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Phosphino-Boryl-Naphthalenes: Geometrically Enforced, Yet Lewis Acid Responsive P → B Interactions

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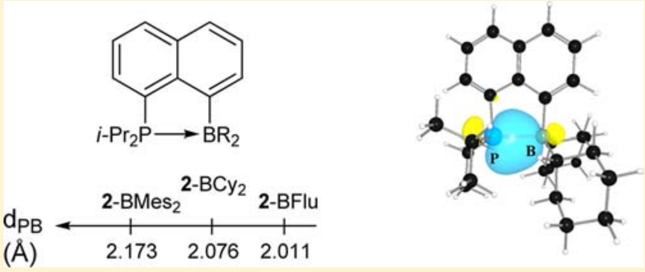
Supporting Information

ABSTRACT: Three naphthyl-bridged phosphine-borane derivatives **2**-BCy$_2$, **2**-BMes$_2$, and **2**-BFlu, differing in the steric and electronic properties of the boryl moiety, have been prepared and characterized by spectroscopic and crystallographic means. The presence and magnitude of the P → B interactions have been assessed experimentally and theoretically. The naphthyl linker was found to enforce the P → B interaction despite steric shielding, while retaining enough flexibility to respond to the Lewis acidity of boron.



INTRODUCTION

Donor−acceptor (D → A) interactions play a major role in chemistry. They are found in a broad variety of chemical structures, including simple Lewis acid/Lewis base adducts (such as the prototypical compound $H_3N \rightarrow BH_3$),[1] hypervalent derivatives (typically met with heavier p-block elements)[2] and coordination complexes (extensively found with s-block metals, transition metals and f-elements). Such compounds find applications in many fields ranging over organic synthesis, catalysis, material science, etc., and thus represent a very fertile ground of research. Two centuries after the seminal discovery of $H_3N \rightarrow BF_3$ by Gay-Lussac,[3] the precise description of dative interactions as well as the accurate estimation of their strength also remain a very active field of research, in particular for computational investigations.[4]

Connecting donor and acceptor moieties through an organic linker has proven most valuable in the study and development of D → A compounds. Indeed, such an intramolecular approach provides some control over the D → A interaction by varying the length and rigidity of the spacer. In that respect, the naphthalene skeleton exhibits unique features, the elements introduced in peripositions being maintained in close proximity (2.5 Å when no deformation occurs).[5] The propensity of such naphthalene derivatives to engage into D → A interactions has been amply substantiated. In particular, amines and phosphines have been combined with a broad variety of Lewis acid moieties.[6] Representative examples involving group 13, 14, and 15 elements as acceptor centers are depicted in Figure 1.

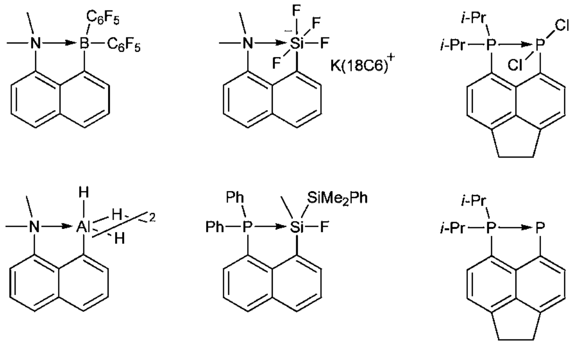


Figure 1. Selected examples of naphthyl-bridged D → A interactions involving group 13−15 elements as Lewis acid moieties.

In recent years, Lewis pairs have attracted tremendous interest,[7] following the discovery of Stephan and Erker that phosphine-boranes, in which P → B interactions are prevented sterically and/or geometrically, are capable to readily activate and transfer dihydrogen.[8] Accordingly, the factors controlling the formation and magnitude of P → B interactions are attracting renewed interest.[9]

In this context, and as an extension of our work on *o*-phenylene bridged phosphine-boranes (PB),[10] we turned our attention to the naphthyl spacer and report here a detailed study of P → B interactions in such systems. According to a SciFinder database search, the only examples of such PB derivatives described so far are the boryl-dichlorophosphino-naphthalenes **A** recently prepared by Sasamori and Tokitoh

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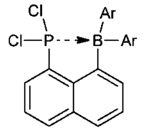
(Chart 1), en route to the corresponding 1-phospha-2-boraacenaphthenes. The presence or lack of P → B interactions in compounds **A**[11] was inferred by ^{11}B NMR spectroscopy. Accordingly, sterically demanding substituents around boron were proposed to prevent the intramolecular dative bond.

Chart 1



A

Ar = Mes, 2,6-$Me_2C_6H_3$, 3,5-$(t\text{-}Bu)_2C_6H_3$

Here we report the synthesis and thorough characterization of three naphthyl PB derivatives featuring boryl groups of different steric and electronic properties.[12] The naphthyl backbone is shown to enforce P → B interaction despite steric shielding, while retaining enough flexibility to respond to the Lewis acidity of boron. The magnitude of the involved P → B interactions has been carefully assessed by considering various experimental and computational descriptors (spectroscopic, geometric and electronic).

■ RESULTS AND DISCUSSION

The three PB naphthyl derivatives **2**-BCy_2, **2**-$BMes_2$, and **2**-BFlu were synthesized in two steps following the same strategy as with the *o*-phenylene linker (Scheme 1, Table 1).[13] Starting from 1,8-diiodonaphthalene, the diisopropylphosphino group was introduced first by iodine–lithium–phosphorus exchange. After purification by flash chromatography, compound **1** was obtained as a yellow oil in 45% yield.[14] The different boryl groups were then installed by iodine–lithium exchange followed by electrophilic trapping with the corresponding halogenoborane $ClBCy_2$, $FBMes_2$ or ClBFlu.

