

Exploring the Reactivity of B-Connected Carboranylphosphines in Frustrated Lewis Pair Chemistry: A New Frame for a Classic System

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Dedicated to Professor Peter Junk on the occasion of his 60th birthday.

Abstract: The primary phosphines MesPH₂ and tBuPH₂ react with 9-iodo-*m*-carborane yielding B9-connected secondary carboranylphosphines 1,7-H₂C₂B₁₀H₉-9-PHR (R = 2,4,6-Me₃C₆H₂ (Mes; **1 a**), tBu (**1 b**)). Addition of tris(pentafluorophenyl)borane (BCF) to **1 a, b** resulted in the zwitterionic compounds 1,7-H₂C₂B₁₀H₉-9-PHR(*p*-C₆F₄)BF(C₆F₅)₂ (**2 a, b**) through nucleophilic *para* substitution of a C₆F₅ ring followed by fluoride transfer to boron. Further reaction with Me₂SiHCl prompted a H–F exchange yielding the zwitterionic compounds 1,7-H₂C₂B₁₀H₉-9-PHR(*p*-C₆F₄)BH(C₆F₅)₂ (**3 a, b**). The reaction of **2 a, b** with one equivalent of R'MgBr (R' = Me, Ph) gave the extremely water-sensitive frustrated Lewis pairs 1,7-H₂C₂B₁₀H₉-9-PR(*p*-C₆F₄)B(C₆F₅)₂ (**4 a, b**). Hydrolysis of the B–C₆F₄ bond in **4 a, b**

gave the first tertiary B-carboranyl phosphines with three distinct substituents, 1,7-H₂C₂B₁₀H₉-9-PR(*p*-C₆F₄H) (**5 a, b**). Deprotonation of the zwitterionic compounds **2 a, b** and **3 a, b** formed anionic phosphines [1,7-H₂C₂B₁₀H₉-9-PR(*p*-C₆F₄)BX(C₆F₅)₂][−][DMSOH]⁺ (R = Mes, X = F (**6 a**), R = tBu, X = F (**6 b**); R = Mes, X = H (**7 a**), R = tBu, X = H (**7 b**)). Reaction of **2 a, b** with an excess of Grignard reagents resulted in the addition of R' at the boron atom yielding the anions [1,7-H₂C₂B₁₀H₉-9-PR(*p*-C₆F₄)BR'(C₆F₅)₂][−] (R = Mes, R' = Me (**8 a**), R = tBu, R' = Me (**8 b**); R = Mes, R' = Ph (**9 a**), R = tBu, R' = Ph (**9 b**)) with [MgBr(Et₂O)_{*n*}]⁺ as counterion. The ability of the zwitterionic compounds **3 a, b** to hydrogenate imines as well as the Brønsted acidity of **3 a, b** were investigated.

Introduction

Since the first metal-free hydrogen activation by a frustrated Lewis pair (FLP) was reported,^[1] the concept of unquenched Lewis acidity and basicity has given rise to various systems capable not only of hydrogen splitting^[2] but also of activating unsaturated small molecules, including CO₂,^[3] CO,^[4] SO₂,^[5] N₂O,^[6] NO,^[7] alkenes^[8] and alkynes.^[9] Various different backbones have been employed in frustrated Lewis pairs, such as naphthalene,^[10] binaphthalene^[11] or ferrocene,^[12–14] expanding the structural versatility. Dicarba-*closo*-dodecaboranes (carboranes), which are icosahedral 12-vertex boron-carbon clusters,^[15] come with an intriguing set of properties appealing to the field of frustrated Lewis pairs such as an extensive steric demand

(the van der Waals volume of *meta*-carborane ($V_{\text{vdW}} = 143 \text{ \AA}^3$) even surpasses that of adamantane ($V_{\text{vdW}} = 136 \text{ \AA}^3$)^[16]) or a substantial dichotomy regarding the electronic effect on substituents. Thus, depending on the position of the substitution, a strong electron-withdrawing or a strong electron-donating effect are exerted on a substituent (Figure 1).^[17]

C-connected carboranyl phosphines have been known since 1963^[18] and have received a steadily increasing attention also with a focus on possible applications.^[19,20,21] In contrast, phosphine substitution at the electron-rich B9-position, albeit with very low yields, has only first been reported in 1992 by Bregadze et al.,^[22] and was followed up by Spokoiny, Buchwald and co-workers in 2012, providing a facile synthesis for electron-rich tertiary B9-connected carboranyl phosphines (Figure 2).^[23,24]

However, only a very small number of compounds containing a carborane moiety has been studied (or even synthesized) as part of a frustrated Lewis pair (Figure 2).^[25–27]

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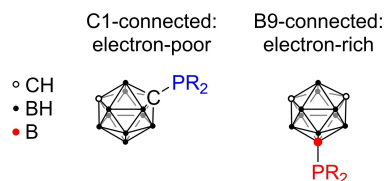


Figure 1. Dichotomy regarding the electronic effect of a carboranyl moiety on phosphine substituents.

