Chapter 2. Bis(phosphino)borates: a new family of monoanionic chelating phosphine ligands

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2.1. Introduction

Phosphines, perhaps more than any other single ligand class, play a central role in both organic and inorganic chemistry.[1] Little attention, however, has focused on anionic derivatives of these popular ligands.[2-8] To expand the range of anionic bis(phosphines), our group recently introduced the anionic bis(phosphino)borate ligand [Ph_2BP_2] ([Ph_2BP_2] = [$Ph_2B(CH_2PPh_2)_2]^-$).[9,10] The [Ph_2BP_2] ligand is unique in that it preserves the essential properties of a neutral bis(phosphine) chelate while also being anionic in nature. Its chemical properties derive in part from the borate charge covalently attached to the alkyl chain of the ligand backbone (Figure 2.1).

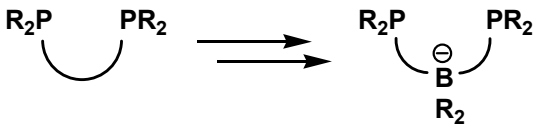


Figure 2.1. Development of anionic bidentate phosphines by covalently linking a borate into the ligand.

Use of an anionic borate unit to template di- and tripodal donor ligands has been widely exploited since Trofimenko's early work.[11] The (phosphino)borate ligands are distinct, however, in that they introduce electronic and steric properties chemically divergent from previous borate-based systems. Moreover, despite the diverse areas to which they might be applied, the chemistry of (phosphino)borate ligands is essentially unexplored. To make these ligand systems more synthetically accessible, we have initiated studies to develop reliable protocols for their synthesis. In this context, this chapter describes detailed methods for the preparation of a series of bis(phosphino)borate ligands containing diverse electronic and steric properties. Certain methods that met with limited success are noted as this type of information will likely prove useful in the continued development of this promising ligand family.

The general method chosen for preparing bis(phosphino)borate ligands relies on the delivery of a phosphinoalkyl carbanion to a borane electrophile. The advantage of this strategy is its convergent approach: many borane electrophiles and appropriate carbanions are synthetically accessible. Also, the synthesis of borate-based ligands by nucleophilic addition to borane precursors has precedence in the literature,[12,13] Riordan's recent work being perhaps most related.

The synthesis of (phosphino)borate ligands required a survey of conditions compatible with clean phosphine carbanion delivery to haloborane reagents due to the possibility of kinetically problematic side reactions. While we have yet to establish a truly general strategy since phosphines like those described herein require somewhat customized methods of synthesis, significant progress towards a simple and generally effective approach to these bidentate systems has been realized. Reaction solvents, reaction temperatures, and the use of phosphine-protecting groups are among the variables we consider in the present study. Cation exchange protocols are also emphasized as we have found specific salt derivatives to be synthetically useful in separate ongoing work.

In the results that follow, we discuss how each of the bis(phosphino)borates shown in Figure 2.2 was prepared, adhering to the following format for presenting this data:

(i) Methodology for generating diarylchloroborane electrophiles of the form R_2BCl;

(ii) Methodology for generating phosphine carbanions of the general form "$R_2PCH_2^-$" including the potential synthetic advantages/disadvantages of phosphine-protection protocols;

(iii) Generation of lithium salts of the form $[R_2B(CH_2PPh_2)_2][Li]$;

(iv) Generation of lithium salts of the form $[Ph_2B(CH_2PR_2)_2][Li]$;

(v) Methodology for generating synthetically useful ammonium and thallium salts of bis(phosphino)borates.

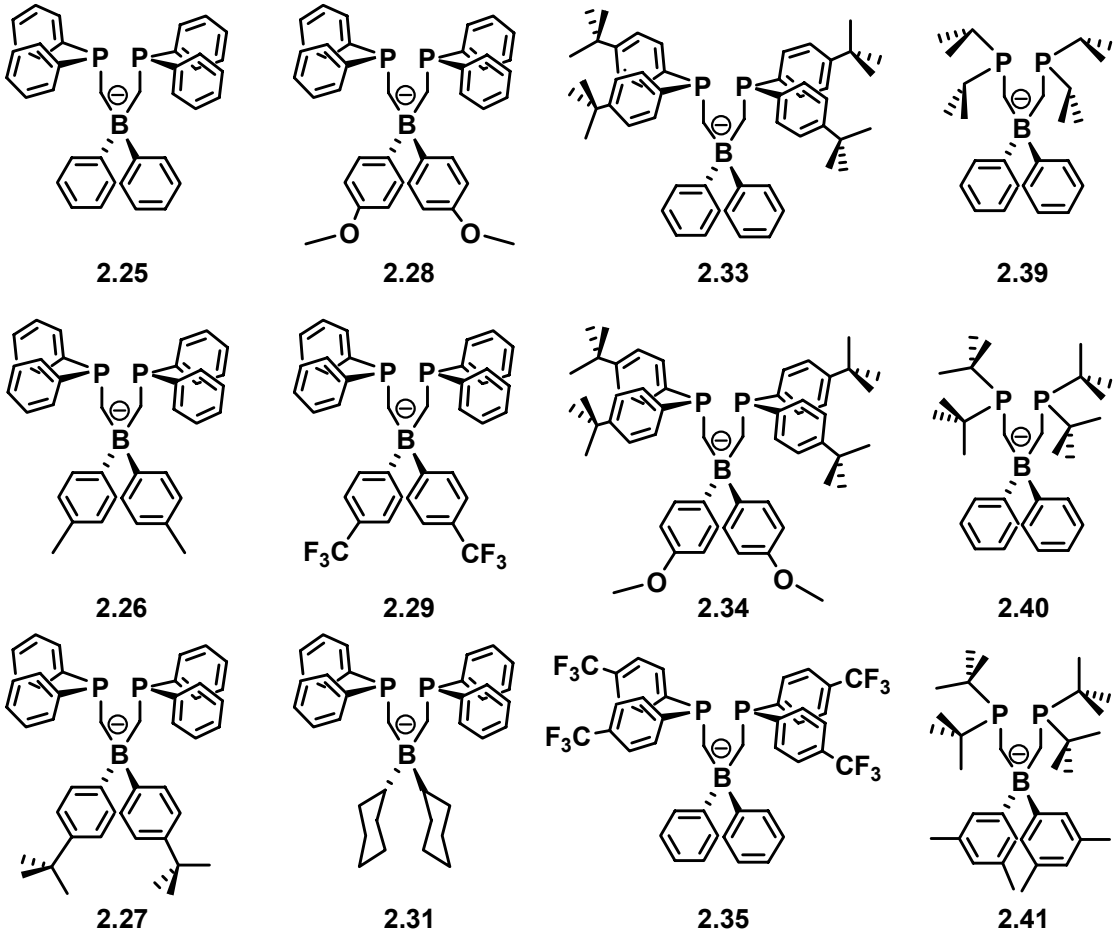


Figure 2.2. Representative drawings of the bis(phosphino)borates discussed.

2.2. Results and discussion

2.2.1. Boron synthons

It was desirable to preferentially study aryl-containing borates due to their typically enhanced stability[14] compared to alkyl borates. We therefore chose to pursue the use of diarylhaloborane synthons. Arylhaloboranes have been prepared previously by a variety of methods,[15-20] the most common of which rely on metathesis of haloboranes with aryl tin reagents. Since detailed methods for the direct and efficient synthesis of a variety of diarylhaloboranes have not been previously described, experimental procedures for the production of several R_2BCl reagents are provided herein. We acknowledge an important lead from the laboratories of Chivers[19a] and Piers,[19b] who provided a reliable method for the preparation of $(C_6F_5)_2BCl$ from disproportionation of $Me_2Sn(C_6F_5)_2$ and BCl_3.

The first step in a two-step procedure required the preparation of dimethyldiaryltin reagents, many of which have been described in the literature previously.[21-28] A wide variety of dimethyldiaryltin reagents are readily synthesized from dimethyltindichloride and an appropriate aryl-Grignard or aryl-lithium reagent. These reactions result in high isolated yields of dimethyldiaryltin compounds Me_2SnR_2 (R = Ph (**2.1**),[21-24] *p*-MePh (**2.2**),[21-23,25] *m,m*-$(CH_3)_2$Ph (**2.3**), *p*-^{t}BuPh (**2.4**),[26] *p*-MeOPh (**2.5**),[22,23,27] *p*-CF_3Ph (**2.6**),[22] *o*-MeOPh (**2.7**),[23] *o,o*-$(MeO)_2$Ph (**2.8**),[28] *o*-CF_3Ph (**2.9**)). In our hands, alkyl, ether, and fluoro substituted diaryl tin reagents were successfully prepared (Figure 2.3).

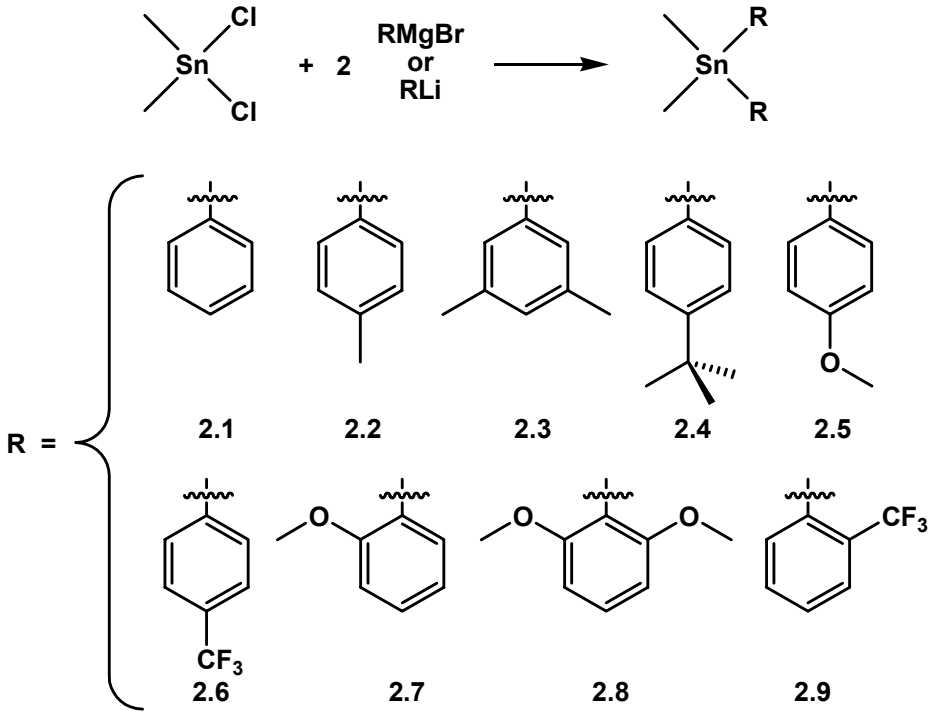


Figure 2.3. Preparation of dimethyldiaryltin reagents containing various functional aryl groups.

In a second step, diarylchloroboranes were generated using modified conditions of the Chivers/Piers methodology. A heptane solution of BCl_3 was introduced into a sealable reaction vessel containing the dimethyldiaryltin reagent in heptane. The sealed vessel was then heated in an oil bath maintained at 100 ºC for 24 to 72 h, depending on the tin reagent used. Use of a heptane solution at 100 ºC was chosen for reasons of simplicity and safety: previous methods employed hexanes at temperatures exceeding the boiling point of the solvent in a closed system, which we preferred to avoid. Additionally, BCl_3 can be purchased commercially as a heptane solution. The necessary reaction time was dependent upon the electronic nature of the aryl substituent: electron-poor aromatics required longer reaction times to reach completion, whereas electron-rich aromatics transferred more quickly. These observations are consistent with an electrophilic attack by the boron center on the aryl ring. Cooling of the vessel resulted in

the spontaneous crystallization of the dimethyltindichloride byproduct, which provided for easy recovery of this somewhat expensive and toxic starting material. The recovered Me_2SnCl_2 was collected by filtration and then purified for reuse via subsequent sublimation. Removal of the reaction volatiles from the resultant solution under reduced pressure at ambient temperature provided the desired diarylchloroborane reagents, typically in very pure form. Where necessary, we have found that the isolated borane product can be recrystallized from hydrocarbon solutions (e.g., petroleum ether, hexanes). Yields for these preparations when carried out on 5 to 10 g scales were greater than 70% for all but one case (Figure 2.4). In addition to the unsubstituted aryl borane Ph_2BCl (**2.10**),[15,16] we have successfully produced substituted diarylchloroboranes using this methodology incorporating either electron-donating ((*p*-$MePh)_2BCl$, **2.11**;[16,17] (*p*-^{t}$BuPh)_2BCl$, **2.13**; (*p*-$MeOPh)_2BCl$, **2.14**[16,18]) or electron-withdrawing ((*p*-$CF_3Ph)_2BCl$, **2.15**) substituents at the *para* position. Additionally, the *meta* substituted borane (*m,m*-$(CH_3)_2Ph)_2BCl$ (**2.12**) was prepared by the same method. Substitution at the *ortho* position has proven more problematic. For example, attempts to incorporate *ortho* substituted methoxy aryl groups resulted in cleavage at the aryl methyl ether linkage, generating complex reaction mixtures. Given the known ability of Lewis acidic haloboranes to cleave ethers, particularly methyl aryl ethers,[29] this was not surprising. Attempts to place a sterically encumbering CF_3 group in an *ortho* position were also unsuccessful.

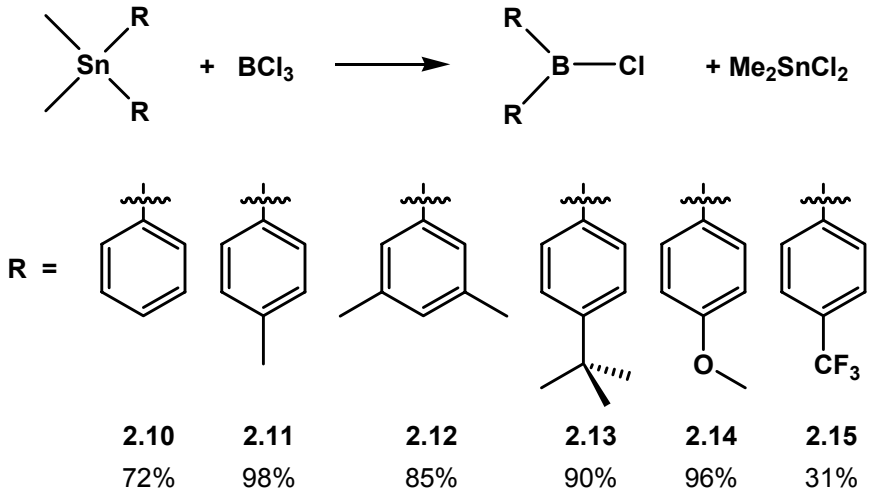
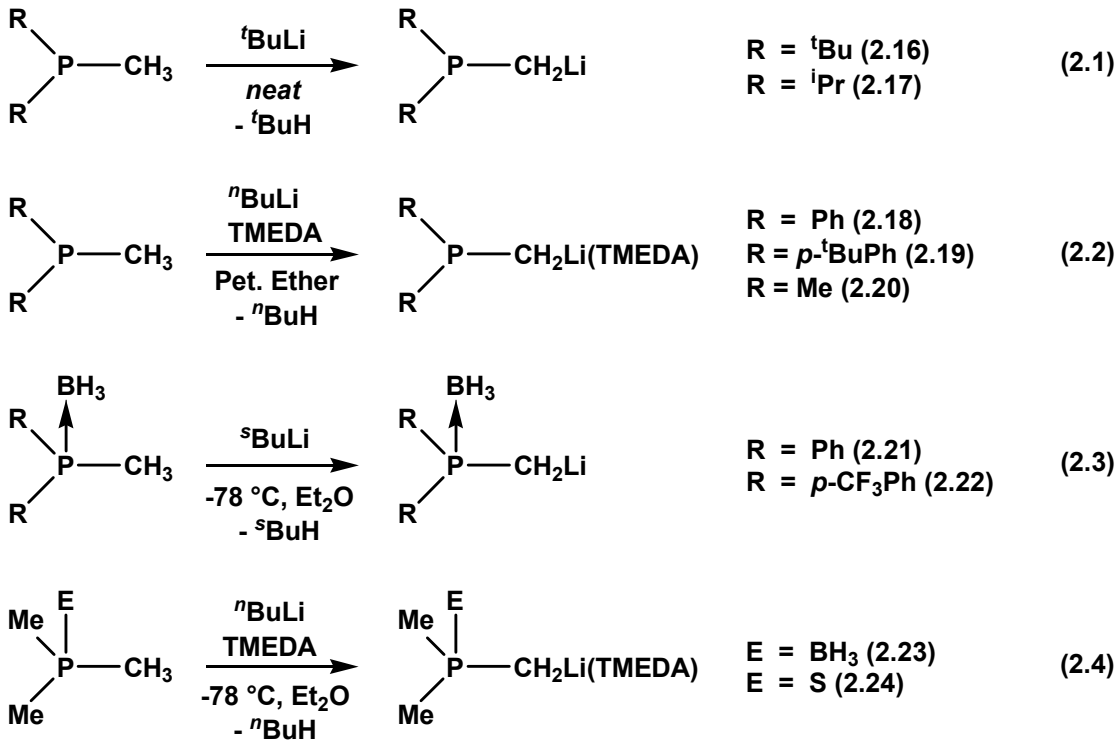


Figure 2.4. Preparation of diarylchloroboranes containing various functional aryl groups.

