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Tris(borane) Adducts of Diphosphanylmethanides: The $[H_3BCH(PPh_2BH_3)_2]^-$ Anion and Its Alkali Metal Complexes

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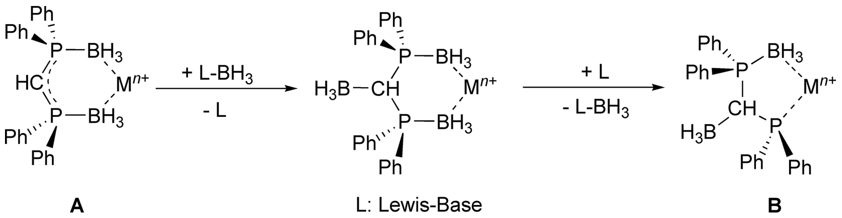
The reactivity of lithium complexes that contain the borane-modified diphoshanylmethanide ligand $[CH(PPh_2BH_3)_2]^-$ towards different Lewis base adducts of BH_3 was studied to gain further insight into the mechanism of the isomerization of this derivative, which formally proceeds through a shift of one BH_3 group from the phosphorus atom to the carbon atom. Whereas the use of $BH_3{\cdot}THF$ in THF only resulted in the thf adduct of the starting material, $[Li\{CH(PPh_2BH_3)_2\}(thf)_2]$ (**1**), the application of $BH_3{\cdot}SMe_2$ in toluene resulted in the formation of the novel compound $[(Li\{H_3BCH(PPh_2BH_3)_2\})_\infty]$ (**2**). The subsequent addition of ethereal ligands led to the isolation of $[Li\{H_3BCH(PPh_2BH_3)_2\}(Me_4thf)]$ (**3**) and $[Li\{H_3BCH(PPh_2BH_3)_2\}(thf)_3]$ (**4**). Treatment of these complexes with stronger Lewis bases such as *N*,*N*,*N′*,*N′*-tetramethylethane-1,2-diamine (tmeda) results in the removal of one phosphorus-bound BH_3 molecule and the formation of the $[Ph_2PCH(BH_3)PPh_2BH_3]^-$ anion. These results indicate that the isomerization of $[CH(PPh_2BH_3)_2]^-$ requires an additional BH_3 source and a rather strong Lewis base. Complexes **1**–**4** and the related derivatives $[Li\{CH(PPh_2BH_3)_2\}(Me_4THF)]$ (**5**) and $[K\{H_3BCH(PPh_2BH_3)_2\}(dme)_2]$ (**6**; dme = 1,2-dimethoxyethane) were characterized by multinuclear NMR spectroscopy and by single-crystal X-ray diffraction analysis.

Introduction

The chemistry of phosphane–borane-stabilized carbanions and their metal complexes dates back to the pioneering work of Schmidbaur and co-workers[1] and has recently received renewed interest on account of the importance of the alkali metal derivatives in particular in the synthesis of various phosphane derivatives.[2] Izod and co-workers[3] as well as other groups[4] investigated the coordination chemistry of these ligands towards a variety of main-group metals. Within these derivatives, these ambidentate ligands show different coordination modes that often involve the phosphorus-bound BH_3 groups in addition to the carbanionic carbon atom. The preference of one potential donor over the other is closely related to the chosen metal and the co-ligands that are present. In the case of the complexes of the s-block metals, there is a slight preference for the hydridic hydrogen atoms at the boron center over the carbanion, which is nevertheless often found in the coordination sphere of the metal ions.[3,4] In these complexes, the phosphane–borane moiety shows remarkable stability in the presence of the adjacent nucleophilic carbanion, which allows the broad use of those complexes in organic syntheses.[2] However, in a recent investigation on barium complexes, an isomerization of such a ligand, namely, $[CH(PPh_2BH_3)_2]^-$, by means of a formal shift of one of the BH_3 groups from the phosphorus atom to the carbon atom was observed.[5] Although the mechanism of this rearrangement is not fully understood, this reaction offers a potential strategy for the synthesis of novel anionic phosphane derivatives. Owing to the high importance of phosphanes as ligands in an over-



Scheme 1. Proposed mechanism of the isomerization of the $[CH(PPh_2BH_3)_2]^-$ anion.

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whelming number of catalytic transformations,[6,7] the aforementioned isomerization deserves further investigation.

Additionally, related phosphorus-stabilized methanides bearing BH_3 substituents were observed as products or proposed as intermediates of B–H bond-activation reactions between Li/Cl carbenoids and different BH_3 adducts.[8]

Herein, we evaluate the affinity of alkali metal complexes of $[CH(PPh_2BH_3)_2]^-$ towards different BH_3 transfer agents to test the plausibility of one of the proposed mechanisms (see Scheme 1) for the isomerization of this anion.

Results and Discussion

Lithium complexes that contain anionic $[CH(PPh_2BH_3)_2]^-$ are easily accessible by deprotonation of parent $CH_2(PPh_2BH_3)_2$[9] with commercially available organolithium compounds such as *n*-butyllithium and were therefore chosen as the starting point of this investigation. If this reaction is performed in a solution of diethyl ether, the ether-ligated derivative $[Li\{CH(PPh_2BH_3)_2\}(Et_2O)_2]$ is accessible in crystalline form.[4b] Although the methanide carbon atom does not show a bonding interaction with the lithium cation in this complex, such interactions were found in the related derivative $[Li_2\{CH(PPh_2BH_3)_2\}_2(Et_2O)]$, which can be prepared under modified conditions.[4d] This finding underlines the notion that the methanide carbon atom, which carries a significant part of the negative charge of the anion,[4c] is sufficiently nucleophilic to form bonds with rather hard Lewis acids such as Li^+ and therefore might be suitable to take up an additional BH_3 group under certain conditions. This uptake should result in the formation of the hitherto unknown anion $[H_3BCH(PPh_2BH_3)_2]^-$, an envisioned intermediate[5b] in the isomerization depicted in Scheme 1.

However, the addition of 1 equiv. of $BH_3{\cdot}THF$ (in THF) to a freshly prepared solution of $[Li\{CH(PPh_2BH_3)_2\}(Et_2O)_2]$ in diethyl ether did not lead to the isolation of the desired product but to partial or complete exchange of the neutral diethyl ether ligand and to the isolation of crystalline samples of $[Li\{CH(PPh_2BH_3)_2\}(Et_2O)_{2-n}(thf)_n]$ ($n \approx 1$) and $[Li\{CH(PPh_2BH_3)_2\}(thf)_2]$ (**1**) upon cooling, depending on the conditions applied. An uptake of BH_3 by the anionic ligand was not detected in the isolated crystalline crop. Compound **1** is easily accessible in good yields by recrystallization of the known diethyl ether ligated derivative in THF. The molecular structure of **1** is depicted in Figure S1 (see the Supporting Information).