Scheme 1. Synthesis of the PB Compounds 2-BCy_2, 2-$BMes_2$, and 2-BFlu

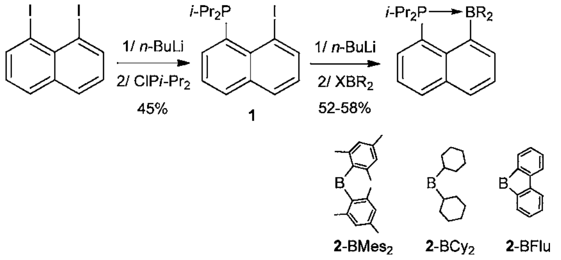


Table 1. Selected Spectroscopic and Crystallographic Data for Compounds 2

	2-$BMes_2$	2-BCy_2	2-BFlu
$\delta^{31}P$ (ppm)	17.4	23.4	25.1
$\delta^{11}B$ (ppm)	16.2	0.1	−8.5
d(PB) (Å)	2.173(4)	2.076(2)	2.011(2)
$\sum_\alpha B$ (°)	341.9(9)	340.7(2)	338.5(5)
PC_1C_2 (°)	111.4(3)	109.4(2)	109.0(2)
BC_3C_2 (°)	119.4(3)	118.0(2)	116.6(2)
PC_1C_3B (°)	2.6(2)	13.1(1)	11.9(2)

We started our investigations with compound **2**-BCy_2. The steric demand and Lewis acidity of the dicyclohexylboryl group is intermediate between those of the dimesitylboryl and borafluorenyl moieties.[13b,15] Compound **2**-BCy_2 was obtained as a white powder in 56% yield. It was characterized in solution by NMR spectroscopy and in the solid state by X-ray diffraction analysis (Table 1). The ^{11}B NMR signal of **2**-BCy_2 (δ = 0.1 ppm) appears at much higher field than those of three-coordinate boron centers (δ = 80.8 ppm for BCy_3)[16] and falls in the typical range of tetracoordinate boron compounds. Consistently, the ^{31}P NMR resonance signal of **2**-BCy_2 (δ = 23.4 ppm) is shifted to low field by about 20 ppm compared to that of its phosphine precursor **1** (δ = 1.6 ppm). These NMR data indicate the presence of a significant P → B interaction in solution.

Crystals of **2**-BCy_2 were obtained from a concentrated pentane solution at −40 °C (Figure 3). The presence of an intramolecular P → B interaction is clearly apparent from the pyramidalization of the boron environment [sum of CBC bond angles $\sum_\alpha B$ = 340.7(20)°] and the short PB distance [2.076(2) Å, vs 1.91 Å for the sum of covalent radii[17]]. There are only few crystallographic data available for P → B interactions supported by C_3 linkers. The only system with perisubstitution is the diphosphino-boryl-anthracene compound described by Akiba [i-Pr_2P → BCat interaction associated with a PB distance of 2.14(1) Å].[18] The PB distance observed in **2**-BCy_2 is shorter and falls in the range of those found by Erker for R_2P → $B(C_6F_5)_2$ interactions supported by flexible aliphatic C_3 linkers (PB distances of 2.06–2.09 Å for R = *t*-Bu, Ph, Mes).[9b,c] In order to accommodate the PB distance, the naphthyl backbone of **2**-BCy_2 significantly distorts both in-plane [bond angles PCC = 109.41(13)° and BCC = 118.02(16)°][19] and out-of-plane [torsion angle PC1C3B = 13.05(10)°].

The study was pursued with compound **2**-$BMes_2$. Despite the steric crowding induced by the bulky substituents at phosphorus and boron, the preparation proceeded smoothly and **2**-$BMes_2$ was isolated in 58% yield after workup. The ^{11}B NMR signal is observed at δ = 16.2 ppm for **2**-$BMes_2$ [vs δ = 79 ppm for $BMes_3$], indicating that the boron center is here also tetracoordinated. The deshielding of the ^{31}P NMR resonance signal (δ = 17.4 ppm for **2**-$BMes_2$) supports the existence of an intramolecular P → B interaction, but the NMR shift is less pronounced than in **2**-BCy_2, suggesting a somewhat weaker interaction in **2**-$BMes_2$. The crystallographic data confirm this view (Figure 3, Table 1), with a pyramidalized environment around boron [$\sum_\alpha B$ = 341.9 (9)°] and a PB distance of 2.173(4) Å. Compared with **2**-BCy_2, the P and B atoms are slightly pushed apart in **2**-$BMes_2$, indicating a somewhat weakened interaction. Nonetheless, the naphthyl spacer supports such donor–acceptor interactions, despite severe steric shielding. It is well-known that the presence of two mesityl groups at boron imparts considerable steric protection and prevents interaction with most Lewis bases, especially bulky ones.[20,21] Notably, the structure adopted by **2**-$BMes_2$ is in some respect opposite to that encountered in frustrated Lewis pairs, in which steric shielding prevent P → B interactions.

To explore further the flexibility of the naphthyl spacer with respect to the P → B interaction, we then investigated compound **2**-BFlu. In contrast with the $BMes_2$ group, the borafluorenyl moiety BFlu is sterically unhindered and very electron deficient (because of its formal antiaromatic character).[22] It was thus considered as an ideal candidate to assess how far the P → B interaction can be strengthened.

