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$Ph_2P(BH_3)Li$: From Ditopicity to Dual Reactivity

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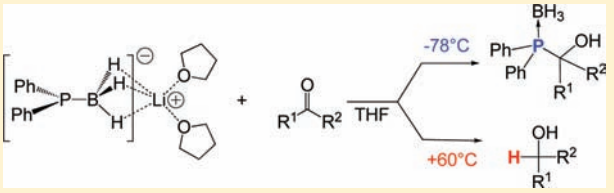
Supporting Information

ABSTRACT: A multinuclear NMR study shows that the deprotonation of diphenylphosphine-borane by *n*-BuLi in THF leads to a disolvated lithium phosphido-borane $Ph_2P(BH_3)Li$ of which Li^+ is connected to the hydrides on the boron and two THF molecules rather than to the phosphorus. This entity behaves as both a phosphination and a reducing agent, depending on the kinetic or thermodynamic control imposed to the reaction medium. Density functional theory computations show that $H_2P(BH_3)Li$ exhibits a ditopic character (the lithium cation can be in the vicinity of the hydride or of the phosphorus). It explains its dual reactivity (H- or P-addition), both routes going through somewhat similar six-membered transition states with low activation barriers.



INTRODUCTION

Phosphine- and amine-boranes[1] are the object of a renewed interest due to their versatile physicochemical properties. Indeed, a flurry of convincing new applications in the fields of P−B polymers,[2] transition metal complexes,[3] and activation of stable molecules (H_2, CO_2)[4] has recently appeared in the literature. Another major application of phosphine-boranes is for the synthesis of sophisticated phosphines, the borane being employed as a temporary protecting group of the phosphorus atom.[5] This application often requires a preliminary deprotonation of the BH_3-protected secondary phosphines, such as **1**, which leads to the corresponding metal phosphido-borane $M(R_2PBH_3)$ **2** where M is generally an alkali (Figure 1, left). These reagents are employed as nucleophilic entities for the synthesis of phosphines ligands by P-reprotonation, alkylation, bromination, or oxidation.[6] Because they have been mostly considered as "in situ" intermediates, these deprotonated derivatives have been rarely studied, and most aspects of their structure and chemical properties are unknown.[7] However, their characteristics could trigger an interest lying far beyond the mere academic curiosity, as they are putative reactants for asymmetric nucleophilic phosphination or precursors for the synthesis of polyphosphinoboranes. We report herein the first in-depth structural investigation of a phosphido-borane in solution as well as unprecedented chemical properties observed with this compound.

RESULTS AND DISCUSSION

NMR spectroscopy looked like the perfect tool to characterize a species bearing four NMR-active nuclei (^1H, ^{11}B, ^{13}C, ^{31}P). The counterion being likely to play a significant role in their reactivity, we also resorted on lithium labeling and prepared the ^6Li-diphenylphosphido-borane **2** (Figure 1, left). This was done by adding, at −78 °C, a THF-d_8 solution of ^6Li-labeled *n*-butyllithium[8] (1 equiv) to diphenylphosphine-borane **1** in the same solvent, directly in an NMR tube. The completion of the deprotonation was confirmed by the absence of signals characteristic of the *P*−*H* hydrogen (Figure 1, right).

The ^6Li (I = 1), ^{11}B (I = 3/2), and ^{31}P (I = 1/2) NMR experiments afforded, at 195 K, one singlet for each nucleus, despite the multiple couplings expected between heteronuclei. A progressive rising of the temperature up to 313 K (40 °C, Figure 2) did not alter the ^6Li-dimension, except for a slight shift at lower field, but revealed the ^1J multiplicities on the ^{11}B and ^{31}P spectra. The absence of P−Li coupling on the ^6Li and ^{31}P spectra, whatever the temperature, remained puzzling, especially as the Li−P coupling constant computed for model compounds exhibiting a P−Li interaction such as those discussed below (Figure 5) is significant (46.5 and 35.3 Hz for disolvated and trisolvated Li^+, respectively).

The key information concerning the location of this nucleus was brought by a complementary bidimensional ^6Li,^1H-HOESY NMR experiment,[9] which revealed a correlation between the signal of the lithium cation and the broad quartet associated with the hydrogen atoms of BH_3 (Figure 3 and S14 in the Supporting

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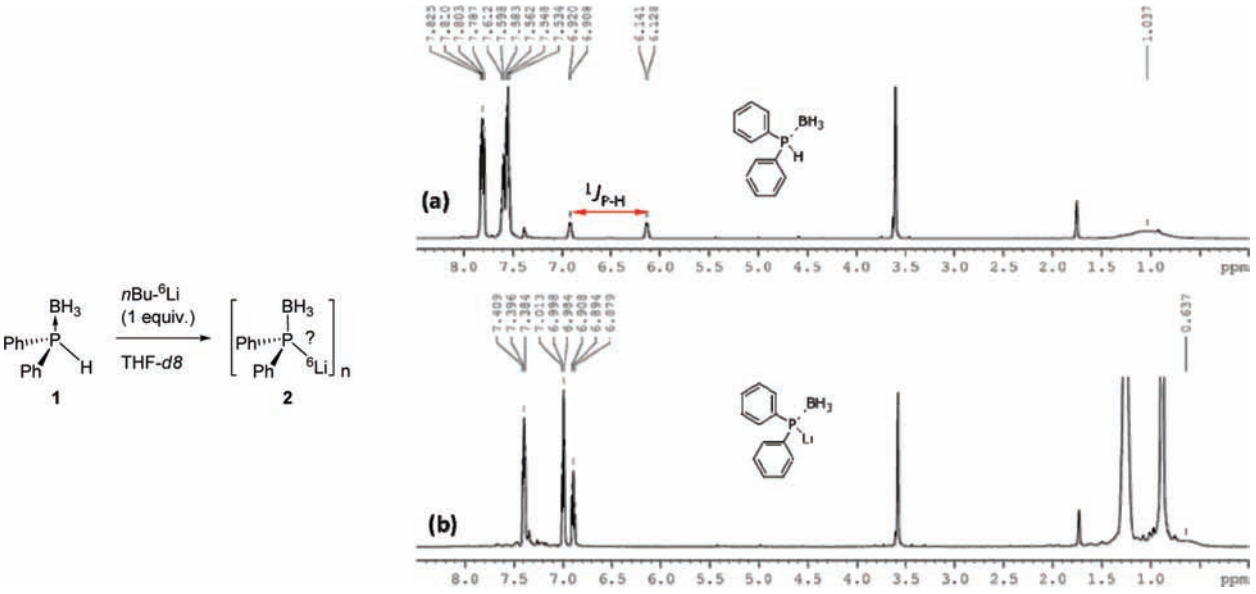

Figure 1. ^{1}H NMR spectra of diphenylphosphine-borane **1** (a) and lithium diphenylphosphido-borane **2** (b) in THF-d_8 at 195 K. The large peaks in the 0.8−1.3 ppm region of (b) are due to butane.

