Monomeric Triphosphinoboranes: Intramolecular Lewis Acid–Base Interactions between Boron and Phosphorus Atoms

Anna Ordyszewska, Natalia Szynkiewicz, Jaroslaw Chojnacki, and Rafał Grubba*

ABSTRACT: Herein, we present the synthesis of the first fully characterized monomeric triphosphinoboranes. The simple reaction of boron tribromide with 3 equiv of bulky lithium phosphide tBu2PLi yielded triphosphinoborane (tBu, P)3B. Triphosphinoboranes with diversified phosphanyl substituents were obtained via a two-step reaction, in which isolable bromodiphosphinoborane (tBu, P)2Br is first formed and then reacts with 1 equiv of less bulky phosphide R2PLi (R2P = Cy3P, iPr2P, tBuPH, or Ph3P). By utilizing this method, we obtained a series of triphosphinoboranes with the general formula (tBu, P)BPR2. On the basis of structural and theoretical studies, two main types of triphosphinoborane structures can be distinguished. In the first type, all three electron lone pairs interact with the formally empty p orbital of the central boron atom, resulting in delocalized π bonding, whereas in the second type, one localized P=−B bond and two P−B bonds are observed. The Lewis acidic–basic properties of triphosphinoboranes during the reaction of (tBu, P)2BPr2 with H2B-SMe2 were analyzed. The P−B bond-containing compound mentioned above not only formed an adduct with BH3 but also activated the B−H bond of the borane molecule, resulting in the incorporation of the BH2 unit into two phosphorus atoms and migration of a hydride to the boron atom of the parent triphosphinoborane. The structures of the triphosphinoboranes were confirmed by single-crystal X-ray analysis, multinuclear nuclear magnetic resonance spectroscopy, and elemental analysis.

1. INTRODUCTION

Nonmetallic systems containing directly linked phosphorus and boron atoms constitute a rapidly expanding area of research in modern chemistry, inter alia, due to their application in the activation of small molecules.1−4 These systems include tricoordinated boron and phosphorus compounds, namely, phosphinoboranes and diphosphinoboranes.5,6

The geometry of P−B systems and their electronic structure are vital for their reactivity. Phosphinoboranes can be divided into two groups. In the first group, the phosphorus and boron atoms are planar and the distance between these atoms is relatively short (double-bond character); in the second group, the P−B bond has a single-bond character, and the phosphorus atom is pyramidal. Most phosphinoboranes have structures somewhere between these two extremes (Chart 1A).1,6

Interestingly, these species can be viewed as intramolecular frustrated Lewis pairs. Stephan showed that phosphinoboranes of the first type, such as R2PB(Cp,F)2 (R = tBu or Cy), can be used in the activation of H2 and the dehydrogenation of ammonia borane.12 However, these systems do not activate CO2, and we showed that this is in line with the electronic structure of the P−B system used, where the lone pair on the P atom is not available for an electrophilic reagent.17 Moreover, we designed and synthesized dianimophosphinoboranes possessing a single P−B bond and an accessible lone pair on the P atom that are capable of activating CO2, N2O, and SO2 under very mild conditions. Recently, the Westcott group reported the synthesis of additional P−B systems named phosphinobororate esters R2PBPin (R = Ph or Cy; Pin = pinacolborane)5 and Ph3PBcat (Bcat = catecholborane); they also reported a phosphinoboration reaction in collaboration with the Stephan group. Broad applicability was shown by applying 1,2-additions to a variety of unsaturated organic compounds: aldehydes, ketones, imines,2,3 N-heterocycles,4 heteroallenes,5 diazobenzene,6 diazomethanes,7,8 acyl chlorides,9 and alkynes.10 These researchers also showed the application of R2PBpin, R2PBMes2, and R2PBcat [R = tBu, Ph, or Mes (Mes = 1,3,5-Me3C6H2)] in reactions with CO2, resulting in the formation of R4PCO2BR2 species. Additionally, access to diphasphoa-ureas was provided by Bcat-containing B/P reagents resulting from double 1,2-phospha-addition to CO2.5,11

Received: November 19, 2021
Published: February 28, 2022
The chemistry of diphosphinoboranes has been explored to a lesser extent than that of other P–B systems (Chart 1B). Most synthesis attempts have been made by Nöth et al.19−21 Recently, we vastly expanded the chemistry of these compounds, not only by the synthesis and isolation of several new diphosphinoboranes22 but also by revealing their potential in the activation of small molecules.23 Our preliminary research on the reactivity of selected diphosphinoboranes revealed that these species react with isocyanates, CO2, and H2. We have also reported the first P–B system that activates both H2 and CO2.23

Having described the straightforward synthetic route and application of diaminophosphinoboranes and diphosphinoboranes, naturally, we decided to investigate the potential of triphosphinoboranes (Chart 1C). To date, there have been no full reports on the synthesis and isolation of species with the general formula (R2P)3B. In the literature, only a single report on the synthesis of triphosphinoborane (Mes2P)2BPMe2 is available, and the structure was confirmed only via 31P and 11B NMR spectroscopy.24 This compound was obtained in the reaction of (Mes2P)2BBr with Me2P Li in toluene. The presence of (Mes2P)3B after the reaction of BBr3 with Mes2PLi, along with other products, was also reported and confirmed by 31P NMR.

Herein, we present a series of the first fully characterized triphosphinoboranes with diversified substituents on the P atoms. Moreover, we elucidate the influence of steric hindrance and the electronic character of the phosphanyl groups on the structure of triphosphinoboranes.

2. RESULTS AND DISCUSSION

To synthesize triphosphinoboranes with the same phosphanyl substituents, we chose a simple method involving the reaction of boron tribromide with lithium phosphides. As precursors of the phosphorus fragments, we used lithium phosphides with diversified substituents on the P atoms such as tBu2PLi (1), Cy2PLi (2), iPr2PLi (3), tBuPhPLi (4), and Ph2PLi (5).24 Thus, we studied the stoichiometry of the reactions of lithium phosphides with boron tribromide. The reactions of equimolar amounts of these reagents in toluene afforded cyclic dimers of 1,1-dibromophosphinoboranes (1a−5a) (Scheme 1). The NMR signatures of these species were very similar to those of previously reported 1,1-dihalogenophosphinoborane dimers (Table 1).1,25 1a was previously synthesized in the reaction of tBu2PH·BBr3 with LiN(SiMe3)2, and its structure was fully confirmed by NMR spectroscopy and X-ray crystallography.25 Bullen and co-workers reported the synthesis of 5a and its iodo derivative by the reaction of Ph2PH with BX3 (X = Br or I) in the presence of Et3N; however, spectroscopic data for 5a were not provided.27,28 Synthetic access to dichlorophosphinoborane dimers was described by Stephan and co-workers, where R2P-BCl2 reacts with BCl3 to form (R2P-BCl2)2 and ClB(C6F5)2.1 Analytically pure samples of 2a−5a were isolated at −30 °C from a concentrated toluene solution with LiN(SiMe3)2, and its structure was fully confirmed by NMR spectroscopy and X-ray crystallography.25

