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CO_2 and Formate Complexes of Phosphine/Borane Frustrated Lewis Pairs

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Abstract: The reaction of a solution of $B(C_6F_4H)_3$ and either iPr_3P or tBu_3P with CO_2 afforded the species $R_3P(CO_2)B(C_6F_4H)_3$ (R = *i*Pr (**1**), *t*Bu (**2**)). In a similar fashion the boranes, $RB(C_6F_5)_2$ (R = hexyl, cyclohexyl (Cy), norbornyl), $ClB(C_6F_5)_2$, or $PhB(C_6F_5)_2$ were combined with tBu_3P and CO_2 to give the species $tBu_3P(CO_2)BR(C_6F_5)_2$ (R = hexyl (**3**), Cy (**4**), norbornyl (**5**), Cl (**6**), Ph (**7**)). Similarly, the compounds $[tBu_3PH][RBH(C_6F_5)_2]$ (R = hexyl (**8**), Cy (**9**), norbornyl (**10**)) were prepared by reaction of the precursor frustrated Lewis pair (FLP) with H_2. Subsequent reactions of **9** and **10** with CO_2 afforded the species $[((C_6F_5)_2BR)_2(\mu\text{-}HCO_2)][tBu_3PH]$ (R = Cy (**11**), norbornyl (**12**)). In related chemistry, combinations of the boranes $RB(C_6F_5)_2$ (R = hexyl, Cy, norbornyl) with tBu_3P treated with an equivalent of formic acid gave $[(C_6F_5)_2BR(HCO_2)][tBu_3PH]$ (R = hexyl (**13**), Cy (**14**), norbornyl (**15**)). Subsequent addition of an additional equivalent of borane provides a second synthetic route to **11** and **12**. Crystallographic studies of compounds **2–6** and **8–14** are reported and discussed. Further understanding of the FLP complexation and activation of CO_2 is provided by computational studies.

Keywords: boranes · carbon dioxide fixation · formate · frustrated Lewis pairs · phosphines

Introduction

The phenomenon of global warming is largely attributable to the increasing concentration of carbon dioxide in the atmosphere.[1] A variety of materials including zeolites, silica gels, aluminas, activated carbons,[2] as well as sophisticated metal–organic frameworks (MOFs)[3] have been developed in an effort to sequester this greenhouse gas. Although these approaches are creative, they are based on large-scale storage of bound CO_2. An alternative to these methods involves the conversion of carbon dioxide to a C_1 chemical feedstock.[4] In fact, some years ago, the conversion of CO_2 to methanol was put forward by Olah et al. as the basis for the "methanol economy".[5] To this end, efforts to develop homogeneous and heterogeneous catalytic processes have targeted the conversion of CO_2 into alternative fuels and organic building blocks.[4,6] A fundamental challenge in this field is the remarkable thermodynamic stability and limited reactivity of CO_2. Although CO_2 reacts with strong nucleophiles and coordinatively unsaturated transition metal species, the presence of hydroxide results in the formation of bicarbonate salts.[7] On the other hand, reactions of main-group systems with CO_2 have only just begun to garner attention. For example, recent reports have described the isolation of a CO_2 adduct of a nitrogen base[8] and the carboxylation of N-heterocyclic carbenes[9] that undergo subsequent catalytic reduction to methanol. Similarly, reactions of CO_2 with silyl, germyl and strontium amides have been described.[10]

Our own efforts have focused on the development of new strategies for the activation of small molecules employing simple main-group systems. Frustrated Lewis pairs (FLPs) have proven to be highly reactive systems derived from the synergistic action of unquenched Lewis acidic and basic sites on the substrate.[11] The first reports of such reactivity demonstrated the activation of H_2 by combinations of sterically encumbered phosphines and boranes and their subsequent use in hydrogenation catalysis.[12] Since then, a broadening range of FLPs has been used in hydrogenation catalysis[13] and in reactivity with a variety of substrates including disulfides, B–H bonds,[14] olefins,[15,16] alkynes,[16,17] cyclopropanes,[18] N_2O,[19] and CO_2.[20–22] Much of this work has been recently reviewed.[11]

In recent work, we have communicated the use of sterically encumbered phosphines and boranes in the reversible binding of CO_2 (Scheme 1, A and B).[20] In subsequent work O'Hare and co-workers demonstrated the stoichiometric reduction of amine/borane FLP–CO_2 complexes to methanol under rather forcing conditions (4 d, 160 °C).[21] Shortly

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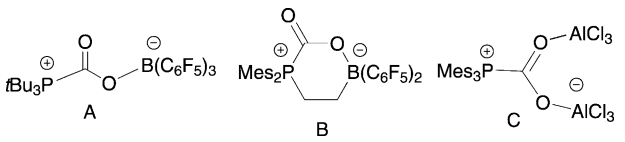
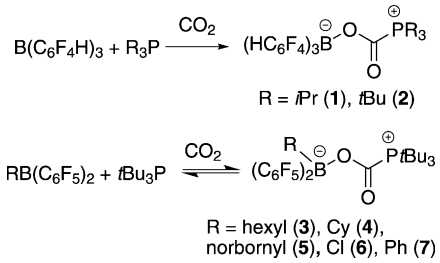


Scheme 1. CO_2 Complexes of FLPs.

thereafter, we demonstrated that P/Al-based FLPs[22a] (Scheme 1, C) react with NH_3BH_3 effecting similar reduction in 5 min at 25 °C.[22b] Most recently, Piers et al. demonstrated that FLP systems could effect the catalytic deoxygenative hydrosilylation of CO_2 to methane.[23a] In this full report, we examine reactions of phosphine/borane FLP systems with CO_2 in greater detail. The impact of variations of the Lewis acids on bound CO_2 and the chemistry that affords related formate derivatives is probed. The understanding of the nature of these systems is further augmented by computational studies.

Results and Discussion

In a fashion similar to that previously communicated for the synthesis of $tBu_3P(CO_2)B(C_6F_5)_3$,[20] reaction of a solution of $B(C_6F_4H)_3$ and either iPr_3P or tBu_3P in CH_2Cl_2 under an atmosphere of carbon dioxide proceeded smoothly to yield the white solids **1** and **2** in 77 and 59%, respectively. These products exhibited $^{31}P\{^1H\}$ NMR resonances at $\delta = 37.3$ and 45.4 ppm, and $^{11}B\{^1H\}$ NMR resonances at $\delta = -2.3$ and -2.4 ppm, respectively, which are in accordance with the quaterization of the boron center.[23b] Both compounds displayed signals at about $\delta = -134$ and -143 ppm in the ^{19}F NMR spectra. The ^{13}C NMR spectra of **1** and **2** showed resonances expected for the constituent phosphorus and boron fragments as well as signals at $\delta = 161.6$ and 162.2 ppm, which exhibited C–P couplings of $J = 112$ and 93 Hz, respectively. These latter signals were consistent with the presence of P–C bonds derived from phosphine binding to CO_2. Infrared spectra showed absorptions at $\tilde{\nu} = 1700$ and 1699 cm^{-1} for **1** and **2**, respectively, attributable to a C=O stretch vibration. Collectively, these data support the formulations of these products as $R_3P(CO_2)B(C_6F_4H)_3$ (R = *i*Pr (**1**), *t*Bu (**2**); Scheme 2).



Scheme 2. Synthesis of compounds **1**–**7**.

It is noteworthy that in contrast with the formation of **1**, reaction of iPr_3P with $B(C_6F_5)_3$ does not result in the capture of CO_2, even under a CO_2 atmosphere. Rather, nucleophilic aromatic substitution at the *para* position of $B(C_6F_5)_3$ by the phosphine yields the zwitterionic isomer $iPr_3P(p\text{-}C_6F_4)B(F)(C_6F_5)_2$.[24] The formation of **1** results from the inability of this FLP to undergo *para*-substitution, thus demonstrating a desirable feature of $B(C_6F_4H)_3$.

The boranes $RB(C_6F_5)_2$ (R = hexyl, cyclohexyl (Cy), norbornyl) were generated through in situ hydroboration of the appropriate olefin precursor by $HB(C_6F_5)_2$. These resulting boranes were then individually combined with tBu_3P under an atmosphere of CO_2, giving the species $R_3P(CO_2)BR(C_6F_5)_2$ (R = hexyl (**3**), Cy (**4**), norbornyl (**5**)) in yields of 75, 71, and 86%, respectively (Scheme 2). These compounds exhibited similar spectroscopic parameters to those described for **1** and **2**. Although these compounds were isolable and stable at low temperature, each of these species was observed to lose CO_2 above -15 °C.

In a similar fashion, reactions of $ClB(C_6F_5)_2$ or $PhB(C_6F_5)_2$ with tBu_3P under a CO_2 atmosphere afforded the compounds $tBu_3P(CO_2)B(C_6F_5)_2R$ (R = Cl (**6**), Ph (**7**)) in 79 and 55% yields (Scheme 2). Similar to **3**–**5** these compounds were also sensitive, undergoing facile loss of CO_2, regenerating the respective FLP. Nonetheless some of these latter species were stable for a few hours in CD_2Cl_2 at room temperature.

