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Bis(phosphino)borates: A New Family of Monoanionic Chelating Phosphine Ligands

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The reaction of dimethyldiaryltin reagents Me_2SnR_2 (R = Ph (**1**), *p*-MePh (**2**), *m,m*-Me_2Ph (**3**), *p*-^{t}BuPh (**4**), *p*-MeOPh (**5**), *p*-CF_3Ph (**6**)) with BCl_3 provided a high-yielding, simple preparative route to the corresponding diarylchloroboranes R_2BCl (R = Ph (**10**), *p*-MePh (**11**), *m,m*-Me_2Ph (**12**), *p*-^{t}BuPh (**13**), *p*-MeOPh (**14**), *p*-CF_3Ph (**15**)). In some cases, the desired diarylchloroborane was not formed from an appropriate tin reagent Me_2SnR_2 (R = *o*-MeOPh (**7**), *o,o*-$(MeO)_2$Ph (**8**), *o*-CF_3Ph (**9**)). The reaction of lithiated methyldiaryl- or methyldialkylphosphines with diarylchloroboranes or dialkylchloroboranes is discussed. Specifically, several new monoanionic bis(phosphino)borates are detailed: $[Ph_2B(CH_2PPh_2)_2]$ (**25**); $[(p\text{-MePh})_2B(CH_2PPh_2)_2]$ (**26**); $[(p\text{-}^t\text{BuPh})_2B(CH_2PPh_2)_2]$ (**27**); $[(p\text{-MeOPh})_2B(CH_2PPh_2)_2]$ (**28**); $[(p\text{-}CF_3Ph)_2B(CH_2PPh_2)_2]$ (**29**); $[Cy_2B(CH_2PPh_2)_2]$ (**30**); $[Ph_2B(CH_2P\{p\text{-}^t\text{BuPh}\}_2)_2]$ (**31**); $[(p\text{-MeOPh})_2B(CH_2P\{p\text{-}^t\text{BuPh}\}_2)_2]$ (**32**); $[Ph_2B(CH_2P\{p\text{-}CF_3Ph\}_2)_2]$ (**33**); $[Ph_2B(CH_2P(BH_3)(Me)_2)_2]$ (**34**); $[Ph_2B(CH_2P(S)(Me)_2)_2]$ (**35**); $[Ph_2B(CH_2P^iPr_2)_2]$ (**36**); $[Ph_2B(CH_2P^tBu_2)_2]$ (**37**); $[(m,m\text{-}Me_2Ph)_2B(CH_2P^tBu_2)_2]$ (**38**). The chelation of diarylphosphine derivatives **25**–**33** and **36** to platinum was examined by generation of a series of platinum dimethyl complexes. The electronic effects of substituted bis(phosphino)borates on the carbonyl stretching frequency of neutral platinum alkyl carbonyl complexes were studied by infrared spectroscopy. Substituents remote from the metal center (i.e. on boron) have minimal effect on the electronic nature of the metal center, whereas substitution close to the metal center (on phosphorus) has a greater effect on the electronic nature of the metal center.

I. Introduction

Phosphines, perhaps more than any other single ligand class, play a central role in both organic and inorganic chemistry.[1] It is striking to note that little attention has been 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

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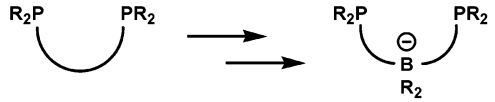
Scheme 1



borate charge fastened into the alkyl chain of the ligand backbone (Scheme 1).

Using 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 untapped. To make these ligand systems more synthetically accessible, we have initiated studies to develop reliable protocols for their synthesis. In this context, we now provide detailed methods for the preparation of a series of bis(phosphino)borate ligands comprising diverse electronic and steric properties. We also make note of certain methods that met with only limited success, realizing this type of information will likely prove equally efficacious in the continued development of this promising ligand family.

The general method we chose 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: a host of 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, Riordan's recent work being perhaps most exemplary.[12]

Specific to (phosphino)borate ligands themselves was a need to survey 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—phosphines like those described herein required somewhat customized methods of synthesis—significant progress toward 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 this study. Cation exchange protocols are also emphasized as we have found, in separate ongoing work, specific salt derivatives to be synthetically most useful.

In the results that follow, we discuss how each of the bis(phosphino)borates shown in Figure 1 was prepared, adhering to the following format for presenting these 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 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.

After the synthetic discussions, we include a consideration of structural, spectroscopic, and electronic properties typical of this emerging class of anionic phosphines. Specifically, we provide infrared spectral data for a series of substituted bis(phosphino)borate−platinum methyl carbonyl complexes and examine the effects of various substitutions upon the carbonyl stretching frequency.

II. Results and Discussion

II.1. Boron Synthons. It was desirable to preferentially study aryl-containing borates due to their typically enhanced stability[13] compared to alkylborates. We therefore chose to pursue the use of diarylhaloborane synthons. Arylhaloboranes have been prepared previously by a variety of methods,[14−19] the most common of which rely on disproportionation of haloboranes with aryl tin reagents. Since detailed descriptions allowing for the direct and efficient synthesis of a variety of diarylhaloboranes have not been previously described, experimental procedures for the production of several R_2-

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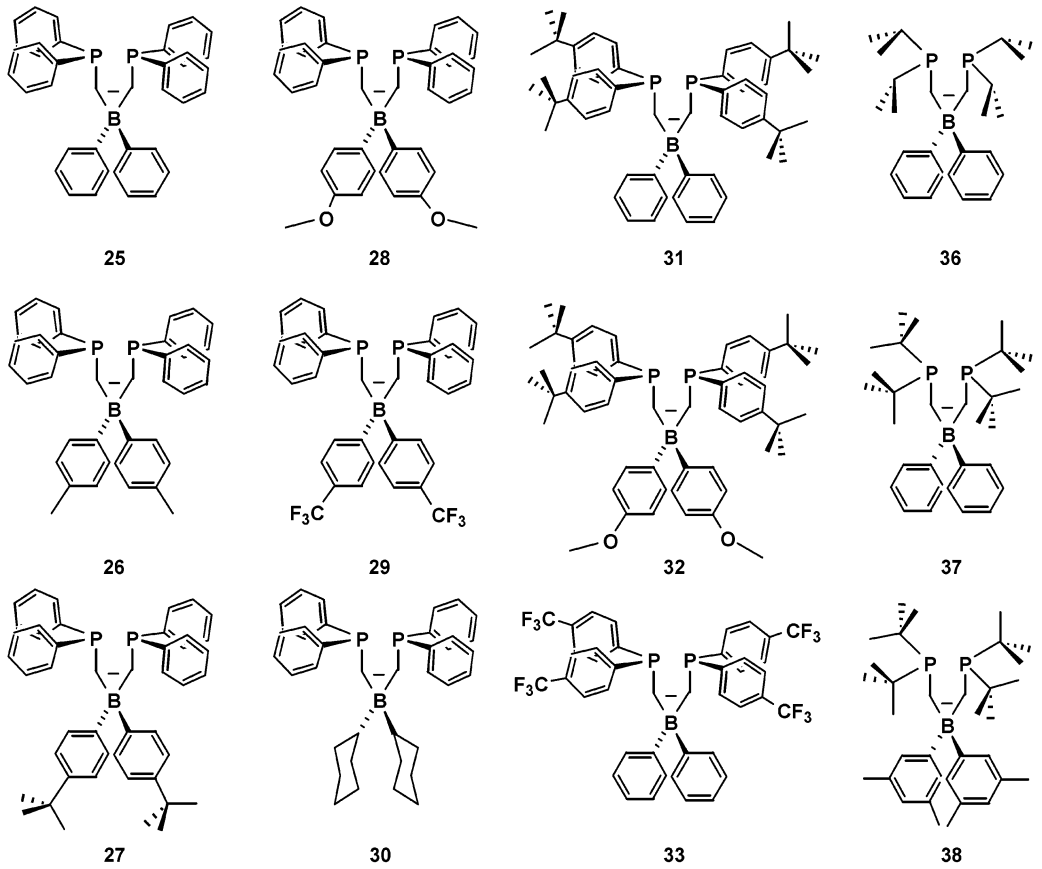
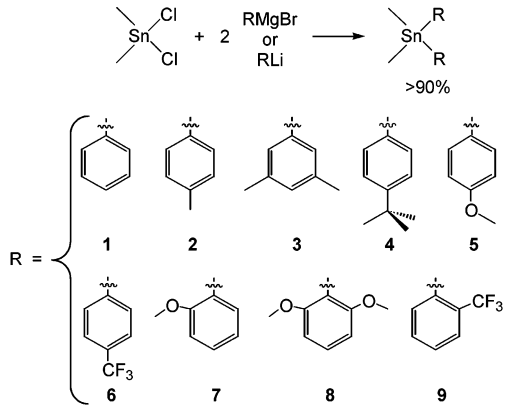


Figure 1. Representative drawings of the bis(phosphino)borates discussed.

BCl reagents are provided herein. We acknowledge an important lead from the laboratories of Chivers[18a] and Piers,[18b] 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.[20−27] A wide variety of dimethyldiaryltin reagents are readily synthesized from dimethyltin dichloride and an appropriate aryl-Grignard or aryllithium reagent. This procedure results in high isolated yields of dimethyldiaryltin compounds Me_2SnR_2 (R = Ph (**1**),[20−23] *p*-MePh (**2**),[20,21,22,24] *m,m*-$(CH_3)_2$Ph (**3**), *p*-^{t}BuPh (**4**),[25] *p*-MeOPh (**5**),[21,22,26] *p*-CF_3Ph (**6**),[21] *o*-MeOPh (**7**),[22] *o,o*-$(MeO)_2$Ph (**8**),[27] *o*-CF_3Ph (**9**)). In our hands, alkyl-, ether-, and fluoro-substituted diaryltin reagents were successfully prepared (Scheme 2).

Scheme 2



In a second step, diarylchloroboranes were generated using modified conditions of the Chivers/Piers methodology.[18] 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 °C for 24−72 h, depending on the tin

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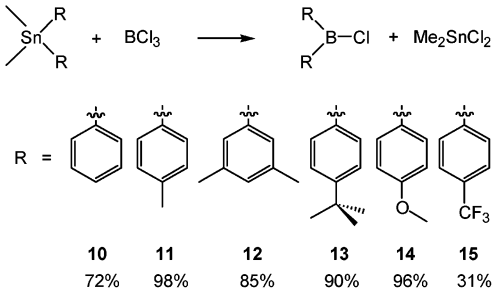
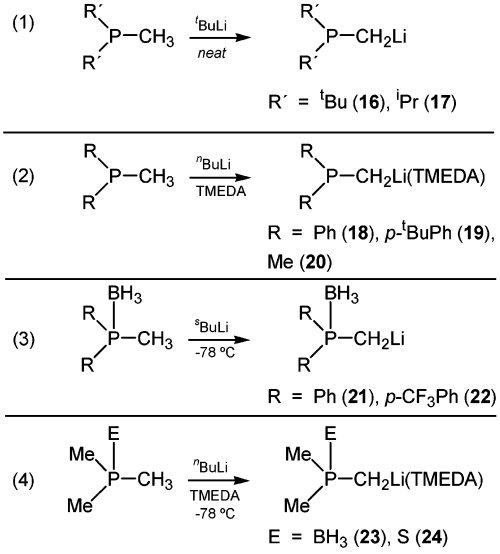
Scheme 3



reagent used. Our choice of incubating a heptane solution at 100 °C was chosen mainly 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 very 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 dimethyltin dichloride byproduct, which provided for easy recovery of this toxic and somewhat expensive 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 easily recrystallized from hydrocarbon solutions (e.g., petroleum ether, hexanes). Yields for these preparations when carried out on 5−10 g scales were greater than 70% for all but one case (Scheme 3). In addition to the parent borane Ph_2BCl (**10**),[14,15] we have successfully produced substituted diarylchloroboranes using this methodology incorporating either electron-donating ((*p*-MePh)$_2$BCl (**11**),[15,16] (*p*-^{t}BuPh)$_2$BCl (**13**), (*p*-MeOPh)$_2$BCl (**14**)[15,17]) or electron-withdrawing ((*p*-CF_3Ph)$_2$BCl (**15**)) substituents at the *para* position. Additionally, the *meta*-substituted borane (*m*,*m*-$(CH_3)_2$-Ph)$_2$BCl (**12**) was prepared by the same method. Substitution at the *ortho* position has proven more problematic. For example, attempts to incorporate *ortho*-substituted methoxyaryl groups resulted in cleavage at the aryl methyl ether linkage, generating complex reaction mixtures (^{1}H and ^{11}B NMR). Given the known ability for Lewis acidic haloboranes to cleave ethers, particularly methyl aryl ethers,[28] this was not surprising. Attempts to place a sterically encumbering CF_3 group in an *ortho* position were also unsuccessful.

