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Amino and Alkyl B-Substituted P-Stabilized Borenium Salts

Marc Devillard,[†] Ghenwa Bouhadir,[†] Sonia Mallet-Ladeira,[‡] Karinne Miqueu,[§] and Didier Bourissou*[,†]

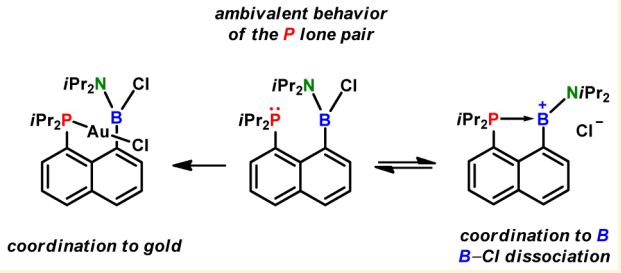
[†]Université de Toulouse, UPS, LHFA (Laboratoire Hétérochimie Fondamentale et Appliquée), and CNRS, LHFA, UMR 5069, 118 route de Narbonne, 31062 Toulouse, France

[‡]Institut de Chimie de Toulouse (FR 2599), 118 route de Narbonne, 31062 Toulouse Cedex 9, France

[§]Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux, Université de Pau et des Pays de l'Adour and CNRS, IPREM UMR 5254, Hélioparc, 2 Avenue du Président Angot, Pau 64053 Cedex 09, France

Supporting Information

ABSTRACT: The ability of the phosphino-naphthyl moiety to stabilize amino- and alkylborenium cations has been studied. Surprisingly, the phosphine–aminochloroborane precursor **2** was found to exist in neutral open form (without P→B interaction) in benzene solution and in the solid state but to ionize spontaneously in chloroform to generate the P-stabilized borenium salt **3**. Addition of gallium trichloride shifts the process forward and affords the corresponding tetrachlorogallate borenium salt **3′**. The phosphine group of **2** remains available for external reactivity, as shown by the ready formation of the corresponding phosphine gold(I) chloride complex **4**. The P-stabilized cyclohexylborenium cation **6** has also been prepared by reacting the corresponding bromoborane **5** with gallium tribromide. Compound **6** is a very rare example of an alkyl-substituted borenium salt. The structures of **2**, **3′**, and **4**–**6** have been unambiguously ascertained by multinuclear NMR spectroscopy and X-ray crystallography.



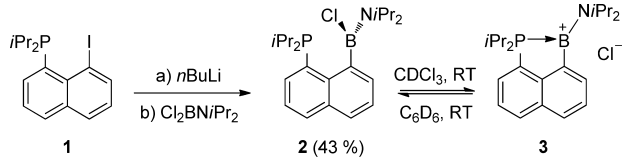
INTRODUCTION

The chemistry of tricoordinate boron cations (borenium cations) has gained new momentum in the past decade.[1] Due to their cationic character and enhanced Lewis acidity, borenium cations are powerful reagents for a variety of stoichiometric and catalytic transformations such as the halo- and hydroboration of alkynes and alkenes,[2] the borylation of arenes,[3] the carboboration of alkynes,[4] and FLP-type hydrogenations.[5] Additionally, they have been recently used as precursors for boryl radicals[6] and borylenes,[7] as well as constituents of superacidic ionic liquids.[8] These developments have strongly stimulated the search and study of new (L→BR_2^+) motifs. In fact, most of the borenium cations known so far involve N-containing Lewis bases (pyridines, N-heterocyclic carbenes),[9] whereas only a handful of P-stabilized borenium cations have been described.[10] In this area, our group has recently introduced a new type of naphthyl-bridged[11] P-stabilized borenium cations.[12] B-mesityl-substituted compounds have been isolated and shown to display rich reactivity (H_2 splitting, 1,2-carboboration, N–H bond cleavage). These results encouraged us to try to extend the structural modularity of such P-stabilized borenium cations. We report here the preparation and complete characterization of B-amino- and B-alkyl-substituted compounds. The structures of the targeted compounds and of their phosphine–borane precursors have been analyzed carefully, revealing an interesting solvent-dependent and reversible B–Cl dissociation process.

RESULTS AND DISCUSSION

The phosphine–aminochloroborane **2** was prepared in one step from 1-iodo-8-(diisopropylphosphino)naphthalene (**1**;[11c] Scheme 1). The ^{31}P NMR chemical shift of **2** in C_6D_6 (δ −11.8 ppm) is nearly identical with that of the starting phosphine **1**, indicating the absence of a P→B interaction in **2**. Consistently, the ^{11}B NMR spectrum displays a broad signal at δ 33.3 ppm characteristic of a tricoordinate aminoborane ($tBu_2NB(Ph)(Cl)$, δ 35 ppm).[13] The absence of a P→B interaction is likely due to the strong π-donating properties of the diisopropylamino substituent that significantly reduce the Lewis acidity of the boron center.