Crystallographic studies confirmed the structures of **2**–**6** (Figures 1–3) in which the CO_2 is bound through the carbon atom to P and to B through one of the O atoms. As the

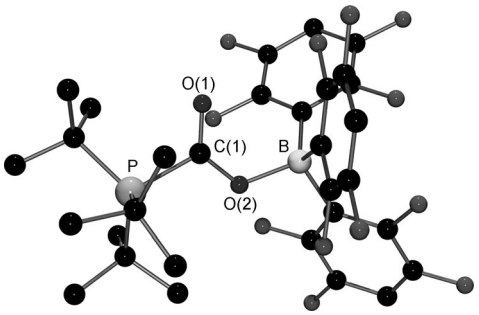


Figure 1. POV depiction of **2**.

phosphine fragments are identical in these species, the P–C bond length in **2**–**6** are indistinguishable averaging 1.89(1) Å with the exception of **5** where the P–C bond length is 1.896(3) Å (Table 1). Although the B–O bond lengths in these compounds range from 1.527(3)–1.592(3), the longest B–O bond length is in **5**. The shortest B–O bond length is 1.527(3) Å in **6**, consistent with the Lewis acidity of $ClB(C_6F_5)_2$. The corresponding C–O bond lengths range from 1.281(5)–1.300(2) Å in **2**–**6**, whereas the terminal C=O bond lengths in **2**, **3**, **4**, and **6** average 1.204(4) Å. Only compound **5** deviates from these typical values. This seems to be attrib-

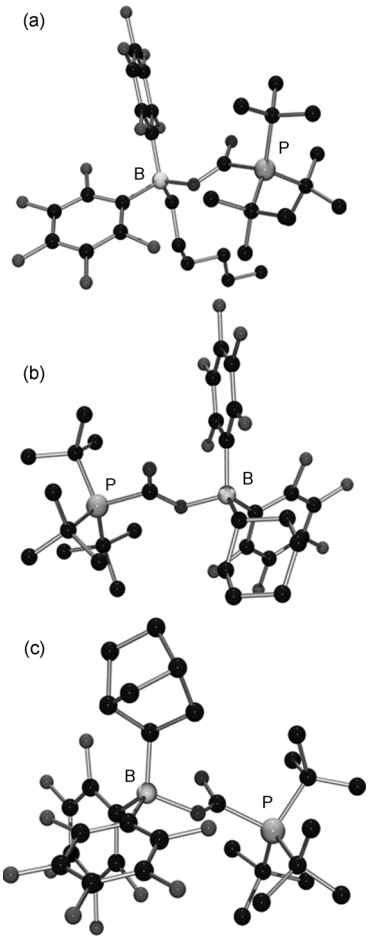


Figure 2. POV depictions of a) **3**, b) **4**, and c) **5**.

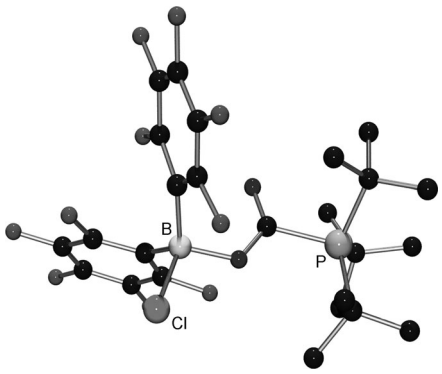


Figure 3. POV depictions of **6**.

uted to a combination of steric bulk of the norbornyl substituent and the lesser Lewis acidity of the borane.

All of the above-described compounds evolve CO_2 upon warming. Indeed in some cases, the compounds were found to be unstable at room temperature. Similarly, exposure of these complexes to H_2 resulted in the liberation of CO_2 and the subsequent heterolytic activation of H_2 to give the corresponding $[t\mathrm{Bu_3PH}][HBR_3]$ salts. To confirm these observations, the compounds $[t\mathrm{Bu_3PH}][RBH(C_6F_5)_2]$ (R = hexyl (**8**), Cy (**9**), norbornyl (**10**)) were prepared initially generating the borane in situ, followed by combination with $t\mathrm{Bu_3P}$ and subsequent exposure to 2 bar H_2 at room temperature. The resulting salts **8**–**10** were isolated in 60, 66, and 77% yield, respectively. These compounds exhibited typical PH and BH spectroscopic signatures. The P–H fragments in **8**–**10** gave rise to ^{1}H NMR signals at $\delta = 5.46$, 5.49, and 5.28 ppm with P,H coupling constants of $J = 436.6$, 437.2, and 432.5 Hz, respectively. The corresponding B–H resonances were observed at $\delta = 2.72$, 2.44, and 2.46 ppm, respectively, with the associated ^{11}B{^{1}H} signals at $\delta = -18.4$, -17.6, and -18.5 ppm, respectively. Analogous preparation of the deuterated analogues $[t\mathrm{Bu_3PD}][RBD(C_6F_5)_2]$ (R = hexyl ([D$_2$]**8**), Cy, ([D$_2$]**9**), norbornyl ([D$_2$]**10**)) were confirmed by the observations of ^{2}H NMR resonances attributable to the P–D fragments at $\delta = 5.45$, 5.49, and 5.30 ppm, respectively, with P,D coupling constants of $J = 66.1$, 66.9, and 66.8 Hz, respectively. The resonances for the corresponding B–D units were observed at $\delta = 2.71$, 2.49, and 2.50 ppm, respectively. The formation of the products **8**, **9**, and **10** was further confirmed by X-ray crystallographic studies (Figure 4). The metric parameters of these salts were unexceptional.

Table 1. Selected bond lengths and IR data for different B/P FLP–CO_2 Complexes.

Compound	P–C [Å]	C–O [Å]	C=O [Å]	O–B [Å]	$\tilde{\nu}$ [cm^{-1}]
A	1.893(1)	1.299(2)	1.208(2)	1.547(2)	1695
B	1.900(3)	1.284(4)	1.209(4)	1.550(4)	1694
2	1.892(2)	1.300(2)	1.203(2)	1.556(2)	1699
3	1.896(4)	1.281(5)	1.208(5)	1.579(5)	1693
4	1.893(3)	1.289(4)	1.206(4)	1.587(4)	1698
5	1.896(3)	1.284(3)	1.210(3)	1.592(3)	1686
6	1.888(2)	1.297(3)	1.201(3)	1.527(3)	1702

Subsequent reactions of **9** and **10** with CO_2 were undertaken. Heating a solution of **9** to 60 °C overnight under CO_2, resulted in the formation of a new species **11**. The product **11** was recrystallized from dichloromethane/pentane affording 45% yield based on one equivalent of **9**. NMR data for **11** revealed a broad ^{11}B NMR resonance at $\delta = 5.1$ ppm, as well as the ^{1}H NMR resonances including a singlet at $\delta = 8.04$ ppm and a ^{13}C{^{1}H} NMR signal at $\delta = 173.4$ ppm. These data are in accordance with the existence of a bridging formate unit. Infrared absorption at $\tilde{\nu} = 1631$ cm^{-1} also supports this proposition. A doublet at $\delta = 5.09$ ppm in the ^{1}H NMR spectrum exhibits P,H coupling of $J = 427.7$ Hz, consistent with the presence of the phosphonium cation $[t\mathrm{Bu_3PH}]^+$, supporting the formulation of **11** as $[t\mathrm{Bu_3PH}][((C_6F_5)_2BCy)_2(\mu\text{-}HCO_2)]$ (Scheme 3). Similarly, the reaction of **10** afforded the analogous species $[t\mathrm{Bu_3PH}][(\mathrm{norbornylB}(C_6F_5)_2)_2(\mu\text{-}HCO_2)]$ (**12**) as a 1:1 mixture of the respective pairs of *rac* and *meso* diastereomers, which exhibited similar core spectral parameters as observed for **11**. The formation of **11** and **12** was confirmed by X-ray crystallography (Figure 5). The anions of these salts are comprised of two borane fragments bridged by a formate unit. The resulting B–O distances in

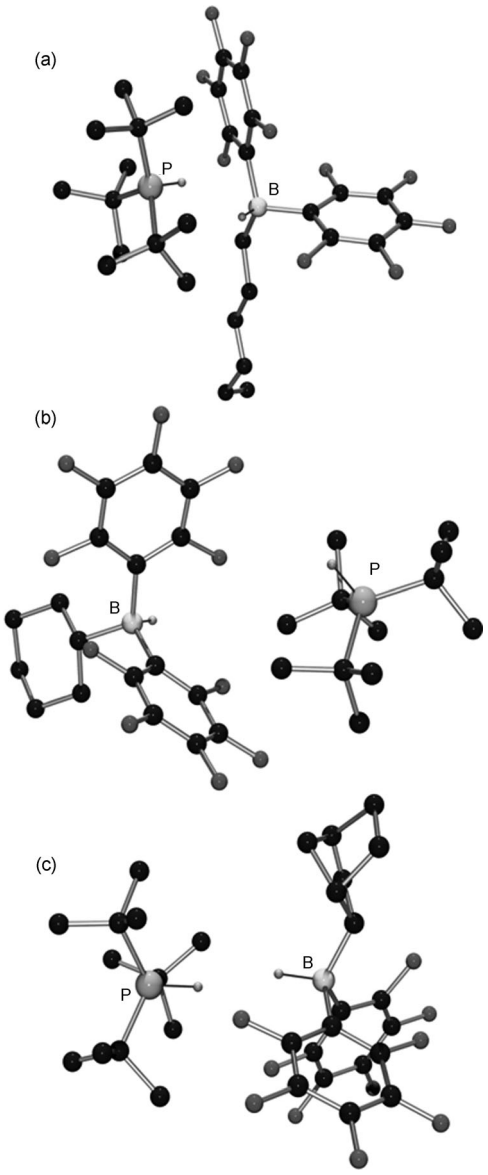
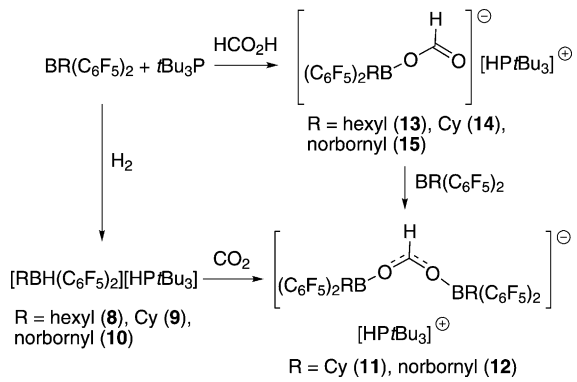


Figure 4. POV depictions of a) **8**, b) **9**, and c) **10**.

the anion of **11** are 1.611(7) and 1.567(7) Å, the corresponding C–O distances in **11** are 1.253(6) and 1.254(6) Å, and



Scheme 3. Synthesis of compounds **8**–**15**.