### Table 1. 31P{1H} and 11B NMR Data of Phosphinoborane Dimers 1a−5a

| compound | δP (ppm) | δB (ppm) | JPB (Hz) |
|----------|----------|----------|----------|
| 1a−16    | 7.0 (sept, tBuP) | −8.2 (t) | 86       |
| 2a       | −24.4 (sept, CyP) | −10.7 (t) | 96       |
| 3a       | −15.8 (sept, iPrP) | −10.8 (t) | 96       |
| 4a       | −11.1 (sept, tBuPhP) | −10.2 (t) | 92       |
| 5a       | −24.2 (sept, PhP) | −10.0 (t) | 97       |

tBu2PH·BBr3 with LiN(SiMe3)2, and its structure was fully confirmed by NMR spectroscopy and X-ray crystallography.25 Bullen and co-workers reported the synthesis of 5a and its iodo derivative by the reaction of Ph2PH with BX3 (X = Br or I) in the presence of Et3N; however, spectroscopic data for 5a were not provided.27,28 Synthetic access to dichlorophosphinoborane dimers was described by Stephan and co-workers, where R2P-BCl2 reacts with BCl3 to form (R2P-BCl2)2 and ClB(C6F5)2.1 Analytically pure samples of 2a−5a were isolated at −30 °C from a concentrated toluene solution.
solution as colorless crystals. The structures of 2a–5a were confirmed by X-ray diffraction (Figures S1–S4).

Next, we tested the reactivity of boron tribromide with an excess of lithium phosphides. The addition of a toluene solution of BBr₃ to 2 equiv of tBu₂PLi (1) suspended in toluene at −50 °C led to the immediate formation of bromodiporphinoborane 1b and a LiBr precipitate, together with small amounts of tBu₂PH and (tBu₂P)₂ (products of hydrolysis and radical side reactions). The δ¹¹B NMR spectra of 1b displayed a downfield-shifted broad singlet at 74.6 ppm, indicating a tricoordinated boron center (Table 2). The δ³¹P{¹H} NMR spectrum of 1b consists of only one broad singlet at 46.2 ppm, which confirms the equivalence of both phosphorus atoms. Compound 1b crystallized from a concentrated petroleum ether solution at −30 °C as red crystals in 83% yield. The formation of monomeric 1b was confirmed by single-crystal X-ray diffraction (Figure 1). The central B1 atom is connected to the P1 and P2 atoms of the tBu₂P phosphanyl groups and the Br1 atom. The geometry around the B1 atom is planar (sum of the angles around the B atom \( \sum B1 = 360 \)°), whereas both phosphanyl groups exhibit pyramidal geometry, with a sum of angles around the P atoms of approximately 324°. The phosphorus–boron distances are approximately 1.91 Å, which are shorter than the expected lengths for single, covalent P–B bonds (sum of the single bond covalent radii for P and B \( \sum r_{coval}(P–B) = 1.96 \) Å).²⁹

In contrast to the reaction involving tBu₂PLi, the reactions of BBr₃ with a 2-fold excess of less bulky lithium phosphides (2–5) exclusively afforded dimers 2a–5a, respectively. Notably, in the case of the reaction using 1, the reverse addition of substrates afforded only analogous dimer 1a. Moreover, the equimolar reaction of 1b with BBr₃ also yielded dimer 1a (Scheme 1).

Next, we studied the influence of a 3-fold excess of phosphorus reagents on the outcome of reactions with BBr₃. In experiments involving tBu₂PLi, NMR spectroscopy revealed the formation of 1b together with new compound 1c, exhibiting broad δ¹¹B NMR and δ³¹P{¹H} resonances at 56.3 and 40.8 ppm, respectively (Scheme 1 and Table 2).

After 24 h, the signals of 1b disappeared, and only resonances attributed to 1c were present in the δ¹¹B and δ³¹P{¹H} NMR spectra of the reaction mixture. This observation suggested that 1b is the intermediate compound that further reacts with the third equivalent of tBu₂PLi to form triphosphinoborane 1c. The downfield-shifted resonance in the δ¹¹B spectra of 1c is consistent with the trigonal planar environment of the boron atom, whereas the presence of only one resonance in the δ³¹P{¹H} spectra of 1c agrees with the structure with three equivalent tBu₂P groups bound to one boron atom. 1c was isolated by low-temperature crystallization from petroleum ether as red crystals in 72% yield. X-ray structure analysis confirmed the formation of triphosphinoborane 1c (Figure 2).

The analogous reactions involving a 3-fold excess of less bulky phosphides 2–5 afforded dimers 2a–5a, respectively, as the main products. Interestingly, during the reaction using tBuPhPLi (4), in addition to main product 4a, trace amounts of triphosphinoborane 4c′ were formed (Scheme 1). A few crystals of 4c′ were grown at low temperature from the petroleum ether solution obtained from washing the crude product 4a (4c′ is only slightly soluble in petroleum ether). We assumed that the concentration of 4c′ in the reaction mixture must be very low, as this product could not be detected using our NMR spectrometer. Moreover, our attempts to optimize the synthesis to obtain significant amounts of 4c′ were unsuccessful. Therefore, 4c′ was characterized using only single-crystal X-ray diffraction (Scheme S5).

The successful isolation of bromodiporphinoborane 1b encouraged us to use this compound in the synthesis of triphosphinoboranes. To our delight, 1b reacted with

---

**Table 2.** δ³¹P{¹H} and δ¹¹B NMR Data of Diporphinoborane (1b) and Triphosphinoboranes (1c–5c)

| Compound | δ³¹P (ppm) | J_{PP} (Hz) | δ¹¹B (ppm) |
|----------|------------|-------------|------------|
| 1b       | 46.2 (bs, tBu₂P) | –           | 74.6 (bs)  |
| 1c       | 40.8 (bs, tBu₂P) | –           | 56.3 (bs)  |
| 2c       | 122.4 (bs, Cy₂P); –1.5 (bs, tBu₂P) | –           | 50.4 (bs)  |
| 3c       | 130.3 (bs, iPr₂P); –2.9 (bs, tBu₂P) | –           | 50.6 (bs)  |
| 4c       | 85.5 (bs, tBuPhPB); 12.4 (bd, tBu₂P) | 106         | 59.6 (bs)  |
| 5c       | 52.3 (bd, tBu₂P); –12.4 (bt, Ph₂P) | 98          | 63.8 (bs)  |