II.2. Phosphine Synthons. The lithiation of unprotected dialkyl- and diarylmethylphosphines has been studied previously, most notably by the collective efforts of Karsch, Schmidbaur, Peterson, and Schore.[29,30] For example, Karsch and Schmidbaur described the deprotonation of MeP^{t}Bu$_2$ and PMe_3 to prepare $LiCH_2P^tBu_2$ (**16**) and Li(TMEDA)CH_2PMe_2 (**20**), respectively[29] (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). We have found that lithiation of MeP^{i}Pr$_2$ can be achieved using conditions similar to those employed by Karsch for the deprotonation of MeP^{t}Bu$_2$. Thus, reaction of neat MeP^{i}Pr$_2$ with desolvated ^{t}BuLi at 60 °C for 24 h provided white solids that, after washing with petroleum ether, reacted cleanly as "^{i}Pr$_2$PCH$_2$Li" (**17**) (eq 1). With respect to diarylmethylphosphines, Peterson and Schore demonstrated that deprotonation of $MePPh_2$ was most effectively accomplished using *n*-BuLi in the presence of TMEDA, thereby producing Li(TMEDA)CH_2PPh_2 (**18**).[30] By analogy, the alkyl-substituted diarylmethylphosphine (*p*-^{t}BuPh)$_2$PMe deprotonated smoothly using similar conditions to precipitate (*p*-^{t}BuPh)$_2$PCH$_2$Li(TMEDA) (**19**) as a yellow solid (eq 2). As a cautionary note, we have found that methyl-substituted arylphosphines, such as (2,4,6-Me_3-Ph)$_2$PMe, can undergo competitive lithiation at the methyl positions of the aryl rings. Additionally, attempts to deprotonate (*p*-CF_3Ph)$_2$PCH$_3$ by this method led to extensive decomposition.

The deprotonation of tertiary phosphines protected by BH_3[31,32] and S[33] has also been scrutinized due to its synthetic utility with respect to preparing chiral phosphines, as was first exemplified by Imamoto and co-workers.[32] 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*-CF_3Ph)$_2$(BH_3)PCH_3, and $Me_2(BH_3)PCH_3$ proceeded cleanly at −78 °C in ethereal solution over the course of a few hours, generating $Ph_2(BH_3)P(CH_2Li)$ (**21**) (eq 3),[32] (*p*-CF_3Ph)$_2$(BH_3)P(CH_2Li) (**22**) (eq 3), and $Me_2(BH_3)P(CH_2Li$-(TMEDA)) (**23**) in situ (eq 4).[31] Similarly, deprotonation of sulfur-protected $Me_2(S)PCH_3$ at −78 °C provided $Me_2(S)$-P(Li(TMEDA)) (**24**) in situ (eq 4). For cases where the reaction of unprotected phosphines with boranes led to



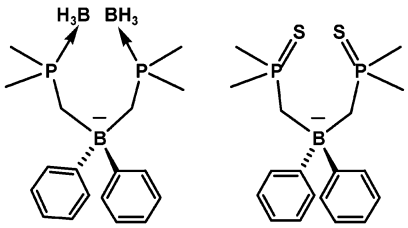
(28) For example: (a) Benton, F. L.; Dillon, T. E. *J. Am. Chem. Soc.* **1942**, *64*, 1128−1129. (b) Burwell, R. L., Jr. *Chem. Rev.* **1954**, *54*, 615−685. (c) Gerrard, W.; Lappert, M. F. *Chem. Rev.* **1958**, *58*, 1081−1111. (d) Guindon, Y.; Yoakim, C.; Morton, H. E. *Tetrahedron Lett.* **1983**, *24*, 2969−2972. (e) Guindon, Y.; Girard, Y.; Yoakim, C. *J. Org. Chem.* **1987**, *52*, 1680−1686.

undesirable results, the ease of synthesis of these reagents makes them attractive carbanion synthons.

II.3.A. Bis(phosphino)borates: Substitution at Boron. Preparation of the bis(phosphino)borate ligands themselves 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 canvassed the condensation of $Ph_2PCH_2Li(TMEDA)$ (**18**) with several different borane electrophiles. The reaction between **18** and a diarylchloroborane in general proceeded cleanly under a single reaction condition (Et_2O/toluene, −78 °C to room temperature). Only the fluorine-containing borane **15** showed any propensity to form undesired side products under these conditions. Thus, preparation of bis(phosphino)-borate ligands from functionalized diarylchloroboranes was achieved by reaction of 2 equiv of **18** with **10**, **11**, and **13**−**15**, to generate $[Ph_2B(CH_2PPh_2)_2][Li(TMEDA)_x]$ (**25**[Li]),[9] $[(p\text{-MePh})_2B(CH_2PPh_2)_2][Li(TMEDA)_x]$ (**26**[Li]), $[(p\text{-}^t\text{BuPh})_2B(CH_2PPh_2)_2][Li(TMEDA)_x]$ (**27**[Li]), $[(p\text{-MeOPh})_2B(CH_2PPh_2)_2][Li(TMEDA)_x]$ (**28**[Li]), and $[(p\text{-}CF_3Ph)_2B(CH_2PPh_2)_2][Li(TMEDA)_x]$ (**29**[Li]). In general, ^{31}P NMR spectra of the crude reaction mixtures established successful synthesis and yield as well as reaction times. Most of the Li(TMEDA) salts of the bis(phosphino)borates described above evinced some solubility in a range of solvents, including toluene, THF, CH_3CN, acetone, and ethanol. The ether- and perfluoroalkyl-substituted derivatives **28** and **29** showed greater solubility (Et_2O, 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, undergoing rapid decomposition upon dissolution. Degradation in chlorinated solvents is not generally problematic when the ligands are coordinated to transition metal ions.

The commercially available 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 $[Cy_2B(CH_2PPh_2)_2][Li(TMEDA)_x]$ (**30**[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 **30**[Li] from diethyl ether or toluene at −30 °C.

An attempt to incorporate another commercially available borane reagent, Mes_2BF (Mes = 2,4,6-Me_3Ph), proved unsuccessful under conditions analogous to those used for other boranes. The absence of reactivity under the conditions examined is most likely due to the high degree of steric hindrance at boron. While not thoroughly explored as yet, more forcing conditions may prove successful for reaction between Mes_2BF and $Ph_2PCH_2Li(TMEDA)$ (**18**).



34 35

Figure 2. Protected alkylbis(phosphino)borates.

II.3.B. 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 methyldiarylphosphines were examined. Reaction of 2 equiv of $(p\text{-}^t\text{BuPh})_2PCH_2Li(TMEDA)$ (**19**) with either Ph_2BCl (**10**) or $(p\text{-MeOPh})_2BCl$ (**14**) under the previously described conditions resulted in the generation of $[Ph_2B(CH_2P\{p\text{-}^t\text{BuPh}\}_2)_2][Li(TMEDA)_x]$ (**31**[Li]) and $[(p\text{-MeOPh})_2B(CH_2P\{p\text{-}^t\text{BuPh}\}_2)_2][Li(TMEDA)_x]$ (**32**[Li]). We also inspected the fluorine-containing synthon $(p\text{-}CF_3Ph)_2PMe$ to generate bis(phosphino)borates. Since direct lithiation of this phosphine was unsuccessful (vide supra), a borane protection strategy was used. Generation of $(p\text{-}CF_3Ph)_2(BH_3)PCH_3$ proceeded readily by addition of $BH_3{\cdot}SMe_2$. Subsequent deprotonation (*s*-BuLi at −78 °C over 2 h) followed by addition of Ph_2BCl provided the protected bis(phosphino)borate $[Ph_2B\{CH_2P(p\text{-}CF_3Ph)_2(BH_3)\}_2][Li]$ (**33**·BH_3[Li]). Removal of the BH_3 protecting groups was accomplished by dissolution of **33**·BH_3 in neat morpholine at 60 °C for 12 h, providing **33**[Li].

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 simple methyl-substituted derivative $[Ph_2B(CH_2PMe_2)_2]$. Direct reaction of $Me_2PCH_2Li(TMEDA)$ (**20**) with diphenylchloroborane 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.[34] In accord with this suggestion, the BH_3-protected carbanion, $Me_2P(BH_3)CH_2Li(TMEDA)$ (**23**), reacted productively with Ph_2BCl (**10**) to produce the desired borate $[Ph_2B(CH_2P(BH_3)Me_2)_2][Li(TMEDA)_x]$ (**34**) (Figure 2). Likewise, the in situ-generated sulfur-protected reagent, $Me_2P(S)CH_2Li$ (**24**), reacted cleanly to afford $[Ph_2B(CH_2P(S)Me_2)_2]$ (**35**) (Figure 2), an intriguing S-donor ligand in its own right.

Attempts to deprotect either the borane- or sulfur-protected borates **34** and **35** have met with very limited success. For example, to deprotect **34**, a host of literature protocols for

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(30) (a) Peterson, D. J. *J. Organomet. Chem.* **1967**, *8*, 199. (b) Schore, N. E.; Benner, L. S.; Labelle, B. E. *Inorg. Chem.* **1981**, *20*, 3200−3208.
(31) Schmidbaur, H. *J. Organomet. Chem.* **1981**, *200*, 287−306 and references therein.
(32) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244−5252.
(33) (a) Mathey, F. *Tetrahedron* **1974**, *30*, 3127−3137. (b) Mathey, F.; Mercier, F. *Tetrahedron Lett.* **1979**, 3081−3084. (c) Chen, C. H.; Brighty, K. E. *Tetrahedron Lett.* **1980**, 4421−4424. (d) Karsch, H. H. *Chem. Ber.* **1982**, *115*, 818−822. (e) Corey, E. J.; Chen, Z.; Tanoury, G. J. *J. Am. Chem. Soc.* **1993**, *115*, 11000−11001. (f) Muci, A. R.; Campos, K. R.; Evans, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 9075−9076.
(34) Karsch et al. have reported similar results using aluminum electrophiles. See ref 4.

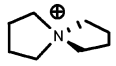
deprotecting phosphine−boranes were tried. These included heating the borane-protected borate in neat morpholine or diethylamine,[32] refluxing in toluene with an excess of DABCO,[35] reaction with $HBF_4 \cdot Me_2O$,[36] and attempting to reduce it by Pd/C in ethanol.[37] Additionally, heating **34** in toluene with an excess of PMe_3, or even in neat $^nBu_3P$, 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 **35** 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 $^nBu_3P$.[42] Also, attempts to reduce **35** 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 chemically challenging than deprotection of the corresponding aryl-substituted derivatives*. This is presumably due to a very high degree of thermodynamic stability in the anionic (alkylphosphino)borate-to-borane adduct complexes.

Because the simple methyl-substituted phosphines proved reluctant to release their protection groups, we examined bulkier alkyl carbanions with the hope that steric crowding would disfavor formation of the Lewis acid ← base adducts and therefore not require phosphine protection. We were gratified to find that $^iPr_2PCH_2Li$ (**17**) reacted with Ph_2BCl (**10**) in a mixture of THF and Et_2O to produce the target ligand $[Ph_2B(CH_2P^iPr_2)_2][Li(THF)_2]$ (**36**[Li]) in good yield (essentially quantitative by ^{31}P NMR). In similar fashion, 2 equiv of $^tBu_2PCH_2Li$ (**16**) reacted with Ph_2BCl (**10**) in Et_2O/THF to form $[Ph_2B(CH_2P^tBu_2)_2][Li(OEt_2)]$ (**37**[Li]). Once again, the reaction proceeded very cleanly according to the crude ^{31}P NMR spectrum. Both **36**[Li] and **37**[Li] could be crystallized from Et_2O at −30 °C. The related ligand [(*m*,*m*-$Me_2Ph)_2B(CH_2P^tBu_2)_2$][Li($OEt_2$)] (**38**[Li]), was also prepared by room-temperature reaction of 2 equiv of $^tBu_2PCH_2Li$ (**16**) with (*m*,*m*-$Me_2Ph)_2BCl$ (**12**) in Et_2O/THF and crystallized from Et_2O at −30 °C. High isolated crystalline yields of alkyl-substituted bis(phosphino)borates have 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 **36**−**38** to be appreciably less stable than their aryl substituted counterparts. This was true with respect to oxidation, hydrolysis, and also thermal decomposition*.

II.4. Generation of Ammonium and Thallium Salts. Under many conditions, the lithium and Li(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 highly dependent on the nature of the countercation. We therefore explored the salt exchange of several bis(phosphino)borates. Although we have chosen to specifically describe the formation of ASN (ASN = 5-azoniaspiro[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.[45]

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

[BP_2] = bis(phosphino)borate$^-$
[Li] = Li(solvent)$^+$ or Li(TMEDA)$^+$
[R_4N] = nBu_4N^+, Et_4N^+, ASN$^+$
[X] = Br^-, Cl^-

ASN$^+$ = 

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

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

Salt exchange was straightforward for alkyl-substituted aryl borates **25**−**27** and **31**. The poor solubility of the ammonium bis(phosphino)borates in EtOH provided a general means for removing (TMEDA)Li halide. The generation of tetraalkylammonium salts by direct salt metathesis using ammonium halides in ethanol succeeded for **25**[Li], **26**[Li], **27**[Li], and **31**[Li], providing $[Ph_2B(CH_2PPh_2)_2]$[ASN] (**25**[ASN]),[9] [(*p*-$MePh)_2B(CH_2PPh_2)_2$][ASN] (**26**[ASN]), [(*p*-$^tBuPh)_2B(CH_2$-$PPh_2)_2$][ASN] (**27**[ASN]), and $[Ph_2B(CH_2P\{p\text{-}^tBuPh\}_2)_2]$-[ASN] (**31**[ASN]).

