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Alkenylborane-Derived Frustrated Lewis Pairs: Metal-Free Catalytic Hydrogenation Reactions of Electron-Deficient Alkenes

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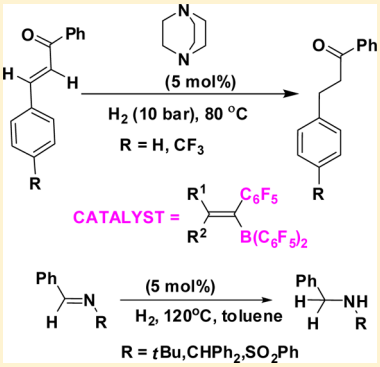
Supporting Information

ABSTRACT: A series of alkenylboranes were prepared by 1,1-carboboration routes and used as Lewis acid components for the generation of frustrated Lewis pairs (FLPs). The reactions of 1-alkynes with $B(C_6F_5)_3$ gave the $RCH{=}C(C_6F_5)B(C_6F_5)_2$ systems **4a** (R = *n*-C_3H_7), **4b** (R = *n*-C_4H_9), **4c** (R = Ph), and **4d** (R = *t*-C_4H_9), respectively. The alkenylborane/tBu_3P FLPs derived from compounds **4a**–**d** reacted rapidly with dihydrogen (2.5 bar) at ambient temperature. The bulky system **4d** left the C=C double bond of the alkenylborane unsaturated and gave the dihydrogen cleavage product $[tBu_3PH][tBuCH{=}C(C_6F_5)BH(C_6F_5)_2]$ (**10d**). In contrast, the less bulky systems **4a**/tBu_3P and **4b**/tBu_3P split dihydrogen under these conditions and had their C=C double bonds cleanly reduced to yield the corresponding 1-pentafluorophenylalkyl hydridoborate salts $[tBu_3PH][RCH_2CH(C_6F_5)BH(C_6F_5)_2]$ **9a** (R = *n*-C_3H_7) and **9b** (R = *n*-C_4H_9), respectively. The **4c**/tBu_3P FLP gave a mixture of both product types (**9c**/**10c**). 1,1-Carboboration of symmetrical internal alkynes gave the alkenylboranes $R_2C{=}C(C_6F_5)B(C_6F_5)_2$ **4e** (R = C_2H_5), **4f** (R = *n*-C_3H_7), **4g** (R = Ph), and **4h** (R = *p*-MeC_6H_4), respectively. The **4e**–**h**/tBu_3P FLPs cleaved dihydrogen under mild conditions but retained their C=C double bonds to give the respective $[tBu_3PH][R_2C{=}C(C_6F_5)BH(C_6F_5)_2]$ products (**10e**–**h**). Selected examples of these alkenylboranes undergo FLP reactions acting as catalysts for the hydrogenation of imines. Perhaps most remarkably, some of these alkenylboranes retain the C=C double bonds under FLP/H_2 reaction conditions and heterolytically split dihydrogen in the presence of the Lewis base DABCO and catalyze the hydrogenation of the electron-poor C=C double bonds of diaryl-substituted enones.

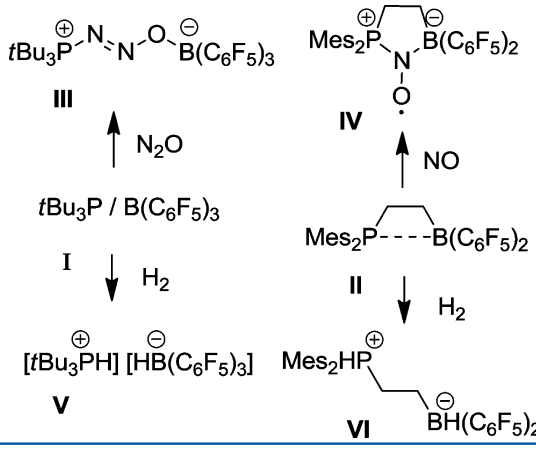


INTRODUCTION

Frustrated Lewis pair (FLP) chemistry has seen numerous advances in recent years, and the interest in and impact of the field continue to grow.[1] The inter- or intramolecular combination of sterically congested strong Lewis acids[2] and Lewis bases has allowed for the observation of a variety of unusual synergistic reactions with a number of small molecules. To date, most, but not all,[3] Lewis acids employed have been boron-based. On the other hand, a broader selection of phosphorus-,[2a,4] nitrogen-,[4o,5] or even carbon-based[6] Lewis bases have been employed. The inter- and intramolecular FLPs typified by systems I and II (Chart 1)[7] were shown to react with alkenes[8] or alkynes,[8c,9] conjugated dienes, diynes, and enynes,[9c,10] and a great variety of carbonyl compounds,[3f,11] including carbon dioxide.[12] Moreover, system I was found to bind N_2O,[13] while the intramolecular system II captures NO.[14]

Most remarkable is the ability of many FLPs to react with dihydrogen[7a,15] to effect heterolytic cleavage, affording the respective phosphonium hydridoborate salt (V from I) or the zwitterion (VI from II, Chart 1). Even more surprisingly, a number of such systems may serve as metal-free catalysts for the hydrogenation of some organic substrates.[1a,f,4f,o,5l,16] To date, a wide variety of systems able to heterolytically cleave dihydrogen have been utilized to catalytically hydrogenate imines, dimines,[1a]

Chart 1



and *N*-heterocycles.[1a,4e,n,o,5l−n,17] Moreover, reduction of electron-rich alkenes such as enamines, conjugated dienamines and even silyl enol ethers has been reported.[18] Most recently Stephan and co-workers have reported the stoichiometric reduction of

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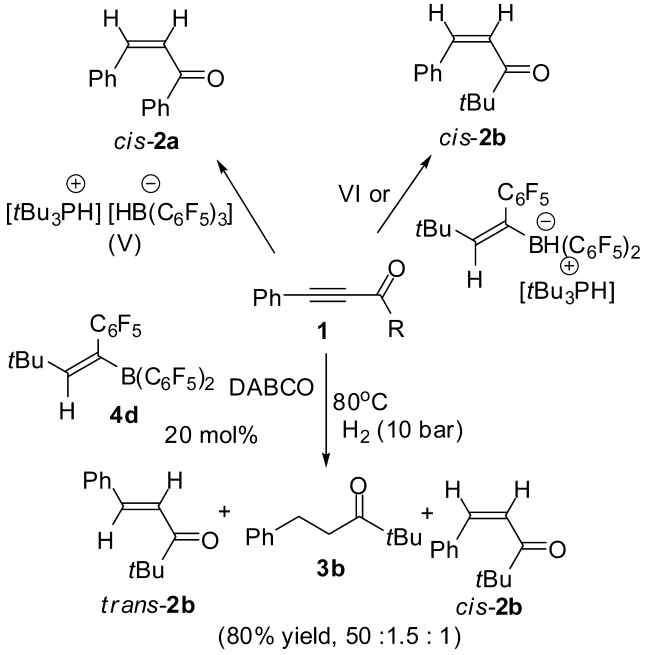
aniline derivatives to the corresponding cyclohexylamines.[19] For all of these electron-rich substrates, the reductions are thought to proceed *via* initial proton transfer to generate an activated substrate (i.e., iminium ions or analogues) followed by hydride delivery from the borohydride.

Although the field of the FLPs is quite young, metal-free catalyzed hydrogenation of these electron-rich substrates is already becoming established. In contrast, both the stoichiometric and catalytic reduction chemistry of synthetically important electron-poor conjugated enones or ynones and related organic substances by FLP/H_2 systems is still in its infancy. Indeed, only a few examples of such reductions have been described. For example, Soós et al.[5g] have described the catalytic hydrogenation of the α,β-unsaturated terpenoid ketone carvone by the mesityl-$B(C_6F_5)_2$/DABCO frustrated Lewis pair. Erker and co-workers recently reported[20] that both the H_2-activated forms (Chart 1, V and VI) of the FLPs I and II, respectively, were able to stoichiometrically hydrogenate the ynones **1a** (R = Ph) and **1b** (R = *t*Bu) to the corresponding *cis*-enones (*cis*-**2a**, **2b**) (Chart 2).

Chart 2. Hydrogenation of the Ynones to the Corresponding *cis*-Enones



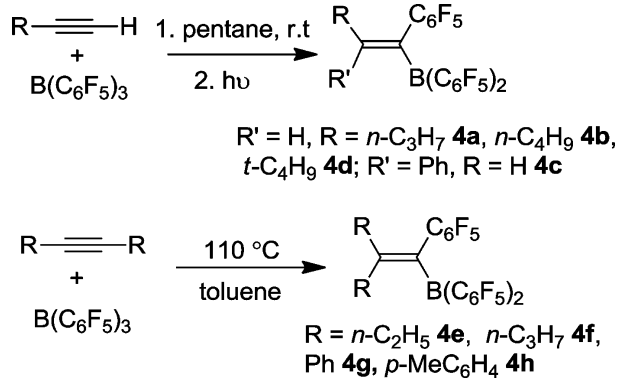
Since it is likely that the FLP/H_2 enone and ynone reactions proceed by hydride addition followed by proton transfer, a slightly less Lewis acidic borane that yields a more hydridic borate should prove to be advantageous. Indeed we have communicated that an alkenylborane (**4d**), derived from a 1,1-carboboration reaction,[21] is a Lewis acid[20] that in combination with the Lewis base tBu_3P and dihydrogen cleanly effects the stoichiometric *cis*-reduction of ynones. The use of 1,4-diazabicyclo[2.2.2]octane (DABCO) as the Lewis base required slightly more forcing conditions to hydrogenate the ynone **1b**, although this was achieved catalytically (Chart 2).

In this paper, we report the use of such bulky alkenylboranes for the hydrogenation reactions of α,β-unsaturated carbonyl compounds. In addition, as these alkenylboranes are themselves electron-poor olefins, the potential for "self" C=C double-bond hydrogenation under our typical reaction conditions was investigated. Herein, we report that selected examples of such bulky alkenylborane systems are active catalysts for the hydrogenation of imines and a few conjugated enone model substrates. These results provide a broader scope of substrates where FLP hydrogenations are useful. Moreover, these data provide insight into the structure−activity relationship of boranes in such metal-free hydrogenations.

RESULTS AND DISCUSSION

Synthesis of Alkenylboranes. It has been previously communicated that alkenylboranes are accessible from the reaction of $B(C_6F_5)_3$ with alkynes.[8c,9a−f,22] The profound ability of $B(C_6F_5)_3$ to undergo a rapid 1,1-carboboration reaction with many terminal alkynes affords a series of alkenylboranes of formulas $RCH{=}C(C_6F_5)B(C_6F_5)_2$. Mechanistically, such reactions are thought to proceed by borane interaction with the alkyne, prompting a 1,2-hydrogen migration along the alkyne carbon framework and concomitant 1,2-C_6F_5 shift from boron to the former terminal alkynyl carbon atom (C1), yielding the alkenylborane. Initially, the 1,1-carboboration sequence is not stereoselective, giving a mixture of *Z*- and *E*-alkenylborane isomers. Subsequent photolysis (HPK 125, Pyrex) for many systems results in efficient *E*- to *Z*-alkenylborane isomerization, allowing *Z*-alkenylboranes to be obtained in high yields. A typical example is the preparation of *Z*-$CH_3(CH_2)_2CH{=}C(C_6F_5)B(C_6F_5)_2$ (**4a**). This species is obtained as a white solid in 90% yield from a one-pot/two-step process of 1,1-carboboration and photolysis (Scheme 1). In an analogous manner, the *Z*-alkenylboranes **4b**

Scheme 1. Synthesis of Alkenylboranes



(R = *n*-butyl), **4c** (R = Ph; *E*/*Z* = 30:1 mixture), and **4d** (R = *t*Bu) were prepared.

A second series of alkenylboranes (**4e−h**) were derived from the analogous 1,1-carboboration reactions employing internal alkynes. In these cases elevated temperatures were required to yield the respective tetra-substituted alkenes bearing a geminal pair of R groups at one end and a $C_6F_5/B(C_6F_5)_2$ pair of substituents at the other. Treatment of the respective symmetrically substituted alkynes with $B(C_6F_5)_3$ at 110 °C in toluene consequently gave the alkenylboranes **4e−h** in good yield (Scheme 1). These 1,1-carboborations are further supported by the crystallographic characterization of **4e** (Figure 1).