---

**Figure 1.** View of the molecular structure of 1b (50% probability ellipsoids, H atoms omitted).

---

**Figure 2.** View of the molecular structure of 1c (50% probability ellipsoids, H atoms omitted). One molecule from 4/3 molecules present in the independent part of the unit cell is shown.
phosphides 2–5 with the clean formation of new triphosphinoboranes 2c–5c, respectively, as the main products (Scheme 1). The reactions mentioned above proceeded in toluene and even faster in diethyl ether, where the complete conversion of parent 1b into triphosphinoboranes was observed within 24 h. The 11B NMR spectra of 2c–5c consist of a broad resonance in the range of 50.4–63.8 ppm, confirming the formation of monomeric species and the presence of tricoordinated boron atoms (Table 2). The 31P{1H} spectra of 2c–5c show two resonances, one attributed to two equivalent P1 and P2 atoms of tBu3P groups and the other assigned to the P3 atom of a less bulky phosphanyl group such as Cy2P(2c), tPr2P (3c), tBuPhP (4c), or Ph2P (5c). In the case of 2c–4c, the 31P{1H} resonance of the tBu3P group (P1 and P2) has a value ranging from −2.9 to 12.4 ppm, and the P3 resonance of the less bulky phosphanyl group is shifted strongly downfield, with values from 85.5 to 130.3 ppm (Table 2). Interestingly, such a strong downfield shift of phosphorus resonances is not observed for triphosphinoborane 5c. Moreover, in comparison to those of 2c–4c, the relative position of the signals in the 31P{1H} spectrum of 5c is inverted, where the most downfield signal is attributed to the P1 and P2 atoms of the tBu3P group (52.3 ppm), whereas the P3 atom of the Ph3P group resonates at a higher field (−12.4 ppm). Notably, in the 31P{1H} spectra of 4c and 5c, J_{pp} coupling is observed, with values of 106 and 98 Hz, respectively. In the case of other triphosphinoboranes, such coupling was not observed because of the broadness of the signals (2c and 3c) or the equivalence of the three phosphorus atoms (1c).

According to the studies of Power and co-workers, 31P NMR spectroscopy is a very useful tool for the analysis of π interactions in tricoordinated compounds possessing direct P–B bonds. They showed that the large positive value of the chemical shift indicates a significant π interaction between the P and B atoms. Therefore, the strongly downfield-shifted resonances of P3 in the 31P{1H} spectra of 2c–4c suggest the presence of localized multiple bonds between the P3 atom and the B1 atom. Note that for 2c and 3c, the chemical shifts corresponding to the P3 atoms have values (122.4 and 130.3 ppm, respectively) even more positive than those observed for planar phosphinoboranes with P==B bonds possessing strongly electron-withdrawing groups at the B atom [δ = 120.7 ppm for tBu3P==B(C6F5)3]. On the contrary, in the case of 1c and 5c, delocalized π interactions between boron and three phosphorus atoms are expected on the basis of the 31P{1H} NMR data of these species. Compounds 2c–5c were isolated in high yields as crystals from concentrated petroleum ether solutions at −30 °C. Due to the presence of reactive P–B bonds and the low coordination number of both phosphorus and boron centers, triphosphinoboranes 1c–5c rapidly decompose when in contact with air.

The molecular structures of all obtained triphosphinoboranes (1c–5c) were determined by single-crystal X-ray diffraction. The most important parameters of 1c–5c are listed in Table 3. Moreover, to further investigate the electronic structure of triphosphinoboranes, NBO analysis of these species was performed. Depending on the geometry and electronic structure, two main types of triphosphinoboranes can be distinguished. The compounds within the mentioned groups exhibit common structural features; therefore, they will be discussed together. The first group includes triphosphino-

---

Table 3. Selected Bond Lengths and Geometries around the B1 and P1–P3 Atoms for Triphosphinoboranes 1c–5c

| compound | B1–P1 (Å) [WBI] | B1–P2 (Å) [WBI] | B1–P3 (Å) [WBI] | ΣB1 (deg) | ΣP1, ΣP2, ΣP3 (deg) |
|----------|----------------|----------------|----------------|-----------|-------------------|
| 1c       | 1.904(7) b [1.22] | 1.936(9) b [1.22] | 1.913(7) b [1.22] | 353.3 b | 343.4 b 342.3 b 342.7 b |
| 2c       | 2.010(5) [1.00]  | 2.021(5) [1.00]  | 1.799(3) [1.70]  | 359.8    | 327.6 324.3 359.9 |
| 3c       | 1.990(2) [1.00]  | 1.990(1) [1.00]  | 1.792(1) [1.70]  | 360.0    | 328.2 322.8 359.6 |
| 4c       | 1.990(1) [1.02]  | 1.989(1) [1.00]  | 1.810(1) [1.66]  | 359.8    | 326.9 323.8 358.9 |
| 4c'      | 1.918(2) [1.20]  | 1.904(2) [1.23]  | 1.911(2) [1.22]  | 352.3    | 329.1 330.2 330.5 |
| 5c       | 1.953(2) [1.10]  | 1.881(2) [1.35]  | 1.899(2) [1.22]  | 354.5    | 329.9 345.3 336.6 |

"The Wiberg bond indices (WBIs) for the corresponding bonds are provided in brackets. b Average values for 4/3 molecules present in the independent part of the unit cell.

Table 4. Stabilizing Energies E(2) Associated with Electron Delocalization between Donor P Centers and Acceptor B Centers in 1c–5c

| compound | donor | occupancy | acceptor | occupancy | E(2) (kcal/mol) |
|----------|-------|-----------|----------|-----------|----------------|
| 1c       | LP(P1)| 1.71      | LP*(B1)  | 0.65      | 14.97          |
|          | LP(P2)| 1.71      |          |           | 15.14          |
|          | LP(P3)| 1.71      |          |           | 15.04          |
| 2c       | LP(P1)| 1.89      | σ*(P3–B1)| 0.05      | 8.66           |
|          | LP(P2)| 1.90      | σ*(P1–B1)| 0.05      | 7.65           |
| 3c       | LP(P1)| 1.89      | σ*(P3–B1)| 0.05      | 8.98           |
|          | LP(P2)| 1.90      | σ*(P1–B1)| 0.05      | 8.32           |
| 4c       | LP(P1)| 1.89      | σ*(P3–B1)| 0.06      | 9.92           |
|          | LP(P2)| 1.90      | σ*(P1–B1)| 0.05      | 7.87           |
| 4c'      | LP(P1)| 1.76      | LP*(B1)  | 0.61      | 17.83          |
|          | LP(P2)| 1.74      |          |           | 20.93          |
|          | LP(P3)| 1.74      |          |           | 19.18          |
| 5c       | LP(P1)| 1.84      | LP*(B1)  | 0.64      | 3.06           |
|          | LP(P2)| 1.64      |          |           | 29.33          |
|          | LP(P3)| 1.66      |          |           | 28.16          |
Compounds 2c–4c represent the second group of triphosphinoboranes. Their molecular structures are presented in Figure 4. The most striking features of the triphosphinoboranes in this group are the planar geometry around the B1 and P3 atoms and the pyramidal geometry around the P1 and P2 atoms (Table 3). Furthermore, in contrast to those of the triphosphinoboranes in the first group, the P–B bond lengths in the second group are more diversified, with very long P1–B1 and P2–B1 distances of approximately 2.00 Å, a distance even slightly longer than the length of a typical single covalent bond [\( \sum_{\text{cov}}(\text{P} \equiv \text{B}) = 1.96 \text{ Å} \)]\(^{26,30}\) and very short [1.792(1)–1.810(1) Å] P3–B1 distances indicative of the double-bond character of these bonds [\( \sum_{\text{cov}}(\text{P} \equiv \text{B}) = 1.80 \text{ Å} \)]\(^{31}\). The NBO analysis of 2c–4c confirmed the presence of localized \( \pi \) bonds between the P3 and B1 atoms (Figure 5). As expected, the NBO \( \pi(\text{P}3–\text{B}1) \) orbitals of 2c–4c dominate the contribution of the P3 atom (68–70%). Moreover, the calculated Wiberg bond orders for P3–B1 bonds have large values ranging from 1.66 to 1.70, whereas the obtained bond orders for the P1–B1 and P2–B1 bonds are very close to 1 (Table 3). These findings corroborate the \( ^{31}\text{P}[^1\text{H}] \) NMR spectroscopic data of 2c–4c, where strongly downfield-shifted resonances of P3 atoms were observed.