The isolation of **1** underlines the notion that the proposed uptake of an additional BH_3 group requires more forceful conditions. The presence of competing Lewis bases such as diethyl ether and THF, especially when used in large excess as solvent, seems counterproductive for this endeavor. Therefore, the original procedure was modified. Toluene or benzene were used as solvents during deprotonation of the precursor $CH_2(PPh_2BH_3)_2$, and $BH_3{\cdot}SMe_2$ was chosen as the BH_3 source since dimethylsulfane as a rather soft Lewis base was expected to show lower affinity toward the hard Lewis acid BH_3 and therefore would make the methanide carbon atom more competitive as a BH_3 acceptor. The colorless crystalline material obtained was identified by X-ray diffraction analysis as the desired compound $[(Li\{H_3BCH(PPh_2BH_3)_2\})_\infty]$ (**2**), although the rather low quality of the obtained crystals only led to a structural motif of this complex (see Figure 1), thereby preventing further discussion of bond lengths and angles.

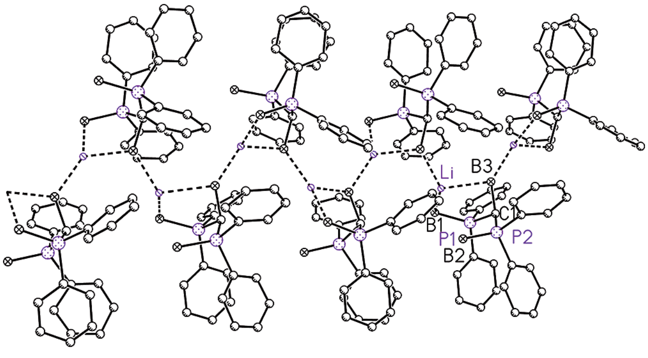


Figure 1. Structural motif of the polymeric chain of $[(Li\{H_3BCH(PPh_2BH_3)_2\})_\infty]$ (**2**). Hydrogen atoms are omitted for clarity.

The complex was insoluble in non-coordinating solvents such as benzene and toluene, which hampered its investigation in solution in the absence of additional Lewis bases. To test the stability of the newly formed anion $[H_3BCH(PPh_2BH_3)_2]^-$ of the lithium complex **2** in the presence of different ethers, a number of these donor ligands were used as additives during recrystallization after successful formation of **2**. Initially, 2,2,5,5-tetramethyltetrahydrofuran (Me_4THF) was applied. Owing to steric crowding around its oxygen atom, this ether should be only weakly nucleophilic and was therefore in our opinion the most suitable candidate to prevent possible removal of labile BH_3 groups. As the result of this experiment, the mononuclear complex $[Li\{H_3BCH(PPh_2BH_3)_2\}(Me_4thf)]$ (**3**) was isolated in crystalline form. The structure of the compound, determined by X-ray diffraction experiments, is shown in Figure 2.

The uptake of the additional BH_3 group by the formerly sp^2-hybridized methanide carbon atom led to sp^3 hybridization of this atom. The observed distance between the carbon atom and the attached boron atom of 1.687(4) Å is slightly longer than the related single bond of 1.638(11) Å observed for isomer **B** (see Scheme 1) in $[Ba_4O\{CH(PPh_2BH_3)_2\}_2\{Ph_2PCH(BH_3)(PPh_2BH_3)\}]$[5] and the value of 1.66(3) Å reported for the carbon–boron single bond of the closely related carbodiphosphorane borane adduct $[\{(\mu\text{-}H)H_4B_2\}\{C(PPh_3)_2\}][B_2H_7]$.[10] The phosphorus–carbon bond lengths of the diphosphanylmethanide moiety in **3** show values of 1.814(2) Å (P1–C1) and 1.817(3) Å (P2–C1), also typical of single bonds. Owing to the change in hybridization, a smaller P1–C1–P2 angle of 116.91(13)° relative to compound **1** [131.59(15)°] was observed. The lithium cation interacts with the hydridic hydrogen atoms of

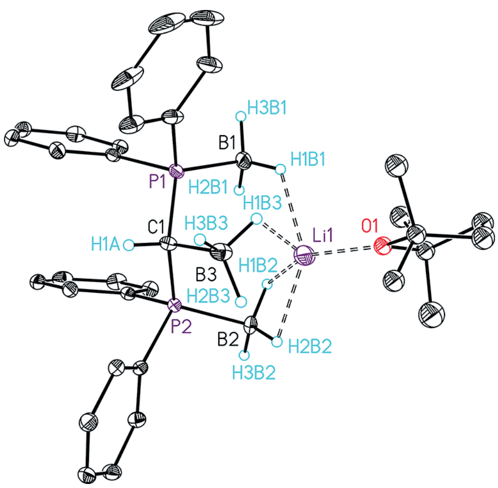


Figure 2. Molecular structure and numbering scheme of $[Li\{H_3BCH(PPh_2BH_3)_2\}(Me_4thf)]$ (**3**). The ellipsoids represent a probability of 40%. Hydrogen atoms except those of the BH_3 groups and at C1 as well as a disorder of the Me_4THF ligand are omitted for clarity. Selected bond lengths [Å] and angles [°]: Li1–H1(B1) 2.21(4), Li1–H1(B2) 2.12(3), Li1–H2(B2) 2.12(4), Li1–H1(B3) 1.97(4), Li1–O1 1.841(7), C1–B3 1.687(4), C1–P1 1.814(2), C1–P2 1.817(3), P1–B1 1.924(3), P2–B2 1.945(3); O1–Li1–H1(B1) 103.7(10), O1–Li1–H1(B2) 132.9(10), O1–Li1–H2(B2) 116.6(11), O1–Li1–H1(B3) 104.1(11), B3–C1–P1 109.18(17), B3–C1–P2 108.16(19), P1–C1–P2 116.91(13), C1–P1–B1 116.55(14), C1–P2–B2 117.09(13).

all three BH_3 moieties of the anionic ligand. Whereas the coordination mode of the BH_3 group at P2 is best described as $\kappa^2(H,H)$ with lithium–hydrogen distances of 2.12(3) and 2.12(4) Å, the other two BH_3 groups show both $\kappa^1(H)$ coordination with a shorter contact between the lithium ion and the carbon-bound BH_3 group [Li1–H1(B3) 1.97(4) Å] and a rather long one to the second phosphorus-bound BH_3 moiety [Li1–H1(B1) 2.21(4) Å]. Together with the oxygen atom of the neutral ether ligand Me_4THF, the three borane moieties form a pseudotetrahedral coordination sphere around the lithium center. The interaction between the cation and Me_4THF seems to be variable. A positional disorder leads to two deviating locations of the ligand relative to the lithium cation. Rather different distances between the metal ion and the oxygen atom of 1.841(7) Å (Li–O1) and 2.045(8) Å (Li–O1A) were observed. Compound **3** is a rare example of a metal complex that contains this coordinated ether ligand[11] and to the best of our knowledge[12] is the first structurally characterized derivative.

Dissolution of **2** and **3** in THF did not lead to reversion of the formation of the anion by liberation of BH_3 as underlined by the NMR spectroscopic data obtained for these complexes in $[D_8]THF$. Despite the enhanced donor capacity of this ether, no formation of complex **1** was detected in solution. Instead, the spectra obtained suggest a breakup of the polymeric structure in the case of **2** as well as rapid replacement of the neutral ligand in **3** by $[D_8]THF$, which leads to essentially identical spectra of these compounds despite the signals of the liberated ligand.