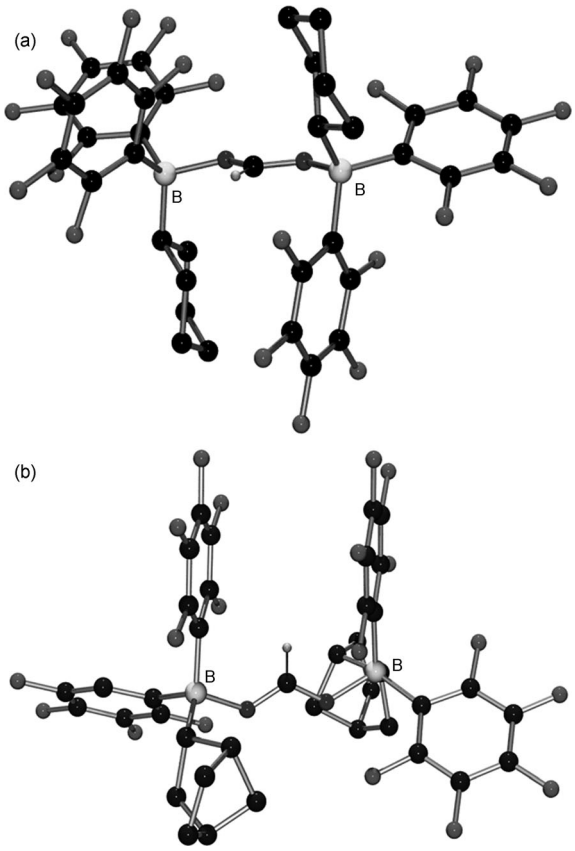


Figure 5. POV depictions of the anions of a) **11** and b) **12**.

the O-C-O angle is 121.2(5)°. The average of these B–O distances is slightly longer than those seen in the recently reported salt $[TMPH][((C_6F_5)_3B)_2(\mu\text{-}HCO_2)]$[23s] (TMP = 2,2,6,6-tetramethylpiperidine; B–O: 1.587(3), 1.584(3) Å; C–O: 1.256(3), 1.268(3) Å), whereas the C–O distances (B(1)–O(1) 1.611(7), B(2)–O(2) 1.567(7), 1.253(6), 1.254(6) Å) in **11** are slightly shorter. The B–O distance of 1.566(4) Å in **12** is similar to that in **11**, whereas the C–O distances of 1.249(3) Å is slightly shorter.

In related chemistry, the boranes $RB(C_6F_5)_2$ (R = hexyl, Cy, norbornyl) were combined with one equivalent of tBu_3P and treated with one equivalent of formic acid. These reactions occur rapidly and afford the formation of the new species **13**–**15**, respectively. These products exhibit ^{31}P and ^{1}H NMR resonances consistent with the presence of the phosphonium cation $[tBu_3PH]^+$. The ^{1}H NMR data also show resonances at $\delta = 8.29$, 8.20, and 8.17 ppm suggesting the formation of the formato–borate anions, thus inferring the formation of these products as $[tBu_3PH][(C_6F_5)_2BR(HCO_2)]$ (R = hexyl (**13**), Cy (**14**), norbornyl (**15**)). X-ray crystallographic studies confirmed these interpretations (Figure 6).

Additionally, some selected compounds were modeled computationally. In general, good congruence between the experimentally measured X-ray geometries and the calculated geometries is observed (Figure 7).[25] However, some de-

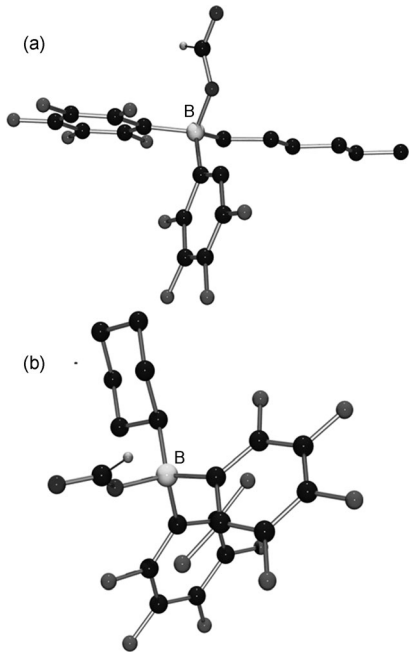


Figure 6. POV depictions of the anions of a) **13** and b) **14**.

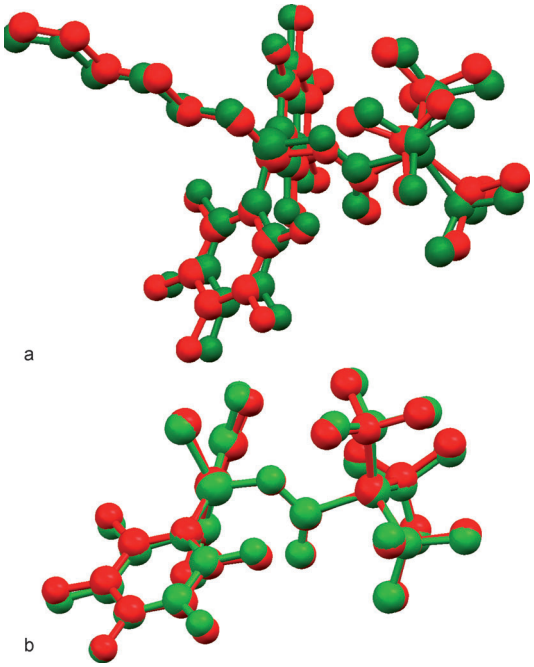


Figure 7. Overlay of X-ray structure (green) and DFT-D2 optimized structure (red) of a) **3** and b) **6**.

viations between computed and experimental structures are seen in the "outer" regions of the bulky substituents. This presumably arises from crystal packing effects.[26] The interaction energies of P*t*Bu$_3$ with the boranes RB(C$_6$F$_5$)$_2$ (*n*-hexyl, R = Cy, Cl, H) were calculated (Table 2a). The formation reaction energy values for compounds **3**, **4**, **6**, and **6a** (see Table 2) were calculated and are reported relative to the reactants (Table 2b) and relative to the FLP and CO_2 (Table 2c). In the following we will focus our discussion on the data from the B2PLYP-D3 calculations, which have an estimated accuracy of about 5–10% (TPSS-D2 data give similar trends, see the Experimental Section).

Table 2. Computed reaction energies of P*t*Bu$_3$ and RB(C$_6$F$_5$)$_2$ (a). b) Formation of **3**, **4**, **6**, and **6a** relative to separate reactants, and c) formation of **3**, **4**, **6**, and **6a** relative to the FLP and CO_2.[a]

	Compound	R	TPSS-D2	B2PLYP-D3//TPSS-D2
a		hexyl	−13.1	−10.4
		Cy	−9.7	−7.3
		Cl	−13.5	−10.8
		H	−27.8	−20.9
b	**3**	hexyl	−28.5	−24.9
	4	Cy	−31.2	−27.1
	6	Cl	−30.6	−28.5
	6a	H	−31.4	−27.7
c	**3**	hexyl	−15.4	−14.5
	4	Cy	−21.5	−19.8
	6	Cl	−17.1	−17.7
	6a	H	−3.6	−6.9

[a] The def2-TZVP basis set was used. All energies are given in [kcal mol^{-1}].

All computed reactions are strongly exothermic. The values for the phosphine–borane interactions (Table 2a) range from −7 to −21 kcal mol^{-1}. The reaction energies for the formation of **3**, **4**, and **6** with respect to free reactants vary only between −25 to −28 kcal mol^{-1}. The smaller energy values with respect to the FLP and CO_2 (Table 2c) simply reflect the different stabilities of the FLP, whereas the energetics of the bonds formed are rather similar. The formation of compound **4** is the most exothermic (see Table 2c). Similarly, the corresponding FLP forms the strongest P–B interactions, although it is almost isoenergetic with the interaction of P*t*Bu$_3$ and CH$_3$(CH$_2$)$_5$B(C$_6$F$_5$)$_2$.

These calculations also provide some insight regarding the impact of borane substituents on the compound stability. Formation of the FLP from P*t*Bu$_3$ and CyB(C$_6$F$_5$)$_2$ results in the highest energy of those calculated. The corresponding values for the FLPs derived from CH$_3$(CH$_2$)$_5$B(C$_6$F$_5$)$_2$ and ClB(C$_6$F$_5$)$_2$ are about 3 kcal mol^{-1} lower and differ by only 0.4 kcal mol^{-1}. This reflects the smaller size of the Cl substituent and the higher flexibility of the *n*-hexyl chain. On the other hand, the *n*-hexyl group is still bulkier than Cl and this leads to a CO_2 uptake energy for **4** that is comparable to the one computed for the formation of **6**.