Moreover, weak interactions were found between the electron lone pairs on the P1 and P2 atoms and the antibonding \( \sigma^* (\text{P}3–\text{B}1) \) and \( \sigma^* (\text{P}1–\text{B}1) \) orbitals for the structures of the second type (Table 4). In the case of 2c–4c, the lack of \( \pi \) donation from P1 and P2 atoms is additionally confirmed by the very small contribution of the boron atom (1%) in NLMOs associated with electron lone pairs of the mentioned phosphorus atoms. The influence of the steric effect of substituents on the P atoms on the structures of the triphosphinoboranes is clear. The introduction of substituents smaller than tBu groups at the P3 atom allows sp\(^2\) hybridization of the P3 atom and formation of localized P3\( \equiv \text{B}1 \) bonds.

Compounds 2c–4c, and their molecular structures are presented in Figure 2 and Figure S5, respectively. They exhibit an almost planar geometry around the B1 atom (for 1c, \( \sum_{\text{B}1} = 353.3^\circ \); for 4c, \( \sum_{\text{B}1} = 352.3^\circ \)), whereas the geometry around all phosphorus atoms is similar and is intermediate between ideal planar and pyramidal (for 1c, average \( \sum_{\text{P}} = 342.8^\circ \); for 4c, average \( \sum_{\text{P}} = 329.9^\circ \)). All three P–B bonds have comparable lengths slightly longer than 1.90 Å, which are between the expected distances for single and double phosphorus–boron bonds [\( \sum_{\text{cov}}(\text{P} \equiv \text{B}) = 1.96 \text{ Å} \), and \( \sum_{\text{cov}}(\text{P} \equiv \text{B}) = 1.80 \text{ Å} \)]\(^{25,31}\). For 1c and 4c, the relatively short P–B distances and the high degree of planarity of \( \text{R}_2\text{P} \) moieties suggested the interaction of a formally empty p orbital on boron with three electron pairs on the P1–P3 atoms. Indeed, NBO analysis confirmed this assumption. The calculated P–B bond orders for 1c and 4c are equal to or slightly greater than 1.20, indicating the partial multiple character of these bonds. The second-order perturbation analysis provides additional information about the \( \pi \) interactions between the Lewis acidic B center and the three Lewis basic P centers (Table 4). The stabilizing energies \( E(2) \), which characterize donor–acceptor interactions between the B and P centers, have values of approximately 15 kcal/mol for 1c and between 17.83 and 20.93 kcal/mol for 4c. Moreover, the triphosphinoboranes of this group exhibit decreased occupancies of the orbitals associated with electron pairs on the P atoms and increased occupancies of the unhybridized p orbitals of the central B atoms. The NBO orbitals of 1c involved in P–B \( \pi \) interactions are presented in Figure 3. The NLMO analysis of 1c and 4c further corroborates the presence of \( \pi \) donation from all three P atoms to the formally empty p orbital of boron and reveals the significant contribution of the B atom (7–13%) in NLMOs attributed to electron lone pairs at P atoms. All of these observations confirm the almost equal and significant \( \pi \) contributions in all three P–B bonds in the triphosphinoboranes in the first group.

![Figure 3](image-url)

Figure 3. View of NBOs of 1c engaged in donor–acceptor \( \pi \) interactions.

![Figure 4](image-url)

Figure 4. View of the molecular structures of 2c–5c (50% probability ellipsoids, H atoms omitted).
Interestingly, 3c combines the structural features of triphosphinoboranes of both aforementioned groups. The X-ray structure of 3c is depicted in Figure 4. Similar to the compounds in the first group, 3c displays an almost planar geometry around the B1 atom and a high degree of planarity of all phosphorus atoms (Table 3). However, in contrast to that of the first group but similar to that of the second group, the geometry around the phosphorus atom and the phosphorus–boron distances are more diversified. In the case of 3c, the planarity of the phosphanyl groups increases in the following order: tBu2P1 < Ph2P3 < tBu2P2. The phosphorus–boron distances decrease in the following order: P1–B3 > P3–B3 > P2–B3 (Table 3). NBO analysis of 3c revealed that the electron pairs on P1–P3 interact with the Lewis acidic boron center to a different extent (Table 4). Calculations of the electron delocalization energies E(2) show that the strength of the interactions mentioned above increases in the following order: P1 → B3 (3.06 kcal/mol), P3 → B3 (28.16 kcal/mol), and P2 → B3 (29.33 kcal/mol). It is worth mentioning that the contribution of the B atom in NLMOs of 3c attributed to electron lone pairs of phosphorus atoms is diversified [LP(P1), 3%; LP(P3), 10%; LP(P2), 17%] and indicates the strongest π donation from the P2 atom and the weakest from the P1 atom. Despite the less bulky phenyl groups at the P3 atom, the structure of 3c does not contain a localized P3=B1 bond, similar to triphosphinoboranes of the second type. We assume that the electron-withdrawing properties of the phenyl groups weaken the donor abilities of the P3 atom; therefore, the extent of delocalization of the electron pair between the P3 and B1 atoms is smaller.

The unusual structural features of triphosphinoboranes, such as the presence of three Lewis basic phosphorus atoms that are directly bound to the Lewis acidic boron center, encouraged us to test their reactivity toward simple adducts of Lewis bases and Lewis acids. For this study, we selected 3c, which exhibits one double and two single P–B bonds and hence a diversified phosphanyl group geometry. 3c reacted cleanly with 2 equiv of H3B·SMe2 in toluene to form 3d (Scheme 2). The end point of the reaction was easily observed by the discoloration of the red toluene solution of 3c. The reactions with a molar ratio of 1:1 afforded a mixture of 3c and 3d, whereas an experiment involving a large excess of borane adduct yielded 3d and unreacted H3B·SMe2. NMR spectroscopic and X-ray diffraction studies indicated that 3c not only forms a classical adduct with BH3 but also activates the B–H bonds within the BH3 moiety.