Reactions of Alkenylboranes with Phosphanes. Efforts to generate FLPs from alkenylboranes required combination with sterically hindered phosphanes. In some cases these mixtures were not inert. For example, a 1:1 mixture of the

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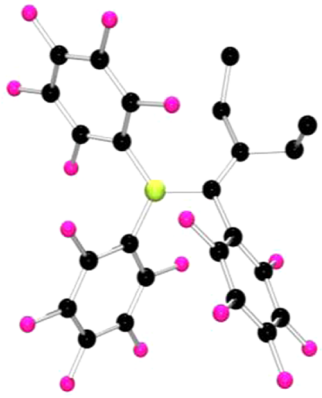
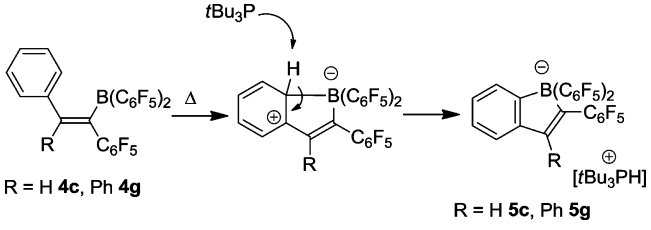


Figure 1. POV-ray depiction of the alkenylborane **4e**. C: black, B: yellow-green, F: pink. Hydrogen atoms are not shown.

phenyl-substituted alkenylboranes **4c** and **4g** and tBu$_3$P react upon heating for 24 h at 80 °C in toluene to form the salt **5g** (Scheme 2). An X-ray diffraction study of **5g** (Figure 2)

Scheme 2. Formation of 5c and 5g



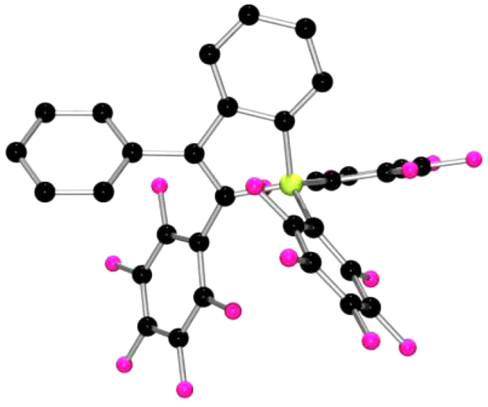
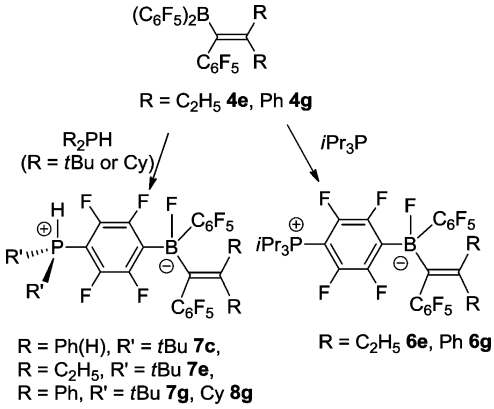


Figure 2. POV-ray depiction of the anion of **5g**. C: black, B: yellow-green, F: pink, Hydrogen atoms are not shown.

identified it as the product of an internal electrophilic aromatic substitution. In this case the borane is bound to the *cis*-oriented vicinal phenyl substituent, while the phosphane is protonated, affording the boracycle **5g**. The product **5c** was similarly obtained from the *E* isomer of **4c** alkenylborane and tBu$_3$P at elevated temperatures. The compound **5c** was also characterized by X-ray diffraction (see Supporting Information).

In contrast, the analogous reactions of the alkenylboranes **4c**, **4e**, and **4g** with iPr$_3$P, tBu$_2$PH, or Cy$_2$PH, resulted in *para*-attack on a C$_6$F$_5$ group on boron, resulting in a nucleophilic aromatic substitution reaction.[23] The fluoride is trapped by the boron electrophile, affording the zwitterionic salts R$_2$C═C(C$_6$F$_5$)BF(C$_6$F$_5$)(C$_6$F$_4$PiPr$_3$) (R = Et **6e**, Ph **6g**), R$_2$C═C(C$_6$F$_5$)BF(C$_6$F$_5$)(C$_6$F$_4$PtBu$_2$H) (R$_2$ = Ph(H) **7c**; R = Et **7e**, Ph **7g**), and

Scheme 3. Formation of 6e, 6g, 7c, 7e, 7g, and 8g



Ph$_2$C═C(C$_6$F$_5$)BF(C$_6$F$_5$)(C$_6$F$_4$PCy$_2$H) (**8g**) (Scheme 3). In some cases these reactions were accelerated at elevated temperatures of 50−70 °C. These reactions are typified by the appearance of the diagnostic broad ^{19}F NMR signals at ca. −180 ppm, reflecting the presence of a BF fragment in addition to the resonances attributable to the C$_6$F$_4$ group. Three of the products (**6e**, **6g**, and **7g**) were characterized by X-ray diffraction (**6g**: Figure 3; **6e**, **7g**: see Supporting Information).

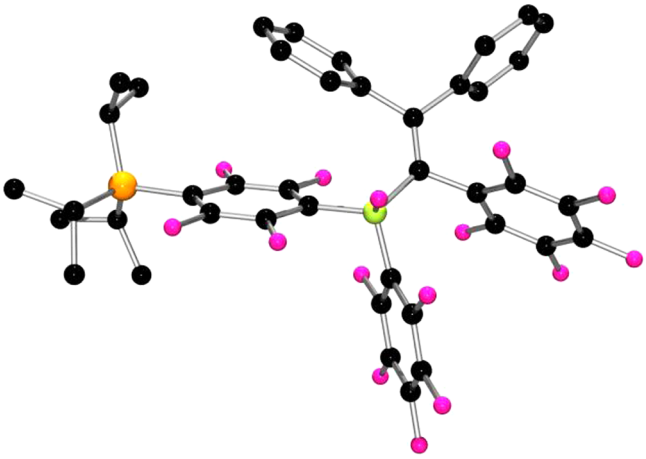


Figure 3. POV-ray depiction of the zwitterion **6g**. C: black, B: yellow-green, F: pink, P: orange. Hydrogen atoms are not shown.

Reactions of Alkenylborane-Derived FLPs with H$_2$. Despite the thermally driven formation of the boracycles **5** and zwitterions **6**−**8**, the alkenylboranes **4** form FLPs with bulky phosphanes that are amenable to heterolytic H−H bond cleavage. For example, the combination of dihydrogen (2.5 bar), the *n*-propyl-substituted alkenylborane **4a**, and tBu$_3$P in toluene overnight at ambient temperature results in the formation of the new species **9a**, which has taken up two equivalents of dihydrogen (Scheme 4). In the ^{1}H and ^{13}C NMR spectra of compound **9a**, signals at 3.23 (^{1}H) and 30.3 (br, ^{13}C) ppm, respectively, are consistent with the presence of a newly formed saturated C$_5$ chain at boron (BCH). The [B]H unit results in a ^{11}B NMR doublet at δ −19.3 ($^1J_{BH} \approx 90$ Hz), and the ^{31}P NMR [P]H doublet resonance is seen at δ 59.2 ($^1J_{PH} \approx 433$ Hz). Compound **9a** was characterized by X-ray diffraction (Figure 4), revealing the hydrogenation of the olefinic fragment of **4a** with the formation of the phosphonium borate [tBu$_3$PH] [CH$_3$(CH$_2$)$_2$-CH$_2$CH(C$_6$F$_5$)BH(C$_6$F$_5$)$_2$], **9a**. The formerly olefinic bond has

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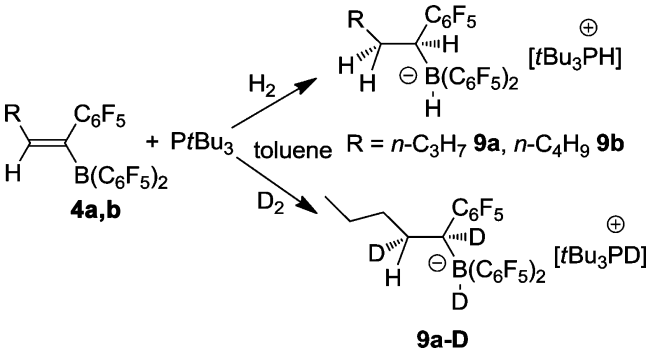
Scheme 4. Formation of 9a, 9b, and 9a-D



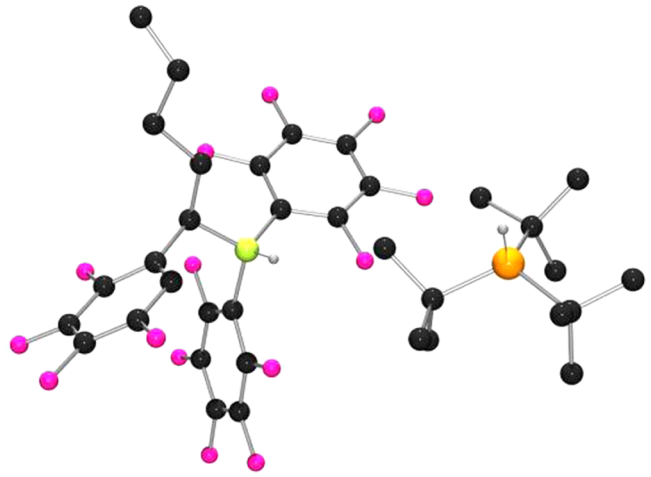


Figure 4. POV-ray depiction of the zwitterion **9a**. C: black, B: yellow-green, F: pink, H: gray, P: orange. Hydrogen atoms except for BH and PH are not shown.

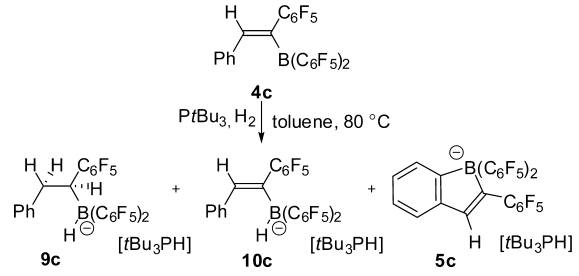
been reduced, as evidenced by the C−C bond length of 1.512(8) Å, while the corresponding B−C bond distance is 1.633(8) Å. The boron center is tetra-coordinated with the C−B1−C angles summing to 334.4°, while the geometry of the [tBu$_3$PH] cation is unexceptional.

The analogous experiment was carried out with dideuterium, **4a**, and tBu$_3$P at 25 °C to afford **9a-D**. The ^{2}H NMR spectrum displayed a pair of [sp^3-C]-D resonances resulting from the saturated hydrocarbon chain at δ 3.19 ([B]CD) and δ 1.85/1.62 (−CDH) as well as a broad [B]D deuteride resonance at δ 2.98 and a [P]D doublet at δ 5.23 ($^1J_{PD} \approx 66$ Hz).[24] The corresponding reaction of the alkenylborane **4b** with tBu$_3$P and H$_2$ yielded the related saturated product **9b** in ca. 80% yield as a white solid (Scheme 4).

The FLP derived from the phenyl-substituted alkenylborane **4c** (*E*:*Z* 30:1) and tBu$_3$P was less reactive. At 25 °C in pentane, clean heterolytic cleavage of dihydrogen was achieved to yield ca. 85% of **10c** after 3 days. In the absence of light, the hydrogenated product was exclusively the *E* isomer, while an uncovered reaction vessel yielded a ca. 1:1 isomeric *E*:*Z* mixture. Under more forcing conditions, i.e., heating under H$_2$ at 80 °C for 15 h in toluene, a 9:2:4 mixture of salts **9c**:**10c**:**5c** resulted (Scheme 5). Nonetheless compound **9c** has been successfully isolated and fully characterized, including an X-ray structure confirming the nature of the salt (Figure 5).

These data are consistent with a trend of decreased reactivity with increasing steric bulk of the substituents at the end of the alkenylborane C=C double bond. This is also seen for the *tert*-

Scheme 5. Formation of 9c and 10c



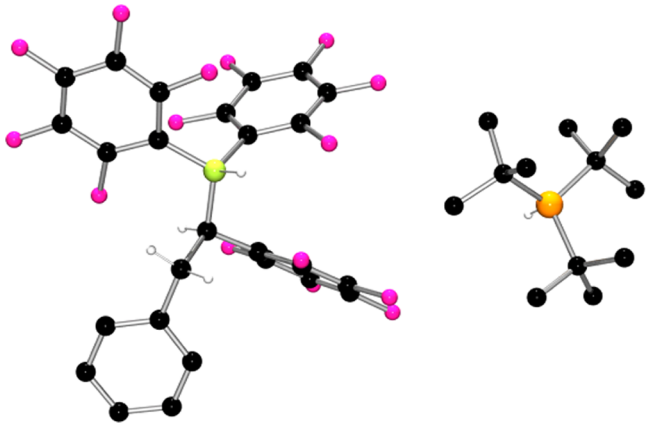
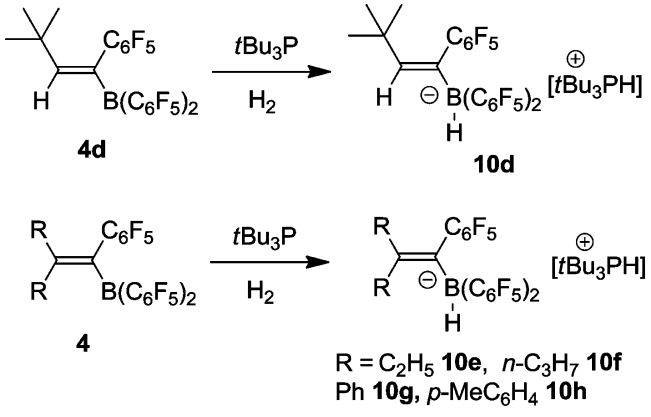


Figure 5. POV-ray depiction of the salt **9c**. C: black, B: yellow-green, F: pink, H: gray, P: orange. Only the PH, BH, CH, and CH$_2$ hydrogen atoms are shown.

butyl-substituted alkenylborane **4d**, as treatment with tBu$_3$P and dihydrogen affords the phosphonium hydridoborate salt **10d**, in which the olefinic moiety is not hydrogenated (Scheme 6). In

Scheme 6. Formation of 10d−h



solution, compound **10d** shows the typical ^{1}H NMR features of the intact alkenyl substituent at boron (^{1}H: δ 5.40), the broad 1:1:1:1 intensity quartet at δ 3.00 ($^1J_{BH} \approx 90$ Hz), and a doublet at δ 5.17 ($^1J_{PH} \approx 431$ Hz) attributable to [B]H and [P]H fragments. The corresponding alkenyl-^{13}C, ^{11}B, and ^{31}P NMR signals were observed at δ 143.1, −18.8, and 59.6, respectively. This phosphonium-alkenylhydridoborate salt **10d** was also characterized by X-ray diffraction (Figure 6). It features the intact C1−C2 (1.329(5) Å) and C=C double bond at boron (C1−B1 1.633(5) Å, B1−C1−C2 124.1(3)°). The trisubstituted alkene also has the *tert*-butyl substituent at C2 (C1−C2−C3 135.0(3)°)

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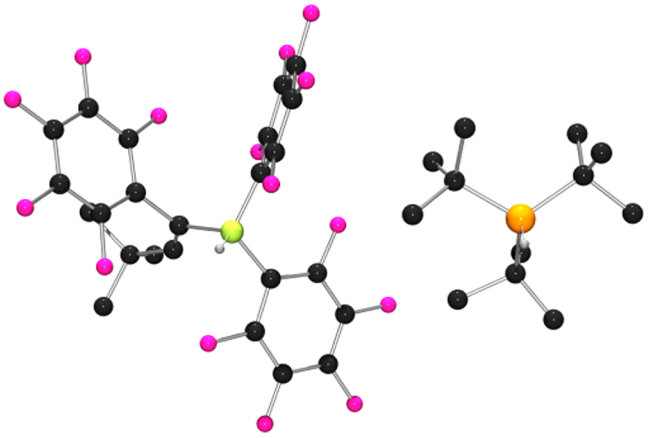


Figure 6. POV-ray depiction of the salt **10d**. C: black, B: yellow-green, F: pink, H: gray, P: orange. Only the PH and BH hydrogen atoms are shown.

and the $-C_6F_5$ group in a *Z*-orientation. The plane of the pentafluorophenyl group at C1 is rotated markedly from the olefinic substituent plane (θ C2−C1−C51−C52 96.2(4)°). The boron and phosphorus atoms are typically pseudotetrahedral, with the C−B−C and C−P−C bonding angles summing to 336.8° and 342.8°, respectively.

