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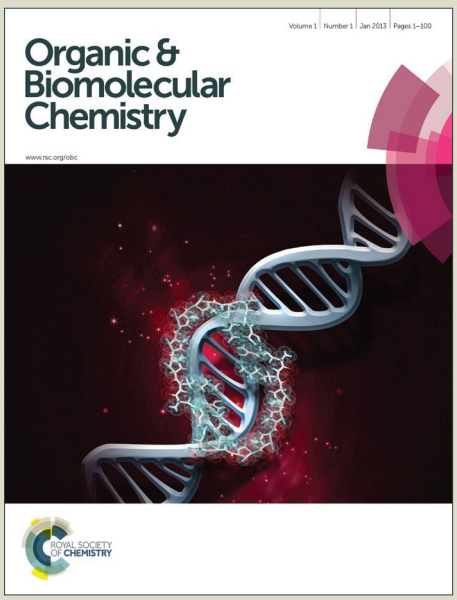

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Direct Synthesis of a Geminal Zwitterionic Phosphonium / Hydridoborate System - Developing an Alternative Tool for Generating Frustrated *Lewis* Pair Hydrogen Activation Systems

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A convenient way to the new class of geminal $Mes_2PH^+/B(C_6F_5)_2H^-$ pairs is presented. It utilizes triflic acid addition to *trans*-$Mes_2PCH{=}CHB(C_6F_5)_2$ followed by triflate/hydride exchange. Thermally induced ring-closure gave a phosphonium/boratacyclopropane zwitterion **8** which formed the $Mes_2PH(CHMe)B(C_6F_5)_2H$ P/B FLP-H_2 product **10** by subsequent treatment with triflic acid and a silane, or alternatively with dihydrogen at 90 °C. The product **10** is an active catalyst for the hydrogenation of a variety of unsaturated organic substrates, including a quinoline derivative. Treatment of **8** with $HB(C_6F_5)_2$ gave a bifunctional borane **14** which selectively reduced carbon monoxide to the formyl stage.

Introduction

Frustrated *Lewis* pairs (FLPs) have shown some remarkable potential for small molecule binding and activation.[1,2] Heterolytic cleavage of the dihydrogen molecule has been the most prominent feature in this chemistry.[3] This activation of H_2 by cooperative action of a pair of complementary main group element functional groups has led to the development of a catalytic metal-free hydrogenation protocol for quite a variety of unsaturated substrate types.[4-6] Usually, the inter- or intra-molecular FLPs were prepared and then converted to the respective zwitterionic H_2-activation products by treatment with dihydrogen. The formation of the vicinal intramolecular P/B FLP **1** and its $[P]H^+/[B]H^-$ H_2-activation product **2** is a typical example (see Chart 1).[7-8] However, there are unfortunate cases where this straightforward approach has so far not been achieved. The family of the geminal $Mes_2P/B(C_6F_5)_2$ FLPs represents an example of such a situation. So far, we had been able to obtain related systems **3** by simple hydroboration only with the $P(C_6F_5)_2$ moiety (see Chart 1) i.e. a *Lewis* base functionality that is not basic enough for the dihydrogen activation process.[9-10] For such situations, we have now developed an attractive principal synthetic alternative that has made a respective $[P]H^+/[B]H^-$ product directly available without involving the isolated free P/B FLP. By this new way we have obtained an active geminal phosphonium/hydrido-borate system that could then be used directly for the actual metal-free catalytic hydrogenation reaction of a variety of unsaturated substrates and we have developed first examples of an interesting follow-up chemistry derived from this new synthetic FLP development. In this article we will briefly outline this unusual but very convenient new way to a catalytically active geminal P/B FLP H_2 system.

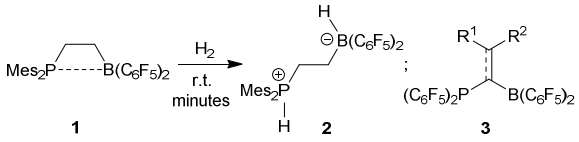

Chart 1. Intramolecular FLP examples

Results and discussion

Formation of the new geminal PH^+/BH^- system

Our synthesis started with dimesitylethynylphosphane (**4**) which was regioselectively hydroborated with *Piers'* borane $[HB(C_6F_5)_2]$[11] to yield compound **5**. It contains a phosphane *Lewis* base (^{31}P NMR: δ -7.7) and a borane *Lewis* acid (^{11}B NMR: δ 53.2) bridged by the *trans*-CH=CH-unit (^{1}H NMR: δ 8.30, 6.66, $^3J_{HH}$ = 18.1 Hz). The structure was confirmed by X-ray diffraction (see Figure 1). The X-ray crystal structure analysis shows that the *Piers'* borane reagent $[HB(C_6F_5)_2]$ has regioselectively added to the carbon-carbon triple bond of the dimesitylphosphanyl substituted acetylene. The resulting central carbon-carbon double bond [C1-C2 1.350(3) Å] in the

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product **5** is *trans*-configured. The bulky substituents show a dihedral angle of θ P1-C1-C2-B1 = 170.3(2)°. The borane is planar-tricoordinate with a sum of bond angles of $\Sigma B1^{CCC}$ 360.0°. It is found in a conjugated orientation with the adjacent C=C double bond [θ C1-C2-B1-C31 -161.6(2)°, C1-C2-B1-C41 17.5(3)°]. The phosphorus atom in compound **5** features a flattened trigonal-pyramidal geometry with $\Sigma P1^{CCC}$ 324.7°.[12]

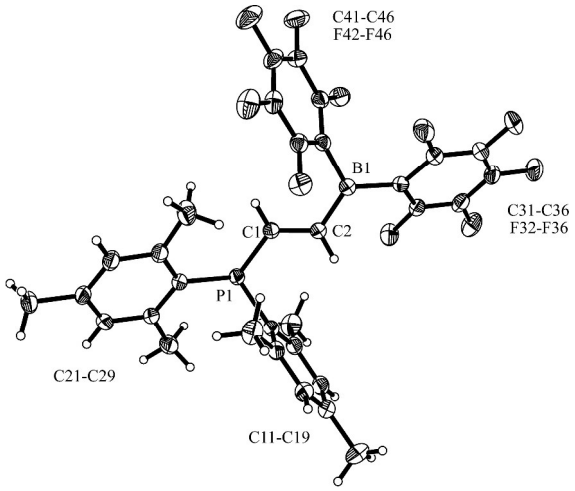


Figure 1. Molecular structure of compound **5** (thermal ellipsoids are shown with 30% probability).