The 31B NMR spectrum of 3d displays a broad multiplet at −23.9 and two broad overlapping multiplets from −33.8 to −38.2 ppm, which are in the characteristic region for the tetracoordinated boron center. The presence of three very broad signals in the 31P(1H) NMR spectrum at 36.2, 29.5, and 4.7 ppm indicates three inequivalent P atoms in the structure of 3d. In contrast to that of 3c, the signal attributed to the phosphorus atom of the PhPr2 group is shifted strongly upfield (3c, 130.3 ppm; 3d, 4.7 ppm), suggesting a lack of P–B π interactions. Furthermore, the 1H NMR spectrum consists of very broad signals that can be attributed to hydrogen atoms directly bound to boron atoms (0.84–2.15 ppm, 3H; 3.37 ppm, 1H). X-ray-quality crystals of 3d were grown from a petroleum ether solution at low temperatures. The molecular structure of 3d is presented in Figure 6. An X-ray diffraction study revealed that the P1 atom formed a coordination bond with the B2 atom of the BH3 moiety. The second borane molecule reacted with 3c to incorporate a BH3 unit between the P2 and P3 atoms and to cause the migration of a hydride moiety to the B1 atom. We assume that the B–H bond activation by 3c proceeds via a stepwise mechanism, where the first step is the coordination of the BH3 molecule to a P atom of the tBu2P group. Then hydride migrates to the B atom of the parent triphosphinoborane, followed by the coordination of the P atom of the iPr3P group to the B atom of the BH3 unit.
Notably, the hydrogen atoms of the BH, BH₂, and BH₃ units were located on the basis of analysis of the Fourier electron density map. It was previously confirmed by ¹¹B NMR spectroscopy that all boron atoms are tetracoordinated. The same coordination number was observed for all P atoms. The P–B bond distances were found to be in the range expected for single covalent bonds [1.951(4)–2.025(3) Å], and no structural evidence for π interaction between P and B atoms was observed. B–H bond activation in BH₃ compounds by nonmetallc systems is very rare. An example of this kind of reactivity is the 1,1-addition of BH₂ to carbenoids³³ that to date, there have been no reports on BH₃ activation by systems containing P–B bonds.

3. CONCLUSIONS

The obtained triphosphinoboranes exhibit unique structural features, where the Lewis acidic boron center is directly bonded to three Lewis basic phosphorus centers. We showed that the electronic and steric properties of phosphanyl substituents have a significant influence on the structure of triphosphinoboranes, where structures with delocalized or localized P–B π bonding were obtained. The ambiphilic nature of triphosphinoboranes together with the low coordination number of reactive phosphorus and boron centers makes these species very attractive in the activation of small molecules. The Lewis acidic–basic properties of triphosphinoboranes were manifested in the reaction with a borane adduct, where B–H bond activation was observed. Currently, reactivity investigations of these P–B bond systems toward a wide range of small inorganic and organic molecules are in progress.

4. EXPERIMENTAL SECTION

General Information. All experiments were performed under an inert gas (argon) atmosphere. All manipulations were carried out using Schlenk, standard vacuum, and glovebox techniques. Petroleum ether, toluene, and diethyl ether were purified and dried using Na/K and benzophenone. C₆D₆ was purified with Na. Literature methods were followed for the synthesis of phosphides.²⁵ BBr₃ and BH₃·SMe₂ were purchased from commercial sources and used without further purification. A BBr₃ solution in toluene and BMS (H₃B·Et₂O) at ambient temperature. Inorganic Chemistry pubs.acs.org/IC

Crystallographic data for all structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 2114349–2114360. The data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/structures.

Elemental analyses were performed using a Vario El Cube CHNS apparatus at the University of Gdańsk. The lower value of carbon in elemental analyses of several compounds reported herein is caused by the extreme sensitivity of the triphosphinoboranes.

Synthesis of (Cy₃PBBr₂)₂ (2a). To the suspension of 163 mg (0.8 mmol) of Cy₃PBr in 4 mL of toluene was added dropwise the solution of 1 mL (0.8 mmol, 0.8 M) of BBr₃ in toluene at −30 °C. After the reaction mixture had been warmed to room temperature, toluene was evaporated under reduced pressure. The solid residue was partially dissolved in petroleum ether; LiBr was removed by filtration, and the solute was concentrated to a volume of 2 mL. The residue that was not soluble in petroleum ether was redissolved in toluene. Colorless crystals of 2a (179 mg, 0.244 mmol, 61% yield) suitable for X-ray diffraction analysis were isolated from the concentrated toluene fraction at −30 °C: ¹H NMR (C₆D₆, 400 MHz, 298 K) δ 1.06 (m, 4H, CH₂), 1.28 (m, 8H, CH₂), 1.59 (m, overlapped 2H, CH), 2.58 (m, overlapped, 8H, CH₂), 2.98 (m, 4H, PCH). ¹¹B NMR (C₆D₆, 128 MHz, 298 K) δ −10.6 (t, J₁/P = 96 Hz, Cy₃PBr₂); ¹³P{¹H} NMR (C₆D₆, 162 MHz, 298 K) δ −24.2 (sept, J₂/P = 96 Hz, Cy₃PBr₂), −28.0 (s, Cy₃P); ¹³C{¹H} NMR (C₆D₆, 100 MHz, 298 K) δ 26.0 (5C, 2H, CH₂), 29.7 (t, J₂/C = 5.4 Hz, CH₂), 74.1 (s, CH₂), 10.4 (s, CH₂), 124.5 (C, 1H); elemental analysis calcd for C₂₄H₄₄B₄Br₄P₂ (M = 735.79 g/mol) 39.18% C and 6.03% H, found 39.12% C and 6.07% H.

Synthesis of (iPr₂PBBr₂)₂ (3a). To the suspension of 100 mg (0.8 mmol) of iPr₂PBr in 4 mL of toluene was added dropwise the solution of 1 mL (0.8 mmol, 0.8 M) of BBr₃ in toluene at −30 °C. After the reaction mixture had been warmed to room temperature, toluene was evaporated under reduced pressure. The solid residue was partially dissolved in petroleum ether; LiBr was removed by filtration, and the solute was concentrated to a volume of 2 mL. The residue that was not soluble in petroleum ether was redissolved in toluene. Colorless crystals of 3a (175 mg, 0.246 mmol, 62% yield) suitable for X-ray diffraction analysis were isolated from the concentrated toluene fraction at −30 °C: ¹H NMR (C₆D₆, 400 MHz, 298 K) δ 1.29 (dd, J₁/H = 7 Hz, J₂/H = 15 Hz, 2H, (CH₂)₂CH₂), 2.96 (m, 4H, (CH₂)₂CH₂); ¹¹B NMR (C₆D₆, 128 MHz, 298 K) δ −10.7 (t, J₁/P = 96 Hz, iPr₂PBr₂); ¹³P{¹H} NMR (C₆D₆, 162 MHz, 298 K) δ −15.8 (sept, J₂/P = 96 Hz, (iPr₂PBr₂)), ¹³C{¹H} NMR (C₆D₆, 100 MHz, 298 K) δ 19.3 (C, 2H, CH₂), 25.6 (t, J₂/C = 14 Hz, CH₂), elemental analysis calcd for C₁₄H₂₀B₂Br₂P₂ (M = 575.54 g/mol) 25.04% C and 4.90% H, found 25.32% C and 4.61% H.