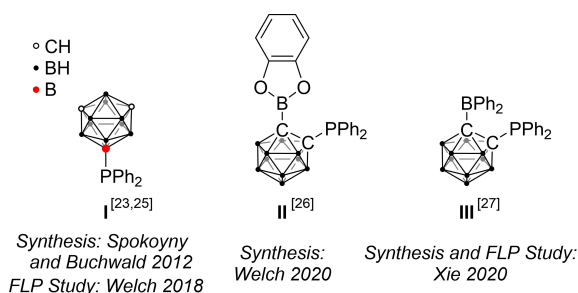
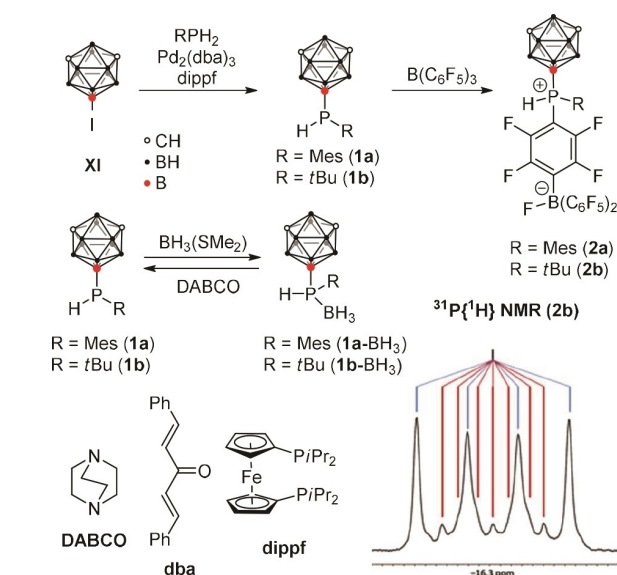


Figure 2. Known examples of carborane derivatives studied in the context of FLPs and/or featuring an intramolecular FLP.

Given the attractive steric and electronic characteristics of carborane, we set out to study the potential use of B9-connected *meta*-carboranyl phosphines as Lewis bases in FLP chemistry by using the significant electron-donating effect exhibited by the carborane cluster.^[28]

On the one hand, the substituents at phosphorus other than the carborane moiety require a certain bulk to prevent the formation of Lewis adducts when combined with the Lewis acid tris(pentafluorophenyl)borane (BCF).^[29] On the other hand, employing sterically encumbered phosphines like di-*tert*-butylphosphine was reported to be unsuitable for the phosphination of the B9-position.^[23] We have chosen a different approach and focused on the synthesis of secondary *B*-carboranyl phosphines, which do not provide the necessary steric bulk on their own. However, the reaction with BCF should prompt a nucleophilic *para* substitution of a C₆F₅ ring,^[30] yielding zwitterionic compounds featuring a C₆F₄ bridge, one of the recurring motifs in FLP chemistry (Figure 3),^[1,12,14,31–33] thus, ultimately preventing the formation of Lewis adducts. The neutral FLP forms of such compounds are known to be able to reversibly activate dihydrogen,^[1] catalyze hydrogenation reactions of imines and aziridines,^[34] heterolytically cleave disulfides,^[35] afford macrocyclic species with alkynes,^[36] and to form zwitterionic phosphine complexes.^[37]



Scheme 1. Syntheses of compounds **1a**, **b**, **1a-BH₃**, **1b-BH₃** and **2a**, **b**. The $^{31}\text{P}\{^1\text{H}\}$ NMR signal of **2b** is displayed as the sum of a 1:1:1:1 quartet (blue; $^{31}\text{P}-^{11}\text{B}$ coupling) and a 1:1:1:1:1:1:1 septet (red; $^{31}\text{P}-^{10}\text{B}$ coupling). Compounds **1a** and **1b**, as well as all compounds derived from them, are *P*-chiral and were obtained as racemic mixtures. For clarity, in this and all following figures and schemes, only one enantiomer is shown.

Results and Discussion

Secondary B-carboranyl phosphines

Reaction of 9-iodo-*m*-carborane (XI)^[38] with the respective primary phosphines MesPH₂ or *t*BuPH₂ resulted in the formation of the first B9-connected secondary carboranyl phosphines **1a** and **1b** (Scheme 1).^[39] In marked contrast to **1a**, **1b** is highly air-sensitive. Both phosphines were converted to the borane adduct **1a-BH₃** and **1b-BH₃**, purified by column chromatography and subsequently deprotected with DABCO (1,4-diazabicyclo[2.2.2]octane) to give pure **1a** and **1b**.

The ^{31}P NMR spectra exhibit signals which, remarkably, are only slightly shifted downfield relative to those of the primary phosphines RPH₂ (**1a**: $\delta = -145.1$ ppm, $\Delta\delta = 15$ ppm; **1b**: $\delta = -69.9$ ppm, $\Delta\delta = 11$ ppm).^[40] In the case of **1a**, the chemical shift is even substantially lower than that of (CH₃)₂PH ($\delta =$

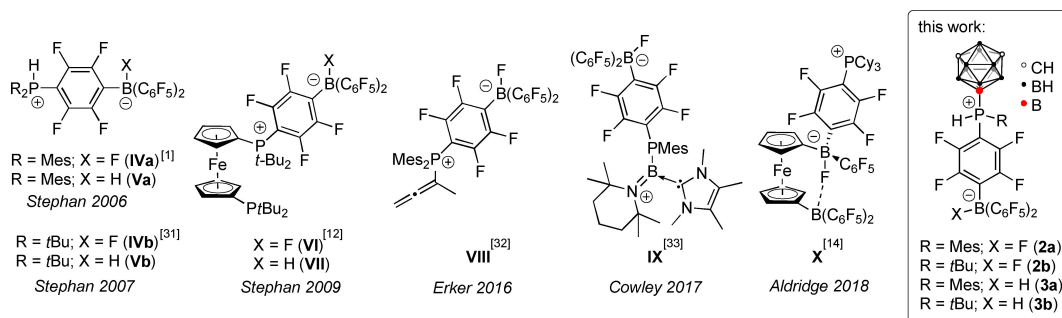


Figure 3. Selected examples of C₆F₄-bridged zwitterionic compounds in FLP chemistry.