Only the theoretically considered compound **6a** differs from the others as it gives rise to the lowest FLP self-quench energy of all tested compounds as well as the smallest reaction energy relative to the FLP (−6.9 kcal mol^{-1}). This infers a preference for the formation of the FLP as the reaction with CO_2 does not seem feasible as the energy gain for this step is comparatively small and may even generate a loss upon consideration of entropic corrections. Nonetheless, it is noteworthy that the overall reaction energy of **6a** is very similar to that of compound **6**, which suggests similar behavior towards release of CO_2.

Conclusion

In summary, a variety of FLPs comprised of phosphine and an electrophilic borane have been shown to bind CO_2 affording zwitterionic products of the form $R_3PCO_2B(C_6F_5)_2R'$. These reactions were probed experimentally and computationally. These species liberate CO_2 under mild conditions. Nonetheless, the compounds $[tBu_3PH][RBH(C_6F_5)_2]$, prepared through reaction of the precursor FLP with H_2, react with CO_2 to give the species $[((C_6F_5)_2BR)_2(\mu\text{-}HCO_2)][tBu_3PH]$. In related chemistry, phosphine/borane FLP combinations react with formic acid to give the species $[((C_6F_5)_2BR(HCO_2)][tBu_3PH]$. This chemistry demonstrates that although FLPs can capture CO_2 and formate fragments, the thermal instability of the CO_2 adducts precludes derivatization. It is for this reason that we now are exploring new FLP systems that offer stronger Lewis acids. Efforts to employ such new FLPs to effect reduction of CO_2 or to utilize CO_2 in synthetic chemistry are underway.

Experimental Section

General considerations: All manipulations were performed on a double-manifold N_2 (H_2)/vacuum line with Schlenk-type glassware or in an N_2-filled inert atmospheres glovebox. The N_2 and H_2 gases were dried by passage through a Dririte column. Solvents (Aldrich) were dried by using an Innovative Technologies solvent system (toluene, hexane, pentane, CH_2Cl_2). NMR spectra were obtained on a Bruker ARX 300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz), Bruker Avance 400 MHz spectrometer (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{19}F: 376 MHz, ^{11}B: 128 MHz, ^{31}P: 162 MHz) or, Varian Inova 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 470 MHz, ^{11}B: 160 MHz). ^{1}H NMR and ^{13}C NMR chemical shifts (δ) are given relative to TMS and referenced to the solvent signal (^{19}F relative to external $CFCl_3$; ^{11}B relative to external $BF_3{\cdot}Et_2O$). NMR assignments are supported by additional 1D and 2D NMR experiments. Assignments marked with a superscript t are tentative assignments extracted from the COSY, GHMBC and GHSQC NMR experiments. NMR spectra were recorded in CD_2Cl_2 unless otherwise stated and chemical shifts are reported in ppm. NMR solvents were purchased from Cambridge Isotopes, dried over CaH_2 (CD_2Cl_2 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). The boranes $RB(C_6F_5)_2$ (R = $(CH_2)_5CH_3$, Cy, (norbornyl), Cl, Ph) were prepared by literature methods.[27]

Synthesis of $R_3P(CO_2)B(p\text{-}C_6F_4H)_3$ (R=*i*Pr (1), *t*Bu (2)): These compounds were prepared in a similar fashion and thus only one synthetic protocol is detailed. A solution of $B(p\text{-}C_6F_4H)_3$ (81.0 mg, 0.177 mmol) in dichloromethane (2 mL) was mixed with iPr_3P (290.0 mg of a 10 wt% solution in hexane, 0.181 mmol) and cooled to − 64 °C. The solution was pressurized with CO_2 and allowed to warm to ambient temperature. The reaction mixture gradually became turbid. After stirring overnight, all volatiles were removed in vacuo at 0 °C to yield the crude product as a colorless, powdery residue. The residue was extracted with cold dichloromethane (3×2 mL) and pentane (ca. 2 mL) was added in a dropwise fashion. The mixture was filtered and the mother liquor was evaporated to dryness in vacuo. The colorless residue was recrystallized by storing a cold, saturated dichloromethane/pentane solution (ca. 1:1) at −35 °C for several days. Analytical data for **1**: yield: 90.0 mg (136.0 mmol, 77%); ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 6.87 (tt, ^3J(H,F) = 9.6, ^4J(H,F) = 7.0 Hz, 3H; *p*-CH), 2.79 (dsept, ^2J(P,H) = 14.0, ^3J(H,H) = 7.1 Hz, 3H; *i*Pr), 1.41 ppm (dd, ^3J(P,H) = 16.5, ^3J(H,H) = 7.1 Hz, 18H; *i*Pr); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K): δ = 161.3 (d, ^1J(P,C) = 112 Hz, PCO_2), 148.4 (dm, ^1J(F,C) = 235 Hz, *o*-C_6F_4H), 146.0 (dm, ^1J(F,C) = 240 Hz, *m*-C_6F_4H), 127.4 (br, *i*-C_6F_4H), 103.7 (t, ^2J(F,C) = 23 Hz, *p*-CH), 22.2 (d, ^1J(P,C) = 34.5 Hz, *i*Pr), 17.0 ppm (d, ^2J(P,C) = 3 Hz, *i*Pr); ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ = −134.7 (m, 6F; *o*-C_6F_4H), −143.1 ppm (m, 6F; *m*-C_6F_4H); ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2, 298 K): δ = −2.3 ppm (br); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 298 K): δ = 37.3 ppm; IR (KBr): $\tilde{\nu}$ = 1700 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{28}H_{24}BF_{12}O_2P$ (662.2): calcd: C 50.78, H 3.65; found: C 50.88, H 3.89.

Analytical data for **2**: yield: 180.0 mg (0.256 mmol, 59%); ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 6.85 (tt, ^3J(H,F) = 9.7, ^4J(H,F) = 6.9 Hz, 3H; *p*-CH), 1.60 ppm (d, ^3J(P,H) = 14.5 Hz, 27H; *t*Bu);^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K): δ = 162.2 (d, ^1J(P,C) = 93.0 Hz, PCO_2), 148.2 (dm, ^1J(F,C) = 237 Hz, *o*-C_6F_4H), 146.0 (dm, ^1J(F,C) = 245 Hz, *m*-C_6F_4H), 127.2 (br, *t*Bu), 103.5 (t, ^2J(F,C) = 23.0 Hz, *p*-CH), 41.3 (d, ^1J(P,C) = 19.5 Hz, *t*Bu), 30.7 ppm (*t*Bu); ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ = −133.8 (m, 6F; *o*-C_6F_4H), −143.2 ppm (m, 6F; *m*-C_6F_4H); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 298 K): δ = 45.4 ppm; ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2, 298 K): δ = −2.4 ppm; IR (KBr): $\tilde{\nu}$ = 1699 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{31}H_{30}BF_{12}O_2P$ (704.33): C 52.86, H 4.29; found C 53.05, H 4.47.

Synthesis of $tBu_3P(CO_2)BR(C_6F_5)_2$ (R=hexyl (3), Cy (4), norbornyl (5)): These compounds were prepared in a similar fashion and thus only one synthetic protocol is detailed. $(C_6F_5)_2BH$ (111.0 mg, 0.316 mmol) was suspended in pentane (2 mL). Through a syringe 1-hexene (40 μL, 0.316 mmol) was added and the solution was stirred for 10 min. Afterwards, tBu_3P (64.0 mg, 0.316 mmol) was also dissolved in pentane (1 mL) and added to the first solution. The reaction flask was cooled down to −50 °C, degassed and then filled with CO_2 (2.0 bar) and stirred for 5 min. The immediately precipitated white solid was separated from the pentane solution by removing the solvent with a cannula and the product was dried in vacuo for 5 min also at low temperature. Crystals suitable for X-ray analysis were obtained from a dichloromethane solution by slow diffusion of pentane at −35 °C. Analytical data for **3**: yield: 160 mg (0.237 mmol, 75%); ^{1}H NMR (400 MHz, CD_2Cl_2, 243 K): δ = 1.57 (d, ^3J(P,H) = 14.3 Hz, 27H; *t*Bu), 1.18 (m, 2H; 5-H), 1.16 (m, 2H; 3-H), 1.12 (m, 2H; 4-H), 1.01 (m, 2H; 1-H), 0.88 (m, 2H; 2-H), 0.79 ppm (t, ^3J(H,H) = 6.1 Hz, 3H; 6-H); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 243 K): δ = 160.9 (d, ^1J(P,C) = 92.3 Hz, PCO_2), 148.1 (dm, ^1J(F,C) ≈ 239 Hz, *o*-C_6F_5), 137.9 (dm, ^1J(F,C) ≈ 247 Hz, *p*-C_6F_5), 136.5 (dm, ^1J(F,C) ≈ 247 Hz, *m*-C_6F_5), 122.5 (br, *i*-C_6F_5), 40.2 (d, ^1J(P,C) = 19.8 Hz, *t*Bu), 33.6 (C-3), 32.2 (C-4), 30.0 (*t*Bu), 26.6 (C-2), 23.5 (C-1), 22.9 (C-5), 14.2 ppm (C-6); ^{19}F NMR (377 MHz, CD_2Cl_2, 243 K): δ = −133.8 (dd, ^3J(F,F) = 24.7, ^4J(F,F) = 7.6 Hz, 2F; *o*-C_6F_5), −161.9 (t, ^3J(F,F) = 20.6 Hz, 1F; *p*-C_6F_5), −166.1 ppm (m, 1F; *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 4.2 ppm]; ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 243 K): δ = 41.3 ppm ($\nu_{1/2}$ ≈ 2 Hz); temperature of CO_2 loss: −14 °C; IR (KBr): $\tilde{\nu}$ = 1693 cm^{-1} (s, C=O); elemental analysis calcd (%) for $C_{31}H_{40}BF_{10}O_2P$ (676.4): C 55.04, H 5.96; found: C 55.26, H 6.31.

