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Coordinating Anions: (Phosphino)tetraphenylborate Ligands as New Reagents for Synthesis

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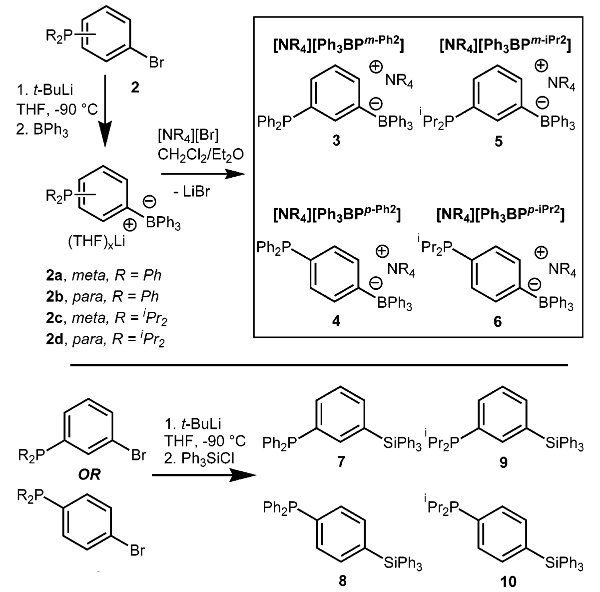
Anionic, electron-releasing phosphines that incorporate a borate counteranion within the ligand framework are promising reagents for organometallic catalysis. This report describes the synthesis of a new class of monodentate tertiary phosphines built upon the commonly employed tetraphenylborate anion. These new phosphines are highly stable and strongly electron-releasing and readily coordinate transition metals. Moreover, they are promising reagents for catalysis, as demonstrated by their ability to promote the Suzuki cross-coupling of aryl chloride substrates.

Whereas monodentate neutral phosphine ligands find utility in nearly all areas of chemical synthesis,[1] comparatively little attention has been devoted to structurally related anionic derivatives. The diphenylphosphidoboratabenzene ligand of Fu provides one of the noteworthy exceptions.[2] This system features a triphenylphosphine-type ligand rendered anionic by a boratabenzene subunit, the latter of which has itself been offered as an intriguing cyclopentadienyl alternative.[3] Given the growing interest in sterically demanding, electron-releasing phosphines (and carbenes) for homogeneous catalysis,[4] access to electron-rich, anionic phosphines would provide a timely complement to these increasingly popular ligands. One conceptual way to generate such species, while at the same time preserving desirable properties inherent to tertiary phosphines, is to embed a borate counteranion within the phosphine donor framework. This approach has already found utility with respect to developing catalytically active, zwitterionic organometallic species.[5] In this paper, we introduce a new series of monodentate phosphines templated upon the tetraphenylborate anion and briefly discuss aspects of their stability, their transition-metal binding affinity, their comparative electron-releasing character, and their potential as reagents for organic synthesis.

Scheme 1



The delivery of lithiated carbanions of methyldiarylphosphines (i.e., $\mathrm{LiCH_2PAr_2}$) and methyldialkylphosphines (i.e., $\mathrm{LiCH_2PR_2}$) to borane electrophiles in the preparation of tri- and bidentate (phosphino)borates has been explored.[6] For example, addition of 3 equiv of $\mathrm{LiCH_2P^iPr_2}$ to $\mathrm{PhBCl_2}$ provides the tridentate anion $[\mathrm{PhB(CH_2P^iPr_2)_3}]^-$,[6a] whereas addition of 2 equiv of $\mathrm{LiCH_2P^iPr_2}$ to $\mathrm{Ph_2BCl}$ provides the bidentate anion $[\mathrm{Ph_2B(CH_2P^iPr_2)_2}]^-$.[6b] A similar protocol exploiting triphenylborane as the electrophile of choice provides related monodentate ligands. For example, the addition of $\mathrm{(TMEDA)LiCH_2PPh_2}$ to $\mathrm{BPh_3}$ generates $[\mathrm{(TMEDA)Li}][\mathrm{Ph_2PCH_2BPh_3}]$ (**1**) in good yield.