–99 ppm), the compound that usually defines the lower end of the chemical shift range for secondary phosphines.^[41] Similar to previously reported tertiary *B*-carboranyl phosphines including **1**,^[23] the coupling to the B9 atom is visible, as well as coupling to the respective proton ($^1J_{P,H} = 215$ Hz (**1 a**), 200 Hz (**1 b**)).

The molecular structures of **1 a**, **1 a**-BH₃ and **1 b**-BH₃ were confirmed by single-crystal X-ray diffraction (Figure 4). All compounds crystallize in monoclinic space groups^[42] and

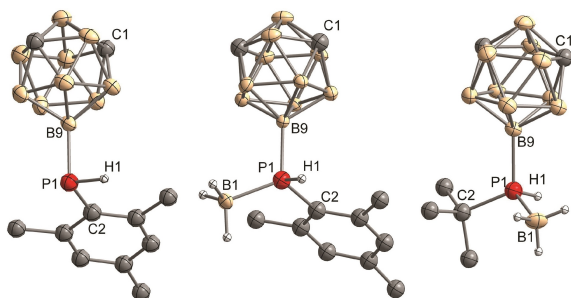


Figure 4. Molecular structures of **1 a** (left), **1 a**-BH₃ (middle) and **1 b**-BH₃ (right) in the solid state with thermal ellipsoids drawn at the 50% probability level. Only the non-oxidized molecule in the asymmetric unit is depicted for **1 a**, and in the case of **1 b**-BH₃, only the molecule with the highest site occupancy factor (0.92) is depicted.^[42] Hydrogen atoms (except for PH and BH₃) are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for **1 a**, **1 a**-BH₃ and **1 b**-BH₃.^[a]

	1 a ^[b]	1 a -BH ₃	1 b -BH ₃ ^[c]
P1–B9	1.945(3)	1.927(3)	1.940(2)
P1–C2	1.840(2)	1.816(3)	1.847(2)
P1–B1	–	1.940(3)	1.933(2)
B9–P1–C2	104.7(1)	108.7(1)	113.1(1)
B9–P1–B1	–	113.9(1)	113.7(1)

[a] Numbering scheme according to Figure 4. [b] For **1 a**, only the values for the non-oxidized molecule in the asymmetric unit are given. [c] For **1 b**-BH₃, only the values for the molecule with the highest site occupancy factor (0.92) in the asymmetric unit are given.

feature B_{carb}–P bond lengths that compare well with other phosphinoboranes (Table 1).^[43] Compound **1 a** co-crystallized with a small quantity (11%) of the corresponding phosphine oxide, showing the compound's extreme sensitivity to oxygen.

Zwitterionic compounds

Like organic secondary phosphines, the secondary *B*-carboranyl phosphines **1 a**, **b** react with BCF to give the zwitterionic compounds **2 a** and **2 b** through nucleophilic *para* substitution of a C₆F₅ ring followed by fluoride transfer to boron (Scheme 1). Colorless crystals of **2 a** suitable for X-ray structure analysis were obtained from dichloromethane at room temperature (Figure 5). **2 a** crystallizes in the triclinic space group *P* $\bar{1}$ with two molecules in the unit cell. The P–B bond length in **2 a** (1.926(5) Å) is comparable to that of the starting material, and the B–F bond length (1.429(5) Å) is in accordance with similar anions.^[44] As in **IVb**, intermolecular P–H...F–B interactions (2.507(3) Å) can be observed (Figure 5, left) and the C₆F₄ rings participate in offset π -stacking (Table 2).^[45]

The multiplet in the ³¹P{¹H} NMR spectra of **2 a**, **b** is significantly shifted to lower field compared to **1 a**, **b** (Table 3). The multiplet represents the sum of two independent signals stemming from coupling with the isotopologues ¹⁰B (*I* = 3, *N* = 20%) and ¹¹B (*I* = 3/2, *N* = 80%) of the B9 atom (Figure 4). As ¹J_{PX} coupling constants generally increase with a lower electron density on phosphorus, they dramatically increase on formation of a phosphonium moiety in **2 a**, **b**.^[41] Since the ¹J_{P,¹¹B} coupling constants in **2 a**, **b** are substantially larger than those of the starting materials **1 a**, **b**, the signal is displayed as the sum of a 1:1:1:1 quartet (¹J_{P,¹¹B} = 168 Hz (**2 a**), 154 Hz (**2 b**)) and a 1:1:1:1:1:1:1 septet (¹J_{P,¹⁰B} = 55 Hz (**2 a**), 51 Hz (**2 b**)) in a 4:1 ratio, mirroring the natural abundance of the two isotopes (Scheme 1).^[46] When compared to the previously reported compounds by Stephan et al., R₂PH(*p*-C₆F₄)BF(C₆F₅)₂ (R = Mes (**IVa**),^[1] *t*Bu (**IVb**)^[31]), replacement of an organic substituent with