Triflic acid was then added[11c,13] to compound **5** to give the phosphonium compound **6** [PH^+: δ 7.90 ($^1J_{PH}$ = 475.3 Hz) (^{1}H); δ -16.8 (^{31}P)]. The triflate anion was found covalently attached at the boron atom. This was confirmed by X-ray diffraction (see Figure 2). The X-ray crystal structure analysis shows the -OSO_2CF_3 group covalently bonded to the boron atom [B1-O1 1.573(3) Å] which now has altered into a pseudo-tetrahedral coordination geometry ($\Sigma B1^{CCC}$ 333.4°). The phosphorus base at the opposite end of the *trans*-B1-C2=C1-P1 framework with [B1-C2 1.594(4) Å, C2-C1 1.322(4) Å, C1-P1 1.777(3) Å, angles B1-C2-C1 128.0(2)°, C2-C1-P1 122.5(2)°] has become protonated ($\Sigma P1^{CCC}$ 342.2°).

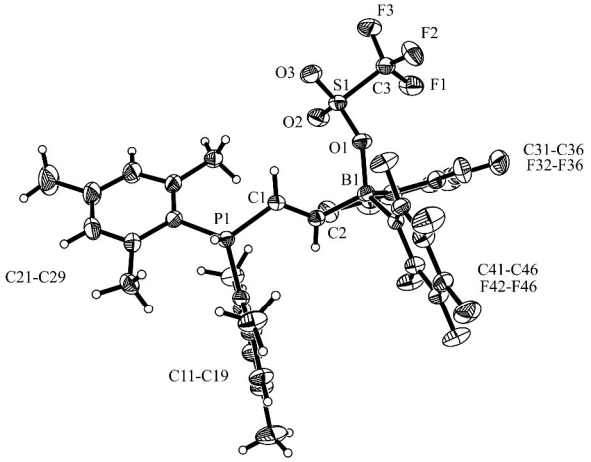
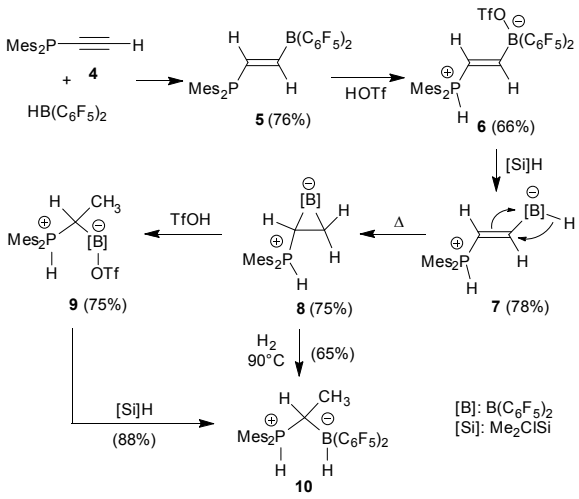


Figure 2. A view of the molecular structure of compound **6** (thermal ellipsoids are shown with 30% probability).

In solution, compound **6** shows a typical borate ^{11}B NMR resonance at δ 0.7 [^{31}P: δ -16.8 ($^1J_{PH} \approx$ 475 Hz)]. The ^{19}F NMR spectrum features the typical ratio of *o,p,m*-resonances of the pair of C_6F_5 substituents at boron and a separate ^{19}F NMR signal of the -OSO_2CF_3 group at δ -78.6. The connecting C=C unit in compound **6** is *trans*-configured [^{1}H NMR: δ 7.67, 6.43 ($^3J_{HH}$ = 19.0 Hz), ^{13}C: δ 174.1 ([B]CH), 107.9 ([P]CH)]. The OTf substituent at the borate anion terminus of compound **6** was then exchanged to hydride by treatment with chlorodimethylsilane (CH_2Cl_2, 1h at r.t.) to give the *trans*-CH=CH-bridged phosphonium/hydridoborate system **7** (see Scheme 1).

Both the PH^+ proton (δ 7.82, $^1J_{PH}$ = 469.3 Hz, with corresponding ^{31}P NMR signal at δ = -18.3) and the BH^- hydride signal (broad partially relaxed 1:1:1:1 quartet at δ 3.24, with corresponding ^{11}B NMR signal at δ = -21.6, $^1J_{BH}$ = 89.0 Hz) were located. The ^{1}H/^{13}C NMR spectra feature of the *trans*-CH=CH-bridge occur at δ 8.02, 5.74 ($^3J_{HH}$ = 18.3 Hz) and δ 189.1/101.5, respectively.



Scheme 1. Synthesis of compound **10**

Thermolysis of compound **7** in toluene solution (30 min, 110 °C) resulted in a clean and complete rearrangement to the zwitterionic phosphonium/boratacyclopropane isomer **8**.[14] The X-ray crystal structure analysis (see Figure 3) shows the newly formed anionic heterocyclic three-membered ring [B1-C1 1.660(3) Å, B1-C2 1.563(3) Å, C1-C2 1.535(3) Å]. The boron atom is four-coordinate; it has the pair of C_6F_5 substituents bonded to it [B1-C31 1.614(3) Å, B1-C41 1.608(3) Å, angle C31-B1-C41 112.2(2)°, C1-B1-C2 56.8(1)°]. The Mes_2P(H)-substituent is found attached at carbon atom C1 of the ring [C1-P1 1.749(2) Å]. The phosphorus atom also shows a distorted pseudotetrahedral coordination geometry ($\Sigma P1^{CCC}$ 342.5°).

The NMR spectra of compound **8** show typical cyclopropane features [^{1}H: δ 1.17 (CH), δ 1.00, 0.85 (CH_2); ^{13}C: δ 12.4 (CH_2), δ 4.2 (CH, $^1J_{PC}$ = 62.3 Hz)]. The ^{11}B NMR signal was observed at δ -23.8 and the signals of the PH unit were located at δ -1.1 (^{31}P) and 6.94 (^{1}H, $^1J_{PH}$ = 464.4 Hz), respectively. Due to the newly formed chiral carbon center (C1) compound **8** shows the

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^{19}F NMR resonances of a pair of diastereotopic C_6F_5 groups at boron and the ^{1}H/^{13}C NMR signals of a pair of diastereotopic mesityl groups at phosphorus (for details see the Supporting Information).