The data obtained in $[D_8]THF$ (see the Experimental Section and the Supporting Information) suggest that the negative charge in these complexes is localized at the carbon-bound BH_3 group. The hydridic hydrogen atoms of this group resonated at rather high field strength and gave a broad signal centered at $\delta_H = 0.30$ ppm. In contrast, the hydrogen atoms of the phosphorus-bound BH_3 groups and of the central methanide subunit are significantly deshielded relative to compound **1**, and chemical shifts of $\delta_H = 1.22$ ($P–BH_3$; **1**: $\delta_H = 0.84$ ppm) and 3.07 ppm (P_2CH; **1**: $\delta_H = 0.68$ ppm), respectively, were observed. In the ^{13}C and ^{31}P NMR spectra, the PCHP subunit gave rise to signals at $\delta_C = 15.6$ ppm and $\delta_P = 22.1$ ppm, whereas two signals with relative integrals of 2:1 were observed in the ^{11}B NMR spectrum at $\delta_B = -37.4$ (PBH_3) and –30.8 ppm (CBH_3).

To relate the solution data of the $[D_8]THF$-ligated compound formed during the NMR spectroscopic investigation with additional data and to see how the use of a stronger donor solvent such as THF might affect the interaction between anion and cation, the thf-ligated complex $[Li\{H_3BCH(PPh_2BH_3)_2\}(thf)_3]$ (**4**) was prepared in crystalline form. As shown in Figure 3, the complex contains three-coordinated THF molecules per lithium center, which leaves one coordination site of the preferably tetracoordinated lithium cation for the interaction with the anionic ligand. This interaction takes place through the carbon-

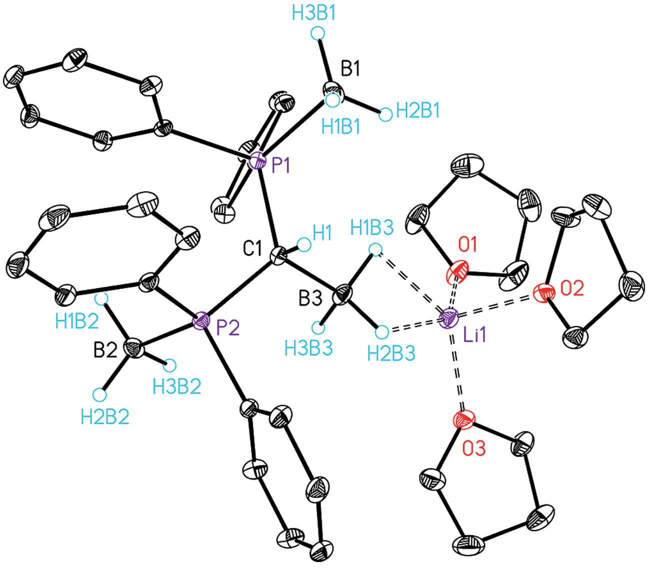
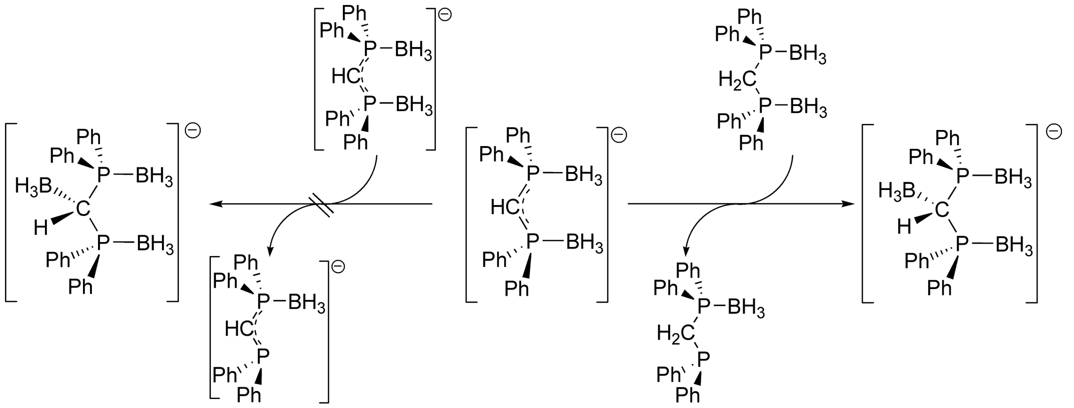


Figure 3. Molecular structure and numbering scheme of $[Li\{H_3BCH(PPh_2BH_3)_2\}(thf)_3]\cdot toluene$ (**4**). The ellipsoids represent a probability of 40%. Hydrogen atoms except those of the BH_3 groups and at C1 as well as the co-crystallized toluene are omitted for clarity. Selected bond lengths [Å] and angles [°]: Li1–H1(B3) 1.994(18), Li1–H2(B3) 2.141(17), Li1–O1 1.965(3), Li1–O2 1.973(3), Li1–O3 1.954(2), C1–B3 1.6691(18), C1–P1 1.8329(12), C1–P2 1.8207(12), P1–B1 1.9257(15), P2–B2 1.9354(15); O1–Li1–O2 100.05(11), O1–Li1–O3 108.14(12), O1–Li1–H1(B3) 95.5(5), O1–Li1–H2(B3) 145.8(5), O2–Li1–O3 98.96(11), O2–Li1–H1(B3) 107.4(5), O2–Li1–H2(B3) 100.9(5), O3–Li1–H1(B3), 140.7(5), O3–Li1–H2(B3) 94.9(5), B3–C1–P1 111.41(8), B3–C1–P2 112.87(9), B3–C1–H1 106.1(10), P1–C1–P2 119.93(6), P1–C1–H1 100.0(9), P2–C1–H1 104.5(10), C1–P1–B1 107.36(7), C1–P2–B2 120.06(6).



Scheme 2. Reactivity of $[CH(PPh_2BH_3)_2]^-$ towards neutral and anionic phosphane–borane adducts.

bound BH_3 group, which shows an unsymmetrical κ^2-coordination mode [Li1–H1(B3) 1.994(18) Å, Li1–H2(B3) 2.141(17) Å]. The two other BH_3 groups show no close contacts with the lithium ion and are oriented away from each other to minimize electrostatic repulsion.

The significance of complexes such as **2**–**4** for the isomerization of $[CH(PPh_2BH_3)_2]^-$ to $[H_3BCH(PPh_2BH_3)(PPh_2)]^-$ was further investigated, since in the original procedure for the synthesis of $[Ba_4O\{CH(PPh_2BH_3)_2\}_2\{Ph_2PCH(BH_3)(PPh_2BH_3)\}]$,[5] the addition of an external BH_3 source was not mentioned. It was envisioned that the anionic ligand $[CH(PPh_2BH_3)_2]^-$ is not only a suitable BH_3 group acceptor as proven by the synthesis of **2**–**4**, but also a potential donor. This would lead to a redistribution of BH_3 groups between two bis(borane) adducts $[CH(PPh_2BH_3)_2]^-$ to form a monoborane adduct $[Ph_2PCHPPh_2BH_3]^-$ in addition to the $[H_3BCH(PPh_2BH_3)_2]^-$ anion already observed in complexes **2**–**4** (see Scheme 2, left). However, heating of a freshly prepared sample of $[(Li\{CH(PPh_2BH_3)_2\})_n]$ in toluene without additional donors to 80 °C for 12 h did not result in any noticeable redistribution of BH_3 groups, as judged by NMR spectroscopy. The addition of 2 equiv. of Me_4THF as a potential BH_3 "shuttle" does not change the outcome of this experiment with respect to the bonding situation of the BH_3 groups but led to the isolation of $[Li\{CH(PPh_2BH_3)_2\}(Me_4thf)]$ (**5**) (see Figure S2 in the Supporting Information).