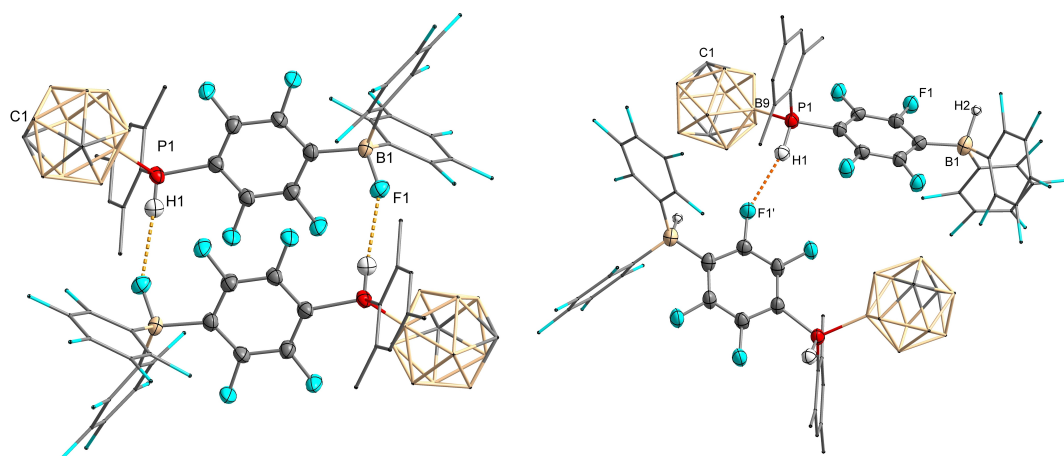


Figure 5. Molecular structures of **2 a** (left) and **3 a** (right) in the solid state with thermal ellipsoids drawn at the 50% probability level. The carboranyl, mesityl and C₆F₅ substituents are represented as wire frames. The hydrogen atoms (except for PH and BH groups other than the carboranyl moiety) and disorders are omitted for clarity. The dashed lines show the intermolecular PH...FB or PH...FC interactions.

Table 2. Selected bond lengths [Å], distances [Å], and angles [°] for **2a**, **3a** and **3b**.^[a]

	2a	3a	3b
P1–B9	1.926(5)	1.934(4)	1.929(2)
P1–C _{sub} ^[b]	1.795(5)	1.800(4)	1.840(3)
P–C ₆ F ₄	1.807(5)	1.797(3)	1.790(2)
B9–P1–C _{sub} ^[b]	114.6(2)	114.1(2)	119.4(1)
B9–P–C ₆ F ₄	116.7(2)	118.9(2)	112.4(1)
H1–P1–B1–X ^[c]	12.7(2)	174.7(1)	132.3(2)
d ^[d]	3.395	6.048	5.591

[a] Numbering scheme according to Figures 5 and 6. [b] Sub = substituent (R = Mes for **2a** and **3a**; R = *t*Bu for **3b**). [c] X = F1 for **2a**; X = H2 for **3a** and **3b**. [d] Distance between planes defined by the C₆F₄ rings of two neighboring molecules.

a carboranyl moiety results in a considerable shielding of the phosphorus nucleus due to the increased electron donating

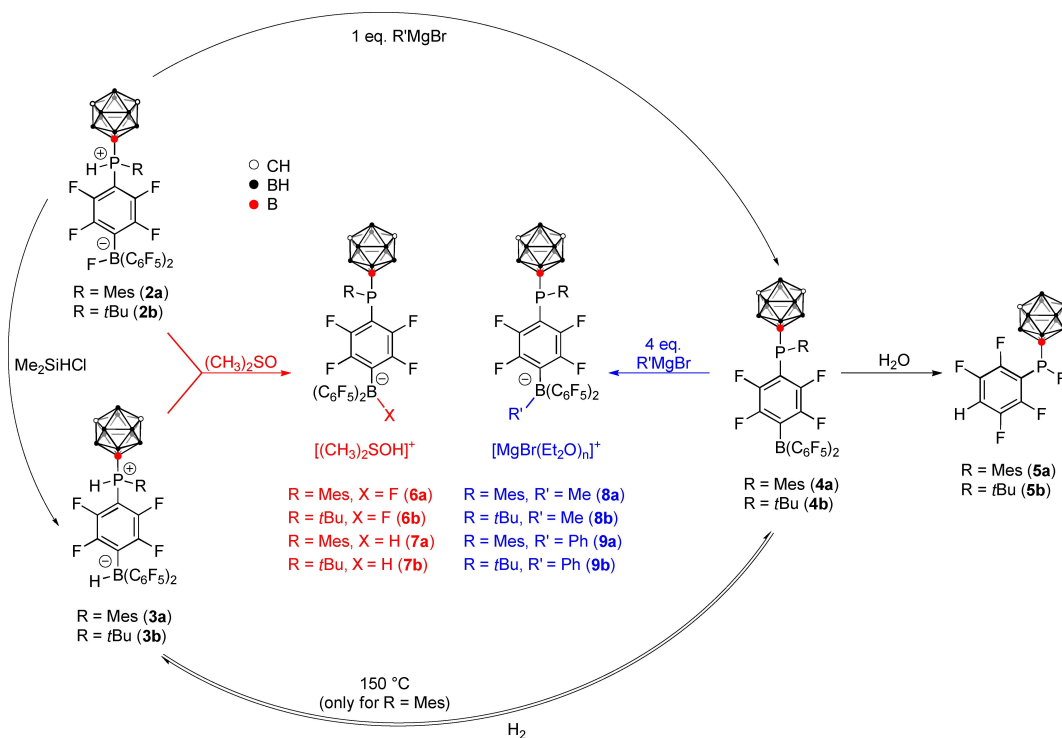
effect (Table 3). A shift to lower field and larger coupling constants compared to **1a**, **b** are also observed in the ¹H NMR spectra of **2a**, **b** for the doublets corresponding to the respective PH fragment. In **2b**, four signals are observed in the ¹⁹F{¹H} NMR spectrum for the C₆F₄ ring, indicating magnetic inequivalence of the fluorine atoms and thus hindered rotation about the P–C₆F₄ at 25 °C, similar to the effect found in **Vb**.^[31] In order to obtain a phosphonium-borate species that is capable of losing H₂ and thus generating an FLP, the boron fluoride moiety needed to be replaced by a boron hydride group.^[1,31] The reaction of **2a**, **b** with Me₂SiHCl prompted a H–F exchange yielding the zwitterionic compounds **3a** and **3b** (Scheme 2).^[1]