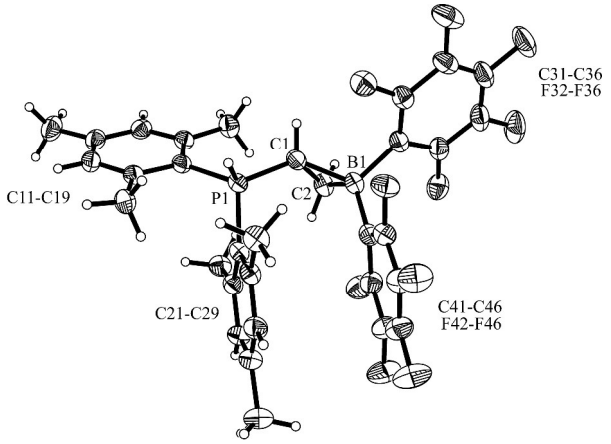

Figure 3. Molecular structure of compound **8** (thermal ellipsoids are shown with 30% probability).

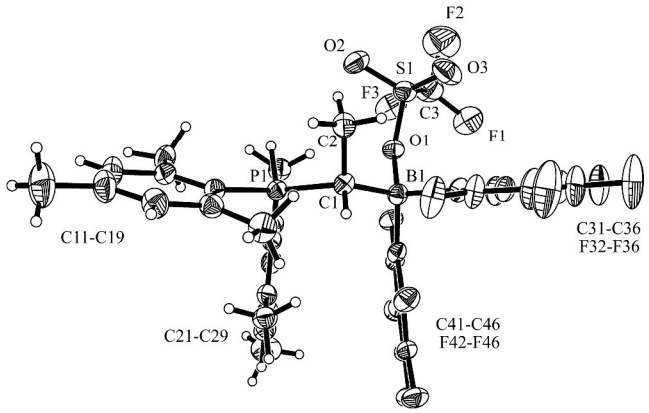

Figure 4. A view of the molecular structure of the HOTf addition product **9** (thermal ellipsoids are shown with 30% probability).

Treatment of the zwitterion **8** with triflic acid resulted in a selective protonolytic ring opening of the heterocyclic three-membered ring to give compound **9** in 75% yield. In solution, it shows heteronuclear magnetic resonance signals at δ 3.6 (^{11}B), δ -1.2 (^{31}P) and δ -76.8 (^{19}F NMR of the CF_3 group). At 233 K compound **9** showed a total of ten ^{19}F NMR signals of the pair of diastereotopic C_6F_5 substituents at boron, indicating hindered rotation around the B-C vectors. Compound **9** shows a typical pattern of ^{1}H NMR signals of the -$CHCH_3$ unit [δ 3.72 (CH), δ 1.67 (dd, $^{3}J_{PH}$ = 24.2 Hz, $^{3}J_{HH}$ = 6.9 Hz (CH_3); ^{13}C: δ 19.5, 14.9)]. Compound **9** was characterized by X-ray diffraction. The view of the structure (Figure 4) confirms that the boratacyclopropane ring of the product **8** has been opened protonolytically. This resulted in the formation of a methyl group (C2) attached at the methine carbon atom C1 that is found bridging between boron and phosphorus [C1-C2 1.552(5) Å, B1-C1 1.662(5) Å, P1-C1 1.816(3) Å, angle B1-C1-P1 116.0(2)°]. The triflate anion has become attached to boron [B1-O1 1.571(5) Å] and the phosphorus atom is protonated ($\Sigma P1^{CCC}$ 344.0°). In the crystal, product **9** exhibits a conformation that shows the C1-C2 vector in a gauche-like orientation with the B1-O1 triflate group [θ C2-C1-B1-O1 -61.1(4)°].

Subsequent treatment of compound **9** with $Me_2Si(H)Cl$ resulted in clean removal of the OTf group from boron with formation of the borohydride product **10**, which was isolated in 88% yield. Alternatively, ring opening of **8** was achieved directly by treatment with dihydrogen at elevated temperature (90 °C, overnight in toluene, 2.5 bar H_2) to give compound **10** (see Scheme 1). We isolated it after workup involving crystallization from dichloromethane/pentane in 65% yield.

The geminal phosphonium/hydridoborate zwitterion **10** was characterized by X-ray diffraction (see Figure 5). It features bonds between carbon atom C1 and phosphorus [P1-C1 1.805(3) Å] and boron [B1-C1 1.669(5) Å, angle B1-C1-P1 107.2(2)°]. Carbon atom C1 also bears the newly formed methyl group that was derived from opening of the boratacyclopropane ring of the product **8** in the course of the hydrogenolysis reaction [C1-C2 1.566(6) Å]. Both the phosphorus and the boron atoms in compound **10** feature pseudotetrahedral coordination geometries ($\Sigma P1^{CCC}$ 343.8°, $\Sigma B1^{CCC}$ 336.4°). In solution, we have located both the hydride ^{1}H NMR signal of the hydridoborate subunit [δ 2.89, ^{11}B: δ -20.0 ($^{1}J_{BH}$ = 90.5 Hz)] and the phosphonium proton [δ 7.06 ($^{1}J_{PH}$ = 463.9 Hz), ^{31}P: δ 6.3]. The ^{1}H NMR spectrum feature of the ethylidene bridge occur at δ 3.26 (CH) and δ 1.13 (CH_3) [^{13}C: δ 17.3 (CH), δ 15.8 (CH_3)].

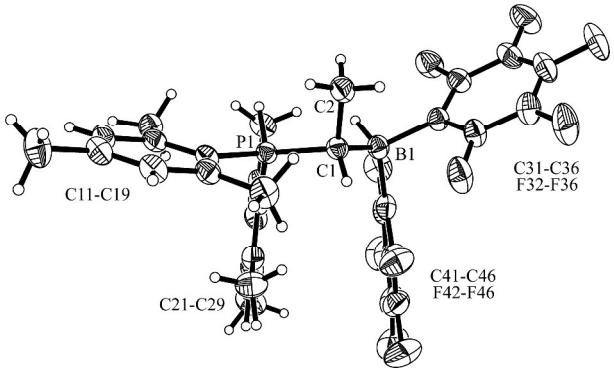

Figure 5. A view of the molecular structure of the geminal phosphonium/ hydridoborate system **10** (thermal ellipsoids are shown with 30% probability).