Scheme 1. Synthesis and Structure of a Phosphine–Aminochloroborane: Solvent-Dependent Equilibrum between the Neutral Open Structure 2 and the P-Stabilized Borenium Salt 3



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For further structural insight, a single crystal of **2** was analyzed by X-ray diffraction (Figure 1). As in benzene

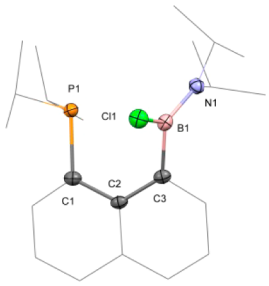


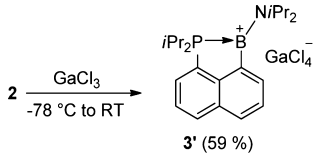
Figure 1. X-ray crystal structure of **2**. The *i*Pr groups and the naphthyl spacer are simplified, and the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−C1 1.829(2), B1−Cl1 1.830(3), B1−C3 1.589(3), B1−N1 1.385(3); Cl1−B1−C3 112.4(2), Cl1−B1−N1 120.9(2), N1−B1−C3 123.9(2); P1−C1−C3−B1 20.0(1).

solution, the phosphine−borane adopts a neutral open structure in the solid state. The P−B distance (2.867(2) Å) is much longer than the sum of covalent radii (1.91 Å).[14] Both the boron and nitrogen atoms are in trigonal-planar environments ($\sum_{\alpha}$B = 357.2°, $\sum_{\alpha}$N = 359.7°), and the N−B bond is short (1.385(3) Å, in comparison with the sum of covalent radii of 1.55 Å), indicating significant double-bond character.[15]

Surprisingly, **2** displays rather different spectroscopic data in $CDCl_3$ solution. The ^{31}P NMR resonance signal moves from δ −11.8 ppm in C_6D_6 to δ 11.3 ppm in $CDCl_3$. This large downfield shift ($\Delta\delta$ = 23.1 ppm) supports the establishment of a substantial P→B interaction in chloroform. In the meantime, the ^{11}B NMR signal (δ 37.2 ppm in $CDCl_3$) remains in the range of tricoordinate aminoboranes. We surmised that the solvent dependence of the NMR data was the result of B−Cl dissociation with formation of the phosphine-stabilized borenium salt **3**, in line with the polar nature of the chlorinated solvent (vs apolar character of benzene). Note that high-resolution mass spectrometric analysis of **2** (HRMS, CI, CH_4) gives the isotopic mass of the cation **3**, in line with facile B−Cl dissociation. The experimental observations have been corroborated computationally (the relative stabilities of the two forms have been evaluated by DFT in benzene and chloroform).[16] In addition, attempts to crystallize **3** yielded crystals of **2**, showing the reversibility of the chloride dissociation at boron. Nucleophilic displacement of a halogen atom (or a trifluoromethanesulfonate group) at boron by an external base to generate a borenium salt is quite well-known with N-based donors such as pyridine, lutidine, and phenantroline.[17] However, reversible B−X bond cleavage as observed between **2** and **3** is, to the best of our knowledge, unprecedented.

To further ascertain the structure of **3**, **2** was then reacted with a gallium salt (Scheme 2), which we have shown to be a suitable halide scavenger to generate borenium cations.[12] Mixing **2** with $GaCl_3$ at low temperature in toluene led to the precipitation of a white powder (**2** is soluble in toluene). NMR analysis of the isolated solid in $CDCl_3$ showed the formation of the single species **3′** with ^{31}P and ^{11}B resonance signals ($\delta(^{31}P)$ 13.0 ppm and $\delta(^{11}B)$ 37.9 ppm) very similar to those of **3**. Crystals of **3′** were grown from a saturated dichloromethane solution at room temperature. X-ray diffraction analysis (Figure 2) confirmed the chloride

Scheme 2. Synthesis of the Borenium Salt 3′ by Chloride Abstraction with Gallium Trichloride



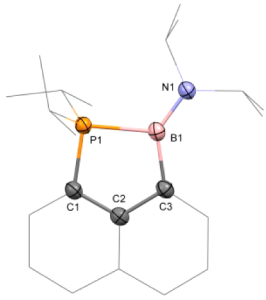
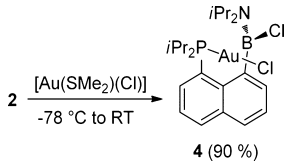


Figure 2. X-ray crystal structure of **3′**. The *i*Pr groups and the naphthyl spacer are simplified, and the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−C1 1.791(2), N1−B1 1.384(2), B1−C3 1.579(2), P1−B1 1.989(2); N1−B1−C3 135.7(2), C3−B1−P1 102.7(1), N1−B1−P1 121.6(1); P1−C1−C3−B1 −1.24(8).

abstraction and the formation of a borenium tetrachlorogallate salt.[18] The ion pair is well separated (the shortest Cl···B bond distance amounts to 6.188(2) Å), and the boron center is tricoordinate. It is engaged in strong P→B interactions (P−B distance 1.989(2) Å)[19] and stabilized by π donation from the N*i*Pr$_2$ substituents. As in the chloroborane **2**, the B−N distance (1.384(2) Å) is short and has significant double-bond character. Note that the whole (naphthyl)PBN skeleton is flat, the coordination planes of B and N as well as the mean plane of the naphthyl bridge being almost coplanar.

The absence of P→B interactions in **2** is unusual and contrasts with the closed form adopted by most naphthyl-bridged phosphine−boranes.[6,11,20] However, given the constraint imposed by the naphthyl moiety and the tendency of **2** for B−Cl dissociation, it is questionable if the phosphine moiety of **2** remains available for external reactivity. To this end, the phosphine−borane **2** was reacted with [Au(SMe$_2$)(Cl)] with the aim of forming the corresponding phosphine gold(I) chloride complex (Scheme 3). Gratifyingly, ^{31}P NMR

Scheme 3. Preparation of the Gold(I) Complex 4



monitoring indicated that a clean reaction readily took place. Within 20 min at room temperature, **2** was completely consumed and complex **4** was formed as the sole product. Its ^{31}P NMR chemical shift (δ 65.6 ppm) falls in the typical range for [(R_3P)AuCl] complexes.[21] The formation of the expected compound **4** was further confirmed by HRMS as well as elemental analysis.