2.2.2. Phosphine synthons

The lithiation of unprotected dialkyl- and diarylmethyl phosphines has been studied previously, most notably by the collective efforts of Karsch, Schmidbaur, Peterson, and Schore.[30,31] Karsch and Schmidbaur have described the deprotonation of $^{t}Bu_2PMe$ and PMe_3 to prepare $^{t}Bu_2PCH_2Li$ (**2.16**) and Me_2PCH_2Li(TMEDA) (**2.20**) respectively (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine). We have found that lithiation of $^{i}Pr_2PMe$ can be achieved using conditions similar to those employed by Karsch for the deprotonation of $^{t}Bu_2PMe$. Thus, reaction of neat $^{i}Pr_2PMe$ with desolvated $^{t}BuLi$ at 60 ºC for 24 h provided white solids that, after washing with petroleum ether, reacted cleanly as $^{i}Pr_2PCH_2Li$ (**2.17**) (eq 2.1). With respect to diarylmethyl phosphines, Peterson and Schore demonstrated that deprotonation of Ph_2PMe was accomplished most effectively using $^{n}BuLi$ in the presence of TMEDA, thereby producing Ph_2PCH_2Li(TMEDA) (**2.18**). By analogy, the alkyl-substituted diarylmethyl phosphine (p-$^{t}BuPh)_2PMe$ deprotonated smoothly using similar conditions to precipitate (p-$^{t}BuPh)_2PCH_2Li$(TMEDA) (**2.19**) as a yellow solid (eq 2.2). As a

cautionary note, we have found that methyl-substituted arylphosphines, such as $(2,4,6\text{-}Me_3Ph)_2PMe$, can undergo competitive lithiation at the methyl positions of the aryl rings. Additionally, attempts to deprotonate $(p\text{-}CF_3Ph)_2PMe$ by this method led to extensive decomposition.



The deprotonation of tertiary phosphines protected by BH_3[32,33] and S[34] has also been studied due to its synthetic utility with respect to preparing chiral phosphines, as was first exemplified by Imamoto and coworkers. The advantage of phosphine protection is that, owing to its increased acidity, the methyl group undergoes deprotonation much more rapidly. For example, the deprotonation of $Ph_2(BH_3)PCH_3$, $(p\text{-}CF_3Ph)_2(BH_3)PCH_3$, and $Me_2(BH_3)PCH_3$ proceeded cleanly at -78 ºC in ethereal solution over the course of a few hours using ^{s}BuLi or ^{n}BuLi/TMEDA, generating $Ph_2(BH_3)PCH_2Li$ (**2.21**) (eq 2.3), $(p\text{-}CF_3Ph)_2(BH_3)PCH_2Li$ (**2.22**) (eq 2.3), and $Me_2(BH_3)PCH_2Li(TMEDA)$ (**2.23**) *in situ* (eq 2.4). Similarly, deprotonation of sulfur-

protected $Me_2(S)PCH_3$ using ^{n}BuLi/TMEDA at -78 ºC provided $Me_2(S)PCH_2Li(TMEDA)$ (**2.24**) *in situ* (eq 2.4). For cases where the reaction of unprotected phosphines with boranes led to undesirable results, the ease of synthesis of these reagents makes them attractive carbanion synthons.

2.2.3. Bis(phosphino)borates: substitution at boron

The synthesis of bis(phosphino)borate ligands was accomplished in a straightforward manner by condensation of the lithio phosphine reagents with borane electrophiles. To examine the generality of this approach, we first studied the condensation of $Ph_2PCH_2Li(TMEDA)$ (**2.18**) with several different borane electrophiles. The reaction between **2.18** and a diarylchloroborane in general proceeded cleanly under a single reaction condition (Et_2O/toluene, -78 ºC to room temperature). Only the fluorine-containing borane **2.15** showed any propensity to form undesired side-products under these conditions. Thus, the preparation of bis(phosphino)borate ligands from functionalized diarylchloroboranes was achieved by reaction of two equivalents of **2.18** with **2.10**, **2.11**, **2.13**, **2.14**, and **2.15**, to generate $[Ph_2B(CH_2PPh_2)_2][Li(TMEDA)_x]$ (**2.25**[Li]), $[(p\text{-}MePh)_2B(CH_2PPh_2)_2][Li(TMEDA)_x]$ (**2.26**[Li]), $[(p\text{-}^{t}BuPh)_2B(CH_2PPh_2)_2][Li(TMEDA)_x]$ (**2.27**[Li]), $[(p\text{-}MeOPh)_2B(CH_2PPh_2)_2][Li(TMEDA)_x]$ (**2.28**[Li]), and $[(p\text{-}CF_3Ph)_2B(CH_2PPh_2)_2][Li(TMEDA)_x]$ (**2.29**[Li]). In general, $^{31}P\{^{1}H\}$ NMR spectra of the crude reaction mixtures established successful syntheses and yields as well as reaction times. Most of the Li(TMEDA) salts of the bis(phosphino)borates described above showed some solubility in a range of solvents, including toluene, THF, CH_3CN, acetone, and ethanol. The ether- and perfluoroalkyl-substituted derivatives **2.28** and **2.29** showed greater solubility in Et_2O and benzene. We note that all of the bis(phosphino)borate

ligands, including those described below, are incompatible with the halogenated solvents $CHCl_3$ and CH_2Cl_2.

Since it had been described in the literature, we attempted to prepare a bis(phosphino)borate using the perfluoronated diaryl borane $(C_6F_5)_2BCl$. Direct reaction of two equivalents of $Ph_2PCH_2Li(TMEDA)$ (**2.18**) with $(C_6F_5)_2BCl$ at low temperature formed a large number of uncharacterized products as observed in the $^{31}P\{^1H\}$, $^{11}B\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectra of the reactions. The presence of new fluorine containing products that were not consistent with the C_6F_5 group suggested that the carbanion **2.18** was too reactive. Accordingly, two equivalents of $Ph_2(BH_3)PCH_2Li$ (**2.21**) reacted with $(C_6F_5)_2BCl$ at -78 °C to cleanly generate $[(C_6F_5)_2B\{CH_2P(BH_3)(Ph)_2\}_2][Li(solvent)_x]$ (**2.30**·BH_3[Li]), which was characterized by $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectroscopy. The deprotection of **2.30**·BH_3[Li] was not studied; however, we suspect that the presence of the perfluoronated aryl groups ought to increase the ease of deprotection (*vide infra*).

Several commercially available borane reagents were examined for their ability to generate bis(phosphino) borates. For example, the synthon bis(cyclohexyl)chloroborane also provided successful entry into bis(phosphino)borate chemistry. Using the same methodology as for $[Ph_2BP_2]$, the analogous ligand $[Cy_2B(CH_2PPh_2)_2][Li(TMEDA)_x]$ (**2.31**[Li]) was prepared. Preparation proceeded cleanly, and the product was purified for use by washing with petroleum ether. Further purification to remove any remaining lithium chloride salts was achieved by crystallization of **2.31**[Li] from diethyl ether or toluene at -30 ºC. An attempt to incorporate another commercially available borane reagent, Mes_2BF (Mes = 2,4,6-Me_3Ph), proved unsuccessful. The absence of reactivity under the conditions examined is most likely due to the high degree of steric hindrance at

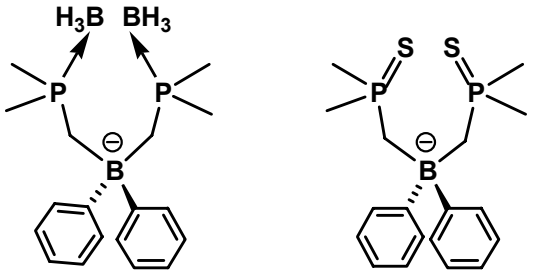
boron. Finally, the non-halogenated borane precursor, *B*-methoxy-9-BBN (9-methoxy-9-borabicyclo[3.3.1]nonane), was cursorily examined. The reaction of a 1.0 M hexanes solution of *B*-methoxy-9-BBN with two equivalents of $Ph_2PCH_2Li(TMEDA)$ (**2.18**) in diethyl ether at -78 °C provided white solids containing a mixture of two products as determined by $^{31}P\{^1H\}$ and $^{11}B\{H\}$ NMR spectroscopy. The products are consistent with the formation of $[BBN\text{-}B,B\text{-}(CH_2PPh_2)_2][Li(TMEDA)_x]$ (**2.32**[Li]) and $[BBN\text{-}B\text{-}(CH_2PPh_2)\text{-}B\text{-}(OMe)][Li(TMEDA)_x]$ based on the $^{11}B\{H\}$ NMR spectrum of the mixture. Thus, it appears that boronic esters may be suitable reagents for the preparation of (phosphino)borates.

2.2.4. Bis(phosphino)borates: substitution at phosphorus

We next examined the reactivity of several R_2PCH_2Li reagents with borane electrophiles. Substituted aryl groups can provide different electronic and steric environments around a coordinated metal in addition to variable solubility. Two substituted methyldiaryl phosphines were examined. Reaction of two equivalents of $(p\text{-}^tBuPh)_2PCH_2Li(TMEDA)$ (**2.19**) with either Ph_2BCl (**2.10**) or $(p\text{-}MeOPh)_2BCl$ (**2.14**) under the previously described conditions resulted in the generation of $[Ph_2B\{CH_2P(p\text{-}^tBuPh)_2\}_2][Li(TMEDA)_x]$ (**2.33**[Li]) and $[(p\text{-}MeOPh)_2B\{CH_2P(p\text{-}^tBuPh)_2\}_2][Li(TMEDA)_x]$ (**2.34**[Li]). We also inspected the fluorine-containing synthon $(p\text{-}CF_3Ph)_2PCH_3$ (**2.43**) to generate bis(phosphino)borates. Since direct lithiation of this phosphine was unsuccessful (*vide supra*), a borane protection strategy was used. Generation of $(p\text{-}CF_3Ph)_2(BH_3)PCH_3$ (**2.44**) proceeded readily by addition of $BH_3{\cdot}SMe_2$ to **2.43**. Subsequent deprotonation of **2.44** (^{s}BuLi at -78 ºC over 2 h) followed by addition of Ph_2BCl (**2.10**) provided the protected bis(phosphino)borate $[Ph_2B\{CH_2P(p\text{-}CF_3Ph)_2(BH_3)\}_2][Li]$ (**2.35**$\cdot BH_3$[Li]). Removal of

the BH_3 protecting groups was accomplished by dissolution of **2.35**·BH_3 in neat morpholine at 60 ºC for 12 h, generating $[Ph_2B\{CH_2P(p\text{-}CF_3Ph)_2\}_2][Li]$ (**2.35**[Li]). The reaction of $(p\text{-}CF_3Ph)_2(BH_3)PCH_2Li$ (**2.22**), generated *in situ* at -78 °C, with $(C_6F_5)_2BCl$ was also examined. The major reaction product appears to be $[(C_6F_5)_2B\{CH_2P(p\text{-}CF_3Ph)_2(BH_3)\}_2][Li(solvent)_x]$ (**2.36**·BH_3[Li]) based on $^{31}P\{^1H\}$, $^{19}F\{^1H\}$, and $^{11}B\{H\}$ NMR spectroscopy. Deprotection of the phosphines could be accomplished over three days by dissolving **2.36**·BH_3[Li] in morpholine at ambient temperature, although a second product was observed as a result of the deprotection.

We also desired to extend our ability to substitute bis(phosphino)borate ligands by examining alkyl substituents on phosphorus. To this end, we attempted to prepare the methyl-substituted derivative $[Ph_2B(CH_2PMe_2)_2]^-$. Direct reaction of Me_2PCH_2Li(TMEDA) (**2.20**) with Ph_2BCl (**2.10**) resulted in the formation of multiple products. We presume this to be due to the competitive formation of Lewis acid/base complexes that prevent nucleophilic carbanion addition to the borane center. Karsch *et al.* have reported similar results using aluminum electrophiles. In accord with this suggestion, the BH_3-protected carbanion, $Me_2(BH_3)PCH_2Li$(TMEDA) (**2.23**), reacted productively with **2.10** to produce the desired borate $[Ph_2B\{CH_2P(BH_3)(Me)_2\}_2][Li(TMEDA)_x]$ (**2.37**) (Figure 2.5). Likewise, the *in situ*-generated sulfur-protected reagent, $Me_2(S)PCH_2Li$ (**2.24**), reacted cleanly to afford $[Ph_2B\{CH_2P(S)(Me)_2\}_2]$ (**2.38**) (Figure 2.5), a potential S-donor ligand on its own.



2.37 2.38

Figure 2.5. Protected alkyl bis(phosphino)borates **2.37** and **2.38**.

Attempts to deprotect either the borane- or sulfur-protected borates **2.37** and **2.38** have met with very limited success. For example, to deprotect **2.37**, many literature protocols were examined for deprotecting phosphine-boranes. These included heating borane-protected **2.37** in neat morpholine or diethylamine, refluxing **2.37** in toluene with an excess of DABCO,[35] reacting **2.37** with $HBF_4{\cdot}Me_2O$,[36] and attempting to reduce **2.37** using Pd/C in ethanol.[37] Additionally, heating **2.37** in toluene with an excess of PMe_3 or in neat $^{n}Bu_3P$ was examined. None of these methods were successful in that, even for those methods that did evince some degree of productive deprotection, isolation of synthetically viable sources of the deprotected $[Ph_2B(CH_2PMe_2)_2]^-$ could not be accomplished. Likewise, either decomposition or no reaction at all resulted for the attempted deprotection of **2.38** using previously reported routes, such as $Cl_3SiSiCl_3$,[38] $MeOTf/(Me_2N)_3P$,[39] $MeOTf/RS^-$,[40] lithium aluminum hydride in refluxing dioxane,[41] and $^{n}Bu_3P$.[42] Also, attempts to reduce **2.38** with sodium naphthalide,[43] or magnesium anthracene were equally unsuccessful. In general, we therefore note that direct deprotection of the alkyl-substituted (phosphino)borate ligands was far more challenging than deprotection of the corresponding aryl-substituted derivatives. This is presumably due to the thermodynamic stability of the anionic (alkylphosphino)borate-to-borane adduct complexes.

Because the methyl-substituted phosphines proved reluctant to release their protecting groups, we examined bulkier alkyl carbanions hypothesizing that steric crowding would disfavor formation of the Lewis acid/base adducts and therefore not require phosphine protection. We found that $^{i}Pr_2PCH_2Li$ (**2.17**) reacted with Ph_2BCl (**2.10**) in a mixture of THF and Et_2O to produce the target ligand $[Ph_2B(CH_2P^{i}Pr_2)_2][Li(THF)_2]$ (**2.39**[Li]) in good yield (essentially quantitative as seen in $^{31}P\{^{1}H\}$ NMR spectra). In similar fashion, two equivalents of $^{t}Bu_2PCH_2Li$ (**2.16**) reacted with **2.10** in Et_2O/THF to form $[Ph_2B(CH_2P^{t}Bu_2)_2][Li(OEt_2)]$ (**2.40**[Li]). Once again, the reaction proceeded very cleanly according to crude $^{31}P\{^{1}H\}$ NMR spectra. Both **2.39**[Li] and **2.40**[Li] could be crystallized from Et_2O at -30 ºC. The related ligand $[(m,m\text{-}Me_2Ph)_2B(CH_2P^{t}Bu_2)_2][Li(OEt_2)]$ (**2.41**[Li]), was also prepared by room temperature reaction of two equivalents of **2.16** with $(m,m\text{-}Me_2Ph)_2BCl$ (**2.12**) in Et_2O/THF and crystallized from Et_2O at -30 ºC. High isolated crystalline yields of alkyl-substituted bis(phosphino)borates has proven difficult due to their increased solubility; however, spectra of the crude reactions typically show the presence of a single major product. In general, we have found the alkyl substituted (phosphino)borates **2.39**, **2.40**, and **2.41** to be appreciably less stable than their aryl substituted counter-parts. This was true with respect to oxidation, hydrolysis, and thermal decomposition.