Reactivity studies

We tried to find out more about the unusual hydrogenolytic ring opening reaction of **8** to give **10**. Therefore, we performed a few additional reactions with the phosphonium/borata-cyclopropane zwitterion **8**. Treatment with potassium hydride resulted in a clean deprotonation of the phosphonium unit to give the Mes_2P-substituted boratacyclopropane salt **11** [NMR: δ -4.4 (^{31}P), δ -26.8 (^{11}B), δ 1.62, 0.61 ($^{3}J_{PH}$ = 25.4 Hz), 0.18 ($^{3}J_{PH}$ = 10.1 Hz) (^{1}H, -CH-CH_2-)]. Its treatment with benzylbromide gave the zwitterionic benzylphosphonium/ boratacyclopropane product **12** isolated as colorless crystals in

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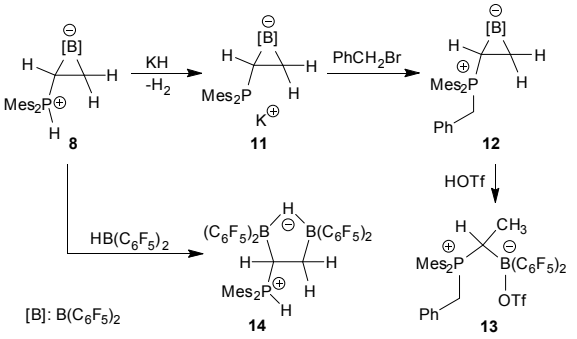
82% yield (see Scheme 2) [NMR: δ 33.7 (^{31}P), δ -23.1 (^{11}B)]. Compound **12** showed an AB ^{1}H NMR type pattern of the diastereotopic benzylic hydrogens adjacent to phosphorus [δ 4.45, 4.22, ($^{2}J_{PH} \approx {}^{2}J_{HH}$ = 13.4 Hz); ^{13}C: δ 39.3 ($^{1}J_{PC}$ = 49.5 Hz)] and the ^{13}C NMR signals of the boratacyclopropane unit at δ 12.1 (CH_2) and 10.4 (CH), respectively.



Scheme 2. Reaction of compound **8**

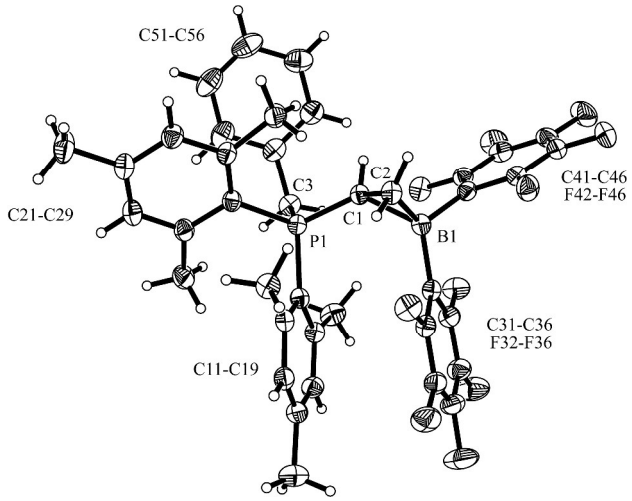


Figure 6. Molecular structure of compound **12** (thermal ellipsoids are shown with 30% probability).

Compound **12** was characterized by X-ray diffraction (see Figure 6). It shows structural features of the boratacyclopropane subunit [B1-C1 1.675(3) Å, B1-C2 1.574(3) Å, C1-C2 1.523(3) Å, angle C1-B1-C2 55.8(1)°] that are very similar to those of the related phosphonium/boratacyclopropane compound **8** (see above). In **12** the P1-C3 linkage of the newly introduced benzyl substituent amounts to 1.845(2) Å.

Compound **12** was also exposed to a dihydrogen atmosphere at elevated temperature. In contrast to the PH^+ containing system **8**, the P-benzyl$^+$ analogue **12** did not undergo ring-opening under comparable conditions, but it was cleanly opened by triflic acid to give **13** (see Scheme 2). The ring opened product **13** was characterized by C,H elemental analysis, by NMR spectroscopy and by X-ray diffraction. The X-ray crystal structure analysis of compound **13** (see Figure 7) showed the presence of the Mes_2P-benzyl moiety [P1-C3 1.840(3) Å] and the newly introduced triflate substituent at boron [B1-O1 1.579(4) Å]. The boratacyclopropane unit of its precursor **12** had been opened by addition of the proton to give a methyl group (C2) attached at the bridging sp^3-carbon atom C1 [C1-C2 1.547(4) Å, B1-C1 1.652(5) Å, P1-C1 1.844(3) Å, angle B1-C1-P1 118.5(2)°]. Overall, the structural parameters of the zwitterionic P-benzyl/B-OTf product **13** are similar to those of the related PH/B-OTf compound **9** (see above).

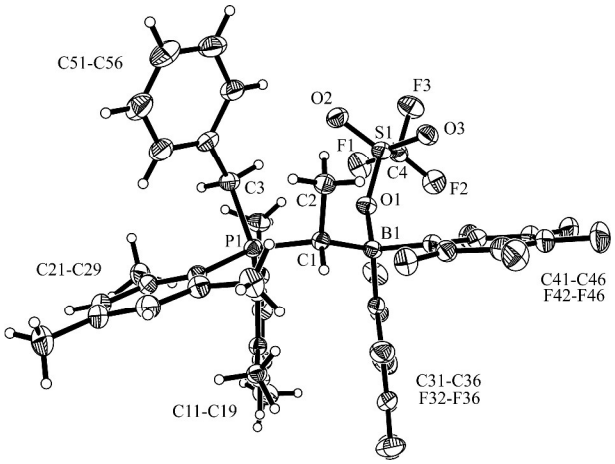


Figure 7. A projection of the molecular structure of the ethylidene-bridged P-benzyl/B-OTf zwitterion **13** (thermal ellipsoids are shown with 30% probability).

