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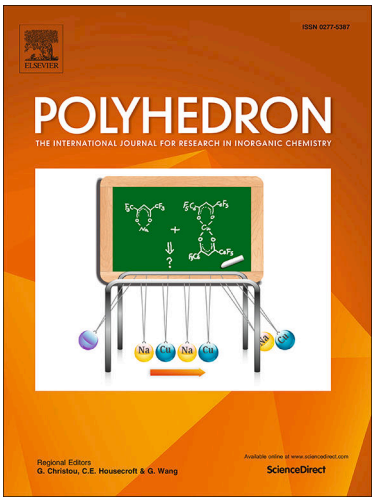

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Reactivity of bulky aminophosphanes towards small molecules: activation of dihydrogen and carbon dioxide by aminophosphane/borane frustrated Lewis pairs

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Abstract

A series of mono- and bisaminophosphanes with formulas $R_2NPR'R''$ and $(R_2N)_2PR'$ (R = *i*Pr, Cy; R' = Ph, Cy; R'' = *i*Pr) were structurally characterized by X-ray structural analysis, NMR spectroscopy and computational methods. The common structural futures of these species are short and polarized P-N bonds, a pyramidal geometry at the P atom and an almost planar geometry at the N atoms. According to DFT calculations, these compounds are highly nucleophilic, with nucleophilic centers located on the N and P atoms. Except for species containing a PPh_2 moiety, the obtained aminophosphanes are air-stable and do not react with water. They form stable frustrated Lewis pairs with BPh_3 or $B(C_6F_5)_3$. Mono- and bisaminophosphanes in the presence of $B(C_6F_5)_3$ activate dihydrogen and carbon dioxide at room temperature.

Keywords: main group chemistry; phosphanes; boranes; frustrated Lewis pairs; dihydrogen; carbon dioxide.

Introduction

Aminophosphanes are a class of P-tricoordinate compounds containing one to three polar P-N bonds and constitute a richly represented and widely studied family of phosphanes.[1–3] Based on the number of amino groups bound to the P atom, they may be classified as mono-, di- or trisaminophosphanes, and based on the number of hydrogen atoms attached to the nitrogen atom, each group may be subdivided into dialkylamino- $R_xP(NR'R'')_{3-x}$, monoalkylamino- $R_xP(NHR')_{3-x}$ and aminophosphanes $R_xP(NH_2)_{3-x}$; mono-, bis- and tris(dialkylamino)phosphanes are of the greatest interest because of their stability.[1,2,4,5] Systems with N-H bonds tend to condense to form oligomers, and this process is enhanced as the number of amino substituents increases and the steric bulk of these substituents decreases.[4] Moreover, the N-**H** atom is labile and can easily migrate from the nitrogen atom to the phosphorus atom, forming two isomers: R_2P-N(H)R' and $R_2P(H)$=NR'.[5]

Because their chirality, nucleophilicity, and reactivity towards metal complexes of phosphanes strongly depend on the substituents, attaching amino groups to the P center significantly broadens the scope of properties that can be tailored to specific applications. The nitrogen atom may constitute the stereogenic center of the molecule itself or generate a P stereogenic center as an amino substituent on phosphanes bearing three different groups, yielding chiral phosphorus ligands for use in asymmetric catalysis.[6] The introduction of nitrogen atoms as additional reactive sites increases their reactivity due to the presence of both hard (N) and soft (P) Lewis basic centers in one molecule. Therefore, in reactions with Lewis acids, aminophosphanes may behave as ambident reagents, with the P atoms being a basic center when soft acids are used as reagent partners and conversely, with the nitrogen atoms serving as bases when reacting with hard acids.[7] Despite the π-electron transfer from neighboring nitrogen atoms, the nucleophilicity of aminophosphanes depends mainly on the availability of the lone pair on the phosphorus atom; therefore, their nucleophilicity is similar to that of tertiary alkyl amines and phosphanes.[8] This indicates that steric effects (steric hindrance of the P and N substituents) rather than electronic effects are crucial in reactions with electrophiles.[2]

The condensation reaction between a phosphorus(III) halide and the respective primary or secondary amine(s) RR'NH is the most convenient method to synthesize aminophosphanes.[1,2,9–14] This method is widely used because of its readily available and inexpensive reagents, easy isolation process, and overall reaction yields ranging from

approximately 50 to 80%. To obtain mono- and bisaminophosphanes, the condensation reaction should be preceded by the introduction of alkyl, aryl or alkoxy groups in the reaction of PCl_3 with the respective organometallic reagent or alcohol due to the labile nature of the P–N bonds.[2,10,14] Therefore, aminophosphanes are generally air- and moisture-sensitive, and polar P-N bond(s) undergo hydrolysis.[5,15] Nevertheless, aminophosphanes are widely applicable as catalysts in polymerization processes and peptide synthesis[2,16] or as versatile ligands for the synthesis of transition metal complexes, which in turn supports a wide variety of organic reactions.[1,17] They may also serve as synthons to obtain a variety of inorganic heterocycles and as precursors for the synthesis of fire retardants, chemotherapeutic agents, sterilizing agents, and effective insecticides.[2]

Although aminophosphanes have a long-standing history in main-group-element chemistry, there are no reports on their reactivity as Lewis basic components in one of the most attention-grabbing groups of nonmetallic catalysts, frustrated Lewis pairs (FLPs).[18–21] These pairs are inter- or intramolecular combinations of Lewis acids and Lewis bases that, because of steric encumbrance[22,23] or reduced electronic overlap[24–27] of the reactive centers, do not form classic Lewis adducts. Such systems exhibit unusual reactivity towards small molecules – for example, FLPs are capable of activating H_2,[28–31] CO_2,[32–34] CO,[35] N_2O,[36,37] NO,[38] or SO_2[39–42]. Even simple combinations of Lewis acids (mostly boranes) with amines,[31,41,43,44] imines[18,45] or phosphanes[40,45,46] can split dihydrogen molecules heterolytically under ambient conditions to form salts that may serve as effective catalysts in the hydrogenation of unsaturated organic compounds.[28–31] There are only a few examples of nonmetallic compounds with P-N bonds that were proven to activate small molecules. Among this class of compounds, superbases attract the most attention.[47,48] Equimolar mixtures of Verkade superbase[49,50] or phosphazene[50], with weak Lewis acids (BPh_3 or $HBMe_2$) form FLPs that split H_2, while amidophosphoranes fix CO_2 molecules between the P-N bonds.[51] Interestingly, reactions of the classical adduct of Verkade superbase and strong Lewis acid $B(C_6F_5)_3$ with CO_2, PhNCO, PhNSO, or $PhCH_2N_3$ led to the insertion of these molecules into the P-B bond.[52]

One of the main interests of our group is the application of compounds containing p-block elements and possessing polarized covalent bonds to the activation of small molecules. Recently, we reported on the reactivity of $(R_2N)_2$P-P*t*Bu_2, unsymmetrical bis(dialkylamino)-substituted diphosphanes[53] that, in combination with BPh_3 acting as a catalyst, incorporated CO_2 molecules into the polar P-P bond to form $(R_2N)_2$P-O-C(O)-P*t*Bu_2.[54] Moreover, we

showed that diaminophosphinoboranes can act as intramolecular FLPs and react with CO_2 or SO_2 via the insertion of these molecules into polarized P-B bonds[55][56] We decided to include systems with polarized P-N bonds, such as aminophosphanes, in our research program. Herein, we report the structures of a series of mono- and bisaminophosphanes with bulky substituents and their reactivity towards small molecules.

Results and discussion

Syntheses and structures of mono- and bisaminophosphanes

For the reactivity studies, we selected a series of aminophosphanes bearing bulky *i*Pr$_2$N (**1**-**3**) or Cy$_2$N (**4**-**6**) amino groups (Chart 1). We assumed that these substituents would increase the stability of the obtained compounds and facilitate the formation of crystalline products. Moreover, in these species, the P atom bears phenyl (**1**, **2**, **4**-**6**), cyclohexyl (**3**), or isopropyl substituents (**6**). In this group of compounds, three monoaminophosphanes (**2**, **5**, **6**) and three bisaminophosphanes (**1**, **3**, **4**) were obtained. The syntheses of **1**,[57] **2**,[58] **4**,[59] and **5**[60] were previously reported; however, solid-state structures for these aminophosphanes remained unavailable.

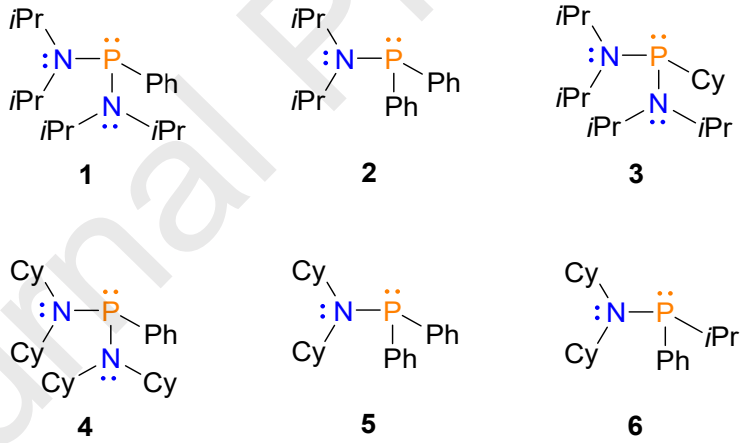
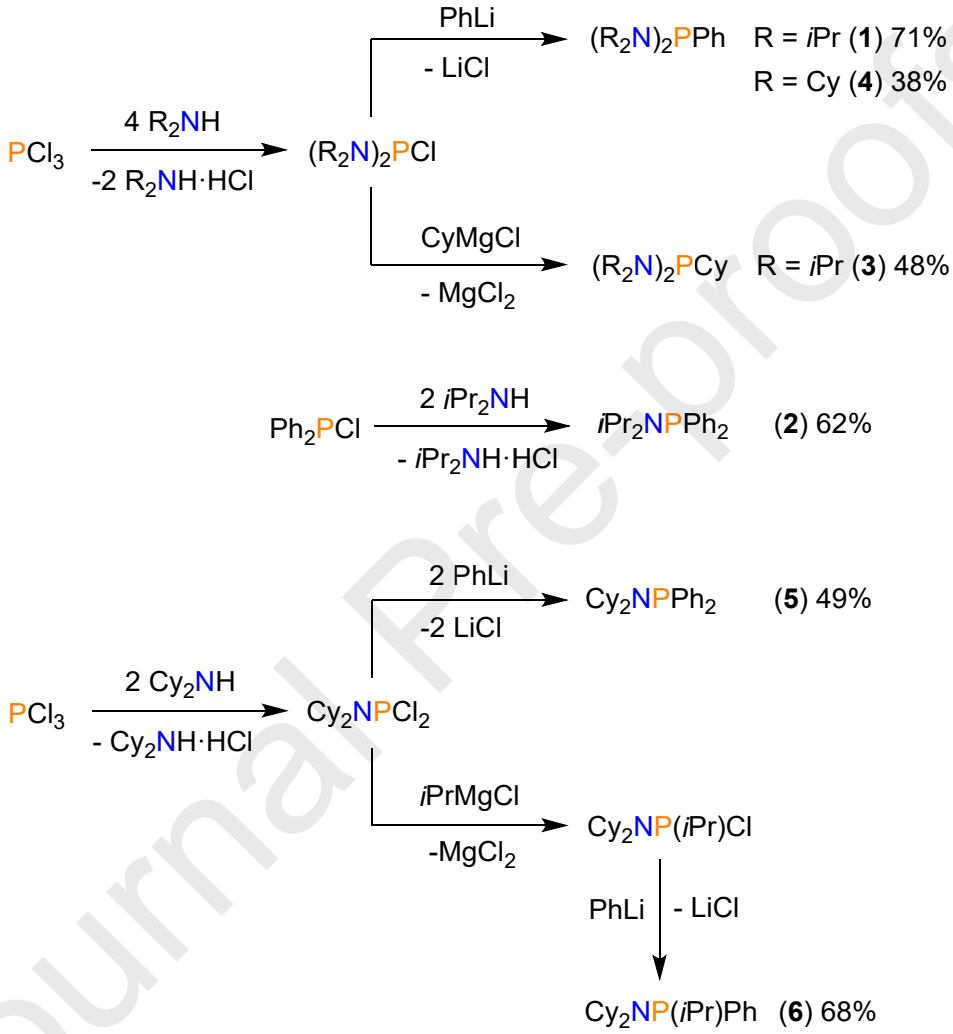


Chart 1 Mono- and bisaminophosphanes selected for the reactivity studies.