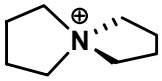
2.2.5. Generation of ammonium and thallium salts

Under many conditions, the lithium and lithium(TMEDA) salts of bis(phosphino)borates prove to be excellent reagents themselves; however, we have also found ammonium and thallium reagents to be effective for the metalation of transition metal precursors.[8c-e,h,9,10] The reaction products of such reactions are often dependent on

the nature of the counter-cation. We therefore explored the cation exchange of several bis(phosphino)borates. Although we have chosen to specifically describe the formation of ASN (ASN = 5-azonia-spiro[4.4]nonane) salts[44] here owing to the crystallinity they impart on coordinated metal salts, similar protocols are also effective for commercially available ammonium salts, such as tetrabutylammonium bromide and tetraethylammonium chloride. For reference, the experimental data for the $[^{n}Bu_4N]^+$ and $[Et_4N]^+$ salts of $[Ph_2B(CH_2PPh_2)_2]^-$ have been included.

$$[BP_2][Li] + [R_4N][X] \longrightarrow [BP_2][R_4N] + [Li][X] \quad (2.5)$$

$[BP_2]$ = bis(phosphino)borate$^-$
$[Li]$ = Li(solvent)$^+$ or Li(TMEDA)$^+$
$[R_4N]$ = $^{n}Bu_4N^+$, Et_4N^+, ASN$^+$
$[X]$ = Br^-, Cl^-

ASN = 

$$[BP_2][Li] + [Tl][X] \longrightarrow [BP_2][Tl] + [Li][X] \quad (2.6)$$

$[BP_2]$ = bis(phosphino)borate$^-$
$[Li]$ = Li(solvent)$^+$ or Li(TMEDA)$^+$
$[X]$ = NO_3^- or PF_6^-

Cation exchange was straightforward for alkyl-substituted aryl borates **2.25**, **2.26**, **2.27**, and **2.33**. The poor solubility of the ammonium bis(phosphino)borates in EtOH provided a general means for removing (TMEDA)lithium halide. The generation of tetra-alkyl ammonium salts by direct salt metathesis using ammonium halides in ethanol succeeded for **2.25**[Li], **2.26**[Li], **2.27**[Li], and **2.33**[Li], providing $[Ph_2B(CH_2PPh_2)_2][ASN]$ (**2.25**[ASN]), $[(p\text{-}MePh)_2B(CH_2PPh_2)_2][ASN]$ (**2.26**[ASN]), $[(p\text{-}^{t}BuPh)_2B(CH_2PPh_2)_2]$ [ASN] (**2.27**[ASN]), and $[Ph_2B\{CH_2P(p\text{-}^{t}BuPh)_2\}_2][ASN]$ (**2.33**[ASN]).

In contrast, cation exchange for the MeO- and CF_3-substituted aryl borates **2.28**[Li] and **2.29**[Li] was problematic due to their respective solubilities. The

preparation of [(*p*-CF_3Ph)$_2$B(CH_2PPh_2)$_2$][ASN] (**2.29**[ASN]) by dissolution in acetone with ASNBr followed by filtration, concentration, and crystallizing at -35 ºC did prove successful. The synthesis of [(*p*-MeOPh)$_2$B(CH_2PPh_2)$_2$][ASN] (**2.28**[ASN]), however, was much more challenging. The most favorable results were obtained by generating the BH_3-protected phosphine ligand by deprotonation of $Ph_2(BH_3)PCH_3$, followed by reaction with **2.14** to form [(*p*-MeOPh)$_2$B{$CH_2P(Ph)_2(BH_3)$}$_2$][Li(solvent)$_x$] (**2.28**·BH_3[Li]) and then carrying out salt metathesis in ethanol with ASNBr. The resulting product, [(*p*-MeOPh)$_2$B{$CH_2P(Ph)_2(BH_3)$}$_2$][ASN] (**2.28**·BH_3[ASN]), can be converted through borane deprotection to the desired compound, **2.28**[ASN], albeit with a reduction in yield of the ligand. The use of a phosphine-borane adduct precursor for the cation metathesis step may prove ultimately beneficial for certain ligand derivatives. Deprotonation of various (aryl)$_2(BH_3)PCH_3$ complexes occurs much more readily than those of the corresponding phosphines, and the resulting bis(phosphino)borate products are likely to be more stable to air and moisture than their unprotected counterparts. Similarly, phosphine-sulfides may also prove to be effective reagents for preparation of bis(phosphino)borates. The limitation for using either borane- or sulfide-protected phosphines to synthesize bis(phosphino)borates is the possibility for the successful and high-yielding deprotection of the product.

To examine thallium salt formation with phenyl-substituted bis(phosphino)borates, we prepared the compound, [$Ph_2B(CH_2PPh_2)_2$][Tl] (**2.25**[Tl]). Salt exchange occurred upon combination of EtOH solutions of **2.25**[Li] and $TlPF_6$. Over 30 min, off-white solids precipitated which were collected and further purified by crystallization from THF. For this cation exchange, it was not necessary that **2.25**[Li] be

rigorously isolated from additional LiCl. It remains in the EtOH solution, as does any excess $TlPF_6$. Purified **2.25**[Tl] displayed several noteworthy properties. First, its NMR spectra were best obtained in THF-d_8, as the product displays poor solubility in other hydrocarbon or polar solvents, including benzene, toluene, acetone, and acetonitrile. Second, although ^{1}H NMR spectra of **2.25**[Tl] were obtained that showed no remarkable features, the expected $^{31}P\{^1H\}$ NMR resonances were difficult to detect at ambient temperature. This contrasts the $^{31}P\{^1H\}$ NMR spectrum obtained of crude **2.25**[Tl], which shows a broad singlet at 57 ppm. Examination of a THF-d_8 solution of **2.25**[Tl] demonstrated that a temperature-dependent exchange phenomenon was operative. Thus, at low temperature (-65 ºC), the $^{31}P\{^1H\}$ NMR spectrum showed a doublet centered at 52.5 ppm, with a typical, large phosphorus-thallium coupling constant of 4166 Hz. Upon warming, the peaks coalesced between -20 and 0 ºC. Further warming to 55 ºC provided a broad singlet at 57.9 ppm (Figure 2.6).

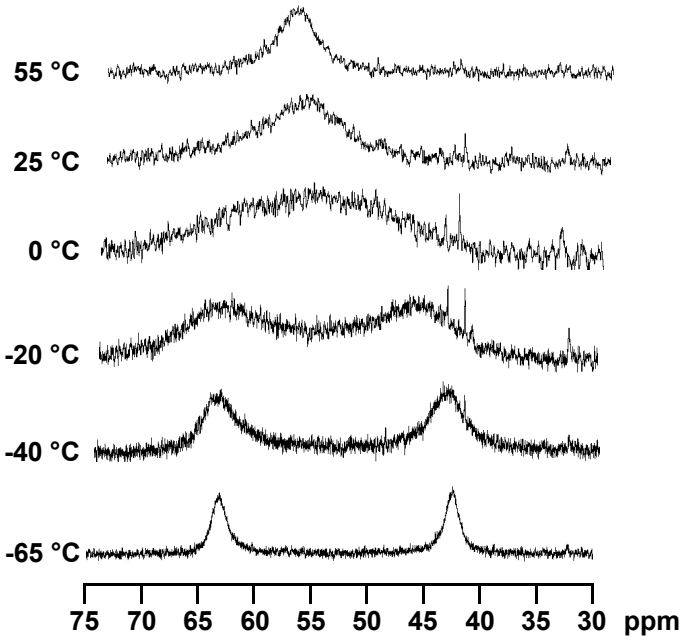


Figure 2.6. $^{31}P\{^1H\}$ NMR spectra of **2.25**[Tl] at -65, -40, -20, 0, 25 and 55 ºC.

A thallium adduct of **2.41** was also synthesized. Salt exchange was effected by stirring a toluene solution of **2.41**[Li] with thallium nitrate. A similar method works equally well for related **2.40**[Li]. The thallium-phosphorus coupling constant observed in the $^{31}P\{^{1}H\}$ NMR spectrum for **2.41**[Tl] in benzene is exceptionally large (6334 Hz), but is reduced upon dissolution of **2.41**[Tl] in a more polar solvent such as THF (5933 Hz). This change in the P-Tl coupling constant likely reflects the greater ability of THF solvent to coordinate to the thallium cation relative to benzene solvent or an aromatic ring of a bis(phosphino)borate molecule (*vide infra*).

2.2.6. Structural and spectroscopic data for bis(phosphino)borates

In general, bis(phosphino)borates contain relatively unremarkable spectral properties. Several features of note come from the wide variety of NMR active nuclei (^{1}H, ^{13}C, ^{31}P, ^{11}B). In all cases, $^{11}B\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were useful for analyzing the contents of crude reaction mixtures. The desired tetra-alkyl substituted borates have distinctive $^{11}B\{^{1}H\}$ NMR chemical shifts and sharp resonances which allow for easy identification. All of the aryl-substituted phosphines provided $^{31}P\{^{1}H\}$ NMR chemical shifts within a narrow range (-6 to -12 ppm), providing a second diagnostic handle. Because of the large number of NMR active nuclei, some specific resonances were distinctly altered: *ipso* carbons attached to boron were typically observed as broad quartets in $^{13}C\{^{1}H\}$ NMR spectra (155 to 175 ppm), methylene carbons and protons between boron and phosphorus were significantly broadened, and uncoordinated bis(phosphino)borates often evinced coupling between phosphorus and boron ($^{2}J_{P\text{-}B}$) in their $^{31}P\{^{1}H\}$ NMR spectra.

In order to provide structural data for this new ligand class, X-ray diffraction studies were carried out on a few select derivatives. The phenyl substituted

bis(phosphino)borate [Ph_2BP_2] (**2.25**) was crystallized as its lithium(TMEDA)$_2$ salt, and a representation of its structural data is shown in Figure 2.7. As can be seen from the figure, even in the absence of an alkali metal cation, the ligand adopts a conformation that is poised to accept a metal ion.

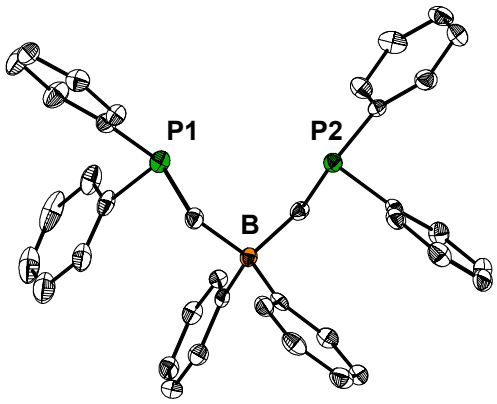


Figure 2.7. Displacement ellipsoid representation (50%) of [$Ph_2B(CH_2PPh_2)_2$][Li(TMEDA)$_2$] (**2.25**[Li]). Hydrogen atoms and [Li(TMEDA)$_2$] cation are omitted for clarity.

The related thallium salt of **2.25** was also studied by X-ray crystallography to further probe the exchange phenomenon described above. A structural determination of crystalline **2.25**[Tl] revealed a coordination polymer structure where the thallium cation joins two bis(phosphino)borate molecules by coordinating to one phosphorus atom and one borate aryl ring from each molecule (Figure 2.8). Based on the structural determination, the $^{31}P\{^1H\}$ NMR data is best explained by a highly labile binding of thallium to phosphorus. Note that the thallium atom is four-coordinate and is best described by two Tl-P interactions and two η^6-aryl interactions. The Tl-C_{aryl} distances range from 3.239(3) to 3.403(4) Å. This contrasts the coordination observed for a related bis(phosphino)borate-thallium complex (*vide infra*).

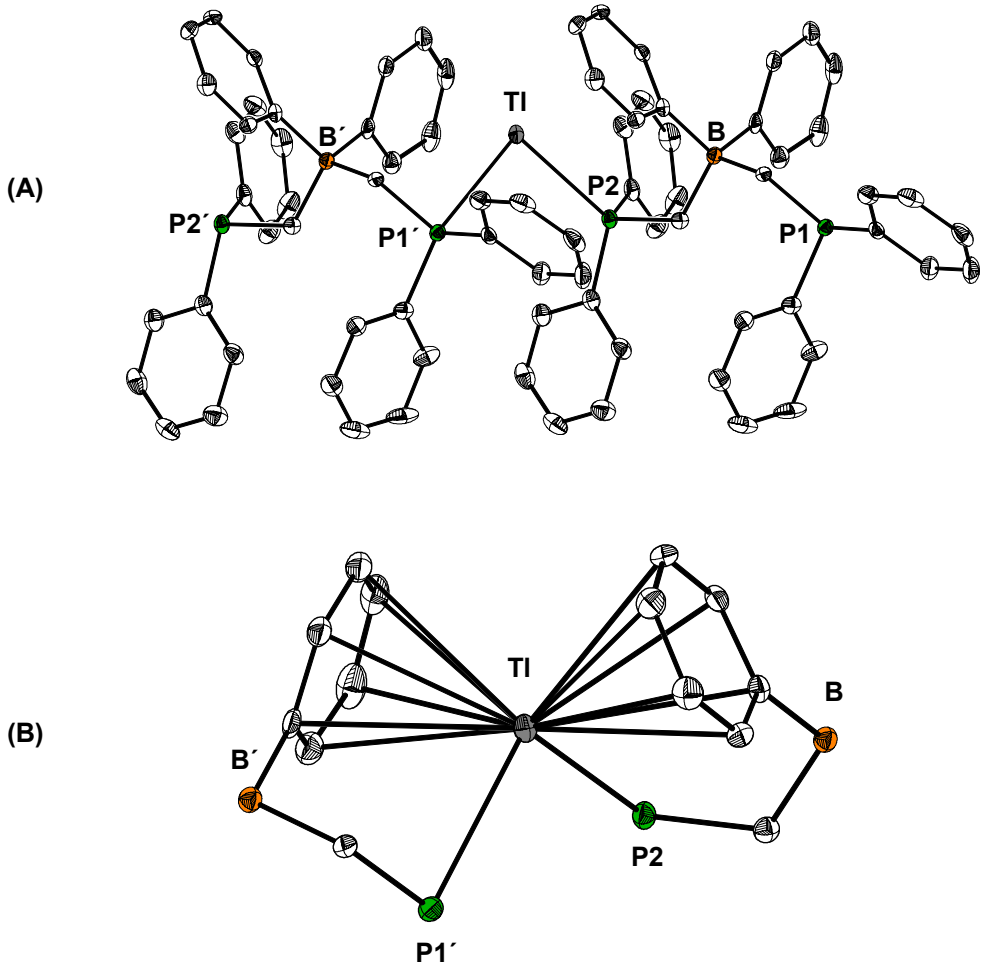


Figure 2.8. (A) Displacement ellipsoid representation (50%) of $\{[Ph_2B(CH_2PPh_2)_2][Tl]\}_n$ (**2.25**[Tl]), showing two anionic bis(phosphino)borate units and one interconnecting thallium. Hydrogen atoms are omitted for clarity. (B) Expanded view of the thallium coordination sphere. Selected interatomic distances (Å) and angles (°): P1´-Tl, 3.0283(9); P2-Tl, 3.0231(9); Tl-C_{aryl}(avg), 3.311(5).

Crystals of alkyl-substituted bis(phosphino)borates **2.39**[Li] and **2.40**[Li] were also studied by X-ray diffraction. Structural representations are shown in Figure 2.9. Common to both structures is the coordination of the lithium cation by the bis(phosphino)borate. Interestingly, the two structures provide different coordination numbers for the lithium cations. The sterically encumbering *tert*-butyl groups of **2.40**[Li]

restrict the coordination environment around lithium to three-coordinate, allowing only a single diethyl ether molecule to coordinate. In contrast, the structure of the lithium ion in **2.39**[Li] is more typically four-coordinate, with two THF molecules coordinated to the lithium cation.

