 2). From the dynamic $^{31}$P NMR spectra an activation barrier of $\Delta G^{\neq}_{enant}$ (223 K) = 10.0 ± 0.3 kcal mol$^{-1}$ was estimated for this conformational equilibration process (see the ESI†).

The results were augmented by a study of the reaction of the intramolecular FLP[12] derived from the hydroboration of cyclohexenyldimesitylphosphane with Piers' borane $[HB(C_6F_5)_2]$.[13] FLP **5** reacts readily with $SO_2$ to give the cyclic adduct **6** (Scheme 1). In this case the FLP framework itself contains a pair of chiral carbon centers. The resulting stereochemistry from the hydroboration affords the single diastereoisomer that has the –$PMes_2$ and –$B(C_6F_5)_2$ groups *trans*-1,2-attached (*rac-trans*-**5**; this study involves only racemic compounds).[14] Introduction of the stereogenic sulfur center in **6** leads to the formation of a pair of diastereomers of **6** in a *ca.* 1 : 1.3 ratio [$^{31}$P NMR (193 K): $\delta =$ 60.5 ppm and $\delta = 41.1$ ppm]. Each diastereoisomer exhibits conformational equilibria similar to those observed for the monocyclic FLP/$SO_2$ adducts **4a**/**b** (*vide supra*). At higher temperature (308 K) the reversible equilibration between the diastereoisomers of **6**, by epimerization at sulfur, was evidenced by a $^{31}$P, $^{31}$P-NOESY experiment (see the ESI†). The X-ray crystal structure analysis of **6** confirmed that the phosphane component of the FLP **5** had added to the sulfur atom of sulfur dioxide. The diastereomers of **6** are present in a 3 : 1 ratio in the crystal (Fig. 3). The major adduct **6** shows typical bond lengths of P1–S1: 2.362(1) Å, S1–O(2A): 1.407(2) Å, S1–O1: 1.547(2) Å, O1–B1: 1.568(3) Å and bond angles C1–P1–S1: 102.80(7)°, P1–S1–O(2A): 114.82(11)°, O(2A)–S1–O1: 116.5(12)°, S1–O1–B1: 122.51(14)°, O1–B1–C6: 108.79(18)°.

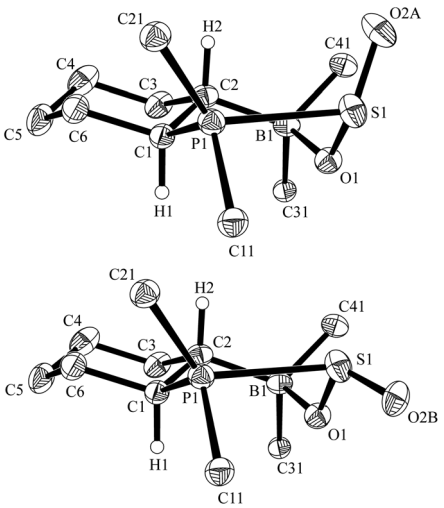



**Fig. 3** View of the molecular structures of the pair of diastereomers of the FLP-$SO_2$ adduct **6** in the crystal (top 75%, bottom: 25%) (thermal ellipsoids are shown with 30% probability; For clarity only the ipso-carbons of aryl ring at B and P are shown).

The FLP-$SO_2$ adducts **4a** and **6** were also characterized by $^{31}P$ and $^{11}B$ solid state NMR spectroscopy (see Fig. 4). The $^{31}P\{^1H\}$ CP MAS NMR spectrum of **4a** shows a pair of resonances at 39.9 and 28.7 ppm in an intensity ratio of about 1 : 3 probably originating from the two [B]–O–(O)S–[P] ring conformers. The unusually broad line shape suggests some fluxional character in the solid state. The line shape simulation for the $^{11}B$ MAS NMR spectrum of **4a** reveals two resonances at about 1 ppm with quadrupolar coupling constants $C_Q$ of 1.6 and 1.9 MHz and nearly identical asymmetry parameters $\eta$ of about 0.5. The experimental $C_Q$ and $\eta$ values are much closer to those calculated for the [B]–O–(O)S–[P] isomer than to those calculated for the [B]–S(O)–O–[P] isomers **4a**′-ax. and **4a**′-eq. (see Table 1). Thus, the formation of the latter isomers can be ruled out for all the $SO_2$ adducts studied here.