The isolation of **5** underlines the notion that the phosphorus–boron bond of the $[CH(PPh_2BH_3)_2]^-$ anion is too strong to be broken under the applied conditions. Nonetheless, the initial report[5] holds a clue about another BH_3 source. It was mentioned that during transfer of $[CH(PPh_2BH_3)_2]^-$ from potassium to barium substantial amounts of parent $CH_2(PPh_2BH_3)_2$ were formed. Since this substance is a neutral molecule, it should be a more feasible BH_3 donor than its anionic counterpart owing to a diminished electrostatic attraction between the leaving BH_3 group and the remaining Lewis base. Heating a sample of $[(Li\{CH(PPh_2BH_3)_2\})_n]$ in toluene in the presence of substoichiometric amounts of $CH_2(PPh_2BH_3)_2$ indeed led to consumption of $CH_2(PPh_2BH_3)_2$, and the formation of compound **2** and $Ph_2PCH_2PPh_2BH_3$[5b,13] (major products) in addition to further byproducts as judged by ^{31}P NMR spectroscopic investigation of the product mixture (see the Supporting Information). The reaction is not limited to lithium complexes but also works in the case of derivatives that contain the softer Lewis acid potassium. Consequently, a crystalline mixture of $[K\{H_3BCH(PPh_2BH_3)_2\}(dme)_2]$ (**6**; dme = 1,2-dimethoxyethane) and $Ph_2PCH_2PPh_2BH_3$ was observed from the reaction of $[(K\{CH(PPh_2BH_3)_2\})_\infty]$[5] and $CH_2(PPh_2BH_3)_2$ after recrystallization from a mixture

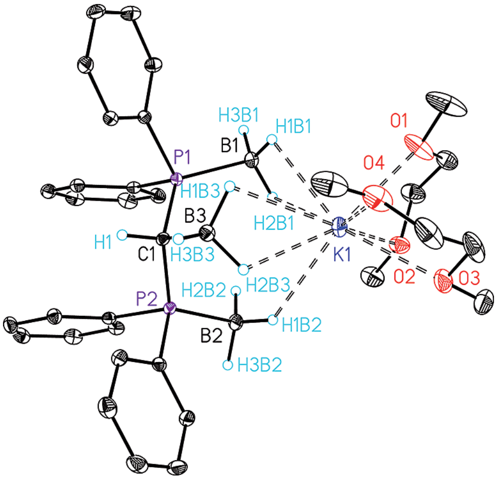


Figure 4. Molecular structure and numbering scheme of $[K\{H_3BCH(PPh_2BH_3)_2\}(dme)_2]$ (**6**). The ellipsoids represent a probability of 40%. Hydrogen atoms except those of the BH_3 groups and at C1 are omitted for clarity. Selected bond lengths [Å] and angles [°]: K1–H1(B1) 2.74(3), K1–H2(B1) 2.86(3), K1–H1(B2) 2.98(3), K1–H1(B3) 2.91(3), K1–H2(B3) 2.64(3), K1–O1 2.723(2), K1–O2 2.7714(18), K1–O3 2.816(2), K1–O4 2.765(2), C1–B3 1.694(3), C1–P1 1.825(2), C1–P2 1.816(2), P1–B1 1.950(3), P2–B2 1.916(2); O1–K1–O2 62.33(6), O1–K1–O3 79.82(7), O1–K1–O4 83.20(7), O1–K1–H1(B1) 78.8(6), O1–K1–H2(B1) 91.2(6), O1–K1–H1(B2) 140.3(5), O1–K1–H1(B3) 118.3(5), O1–K1–H2(B3) 156.6(6), O2–K1–O3 79.04(7), O2–K1–O4 130.82(7), O2–K1–H1(B1) 99.7(6), O2–K1–H2(B1) 72.3(6), O2–K1–H1(B2) 80.0(5), O2–K1–H1(B3) 149.8(5), O2–K1–H2(B3) 139.1(6), O3–K1–O4 60.15(8), O3–K1–H1(B1) 156.4(6), O3–K1–H2(B1) 150.9(6), O3–K1–H1(B2) 106.0(5), O3–K1–H1(B3) 131.0(5), O3–K1–H2(B3) 110.0(6), O4–K1–H1(B1) 107.1(6), O4–K1–H2(B1) 146.7(6), O4–K1–H1(B2) 134.4(5), O4–K1–H1(B3) 76.4(5), O4–K1–H2(B3) 83.7(6), B3–C1–P1 108.77(14), B3–C1–P2 111.30(14), P1–C1–P2 115.40(11), C1–P1–B1 120.96(11), C1–P2–B2 118.15(11).

Scheme 3. Reactivity of the $[H_3BCH(PPh_2BH_3)_2]^-$ anion towards tmeda.

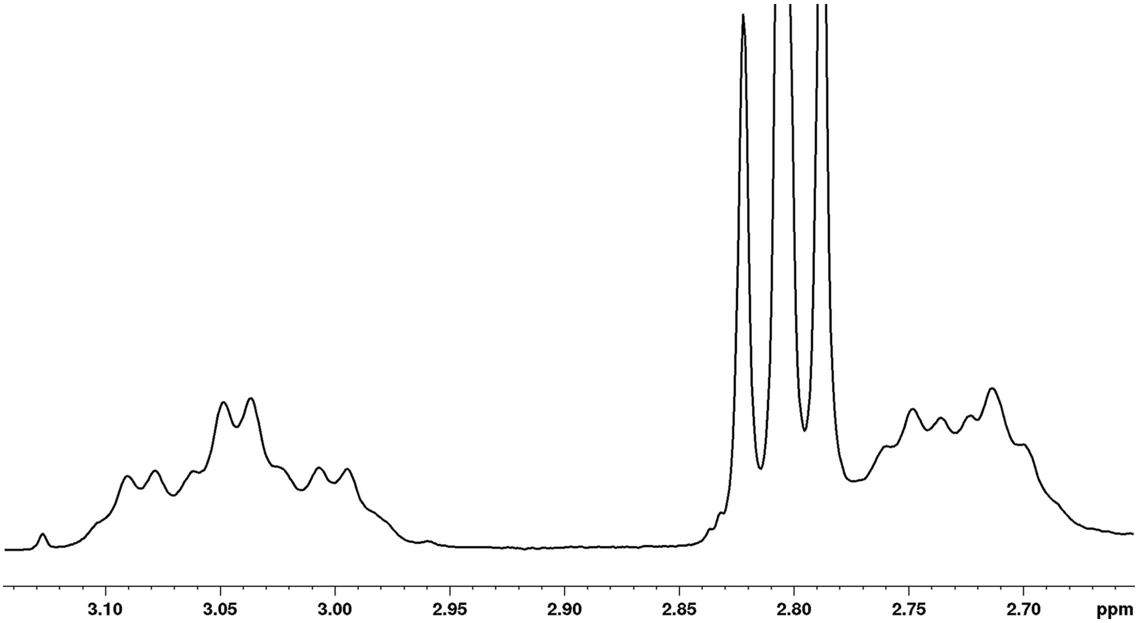


Figure 5. Part of the ^1H NMR spectrum of the reaction mixture of **2** and tmeda in [D$_8$]THF. Left: P_2CHB moiety of **2**. Center: CH_2 group of $Me_2NCH_2CH_2N(BH_3)Me_2$. Right: P_2CHB moiety of Li[$Ph_2PCH(BH_3)(PPh_2BH_3)$].