Following the same trend, the alkenylboranes **4e−h**, containing tetra-substituted C═C double bonds, react similarly with dihydrogen in the presence of tBu$_3$P. In all these cases the tetra-substituted C═C double bonds of the boron Lewis acid compounds remained intact, but the P/B pairs effected rapid heterolytic dihydrogen splitting to afford the phosphonium-hydridoborate salts **10e** (R = C_2H_5), **10f** (R = *n*-C_3H_7), **10g** (R = Ph), and **10h** (R = *p*-MeC_6H_4) in good yields (Scheme 6). Compounds **10e−g** were characterized by X-ray diffraction (**10e**: Figure 7; **10f**, **10g**: see the Supporting Information). The

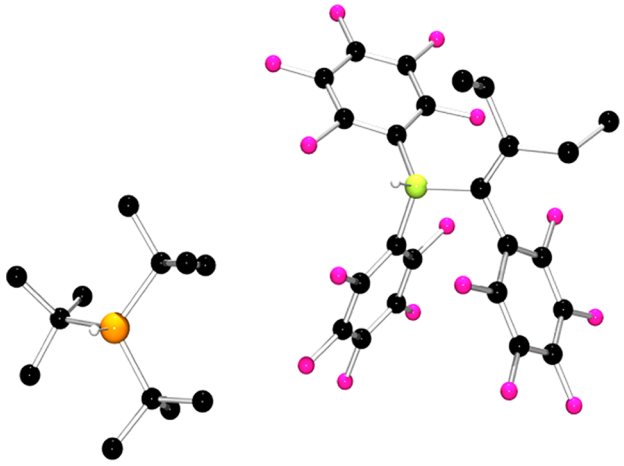
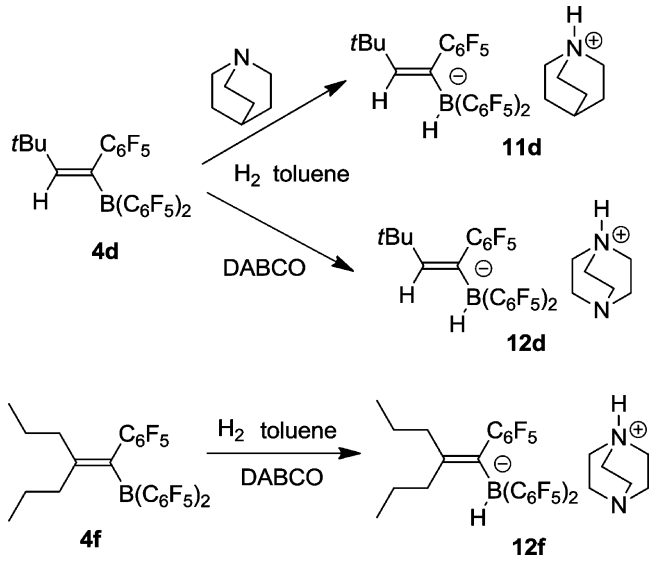


Figure 7. POV-ray depiction of the salt **10e**. C: black, B: yellow-green, F: pink, H: gray, P: orange. Only the PH and BH hydrogen atoms are shown.

aryl-substituted alkenylborane (**4g** and **4h**)/tBu$_3$P FLPs were found to be less reactive toward dihydrogen compared to alkyl-substituted alkenylboranes/tBu$_3$P FLPs toward dihydrogen splitting under similar reaction conditions. Thus, more forcing conditions (60 bar H_2 and 80 °C) were used to generate the aryl-substituted phosphonium alkenylhydridoborate salts, **10g** and **10h**, respectively (Scheme 6).

Analogous reactions employing nitrogen-based Lewis bases and dihydrogen were also briefly investigated. To this end, compound **4d** and either 1-azabicylo[2.2.2]octane (quinuclidine) or DABCO were combined under 60 bar of dihydrogen at room temperature. This led to the rapid formation of the respective ammonium hydridoborate salts **11d** and **12d** (Scheme 7).

Scheme 7. Synthesis of 11d, 12d, and 12f



Compound **11d** was characterized by X-ray diffraction (see the Supporting Information). In a similar fashion, the FLP derived from the tetra-substituted alkenylborane **4f** and the DABCO Lewis base with dihydrogen under identical conditions gave the corresponding ammonium hydridoborate salt **12f** (Scheme 7).

Catalytic Hydrogenation of Imines. The ability of electron-deficient boranes to effect catalytic hydrogenations of imines has been previously demonstrated. This results in part from the ability of the Lewis acid and substrate imine to effect heterolytic cleavage of dihydrogen. As the alkenylboranes described herein have been shown to be sufficiently electrophilic to participate in such activation of dihydrogen, several of these alkenylboranes were evaluated in catalytic hydrogenation of imines. Compounds **4c**, **4e**, and **4g** were employed in the catalytic hydrogenations of several imine substrates (Table 1) using a catalyst loading of 5 mol % at 120 °C. Reactions were performed at dihydrogen pressures of 5 and 110 bar. In the case of the prototypical sterically encumbered imine, Ph(H)C═NtBu, **4c** and **4e** proved to be effective catalysts, each resulting in quantitative hydrogenations after 12 h. In contrast, species **4g** was ineffective, resulting in only 11% yield of the hydrogenated amine after 24 h at 110 bar of dihydrogen at 120 °C. Using the sterically bulky substrate Ph(H)C═NCHPh$_2$, of the three catalysts only **4e** was effective and only under high pressure conditions, while for the substrate Ph(H)C═NSO_2Ph, the alkenylboranes were ineffective at low pressure and displayed marginal activity even at higher dihydrogen pressure. Collectively, these data infer that increased steric congestion in either these hydridoborate anions or substrates is problematic for hydride delivery to transient iminium cations. Moreover, reduced Lewis basicity at the nitrogen centers does not result in efficient hydrogen activation.

Catalytic Hydrogenation of Conjugated Enones. It had also been shown that a conjugated ynone can be slowly

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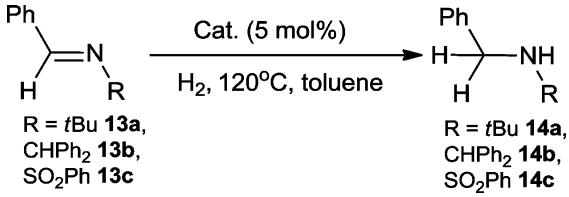
Table 1. Imine Hydrogenations[a]



R = *t*Bu **13a**, $CHPh_2$ **13b**, SO_2Ph **13c**

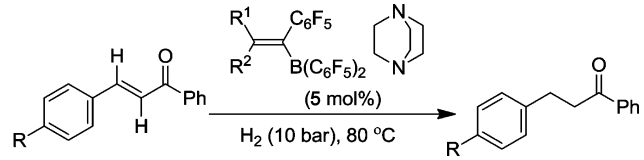
R = *t*Bu **14a**, $CHPh_2$ **14b**, SO_2Ph **14c**

imine substrate	cat.	*T* (h)	yield (%) (5 bar)	yield (%) (110 bar)
13a	**4c**	12	>99	>99
13a	**4e**	12	>99	>99
13a	**4g**	24	6	11
13b	**4c**	12	19	35
13b	**4e**	12	20	>99
13b	**4g**	24	0	trace
13c	**4c**	24	0	2
13c	**4e**	24	trace	11
13c	**4g**	24	0	18

[a]Performed employing 5 mol % catalyst at 120 °C.

hydrogenated to the saturated ketone by a catalytic amount of the FLP derived from the alkenylborane **4d** and the amine Lewis base DABCO.[20] Herein, the hydrogenation of a small series of enones with sufficiently bulky substituents at both the ketone and alkene ends was studied (Table 2). Initially 5 mol % of the

Table 2. Catalytic Enone Hydrogenations[a]



R = H **15a**, CF_3 **15b**

R = H **16a**, CF_3 **16b**

enone	alkenylborane	conversion (%)[b]	yield (%)
15a	**4a**	2	
15a	**4d**	81	74
15a	**4f**	50	47
15a[c]	**4f**	>99	92
15a	**4h**	trace	
15b	**4d**	>99	91
15b	**4f**	40	34

[a]5 mol % FLP catalyst, 10 bar of H_2, 80 °C, 48 h in d_6-benzene. [b]Determined by ^{1}H NMR spectroscopy. [c]40 bar of H_2.

respective FLP was employed, and the reactions were carried out at 10 bar dihydrogen pressure for 48 h at 80 °C in benzene-d_6. The catalyst **4d**/DABCO was the most effective catalyst of the series. Under our standard conditions, monitoring by NMR spectroscopy revealed 81% conversion of the enone **15a** to the saturated ketone **16a**. On the other hand, the tetra-substituted alkenylborane **4f** gave a slightly inferior catalyst under the same conditions; however, it led to a quantitative conversion of **15a** to **16a** under slightly more forcing conditions (40 bar H_2). Both the more bulky diaryl-substituted alkenylborane **4h** and the much less sterically congested system **4a** made very poor catalysts. In the latter case, the observed reactivity of **4a** with dihydrogen might be responsible for this unfavorable behavior (see above). The introduction of a strongly electron-withdrawing substituent at the distal aryl ring of the enone **15b** accelerated the FLP hydrogenation of the electron-poor C═C double bond with the **4d**/DABCO catalyst. In contrast, the respective *p*-methoxy derivative **15c** was not reduced under these conditions. These results indicate that hydride transfer from the *in situ* formed alkenylhydridoborate anion derived from the alkenylborane under FLP conditions might be the decisive factor in achieving the requisite reactivity for selective hydrogenation of electron-deficient olefins. It seems that the alkenylboranes used here display the appropriate balance between sufficient Lewis acidity and steric bulk to allow for dihydrogen activation by the respective FLPs. At the same time they feature sufficiently reduced electrophilicity to make the resulting hydridoborate nucleophilic enough to attack at the Michael position of the enone. Whether this process is Lewis or Brønsted acid catalyzed remains an open question; also the specific role of the DABCO Lewis base or its conjugate DABCO-H^+ Brønsted acid remains unsolved.

■ CONCLUSIONS

We conclude that 1,1-carboboration reactions of alkynes with $B(C_6F_5)_3$ result in the formation of a series of useful alkenylborane systems. These form reactive FLPs upon addition of a suitable bulky Lewis base. Exposure of these FLPs to dihydrogen in all cases studied here leads to rapid heterolytic cleavage of dihydrogen. In the cases of sufficient steric bulk of the substituents at the alkenyl C═C double bond this results in the formation of the respective alkenylhydridoborate/phosphonium salts. Remarkably, the less sterically crowded examples undergo a concomitant efficient hydrogenation of the C═C double bond, giving the corresponding saturated 1-pentafluorophenylalkylhydridoborate/phosphonium salts in high yield. In contrast, some FLPs derived from the alkenylboranes proved resistant to hydrogenation of the C═C double bond under typical reaction conditions. In addition, the combination of the alkenylborane **4d** and DABCO was shown to give an active catalyst for the hydrogenation of enone substrates. This work illustrates that judicious control of the nature of a FLP hydrogenation catalysts can permit the reduction of a broadening scope of substrates.

■ EXPERIMENTAL SECTION

General Considerations. All reactions involving air- and/or moisture-sensitive compounds were carried out under an inert gas atmosphere (Münster: argon purchased from Westfalen AG; Toronto: nitrogen) using Schlenk-type glassware and a glovebox (Münster: glovebox 150 B-G II from MBraun; Toronto: gloveboxes from Innovative Technology, Vacuum Atmospheres, and MBraun). All other manipulations were performed on a double-manifold N_2 (H_2)/vacuum line with Schlenk-type glassware or in an N_2-filled inert atmosphere glovebox. The N_2 and H_2 gases were dried by passage through a Drierite column. Solvents (Aldrich) were dried using an Innovative Technologies solvent system (toluene, hexanes, pentane, CH_2Cl_2). NMR spectra were obtained on a Bruker ARX 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz), Bruker Avance 400 MHz, or Varian Inova 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 470 MHz, ^{11}B: 160 MHz) spectrometer. For ^{1}H NMR and ^{13}C NMR chemical shifts (δ) are given relative to TMS and referenced to the solvent signal (^{19}F rel. to external $CFCl_3$; ^{11}B rel. to external $BF_3{\cdot}Et_2O$). NMR assignments are supported by additional 1D and 2D NMR experiments. NMR spectra were recorded at 25 °C unless otherwise stated, and chemical shifts are reported in ppm. NMR solvents were purchased from Cambridge Isotopes, dried over CaH_2 (CD_2Cl_2, C_6D_5Br, and $CDCl_3$), vacuum distilled prior to use, and stored over 4 Å molecular sieves in the glovebox. Elemental analyses were performed on a Elementar Vario El III. IR spectra were recorded on a Varian 3100 FT-IR (Excalibur Series). Melting points were obtained with a DSC Q20 (TA Instruments). ESI mass spectra recorded on a Bruker Daltonics MicroTof.