Analytical data for **4**: yield: 140 mg (0.208 mmol, 71%); ^{1}H NMR (500 MHz, CD_2Cl_2, 243 K): δ = 1.54 (d, ^3J(P,H) = 14.3 Hz, 27H; *t*Bu), 1.58/1.18, 1.57/1.00, 1.44/0.51 (each m, Σ10H; CH_2), 1.23 ppm (m, 1H; 1-H); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 243 K): δ = 161.3 (d, ^1J(P,C) = 91.9 Hz, PCO_2), 147.4 (dm, ^1J(F,C) ≈ 232 Hz, *o*-C_6F_5), 136.4 (dm, ^1J(F,C) ≈ 240 Hz, *m*,*p*-C_6F_5), not observed (*i*-C_6F_5), 40.2 (d, ^1J(P,C) = 19.3 Hz, *t*Bu), 32.0 (br, C-1), 29.9, 28.6, 27.6 (br, CH_2), 29.9 ppm (*t*Bu); ^{19}F NMR (470 MHz, CD_2Cl_2, 243 K): δ = −132.0 (br, 2F; *o*-C_6F_5), −161.6 (br, 1F; *p*-C_6F_5), −166.0 ppm (br, 2F; *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 4.4 ppm]; ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 243 K): δ = 41.0 ppm ($\nu_{1/2}$ ≈ 9 Hz); temperature of CO_2 loss: −16 °C; IR (KBr): $\tilde{\nu}$ = 1698 cm^{-1} (s, C=O); elemental analysis calcd (%) for $C_{31}H_{38}BF_{10}O_2P$ (674.4): C 55.21, H 5.68; found: C 55.01, H 5.77.

Analytical data for **5**: yield: 340 mg (0.495 mmol, 86%). At low temperature the solubility of **5** is very poor. At room temperature the system released CO_2 partially, leading to an equilibrium of (norbornyl)$B(C_6F_5)_2$/$PtBu_3$ and compound **5** in a ratio of 4:1. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 2.05/196 (each m, 1H; 1,4-H), 1.61 (d, ^3J(P,H) = 14.2 Hz, 27H; *t*Bu), 1.42/1.17 (each m, 2H; 5-H^t), 1.41/1.28 (each m, 2H; 6-H^t), n.o. (2-

H), 1.31 (m, 4H; 3-H^t), 0.74/0.28 ppm (each br m, 2H; 7-H^t); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ = n.o. (CO), 39.7, 37.0 (C-1,4), 40.6 (*t*Bu), 37.1 (C-7), 34.9 (C-3^t), n.o. (C-2), 34.6 (C-6^t), 30.4 (*t*Bu), 29.2 ppm (C-5^t); ^{19}F NMR (470 MHz, CD_2Cl_2, 243 K): $\delta = -130.2$ (br, 2F; *o*-C_6F_5), −151.1 (br, 1F; *p*-C_6F_5), −162.3 ppm (br, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 11.2 ppm] [(norbornyl)B(C_6F_5)$_2$/P*t*Bu$_3$: ca. 80%]; ^{19}F NMR (470 MHz, CD_2Cl_2, 243 K): $\delta = -130.5$, −131.5 (each br, 2F; *o*-C_6F_5), −161.7, −162.1 (each t, ^3J(F,F) = 20.2 Hz, 1F; *p*-C_6F_5), −166.37, −166.43 ppm (each m, 2F; *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p} \approx (4.5 \pm 0.3)$ ppm] [**5**: ca. 20%]; ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 298 K): δ = 62.4 ($\nu_{1/2} \approx 3$ Hz, *t*Bu$_3$P: ca. 80%), 57.8 ($\nu_{1/2} \approx 2$ Hz, *t*Bu$_3$PH$^+$: traces], 42.5 ppm ($\nu_{1/2} \approx 3$ Hz, **5**: ca. 20%]; temperature of CO_2 loss: −16 °C; IR (KBr): $\tilde{\nu}$ = 1686 cm^{-1} (s, C=O); elemental analysis calcd (%) for: $C_{32}H_{38}BF_{10}O_2P$ (686.4): C 55.99, H 5.58; found: C 55.08, H 5.23.

Preparation of *t*Bu$_3$P(CO$_2$)B(C_6F_5)$_2$Cl (6): A 50 mL schlenk flask was charged with ClB(C_6F_5)$_2$ (150.0 mg, 0.394 mmol) and *t*Bu$_3$P (80.0 mg, 0.395 mmol) in bromobenzene (10 mL). The bright yellow solution was degassed and backfilled with CO_2 (1 bar). The reaction mixture was then stirred for two hours at room temperature. At this time, pentane (20 mL) was added precipitating an off-white solid. The solvent was decanted and the crude product was washed with pentane (3×5 mL). The product **6** was then dried in vacuo for two hours. Yield: 193.0 mg (79%). Crystals suitable for X-ray diffraction were grown from a layered CH_2Cl_2/cyclohexane solution at 25 °C. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 1.68 ppm (d, ^3J(P,H) = 14.5 Hz, *t*Bu); ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ = 161.0 (d, ^1J(P,C) = 93.4 Hz, PCO_2), 147.8 (dm, ^1J(F,C) ≈ 238 Hz, *o*-C_6F_5), 140.0 (dm, ^1J(F,C) ≈ 256 Hz, *p*-C_6F_5), 137.0 (dm, ^1J(F,C) ≈ 256 Hz, *m*-C_6F_5), n.o. (*i*-C_6F_5), 41.3 (d, ^1J(P,C) = 19.4 Hz, *t*Bu), 30.5 ppm (*t*Bu); ^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): $\delta = -133.8$ (m, 2F; *o*-C_6F_5), −159.5 (t, ^3J(F,F) = 20.3 Hz, 1F; *p*-C_6F_5), −165.6 ppm (m, 2F; *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 6.1 ppm]; ^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 298 K): δ = 2.1 ppm ($\nu_{1/2} \approx 150$ Hz); ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 298 K): δ = 45.0 ppm ($\nu_{1/2} \approx 2$ Hz); IR (KBr): $\tilde{\nu}$ = 1702 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{25}H_{27}BClF_{10}O_2P$ (626.7): C, 47.88; H, 4.34, found: C, 47.89; H, 4.46.

Preparation of *t*Bu$_3$PCO$_2$B(C_6F_5)$_2$Ph (7): A 100 mL Schlenk flask was charged with PhB(C_6F_5)$_2$ (0.100 g, 0.237 mmol) and *t*Bu$_3$P (0.048 g, 0.237 mmol) in pentane (10 mL) and bromobenzene (1 mL). The reaction mixture was degassed and backfilled with CO_2 (1 bar). The reaction instantly became cloudy and was stirred for a further 12 h. The white precipitate was allowed to settle and the solvent was decanted. The product was washed with pentane (3×5 mL) and dried in vacuo for 2 h. Yield: 0.087 g (55%); ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 7.68 (d, ^3J(H,H) = 7.4 Hz, 2H; *o*-C_6H_5), 7.30 (t, ^3J(H,H) = 7.6 Hz, 2H; *m*-C_6H_5), 7.15 (t, ^3J(H,H) = 7.3 Hz, 1H; *p*-C_6H_5), 1.16 ppm (d, ^3J(P,H) = 14.0 Hz, 27H; *t*Bu); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K): δ(partial) = 160.8 (d, ^1J(P,C) = 92.0 Hz, PCO_2); 147.4 (br d, ^1J(C,F) = 240 Hz, *o*-C_6F_5); 138.4 (br d, ^1J(C,F) = 253 Hz, *p*-C_6F_5); 136.4 (br d, ^1J(C,F) = 243 Hz, *m*-C_6F_5); 131.4 (*p*-C_6H_5); 126.5 (*o*-C_6H_5); 125.0 (*m*-C_6H_5); 39.4 (d, ^1J(P,C) = 20.0 Hz, *t*Bu); 29.3 ppm (*t*Bu); ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ = −130.5 (d, ^3J(F,F) = 23.0 Hz, 4F; *o*-C_6F_5), −160.0 (t, ^3J(F,F) = 21.0 Hz, 2F; *p*-C_6F_5), −164.7 ppm (m, 4F; *m*-C_6F_5); ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2, 298 K): δ = 0.83 ppm; ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 298 K): δ = 43.9 ppm (d, ^1J(P,C) = 92 Hz); IR (KBr): $\tilde{\nu}$ = 1695 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{31}H_{32}BF_{10}O_2P$ (668.3): C 55.67, H 4.83; found: C 55.60, H 5.09.

Preparation of [*t*Bu$_3$PH][RBH(C_6F_5)$_2$] (R = hexyl (8), Cy (9), norbornyl (10)): These compounds were prepared in a similar fashion and thus only one preparation is detailed. (C_6F_5)$_2$BH (165.0 mg, 0.477 mmol) was suspended in pentane (2 mL). Through a syringe 1-hexene (60 μL, 0.477 mmol) was added dropwise and the mixture was stirred for 10 min. *t*Bu$_3$P (94.0 mg, 0.477 mmol) was also dissolved in pentane (2 mL) and added to the first solution. The degassed reaction flask was then filled with H_2 (2.0 bar) at ambient temperature for 10 min and stirred overnight. The precipitated white solid was separated from the pentane solution by removing the solvent with a cannula. The product was washed with pentane (2×4 mL) and dried in vacuo for two hours. Crystals suitable for X-ray analysis were obtained from a dichloromethane solution by slow diffusion of pentane at −35 °C.