Colorless crystals of **3a** (Figure 5, right) and **3b** (Figure 6) suitable for X-ray structure analysis were obtained from dichloromethane at room temperature. While H1 and F1 in **2a** are arranged in a *syn*-periplanar conformation about the C₆F₄ ring ($\theta = 12.7(2)^\circ$) to accommodate intermolecular P–H...F–B

Table 3. Selected chemical shifts (in ppm) and coupling constants *J* (in Hz).

	¹ H NMR [PH]	³¹ P NMR	¹ J _{P,H}	¹¹ B NMR [B(C ₆ F ₅) ₂ X] (X = H or F)	¹ J _{B,X} (X = H or F)
IVa ^[1]	8.49	–37.9	502	0.4	62
IVb ^[31]	6.23	34.0	462	0.4	62
Va ^[1]	8.52	–37.7	503	–25.2	85
Vb ^[31]	6.32	34.2	465	–25.2	82
1a	3.90	–145.1	215	–	–
1b	2.99	–69.9	199	–	–
2a	7.48	–54.7	458	–0.6	65
2b	6.32	–16.5	449	–0.4	^a
3a	7.48	–54.7	457	–25.2	93
3b	6.32	–16.5	449	–24.9	92

[a] Unresolved coupling.

**Scheme 2.** Syntheses of compounds **3a**, **b–9a**, **b**.

interactions (2.507(3) Å), the torsion angle H–P...B–H in **3a** is much larger ($\theta = 174.7(1)^\circ$), resulting in an *anti*-periplanar conformation. However, unlike in **Va** in which the PH moiety is not interacting with neighboring molecules,^[1] the PH proton in **3a** is still able to participate in intermolecular interactions and forms a P–H...F–C contact (2.400(3) Å) that is even shorter than the interaction in **2a** (Figure 5). Even though the hydrogen atom in the (*p*-C₆F₄)BH(C₆F₅)₂ fragment is not observed in the ¹H NMR spectrum following the H–F exchange, the corresponding signal of the boron atom is considerably shifted upfield in the ¹¹B NMR spectrum, comparing well with other compounds containing the (*p*-C₆F₄)BH(C₆F₅)₂ moiety (Table 3).

Paths to frustrated Lewis Pairs

The generation of the desired FLP species **4a** was attempted by thermal elimination of H₂ from the phosphonium-borate **3a**.^[1,47] When **3a** was heated to 150 °C in bromobenzene to induce loss of H₂, the initially colorless solution first turned yellow and after time changed to dark red and a new signal in the ³¹P NMR spectrum at –75 ppm appeared that did not show proton coupling. However, the expected FLP **4a** could not be isolated after work up of the reaction mixture; only the tertiary *B*-carboranyl phosphine **5a** (³¹P NMR: –75 ppm) was obtained that was apparently formed through cleavage of the B–C₆F₄ bond (Scheme 2). Cedillo et al. have shown through DFT calculations on Mes₂PH(*p*-C₆F₄)BH(C₆F₅) (**Va**) that the formation of two fragments by cleavage of the B–C₆F₄ bond is thermodynamically favored over the experimentally observed release of a dihydrogen molecule.^[48] Thus, to understand whether the *meta*-carborane moiety supports the dihydrogen release from **3a** or cleavage of the B–C₆F₄ bond, DFT calculations (employing the same proposed intermediates) were carried out for the corresponding reactions (Scheme 3).

While the computed energies of the first intermediates **H1** and **P1** of both the hydride and proton shift are almost identical, the second and third intermediates of the hydride shift **H2** and **H3** are energetically more favored than the corresponding steps in the proton shift **P2** and **P3**. For both pathways, the final intermediate undergoes cleavage of the P–C bond (hydride shift, for **H3**) or the B–C bond (proton shift, for **P3**), yielding products in which the proton (**5a**) or hydride (**XII**) would be attached to the *para*-carbon atom relative to their starting position. Of the possible products formed from the zwitterion (namely **1a**/**XII** through P–C bond cleavage, **4a**/H₂ (FLP behavior) and **5a**/**XIII** through B–C bond cleavage), only the nucleophilic substitution through the hydride shift and P–C bond cleavage is exothermic (Scheme 3). Although the high temperature employed (150 °C) should provide enough energy to even support a pathway that is overall slightly endothermic, namely the H₂ elimination, obviously a hydride shift with P–C bond cleavage is favored and thus, the observed formation of **5a** clearly did not occur as a part of this proposed mechanism.