In solution, compound **13** is characterized by NMR resonances at δ 5.1 (^{11}B), δ 38.6 (^{31}P) and -75.9 (^{19}F of OSO_2CF_3). The compound shows the ^{19}F NMR signals of a pair of diastereotopic C_6F_5 groups at boron (with hindered rotation on the ^{19}F NMR time scale at low temperature) and similarly the ^{1}H/^{13}C NMR resonances of the diastereotopic mesityl group at phosphorus. The benzylic methylene protons are also diastereotopic as expected, and give rise to a typical pattern at δ 4.94/4.40. The ^{1}H/^{13}C NMR spectra feature of the bridging ethylidene unit occur at δ 3.95 / 25.1 (CH) and δ 1.84 / 17.2 (CH_3), respectively.

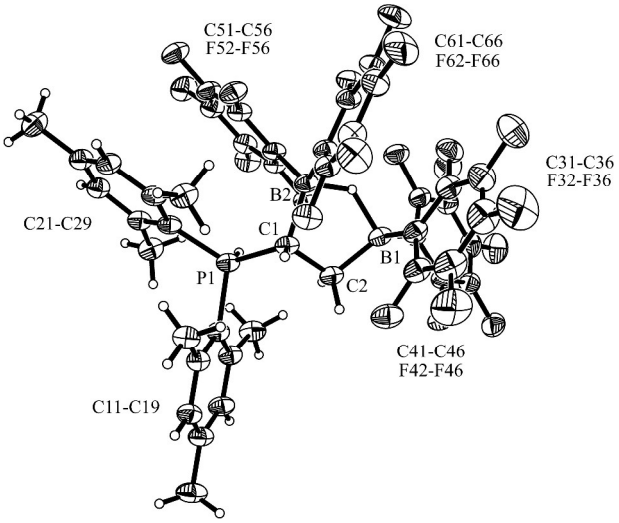


Figure 8. A view of the molecular structure of compound **14** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (deg): C1-

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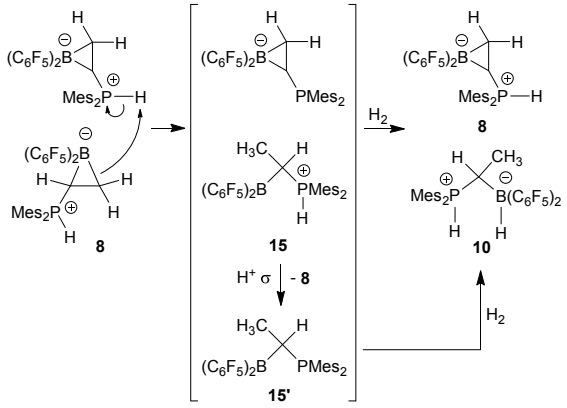
P1 1.816(2), C1-B2 1.664(3), C1-C2 1.558(3), C2-B1 1.602(4), $\Sigma P1^{CCC}$ 347.2, $\Sigma B1^{CCC}$ 347.0, $\Sigma B2^{CCC}$ 349.3, B1-C1-C2-B2 22.9(2).

Compound **8** also underwent rapid opening of the boratacyclopropane ring by treatment with the *Lewis* acid $[HB(C_6F_5)_2]$. Workup gave the zwitterionic product **14** in 65% yield [NMR: δ -2.2 (^{31}P), ^{1}H: δ 2.09 (BH), δ 7.01 ($^{1}J_{PH}$ = 460.8 Hz, PH), δ 4.09, 2.09, 1.87 ($CHCH_2$)]. The product **14** was characterized by X-ray diffraction (see Figure 8). The structure shows a central five-membered [B]-H-[B] containing heterocycle that was formed by opening of the boratacyclopropane ring system. It has the Mes_2PH^+-substituent attached.

From these experimental observations it had become evident that the ring opening of the boratacyclopropane ring was readily achieved by protonolysis. It was, therefore, likely that the phosphonium $[P]H^+$ served as the necessary *Brønsted* acid also in the hydrogenolytic ring-opening reaction. Quantum chemical calculations[15,16] rapidly ruled out any direct reaction of H_2 with a B1-C2 σ-bond or a preceeding intramolecular conversion to the geminal FLP Mes_2P-$CH(CH_3)$-$B(C_6F_5)_2$ (**15'**), although the **8** to **15'** isomerization was calculated to be almost thermoneutral. According to our density functional theory (DFT) analysis the isomerisation of **8** to the (not experimentally observed) geminal FLP **15'** is substantially kinetically hindered ($\Delta G^{\ddagger}_{calc}$ ~ 55 kcal mol^{-1}), even though the subsequent reaction of the FLP **15'** with dihydrogen would be feasible ($\Delta G^{\ddagger}_{calc}$ ~ 17 kcal mol^{-1}) (for details see the Supporting Information). However, we found some indication that the reaction might proceed intermolecularly via a mutual protonation/de-protonation reaction between two species of **8**. This would generate the not directly observed salt **15** which would be an alternative candidate for the heterolytic splitting of the dihydrogen to eventually form the observed phosphonium/ hydridoborate zwitterion **10** (see Scheme 3). Alternatively a further proton transfer might then generate the geminal FLP **15'** which, according to the DFT analysis, would react with dihydrogen to give compound **10**.



Scheme 3. A possible pathway of the formation of compound **10**

Catalytic hydrogenation

The new directly prepared geminal phosphonium/hydridoborate zwitterion, which formally represents the dihydrogen activation product of the non-observed C_1-bridged P/B FLP **15'**, has served as a catalyst in the metal-free hydrogenation of a variety of unsaturated organic substrates (see Table 1). Under the applied standard test condition (90 °C, 50 bar H_2, D_2-dichloromethane solution) complete conversion was achieved upon hydrogenation of a bulky imine to the secondary amine,[4b] of a tetra-substituted enamine to the *tert*-amine,[4a,17] of a silylenolether to the silylated alcohol,[18] and even of a substituted quinoline to the respective tetrahydroquinoline product.[19] The respective products were in each case isolated in reasonable yields (see Table 1 and the Supporting Information).

Table 1. Metal-free catalyzed hydrogenation of a small series of substrates with the $[P]H^+/[B]H^-$ system **10**[a]

	substrate	product	substrate mg (mmol)	**10** mol%	reaction time (h)	conv. (iso.)
1			209 (1.0)	10	36	>99% (86%)
2			215 (1.0)	10	36	>99% (60%)
3			192 (1.0)	10	36	>99% (62%)
4			143 (1.0)	10	36	>99% (70%)

[a] 90 °C, 50 bar H_2, in D_2-dichloromethane solution.