The first step of the syntheses was the condensation of phosphorus trichloride with the secondary amine *i*Pr$_2$NH or Cy$_2$NH (Scheme 1). For the syntheses of mono- and bisaminophosphanes, two- and four-fold excesses, respectively, of the secondary amine were used. In the second step, the obtained amino(chloro)phosphanes reacted with the appropriate organolithium or/and Grignard reagent. In the synthesis of **2**, we used a modified literature

method[58] where commercially available Ph_2PCl reacted with two equivalents of iPr_2NH. Notably, attempts to introduce bulkier alkyl groups such as *t*Bu at the P atom were unsuccessful. According to ^{31}P NMR spectroscopy, reactions of the mentioned amino(chloro)phosphanes with *t*BuLi or reactions of *tert*-butyl-substituted mono- and dichlorophosphanes with R_2NH (R= *i*Pr, Cy) did not occur at all, or only very weak signals attributable to the desired products were observed.



Scheme 1 Syntheses of mono- and bisaminophosphanes.

The ^{31}P NMR chemical shifts of aminophosphanes were in the range of 37.9 ppm to 64.9 ppm (Table 1). The signals of bisaminophosphanes (**1**, **3**, **4**) are more downfield shifted compared to the signals of monoaminophosphanes (**2**, **5**, **6**). Analytically pure crystalline compounds **1**-**6** were obtained by extraction of the crude products with petroleum ether (**1**, **3**) or toluene (**2**, **4**-

6) followed by crystallization at -20°C (**1**, **2**, **4**-**6**) or +4°C (**3**). Although the syntheses of **1**-**6** were almost quantitative, the yields of the crystalline products varied from 38% to 71%.

Table 1 $^{31}P\{^{1}H\}$ NMR data for the aminophosphanes (**1**-**6**) together with $^{31}P\{^{1}H\}$ NMR and ^{11}B NMR data for the products of the activation of H_2 (**1a**-**6a**) and CO_2 (**1b**, **3b**, **4b**, **6b**) by aminophosphane/borane FLPs.

No.	δ $^{31}P\{^{1}H\}$ [ppm]	$^{1}J_{P-H}$ [Hz]	δ ^{11}B [ppm]	$^{1}J_{B-H}$ [Hz]
1	59.5			
2	37.9			
3	57.7			
4	64.9			
5	41.3			
6	41.7			
1a	17.0	534	-25.0	89
2a	15.5	519	-24.7	88
3a	28.2	519	-25.0	92
4a	19.0	539	-24.9	90
5a	16.1	521	-25.0	90
6a	33.9	495	-24.7	90
1b	36.4		-2.6	
3b	50.2		-2.8	
4b	39.9		-2.7	
6b	39.1		-2.1	

Solid-state structures of all the isolated aminophosphanes were determined by single-crystal X-ray structure analysis. The X-ray structures of **1**-**6** are presented in Figure 1. Compounds **1**-**6** exhibit common structural features that are characteristic of the whole family of aminophosphanes: planar geometry of the N atoms, pyramidal geometry of the P atoms, and relatively short P-N distances (Table 2). Interestingly, in the case of bisaminophosphanes **1**, **3**, and **4**, the geometries around the P atoms are more flattened. The P-N bond lengths are in the narrow range of 1.681(2) Å – 1.705(3) Å, in between the single and double covalent P-N bond

lengths of 1.820 Å[61] and 1.620 Å[62], respectively. The determined distances are within the range of 1.661 Å – 1.723 Å reported previously for P-N bonds in aminophosphanes.[63–70]

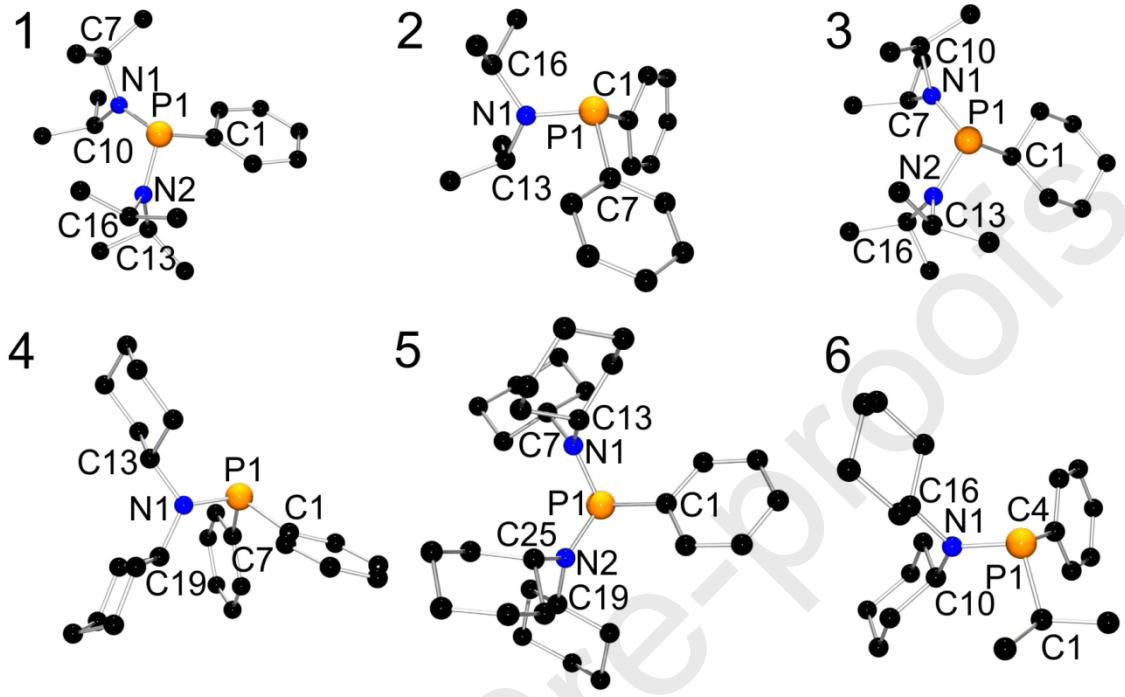


Figure 1 X-ray structures of aminophosphanes **1**-**6** showing the atom-numbering scheme. H atoms have been omitted for clarity.

Table 2 P-N bond distances and geometries at the P and N atoms in aminophosphanes **1**-**6**.

No.	P1-N1 [Å]	P1-N2 [Å]	ΣP1 [°]	ΣN1 [°]	ΣN2 [°]
1	1.696(3)	1.698(4)	317.02	359.17	359.40
2	1.681(2)		310.91	357.34	
3	1.705(3)	1.712(3)	314.49	359.90	359.89
4	1.698(2)	1.703(2)	313.60	359.68	359.37
5	1.690(2)		310.76	357.54	
6	1.6933(9)		308.07	358.82	

The structural features of **1**-**6** were investigated by DFT methods (see the ESI for details). NBO analysis indicates that the N atoms exhibit sp^2 hybridization and lone pairs at these atoms display an almost pure p character. Otherwise, the lone pairs at the P atoms have significant s character (48-50%), whereas the p orbitals of the P atoms are involved mainly in the formation

of P-C and P-N bonds (s character contribution of only 16-17%). The NBO orbitals attributed to the lone pairs on the N atoms for the representative aminophosphane **6** are presented in Figure 2. The decreased occupancies of NBO orbitals attributed to the lone pair orbitals of the N atoms and increased occupancies of antibonding σ*(P) orbitals suggest significant π-interactions between these orbitals (negative hyperconjugation). This is in accord with the structural features of aminophosphanes, such as short P-N bonds and planar amino groups. According to Hirshfeld population analysis, P-N bonds are polarized towards the N atom, where higher polarization is observed for bisaminophosphanes (**1**, **3**, **4**) than for other compounds (Figures S91-S96). For representative compound **1**, the Hirshfeld charges on P and N atoms have values of +0.159 (P1), -0.116 (N1), and -0,119 (N2). Fukui function analysis revealed that the values of the condensed nucleophilic Fukui function for P and N atoms are very similar, which indicates that both nitrogen and phosphorus atoms may constitute the nucleophilic center of aminophosphanes when reacting with an electrophile (Table S4). Similarly, the HOMO orbitals of **1**-**6** are located mainly at these atoms (Figures S85-S90).

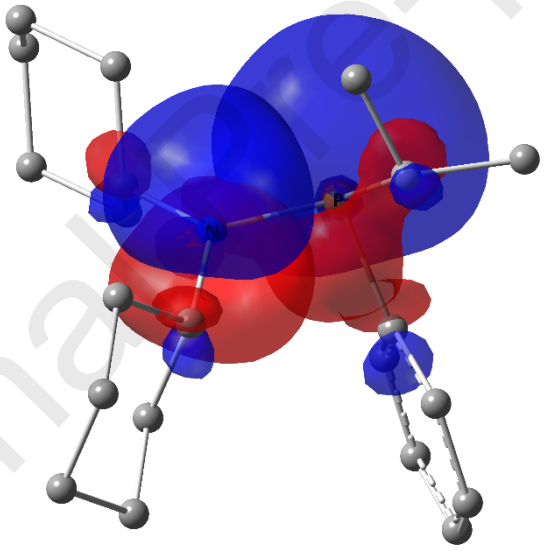
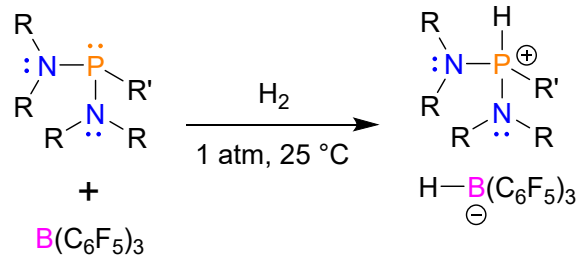


Figure 2 The NBO orbitals of **6** associated with lone pairs on the nitrogen and phosphorus atoms.

Reactivity of mono- and bisaminophosphanes towards small molecules

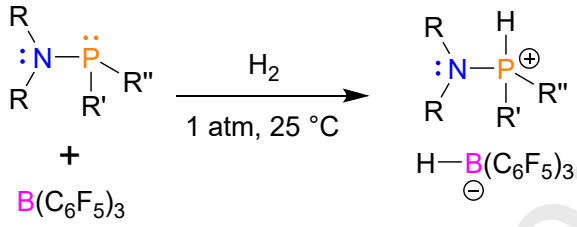
Reactions of THF solutions of **1**-**6** with water under an ambient air atmosphere were performed. Surprisingly, P-N bond hydrolysis was not observed. In the case of aminophosphanes possessing PPh_2 groups (**2**, **5**), oxidation to the respective phosphane oxides $R_2NP(=O)Ph_2$[71] occurred. The other aminophosphanes (**1**, **3**, **4**, **6**) were stable under these reaction conditions.