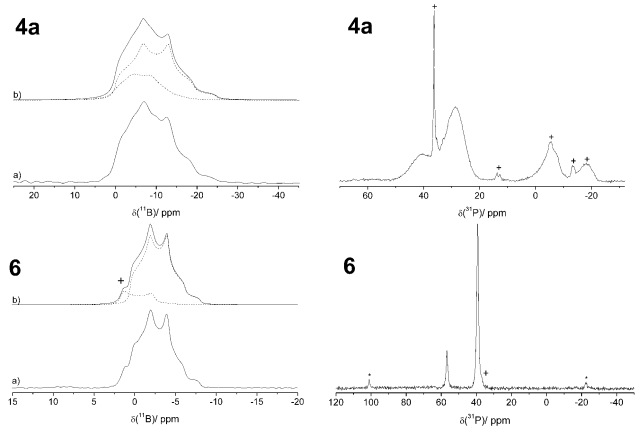



**Fig. 4** Left: $^{11}B\{^1H\}$ MAS NMR spectra of **4a** and **6** (a) acquired at 7.1 T and 11.7 T, respectively, with their corresponding line shape simulations (b). Right: $^{31}P\{^1H\}$ CP MAS spectrum of **4a** acquired at 7.1 T and $^{31}P\{^1H\}$ MAS NMR spectrum of **6** acquired at 9.4 T. * mark spinning sidebands, + impurities.

**Table 1** Experimentally and theoretically determined $^{11}B$ NMR parameters for the [B]–O–(O)S–[P] and [B]–S(O)–O–[P] conformers of **4a** and **6**. [Chemical shifts are calculated on a B3-LYP/def2-TZVP, electric field gradients on a B97-D/def2-TZVP (mod.) level of theory (for the full AO basis set see ref. 16)]

| | $\delta_{CS}^{iso}$/ ppm ±0.5 | $C_Q$/ MHz ±10% | $\eta$ ±0.1 | $\delta_{CS}^{iso}$/ppm (calc.) | $C_Q$/MHz (calc.) | $\eta$ (calc.) |
|---|---|---|---|---|---|---|
| **4a** | 1.0 | 1.62 | 0.46 | 1.6[a] | 2.21[a] | 0.35[a] |
| | 1.0 | 1.92 | 0.48 | 2.2[b] | 2.15[b] | 0.37[b] |
| | | | | −4.4[c] | 1.16[c] | 0.71[c] |
| | | | | −5.4[d] | 1.00[d] | 0.56[d] |
| **6** | 2.5[i] | 1.80[i] | 0.01[i] | −2.6[e] | 1.95[e] | 0.43[e] |
| | 0.9 | 1.88 | 0.50 | 0.4[f] | 2.02[f] | 0.44[f] |
| | | | | −2.8[g] | 1.05[g] | 0.74[g] |
| | | | | −1.5[h] | 1.25[h] | 0.57[h] |

[a] Fully geometry optimized structure of **4a**-ax. [b] Fully geometry optimized structure of **4a**-eq. [c] Fully geometry optimized structure of **4a**′-ax. [d] Fully geometry optimized structure of **4a**′-eq. [e] Geometry of **6**-ax. taken from the crystal structure. [f] Geometry of **6**-eq. taken from the crystal structure. [g] Fully geometry optimized structure of **6**′-ax. [h] Fully geometry optimized structure of **6**′-eq. [i] Assigned to an impurity.

Fig. 5 shows results from $^{11}B\{^{31}P\}$ *R*otational *E*cho *DO*uble *R*esonance (REDOR)[15,16] experiments for measuring the boron-phosphorus distances in **4a** and **6**. In contrast to previous results on non-reacted FLPs with much shorter B···P distances,[16] no dipolar oscillation typical of spin pairs are seen in these curves. Most likely, these oscillations are damped out due to subtle differences in the B···P distances for the different conformers and/or slow dynamic processes as suspected for **4a**. For the distance determination, we use the fact that at short evolution times ($\Delta S/S_0 < 0.25$) these curves are well approximated by parabolae, whose curvatures are proportional to the squared dipolar coupling constants.[17] With the B···P internuclear distance for **6** known from the crystal structure (3.463(4) Å) we can use the REDOR curve of this compound (Fig. 5a) for calibrating analogous results obtained on **4a**. We find a boron-phosphorus distance of 3.72 Å ± 0.2 Å in good agreement with the theoretically expected value (3.495 Å/3.506 Å) in the gas phase. Within the experimental error limit it also agrees well with the B···P internuclear distances of 3.501(2) Å and 3.537(6) Å for the two conformers determined from the crystal structure of **4b**. The $^{31}P\{^1H\}$ MAS NMR spectrum of a sample of **6** reveals two resonances at 56.5 and 39.1 ppm, respectively, close to the