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The imines[25b,c] **13** and the enones[25a] **15** were prepared by literature methods. $B(C_6F_5)_3$ was prepared according to a literature procedure[2c,d] and purified by two successive sublimations (Toronto). The syntheses of compounds **4a**−**h** were described in our previously published papers.[22] Crystals of **4e** suitable for X-ray diffraction were grown from a concentrated pentane solution at −40 °C for one week.

Synthesis of [Et_2C═$C(C_6F_5)B(C_6F_5)_2$], 4e. In a glovebox, a 50 mL glass tube wrapped with aluminum foil, equipped with a small stir bar and a Teflon screw tap, was charged with a solution of $B(C_6F_5)_3$ (512 mg, 1.00 mmol) in toluene (15 mL). While mixing, 3-hexyne was added *via* syringe (0.34 mL, 3.00 mmol), resulting in a light brown solution. The solution was allowed to mix for 12 h at 120 °C. After cooling to 25 °C, all volatiles were removed and the crude product was recrystallized from pentane at −40 °C to yield a pale brown powder in 78% yield. Crystals suitable for X-ray diffraction were grown from a concentrated pentane solution at −40 °C for one week. Anal. Calcd (%) for $C_{24}H_{10}BF_{15}$: C 48.52, H 1.70. Found: C 48.21, H 1.84. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 2.51 (m, 2H, $^3J_{H-H}$ = 7.43 Hz, CH_2), 2.32 (m, 2H, $^3J_{H-H}$ = 7.4 Hz,CH_2), 1.12 (t, 3H, $^3J_{H-H}$ = 7.4 Hz, CH_3), 1.07 (t, 3H, $^3J_{H-H}$ = 7.4 Hz, CH_3). ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ −129.8 (m, 4F, *o*-$B(C_6F_5)_2$), −139.3 (m, 2F, *o*-C_6F_5), −148.2 (t, 2F, $^3J_{F-F}$ = 19.9 Hz, *p*-$B(C_6F_5)_2$), −156.0 (t, 1F, $^3J_{F-F}$ = 20.7 Hz, *p*-C_6F_5), −161.3 (m, 4F, *m*-$B(C_6F_5)_2$), −162.5 (m, 2F, *m*-C_6F_5). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ 60.9 (br s). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K): δ 182.6 (Et_2C═), 146.9 (dm, $^1J_{C-F}$ = 248 Hz, CF), 143.8 (dm, $^1J_{C-F}$ = 244 Hz, CF), 143.4 (dm, $^1J_{C-F}$ = 258 Hz, CF), 140.4 (dm, $^1J_{C-F}$ = 253 Hz, CF), 137.4 (dm, $^1J_{C-F}$ = 253 Hz, CF), 137.2 (dm, $^1J_{C-F}$ = 252 Hz, CF), 126.6 (br, ═CB), 116.9 (tm, $^2J_{C-F}$ = 20.7 Hz, *ipso*-C_6F_5), 114.6 (br, *ipso*-$B(C_6F_5)_2$), 29.9 (CH_2), 29.2 (CH_2), 14.6 (CH_3), 11.7 (CH_3). X-ray data: *a* = 10.9155(7) Å, *b* = 9.9660(7) Å, *c* = 11.6419(8) Å, β = 115.278(2)°, *V* = 1145.18(13) Å^3, *Z* = 2, monoclinic, space group: $P2_1$, 3972 observed reflections ($I \geq 2\sigma(I)$), 490 refined parameters, R1 = 0.0294, wR2(all) = 0.688, GOF = 1.024.

Synthesis of [tBu_3PH][$HC(C_6H_4)$═$C(C_6F_5)B(C_6F_5)_2$], 5c. In a glovebox, a 50 mL glass tube equipped with a small stir bar and a Teflon screw top was charged with a solution of (*E*)- and (*Z*)-**4c** (30:1) (77 mg, 0.12 mmol) and tBu_3P (25 mg, 0.12 mmol) in toluene (3 mL). The yellow solution was placed in an oil bath at 80 °C for 3 days. The solvent was removed under vacuum, and the crude oil was washed with pentane (3 × 5 mL) to yield 69% of the product as a white precipitate. Anal. Calcd (%) for $C_{38}H_{33}BF_{15}P$: C 55.90, H 4.07. Found: C 55.82, H 4.15. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.27 (d, 1H, $^3J_{H-H}$ = 7.1 Hz, C_6H_4), 7.19 (s, 1H, C(H)═), 7.09 (d, 1H, $^3J_{H-H}$ = 7.1 Hz, C_6H_4), 6.91 (tm, 1H, $^3J_{H-H}$ = 7.10 Hz, C_6H_4), 6.81 (t, 1H, $^3J_{H-H}$ = 7.1 Hz, C_6H_4), 4.87 (d, 1H, $^1J_{H-P}$ = 429 Hz, PH), 1.52 (d, 27H, $^3J_{H-P}$ = 15.7 Hz, *t*Bu). ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ −131.2 (m, 4F, *o*-$B(C_6F_5)_2$), −140.0 (m, 2F, *o*-C_6F_5), −163.6 (t, 1F, $^3J_{F-F}$ = 21.1 Hz, *p*-C_6F_5), −165.4 (t, 2F, $^3J_{F-F}$ = 21.1 Hz, *p*-$B(C_6F_5)_2$), −166.8 (m, 2F, *m*-C_6F_5), −167.5 (m, 4F, *m*-$B(C_6F_5)_2$). ^{31}P NMR (162 MHz, CD_2Cl_2, 298 K): δ 60.2 ($^1J_{H-P}$ = 429 Hz, PH). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ −10.0; ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K) partial: δ 149.7 (^{Ph}CC(H)═), 142.1 (C(H)═), 128.5 (C_6H_4), 124.4 (C_6H_4), 124.3 (C_6H_4), 120.5 (C_6H_4), 37.7 (d, $^1J_{C-P}$ = 27.1 Hz, *t*Bu), 30.0 (*t*Bu). X-ray data: *a* = 11.2573(6) Å, *b* = 11.8997(6) Å, *c* = 15.2899(8) Å, α = 78.641(3)°, β = 71.732(3)°, γ = 67.422(2)°, *V* = 1789.05(16) Å^3, *Z* = 2, triclinic, space group $P\bar{1}$, 6288 observed reflections ($I \geq 2\sigma(I)$), 505 refined parameters, R1 = 0.0566, wR2(all) = 0.1546, GOF = 1.018.

Synthesis of [tBu_3PH][$PhC(C_6H_4)$═$C(C_6F_5)B(C_6F_5)_2$], 5g. Compound **4g** (28 mg, 0.041 mmol) and tBu_3P (8 mg, 0.041 mmol) were dissolved in toluene (0.5 mL) in a Teflon screw cap 50 mL glass bomb with a small stir bar. The mixture was allowed to heat at 80 °C for 3 days. The solvent was removed under vacuum, and the crude oil was washed with pentane (3 × 5 mL) to yield the product as a white precipitate in 52% yield. Anal. Calcd (%) for $C_{44}H_{37}BF_{15}P$: C 59.21, H 4.18. Found: C 58.69, H 4.38. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.25−7.10 (m, 6H, Ph, C_6H_4), 6.94−6.85 (m, 3H, Ph, C_6H_4), 4.85 (d, 1H, $^1J_{H-P}$ = 427 Hz, PH), 1.52 (d, 27H, $^3J_{H-P}$ = 15.7 Hz, *t*Bu). ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ −132.2 (m, 4F, *o*-$B(C_6F_5)_2$), −141.1 (m, 2F, *o*-C_6F_5), −163.8 (t, 1F, $^3J_{F-F}$ = 20.7 Hz, *p*-C_6F_5), −166.2 (t, 2F, $^3J_{F-F}$ = 20.7 Hz, *p*-$B(C_6F_5)_2$), −167.9 (m, 2F, *m*-C_6F_5), −168.4 (m, 4F, *m*-$B(C_6F_5)_2$). ^{31}P NMR (162 MHz, CD_2Cl_2, 298 K): δ 58.3 ($^1J_{H-P}$ = 427 Hz, PH). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ −9.39. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K) partial: δ 130.0, 129.4 (Ph), 128.3 (Ph), 126.6, 124.6, 124.3, 120.0, 38.1 (d, $^1J_{C-P}$ = 26.6 Hz, *t*Bu), 30.4 (*t*Bu). X-ray data: *a* = 11.2252(3) Å, *b* = 18.7357(5) Å, *c* = 19.1203(6) Å, *V* = 4021.2(2) Å^3, *Z* = 4, orthorhombic, space group $P2_12_12_1$ 7084 observed reflections ($I \geq 2\sigma(I)$), 559 refined parameters, R1 = 0.0459, wR2(all) = 0.1211, GOF = 1.050.

Synthesis of R_2C═$C(C_6F_5)BF(C_6F_5)(C_6F_4PiPr_3)$ (R = Et 6e, Ph 6g), R_2C═$C(C_6F_5)BF(C_6F_5)(C_6F_4PtBu_2H)$ (R_2 = Ph(H) 7c; R = Et 7e, Ph 7g), and Ph_2C═$C(C_6F_5)BF(C_6F_5)(C_6F_4PCy_2H)$, 8g. These compounds were prepared in a similar fashion, and thus only one preparation is detailed. In some cases elevated temperatures and prolonged periods were employed. To a yellow solution of **4g** (107 mg, 0.13 mmol) in toluene (1 mL) was added $iPPr_3$ (25 mg, 0.16 mmol). After 16 h at 25 °C, a white precipitate was observed. The reaction was allowed to stir for 48 h at 25 °C, before adding pentane (3 × 2 mL). The solvent was decanted, and the product was dried *in vacuo* to yield **6g** (82%) as a white solid.

6e: 25 °C for 16 h, 70% yield as a white solid. Anal. Calcd (%) for $C_{33}H_{31}BF_{15}P$: C 52.54, H 4.14. Found: C 52.55, H 4.44. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 3.26 (m, 3H, *i*Pr), 2.27 (m, 2H, CH_2), 1.91 (m, 2H, CH_2), 1.48 (dd, $^3J_{H-P}$ = 17.8 Hz, $^3J_{H-H}$ = 7.1 Hz, 18H, *i*Pr), 0.89 (t, 3H, $^3J_{H-H}$ = 7.4 Hz, CH_3), 0.74 (t, 3H, $^3J_{H-H}$ = 7.4 Hz, CH_3). ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ −126.3 (br, 2F, C_6F_4), −131.6 (m, 2F, *p*-C_6F_4), −133.0 (m, 2F, *o*-BC_6F_5), −139.4 (m, 1F, *o*-CC_6F_5), −140.2 (br, 1F, *o*-CC_6F_5), −162.5 (t, 1F, $^3J_{F-F}$ = 19.2 Hz, *p*-C_6F_5), −163.6 (t, 1F, $^3J_{F-F}$ = 20.8 Hz, *p*-C_6F_5), −166.8−167.0 (m, 4F, *m*-BC_6F_5, *m*-CC_6F_5), −185.5 (br, 1F, BF). ^{31}P{^{1}H} NMR (400 MHz, CD_2Cl_2, 298 K): δ 52.1 (m). ^{11}B NMR (128 MHz, CD_2Cl_2 298 K): δ 0.34 (d, $^1J_{B-F}$ = 48.0 Hz). ^{13}C{^{1}H} NMR (400 MHz, CD_2Cl_2, 298 K) partial: δ 150.5 (Et_2C═), 149.3 (dm, $^1J_{C-F}$ = 250 Hz, CF), 147.9 (dm, $^1J_{C-F}$ = 240 Hz, CF), 146.3 (dm, $^1J_{C-F}$ = 254 Hz, CF), 143.6 (dm, $^1J_{C-F}$ = 246 Hz, CF), 137.6 (dm, $^1J_{C-F}$ = 247 Hz, CF), 136.7 (dm, $^1J_{C-F}$ = 248 Hz, CF), 130.6 (br, ═CB), 124.1 (br, *ipso*-BC_6F_5), 122.7 (tm, $^2J_{C-F}$ = 24.5 Hz, *ipso*-CC_6F_5), 87.8 (dt, $^1J_{C-P}$ = 70.7 Hz, $^2J_{C-F}$ = 18.0 Hz, *ipso*-PC_6F_4), 26.2 (CH_2), 25.9 (CH_2), 23.5 (dm, $^1J_{C-P}$ = 40.9 Hz, *i*Pr), 16.8 (*i*Pr), 12.0 (CH_3), 11.8 (CH_3). X-ray data: *a* =18.4883(10) Å, *b* =18.5351(11) Å, *c* = 19.2487(11) Å, *V* = 6596.2(7) Å^3, Z = 8, orthorhombic, space group *Pbca*, 5803 observed reflections ($I \geq 2\sigma(I)$), 451 refined parameters, R1 = 0.0516, wR2(all) = 0.1501, GOF = 1.039.