In contrast, cation exchange for the MeO- and CF_3-substituted arylborates **28**[Li] and **29**[Li] was problematic due to their respective solubilities. The preparation of [(*p*-$CF_3Ph)_2B(CH_2PPh_2)_2$][ASN] (**29**[ASN]) by dissolution in acetone with (ASN)Br followed by filtration, concentration, and crystallizing at −35 °C did prove successful. The synthesis of [(*p*-$MeOPh)_2B(CH_2PPh_2)_2$][ASN] (**28**[ASN]), however, was much more challenging. The most favorable results were obtained by generating the BH_3-protected phosphine ligand by deprotonation of $MePPh_2 \cdot BH_3$ followed by reaction with **14** to form [(*p*-MeOPh)$_2$B{$CH_2P(Ph)_2$-(BH_3)}$_2$][Li(solvent)$_x$] (**28**·BH_3[Li]) and then carrying out salt metathesis in ethanol with (ASN)Br. The resulting product, [(*p*-MeOPh)$_2$B{$CH_2P(Ph)_2(BH_3)$}$_2$][ASN] (**28**·BH_3-[ASN]), can be converted through borane deprotection to

(35) Brisset, H.; Gourdel, Y.; Pellon, P.; Le Corre, M. *Tetrahedron Lett.* **1993**, 4523−4526.
(36) McKinstery, L.; Livinghouse, T. *Tetrahedron* **1995**, *51*, 7655−7666.
(37) Couturier, M.; Tucker, J. L.; Andresen, B. M.; Dubé, P.; Negri, J. T. *Org. Lett.* **2001**, *3*, 465−467.
(38) (a) Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7012−7023. (b) Zon, G.; DeBruin, K. E.; Naumann, K.; Mislow, K. *J. Am. Chem. Soc*. **1969**, *91*, 7023−7027.
(39) Omelańczuk, J.; Mikołajczyk, M. *Tetrahedron Lett.* **1984**, *25*, 2493−2496.
(40) Omelańczuk, J.; Mikołajczyk, M. *J. Am. Chem. Soc.* **1979**, *101*, 7292−7295.
(41) (a) King, R. B.; Cloyd, Jr., J. C. *J. Am. Chem. Soc*. **1975**, *97*, 46−52. (b) King, R. B.; Cloyd, Jr., J. C. *J. Am. Chem. Soc.* **1975**, *97*, 53−60.
(42) Gorla, F.; Venanzi, L. M.; Albinati, A. *Organometallics* **1994**, *13*, 43−54.
(43) Olah, G. A.; Hehemann, D. *J. Org. Chem.* **1977**, *42*, 2190.
(44) Blicke, F. F.; Hotelling, E. B. *J. Am. Chem. Soc.* **1954**, *76*, 5099−5103.
(45) For reference, we have included the [$^nBu_4N$] and [Et_4N] salts of $[Ph_2B(CH_2PPh_2)_2]$ in the experimental data.

the desired compound, **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 either borane- or sulfide-protected phosphines is the possibility for their successful and high-yielding deprotection.

To examine the ability to form thallium salts of phenyl-substituted bis(phosphino)borates, we prepared the compound $[Ph_2B(CH_2PPh_2)_2][Tl]$ (**25**[Tl]). Salt exchange occurred upon combination of EtOH solutions of **25**[Li] and $TlPF_6$. Over 30 min, off-white solids precipitated which were collected and further purified by crystallization from THF. For this salt exchange, it was not necessary that **25**[Li] be rigorously pure from additional LiCl. It remains in the EtOH solution, as does any excess $TlPF_6$. Purified **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 **25**[Tl] were obtained that showed no remarkable features, the ^{31}P NMR signals were difficult to detect at ambient temperature. This contrasts the ^{31}P NMR spectrum obtained of crude **25**[Tl], which shows a broad singlet at 57 ppm. Examination of a THF-d_8 solution of **25**[Tl] demonstrated that a temperature-dependent exchange phenomenon was operative. Thus, at low temperature (−65 °C), the ^{31}P 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 °C. Further warming to 55 °C provided a broad singlet at 57.9 ppm.

A thallium adduct of **38** was also synthesized. Salt exchange was effected by stirring a toluene solution of **38**[Li] with thallium nitrate. (A similar method works equally well for related **37**[Li].) The thallium−phosphorus coupling constant observed for **38**[Tl] in benzene is exceptionally large (6334 Hz) but is reduced upon dissolution 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).

II.5. 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 and ^{31}P NMR were useful for analyzing the contents of crude reaction mixtures. The desired tetraalkyl-substituted borates have distinctive ^{11}B NMR chemical shifts and sharp resonances which allow for easy identification. All of the aryl-substituted phosphines

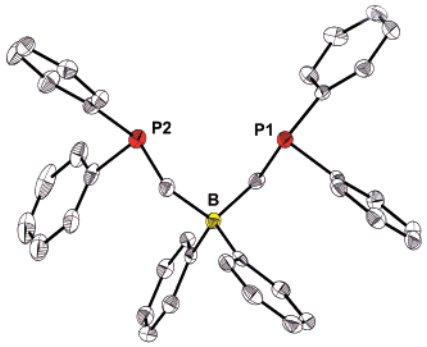


Figure 3. A 50% displacement ellipsoid representation of $[Ph_2B(CH_2PPh_2)_2][Li(TMEDA)_2]$ (**25**[Li]). Hydrogen atoms and the $[Li(TMEDA)_2]$ cation are omitted for clarity.

provided ^{31}P 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 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 ($^2J_{P-B}$).

To provide structural data for this new ligand class, X-ray diffraction studies were carried out on select derivatives. The previously described bis(phosphino)borate $[Ph_2BP_2]$ (**25**) was crystallized as its $Li(TMEDA)_2$ salt, and a representation of its structural data is shown in Figure 3. As can be seen from the figure, even in the absence of an alkali metal cation, the ligand adopts a confirmation well-poised to accept a metal ion.

The related thallium salt of **25** was also studied by X-ray crystallography to further probe the intriguing exchange phenomenon eluded to above. A structural determination of crystalline **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 4). On the basis of the structural determination, the ^{31}P NMR data is best explained by a highly labile binding of thallium by 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 (see Supporting Information for greater detail). This contrasts the coordination observed for a related bis-(phosphino)borate−thallium complex (vide infra).

Crystals of alkyl-substituted bis(phosphino)borates **36**[Li] and **37**[Li] were also studied by X-ray diffraction. Structural representations are shown in Figures 5 and 6. 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 **37**[Li] restrict the coordination environment around lithium to 3-coordinate, allowing only a single diethyl ether molecule to coordinate. In contrast, the structure of the lithium ion in **36**[Li] is more typically 4-coordinate, with two THF molecules coordinated to the lithium cation.

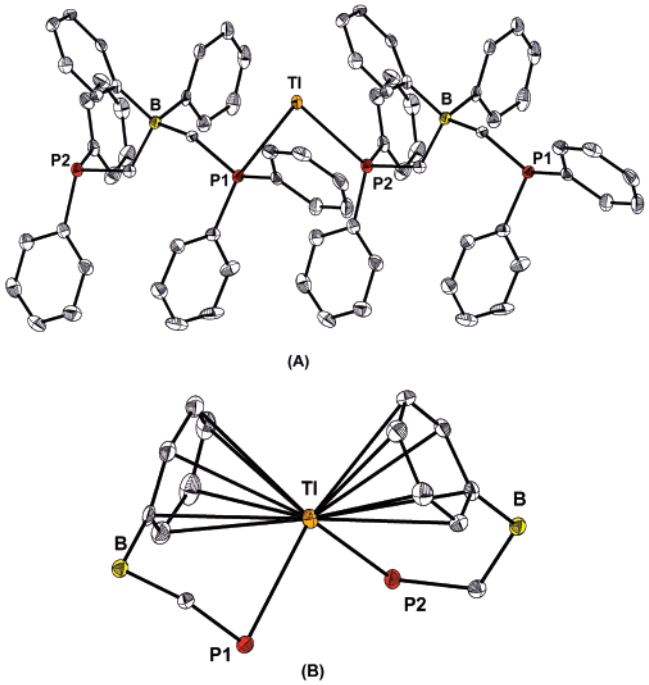


Figure 4. (A) A 50% displacement ellipsoid representation of $\{[Ph_2B(CH_2PPh_2)_2][Tl]\}_n$ (**25**[Tl]), showing two anionic bis(phosphino)borate units and one interconnecting thallium. Hydrogen atoms are omitted for clarity. (B) Expanded view of the thallium coordination sphere. Selected interatomic distances (Å) and angles (deg): P1−Tl, 3.0283(9); P2−Tl, 3.0231(9); Tl−C_{aryl}(av), 3.311(5).

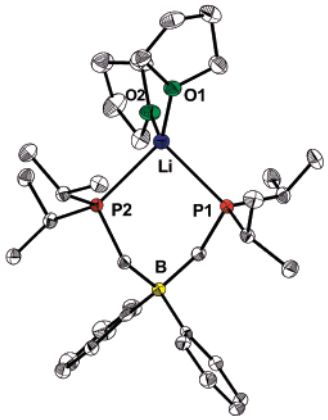


Figure 5. A 50% displacement ellipsoid representation of $[Ph_2B(CH_2P^iPr_2)_2][Li(THF)_2]$ (**36**[Li]). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Li−P1, 2.608(3); Li−P2, 2.596(3); Li−O1, 1.962(3); Li−O2, 1.928(3); Li−B, 4.197(3); P1−Li−P2, 91.07(9); 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).

An X-ray diffraction experiment carried out on crystals of **38**[Tl] grown from benzene showed a structure distinct from **25**[Tl] in that the thallium cation is coordinated by two phosphines and garners additional electron density from the aryl ring of an adjacent arylborate group (Figure 7). The thallium center in **38**[Tl] is best described as three-coordinate, with two phosphine donors and a single η^2-aryl interaction (see Supporting Information for greater detail). The nominally 3-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.

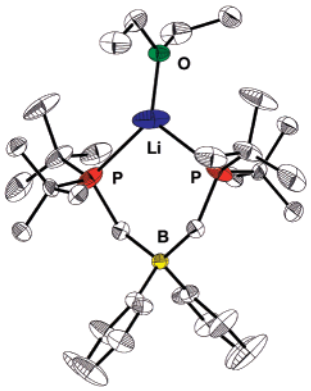


Figure 6. A 50% displacement ellipsoid representation of $[Ph_2B(CH_2P^tBu_2)_2][Li(OEt_2)]$ (**37**[Li]). Hydrogen atoms and disordered positions are omitted for clarity. Selected interatomic distances (Å) and angles (deg): P−Li, 2.485(4); Li−O, 1.926(8); B−Li, 4.092(8); P−Li−O, 121.31(14); P−Li−P, 99.5(2).

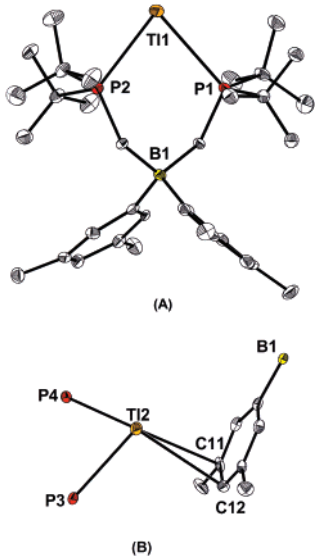


Figure 7. (A) A 50% displacement ellipsoid representation of $[(m,m\text{-}(CH_3)_2Ph)_2B(CH_2P^tBu_2)_2][Tl]$ (**38**[Tl]). Hydrogen atoms and second molecule of the asymmetric unit are omitted for clarity. Selected interatomic distances (Å) and angles (deg): P1−Tl1, 2.9919(12); P2−Tl1, 2.9426(11); 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 (deg): P3−Tl2, 2.9788(12); P4−Tl2, 2.9406(11); C11−Tl2, 3.388(4); C12−Tl2, 3.353(4).

II.6. Discussion of Electronic Properties Characteristic of Bis(phosphino)borate Ligands. Our remaining objective is to consider the electronic properties of the bis(phosphino)borate ligands that have been described herein. To do this, we report the spectroscopic characterization of a series of neutral, platinum(II) carbonyl complexes supported by these ligands. A key issue we consider is whether a zwitterionic description is most appropriate for neutral complexes supported by these new ligands.