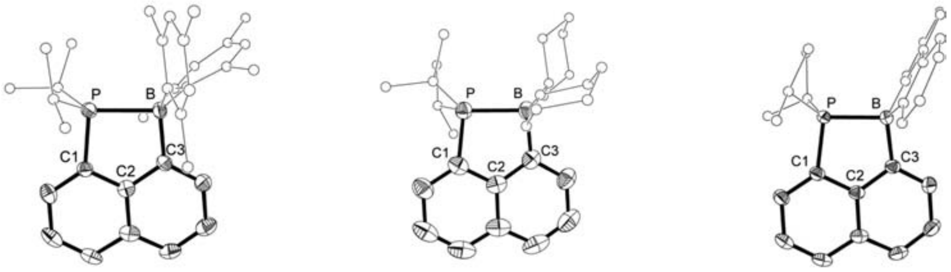


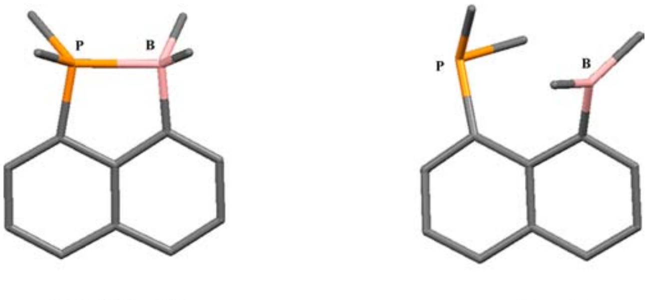
Figure 3. Molecular structure of **2**-BMes$_2$, **2**-BCy$_2$, and **2**-BFlu with thermal ellipsoids drawn at 50% probability. For clarity, the hydrogen atoms and solvent molecules are omitted, and the substituents at P and B are simplified.

Compound **2**-BFlu was isolated in 52% yield. It is stable at room temperature under inert atmosphere, whereas the corresponding *o*-phenylene bridged derivative[13b] rapidly decomposes under the same conditions. The ^{11}B and ^{31}P NMR signals of **2**-BFlu ($\delta = -8.5$ and 25.1 ppm, respectively) are diagnostic of a strong intramolecular P → B interaction (Table 1). Consistently, the X-ray diffraction study (Figure 3) revealed a strong pyramidalization of the boron environment [$\sum_\alpha$B = 338.45(5)°] and a very short PB distance [2.011(2) Å, at the lower limit of those reported to date for phosphine → borane adducts].[23] The strong P → B interaction induces significant distortions of the naphthyl backbone [in-plane: PCC = 108.98(13)° and BCC = 116.60(16)°; out-of-plane: PC1C3B = 11.90°].

Between the two extreme cases **2**-BMes$_2$ and **2**-BFlu, the magnitude of the P → B interaction varies significantly, as shown by the substantial decrease of the PB distance from 2.173(4) to 2.011(2) Å.[24] It is remarkable that on one hand, the naphthyl spacer can compensate for severe steric shielding and enforce D → A interaction thanks to its rigidity, and that on the other hand, it retains enough flexibility for the P → B interaction to respond significantly to the variation of the boron Lewis acidity.

The phosphine → borane interactions of the naphthyl derivatives were then examined by DFT calculations at the B3PW91/6-31G** level of theory.[25] The model compound **3** (featuring Me groups at the B and P atoms) as well as the full molecules **2**-BCy$_2$, **2**-BMes$_2$, and **2**-BFlu were investigated.

In line with previous observations for *o*-phenylene bridged diphosphine- and triphosphine-boranes,[9a] two minima were found on the potential energy surface of the model compound **3** (Figure 4). In the *closed* form **3*c***, the PB distance is short (2.025 Å) and the boron environment is strongly pyramidalized ($\sum\alpha$B = 340.40°), while in the *open* form **3*o***, there is no P → B interaction (B···P: 3.690 Å, $\sum\alpha$B = 358.8°), the phosphorus-centered pyramid pointing opposite to the 2p(B) vacant orbital. The *closed* form **3*c*** is lower in energy than the *open* form **3*o*** by as much as 27 kcal/mol. This contrasts with the small energy difference predicted between the two forms of the corresponding *o*-phenylene bridged phosphine-borane (~3.0 kcal/mol at the same level of theory) and provides some quantitative estimation of the influence of the spacer on the strength of the P → B interaction.



closed form **3*c***

open form **3*o***

Figure 4. Optimized geometries of *closed* and *open* forms of the model compound **3**. For clarity, the hydrogen atoms are omitted.

In compounds **2**, the phosphorus substituents cannot point to boron because of steric reasons, and only the *closed* forms were found as minima on the respective potential energy surfaces. The optimized geometries (Table 2) reproduce well the X-ray data (largest deviation of 0.1 Å in the PB bond distance and 2° in the bond angles). In agreement with the experimental observations, the PB distance decreases with increasing the Lewis acidity of the boron center (from 2.270 in **2**-BMes$_2$ to 2.040 Å in **2**-BFlu). The pyramidalization around boron increases in the same series ($\sum\alpha$B varies from 337.4° in **2**-BFlu to 345.4° in **2**-BMes$_2$). The progressive strengthening of the P → B interaction from BMes$_2$ to BCy$_2$, and BFlu, is also apparent from the associated Wiberg bond orders (WBI), which increase from 0.74 in **2**-BMes$_2$ to 0.81 in **2**-BCy$_2$ and 0.88 in **2**-BFlu.