6g: Anal. Calcd (%) for $C_{41}H_{31}BF_{15}P$: C 57.90, H 3.67. Found: C 58.21, H 4.14. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.38 (d, 2H, $^3J_{H-H}$ = 7.4 Hz, *o*-Ph), 7.12−7.09 (m, 4H, *o*,*m*-Ph), 7.04−6.97 (m, 3H, *m*-Ph, *p*-Ph), 6.92 (t, 1H, $^3J_{H-H}$ = 7.4 Hz, *p*-Ph), 3.07 (m, 3H, *i*Pr), 1.33 (dd, $^3J_{H-P}$ = 17.6 Hz, $^3J_{H-H}$ = 6.4 Hz, 18H, *i*Pr). ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ −124.7 (br, 2F, C_6F_4), −132.2 to 132.3 (br, 4F, *o*-BC_6F_5, *p*-C_6F_4), −138.3 (m, 1F, *o*-CC_6F_5), −138.8 (br, 1F, *o*-CC_6F_5), −162.1 (t, 1F, $^3J_{F-F}$ = 20.2 Hz, *p*-BC_6F_5), −162.3 (t, 1F, $^3J_{F-F}$ = 20.7 Hz, *p*-CC_6F_5), −166.7 (m, 1F, *m*-CC_6F_5), −166.9 (m, 1F, *m*-CC_6F_5), −167.1 (m, 2F, *m*-BC_6F_5), −180.1 (br, 1F, BF). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 298 K): δ 52.0 (m). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ 0.59 (d, $^1J_{B-F}$ = 52.5 Hz). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K) partial: δ 149.6 (Ph_2C═), 149.4 (dm, $^1J_{C-F}$ = 251 Hz, CF), 147.8 (dm, $^1J_{C-F}$ = 242 Hz, CF), 145.9 (*i*-Ph), 143.9 (*i*-Ph), 143.3 (dm, $^1J_{C-F}$ = 242 Hz, CF), 138.0 (dm, $^1J_{C-F}$ = 244 Hz, CF), 136.8 (dm, $^1J_{C-F}$ = 245 Hz, CF), 129.6 (*o*-Ph), 128.0 (*o*-Ph), 127.5 (*m*-Ph), 126.6 (*m*-Ph), 126.0 (*p*-Ph), 125.8 (*p*-Ph), 123.4 (br, *ipso*-BC_6F_5), 123.2 (tm, $^2J_{C-F}$ = 22.0 Hz, *ipso*-CC_6F_5), 87.7 (dtm, $^1J_{C-P}$ = 72.0 Hz, $^2J_{C-F}$ = 18.2 Hz, *ipso*-PC_6F_4), 23.4 (dm, $^1J_{C-P}$ = 41.9 Hz, *i*Pr), 16.9 (*i*Pr). X-ray data: *a* = 11.0573(6) Å, *b* = 13.0147(7) Å, *c* = 13.9942(7) Å, α = 81.889(2)°, β = 88.595(3)°, γ = 85.825(2)°, *V* = 1988.23(18) Å^3, *Z* = 2, triclinic, space group $P\bar{1}$, 6992 observed reflections ($I \geq 2\sigma(I)$), 523 refined parameters, R1 = 0.0579, wR2(all) = 0.1739, GOF = 1.045.

7c: 50 °C for 48 h, 66% yield. Anal. Calcd (%) for $C_{34}H_{25}BF_{15}P$: C 53.71, H 3.31. Found: C 53.50, H 3.50. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.17 (t, 2H, $^3J_{H-H}$ = 7.1 Hz, *m*-Ph), 7.13 (t, 1H, $^3J_{H-H}$ = 7.1 Hz, *p*-Ph), 6.98 (d, 2H, $^3J_{H-H}$ = 7.1 Hz, *o*-Ph), 6.81 (s, 1H, C(H)═), 6.33 (d, 1H, $^1J_{H-P}$ = 462 Hz, PH), 1.60 (d, 18H, $^3J_{H-P}$ = 19.3 Hz, *t*Bu). ^{19}F NMR

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(377 MHz, d_8-THF, 298 K): δ −127.0 (br, 1F, C_6F_4), −127.3 (m, 1F, *p*-C_6F_4), −127.7 (br, 1F, C_6F_4), −131.5 (m, 2F, *o*-BC_6F_5), −133.6 (m, 1F, C_6F_4), −138.7 (m, 1F, *o*-CC_6F_5), −142.2 (m, 1F, *o*-CC_6F_5), −163.3 (t, 1F, $^3J_{F-F}$ = 20.3 Hz, *p*-BC_6F_5), −163.5 (t, 1F, $^3J_{F-F}$ = 20.7 Hz, *p*-CC_6F_5), −166.8 (m, 1F, *m*-CC_6F_5), −167.6 to −167.7 (m, 3F, *m*-BC_6F_5, *m*-CC_6F_5), −193.0 (br, 1F, BF). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 298 K): δ 33.4 (br). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ 1.49 (d, $^1J_{B-F}$ = 50.8 Hz, BF). $^{13}C\{^1H\}$ NMR (101 MHz, d_8-THF, 298 K) partial: δ 148.9 (dm, $^1J_{C-F}$ = 244 Hz, CF), 148.4 (dm, $^1J_{C-F}$ = 244 Hz, CF), 145.0 (dm, $^1J_{C-F}$ = 248 Hz, CF), 143.7 (dm, $^1J_{C-F}$ = 249 Hz, CF), 142.8 (dm, $^1J_{C-F}$ = 240 Hz, CF), 139.5 (*ipso*-Ph), 138.0 (dm, $^1J_{C-F}$ = 247 Hz, CF), 137.0 (dm, $^1J_{C-F}$ = 247 Hz, CF), 136.6 (dm, $^1J_{C-F}$ = 246 Hz, CF), 136.3 (dm, $^1J_{C-F}$ = 247 Hz, CF), 134.8 (C(H)═), 127.6 (*o*,*m*-Ph), 125.9 (*p*-Ph), 123.8 (br, *i*-BC_6F_5), 120.5 (tm, $^2J_{C-F}$ = 22.8 Hz, *i*-CC_6F_5), 90.1 (dtm, $^1J_{C-P}$ = 70.0 Hz, $^2J_{C-F}$ = 19.3 Hz, *ipso*-PC_6F_4), 35.5 (d, $^1J_{C-P}$ = 31.6 Hz, *t*Bu), 26.6 (*t*Bu).

7e: 50 °C, 48 h, 99% yield. Anal. Calcd (%) for $C_{32}H_{29}BF_{15}P$: C 52.19, H 3.95. Found: C 52.56, H 4.41. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 6.33 (d, 1H, $^1J_{H-P}$ = 466 Hz, PH), 2.25 (m, 2H, CH_2), 1.90 (m, 2H, CH_2), 1.59 (d, 18H, $^3J_{H-P}$ = 19.0 Hz, *t*Bu), 0.88 (t, 3H, $^3J_{H-H}$ = 7.4 Hz, CH_3), 0.72 (t, 3H, $^3J_{H-H}$ = 7.4 Hz, CH_3). ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ −125.6 (br, 1F, C_6F_4), −126.2 (br, 1F, C_6F_4), −126.5 (m, 1F, *p*-C_6F_4), −133.0 (m, 3F, *o*-BC_6F_5, C_6F_4), −139.4 (m, 1F, *o*-CC_6F_5), −140.3 (br, 1F, *o*-CC_6F_5), −162.4 (t, 1F, $^3J_{F-F}$ = 20.8 Hz, *p*-C_6F_5), −163.6 (t, 1F, $^3J_{F-F}$ = 20.8 Hz, *p*-C_6F_5), −166.7 to 166.9 (m, 4F, *m*-BC_6F_5, *m*-CC_6F_5), −184.5 (br, 1F, BF). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 298 K): δ 33.1 (br). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ 0.39 (d, J_{B-F} = 40.8 Hz, BF). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 298 K) partial: δ 150.6 (Et_2C═), 149.3 (dm, $^1J_{C-F}$ = 252 Hz, CF), 142.0 (dm, $^1J_{C-F}$ = 240 Hz, CF), 143.7 (dm, $^1J_{C-F}$ = 240 Hz, CF), 138.5 (dm, $^1J_{C-F}$ = 249 Hz, CF), 137.6 (dm, $^1J_{C-F}$ = 252 Hz, CF), 136.7 (dm, $^1J_{C-F}$ = 246 Hz, CF), 131.6 (br, ═CB), 123.9 (br, *i*-BC_6F_5), 122.6 (tm, $^2J_{C-F}$ = 22.0 Hz, *ipso*-CC_6F_5), 88.7 (m, *ipso*-PC_6F_4), 36.0 (d, $^1J_{C-P}$ = 30.9 Hz, *t*Bu), 27.6 (*t*Bu), 26.2 (CH_2), 25.9 (CH_2), 12.0 (CH_3), 11.8 (CH_3).

7g: 70 °C for 48 h, 42% yield off-white solid. Anal. Calcd (%) for $C_{40}H_{29}BF_{15}P$: C 57.44, H 3.49. Found: C 57.19, H 3.70. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.40 (d, 2H, $^3J_{H-H}$ = 7.0 Hz, *o*-Ph), 7.30 (m, 1H, *p*-Ph), 7.13 (m, 4H, *o*,*m*-Ph), 7.02 (t, 2H, $^3J_{H-H}$ = 7.0 Hz, *m*-Ph), 6.95 (m, 1H, *p*-Ph), 6.27 (d, 1H, $^1J_{H-P}$ = 465 Hz, PH), 1.57 (d, 18H, $^3J_{H-P}$ = 19.2 Hz, *t*Bu). ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ −124.2 (br, 1F, C_6F_4), −124.5 (br, 1F, C_6F_4), −127.1 (m, 1F, *p*-C_6F_4), −132.4 (m, 2F, *o*-BC_6F_5), −133.5 (m, 1F, C_6F_4), −138.3 (m, 1F, *o*-CC_6F_5), −139.0 (m, 1F, *o*-CC_6F_5), −161.9 (t, 1F, $^3J_{F-F}$ = 20.4 Hz, *p*-BC_6F_5), −162.2 (t, 1F, $^3J_{F-F}$ = 20.4 Hz, *p*-CC_6F_5), −166.6 (m, 1F, *m*-CC_6F_5), −166.8 (m, 1F, *m*-CC_6F_5), −166.9 (m, 2F, *m*-BC_6F_5), −179.0 (br, 1F, BF). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 298 K): δ 33.1 (br). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ 0.68 (d, $^1J_{B-F}$ = 52.3 Hz, BF). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 298 K): δ partial: 149.8 (Ph_2C═), 148.9 (dm, $^1J_{C-F}$ = 251 Hz, CF), 148.2 (dm, $^1J_{C-F}$ = 247 Hz, CF), 145.9 (dm, $^1J_{C-F}$ = 244 Hz, CF), 146.3 (*i*-Ph), 144.3 (*ipso*-Ph), 143.8 (dm, $^1J_{C-F}$ = 244 Hz, CF), 138.1 (dm, $^1J_{C-F}$ = 249 Hz, CF), 136.7 (dm, $^1J_{C-F}$ = 244 Hz, CF), 129.9 (*o*-Ph), 128.3 (*m*-Ph), 127.9 (*o*-Ph), 127.0 (*m*-Ph), 126.4 (*p*-Ph), 126.2 (*p*-Ph), 123.6 (br, *ipso*-BC_6F_5), 123.5 (tm, $^2J_{C-F}$ = 21.2 Hz, *ipso*-CC_6F_5), 89.1 (dtm, $^1J_{C-P}$ = 73.6 Hz, $^2J_{C-F}$ = 17.8 Hz, *i*-PC_6F_4), 36.1 (d, $^1J_{C-P}$ = 31.3 Hz, *t*Bu), 36.0 (d, $^1J_{C-P}$ = 31.3 Hz, *t*Bu), 27.7 (*t*Bu), 27.6 (*t*Bu). X-ray data: a = 9.8745(6) Å, b = 18.2413(10) Å, c = 23.7744(13) Å, V = 4282.3(4) Å^3, Z = 4, orthorhombic, space group $P2_12_12_1$, 9855 observed reflections ($I \geq 2\sigma(I)$), 565 refined parameters, R1 = 0.0728, wR2(all) = 0.2161, GOF = 1.037. **8g:** 70 °C for 24 h, 64% yield. Anal. Calcd (%) for $C_{44}H_{33}BF_{15}P$: C 59.48, H 3.74. Found: C 59.51, H 3.98. ^1H NMR (400 MHz, d_8-THF, 298 K): δ 7.41 (d, 2H, $^3J_{H-H}$ = 7.5 Hz, *o*-Ph), 7.13 (d, 2H, $^3J_{H-H}$ = 7.6 Hz, *o*-Ph), 7.06 (t, 2H, $^3J_{H-H}$ = 7.6 Hz, *m*-Ph), 7.03 (d, 1H, $^1J_{H-P}$ = 496 Hz, PH), 7.00−6.89 (m, 2H, *p*-Ph, *p*-Ph), 6.97 (t, 2H, $^3J_{H-H}$ = 7.5 Hz, *m*-Ph), 3.00 (br, 2H, Cy), 2.17 − 1.34 (br m, 20H, Cy). ^{19}F NMR (377 MHz, d_8-THF, 298 K): δ −124.5 (br, 2F, C_6F_4), −132.3 (br, 2F, *o*-BC_6F_5), −132.9 (br d, 2F, C_6F_4), −138.4 (m, 1F, *o*-CC_6F_4), −139.0 (br, 1F, *o*-CC_6F_4), −162.0 (t, 1F, $^3J_{F-F}$ = 20.2 Hz, *p*-C_6F_5), −162.3 (t, 1F, $^3J_{F-F}$ = 21.5 Hz, *p*-C_6F_5), −166.8 to −167.0 (m, 4F, *m*-BC_6F_5, *m*-CC_6F_5), −179.8 (br, 1F, BF). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 298 K): δ 11.0 (br s). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ 0.48 (br, BF). $^{13}C\{^1H\}$ NMR (101 MHz, d_8-THF, 298 K) partial: δ 149.6 (Ph_2C═), 148.4 (dm, $^1J_{C-F}$ = 247 Hz, CF), 148.0 (dm, $^1J_{C-F}$ = 247 Hz, CF), 146.1 (*i*-Ph), 145.6 (dm, $^1J_{C-F}$ = 252 Hz, CF), 145.4 (dm, $^1J_{C-F}$ = 252 Hz, CF), 143.8 (*ipso*-Ph), 143.4 (dm, $^1J_{C-F}$ = 247 Hz, CF), 137.7 (dm, $^1J_{C-F}$ = 247 Hz, CF), 136.2 (dm, $^1J_{C-F}$ = 250 Hz, CF), 129.7 (*o*-Ph), 128.0 (*o*-Ph), 127.1 (*m*-Ph), 126.2 (*m*-Ph), 125.7 (*p*-Ph), 125.4 (*p*-Ph), 123.9 (tm, $^2J_{C-F}$ = 20.8 Hz, *i*-CC_6F_5), 87.5 (br, *ipso*-PC_6F_4), 28.6 (d, $^1J_{C-P}$ = 41.7 Hz, P-Cy), 26.3 (d, $^2J_{C-P}$ = 3.3 Hz, Cy), 25.5 (d, $^3J_{C-P}$ = 15.6 Hz, Cy), 24.8 (Cy).