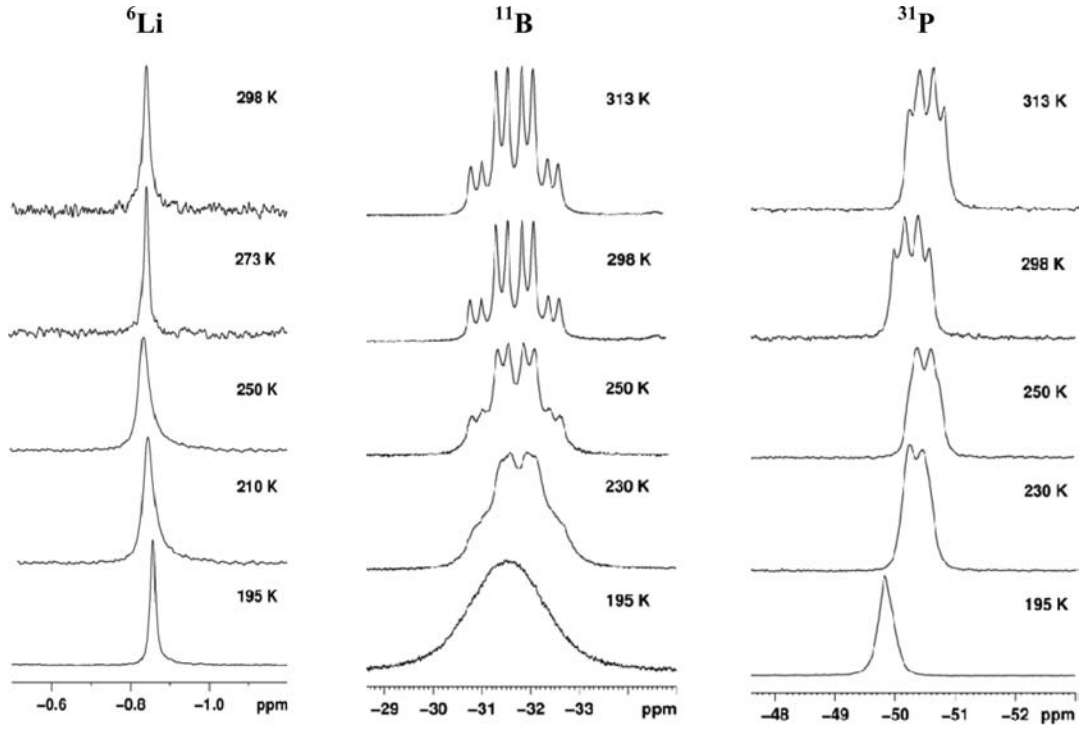

Figure 2. NMR spectra of $Ph_2P(BH_3)Li$ **2** in THF-d_8 at 195−313 K.

Information), suggesting a spatial proximity between these nuclei. This result, in perfect accord with a solid-state structure proposed by Müller and Brand on the basis of X-ray data obtained in a similar case,[7] justifies the absence of P−Li coupling. It also fits nicely observations reported about the hydride−metal interaction in other P−B−H−M systems involving lithium or transition metals.[10]

The degree of oligomerization and solvation of **2**[11] was also evaluated thanks to a ^{1}H-DOSY NMR experiment[12] (Figure 4, left). Run in the presence of three internal references in THF-d_8 at 195 K, this experiment led to the estimation of the molecular weight of the main species in solution to MW = 370 (Figure 4, right), pointing the finger at a disolvated lithium phosphido-borane monomer (MW = 363) rather than a dimer, even unsolvated (MW = 438).

Computations were carried out to get additional information on the competition between the possible coordination modes at lithium. The structure of $[H_2P(BH_3)]Li$, taken as a model

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phosphido-borane, solvated by one to three Me_2O molecules[13] (used as a model for THF) was first optimized. Isomers locating the lithium around the hydrides, the phosphorus, or both were considered (Figure 5). Overall, the structures exhibiting the lowest Gibbs free energies are in line with those deduced from the NMR data as all structures lying within 3 kcal mol^{-1} from the global minimum exhibit H−Li interactions. Nevertheless, two structures exhibiting only a P−Li interaction are found close above (between 3.8 and 5.6 kcal mol^{-1}).

A closer look at the above data suggests that a dual reactivity based on both P and H centers can be expected and **2** should behave either as a classical phosphorus nucleophile (Scheme 1, route 1) or as a source of hydrides (parallel to $NaBH_3CN$, route 2), the latter reactivity being unknown for phosphido-boranes. In both cases, the Li cation would behave as the activating Lewis acid toward the carbonyl, and the counterion (P or H) occupying an adequate position in the carbonyl surrounding will be the natural nucleophile to engage in the transition state en route to the 1,2-addition. The following results demonstrated the validity of this hypothesis.

The dual reactivity of **2** was tested toward carbonyl derivatives (Table 1). Addition of aldehydes, benzaldehyde or *p*-cyanobenzaldehyde, to **2** in THF led, upon quenching at −78 °C with 1 equiv of 2 M HCl in diethylether, to the exclusive formation of the phosphine-borane adducts **3a** and **3b**, respectively (entries 1 and 3). In sharp contrast, the same experiment run at +60 °C led to the exclusive formation of the reduction products **4a** and **4b** (entries 2 and 4) in high yields. The less reactive ketones, cyclohexanone and 2-heptanone, showed a similar behavior: formation of the phosphination products **3c** and **3d**, respectively, at low temperature (entries 5 and 7) and of the reduction products **4c** and **4d** upon heating (entries 6 and 8).

All of the new compounds were fully characterized by NMR and HRMS. In the case of **3b**, single crystals were grown by slow diffusion of pentane into an ethyl acetate solution at room temperature. Its structure was unambiguously confirmed by X-ray diffraction analysis (Figure 6 and Supporting Information).