of toluene and dme. Attempts to separate **6** from this mixture failed. Nevertheless, the molecular structure of **6** was determined by X-ray diffraction analysis (see Figure 4). As expected, the larger potassium cation shows a higher coordination number than the lithium cation. In **6** the potassium center is surrounded by the four oxygen atoms of the dme ligands and the three BH_3 groups of the anionic ligand in an irregular arrangement. The average potassium–oxygen bond in **6** has a length of 2.769(2) Å, whereas the five potassium–hydrogen bonds are 2.83(3) Å long on average. The anionic ligand itself shows interatomic distances and angles comparable to the values observed in **3** and **4**.

As described above, alkali metal complexes that contain the novel anionic ligand $[H_3BCH(PPh_2BH_3)_2]^-$ are rather stable in the presence of ethereal Lewis bases like THF. Against stronger bases such as *N*,*N*,*N′*,*N′*-tetramethylethane-1,2-diamine (tmeda), partial loss of a phosphorus-bound BH_3 group was observed in solution (see Scheme 3). The ^{31}P NMR spectrum of the reaction mixture of **2** and tmeda in [D$_8$]THF shows the presence of a new species related to signals at $\delta_P = 22.8$ and –8.8 ppm. The latter signal stems from an unprotected phosphane moiety. In the ^1H NMR spectrum, the methanide subunit of this species shows a broadened multiplet at $\delta_H = 2.73$ ppm (see Figure 5), which is indicative of the still attached BH_3 group. Although this compound was only characterized in solution, the NMR spectroscopic data indicates that this lithium complex contains the same $[Ph_2PCH(BH_3)(PPh_2BH_3)]^-$ anion as observed in the barium complex $[Ba_4O\{CH(PPh_2BH_3)_2\}_2\{Ph_2PCH(BH_3)(PPh_2BH_3)\}]$.[5] This result demonstrates that the complexes under investigation are indeed potential intermediates in the isomerization of $[CH(PPh_2BH_3)_2]^-$.

Conclusion

A straightforward strategy for the synthesis of lithium complexes that contain the novel tris(borane) adduct of diphosphanylmethanide was developed by using $BH_3{\cdot}SMe_2$ as a borane source. During their synthesis, the use of toluene proved superior to ethereal solvents. Nevertheless, the product of the reaction under these conditions, $[(Li\{H_3BCH(PPh_2BH_3)_2\})_\infty]$ (**2**), is, once formed, stable in the presence of ethers. Whereas the derivative $[Li\{H_3BCH(PPh_2BH_3)_2\}(Me_4thf)]$ (**3**) contained one ether molecule per lithium center, the utilization of THF resulted in the derivative $[Li\{H_3BCH(PPh_2BH_3)_2\}(thf)_3]$ (**4**), which showed reduced interactions between the lithium cation and the anionic ligand owing to the uptake of three neutral

THF molecules. The isolated compounds can act as borane sources themselves in the presence of stronger Lewis bases such as tmeda. In the presence of this substance, a phosphorus-bound BH_3 group is partially removed and the anionic phosphane ligand $[Ph_2PCH(BH_3)(PPh_2BH_3)]^-$ is formed. This result indicates that the tris(borane) adducts of bis(diphenylphosphanyl)methanide are potential intermediates in the isomerization of $[CH(PPh_2BH_3)_2]^-$ to $[Ph_2PCH(BH_3)(PPh_2BH_3)]^-$. However, this process requires an external borane source as well as a sufficiently strong Lewis base. Whether this simple strategy can be adapted to the synthesis of other α-BH_3-modified phosphanes is under current investigation.

In addition, two unique metal complexes that contain the sterically crowded ether ligand Me_4THF, namely, $[Li\{H_3BCH(PPh_2BH_3)_2\}(Me_4thf)]$ (**3**) and $[Li\{CH(PPh_2BH_3)_2\}(Me_4thf)]$ (**5**), were synthesized and structurally characterized.

Experimental Section

General Methods: All manipulations were carried out under argon by using standard Schlenk techniques. THF, 2,2,5,5-tetramethyltetrahydrofuran, diethyl ether, toluene, and benzene were dried with KOH and distilled from sodium/benzophenone under argon; deuterated THF was dried with sodium, degassed, and saturated with argon. The yields given are not optimized. ^{1}H, ^{7}Li{^{1}H}, ^{11}B{^{1}H}, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded with Bruker AC 400 or AC 600 spectrometers. Chemical shifts are reported in parts per million relative to Me_4Si as an external standard. The residual signals of [D$_8$]THF were used as internal standard in the ^{1}H and ^{13}C NMR spectra. ^{7}Li, ^{11}B, and ^{31}P NMR spectroscopic shifts are referenced to LiCl in D_2O, 15% $BF_3{\cdot}OEt_2$ in $CDCl_3$, and 85% H_3PO_4 as external standard, respectively. Coupling constants are given in Hertz. $BH_3{\cdot}THF$ and $BH_3{\cdot}SMe_2$ were purchased from Aldrich. $CH_2(PPh_2BH_3)_2$ was synthesized according to a known procedure.[9]