Synthesis of [*t*Bu$_3$PH][CH$_3$(CH$_2$)$_3$CH(C$_6$F$_5$)BH(C$_6$F$_5$)$_2$], 9a. A solution of **4a** (58 mg, 0.1 mmol) and *t*Bu$_3$P (20 mg, 0.1 mmol) in toluene (2 mL) was degassed, and the reaction flask filled with H_2 (2.5 bar). The reaction mixture was stirred overnight under H_2 (2.5 bar), and pentane (10 mL) was added, after which the supernatant was decanted. Crystallizing the residue with CH_2Cl_2/pentane (v/v = 1:3, 4 mL) at −35 °C and then drying *in vacuo* afforded **9a** as a white powder (68 mg, 87%). Crystals suitable for X-ray crystal structure analysis were grown by a CH_2Cl_2/pentane (v/v = 1:3) solution of **9a** at −35 °C. Anal. Calcd for $C_{35}H_{39}BF_{15}P$: C, 53.45; H, 5.00. Found: C, 53.31; H, 5.10. ^1H NMR (600 MHz, CD_2Cl_2, 298 K): δ 5.29 (d, $^1J_{PH}$ = 433.5 Hz, 1H, PH), 3.23 (br t, $^3J_{HH}$ = 10.1 Hz, 1H, BCH), 2.94 (1:1:1:1 q, $^1J_{BH} \approx$ 95 Hz, BH), 1.88/1.64 (each m, each 1H, $^{CH}CH_2$), 1.67 (d, $^3J_{PH}$ = 15.7 Hz, 27H, *t*Bu), 1.27/1.20 (each m, each 1H, $^{Me}CH_2$), 1.12 (m, 2H, CH_2), 0.80 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 298 K): δ 38.0 (d, $^1J_{PC}$ = 27.1 Hz, *t*Bu), 33.5 (CH_2), 33.0 ($^{CH}CH_2$), 30.3 (d, $^2J_{PC}$ = 5.9 Hz, *t*Bu), 30.3 (br, BCH), 23.2 ($^{Me}CH_2$), 14.4 (CH_3), [C_6F_5 not listed]. ^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): δ −132.6 (m, 4F), −140.9 (br, 1F), −143.7 (br, 1F) (*o*-C_6F_5), −164.6 (t, $^3J_{FF}$ = 20.3 Hz), −164.9 (t, $^3J_{FF}$ = 20.3 Hz), −166.2 (t, $^3J_{FF}$ = 21.3 Hz) (each 1F, *p*-C_6F_5), −167.3 (m, 4F), −167.5 (m, 2F) (*m*-C_6F_5). $^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 298 K): δ −19.3 ($\nu_{1/2} \approx$ 60 Hz). ^{11}B NMR (192 MHz, CD_2Cl_2, 298 K): δ −19.3 (d, $^1J_{BH}$ = 90.6 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 298 K): δ 59.2 ($\nu_{1/2} \approx$ 3 Hz). ^{31}P NMR (202 MHz, CD_2Cl_2, 298 K): δ 59.2 (dm, $^1J_{PH} \approx$ 433 Hz). X-ray data: a = 9.9252(3) Å, b = 20.0004(11) Å, c = 18.3802(7) Å, β = 93.002(3)°, V = 3643.6(3) Å^3, Z = 4, monoclinic, space group $P2_1/n$, 4875 observed reflections ($I \geq 2\sigma(I)$), 490 refined parameters, R1 = 0.0889, wR2(all) = 0.2672, GOF = 1.067.

Synthesis of [*t*Bu$_3$PH][CH$_3$(CH$_2$)$_4$CH(C$_6$F$_5$)BH(C$_6$F$_5$)$_2$], 9b. A similar procedure to that mentioned above for the preparation of compound **9a** was carried out by using starting material **4b** to yield **9b** as a white powder (66 mg, 82%). Anal. Calcd for $C_{36}H_{41}BF_{15}P$: C, 54.02; H, 5.16. Found: C, 53.86; H, 5.25. ^1H NMR (500 MHz, CD_2Cl_2, 298 K): δ 5.31 (d, $^1J_{PH}$ = 433.8 Hz, 1H, PH), 3.23 (br t, $^3J_{HH}$ = 10.1 Hz, 1H, BCH), 2.93 (br, BH), 1.88/1.64 (each m, each 1H, $^{CH}CH_2$)[1], 1.68 (d, $^3J_{PH}$ = 15.7 Hz, 27H, *t*Bu), 1.21/1.18 (each m, each 1H, $^{Me}CH_2$)[1], 1.23/1.18 (each m, each 1H, 4-CH_2)[1], 1.14 (m, 2H, 3-CH_2)[1], 0.81 (m, 3H, CH_3) [[1] from ghsqc experiment]. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298 K): δ 38.0 (d, $^1J_{PC}$ = 27.1 Hz, *t*Bu), 33.3 ($^{CH}CH_2$), 32.5 (C4), 30.9 (C3), 30.3 (*t*Bu), 30.2 (br, B-CH), 23.2 ($^{Me}CH_2$), 14.3 (CH_3) [C_6F_5 not listed]. ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): δ −132.6 (m, 4F), −140.9 (br, 1F), −143.7 (br, 1F) (*o*-C_6F_5), −164.6 (t, $^3J_{FF}$ = 20.3 Hz), −164.9 (t, $^3J_{FF}$ = 20.3 Hz), −166.2 (t, $^3J_{FF}$ = 21.3 Hz) (each 1F, *p*-C_6F_5), −167.3 (m, 4F), −167.5 (m, 2F) (*m*-C_6F_5). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 298 K): δ −19.3 ($\nu_{1/2} \approx$ 70 Hz). ^{11}B NMR (160 MHz, CD_2Cl_2, 298 K): δ −19.3 (d, $^1J_{BH}$ = 93.1 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 298 K): δ 59.1 ($\nu_{1/2} \approx$ 3 Hz). ^{31}P NMR (202 MHz, CD_2Cl_2, 298 K): δ 59.1 (dm, $^1J_{PH}$ = 433.9 Hz).

Synthesis of [*t*Bu$_3$PH][PhCH$_2$CH(C$_6$F$_5$)BH(C$_6$F$_5$)$_2$], 9c. In a glovebox, a 50 mL glass tube equipped with a small stir bar and a Teflon screw top was charged with a solution of (*E*)- and (*Z*)-**4c** (30:1) (77 mg, 0.12 mmol) and *t*Bu$_3$P (25 mg, 0.12 mmol) in toluene (1 mL). The yellow solution was degassed three times through a freeze−pump−thaw cycle on the vacuum/H_2 line and filled with H_2 (4 bar) at −196 °C. After the addition of H_2 the reaction tube was allowed to mix at 80 °C for 15 h. The product was precipitated from solution by adding pentane (20 mL) dropwise. The crude product was dried under vacuum and shown to be a mixture of **5c**, **9c**, and **10c** in a 4:9:2 ratio. Crystals of **9c** suitable for X-ray diffraction were grown from a layered C_6D_5Br/hexane solution at 25 °C and isolated in ca. 30% yield. Anal. Calcd (%) for

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$C_{38}H_{37}BF_{15}P$: C 55.63; H 4.55. Found: C 55.17, H 4.73. ^{1}H NMR (400 MHz, C_6D_5Br, 298 K): δ 7.37 (d, 2H, $^3J_{H-H}$ = 7.6 Hz, *o*-Ph), 7.10 (t, 2H, $^3J_{H-H}$ = 7.6 Hz, *m*-Ph), 6.95 (t, 1H, $^3J_{H-H}$ = 7.6 Hz, *p*-Ph), 4.67 (d, 1H, $^1J_{H-P}$ = 434 Hz, PH), 4.14 (br m, 1H, CHB), 3.43 (m, 2H, CH_2Ph), 3.42 (br, 1H, BH), 1.07 (d, 27H, $^3J_{H-P}$ = 15.7 Hz; *t*Bu). ^{19}F NMR (377 MHz, C_6D_5Br, 298 K): −131.1 (m, 2F, *o*-B(C_6F_5)$_2$), −131.2 (m, 2F, *o*-B(C_6F_5)$_2$), −139.5 (m, 1F, *o*-C_6F_5), −142.1 (m, 1F, *o*-C_6F_5), −162.5 (t, 1F, $^3J_{F-F}$ = 20.9 Hz, *p*-B(C_6F_5)$_2$), −162.7 (t, 1F, $^3J_{F-F}$ = 21.1 Hz, *p*-B(C_6F_5)$_2$), −163.7 (t, 1F, $^3J_{F-F}$ = 22.0 Hz, *p*-C_6F_5), −165.3 (m, 1F, *m*-B(C_6F_5)$_2$), −165.5 (m, 1F, *m*-B(C_6F_5)$_2$), −165.8 (m, 1F, *m*-C_6F_5), −166.2 (m, 1F, *m*-BC_6F_5). ^{31}P{^{1}H} NMR (162 MHz, C_6D_5Br, 298 K): δ 58.5. ^{11}B NMR (128 MHz, C_6D_5Br, 298 K): δ −18.7 (br, BH). ^{13}C{^{1}H} NMR (101 MHz, C_6D_5Br, 298 K) partial: δ 145.2 (*ipso*-Ph), 128.5 (*o*-Ph), 128.1 (*m*-Ph), 125.3 (*p*-Ph), 39.4 (CH_2Ph), 36.7 ($^1J_{C-P}$ = 27.1 Hz, *t*Bu), 33.4 (br, CHB), 29.3 (*t*Bu). X-ray data: *a* = 37.440(3) Å, *b* = 9.7274(6) Å, *c* = 24.1227(17) Å, β = 120.714(3)°, *V* = 7553.0(9) Å^3, *Z* = 8, monoclinic, space group *C*2/*c*, 6652 observed reflections ($I \geq 2\sigma(I)$), 509 refined parameters, R1 = 0.0528, wR2(all) = 0.1413, GOF = 1013.

Synthesis of [*t*Bu$_3$PH][Ph(H)C═C(C_6F_5)BH(C_6F_5)$_2$], 10c. In a glovebox, a 50 mL glass tube equipped with a small stir bar and a Teflon screw top was charged with a solution of (*E*)- and (*Z*)-**4c** (30:1) (77 mg, 0.12 mmol) and *t*Bu$_3$P (25 mg, 0.12 mmol) in pentane (40 mL). The reaction flask was immediately covered with aluminum foil. The bright yellow solution was degassed three times through a freeze−pump−thaw cycle on the vacuum/H_2 line and filled with H_2 (4 bar) at −196 °C. After the addition of H_2 the reaction tube was allowed to mix at 25 °C for 3 days. A white precipitate was observed in the reaction tube as the solution gradually became colorless. The *E* isomer of the product was isolated in 86% yield. Anal. Calcd (%) for $C_{38}H_{37}BF_{15}P$: C 55.63; H 4.55. Found: C 55.17, H 4.73.

The same procedure above was repeated without covering the reaction tube, yielding a white precipitate, which was isolated in 88% yield and proved to be a mixture of the *E* and *Z* isomers.

Resonances common to both *E* and *Z* isomers: ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.12 (m, 2H, *m*-Ph), 7.03 (m, 1H, *p*-Ph), 5.10 (d, 1H, $^1J_{H-P}$ = 431 Hz, PH), 1.67 (d, 27H, $^3J_{H-P}$ = 15.7 Hz, *t*Bu). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 298 K): δ 58.2. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K): δ 148.2 (dm, $^1J_{C-F}$ = 234 Hz, CF), 147.7 (dm, $^1J_{C-F}$ = 234 Hz, CF), 143.1 (dm, $^1J_{C-F}$ = 243 Hz, CF), 142.8 (dm, $^1J_{C-F}$ = 241 Hz, CF), 126.1 (*ipso*-B(C_6F_5)$_2$), 123.8 (tm, $^2J_{C-F}$ = 23 Hz, *i*-C_6F_5), 37.6 (d, $^1J_{C-P}$ = 26.8 Hz, *t*Bu), 29.9 (*t*Bu).