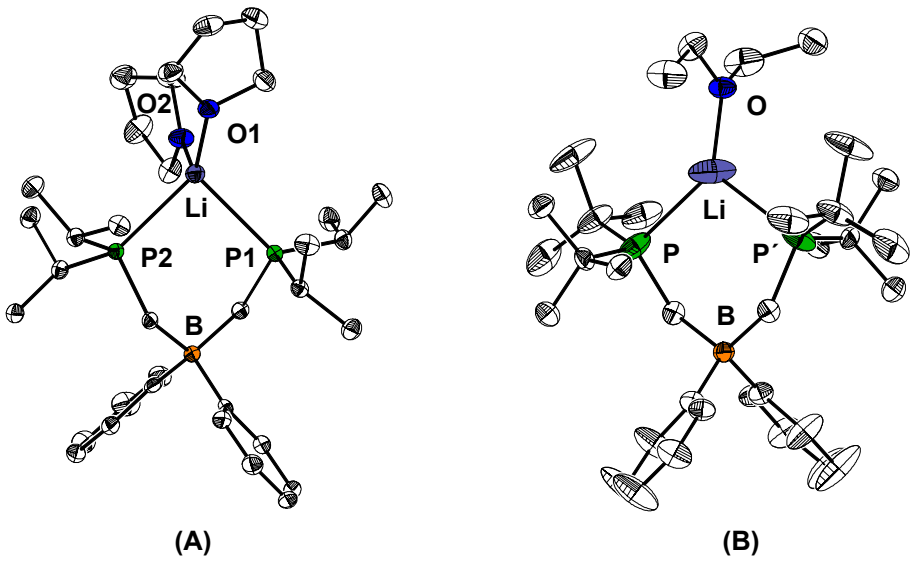


Figure 2.9. Displacement ellipsoid representation (50%) of (A) $[Ph_2B(CH_2P^iPr_2)_2][Li(THF)_2]$ (**2.39**[Li]) and (B) $[Ph_2B(CH_2P^tBu_2)_2][Li(OEt_2)]$ (**2.40**[Li]). Hydrogen atoms and disordered positions are omitted for clarity. Selected interatomic distances (Å) and angles (°), for **2.39**[Li]: Li-P1, 2.608(3); Li-P2, 2.596(3); Li-O1, 1.962(3); Li-O2, 1.928(3); Li-B, 4.197(3); P1-Li-P2, 91.07(9); O1-Li-O2, 104.93(14); P1-Li-O1, 116.77(13); P2-Li-O2, 107.46(13); P1-Li-O2, 112.56(13); P2-Li-O1, 123.68(13). For **2.40**[Li]: P-Li, 2.485(4); Li-O, 1.926(8); B-Li, 4.092(8); P-Li-O, 121.31(14); P-Li-P´, 99.5(2).

An X-ray diffraction experiment carried out on crystals of **2.41**[Tl] grown from benzene showed a structure distinct from **2.25**[Tl] in that the thallium cation is coordinated by two phosphines and acquires additional electron density from the aryl ring of an adjacent arylborate group (Figure 2.10). The thallium center in **2.41**[Tl] is best described as three-coordinate, with two phosphine donors and a single η^2-aryl interaction.

The nominally three-coordinate structures determined for both the lithium and thallium adducts of the sterically crowded $[Ph_2B(CH_2P^tBu_2)_2]^-$ ligand provide a promising lead for developing low-coordinate transition metal chemistry based upon this particular ligand type.

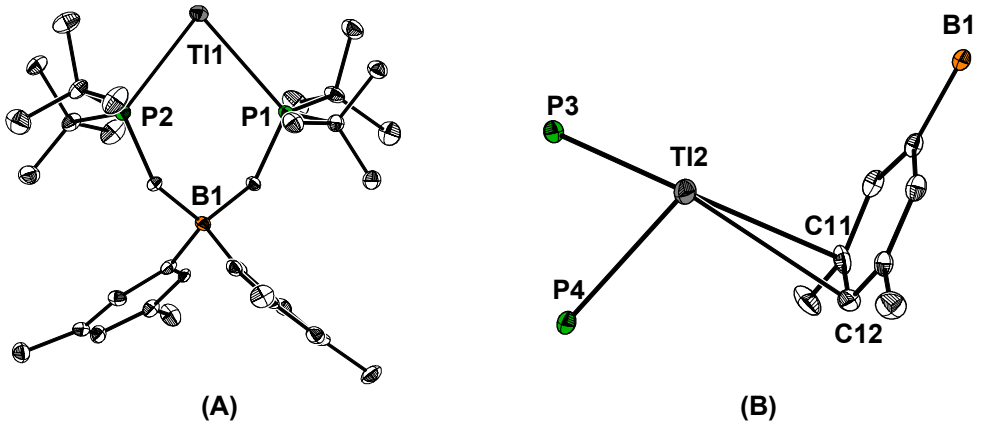


Figure 2.10. (A) Displacement ellipsoid representation (50%) of $[(m,m\text{-}(CH_3)_2Ph)_2B(CH_2P^tBu_2)_2][Tl]$ (**2.41**[Tl]). Hydrogen atoms and second molecule of the asymmetric unit are omitted for clarity. Selected interatomic distances (Å) and angles (°): P1-Tl1, 2.9919(12); P2-Tl1, 2.9426(11); B1-Tl1, 4.786(5); P1-Tl1-P2, 78.75(3). (B) Intermolecular interactions within the asymmetric unit, emphasizing the thallium coordination sphere. Selected interatomic distances (Å) and angles (°): P3-Tl2, 2.9788(12); P4-Tl2, 2.9406(11); C11-Tl2, 3.388(4); C12-Tl2, 3.353(4).

2.3. Conclusion

This chapter has outlined a general synthetic protocol used to prepare a new family of bis(phosphino)borate ligands. The methods described provide a path to construct ligands of these types with varying substitution patterns at both the borate and phosphine donor positions. These same protocols are proving successful in the synthesis of tris(phosphino)borate ligands.[45] While the protocols are in general effective, problematic scenarios can arise. Most noteworthy is the synthesis of less sterically

encumbered derivatives, as in our attempted synthesis of the anion $[Ph_2B(CH_2PMe_2)_2]^-$. Clean delivery of two equivalents of carbanion to the borane electrophile proved problematic in this case. While this problem can be circumvented by an initial phosphine protection step, deprotection protocols that afford the desired ligand are non-trivial. The high σ-donor strength of the $[Ph_2B(CH_2PMe_2)_2]^-$ anion is an excellent example that illustrates when deprotection becomes extremely problematic. For arylphosphine donors, protection/deprotection protocols are more straightforward, and in certain cases are required, as for the case of ligand **2.35**. Fortunately, alkyl-substituted ligands, such as $[Ph_2B(CH_2P^iPr_2)_2]^-$ (**2.39**) and $[Ph_2B(CH_2P^tBu_2)_2]^-$ (**2.40**), are readily prepared without protection. Alkyl-substituted systems appear to be generally accessible, at least for cases where problematic Lewis acid-base donor adducts can be kinetically avoided in the carbanion delivery step.

For synthetic utility, this chapter has also provided protocols for preparing lithium, thallium, and ammonium salt derivatives of the bis(phosphino)borates. We note that the thallium and ammonium salts have proven effective in the formation in the preparation of transition metal complexes. Also, the reaction product profile can be highly dependent on which counter-cation is used. We anticipate that these monoanionic bidentate phosphine ligands will provide rich coordination chemistry that will compliment the body of literature on known neutral phosphine donors.

2.4. Experimental section

2.4.1. General considerations

Unless otherwise noted, all syntheses were carried out in the absence of water and dioxygen, using standard Schlenk and glovebox techniques. Acetonitrile,

tetrahydrofuran, diethyl ether, dichloromethane, toluene, benzene, and petroleum ether were deoxygenated and dried by thorough sparging with N_2 gas followed by passage through an activated alumina column. Pentane and hexanes were deoxygenated by repeated evacuation under reduced pressure followed by introduction of dinitrogen and were dried by storing over 3-Å molecular sieves. *p*-Dioxane was dried and distilled over sodium/benzophenone under dinitrogen. Hydrocarbon and ethereal solvents were typically tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. Ethanol and acetone were dried and distilled over calcium sulfate under dinitrogen. Morpholine, TMEDA, and diethylamine were dried and distilled from KOH under dinitrogen. Deuterated chloroform, benzene, dichloromethane, THF, acetonitrile, and acetone were purchased from Cambridge Isotope Laboratories, Inc. and were degassed by repeated freeze-pump-thaw cycles and dried over activated 3-Å molecular sieves prior to use.

NMR spectra were recorded at ambient temperature on Varian Mercury 300 MHz and Inova 500 MHz, and Jeol 400 MHz spectrometers, unless otherwise noted. ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts are reported in ppm (δ) and referenced to residual solvent as determined relative to Me_4Si (0 ppm). $^{31}P\{^{1}H\}$ NMR, $^{11}B\{^{1}H\}$ NMR, and $^{19}F\{^{1}H\}$ NMR chemical shifts are reported in ppm (δ) relative to an external standard (0 ppm) of 85% H_3PO_4, neat $BF_3{\cdot}Et_2O$, and neat $CFCl_3$, respectively. Abbreviations for reported signal multiplicities are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. IR spectra were recorded in a KBr solution cell, as a KBr pellet, or as a Nujol mull between KBr plates at 2 cm^{-1} resolution on a Bio-Rad Excalibur FTS 3000 spectrometer controlled by Win-IR Pro software. MS data were obtained by

injection of a solution onto a Hewlett-Packard 1100MSD mass spectrometer (ES MS) or an Agilent 5973 mass selective detector (GC MS). Elemental analyses were performed by Desert Analytics, Tucson, AZ. X-ray diffraction experiments were carried out by the Beckmann Institute Crystallographic Facility on a Bruker Smart 1000 CCD diffractometer.

2.4.2. Starting materials and reagents

Ph_2PMe,[46] $Ph_2PCH_2Li(TMEDA)$, $^tBu_2PCl$,[47] $^tBu_2PMe$,[48] $^tBu_2PCH_2Li$, $Me_2PCH_2Li(TMEDA)$, $(Ph)_2(BH_3)PCH_3$, and 5-azonia-spiro[4.4]nonane bromide (ASNBr), were prepared by literature methods. $^iPr_2PMe$[49] was prepared by reaction of $^iPr_2PCl$ with MeLi and isolation of the product by distillation. $Me_3P(BH_3)$[50] was prepared by reaction of PMe_3 with $BH_3{\cdot}SMe_2$. $S{=}PMe_3$[51] was prepared by the addition of elemental sulfur to a toluene solution of PMe_3 and collecting the precipitate. All other chemicals were purchased from Aldrich, Strem, Alfa Aesar, Gileste, or Matrix Scientific and used without further purification.

2.4.3. Syntheses of compounds

General method A: preparation of Me_2SnR_2. Aryl Grignard reagents were either purchased or generated by standard methods using magnesium and an appropriate aryl bromide. A flask containing the aryl Grignard reagent was cooled to -78 ºC in a dry ice/acetone bath. One half of an equivalent of solid Me_2SnCl_2 was added under a counterflow of dinitrogen. The reaction was stirred at -78 ºC for 20 min, then the bath was removed and the reaction allowed to warm to room temperature and stir over several hours. Volatiles were removed under reduced pressure. Hexanes (100 mL) were added to the resulting solids, and the suspension was filtered over Celite. Residual solids were washed with hexanes (4 x 75 mL), and the combined organic solutions were concentrated

by rotary evaporation, providing the desired Me_2SnR_2 as either an oil or a solid. Further purification of the product can be achieved by crystallization or distillation under heat and vacuum. (*Note:* several of the dimethyldiaryltin complexes reported herein have appeared previously in the literature. For those cases, relevant citations are given. NMR data in readily available deuterated solvents (e.g., $CDCl_3$, C_6D_6) are included for completeness.)

$(CH_3)_2Sn(C_6H_5)_2$ (2.1).[21-24] Following General Method A, pale yellow oil (24.3020 g, 77.6%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (m, 4H), 7.36 (m, 6H), 0.53 (s, 6H, $^2J_{Sn-H}$ = 54 Hz).

$(CH_3)_2Sn(C_6H_4$-*p*-$Me)_2$ (2.2).[21-23,25] Following General Method A, white solids (12.3836 g, 96.9%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (d, 4H, J_{Sn-H} = 45 Hz), 7.27 (d, 4H), 2.44 (s, 6H), 0.57 (s, 6H, $^2J_{Sn-H}$ = 55 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 138.5, 137.0, 136.4 (J_{Sn-C} = 38 Hz), 129.3 (J_{Sn-C} = 50 Hz), 21.6, -9.8 ($^1J_{Sn-C}$ = 356 Hz).

$(CH_3)_2Sn(C_6H_3$-*m*,*m*-$Me_2)_2$ (2.3). Following General Method A, white solids (19.4541 g, 87.9%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21 (s, 4H, J_{Sn-H} = 48 Hz), 7.05 (s, 2H), 2.38 (s, 12H), 0.55 (s, 6H, $^2J_{Sn-H}$ = 55 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 140.6, 137.7 (J_{Sn-C} = 49 Hz), 134.1 (J_{Sn-C} = 36 Hz), 130.5 (J_{Sn-C} = 11 Hz), 21.5, -9.8 ($^1J_{Sn-C}$ = 360 Hz). Anal. Calcd. for $C_{18}H_{24}Sn$: C, 60.21; H, 6.74. Found: C, 59.95; H, 6.74.

$(CH_3)_2Sn(C_6H_4$-*p*-^{t}Bu$)_2$ (2.4). Following General Method A, white solids (18.1831 g, 96.2%).

^{1}H NMR (300 MHz, C_6D_6): δ 7.51 (d, 4H), 7.32 (d, 4H), 1.24 (s, 18H), 0.45 (s, 6H, $^{2}J_{Sn-H}$ = 54 Hz). $^{13}C\{^{1}H\}$ NMR (125.7 MHz, $CDCl_3$): δ 151.6, 137.3, 136.3 (J_{Sn-C} = 38 Hz), 125.5 (J_{Sn-C} = 48 Hz), 34.8, 31.5, -9.8 ($^{1}J_{Sn-C}$ = 364 Hz). Anal. Calcd. for $C_{22}H_{32}Sn$: C, 63.64; H, 7.77. Found: C, 63.53; H, 7.99.

$(CH_3)_2Sn(C_6H_4$-*p*-OMe$)_2$ (2.5).[22,23,27] Following General Method A, oil which solidified upon standing (13.7652 g, 83.3%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (d, 4H), 7.07 (d, 4H), 3.94 (s, 6H), 0.61 (s, 6H, $^{2}J_{Sn-H}$ = 55 Hz). $^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$): δ 160.3, 137.5 (J_{Sn-C} = 42 Hz), 131.1, 114.3 (J_{Sn-C} = 53 Hz), 55.1, -9.7 ($^{1}J_{Sn-C}$ = 358 Hz).

$(CH_3)_2Sn(C_6H_4$-*p*-$CF_3)_2$ (2.6).[22] Following General Method A, orange oil (14.9446 g, 94.4%).

^{1}H NMR (300 MHz, C_6D_6): δ 7.40 (d, 4H), 7.19 (d, 4H, J_{Sn-H} = 43.8 Hz), 0.27 (s, 6H, $^{2}J_{Sn-H}$ = 54.3 Hz). $^{19}F\{^{1}H\}$ NMR (282.1 MHz, C_6D_6): δ -63.5.

$(CH_3)_2Sn(C_6H_4$-*o*-OMe$)_2$ (2.7).[23] Following General Method A, white crystalline solids (16.2126 g, 98.7%).

^{1}H NMR (300 MHz, C_6D_6): δ 7.52 (dd, 2H, J_{Sn-H} = 52.2 Hz), 7.20 (ddd, 2H), 6.94 (dt, 2H), 6.54 (br d, 2H), 3.24 (s, 6H), 0.65 (s, 6H, $^{2}J_{Sn-H}$ = 56.1 Hz). $^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$): δ 164.0, 137.3 (J_{Sn-C} = 26.6 Hz), 130.2, 129.8, 121.2 (J_{Sn-C} = 47.4 Hz), 109.4, 55.5, -8.5 ($^{1}J_{Sn-C}$ = 375 Hz). Anal. Calcd. for $C_{16}H_{20}O_2Sn$: C, 52.93; H, 5.55. Found: C, 52.20; H, 5.55.

$(CH_3)_2Sn(C_6H_3$-*o*,*o*-$(OMe)_2)_2$ (2.8).[28] Prepared by the previously reported method (deprotonation of 1,3-(dimethoxy)benzene followed by quenching with Me_2SnCl_2), white solids (11.3345 g, 55.8%).

^{1}H NMR (300 MHz, C_6D_6): δ 7.16 (t, 4H), 6.34 (d, 4H), 3.27 (s, 6H), 0.89 (s, 6H, $^{2}J_{Sn-H}$ = 58.5 Hz).