Synthesis of $[Li\{CH(PPh_2BH_3)_2\}(thf)_2]$ (1): Solid $CH_2(PPh_2BH_3)_2$ (0.666 g, 1.62 mmol) was suspended in diethyl ether (20 mL), and a solution of *n*-butyllithium (1.0 mL of a 1.6 M hexane solution, 1.6 mmol) was added with a syringe to the stirred suspension at ambient temperature. After the formation of a clear solution, THF (1.5 mL) was added, and the resulting solution was stored at 0 °C. After 24 h, the resulting white precipitate was collected with a Schlenk frit and dried under vacuum. Yield: 0.813 g (1.45 mmol, 89.5%, crude product). The compound partially lost coordinated THF upon prolonged drying. In some cases, the product partially contained diethyl ether beside coordinated THF. In these cases, the crude product was recrystallized from THF (ambient temperature to –20 °C) to obtain pure **1**. ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 0.68 (s, 1 H, P_2CH), 0.84 (br., 6 H, PBH_3), 1.76 (m, 8 H, CH_2 THF), 3.62 (m, 8 H, OCH_2 THF), 7.10 (m, 12 H, *m*-CH, *p*-CH Ph), 7.71 (m, 8 H, *o*-CH Ph) ppm. ^{7}Li{^{1}H} NMR (155 MHz, [D$_8$]THF, 25 °C): δ = –0.6 (s) ppm. ^{11}B{^{1}H} NMR (128 MHz, [D$_8$]THF, 25 °C): δ = –33.6 (br.) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]THF, 25 °C): δ = 5.1 (t, $^{1}J_{C,P}$ = 77.4 Hz, 1 C, P_2CH), 26.3 (s, 2 C, CH_2 THF), 68.2 (s, 2 C, OCH_2 THF), 127.1 (d, $^{3}J_{C,P}$ = 8.8 Hz, 8 C, *m*-CH Ph), 127.8 (d, $^{4}J_{C,P}$ = 1.6 Hz, 4 C, *p*-CH Ph), 133.2 (d, $^{2}J_{C,P}$ = 9.1 Hz, 8 C, *o*-CH Ph), 142.9 (dd, $^{1}J_{C,P}$ = 55.4, $^{3}J_{C,P}$ = 1.4 Hz, 4 C, *i*-C Ph) ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF, 25 °C): δ = 14.4 (br.) ppm. Suitable crystals of **1** for X-ray diffraction analysis were obtained directly from the reaction mixture.

Synthesis of $[(Li\{H_3BCH(PPh_2BH_3)_2\})_\infty]$ (2): $BH_3{\cdot}SMe_2$ (0.1 mL, 1.69 mmol) was added with a syringe at ambient temperature to a stirred solution of $[(Li\{CH(PPh_2BH_3)_2\})_n]$, freshly prepared from $CH_2(PPh_2BH_3)_2$ (0.281 g, 0.68 mmol) and *n*-butyllithium (0.43 mL, 0.69 mmol, 1.6 M in hexane) in benzene (5 mL). Afterwards, the reaction mixture was stirred for an additional 30 min. The white precipitate that formed was collected with a Schlenk frit and dried under vacuum. Yield: 0.245 g (0.57 mmol, 83.2%). $C_{25}H_{30}B_3LiP_2$ (431.835): calcd. C 69.53, H 7.00; found C 69.21, H 7.63. ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 0.30 (br., 3 H, CBH_3), 1.22 (br., 6 H, PBH_3), 3.07 (m, 1 H, P_2CHB), 7.05 (m, 8 H, *m*-CH Ph), 7.10 (m, 4 H, *p*-CH Ph), 7.78 (m, 8 H, *o*-CH Ph) ppm. ^{7}Li{^{1}H} NMR (233 MHz, [D$_8$]THF, 25 °C): δ = –1.1 (s) ppm. ^{11}B{^{1}H} NMR (128 MHz, [D$_8$]THF, 25 °C): δ = –37.4 (br., 2 B, PBH_3), –30.8 (br., 1 B, CBH_3) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]THF, 25 °C): δ = 15.6 (br., 1 C, P_2CHB), 127.5 (d, $^{3}J_{C,P}$ = 9.5 Hz, 4 C, *m*-CH Ph), 127.8 (d, $^{3}J_{C,P}$ = 9.5 Hz, 4 C, *m*-CH Ph), 129.4 (d, $^{4}J_{C,P}$ = 1.0 Hz, 2 C, *p*-CH Ph), 129.6 (d, $^{4}J_{C,P}$ = 1.0 Hz, 2 C, *p*-CH Ph), 134.1 (d, $^{2}J_{C,P}$ = 8.4 Hz, 4 C, *o*-CH Ph), 134.2 (d, $^{1}J_{C,P}$ = 50.8 Hz, 2 C, *i*-C Ph), 134.4 (d, $^{2}J_{C,P}$ = 8.4 Hz, 4 C, *o*-CH Ph), 135.0 (dd, $^{1}J_{C,P}$ = 54.4, $^{3}J_{C,P}$ = 6.5 Hz, 2 C, *i*-C Ph) ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF, 25 °C): δ = 22.1 (br.) ppm. Crystals of **2** for X-ray diffraction experiments could be obtained directly from the reaction mixture when $BH_3{\cdot}SMe_2$ was added without stirring at ambient temperature, and the resulting mixture was left undisturbed for 18 h.

Synthesis of $[Li\{H_3BCH(PPh_2BH_3)_2\}(Me_4thf)]$ (3): Solid $CH_2(PPh_2BH_3)_2$ (0.314 g, 0.76 mmol) was suspended in toluene (5 mL), and a solution of *n*-butyllithium (0.48 mL of 1.6 M hexane solution, 0.77 mmol) was added with a syringe to the stirred suspension at ambient temperature. After 5 min of stirring, $BH_3{\cdot}SMe_2$ (0.1 mL, 1.69 mmol) was added by syringe to the clear solution. The resulting white solid dissolved upon addition of 2,2,5,5-tetramethyltetrahydrofuran (1 mL). The clear solution was stored at –20 °C overnight to give a white precipitate. The product was collected with a Schlenk frit and dried under vacuum. Yield: 0.358 g (0.64 mmol, 83.9%). ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 0.30 (br., 3 H, CBH_3), 1.17 (s, 12 H, CH_3 Me_4THF), 1.21 (br., 6 H, PBH_3), 1.81 (s, 4 H, CH_2 Me_4THF), 3.07 (m, 1 H, P_2CHB), 7.05 (m, 8 H, *m*-CH Ph), 7.10 (m, 4 H, *p*-CH Ph), 7.78 (m, 8 H, *o*-CH Ph) ppm. ^{7}Li{^{1}H} NMR (155 MHz, [D$_8$]THF, 25 °C): δ = –1.1 (s) ppm. ^{11}B{^{1}H} NMR (128 MHz, [D$_8$]THF, 25 °C): δ = –37.4 (br., 2 B, PBH_3), –30.8 (br., 1 B, CBH_3) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]THF, 25 °C): δ = 15.6 (br., 1 C, P_2CHB), 30.1 (s, 4 C, CH_3 Me_4THF), 39.4 (s, 2 C, CH_2 Me_4THF), 81.0 (s, 2 C, OC Me_4THF), 127.5 (d, $^{3}J_{C,P}$ = 9.5 Hz, 4 C, *m*-CH Ph), 127.7 (d, $^{3}J_{C,P}$ = 9.5 Hz, 4 C, *m*-CH Ph), 129.4 (d, $^{4}J_{C,P}$ = 2.3 Hz, 2 C, *p*-CH Ph), 129.6 (d, $^{4}J_{C,P}$ = 1.9 Hz, 2 C, *p*-CH Ph), 134.1 (d, $^{2}J_{C,P}$ = 8.6 Hz, 4 C, *o*-CH Ph), 134.2 (d, $^{1}J_{C,P}$ ≈ 53 Hz, 2 C, *i*-C Ph), 134.4 (d, $^{2}J_{C,P}$ = 8.5 Hz, 4 C, *o*-CH Ph), 135.0 (dd, $^{1}J_{C,P}$ = 54.4, $^{3}J_{C,P}$ = 6.5 Hz, 2 C, *i*-C Ph) ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF, 25 °C): δ = 22.0 (br.) ppm. Suitable crystals of **3** for X-ray diffraction experiments were obtained directly from the reaction mixture at –40 °C.