Synthesis of (BuPhPBBr₂)₂ (4a). To the suspension of 136 mg (0.8 mmol) of BuPhPBr in 4 mL of toluene was added dropwise the solution of 1 mL (0.8 mmol, 0.8 M) of BBr₃ in toluene at −30 °C. After the reaction mixture had been warmed to room temperature, toluene was evaporated under reduced pressure. The solid residue was partially dissolved in petroleum ether; LiBr was removed by filtration, and the solute was concentrated to a volume of 2 mL. The residue that was not soluble in petroleum ether was redissolved in toluene. Colorless crystals of 4a (64 mg, 0.096 mmol, 24% yield; lower crystallization yield due to the partial solubility of 4a in petroleum ether) suitable for X-ray diffraction analysis were isolated from the concentrated toluene fraction at −30 °C: ¹H NMR (C₆D₆, 400 MHz, 298 K) δ 1.41 (m, 18H, (CH₂)₃C), 6.94 (m, overlapped, 6H, CH₃para and C-Hwasench), 7.90 (m, 4H, C-Hortho), 8.14 (m, 2H, C-Hmeta and C-Hpara)), ¹¹B NMR (C₆D₆, 128 MHz, 298 K) δ −10.2 (t, J₁/P = 92 Hz (BuPhPBr₂)), ¹³P{¹H} NMR (C₆D₆, 162 MHz, 298 K) δ −5.7 (s, BuPhPBr₂), ¹³C{¹H} NMR (C₆D₆, 100 MHz, 298 K) δ 19.3 (C, 2H, CH₂), 25.6 (t, J₂/C = 14 Hz, CH₂), elemental analysis calcd for C₁₄H₂₀B₂Br₂P₂ (M = 671.62 g/mol) 35.78% C and 4.20% H, found 35.62% C and 4.46% H.

Synthesis of (Ph₂PBBr₂)₂ (5a). To the suspension of 96 mg (0.5 mmol) of Ph₂PBr in 4 mL of toluene was added dropwise the solution of 0.625 mL (0.5 mmol, 0.8 M) of BBr₃ in toluene at −30 °C. After the reaction mixture had been warmed to room temperature, toluene was evaporated under reduced pressure. The solid residue was partially dissolved in petroleum ether; LiBr was removed by filtration, and the solute was concentrated to a volume of 2 mL. The residue that was not soluble in petroleum ether was redissolved in toluene. Colorless crystals of 5a (165 mg, 0.232 mmol, 58% yield) suitable for X-ray diffraction analysis were isolated from the concentrated toluene fraction at −30 °C: ¹H NMR (C₆D₆, 400 MHz, 298 K) δ 6.92 (m, 10H, CH), 10.1 (t, J₁/H = 97 Hz, Ph₂PBr₂); ¹³P{¹H} NMR (C₆D₆, 162 MHz, 298 K) δ −24.2 (sept, J₂/P = 97 Hz, Ph₂PBr₂), −40.7 (s, Ph₂P); ¹³C{¹H} NMR (C₆D₆, 100 MHz, 298 K) δ 126.4 (t, J₂/C = 30 Hz, C), 128.5 (t, J₂/C = 6 Hz, C), 131.2 (s, C).
C₄H₇BuBr₂BP₂ (M = 711.60 g/mol) 40.51% C and 2.83% H, found 40.61% C and 2.98% H.

Synthesis of (Bu₂BP₂)Br (1b). To the suspension of 608 mg (4.0 mmol) of Bu₂PLi in 6 mL of toluene was added the solution of 2.5 mL (2.0 mmol, 0.8 M) of BBr₃ in toluene at –50 °C. After the reaction mixture had been warmed to room temperature, the reaction mixture was stirred for 9 days, and toluene was evaporated under reduced pressure. The solid residue was dissolved in petroleum ether; LiBr was removed by filtration, and the solute was concentrated to a volume of 2 mL. Red crystals of 1b (0.641 g, 1.67 mmol, 83% yield) were isolated at –30 °C. After being warmed to room temperature, the reaction mixture was stirred for 72 h, and then toluene was evaporated under reduced pressure. The solid residue was dissolved in petroleum ether; LiBr was removed by filtration, and the solute was concentrated to a volume of 1.5 mL. Red crystals of 1c (161 mg, 0.36 mmol, 72% yield) were isolated at 43°C. After being warmed to room temperature, the reaction mixture was stirred for 9 days, and toluene was evaporated under reduced pressure. The solid residue was dissolved in petroleum ether; LiBr was removed by filtration, and the solute was concentrated to a volume of 2 mL. Red crystals of 2c (189 mg, 0.388 mmol, 78% yield) were isolated at –30 °C: 1H NMR (CD₂Cl₂, 400 MHz, 298 K) δ 1.50 (s, 13H, (CH₃)₃C), 2.04 (m, overlapped, 4H, CH (Cy)), 3.24 (m, overlapped, 2H, CH (Cy)), 11B NMR (CD₂Cl₂, 128 MHz, 298 K) δ 50.9 (broad s, (Bu₂P₂)BP₂Cy); 13P{¹H} NMR (CD₂Cl₂, 128 MHz, 298 K) δ 122.4 (broad s, CyP₂), 1.7 (d, JHH = 6 Hz, 2H, B), 17 (d, JHH = 6 Hz, 2H, B), 11B NMR (CD₂Cl₂, 128 MHz, 298 K) δ 0.70 (broad s, (Bu₂P₂)BP₂P₂); 13P{¹H} NMR (CD₂Cl₂, 128 MHz, 298 K) δ 130.1 (broad s, iP₃P₂B); –3.2 (d, JHP = 88 Hz, Bu₂BP₂); 11B NMR (CD₂Cl₂, 128 MHz, 298 K) δ 235.3 (d, JHB = 6 Hz, (CH₃)₂CH), 28.6 (m, (CH₃)₂CH), 33.3 (m, (CH₃)₂CH), 33.9 (m, (CH₃)₂CH); elemental analysis calcld for C₂H₇BuCl₂BP₂ (M = 418.36 g/mol) 63.16% C and 12.05% H, found 62.37% C and 11.85% H.