Analytical data for **8**: yield: 180.0 mg (0.284 mmol, 60%); ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 5.46 (d, ^1J(P,H) = 436.6 Hz, 1H; PH), 2.72 (br, 1H; BH), 1.64 (d, ^3J(P,H) = 15.6 Hz, 27H; *t*Bu), 1.28, 1.25, 1.23, 1.10. 0.80 (each m, 2H; CH_2), 0.85 ppm (t, ^3J(H,H) = 6.8 Hz, 3H; 6-H); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ = 148.5 (dm, ^1J(F,C) ≈ 238 Hz, *o*-C_6F_5), 137.6 (dm, ^1J(F,C) ≈ 247 Hz, *p*-C_6F_5), 136.6 (dm, ^1J(F,C) ≈ 245 Hz, *m*-C_6F_5), 129.8 (br, *i*-C_6F_5), 37.9 (d, ^1J(P,C) = 27.3 Hz, *t*Bu), 34.2, 32.8, 31.4 (br), 23.4 (br), 23.3 (CH_2), 30.3 (*t*Bu), 14.4 ppm (C-6); ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): $\delta = -132.9$ (m, 2F; *o*-C_6F_5), −165.8 (br, 1F; *p*-C_6F_5), −167.6 ppm (m, 2F; *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 1.8 ppm]; ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 298 K): $\delta = -18.4$ ($\nu_{1/2} \approx 200$ Hz); ^{31}P NMR (202 MHz, CD_2Cl_2, 298 K): δ = 57.7 (dm, ^1J(P,H) ≈ 437 Hz); elemental analysis calcd (%) for $C_{30}H_{42}BF_{10}P$ (634.4): C 56.80, H 6.67; found: C 56.27, H 6.40.

Analytical data for **9**: yield: 203.0 mg (0.321 mmol, 66%); ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 5.49 (d, ^1J(P,H) = 437.2 Hz, 1H; PH), 2.44 (br m, 1H; BH), 1.66 (d, ^3J(P,H) = 15.6 Hz, 27H; *t*Bu), 1.64/1.17 (each m, 1H; $^4CH_2$), 1.61/1.21 (each m, 2H; $^{3,5}CH_2^t$), 1.49/0.84 (each m, 2H; $^{2,6}CH_2^t$), 1.09 ppm (br, 1H; 1-H); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ = 148.2 (dm, ^1J(F,C) ≈ 226 Hz, *o*-C_6F_5), 137.2 (dm, ^1J(F,C) ≈ 246 Hz, *p*-C_6F_5), 136.5 (dm, ^1J(F,C) ≈ 246 Hz, *m*-C_6F_5), 129.1 (br, *i*-C_6F_5), 37.9 (d, ^1J(P,C) = 25.9 Hz, *t*Bu), 35.2 ($^{2,6}CH_2^t$), 30.7 (br, C-1), 30.3 (*t*Bu), 29.6 ppm ($^{3,5}CH_2^t$), 28.6 ($^4CH_2$); ^{19}F NMR (470 MHz, 298 K, CD_2Cl_2): $\delta = -132.0$ (m, 2F; *o*-C_6F_5), −166.0 (m, 1F; *p*-C_6F_5), −167.6 ppm (m, 2F; *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 1.6 ppm]; ^{11}B NMR (160 MHz, 298 K, CD_2Cl_2): $\delta = -17.6$ ppm (d, ^1J(B,H) ≈ 88 Hz); ^{31}P NMR (202 MHz, 298 K, CD_2Cl_2): δ = 57.7 ppm (dm, ^1J(P,H) = 437 Hz); elemental analysis calcd (%) for $C_{30}H_{40}BF_{10}P$ (632.4): C 56.98, H 6.38; found: C 56.43, H 6.38.

Analytical data for **10**: yield: 144 mg (0.223 mmol, 77%); ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 5.28 (d, ^1J(P,H) = 432.5 Hz, 1H; PH), 2.46 (1:1:1:1 q {partial relaxed}, 1H; BH), 2.03 (m, 1H; 4-H^t), 1.71 (m, 1H; 1-H^t), 1.65 (d, ^3J(P,H) = 15.7 Hz, 27H; *t*Bu), 1.59/0.87 (each m, 1H; $^7CH_2^t$), 1.44/1.19 (each m, 1H; $^5CH_2^t$), 1.43/1.12 (each m, 1H; $^6CH_2^t$), 1.18 (m, 1H; 2-H), 1.13/1.00 ppm (each m, 1H; $^3CH_2^t$); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ = 147.5 (dm, ^1J(F,C) ≈ 233 Hz, *o*-C_6F_5), 137.5 (dm, ^1J(F,C) ≈ 237 Hz, *p*-C_6F_5), 136.7 (dm, ^1J(F,C) ≈ 245 Hz, *m*-C_6F_5), 129.8 (br, *i*-C_6F_5), 42.2 (br, C-1^t), 38.5 (br, $^3CH_2^t$), 38.4 (br, C-4^t), 38.0 (d, ^1J(P,C) = 27.0 Hz, *t*Bu), 36.6 (br, $^7CH_2^t$), 34.8 (br, C-2), 34.3 (br, $^5CH_2^t$), 30.3 (*t*Bu), 30.2 ppm (br, $^6CH_2^t$); ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): $\delta = -131.9$ (m, 2F; *o*-$C_6F_5^A$), −132.2 (m, 2F; *o*-$C_6F_5^B$), −166.0 (t, ^3J(F,F) = 20.3 Hz, 1F; *p*-$C_6F_5^A$), −166.1 (t, ^3J(F,F) = 20.2 Hz, 1F; *p*-$C_6F_5^B$), −167.6 (m, 2F; *m*-$C_6F_5^B$), −167.7 ppm (m, 2F; *m*-$C_6F_5^A$), [$\Delta\delta^{19}F_{m,p}$ = 1.7^A, 1.5^B ppm]; ^{11}B NMR (160 MHz, CD_2Cl_2, 298 K): $\delta = -18.5$ (d, ^1J(B,H) ≈ 90 Hz); ^{31}P NMR (202 MHz, CD_2Cl_2, 298 K): δ = 58.7 (dm, ^1J(P,H) ≈ 433 Hz); elemental analysis calcd (%) for $C_{31}H_{40}BF_{10}P$ (644.4): C 57.78, H 6.26; found: C 57.68, H 6.20.

Generation of [*t*Bu$_3$PD][RBD(C_6F_5)$_2$] (R = hexyl ([D$_2$]8), Cy ([D$_2$]9), norbornyl ([D$_2$]10)): These compounds were prepared in a similar fashion and thus only one preparation is detailed. HB(C_6F_5)$_2$ (165.0 mg, 0.477 mmol) was suspended in pentane (2 mL). Through a syringe 1-hexene (60 μL, 0.477 mmol) was added dropwise and the mixture was stirred for 10 min. *t*Bu$_3$P (94.0 mg, 0.477 mmol) was also dissolved in pentane (2 mL) and added to the first solution. The degassed reaction flask was then filled with D_2 (2.0 bar) at ambient temperature for 10 min and stirred overnight. The precipitated white solid was separated from the pentane solution by removing the solvent with a cannula. The product was washed with pentane (2×4 mL) and dried in vacuo for two hours.

Analytical data for [D$_2$]**8**: yield: 212.0 mg (0.333 mmol, 70%); ^{2}H NMR (77 MHz, CH_2Cl_2, 298 K): δ = 5.45 (d, ^1J(P,D) = 66.1 Hz, 1D; PD), 2.72 ppm (br, 1D; BD).

Analytical data for [D$_2$]**9**: yield: 116.0 mg (0.183 mmol, 75%); ^{2}H NMR (77 MHz, CH_2Cl_2, 298 K): δ = 5.49 (d, ^1J(P,D) = 66.9 Hz, 1D; PD), 2.49 ppm (br, 1D; BD).

Analytical data for [D$_2$]**10**: yield: 212 mg (0.328 mmol, 77%); ^{2}H NMR (77 MHz, CH_2Cl_2, 298 K): δ = 5.30 (d, ^1J(P,D) = 66.8 Hz, 1D; PD), 2.50 ppm (br, 1D; BD);

Synthesis of [tBu$_3$PH][$(C_6F_5)_2$BR)$_2$(μ-HCO$_2$)] (R = Cy (11), norbornyl (12)): These compounds were prepared in an analogous manner and thus only one preparation is detailed. In addition these species were prepared by two methods.

Method 1: Compound **9** (203.0 mg, 0.321 mmol) was dissolved in bromobenzene (6 mL), the solution was added to a thick-walled reaction flask, degassed and filled with CO_2. The reaction mixture was heated to 60 °C overnight. Afterwards, the solvent was removed in vacuo and the crude product was recrystallized from a dichloromethane/pentane mixture (1:1). Crystals of **11** suitable for X-ray analysis were obtained from dichloromethane by slow diffusion of pentane at −35 °C.

Method 2: $(C_6F_5)_2$BH (375.0 mg, 1.084 mmol) was dissolved in bromobenzene (3 mL). Through a syringe cyclohexene (110 μL, 1.084 mmol) was added dropwise and the solution was stirred for 10 min. tBu$_3$P (110.0 mg, 0.542 mmol) was also dissolved in bromobenzene (2 mL) and added to the first solution. Afterwards, formic acid (20 μL, 0.542 mmol) was added through a syringe and the reaction mixture was stirred overnight at ambient temperature. After removal of half of the solvent and addition of pentane (12 mL), the suspension was stored in a freezer for one hour. Afterwards, the solvent was removed with a syringe and washed twice with pentane (2 × 10 mL) and dried in vacuo for one hour.