Carbon monoxide reduction

While carbon monoxide reacts readily with trialkyl boranes to give carbon-carbon coupled products,[20] CO is not reduced by [B]-H boranes. Chart 2 shows two striking examples: diborane reacts with carbon monoxide (at elevated pressure and temperature) only to form borane carbonyl [H_3B-CO (**16**)]. This had been described by Schlesinger et al as early as 1937.[21,22] Borane carbonyl (**16**) is a low-boiling liquid (b.p. -64 °C), it rapidly looses CO under specific conditions. We recently reported the related formation of the carbonyl of *Piers'* borane [$(C_6F_5)_2BH{\cdot}CO$ (**17**)], which was even characterized by an X-ray crystal structure analysis.[23]

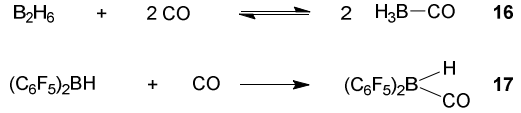


Chart 2. Formation of borane carbonyls

This situation was dramatically changed by applying FLP chemistry. The thermodynamic restriction imposed on the borane CO reduction is lifted at a variety of vicinal P/B FLP templates. As a typical example, compound **18** reacts with CO and $HB(C_6F_5)_2$ to give the product **19**, which is a formylborane stabilized at the P/B template (see Chart 3).[24] This and a variety of related examples have been used to initiate a genuine formylborane derived chemistry.[23] We have assumed that the borane CO reduction may take place by means of the 1,2-P/B

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FLP addition to the borane carbonyl to generate the reactive intermediate **20**, followed by internal borohydride reduction of the activated CO unit.[24]

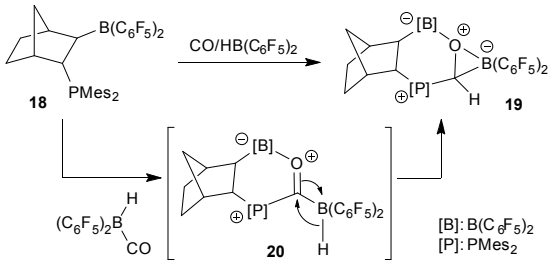
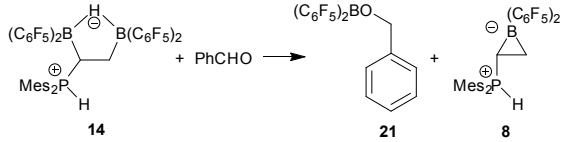


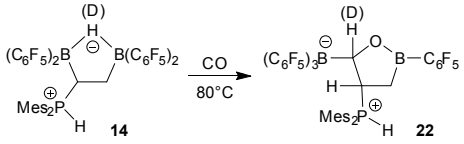
Chart 3. CO reaction at a FLP template

In the course of this study we have now found a closely related example of a CO reduction to the formylborane stage. It utilizes the reducing property of the $HB(C_6F_5)_2$ addition product **14** to the zwitterionic boratacyclopropane **8**. This was first observed when we treated the H-bridged BBP system **14** (see Scheme 4) with benzaldehyde. This gave the reduction product **21** of benzaldehyde and reformed the phosphonium/boratacyclo-propane starting material **8** (see Scheme 4, for details see the Supporting Information). This indicated that the compound **14** might serve as a source of *Piers'* borane under specific conditions.



Scheme 4. Benzaldehyde reaction by compound **14**

This encouraged us to treat compound **14** with carbon monoxide. The reaction was carried out in CH_2Cl_2 at 2.5 bar CO pressure overnight at 80 °C. Workup of the reaction mixture involving column chromatography gave the product **22** in 60% yield (see Scheme 5). Compound **22** was characterized by C,H elemental analysis, by spectroscopy and by X-ray diffraction.



Scheme 5. Reaction of carbon monoxide by compound **14**

The X-ray crystal structure analysis has revealed that carbon monoxide was reduced to the formylborate stage.[25] The newly formed formyl moiety is found C-attached at carbon atom C1 of the framework and O-attached at the ring boron atom B1. In this situation the "formyl" C3-O1 bond is long at 1.473(4) Å. Boron atom B1 has only a single C_6F_5 substituent attached, but the adjacent O1-B1 bond is rather short [1.343(5) Å] indicating some oxygen-boron π interaction. The framework has the $B(C_6F_5)_3$ substituent attached at carbon atom C3 and the remaining $P(H)Mes_2$ group at C1 (see Figure 9).

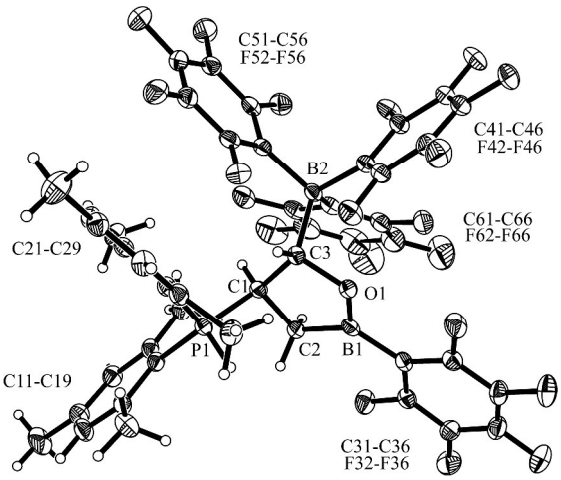
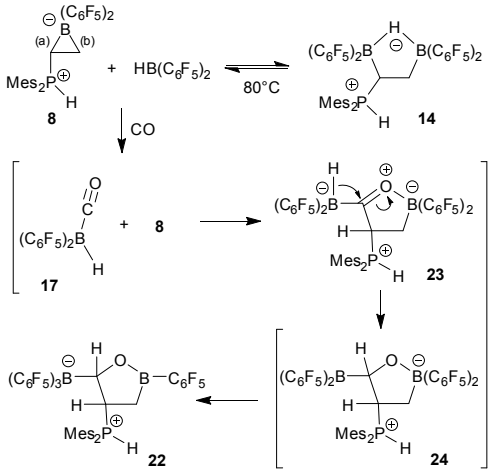


Figure 9. Molecular structure of compound **22** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (deg): C1-P1 1.804(4), C1-C2 1.554(5), C1-C3 1.556(5), C2-B1 1.581(6), B1-O1 1.343(5), C3-O1 1.473(4), B2-C3 1.671(6), B1-O1-C3 112.8(3), P1-C1-C2-B1 -108.6(3), P1-C1-C3-B2 -138.7(3).