Synthesis of (Bu₂BP₂)BPh₂ (4c). To the suspension of 86 mg (0.5 mmol) of Bu₂PhLi in 4 mL of toluene was added the solution of 190 mg (0.5 mmol) of (Bu₂BP₂)Br in 3 mL of toluene at –40 °C. After being warmed to room temperature, the reaction mixture was stirred for 5 min, and then toluene was evaporated under reduced pressure. The solid residue was dissolved in petroleum ether; LiBr was removed by filtration, and the solute was concentrated to a volume of 2 mL. Large red crystals of 4c (189 mg, 0.388 mmol, 78% yield) were isolated at –30 °C: 1H NMR (CD₂Cl₂, 400 MHz, 298 K) δ 1.48 (broad s, (Bu₂P₂BP₂)BP₂); 13P{¹H} NMR (CD₂Cl₂, 128 MHz, 298 K) δ 59.7 (broad s, (Bu₂P₂BP₂)BP₂); 13C{¹H} NMR (CD₂Cl₂, 128 MHz, 298 K) δ 86.2 (broad s, (Bu₂P₂BP₂)BP₂); 19.6 (s, Bu₂P₂BP₂, 19.1%); 12.4 (broad d, JHP = 106 Hz, (Bu₂P₂BP₂), –5.6 (s, Bu₂P₂BP₂, 2.6%); 11B NMR (CD₂Cl₂, 100 MHz, 298 K) δ 63.8 (m, overlapped, (CH₃)₂CP₂Ph), 34.0 (m, overlapped, (CH₃)₂CP₂Ph), 34.7 (dd, JCH = 10 Hz, JCP = 11 Hz, (CH₃)₂CP₂Ph), 19.2 (s, (CH₃)₂CP₂Ph), 137.3 (d, JCP = 9 Hz, (CH₃)₂CP₂Ph), 129.2 (d, JCP = 2 Hz, C-Cl), 135.5 (m, C), 138.2 (d, JCP = 7 Hz, C-Cl); elemental analysis calcld for C₂H₈BP₂ (M = 446.41 g/mol) 66.95% C and 10.80% H, found 66.03% C and 10.54% H.
(dd, \( J_{HH} = 7 \) Hz, \( J_{CP} = 14 \) Hz, 3H, (CH\(_3\))\(_3\)CH), 1.17 (dd, \( J_{HH} = 7 \) Hz, \( J_{CP} = 12 \) Hz, 3H, (CH\(_3\))\(_2\)CH), 1.22 (dd, \( J_{HH} = 7 \) Hz, \( J_{CP} = 15 \) Hz, 3H, (CH\(_3\))\(_2\)CH), 1.31 (dd, \( J_{HH} = 7 \) Hz, \( J_{CP} = 15 \) Hz, 3H, (CH\(_3\))\(_2\)CH), 1.37 (broad d, 18H, (CH\(_3\))\(_3\)C), 1.41 (dd, \( J_{HH} = 8 \) Hz, \( J_{CP} = 13 \) Hz, 18H, (CH\(_3\))\(_2\)CH), 2.20 (m, 1H, (CH\(_3\))\(_2\)CH), 2.36 (m, 1H, (CH\(_3\))\(_2\)CH), 3.37 (very broad d, 1H, BHH): \(^{1}^1^B\) NMR \((C\text{D}_2\text{O}, 128 \text{ MHz}, 298 \text{ K}) \delta = 23.9 \) (broad quintet, \( J_{CP} = 3 \text{ Hz} \), (CH\(_3\))\(_3\)C), 35.8 (dd, 1\( J_{CP} = 2 \) Hz, (CH\(_3\))\(_2\)CH), 21.4 (broad d, \( J_{CP} = 2 \) Hz, (CH\(_3\))\(_2\)CH), 22.4 (dd, \( J_{CP} = 19 \) Hz, \( J_{HH} = 13 \) Hz, 18H, (CH\(_3\))\(_2\)CH), 21.1 (dd, \( J_{CP} = 19 \) Hz, \( J_{HH} = 14 \) Hz, 3H, (CH\(_3\))\(_3\)C), 30.0 (broad d, \( J_{CP} = 2 \) Hz, (CH\(_3\))\(_2\)CH), 1.37 (broad d, 18H, (CH\(_3\))\(_3\)C), 1.41 (dd, \( J_{HH} = 446.03 \) g/mol) 59.24% C and 12.65% H, found 58.46% C and 12.63% H.

**REFERENCES**

(1) Geier, S. J.; Gilbert, T. M.; Stephan, D. W. Synthesis and Reactivity of the Phosphinoboranes \( \text{R}_2\text{PB}(\text{C}_2\text{F}_5)_2 \). *Inorg. Chem.* 2011, 50, 336–344.

(2) Daley, E. N.; Vogels, C. M.; Geier, S. J.; Decken, A.; Doherty, S.; Westcott, S. A. The Phosphinoboration Reaction. *Angew. Chem., Int. Ed.* 2015, 54 (7), 2121–2125.

(3) Kindervater, M. B.; Binder, J. F.; Baird, S. R.; Vogels, C. M.; Geier, S. J.; Macdonald, C. L. B.; Westcott, S. A. The Phosphinoboration of 2-Diphenylphosphino Benzaldehyde and Related Aldimines. *J. Organomet. Chem.* 2019, 880, 378–385.

(4) Geier, S. J.; Vogels, C. M.; Mellone, N. R.; Daley, E. N.; Decken, A.; Doherty, S.; Westcott, S. A. The Phosphinoboration of N-Heterocycles. *Chem. - Eur. J.* 2017, 23 (58), 14485–14499.

(5) Geier, S. J.; Lafortune, J. H. W.; Zhu, D.; Kosnik, S. C.; Macdonald, C. L. B.; Stearns, D. W.; Westcott, S. A. The Phosphinoboration of Carbodiimides, Isocyanates, Isothiocyanates and CO\(_2\). *Dalton Trans.* 2017, 46 (33), 10876–10885.

(6) Lafortune, J. H. W.; Trogimova, A.; Cummings, H.; Westcott, S. A.; Stephan, D. W. Phosphinoboration of Diazobenzene: Intramolecular FLP Synthon for PN2B-Derived Heterocycles. *Chem. - Eur. J.* 2019, 25 (54), 12521–12525.

(7) Trogimova, A.; Lafortune, J. H. W.; Qu, Z. W.; Westcott, S. A.; Stephan, D. W. 1,1-Phosphinoboration of Diazomethanes. *Chem. Commun.* 2019, 55 (80), 12100–12103.

(8) Zhu, D.; Qu, Z. W.; Stephan, D. W. Addition Reactions and Diazomethane Capture by the Intramolecular P-O-B FLP:: \( \text{R}_2\text{PB} \text{OBcat.} \) *Dalton Trans.* 2020, 49 (3), 901–910.