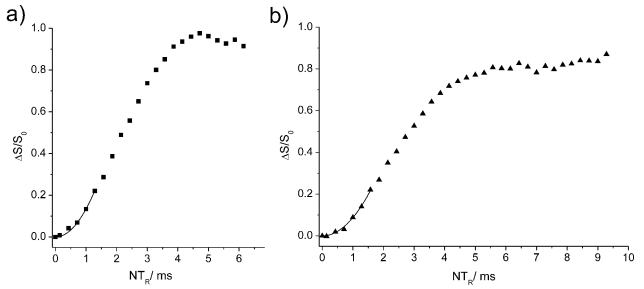



**Fig. 5** $^{11}B\{^{31}P\}$ REDOR curves for **6** (a) and **4a** (b) and corresponding parabolic approximations in the limit of short evolution times (for more details see ESI†).

**Table 2** Free reaction enthalpies ($\Delta G$ in kcal mol$^{-1}$) for the formation of the different isomers of **4a** and **6** in bromobenzene

| Conformer | **4a** | *rac*-(*R*,*R*,$^{S}$*R*) **6** |
|---|---|---|
| [B]–O–(O)S–[P], eq. | −7.9 | −6.2 |
| [B]–O–(O)S–[P], ax. | −7.7 | −6.7 |
| [B]–S(O)–O–[P], eq. | −3.6 | −5.1 |
| [B]–S(O)–O–[P], ax. | −7.1 | −4.5 |
| [B]–S(O)$_2$–[P] | 6.7 | 2.5 |

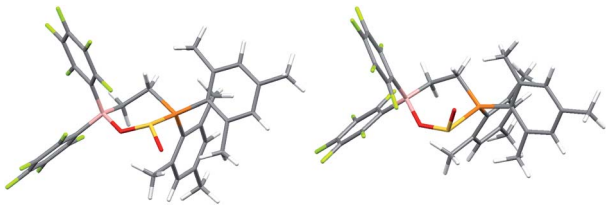


**Fig. 6** The DFT calculated [B]–O–(O)S–[P] isomers of compound **4a**: (a) with $O_{exocycl.}$ equatorial and (b) with $O_{exocycl.}$ axial (color code: C grey, P orange, B purple, S yellow, O red, F green, H white).

respective $^{31}$P NMR chemical shifts found for the pair of diastereoisomers of **6** in solution (see above). In the solid state these two species were initially formed in a *ca.* 1 : 5 ratio which over a period of 25 days changed to 1 : 10. In contrast to **4a** both diastereomers possess nearly identical $^{11}$B quadrupolar coupling parameters since only one resonance is detected in the $^{11}$B MAS NMR spectrum.

The FLP + $SO_2$ reaction was investigated by state of the art DFT calculations [B2PLYP-D3/def2-TZVP//TPSS-D3/def2-QZVPP + COSMO-RS solvent corrections,[18–23] estimated accuracy absolute about 1 kcal mol$^{-1}$ for free enthalpies (for further details see the ESI†)]. As there were no X-ray data available for compound **4a** several structural alternatives were tested. We investigated the observed [B]–O–(O)S–[P] conformational isomers **4a**-eq. and **4a**-ax. (see Table 2 and Fig. 6) as well as their hypothetical [B]–S(O)–O–[P] regioisomers (**4a**′-eq. and **4a**′-ax.). The latter were found to be slightly less favourable than the observed **4a**-eq./ax. pair (calculated for a bromobenzene solution). In addition the formation of the alternative five-membered isomer, [B]–S(O)$_2$–[P], was computed to be highly thermodynamically unfavourable with reaction (free) enthalpies of *ca.* 7–14 kcal mol$^{-1}$ higher than for any of the six-membered products.