Analytical data for **11**: Method 1: yield: 95.0 mg (0.067 mmol, 45 %; maximum yield: 50 %); Method 2: yield: 545.0 mg (0.493 mmol, 91 %); ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 8.04 (s, 1H; CHO_2), 5.09 (d, ^1J(P,H) = 427.7 Hz, 1H; PH), 1.66 (d, ^3J(P,H) = 15.8 Hz, 27H; tBu), 1.62/1.04 (each m, 2H; $^4CH_2$), 1.60/1.20 (each m, 4H; $^{3,5}CH_2^t$), 1.50/0.61 (each m, 4H; $^{2,6}CH_2^t$), 1.27 ppm (m, 2H; 1-H); ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ = 173.4 (HCO), 147.8 (dm, ^1J(F,C) ≈ 242 Hz, o-C_6F_5), 139.2 (dm, ^1J(F,C) ≈ 248 Hz, p-C_6F_5), 137.3 (dm, ^1J(F,C) ≈ 250 Hz, m-C_6F_5), 121.3 (br, i-C_6F_5), 38.1 (d, ^1J(P,C) = 27.0 Hz, tBu), 32.1 (br, C-1), 30.3 (tBu), 30.0 ($^{2,6}CH_2^t$), 28.8 ($^{3,5}CH_2^t$), 27.9 ppm ($^4CH_2$); ^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): δ = −132.6 (m, 2F; o-C_6F_5), −161.1 (t, ^3J(F,F) = 20.4 Hz, 1F; p-C_6F_5), −165.7 ppm (m, 2F; m-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 5.6 ppm]; ^{11}B NMR (192 MHz, CD_2Cl_2, 298 K): δ = 5.1 ppm ($\upsilon_{1/2}$ ≈ 500 Hz); ^{31}P NMR (243 MHz, 298 K, CD_2Cl_2): δ = 60.5 (dm, ^1J(P,H) ~428 Hz); IR (KBr): $\tilde{\nu}$ = 1631 cm^{-1} (s); elemental analysis calcd (%) for $C_{49}H_{52}B_2F_{20}O_2P$ (1105.5): C 53.24, H 4.74; found: C 52.83, H 4.61.

Analytical data for **12**: Method 1: yield: 75.0 mg (0.066 mmol, 46 %; maximum yield: 50 %); Method 2: yield: 417.0 mg (0.369 mmol, 71 %); 1:1 mixture of pairs of diastereomers; ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 8.04 (s, 1H; CHO_2), 5.13 (d, ^1J(P,H) = 428.9 Hz, 1H; PH), 1.99 (m, 2H; 4-H^t), 1.92/1.91 (each m, Σ2H; 1-H^t), 1.66 (d, ^3J(P,H) = 15.8 Hz, 27H; tBu), 1.42/1.12 (each m, 2H; 5-H^t), 1.40/1.22 (each m, 2H; 6-H^t), 1.30 (m, 2H; 2-H), 1.17 (m, 4H; 3-H^t), 0.79/0.70 ppm (each br m, 2H; 7-H^t); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ = 172.7, 172.6 (CHO_2), 147.9 (dm, ^1J(F,C) ≈ 244 Hz, o-C_6F_5), 139.2 (dm, ^1J(F,C) ≈ 252 Hz, p-C_6F_5), 137.3 (dm, ^1J(F,C) ≈ 246 Hz, m-C_6F_5), 121.7 (br, i-C_6F_5), 39.8 (C-1^t), 38.1 (d, ^1J(P,C) = 26.8 Hz, tBu), 37.4, 37.32 (C-4^t), 37.30. 37.28 (m, C-7^t), 35.1 (br, C-3^t), 34.7 (br, C-2), 34.5, 34.4 (C-6^t), 30.4 (tBu), 29.2 ppm (br, C-5^t); ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): δ = −131.9, −132.0, (each m, 2F; o-$C_6F_5^A$), −132.9, −133.0, (each m, 2F; o-$C_6F_5^B$), −160.6, −160.7 (each t, ^3J(F,F) = 20.0 Hz, 1F; p-$C_6F_5^A$), −161.3, −161.4 (each t, ^3J(F,F) = 19.9 Hz, 1F; p-$C_6F_5^B$), −165.4, −165.5 (each m, 2F; m-$C_6F_5^A$), −165.8, −165.9 ppm (each m, 2F; m-$C_6F_5^B$); ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 298 K): δ = 4.3 ppm ($\upsilon_{1/2}$ ≈ 500 Hz); ^{31}P NMR (202 MHz, CD_2Cl_2, 298 K): δ = 60.1 (dm, ^1J(P,H) ≈ 429 Hz); IR (KBr): $\tilde{\nu}$ = 1638 (s); elemental analysis calcd (%) for $C_{51}H_{52}B_2F_{20}O_2P$ (1129.5): C 54.23, H 4.64; found C 54.09, H 3.42.

Synthesis of [tBu$_3$PH][$(C_6F_5)_2$BR(O_2CH)] (R = hexyl (13), Cy (14), norbornyl (15)): These compounds were prepared in a similar fashion and thus only one preparation is detailed. HB$(C_6F_5)_2$ (150.0 mg, 0.434 mmol) was dissolved in toluene (4 mL). Through a syringe 1-hexene (54 μL, 0.434 mmol) was added dropwise and stirred for 10 min. tBu$_3$P (88.0 mg, 0.434 mmol) was also dissolved in toluene (2 mL) and added to the first solution. Afterwards, formic acid (16 μL, 0.434 mmol) was added through a syringe and the reaction mixture was stirred for one hour at ambient temperature. After addition of pentane (10 mL) a white solid precipitated from the solution and the supernatant solution was decanted. The product was washed with pentane (2 × 10 mL) and dried in vacuo for one hour. Crystals suitable for X-ray analysis were obtained from dichloromethane by slow diffusion of pentane at −35 °C.

Analytical data for **13**: yield: 250.0 mg (0.368 mmol, 85 %); ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 8.29 (s, 1H; CHO_2), 5.81 (br d, ^1J(P,H) = 448.9 Hz, 1H; PH), 1.64 (d, ^3J(P,H) = 15.1 Hz, 27H; tBu), 1.25, 1.23, 1.21, 1.05 (each m, 2H; CH_2), 1.01 (m, 2H; 1-H), 0.84 ppm (m, 3H; 6-H); ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ = 166.4 (HCO_2), 148.0 (dm, ^1J(F,C) ≈ 237 Hz, o-C_6F_5), 138.6 (dm, ^1J(F,C) ≈ 254 Hz, p-C_6F_5), 137.2 (dm, ^1J(F,C) ≈ 237 Hz, m-C_6F_5), n.o. (i-C_6F_5), 37.7 (d, ^1J(P,C) = 27.4 Hz, tBu), 30.3 (tBu), 34.0, 32.6, 26.6, 23.3 (CH_2), 25.2 (br, C-1), 14.4 ppm (C-6); ^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): δ = −133.9 (m, 2F; o-C_6F_5), −163.3 (t, ^3J(F,F) = 20.7 Hz, 1F; p-C_6F_5), −166.8 ppm (m, 2F; m-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 3.5 ppm]; ^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 298 K): δ = 0.6 ppm ($\upsilon_{1/2}$ ≈ 200 Hz); ^{31}P NMR (243 MHz, CD_2Cl_2, 298 K): δ = 55.1 (br d, ^1J(P,H) ≈ 450 Hz); IR (KBr): $\tilde{\nu}$ = 1682 (s), 1644 (m), 1515 cm^{-1} (s); elemental analysis calcd (%) for $C_{31}H_{42}BF_{10}O_2P$ (678.4): C 54.88, H 6.24; found: C 54.80, H 5.91.

Analytical data for **14**: yield: 230.0 mg (0.340 mmol, 78 %); ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 8.20 (s, 1H; CHO_2), 5.82 (br d, ^1J(P,H) = 443.2 Hz, 1H; PH), 1.64 (d, ^3J(P,H) = 15.5 Hz, 27H; tBu), 1.65/1.25 (each m, 2H; $^{3,5}CH_2^t$), 1.63/1.07 (each m, 1H; $^4CH_2$), 1.62/0.72 (each m, 2H; $^{2,6}CH_2^t$), 1.30 ppm (br, 1H; 1-H); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ = 166.4 (HCO_2), 148.2 (dm, ^1J(F,C) = 237 Hz, o-C_6F_5), 138.3 (dm, ^1J(F,C) = 245 Hz, p-C_6F_5), 136.6 (dm, ^1J(F,C) = 247 Hz, m-C_6F_5), 124.6 (br, i-C_6F_5), 37.7 (d, ^1J(P,C) = 27.4 Hz, tBu), 33.3 (br, C-1), 30.6 ($^{2,6}CH_2^t$), 30.3 (tBu), 29.3 ($^{3,5}CH_2^t$), 28.3 ppm ($^4CH_2$); ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): δ = −132.3 (m, 2F; o-C_6F_5), −163.0 (t, ^3J(F,F) = 20.3 Hz, 1F; p-C_6F_5), −166.4 ppm (m, 2F; m-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 3.4 ppm]; ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 298 K): δ = 1.5 ppm ($\upsilon_{1/2}$ ≈ 200 Hz); ^{31}P NMR (202 MHz, CD_2Cl_2, 298 K): δ = 55.4 ppm (dm, ^1J(P,H) ≈ 444 Hz); IR (KBr): $\tilde{\nu}$ = 1689 (s), 1645 (m), 1516 (s), 1464 cm^{-1} (s); elemental analysis calcd (%) for $C_{31}H_{40}BF_{10}O_2P$ (676.4): C 55.08, H 5.96; found: C 54.64, H 5.71.