E isomer: ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.49 (d, 2H, $^3J_{H-H}$ = 7.74 Hz, *o*-Ph), 6.63 (s, 1H, C(H)═), 3.90 (br q, 1H, $^1J_{H-B}$ = 90.8 Hz, BH). ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ −131.1 (m, 4F, *o*-B(C_6F_5)$_2$, −141.7 (m, 2F, *o*-C_6F_5), −163.7 (t, 1F, $^3J_{F-F}$ = 20.7 Hz, *p*-C_6F_5), −164.5 (t, 2F, $^3J_{F-F}$ = 20.0 Hz, *p*-B(C_6F_5)$_2$, −166.7 (m, 2F, *m*-C_6F_5), −167.6 (m, 2F, *m*-B(C_6F_5)$_2$. ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ −21.9 (d, $^1J_{B-H}$ = 90.8 Hz, BH). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K): δ140.2 (*ipso*-Ph), 136.1 (Ph(H)C═), 129.2 (*o*-Ph), 126.9 (*m*-Ph), 125.2 (*p*-Ph).

Z isomer: ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 6.92 (d, 2H, $^3J_{H-H}$ = 7.74 Hz, *o*-Ph), 6.54 (s, 1H, C(H)═), 3.35 (br q, 1H, $^1J_{H-B}$ = 90.8 Hz, BH). ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ −131.1 (m, 4F, *o*-B(C_6F_5)$_2$), −141.3 (m, 2F, *o*-C_6F_5), −163.3 (t, 1F, $^3J_{F-F}$ = 21.4 Hz, *p*-C_6F_5), −164.3 (t, 2F, $^3J_{F-F}$ = 19.8 Hz, *p*-B(C_6F_5)$_2$), −165.8 (m, 2F, *m*-C_6F_5), −167.5 (m, 4F, *m*-B(C_6F_5)$_2$). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ −19.4 (d, $^1J_{B-H}$ = 90.8 Hz, BH);. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K): δ 140.3 (*ipso*-Ph), 133.4 (Ph(H)C═), 128.2 (*m*-Ph), 127.8 (*o*-Ph), 125.8 (*p*-Ph).

Synthesis of [*t*Bu$_3$PH][*t*Bu(H)C═C(C_6F_5)BH(C_6F_5)$_2$], 10d. A similar procedure to that mentioned above for compound **9a** was carried out by using starting material **4d** to yield **10d** as a white powder (73 mg, 91%). Crystals suitable for X-ray crystal structure analysis were grown from a CH_2Cl_2/pentane (v/v = 1:3) solution after 12 d at −35 °C. Anal. Calcd for $C_{36}H_{39}BF_{15}P + 3/4CH_2Cl_2$: C, 51.20; H, 4.73. Found: C, 51.07; H, 4.47. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ 5.40 (br s, 1H, ═CH), 5.17 (d, $^1J_{PH}$ = 431.3 Hz, 1H, PH), 3.00 (1:1:1:1 q, $^1J_{BH}$ = 93.1 Hz, 1H, BH), 1.63 (d, $^3J_{PH}$ = 15.7 Hz, 27H, *t*BuP), 0.80 (s, 9H, *t*Bu). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ 143.1 (═CH), n.o. (═CB), 38.0 (d, $^1J_{PC}$ = 26.8 Hz, *t*BuP), 34.7 (*t*Bu), 30.32 (*t*Bu), 30.31 (*t*BuP) [C_6F_5 not listed]. ^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): δ −130.9 (br m, 4F, *o*), −165.0 (t, $^3J_{FF}$ = 20.3 Hz, 2F, *p*), −168.0 (m, 4F, *m*) (BC_6F_5), −140.9 (br m, 2F, *o*), −164.9 (t $^3J_{FF}$ = 21.4 Hz, 1F, *p*), −167.0 (m, 2F, *m*) (C_6F_5). ^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 298 K): δ −18.8 ($\nu_{1/2} \approx$ 50 Hz). ^{11}B NMR (192 MHz, CD_2Cl_2, 298 K): δ −18.8 (d, $^1J_{BH}$ = 91.4 Hz). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 298 K): δ 59.6 ($\nu_{1/2} \approx$ 3 Hz). ^{31}P NMR (202 MHz, CD_2Cl_2, 298 K): δ 59.6 (dm, $^1J_{PH} \approx$ 433 Hz). X-ray data: *a* = 10.2586(3) Å, *b* = 12.1826(5) Å, *c* = 16.1736(5) Å, α = 89.894(3)°, β = 77.848(2)°, γ = 71.794(4)°, *V* = 1872.7(1) Å^3, *Z* = 2, triclinic, space group $P\bar{1}$, 5818 observed reflections ($I \geq 2\sigma(I)$), 496 refined parameters, R1 = 0.0729, wR2(all) = 0.2201, GOF = 1.152.

Synthesis of [*t*Bu$_3$PH][Et$_2$C═C(C_6F_5)BH(C_6F_5)$_2$], 10e. Compound **4e** (28 mg, 0.047 mmol) and *t*Bu$_3$P (9 mg, 0.047 mmol) were dissolved in C_6D_5Br (0.5 mL) in a Teflon cap sealed J-Young tube. The brown solution was degassed three times through a freeze−pump−thaw cycle on the vacuum/H_2 line and filled with H_2 (4 bar) at −196 °C. After the addition of H_2 the reaction tube was allowed to sit in an 80 °C oil bath for 16 h. To isolate the salt, the reaction mixture was layered with hexane and placed in −40 °C freezer overnight to yield 98% of a white precipitate. Crystals suitable for X-ray diffraction were grown from a layered dichloromethane/hexane solution at −40 °C. Anal. Calcd (%) for $C_{32}H_{29}BF_{15}P$: C 54.15, H 4.92. Found: C 54.62, H 4.92. ^{1}H NMR (400 MHz, C_6D_5Br, 298 K): δ 4.73 (d, 1H, $^1J_{H-P}$ = 436 Hz, PH), 4.00 (br, 1H, BH), 2.48 (m, 2H, $^3J_{H-H}$ = 7.6 Hz, CH_2), 2.03 (m, 2H, $^3J_{H-H}$ = 7.3 Hz, CH_2), 1.07 (d, 27H, $^3J_{H-P}$ = 16 Hz, *t*Bu), 1.00 (t, 3H, $^3J_{H-H}$ = 7.6 Hz, CH_3), 0.97 (t, 3H, $^3J_{H-H}$ = 7.3 Hz, CH_3). ^{19}F NMR (377 MHz, C_6D_5Br, 298 K): δ −129.7 (br, 4F, *o*-B(C_6F_5)$_2$, −139.2 (br, 2F, *o*-C_6F_5), −163.4 (t, 1F, $^3J_{F-F}$ = 21.6 Hz, *p*-C_6F_5), −163.7 (t, 2F, $^3J_{F-F}$ = 20.5 Hz, *p*-B(C_6F_5)$_2$), −166.0 (m, 2F, *m*-C_6F_5), −166.4 (m, 4F, *m*-B(C_6F_5)$_2$). ^{31}P NMR (162 MHz, C_6D_5Br, 298 K): δ 57.7 (PH, $^1J_{H-P}$ = 436 Hz). ^{11}B NMR (128 MHz, C_6D_5Br, 298 K): δ −21.0 (br, BH). ^{13}C {^{1}H} NMR (101 MHz, C_6D_5Br, 298 K) partial: δ 148.4 (dm, $^1J_{C-F}$ = 233 Hz, CF), 148.3 (dm, $^1J_{C-F}$ = 236 Hz, CF), 146.2 (Et_2C═), 143.3 (dm, $^1J_{C-F}$ = 239 Hz, CF), 137.4 (dm, $^1J_{C-F}$ = 243 Hz, CF), 137.2 (dm, $^1J_{C-F}$ = 247 Hz, CF), 136.6 (dm, $^1J_{C-F}$ = 245 Hz, CF), 36.7 (d, $^1J_{C-P}$ = 27.1 Hz, *t*Bu), 29.2 (*t*Bu), 26.6 (CH_2), 26.0 (CH_2), 13.2 (CH_3), 12.4 (CH_3). X-ray data: *a* = 8.8564(10) Å, *b* = 12.5788(15) Å, *c* = 17.423(2) Å, α = 81.339(5)°, β = 79.730(5)°, γ = 73.098(6)°, *V* = 1817.3(4) Å^3, *Z* = 2, triclinic, space group $P\bar{1}$, 6402 observed reflections ($I \geq 2\sigma(I)$), 489 refined parameters, R1 = 0.0507, wR2(all) = 0.1169, GOF = 1.004.

Synthesis of [*t*Bu$_3$PH][(C_3H_7)$_2$C═C(C_6F_5)BH(C_6F_5)$_2$], 10f. A similar procedure to that mentioned above for the synthesis of compound **9a** was carried out by using the starting material **4f** to yield **10f** as a white powder (63 mg, 76%). Crystals suitable for X-ray crystal structure analysis were grown from a CH_2Cl_2/cyclopentane (v/v = 1:5) solution of **10f** at −35 °C. Anal. Calcd for $C_{38}H_{43}BF_{15}P$: C, 55.22; H, 5.24. Found: C, 54.76; H, 5.11. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ 5.19 (d, $^1J_{PH}$ = 432.0 Hz, 1H, PH), 3.42 (br, 1:1:1:1 q, $^1J_{BH} \approx$ 92 Hz, 1H, BH), 2.15 (m, 2H, ═CH_2^A), 1.76 (m, 2H, ═CH_2^B), 1.65 (d, $^3J_{PH}$ = 15.7 Hz, 27H, P*t*Bu), 1.29 (m, 2H, CH_2^A), 1.27 (m, 2H, CH_2^B), 0.71 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_3^B), 0.70 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_3^A). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ 144.2 (═C^{Pr}), 132.6 (br, ═CB)[1], 38.0 (d, $^1J_{PC}$ = 27.7 Hz, *t*Bu), 36.5 (═CH_2^B), 36.0 (═CH_2^A), 30.3 (*t*Bu), 21.6 (CH_2^B), 21.3 (CH_2^A), 14.7 (CH_3^A), 14.5 (CH_3^B) [C_6F_5 not listed; [1] from GHMBC experiment]. ^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): δ −131.2 (br m, 4F, *o*), −165.4 (t, $^3J_{FF}$ = 20.3 Hz, 2F, *p*), −168.0 (m, 4F, *m*) (B C_6F_5), −140.5 (br m, 2F, *o*), −165.2 (t, $^3J_{FF}$ = 21.0 Hz, 1F, *p*), −167.5 (m, 2F, *m*) (C_6F_5). ^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 298 K): δ −21.6 ($\nu_{1/2} \approx$ 50 Hz). ^{11}B NMR (192 MHz, CD_2Cl_2, 298 K): δ −21.6 (d, $^1J_{BH} \approx$ 91 Hz). ^{31}P{^{1}H} NMR (242 MHz, CD_2Cl_2, 298 K): δ 59.6 ($\nu_{1/2} \approx$ 3 Hz). ^{31}P NMR (242 MHz, CD_2Cl_2, 298 K): δ 59.6 (dm, $^1J_{PH} \approx$ 432 Hz). X-ray data: *a* = 13.2049(3) Å, *b* = 16.7532(4) Å, *c* = 17.8062(6) Å, β = 98.306(2)°, *V* = 3897.85(18) Å^3, *Z* = 4, monoclinic, space group $P2_1/n$, 6021 observed reflections ($I \geq 2\sigma(I)$), 513 refined parameters, R1 = 0.0415, wR2(all) = 0.1103, GOF = 1.047.

Synthesis of [*t*Bu$_3$PH][Ph$_2$C═C(C_6F_5)BH(C_6F_5)$_2$], 10g. A solution of **4g** (69 mg, 0.1 mmol) and *t*Bu$_3$P (20 mg, 0.1 mmol) was dissolved in toluene (1 mL), and the reaction mixture was kept under a

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hydrogen atmosphere of 60 bar (by using an autoclave system) and heated at 80 °C for a period of 24 h. To isolate the salt, the reaction mixture was layered with heptane and placed in a −35 °C freezer overnight to yield a pale brown precipitate. The supernatant was decanted, and washing the residue with pentane twice (2 × 2 mL) and drying *in vacuo* afforded **10g** as a white powder (65 mg, 72%). Crystals suitable for X-ray crystal structure analysis were grown from a CH_2Cl_2/heptane (v/v = 1:4) solution of **10g** at room temperature. Anal. Calcd for $C_{44}H_{39}BF_{15}P$: C, 59.08; H, 4.39. Found: C, 58.81; H, 4.36. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ 7.29 (m, 2H, *o*-Ph^B), 7.04 (m, 4H, m.*o*-Ph^A), 6.97 (m, 2H, *m*-Ph^B), 6.96 (m, 1H, *p*-Ph^A), 6.89 (m, 1H, *p*-Ph^B), 5.11 (d, $^1J_{PH}$ = 429.6 Hz, 1H, PH), 3.62 (br, 1:1:1:1 q, $^1J_{HB} \approx$ 93 Hz, 1H, BH), 1.65 (d, $^3J_{PH}$ = 15.9 Hz, 27H, *t*Bu). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): n.o. (=CB), 147.2 (*i*-Ph^A), 145.4 (=C^{Ph}), 145.0 (*i*-Ph^B), 129.8 (*o*-Ph^B), 128.8 (*o*-Ph^A), 127.7 (*m*-Ph^A), 126.8 (*m*-Ph^B), 125.7 (*p*-Ph^A), 125.4 (*p*-Ph^B), 38.1 (d, $^1J_{PC}$ = 26.8 Hz, *t*Bu), 30.4 (*t*Bu) [C_6F_5 not listed]. ^{19}F{^{1}H} NMR (564 MHz, CD_2Cl_2, 298 K): δ −130.7 (br m, 4F, *o*), −165.3 (t, $^3J_{FF}$ = 20.2 Hz, 2F, *p*), −168.3 (m, 4F, *m*) (BC_6F_5), −140.0 (m, 2F, *o*), −163.8 (t, $^3J_{FF}$ = 21.1 Hz, 1F, *p*), −167.3 (m, 2F, *m*) (C_6F_5). ^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 298 K): δ −21.5 ($\nu_{1/2} \approx$ 50 Hz). ^{11}B NMR (192 MHz, CD_2Cl_2, 298 K): δ −21.5 (d, $^1J_{BH} \approx$ 91 Hz). ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 298 K): δ 60.0 ($\nu_{1/2} \approx$ 4 Hz). ^{31}P NMR (243 MHz, CD_2Cl_2, 298 K): δ 60.0 (dm, $^1J_{PH} \approx$ 430 Hz). X-ray data: a = 13.3052(2) Å, b = 15.4057(4) Å, c = 20.3224(5) Å, V = 4165.60(16) Å^3, Z = 4, orthorhombic, space group $P2_12_12_1$, 6975 observed reflections ($I \geq 2\sigma(I)$), 567 refined parameters, R1 = 0.0352, wR2(all) = 0.0858, GOF = 1.052.