The relative free enthalpies of all four six-membered isomers of **4a** (and similarly of **6** see Table 2) fall in a rather narrow range of about 4 kcal mol$^{-1}$ for **4a** and 2 kcal mol$^{-1}$ for **6**. The [B]–O–(O)S–[P] isomer **6**-ax. is computed to be the thermodynamically most stable product. Although this would suggest the observed regioselectivity is under thermodynamic control, it should be noted that the error of the computations infer the first two isomers of **6** (and 1,2,4 of **4a**) are more or less isoexergonic.

We investigated the possible pathways of the observed facile enantiomerization process at sulfur in **4a** by DFT and found that a true inversion process at the sulfur atom would be far too high in energy (~50 kcal mol$^{-1}$). However, due to the calculations rapid reversible P–S bond rupture provides a viable pathway of enantiomerization at sulfur in such a system.

## Conclusions

This study shows that FLPs react with remarkable ease with sulfur dioxide. The formation of the respective [B]–O–(O)S–[P] isomers has been observed by X-ray diffraction in three cases and by $^{11}$B solid state NMR/DFT calculations in two selected cases although the [B]–S(O)–O–[P] isomers are thermodynamically feasible according to the DFT calculations. FLP-$SO_2$ adduct formation has remarkably low kinetic barriers, making these adducts readily available for further reactivity studies.

## Experimental

### Synthesis of compound 3

A solution of $B(C_6F_5)_3$ (25 mg, 0.049 mmol) and $t$Bu$_3$P (10 mg, 0.049 mmol) in $C_6H_5Br$ (1 mL) was degassed and filled with $SO_2$ (1 bar). The sample was sealed and allowed to react overnight to afford $t$Bu$_3$PS(O)OB$(C_6F_5)_3$ (**3**) as a white powder (31 mg, 0.039 mmol, 80%). Crystals suitable for X-ray crystal structure analysis were obtained by crystallization from $CH_2Cl_2$. Anal. calcd (%) for $C_{30}H_{27}BF_{15}O_2PS$: C, 46.29; H, 3.50; found: C, 45.84; H, 3.40. $^1$H NMR (400 MHz, 298 K, [d$_2$]-dichloromethane) $\delta$ = 1.43 (d, $J_{PH}$ = 14.1 Hz, 27H, $t$Bu). $^{11}$B NMR (128 MHz) $\delta$ = 0.3 ($\nu_{1/2}$ ~ 200 Hz). $^{31}$P NMR (162 MHz) $\delta$ = 67.8.

### X-ray crystal structure analysis of 3

Formula $C_{30}H_{27}BF_{15}O_2PS$, $M$ = 778.36, colourless crystal, 0.24 × 0.22 × 0.19 mm, $a$ = 9.4942(4), $b$ = 29.0008(13), $c$ = 11.5368(5) Å, $\beta$ = 90.018(2)°, $V$ = 3176.5(2) Å$^3$, $\rho_{calc}$ = 1.628 g cm$^{-3}$, $\mu$ = 0.270 mm$^{-1}$, empirical absorption correction (0.937 ≤ $T$ ≤ 0.950), $Z$ = 4, monoclinic, space group $P2_1/c$ (No. 14), $\lambda$ = 0.71073 Å, $T$ = 150(2) K, $\omega$ and $\varphi$ scans, 30506 reflections collected ($\pm h$, $\pm k$, $\pm l$), 8222 independent ($R_{int}$ = 0.040) and 6900 observed reflections [$I > 2\sigma(I)$], 452 refined parameters, $R$ = 0.034, $wR^2$ = 0.072, max. (min.) residual electron density 0.37 (−0.43) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