$(CH_3)_2Sn(C_6H_4$-*o*-$CF_3)_2$ (2.9). Following General Method A, amber oil (19.7956 g, 90.3%).

^{1}H NMR (300 MHz, C_6D_6): δ 7.48 (dd, 2H), 7.39 (br d, 4H), 6.96 (m, 4H), 0.57 (s, 6H, $^{2}J_{Sn-H}$ = 57.0 Hz). $^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$): δ 139.6 (br), 137.9 (J_{Sn-C} = 26.5 Hz), 131.2 (J_{Sn-C} = 42.8 Hz), 129.0 (J_{Sn-C} = 9.1 Hz), 126.2 (q, $^{1}J_{F-C}$ = 4.5 Hz, J_{Sn-C} = 31.7 Hz), -6.2 (septet, J_{F-C} = 2.6 Hz, $^{1}J_{Sn-C}$ = 392 Hz). $^{19}F\{^{1}H\}$ NMR (282.1 MHz, C_6D_6): δ -60.4. Anal. Calcd. for $C_{16}H_{14}F_6Sn$: C, 43.78; H, 3.21. Found: C, 42.90; H, 3.48.

General method B: preparation of R_2BCl. To a thick-walled vessel with a stirbar and sealable teflon valve was added an appropriate dimethyldiaryltin compound (approx. 10-15 g) and heptane (25 mL). One equivalent of a solution of BCl_3 in heptane (approx. 25 mL of a 1 M solution) was added to the vessel at room temperature and the vessel was sealed. After stirring at room temperature for 30 min, the reaction was placed in a oil bath maintained at 100 ºC and was stirred for 24-48 h at 100 ºC. The vessel was removed from the oil bath and allowed to cool, causing dimethyltindichloride to crystallize from the mixture. The resulting solution was decanted from the white crystals. Removal of volatiles under reduced pressure provided crude diarylchloroborane. If necessary, recrystallization from hydrocarbon solvent (e.g., petroleum ether) at -35 ºC provided pure diarylchloroborane. If any dimethyltindichloride was observed by ^{1}H NMR spectroscopy, it was removed by vacuum sublimation.

$(C_6H_5)_2BCl$ (2.10).[15,16] Following General Method B, colorless crystalline solids (5.403 g, 72.8%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (d, 2H), 7.65 (t, 2H), 7.54 (t, 1H). $^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$): δ 137.2, 133.1, 128.0. $^{11}B\{^{1}H\}$ NMR (128.3 MHz, $CDCl_3$): δ 62.8.

(*p*-$MeC_6H_4)_2BCl$ (2.11).[16,17] Following General Method B, white solids (4.7058 g, 98.0%).

^{1}H NMR (300 MHz, C_6D_6): δ 7.98 (d, 4H, $^{3}J_{H-H}$ = 8.1 Hz), 7.01 (d, 4H, $^{3}J_{H-H}$ = 8.1 Hz), 2.06 (s, 6H). $^{13}C\{^{1}H\}$ NMR (75.4 MHz, C_6D_6): δ 144.0, 138.1, 129.3, 22.0. $^{11}B\{^{1}H\}$ NMR (128.3 MHz, C_6D_6): δ 61.6.

(*m*,*m*-$Me_2C_6H_3)_2BCl$ (2.12). Following General Method B, white solids (5.3505 g, 85.6%).

^{1}H NMR (300 MHz, C_6D_6): δ 7.74 (s, 4H), 6.94 (s, 2H), 2.11 (s, 12H). $^{13}C\{^{1}H\}$ NMR (75.4 MHz, C_6D_6): δ 137.6, 135.5, 135.2, 21.5. $^{11}B\{^{1}H\}$ NMR (128.3 MHz, C_6D_6): δ 62.6. Anal. Calcd. for $C_{16}H_{18}BCl$: C, 74.90; H, 7.07. Found: C, 74.59; H, 7.32.

(*p*-$^{t}BuC_6H_4)_2BCl$ (2.13). Following General Method B, white crystalline solids (5.2415 g, 90.6%).

^{1}H NMR (300 MHz, C_6D_6): δ 8.08 (d, 4H, $^{3}J_{H-H}$ = 7.8 Hz), 7.33 (d, 4H, $^{3}J_{H-H}$ = 7.8 Hz), 1.19 (s, 18H). $^{13}C\{^{1}H\}$ NMR (75.4 MHz, C_6D_6): δ 156.5, 137.7, 125.2, 35.0, 31.0. $^{11}B\{^{1}H\}$ NMR (128.3 MHz, C_6D_6): δ 61.8. Anal. Calcd. for $C_{20}H_{26}BCl$: C, 76.82; H, 8.38. Found: C, 76.00; H, 8.56.

(*p*-$MeOC_6H_4)_2BCl$ (2.14).[16,18] Following General Method B, white solids (6.2865 g, 96.5%).

^{1}H NMR (300 MHz, C_6D_6): δ 8.06 (d, 4H, $^{3}J_{H-H}$ = 8.1 Hz), 6.79 (d, 4H, $^{3}J_{H-H}$ = 8.1 Hz), 3.23 (s, 6H). $^{13}C\{^{1}H\}$ NMR (75.4 MHz, C_6D_6): δ 164.4, 140.2, 114.2, 55.1.

$^{11}B\{^{1}H\}$ NMR (128.3 MHz, C_6D_6): δ 59.4. Anal. Calcd. for $C_{20}H_{26}BCl$: C, 64.54; H, 5.42. Found: C, 64.47; H, 5.30.

(*p*-$CF_3C_6H_4)_2BCl$ (2.15). Following General Method B, colorless crystalline solids (3.5460 g, 31.0%).

^{1}H NMR (300 MHz, C_6D_6): δ 7.54 (d, $^{3}J_{H-H}$ = 7.5 Hz), 7.35 (d, $^{3}J_{H-H}$ = 7.5 Hz). $^{19}F\{^{1}H\}$ NMR (282.1 MHz, C_6D_6): δ -63.9. $^{11}B\{^{1}H\}$ NMR (128.3 MHz, C_6D_6): δ 61.5. Anal. Calcd. for $C_{14}H_8BClF_6$: C, 49.98; H, 2.40. Found: C, 50.37; H, 2.51.

$^{i}Pr_2P(CH_2Li)$ (2.17). (*Caution*: This procedure evolves gas in a sealed system. Use appropriate precautions, including periodic venting of the vessel to release pressure.) A solution of ^{t}BuLi in pentane (30 mL, 1.7 M, 51 mmol), was placed in a 250 mL thick-walled sealable vessel. Volatiles were removed under reduced pressure, providing solid ^{t}BuLi. To the white solids was added neat $^{i}Pr_2PMe$ (6.694 g, 51.03 mmol). The reaction vessel was evacuated and sealed. The reaction was heated to 60 ºC for 20 h, venting periodically to release pressure, during which time yellow-white solids formed. The vessel was cooled to room temperature and the resulting solids were collected by filtration and washed with petroleum ether (3 x 20 mL). The resulting white solids were dried under reduced pressure, providing **2.17** (5.5217 g, 78.4%).

$^{31}P\{^{1}H\}$ NMR (121.4 MHz, THF): δ 22.8.

(*p*-^{t}BuPh)$_2$PCH$_2$Li(TMEDA) (2.19). A solution of ^{n}BuLi in hexanes (2.20 mL, 1.6 M, 3.52 mmol) was added to a stirring room temperature petroleum ether solution of TMEDA (532 μl, 3.52 mmol) and (*p*-^{t}BuPh)$_2$PMe (1.0990 g, 3.5176 mmol). Upon addition, the mixture turned orange. The mixture was stirred at room temperature for 4 days, precipitating a pale yellow product solid. The solids were collected by filtration

and washed with petroleum ether (2 x 2 mL). Drying the solids under reduced pressure provided **2.19** as pale yellow solids (1.1358 g, 74.3%).

^{1}H NMR (300 MHz , C_6D_6,/THF-d_8 10:1): δ 7.85 (dd, 4H), 7.22 (d, 4H), 2.20 (s, 4H), 2.05 (s, 12H), 1.22 (s, 18H), 0.06 (d, 2H). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6/THF-d_8 10:1) δ -1.26.

[$Ph_2B(CH_2PPh_2)_2$][$Li(TMEDA)_2$] ([Ph_2BP_2][Li], 2.25[Li]). Solid pale yellow Ph_2PCH_2Li(TMEDA) (4.82 g, 15.0 mmol) was dissolved in diethyl ether (180 mL) in a Schlenk flask with a stir bar and sealed with a septum. The reaction vessel was cooled to -78 ºC in a dry ice/acetone bath. Ph_2BCl (1.514 g, 7.553 mmol), dissolved in toluene (10 mL), was introduced dropwise via syringe to the cooled reaction flask. The reaction was stirred and warmed gradually to room temperature over 14 h, providing a pale yellow precipitate. Volatiles were removed under reduced pressure, and the resulting solids were isolated in a drybox on a sintered glass frit and washed with diethyl ether (5 x 10 mL). Drying under reduced pressure provided pale yellow solid [$Ph_2B(CH_2PPh_2)_2$][$Li(TMEDA)_2$] (5.67 g, **2.25**[Li]).

^{1}H NMR (300 MHz, acetone-d_6): δ 7.29 (br, 4H, *ortho* $B(C_6H_5)_2$), 7.16 (m, 8H, *ortho* $P(C_6H_5)_2$), 6.98 (m, 12H, *meta* $B(C_6H_5)_2$ and $P(C_6H_5)_2$), 6.72 (tt, 4H, *para* $P(C_6H_5)_2$), 6.60 (tt, 2H, *para* $B(C_6H_5)_2$), 2.34 (s, 8H, $Me_2N(CH_2)_2NMe_2$), 2.17 (s, 24H, $(CH_3)_2N(CH_2)_2N(CH_3)_2$), 1.64 (br, 4H, $Ph_2B(CH_2PPh_2)_2$). ^{13}C{^{1}H} NMR (75.4 MHz, CD_3CN): δ 163 (br, *ipso* $B(C_6H_5)_2$), 147.60 (d, *ipso* $P(C_6H_5)_2$, $^{1}J_{P\text{-}C}$ = 22 Hz), 135.19 (s, *ortho* $B(C_6H_5)_2$), 133.62 (d, *ortho* $P(C_6H_5)_2$, $^{2}J_{P\text{-}C}$ = 19 Hz), 128.26 (s, *meta* $P(C_6H_5)_2$, $^{3}J_{P\text{-}C}$ = 5.8 Hz), 127.28 (s, *para* $P(C_6H_5)_2$), 126.32 (s, *meta* $B(C_6H_5)_2$), 118.36 (s, *para* $B(C_6H_5)_2$), 57.47 ($Me_2N(CH_2)_2NMe_2$), 46.19 ($(CH_3)_2N(CH_2)_2N(CH_3)_2$), 25.66 (br,

[$Ph_2B(CH_2PPh_2)_2$]). $^{31}P\{^1H\}$ NMR (121.4 MHz, acetone-d_6): δ -8.34 ($^2J_{P\text{-}B}$ = 11 Hz). $^{11}B\{^1H\}$ NMR (160.4 MHz, CD_3CN): δ -12.8.

[$Ph_2B(CH_2PPh_2)_2$][ASN] ([Ph_2BP_2][ASN], 2.25[ASN]). Solid [$Ph_2B(CH_2PPh_2)_2$][$Li(TMEDA)_2$] was dissolved in ethanol (40 mL). ASNBr (1.8 g, 8.7 mmol) was dissolved in ethanol (8 mL) and added to stirring **2.25**[Li]. A white precipitate formed immediately. The mixture was stirred for 10 min, and white solids were subsequently collected by filtration. The solids were washed with ethanol (2 x 10 mL) and diethyl ether (3 x 10 mL) and dried under reduced pressure for 24 h, providing **2.25**[ASN] as a pure, white solid (4.30 g, 6.23 mmol, 83.1%).

^1H NMR (300 MHz, acetone-d_6): δ 7.29 (br, 4H, *ortho* $B(C_6H_5)_2$), 7.17 (m, 8H, *ortho* $P(C_6H_5)_2$), 7.00 (m, 12H, *meta* $B(C_6H_5)_2$ and $P(C_6H_5)_2$), 6.74 (m, 4H, *para* $P(C_6H_5)_2$), 6.62 (m, 2H, *para* $B(C_6H_5)_2$), 3.65 (m, 8H, $((CH_2CH_2)_2)_2N$), 2.23 (m, 8H, $((CH_2CH_2)_2)_2N$), 1.64 (br, 4H, $Ph_2B(CH_2PPh_2)_2$). $^{13}C\{^1H\}$ NMR (125.7 MHz, acetone-d_6): δ 165 (br, *ipso* $B(C_6H_5)_2$), 147.4 (d, *ipso* $P(C_6H_5)_2$, $^1J_{P\text{-}C}$ = 22 Hz), 134.7 (s, *ortho* $B(C_6H_5)_2$), 133.6 (d, *ortho* $P(C_6H_5)_2$, $^2J_{P\text{-}C}$ = 19 Hz), 127.1 (s, *meta* $P(C_6H_5)_2$, $^3J_{P\text{-}C}$ = 6 Hz), 126.0 (s, *para* $P(C_6H_5)_2$), 125.3 (s, *meta* $B(C_6H_5)_2$), 121.5 (s, *para* $B(C_6H_5)_2$), 63.1 ($(((CH_2CH_2)_2)_2N$), 25.7 (br, [$Ph_2B(CH_2PPh_2)_2$]), 22.1 ($(((CH_2CH_2)_2)_2N$). $^{31}P\{^1H\}$ NMR (121.4 MHz, acetone-d_6): δ -8.78 ($^2J_{P\text{-}B}$ = 10.0 Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, acetone-d_6): δ -12.6. Anal. Calcd. for $C_{46}H_{50}BNP_2$: C, 80.11; H, 7.31; N, 2.03. Found: C, 79.89; H, 7.45; N, 2.15.

[$Ph_2B(CH_2PPh_2)_2$][Et_4N] ([Ph_2BP_2][TEA], 2.25[TEA]). A solution of [$Ph_2B(CH_2PPh_2)_2$][Li(TMEDA)] (500 mg, 0.592 mmol) in EtOH (8 mL) was added to a stirring solution of Et_4NBr (186.5 mg, 0.887 mmol) in EtOH (4 mL) at room temperature.

Within minutes, a white precipitate formed. After 30 minutes, the solids were collected by filtration. The solids were washed with EtOH (3 x 5 mL) and Et_2O (2 x 3 mL). The solids were dried under reduced pressure providing **2.25**[TEA] (374 mg, 91%).

^{1}H NMR (300 MHz, acetone-d_6): δ 7.29 (m, 4H), 7.16 (m, 8H), 6.99 (m, 12H), 6.73 (t, 4H), 6.13 (t, 2H), 3.46 (q, 8H), 1.64 (br, 4H), 1.37 (tt, 12H). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-d_6): δ -8.6 (br d, $^2J_{P\text{-}B}$ = 13 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, acetone-d_6): δ -12.9.

[$Ph_2B(CH_2PPh_2)_2$][^{n}Bu_4N] ([Ph_2BP_2][TBA], 2.25[TBA]). Solid [$Ph_2B(CH_2PPh_2)_2$][Li(TMEDA)] (3.51 g, 4.42 mmol) was dissolved in EtOH (20 mL). Stirring, an EtOH solution (15 mL) of ^{n}Bu_4NCl (1.424 g, 4.42 mmol) was added dropwise. White solids began precipitating immediately upon addition. After the addition was complete, the reaction was stirred for 30 min. The white solids were collected by filtration and washed with EtOH (30 mL) and Et_2O (50 mL). The white solids were dried under reduced pressure, providing **2.25**[TBA] (3.13 g, 88%).

^{1}H NMR (300 MHz, acetone-d_6): δ 7.29 (br, 4H), 7.17 (m, 8H), 7.00 (m, 12H), 6.73 (m, 4H), 6.61 (t, 2H), 3.42 (m, 8H), 1.81 (m, 8H), 1.65 (br, 4H), 1.41 (sextet, 8H), 0.97 (t, 12H). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-d_6): δ -8.8 (q, $^2J_{P\text{-}B}$ = 10 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, acetone-d_6): δ -12.6.