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10.1021/ic0350234 CCC: $27.50

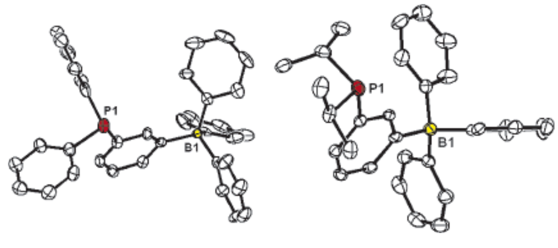

Figure 1. Displacement ellipsoid representations (50%) of **3** (left) and **5** (right). Both phosphines were crystallized as ammonium salt derivatives (cations omitted). See Supporting Information for crystallographic details.

An alternative and potentially more general strategy is to exchange the methylene linker for an aryl linker. This latter approach in effect provides a tetraarylborate counteranion featuring a coordinating phosphine donor. As a number of known halo-substituted arylphosphines are precursors to lithio arylcarbanions,[7] a diverse family of anionic phosphines can be envisioned. Several meta- and para-substituted bromoarylphosphines (**2a**−**d**) were prepared to examine this approach (Scheme 1).

Reaction of the para- and meta-substituted bromoarylphosphines with a single equivalent of t-BuLi (−90 °C, THF) generated the required arylcarbanions. The solutions were subsequently quenched by low temperature addition of triphenylborane. This protocol afforded reasonably high crude yields (>70%) of the desired (phosphino)borate species, as ascertained by ^{11}B and ^{31}P NMR spectroscopy. These lithium species were converted in situ to their more conveniently isolated ammonium salt derivatives, **3**−**6**, by salt exchange with $[NR_4][Br]$ in dichloromethane solution ($NR_4 = NBu_4$, NEt_4, and ASN = 5-azonia-spiro[4.4]nonane). The solid-state structures of the ammonium salts of **3** and **5** (Figure 1, also see Supporting Information) establish the structural integrity of these borates, and compare well with structural data for related neutral phosphines (e.g., PPh_3 and Ph^iPr_2P).[8] For comparative purposes, the isostructural neutral silane ligands were also prepared (Scheme 1) via low temperature generation of the arylcarbanion (as above) and subsequent quenching with triphenylsilyl chloride. This procedure afforded consistently high crude yields (> 90% by ^{31}P NMR) of the desired (phosphino)silanes (**7**−**10**).

The anionic phosphine salts **3**−**6** are appreciably soluble in alcohols (e.g., EtOH), acetonitrile, tetrahydrofuran, chlorinated solvents, and acetone.[9] Their stability in $CHCl_3$ and CH_2Cl_2 is distinct from those of **1** and related methylene-bridged (phosphino)borates, which tend to degrade rather rapidly in such solvents.[6b] Moreover, ligands **3**−**6** proved very stable to both air oxidation and hydrolysis. For example, **3**−**6** afforded no discernible oxidation products (^{31}P NMR) over a period of 2 weeks under an atmosphere of air in acetone solution. This stability again contrasts that of methylene-bridged **1**, which was oxidized very rapidly by air in acetone solution, and also underwent gradual hydrolysis to release $MePPh_2$ upon exposure to water.