The formation of **5a** can, however, be attributed to hydrolysis (Scheme 2), even though precautions were taken to eliminate even traces of water. Even trace amounts of water

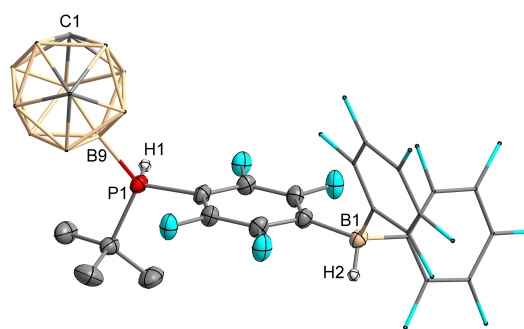


Figure 6. Molecular structure of **3b** in the solid state with thermal ellipsoids drawn at the 50% probability level. The carboranyl and C₆F₅ substituents are represented as wire frames, and the hydrogen atoms (except for PH and BH other than the carboranyl moiety) are omitted for clarity.

cause hydrolysis of the B–C₆F₄ bond in **4a**, as was confirmed by deliberately adding small amounts of D₂O resulting in formation of the corresponding deuterated **5a** containing a *p*-C₆F₄D moiety. This is in agreement with earlier reports that even extensive drying is unable to prevent boranes from scavenging trace amounts of water in the absence of other donors.^[49]

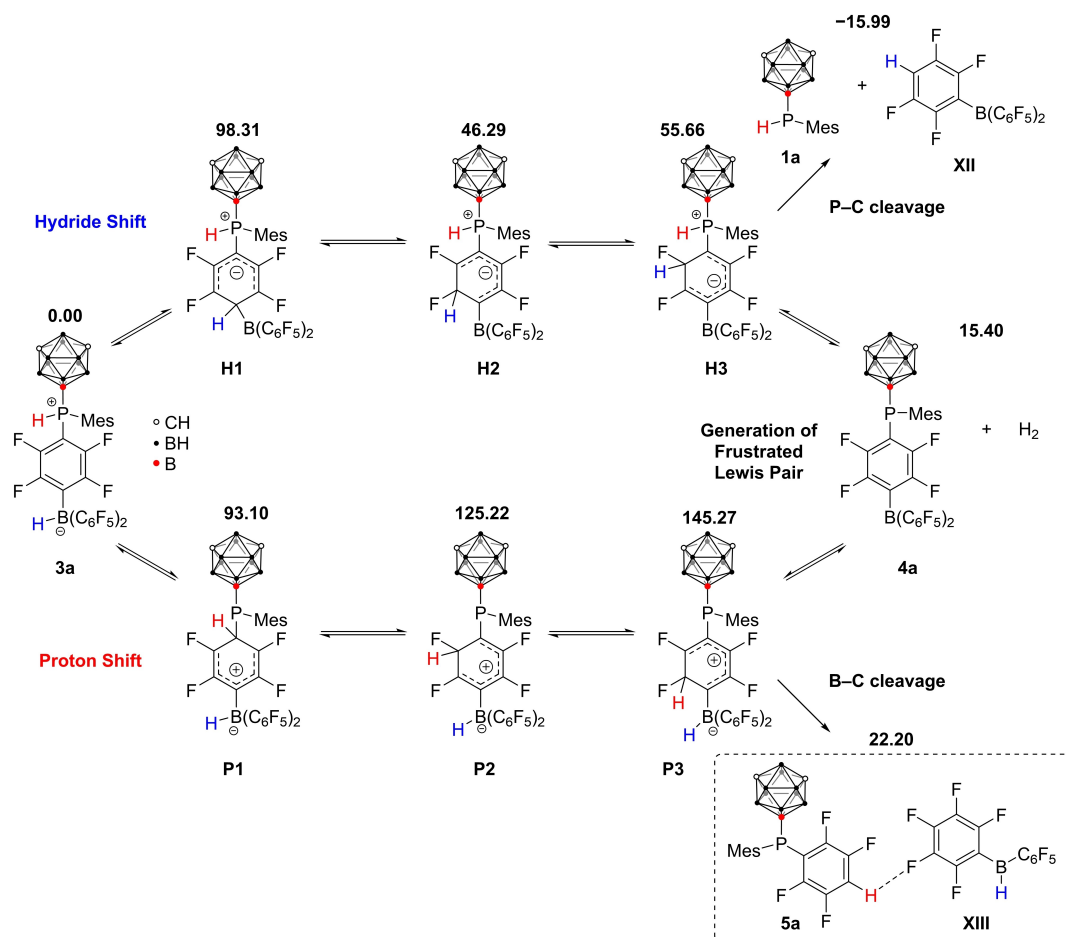
When the thermolysis of **3a** was conducted in rigorously dried solvents, a new prominent signal at –68 ppm, besides a small signal for **5a** at –75 ppm, was observed in the ³¹P{¹H} NMR spectrum, which was tentatively assigned to FLP **4a**. An alternative route is the reaction of **2a** with MeMgBr (Scheme 2)^[31] resulting in formation of **4a** according to the ³¹P NMR spectrum. While **4b** was not accessible by H₂ release from **3b**, this route with a Grignard reagent also provided access to **4b** (Scheme 2).

Interestingly, on heating of **2a** at 150 °C in bromobenzene for 48 h, signals at –68 ppm (**4a**) and –75 ppm (**5a**) could be observed in the ³¹P NMR spectrum, suggesting the formation of **4a** through release of hydrogen fluoride. As there is no hydride present in **2a**, a hydride shift is not possible, and the reaction is forced to follow a proton shift path. To exclude the possibility of a fluoride shift, since sigmatropic fluorine migrations are known in literature,^[50] the first intermediate for this pathway was calculated (see computational details in the Supporting Information); the calculation confirmed that this state would be energetically highly unfavorable, suggesting a strong bias for the proton shift.