Analytical data for **15**: yield: 280.0 mg (0.407 mmol, 70 %); ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 8.17 (s, 1H; CHO_2), 5.81 (d, ^1J(P,H) = 448.2 Hz, 1H; PH), 2.05 (m, 1H; 1-H^t), 2.01 (m, 1H; 4-H^t), 1.65 (d, ^3J(P,H) = 15.5 Hz, 27H; tBu), 1.44/1.31 (each m, 1H; 5-H^t), 1.44/1.15 (each m, 1H; 6-H^t), 1.35 (m, 1H; 2-H), 1.27/1.12 (each m, 1H; 3-H^t), 0.92/0.84 ppm (each br m, 1H; 7-H^t); ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ = 165.9 (HCO_2), 148.1 (dm, ^1J(F,C) ≈ 238 Hz, o-C_6F_5), 138.3 (dm, ^1J(F,C) ≈ 260 Hz, p-C_6F_5), 137.2 (dm, ^1J(F,C) ≈ 239 Hz, m-C_6F_5), 125.4 (br, i-C_6F_5), 40.2 (C-1^t), 37.7 (d, ^1J(P,C) = 27.2 Hz, tBu), 37.5 (C-4^t), 37.4 (C-7), 35.7 (br, C-2), 35.5 (C-3^t), 34.7 (C-5^t), 30.3 (tBu), 29.4 ppm (C-6^t); ^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): δ = −132.1 (m, 2F; o-$C_6F_5^A$), −133.3 (m, 2F; o-$C_6F_5^B$), −162.6 (t, ^3J(F,F) = 20.0 Hz, 1F; p-$C_6F_5^A$), −163.4 (t, ^3J(F,F) = 20.5 Hz, 1F; p-$C_6F_5^B$), −166.4 (m, 2F; m-$C_6F_5^A$), −166.8 ppm (m, 2F; m-$C_6F_5^B$) [$\Delta\delta^{19}F_{m,p}$ = 3.8^A, 3.4^B ppm]; ^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 298 K): δ = 1.0 ppm ($\upsilon_{1/2}$ ≈ 170 Hz); ^{31}P NMR (243 MHz, CD_2Cl_2, 298 K): δ = 55.5 ppm (dm, ^1J(P,H) ≈ 450 Hz); IR (KBr): $\tilde{\nu}$ = 1681 (s), 1645 (m), 1515 (s), 1464 cm^{-1} (s); elemental analysis calcd (%) for $C_{32}H_{40}BF_{10}O_2P$ (688.4): C 55.83, H 5.86; found: 55.42, H 5.49.

X-ray data collection and reduction (Toronto): Crystals were coated in Paratone-N oil in a glovebox, mounted on a MiTegen Micromount and placed under an N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data were collected on a Bruker Apex II diffractometer with $Mo_{K\alpha}$ radiation (λ = 0.71069). The frames were integrated with the Bruker SAINT[36] software package by using a narrow-frame algorithm. Data were corrected for absorption effects by using the empirical multi-scan method (SADABS[37]).

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, both with APEXII detectors, in case of Mo radiation a rotating anode generator equipped with Montel mirrors was used. The frames were integrated with

the DENZO[38] software package including absorption corrections by using the empirical multi-scan method.

Structure solution and refinement (Toronto): Non-hydrogen atomic scattering factors were taken from the literature tabulations.[28] The heavy atom positions were determined by using direct methods employing the SHELXTL[39] direct methods routine. 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, minimizing the function $\omega(F_o-F_c)^2$ where the weight ω is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, anisotropic temperature factors were assigned to all non-hydrogen atoms except in cases 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. Hydrogen-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. The hydrogen-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 by using direct or Patterson methods employing the SHELXS[40] routine. 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

Table 3. Crystallographic data.

	2·CH_2Cl_2	**3**	**4**·CH_2Cl_2	**5**·CH_2Cl_2	**6**
formula	$C_{32}H_{32}BCl_2F_{12}O_2P$	$C_{31}H_{40}BF_{10}O_2P$	$C_{32}H_{40}BCl_2F_{10}O_2P$	$C_{33}H_{40}BCl_2F_{10}O_2P$	$C_{25}H_{27}BClF_{10}O_2P$
M [g mol^{-1}]	789.26	676.41	759.32	771.33	626.70
crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$C2/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a [Å]	37.5992(19)	9.0306(3)	9.4143(1)	9.4213(5)	32.4596(9)
b [Å]	9.1190(5)	17.9639(7)	11.9296(1)	11.8188(6)	8.6466(3)
c [Å]	21.6909(11)	21.8857(9)	16.8587(1)	17.1466(9)	22.3184(8)
α [°]	90.00	90.00	81.528(1)	81.847(2)	90.00
β [°]	114.066(2)	100.321(2)	76.336(1)	75.654(3)	119.588(3)
γ [°]	90.00	90.00	71.861(1)	72.219(3)	90.00
V [Å^3]	6790.6(6)	3493.0(2)	1742.77(3)	1756.82(16)	5447.20(3)
Z	8	4	2	2	8
λ [Å]	0.71073	1.54178	1.54178	1.54178	1.54178
T [K]	150(2)	223(2)	223(2)	223(2)	223(2)
ρ_{calcd} [g cm^{-3}]	1.544	1.286	1.447	1.458	1.528
R_{int}	0.0677	0.058	0.077	0.053	0.044
μ [cm^{-1}]	0.335	14.11	28.57	28.44	26.46
total data	71040	47055	22342	22979	17806
unique data	10291	6216	6029	6161	4810
data $>2\sigma(F_O^2)$	7198	5245	4406	5085	4195
variables	460	350	442	470	370
$R(>2\sigma)$	0.0538	0.095	0.053	0.054	0.042
R_w	0.1627	0.281	0.131	0.146	0.115
GOF	1.026	1.039	1.014	1.027	1.021

	9	**10**	**11**	**12**	**13**	**14**·CH_2Cl_2
formula	$C_{30}H_{42}BF_{10}$	$C_{31}H_{40}BF_{10}P$	$C_{49}H_{42}B_2F_{20}O_2P$	$C_{51}H_{51}B_2F_{20}O_2P$	$C_{31}H_{40}BF_{10}O_2P$	$C_{32}H_{44}BCl_2F_{10}O_2P$
M [g mol^{-1}]	634.42	644.41	1095.42	1128.51	676.41	763.35
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$C2/c$	$P2_12_12_1$	$P\bar{1}$
a [Å]	20.1797(5)	11.7360(2)	15.6851(11)	15.5966(11)	9.0103(2)	9.0425(2)
b [Å]	17.3034(5)	23.5022(5)	16.2344(13)	18.1216(8)	14.8207(3)	12.2269(2)
c [Å]	20.1334(5)	12.3519(3)	20.0983(15)	18.3225(5)	24.2492(6)	17.8775(4)
α [°]	90.00	90.00	90.00	90.00	90.00	70.717(7)
β [°]	112.293(2)	111.8070(10)	104.151(2)	93.638(3)	90.00	83.012(7)
γ [°]	90.00	90.00	90.00	90.00	90.00	88.212(6)
V [Å^3]	6504.7(3)	3163.12(12)	4962.5(6)	5168.1(5)	3238.21(13)	1851.74(7)
Z	8	4	4	4	4	2
λ [Å]	1.54178	0.71073	0.71073	1.54178	0.71073	0.71073
T [K]	223(2)	150(2)	150(2)	223(2)	223(2)	223(2)
ρ_{calcd} [g cm^{-3}]	1.296	1.353	1.466	1.482	1.387	1.369
R_{int}	0.062	0.0523	0.0543	0.055	0.049	0.049
μ [cm^{-1}]	14.30	0.166	0.170	14.82	1.70	2.97
total data	52378	27924	35999	22832	22953	17365
unique data	11422	7175	8727	4448	7560	8615
data $>2\sigma(F_O^2)$	8049	4757	5796	3576	6669	7075
variables	777	388	691	402	416	443
$R(>2\sigma)$	0.075	0.0713	0.099	0073	0.089	0.070
R_w	0.224	0.2069	0.2682	0.215	0.261	0.173
GOF	1.010	1.028	1.029	1.008	1.099	1.083

on F^2 employing the SHELXL[41] routine. In the final cycles of each refinement, anisotropic temperature factors were assigned to all non-hydrogen atoms except in cases 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 atom 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. Hydrogen-atom temperature factors were fixed at 1.20 or 1.50 times the isotropic temperature factor of the carbon 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.

For the crystallographic data see Table 3. Additional data for the structural studies are deposited in the Cambridge Crystallographic database. CCDC-806867 (**2**), 806868 (**3**), 806869 (**4**), 806870 (**5**), 806871 (**6**), 806872 (**7**), 806873 (**8**), 806874 (**9**), 806875 (**10**), 806876 (**11**), 806877 (**12**), and 806878 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational studies: Selected compounds have been investigated by means of state-of-the-art quantum chemical methods. As a starting point we used the X-ray structures and performed geometry optimizations with the *meta*-GGA density functional TPSS[25] applying the large Gaussian AO basis set def2-TZVP,[29] the resolution of the identity approximation[30] and an empirical dispersion correction (DFT-D2)[31] as provided by the ORCA 2.7 (rev. 1383) program package.[32] Subsequent single-point calculations with the accurate double-hybrid functional B2PLYP[33] and the same basis set have been carried out by using the Turbomole 6.0 suite of programs.[34] Because inter- and intramolecular dispersion interactions play a crucial role in systems like FLPs with bulky and weakly interacting substituents, the newly developed DFT-D3 dispersion correction was consistently applied.[35]

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