Such a dramatic sensitivity to temperature hints that **3** could be a kinetic product and **4** could be the thermodynamic one. To probe the reversibility of the phosphination reaction,[15] a cross-over experiment was designed that consisted of adding 1 equiv of the highly electrophilic *p*-cyanobenzaldehyde to an equimolar solution of phosphination adduct **3a** deprotonated by *n*-butyllithium in THF at −68 °C (Scheme 2). The medium was warmed to +5 °C, then cooled to −68 °C before quenching by 1 equiv of HCl in diethylether. The NMR analysis of the crude product showed the formation of benzaldehyde and compound **3b** (isolated in 63% yield), which results from the addition of **2** to *p*-cyanobenzaldehyde. This result supports a reversible *P*-nucleophilic addition of the phosphide.

The details of the mechanism of the phosphination and the hydride transfer were examined in a second DFT study using $[H_2P(BH_3)Li][OMe_2]_2$ as a model of solvated phosphido-borane and formaldehyde as a canonic electrophile (Figure 7 and Table 2 for geometrical data).

The phosphination path (Figure 7A, left part) is straightforward: it takes place with no activation barrier (0.5 kcal/mol) through a very early transition state (where d_{P-C} = 3.52 Å, Figure 7B) and with a minor decoordination of the Li^+ from the hydrides (d_{H-Li} = 1.85 in **SM1** and **TS1** to 2.07 Å in **P1**).[16]

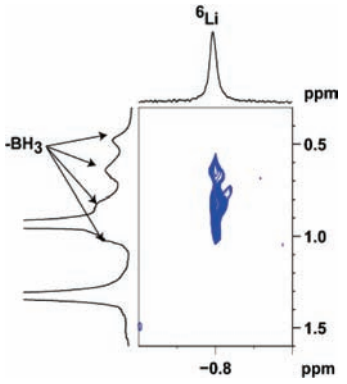
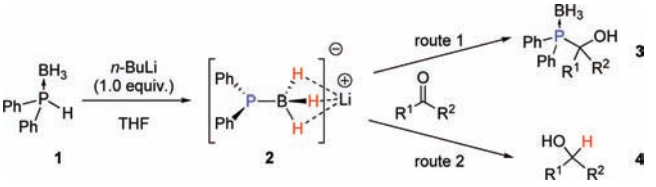


Figure 3. Blow-up of the $^6Li,^1H$-HOESY spectrum of lithium diphenylphosphidoborane **2**, in THF-d_8 at 250 K (−23 °C). The full spectrum is available in the Supporting Information.

Scheme 1. Possible Reactivities of Lithium Phosphidoborane 2



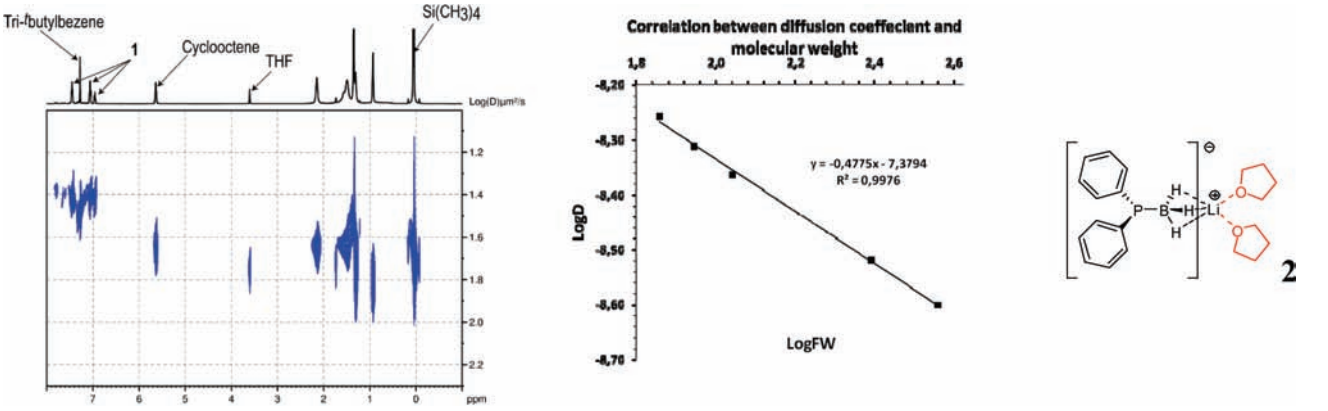


Figure 4. ^1H-DOSY spectrum of **2** in THF-d_8 at 195 K in the presence of three internal references (left), deduced correlation function (middle), and proposed structure (right).

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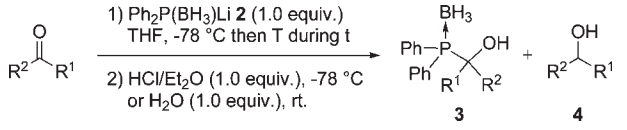
Table 1. Reactivity of 2 with Carbonyl Derivatives at Different Temperatures (°C)



entry	substrate	T (°C)	t (min)	3/4[a]	yield (%)
1	benzaldehyde	−78	1	100/0	91 (**3a**)
2	benzaldehyde	60	10	0/100	79 (**4a**)
3	*p*-cyanobenzaldehyde	−78	1	100/0	90 (**3b**)
4	*p*-cyanobenzaldehyde	60	45	0/100	87 (**4b**)
5	cyclohexanone	−78	1	100/0	89 (**3c**)
6	cyclohexanone	60	60	0/100	81 (**4c**)
7	2-heptanone	−78	1	100/0	91 (**3d**)
8	2-heptanone	60	90	0/100	82 (**4d**)

[a] Determined from ^{1}H NMR ratio.

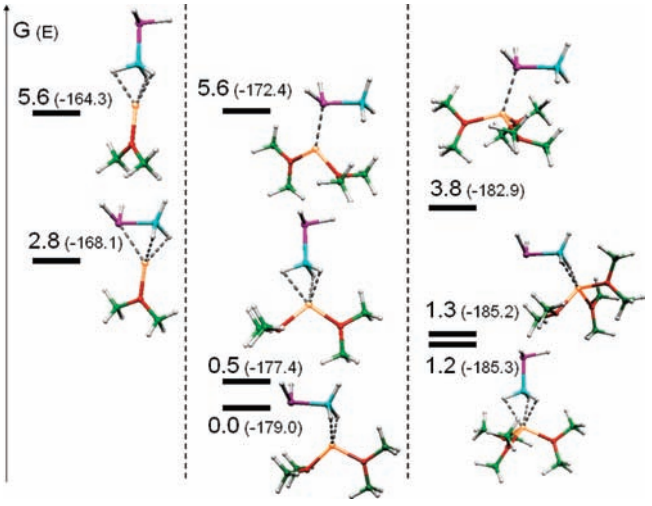


Figure 5. Gibbs free energies (kcal/mol, relative to the lowest structure) and interactions energies[14] (kcal/mol, in parentheses) of [$H_2P(BH_3)Li$] solvated by n molecules of Me_2O [n = 1 (left), 2 (middle), and 3 (right)]. P (pink), Li (orange), B (blue), C (green), H (white), O (red).