Reactivity of frustrated Lewis pairs

In contrast to the zwitterionic phosphonium-borates, the frustrated Lewis pairs **4a** and **4b** possess unquenched acidic (empty orbital at boron) and basic centers (lone pair of electrons at phosphorus) which are available for interaction with other molecules.^[51] Subsequently, we present our investigations of the reactivity of these centers.

After generating **4a** and **4b** (both generated in situ), their ability to split dihydrogen was confirmed by applying a H₂



Scheme 3. Proposed reaction mechanism (RIJK-DSD PBEP86-D3BJ/def2 TZVP energies relative to the reactant are shown in kJ mol^{-1}).

atmosphere (1100 mbar), which resulted in the formation of **3a** and **3b** over 48 h (Scheme 2).

There are many examples of FLP systems showing water activation; however, the reaction usually stops at the HO–H bond cleavage step^[52] with few examples being able to form dihydrogen through the reduction of H_2O .^[53] Although the boron-carbon bond is usually not readily attacked by water,^[54] there is one example of water-induced B–C bond cleavage reported by Piers et al. in which bis(pentafluorophenyl)boryl-ferrocene rapidly forms FCH and $\text{B(OH)(C}_6\text{F}_5)_2$ upon treatment with water.^[55] In a similar fashion, addition of H_2O to FLPs **4a**, **b** offers a suitable route to **5a**, **b**. In the ^{19}F NMR spectra of **5a**, **b**, fluorine-proton coupling can be observed for the $\text{C}_6\text{F}_4\text{H}$ group; for **5b**, four signals are present, indicating the maintained hindered rotation about the P– C_6F_4 bond. Both compounds **5a** and **5b** expand the scope of B9-connected carboranyl phosphines to this new class of chiral (racemic) tertiary B-carboranyl phosphines and enrich the library of P-chiral (racemic) phosphines with a carborane backbone.^[20,21,56] They appear to be intriguing ligands for transition metal complexes^[57] as P-stereogenic tertiary phosphines are of continuing interest for application in enantioselective catalysis.^[58]

Anionic phosphine ligands

Due to the low solubility of the zwitterionic compounds **2a**, **b** and **3a**, **b** even in more polar solvents like CH_2Cl_2 , a variety of solvents was tested. Unexpectedly, we observed the complete deprotonation of the zwitterionic phosphonium-borates when DMSO was used as a solvent yielding the anionic phosphines **6a**, **b** and **7a**, **b**, respectively, with $[(\text{CH}_3)_2\text{SOH}]^+$ as counterion (Scheme 2). Accordingly, no PH signals were observed in the ^1H NMR spectrum and no ^{31}P – ^1H coupling in the ^{31}P NMR spectrum, but an upfield shift of the signal (Table 4). The number of phosphine ligands incorporating a borate moiety and thus rendering the ligand anionic, has steadily increased in recent

Table 4. Selected chemical shifts (in ppm).

	$^{31}\text{P}\{^1\text{H}\}$ NMR	$^{11}\text{B}\{^1\text{H}\}$ NMR $[\text{B}(\text{C}_6\text{F}_5)_2\text{R}]$ (R=H, F, Me or Ph)		$^{31}\text{P}\{^1\text{H}\}$ NMR	$^{11}\text{B}\{^1\text{H}\}$ NMR $[\text{B}(\text{C}_6\text{F}_5)_2\text{R}]$ (R=H, F, Me or Ph)
5a	–75.6	–	5b	–44.3	–
6a	–79.9	–0.9	6b	–47.7	–0.9
7a	–80.7	–25.7	7b	–48.5	–25.6
8a	–80.3	–14.3	8b	–48.5	–14.4
9a	–80.0	–12.2	9b	–48.1	–12.5

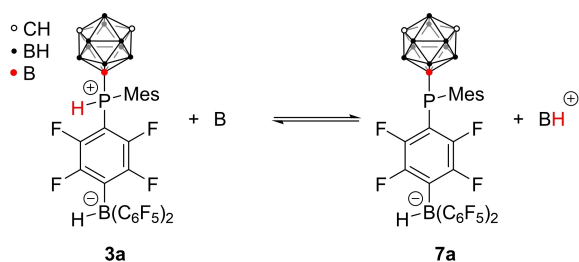
years.^[37,59] This is undoubtedly due to their ability to form zwitterionic transition metal complexes and their potential application in catalysis.^[60]

We have, therefore, further investigated the deprotonation reaction. Although DMSO (pK_a of the conjugated acid (pK_{aH}) = -1.5)^[61] has a higher basicity than water,^[62] the fact that only signals of the deprotonated species are visible in the ^{31}P NMR spectrum, when the zwitterionic compounds are dissolved in DMSO, reveals the acidity of the PH proton in the solvent.^[63] This is reminiscent of the previously reported deprotonation of phosphonium-borates,^[37] however, strong bases like SIMes (1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene) (pK_{aH} = 21.3)^[64] or PtBu_3 (pK_{aH} = 10.6)^[65] were employed in these reactions. Exemplarily, stoichiometric reactions of **3a** with various amines (B) with varying pK_{aH} values (see the Supporting Information for details)^[66] were conducted (Scheme 4).