### Preparation of compound 4a

Compound **2a**, was generated *in situ* from dimesitylvinylphosphane (100 mg, 0.34 mmol, 1.0 eq.) and bis(pentafluorophenyl)-borane (117 mg, 0.34 mmol, 1.0 eq.) in *n*-pentane. $SO_2$ was introduced (−78 °C, 0.8 bar, 10 min.). After stirring the reaction mixture for 1.5 h workup gave compound **4a** (198 mg, 83%) as a white solid. M.p.: 103 °C. Anal. calcd (%) for $C_{32}H_{26}BF_{10}O_2PS$: C, 54.41; H, 3.71; found C, 54.88; H, 3.91. $^1$H NMR (500 MHz, 298 K, [d$_2$]-dichloromethane): $\delta$ = 7.00 (d, $^4J_{PH}$ = 3.6 Hz, 4H, *m*-Mes$^A$), 6.99 (d, $^4J_{PH}$ = 3.9 Hz, 4H, *m*-Mes$^B$), 3.75/2.93 (each m, each 1H, $CH_2^P$), 2.45 (br s, 6H, *o*-$CH_3^{MesA}$), 2.41 (br s, 6H, *o*-$CH_3^{MesB}$), 2.31 (s, 6H, *p*-$CH_3^{MesA,B}$), 1.88/1.23 (each m, each 1H, $CH_2^B$). $^{13}$C{$^1$H} NMR (126 MHz): $\delta$ = 144.9, 144.8 (each s,

*p*-Mes$^{A,B}$), 144.1 (d, $^{2}J_{PC}$ = 7.0 Hz, *o*-Mes$^{B}$), 143.4 (d, $^{2}J_{PC}$ = 5.6 Hz, *o*-Mes$^{A}$), 132.2 (d, $^{3}J_{PC}$ = 10.8 Hz, *m*-Mes$^{B}$), 131.6 (d, $^{3}J_{PC}$ = 9.8 Hz, *m*-Mes$^{A}$), 122.2 (d, $^{1}J_{PC}$ = 39.3 Hz, *i*-Mes$^{A}$), 118.3 (d, $^{1}J_{PC}$ = 52.5 Hz, *i*-Mes$^{B}$), 23.4 (br, *o*-$CH_3^{MesA}$), 23.1 (br, *o*-$CH_3^{MesB}$), 22.7 (d, $^{1}J_{PC}$ = 22.9 Hz, $CH_2^{P}$), 21.3, 21.2 (each s, *p*-$CH_3^{MesA,B}$), 11.4 (br, $CH_2^{B}$), [$C_6F_5$ not listed]. $^{11}B\{^{1}H\}$ NMR (160 MHz): $\delta$ = 1.2 ($\nu_{1/2} \approx$ 400 Hz). $^{19}F$ NMR (470 MHz): $\delta$ = −134.9 (m, 2F, *o*), −160.6 (m, 1F, *p*), −165.7 (m, 2F, *m*), $\Delta\delta^{19}F_{p,m}$ = 5.1 [$C_6F_5^{A}$]; −135.5 (m, 2F, *o*), −160.7 (m, 1F, *p*), −165.7 (m, 2F, *m*), $\Delta\delta^{19}F_{p,m}$ = 4.7 [$C_6F_5^{B}$]. $^{31}P\{^{1}H\}$ NMR (202 MHz): $\delta$ = 33.3 ($\nu_{1/2} \approx$ 20 Hz).