This addition product lies only 8.3 kcal/mol below the starting material.

By contrast, the reduction process (Figure 7A, right) follows a multistep path, requiring (i) a rearrangement within the original aldehyde complex (**SM1**) favoring its interaction with the "hydride side" of the lithium, such that the π_{CO} bond can interact with the lithium cation[17] (hydride−carbonyl distance is shortened: 2.21 Å in **SM2**); (ii) a hydride transfer to the aldehyde to afford an alkoxide exhibiting an elongated C−H bond (1.28 Å), the same proton being involved in an agostic bond with the boron atom (d_{B-H} = 1.40 Å in **IR2**);[16] and (iii) a rearrangement of this primary product to form a very stable heterodimer (−31.5 kcal/mol with respect to the starting docking complex) between the lithium alkoxide and the PH_2BH_2. This complex is organized around a four-membered P−B−O−Li quadrilateral (**P2**) in which both the Lewis base and the Lewis acid characters of ambiphilic PH_2BH_2 are expressed (d_{P-Li} = 2.45 Å and d_{B-O}= 1.54 Å).[18] The

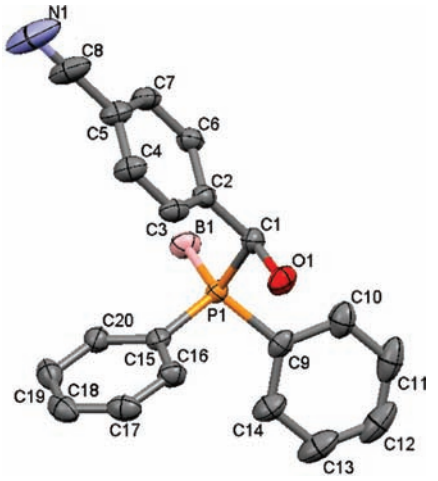
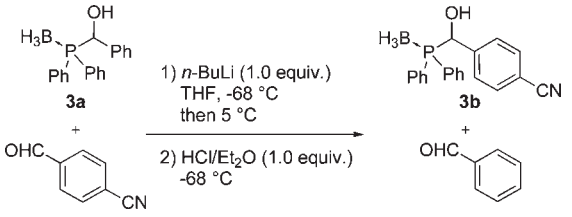


Figure 6. X-ray structure of **3b**.

Scheme 2. Reaction of the Phosphination Adduct 3a and *p*-Cyanobenzaldehyde in the Presence of *n*-BuLi



energy barrier of the overall sequence is +9.2 kcal/mol as the (i) and (ii) steps are reversible.

This part of the DFT computations also helps to understand through which mechanism(s) **3** is related to **4** (Scheme 3). Two hypotheses can be proposed: (i) a back-elimination of the phosphide (mechanism A, step 1) followed by an independent and irreversible hydride transfer (step 2); and (ii) a direct intramolecular hydride transfer simultaneous to, or immediately followed by, the departure of the phosphorus appendage (mechanism B). The above theoretical data suggest that the nonactivated phosphination should be the only reaction occurring at low temperature. Its product lies high enough in energy for the reaction to be reversible, allowing the irreversible reduction pathway to become competitive upon rising of the temperature. Thus, while the computed figures are in good agreement with mechanism A, a TS corresponding to the hydride transfer of mechanism B could not be located for an intramolecular version of the reaction.

CONCLUDING REMARKS

A multinuclear (^{1}H, ^{6}Li, ^{11}B, ^{13}C, ^{31}P) NMR spectroscopic study showed that the deprotonation of diphenylphosphine-borane **1** by butyllithium in THF leads quantitatively to a lithium phosphido-borane of which Li^+ is directly connected to the hydrides borne by the boron, in line with data obtained in the solid phase.[7] This result suggested that $Ph_2P(BH_3)Li$ could act as a dual phosphination and reducing agent in THF, depending on the control (kinetic or thermodynamic) imposed by the reaction conditions. We have shown that these two pathways are indeed

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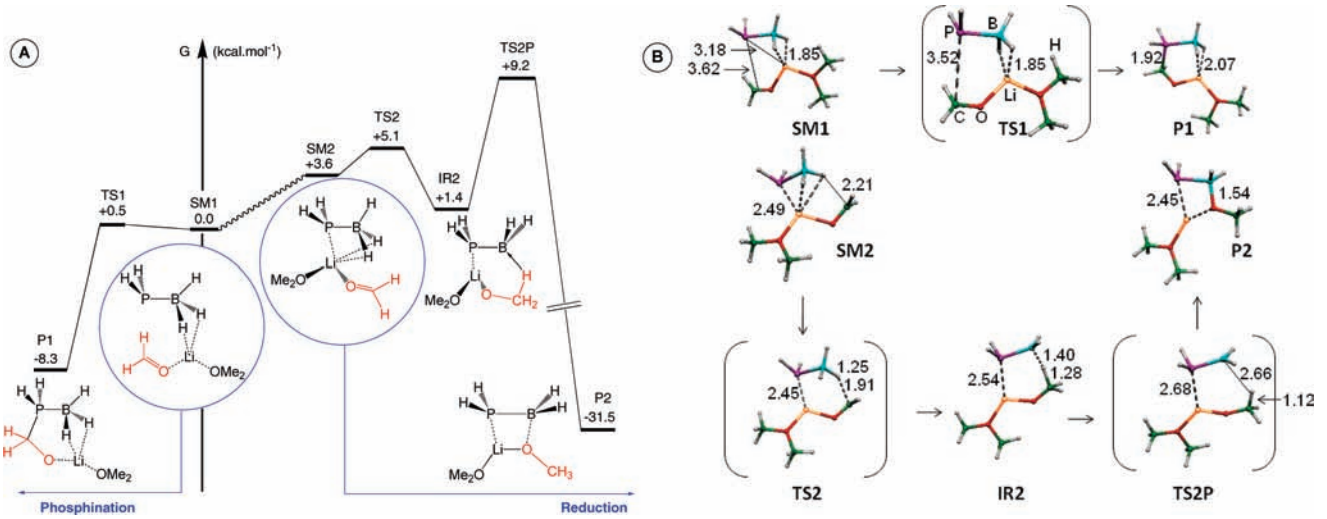


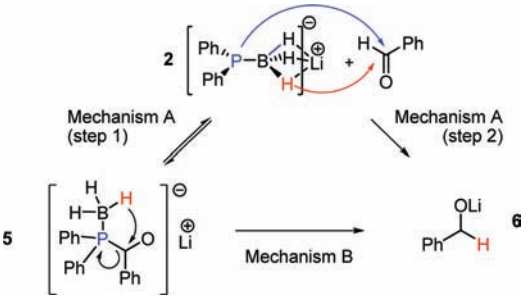
Figure 7. (A) Gibbs free energies (kcal/mol) with respect to **SM1** for phosphination versus reduction. Full lines stand for steps of which connectivity was confirmed, and curled lines stand for a postulated easy interconversion. (B) Optimized structures of stationary points and transition states of the phosphination (top) and reduction (bottom) pathways. The atom color codes are featured on **TS1**. Distances are in angstroms.