(9) Murphy, M. C.; Trogimova, A.; Lafortune, J. H. W.; Vogels, C. M.; Geier, S. J.; Binder, J. F.; Macdonald, C. L. B.; Stearns, D. W.; Westcott, S. A. The Phosphinoboration of Acyl Chlorides. *Dalton Trans.* 2020, 49 (16), 5092–5099.

(10) Fritzemeier, R. G.; Nekvinda, J.; Vogels, C. M.; Rosenblum, C. A.; Slezebnick, C.; Westcott, S. A.; Santos, W. L. Organocatalytic Trans Phosphinoboration of Internal Alkynes. *Angew. Chem., Int. Ed.* 2020, 59 (34), 14358–14362.

(11) Lafortune, J. H. W.; Qu, Z. W.; Bamford, K. L.; Trogimova, A.; Westcott, S. A.; Stephan, D. W. Double Phosphinoboration of CO\(_2\): A Facile Route to Diphospha-Ureas. *Chem. - Eur. J.* 2019, 25 (52), 12063–12067.

(12) Geier, S. J.; Gilbert, T. M.; Stephan, D. W. Activation of H\(_2\) by Phosphinoboranes \( \text{R}_2\text{PB}(\text{C}_2\text{F}_5)_2 \). *J. Am. Chem. Soc.* 2008, 130, 12632–12633.

(13) Price, A. N.; Nichol, G. S.; Cowley, M. J. Phosphoboranes: Accessible Reagents for the Synthesis of C–C/P–B Isoteres. *Angew. Chem.* 2017, 129 (33), 10085–10089.

(14) Pestana, D. C.; Power, P. N. Nature of the Boron-Phosphorus Bond in Monomeric Phosphinoboranes and Related Compounds. *J. Am. Chem. Soc.* 1991, 113 (22), 8426–8437.

(15) Paine, R. T.; Nöth, H. Recent Advances in Phosphinoborane Chemistry. *Chem. Rev.* 1995, 95, 343–379.

(16) Bailey, J. A.; Pringle, P. G. Monomeric Phosphinoboranes. *Coord. Chem. Rev.* 2015, 297–298, 77–90.

(17) Szymkiewicz, N.; Ordyzewska, A.; Chojnacki, J.; Grubba, R. Diaminosuphophosphate: Effective Reagents for Phosphinoboration of CO\(_2\). *RSC Adv.* 2019, 9 (48), 27749–27753.

(18) Szymkiewicz, N.; Chojnacki, J.; Grubba, R. Activation of N\(_2\)O and SO\(_2\) by the P-B Bond System. Reversible Binding of SO\(_2\) by the P-B Gamal Frustrated Lewis Pair. *Inorg. Chem.* 2020, 59 (9), 6332–6337.

(19) Dou, D.; Westerhausen, M.; Wood, G. L.; Linti, G.; Duesler, E. N.; Noth, H.; Paine, R. T. Synthesis and Reaction Chemistry of Aminophosphinylboranes. *Chem. Ber.* 1993, 126, 379–397.

(20) Nöth, H.; Schrägle, W. Monomere Phosphinoborane. *Angew. Chem.* 1962, 74, 587.

(21) Nöth, H.; Sze, S. N. Beiträge zur Chemie des Bors, XCIX [1] Borylphosphin-Metallcarbonyle der VI. Nebengruppe. *Z. Naturforsch.* B 1978, 33, 1313–1317.
(22) Ordyszewska, A.; Szyrkiewicz, N.; Perzanowski, E.; Chojnacki, J.; Wiśniewska, A.; Grubba, R. Structural and Spectroscopic Analysis of a New Family of Monomeric Diphosphinoboranes. *Dalton Trans.* 2019, 48 (33), 12482−12495.

(23) Szyrkiewicz, N.; Ordyszewska, A.; Chojnacki, J.; Grubba, R. Diphosphinoboranes as Intramolecular Frustrated Lewis Pairs: P-B-P Bond Systems for the Activation of Dihydrogen, Carbon Dioxide, and Phenyl Isocyanate. *Inorg. Chem.* 2021, 60 (6), 3794−3806.

(24) Heinz Karsch, H.; Hanika, G.; Huber, B.; Riede, J.; Müller, G. Monomere Phosphinoboran: Synthese Eines Tetraalkylphosphinoborans Und Seine Umwandlung Unter Retro- Und Re-Hydroborierung Zu Einem Dimeren Phosphinoboran Sowie Synthese Eines Triphosphinoborans. *J. Organomet. Chem.* 1989, 361 (2), C25−C29.

(25) Kaniewska, K.; Dragulescu-Andrasi, A.; Ponikiewski, L.; Pikies, J.; Stoian, S. A.; Grubba, R. Syntheses, Structures and Reactivity of Terminal Phosphido Complexes of Iron (II) Supported by a -Diketiminato Ligand. *Eur. J. Inorg. Chem.* 2018, 2018, 4298−4308.

(26) Dornhaus, F.; Scholz, S.; Sänger, I.; Bolte, M.; Wagner, M.; Lerner, H.-W. A Comparative Study on the Structural and Chemical Properties of Group 13−15 Element Addition Compounds tBu3PH-EX3 (E = B, Al, Ga, In; X = Cl, Br). *Z. Anorg. Allg. Chem.* 2009, 635 (13−14), 2263−2272.

(27) Gee, W.; Shaw, R. A.; Smith, B. C.; Bullen, G. J. *Proc. Chem. Soc.* 1961, 397.

(28) Bullen, G. J.; Mallinson, P. R. Molecular Structures of Cycloborataphosphonians. Part I. Crystal Structure of 2,2,4,4-Tetraido-1,1,3,3-Tetraphenylcyclodiborataphosphoniane. *J. Chem. Soc., Dalton Trans.* 1972, 11, 1143.

(29) Pyykö, P.; Atsumi, M. Molecular Single-Bond Covalent Radii for Elements 1−118. *Chem. - Eur. J.* 2009, 15 (1), 186−197.

(30) Pestana, D. C.; Power, P. P. Synthesis and Spectroscopic and Structural Characterization of PhB[P(Mes)BMes2]: A Boron-Phosphorus Analogue of the Pentadienyl Cation. *Organometallics* 1992, 11 (1), 98−103.

(31) Pyykö, P.; Atsumi, M. Molecular Double-Bond Covalent Radii for Elements Li-E112. *Chem. - Eur. J.* 2009, 15 (46), 12770−12779.

(32) Heuclin, H.; Ho, S. Y. F.; Le Goff, X. F.; So, C. W.; Mézailles, N. Facile B-H Bond Activation of Borane by Stable Carbenoid Species. *J. Am. Chem. Soc.* 2013, 135 (24), 8774−8777.

(33) Lastovickova, D. N.; Bielawski, C. W. Diamidocarbene Induced B-H Activation: A New Class of Initiator-Free Olefin Hydroboration Reagents. *Organometallics* 2016, 35 (5), 706−712.