The impetus to describe neutral complexes supported by (phosphino)borate ligands as zwitterionic derives from the lack of simple resonance contributors that can efficiently delocalize the anionic borate charge to the coordinated metal center. From an electron-counting perspective, the zwitterionic formulation suggests that metal complexes supported by bis(phosphino)borates be regarded as cationic complexes chelated by an L_2, 4-electron-donor ligand.[46] This electronic

Table 1. ^{31}P NMR Signals and Carbonyl Stretching Frequencies for Bis(phosphino)borate−Platinum Methyl Carbonyl Complexes **49**−**58**

complex	^{31}P NMR, δ ($^{1}J_{Pt-P}$, Hz)	ν_{CO} (cm^{-1})[c]
$[Ph_2B(CH_2PPh_2)_2]Pt(Me)(CO)$ (**49**)	20.15 (3053), 15.53 (1637)[a]	2094
$[(p\text{-}MePh)_2B(CH_2PPh_2)_2]Pt(Me)(CO)$ (**50**)	20.33 (3062), 15.92 (1645)[a]	2094
$[(p\text{-}^tBuPh)_2B(CH_2PPh_2)_2]Pt(Me)(CO)$ (**51**)	20.00 (3044), 15.32 (1639)[b]	2094
$[(p\text{-}MeOPh)_2B(CH_2PPh_2)_2]Pt(Me)(CO)$ (**52**)	19.89 (3053), 15.43 (1640)[b]	2094
$[(p\text{-}CF_3Ph)_2B(CH_2PPh_2)_2]Pt(Me)(CO)$ (**53**)	18.75 (3061), 14.24 (1631)[b]	2097
$[Cy_2B(CH_2PPh_2)_2]Pt(Me)(CO)$ (**54**)	20.42 (3037), 16.23 (1646)[a]	2092
$[Ph_2B(CH_2P\{p\text{-}^tBuPh\}_2)_2]Pt(Me)(CO)$ (**55**)	17.48 (3030), 12.68 (1641)[b]	2091
$[(p\text{-}MeOPh)_2B(CH_2P\{p\text{-}^tBuPh\}_2)_2]Pt(Me)(CO)$ (**56**)	17.65 (3034), 12.93 (1642)[a]	2091
$[Ph_2B(CH_2P\{p\text{-}CF_3Ph\}_2)_2]Pt(Me)(CO)$ (**57**)	20.85 (3090), 16.84 (1616)[a]	2105
$[Ph_2B(CH_2P^iPr_2)_2]Pt(Me)(CO)$ (**58**)	40.28 (1666), 30.81 (2942)[b]	2079

[a] $CDCl_3$. [b] CD_2Cl_2. [c] CH_2Cl_2.

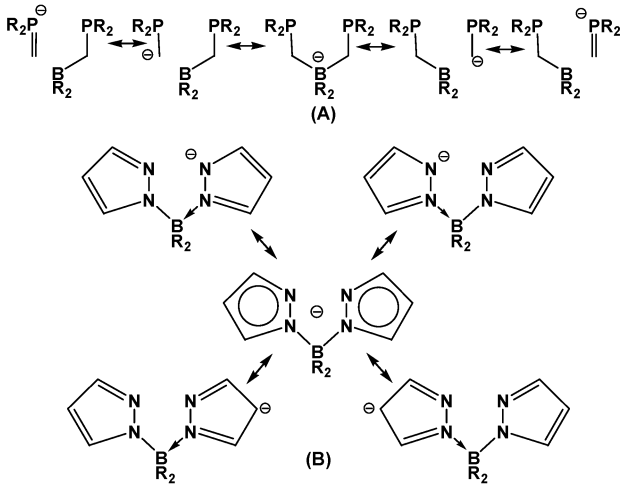


Figure 8. Selected resonance contributors for (A) bis(phosphino)borates and (B) bis(pyrazolyl)borates.

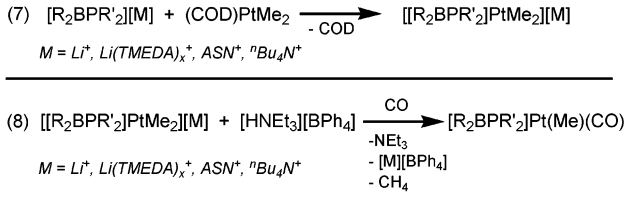
description is distinct from the delocalized description typically offered for the related families of bis- and tris-(pyrazolyl)borates.[11,46] In the (pyrazolyl)borates, the borate charge is presumed to be more uniformly distributed due to important resonance contributors that fully delocalize the borate charge. In the extreme, electron-counting schemes designate bis(pyrazolyl)borates as LX-type, 3-electron-donors, whereas bis(phosphino)borates can be classified as 4-electron, L_2-donor ligands coordinated to a formal cation. To underscore and clarify this distinction, Figure 8 provides several conceivable resonance forms for a hypothetical bis-(phosphino)borate complex and several reasonable resonance forms of the bis(pyrazolyl)borate system. Some structures shown for the bis(phosphino)borate system emphasize an ylide resonance contributor of these anions.

To comparatively probe electronic factors, we have reported infrared data for neutral metal carbonyl complexes supported by both (phosphino)- and (amino)borate ligands and have compared these data to that of their isostructural but formally cationic carbonyl analogues.[8d,9b,10,47] The results of these model studies are collectively summarized as follows: despite the utility in the zwitterionic descriptor, CO stretching frequencies recorded for the neutral systems are invariably much lower in energy than their corresponding cationic systems. This fact intimates that (phosphino)borate ligands are appreciably more electron-releasing than their neutral ligand congeners. Data consistent with this summary has now been examined for several model carbonyl systems featuring different metals (Fe, Ru, Rh, Co, Pd, Pt) in a range of stereochemical environments (trigonal pyramidal, square pyramidal, square planar, and octahedral).[8d,9b,10,47,48]

Given these data, it is surprising how well the overall reactivity of the zwitterionic systems we have thus far examined compares with their isostructural but cationic cousins. Clearly, the anionic field of the borate charge is experienced by the coordinated metal center in these complexes but does not significantly detract from their ability to mediate transformations typical of their more electrophilic, cationic cousins.[9,10,47]

Of obvious concern is to consider the degree to which infrared CO data are actually reflective of the electronic distribution for these systems. We therefore collected infrared data for the series of platinum complexes shown in Table 1 to tune electronic effects at a position remote from the coordinated metal center and to determine whether the CO stretching frequency would be sensitive to such tuning.

As for the preparation of $[Ph_2BP_2]Pt(Me)(CO)$,[9b] the dimethyl complexes were prepared by reaction of the bis-(phosphine) ligand with $(COD)PtMe_2$, which in most cases led to rapid and quantitative displacement of cyclooctadiene (eq 7). The sterically encumbered ligand **37** (and its relative **38**) was the only phosphine ligand that failed to displace cyclooctadiene, even at elevated temperatures (80 °C). Subsequent protonation of each dimethyl complex by an ammonium salt (e.g., $[HNEt_3][BPh_4]$) in THF, followed by introduction of an atmosphere of CO, cleanly generated the desired neutral methyl carbonyl complexes $[R_2B(CH_2PR'_2)_2]$-Pt(Me)(CO) (**49**−**58**, eq 8). Their IR spectra were recorded in CH_2Cl_2 solution (KBr cell) to provide the relevant CO stretching frequencies (Table 1).



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As can be seen from the infrared data, variation of the borate backbone by systematic *para* substitution on the phenyl ring (e.g., −H, $-CH_3$, $-^tBu$, −OMe, $-CF_3$) has rather little effect on the observed CO stretching frequencies. Indeed, aside from the CF_3-substituted derivative, each of the complexes shown provides an indistinguishable CO stretching frequency of 2094 cm^{-1}. The difference in the observed CO stretching frequency ($\Delta\nu_{CO}$) between the MeO-substituted and the CF_3-substituted derivatives is only 3 cm^{-1}. This modest difference is striking in view of the large difference in the CO stretching frequency ($\Delta\nu_{CO} = +24$ cm^{-1}) measured between $[Ph_2BP_2]$Pt(Me)(CO) and its cationic counterpart $[(Ph_2SiP_2)PtMe(CO)][BAr_4]$ ($Ph_2SiP_2 = Ph_2Si(CH_2PPh_2)_2$).[9b] Replacement of the diaryl backbone by a dialkyl backbone, as in the Cy_2B derivative, provides a slightly more electron-releasing ligand. Perhaps expectedly, more pronounced effects are observed by *para* substitution at the arylphosphine donor positions. For example, the electron-releasing *para-tert*-butyl-substituted derivative, **55**, has a ν_{CO} at 2091 cm^{-1}, whereas the *para*-CF_3-substituted derivative, **57**, provides a ν_{CO} at 2105 cm^{-1}, a 14 cm^{-1} difference. The sensitivity of the CO stretching frequency as a function of variation at the borate backbone in these *neutral* complexes appears to be quite small (2−3 cm^{-1}) or negligible. Variation at the phosphine donors has an appreciably more pronounced effect. This outcome is consistent with describing the borate unit as electronically insulated, at least to some degree.

To reconcile this conclusion with the comparative infrared data for the neutral versus cationic platinum carbonyl complexes, it needs to be underscored that the absolute magnitude in $\Delta\nu_{CO}$ measured between a zwitterionic complex (e.g., $[Ph_2BP_2]$Pt(Me)(CO)) and a cationic complex (e.g., $[(Ph_2SiP_2)Pt(Me)(CO)][BAr_4]$) is somewhat misleading for the following reason. In cationic late metal carbonyls, where π-back-bonding is relatively weak, strong polarization of the CO σ-bond by the cationic complex is anticipated.[49] This raises the energy of the force constant F_{CO} dramatically, and in extreme cases, polarization can dominate the observed F_{CO}. In this context, cationic complexes such as $[(Ph_2SiP_2)PtMe]^+$ are expected to have characteristically high force constants F_{CO} due to a strong polarization effect. This effect will be much reduced for CO coordinated to a neutral $[Ph_2BP_2]$PtMe fragment, regardless of whether its charge is distributed asymmetrically due to a zwitterionic resonance contributor. We therefore caution that the absolute magnitude of $\Delta\nu_{CO}$ is not so reliable a gauge of relative back-bonding ability between complexes that are *formally* cationic and complexes that are *formally* neutral. Large differences in polarization between isostructural cationic and neutral complexes likely compete with the electronic contributors of σ donation, π-back-bonding, and/or π-acceptor character that we typically rely upon to correlate measured $\Delta\nu_{CO}$ values to the electron-releasing character of a ligand. This dilemma of variable polarization is avoided within a contiguous series of neutral carbonyl complexes, such as those provided in Table 1. The relative ν_{CO} values recorded are more reflective of relative "electron-releasing" character.

It is interesting to also note that the subtle differences recorded for the IR data are also manifest in the respective ^{31}P NMR shifts of the methyl carbonyl complexes. The magnitude of the separation (between 4 and 5 ppm) between the two signals remains fairly constant across the series, and complexes with identical ν_{CO} stretches exhibit nearly identical ^{31}P NMR shifts, as well as NMR coupling constants.

From the spectroscopic data collected in Table 1, it is reasonable to conclude that electronic variation by substitution at the arylborate unit of the bis(phosphino)borate ligands has only a small, if any, electronic impact on the electron-releasing character of the phosphine ligands. This view is consistent with the zwitterionic resonance contributor for neutral complexes derived from these ligands. Data reported elsewhere, however, that compare the electrophilicity of these zwitterions with their isostructural cations strongly suggest that the zwitterions are appreciably more electron-rich.[9b,10,47] Considering both sets of data collectively, one can therefore anticipate a step change in the relative electrophilicity of a metal center on moving from a neutral to a formally cationic system, regardless of whether the neutral system is formally zwitterionic. In other words, the anionic (phosphino)borates are clearly more electron-releasing than their neutral counterparts—a chemically plausible outcome. However, the degree to which the borate charge is actually disseminated throughout the complex is perhaps overly emphasized by infrared data that compare a cationic to a neutral system.

Conclusion

This paper 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 efficacious in the synthesis of tris(phosphino)-borate ligands.[50] While the protocols are in general effective, we have uncovered problematic scenarios that 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 carbanion delivery 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 nontrivial. 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 far more straightforward and, in certain cases, are required, as for the case of ligand **33**. Fortunately, alkyl-substituted ligands, such as $[Ph_2B(CH_2P^iPr_2)_2]$ and $[Ph_2B(CH_2P^tBu_2)_2]$, are readily prepared without protection.

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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 paper has also provided protocols for preparing lithium, thallium, and ammonium salt derivatives of the bis(phosphino)borates. While detailed studies of the reactivity of these derivatives with transition metal precursors is reserved for future reports, we note that the thallium and ammonium salts have proven effective to date in our laboratories. Also, the reaction product profile can be highly dependent on which countercation is used.

Finally, we have discussed the electron-releasing character of these anionic phosphine ligands. While this latter issue is not fully resolved, we can conclude that (phosphino)borates are generally more electron-releasing than their neutral phosphine analogues, despite the fact that the borate unit is not delocalized by conventional resonance contributors. This latter conclusion suggests that neutral complexes supported by (phosphino)borate ligands will be more electron-rich than their cationic counterparts. Whether a zwitterionic description is most appropriate for a neutral complex supported by a (phosphino)borate ligand obviously depends on the degree of charge delocalization. Measuring the degree of charge delocalization, and the electronic mechanism by which delocalization occurs, is not reliably done through infrared carbonyl studies. Such model studies do, however, speak to the *relative* electron-richness of each complex discussed herein. At present, we suggest that a zwitterionic description is useful if it predicts a complex's chemical reactivity. A diverse set of model studies have shown that neutral complexes supported by (phosphino)borate ligands will mediate transformations typical of their more conventional, cationic counterparts. In this sense, our classification of these neutral complexes as "zwitterionic" is meaningful.