In solution, compound **22** shows the $^1H/^{13}C$ resonances of the incorporated formyl moiety at δ 6.09 ($^3J_{PH}$ = 30.3 Hz) / δ 84.2. The ^1H NMR signals of the remaining five-membered heterocyclic framework occur at δ 3.90 (CH), and δ 1.47 / 1.21 (CH_2). Compound **22** exhibits two ^{11}B NMR signals, one of the endocyclic slightly *Lewis* acidic borane (δ 42.7) and one of the pending $B(C_6F_5)_3$ borate unit (δ -12.9) and compound **22** shows the [P]H resonances at δ -5.6 (^{31}P) and δ 6.97 (^1H) ($^1J_{PH}$ = 457 Hz), respectively.



Scheme 6. A possible pathway of the formation of the CO reduction product **22**

The borohydride reduction of CO was additionally confirmed by an experiment using the deuterium labelled $DB(C_6F_5)_2$ reagent. Its reaction with the phosphonium/boratacyclopropane system **8** gave the product **14-D** (see Scheme 5). It was characterized by ^2H NMR spectroscopy and showed the broad $[B]^2H$ resonance at δ 2.1 (the corresponding $^1H/^2H$ NMR spectra are depicted in the Supporting Information section).

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Treatment of **14-D** with CO under the usual condition then gave the formylborane product **22-D** (isolated in 53% yield after column chromatography). The $^{1}H/^{2}H$ NMR spectra revealed selective deuterium incorporation at the formyl group (i.e. -CD-O[B]) shown by the broad ^{2}H NMR at δ 6.3.

We assume a reaction scheme of the formation of the CO reduction product that is related to the formation of the FLP/formylborane product **19** (see Chart 3 and Scheme 6). It may be that reversibility of the formation of **14** from **8** and $HB(C_6F_5)_2$ under the harsh reaction conditions allows for the in situ generation of the borane carbonyl $(C_6F_5)_2B(H)\cdot CO$ (**17**), a compound that we had previously isolated and characterized by X-ray diffraction.[23] This could then add to **8** and have the H[B]-C≡O unit reduced *via* possible intermediates **23**/**24** in a similar fashion as obtained for the FLP-formylborane formation shown in Chart 3.

Conclusions

Our new reaction has made a novel type of active geminal FLP derivatives readily available that cannot be made by the conventional hydroboration route because of its wrong regioselectivity. Our study utilizes the formation of the phosphonium substituted boratacyclopropane moiety by means of a ring-closing rearrangement reaction of the respective alkenylhydridoborate isomer in conjunction with its subsequent hydrogenolytic ring opening reaction. There is evidence that the latter reaction is *Brønsted* acid induced. Our reaction sequence has consequently arrived directly at the FLP-phosphonium/hydridoborate state **10**, which is the formal hydrogen activation product of the respective geminal P/B FLP **15'**. It might actually be that this sensitive P/B *Lewis* base/*Lewis* acid system is involved in the protonolytic ring-opening reaction under dihydrogen. First tests have shown that the system **10** is even stable toward small amounts of water added to its solution in e.g. CH_2Cl_2 (for details see the Supporting Information). The new geminal P/B FLP-H_2 system made available by means of our new synthesis is an active catalyst for the metal-free hydrogenation of a variety of substrates, among them the heterocyclic quinoline system (see Table 1), although it is less active than e.g. the related vicinal P/B FLP system **1** or **18** (see above). However, the system **8** provides a template for the borane reduction of carbon monoxide to the formyl stage. We expect such geminal P/B FLP related system to further enhance the synthetic and catalytic potential of intramolecular frustrated *Lewis* pair chemistry.

Experimental section

Synthesis of compound 5.

The combination of a toluene (2.0 mL) solution of dimesitylethynylphosphane (**4**) (206 mg, 0.70 mmol) with a toluene (2.0 mL) solution of bis(pentafluorophenyl)borane (242 mg, 0.70 mmol) give instantaneously a yellow solution. After stirring the reaction mixture at r.t. for 30 min, it was stored at r.t. overnight to give some deep yellow crystalline material. The solid was collected and dried *in vacuo* to give compound **5** (340 mg, 0.53 mmol, 76%). Single crystals of compound **5** suitable for the X-ray crystal structure analysis were obtained by storing a saturated toluene solution of compound **5** at r.t. for several days. Anal. Calcd. for $C_{32}H_{24}BF_{10}P$: C, 60.03; H, 3.78. Found: C, 59.96; H, 3.70.

Synthesis of compound 6.

Triflic acid (75 mg, 0.50 mmol) was added to a toluene solution (10 mL) of compound **5** (320 mg, 0.50 mmol). The reaction mixture was stirred at r.t. for 30 min to give a light yellow solution. Subsequently all volatiles were removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (2 mL). Then pentane (10 mL) was added to form a suspension. Compound **6** (260 mg, 0.33 mmol, 66%) was obtained as white powder after filtration of the suspension and drying of the residue *in vacuo* overnight. Single crystals of compound **6** suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **6** in CH_2Cl_2 at -30 °C. Anal. Calcd. for $C_{33}H_{25}BF_{13}O_3PS$: C, 50.15; H, 3.19. Found: C, 49.92; H, 3.00.

Synthesis of compound 7.

Excess $Me_2Si(H)Cl$ (0.2 mL, 1.8 mmol) was slowly added to a CH_2Cl_2 (4 mL) solution of compound **6** (320 mg, 0.40 mmol). Then the reaction mixture was stirred at r.t. for 1 h. Subsequently all volatiles were removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (2 mL). Then pentane (10 mL) was added to give a suspension. The solution was removed by cannula to give compound **7** (200 mg, 0.31 mmol, 78%) as white powder which was dried *in vacuo* overnight. Anal. Calcd. for $C_{32}H_{26}BF_{10}P$: C, 59.84; H, 4.08. Found: C, 59.69; H, 3.96.

Synthesis of compound 8.