Table 2. Selected Geometric Data for Compounds 2, as Calculated at the B3PW91/6-31G Level of theory**

	2-BMes$_2$	**2**-BCy$_2$	**2**-BFlu
d(PB) (Å)	2.270	2.169	2.040
$\sum_\alpha$B (°)	345.4	345.1	337.4
PC$_1$C$_2$ (°)	112.56	110.65	109.74
BC$_3$C$_2$ (°)	121.67	119.50	117.88
PC$_1$C$_3$B (°)	7.8	15.0	−6.6

Natural bond orbital (NBO)[26] analyses also provide valuable information about the P → B interactions (Table 3). The natural population analysis (NPA) charges clearly indicate some electron transfer from phosphorus to boron. The charge of the P*i*-Pr$_2$ fragment is positive and increases from **2**-BMes$_2$ (0.74) to **2**-BCy$_2$ (0.81), and **2**-BFlu (0.88), while the charge of the BR$_2$ fragment is negative and decreases in the same series (from −0.21 in **2**-BMes$_2$ to −0.25 in **2**-BCy$_2$, and −0.43 in **2**-BFlu). In the NBO analysis, polarized σ_{PB} bonds were found at the first order (Figure 5a). The contribution of phosphorus prevails (60−70%), but the participation of boron is noticeable (30−40%) and increases from **2**-BMes$_2$ to **2**-BCy$_2$, and **2**-BFlu. This trend can be explained by simple molecular orbital considerations. Indeed, the higher the Lewis acidity of boron, the smaller is the energy gap between the boron vacant orbital

Table 3. Selected Results of the Computational Analysis of Compounds **2**

	2-BMes$_2$	**2**-BCy$_2$	**2**-BFlu
	NBO analyses		
WBI	0.74	0.81	0.88
NPA charges			
P*i*-Pr$_2$	0.82	0.87	0.99
BR$_2$	−0.21	−0.25	−0.43
%P in σ_{PB} (%s/%p)	70.0 (30.6/69.3)	67.8 (32.4/67.5)	61.2 (31.2/68.7)
%B in σ_{PB} (%s/%p)	30.0 (12.8/87.1)	32.2 (14.3/85.6)	38.8 (18.8/81.1)
	AIM analyses		
BCP (P−B)			
$\rho(r)$ (e.bohr^{-3})	0.06	0.08	0.10
$\nabla^2\rho(r)$ (e.bohr^{-5})	−0.04	−0.08	−0.11
$H(r)$	−0.031	−0.050	−0.083
δ(P,B)	0.328	0.353	0.400

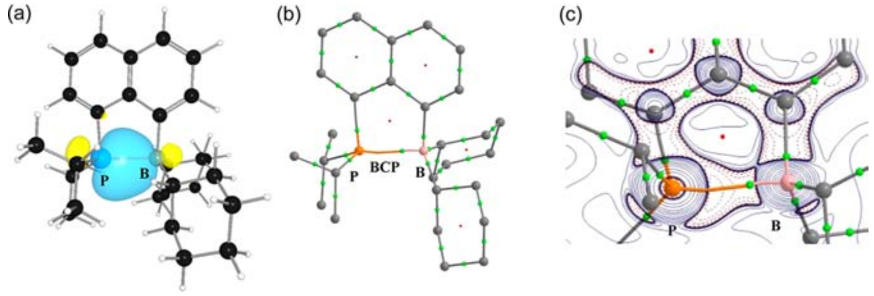


Figure 5. (a) Plot of the NBO σ_{PB} orbital of **2**-BCy$_2$ (cutoff: 0.04). (b) Simplified AIM molecular graph for **2**-BCy$_2$; the hydrogen atoms and the BCP associated to the C−H bonds are omitted for clarity. (c) Contour plot of the Laplacian $\nabla^2\rho$(BCP) of **2**-BCy$_2$ in the P(naphthyl)B plane, with charge accumulation ($\nabla^2\rho(r)<0$) in blue lines and charge depletion ($\nabla^2\rho(r)>0$) in dashed lines.

2p(B) and the phosphorus lone pair n_P, thus the more the two atomic orbitals mix and the more stabilizing is the donor−acceptor interaction. Accordingly, the less polarized σ_{PB} bond (61.2% P/38.8% B) is found in compound **2**-BFlu featuring the strongest P → B interaction.

Finally, the P → B interactions in compounds **2** were analyzed by atoms in molecules (AIM) calculations.[27] The electron density maps (Figure 5b) show the presence of bond paths between the phosphorus and boron atoms with localized bond critical points (BCP). The electron density $\rho(r)$ at the BCP increases from 0.06 e.bohr^{-3} for **2**-BMes$_2$, to 0.08 e.bohr^{-3} for **2**-BCy$_2$, and 0.10 e.bohr^{-3} for **2**-BFlu, corroborating the strengthening of the P → B interaction as the Lewis acidity of boron increases. In agreement with the donor−acceptor character of the P → B interactions, the Laplacian $\nabla^2\rho(r)$ (Figure 5c) and local electronic energy density $H(r)$ at the BCP are small and negative.[28] The sharing of electrons between P and B was assessed by considering the delocalization index δ(B,P), often called bond order, as introduced by Bader.[27c,29] δ(B,P) follows the same trend as the electron density and Wiberg bond index, increasing from 0.328 in **2**-BMes$_2$, to 0.353 in **2**-BCy$_2$, and 0.400 in **2**-BFlu.