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The precise structure of **4** was further ascertained by X-ray crystallography (Figure 3). The gold is dicoordinate and only

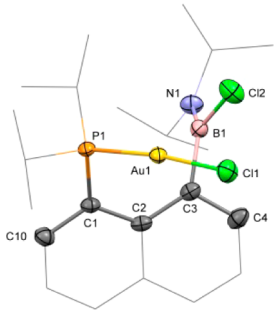


Figure 3. X-ray crystal structure of **4**. The *i*Pr groups and the naphthyl spacer are simplified, and the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−C1 1.829(2)(2), B1−Cl2 1.785(2), B1−C3 1.581(2), B1−N1 1.393(2), P1−Au1 2.238(1), Au1−Cl1 2.297(1); Cl2−B1−C3 118.3(1), Cl2−B1−N1 119.4(1), N1−B1−C3 121.2(1), P1−Au1−Cl1 173.06(2); P1−C1−C3−B1 −43.9(1), C3−C1−P1−Au1 −48.20(7).

slightly deviates from a linear geometry[22] (P−Au−Cl bond angle 173.1°). The borane moiety and AuCl fragment lie on both sides of the naphthyl bridge, with significant displacement of the C1P1 and C3B1 axes from the mean plane (by 15.2 and 22.2°, respectively) due to severe steric congestion. The boron center is trigonal planar ($\sum_{\alpha}$B = 358.9°) and remains far away from the gold atom (the AuB distance is very long at 3.608(2) Å), ruling out any conceivable Au→B interaction.[23] The π-donating amino substituent reduces the Lewis acidity of boron and does not favor its coordination to gold as a σ-acceptor ligand.[24] It is also worth mentioning that oxidative addition of the B−Cl bond to gold was not observed either, despite the P-chelation.[25,26]

Having prepared and characterized P-stabilized borenium cations featuring aryl and amino groups at boron, we then wondered if the same approach could be extended to alkylborenium cations. In comparison with aryl and amino substituents, alkyl groups are obviously weak donors (with only inductive effects and eventually hyperconjugation) and, in fact, only a very few alkylborenium cations have been reported so far (Figure 4).[27−29]

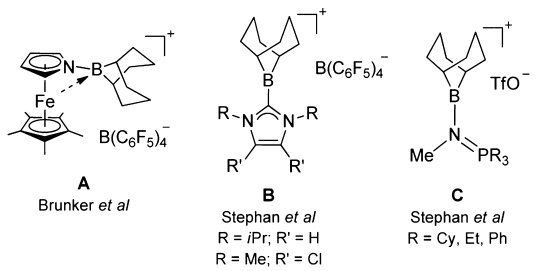
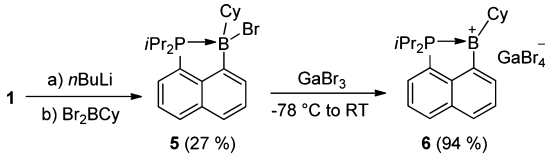


Figure 4. Known alkylborenium cations (9-BBN derivatives stabilized by azaferrocene, NHC, or phosphinimine Lewis bases).

In 2014, Brunker and co-workers explored the chemistry of pentamethylazaferrocene borenium cations and prepared the 9-borabicyclo[3.3.1]nonane (9-BBN) compound **A** by reacting the corresponding BH_2 borenium cation with 1,5-cyclooctadiene (double hydroboration).[27] The 9-BBN borenium cation **A** was characterized by means of ^{11}B NMR analysis (δ 68.0 ppm), and DFT calculations performed on the parent borenium cation indicated significant stabilization by electron donation from the N center and the Fe atom to boron. In parallel, Stephan et al. reported several NHC-stabilized 9-BBN borenium cations **B**.[28] They were synthesized by hydride abstraction, characterized by NMR spectroscopy as well as X-ray diffraction, and applied to metal-free imine hydrogenation catalysis. A series of phosphinimine-stabilized 9-BBN borenium cations **C** were also recently prepared by methylation of the corresponding N-boryl phosphinimines.[29] ^{11}B NMR spectroscopy and X-ray diffraction analyses indicated strong donation of the phosphinimine moiety to the boron center, resulting in significant B═N double-bond character and concentration of the positive charge at phosphorus. Thus, all known alkyl borenium cations derive from the bicyclic 9-borabicyclo[3.3.1]-nonane framework and involve extensive delocalization of the positive charge at boron toward a N-containing moiety (azaferrocene, NHC, or phosphinimine).

Starting from 1-iodo-8-(diisopropylphosphino)naphthalene (**1**),[11c] we targeted a P-stabilized borenium cation featuring a simple alkyl group at boron. First, the phosphine−alkylborane **5** was prepared in a way similar to that for **2**, using cyclohexyldibromoborane as an electrophile (Scheme 4). The

Scheme 4. Synthesis of the Cyclohexyl-Substituted P-Stabilized Borenium Salt 6 by Bromide Abstraction



presence of a strong P→B interaction both in solution and in the solid state is apparent from the ^{31}P (δ 16.4 ppm) and ^{11}B (δ 2.0 ppm) NMR chemical shifts, as well as the short P−B distance (2.021(3) Å) in the crystal structure.[16] The neutral closed form adopted by **5** confirms the key role played by the strongly π donating amino substituent in the open structure of **2** (no trace of an ion pair structure analogous to **3** was detected for **5**).