Heating a solution of compound **7** (200 mg, 0.31 mmol) in toluene (10 mL) at 110 °C for 30 min gave a deep yellow solution. Then all volatiles were removed *in vacuo* and the residue was dissolved in pentane (5 mL). Subsequently the solution was stored at -30 °C overnight to give yellow crystalline material. The solid was collected and dried *in vacuo* overnight to give compound **8** (150 mg, 0.23 mmol, 75%). Single crystals of compound **8** suitable for the X-ray crystal structure analysis were obtained by storing solution of compound **8** in pentane at -30 °C for several days. Anal. Calcd. for $C_{32}H_{26}BF_{10}P$: C, 59.84; H, 4.08. Found: C, 59.51; H, 4.44.

Synthesis of compound 9.

Triflic acid (30 mg, 0.20 mmol) was added to the CH_2Cl_2 (5 mL) solution of compound **8** (128 mg, 0.20 mmol). The color of the yellow solution disappeared immediately. After stirring the reaction mixture at r.t. for another 10 min, all volatiles were removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (1 mL) and then pentane (5 mL) was added. After storing this solution at -30 °C overnight, some colorless solid was obtained. The solid was collected and dried *in vacuo* overnight to give

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compound **9** (120 mg, 0.15 mmol, 75%). Single crystals of **9** suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **9** in CH_2Cl_2 at -30 °C. Anal. Calcd. for $C_{33}H_{27}BF_{13}O_3PS$: C, 50.02; H, 3.43. Found: C, 49.91; H, 3.43.

Synthesis of compound 10.

Excess $Me_2Si(H)Cl$ (0.1 mL, 0.90 mmol) was slowly added to a CH_2Cl_2 (2 mL) solution of compound **9** (125 mg, 0.16 mmol). Then the reaction mixture was stirred at 90 °C for 0.5 h. Subsequently all volatiles were removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (1 mL). Then pentane (5 mL) was added. The obtained solution was stored at -30 °C overnight to give crystalline material. The solid was collected and dried *in vacuo* overnight to give compound **10** (91 mg, 0.14 mmol, 88%).

Synthesis of compound 11.

KH (16 mg, 0.40 mmol) was added to the THF solution (4 mL) of compound **8** (200 mg, 0.31 mmol). The reaction mixture was stirred at r.t. for 0.5 h (some gas bubbles were observed during the reaction). Then all volatiles were removed *in vacuo* and the residue was dissolved in CH_2Cl_2/pentane (1 mL/5 mL). Subsequently the solution was stored at -30 °C overnight to give a colorless crystalline material. The solid was collected and dried *in vacuo* for 1 h to give compound **11** with coordinating ¼ THF (140 mg, ≈ 0.2 mmol, ≈ 50 %).

Synthesis of compound 12.

Benzyl bromide (50 mg, 0.29 mmol) was added to a THF solution (5 mL) of compound **11** (200 mg, ≈ 0.28 mmol) to give a suspension immediately. The suspension was stirred at r.t. for 10 min. Then the solid was filtrated off. All volatiles of the solution were removed *in vacuo* and the resulting residue was dissolved in CH_2Cl_2/pentane (1 mL/5 mL). Subsequently the solution was stored at -30 °C overnight to give a colorless crystalline material. The solid were collected and dried *in vacuo* overnight to give compound **12** (160 mg, 0.23 mmol, 82%). Single crystals of compound 12 suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a CH_2Cl_2 solution of compound **12** at -30 °C. Anal. Calcd. for $C_{39}H_{32}BF_{10}P$: C, 63.95; H, 4.40. Found: C, 63.45; H, 4.50.

Synthesis of compound 13.

Triflic acid (30 mg, 0.20 mmol) was added to the CH_2Cl_2 (4 mL) solution of compound **12** (150 mg, 0.20 mmol) to give a colorless solution. The solution was stirred at r.t. for 10 min. Then all volatiles were removed *in vacuo* and pentane (5 mL) was added to the residue to give a suspension. Subsequently the formed solid was collected and dried overnight in *vacuo* to give compound **13** (130 mg, 0.15 mmol, 75%). Crystals of compound **13** suitable for the X-ray single crystal structure analysis were obtained by slow diffusion of pentane to a CH_2Cl_2 solution of compound **13** at -30 °C. Anal. Calcd. for $C_{40}H_{33}BF_{13}PS$: C, 54.44; H, 3.77. Found: C, 54.69; H, 3.56.

Synthesis of compound 14.

Mixing of compound **8** (200 mg, 0.31 mmol) and $HB(C_6F_5)_2$ (107 mg, 0.31 mmol) in CH_2Cl_2 (10 mL) gave a suspension. The reaction mixture was stirred at r.t. for another 1h. Then the solid was collected and dried *in vacuo* overnight to give compound **14** (200 mg, 0.20 mmol, 65%). Single crystals of compound **14** suitable for the X-ray single crystal structure analysis were obtained by storing a saturated CH_2Cl_2 solution of compound **14** at r.t. for several days. Anal. Calcd. for $C_{44}H_{27}B_2F_{20}P$: C, 53.48; H, 2.75. Found: C, 53.83; H, 2.38.

Synthesis of compound 22.

Compound **13** (300 mg, 0.30 mmol) was dissolved in CH_2Cl_2 (10 mL). Then the solution was degassed and purged with CO gas (2.5 bar). After heating the reaction mixture at 80 °C overnight, all volatiles were removed *in vacuo* at rt and the remaining residue was purified by column chromatography [silica gel, CH_2Cl_2] to give compound **22** (183 mg, 0.18 mmol, 60%). Single crystals of compound **22** suitable for the X-ray single crystal structure analysis were obtained by storing a saturated CH_2Cl_2 solution of compound **22** at r.t. for several days. Anal. Calcd. for $C_{45}H_{27}B_2F_{20}OP$ (1016.26 g/mol): C, 53.18; H, 2.68. Found: C, 53.06; H, 2.77.

Compound 10 catalyzed hydrogenation reaction.

General procedure: compound **10** (0.1 mmol) and the respective substrate were mixed in CD_2Cl_2 (2 mL) using a special ampule[4a] (10 mL) with magnetic stirrer. Subsequently the ampule was put into an autoclave and H_2 gas (50 bar) was applied. Then the reaction mixture was stirred at 90 °C for 36 h. The obtained reaction mixture was directly characterized by ^1H NMR spectroscopy. The conversion was estimated by integration of suitable ^1H NMR signals.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Details of the experiments, characterization of all compounds and crystal structure data as CIF files (CCDC numbers are 1034881 to 1034888 and 1045775). See DOI: 10.1039/b000000x/

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