Synthesis of $[Li\{H_3BCH(PPh_2BH_3)_2\}(thf)_3]{\cdot}1toluene$ (4): Solid $CH_2(PPh_2BH_3)_2$ (0.290 g, 0.70 mmol) was suspended in toluene (5 mL), and a solution of *n*-butyllithium (0.38 mL of 1.6 M hexane solution, 0.70 mmol) was added with a syringe to the stirred suspension at ambient temperature. After 5 min of stirring, $BH_3{\cdot}SMe_2$ (0.1 mL, 1.69 mmol) was added to the clear solution. The resulting white solid dissolved upon addition of THF (1 mL). The solution was concentrated under vacuum until the remaining oil started to crystallize. The product was suspended in toluene (5 mL), removed by filtration, and dried under vacuum. The compound partially lost coordinated THF upon drying. Yield: 0.256 g (0.35 mmol, 49.1%). ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 0.30 (br., 3 H, CBH_3), 1.22 (br., 6 H, PBH_3), 1.77 (m, CH_2 THF), 2.31 (s, 3 H, CH_3 toluene), 3.07 (m, 1 H, P_2CHB), 3.62 (m, OCH_2 THF), 7.05 (m, 8 H, *m*-CH Ph), 7.10 (m, 4 H, *p*-CH Ph), 7.13 (m, 3 H, *o*-CH, *p*-CH toluene), 7.19 (m, 2 H, *m*-CH toluene), 7.79 (m, 8 H, *o*-CH Ph) ppm. $^{7}Li\{^{1}H\}$ NMR (155 MHz, [D$_8$]THF, 25 °C): δ = –1.1 (s) ppm. $^{11}B\{^{1}H\}$ NMR (128 MHz, [D$_8$]THF, 25 °C): δ = –37.4 (br., 2 B, PBH_3), –30.8 (br., 1 B, CBH_3) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, [D$_8$]THF, 25 °C): δ = 15.7 (br., 1 C, P_2CHB), 21.4 (s, 1 C, CH_3 toluene), 26.4 (s, CH_2 THF), 68.3 (s, OCH_2 THF), 126.1 (s, 1 C, *p*-CH toluene), 127.6 (d, $^{3}J_{C,P}$ = 9.6 Hz, 4 C, *m*-CH Ph), 127.9 (d, $^{3}J_{C,P}$ = 9.6 Hz, 4 C, *m*-CH Ph), 128.9 (s, 2 C, *m*-CH toluene), 129.6 (d, $^{4}J_{C,P}$ = 1.8 Hz, 2 C, *p*-CH Ph), 129.7 (s, 2 C, *o*-CH toluene), 129.7 (d, $^{4}J_{C,P}$ = 2.0 Hz, 2 C, *p*-CH Ph), 134.3 (d, $^{2}J_{C,P}$ = 8.0 Hz, 4 C, *o*-CH Ph), 134.5 (d, $^{2}J_{C,P}$ = 8.0 Hz, 4 C, *o*-CH Ph), 134.3 (d, $^{1}J_{C,P} \approx 50$ Hz, 2 C, *i*-C Ph), 135.1 (dd, $^{1}J_{C,P}$ = 54.3, $^{3}J_{C,P}$ = 6.6 Hz, 2 C, *i*-C Ph), 138.4 (s, 1 C, *i*-C toluene) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz, [D$_8$]THF, 25 °C): δ = 22.1 (br.) ppm. Suitable crystals of **4** for X-ray diffraction experiments were obtained by layering a saturated solution of **4** in a mixture of toluene and THF with *n*-heptane at –10 °C.

Synthesis of $[Li\{CH(PPh_2BH_3)_2\}(Me_4thf)]$ (5): Solid $CH_2(PPh_2BH_3)_2$ (0.349 g, 0.85 mmol) was suspended in toluene (8 mL), and a solution of *n*-butyllithium (0.55 mL of 1.6 M hexane solution, 0.88 mmol) was added to the stirred suspension at ambient temperature. Hexane and butane were removed by distillation under reduced pressure. The resulting white precipitate dissolved upon addition of Me_4THF (0.224 g, 1.75 mmol). The pale yellow solution was heated to 80 °C for 18 h. After cooling to ambient temperature, the resulting white precipitate was collected with a Schlenk frit and dried under vacuum. Yield: 0.333 g (0.61 mmol, 72.0%). ^{1}H NMR (600 MHz, [D$_8$]THF, 25 °C): δ = 0.64 (s, 1 H, P_2CH), 0.84 (br., 6 H, PBH_3), 1.17 (m, 12 H, CH_3 Me_4THF), 1.81 (m, 4 H, CH_2 Me_4THF), 7.09 (m, 12 H, *m*,*p*-CH), 7.69 (m, 8 H, *o*-CH) ppm. $^{7}Li\{^{1}H\}$ NMR (233 MHz, [D$_8$]THF, 25 °C): δ = –0.6 (s) ppm. $^{11}B\{^{1}H\}$ NMR (193 MHz, [D$_8$]THF, 25 °C): δ = –33.9 (br.) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, [D$_8$]THF, 25 °C): δ = 5.3 (t, $^{1}J_{C,P}$ = 77.6 Hz, 1 C, P_2CH), 30.2 (s, 4 C, CH_3 Me_4THF), 39.5 (s, 2 C, CH_2 Me_4THF), 81.1 (s, 2 C, OC Me_4THF), 127.3 (d, $^{3}J_{C,P}$ = 9.9 Hz, 8 C, *m*-CH Ph), 127.9 (s, 4 C, *p*-CH Ph), 133.2 (d, $^{2}J_{C,P}$ = 8.8 Hz, 8 C, *o*-CH Ph), 143.1 (d, $^{1}J_{C,P}$ = 57.4 Hz, 4 C, *i*-C Ph) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz, [D$_8$]THF, 25 °C): δ = 14.3 (br.) ppm. Suitable crystals of **7** for X-ray diffraction experiments were obtained from the mother liquor of the reaction at –20 °C.