The structural features of aminophosphanes **1-6**, where two or three Lewis basic centers are surrounded by bulky substituents, encouraged us to test their reactivity as basic components of FLPs in reactions with small molecules. Indeed, **1-6** formed "stable" FLPs with boranes such as BPh_3 or $B(C_6F_5)_3$. According to $^{31}P\{^1H\}$ and ^{11}B NMR spectroscopy, we did not observe the formation of classic Lewis acid-base adducts or decomposition products in a benzene-d_6 solution at room temperature. The FLPs of **1-6** with $B(C_6F_5)_3$ were found to be active. Benzene-d_6 solutions containing each aminophosphane **1-6** and $B(C_6F_5)_3$ were covered by a H_2 atmosphere (1 atm) at room temperature. After overnight stirring, the formation of two phases was observed, and their composition was determined by ^1H, ^{13}C, $^{31}P\{^1H\}$, $^{19}F\{^1H\}$, and ^{11}B spectroscopy. The upper phase consisted mainly of solvent and traces of unreacted aminophosphane and borane. The $^{31}P\{^1H\}$ NMR spectrum of the lower oily phase contains signals in the range of 15.5-33.9 ppm, which are significantly shifted upfield from the signals from the parent aminophosphanes. Furthermore, the reaction products exhibited a large $^1J_{P\text{-}H}$ value (495-534 Hz) characteristic of tetracoordinated P centers with P-H functions.[72] The ^{11}B NMR spectra of the lower oily phases displayed a doublet at approximately -25 ppm with a $^1J_{B\text{-}H}$ value of approximately 90 Hz, whereas the $^{19}F\{^1H\}$ spectrum contained three signals at approximately -133 ppm, -164 ppm and -167 ppm. These NMR data are in agreement with those reported for the $[H\text{-}B(C_6F_5)_3]^-$ anion.[72] Collectively, the NMR spectroscopy data indicated the formation of phosphonium borate salts with formulas $[(R_2N)_2R'PH]^+[HB(C_6F_5)_3]^-$ (**1a**, **3a**, **4a**) or $[(R_2N)R'R''PH]^+[HB(C_6F_5)_3]^-$ (**2a**, **5a**, **6a**) as the main components of the lower oily phases (Scheme 2). Notably, we did not observe the formation of the ammonium borate salts $[[(R_2NH)(R_2N)R'P]^+[HB(C_6F_5)_3]^-$ or $[(R_2NH)R'R''P]^+[HB(C_6F_5)_3]^-$ similar to the products of reactions of amine/borane FLPs with dihydrogen.[31] The observed reaction pattern can be explained by better accessibility of the P lone pair than of the N lone pair (Figure 2) and the fact that the latter pair is involved in π-interactions with phosphorus atoms.



1 (R= *i*Pr, R'= Ph)
3 (R= *i*Pr, R'= Cy)
4 (R= Cy, R'= Ph)

1a (R= *i*Pr, R'= Ph)
3a (R= *i*Pr, R'= Cy)
4a (R= Cy, R'= Ph)



2 (R= *i*Pr, R'R''= Ph)
5 (R= Cy, R'R''= Ph)
6 (R= Cy, R'= Ph, R''= *i*Pr)

2a (R= *i*Pr, R'R''= Ph)
5a (R= Cy, R'R''= Ph)
6a (R= Cy, R'= Ph, R''= *i*Pr)

Scheme 2 Activation of dihydrogen by aminophosphane/borane FLPs.

Generally, **1a-6a** had a low tendency to crystallize; however, in the case of **1a**, **3a,** and **4a,** small amounts of crystals suitable for X-ray analysis were obtained from pentane solution at +4°C. The solid-state structures of **1a**, **3a,** and **4a** are presented in Figure 3. X-ray analysis confirmed the formation of phosphonium borate salts. Hydrogen atoms directly bound to phosphorus and boron were found in the Fourier electron density map. In the structures of **1a** and **3a,** the P-H and H-B functionalities face each other, with H···H distances of 3.44(3) Å and 2.53(5) Å, respectively. The H···H distances in **3a** are significantly shorter than those observed previously for $[t\mathrm{Bu_3PH}]^+[\mathrm{HB(C_6F_5)_3}]^-$ (2.75 Å).[72] The phosphonium cations **1a**, **3a**, and **4a** retain planar geometry at the nitrogen atoms but exhibit slightly shorter P-N bonds (1,625(2) Å – 1.649(2) Å) than do the parent aminophosphanes (1.698(4) Å – 1.712(3) Å).

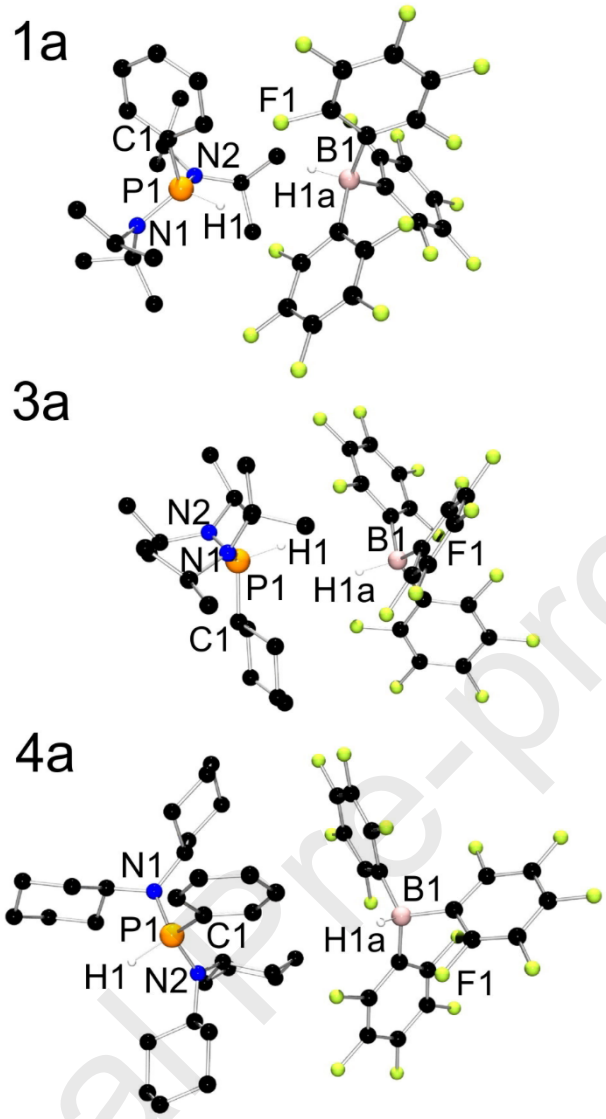
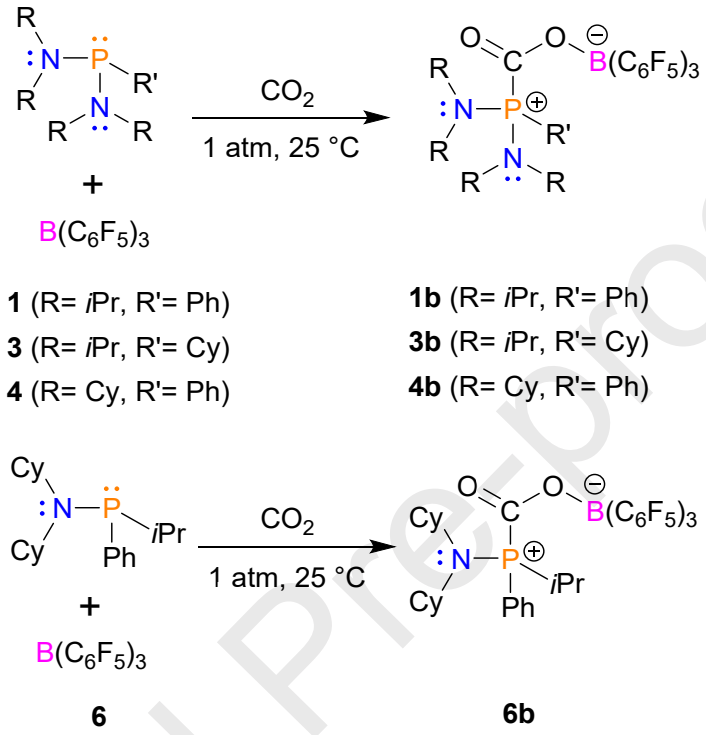


Figure 3 X-ray structures of the products of dihydrogen activation by aminophosphane/borane FLPs (**1a**, **3a**, and **4a**) showing the atom-numbering scheme. All H atoms except for P-H and B-H have been omitted for clarity.

FLPs **1**-**6** with $B(C_6F_5)_3$ react with gaseous CO_2 (1 atm) in benzene-d_6 at room temperature. The reactions involving **1**, **3**, **4** or **6** led to the formation of zwitterionic salts $(R_2N)_2R'PC(O)OB(C_6F_5)_3$ (**1b**, **3b**, **4b**) or $(Cy_2N)Ph$*i*$PrPC(O)OB(C_6F_5)_3$ (**6b**) (Scheme 3). Products **1b**, **3b**, and **4b** precipitated from the reaction solution as a white solid. The mixture of aminophosphanes containing PPh_2 groups (**2**, **5**) and $B(C_6F_5)_3$ did not form stable adducts with CO_2. The products of these reactions decomposed rapidly to symmetrical Ph_2P-PPh_2 and a complex mixture of unidentified compounds, which suggests that subsequent radical reactions occurred in the reaction mixture. The identity of isolated CO_2 activation products was confirmed by means of ^{1}H, ^{13}C, ^{31}P, ^{11}B, ^{19}F spectroscopy (**1b**, **3b**, **4b**, and **6b**) and single-

crystal X-ray diffraction (**1b**). The $^{31}P\{^{1}H\}$ spectra of the mentioned products display singlets in the range of 36.4 ppm – 50.2 ppm, whereas the ^{11}B spectra show singlets between -3 ppm and -2 ppm. Furthermore, characteristic downfield doublets attributed to the C=O group at 162.9 ppm – 163.9 ppm ($^{1}J_{C\text{-}P}$ = 133.6 Hz – 178.4 Hz) are visible in the ^{13}C spectra. These spectroscopic data are in accord with the spectroscopic data of tBu$_3$PC(O)OB(C$_6$F$_5$)$_3$.[34]



Scheme 3 Activation of carbon dioxide by aminophosphane/borane FLPs.

The X-ray structure of zwitterion **1b** is depicted in Figure 4. The P1-C1 and B1-O1 distances, with values of 1.899(2) Å and 1.535(3) Å, respectively, are very close to those observed for zwitterionic species with the P-C(=O)O-B structural motif.[34] The P1 and B1 atoms exhibit pseudotetrahedral geometries, whereas the geometries around the C1 atom of the CO_2 moiety and the N1 and N2 atoms of the amino groups are planar. Of note is that the FLPs of **1**-**6** with BPh_3 were found to be inactive towards hydrogen and carbon dioxide.