■ CONCLUSION

Compounds **2**-BMes$_2$, **2**-BCy$_2$, and **2**-BFlu are rare examples of naphthyl-bridged phosphine-boranes. The involved P → B interactions have been thoroughly analyzed by experimental and computational means, substantiating a dual character of the naphthyl linker. On the one hand, it can overwhelm important steric crowding and enforce unfavorable P → B interaction thanks to its rigidity. On the other hand, it retains enough flexibility for the P → B interaction to respond significantly to the variation of the boron Lewis acidity, both geometrically and electronically. Future work will seek to explore further the chemistry of donor−acceptor naphthyl systems, from both structural and reactivity standpoints.

■ EXPERIMENTAL SECTION

General Comments. All reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. All solvents were purged with argon and dried using an MBraun Solvent Purification System (SPS). ^{1}H, ^{11}B, ^{13}C and ^{31}P NMR spectra were recorded on Bruker, AMX 400, Avance 500 and Avance 300 spectrometers. Chemical shifts are expressed with a positive sign, in parts per million, calibrated to residual ^{1}H (7.24 ppm) and ^{13}C (77.16 ppm) solvent signals, external $BF_3{\cdot}OEt_2$ and 85% H_3PO_4. Otherwise stated, NMR spectra were recorded at 293 K. Chloroborafluorene was synthesized according to literature procedure.[30]

Compound 1. 2.00 mL of solution of *n*-BuLi (1.60 M in hexanes, 3.22 mmol) were added dropwise to 1.165 g (3.070 mmol) of 1,8-diiodonaphtalene solution in THF (40 mL) at −78 °C and the reaction mixture was stirred 1 h at this temperature. After the subsequent addition of 488 μL of chlorodiisopropylphosphine (3.07 mmol), the reaction mixture was stirred at rt overnight. The volatiles were then removed under a vacuum, and the residue was purified by flash chromatography on silica gel (eluant: pentane) affording the expected compound as a yellow oil with a 45% yield. ^{1}H NMR (300.2 MHz, C_6D_6) δ = 0.94 (dd, 6H, $^3J_{H-P}$ = 12.7 Hz, $^3J_{H-H}$ = 7.0 Hz, CH_{3iPr}), 1.15 (dd, 6H, $^3J_{HP}$ = 13.7 Hz, $^3J_{H-H}$ = 7.0 Hz, CH_{3iPr}), 2.08 [(pseudo)sept-d, 2H, $^2J_{H-P}$ = 2.2 Hz, $^3J_{H-H}$ = 7.0 Hz, CH_{iPr}], 6.59 (pseudo-t, 2H, J = 7.5 Hz, $H_{arom.}$), 7.39−7.45 (m, 2H, $H_{arom.}$), 7.60−7.65 (m, 1H, $H_{arom.}$), 8.24 (dd, 1H, $^3J_{H-H}$ = 7.4 Hz, $^4J_{HH}$ = 1.3 Hz, $H_{arom.}$); ^{13}C{^{1}H} (125.81 MHz, C_6D_6) δ = 20.3 (d, $^2J_{C-P}$ = 20.5 Hz, CH_{3iPr}), 21.0 (d, $^2J_{C-P}$ = 14.2 Hz, CH_{3iPr}), 27.3 (d, $^1J_{C-P}$ = 20.7 Hz, CH_{iPr}), 125.1 (s, $CH_{arom.}$), 126.5 (s, $CH_{arom.}$), 128.9 (d, J_{C-P} = 57.7 Hz, C$_{\text{quat.}}$), 130.3 (d, $J_{\text{C−P}}$ = 1.7 Hz, CH$_{\text{arom.}}$), 130.7 (s, CH$_{\text{arom.}}$), 134.5 (d, $J_{\text{C−P}}$ = 1.9 Hz, CH$_{\text{arom.}}$), 136.2 (d, $J_{\text{C−P}}$ = 3.9 Hz, C$_{\text{quat.}}$), 137.1 (d, $J_{\text{C−P}}$ = 35.9 Hz, C$_{\text{quat.}}$), 138.6 (d, $J_{\text{C−P}}$ = 20.0 Hz, C$_{\text{quat.}}$), 143.8 (s, CH$_{\text{arom.}}$); ^{31}P{^{1}H} (121.49 MHz, C_6D_6) δ = 7.9.