Table 2. Main Distances (in Å) along the Phosphination and Reduction Pathways

	P1	TS1	M1	M2	TS2	IR2	TS2P	P
Li−P	3.067	3.308	3.181	2.491	2.451	2.537	2.688	2.454
Li−H	1.971	1.845	1.848	1.922	2.543			
	2.155	1.837	1.847	2.649	2.909			
Li−O(=C)	1.772	1.937	1.959	1.956	1.866	1.755	1.666	1.795
P−B	1.965	2.003	2.005	2.015	2.003	1.964	1.9	2.031
C=O	1.347	1.224	1.223	1.227	1.238	1.303	1.374	1.413
P−C	1.924	3.517	3.617					
C−H				2.212	1.909	1.275	1.118	1.099
B−H	1.221	1.238	1.238	1.235	1.251	1.199	1.189	1.215
	1.219	1.237	1.238	1.238	1.224	1.199	1.189	1.215
	1.202	1.206	1.205	1.204	1.206	1.398	2.658	2.731
B−O						3.287	3.522	1.538

competitive, one being reversible (the phosphination) in contrast to the other (reduction). The DFT results are fully consistent with these observations. Theory indeed suggests that when $Ph_2P(BH_3)Li$ is reacted with a carbonyl derivative (aldehyde or ketone), the reaction will expectedly start with a docking of the oxygen of the electrophile on the Li^+. The unforeseen ditopic character of this reagent then explains that two pathways compete in the following, both H- and P- 1,2-additions being possible. Their respective occurrence corresponds to a simple switch between the two opposite head-to-tail arrangements of the P−B−H and C−O−Li triads. At low temperature, the lithium is mainly located toward the hydrides, and the phosphination is favored. At higher temperature, the lithium moves toward the phosphorus and give its chance to the reduction. The parallel between these two reactions explains that they finally proceed through similar six-membered transition states with a low activation barrier (no dimer or rearrangement needed, Figure 8). Underlying all of these observations is the exceptional strength of the donor−acceptor P−B bond,[19] which survives all of the transformations undergone by this system.

Scheme 3. Two Possible Routes Connecting Phosphination Product 5 to Reduction Product 6



EXPERIMENTAL SECTION

All of the reactions were carried out under argon or nitrogen atmosphere. Argon was dried and deoxygenated by bubbling through a commercial solution of butyllithium in hexane. Tetrahydrofuran-d_8 was distilled over sodium and benzophenone. Tetrahydrofuran and toluene were purified by an Innovative Pure Solvent Device (activated alumina column containing a copper catalyst and molecular sieves). Pentane, 1-bromobutane, benzaldehyde, cyclohexanone, and 2-heptanone were dried by stirring over CaH_2 and then distilled. Commercial ^{6}Li (95%) purchased from Aldrich was washed in freshly distilled pentane. Structural NMR experiments were carried out by using Bruker AVIII 400 and DMX 500 spectrometers (Bruker, Wissembourg, France). The Bruker AVIII 400 was equipped with a 10 A gradient amplifier and a 5 mm BBFO probe including shielded *z*-gradients. The Bruker Avance DMX 500 was equipped with a 10 A gradient amplifier and a 5 mm {^{1}H−X} BBI or 5 mm {^{1}H, ^{6}Li, ^{13}C, and ^{15}N} quadruple-resonance probe. Measuring frequencies were 400 or 500 MHz for ^{1}H, 160 MHz for ^{11}B, 162 or 202 MHz for ^{31}P, 100 or 125 MHz for ^{13}C, and 73 MHz for ^{6}Li. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm using the residual peak of chloroform-*d* (7.26 and 77.16 ppm) or THF-d_8 (1.73 and 25.37 ppm) as internal standards. ^{11}B and ^{31}P NMR spectra were referenced (δ = 0.0 ppm) to calculated boron and phosphorus frequencies in $BF_3\cdot Et_2O$ and 85% H_3PO_4 references compounds, respectively.[20] ^{6}Li spectra were referenced to the external 0.30 M ^{6}LiCl solution in THF-d_8 (δ = 0.0 ppm). Coupling constants are reported in

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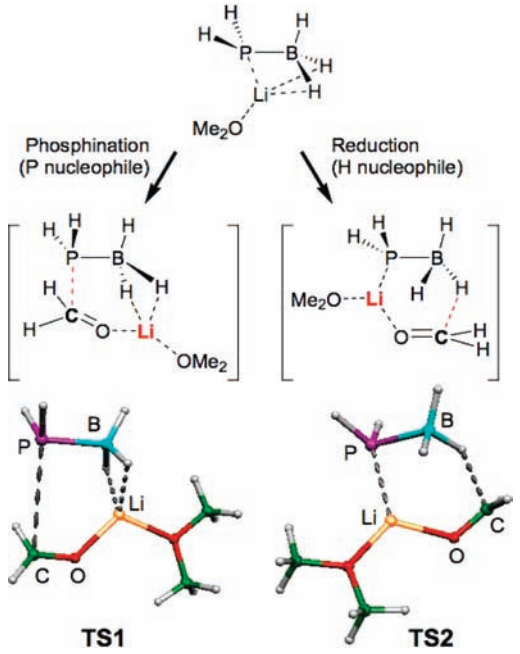

Figure 8. Schematic (top) and optimized (bottom) TS's for phosphination (left) versus reduction (right) of HCHO by $[H_2P(BH_3)Li]-(OMe_2)_2$.

hertz (Hz). Abbreviations are used as follows: s = singlet, d = doublet, q = quadruplet, m = multiplet, br = broad. IR spectra were recorded on a Spectrum One Perkin-Elmer spectrometer, and only the strongest or structurally most important peaks are listed. Melting points were measured on a Gallenkamp Melting Point Apparatus. High resolution mass spectroscopy was performed on a Q-TOF Micro Waters spectrometer or Waters LPC Premier.