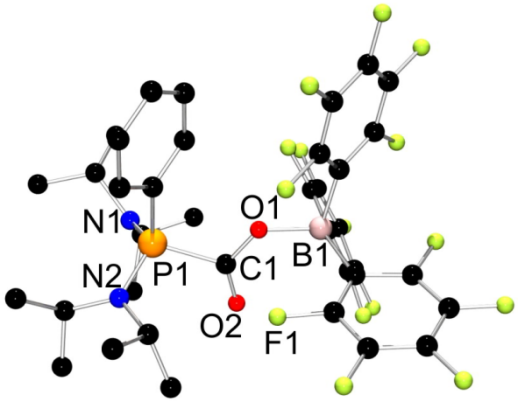


Figure 4 X-ray structures of the product of the activation of carbon dioxide by an aminophosphane/borane FLP (**1b**) showing the atom-numbering scheme. H atoms have been omitted for clarity.

Interestingly, despite the presence of highly polarized P-N in **1**-**6**, the products of CO_2 insertion into P-N bonds were not observed. The reactivity of aminophosphane/borane FLPs towards CO_2 is in strong contrast to the reactivity of diphosphane/borane FLPs, where CO_2 was inserted into a polarized P-P bond.[54] The reactions involving combinations of aminophosphanes **1**-**6** and $B(C_6F_5)_3$ with dihydrogen or carbon dioxide were not reversible. We did not observe regeneration of the parent compounds even under vacuum or elevated temperatures. It is worth mentioning that combinations of aminophosphanes with the weaker Lewis acid BPh_3 did not activate dihydrogen and carbon dioxide under the same mild conditions.

Conclusions

Our studies reveal that aminophosphanes **1**-**6** possessing bulky substituents can be successfully applied as basic components of frustrated Lewis pairs. These Lewis bases bearing the P-N structural motif are relatively easy to synthesize and in contrast to the great majority of aminophosphanes, they did not undergo oxidation or hydrolysis of the P-N bonds in ambient air (except for **2** and **5** bearing the PPh_2 group). These features make them attractive reagents for the activation of small molecules. Indeed, the combinations of **1**-**6** and $B(C_6F_5)_3$ form "stable" FLPs that activate dihydrogen and carbon dioxide at room temperature and under 1 atm of gaseous reagents. The structural features of aminophosphanes such as the presence of accessible lone pair at the P atom and the involvement of the lone pair at N atoms in π-interactions with σ*(P) antibonding orbitals, explain their reactivity towards small molecules. The reactions of FLPs containing aminophosphane as a basic component with H_2 led to

phosphonium borate salts possessing P-H function, whereas reaction with CO_2 led to the formation of a new P-C bond. The less accessible lone pairs at N atoms did not interact with small molecules, moreover, products of the insertion of small molecules into polarized P-N bonds were not observed. The studies on the reactivity of products of H_2 activation – phosphonium borate salts with P-N structural motif – are currently in progress and will be published due to course.

Materials and methods

All manipulations were performed under an Ar atmosphere in flame-dried Schlenk-type glassware on a vacuum line or in a dry box. Solvents, tetrahydrofuran, and toluene were dried over K/benzophenone and distilled under argon. Diethyl ether was dried over Na/benzophenone and distilled under argon. Pentane and petroleum ether were dried over sodium-potassium alloy and also distilled under argon. Solvents for NMR spectroscopy, C_6D_6, and $CDCl_3$, were purified with metallic sodium and P_2O_5, respectively. Literature methods were used for the synthesis of $(i\text{Pr}_2\text{N})_2\text{PCl}$[73], $(i\text{Pr}_2\text{N})\text{PCl}_2$[74], $(\text{Cy}_2\text{N})_2\text{PCl}$[75], $\text{Cy}_2\text{N-PCl}_2$[74]. $B(C_6F_5)_3$, CyMgCl, *i*PrMgCl, Ph_2PCl, PhLi were purchased from commercial and used as received. NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer at ambient temperature (external standard TMS for ^1H, ^{13}C; H_3PO_4 for ^{31}P, $BF_3{\cdot}Et_2O$ for ^{11}B, $CFCl_3$ for ^{19}F). Data were processed using Bruker's Topspin 3.5 software. For previously reported **1**,[57] **2**,[58] **4**,[59] and **5**[60] completed NMR data are provided.

Diffraction data of described compounds were collected on an IPDS 2T dual-beam diffractometer (STOE&Cie GmbH, Darmstadt, Germany) at 120.0(2) K using Mo*K*α radiation of a microfocus X-ray source (GeniX 3D Mo HighFlux, Xenocs, Sassenage, France, 50 kV, 1.0 mA, λ = 0.71069 Å) for **1**, **3**, **5**, **6**, **1a**, **3a**, **4a**, **1b**) and Cu*K*α radiation of a microfocus X-ray source (GeniX 3D Cu HighFlux, Xenocs, 50 kV, 0.6 mA, λ = 1.54186 Å) for structures **2** and **5**. Good quality single-crystal specimens of **1** – **6**, **1a**, **3a**, **4a**, and **1b** were manually selected for the X-ray diffraction experiments. The investigated crystal was thermostated in the nitrogen stream at 120 K using CryoStream-800 device (Oxford CryoSystem, UK) during the entire experiment. Data collection and data reduction were controlled by X-Area 1.75 program.[76] The structures were solved with the Shelxt method[77,78] and refined using the program packages Olex2[79,80] and SHELX-2014.[77,78] All non-hydrogen atoms were refined with anisotropic displacement parameters. All H-atoms were refined with isotropic displacement

parameters. Hydrogen atoms were placed in idealized positions and refined with usual restraints of the riding model, except P-H and B-H hydrogen atoms which were refined as an independent.

Specific details for individual structures: Structure **1** was refined with whole molecule disordered over two positions with site occupation factors of 0.6103/0.3097(10). A similar disorder was already reported for other aminophosphanes.[81] In order to stabilize positions of chemically bonded atoms, restraints for N1-C and N2-C bond lengths were applied in both parts to make them equal (SADI command). Similarly, restraints to make even bond lengths in C1-C6 rings in both parts were added. Two structures, **2** and **4**, were determined using the Cu X-ray source (due to failure of Mo-lamp) and in those cases, absorption correction was performed, being necessary. The structure of **2** was solved by SHELXT procedure and refined with the SHELXL program with no special treatment. It just turned out to be necessary to omit two reflections affected by beam stop holder shadow. The structure of **3** was also refined as disordered with the whole molecule occupying two positions with a probability of 0.8154/0.1846(15). Similarly, as for **1**, restraints for N-C and additionally on P-N bond lengths in both parts of **3** were applied. Structure **4** turned out to contain two independent molecules in the asymmetric unit, (Z = 8 in the space group $P2_1/n$) but required no special procedures for determination (except omitting of two bad reflections). Structures of **5** and **6** were determined using routine procedures. In the structure of **1a**, we refined the structure with atom P1 disordered over two positions with site occupation factors of 0.8638/0.1362(18) to absorb a relatively high electron density peak close to the atom. Due to the low occupation factor of the second part, it would be speculative to determine the position of the rest light atoms in that part. Hydrogen atoms in groups P1-H1 and B1-H1A were found in the Fourier electron density map and refined without restraints. No disorder was found in structures **3a** and **4a**, and the same procedure was applied for the determination of P-H and B-H hydrogen atom positions. Finally, structure **1b** was refined with a disorder of the *iso*propyl group C8-C9-C10 over two positions with site occupation factors of 0.559/0.441(8).

For more crystallographic details see ESI. The crystal structure analyses were performed on an STOE IPDS II diffractometer.

Elemental analysis was performed at the University of Gdańsk using a Vario El Cube CHNS apparatus.

Synthesis procedures

Synthesis of (iPr$_2$N)$_2$PPh (1)

PhLi (2.15 mL, 4.0 mmol, 1.9 M in dibutyl ether) was added dropwise to a stirred solution of (iPr$_2$N)$_2$PCl (1.080 g, 4.0 mmol) in Et$_2$O (20 mL) at 0^{o}C. The mixture was allowed to warm to room temperature and stirred overnight. Filtration to remove the white precipitate, followed by the removal of the solvent under reduced pressure, produced a light yellow residue. The crude product was extracted with petroleum ether (6 mL) and filtered. Slow cooling of the resulting solution to -20^{o}C gave suitable crystals for X-ray diffraction. Yield: 0.890 g (71%).

Elemental analysis: Calc. for $C_{18}H_{33}N_2P$: C: 70.09; H: 10.784; N: 9.08. Found: C: 70.05; H: 10.746; N: 9.04.

$^{31}P\{^1H\}$ NMR (C_6D_6): δ 59.5 (s).

^1H NMR (C_6D_6): δ 7.72 (tm, $^3J_{H-H}$ = 7.4 Hz, 2H, *o*-C***H***); 7.25 (td, $^3J_{H-H}$= 7.4 Hz, $^4J_{P-H}$ = 2.2 Hz, 2H, *m*-C***H***); 7.10 (td, $^3J_{H-H}$ = 7.4 Hz, $^4J_{H-H}$ = 1.1 Hz, 1H, *p*-C***H***); 3.32 (dsept, $^3J_{H-H}$ = 6.6 Hz, $^3J_{P-H}$ = 2.2 Hz, 4H, C***H***(CH$_3$)$_2$); 1.24 (d, $^3J_{H-H}$ = 6.6 Hz, 12H, CH(C***H***$_3$)$_2$); 1.17 (d, $^3J_{H-H}$ = 6.6 Hz, 12H, CH(C***H***$_3$)$_2$).

$^{13}C\{^1H\}$ NMR (C_6D_6): δ 145.1 (d, $^1J_{C-P}$ = 5.5 Hz, *ipso*-***C***P); 131.0 (d, $^2J_{C-P}$ = 21.1 Hz, *o*-***C***H); 127.6 (d, $^3J_{C-P}$ = 4.5 Hz, *m*-***C***H); 126.7 (d, $^4J_{C-P}$ = 1.8 Hz, *p*-***C***H); 47.7 (d, $^2J_{C-P}$ = 11.7 Hz, ***C***H(CH$_3$)$_2$); 24.2 (d, $^3J_{C-P}$ = 6.4 Hz, CH(***C***H$_3$)$_2$); 24.1 (d, $^3J_{C-P}$ = 7.9 Hz, CH(***C***H$_3$)$_2$).

Synthesis of (iPr$_2$N)PPh$_2$ (2)

Ph$_2$PCl (3.14 mL, 17.5 mmol, 1.229 g/mL) in Et$_2$O (5 mL) was added dropwise to a stirred solution of iPr$_2$NH (4.91 mL, 35.0 mmol, 0.722 g/mL) in Et$_2$O (15 mL) at 0^{o}C. The mixture was allowed to warm to room temperature and stirred overnight. Filtration to remove the white precipitate, followed by the removal of the solvent under reduced pressure, produced a light yellow residue. The crude product was extracted with toluene (30 mL) and filtered. Slow cooling of the resulting solution to -20^{o}C gave suitable crystals for X-ray diffraction. Yield: 3.086 g (62%).

Elemental analysis: Calc. for $C_{18}H_{24}NP$: C: 75.76; H: 8.477; N: 4.91. Found: C: 75.47; H: 8.231; N: 4.71.

$^{31}P\{^1H\}$ NMR (C_6D_6): δ 37.9 (s).