Compound 2-BCy$_2$. 375 μL of *n*-BuLi (1.60 M in hexanes, 0.60 mmol) were added dropwise to 222 mg (0.60 mmol) of 1-iodo-8-diisopropylphosphinonaphtalene in solution in diethylether (2.3 mL) at −50 °C. After stirring 30 min at this temperature, the solution was filtered off and the resulting yellow solid was washed with diethylether (2 × 1 mL) at −50 °C. The solid was then dissolved in 2.3 mL of toluene, and dicyclohexylchloroborane (1.0 M in hexanes, 0.6 mmol, 600 μL) was added dropwise at −78 °C. The reaction mixture was stirred at rt overnight. The volatiles were then removed under a vacuum; the residue was dissolved in pentane (5 mL) and filtrated through a plug of Celite. Compound **2**-BCy$_2$ was obtained as colorless crystals suitable for X-ray diffraction analysis from a concentrated solution of pentane −40 °C in 56% yield. mp 176 °C. HRMS *m*/*z* (CI, CH_4): exact mass calculated $C_{48}H_{42}BP$,421.3195; found, 421.3210; elementary analysis: calculated C,79.99; H,10.07 found C,80.21; H,10.47. ^{1}H NMR (300.18 MHz, C_6D_6) δ = 0.81 (dd, 6H, $^{3}J_{\text{H−P}}$ = 13.2 Hz, $^{3}J_{\text{H−H}}$ = 7.1 Hz, CH$_{3i\text{Pr}}$), 0.95 (dd, 6H, $^{3}J_{\text{H−P}}$ = 13.2 Hz, $^{3}J_{\text{H−H}}$ = 7.1 Hz, CH$_{3i\text{Pr}}$), 1.16−1.61 (m, 12H, H$_{\text{Cy}}$), 1.70−1.88 (m, 6H, H$_{\text{Cy}}$), 1.96−2.20 (m, 4H, H$_{\text{Cy}}$), 2.27 [(pseudo)sept-d, 2H, $^{3}J_{\text{H−H}}$ = 7.1 Hz, $^{2}J_{\text{H−P}}$ = 8.3 Hz, CH$_{i\text{Pr}}$], 7.14−7.26 (m, 2H, H$_{\text{arom.}}$), 7.49−7.59 (m, 2H, H$_{\text{arom.}}$), 7.72 (d-mult, 1H, $^{3}J_{\text{H−H}}$ = 6.1 Hz, H$_{\text{arom.}}$), 7.76 (d-mult, 1H, $^{3}J_{\text{H−H}}$ = 7.8 Hz, H$_{\text{arom.}}$); ^{13}C{^{1}H} (125.81 MHz, C_6D_6) δ = 18.3 (d, $^{2}J_{\text{C−P}}$ = 0.8 Hz, CH$_{3i\text{Pr}}$), 19.1 (s, CH$_{3i\text{Pr}}$), 22.6 (d, $^{1}J_{\text{C−P}}$ = 18.0 Hz, CH$_{i\text{Pr}}$), 28.2 (s, CH$_{2\text{Cy}}$), 29.7 (s, CH$_{2\text{Cy}}$), 30.2 (s, CH$_{2\text{Cy}}$), 32.1 (d, $J_{\text{C−P}}$ = 7.5 Hz, CH$_{2\text{Cy}}$), 33.8 (d, $J_{\text{C−P}}$ = 6.1 Hz, CH$_{2\text{Cy}}$), 123.3 (d, $J_{\text{C−P}}$ = 1.8 Hz, CH$_{\text{arom.}}$), 124.8 (d, $J_{\text{C−P}}$ = 6.7 Hz, CH$_{\text{arom.}}$), 126.5 (s, CH$_{\text{arom.}}$), 127.9 (d, $J_{\text{C−P}}$ = 2.4 Hz, CH$_{\text{arom.}}$), 128.7 (d, $J_{\text{C−P}}$ = 16.4 Hz, CH$_{\text{arom.}}$), 130.2 (d, $J_{\text{C−P}}$ = 45.6 Hz, C$_{\text{quat.}}$), 130.9 (d, $J_{\text{C−P}}$ = 2.1 Hz, CH$_{\text{arom.}}$), 132.7 (d, $J_{\text{C−P}}$ = 9.2 Hz, C$_{\text{quat.}}$), 145.5 (d, $J_{\text{C−P}}$ = 29.6 Hz, C$_{\text{quat.}}$), the three carbon atoms in α position of the boron atom are not observed; ^{11}B{^{1}H} (128.4 MHz, $CDCl_3$) δ = 0.1; ^{31}P{^{1}H} (121.49 MHz, $CDCl_3$) δ = 23.4.