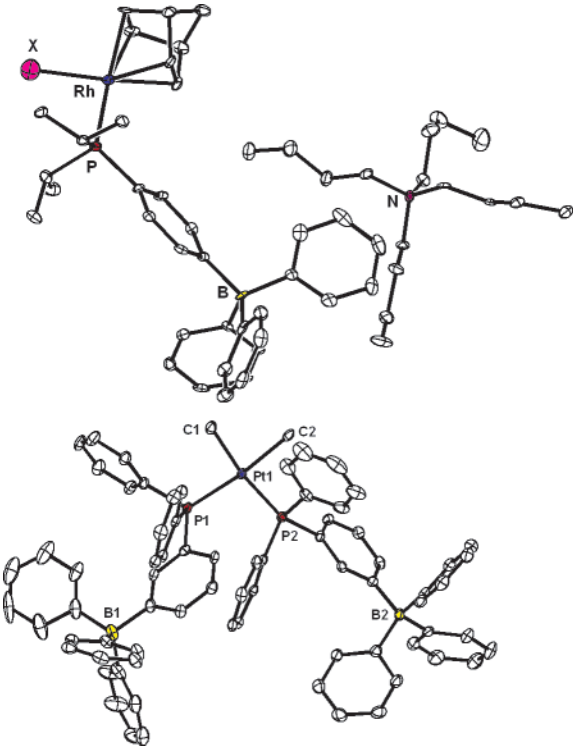

Figure 2. Displacement ellipsoid representations (50%) of $\{^nBu_4N\}\{[Ph_3BP^{p\text{-}iPr_2}]RhX(NBD)\}$ (**11**, top) and $\{^nBu_4N\}_2\{[Ph_3BP^{m\text{-}Ph_2}]_2PtMe_2\}$ (**12**, bottom).[10] The two ASN countercations of **12** have been omitted for clarity.

To benchmark the binding affinity of ligands **3**−**6**, their reactivity with $\{(NBD)RhCl\}_2$ and $(COD)PtMe_2$ (COD = cyclooctadiene, NBD = norbornadiene) was surveyed. Addition of **6** as a tetra-*n*-butylammonium salt to $\{(NBD)RhCl\}_2$ provided the molecular salt $\{^nBu_4N\}\{[Ph_3BP^{p\text{-}iPr_2}]RhCl(NBD)\}$ (**11**), whose solid-state structure is shown in Figure 2.[10] This anion is a promising precursor to zwitterionic rhodium species upon formal release of $[^nBu_4N][Cl]$. Indeed, addition of $[Tl][PF_6]$ precipitates TlCl instantly to give a benzene soluble species with a single resonance in the ^{31}P NMR ($^1J_{Rh-P} = 166$ Hz). The ligands **3**, **4**, and **5** also reacted with $\{(NBD)RhCl\}_2$ to give analogous salt products. With respect to platinum, addition of 2 equiv of an ammonium salt of **3**−**6** to $(COD)PtMe_2$ afforded in each case disubstitution and the *cis* isomer exclusively: $\{ASN\}_2\{(Ph_3BP^{m\text{-}Ph_2})_2PtMe_2\}$ (**12**), $\{NBu_4\}_2\{[Ph_3BP^{p\text{-}Ph_2}]_2PtMe_2\}$ (**13**), $\{NBu_4\}_2\{[Ph_3BP^{m\text{-}iPr_2}]_2PtMe_2\}$ (**14**), and $\{NBu_4\}_2\{[Ph_3BP^{p\text{-}iPr_2}]_2PtMe_2\}$ (**15**).[11] The ^{31}P NMR shifts and coupling constants of complexes **12** and **13** (28.63, ppm, $^1J_{Pt-P} = 1947$ Hz; and 27.47 ppm, $^1J_{Pt-P} = 1935$ Hz, respectively) compare well with literature values for *cis*-$(PPh_3)_2PtMe_2$ (27.7 ppm, $^1J_{Pt-P} = 1900$ Hz).[11,12] The isopropyl derivatives **14** and **15** are

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(9) Ligand solubility is highly dependent on the ammonium salt used. For example, the ASN salt of **3** is sparingly soluble in THF, while the $^nBu_4N$ salts of **4**−**6** and the $Li(TMEDA)_2$ salt of **1** are highly soluble in THF.

(10) The structural data obtained for complex **11** revealed the presence of a bromide impurity, which was present in the original batch of **6** that produced the crystal (see Supporting Information). The data are satisfactorily modeled with the halide occupancy as 60% Br and 40% Cl.

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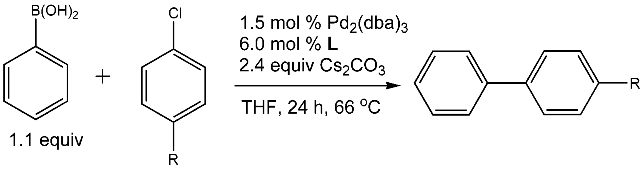
Table 1. Examination of the Efficiency of Ligands **5**, **9**, and P^iPr_2Ph To Facilitate Suzuki Cross-Coupling between Phenylboronic Acid and *p*-Chlorotoluene, *p*-Chloroacetophenone, or 1,4-Dichlorobenzene