Formation of $[K\{H_3BCH(PPh_2BH_3)_2\}(dme)_2]$ (6): Solid $[(K\{CH(PPh_2BH_3)_2\})_\infty]$ (105 mg, 0.23 mmol) was suspended in toluene (5 mL). After the addition of solid $CH_2(PPh_2BH_3)_2$ (96 mg, 0.24 mmol), the resulting suspension was heated to 80 °C (bath temperature) for 30 h. Afterwards, the reaction mixture was allowed to reach ambient temperature. Thereafter, dme (0.5 mL) was added, and reaction mixture was stirred for 30 min. The remaining solids were removed by filtration, and the clear solution was stored at –20 °C for 2 d. The resulting crystalline mixture was isolated by decantation and consisted predominantly of **6** in addition to $Ph_2PCH_2PPh_2BH_3$ and minor amounts of the starting material. Attempts to further purify **6** failed. Yield: 74 mg (crude product). Analytical data of **6**: ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 0.2–1.7 (br., 9 H, BH_3), 3.03 (m, 1 H, P_2CHB), 3.28 (s, 12 H, OCH_3 dme), 3.44 (s, 8 H, OCH_2 dme), 6.78 (m, 4 H, *m*-CH Ph), 6.90 (m, 2 H, *p*-CH Ph), 7.23 (m, 6 H, *m*-CH, *p*-CH Ph), 7.35 (m, 4 H, *o*-CH Ph), 7.92 (m, 4 H, *o*-CH Ph) ppm. $^{11}B\{^{1}H\}$ NMR (128 MHz, [D$_8$]THF, 25 °C): δ = –37.8 (br., 2 B, PBH_3), –28.6 (br., 1 B, CBH_3) ppm. $^{13}C\{^{1}H\}$ NMR (100.6 MHz, [D$_8$]THF, 25 °C): δ = 13.0 (br., 1 C, P_2CHB), 58.8 (s, 4 C, CH_3 dme), 72.6 (s, 4 C, OCH_2 dme), 127.7 (m, 8 C, *m*-CH Ph), 129.4 (m, 4 C, *p*-CH Ph), 133.6 (m, 8 C, *o*-CH Ph), 135.6 (d, $^{1}J_{C,P}$ = 45.8 Hz, 2 C, *i*-C Ph), 135.9 (d, $^{1}J_{C,P}$ = 72.3 Hz, 2 C, *i*-C Ph) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz, [D$_8$]THF, 25 °C): δ = 21.2 (br.) ppm. Suitable crystals of **6** for X-ray diffraction experiments were obtained directly from the reaction mixture at –20 °C.

Reaction of $[Li\{H_3BCH(PPh_2BH_3)_2\}([D_8]thf)_3]$ with tmeda: A solution of compound **4** was generated in situ from **2** (19.5 mg, 0.045 mmol) and [D$_8$]THF (0.4 mL), which was transferred to a valved NMR spectroscopy tube. Afterwards, an excess amount of tmeda (0.15 mL, 0.99 mmol) was added. The resulting mixture was shaken for a few seconds and allowed to stand at ambient temperature for an additional 24 h. Thereafter, the mixture was characterized by multinuclear NMR spectroscopy. In addition to residual starting materials, $Li\{Ph_2PCH(BH_3)(PPh_2BH_3)\}$ and $Me_2NCH_2CH_2N(BH_3)Me_2$ are the predominantly formed products.

Analytical Data of $Li\{Ph_2PCH(BH_3)(PPh_2BH_3)\}$: ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 0.26 (br. m, 3 H, BH_3), 0.70–1.65 (m, 3 H, PBH_3), 2.73 (br. m, 1 H, P_2CHB), 6.73 (m, 2 H, CH Ph), 6.78 (m, 1 H, CH Ph), 6.93 (m, 2 H, CH Ph), 6.99 (m, 1 H, CH Ph), 7.02–7.18 (m, 7 H, CH Ph), 7.57 (m, 2 H, CH Ph), 7.65 (m, 2 H, CH Ph), 7.70–7.85 (m, 3 H, CH Ph) ppm. $^{11}B\{^{1}H\}$ NMR (128 MHz, [D$_8$]THF, 25 °C): δ = –40.8 (br., 1 B, PBH_3), –31.4 (br., 1 B, CBH_3) ppm. $^{13}C\{^{1}H\}$ NMR (100.6 MHz, [D$_8$]THF, 25 °C): δ = 14.8 (br., 1 C, P_2CHB), 127.2 (s, 1 C, *p*-CH Ph), 127.45 (d, $^{3}J_{C,P}$ = 7.2 Hz, 2 C, *m*-CH Ph), 127.5–127.8 (m, 7 C, 6 *m*-CH, *p*-CH Ph), 129.3 (br., 2 C, *p*-CH Ph), 133.7–134.0 (m, 4 C, *o*-CH Ph), 134.4 (d, $^{2}J_{C,P}$ = 21.3 Hz, 2 C, *o*-CH Ph), 134.9 (d, $^{2}J_{C,P}$ = 20.8 Hz, 2 C, *o*-CH Ph), 135.9 (d, $^{1}J_{C,P}$ = 49.2 Hz, 1 C, *i*-C Ph), 136.4 (dd, $^{1}J_{C,P}$ = 55.3, $^{3}J_{C,P}$ = 6.3 Hz,1 C, *i*-C Ph), 143.5 (d, $^{1}J_{C,P}$ = 22.1 Hz, 1 C, *i*-C Ph), 143.9 (pseudo-t, $^{1}J_{C,P} \approx {}^{3}J_{C,P} \approx 14.2$ Hz, 1 C, *i*-C Ph) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz, [D$_8$]THF, 25 °C): δ = –8.8 (d, $^{2}J_{P,P}$ = 65.7 Hz, 1 P, PPh_2), 22.7 (br., 1 P, PPh_2BH_3) ppm.

Analytical Data of $Me_2NCH_2CH_2N(BH_3)Me_2$: ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 2.19 (s, 6 H, NMe_2), 2.55 (s, 6 H, $BNMe_2$), 2.61 (t, $^{3}J_{H,H}$ = 6.8 Hz, 2 H, CH_2), 2.81 (t, $^{3}J_{H,H}$ = 6.8 Hz, 2 H, CH_2) ppm; the signal of the BH_3 group overlaps with the signals of the BH_3 groups of $Li\{Ph_2PCH(BH_3)(PPh_2BH_3)\}$. $^{11}B\{^{1}H\}$ NMR (128 MHz, [D$_8$]THF, 25 °C): δ = –10.8 (s, 1 B, NBH_3) ppm. $^{13}C\{^{1}H\}$ NMR (100.6 MHz, [D$_8$]THF, 25 °C): δ = 46.0 (s, 2 C, NMe_2), 52.0 (s, 2 C, $BNMe_2$), 55.4 (s, 1 C, CH_2) 62.3 (s, 1 C, CH_2) ppm.

Structure Determinations: The intensity data for the compounds were collected with a Nonius KappaCCD diffractometer by using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.[14,15] The structures were solved by direct methods (SHELXS[16]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[16]). The hydrogen atoms of compounds **5** and **6** (without the hydrogen atoms attached to C26) as well as the hydrogen atoms of the borane groups of **1**, **3**, and **4** were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. The non-disordered, non-hydrogen atoms were refined anisotropically.[16] Crystallographic data as well as structure solution and refinement details are summarized in Table S1 (see the Supporting Information). XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structural representations. The crystals of **2** were extremely thin and of low quality, which resulted in a substandard data set. However, the structure is sufficient to show connectivity and geometry. We will only publish the conformation of the molecule and the crystallographic data. We will not deposit the data of **2** in the Cambridge Crystallographic Data Centre database. CCDC-1010309 (**1**), -1010310 (**3**), -1010312 (**4**), -1010313 (**5**), and -1010314 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): NMR spectra of complexes **1**–**5** as well as additional NMR spectroscopic data, molecular structures of compounds **1** and **5**, and crystallographic data for all structures.

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