Experimental Section

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 at atmospheric pressure. Hydrocarbon and ethereal solvents were typically tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran 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. Ph_2PMe,[51] Ph_2PCH_2Li(TMEDA),[30] $^tBu_2PCl$,[52] $^tBu_2PMe$,[53] $^tBu_2P(CH_2Li)$,[29] Me_2PCH_2Li(TMEDA),[29] $(Ph)_2(BH_3)PCH_3$,[32] $[Ph_2B(CH_2PPh_2)_2][Li(TMEDA)_2]$,[9] $[Ph_2B(CH_2PPh_2)_2][ASN]$,[9] $[Ph_2BP_2Pt(Me)_2][ASN]$,[9] $[Ph_2BP_2]Pt(Me)(CO)$,[9b] 5-azoniaspiro[4.4]nonane bromide (ASNBr),[44] $(COD)PtCl_2$,[54] $(COD)PtMe_2$,[55] and $[HNEt_3][BPh_4]$[56] were prepared by literature methods. $^iPr_2PMe$[57] was prepared by reaction of $^iPr_2PCl$ with MeLi and isolation of the product by distillation. $Me_3P(BH_3)$[58] was prepared by reaction of PMe_3 with $BH_3{\cdot}SMe_2$. $SPMe_3$[59] 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, or Matrix Scientific and used without further purification. NMR spectra were recorded at ambient temperature on Varian Mercury 300 MHz and Inova 500 MHz and Joel 400 MHz spectrometers, unless otherwise noted. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts were referenced to residual solvent as determined relative to Me_4Si (0 ppm). $^{31}P\{^1H\}$ NMR, $^{11}B\{^1H\}$ NMR, and $^{19}F\{^1H\}$ NMR chemical shifts are reported 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 at 2 cm^{-1} resolution on a Bio-Rad Excalibur FTS 3000 spectrometer controlled by Win-IR Pro software using a KBr solution cell. 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 P4 CCD diffractometer.

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 °C in a dry ice/acetone bath. A 0.5 equiv amount of solid Me_2SnCl_2 was added under a counterflow of dinitrogen. (*Note! Me_2SnCl_2 is highly toxic. Use appropriate precautions when handling this material.*) The reaction was stirred at −78 °C for 20 min, and then the bath was removed and the reaction allowed to warm to rt 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 × 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.)

$(CH_3)_2Sn(C_6H_5)_2$ (1).[20,21,22,23] Following general method A, a pale yellow oil was generated (24.3020 g, 77.6%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.54 (m), 7.36 (m), 0.53 (s, $^2J_{Sn-H}$ = 54 Hz).

$(CH_3)_2Sn(C_6H_4$-*p*-$Me)_2$ (2).[20,21,22,24] Following general method A, white solids were generated (12.3836 g, 96.9%). ^1H NMR (300

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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*-$Me_2)_2$ (3). Following general method A, white solids were generated (19.4541 g, 87.9%). ^1H 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$)_2$ (4).[25] Following general method A, white solids were generated (18.1831 g, 96.2%). ^1H NMR (300 MHz, C_6D_6): δ 7.51 (d, 4H), 7.32 (d, 4H), 1.24 (s, 18H), 0.45 (s, 6H, $^2J_{Sn-H}$ = 54 Hz). $^{13}C\{^1H\}$ 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 ($^1J_{Sn-C}$ = 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$)_2$ (5).[21,22,26] Following general method A, an oil which solidified upon standing was generated (13.7652 g, 83.3%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.57 (d, 4H), 7.07 (d, 4H), 3.94 (s, 6H), 0.61 (s, 6H, $^2J_{Sn-H}$ = 55 Hz). $^{13}C\{^1H\}$ 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 ($^1J_{Sn-C}$ = 358 Hz).

$(CH_3)_2Sn(C_6H_4$-*p*-$CF_3)_2$ (6).[21] Following general method A, an orange oil was generated (14.9446 g, 94.4%). ^1H 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, $^2J_{Sn-H}$ = 54.3 Hz). ^{19}F NMR (282.1 MHz, C_6D_6): δ −63.5.

$(CH_3)_2Sn(C_6H_4$-*o*-OMe$)_2$ (7).[22] Following general method A, white crystalline solids were generated (16.2126 g, 98.7%). ^1H 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, $^2J_{Sn-H}$ = 56.1 Hz). $^{13}C\{^1H\}$ 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 ($^1J_{Sn-C}$ = 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*-$(OMe)_2)_2$ (8).[27] This was prepared by the previously reported method (deprotonation of 1,3-(dimethoxy)-benzene followed by quenching with Me_2SnCl_2), yielding white solids (11.3345 g, 55.8%). ^1H NMR (300 MHz, C_6D_6): δ 7.16 (t, 4H), 6.34 (d, 4H), 3.27 (s, 6H), 0.89 (s, 6H, $^2J_{Sn-H}$ = 58.5 Hz).

$(CH_3)_2Sn(C_6H_4$-*o*-$CF_3)_2$ (9). Following general method A, an amber oil was generated (19.7956 g, 90.3%). ^1H NMR (300 MHz, C_6D_6): δ 7.48 (dd, 2H), 7.39 (br d, 4H), 6.96 (m, 4H), 0.57 (s, 6H, $^2J_{Sn-H}$ = 57.0 Hz). $^{13}C\{^1H\}$ 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, J_{F-C} = 4.5 Hz, J_{Sn-C} = 31.7 Hz), −6.2 (septet, J_{F-C} = 2.6 Hz, $^1J_{Sn-C}$ = 392 Hz). ^{19}F 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 stir bar and sealable Teflon valve was added an appropriate dimethyldiaryltin compound (ca. 10−15 g) and heptane (25 mL). A 1 equiv amount of a solution of BCl_3 in heptane (ca. 25 mL of a 1 M solution) was added to the vessel at rt, and the vessel was sealed. After being stirred at rt for 30 min, the reaction was placed in a oil bath maintained at 100 °C and was further stirred for 24−48 h at 100 °C. The vessel was removed from the oil bath and allowed to cool, causing dimethyltin dichloride to crystallize from the mixture. The resulting solution was decanted from the white crystals. (*Note! Me_2SnCl_2 is highly toxic. Use appropriate precautions when handling and recovering this material.*) Removal of volatiles under reduced pressure provided crude diarylchloroborane. If necessary, recrystallization from hydrocarbon solvent (e.g. petroleum ether) at −35 °C provided pure diarylchloroborane. If any dimethyltin dichloride was observed by ^1H NMR spectroscopy, it was removed by vacuum sublimation.

$(C_6H_5)_2BCl$ (10).[14,15] Following general method B, colorless crystalline solids were generated (5.403 g, 72.8%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.05 (d), 7.65 (t), 7.54 (t). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 137.2, 133.1, 128.0. $^{11}B\{^1H\}$ NMR (128.3 MHz, $CDCl_3$): δ 62.8.

$(p$-$MeC_6H_4)_2BCl$ (11).[15,16] Following general method B, white solids were generated (4.7058 g, 98.0%). ^1H NMR (300 MHz, C_6D_6): δ 7.98 (d, 4H, $^3J_{H-H}$ = 8.1 Hz), 7.01 (d, 4H, $^3J_{H-H}$ = 8.1 Hz), 2.06 (s, 6H). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ 144.0, 138.1, 129.3, 22.0. $^{11}B\{^1H\}$ NMR (128.3 MHz, C_6D_6): δ 61.6.

$(m,m$-$Me_2C_6H_3)_2BCl$ (12). Following general method B, white solids were generated (5.3505 g, 85.6%). ^1H NMR (300 MHz, C_6D_6): δ 7.74 (s, 4H), 6.94 (s, 2H), 2.11 (s, 12H). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ 137.6, 135.5, 135.2, 21.5. $^{11}B\{^1H\}$ 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}Bu$C_6H_4)_2BCl$ (13). Following general method B, white crystalline solids were generated (5.2415 g, 90.6%). ^1H NMR (300 MHz, C_6D_6): δ 8.08 (d, 4H, 7.8 Hz), 7.33 (d, 4H, 7.8 Hz), 1.19 (s, 18H). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ 156.5, 137.7, 125.2, 35.0, 31.0. $^{11}B\{^1H\}$ 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.

$(p$-$MeOC_6H_4)_2BCl$ (14).[15,17] Following general method B, white solids were generated (6.2865 g, 96.5%). ^1H NMR (300 MHz, C_6D_6): δ 8.06 (d, 4H, J = 8.1 Hz), 6.79 (d, 4H, J = 8.1 Hz), 3.23 (s, 6H). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ 164.4, 140.2, 114.2, 55.1. $^{11}B\{^1H\}$ 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.

$(p$-$CF_3C_6H_4)_2BCl$ (15). Following general method B, colorless crystalline solids were generated (3.5460 g, 31.0%). ^1H NMR (300 MHz, C_6D_6): δ 7.54 (d, J_{H-H} = 7.5 Hz), 7.35 (d, J_{H-H} = 7.5 Hz). ^{19}F NMR (282 MHz, C_6D_6): δ −63.9. $^{11}B\{^1H\}$ NMR (121.3 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$_2$P(CH$_2$Li) (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 (0.891 mL, 1.7M, 1.51 mmol) was placed in a 50 mL thick-walled sealable vessel. Volatiles were removed under reduced pressure, providing solid ^{t}BuLi. To the white solids was added neat ^{i}Pr$_2$PMe (185.6 mg, 1.404 mmol). The reaction vessel was evacuated and sealed. The reaction was heated to 60 °C for 20 h, during which time yellow-white solids formed. The vessel was cooled to rt, and the resulting solids were collected by filtration and washed with petroleum ether (3 × 2 mL). The resulting white solids were dried under reduced pressure, providing **17** (140.0 mg, 72.2%). $^{31}P\{^1H\}$ NMR (121.4 MHz, THF): δ 22.8.

$(p$-^{t}BuPh$)_2$PCH$_2$Li(TMEDA) (19). A solution of *n*-BuLi in hexanes (2.20 mL, 1.6 M, 3.52 mmol) was added to a stirring rt 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 rt for 4 d, precipitating a pale yellow product solid. The solids were collected by filtration and washed with petroleum ether (2 × 2 mL). Drying the solids under reduced pressure provided **19** as pale yellow solids (1.1358 g, 74.3%). ^1H NMR (300 MHz, 10:1 C_6D_6/THF-d_8): 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 NMR (121.4 MHz, 10:1 C_6D_6/THF-d_8): δ −1.26.

[$Ph_2B(CH_2PPh_2)_2$][Et_4N] (25[TEA]). The precursor [$Ph_2B(CH_2PPh_2)_2$][Li(TMEDA)] was prepared as previously described.[9] A solution of **25**[Li] (500 mg, 0.592 mmol) in EtOH (8 mL) was added to a stirring solution of [NEt_4][Br] (186.5 mg, 0.887 mmol) in EtOH (4 mL) at room temperature. Within minutes, a white precipitate formed. After 30 min, the solids were collected by filtration. The solids were washed with EtOH (3 × 5 mL) and Et_2O (2 × 3 mL). The solids were dried under reduced pressure providing **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 (d, $^2J_{P-B}$ = 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] (25[TBA]). The precursor [$Ph_2B(CH_2PPh_2)_2$][Li(TMEDA)] was prepared as previously described.[9] Solid **25**[Li] (3.51 g, 4.42 mmol) was dissolved in EtOH (20 mL). With stirring, an EtOH solution (15 mL) of [^{n}Bu_4N][Cl] (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 **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 ($^2J_{P-B}$ = 10 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, acetone-d_6): δ −12.6.

{**[$Ph_2B(CH_2PPh_2)_2$][Tl]**}$_n$ **(25[Tl]).** The precursor [$Ph_2B(CH_2PPh_2)_2$][Li(TMEDA)] was prepared as previously described.[9] Solid **25**[Li] (284.4 mg) was dissolved in EtOH (1.5 mL). With 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 **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, $^3J_{Tl-H}$ = 9.6 Hz). ^{31}P{^{1}H} NMR (202.4 Hz, THF-d_8, 55 °C): δ 57.9. ^{31}P{^{1}H} NMR (202.4 Hz, THF-d_8, −65 °C): δ 52.6 (br d, $^1J_{Tl-P}$ = 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_2PPh_2)$_2$][Li(TMEDA)] (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 °C 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 rt 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 × 30 mL), providing pale yellow solid **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, $^2J_{B-P}$ = 9.2 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, acetone-d_6): δ −12.9.

[(*p*-MePh)$_2$B(CH_2PPh_2)$_2$][ASN] (26[ASN]). Crude **26**[Li] (289.3 mg, 0.3482 mmol) was dissolved in ethanol (4 mL). Solid (ASN)-Br (80.4 mg, 0.390 mmol) was dissolved in ethanol (2 mL) and added to stirring **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 × 2 mL). The solids were dried under reduced pressure, providing white **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, $^2J_{B-P}$ = 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_2PPh_2)$_2$][Li(TMEDA)$_2$] (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 °C 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 rt 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 × 30 mL), providing pale yellow solid **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{^{1}H} NMR (121.4 MHz, CD_3CN): δ −10.05 (q, $^2J_{B-P}$ = 11.5 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, CD_3-CN): δ −13.3.

[(*p*-^{t}BuPh)$_2$B(CH_2PPh_2)$_2$][ASN] (27[ASN]). Solid **27**[Li] (589.6 mg, 0.6451 mmol) was dissolved in ethanol (9 mL). Solid (ASN)-Br (138.2 mg, 0.6705 mmol) was dissolved in ethanol (3 mL) and added to stirring **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 **27**[ASN] (357.4 mg, 68.1%). ^{1}H 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{^{1}H} 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{^{1}H} NMR (121.4 MHz, CD_3CN): δ −10.04. ^{11}B{^{1}H} 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_2PPh_2)$_2$][Li(TMEDA)$_2$] (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 °C 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 rt 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 × 10 mL), providing off-white solid **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). $^{13}C\{^1H\}$ 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). $^{31}P\{^1H\}$ NMR (121.4 MHz, acetone-d_6): δ −8.46 (q, $^2J_{B-P}$ = 10.9 Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, acetone-d_6): δ −13.7.