^{1}H NMR (C_6D_6): δ 7.58 (m, 4H, *o*-C***H***); 7.15 (m, 4H, *m*-C***H***, overlapped with solvent), 7.09 (m, 2H, *p*-C***H***); 3.29 (dsept, $^{3}J_{H-H}$ = 6.6 Hz, $^{3}J_{P-H}$ = 2.5 Hz, 2H, C***H***$(CH_3)_2$); 1.04 (d, $^{3}J_{H-H}$ = 6.6 Hz, 12H, CH(C***H***$_3)_2$).

^{13}C{^{1}H} NMR (C_6D_6): δ 141.0 (d, $^{1}J_{C-P}$ = 14.0 Hz, *ipso*-***C***P); 132.5 (d, $^{2}J_{C-P}$ = 20.5 Hz, *o*-***C***H); 128.0 (d, $^{3}J_{C-P}$ = 5.9 Hz, *m*-***C***H, overlapped with *p*-***C***H and solvent); 128.0 (s, *p*-***C***H, overlapped with *m*-CH and solvent); 47.4 (d, $^{2}J_{C-P}$ = 9.1 Hz, ***C***H$(CH_3)_2$); 23.6 ppm (d, $^{3}J_{C-P}$ = 6.7 Hz, CH(***C***H$_3)_2$).

Synthesis of (*i*Pr$_2$N)$_2$PCy (3)

CyMgCl (3.11 mL, 4.0 mmol, 1.3 M in THF) was added dropwise to a stirred solution of (*i*Pr$_2$N)$_2$PCl (1.080 g, 4.0 mmol) in THF (20 mL) at 0^{o}C. The mixture was allowed to warm to room temperature and stirred overnight. Filtration to remove the white precipitate, followed by the removal of the solvent under reduced pressure, produced a light yellow residue. The crude product was extracted with petroleum ether (20 mL) and filtered. Slow cooling of the resulting solution to +4^{o}C gave suitable crystals for X-ray diffraction. Yield: 0.608 g (48%).

Elemental analysis: Calc. for $C_{18}H_{39}N_2P$: C: 68.74; H: 12.500; N: 8.91.Found: C: 68.51; H: 12.252; N: 8.83.

^{31}P{^{1}H} NMR (C_6D_6): δ 57.7 (s).

^{1}H NMR (C_6D_6): δ 3.27 (dsept, $^{3}J_{H-H}$ = 6.6 Hz, $^{3}J_{P-H}$ = 3.4 Hz, 4H, C***H***$(CH_3)_2$); 2.02 – 1.66 (m, 6H, overlapped signals of C***H*** or C***H***$_2$ of Cy); 1.41 – 1.25 (m, 5H, overlapped signals of C***H*** and C***H***$_2$ of Cy); 1.23 (d, $^{3}J_{H-H}$ = 6.6 Hz, 12H, CH(C***H***$_3)_2$); 12 (d, $^{3}J_{H-H}$ = 6.7 Hz, 12H, CH(C***H***$_3)_2$).

^{13}C{^{1}H} NMR (C_6D_6): δ 46.9 (d, $^{2}J_{C-P}$ = 10.1 Hz, ***C***H$(CH_3)_2$); 34.6 (s, ***C***H of Cy); 30.6 (d, $^{2}J_{C-P}$ = 21.5 Hz, ***C***H$_2$ of Cy); 27.4 (d, $^{3}J_{C-P}$ = 12.9 Hz, ***C***H$_2$ of Cy); 26.8 (bs, ***C***H$_2$ of Cy); 24.7 (d, $^{3}J_{C-P}$ = 6.6 Hz, CH(***C***H$_3)_2$); 24.2 (d, $^{3}J_{C-P}$ = 6.2 Hz, CH(***C***H$_3)_2$).

Synthesis of (Cy$_2$N)$_2$PPh (4)

PhLi (2.15 mL, 4.0 mmol, 1.9 M in dibutyl ether) was added dropwise to a stirred solution of (Cy$_2$N)$_2$PCl (0.942 g, 4.0 mmol) in Et$_2$O (15 mL) at 0^{o}C. The mixture was allowed to warm to room temperature and stirred overnight. Filtration to remove the white precipitate, followed by

the removal of the solvent under reduced pressure, produced a light yellow residue. The crude product was extracted with toluene (15 mL) and filtered. Slow cooling of the resulting solution to -20ºC gave suitable crystals for X-ray diffraction. Yield: 0.704 g (38%).

Elemental analysis: Calc. for $C_{30}H_{49}N_2P$: C: 76.88; H: 10.538; N: 5.98. Found: C: 76.62; H: 10.491; N: 5.90.

$^{31}P\{^1H\}$ NMR (C_6D_6): δ 64.9 (s).

^1H NMR (C_6D_6): δ 7.83 (tm, $^3J_{H-H}$= 7.5 Hz, 2H, *o*-C***H***); 7.26 (td, $^3J_{H-H}$= 7.5 Hz, $^4J_{P-H}$= 1.9 Hz, 2H, *m*-C***H***); 7.09 (td, $^3J_{H-H}$= 7.5 Hz, $^4J_{H-H}$= 1.0 Hz, 1H, *p*-C***H***); 2.97 (m, 4H, overlapped signals of C***H*** of Cy); 2.00 – 0.95 (m, 40H, overlapped signals of C$\boldsymbol{H}_2$ of Cy).

$^{13}C\{^1H\}$ NMR (C_6D_6): δ 145.7 (d, $^1J_{C-P}$ = 9.2 Hz, *ipso*-***C***P); 131.0 (d, $^2J_{C-P}$ = 21.9 Hz, *o*-***C***H); 127.5 (d, $^3J_{C-P}$ = 4.8 Hz, *m*-***C***H); 126.6 (d, $^4J_{C-P}$ = 1.3 Hz, *p*-***C***H); 57.7 (d, $^2J_{C-P}$ = 9.7 Hz, overlapped signals of ***C***H of Cy); 35.5 (d, $^4J_{C-P}$ = 6.3 Hz, overlapped signals of ***C***H_2 of Cy); 34.9 (d, $^4J_{C-P}$ = 7.5 Hz, overlapped signals of ***C***H_2 of Cy); 26.9 (d, $^3J_{C-P}$ = 17.5 Hz, overlapped signals of ***C***H_2 of Cy); 25.8 (s, overlapped signals of ***C***H_2 of Cy).

Synthesis of $(Cy_2N)PPh_2$ (5)

PhLi (8.63 mL, 16.4 mmol, 1.9 M in dibutyl ether) was added dropwise to a stirred solution of $(Cy_2N)PCl_2$ (2.31 g, 8.2 mmol) in Et_2O (30 mL) at 0ºC. The mixture was allowed to warm to room temperature and stirred overnight. Filtration to remove the white precipitate, followed by the removal of the solvent under reduced pressure, produced a light yellow residue. The crude product was extracted with toluene (25 mL) and filtered. Slow cooling of the resulting solution to -20ºC gave suitable crystals for X-ray diffraction. Yield: 1.423 g (49%).

Elemental analysis: Calc. for $C_{24}H_{32}NP$: C: 78.87; H: 8.825; N: 3.83. Found: C: 79.07; H: 8.864; N: 3.81.

$^{31}P\{^1H\}$ NMR (C_6D_6): δ 41.3 (s).

^1H NMR (C_6D_6): δ 7.66 (m, 4H, *o*-C***H***); 7.18 (m, 4H, *m*-C***H***, overlapped with solvent); 7.10 (m, 2H, *p*-C***H***, signals overlapped with solvent); 2.93 (m, 2H, overlapped signals of C***H*** of Cy); 1.73 – 1.54 (m, 10H, overlapped signals of C$\boldsymbol{H}_2$ of Cy); 1.50 – 1.40 (bd, 2H, overlapped signals

of C***H***$_2$ of Cy); 1.37 – 1.25 (m, 2H, overlapped signals of C***H***$_2$ of Cy); 1.16 – 0.82 (m, 6H, overlapped signals of C***H***$_2$ of Cy).

$^{13}C\{^1H\}$ NMR (C_6D_6): δ 141.5 (d, $^1J_{C-P}$ = 14.9 Hz, *ipso*-***C***P); 132.5 (d, $^2J_{C-P}$ = 20.5 Hz, *o*-***C***H); 128.0 (d, $^3J_{C-P}$ = 5.5 Hz, *m*-***C***H, overlapped *p*-CH and solvent); 128.0 (s, *p*-***C***H, overlapped with *m*-CH and solvent); 57.0 (bs, ***C***H of Cy); 34.9 (bs, ***C***H$_2$ of Cy); 26.5 (s, ***C***H$_2$ of Cy); 25.7 (s, ***C***H$_2$ of Cy).

Synthesis of (Cy$_2$N)P(*i*Pr)Ph (6)

*i*PrMgCl (3.20 mL, 6.4 mmol, 2 M in Et_2O) was added dropwise to a stirred solution of (Cy$_2$N)PCl$_2$ (1.806 g, 6.4 mmol) in Et_2O (35 mL) at 0^{o}C. The mixture was allowed to warm to room temperature and stirred overnight. Filtration to remove the white precipitate, followed by the removal of the solvent under reduced pressure, produced a light yellow residue. The crude product was extracted with toluene (15 mL) and filtered. Slow cooling of the resulting solution to -20^{o}C gave light yellow crystals of (Cy$_2$N)P(*i*Pr)Cl (1.254 g, 4.3 mmol, yield 67%). The purity of the obtained product was confirmed by NMR spectroscopy. Thereafter, PhLi (2.26 mL, 4.3 mmol, 1.9 M in dibutyl ether) was added dropwise to a stirred solution of (Cy$_2$N)P(*i*Pr)Cl (1.254 g, 4.3 mmol) in Et_2O (25 mL) at 0^{o}C. The mixture was allowed to warm to room temperature and stirred overnight. Filtration to remove the white precipitate, followed by the removal of the solvent under reduced pressure, produced a white residue. The crude product was extracted with toluene (10 mL) and filtered. Slow cooling of the resulting solution to -20^{o}C gave suitable crystals for X-ray diffraction. Yield: 0.972 g (68%).

Elemental analysis: Calc. for $C_{21}H_{34}NP$: C: 76.09; H: 10.339; N: 4.23. Found: C: 76.09; H: 10.257; N: 4.20.

$^{31}P\{^1H\}$ NMR (C_6D_6): δ 41.7 (s).

^1H NMR (C_6D_6): δ 7.65 (tm, $^3J_{H-H}$ = 6.8 Hz, 2H, *o*-C***H***); 7.18 (m, 2H, *m*-C***H***, overlapped with solvent); 7.11 (m, 1H, *p*-C***H***, overlapped with solvent); 2.79 (bs, 2H, overlapped signals of C***H*** of Cy); 2.35 (sept, $^3J_{H-H}$ = 6.8 Hz, 1H, C***H***(CH$_3$)$_2$), 1.78 – 1.44 (m, 10H, overlapped signals of ***C***H$_2$ of Cy); 1.36 – 0.91 (m, 10H, overlapped signals of ***C***H$_2$ of Cy, overlapped with CH(C***H***$_3$)$_2$); 1.28 (dd, $^3J_{P-H}$ = 15.0 Hz, $^3J_{H-H}$ = 6.8 Hz, 3H, CH(C***H***$_3$)$_2$); 0.96 (dd, $^3J_{P-H}$ = 17.9 Hz, $^3J_{H-H}$ = 6.8 Hz, 3H, CH(C***H***$_3$)$_2$).