### Synthesis of compound 4b

Compound **2b**, was generated *in situ* from (1-methylethenyl)dimesitylphosphane (24.8 mg, 0.08 mmol, 1.0 eq.) and bis-(pentafluorophenyl)borane (27.6 mg, 0.08 mmol, 1.0 eq.) in toluene (2 mL). The solution was briefly exposed to sulfur dioxide at −78 °C (5 min, 1.8 bar, this provided for minimal condensation of $SO_2$). The reaction mixture was stirred for 45 min. The excess $SO_2$ was vented and the obtained reaction mixture was covered with precooled *n*-pentane (5 mL) and stored at −36 °C to finally get compound **4b** as colorless crystals which were suitable for X-ray crystal structure analysis. Two diastereomers of **4b** were found in [$d_2$]-dichloromethane solution at 299 K (ratio: 84/16). M.p.: 126 °C. $^{11}B\{^{1}H\}$ NMR (160 MHz, $CD_2Cl_2$, 299 K): $\delta$ = 1.3 ($\nu_{1/2} \approx$ 450 Hz). $^{31}P\{^{1}H\}$ NMR (202 MHz, $CD_2Cl_2$, 299 K): $\delta$ = 51.2 ($\nu_{1/2} \approx$ 10 Hz, 16%), 39.5 ($\nu_{1/2} \approx$ 10 Hz, 84%). $^{31}P\{^{1}H\}$ NMR (202 MHz, $CD_2Cl_2$, 198 K): $\delta$ = 55.4 ($\nu_{1/2} \approx$ 15 Hz, 8%), 50.3 ($\nu_{1/2} \approx$ 35 Hz, 3%), 39.0 ($\nu_{1/2} \approx$ 25 Hz, 58%), 37.8 ($\nu_{1/2} \approx$ 30 Hz, 31%). *Major diastereomer [84%]:* $^{1}H$ NMR (500 MHz, $CD_2Cl_2$, 299 K): $\delta$ = 7.02 (d, $^{4}J_{PH}$ = 3.6 Hz, 2H, *m*-Mes$^{A}$), 7.00 (d, $^{4}J_{PH}$ = 3.6 Hz, 2H, *m*-Mes$^{B}$), 4.14 (m, 1H, $CH^{P}$), 2.38 (br, 6H, *o*-$CH_3^{MesA}$), 2.35 (br, 6H, *o*-$CH_3^{MesB}$), 2.325 (br m, 3H, *p*-$CH_3^{MesA}$), 2.318 (br m, 3H, *p*-$CH_3^{MesB}$), 1.82 (dd, $^{3}J_{PH}$ = 27.8 Hz, $^{3}J_{HH}$ = 16.4 Hz, 1H, $CH_2^{B}$), 1.41 (dd, $^{3}J_{PH}$ = 18.1 Hz, $^{3}J_{HH}$ = 7.0 Hz, 3H, $CH_3^{P}$), 1.30 (m, 1H, $CH_2^{B}$). $^{13}C\{^{1}H\}$ NMR (126 MHz): $\delta$ = 144.6 (d, $^{4}J_{PC}$ = 3.1 Hz, *p*-Mes$^{A}$), 144.3 (d, $^{4}J_{PC}$ = 3.8 Hz *p*-Mes$^{B}$), 144.0 (d, $^{2}J_{PC}$ = 5.6 Hz *o*-Mes$^{A}$), 143.6 (br d, $^{2}J_{PC}$ = 6.6 Hz *o*-Mes$^{B}$), 132.5 (br d, $^{3}J_{PC}$ = 11.4 Hz, *m*-Mes$^{B}$), 131.69 (d, $^{3}J_{PC}$ = 9.9 Hz, *m*-Mes$^{A}$), 120.4 (d, $^{1}J_{PC}$ = 49.6 Hz, *i*-Mes$^{B}$), 120.3 (d, $^{1}J_{PC}$ = 36.1 Hz, *i*-Mes$^{A}$) 31.1 (d, $^{1}J_{PC}$ = 15.0 Hz, $CH^{P}$), 24.6 (br, *o*-$CH_3^{MesA}$)$^{t}$, 23.3 (d, $^{3}J_{PC}$ = 4.1 Hz, *o*-$CH_3^{MesB}$)$^{t}$, 22.3 (br d, $^{2}J_{PC}$ = 7.9 Hz, $CH_3^{P}$), 21.19, 21.18 (each d, each $^{5}J_{PC}$ = 1.8 Hz, *p*-$CH_3^{MesA,B}$), 21.1 (br, $CH_2^{B}$), [$C_6F_5$ not listed]. $^{19}F$ NMR (470 MHz): $\delta$ = −135.4 (m, 2F, *o*), −160.6 (t, $^{1}J_{FC}$ = 20.4 Hz, 1F, *p*), −165.7 (m, 2F, *m*), $\Delta\delta^{19}F_{p,m}$ = 5.1 [$C_6F_5^{A}$]; −135.6 (m, 2F, *o*), −161.1 (t, $^{1}J_{FC}$ = 20.4 Hz, 1F, *p*), −165.5 (m, 2F, *m*), $\Delta\delta^{19}F_{p,m}$ = 4.4 [$C_6F_5^{B}$]. *Minor diastereomer [16%]:* $^{1}H$ NMR (500 MHz): $\delta$ = 7.04 (d, $^{4}J_{PH}$ = 3.7 Hz, 2H, *m*-Mes$^{A}$), 7.01 (d, $^{4}J_{PH}$ = 3.6 Hz, 2H, *m*-Mes$^{B}$), 3.36 (m, 1H, $CH^{P}$), 2.37 (br, 6H, *o*-$CH_3^{MesA}$), 2.34 (br, 6H, *p*-$CH_3^{MesA,B}$), 2.27 (br, 6H, *o*-$CH_3^{MesB}$), 2.04 (m, 1H, $CH_2^{B}$), 1.68 (dd, $^{3}J_{PH}$ = 27.5 Hz, $^{3}J_{HH}$ = 16.4 Hz, 1H, $CH_2^{B}$), 1.406 (dd, $^{3}J_{PH}$ = 17.9 Hz, $^{3}J_{HH}$ = 7.1 Hz, 3H, $CH_3^{P}$). $^{13}C\{^{1}H\}$ NMR (126 MHz): $\delta$ = 144.4 (d, $^{4}J_{PC}$ = 3.3 Hz), 144.3$^{t}$ (d, $^{4}J_{PC}$ = 3.8 Hz) (*p*-Mes$^{A,B}$), 144.1 (d, $^{2}J_{PC}$ = 6.3 Hz, *o*-Mes$^{A}$), 142.9 (d, $^{2}J_{PC}$ = 6.3 Hz, *o*-Mes$^{B}$), 132.2 (d, $^{3}J_{PC}$ = 10.6 Hz, *m*-Mes$^{B}$), 131.67 (d, $^{3}J_{PC}$ = 10.8 Hz, *m*-Mes$^{A}$), 121.5 (d, $^{1}J_{PC}$ = 44.8 Hz, *i*-Mes$^{B}$), 121.1 (d, $^{1}J_{PC}$ = 34.5 Hz, *i*-Mes$^{A}$), 33.6 (d, $^{1}J_{PC}$ = 11.7 Hz, $CH^{P}$), 24.4 (br, *o*-$CH_3^{MesA}$), 23.7 (d, $^{3}J_{PC}$ = 3.5 Hz, *o*-$CH_3^{MesB}$), 21.6 (d, $^{2}J_{PC}$ = 12.6 Hz, $CH_3^{P}$), n.o. (*p*-$CH_3^{Mes}$), 20.2 (br, $CH_2^{B}$), [$C_6F_5$ not listed; $^{t}$ tentative assignment]. $^{19}F$ NMR (470 MHz): $\delta$ = −134.5 (m, 2F, *o*), −161.0 (t, $^{1}J_{FC}$ = 20.4 Hz, 1F, *p*), −165.9 (m, 2F, *m*), $\Delta\delta^{19}F_{p,m}$ = 5.1 [$C_6F_5^{A}$]; −134.7 (m, 2F, *o*), −159.9 (t, $^{1}J_{FC}$ = 20.4 Hz, 1F, *p*), −165.0 (m, 2F, *m*), $\Delta\delta^{19}F_{p,m}$ = 4.4 [$C_6F_5^{B}$].