Compound 2-BMes$_2$. 235 μL of *n*-BuLi (2.50 M in hexanes,0.60 mmol) and 158 mg (0.60 mmol) of dimesitylfluoroborane in solution of toluene (2 mL) were successively added at −50 °C and −78 °C to a 1-iodo-8-diisopropylphosphinonaphtalene solution (222 mg, 0.6 mmol) in toluene (2 mL). After warming to rt, the volatiles were removed under a vacuum, the residue was dissolved in pentane (2 × 5 mL), and the salts were removed by filtration. After concentration of the solution at rt, compound **2**-BMes$_2$ is obtained as colorless crystals suitable for X-ray diffraction analysis in 58% yield. mp 176 °C. *m*/*z* (EI, 70 eV): 492 [M]$^+$. ^{1}H NMR (400.1 MHz, $CDCl_3$) δ = 0.45 (dd, 3H, $^{3}J_{\text{H−P}}$ = 12.0 Hz, $^{3}J_{\text{H−H}}$ = 7.2 Hz, CH$_{3i\text{-Pr}}$), 1.12 (s, 3H, CH$_{3\text{Mes}}$), 1.13 (dd, 3H, $^{3}J_{\text{H−P}}$ = 12.0 Hz, $^{3}J_{\text{H−H}}$ = 7.2 Hz, CH$_{3i\text{-Pr}}$), 1.34 (dd, 3H, $^{3}J_{\text{H−P}}$ = 12,0 Hz, $^{3}J_{\text{H−H}}$ = 7.2 Hz, CH$_{3i\text{-Pr}}$), 1.36 (dd, 3H, $^{3}J_{\text{H−P}}$ = 12,0 Hz, $^{3}J_{\text{H−H}}$ = 7.2 Hz, CH$_{3i\text{-Pr}}$), 1.86 (s, 3H, CH$_{3\text{Mes}}$), 2.01 (s, 3H, CH$_{3\text{Mes}}$), 2.24 (s, 3H, CH$_{3\text{Mes}}$), 2.26 (s, 3H, CH$_{3\text{Mes}}$), 2.33 (s, 3H, CH$_{3\text{Mes}}$), 2.46 [(pseudo)sept-d, 1H, $^{2}J_{\text{H−P}}$ = 14.0 Hz, $^{3}J_{\text{H−H}}$ = 7.2 Hz, CH$_{i\text{-Pr}}$], 2.70 [(pseudo)sept-d, 1H, $^{2}J_{\text{H−P}}$ = 14,0 Hz, $^{3}J_{\text{H−H}}$ = 7.2 Hz, CH$_{i\text{-Pr}}$], 6.50 (s, 1H, H$_{\text{Mes}}$), 6.79 (s, 1H, H$_{\text{Mes}}$), 6.82 (s, 2H, H$_{\text{Mes}}$), 7.46 (m, 2H, H$_{\text{arom.}}$), 7.58 (dd, 1H, $^{3}J_{\text{H−H}}$ = 6,6 Hz, $^{3}J_{\text{H−H}}$ = 7.6 Hz, H$_{\text{arom.}}$), 7.75 (dd, 1H, $^{3}J_{\text{H−H}}$ = 7.2 Hz, $^{4}J_{\text{H−H}}$ = 1.9 Hz, H$_{\text{arom.}}$), 7.78 (pseudo-t, 1H, $^{3}J_{\text{H−H}}$ = 6.6 Hz, $^{3}J_{\text{H−P}}$ = 6.6 Hz, H$_{\text{arom.}}$), 8.04 (d, 1H, $^{3}J_{\text{H−H}}$ = 7.6 Hz, H$_{\text{arom.}}$); ^{13}C{^{1}H} (101.6 MHz, 298 K, $CDCl_3$) δ = 18.1 (s, CH$_{3i\text{-Pr}}$), 19.2 (s, CH$_{3\text{i-Pr}}$), 20.0 (s, CH$_{3i\text{-Pr}}$), 21.2 (d, $^{2}J_{\text{C−P}}$ = 3.0 Hz, CH$_{3i\text{-Pr}}$), 21.3 (s, 2C, CH$_{3\text{Mes}}$), 25.8 (s, CH$_{3\text{Mes}}$), 26.0 (d, $J_{\text{C−P}}$ = 2.0 Hz, CH$_{3\text{Mes}}$), 26.3 (s, CH$_{3\text{Mes}}$), 26.6 (s, CH$_{3\text{Mes}}$), 26.8 (d, $^{1}J_{\text{C−P}}$ = 16.0 Hz, CH$_{i\text{-Pr}}$), 30.3 (s, CH$_{i\text{-Pr}}$), 125.0 (d, $^{4}J_{\text{C−P}}$ = 5.0 Hz, CH$_{\text{Napht}}$), 125.3 (s, CH$_{\text{Napht}}$), 127.9 (d, $J_{\text{C−P}}$ = 1.0 Hz, CH$_{\text{Napht}}$), 128.4 (s, CH$_{\text{Mes}}$), 128.4 (s, CH$_{\text{Mes}}$), 128.9 (s, C$_{\text{quat.}}$), 129.2 (s, CH$_{\text{Napht}}$), 129.7 (d, J$_{\text{C−P}}$ = 4 Hz, CH$_{\text{Mes}}$), 129.8 (s, CH$_{\text{Mes}}$), 130.3 (s, CH$_{\text{Mes}}$), 131.1 (d, $^{3}J_{\text{C−P}}$ = 1.0 Hz, CH$_{\text{Napht}}$), 132.9 (d, $J_{\text{C−P}}$ = 14.0 Hz, C$_{\text{quat.}}$), 133.0 (d, $^{2}J_{\text{C−P}}$ = 15.0 Hz, CH$_{\text{Napht}}$), 135.1 (s, C$_{\text{quat.}}$), 136.2 (d, $J_{\text{C−P}}$ = 4.0 Hz, C$_{\text{quat.}}$), 140.7 (d, $J_{\text{C−P}}$ = 4 Hz, C$_{\text{quat.}}$), 142.2 (d, $J_{\text{C−P}}$ = 10.0 Hz, C$_{\text{quat.}}$), 142.5 (d, $J_{\text{C−P}}$ = 9.0 Hz, C$_{\text{quat.}}$), 143.9 (d, $J_{\text{C−P}}$ = 33 Hz, C$_{\text{quat.}}$), 144.0 (s, C$_{\text{quat.}}$), 144.3 (s, C$_{\text{quat.}}$), 147.8 (s, C$_{\text{quat.}}$), 156.5 (d, $J_{\text{C−P}}$ = 16.0 Hz, C$_{\text{quat.}}$); ^{11}B{^{1}H} (128.4 MHz, 298 K, $CDCl_3$) δ = 16.2; ^{31}P{^{1}H} (162.0 MHz, 298 K, $CDCl_3$) δ = 17.4.