$^{13}C\{^1H\}$ NMR (C_6D_6): δ 140.5 (d, $^1J_{C-P}$ = 22.4 Hz, *ipso*-***C***P); 132.8 (d, $^2J_{C-P}$ = 21.4 Hz, *o*-***C***H); 128.3 (bs, *p*-***C***H); 127.9 (d, $^3J_{C-P}$ = 6.2 Hz, *m*-***C***H); 34.9 (bs, ***C***H of Cy); 26.7 (s, ***C***H_2 of Cy); 26.5 (s, ***C***H_2 of Cy); 25.7 (s, ***C***H_2 of Cy); 21.7 (d, $^1J_{C-P}$ = 6.36 Hz, ***C***$H(CH_3)_2$); 19.8 (d, $^2J_{C-P}$ = 19.8 Hz, ***C***$H(CH_3)_2$); 18.2 (d, $^2J_{C-P}$ = 27.5 Hz, $CH(\boldsymbol{C}H_3)_2$).

H_2 activation

General procedure for H_2 activation: appropriate aminophosphane (0.25 mmol) and $B(C_6F_5)_3$ (0.128 g, 0.25 mmol) was dissolved in C_6D_6 (3 mL). The resulting reaction mixture was subjected to a few freeze-pump-thaw cycles and subsequently exposed to 1 atm of H_2 at 78 K. The mixture was allowed to warm to room temperature and stirred overnight. After that time, two phases could be seen.

The oil phase was separated and the volatiles were removed *in vacuo*. The residue was extracted with pentane (3 mL). Slow cooling of resulting solution to +4°C gave small amount of crystals of **1a**, **3a**, and **4a** suitable for X-ray diffraction.

Samples, obtained by the dissolution of **1a** – **6a** oil phase (0.1 mL) in $CDCl_3$ (0.6 mL), were measured via NMR spectroscopy. Given yield refers to the amount of obtained oil phase.

Synthesis of $[(i\mathrm{Pr}_2\mathrm{N})_2\mathrm{PhPH}]^+[\mathrm{HB}(\mathrm{C}_6\mathrm{F}_5)_3]^-$ (1a)

Yield: 0.186 g (90%).

Elemental analysis: Calc. for $C_{36}H_{35}BF_{15}N_2P$: C: 52.57; H: 4.289; N: 3.41. Found: C: 52.10; H: 4.348; N: 3.45.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 17.0 (s) ($^1J_{P-H}$ = 534.0 Hz).

^{11}B NMR ($CDCl_3$): δ -25.0 (bd, $^1J_{B-H}$ = 89.4 Hz).

^1H NMR ($CDCl_3$): δ 7.96 (d, $^1J_{P-H}$ = 534.0 Hz, 1H, P***H***); 7.91 – 7.70 (m, 5H, overlapped signals of *o*-C***H***, *m*-C***H***, and *p*-C***H***); 4.15 (bd, $^1J_{B-H}$ = 89.4 Hz, 1H, B***H***); 3.78 (dsept, $^3J_{H-H}$ = 6.9 Hz, $^3J_{P-H}$ = 3.3 Hz, 4H, C***H***$(CH_3)_2$); 1.42 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, $CH(C\boldsymbol{H}_3)_2$); 1.29 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, $CH(C\boldsymbol{H}_3)_2$).

^{19}F $\{^1H\}$ NMR ($CDCl_3$): δ -133.1 (d, $^3J_{F-F}$ = 19.2 Hz, 6F, *o*-C_6F_5); -163.8 (t, $^3J_{F-F}$ = 20.4 Hz, 3F, *p*-C_6F_5); -166.8 (td, $^3J_{F-F}$ = 22.3 Hz, $^4J_{F-F}$ = 7.0 Hz, 6F, *m*-C_6F_5).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 148.4 (dm, $^{1}J_{C-F}$ = 236.3 Hz, *o*-***C***F); 138.0 (dm, $^{1}J_{C-F}$ = 245.8 Hz, *p*-***C***F); 136.6 (dm, $^{1}J_{C-F}$ = 246.5 Hz, *m*-***C***F); 135.8 (d,$^{4}J_{C-P}$ = 3.25 Hz, *p*-***C***H); 131.5 (d, $^{3}J_{C-P}$ = 13.9 Hz, *m*-***C***H); 130.4 (d, $^{2}J_{C-P}$ = 14.9 Hz, *o*-***C***H); 125.4 (bs, *ipso*-***C***B); 123.0 (d, $^{1}J_{C-P}$ = 124.3 Hz, *ipso*-***C***P); 48.3 (d, $^{2}J_{C-P}$ = 4.7 Hz, ***C***H$(CH_3)_2$); 22.9 (d, $^{3}J_{C-P}$ = 2.7 Hz, CH(***C***$H_3)_2$); 22.0 (d, $^{3}J_{C-P}$ = 3.1 Hz, CH(***C***$H_3)_2$).

Synthesis of [(*i*Pr_2N)Ph_2PH]$^+$[HB($C_6F_5)_3$]$^-$ (2a)

Yield: 0.178 g (89%).

Elemental analysis: Calc. for $C_{36}H_{26}BF_{15}NP$: C: 54.09; H: 3.278; N: 1.75. Found: C: 54.17; H: 3.332; N: 1.59.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 15.5 (s) ($^{1}J_{P-H}$ = 519.0 Hz).

^{11}B NMR ($CDCl_3$): δ -24.7 (bd, $^{1}J_{B-H}$ = 88.2 Hz).

^{1}H NMR ($CDCl_3$): δ 8.50 (d, $^{1}J_{P-H}$ = 519.0 Hz, 1H, P***H***); 7.95 – 7.88 (m, 2H overlapped signals of *o*-C***H***, *m*-C***H***, *and p*-C***H***); 7.80 – 7.73 (m, 7H, overlapped signals of *o*-C***H***, *m*-C***H***, *and p*-C***H***); 7.52 – 7.35 (m, 1H, overlapped signals of *o*-C***H***, *m*-C***H***, and *p*-C***H***); 4.09 (bd, $^{1}J_{B-H}$ = 88.2 Hz, 1H, B***H***); 3.73 (dsept, $^{3}J_{H-H}$ = 6.7 Hz, $^{3}J_{P-H}$ = 3.2 Hz, 2H, C***H***$(CH_3)_2$); 1.37 (d, $^{3}J_{H-H}$ = 6.7 Hz, 9H, CH(C***H***$_3)_2$).

^{19}F $\{^{1}H\}$ NMR ($CDCl_3$): δ -133.1 (d, $^{3}J_{F-F}$ = 19.7 Hz, 6F, *o*-C_6F_5); -163.3 (t, $^{3}J_{F-F}$ = 20.4 Hz, 3F, *p*-C_6F_5); -166.4 (td, $^{3}J_{F-F}$ = 22.3 Hz, $^{4}J_{F-F}$ = 7.1 Hz, 6F, *m*-C_6F_5).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 148.3 (dm, $^{1}J_{C-F}$ = 234.3 Hz, *o*-***C***F); 138.1 (dm, $^{1}J_{C-F}$ = 243.9 Hz, *p*-***C***F); 136.6 (dm, $^{1}J_{C-F}$ = 249.0 Hz, *m*-***C***F); 136.2 (s, *p*-***C***H); 133.1 (d, $^{3}J_{C-P}$ = 12.6 Hz, *m*-***C***H); 130.7 (d, $^{2}J_{C-P}$ = 13.9 Hz, *o*-***C***H); 124.9 (bs, *ipso*-***C***B); 117.8 (d, $^{1}J_{C-P}$ = 99.5 Hz, *ipso*-***C***P); 48.8 (s, ***C***H$(CH_3)_2$); 22.4 (bs, CH(***C***$H_3)_2$); 19.1 (s, CH(***C***$H_3)_2$

Synthesis of [(*i*Pr_2N)$_2$CyPH]$^+$[HB($C_6F_5)_3$]$^-$ (3a)

Yield: 0.192 g (93%).

Elemental analysis: Calc. for $C_{36}H_{41}BF_{15}N_2P$: C: 52.19; H: 4.988; N: 3.38. Found: C: 51.63; H: 4.923; N: 3.30.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 28.2 (s) ($^{1}J_{P-H}$ = 519.4 Hz).

^{11}B NMR ($CDCl_3$): δ -25.0 (bd, $^1J_{B-H}$ = 91.5 Hz).

^{1}H NMR ($CDCl_3$): δ 6.83 (dd, $^1J_{P-H}$ = 519.4 Hz, $^3J_{H-H}$ = 7.5 Hz, 1H, P***H***); 3.97 (bd, $^1J_{B-H}$ = 91.5 Hz, 1H, B***H***, overlapped with C***H***$(CH_3)_2$); 3.67 (dsept, $^3J_{H-H}$ = 6.8 Hz, $^3J_{P-H}$ = 1.9 Hz, 2H, C***H***$(CH_3)_2$); 2.60 (bs, 1H, C***H*** of Cy); 2.14 – 1.88 (m, 5H, overlapped signals of C***H*** or C$\boldsymbol{H}_2$ of Cy); 1.56 – 1.29 (m, 5H, overlapped signals of C***H*** or C$\boldsymbol{H}_2$ of Cy, overlapped with CH(C$\boldsymbol{H}_3)_2$); 1.43 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, CH(C$\boldsymbol{H}_3)_2$); 1.38 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, CH(C$\boldsymbol{H}_3)_2$).

^{19}F {^{1}H} NMR ($CDCl_3$): δ -133.0 (d, $^3J_{F-F}$ = 19.6 Hz, 6F, *o*-C_6F_5); -163.9 (t, $^3J_{F-F}$ = 20.1 Hz, 3F, *p*-C_6F_5); -166.8 (td, $^3J_{F-F}$ = 21.3 Hz, $^4J_{F-F}$ = 6.9 Hz, 6F, *m*-C_6F_5).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.5 (dm, $^1J_{C-F}$ = 237.5 Hz, *o*-***C***F); 138.0 (dm, $^1J_{C-F}$ = 243.2 Hz, *p*-***C***F); 136.6 (dm, $^1J_{C-F}$ = 245.6 Hz, *m*-***C***F); 125.5 (bs, *ipso*-***C***B); 49.2 (d, $^2J_{C-P}$ = 2.8 Hz, ***C***H$(CH_3)_2$); 34.7 (d, $^1J_{C-P}$ = 82.3 Hz, P***C***H of Cy); 28.3 (s, ***C***H_2 of Cy); 26.3 (d, $^2J_{C-P}$ = 17.2 Hz, ***C***H_2 of Cy); 25.0 (bs, ***C***H_2 of Cy); 23.2 (d, $^3J_{C-P}$ = 2.7 Hz, CH(***C***$H_3)_2$); 23.2 (d, $^3J_{C-P}$ = 2.0 Hz, CH(***C***$H_3)_2$).

Synthesis of $[(Cy_2N)_2PhPH]^+[HB(C_6F_5)_3]^-$ (4a)

Yield: 0.205 g (84%).

^{31}P{^{1}H} NMR ($CDCl_3$): δ 19.0 (s) ($^1J_{P-H}$ = 538.7 Hz, $^3J_{P-H}$ = 14.7 Hz).

^{11}B NMR ($CDCl_3$): δ -24.9 (bd, $^1J_{B-H}$ = 89.7 Hz).