Then, compound **5** was treated with 1 equiv of $GaBr_3$ in toluene at room temperature. A clear yellow oil rapidly precipitated. After workup, the new compound **6** was obtained in 94% yield. Its ^{11}B NMR resonance signal at δ 76.9 ppm is consistent with the formation of a cationic tricoordinate boron center. Consistently, the ^{31}P NMR signal of **5** appears at δ 21.4 ppm. It is shifted downfield by 5.1 ppm from that of **5**, indicating some strengthening of the P→B interaction upon bromide abstraction at boron. The ^{1}H NMR spectrum also reveals the higher symmetry of **6** in comparison to that of **5**. The two isopropyl groups at phosphorus are magnetically equivalent in **6**, in line with the loss of chirality at boron induced by the change in coordination number (from tetra- to tricoordinate). Note also that the HRMS analysis of **6** (electrospray ionization) shows the isotopic peak expected for the P-stabilized cyclohexylborenium cation [iPr$_2$P(naph)-BCy]$^+$ at m/z 336.2289.

Single crystals of **6** suitable for X-ray diffraction analysis were obtained from a saturated dichloromethane solution at room temperature (Figure 5). The boron atom is tricoordinate (the shortest Br···B distance is as long as 4.287(5) Å and is in a planar environment ($\sum_{\alpha}$B = 359.9°). The P−B distance is

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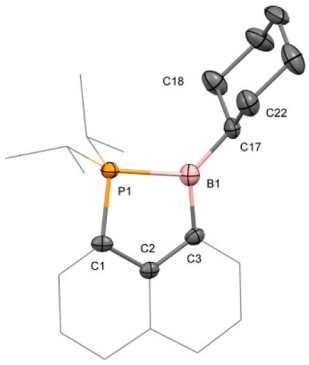

Figure 5. X-ray crystal structure of **6**. The *i*Pr groups and the naphthyl spacer are simplified, and the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−C1 1.793(4), C17−B1 1.535(6), B1−C3 1.521(6), P1−B1 2.004(4); C17−B1−C3 130.5(4), C3−B1−P1 100.7(3), C17−B1−P1 128.7(3), C22−C17−B1 112.7(3), C18−C17−B1 113.6(3); P1−C1−C3−B1 −9.5(2).

short at 2.004(4) Å, a value comparable to those found in related borenium cations featuring a mesityl or an amino group at boron (1.97−2.00 Å).[12b] It is likely that the length and strength of the P→B interaction in these cations are dictated by a combination of electronic and steric factors.[30] The mean plane of the cyclohexyl group is roughly perpendicular to that of the naphthyl spacer (83.1°), minimizing steric constraints. The boron atom sits in an equatorial position of the cyclohexyl chair.

■ CONCLUSION

The phosphino-naphthyl moiety has been shown to efficiently stabilize amino- and alkylborenium cations. The phosphine−aminochloroborane precursor **2** has been characterized in both its neutral open form and closed ion pair structure. Upon interacting with the adjacent boron center, the phosphorus atom induces B−Cl dissociation. The process is reversible and solvent dependent. Despite the rigidity of the naphthyl spacer, the steric hindrance around phosphorus, and its tendency to coordinate to boron, the phosphine group of **2** remains available for external reactivity, as shown by the formation of the gold(I) chloride complex **4**. Using the same approach, the cyclohexylborenium cation **6** was isolated and fully characterized. It is a rare example of an alkylborenium cation and the first not derived from the bicyclic 9-BBN framework. This work provides interesting insights into naphthyl-bridged P/B compounds and extends the variety of P-stabilized borenium cations. Future work will aim at exploiting this structural modularity to tune the Lewis acidity and reactivity of the boron center.

■ EXPERIMENTAL SECTION

General Experimental Considerations. All reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. All solvents were sparged with argon and dried using an MBRAUN Solvent Purification System (SPS). ^{1}H, ^{13}C, ^{11}B, and ^{31}P NMR spectra were recorded at 293 K on Bruker Avance 500, 400, and 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 (0 ppm), respectively. Mass spectra were recorded on a Waters LCT mass spectrometer. Dichloro(diisopropylamino)borane[31] was synthesized as previously described. Whenever possible, the purity of the new compounds was assessed by elemental analyses. Otherwise, the absence of detectable amounts of organic impurities was established by high-field multinuclear NMR spectroscopy.

Dibromocyclohexylborane. The synthesis was adapted from the literature procedure.[32] To a neat mixture of neat boron tribrmide (5.0 g, 20.0 mmol) and cyclohexene (2.02 mL, 20.0 mmol, 1 equiv) was added dropwise a solution of chlorodimethylsilane (2.22 mL, 20.0 mmol, 1 equiv) in pentane (10 mL) at −78 °C. The solution was then warmed slowly to room temperature and stirred at room temperature for an additional 9 h, giving a colorless solution. The volatiles were removed at room temperature under vacuum, and the desired dibromoborane was obtained as a colorless oil after vacuum distillation (63% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.15−2.01 (m, 11H, CH_{Cy}, CH_{2Cy}). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, δ): 26.3 (s, $CH_2(\delta)$), 26.5 (s, $CH_2(\beta$ or $\chi)$), 29.3 (s, $CH_2(\beta$ or $\chi)$), 43.7 (s br $CH(\alpha)$). $^{11}B\{^{1}H\}$ NMR (96 MHz, $CDCl_3$, δ): 66.3.