[(*p*-MeOPh)$_2$B{CH$_2$P(Ph)$_2$(BH$_3$)}$_2$][ASN] (28·BH$_3$[ASN]). Colorless oil MePPh$_2$(BH$_3$) (0.9615 g, 4.492 mmol) was dissolved in Et$_2$O (100 mL) in a Schlenk flask with a stir bar and sealed with a septum. The flask was cooled to −78 °C in a dry ice/acetone bath. To the stirring reaction was added a solution of *s*-BuLi in cyclohexane (3.5 mL, 1.3M, 4.6 mmol). The reaction was stirred and maintained at −78 °C 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 rt over 14 h. Volatiles were removed under reduced pressure, providing white solids. ($^{31}P\{^1H\}$ NMR 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). With stirring, an EtOH solution (4 mL) of (ASN)Br (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 **28**·BH$_3$[ASN] (1.6137 g, 92.3%). ^1H 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). $^{13}C\{^1H\}$ 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). $^{31}P\{^1H\}$ NMR (121.4 MHz, acetone-d_6): δ 21.3. $^{11}B\{^1H\}$ 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] (28[ASN]). Solid **28**·BH$_3$[ASN] (393.8 mg, 0.5066 mmol) was suspended in morpholine (10 mL). The reaction was stirred and heated to 60 °C for 72 h. $^{31}P\{^1H\}$ NMR analysis of the reaction showed the formation of predominantly one major product and several (ca. 5) minor side products. Volatiles were removed under reduced pressure. The resulting solids were washed with toluene (2 × 1 mL) and Et$_2$O (2 × 1 mL). Drying under reduced pressure provided a white foam (215.7 mg, 56.8%). ^1H 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). $^{13}C\{^1H\}$ 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. $^{31}P\{^1H\}$ NMR (121.4 MHz, acetone-d_6): δ −8.4. $^{11}B\{^1H\}$ NMR (128.3 MHz, acetone-d_6): δ −12.4.

[(*p*-CF$_3$Ph)$_2$B(CH$_2$PPh$_2$)$_2$][Li(TMEDA)$_2$] (29[Li]). Solid pale yellow Ph$_2$PCH$_2$Li(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 °C in a dry ice/acetone bath under a positive pressure of dinitrogen. Solid **15** (1.1011 g, 3.2725 mmol) was dissolved in toluene (8 mL), and the solution was added dropwise by syringe over 5 min to the cooled flask. The reaction became brown as it was stirred at −78 °C 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 × 5 mL) and dried under reduced pressure, providing crude **29**[Li] (2.3626 g, 77.3%). ^1H 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, $^2J_{P-B}$ = 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$_3$Ph)$_2$B(CH$_2$PPh$_2$)$_2$][ASN] (29[ASN]). Crude **29**[Li] (376.3 mg, 0.401 mmol) was dissolved in acetone along with approximately 1 equiv of (ASN)Br. 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$_2$O, and crystallization at −30 °C provided **29**[ASN] (186.3 mg, 56.3%). ^1H 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.

[Cy$_2$B(CH$_2$PPh$_2$)$_2$][Li(TMEDA)$_2$] (30[Li]). Solid yellow Ph$_2$PCH$_2$Li(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 °C in a dry ice/acetone bath. A solution of Cy$_2$BCl (491.6 mg, 2.312 mmol) dissolved in toluene (5 mL), was introduced dropwise via syringe to the cooled reaction flask. The reaction was stirred and warmed gradually to rt 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 × 30 mL), providing pale yellow solid **30**[Li] (1.2134 g, 64.4%). Crystallization from toluene at −30 °C provided analytically pure **30**[Li]. ^1H 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). $^{13}C\{^1H\}$ 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). $^{31}P\{^1H\}$ NMR (121.4 MHz, acetone-d_6): δ −6.18. $^{11}B\{^1H\}$ 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.

[Ph$_2$B(CH$_2$P{*p*-^{t}BuPh}$_2$)$_2$][Li(TMEDA)$_x$] (31[Li]). The same method as for **26**[Li] yielded pale yellow solids, 0.9618 g, 75.8%. ^1H 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). $^{13}C\{^1H\}$ 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). $^{31}P\{^1H\}$ NMR (121.4 MHz, acetone-d_6): δ −12.40. $^{11}B\{^1H\}$ NMR (128.3 MHz, acetone-d_6): δ −12.2.

[Ph$_2$B(CH$_2$P{*p*-^{t}BuPh}$_2$)$_2$][ASN] (31[ASN]). The same method as for **26**[Li] yielded white solids, 0.6900 g, 80.0%. ^1H 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). $^{31}P\{^1H\}$ 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)$_x$] (32[Li]). Solid **19** (509.3 mg, 1.172 mmol) was suspended in Et$_2$O (20 mL) in a Schlenk flask with a stir bar and septum. The reaction vessel was cooled to −78 °C 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

32[Li] to precipitate upon standing (272.6 mg, 47.8%). ^{1}H NMR (300 MHz, C_6D_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 (36H). ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_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$_2$B{CH$_2$P(*p*-CF$_3$Ph)$_2$(BH$_3$)}$_2$][Li(THF)$_x$] (33·BH$_3$[Li]). A diethyl ether solution (100 mL) of MeP(*p*-CF$_3$Ph)$_2$(BH$_3$) (1.3411 g, 3.8312 mmol) was placed in a Schlenk flask with a stir bar and a septum and cooled to −78 °C in a dry ice/acetone bath. A solution of *sec*-butyllithium in cyclohexane (3.0 mL, 1.3 M, 3.9 mmol) was added by syringe, and the reaction was stirred and maintained at −78 °C. After 3 h, a toluene solution (6 mL) of Ph$_2$BCl 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 × 5 mL). The solids were dissolved in diethyl ether (12 mL) and filtered over Celite. Removal of volatiles under reduced pressure provided crude **33**·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$_2$B(CH$_2$P{*p*-CF$_3$Ph}$_2$)$_2$][ASN] (33[ASN]). Crude **33**·BH$_3$[Li] (485.6 mg, 0.514 mmol) was dissolved in CH_2Cl_2 (2 mL). With stirring, a CH_2Cl_2 solution (2 mL) of (ASN)Br (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 redissolved 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 °C for 12 h. Examination of an aliquot by ^{31}P 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 × 2 mL), providing white solids. Crystallization of the white solids from THF/petroleum ether provided analytically pure **33**[ASN] (210.6 mg, 42.6%). ^{1}H 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{^{1}H} 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-{^{1}H} NMR (121.4 MHz, acetone-d_6): δ −6.74. ^{19}F{^{1}H} NMR (282 MHz, acetone-d_6): δ −62.7. ^{11}B{^{1}H} 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.

[Ph$_2$B(CH$_2$P(CH$_3$)$_2$(BH$_3$))$_2$][Li(TMEDA)] (34). Solid PMe$_3$·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 °C in a dry ice/acetone bath. A 1.6 M solution of *n*-butyllithium (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 °C. A toluene solution (8 mL) of Ph$_2$BCl (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 × 10 mL), providing **34** (3.3948 g, 97.8%). The material can be crystallized from pentane vapor diffusion into a benzene solution, providing analytically pure [Ph$_2$B(CH$_2$P(CH$_3$)$_2$-(BH$_3$))$_2$][Li(TMEDA)]. ^{1}H 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{^{1}H} 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{^{1}H} NMR (121.4 MHz, C_6D_6): δ 1.23 (m). ^{11}B{^{1}H} NMR (128.3 MHz, C_6D_6): δ −13.3 (s, Ph$_2$*B*P$_2$), −34.2 (d, Ph$_2$B(P(*B*H$_3$))$_2$, $^1J_{P-B}$ = 71 Hz). ES MS (CH_3CN) (*m*/*z*): calcd for $C_{18}H_{32}B_3P_2$, 343.2; found, 343.2. 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$_2$B(CH$_2$P(CH$_3$)$_2$(S))$_2$][Li(TMEDA)] (35). Solid SPMe$_3$ (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 °C in a dry ice/acetone bath. A solution of *n*-butyllithium (2.86 mL, 1.6M, 4.58 mmol) was added dropwise via syringe to the reaction. The reaction was stirred at −78 °C for 3 h. A toluene solution (5 mL) of Ph$_2$BCl (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 × 10 mL), providing white solids. Crystallization from Et_2O at −30 °C provided analytically pure **35** (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, J_{P-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, $^1J_{P-C}$ = 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$_2$B(CH$_2$P^{i}Pr$_2$)$_2$][Li(THF)$_2$] (36[Li]). Solid white ^{i}Pr$_2$P(CH$_2$-Li) (474.2 mg, 3.433 mmol) was dissolved in THF (3 mL), creating a yellow solution. Separately, Ph$_2$BCl 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 × 2 mL) and redissolved in Et_2O (6 mL). Repeated crystallization and concentration of the Et_2O solution at −30 °C provided several crops of colorless crystals of **36**[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, $^2J_{P-B}$ = 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$_2$B(CH$_2$P^{t}Bu$_2$)$_2$][Li(OEt$_2$)] (37[Li]). An Et_2O suspension (200 mL) of ^{t}Bu$_2$PCH$_2$Li (**16**) (7.3328 g, 44.14 mmol) was cooled in a Schlenk flask with a stir bar and a septum to −78 °C in a dry ice/acetone bath. An Et_2O solution (50 mL) of Ph$_2$BCl (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 °C provided **37**[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, $^3J_{P-H}$ = 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, $^2J_{B-P}$ = 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$_2$Ph)$_2$B(CH$_2$P^{t}Bu$_2$)$_2$][Li(OEt$_2$)] (38[Li]). Solid ^{t}Bu$_2$PCH$_2$Li (**16**) (562.6 mg, 3.385 mmol) was dissolved in a mixture of THF and diethyl ether (3 mL/7 mL). With stirring, a diethyl ether solution (5 mL) of (*m*,*m*-Me$_2$Ph)$_2$BCl (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 °C provided colorless crystalline **38**[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, $^1J_{B-C}$ = 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] (38[Tl]). Solid **38**[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 × 2 mL) and dried under reduced pressure, providing **38**[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, $^3J_{P-H}$ = 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, $^1J_{Tl-P}$ = 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.

General Method C: Preparation of Bis(phosphino)borate−Platinum Dimethyl Complexes [[R$_2$B(CH$_2$PR′$_2$)$_2$]PtMe$_2$][X] (40−48). A solution of CODPtMe$_2$ in THF was added to a stirring solution or suspension of 1 equiv of the bis(phosphino)borate in THF. After 1 h, the reaction had gone to completion, as evinced by a ^{31}P NMR spectrum of a homogeneous reaction aliquot. The resulting solution was concentrated to dryness under reduced pressure. The resulting white or off-white solids were typically washed repeatedly with Et_2O or petroleum ether to remove residual cyclooctadiene and then were dried under reduced pressure. Purity was assessed by examination of the NMR spectra (^{1}H, ^{13}C, ^{31}P, ^{11}B). Yields are reported for compounds where greater than 100 mg was isolated.

[[(*p*-MePh)$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)$_2$][ASN] (40). Following general method C, off-white solids were generated (209.7 mg, 96.7%). ^{1}H NMR (300 MHz, acetone-d_6): δ 7.38 (m, 8H), 7.11 (m, 4H), 7.05 (m, 8H), 6.79 (d, 4H), 6.47 (d, 4H), 3.67 (m, 8H), 2.24 (m, 8H), 2.09 (s, 6H), 1.91 (br, 4H), 0.08 (t, 6H, Pt(CH_3)$_2$, $^3J_{P-H}$ = 6.0 Hz, $^2J_{Pt-H}$ = 67 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, acetone-d_6): δ 163 (q), 140.8 (d), 134.7, 134.1, 130.5, 128.5, 127.9, 127.6, 64.2, 23.4 (br), 23.3, 21.7, 5.9 (dd, Pt(CH_3)$_2$, $^1J_{Pt-C}$ = 600 Hz, $^2J_{P-C}$ = 9.2, 103 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-d_6): δ 20.70 ($^1J_{Pt-P}$ = 1895 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, acetone-d_6): δ −13.6. Anal. Calcd for $C_{50}H_{60}BNP_2Pt$: C, 63.69; H, 6.41; N, 1.49. Found: C, 63.43; H, 6.74; N, 1.76.

[[(*p*-^{t}BuPh)$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)$_2$][ASN] (41). Following general method C, white solids were generated (172.3 mg, 94.4%). ^{1}H NMR (300 MHz, acetone-d_6): δ 7.40 (tt, 8H), 7.06 (m, 12H), 6.83 (br d, 4H), 6.70 (d, 4H), 3.69 (m, 8H), 2.25 (m, 8H), 2.00 (br, 4H), 1.22 (s, 18H), 0.07 ("t", 6H, Pt(CH_3)$_2$, $^2J_{Pt-H}$ = 67 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, acetone-d_6): δ 163 (br q), 144.3, 141.0, 135.2, 133.9, 129.0, 128.1, 123.9, 64.6, 35.2, 33.1, 23.8 (br), 23.7, 6.2 (dd, Pt(CH_3)$_2$, $^1J_{Pt-C}$ = 600 Hz, $^2J_{P-C}$ = 9, 100 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-d_6): δ 20.74. ^{11}B{^{1}H} NMR (128.3 MHz, acetone-d_6): δ −14.2. Anal. Calcd for $C_{56}H_{72}BNP_2Pt$: C, 65.49; H, 7.07; N, 1.36. Found: C, 65.68; H, 6.94; N, 1.30.