{[$Ph_2B(CH_2PPh_2)_2$][Tl]}$_n$ ([Ph_2BP_2][Tl], 2.25[Tl]). Solid [$Ph_2B(CH_2PPh_2)_2$][Li(TMEDA)] (284.4 mg) was dissolved in EtOH (1.5 mL). Stirring, an EtOH solution (1.5 mL) of $TlPF_6$ (145.3 mg, 0.416 mmol) was added. Precipitation of off-white solids occurred as the solution was stirred over 30 min. After 30 min, the solids were isolated by filtration and washed with EtOH (1 mL). The solids were then dissolved

in THF (6 mL) and filtered, and from the resulting solution, colorless **2.25**[Tl] was crystallized by vapor diffusion of petroleum ether (276.3 mg, 86.5%).

^{1}H NMR (300 MHz, THF-d_8): δ 7.41 (m, 8H), 7.12 (m, 16H), 6.91 (m, 6H), 2.32 (br d, 4H, $^{3}J_{Tl-H}$ = 9.6 Hz). ^{31}P{^{1}H} NMR (202.4 Hz, THF-d_8, 55 ºC): δ 57.9. ^{31}P{^{1}H} NMR (202.4 Hz, THF-d_8, -65 ºC): δ 52.6 (br d, $^{1}J_{Tl-P}$ = 4166 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, THF-d_8): δ -12.2. Anal. Calcd. for $C_{38}H_{34}BP_2Tl$: C, 59.44; H, 4.46. Found: C, 59.63; H, 4.52.

[(*p*-MePh)$_2$B(CH$_2$PPh$_2$)$_2$][Li(TMEDA)] (2.26[Li]). Solid yellow Ph_2PCH_2Li(TMEDA) (1.3999 g, 4.3510 mmol) was suspended in diethyl ether (100 mL) in a Schlenk flask with a stir bar and sealed with a septum. The reaction vessel was cooled to -78 ºC in a dry ice/acetone bath. A solution of (*p*-MePh)$_2$BCl (498.3 mg, 2.180 mmol) dissolved in toluene (5 mL), was introduced dropwise via syringe to the cooled reaction flask. The reaction was stirred and warmed gradually to room temperature over 14 h, providing a pale yellow precipitate. Volatiles were removed under reduced pressure, and the resulting solids were isolated in the drybox on a sintered glass frit and washed with petroleum ether (3 x 30 mL), providing pale yellow solid **2.26**[Li] (1.1907 g, 65.7%).

^{1}H NMR (300 MHz, acetone-d_6): δ 7.15 (m, 12H), 6.97 (m, 12H), 6.53 (d, 4H), 2.36 (s, 4H), 2.19 (s, 12H), 2.09 (s, 6H), 1.61 (br, 4H). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-d_6): δ -8.36 (q, $^{2}J_{B-P}$ = 9.2 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, acetone-d_6): δ -12.9.

[(*p*-MePh)$_2$B(CH$_2$PPh$_2$)$_2$][ASN] (2.26[ASN]). Crude **2.26**[Li] (289.3 mg, 0.3482 mmol) was dissolved in ethanol (4 mL). Solid ASNBr (80.4 mg, 0.390 mmol) was dissolved in ethanol (2 mL) and added to stirring **2.26**[Li]. Immediately, a white

precipitate formed. The mixture was stirred for 15 min. The supernatant was decanted, and the white solids were subsequently collected by filtration and washed with Et_2O (2 x 2 mL). The solids were dried under reduced pressure, providing white **2.26**[ASN] (199.4 mg, 79.8%).

^{1}H NMR (300 MHz, acetone-d_6): δ 7.16 (m, 12H), 7.00 (m, 12H), 6.55 (d, 4H), 3.59 (m, 8H), 2.19 (m, 8H), 2.10 (s, 6H), 1.61 (br, 4H). ^{13}C{^{1}H} NMR (125.7 MHz, acetone-d_6): δ 163 (q), 148.1 (d), 135.3, 133.8 (d), 130.1, 127.8, 126.9, 126.6, 63.6, 26.6 (br), 22.8, 21.4. ^{31}P{^{1}H} NMR (121.4 MHz, acetone-d_6): δ -8.47 (q, $^2J_{B\text{-}P}$ = 11.5 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, acetone-d_6): δ -12.1. Anal. Calcd. for $C_{48}H_{54}BNP_2$: C, 80.33; H, 7.58; N, 1.95. Found: C, 78.66; H, 7.46; N, 1.81.

[(*p*-^{t}BuPh)$_2$B(CH$_2$PPh$_2$)$_2$][Li(TMEDA)$_2$] (2.27[Li]). Solid yellow Ph_2PCH_2Li(TMEDA) (1.9698 g, 6.1223 mmol) was suspended in diethyl ether (100 mL) in a Schlenk flask with a stir bar and sealed with a septum. The reaction vessel was cooled to -78 ºC in a dry ice/acetone bath. A solution of (*p*-^{t}BuPh)$_2$BCl (957.9 mg, 3.064 mmol) dissolved in toluene (10 mL), was introduced dropwise via syringe to the cooled reaction flask. The reaction was stirred and warmed gradually to room temperature over 4 h. Volatiles were removed under reduced pressure providing pale yellow solids and yellow oil. The flask was taken into the drybox, and petroleum ether (50 mL) was added. The mixture was stirred for 10 min, and the resulting solids were isolated on a sintered glass frit and washed with petroleum ether (3 x 30 mL), providing pale yellow solid **2.27**[Li] (2.2105 g, 78.9%).

^{1}H NMR (300 MHz, CD_3CN): δ 7.15 (m, 12H), 7.05 (m, 12H), 6.89 (d, 4H), 2.36 (s, 4H), 2.23 (s, 12H), 1.46 (br, 4H), 1.23 (s, 18H). ^{13}C{^{1}H} NMR (125.7 MHz,

CD_3CN): δ 163 (br), 147.9 (br), 144.7, 134.9, 133.7 (d), 128.3 (d),127.3, 123.2, 57.7, 46.3, 34.5, 32.1, 26.3 (br). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_3CN): δ -10.05 (q, $^2J_{B\text{-}P}$ = 11.5 Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, CD_3CN): δ -13.3.

[(*p*-^{t}BuPh)$_2$B(CH$_2$PPh$_2$)$_2$][ASN] (2.27[ASN]). Solid **2.27**[Li] (589.6 mg, 0.6451 mmol) was dissolved in ethanol (9 mL). Solid ASNBr (138.2 mg, 0.6705 mmol) was dissolved in ethanol (3 mL) and added to stirring **2.27**[Li]. After 5 min, a white precipitate formed. The mixture was stirred for 30 min and allowed to settle. The supernatant was decanted, and the white solids were subsequently collected by filtration and washed with Et_2O (1 mL). The solids were dried under reduced pressure, providing white **2.27**[ASN] (357.4 mg, 68.1%).

^1H NMR (300 MHz, CD_3CN): δ 7.17 (br, 12H), 7.08 (br, 12H), 6.90 (d, 4H), 3.40 (m, 8H), 2.12 (m, 8H), 1.49 (br, 4H), 1.24 (s, 18H). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_3CN): δ 162.8 (q), 148.0, 135.2, 133.9, 128.5, 127.5, 123.4, 64.0, 34.7, 32.3, 26.2 (br), 22.9. $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_3CN): δ -10.04. $^{11}B\{^1H\}$ NMR (128.3 MHz, CD_3CN): δ -13.2. Anal. Calcd. for $C_{54}H_{66}BNP_2$: C, 80.88; H, 8.30; N, 1.75. Found: C, 81.14; H, 8.12; N, 1.93.

[(*p*-MeOPh)$_2$B(CH$_2$PPh$_2$)$_2$][Li(TMEDA)$_2$] (2.28[Li]). Solid yellow Ph_2PCH_2Li(TMEDA) (1.8666 g, 5.8016 mmol) was suspended in diethyl ether (70 mL) in a Schlenk flask with a stir bar and sealed with a septum. The reaction vessel was cooled to -78 ºC in a dry ice/acetone bath. A solution of (*p*-MeOPh)$_2$BCl (755.9 mg, 2.902 mmol) dissolved in toluene (5 mL), was introduced dropwise via syringe to the cooled reaction flask. The reaction was stirred and warmed gradually to room temperature over 12 h. Volatiles were removed under reduced pressure providing pale

yellow solids. The flask was taken into the drybox, and petroleum ether (20 mL) was added. The mixture was stirred for 10 min, and the resulting solids were isolated on a sintered glass frit and washed with diethyl ether (2 x 10 mL), providing off-white solid **2.28**[Li] (2.1055 g, 84.1%).

^{1}H NMR (300 MHz, acetone-d_6): δ 7.17 (m, 12H), 6.99 (m, 12H), 6.34 (d, 4H), 3.60 (s, 6H), 2.37 (s, 8H), 2.20 (s, 24H), 1.61 (br, 4H). ^{13}C{^{1}H} NMR (125.7 MHz, acetone-d_6): δ 157 (br), 148.2 (d), 135.8, 133.7 (d), 129.3 (d), 127.8 (d), 126.5, 111.9, 58.2, 55.0, 46.2, 27 (br). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-d_6): δ -8.46 (q, $^{2}J_{B\text{-}P}$ = 10.9 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, acetone-d_6): δ -13.7.

[(*p*-MeOPh)$_2$B{CH$_2$P(Ph)$_2$(BH$_3$)}$_2$][ASN] (2.28·BH$_3$[ASN]). Colorless oil Ph$_2$(BH$_3$)PCH$_3$ (0.9615 g, 4.492 mmol) was dissolved in Et$_2$O (100 mL) in a Schlenk flask with a stirbar and sealed with a septum. The flask was cooled to -78 ºC in a dry ice/acetone bath. To the stirring reaction was added a solution of ^{s}BuLi in cyclohexane (3.5 mL, 1.3 M, 4.6 mmol). The reaction was stirred and maintained at -78 ºC for 3 h. After 3 h, a toluene solution (5 mL) of (*p*-MeOPh)$_2$BCl (585.9 mg, 2.249 mmol) was added by syringe, causing the rapid formation of white solids. The reaction was stirred and allowed to gradually warm to room temperature over 14 h. Volatiles were removed under reduced pressure, providing white solids. ^{31}P{^{1}H} NMR spectroscopic analysis of a portion of the crude reaction in THF showed the formation of a single product. The white solids were dissolved in EtOH (10 mL). Stirring, an EtOH solution (4 mL) of ASNBr (469.3 mg, 2.277 mmol) was added slowly, and white precipitate formed immediately. The mixture was stirred for 20 min. The solids were collected by filtration

and washed with EtOH (2 mL). The solids were dried under reduced pressure, providing analytically pure **2.28**·BH_3[ASN] (1.6137 g, 92.3%).

^{1}H NMR (300 MHz, acetone-d_6): δ 7.45 (m, 8H), 7.12 (m, 12H), 6.88 (br d, 4H), 6.10 (d, 4H), 3.69 (m, 8H), 3.57 (s, 6H), 2.24 (m, 8H), 2.2 (br d, 4H), 0.5-1.6 (br, 6H). ^{13}C{^{1}H} NMR (125.7 MHz, acetone-d_6): δ 155.7, 153 (br), 137.9 (d), 135.2, 132.4 (d), 128.4, 127.3 (d), 110.8, 69.3, 63.7, 22.8, 20.5 (br). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-d_6): δ 21.3. ^{11}B{^{1}H} NMR (128.3 MHz, acetone-d_6): δ -13.2, -36.0. Anal. Calcd. for $C_{48}H_{60}B_3NO_2P_2$: C, 74.16; H, 7.78; N, 1.80. Found: C, 74.36; H, 7.89; N, 1.90.

[(*p*-MeOPh)$_2$B(CH$_2$PPh$_2$)$_2$][ASN] (2.28[ASN]). Solid **2.28**·BH_3[ASN] (393.8 mg, 0.5066 mmol) was suspended in morpholine (10 mL). The reaction was stirred and heated to 60 ºC for 72 h. ^{31}P{^{1}H} NMR spectroscopic analysis of the reaction showed the formation of predominantly one major product and approximately five minor side-products. Volatiles were removed under reduced pressure. The resulting solids were washed with toluene (2 x 1 mL) and Et_2O (2 x 1 mL). Drying under reduced pressure provided a white foam (215.7 mg, 56.8%).

^{1}H NMR (300 MHz, acetone-d_6): δ 7.17 (m, 12H), 7.00 (m, 12H), 6.35 (d, 4H), 3.66 (m, 8H), 3.61 (s, 6H), 2.22 (m, 8H), 1.60 (br, 4H). ^{13}C{^{1}H} NMR (125.7 MHz, acetone-d_6): δ 157.5 (br q), 148.2 (d), 135.9, 133.9, 133.8, 127.8, 126.6, 111.9, 63.7, 55.0, 27 (br), 22.8. ^{31}P{^{1}H} NMR (121.4 MHz, acetone-d_6): δ -8.4. ^{11}B{^{1}H} NMR (128.3 MHz, acetone-d_6): δ -12.4.

[(*p*-CF$_3$Ph)$_2$B(CH$_2$PPh$_2$)$_2$][Li(TMEDA)$_2$] (2.29[Li]). Solid pale yellow Ph_2PCH_2Li(TMEDA) (2.0950 g, 6.5115 mmol) was suspended in diethyl ether (70 mL)

in a Schlenk flask equipped with a stir bar and sealed with a septum. The flask was cooled to -78 ºC in a dry ice/acetone bath under a positive pressure of dinitrogen. Solid (p-$CF_3Ph)_2BCl$ (1.1011 g, 3.2725 mmol) was dissolved in toluene (8 mL) and added dropwise by syringe over 5 min to the cooled flask. The reaction became brown as it was stirred at -78 ºC for 2 h. The flask was allowed to warm gradually and stir for an additional 3 h. Volatiles were removed under reduced pressure, providing brown solids. Toluene (8 mL) was added to the solids, providing a heterogeneous mixture. The supernatant was decanted, and the resulting solids were washed with petroleum ether (3 x 5 mL) and dried under reduced pressure, providing crude **2.29**[Li] (2.3626 g, 77.3%).

^{1}H NMR (300 MHz, acetone-d_6): δ 7.28 (br, 4H), 7.17 (br, 8H), 7.00 (m, 12H), 6.94 (d, 4H), 2.36 (s, 8H), 2.19 (s, 24H), 1.72 (br, 4H). $^{31}P\{^1H\}$ NMR (121.4 MHz, THF): δ -9.8 (q, $^2J_{P\text{-}B}$ = 9.8 Hz). $^{19}F\{^1H\}$ NMR (282.1 MHz, THF): δ -62.3. $^{11}B\{^1H\}$ NMR (128.3 MHz, THF): δ -12.7.

[(p-$CF_3Ph)_2B(CH_2PPh_2)_2$][ASN] (2.29[ASN]). Crude **2.29**[Li] (376.3 mg, 0.401 mmol) was dissolved in acetone along with approximately one equivalent of ASNBr. The solution was stirred for 30 min, and the resulting mixture was filtered. Volatiles were removed under reduced pressure. The solids were redissolved in a minimum of Et_2O, and crystallization at -30 ºC provided **2.29**[ASN] (186.3 mg, 56.3%).

^{1}H NMR (300 MHz, acetone-d_6): δ 7.30 (br, 4H), 7.17 (br, 8H), 7.01 (m, 12H), 6.96 (m, 4H), 3.73 (m, 8H), 2.27 (m, 8H), 1.72 (br, 4H). $^{13}C\{^1H\}$ NMR (75.4 MHz, acetone-d_6): δ 146.9, 135.1, 133.7 (d), 128.1, 127.0, 124.0 (q), 122.4, 63.7, 25 (br), 22.8. $^{31}P\{^1H\}$ NMR (121.4 MHz, acetone-d_6): δ -10.04. $^{19}F\{^1H\}$ NMR (282.1 MHz,

acetone-d_6): δ -61.5. $^{11}B\{^1H\}$ NMR (128.3 MHz, acetone-d_6): δ -11.3. Anal. Calcd. for $C_{48}H_{48}BF_6NP_2$: C, 69.83; H, 5.86; N, 1.70. Found: C, 68.28; H , 5.85; N, 1.84.