Compound 1. The synthesis was adapted from the literature procedure.[26a] A *n*BuLi solution (1.6 M in hexanes, 4.94 mL, 7.90 mmol, 1 equiv) was added dropwise to a 1,8-diiodonaphthalene solution (3.30 g, 7.90 mmol) in THF (100 mL) at −78 °C, and the reaction mixture was stirred for 1 h 30 min at this temperature. After the subsequent addition of chlorodiisopropylphosphine (1.26 mL, 7.90 mmol, 1 equiv), the reaction mixture was warmed to room temperature overnight. The volatiles were then removed under vacuum, and the residue was extracted with toluene (2 × 30 mL). The toluene solution was filtered over Celite and then concentrated until dryness, giving a yellow oil. The oil was finally dissolved in dichloromethane and filtered through a plug of silica. After removal of the volatiles under vacuum, the expected phosphine was obtained as a bright yellow oil in 90% yield. ^{1}H NMR (300 MHz, C_6D_6, δ): 0.94 (dd, 6H, $^{3}J_{HP}$ = 12.6 Hz, $^{3}J_{HH}$ = 6.9 Hz, CH_{3iPr}), 1.15 (dd, 6H, $^{3}J_{HP}$ = 13.6 Hz, $^{3}J_{HH}$ = 6.9 Hz, CH_{3iPr}), 2.09 (dsept, 2H, $^{2}J_{HP}$ = 2.2 Hz, $^{3}J_{HH}$ = 6.9 Hz, CH_{iPr}), 6.60 (pseudo-t, 1H, J = 7.7 Hz, H_{Naphth}), 7.13 (m, 1H, H_{Naphth}), 7.42 (m, 2H, H_{Naphth}), 7.63 (m, 1H, H_{Naphth}), 8.25 (dd, J = 7.4 Hz, $^{3}J_{HH}$ = 1.3 Hz, H_{Naphth}). $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, δ): −7.9.

Compound 2. A *n*BuLi solution (1.6 M in hexanes, 4.8 mL, 7.67 mmol, 1 equiv) was added dropwise to a solution of 1-iodo-8-(diisopropylphosphino)naphthalene (**1**; 2.84 g, 7.67 mmol) in diethyl ether (5 mL) at −50 °C with stirring. Stirring the reaction mixture for an additional 1 h at this temperature led to the precipitation of a yellow solid. The mother liquor was then eliminated via cannula, and the solid was washed with diethyl ether (5 mL). The solid was then dried under vacuum at room temperature and solubilized in toluene (10 mL) at −78 °C. Dichloro(diisopropylamino)borane (1.39 g, 7.67 mmol, 1 equiv) in solution in toluene (10 mL) was then added dropwise at the same temperature with stirring. After completion of the addition, the reaction mixture was warmed to room temperature overnight, giving a suspension that was filtered over Celite. The resulting toluene solution was concentrated to dryness, giving a yellowish solid. This solid was then washed with dichloromethane (2 × 5 mL), leading to the desired compound **2** as a white powder in 43% yield. Crystals suitable for X-ray diffraction analysis were obtained from a saturated toluene solution at room temperature. ^{1}H NMR (500 MHz, C_6D_6, δ): 0.63−1.54 (m, 24H, CH_{3iPr}), 2.02 (br, 2H, CH_{PiPr}), 3.56 (sept., 2H, $^{3}J_{HH}$ = 6.6 Hz, CH_{NiPr}), 7.29 (m, 1H, H_{Naphth}), 7.32 (m, 1H, H_{Naphth}), 7.49 (ddd, 1H, J_{HP} = 3.4 Hz, J_{HH} = 7.0 Hz, J_{HH} = 1.2 Hz, H_{Naphth}), 7.61 (d, 2H, J_{HH} = 7.4 Hz, H_{Naphth}), 7.68 (dd, 1H, J_{HH} = 8.2 Hz, J_{HH} = 1.2 Hz, H_{Naphth}). $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, δ): 19.8 (br, CH_{3PiPr}), 20.8 (br, 2C, CH_{3PiPr}), 20.9 (br, 2C, CH_{3NiPr}), 21.2 (br, CH_{3PiPr}), 23.3 (br 2C, CH_{3NiPr}), 27.1 (br, 2C, CH_{PiPr}), 48.9 (br, 2C, CH_{NiPr}), 125.0 (d, J_{CP} = 1.4 Hz, CH_{Naphth}), 125.8 (s, CH_{Naphth}), 129.0 (d, J_{CP} = 2.0 Hz, CH_{Naphth}), 130.4 (d, J_{CP} = 3.2 Hz, CH_{Naphth}), 130.7 (d, J_{CP} = 1.2 Hz, CH_{Naphth}), 131.2 (d, J_{CP} = 2.6 Hz, CH_{Naphth}), 134.6 (d, J_{CP} = 6.3 Hz, C_{quat}, 135.4 (d, J_{CP} = 9.4 Hz, C_{quat}), 140.6 (d, J_{CP} = 28.8 Hz, C_{quat}), 143.2 (br, B−C). $^{11}B\{^{1}H\}$ NMR (96 MHz, C_6D_6, δ): 33.3. $^{31}P\{^{1}H\}$ NMR (203 MHz, C_6D_6, δ): −11.8. HRMS (CI, CH_4): exact mass (monoisotopic) calcd for $[C_{22}H_{34}BNP]^+$, [M − Cl]$^+$, 354.2522; found, 354.2526.

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Compound 3. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$, δ): 37.2. $^{31}P\{^1H\}$ NMR (203 MHz, $CDCl_3$, δ): 11.3.