[[(*p*-MeOPh)$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)$_2$][ASN] (42). Following general method C, **42** was generated. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.40 (m, 8H), 7.09 (m, 12H), 6.78 (br d, 4H), 6.28 (m, 4H), 3.63 (m, 8H), 3.62 (s, 6H), 2.21 (m, 8H), 1.90 (br d, 4H), 0.09 (dd, 6H, Pt−CH_3, $^2J_{Pt-H}$ = 68 Hz, $^3J_{P-H}$ = 6, 6 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, acetone-d_6): δ 159 (br), 140.8, 134.9, 134.7, 129.8, 128.7, 127.9, 112.9, 64.4, 55.7, 24 (br), 23.4, 6.1 (dd, Pt-CH_3, $^1J_{Pt-C}$ = 605 Hz, $^2J_{P-C}$ = 10, 100 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-d_6): δ 20.49 ($^1J_{Pt-P}$ = 1893 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, acetone-d_6): δ −13.7.

[[(*p*-CF$_3$Ph)$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)$_2$][ASN] (43). Following general method C, **43** was generated. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.40 (m, 8H), 7.10 (m, 12H), 6.95 (m, 8H), 3.74 (m, 8H), 2.27 (m, 8H), 2.01 (br, 4H), 0.07 ("t", 6H, Pt(CH_3)$_2$, $^2J_{Pt-H}$ = 68 Hz, $^3J_{P-H}$ = 6.3 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, acetone-d_6): δ 172 (br q), 139.4 (m), 134.2 (m), 133.3, 128.5, 127.4 (m), 124.0 (q), 122.7, 63.7, 22.8, 22.7 (br), 5.5 (dd, Pt(CH_3)$_2$, $^1J_{Pt-C}$ = 600 Hz, $^2J_{P-C}$ = 9.7, 103 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-d_6): δ 19.33 (J_{Pt-P} = 1880 Hz). ^{19}F{^{1}H} NMR (282.1 MHz, acetone-d_6): δ −61.6. ^{11}B{^{1}H} NMR (128.3 MHz, acetone-d_6): δ −13.5.

[[Cy$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)$_2$][Li(TMEDA)$_2$] (44). Following general method C, **44** was generated. ^{1}H NMR (300 MHz, C_6D_6): δ 7.92 (m, 8H), 7.14 (m, 12H), 2.21 (s, 8H), 1.88 (m, 32H), 1.3−1.6 (m, 24H), 1.09 (m, 2H), 0.21 (br s, 6H, Pt−CH_3, $^2J_{Pt-H}$ = 54 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6): δ 141 (m), 135.0 (m), 128.9, 127.9 (m), 68.2, 56.3, 45.3, 39.8 (br), 33.5, 31.4, 19.7 (br), 2.2 (dd, Pt(CH_3)$_2$, $^1J_{Pt-C}$ = 530 Hz, $^2J_{P-C}$ = 8.9, 96 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 17.39 ($^1J_{Pt-P}$ = 2037 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, C_6D_6): δ −13.2.

[[Ph$_2$B(CH$_2$P{*p*-^{t}BuPh}$_2$)$_2$]Pt(Me)$_2$][ASN] (45). Following general method C, white solids were generated (108.5 mg, 98.6%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.86 (t, 8H, J = 8.4 Hz), 7.24 (br d, 4H, J = 7.2 Hz), 7.17 (d, 8H, J = 7.8 Hz), 6.76 (m, 4H), 6.70 (m, 2H), 2.53 (br d, 4H), 1.65 (m, 8H), 1.29 (s, 36H), 0.85 (m, 8H), 0.65 (s, 6H, Pt(CH_3)$_2$, $^2J_{Pt-H}$ = 67 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6): δ 166.9 (q, J_{B-C} = 54 Hz), 150.6, 137.0 (m), 134.6 (m), 133.2, 126.4, 124.3, 121.8, 62.3, 34.9, 32.0, 23.4 (br), 21.8, 6.6 (dd, Pt(CH_3)$_2$, $^1J_{Pt-C}$ = 595 Hz, $^2J_{P-C}$ = 9.7, 103 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 16.22 ($^1J_{Pt-P}$ = 1890 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, C_6D_6): δ −14.6. Anal. Calcd for $C_{64}H_{88}BNP_2$-Pt: C, 67.47; H, 7.79; N, 1.23. Found: C, 67.47; H, 7.55; N, 1.07.

[[(*p*-MeOPh)$_2$B(CH$_2$P{*p*-^{t}BuPh}$_2$)$_2$]Pt(Me)$_2$][Li(TMEDA)] (46). Following general method C, **46** was generated. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.35 (8H, m), 7.10 (8H, d), 6.75 (4H, d), 6.25 (4H, d), 3.61 (6H, s), 2.36 (4H, s), 2.18 (12H, s), 1.88 (4H, bd), 1.29 (36H, s), 0.10 (t, 6H, Pt(CH_3)$_2$, $^2J_{Pt-H}$ = 67 Hz, $^3J_{P-H}$ = 5 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, acetone-d_6): δ 158 (br), 156.1, 150.4, 134.3 (m), 134.1, 124.1 (m), 112.1, 59.7, 46.2, 35.0, 31.9, 24 (br), 5.2 (dd, Pt(CH_3)$_2$). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-

d_6): δ 15.95 ($^1J_{Pt-P}$ = 2033 Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, acetone-d_6): δ −14.2.

[[Ph$_2$B(CH$_2$P{*p*-CF$_3$Ph}$_2$)$_2$]Pt(Me)$_2$][ASN] (47). Following general method C, **47** was generated. ^{1}H NMR (300 MHz, CD_3CN): δ 7.50 (m, 8H), 7.40 (m, 8H), 6.75 (br, 4H), 6.65 (m, 6H), 3.38 (m, 8H), 2.10 (m, 8H), 2.03 (br m, 4H), −0.06 ("t", Pt(C*H*$_3$)$_2$, $^2J_{Pt-H}$ = 68 Hz, $^3J_{P-H}$ = 5.7 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_3CN): δ 164 (br), 142.7 (m), 133.8 (m), 132.1, 129.4 (q), 126.0, 123.7 (m), 121.9, 117.5, 63.0, 22.0, 21 (br), 4.8 (dd, Pt(*C*H$_3$)$_2$, $^1J_{Pt-C}$ = 632 Hz, $^2J_{P-C}$ = 9.3, 102 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_3CN): δ 21.32 ($^1J_{Pt-P}$ = 1848 Hz). $^{19}F\{^1H\}$ NMR (282.1 MHz, CD_3CN): δ −63.1. $^{11}B\{^1H\}$ NMR (128.3 MHz, CD_3CN): δ −14.2.

[[Ph$_2$B(CH$_2$P^{i}Pr$_2$)$_2$]Pt(Me)$_2$][^{n}Bu$_4$N] (48). Following general method C, to the resulting THF solution was added 1 equiv of ^{n}Bu$_4$NBr. After removal of volatiles under reduced pressure, the white solids were washed with Et_2O (2 × 2 mL). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.50 (br, 4H), 6.97 (t, 4H), 6.77 (t, 2H), 2.82 (m, 8H), 2.15 (m, 4H), 1.2−1.5 (m, 20H), 1.04 (m, 24H), 0.93 (dd, 12H), 0.14 (t, 6H, $^2J_{Pt-H}$ = 64 Hz, $^3J_{P-H}$ = 5.1 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2): δ 169.2 (q, $^1J_{B-C}$ = 50 Hz), 132.1, 126.4, 121.9, 59.3 (N*C*H$_2$CH$_2$CH$_2$CH$_3$), 24.6 (q), 24.4 (NCH$_2$*C*H$_2$-CH$_2$CH$_3$), 20.3 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 19.8 (m), 18.8 (m), 14.0 (NCH$_2$CH$_2$CH$_2$*C*H$_3$), 7.9 (br), 1.2 (dd, Pt(*C*H$_3$)$_2$, $^1J_{Pt-C}$ = 564 Hz, $^2J_{P-C}$ = 11.4, 102 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ 24.75 ($^1J_{Pt-P}$ = 1961 Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, CD_2Cl_2): δ −15.7. Anal. Calcd for $C_{44}H_{84}BNP_2Pt$: C, 59.05; H, 9.46; N, 1.57. Found: C, 59.10; H, 9.53; N, 1.61.

General Method D: Preparation of Bis(phosphino)borate−Platinum Methyl Carbonyl Complexes [R$_2$B(CH$_2$PR′$_2$)$_2$]Pt(Me)(CO) (50−58). A solution of the bis(phosphino)borate−platinum dimethyl anion was dissolved in THF. A THF solution containing 1 equiv of [Et$_3$NH][BPh$_4$] was added to the stirring reaction mixture. After 15−20 min, the solution was filtered into a flask with a sidearm, removing any solid precipitate ([X][BPh$_4$]). The flask was sealed with a septum. A stream of CO gas was introduced through the sidearm, and the flask was flushed with CO for 10 min. The sealed flask was then stirred for an additional 60 min, after which time volatiles were removed under reduced pressure.

[(*p*-MePh)$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)(CO) (50). Following general method D, **50** was generated. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21−7.44 (m, 20H), 6.94 (d, 4H), 6.74 (d, 4H), 2.27 (s, 6H), 2.13 (br m, 4H), 0.57 (t, 3H, Pt(C*H*$_3$), $^3J_{P-H}$ = 5.7 Hz, $^2J_{Pt-H}$ = 58 Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$): δ 180.6 (dd, Pt-*C*O, $^1J_{Pt-C}$ = 1286 Hz, $^2J_{Pt-p}$ = 7.4, 131 Hz), 159 (br, *ipso* B(C$_6$H$_5$)$_2$), 136.5 (d, $^1J_{P-C}$ = 48.5 Hz), 133.5, 132.5, 132.4, 131.7, 131.4 (d, $^1J_{P-C}$ = 57 Hz), 130.3, 129.9, 128.3 (m), 128.1 (m), 127.5, 21.3, 18.0 (br), 16.8 (br), −2.8 (d, Pt(*C*H$_3$), $^2J_{P-C}$ = 61 Hz, $^1J_{Pt-C}$ = 416 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 20.33 ($^1J_{Pt-P}$ = 3062 Hz, $^2J_{P-P}$ = 31 Hz), 15.92 ($^1J_{Pt-P}$ = 1645 Hz, $^2J_{P-P}$ = 31 Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, $CDCl_3$): δ −13.9. IR (CH_2Cl_2): ν_{CO} = 2094 cm^{-1}.

[(*p*-^{t}BuPh)$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)(CO) (51). Following general method D, **51** was generated. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.30 (m, 10H), 7.20 (m, 8H), 7.05 (t, 2H), 6.81 (m, 8H), 2.16 (m, 4H), 1.24 (s, 18H), 0.42 (t, 3H, Pt(C*H*$_3$), $^2J_{Pt-H}$ = 58 Hz, $^3J_{P-H}$ = 6.0 Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2): δ 180.9 (dd, Pt-*C*O), $^2J_{P-C}$ = 7.4, 131 Hz), 159 (br), 145.1, 136.6 (d), 136.5, 134.0 (m), 133.2 (m), 131.8, 130.8 (d), 130.5 (d), 128.6 (d), 128.4 (d), 123.7, 34.3, 32.0, 19 (br), 17 (br), −2.8 (dd, Pt(*C*H$_3$)). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ 20.00 ($^1J_{Pt-P}$ = 3044 Hz, $^2J_{P-P}$ = 32 Hz), 15.32 ($^1J_{Pt-P}$ = 1639 Hz, $^2J_{P-P}$ = 32 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, THF): δ 20.38 ($^1J_{Pt-P}$ = 3038 Hz, $^2J_{P-P}$ = 32 Hz), 15.94 ($^1J_{Pt-P}$ = 1645 Hz, $^2J_{P-P}$ = 32 Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, CD_2Cl_2): δ −15.1. IR (CH_2Cl_2): ν_{CO} = 2094 cm^{-1}.

[(*p*-MeOPh)$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)(CO) (52). Following general method D, **52** was generated. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.2−7.4 (m, 16H), 7.04 (t, 2H), 6.89 (t, 2H), 6.78 (d, 4H), 6.39 (d, 4H), 3.69 (s, 6H), 2.09 (br m, 4H), 0.47 (t, 3H, Pt(C*H*$_3$), $^2J_{Pt-H}$ = 58 Hz, $^3J_{P-H}$ = 5.7 Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2): δ 180.9 (dd, Pt(*C*O)), 154 (br), 136.5, 133.9 (m), 133.1, 132.9 (m), 130.8, 130.5, 128.7 (d), 128.5 (d), 126.4, 122.4, 112.6, 55.4, 18.8 (br), 17.1 (br), −2.8 (dd, Pt(*C*H$_3$)). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ 19.89 ($^1J_{Pt-P}$ = 3053 Hz, $^2J_{P-P}$ = 32 Hz), 15.43 ($^1J_{Pt-P}$ = 1640 Hz, $^2J_{P-P}$ = 32 Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, CD_2Cl_2): δ −14.6. IR (CH_2Cl_2): ν_{CO} = 2094 cm^{-1}.