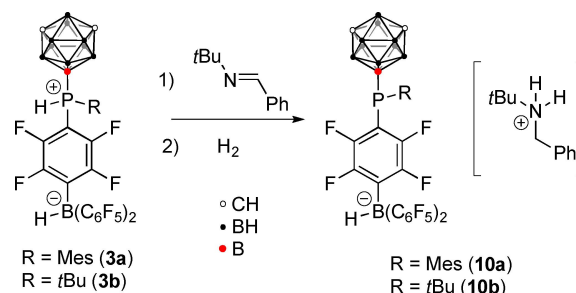
The pK_a value of **3a** in THF was determined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (see the Supporting Information for details) as $pK_a(\text{THF}) = 4.6$, which is comparable to the pK_a value of $[\text{PHCyPh}_2][\text{BF}_4]$ ($pK_a(\text{CD}_2\text{Cl}_2) = 4.3$).^[67]

A different path to anionic phosphines is the formation of "ate" complexes by reaction of FLPs **4a, b** with organomagnesium halides (MeMgBr or PhMgBr). Grignard reagents have commonly been used in the formation of weakly coordinating tetraorganoborates.^[68] When they are used in excess during the formation of FLPs **4a, b** from **2a, b**, substitution at the boron center occurs resulting in the clean formation of the anionic phosphines **8a, b** or **9a, b** (Scheme 2); the signals in the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (Table 4) are in the same range as for other tetracoordinated organoborate moieties.^[69]

Anionic phosphines with fluorinated borate moieties are very intriguing as ligands, as a weak interaction between the cationic metal complex and the anion is generally favorable in the field of homogeneous catalysis.^[70] This is exemplified by an increased reaction rate in asymmetric hydrogenation reactions for fluorinated tetraarylborates $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and BARF ($[\text{B}(\text{CF}_3)_2\text{C}_6\text{H}_3)_4]^-$).^[71] Furthermore, the influence of the borate group in anionic (phosphino)tetraphenylborate ligands has recently been examined and was shown to increase the electron-donating power of the lone pair of electrons at phosphorus.^[72]



Scheme 4. Acid–base equilibrium of **3a** and **7a** with various amines (B). B = triethylamine, 4-Br-aniline, *N*-Me-aniline, aniline, pyridine and 2-MeO-pyridine.



Scheme 5. Hydrogenation of imine $t\text{BuN}=\text{C}(\text{H})\text{Ph}$ with **3a, b** and subsequent formation of the phosphine borates **10a, b**.

Hydrogenation of imines

The reduction of imines is of immense importance in the synthesis of pharmaceuticals and in the fine chemical industries.^[73] As the zwitterionic compounds **Va, b** (Figure 3) act as catalysts in the hydrogenation of imines, we have investigated the performance of the corresponding zwitterionic carborane-based derivatives **3a, b** in the reaction with $t\text{BuN}=\text{C}(\text{H})\text{Ph}$ (the imine that previously showed the most promising results with **Va, b**).^[34] Upon addition of the imine, the reaction solutions immediately turned yellow indicating the formation of FLPs **4a, b**. Complete hydrogenation was achieved by applying a H_2 atmosphere (1100 mbar) and heating at 110°C for 2 h, after which no signals of $t\text{BuN}=\text{C}(\text{H})\text{Ph}$ remained in the ^1H NMR spectrum and formation of **10a, b** was observed (Scheme 5). Addition of another equivalent of imine under a H_2 atmosphere also resulted in complete hydrogenation (see experimental details and spectra in the Supporting Information).

Conclusion

The first B9-connected secondary carboranyl phosphines **1a** and **1b** have been obtained, giving access to an intriguing new class of electron-rich secondary phosphines. With tris(pentafluorophenyl)borane, the zwitterionic species **2a** and **2b** were formed by nucleophilic *para*-substitution of a pentafluorophenyl substituent; H/F exchange was facilitated with Me_2SiHCl to give **3a, b** which can be regarded as the products of dihydrogen splitting by a frustrated Lewis pair. Consequently, attempts were undertaken to eliminate dihydrogen from **3a, b** to generate the parent FLPs **4a, b**. However, the reaction of **2a, b** with Grignard reagents proved superior to a thermal dehydrogenation of **3a, b** in preparing FLPs **4a, b**. While **4a, b** could not be isolated, they could be prepared in situ and used for further reactions, such as dihydrogen splitting resulting in the formation of zwitterions **3a, b**. Furthermore, targeted hydrolysis of the B– C_6F_4 bond yielded the first tertiary B-connected carboranyl phosphines **5a, b** with three different substituents. Additionally, an intriguing set of anionic phosphine borates was obtained either by deprotonation of the phosphonium borates **2a, b** and **3a, b** in DMSO, leading to the anionic compounds **6a, b** and **7a, b**, or through the reaction of

FLPs **4a**, **b** with Grignard reagents, giving the tetraorganoborates **8a**, **b** and **9a**, **b**. Finally, the zwitterionic compounds **3a**, **b** were shown to hydrogenate imines.

We are now exploring the capability of the anionic phosphine ligands to form zwitterionic transition metal complexes and their catalytic potentials.

Experimental Section

Experimental details, NMR spectra, crystallographic characterization, and computational details are available in the Supporting Information.

Deposition Numbers 2114689 (for **1a**), 2145529 (for **1a**-BH₃), 2114687 (for **1b**-BH₃), 2114666 (for **2a**), 2114668 (for **3a**), 2115031 (for **3b**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: anions · carboranes · dihydrogen activation · frustrated Lewis pairs · phosphorus · zwitterions

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