$[(C_6F_5)_2B\{CH_2P(BH_3)(Ph)_2\}_2][Li(solvent)_x]$ (2.30·BH_3[Li]). Colorless oil $Ph_2(BH_3)PCH_3$ (528.3 mg, 2.468 mmol) was dissolved in diethyl ether (10 mL) in a Schlenk flask with a stir bar and sealed with a septum. The reaction vessel was cooled to -78 ºC in a dry ice/acetone bath. A solution of *sec*-butyl lithium in cyclohexane (2.1 mL, 1.3 M, 2.7 mmol) was added by syringe, and the reaction was stirred and maintained at -78 ºC. After 2 h, a toluene solution (4 mL) of $(C_6F_5)_2BCl$ (469.8 mg, 1.235 mmol) was added by syringe to the reaction. The resulting mixture was stirred and allowed to gradually warm over 18 h, providing a pale brown solution with white solids. Volatiles were removed under reduced pressure. The resulting solids were washed with petroleum ether (5 mL) and dissolved in diethyl ether (5 mL). The solution was filtered, removing white solids. Volatiles were removed under reduced pressure to provide a foam that was triturated under petroleum ether (3 x 3 mL). Drying under reduced pressure provided a foam that was analyzed by NMR spectroscopy.

$^{31}P\{^1H\}$ NMR (121.4 MHz, THF): δ 19.53. $^{11}B\{^1H\}$ NMR (128.3 MHz, THF): δ -13.8 ($[(C_6F_5)_2\mathit{B}\{CH_2P(BH_3)(Ph)_2\}_2]$), -37.8 (br, $[(C_6F_5)_2B\{CH_2P(\mathit{B}H_3)(Ph)_2\}_2]$).

$[Cy_2B(CH_2PPh_2)_2][Li(TMEDA)_2]$ (2.31[Li]). Solid yellow Ph_2PCH_2Li(TMEDA) (1.4744 g, 4.5739 mmol) was suspended in diethyl ether (100 mL) in a Schlenk flask with a stir bar and sealed with a septum. The reaction vessel was cooled to -78 ºC in a dry ice/acetone bath. A solution of Cy_2BCl (491.6 mg, 2.313 mmol) dissolved in toluene (5 mL), was introduced dropwise via syringe to the cooled reaction flask. The reaction was stirred and warmed gradually to room temperature over 14 h,

providing a pale yellow precipitate. Volatiles were removed under reduced pressure, and the resulting solids were isolated by filtration and washed with petroleum ether (3 x 30 mL), providing pale yellow solid **2.31**[Li] (1.2134 g, 64.4%). Crystallization from toluene at -30 ºC provided analytically pure **2.31**[Li].

^{1}H NMR (300 MHz, acetone-d_6): δ 7.39 (m, 8H), 7.09 (m, 12H), 2.34 (s, 8H), 2.17 (s, 24H), 1.63 (br d, 4H), 1.47 (br d, 4H), 0.8-1.2 (m, 16H), 0.31 (m, 2H). ^{13}C{^{1}H} NMR (125.7 MHz, acetone-d_6): δ 149.3 (d), 133.9 (d), 217.8 (d), 126.6, 69.3, 58.3, 46.1, 37 (br), 32.6, 31.0, 22 (br). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-d_6): δ -6.18. ^{11}B{^{1}H} NMR (128.3 MHz, acetone-d_6): δ -13.1. Anal. Calcd. for $C_{50}H_{78}BLiN_4P_2$: C, 73.70; H, 9.10; N, 6.50. Found: C, 74.10; H, 9.65; N, 6.88.

[BBN-*B*,*B*-(CH$_2$PPh$_2$)$_2$][Li(TMEDA)$_x$] (2.32[Li]). Solid Ph_2PCH_2Li(TMEDA) (595.9 mg, 1.852 mmol) was suspended in diethyl ether (50 mL) in a Schlenk flask with a stir bar and sealed with a septum. The reaction vessel was cooled to -78 ºC in a dry ice/acetone bath. A hexanes solution of *B*-methoxy-9-BBN (930 μL, 1.0 M, 0.93 mmol) was introduced dropwise via syringe to the cooled reaction flask. The reaction was stirred at -78 °C for 2 h and then warmed to room temperature and stirred for 2 h, providing a pale yellow solution with white precipitate. Volatiles were removed under reduced pressure, and the resulting solids were analyzed by NMR spectroscopy.

^{31}P{^{1}H} NMR (121.4 MHz, C_6H_6): δ -7.7 (q, [BBN-*B*,*B*-(CH$_2$*P*Ph$_2$)$_2$], J = 59 Hz), -9.8 (q, [BBN-*B*-(CH$_2$*P*Ph$_2$)-*B*-(OMe)], J = 35 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, C_6H_6): δ -0.1 ([*B*BN(CH$_2$PPh$_2$)(OMe)]), -14.6 ([*B*BN(CH$_2$PPh$_2$)$_2$]).

[Ph$_2$B{CH$_2$P(*p*-^{t}BuPh)$_2$}$_2$][Li(TMEDA)] (2.33[Li]). Same method as **2.26**[Li]. Pale yellow solids, 0.9618 g, 75.8%.

^{1}H NMR (300 MHz, acetone-d_6): δ 7.25 (br, 4H), 7.15 (m, 8H), 7.05 (m, 8H), 6.67 (t, 4H), 6.57 (t, 2H), 2.36 (s, 4H), 2.20 (s, 12H), 1.66 (br, 4H), 1.23 (s, 36H). ^{13}C{^{1}H} NMR (125.7 MHz, acetone-d_6): δ 166.3 (br), 148.8, 144.5, 135.2, 133.4, 125.7, 124.5, 121.9, 58.2, 46.1, 34.8, 31.7, 26.0 (br). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-d_6): δ -12.40. ^{11}B{^{1}H} NMR (128.3 MHz, acetone-d_6): δ -12.2.

[Ph$_2$B{CH$_2$P(*p*-^{t}BuPh)$_2$}$_2$][ASN] (2.33[ASN]). Same method as **2.26**[Li]. White solids, 0.6900 g, 80.0%.

^{1}H NMR (300 MHz, acetone-d_6): δ 7.25 (br, 4H), 7.15 (dd, 8H), 7.05 (d, 8H), 6.67 (t, 4H), 6.56 (t, 2H), 3.77 (m, 8H), 2.30 (br, 4H), 2.05 (m, 8H), 1.24 (s, 36H). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-d_6): δ -12.36. Anal. Calcd. for $C_{62}H_{82}BNP_2$: C, 81.47; H, 9.04; N, 1.53. Found: C, 81.07; H, 9.36; N, 1.50.

[(*p*-MeOPh)$_2$B{CH$_2$P(*p*-^{t}BuPh)$_2$}$_2$][Li(TMEDA)] (2.34[Li]). Solid **2.19** (509.3 mg, 1.172 mmol) was suspended in Et$_2$O (20 mL) in a Schlenk flask with a stirbar and septum. The reaction vessel was cooled to -78 ºC under dinitrogen using a dry ice/acetone bath. A toluene solution (3 mL) of (*p*-MeOPh)$_2$BCl (153.0 mg, 0.5873 mmol) was added to the stirring cold reaction by syringe. The reaction was stirred and gradually warmed over 12 h. Volatiles were removed under reduced pressure, providing a tan oil. The products were dissolved in toluene (30 mL) and filtered. The solution was concentrated, and addition of petroleum ether caused white solid **2.34**[Li] to precipitate upon standing (272.6 mg, 47.8%).

^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.54 (br d, 4H), 7.46 (m, 8H), 7.16 (d, 8H), 6.72 (d, 4H), 3.47 (6H), 2.22 (br, 4H), 1.68 (br, 12H), 1.4 (br, 4H), 1.25 (s, 36H). ^{13}C{^{1}H} NMR (125.7 MHz, C$_6$D$_6$): δ 157 (br), 156.6, 150.5, 139.7, 134.9, 133.7 (m), 125.3, 112.8, 57.0,

55.0, 46.5, 34.9, 31.8, 24 (br d). $^{31}P\{^{1}H\}$ NMR (121.4 MHz, C_6D_6): δ -13.4. $^{11}B\{^{1}H\}$ NMR (128.3 MHz, C_6D_6): δ -13.4.

$[Ph_2B\{CH_2P(p\text{-}CF_3Ph)_2(BH_3)\}_2][Li(THF)_x]$ (2.35·BH_3[Li]). A diethyl ether solution (100 mL) of $(p\text{-}CF_3Ph)_2(BH_3)PCH_3$ (1.3411 g, 3.8312 mmol) was placed in a Schlenk flask with a stir bar and a septum and cooled to -78 ºC in a dry ice/acetone bath. A solution of *sec*-butyl lithium in cyclohexane (3.0 mL, 1.3 M, 3.9 mmol) was added by syringe, and the reaction was stirred and maintained at -78 ºC. After 3 h, a toluene solution (6 mL) of Ph_2BCl (386.1 mg, 1.926 mmol) was added by syringe to the reaction. The resulting mixture was stirred and allowed to gradually warm over 12 h. Volatiles were removed under reduced pressure, providing a pale yellow foam. The foam was dissolved in THF (10 mL) and transferred into a 20 mL scintillation vial. Volatiles were removed under reduced pressure, and the resulting foam was washed with petroleum ether (2 x 5 mL). The solids were dissolved in diethyl ether (12 mL) and filtered over Celite. Removal of volatiles under reduced pressure provided crude **2.35**·BH_3[Li] (1.3756 g).

^{1}H NMR (300 MHz, acetone-d_6): δ 7.64 (t, 8H), 7.50 (d, 8H), 6.90 (br, 4H), 6.46 (m, 6H), 3.62 (m, THF), 2.39 (br d, 4H), 1.79 (m, THF), 0.7-1.7 (br, 6H). $^{13}C\{^{1}H\}$ NMR (125.7 MHz, acetone-d_6): δ 142.6 (d), 135.1, 133.6 (d), 130.8 (q), 125.8, 125.0 (m), 123.0, 68.1 (THF), 26.2 (THF), 19 (br). $^{31}P\{^{1}H\}$ NMR (121.4 MHz, acetone-d_6): δ 24.0. $^{19}F\{^{1}H\}$ NMR (282.1 MHz, acetone-d_6): δ -63.2. $^{11}B\{^{1}H\}$ NMR (128.3 MHz, acetone-d_6): δ -13.0, -35.6 (br).

$[Ph_2B\{CH_2P(p\text{-}CF_3Ph)_2\}_2]$[ASN] (2.35[ASN]). Crude **2.35**·BH_3[Li] (485.6 mg, 0.514 mmol) was dissolved in CH_2Cl_2 (2 mL). Stirring, a CH_2Cl_2 solution (2 mL) of

ASNBr (106.2 mg, 0.515 mmol) was added. After 20 min, the hazy solution was filtered over Celite, washing with CH_2Cl_2 (1 mL). The combined organic layers were dried under reduced pressure, providing a pale yellow foam. The foam was dissolved in CH_2Cl_2 (2 mL) and filtered over Celite, washing with CH_2Cl_2 (1 mL). The combined organic layers were dried under reduced pressure, providing a pale yellow foam, which was subjected to the filtration procedure one additional time. The resultant foam was dissolved in neat morpholine (2 mL) and heated to 60 ºC for 12 h. Examination of an aliquot by $^{31}P\{^1H\}$ NMR spectroscopy showed the formation of one dominant product. Volatiles were removed under reduced pressure, and the yellow oil was washed with diethyl ether (3 x 2 mL), providing white solids. Crystallization of the white solids from THF/petroleum ether provided analytically pure **2.35**[ASN] (210.6 mg, 42.6%).

^1H NMR (300 MHz, acetone-d_6): δ 7.32 (m 16H), 7.15 (br d, 4H), 6.69 (t, 4H), 6.61 (m, 2H), 3.75 (m, 8H), 2.28 (m, 8H), 1.75 (br s, 4H). $^{13}C\{^1H\}$ NMR (125.7 MHz, acetone-d_6): δ 152.4 (d), 134.9, 134.1 (m), 128.7 (q), 126.2, 124.7 (d), 122.7, 63.6, 24.9 (br), 22.8. $^{31}P\{^1H\}$ NMR (121.4 MHz, acetone-d_6): δ -6.74. $^{19}F\{^1H\}$ NMR (282.1 MHz, acetone-d_6): δ -62.7. $^{11}B\{^1H\}$ NMR (128.3 MHz, acetone-d_6): δ -12.2. Anal. Calcd. for $C_{50}H_{46}BF_{12}NP_2$: C, 62.45; H, 4.82; N, 1.46. Found: C, 62.40; H, 4.94; N, 1.69.

$[(C_6F_5)_2B\{CH_2P(BH_3)(p\text{-}CF_3Ph)_2\}_2][Li(solvent)_x]$ (2.36·BH_3[Li]). A diethyl ether solution (10 mL) of $(p\text{-}CF_3Ph)_2(BH_3)PCH_3$ (532.5 mg, 1.521 mmol) was placed in a Schlenk flask with a stir bar and a septum and cooled to -78 ºC in a dry ice/acetone bath. A solution of *sec*-butyl lithium in cyclohexane (1.3 mL, 1.3 M, 1.7 mmol) was added by syringe, and the reaction was stirred and maintained at -78 ºC. After 2 h, a toluene solution (3 mL) of $(C_6F_5)_2BCl$ (289.6 mg, 0.7613 mmol) was added by syringe to the

reaction. The resulting mixture was stirred and allowed to gradually warm over 18 h to provide a pale yellow reaction mixture. Volatiles were removed under reduced pressure. The resulting solids were dissolved in diethyl ether (7 mL) filtered over Celite, removing white solids. Volatiles were removed under reduced pressure to provide a foam. The foam was washed with petroleum ether (3 x 1 mL) and dried under reduced pressure.

$^{31}P\{^{1}H\}$ NMR (121.4 MHz, THF): δ 22.3 (br). $^{11}B\{^{1}H\}$ NMR (128.3 MHz, THF): δ -14.0 ($[(C_6F_5)_2B\{CH_2P(BH_3)(p\text{-}CF_3Ph)_2\}_2]$), -37.4 (br, $[(C_6F_5)_2B\{CH_2P(BH_3)(p\text{-}CF_3Ph)_2\}_2]$).

$[(C_6F_5)_2B\{CH_2P(BH_3)(p\text{-}CF_3Ph)_2\}_2][ASN]$ (2.36·BH_3[ASN]). Solid **2.36**·BH_3[Li] (141.4 mg, 135 μmol) and solid ASNBr (27.8 mg, 135 μmol) were dissolved in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 20 min, during which time white solids precipitated. The reaction mixture was filtered, and volatiles were removed under reduced pressure. The resulting solids were dissolved in toluene (2 mL) and layered with petroleum ether. Over several days, white solids formed.

^{1}H NMR (300 MHz, acetone-d_6): δ 7.82 (t, 8H, J = 8.7), 7.68 (d, 8H, J = 7.5 Hz), 3.77 (m, 8H), 2.79 (br, 4H), 2.28 (m, 8H), 1.2 (br, 6H, P-BH_3). $^{31}P\{^{1}H\}$ NMR (121.4 MHz, acetone-d_6): δ 24.1 (br). $^{19}F\{^{1}H\}$ NMR (282.1 MHz, acetone-d_6): δ -59.2 (s, P(p-CF_3Ph)$_2$), -127.3 (br), -160.1 (t), -162.4 (br).

$[(C_6F_5)_2B\{CH_2P(p\text{-}CF_3Ph)_2\}_2][ASN]$ (2.36[ASN]). Solid **2.36**·BH_3[ASN] was dissolved in morpholine (1 mL). Monitoring the reaction by $^{31}P\{^{1}H\}$ NMR spectroscopy showed that the starting material was consumed after 3 days to provide a mixture of two products. $^{31}P\{^{1}H\}$ NMR (121.4 MHz, morpholine): δ -8.7, -9.2.

$[Ph_2B\{CH_2P(CH_3)_2(BH_3)\}_2][Li(TMEDA)]$ (2.37). Solid $PMe_3{\cdot}BH_3$ (1.0713 g, 11.915 mmol) and TMEDA (1.3893 g, 11.955 mmol) were dissolved in diethyl ether (100 mL) in a 250 mL Schlenk flask equipped with a stir bar and septum under dinitrogen. The flask was cooled to -78 ºC in a dry ice/acetone bath. A 1.6 M solution of *n*-butyl lithium (7.6 mL, 12 mmol) was added dropwise via syringe to the reaction. The reaction stirred and warmed gradually to ambient temperature over 12 h and was cooled again to -78 ºC. A toluene solution (8 mL) of Ph_2BCl (1.1950 g, 5.9607 mmol) was added dropwise via syringe to the cooled reaction, and the mixture was allowed to stir and warm gradually over 4 h. Volatiles were removed under reduced pressure, providing white solids. The solids were collected on a frit and washed with diethyl ether (3 x 10 mL), providing **2.37** (3.3948 g, 97.8%). The material can be crystallized from pentane vapor diffusion into a benzene solution, providing analytically pure $[Ph_2B\{CH_2P(CH_3)_2(BH_3)\}_2][Li(TMEDA)]$.