[(*p*-CF$_3$Ph)$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)(CO) (53). Following general method D, **53** was generated. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.15−7.45 (m, 20H), 7.01 (d, 4H), 6.92 (d, 4H), 2.21 (br m, 4H), 0.44 (t, $^2J_{Pt-C}$ = 58 Hz, $^3J_{P-C}$ = 6.0 Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2): δ 180.5 (dd, Pt(*C*O), $^1J_{Pt-C}$ = 1288 Hz, $^2J_{P-C}$ = 6.8, 132 Hz), 167 (br q), 135.9 (d), 134.0 (d), 132.9 (d), 132.3, 131.2 (d), 131.0 (d), 129.5, 128.9 (d), 128.6 (d), 125.1 (q), 123.4, 19 (br), 17 (br), −2.6 (dd, Pt(*C*H$_3$), $^1J_{Pt-C}$ = 415 Hz, $^2J_{P-C}$ = 4.3, 61 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ 18.75 ($^1J_{Pt-P}$ = 3061 Hz, $^2J_{P-P}$ = 31 Hz), 14.24 ($^1J_{Pt-P}$ = 1631 Hz, $^2J_{P-P}$ = 31 Hz). $^{19}F\{^1H\}$ NMR (282.1 MHz, CD_2Cl_2): δ −62.8. $^{11}B\{^1H\}$ NMR (128.3 MHz, CD_2Cl_2): δ −14.7. IR (CH_2Cl_2): ν_{CO} = 2097 cm^{-1}.

[Cy$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)(CO) (54). Following general method D, **54** was generated. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41 (m, 8H), 7.14 (t, 8H), 6.99 (t, 4H), 2.02 (br, 2H), 1.86 (br, 2H), 1.45 (m, 8H), 1.30 (m, 8H), 0.88 (m, 4H), 0.67 (m, 2H), 0.45 (dd, 3H, Pt(C*H*$_3$), $^2J_{Pt-H}$ = 58 Hz, $^3J_{P-H}$ = 6, 6 Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$): δ 181.0 (dd, Pt(*C*O), $^2J_{P-P}$ = 9, 130 Hz), 138.8, 138.4, 133.9 (d), 132.9 (d), 130.4 (d), 130.1 (d), 128.6 (d), 128.3 (d), 56.4 (br), 45.7 (br), 38.7 (br), 16.3 (br), 14.4 (br), −2.0 (dd, Pt(*C*H$_3$), $^1J_{Pt-C}$ = 413 Hz, $^2J_{P-C}$ = 4, 62 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 20.42 ($^1J_{Pt-P}$ = 3037 Hz, $^2J_{P-P}$ = 31 Hz), 16.23 ($^1J_{Pt-P}$ = 1646 Hz, $^2J_{P-P}$ = 31 Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, $CDCl_3$): δ −13.3. IR (CH_2Cl_2): ν_{CO} = 2092 cm^{-1}.

[Ph$_2$B(CH$_2$P{*p*-^{t}BuPh}$_2$)$_2$]Pt(Me)(CO) (55). Following general method D, **55** was generated. $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2): δ 180.8 (d, $^2J_{P-C}$ = 130 Hz), δ 162.5 (br), 153.5, 153.3, 133.3 (m), 133.2 (m), 132.3 (m), 132.2 (m), 131.9, 126.4, 125.2 (d), 125.0 (d), 122.5, 34.7, 34.6, 31.2, 31.1, 18.7 (br), 16.8 (br), 2.4 (dd, Pt(*C*H$_3$), $^1J_{Pt-C}$ = 410 Hz, $^2J_{P-C}$ = 4.3, 62 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ 17.48 ($^1J_{Pt-P}$ = 3030 Hz, $^2J_{P-P}$ = 32 Hz), 12.68 ($^1J_{Pt-P}$ = 1641 Hz, $^2J_{P-P}$ = 32 Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, CD_2Cl_2): δ −14.7. IR (CH_2Cl_2): ν_{CO} = 2091 cm^{-1}.

[(*p*-MeOPh)$_2$B(CH$_2$P{*p*-^{t}BuPh}$_2$)$_2$]Pt(Me)(CO) (56). Following general method D, **56** was generated. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.5 (b, 4H), 7.1 (m, 8H), 6.91 (m, 4H, 6.67 (d, 4H), 6.28 (d, 4H), 3.57 (s, 6H), 1.98 (br, 2H), 1.93 (br, 2H), 1.23 (s, 36H), 0.35 (dd, 3H, Pt(C*H*$_3$), $^2J_{Pt-H}$ = 58 Hz, $^3J_{P-H}$ = 5.7, 5.7 Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$): δ 180.8 (dd, Pt-*C*O, $^2J_{P-C}$ = 130 Hz, $^1J_{Pt-C}$ = 1278 Hz), 163.0 (q, $^1J_{C-B}$ = 51 Hz), 153.4, 153.1, 133.3 (m), 132.9, 132.3 (m), 128.6, 127.2, 125.2 (d), 125.0 (d), 123.3, 112.2, 55.2, 35.0, 34.9, 31.5, 31.4, 18.8 (br), 17.4 (br), −2.5 (dd, Pt(*C*H$_3$), $^2J_{P-C}$ = 4.3, 62 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 17.65 ($^1J_{Pt-P}$ = 3034 Hz, $^2J_{P-P}$ = 31 Hz), 12.93 ($^1J_{Pt-P}$ = 1642 Hz, $^2J_{P-P}$ = 31 Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, $CDCl_3$): δ −14.8. IR (CH_2Cl_2): ν_{CO} = 2091 cm^{-1}.

[Ph$_2$B(CH$_2$P{*p*-CF$_3$Ph}$_2$)$_2$]Pt(Me)(CO) (57). Solid [[Ph$_2$B-(CH$_2$P(*p*-CF$_3$Ph)$_2$)$_2$]PtMe$_2$][ASN] and [Et$_3$NH][BPh$_4$] were dissolved in THF (2 mL). After 15 min, the cloudy mixture was filtered into a J. Young NMR tube and placed under reduced pressure. An

Table 2. X-ray Diffraction Experimental Details for **25**[Li], **25**[Tl], **36**[Li], **37**[Li], and **38**[Tl]

	25[Li]	**25**[Tl]	**36**[Li]	**37**[Li]	**38**[Tl]
chem formula	$C_{50}H_{65}BLiN_4P_2$	$C_{34}H_{58}BP_2Tl$	$C_{34}H_{58}BLiO_2P_2$	$C_{34}H_{60}BLiOP_2$	$C_{38}H_{34}BP_2Tl$
fw	801.75	743.92	578.49	564.51	767.77
T (°C)	−177	−177	−177	−177	−177
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
a (Å)	11.7922(6)	11.7142(9)	11.3226(9)	16.295(3)	8.4192(6)
b (Å)	11.7081(6)	16.4401(13)	15.4574(12)	12.898(2)	12.6996(9)
c (Å)	33.1336(18)	19.1967(15)	20.5142(16)	17.470(3)	15.6565(11)
α (deg)	90	83.288(1)	90	90	95.585(1)
β (deg)	94.062(1)	81.391(1)	94.704(1)	105.480(3)	98.293(1)
γ (deg)	90	72.064(1)	90	90	104.532(1)
V (Å^3)	4563.1(4)	3467.8(5)	3578.3(5)	3538.6(11)	1587.85(19)
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$C2/c$	$P\bar{1}$
Z	4	4	4	4	2
D_{calcd} (g/cm^3)	1.167	1.425	1.074	1.060	1.606
μ (cm^{-1})	1.33	47.70	1.48	1.46	52.13
R1,[a] wR2[a] ($I > 2\sigma(I)$)	0.0608, 0.0862	0.0370, 0.0723	0.0465, 0.0868	0.0517, 0.0896	0.0277, 0.0622

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

atmosphere of CO was introduced to the tube. The reaction was heated at 55 °C for 4 h, after which $^{31}P\{^1H\}$ NMR analysis verified that the reaction had gone to completion. Volatiles were removed under reduced pressure. Dissolution in benzene (2 mL), filtration, and removal of volatiles under reduced pressure provided **57**. ^1H NMR (300 MHz, $CDCl_3$): δ 7.51 (m, 6H), 7.39 (m, 8H), 6.81 (m, 12H), 2.23 (m, 4H), 0.53 (t, 3H, Pt(CH_3), $^2J_{P-H} = 57$ Hz, $^3J_{P-H} = 6$ Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$): δ 179.5 (dd, Pt(*C*O), $^2J_{P-C} = 7.3$, 132 Hz, $^1J_{Pt-C} = 1296$ Hz), 160 (br m), 139.7, 139.3, 133.7 (d), 132.7 (d), 131.8, 127.0, 125.5 (m), 125.2 (m), 123.4, 18.3 (br), 16.3 (br), −1.9 (dd, Pt(*C*H$_3$), $^1J_{Pt-C} = 408$ Hz, $^2J_{P-C} = 4.1$, 61 Hz). $^{19}F\{^1H\}$ NMR (282.1 MHz, $CDCl_3$): δ −64.0, −64.1. $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 20.85 ($^1J_{Pt-P} = 3090$ Hz, $^2J_{P-P} = 32$ Hz), 16.84 ($^1J_{Pt-P} = 1616$ Hz, $^2J_{P-P} = 32$ Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, $CDCl_3$): δ −14.3. IR (CH_2Cl_2): $\nu_{CO} = 2105$ cm^{-1}.

[Ph$_2$B(CH$_2$P^{i}Pr$_2$)$_2$]Pt(Me)(CO) (58). Following general method D, **58** was generated. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.38 (br, 4H), 7.04 (t, 4H), 6.87 (t, 2H), 2.38 (d of septet, 2H), 2.17 (d of septet, 2H), 1.53 (br m, 4H), 1.10 (dd, 12H), 1.02 (dd, 6H), 0.97 (dd, 6H), 0.79 (dd, 3H, Pt(CH_3), $^2J_{Pt-H} = 57$ Hz, $^3J_{P-H} = 5.7$, 4.8 Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2): δ 183.1 (dd, Pt(*C*O), $^2J_{P-C} = 7$, 123 Hz, $^1J_{Pt-C} = 1222$ Hz), 164.2 (q, $^1J_{C-B} = 50$ Hz), 132.0, 127.1, 123.2, 28.9 (m), 28.7 (m), 26.0 (m), 25.7 (m), 20.3 (m), 19.9 (m), 18.8 (m), 18.7 (m), 9.0 (br), 5.5 (br), −8.6 (dd, Pt(*C*H$_3$), $^1J_{Pt-C} = 406$ Hz, $^2J_{P-C} = 6.2$, 61 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ 40.28 ($^1J_{Pt-P} = 1666$ Hz, $^2J_{P-P} = 26$ Hz), 30.81 ($^1J_{Pt-P} = 2942$ Hz, $^2J_{P-P} = 26$ Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, CD_2Cl_2): δ −14.6. IR (CH_2Cl_2): $\nu_{CO} = 2079$ cm^{-1}.

MeP(*p*-^{t}BuPh)$_2$ (59). 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 resultant mixture was warmed to rt and stirred for 2 h. The reaction was quenched with a degassed aqueous ammonium chloride solution (10 wt %, 150 mL). The organic layer was removed by a cannula under nitrogen. The aqueous layer was extracted with dichloromethane (2 × 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 **59** (11.4 g, 85.9%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.35−7.30 (m, 8H), 1.59 (d, $J = 3.6$ Hz, 3H), 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.

MeP(*p*-CF$_3$Ph)$_2$ (60). 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 °C. 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 rt for 2 h. The reaction was quenched with a deoxygenated saturated aqueous solution of [NH_4][Cl] (10 mL). The organic layer was extracted with water (3 × 30 mL) and dried over magnesium sulfate. Removal of the volatiles by rotary evaporation provided **60** as a pale yellow solid (8.6 g, 68%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.63−7.60 (m, 4H), 7.56−7.50 (m, 4H), 1.71−1.69 (m, 3H). $^{13}C\{^1H\}$ 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). $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): δ −59.89. $^{31}P\{^1H\}$ 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.

MeP(*p*-CF$_3$Ph)$_2$(BH$_3$) (61). Solid MeP(*p*-CF_3Ph)$_2$ (1.5709 g, 4.6724 mmol) was dissolved in THF (1 mL). With stirring, a 2.0 M solution of BH_3·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%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.70−7.85 (m, 8H), 1.96 (d, 3H, $J_{P-H} = 10.2$ Hz), 1.0 (br q, 3H, $J_{B-H} = 95$ Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$): δ 134.6 (d), 133.7 (m), 132.5 (d), 126.1 (m), 11.6 (m). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 13.11. $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): δ −64.1. $^{11}B\{^1H\}$ NMR (128.3 MHz, $CDCl_3$): δ −39.5.

General X-ray Experimental Information. Crystals of **25**[Li], **25**[Tl], **36**[Li], **37**[Li], and **38**[Tl] were mounted on a glass fiber with Paratone-N oil. Crystallographic data (Table 2) 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).

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., and copies can be obtained on request, free of charge, by quoting the publication

citation and the deposition numbers 150792 (**25**[Li]), 203701 (**25**[Tl]), 203703 (**36**[Li]), 203700 (**37**[Li]), and 203702 (**38**[Tl]).

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Supporting Information Available: CIF files and tables of crystallographic data for complexes **25**[Li], **25**[Tl], **36**[Li], **37**[Li], and **38**[Tl], including fully labeled thermal ellipsoid plots, crystallographic details, atomic coordinates, equivalent isotropic displacement parameters, anisotropic displacement parameters, and interatomic distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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