Compound 3′. Toluene (2 mL) was added at −78 °C to a neat mixture of **2** (100 mg, 0.26 mmol) and gallium trichloride (45.2 mg, 0.26 mmol, 1 equiv) with stirring. The resulting solution was warmed to room temperature over 20 min and was then concentrated, giving the expected compound as a white precipitate in 59% yield. Crystals suitable for X-ray diffraction analysis were obtained from a saturated dichloromethane solution at room temperature. Mp: 105.5 °C dec. ^1H NMR (400 MHz, $CDCl_3$, δ): 1.22 (dd, 6H, $^3J_{HP}$ = 19.1 Hz, $^3J_{HH}$ = 6.9 Hz, CH_{3PiPr}), 1.43 (dd, 6H, $^3J_{HP}$ = 16.8 Hz, $^3J_{HH}$ = 6.9 Hz, CH_{3PiPr}), 1.57 (d, 6H, $^3J_{HH}$ = 6.1 Hz, CH_{3NiPr}), 1.72 (d, 6H, $^3J_{HH}$ = 7.6 Hz, CH_{3NiPr}), 3.14 (dsept, 2H, $^3J_{HP}$ = 9.3 Hz, $^3J_{HH}$ = 6.9 Hz, CH_{PiPr}), 3.87 (dsept, 1H, $^4J_{HP}$ = 2.1 Hz, $^3J_{HH}$ = 6.1 Hz, CH_{NiPr}), 4.00 (s br, 1H, CH_{NiPr}), 7.80−7.90 (m, 2H, H_{Naphth}), 8.12 (ddd, 1H, $^3J_{HP}$ = 8.1 Hz, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.0 Hz, H_{Naphth}), 8.16 (d br, 1H, $^3J_{HH}$ = 8.2 Hz, H_{Naphth}), 8.27 (d, 1H, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.0 Hz, H_{Naphth}), 8.44 (d br, 1H, $^3J_{HH}$ = 7.0 Hz, H_{Naphth}). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 17.8 (d, 2C, $^2J_{CP}$ = 3.5 Hz, CH_{3PiPr}), 18.2 (s, 2C, CH_{3PiPr}), 22.6 (s br, 2C, CH_{3NiPr}), 23.2 (s br, 2C, CH_{3NiPr}), 24.1 (d, 2C, $^1J_{CP}$ = 33.6 Hz, CH_{PiPr}), 48.1 (s br, CH_{NiPr}), 64.2 (s br, CH_{NiPr}), 117.7 (d, $^1J_{CP}$ = 67.3 Hz, P−C_{Naphth}), 127.4 (d, J_{CP} = 9.8 Hz, CH_{Naphth}), 127.9 (d,. J_{CP} = 1.9 Hz, CH_{Naphth}), 131.8 (d, J_{CP} = 2.9 Hz, CH_{Naphth}), 132.2 (s, CH_{Naphth}), 132.8 (d, J_{CP} = 8.6 Hz, C_{quat}, 133.9 (d, J_{CP} = 2.6 Hz, CH_{Naphth}), 137.8 (s br, CH_{Naphth}), 149.1 (d, J_{CP} = 17.1 Hz, C_{quat}), the carbon atom in α position to boron is not observed. $^{11}B\{^1H\}$ NMR (96 MHz, CD_2Cl_2, δ): 37.9. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, δ): 13.0.

Compound 4. Dichloromethane (3 mL) was added to a mixture of **2** (300 mg, 0.77 mmol) and tetrahydrothiophene gold(I) chloride (321 mg, 0.77 mmol, 1 equiv) at −78 °C with stirring. The suspension was warmed to room temperature over 20 min, giving a colorless solution. This solution was concentrated, saturated with pentane, and filtered. Colorless crystals of the desired complex were obtained at −20 °C (90% yield). Mp: 184.2−195.9 dec. ^1H NMR (300 MHz, CD_2Cl_2, δ): 0.69 (d, 3H, J_{HH} = 6.5 Hz, CH_{3NiPr}), 0.76 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CH_{3NiPr}), 0.94−1.07 (m, 6H, CH_{3iPr}), 1.13 (dd, 3H, $^3J_{HP}$ = 17.6 Hz, $^3J_{HH}$ = 6.8 Hz, CH_{3PiPr}), 1.32−1.52 (m, 9H, CH_{3iPr}), 2.86 (m, 1H, CH_{iPr}), 3.00−3.25 (m, 2H, CH_{iPr}), 4.00 (m, 1H, CH_{iPr}), 7.53 (m, 2H, H_{Naphth}), 7.66 (dd, 1H, $^3J_{HH}$ = 7.1 Hz, J = 1.2 Hz, H_{Naphth}), 7.89 (d br, 1H, $^3J_{HH}$ = 8.0 Hz, H_{Naphth}), 8.00 (d br, 1H, $^3J_{HH}$ = 8.0 Hz, H_{Naphth}), 8.26 (dd, 1H, $^3J_{HH}$ = 7.1 Hz, J_{HP} = 15.8 Hz, H_{Naphth}). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 20 °C, δ): 19.6 (s br, 1C, CH_{3iPr}), 20.4 (d, J_{CP} = 5.6 Hz, 1C, CH_{3iPr}), 21.3 (s br, 1C, CH_{3iPr}), 21.6 (d, 1C, J_{CP} = 4.3 Hz, CH_{3iPr}), 22.3 (s br, 1C, CH_{3iPr}), 22.3 (s br, 1C, CH_{3iPr}), 22.8 (s br, 1C, CH_{3iPr}), 22.8 (s, 1C, CH_{3iPr}), 26.4 (d, 1C, $^1J_{CP}$ = 32.2 Hz, CH_{PiPr}), 27.9 (d, 1C, $^1J_{CP}$ = 31.5 Hz, CH_{PiPr}), 48.5 (s br, 1C, CH_{NiPr}), 50.7 (s br, 1C, CH_{NiPr}), 124.4 (d, 1C, J_{CP} = 13.0 Hz, CH_{Naphth}), 125.1 (d, 1C, $^1J_{CP}$ = 49.0 Hz, P−C_{Naphth}), 125.5 (s, 1C, CH_{Naphth}), 131.1 (d, J_{CP} = 2.7 Hz, 1C, CH_{Naphth}), 133.8 (s br, 1C, CH_{Naphth}), 134.5 (d, 1C, J_{CP} = 2.9 Hz, CH_{Naphth}), 135.0 (d, 1C, J_{CP} = 7.5 Hz, C_{quat}), 136.2 (d, 1C, J_{CP} = 6.7 Hz, C_{quat}), 139.3 (s br, 1C, CH_{Naphth}), the carbon in ipso position at boron is not observed. $^{11}B\{^1H\}$ NMR (96 MHz, CD_2Cl_2, δ): 35.4. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, δ): 65.6. HRMS (CI, CH_4): exact mass (monoisotopic) calcd for $[C_{22}H_{34}BPNAuCl]^+$, $[M - Cl]^+$, 586.1876; found, 586.1880. Anal. Calcd. for $C_{22}H_{34}BPNAuCl_2$; C, 42.47; H, 5.51; N, 2.25. Found: C, 42.25; H, 5.22; N, 2.18.