^1H NMR (300 MHz, C_6D_6): δ 7.69 (d, 4H), 7.36 (tt, 4H), 7.20 (tt, 2H), 2.04 (s, 12H), 1.93 (s, 4H), 1.60 (d, 4H), 0.80 (d, 12H). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6): δ 164 (q, *ipso* $B(C_6H_5)_2$), 134.7, 127.2, 124.0, 57.4, 46.7, 22.7 (m), 15.0 (d). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 1.23 (m). $^{11}B\{^1H\}$ NMR (128.3 MHz, C_6D_6): δ -13.3 (s, Ph_2BP_2), -34.2 (d, $Ph_2B(P(BH_3))_2$, $^1J_{P\text{-}B}$ = 71 Hz). ES MS (CH_3CN): calcd for $C_{18}H_{32}B_3P_2$: 343.2, found: 343.2 [M^-]. Anal. Calcd. for $C_{24}H_{48}B_3LiN_2P_2$: C, 61.86; H, 10.38; N, 6.01. Found: C, 61.84; H, 10.47; N, 5.54.

$[Ph_2B\{CH_2P(CH_3)_2(S)\}_2][Li(TMEDA)]$ (2.38). Solid $S{=}PMe_3$ (494.4 mg, 4.571 mmol) and liquid TMEDA (542.9 mg, 4.672 mmol) were dissolved in diethyl ether (100 mL) in a Schlenk flask equipped with a stir bar and septum. The flask was cooled to -78

ºC in a dry ice/acetone bath. A solution of *n*-butyl lithium (2.86 mL, 1.6 M, 4.58 mmol) was added dropwise via syringe to the reaction. The reaction was stirred at -78 ºC for 3 h. A toluene solution (5 mL) of Ph_2BCl (464.3 mg, 2.316 mmol) was added dropwise via syringe to the cooled reaction, and the mixture was allowed to stir and warm gradually over 12 h. Volatiles were removed under reduced pressure, providing white solids. The solids were collected by filtration and washed with petroleum ether (3 x 10 mL), providing white solids. Crystallization from Et_2O at -30 ºC provided analytically pure **2.38** (1.3138 g, 91.7%).

^{1}H NMR (300 MHz, acetone-d_6): δ 7.34 (br, 4H), 7.02 (tt, 4H), 6.88 (tt, 2H), 2.35 (s, 4H), 2.17 (s, 12H), 1.74 (br d, 4H), 1.04 (d, 12H, $^2J_{P\text{-}H}$ = 12.9 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, acetone-d_6): δ 163 (br), 134.8, 126.9, 123.7, 58.3, 46.1, 35 (br), 24.0 (d, $^1J_{P\text{-}C}$ = 51 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-d_6): δ 43.4. ^{11}B{^{1}H} NMR (128.3 MHz, acetone-d_6): δ -12.5. Anal. Calcd. for $C_{30}H_{58}BN_4P_2S_2$: C, 57.37; H, 8.43; N, 5.58. Found: C, 57.20; H, 8.34; N, 5.76.

$[Ph_2B(CH_2P^iPr_2)_2][Li(THF)_2]$ (2.39[Li]). Solid white $^iPr_2PCH_2Li$ (474.2 mg, 3.433 mmol) was dissolved in THF (3 mL), creating a yellow solution. Separately, Ph_2BCl was dissolved in Et_2O (7 mL) and added slowly to the stirring reaction. The resulting cloudy yellow mixture was stirred for 30 min. The reaction was allowed to settle, and the solution was decanted. Removal of the volatiles under reduced pressure provided a yellow oil. The oil was washed with petroleum ether (2 x 2 mL) and redissolved in Et_2O (6 mL). Repeated crystallization and concentration of the Et_2O solution at -30 ºC provided several crops of colorless crystals of **2.39**[Li] (387.2 mg, 39.1%).

^{1}H NMR (300 MHz, C_6D_6): δ 7.87 (br, 4H), 7.35 (t, 4H), 7.14 (m, 2H), 3.33 (m, 8H), 1.72 (d of septet, 4H), 1.40 (br, 4H), 1.23 (m, 8H), 1.08 (m, 12H), 0.97 (m, 12H). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6): δ 167 (br), 134.2, 127.4, 123.6, 69.0, 25.7, 24.4, 22.1 (d), 22.0 (d), 20.0 (d), 19.9 (d), 18 (br). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 4.94 (q, $^{2}J_{P\text{-}B}$ = 63 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, C_6D_6): δ -13.3. Anal. Calcd. for $C_{30}H_{50}BLiOP_2$: C, 71.15; H, 9.95. Found: C, 70.18; H, 9.65.

[$Ph_2B(CH_2P^tBu_2)_2$][$Li(OEt_2)$] (2.40[Li]). An Et_2O suspension (200 mL) of $^{t}Bu_2PCH_2Li$ (**2.16**) (7.3328 g, 44.14 mmol) was cooled in a Schlenk flask with a stirbar and a septum to -78 ºC in a dry ice/acetone bath. An Et_2O solution (50 mL) of Ph_2BCl (4.4240 g, 22.07 mmol) was added to the stirring reaction. The bath was removed, and the reaction was allowed to warm and stir for 12 h. Volatiles were removed under reduced pressure. The mixture was dissolved in a minimum of Et_2O, removing LiCl solids by filtration. Crystallization of the Et_2O solution at -30 ºC provided **2.40**[Li] (4.28 g, 39.6%).

^{1}H NMR (300 MHz, C_6D_6): δ 8.07 (br d, 4H), 7.23 (t, 4H), 7.00 (t, 2H), 2.79 (q, 4H), 1.51 (br, 4H), 1.15 (d, 36H, $^{3}J_{P\text{-}H}$ = 10.5 Hz), 0.66 (t, 6H). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6): δ 167 (br), 135.6, 127.0, 123.3, 65.8, 32.3 (m), 31.2 (m), 18 (br), 14.9. ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 32.11 (q, $^{2}J_{B\text{-}P}$ = 55 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, C_6D_6): δ -12.3. Anal. Calcd. for $C_{34}H_{60}BLiOP_2$: C, 72.34; H, 10.71. Found: C, 72.10; H, 10.45.

[(*m,m*-$Me_2Ph)_2B(CH_2P^tBu_2)_2$][$Li(OEt_2)$] (2.41[Li]). Solid $^{t}Bu_2PCH_2Li$ (**2.16**) (562.6 mg, 3.385 mmol) was dissolved in a mixture of THF and diethyl ether (3 mL / 7 mL). Stirring, a diethyl ether solution (5 mL) of (*m,m*-$Me_2Ph)_2BCl$ (436.5 mg, 1.701

mmol) was added dropwise. The resulting mixture was stirred for 14 h. Volatiles were removed under reduced pressure. The resulting solids were dissolved in minimal diethyl ether, and the cloudy solution was filtered. Crystallization at -30 ºC provided colorless crystalline **2.41**[Li] (434.6 mg, 41.4%).

^{1}H NMR (500 MHz, THF-d_8): δ 7.18 (s, 4H), 6.24 (s, 2H), 3.34 (q, 6H), 2.07 (s, 12H), 1.08 (t, 4H), 0.83 (d, 36H), 0.73 (br, 4H). ^{13}C{^{1}H} NMR (125.7 MHz, THF-d_8): δ 167.3 (q, $^{1}J_{B\text{-}C}$ = 51 Hz), 135.5, 132.4, 123.3, 68.4, 32.1 (d), 31.7 (d), 26.5, 22.4, 21 (br). ^{31}P{^{1}H} NMR (121.4 MHz, THF-d_8): δ 32.67. ^{11}B{^{1}H} NMR (128.3 MHz, THF-d_8): δ -12.3. Anal. Calcd. for $C_{38}H_{68}BLiOP_2$: C, 73.54; H, 11.04. Found: C, 73.16; H, 11.26.

[(*m*,*m*-Me$_2$Ph)$_2$B(CH$_2$P^{t}Bu$_2$)$_2$][Tl] (2.41[Tl]). Solid **2.41**[Li] (104.3 mg, 0.1683 mmol) was dissolved in toluene (4 mL), forming a colorless solution. Thallium nitrate (49.0 mg, 0.184 mmol) was added to the reaction, and the mixture was stirred for 14 h. The reaction was filtered, and volatiles were removed from the resulting yellow solution under reduced pressure, providing yellow solids. The solids were washed with petroleum ether (2 x 2 mL), and dried under reduced pressure, providing **2.41**[Tl] (109.2 mg, 87.2 %).

^{1}H NMR (300 MHz, C_6D_6): δ 7.55 (s, 4H), 6.75 (s, 2H), 2.64 (br d, 4H), 2.35 (s, 12H), 1.05 (d, 36H, $^{3}J_{P\text{-}H}$ = 12 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6): δ 165 (br), 135.2, 131.9, 125.4, 36.0, 30.9, 22.6, 13.0 (br). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 132.3 (d, $^{1}J_{Tl\text{-}P}$ = 6334 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, C_6D_6): δ -12.5. Anal. Calcd. for $C_{34}H_{58}BP_2Tl$: C, 54.89; H, 7.86. Found: C, 55.25; H, 8.10.

(*p*-^{t}BuPh)$_2$PCH$_3$ (2.42). The Grignard reagent *p*-^{t}BuPhMgBr was generated *in situ* from *p*-^{t}BuPhBr (19.1 g, 89.6 mmol) and excess magnesium turnings in THF (150

mL). The mixture was cannulated slowly over 1 h into a flask containing $MePCl_2$ (4.97 g, 42.5 mmol) dissolved in THF (100 mL) at 0 °C. The resulting mixture was warmed to room temperature and stirred for 2 h. The reaction was quenched with a degassed aqueous ammonium chloride solution (10% by weight, 150 mL). The organic layer was removed by a cannula under nitrogen. The aqueous layer was extracted with dichloromethane (2 x 100 mL). The combined organic layers were dried with anhydrous magnesium sulfate and filtered. The filtrate was concentrated under reduced pressure, and a colorless solid was collected. Spectroscopic data indicated it to be analytically pure **2.42** (11.4 g, 85.9%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35-7.30 (m, 8H), 1.59 (d, 3H, $^2J_{P\text{-}H}$ = 3.6 Hz), 1.30 (s, 18H). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 151.2, 136.5 (d), 131.8 (d), 125.2 (d), 34.6, 31.3, 12.7 (d). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ -29.26. Anal. Calcd for $C_{21}H_{29}P$: C, 80.73; H, 9.36. Found C, 80.53; H, 9.14.

(*p*-CF_3Ph)$_2$PCH$_3$ (2.43). The Grignard reagent *p*-$CF_3PhMgBr$ was generated *in situ* from *p*-CF_3PhBr (16.9514 g, 75.336 mmol) and excess magnesium turnings in Et_2O (200 mL). In a separate flask, liquid $MePCl_2$ (4.3978 g, 37.617 mmol) was dissolved in Et_2O (50 mL) and cooled to 0 ºC. The solution of the aryl Grignard reagent was added slowly by cannula to the cold $MePCl_2$ solution. After addition, the reaction was allowed to stir at room temperature for 2 h. The reaction was quenched with a deoxygenated saturated aqueous solution of H_4NCl (10 mL). The organic layer was extracted with water (3 x 30 mL) and dried over magnesium sulfate. Removal of the volatiles by rotary evaporation provided **2.43** as a pale yellow solid (8.6 g, 68%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63-7.60 (m, 4H), 7.56-7.50 (m, 4H), 1.71-1.69 (m, 3H). $^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$): δ 144.4 (d), 132.5 (d), 130.9 (q), 125.4 (dq), 124.13 (q), 12.41 (d). $^{19}F\{^{1}H\}$ NMR (282.1 MHz, $CDCl_3$): δ -59.89. $^{31}P\{^{1}H\}$ NMR (121.4 MHz, $CDCl_3$): δ -25.04. Anal. Calcd for $C_{15}H_{11}F_6P$: C, 53.59; H, 3.30. Found: C, 53.46; H, 3.22.

(*p*-CF_3Ph)$_2$(BH_3)PCH_3 (2.44). Solid (*p*-$CF_3Ph)_2PCH_3$ (1.5709 g, 4.6724 mmol) was dissolved in THF (1 mL). Stirring, a 2.0 M solution of $BH_3{\cdot}SMe_2$ (2.4 mL, 4.8 mmol) was added slowly. After 30 min, the reaction was quenched with EtOH (1 mL). The resulting solution was concentrated under reduced pressure, providing an oil. The oil was dissolved in Et_2O (4 mL) and filtered over a short silica plug, washing with an additional aliquot of Et_2O (2 mL). The filtered solution was concentrated under reduced pressure, providing a pale yellow oil (1.3411 g, 82.0%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70-7.85 (m, 8H), 1.96 (d, 3H, $^{2}J_{P\text{-}H}$ = 10.2 Hz), 1.0 (br q, 3H, $^{1}J_{B\text{-}H}$ = 95 Hz). $^{13}C\{^{1}H\}$ NMR (125.7 MHz, $CDCl_3$): δ 134.6 (d), 133.7 (m), 132.5 (d), 126.1 (m), 11.6 (m). $^{31}P\{^{1}H\}$ NMR (121.4 MHz, $CDCl_3$): δ 13.11. $^{19}F\{^{1}H\}$ NMR (282.1 MHz, $CDCl_3$): δ -64.1. $^{11}B\{^{1}H\}$ NMR (128.3 MHz, $CDCl_3$): δ -39.5.

2.4.4. X-ray experimental information

Crystals of **2.25**[Li], **2.25**[Tl], **2.39**[Li], **2.40**[Li], and **2.41**[Tl] were mounted on a glass fiber with Paratone-N oil. Crystallographic data were collected on a Bruker SMART 1000 diffractometer with a CCD area detector under a stream of dinitrogen. Data were collected using the Bruker SMART program, collecting ω scans at 5 ϕ settings. Data reduction was performed using Bruker SAINT v6.2. Structure solution

and structure refinement were performed using SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997). All structural representations were produced using the Diamond software program.[52]

Table 2.1. X-ray diffraction experimental details for **2.25**[Li], **2.25**[Tl], **2.39**[Li], **2.40**[Li], and **2.41**[Tl].

	2.25[Li]	**2.25**[Tl]	**2.39**[Li]
CCDC ID	150792	203701	203703
Chemical formula	$C_{50}H_{65}BLiN_4P_2$	$C_{34}H_{58}BP_2Tl$	$C_{34}H_{58}BLiO_2P_2$
Formula weight	801.75	743.92	578.49
T (ºC)	-175	-175	-175
λ (Å)	0.71073	0.71073	0.71073
a (Å)	11.7922(6)	11.7142(9)	11.3226(9)
b (Å)	11.7081(6)	16.4401(13)	15.4574(12)
c (Å)	33.1336(18)	19.1967(15)	20.5142(16)
α (º)	90	83.288(1)	90
β (º)	94.062(1)	81.391(1)	94.704(1)
γ (º)	90	72.064(1)	90
V (Å^3)	4563.1(4)	3467.8(5)	3578.3(5)
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
Z	4	4	4
D_{calcd} (g cm^{-3})	1.167	1.425	1.074
μ (cm^{-1})	1.33	47.70	1.48
*R*1, *wR*2 (I>2σ(I))	0.0608, 0.0862	0.0370, 0.0723	0.0465, 0.0868

Table 2.1. *(continued)*

	2.40[Li]	**2.41**[Tl]
CCDC ID	203700	203702
Chemical formula	$C_{34}H_{60}BLiOP_2$	$C_{38}H_{34}BP_2Tl$
Formula weight	564.51	767.77
T (ºC)	-175	-175
λ (Å)	0.71073	0.71073
a (Å)	16.295(3)	8.4192(6)
b (Å)	12.898(2)	12.6996(9)
c (Å)	17.470(3)	15.6565(11)
α (º)	90	95.585(1)
β (º)	105.480(3)	98.293(1)
γ (º)	90	104.532(1)
V (Å^3)	3538.6(11)	1587.85(19)
Space group	C_2/c	$P\bar{1}$
Z	4	2
D_{calcd} (g cm^{-3})	1.060	1.606
μ (cm^{-1})	1.46	52.13
$R1$, $wR2$ (I>2σ(I))	0.0517, 0.0896	0.0277, 0.0622

$R1 = \Sigma \, | |F_o| - |F_c| | \, / \, \Sigma \, |F_o|$, $wR2 = \{ \Sigma \, [\, w(F_o^2 - F_c^2)^2 \,] \, / \, \Sigma \, [\, w(F_o^2)^2 \,] \, \}^{1/2}$

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