Diphenylphosphine-borane 1. This compound was prepared following the procedure described in the literature[21] (CAS no. 41593-58-2).

Preparation of [^{6}Li] *n*-Butyllithium Salt-Free Solution in Pentane[8,22]. Finely cut 6-lithium metal ribbon (0.3 g, 50 mmol) was introduced in a two-necked round bottomed flask under dry argon. The metallic cuttings were covered with freshly distilled pentane (10 mL). After intensive stirring, the pentane was removed, and the metal was washed twice with the same solvent. A new amount of 10 mL of pentane was introduced, and freshly distilled 1-bromobutane (2.14 mL, 20 mmol) was syringed at room temperature over a period of 4 h. The resulting reaction mixture was stirred for 20 h at room temperature. The hydrocarbon solution was then pumped off the flask with a syringe and directly inserted into centrifugation tubes placed under dry argon. The residual traces of salt were centrifugated, and the clear final solution was collected in a dry flask flushed under dry argon, and then titrated[23] and kept until further use.

Preparation of [^{6}Li] *n*-Butyllithium Salt-Free Solution in Tetrahydrofuran-d_8[8]. A solution of ^{6}Li *n*-butyllithium in pentane prepared as above (2.5 mL) was syringed in a tube fitted with a septum and flushed under dry argon. The tube was then placed under vacuum (20 mmHg) for 1 h to remove the main part of the pentane. Freshly distilled tetrahydrofuran-d_8 was then added at −78 °C to the resulting concentrated solution, and the residual pentane was evaporated at room temperature under vacuum for 1 h. After the mixture was cooled to −78 °C, tetrahydrofuran-d_8 (3−3.5 mL) was added, and the resulting solution was titrated.[23] The solution was kept at −78 °C.

[^{6}Li] Lithium Diphenylphosphido-borane 2 in Tetrahydrofuran-d_8 solution. In a dry NMR tube equipped with a rubber septum were placed diphenylphosphine-borane (20 mg, 0.10 mmol) and freshly distilled tetrahydrofuran-d_8 (0.5 mL). After the mixture was cooled to −78 °C (acetone/dry ice bath), freshly prepared [^{6}Li] *n*-butyllithium (67 μL, 0.10 mmol, 1.5 M in tetrahydrofuran-d_8) was added under dry argon leading to **2** (complete conversion) (CAS no. 145130-18-3).

Representative Procedure for the Addition to Carbonyl Derivatives. Diphenylphosphine-borane (1.0 equiv) and tetrahydrofuran were placed in a dry Schlenk tube equipped with a thermometer. The reactor was cooled at −78 °C, and *n*-butyllithium (1.0 equiv) was added under nitrogen. The aldehyde or ketone (1.0 equiv) was added dropwise at the same temperature followed by precooled hydrochloric acid (1.0 equiv) so as to avoid any increase of the temperature. The reaction mixture was warmed to room temperature and concentrated under reduced pressure. The resulting viscous oil was dissolved in ethyl acetate and water and extracted with ethyl acetate. The combined organic phases were washed with brine, dried over magnesium sulfate, filtered, and concentrated under vacuum.

(1-Hydroxy-1-phenyl)methyldiphenylphosphine-borane 3a. The title compound was prepared from diphenylphosphine-borane **1** (100 mg, 0.50 mmol), *n*-butyllithium (217 μL, 0.50 mmol, 2.3 M in hexane), benzaldehyde (50 μL, 0.50 mmol), and hydrochloric acid (250 μL, 0.50 mmol, 2.0 M in diethylether) in tetrahydrofuran (2.5 mL). The desired product **3a** (153 mg, 91%) was obtained as a colorless oil that solidified on standing (mp = 93 °C) after flash chromatography (ethyl acetate/cyclohexane 15/85) purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86−7.79 (m, 2H), 7.60−7.56 (m, 3H), 7.51−7.47 (m, 3H), 7.41−7.37 (m, 2H), 7.29−7.25 (m, 1H), 7.23−7.20 (m, 2H), 7.07−7.05 (m, 2H), 5.69 (d, $^2J_{P-H}$ = 2.0 Hz, 1H), 2.93 (br s, 1H), 1.39−0.53 (br m, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 136.4 (d, $^2J_{C-P}$ = 1.3 Hz), 134.0 (d, $^2J_{C-P}$ = 7.6 Hz), 133.5 (d, $^2J_{C-P}$ = 7.6 Hz), 131.9 (d, $^4J_{C-P}$ = 2.5 Hz), 131.6 (d, $^4J_{C-P}$ = 2.5 Hz), 128.8 (d, $^3J_{C-P}$ = 10.1 Hz), 128.7 (d, $^3J_{C-P}$ = 10.1 Hz), 128.5 (d, $^5J_{C-P}$ = 2.5 Hz), 128.0 (d, $^4J_{C-P}$ = 2.5 Hz), 127.4 (d, $^3J_{C-P}$ = 3.8 Hz), 126.7 (d, $^1J_{C-P}$ = 54.2 Hz), 125.6 (d, $^1J_{C-P}$ = 52.9 Hz), 73.4 (d, $^1J_{C-P}$ = 36.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.3−26.5 (m). ^{11}B NMR (160 MHz, $CDCl_3$): δ −39.1 to −42.6 (m). IR (neat): 3458, 3059, 2378, 1436. CAS no. 954422-32-3.