Compound 2-BFlu. 375 μL of *n*-BuLi (1.60 M in hexanes, 0.60 mmol) were added dropwise to 222 mg (0.60 mmol) of 1-iodo-8-diisopropylphosphinonaphtalene in diethylether (2.3 mL) at −50 °C, and the reaction mixture was stirred at this temperature for 30 min. The solution was then filtered off and the resulting yellow solid was washed with diethylether (2 × 1 mL) at −50 °C. The solid was then dissolved in toluene (2.3 mL) and a toluene solution (1.6 mL) of chloroborafluorene (119.2 mg, 0.6 mmol) was added at −78 °C. After warming to rt and stirring overnight, the volatiles were removed under a vacuum; the residue was dissolved in pentane (5 mL) and filtered through a plug of Celite. After concentration of the solution, compound **2**-BFlu was obtained at −40 °C as colorless crystals suitable for X-ray diffraction analysis in 52% yield. mp 172 °C. HRMS (CI-CH_4): exact mass calculated for $C_{28}H_{28}BP$,421.2100; found,421.2095. ^{1}H NMR (300.16 MHz, C_6D_6) δ = 0.59 (dd, 6H, $^{3}J_{\text{H−P}}$ = 15.5 Hz, $^{3}J_{\text{H−H}}$ = 7.1 Hz, CH$_{3i\text{Pr}}$), 0.65 (dd, 6H, $^{3}J_{\text{HP}}$ = 14.4 Hz, $^{3}J_{\text{HH}}$ = 7.1 Hz, CH$_{3i\text{Pr}}$), 2.07 [(pseudo)sept-d, 2H, $^{3}J_{\text{H−P}}$ = 10.3 Hz, $^{3}J_{\text{H−H}}$ = 7.1 Hz, CH$_{i\text{Pr}}$], 7.09−7.18 (m, 2H, H$_{\text{arom.}}$), 7.25−7.40 (m, 8H, H$_{\text{arom.}}$), 7.52−7.56 (m, 1H, H$_{\text{arom.}}$), 7.80−7.85 (m, 1H, H$_{\text{arom.}}$), 7.91−7.97 (m, 2H, H$_{\text{arom.}}$); ^{13}C {^{1}H} (125.81 MHz, C_6D_6) δ = 17.7 (d, $^{2}J_{\text{C−P}}$ = 1.7 Hz, CH$_{3i\text{Pr}}$), 18.0 (s, CH$_{3i\text{Pr}}$), 23.1 (d, $^{1}J_{\text{C−P}}$ = 26.4 Hz, CH$_{i\text{Pr}}$), 120.1 (d, $J_{\text{C−P}}$ = 1.0 Hz, CH$_{\text{arom.}}$), 124.0 (d, $J_{\text{C−P}}$ = 1.4 Hz, CH$_{\text{arom.}}$), 125.2 (d, $J_{\text{C−P}}$ = 7.4 Hz, CH$_{\text{arom.}}$), 126.1(d, $J_{\text{C−P}}$ = 2.8 Hz, CH$_{\text{arom.}}$), 127.0 (d, J_{CP} = 2.6 Hz, CH$_{\text{arom.}}$), 128.35 (br, CH$_{\text{arom.}}$), 129.2 (d, $J_{\text{C−P}}$ = 2.2 Hz, CH$_{\text{arom.}}$), 129.5 (d, $J_{\text{C−P}}$ = 14.0 Hz, CH$_{\text{arom.}}$), 129.75 (d, $J_{\text{C−P}}$ = 51.4 Hz, C$_{\text{quat.}}$), 131.3 (d, $J_{\text{C−P}}$ = 2.2 Hz, CH$_{\text{arom.}}$), 132.1 (d, $J_{\text{C−P}}$ = 2.4 Hz, CH$_{\text{arom.}}$), 133.1 (d, $J_{\text{C−P}}$ = 9.3 Hz, C$_{\text{quat.}}$), 146.3 (d, $J_{\text{C−P}}$ = 28.3 Hz, C$_{\text{quat.}}$), 150.4 (d, $J_{\text{C−P}}$ = 5.7 Hz, C$_{\text{quat.}}$), 155.7 (br, C$_{\text{quat.}}$), one quaternary, in α position of the boron atom is not observed; ^{11}B{^{1}H} (96.3 MHz, $CDCl_3$) δ = −8.5; ^{31}P{^{1}H} (121.49 MHz, $CDCl_3$) δ = 25.1.

Crystallographic Analyses. Crystallographic data were collected at 193(2) K on a Bruker-AXS Kappa APEXII Quazar diffractometer (for **2**-BCy$_2$ and **2**-BFlu) and on a Bruker−AXS CCD 1000 diffractometer (for **2**-BMes$_2$), with Mo Kα radiation (λ = 0.71073 Å) using an oil-coated shock-cooled crystal. Phi- and omega-scans were used. Semiempirical absorption correction was employed.[31] The structures were solved by direct methods (SHELXS-97)[32] and refined using the least-squares method on F^2.[33] All non-H atoms were refined with anisotropic displacement parameters. The H atoms were refined isotropically at calculated positions using a riding model with their isotropic displacement parameters constrained to be equal to 1.5 times the equivalent isotropic displacement parameters of their pivot atoms for terminal sp^3 carbon and 1.2 times for all other carbon atoms.

Computational Studies. Calculations were carried out with the Gaussian 09 program[34] at the DFT level of theory using the hybrid functional B3PW91.[35] B3PW91 is Becke's 3 parameters functional, with the nonlocal correlation provided by the Perdew 91 expression. All the atoms have been described with a 6-31G(d,p) double-ζ basis set.[36] Geometry optimizations were carried out without any symmetry restrictions, the nature of the *extrema* (minima or transition state) was verified with analytical frequency calculations. All total energies and Gibbs free energies have been zero-point energy (ZPE) and temperature corrected using unscaled density functional frequencies. Electronic structure of the different complexes was studied using natural bond orbital analysis (NBO-5 program).[37] The NBO orbital (σ_{BP}) obtained from first-order NBO analysis was plotted by using the molecular graphic program NBOView 1.1.[38] The electron density of the optimized structures was subjected to an atoms in molecules analysis (QTAIM analysis)[39] using AIMAll software.[40]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures and analytical data including NMR spectra for **1**, **2**-BCy$_2$, **2**-BMes$_2$, and **2**-BFlu; X-ray crystallographic data for CCDC 923615 (**2**-BCy$_2$), 923616 (**2**-BMes$_2$), and 923617 (**2**-BFlu) (CIF); Cartesian coordinates for the optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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