Compound 5. A *n*BuLi solution (1.6 M in hexanes, 2.45 mL, 3.93 mmol) was added dropwise to a solution of 1-iodo-8-(diisopropylphosphino)naphthalene (1.46 g, 3.93 mmol) in diethyl ether (10.5 mL) at −50 °C. Stirring the reaction mixture for an additional 1 h at this temperature led to the precipitation of a yellow solid. The mother liquor was then eliminated via cannula and the solid was solubilized in toluene (10.5 mL). The resulting solution was then cooled to −78 °C and a dibromocyclohexylborane (997.3 mg, 3.93 mmol) solution in toluene (10.5 mL) was added dropwise at the same temperature with stirring. The reaction mixture was warmed to room temperature overnight. The resulting suspension was then filtered over Celite, and the volatiles were removed under vacuum. The resulting residue was solubilized in the minimum amount of toluene, and this solution was placed at 0 °C, affording colorless crystals of the desired compound in 27% yield. Single crystals suitable for X-ray diffraction analysis were grown from a saturated benzene solution at room temperature. Mp: 128.7−130.2 °C. ^1H NMR (500 MHz, CD_2Cl_2, δ): 0.98 (m, 1H, CH_{Cy}), 1.07 (dd, 3H, $^3J_{HP}$ = 15.2 Hz, $^3J_{HH}$ = 7.1 Hz, CH_{3iPr}), 1.19−1.32 (m, 4H, CH_{2Cy}), 1.27 (dd, 3H, $^3J_{HP}$ = 15.8 Hz, $^3J_{HH}$ = 7.1 Hz, CH_{3iPr}), 1.35 (dd, 3H, $^3J_{HP}$ = 13.6 Hz, $^3J_{HH}$ = 7.1 Hz, CH_{3iPr}), 1.36 (dd, 3H, $^3J_{HP}$ = 14.8 Hz, $^3J_{HH}$ = 7.1 Hz, CH_{3iPr}), 1.62 (m, 1H, CH_{2Cy}), 1.70 (m, 1H, CH_{2Cy}), 1.74 (m, 1H, CH_{2Cy}), 1.77−1.85 (m, 2H, CH_{2Cy}), 1.99 (m, 1H, CH_{2Cy}), 2.73 (dsept, 1H, $^2J_{HP}$ = 8.1 Hz, $^3J_{HH}$ = 7.1 Hz, CH_{iPr}), (dsept, 1H, $^2J_{HP}$ = 12.1 Hz, $^3J_{HH}$ = 7.1 Hz, CH_{iPr}), 7.54−7.60 (m, 2H, H_{Naphth}), 7.68−7.74 (m, 2H, H_{Naphth}), 7.77 (dm, 1H, $^3J_{HH}$ = 6.9 Hz, H_{Naphth}), 7.77 (ddd, 1H, $^3J_{HH}$ = 8.3 Hz, J_{HP} = 1.2 Hz, $^4J_{HH}$ = 0.9 Hz, H_{Naphth}). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, δ): 17.9 (s, CH_{3iPr}), 18.0 (d, $^2J_{CP}$ = 2.6 Hz, CH_{3iPr}), 18.1 (d, $^2J_{CP}$ = 3.6 Hz, CH_{3iPr}), 18.8 (s, CH_{3iPr}), 22.4 (d, $^1J_{CP}$ = 25.4 Hz, CH_{iPr}), 23.8 (d, $^1J_{CP}$ = 30.7 Hz, CH_{iPr}), 27.6 (s, CH_{2Cy}), 28.8 (d, J_{CP} = 1.2 Hz, CH_{2Cy}), 29.0 (s, CH_{2Cy}), 30.0 (d, J_{CP} = 9.8 Hz, CH_{2Cy}), 31.5 (br, CH_{Cy}), 33.9 (d, J_{CP} = 3.8 Hz, CH_{2Cy}), 125.2 (d, J_{CP} = 1.4 Hz, CH_{Naphth}), 125.5 (d, $^1J_{CP}$ = 54.7 Hz, P−C_{Naphth}), 125.8 (d, J_{CP} = 7.9 Hz, CH_{Naphth}), 128.2 (d, J_{CP} = 2.4 Hz, CH_{Naphth}), 128.9 (s, CH_{Naphth}), 130.6 (d, J_{CP} = 13.6 Hz, CH_{Naphth}), 131.5 (d, J_{CP} = 2.4 Hz, CH_{Naphth}), 132.5 (d, J_{CP} = 8.8 Hz, C_{quat}), 143.8 (d, J_{CP} = 24.8 Hz, C_{quat}), 152.0 (br, B−C_{Naphth}). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, δ): 2.0. $^{31}P\{^1H\}$ NMR (203 MHz, CD_2Cl_2, δ): 16.4. HRMS (CI, CH_4): exact mass (monoisotopic) calcd for $[C_{22}H_{30}BBrP]^+$, $[M-H]^+$, 415.1362; found, 415.1380. Anal. Calcd. for $C_{22}H_{31}BBrP$; C, 63.34; H, 7.49. Found: C, 63.08; H, 7.46.