(1-Hydroxy-1-(4-cyanophenyl))methyldiphenylphosphine-borane 3b. This compound was prepared from diphenylphosphine-borane **1** (100 mg, 0.50 mmol), *n*-butyllithium (217 μL, 0.50 mmol, 2.3 M in hexane), *p*-cyanobenzaldehyde (0.40 mL, 0.50 mmol, 1.25 M in tetrahydrofuran, precooled solution), and hydrochloric acid (250 μL, 0.50 mmol, 2.0 M in diethylether) in tetrahydrofuran (2.1 mL). The desired product **3b** (166 mg, 90%) was obtained as a colorless oil that solidified on standing (mp = 117 °C) after flash chromatography (ethyl acetate/cyclohexane 20/80) purification. Single crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into an ethyl acetate solution of **3b** at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81−7.76 (m, 2H), 7.60−7.55 (m, 3H), 7.54−7.39 (m, 7H), 7.17−7.15 (m, 2H), 5.72 (dd, $^3J_{H-H}$ = 5.2 Hz, $^2J_{P-H}$ = 2.9 Hz, 1H), 3.02 (dd, $^3J_{H-P}$ = 7.2 Hz, $^3J_{H-H}$ = 5.2 Hz, 1H), 1.38−0.43 (br m, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 141.8 (d, $^2J_{C-P}$ = 1.2 Hz), 134.0 (d, $^2J_{C-P}$ = 8.7 Hz), 133.3 (d, $^2J_{C-P}$ = 8.7 Hz), 132.3 (d, $^4J_{C-P}$ = 2.5 Hz), 132.0 (d, $^4J_{C-P}$ = 2.5 Hz), 131.6 (d, $^4J_{C-P}$ = 2.2 Hz), 129.0 (d, $^3J_{C-P}$ = 10.0 Hz), 129.0 (d, $^3J_{C-P}$ = 10.0 Hz), 128.0 (d, $^3J_{C-P}$ = 2.2 Hz),126.1 (d, $^1J_{C-P}$ = 54 Hz), 124.6 (d, $^1J_{C-P}$ = 54 Hz), 118.6 (d, $^6J_{C-P}$ = 1.6 Hz), 112.1 (d, $^5J_{C-P}$ = 2.8 Hz), 73.0 (d, $^1J_{C-P}$ = 35 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.7−28.1 (m). ^{11}B NMR (160 MHz, $CDCl_3$): δ −39.0 to −43.3 (m). IR (neat): 3427, 3059, 2384, 2231, 1437. HRMS (ESI) calcd for $[M + Na]^+$: 354.1195, found 354.1202.

(1-Hydroxy)cyclohexyldiphenylphosphine-borane 3c. The title compound was prepared from diphenylphosphine-borane **1** (100 mg, 0.50 mmol), *n*-butyllithium (217 μL, 0.50 mmol, 2.3 M in hexane), cyclohexanone (52 μL, 0.50 mmol), and hydrochloric acid (250 μL, 0.50 mmol, 2.0 M in diethylether) in tetrahydrofuran (2.5 mL).

The desired product **3c** (132 mg, 89%) was obtained as a white solid (mp = 120 °C) after flash chromatography (toluene). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02−7.95 (m, 4H), 7.53−7.49 (m, 2H), 7.49−7.43 (m, 4H), 1.92−1.82 (m, 2H), 1.80−1.72 (m, 3H), 1.70−1.49 (m, 6H), 1.46−0.57 (br m, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 134.4 (d, $^2J_{C-P}$ = 8.1 Hz), 131.4 (d, $^4J_{C-P}$ = 2.5 Hz), 128.7 (d, $^3J_{C-P}$ = 9.6 Hz), 126.5 (d, $^1J_{C-P}$ = 52 Hz), 74.5 (d, $^1J_{C-P}$ = 38 Hz), 32.7 (d, $^2J_{C-P}$ = 7.5 Hz), 25.2 (d, $^4J_{C-P}$ = 1.1 Hz), 20.6 (d, $^3J_{C-P}$ = 9.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.8−28.7 (m). ^{11}B NMR (160 MHz, $CDCl_3$): δ −38.4 to −42.1 (m). IR (neat): 3565, 2944, 2389, 1436. HRMS (ESI) calcd for $[M + Na]^+$: 321.1556, found 321.1568.

(1-Hydroxy-1-methyl)hexyldiphenylphosphine-borane 3d. The title compound was prepared from diphenylphosphine-borane **1** (100 mg, 0.50 mmol), *n*-butyllithium (294 μL, 0.50 mmol, 1.7 M in hexane), 2-heptanone (70 μL, 0.50 mmol), and hydrochloric acid (250 μL, 0.50 mmol, 2.0 M in diethylether) in tetrahydrofuran (2.5 mL). The desired product **3d** (157 mg, 91%) was obtained as a colorless oil after flash chromatography (ethyl acetate/cyclohexane 5/95). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02−7.95 (m, 4H), 7.54−7.48 (m, 2H), 7.48−7.43 (m, 4H), 1.95 (d, $^3J_{H-P}$ = 2.4 Hz, 1H), 1.83−1.68 (m, 2H), 1.44 (d, $^3J_{H-P}$ = 14.2 Hz, 3H), 1.49−1.40 (m, 1H), 1.39−1.29 (m, 1H), 1.39−1.29 (m, 1H), 1.29−1.17 (m, 4H), 0.84 (d, $^3J_{H-H}$ = 7.1 Hz, 3H), 1.40−0.60 (br m, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 134.4 (d, $^2J_{C-P}$ = 8.0 Hz), 134.3 (d, $^2J_{C-P}$ = 8.0 Hz), 131.5 (d, $^4J_{C-P}$ = 2.5 Hz), 131.4 (d, $^4J_{C-P}$ = 2.5 Hz), 127.0 (d, $^1J_{C-P}$ = 51.8 Hz), 126.9 (d, $^1J_{C-P}$ = 51.5 Hz), 75.0 (d, $^1J_{C-P}$ = 37.0 Hz), 37.4 (d, $^3J_{C-P}$ = 9.5 Hz), 32.1 (s), 22.9 (d, $^2J_{C-P}$ = 8.9 H), 22.8 (s), 21.9 (d, $^2J_{C-P}$ = 8.7 Hz), 14.1 (s). ^{31}P NMR (202 MHz, $CDCl_3$): δ 31.9−30.2 (m). ^{11}B NMR (160 MHz, $CDCl_3$): δ −38.5 to −41.7 (m). IR (neat): 3501, 2954, 2383, 2331, 1436. HRMS (API +) calcd for $[M + H - BH_3 - H_2O]^+$: 283.1616, found 283.1611.

Representative Procedure for the Reduction of Carbonyl Compounds. Diphenylphosphine-borane **1** (1.0 equiv) and freshly distilled tetrahydrofuran were placed in a dry Schlenk tube. After the mixture was cooled to −78 °C, *n*-butyllithium (1.0 equiv) was added dropwise followed by the aldehyde or ketone (1.0 equiv) under nitrogen. The reaction mixture was warmed to room temperature, then heated to 60 °C for *x* minutes. After the mixture was cooled to room temperature, water (5.0 equiv) was added, and the solution was concentrated under reduced pressure. The resulting viscous oil was dissolved in ethyl acetate and water and extracted with ethyl acetate. The combined organic phases were washed with brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure.