^{1}H NMR ($CDCl_3$): δ 8.12 (d, $^1J_{P-H}$ = 538.7 Hz, 1H, P***H***); 7.92 – 7.82 (m, 3H, overlapped signals of *m*-C***H***, and *p*-C***H***); 7.73 (m, 2H, *o*-C***H***); 4.00 (bd, $^1J_{B-H}$ = 91.5 Hz, 1H, B***H***); 3.33 (m, 4H, C***H*** of Cy); 2.05 – 1.95 (m, 8H, overlapped signals of C$\boldsymbol{H}_2$ of Cy); 1.95 – 1.85 (m, 4H, overlapped signals of C$\boldsymbol{H}_2$ of Cy); 1.81 – 1.66 (m, 12H, overlapped signals of C$\boldsymbol{H}_2$ of Cy); 1.66 – 1.52 (m, 4H, overlapped signals of C$\boldsymbol{H}_2$ of Cy); 1.47 – 1.23 (m, 8H, overlapped signals of C$\boldsymbol{H}_2$ of Cy); 1.23 – 1.08 (m, 4H, overlapped signals of C$\boldsymbol{H}_2$ of Cy).

^{19}F {^{1}H} NMR ($CDCl_3$):): δ -132.9 (d, $^3J_{F-F}$ = 20.2 Hz, 6F, *o*-C_6F_5); -164.0 (t, $^3J_{F-F}$ = 20.4 Hz, 3F, *p*-C_6F_5); -166.8 (td, $^3J_{F-F}$ = 22.0 Hz, $^4J_{F-F}$ = 7.0 Hz, 6F, *m*-C_6F_5).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.4 (bd, $^1J_{C-F}$ = 242.8 Hz, *o*-***C***F); 138.0 (bd, $^1J_{C-F}$ = 243.8 Hz, *p*-***C***F); 136.6 (bd, $^1J_{C-F}$ = 250.6 Hz, *m*-***C***F); 135.6 (d, $^4J_{C-P}$ = 2.8 Hz, *p*-***C***H); 131.5 (d, $^3J_{C-P}$ = 14.2 Hz, *m*-***C***H); 130.2 (d, $^2J_{C-P}$ = 15.2 Hz, *p*-***C***H); 125.6 (bs, *ipso*-***C***B); 123.8 (d, $^1J_{C-P}$ = 123.6 Hz,

ipso-***C***P); 57.6 (d, $^{2}J_{C-P}$ = 3.6 Hz, ***C***H of Cy); 34.0 (bs, overlapped signals of ***C***H_2 of Cy); 33.1 (bs, overlapped signals of ***C***H_2 of Cy); 26.3 (s, overlapped signals of ***C***H_2 of Cy); 26.2 (s, overlapped signals of ***C***H_2 of Cy); 24.8 (s, overlapped signals of ***C***H_2 of Cy).

Synthesis of $[(Cy_2N)Ph_2PH]^+[HB(C_6F_5)_3]^-$ (5a)

Yield: 0.198 g (90%).

Elemental analysis: Calc. for $C_{42}H_{34}BF_{15}NP$: C: 57.36; H: 3.897; N: 1.59. Found: C: 57.29; H: 4.081; N: 1.21.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 16.1 (s) ($^{1}J_{P-H}$ = 521.4 Hz).

^{11}B NMR ($CDCl_3$): δ -25.0 (bd, $^{1}J_{B-H}$ = 89.9 Hz).

^{1}H NMR ($CDCl_3$): δ 8.30 (d, $^{1}J_{P-H}$ = 521.4 Hz, 1H, P***H***); 7.64 – 7.40 (m, 10H, overlapped signals of *o*-C***H***, *m*-C***H***, and *p*-C***H***); 3.69 (bd, $^{1}J_{B-H}$ = 89.9 Hz, 1H, B***H***); 2.99 (m, 2H, C***H*** of Cy); 1.70 – 1.31 (m, 14H, overlapped signals of C***H***$_2$ of Cy); 1.12 – 0.80 (m, 6H, overlapped signals of C***H***$_2$ of Cy).

^{19}F $\{^{1}H\}$ NMR ($CDCl_3$): δ -133.3 (d, $^{3}J_{F-F}$ = 18.8 Hz, 6F, *o*-C_6F_5); -163.6 (t, $^{3}J_{F-F}$ = 20.1 Hz, 3F, *p*-C_6F_5); -166.7 (td, $^{3}J_{F-F}$ = 22.3 Hz, $^{4}J_{F-F}$ = 7.3 Hz, 6F, *m*-C_6F_5).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 148.1 (dm, $^{1}J_{C-F}$ = 232.1 Hz, *o*-***C***F); 137.7 (dm, $^{1}J_{C-F}$ = 243.2 Hz, *p*-***C***F); 136.4 (dm, $^{1}J_{C-F}$ = 247.5 Hz, *m*-***C***F); 135.8 (s, *p*-***C***H); 132.8 (d, $^{3}J_{C-P}$ = 12.4 Hz, *m*-***C***H); 130.2 (d, $^{2}J_{C-P}$ = 13.7 Hz, *o*-***C***H); 124.7 (bs, *ipso*-***C***B); 117.9 (d, $^{1}J_{C-P}$ = 99.5 Hz, *ipso*-***C***P); 57.3 (s, C***H*** of Cy); 33.2 (s, overlapped signals of ***C***H_2 of Cy); 29.5 (s, overlapped signals of ***C***H_2 of Cy); 25.6 (s, overlapped signals of ***C***H_2 of Cy); 24.4 (s, overlapped signals of ***C***H_2 of Cy); 23.9 (s, overlapped signals of ***C***H_2 of Cy).

Synthesis of $[(Cy_2N)(iPr)PhPH]^+[HB(C_6F_5)_3]^-$ (6a)

Yield: 0.186 g (88%).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 33.9 (s) ($^{1}J_{P-H}$ = 494.5 Hz).

^{11}B NMR ($CDCl_3$): δ -24.7 (bd, $^{1}J_{B-H}$ = 89.8 Hz).

^{1}H NMR ($CDCl_3$): δ 7.89 – 7.66 (m, 5H, overlapped signals of *o*-C***H***, *m*-C***H***, and *p*-C***H***); 7.37 (dd, $^{1}J_{P-H}$ = 494.5 Hz, $^{3}J_{H-H}$ = 9.4 Hz, 1H, P***H***); 3.97 (bd, $^{1}J_{B-H}$ = 89.8 Hz, 1H, B***H***); 3.38 – 2.91 (m, 3H, overlapped signals of C***H*** of Cy, and C***H***$(CH_3)_2$); 2.02 – 1.01 (m, 26H, overlapped signals of C***H***$_2$ of Cy, and CH(C***H***$_3)_2$).

^{19}F {^{1}H} NMR ($CDCl_3$): δ -133.1 (d, $^{3}J_{F-F}$ = 19.0 Hz, 6F, *o*-C_6F_5); -163.4 (t, $^{3}J_{F-F}$ = 20.3 Hz, 3F, *p*-C_6F_5); -166.5 (td, $^{3}J_{F-F}$ = 22.6 Hz, $^{4}J_{F-F}$ = 7.2 Hz, 6F, *m*-C_6F_5).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.4 (dm, $^{1}J_{C-F}$ = 237.1 Hz, *o*-***C***F); 138.0 (dm, $^{1}J_{C-F}$ = 243.5 Hz, *p*-***C***F); 136.7 (dm, $^{1}J_{C-F}$ = 247.8 Hz, *m*-***C***F); 135.8 (d, $^{4}J_{C-P}$ = 2.7 Hz, *p*-***C***H); 137.7 (d, $^{3}J_{C-P}$ = 10.5 Hz, *m*-***C***H); 130.7 (d, $^{2}J_{C-P}$ = 12.6 Hz, *o*-***C***H); 125.0 (bs, *ipso*-***C***B); 119.6 (d, $^{1}J_{C-P}$ = 85.8 Hz, *ipso*-***C***P); 57.7 (d, $^{2}J_{C-P}$ = 1.7 Hz, ***C***H of Cy); 33.6 (d, $^{3}J_{C-P}$ = 15.2 Hz, ***C***H$_2$ of Cy); 25.9 (s, ***C***H$_2$ of Cy); 24.6 (s, ***C***H$_2$ of Cy); 22.3 (d, $^{2}J_{C-P}$ = 60.6 Hz, ***C***H$(CH_3)_2$); 16.8 (d, $^{3}J_{C-P}$ = 2.4 Hz, CH(***C***H$_3)_2$); 16.4 (d, $^{3}J_{C-P}$ = 2.6 Hz, CH(***C***H$_3)_2$).

CO_2 activation

General procedure for CO_2 activation: appropriate aminophosphane (0.25 mmol) and $B(C_6F_5)_3$ (0.128 g, 0.25 mmol) was dissolved in C_6D_6 (3 mL). The resulting reaction mixture was subjected to a few freeze-pump-thaw cycles and subsequently exposed to 1 atm of CO_2 at 78 K. The mixture was allowed to warm to room temperature and stirred overnight. After that time, in the case of the reaction of **1**, **3,** and **4** aminophosphane, white solid precipitated.

The solvent was evaporated and the volatiles were removed *in vacuo*. The residue was extracted with petroleum ether (4 mL) and filtrated. The solvent was evaporated and the crude product was extracted with CH_2Cl_2 (1 mL). Slow cooling of resulting solution to -30^{o}C gave suitable crystals of **1b** for X-ray diffraction in a low yield.

Samples, obtained by the dissolution of **1b**, **3b**, and **4b** white solid (0.020 g) in $CDCl_3$ (0.7 mL) and the sample of **6b** fraction in C_6D_6, were measured via NMR spectroscopy. Given yield refers to the amount of obtained white solid.

Synthesis of (*i*Pr$_2$N)$_2$PhPC(O)OB(C$_6$F$_5$)$_3$ (1b)

Yield: 0.121 g (56%).

^{31}P{^{1}H} NMR ($CDCl_3$): δ 36.4 (s).

^{11}B NMR ($CDCl_3$): δ -2.6 (s).

^{1}H NMR ($CDCl_3$): δ 7.96 (dd, $^{3}J_{P-H}$ = 13.2 Hz, $^{3}J_{H-H}$ = 7.5 Hz, 2H, *o*-C***H***); 7.68 (tm, $^{3}J_{H-H}$ = 7.5 Hz, 1H, *p*-C***H***); 7.46 (td, $^{3}J_{H-H}$= 7.5 Hz, $^{4}J_{P-H}$ = 3.8 Hz, 2H, *m*-C***H***); 2.50 (sept, $^{3}J_{H-H}$= 6.8 Hz, 4H, C***H***$(CH_3)_2$); 1.24 (d, $^{3}J_{H-H}$ = 6.8 Hz, 12H, CH(C***H***$_3)_2$); 1.11 (d, $^{3}J_{H-H}$ = 6.8 Hz, 3H, CH(C***H***$_3)_2$).

^{19}F {^{1}H} NMR ($CDCl_3$): δ -135.6 (bd, $^{3}J_{F-F}$ = 22.3 Hz, 6F, *o*-C_6F_5); -159.9 (t, $^{3}J_{F-F}$ = 20.4 Hz, 3F, *p*-C_6F_5); -165.4 (btd, $^{3}J_{F-F}$ = 22.9 Hz, $^{4}J_{F-F}$ = 7.6 Hz, 6F, *m*-C_6F_5).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 163.9 (d, $^{1}J_{C-P}$ = 175.2 Hz, C=O); 147.8 (dm, $^{1}J_{C-F}$ = 242.4 Hz, *o*-***C***F); 139.3 (dm, $^{1}J_{C-F}$ = 241.5 Hz, *p*-***C***F); 136.7 (dm, $^{1}J_{C-F}$ = 249.1 Hz, *m*-***C***F); 135.2 (d, $^{4}J_{C-P}$ = 2.9 Hz, *p*-***C***H); 134.8 (d, $^{3}J_{C-P}$ = 11.7 Hz, *o*-***C***H); 128.8 (d, $^{2}J_{C-P}$ = 13.4 Hz, *m*-***C***H); 121.3 (d, $^{1}J_{C-P}$ = 107.7 Hz, *ipso*-***C***P); 119.5 (bs, *ipso*-***C***B); 50.0 (d, $^{2}J_{C-P}$ = 5.2 Hz, ***C***H$(CH_3)_2$); 23.8 (d, $^{3}J_{C-P}$ = 3.2 Hz, CH(***C***H$_3)_2$); 23.7 (d, $^{3}J_{C-P}$ = 2.6 Hz, CH(***C***H$_3)_2$).