Compound 6. Toluene (1 mL) was added to a neat mixture of **5** (18.4 mg, 0.044 mmol) and gallium tribromide (13.7 mg, 0.44 mmol, 1 equiv) at room temperature, leading to the precipitation of a clear yellow oil. After 10 min of stirring at the same temperature, the mother liquor was removed via syringe and the oil was dried under vacuum, giving the desired compound as a clear yellow oil in 94% yield. Crystals suitable for X-ray diffraction analysis were obtained from a saturated solution in dichloromethane at room temperature. ^1H NMR (500 MHz, $CDCl_3$, δ): 1.28 (dd, 6H, $^3J_{HP}$ = 19.4 Hz, $^3J_{HH}$ = 7.1 Hz, CH_{3PiPr}), 1.36 (dd, 6H, $^3J_{HP}$ = 17.6 Hz, $^3J_{HH}$ = 7.1 Hz, CH_{3PiPr}), 1.46 (pseudo tt, 1H, J_{HH} = 12.6 Hz, J_{HH} = 3.1 Hz, CH_{2Cy}), 1.55 (m, 2H, CH_{2Cy}), 1.69 (pseudo qd, 2H, J_{HH} = 12.4 Hz, J_{HH} = 3.0 Hz, CH_{2Cy}), 1.89 (m, 1H, CH_{2Cy}), 1.98 (m, 2H, CH_{2Cy}), 2.12 (m, 2H, CH_{2Cy}), 2.69 (dtt, 1H, J_{HP} = 15.8 Hz, J_{HH} = 12.2 Hz, J_{HH} = 2.8 Hz, CH_{Cy}), 3.26 (dsept, 2H, $^2J_{HP}$ = 10.4 Hz, $^3J_{HH}$ = 7.1 Hz, CH_{iPr}), 7.92−8.00 (m, 2H,, H_{Naphth}), 8.24 (dd, 1H, J_{HP} = 8.0 Hz, $^3J_{HH}$ = 7.3 Hz, H_{Naphth}), 8.34 (d, 1H, $^3J_{HH}$ = 8.7 Hz, H_{Naphth}), 8.50 (d, 1H, $^3J_{HH}$ = 8.7 Hz, H_{Naphth}), 8.62 (d, 1H, $^3J_{HH}$ = 6.7 Hz, H_{Naphth}). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, δ): 17.9 (d, 2C, $^2J_{CP}$ = 3.0 Hz, CH_{3PiPr}), 18.1 (s, 2C, CH_{3iPr}), 22.9 (d, 2C, $^1J_{CP}$ = 32.1 Hz, CH_{iPr}), 26.2 (s, $CH_{2Cy(\delta\text{-}B)}$), 27.0 (s, 2C, CH_{2Cy}), 29.7 (d, 2C, J_{CP} = 3.1 Hz, CH_{2Cy}), 35.4 (d, $^2J_{CP}$ = 12.8 Hz, CH_{Cy}), 118.0 (d, $^1J_{CP}$ = 66.7 Hz, P−C_{Naphth}), 128.6 (d, J_{CP} = 9.6 Hz, CH_{Naphth}), 128.7 (s br, CH_{Naphth}), 132.5 (d, J_{CP} = 8.9 Hz, C_{quat}), 132.8 (d, J_{CP} = 3.1 Hz, CH_{Naphth}), 133.6 (d, J_{CP} = 2.7 Hz, CH_{Naphth}), 138.7 (dm, J_{CP} = 11.5 Hz, CH_{Naphth}), 139.0 (d br, J_{CP} = 27.6 Hz, B−C_{Naphth}), 139.2 (s, CH_{Naphth}), 150.6 (d, J_{CP} = 20.4 Hz, C_{quat}). $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, δ): 76.9. $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, δ): 21.4. HRMS (ESI): exact mass (monoisotopic) calcd for $[C_{22}H_{31}BP]^+$, $[M]^+$, 336.2293; found, 336.2289.

Crystal Structure Analyses. The data were collected at low temperature (173(2) or 193(2) K) on a Bruker-AXS APEX II QUAZAR diffractometer equipped with a 30 W air-cooled microfocus source (**3′** and **4**−**6**) or on a Bruker-AXS PHOTON100 D8 VENTURE diffractometer (**2**), using Mo Kα radiation (λ = 0.71073 Å). φ and ω scans were used. An empirical absorption correction with SADABS was applied.[33] The structures were solved by direct methods (SHELXS-97)[34] and refined using the least-squares method on F^2. All non-H atoms were refined with anisotropic displacement parameters. The H atoms on carbon atoms were refined isotropically at calculated positions using a riding model. For **6**, the investigated crystal was twinned. The twin law was determined using TwinRotMat implemented in PLATON5.[35] A refinement with the HKLF 5 option

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of the SHELXL97[34] program was used, and in the final refinement the BASF parameter converges to 0.36.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00737.

NMR spectra and crystallographic data for compounds **2**, **3**, **3′**, and **4**−**6** and computational data (PDF)

Crystallographic data for CCDC 1501657 (**2**), 1501658 (**3′**), 1501659 (**4**), 1501660 (**5**), and 1501661 (**6**) (CIF)

Cartesian coordinates for the calculated structures (XYZ)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for D.B.: dbouriss@chimie.ups-tlse.fr.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

FLP, frustrated Lewis pair; NHC, N-heterocyclic carbene; NMR, nuclear magnetic resonance

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