Synthesis of [*t*Bu$_3$PH][(MeC$_6$H$_4$)$_2$C=C(C$_6$F$_5$)BH(C$_6$F$_5$)$_2$], 10h. A similar procedure to that mentioned above for the preparation of compound **10g** was carried out using the starting material **4h** to yield **10h** as a white powder (76 mg, 81%). Anal. Calcd for $C_{46}H_{43}BF_{15}P$: C, 59.88; H, 4.70. Found: C, 59.59; H, 4.41. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ 7.13 (d, $^3J_{HH}$ = 7.7 Hz, 2H, *o*-tol^A), 6.90 (d, $^3J_{HH}$ = 8.0 Hz 2H, *o*-tol^B), 6.83 (d, $^3J_{HH}$ = 8.0 Hz, 2H, *m*-tol^B), 6.77 (d, $^3J_{HH}$ = 7.7 Hz, 2H, *m*-tol^A), 5.15 (d, $^1J_{PH}$ = 430.7 Hz, 1H, PH), 3.57 (br, 1:1:1:1 q, $^1J_{HB} \approx$ 92 Hz, 1H, BH), 2.17 (s, 3H, CH_3 tol^B), 2.16 (s, 3H, CH_3 tol^A), 1.65 (d, $^3J_{PH}$ = 15.8 Hz, 27H, *t*Bu). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ 145.4 (=C^{tol}), n.o. (=CB), 144.4 (*i*-tol^B), 142.4 (*i*-tol^A), 135.1 (*p*-tol^B), 134.9 (*p*-tol^A), 129.7 (*o*-tol^A), 128.7 (*o*-tol^B), 128.3 (*m*-tol^B), 127.3 (*m*-tol^A), 38.1 (d, $^1J_{PC}$ = 25.2 Hz, *t*Bu), 30.4 (*t*Bu), 21.1 (CH_3^B), 20.9 (CH_3^A) [C_6F_5 not listed]. ^{19}F{^{1}H} NMR (564 MHz, CD_2Cl_2, 298 K): δ −130.7 (br m, 4F, *o*), −165.6 (t, $^3J_{FF}$ = 20.3 Hz, 2F, *p*), −168.4 (m, 4F, *m*) (BC_6F_5), −140.1 (m, 2F, *o*), −164.1 (t, $^3J_{FF}$ = 21.2 Hz, 1F, *p*), −167.4 (m, 2F, *m*) (C_6F_5). ^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 298 K): δ −21.5 ($\nu_{1/2} \approx$ 60 Hz). ^{11}B NMR (192 MHz, CD_2Cl_2, 298 K): δ −21.5 (d, $^1J_{BH} \approx$ 89 Hz). ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 298 K): δ 59.8 ($\nu_{1/2} \approx$ 5 Hz). ^{31}P NMR (243 MHz, CD_2Cl_2, 298 K): δ 59.8 (dm, $^1J_{PH} \approx$ 430 Hz).

Synthesis of [HC(CH$_2$CH$_2$)$_3$NH][*t*Bu(H)C=C(C$_6$F$_5$)BH(C$_6$F$_5$)$_2$], 11d. A solution of **4d** (59 mg, 0.1 mmol) and quinuclidine (11 mg, 0.1 mmol) was dissolved in toluene (2 mL), and the mixture was stirred 24 h under a hydrogen atmosphere of 60 bar (by using the autoclave system). Pentane (10 mL) was added, after which the supernatant was decanted. The residue was then dried *in vacuo* to afford **11d** as a white powder (64 mg, 91%). Crystals suitable for X-ray crystal structure analysis were grown from a CH_2Cl_2/pentane (v/v = 1:3) solution of **11d** at −35 °C. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 6.82 (br, 1H, NH), 5.90 (s, 1H, =CH), 2.75 (br, 1:1:1:1 q, $^1J_{BH} \approx$ 82 Hz, 1H, BH), 2.19 (m, 6H, NCH_2), 1.03 (s, 9H, *t*Bu), 0.84 (m, 1H, CH), 0.60 (m, 6H, CH_2). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ 145.1 (=CH), n.o. (=CB), 46.9 (NCH_2), 35.0 (*t*Bu), 30.4 (*t*Bu), 22.0 (CH_2), 18.1 (CH) [C_6F_5 not listed]. ^{19}F NMR (470 MHz, C_6D_6, 298 K): δ −131.2 (br m, 4F, *o*), −161.2 (t, $^3J_{FF}$ = 20.5 Hz, 2F, *p*), −165.5 (m, 4F, *m*) (B C_6F_5), −140.8 (br m, 2F, *o*), −161.6 (t, $^3J_{FF}$ = 21.4 Hz, 1F, *p*), −165.3 (m, 2F, *m*) (C_6F_5). ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 298 K): δ −17.8 ($\nu_{1/2} \approx$ 40 Hz). ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ −17.8 (d, $^1J_{BH} \approx$ 81 Hz). X-ray data: a = 9.5401(3) Å, b = 19.9821(6) Å, c = 17.8109(5) Å, β = 97.067(2)°, V = 3369.52(17) Å^3, Z = 4, monoclinic, space group $P2_1/c$, 4846 observed reflections ($I \geq 2\sigma(I)$), 503 refined parameters, R1 = 0.0576, wR2(all) = 0.1690, GOF = 1.109.

Synthesis of [N(CH$_2$CH$_2$)$_3$NH][*t*Bu(H)C=C(C$_6$F$_5$)BH(C$_6$F$_5$)$_2$], 12d. A solution of **4d** (59 mg, 0.1 mmol) and 1,4-diazabicyclo[2.2.2]-octane (DABCO, 11 mg, 0.1 mmol) was dissolved in toluene (2 mL), and the mixture was stirred 24 h under a hydrogen atmosphere of 60 bar (by using the autoclave system). Pentane (10 mL) was added, after which the supernatant was decanted. The residue was then dried *in vacuo* to afford **12d** as a white powder (61 mg, 86%). ^{1}H NMR (500 MHz, THF-d_8, 298 K): δ 8.95 (s, 1H, NH), 5.43 (s, 1H, =CH), n.o. (BH), 3.03 (s, 12H, CH_2), 0.80 (s, 9H, *t*Bu). ^{13}C{^{1}H} NMR (126 MHz, THF-d_8, 298 K): δ 143.1 (=CH), n.o. (=CB), 46.3 (CH_2), 35.9 (*t*Bu), 30.6 (*t*Bu) [C_6F_5 not listed]. ^{19}F NMR (470 MHz, THF-d_8, 298 K): δ −130.5 (br m, 4F, *o*), −166.6 (t, $^3J_{FF}$ = 20.1 Hz, 2F, *p*), −169.3 (m, 4F, *m*) (B C_6F_5), −140.6 (m, 2F, *o*), −166.4 (t, $^3J_{FF}$ = 20.8 Hz, 1F, *p*), −168.4 (m, 2F, *m*) (C_6F_5). ^{11}B{^{1}H} NMR (160 MHz, THF-d_8, 298 K): δ −18.7 ($\nu_{1/2} \approx$ 50 Hz). ^{11}B NMR (160 MHz, THF-d_8, 298 K): δ −18.7 (d, $^1J_{BH} \approx$ 92 Hz).

Synthesis of [N(CH$_2$CH$_2$)$_3$NH][(C$_3$H$_7$)$_2$C=C(C$_6$F$_5$)BH(C$_6$F$_5$)$_2$], 12f. A solution of **4f** (62 mg, 0.1 mmol) and 1,4-diazabicyclo[2.2.2]-octane (DABCO, 11 mg, 0.1 mmol) was dissolved in toluene (2 mL), and the mixture was stirred 24 h under a hydrogen atmosphere of 60 bar (by using the autoclave system). Pentane (10 mL) was added, after which the supernatant was decanted. The residue was then dried *in vacuo* to afford **12f** as a white powder (59 mg, 79%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 10.75 (br, 1H, NH), n.o. (BH), 3.14 (s, 12H, CH_2), 2.09 (m, =CH_2^A), 1.78 (m, =CH_2^B), 1.29 (m, CH_2^A), 1.25 (m, CH_2^B), 0.71 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_3^B), 0.67 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_3^A). ^{13}C NMR (126 MHz, CD_2Cl_2, 298 K): δ 144.4 (=C^{Pr}), 132.1 (br, =CB)[1], 45.3 (CH_2), 36.4 (=CH_2^B), 36.2 (=CH_2^A), 21.7 (CH_2^B), 21.2 (CH_2^A), 14.8 (CH_3^A), 14.5 (CH_3^B) [C_6F_5 not listed; [1] from GHMBC experiment]. ^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): δ −131.8 (br m, 4F, *o*), −164.4 (t, $^3J_{FF}$ = 20.2 Hz, 2F, *p*), −167.3 (m, 4F, *m*) (BC_6F_5), −140.1 (br, 2F, *o*), −164.3 (t, $^3J_{FF}$ = 21.1 Hz, 1F, *p*), −167.0 (m, 2F, *m*) (C_6F_5). ^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 298 K): δ −21.6 ($\nu_{1/2} \approx$ 50 Hz). ^{11}B NMR (192 MHz, CD_2Cl_2, 298 K): δ −21.6 (d, $^1J_{BH} \approx$ 88 Hz).

General Procedure for Catalytic Hydrogenation Reactions. *Imines.* (a) Reactions at 5 bar of H_2: In a glovebox, a 100 mL glass bomb equipped with a small stir bar and Teflon screw top was charged with imine (1 mmol), catalyst (0.05 mmol), and dry toluene (2.5 mL). The reaction bomb was degassed three times through a freeze−pump−thaw cycle on the vacuum/H_2 line and filled with H_2 (4 bar) at −196 °C. The flask was then sealed and warmed to room temperature. The reaction was placed in a preheated oil bath set to 120 °C (H_2 pressure: ca. 5 bar). Aliquots were withdrawn at 12 h intervals, and the reaction was monitored by NMR spectroscopy. (b) Reactions at 110 bar of H_2: In a glovebox, a series 4560 mini benchtop Parr Instrument reactors was equipped with six 20 mL vials each containing a small stir bar. The vials were charged with the imine, catalyst, and toluene and loosely capped. The reactor was assembled in the glovebox. The reactor was taken out of the box and connected to a hydrogen line. The line was purged five times with hydrogen from a gas purifier cartridge (Matheson type 452), and then the reactor was purged five times before filling with dihydrogen (behind a blast shield). The reactor was heated with an oil bath to 120 °C for 20 min to equilibrate, and then the H_2 pressure was increased to 110 bar. Aliquots were taken in a glovebox after venting and rapid cooling. Identification of the amine products was by comparison of ^{1}H NMR spectra with literature values.

Enones. Alkenylborane (**4**) (0.025 mmol) and 1,4-diazabicyclo[2.2.2]octane (2.8 mg, 0.025 mmol) were dissolved in C_6D_6 (2 mL), enone (**15**) (0.5 mmol) was added, and the light yellow solution was stirred for 48 h under a hydrogen atmosphere of 10 bar at 80 °C by using an autoclave system. The resulting solution was analyzed by NMR spectroscopy before and after completion of the reaction. The sample contains a mixture of enone (**15**) and ketone (**16**). Afterward the reaction was quenched with 2 mL of pentane (normal pentane with moisture), and then all of the solvent was removed under reduced pressure. Pure ketone was isolated by silica gel chromatography.

X-ray Data Collection and Reduction. (Münster) Crystals were coated in FOMBLIN Y oil, mounted on a glass fiber, and placed under an N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data were collected on Nonius Kappa CCD diffractometers,

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both with APEXII detectors. In the case of Mo radiation a rotating anode generator equipped with Montel mirrors was used. The frames were integrated with the DENZO-SMN software package[26] including absorption corrections[27] using the empirical multiscan method.

Structure Solution and Refinement. (Toronto) Non-hydrogen atomic scattering factors were taken from the literature tabulations.[28] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine.[29] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F^2, minimizing the function $w(F_o - F_c)^2$ where the weight w is defined as $4F_o^2/2\sigma(F_o^2)$, where F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C−H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. H atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C atom to which they are bonded. The H atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Additional details are provided in the Supporting Information.

Structure Solution and Refinement. (Münster). Non-hydrogen atomic scattering factors were taken from the literature tabulations.[28] The heavy atom positions were determined using direct or Patterson methods employing the SHELXS routine.[29] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F^2 employing the SHELXL routine. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C−H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming C−H bond lengths between 0.94 and 0.99 Å depending on the type of the carbon atom. H atom temperature factors were fixed at 1.20 or 1.50 times the isotropic temperature factor of the C atom to which they are bonded. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Additional data for the structural studies are deposited.

■ ASSOCIATED CONTENT

Supporting Information

Synthetic, experimental, and crystallographic details are deposited. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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