Synthesis of (*i*Pr$_2$N)$_2$CyPC(O)OB(C$_6$F$_5$)$_3$ (3b)

Yield: 0.149 g (68%).

^{31}P{^{1}H} NMR ($CDCl_3$): δ 50.2 (s).

^{11}B NMR ($CDCl_3$): δ -2.8 (s).

^{1}H NMR ($CDCl_3$): δ 3.68 (dsept, $^{3}J_{H-H}$ = 6.8 Hz, $^{3}J_{P-H}$ = 2.6 Hz, 4H, C***H***$(CH_3)_2$); 2.23 (m, 1H, C***H*** of Cy); 2.09 (m, 2H, C***H***$_2$ of Cy); 1.83 (m, 2H, C***H***$_2$ of Cy); 1.68 (m, 2H, C***H***$_2$ of Cy); 1.26 (m, 24H, CH(C***H***$_3)_2$); 1.22 – 1.06 (m, 4H, overlapped signals of C***H***$_2$ of Cy);.

^{19}F {^{1}H} NMR ($CDCl_3$): δ -133.5 (bd, $^{3}J_{F-F}$ = 22.8 Hz, 6F, *o*-C_6F_5); -159.9 (t, $^{3}J_{F-F}$ = 20.5 Hz, 3F, *p*-C_6F_5); -165.4 (btd, $^{3}J_{F-F}$ = 23.3 Hz, $^{4}J_{F-F}$ = 7.4 Hz, 6F, *m*-C_6F_5).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 163.6 (d, $^{1}J_{C-P}$ = 164.2 Hz, C=O); 147.8 (dm, $^{1}J_{C-F}$ = 238.8 Hz, *o*-***C***F); 139.3 (dm, $^{1}J_{C-F}$ = 241.4 Hz, *p*-***C***F); 136.7 (dm, $^{1}J_{C-F}$ = 261.3 Hz, *m*-***C***F); 119.7 (bs, *ipso*-***C***B); 49.7 (d, $^{2}J_{C-P}$ = 3.9 Hz, ***C***H$(CH_3)_2$); 38.4 (d, $^{1}J_{C-P}$ = 61.3 Hz, P***C***H of Cy); 28.3 (s, ***C***H$_2$ of Cy); 26.7 (d, $^{2}J_{C-P}$ = 14.4 Hz, ***C***H$_2$ of Cy); 26.1 (d, $^{2}J_{C-P}$ = 2.75 Hz, ***C***H$_2$ of Cy); 25.4 (d, $^{2}J_{C-P}$ = 1.76 Hz, ***C***H$_2$ of Cy); 24.5 (d, $^{3}J_{C-P}$ = 2.9 Hz, CH(***C***H$_3)_2$); 24.4 (d, $^{3}J_{C-P}$ = 3.8 Hz, CH(***C***H$_3)_2$).

Synthesis of (Cy$_2$N)$_2$PhPC(O)OB(C$_6$F$_5$)$_3$ (4b)

Yield: 0.164 g (64%).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 39.9 (s).

^{11}B NMR ($CDCl_3$): δ -2.7 (s).

^{1}H NMR ($CDCl_3$): δ 7.79 (dd, $^{3}J_{P-H}$ = 12.8 Hz, $^{3}J_{H-H}$ = 7.8 Hz, 2H, *o*-C***H***); 7.65 (bt, $^{3}J_{H-H}$ = 7.8 Hz, 1H, *p*-C***H***); 7.36 (td, $^{3}J_{H-H}$= 7.8 Hz, $^{4}J_{P-H}$ = 3.7 Hz, 2H, *m*-C***H***); 3.27 (m, 4H, C***H*** of Cy); 1.91 – 1.84 (m, 4H, overlapped signals of C$\boldsymbol{H}_2$ of Cy); 1.68 – 1.48 (m, 24H, overlapped signals of C$\boldsymbol{H}_2$ of Cy); 1.07 – 0.92 (m, 12H, overlapped signals of C$\boldsymbol{H}_2$ of Cy).

^{19}F $\{^{1}H\}$ NMR ($CDCl_3$): δ -132.8 (bd, $^{3}J_{F-F}$ = 21.5 Hz, 6F, *o*-C_6F_5); -160.1 (t, $^{3}J_{F-F}$ = 20.5 Hz, 3F, *p*-C_6F_5); -165.3 (m, 6F, *m*-C_6F_5).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 162.9 (d, $^{1}J_{C-P}$ = 178.4 Hz, C=O); 147.8 (dm, $^{1}J_{C-F}$ = 245.9 Hz, *o*-***C***F); 139.4 (dm, $^{1}J_{C-F}$ = 249.5 Hz, *p*-***C***F); 136.7 (dm, $^{1}J_{C-F}$ = 251.6 Hz, *m*-***C***F); 134.6 (d, $^{4}J_{C-P}$ = 2.3 Hz, *p*-***C***H); 134.4 (d, $^{3}J_{C-P}$ = 11.2 Hz, *o*-***C***H); 128.5 (d, $^{2}J_{C-P}$ = 13.0 Hz, *m*-***C***H); 122.1 (d, $^{1}J_{C-P}$ = 106.6 Hz, *ipso*-***C***P); 119.3 (bs, *ipso*-***C***B); 59.2 (d, $^{2}J_{C-P}$ = 4.4 Hz, ***C***H of Cy); 35.0 (d, $^{3}J_{C-P}$ = 2.7 Hz, overlapped signals of ***C***H_2 of Cy); 26.8 (d, $^{3}J_{C-P}$ = 5.0 Hz, overlapped signals of ***C***H_2 of Cy); 25.2 (s, overlapped signals of ***C***H_2 of Cy).

Synthesis of (Cy_2N)(*i*Pr)PhPC(O)OB$(C_6F_5)_3$ (6b)

$^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 39.1 (s).

^{11}B NMR (C_6D_6): δ -2.1 (s).

^{1}H NMR (C_6D_6): δ 7.41 (dd, $^{3}J_{P-H}$ = 11.9 Hz, $^{3}J_{H-H}$ = 7.4 Hz, 2H, *o*-C***H***); 7.02 (td, $^{3}J_{H-H}$ = 7.4 Hz, $^{4}J_{H-H}$ = 1.6 Hz, 1H, *p*-C***H***); 6.92 (td, $^{3}J_{H-H}$= 7.4 Hz, $^{4}J_{P-H}$ = 3.5 Hz, 2H, *m*-C***H***); 2.80 (m, 2H, C***H*** of Cy); 2.50 (sept, $^{3}J_{H-H}$ = 6.9 Hz, 1H, C***H***$(CH_3)_2$); 1.78 – 1.63 (m, 2H, overlapped signals of C$\boldsymbol{H}_2$ of Cy); 1.49 – 1.35 (m, 6H, overlapped signals of C$\boldsymbol{H}_2$ of Cy); 1.34 – 1.26 (m, 2H, overlapped signals of C$\boldsymbol{H}_2$ of Cy); 1.10 – 0.81 (m, 8H, overlapped signals of ***C***H_2 of Cy, overlapped with CH(C$\boldsymbol{H}_3)_2$); 0.99 (dd, $^{3}J_{P-H}$ = 19.5 Hz, $^{3}J_{H-H}$ = 6.9 Hz, 3H, CH(C$\boldsymbol{H}_3)_2$); 0.96 (dd, $^{3}J_{P-H}$ = 18.1 Hz, $^{3}J_{H-H}$ = 6.9 Hz, 3H, CH(C$\boldsymbol{H}_3)_2$).

^{19}F $\{^{1}H\}$ NMR (C_6D_6): δ -133.4 (bd, $^{3}J_{F-F}$ = 21.5 Hz, 6F, *o*-C_6F_5); -159.4 (t, $^{3}J_{F-F}$ = 20.7 Hz, 3F, *p*-C_6F_5); -165.1 (btd, $^{3}J_{F-F}$ = 23.4 Hz, $^{4}J_{F-F}$ = 8.2 Hz, 6F, *m*-C_6F_5).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 163.1 (d, $^{1}J_{C-P}$ = 133.6 Hz, C=O); 148.2 (dm, $^{1}J_{C-F}$ = 247.1 Hz, *o*-***C***F); 139.6 (dm, $^{1}J_{C-F}$ = 248.0 Hz, *p*-***C***F); 137.1 (dm, $^{1}J_{C-F}$ = 250.4 Hz, *m*-***C***F); 134.8 (d, $^{4}J_{C-P}$ = 2.6 Hz, *p*-***C***H); 133.4 (d, $^{3}J_{C-P}$ = 9.3 Hz, *o*-***C***H); 128.9 (d, $^{2}J_{C-P}$ = 11.8 Hz, *m*-***C***H); 119.9 (bs, *ipso*-***C***B); 118.2 (d, $^{1}J_{C-P}$ = 84.1 Hz, *ipso*-***C***P); 60.3 (s, ***C***H of Cy); 34.3 (s, overlapped signals of ***C***H_2 of Cy); 33.3 (s, overlapped signals of ***C***H_2 of Cy); 26.6 (d, $^{3}J_{C-P}$ = 20.6 Hz, overlapped signals of ***C***H_2 of Cy); 26.2 (d, $^{3}J_{C-P}$ = 16.7 Hz, overlapped signals of ***C***H_2 of Cy); 25.5 (s, ***C***H$(CH_3)_2$); 24.8 (s, overlapped signals of ***C***H_2 of Cy); 16.4 (d, $^{3}J_{C-P}$ = 2.6 Hz, CH(***C***$H_3)_2$); 15.7 (s, CH(***C***$H_3)_2$).

Appendix A. Supplementary data

CCDC 2003084 – 2003093 contains the supplementary crystallographic data for **1**-**6**, **1a**, **3a**, **4a**, and **6b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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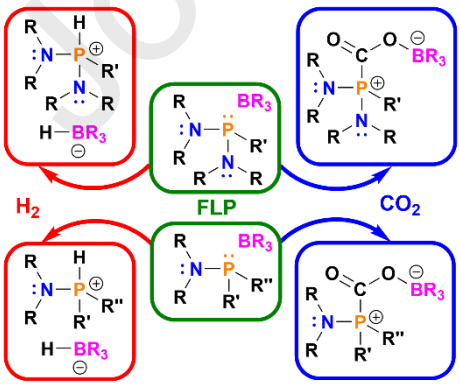
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

The structural analysis of a series of aminophosphanes possessing bulky substituents using X-ray diffraction and DFT methods is presented. The aminophosphanes, as basic components of frustrated Lewis pairs, activate dihydrogen and carbon dioxide under very mild conditions.



The application of aminophosphanes in the activation of dihydrogen and carbon dioxide.