Benzyl Alcohol 4a. The title compound was prepared from diphenylphosphine-borane **1** (200 mg, 1.00 mmol), *n*-butyllithium (0.56 mL, 1.00 mmol, 1.8 M in hexane), and benzaldehyde (101 μL, 1.00 mmol) in tetrahydrofuran (5.0 mL) at 60 °C for 10 min. The desired product **4a** (85 mg, 79%) was obtained as a colorless oil after flash chromatography (ethyl acetate/cyclohexane 5/95). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42−7.35 (m, 5H), 4.66 (s, 1H), 3.03 (br s, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 141.0, 128.6, 127.6, 127.0, 65.1. CAS no. 100-51-6.

4-(Hydroxymethyl)benzonitrile 4b. The title compound was prepared from diphenylphosphine-borane **1** (152 mg, 0.76 mmol), *n*-butyllithium (0.51 mL, 0.76 mmol, 1.5 M in hexane), and *p*-cyanobenzaldehyde (100 mg, 0.76 mmol) in tetrahydrofuran (4.0 mL) at 60 °C for 45 min. The desired product **4b** (88 mg, 87%) was obtained as a white solid (mp = 40 °C;[30] 39−40 °C) after flash chromatography (ethyl acetate/cyclohexane 3/7). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64−7.60 (m, 2H), 7.47−7.44 (m, 2H), 4.76 (s, 2H), 2.16 (br s, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 146.4, 132.4, 127.1, 119.0, 111.2, 64.3. CAS no. 874-89-5.

Cyclohexanol 4c. The title compound was prepared from diphenylphosphine-borane **1** (300 mg, 1.50 mmol), *n*-butyllithium (0.94 mL, 1.50 mmol, 1.6 M in hexane), and cyclohexanone (155 μL, 1.50 mmol) in tetrahydrofuran (7.5 mL) at 60 °C for 1 h. The desired product **4c** (122 mg, 81%) was obtained as a colorless oil after flash chromatography (ethyl acetate/cyclohexane 1/9) and recrystallization in pentane/2-propanol (9/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.59−3.48 (m, 1H), 2.38 (br s, 1H), 1.91−1.79 (m, 2H), 1.75−1.62 (m, 2H), 1.55−1.45 (m, 1H), 1.29−1.18 (m, 4H), 1.18−1.05 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 70.2, 35.4, 25.4, 24.3. CAS no. 108-93-0.

2-Heptanol 4d. The title compound was prepared from diphenylphosphine-borane **1** (800 mg, 4.00 mmol), *n*-butyllithium (2.22 mL, 4.00 mmol, 1.8 M in hexane), and 2-heptanone (0.56 mL, 4.00 mmol) in tetrahydrofuran (10 mL) at 60 °C for 1.5 h. The desired product **4d** (380 mg, 82%) was obtained as a colorless oil after distillation on ball tube followed by filtration on silica with diethyl ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80−3.75 (m, 1H), 1.53 (br s, 1H), 1.46−1.36 (m, 3H), 1.34−1.23 (m, 5H), 1.17 (d, $^3J_{H-H}$ = 6.2 Hz, 3H), 0.88 (t, $^3J_{H-H}$ = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 67.9, 39.3, 31.9, 25.5, 23.3, 22.6, 14.0. CAS no. 543-49-7.

Reversibility of the Phosphination (from 3a to 3b). (1-Hydroxy-1-phenyl)methyldiphenylphosphine-borane **3a** (207 mg, 0.68 mmol) and tetrahydrofuran (4.0 mL) were placed in a dry Schlenk tube equipped with a thermometer. The reactor was cooled at −68 °C (internal temperature), and *n*-butyllithium (453 μL, 0.68 mmol, 1.5 M in hexane) was added under nitrogen followed by a solution of *p*-cyanobenzaldehyde (89 mg, 0.68 mmol, 0.68 M in tetrahydrofuran). The mixture was allowed to warm to 5 °C (internal temperature), and precooled hydrochloric acid (0.34 mL, 0.68 mmol, 2 M in diethyl ether) was added dropwise at −68 °C (internal temperature) so as to avoid any increase of the temperature. The reaction mixture was warmed to room temperature and concentrated under reduced pressure. The resulting viscous oil was dissolved in ethyl acetate (5 mL) and water (5 mL) and further extracted with ethyl acetate (2 × 5 mL). The combined organic phases were washed with brine (10 mL), dried over magnesium sulfate, filtered, and concentrated under reduced pressure to give a crude mixture of (1-hydroxy-1-(4-cyanophenyl))methyldiphenylphosphine-borane **3b** and benzaldehyde. (1-Hydroxy-1-(4-cyanophenyl))methyldiphenylphosphine-borane **3b** (142 mg, 63% yield) was obtained as a white solid after flash chromatography (ethyl acetate/cyclohexane 20/80).

Computational Details. The full geometry optimizations were systematically conducted with no symmetry restraints using the Gaussian 03 program[24] within the framework of the density functional theory (DFT) using the hybrid B3LYP exchange-correlation functional[25] and the 6-31++G** basis set for all atoms as implemented in the Gaussian program, to reproduce both the P−C bond formation and the hydride transfer in a balanced way. This functional and basis set have been shown to properly reproduce structural properties on closely related lithium amidoboranes.[26] Solvation at the lithium cation is ensured via an explicit mode by including one, two, or three dimethylether molecules (as a model for THF)[27,28] coordinated to the lithium. This is essential as it leads to a stronger competition between bi- and tridentate structures, in contrast to the use of nonsolvated lithium.[29] Frequencies were evaluated within the harmonic approximation and used unscaled to compute free enthalpies at either 195 or 298.15 K using the standard protocol. Concerning the relative Gibbs free energies of the isomers, it can be shown that the interaction energy[14] is driving the stability. Thus, for a given degree of solvation, the energies and free enthalpies follow the same ordering. The nature of the transition states was ensured by confirming the presence of a single imaginary frequency. The connection between transition states and minima was ensured by carrying out small displacements of all atoms in the two directions along the imaginary frequency mode and carrying out geometry optimization using these geometries as starting points.

X-ray Structural Analysis Details. The structure was solved using direct methods and refined by full-matrix least-squares analysis on

F^2 with SHELXTL. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. CCDC 813642 contains the supplementary crystallographic data for this Article. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Supporting Information. Full ^{1}H, ^{11}B, ^{13}C, ^{31}P NMR and IR spectra for **3a**−**d**, ^{1}H HOESY spectrum of **2**, and crystal details for **3b**, as well as complete ref 24. This material is available free of charge via the Internet at http://pubs.acs.org.

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