### X-ray crystal structure analysis of 4b

Formula $C_{33}H_{28}BF_{10}O_2PS$, $M$ = 720.39, colourless crystal, 0.20 × 0.13 × 0.05 mm, $a$ = 13.2898(3), $b$ = 13.3521(6), $c$ = 22.5790(9) Å, $\alpha$ = 73.392(3), $\beta$ = 73.073(3), $\gamma$ = 83.328(4)°, $V$ = 3670.7(2) Å$^3$, $\rho_{calc.}$ = 1.304 g cm$^{-3}$, $\mu$ = 1.903 mm$^{-1}$, empirical absorption correction (0.702 ≤ $T$ ≤ 0.910), $Z$ = 4, triclinic, space group $P\bar{1}$ (no. 2), $\lambda$ = 1.54178 Å, $T$ = 223(2) K, $\omega$ and $\varphi$ scans, 53 257 reflections collected (±$h$, ±$k$, ±$l$), 12 647 independent ($R_{int}$ = 0.043) and 10 730 observed reflections [$I > 2\sigma(I)$], 877 refined parameters, $R$ = 0.049, w$R^2$ = 0.145, max. (min.) residual electron density 0.35 (−0.32) e.Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

### Synthesis of compound 6

*Procedure A:* Di(mesityl)cyclohexenylphosphane (120 mg, 0.34 mmol) and $HB(C_6F_5)_2$ (119 mg, 0.34 mmol) dissolved in toluene (2.5 mL) and stirred for 30 min at r.t. to give a yellow solution of **5**. The solution was cooled to −78 °C and $SO_2$ gas was pressurized (2.0 bar) for 3 minutes. Then the solution was covered with *n*-pentane (−30 °C) to finally get compound **6** (136 mg, 52 %) as colourless crystals, which were suitable for X-ray crystal structure analysis. *Procedure B:* Di(mesityl)cyclohexenylphosphane (250 mg, 0.71 mmol) and $HB(C_6F_5)_2$ (247 mg, 0.71 mmol) dissolved in *n*-pentane (15 mL) and stirred for 30 min at r.t. to give a yellow solution of **5**. The solution was cooled to −78 °C and $SO_2$ gas was pressurized (2.0 bar) for 5 minutes. The solvent was removed and the residue was dried at −78 °C. The colourless residue was dissolved in precooled $CH_2Cl_2$ and covered with precooled (−30 °C) *n*-pentane to finally get compound **6** (310 mg, 57 %) as colourless crystals. Anal. calcd (%) for $C_{36}H_{32}PBSO_2F_{10}$: C, 56.86; H, 4.24; found, C; 56.30; H, 4.06. The NMR resonances were not assigned to each diastereoisomer [1 : 1.3 ($^{31}P$)] $^{1}H$ NMR (600 MHz, $CD_2Cl_2$, 193 K) [all resonances are broad] $\delta$ = 7.18/6.97, 7.14/6.93, 7.09/6.80, 7.05/6.87 (each br s, each 1H, *m*,*m*'-Mes)$^{1}$, 3.82, 3.47 (each br., each 1H, PCH), 2.79/2.24(p)/1.64, 2.74/2.30(p)/1.51, 2.67/2.31(p)/1.87, 2.54/2.25(p)/1.74 (each s, each 3H, $CH_3^{Mes}$)$^{1}$, 2.25/1.23, 2.07/0.62, 1.92/0.61, 1.88/1.35, 1.60/1.22, 1.58/1.77, 1.56/1.28, 1.42/0.99 (each br, each 1H, $CH_2$)$^{2}$, 2.31, 1.85 (each br, each 1H, BH)$^{2}$, [$^{1}$ from the gcosy NMR experiment;$^{2}$ from the ghsqc NMR experiment]. $^{11}B\{^{1}H\}$ NMR (192 MHz, $CD_2Cl_2$, 308 K): $\delta$ = 1.8 ($\nu_{1/2} \approx$ 500 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, $CD_2Cl_2$, 193 K): $\delta$ = 60.5 ($\nu_{1/2} \approx$ 30 Hz, [42%]), 41.1 ($\nu_{1/2} \approx$ 40 Hz, [58%]). $^{19}F$ NMR (564 MHz, $CD_2Cl_2$, 193 K): $\delta$ = −128.6, −130.8, −131.7, −132.3, −132.47, −132.53, − 136.3, −139.0 (each br, each 1F, *o*-$C_6F_5$), −158.1, −159.3, −159.7, −160.1 (each br, each 1F, *p*-$C_6F_5$),

−163.6 (1F), −163.9 (1F), −164.5 (5F), −164.9 (1F) (each br, *m*-$C_6F_5$).

### X-ray crystal structure analysis of 6

Formula $C_{36}H_{32}BF_{10}O_2PS$, $M = 760.46$, colourless crystal, 0.28 × 0.15 × 0.06 mm, $a = 10.5993(4)$, $b = 11.8650(4)$, $c = 14.4165(9)$ Å, $\alpha = 92.700(3)$, $\beta = 95.322(2)$, $\gamma = 111.030(13)^\circ$, $V = 1678.66(13)$ Å$^3$, $\rho_{calc.} = 1.504$ g cm$^{-3}$, $\mu = 2.113$ mm$^{-1}$, empirical absorption correction ($0.589 \leq T \leq 0.883$), $Z = 2$, triclinic, space group $P\bar{1}$ (no. 2), $\lambda = 1.54178$ Å, $T = 223(2)$ K, $\omega$ and $\varphi$ scans, 19 387 reflections collected ($\pm h$, $\pm k$, $\pm l$), 5692 independent ($R_{int} = 0.048$) and 4822 observed reflections [$I > 2\sigma(I)$], 476 refined parameters, $R = 0.043$, w$R^2 = 0.116$ max. (min.) residual electron density 0.24 (−0.29) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

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