R	yield^a (%)		
	L = **5**	L = **9**	L = ^{i}**Pr$_2$PPh**
Me	71%	56%	49%
Cl	68%	43%	43%
COMe	74%	38%	49%

[a] Isolated yields reported as the average of two independent runs.

shifted further downfield in their ^{31}P NMR spectra (38.11 ppm, $^1J_{Pt-P} = 1900$ Hz and 36.53 ppm, $^1J_{Pt-P} = 1917$ Hz, respectively). An XRD study of crystals of **12** confirmed its *cis* coordination (Figure 2, also see Supporting Information).

The dianionic species **12**−**15** are highly reactive toward both Bronsted and Lewis acids in THF and acetonitrile solution. For example, stoichiometric addition of $B(C_6F_5)_3$ effected the rapid release of 1 equiv of $[NR_4][Me(B(C_6F_5)_3)]$ (^{1}H, ^{19}F NMR) to produce the corresponding *trans*, monoanionic solvento species $\{NR_4\}\{$*trans*-$[Ph_3BP']_2Pt(Me)(solv)\}$. *trans*-Disposition of the phosphine ligands was inferred from the dramatic increase in the $^1J_{Pt-P}$ coupling constants and the single resonance observed in the ^{31}P NMR spectra. The isostructural but neutral dimethyl complexes $(Ph_3SiP^{p\text{-}iPr_2})_2PtMe_2$ (**16**) and $(Ph_3SiP^{p\text{-}Ph_2})_2PtMe_2$ (**17**) displayed quite distinct reactivity. For example, in the case of **16**, methide abstraction by $B(C_6F_5)_3$ required ca. 12 h and led to the *cis*-mono(solvento) species [*cis*-$(Ph_3SiP^{p\text{-}Ph_2})_2PtMe(solv)][Me(B(C_6F_5)_3]$ (**18**) exclusively as the kinetic product at RT. Slow isomerization of **18** to its thermodynamic *trans* isomer occurred over a period of days in solution. Given the steric similarity between ligands **6** and **10**, the apparently substantial rate difference displayed with respect to *cis* → *trans* isomerization in these mono-solvento adducts is striking and most likely electronic in origin. One plausible explanation is to suggest that the anionic ligand **6** exerts a greater *trans*-influence and thus labilizes solvent molecules in the *trans* position of the kinetic *cis*-phosphine product to a larger extent than for the neutral ligand **10**, thereby facilitating rapid isomerization.

As a final point of interest, we have briefly examined the ability of **3**−**6** to promote Suzuki cross-coupling reactions. Each ligand proved generally effective for the coupling of $PhB(OH)_2$ with typical aryliodide and arylbromide substrates (see Supporting Information). More interesting was the ability of these ligands to facilitate the cross-coupling of aryl chlorides since such substrates typically require electron-rich phosphine promoters.[13] Under conditions recently reported by Fu,[14] we found that $[^nBu_4N][Ph_3BP^{m\text{-}iPr_2}]$ (**5**) promoted the cross-coupling of the three substrates shown in Table 1 in modestly good yield. For comparison, the isostructural but neutral ligand **9**, as well as the more conventional phosphine P^iPr_2Ph, were screened and also found to give the cross-coupled products, albeit in yields that were reproducibly ∼20% lower than the yields obtained using **5**.[15] The appreciable difference in yields likely reflects the greater electron-releasing character of **5**. Assuming oxidative addition of the aryl chloride to be rate-limiting, an anionic $[LPd^0]^-$ fragment would be expected to undergo oxidative addition more rapidly than a neutral LPd^0 fragment.

Infrared model studies of ligands **5** and **9** are consistent with this latter suggestion. For example, refluxing a solution of either **5** or **9** in a THF solution of $Mo(CO)_6$ led, respectively, to the anionic pentacarbonyl complex $\{^nBu_4N\}\{[Ph_3BP^{m\text{-}iPr_2}]Mo(CO)_5\}$ (**19**) and the neutral pentacarbonyl $(Ph_3SiP^{m\text{-}iPr_2})Mo(CO)_5$ (**20**), as confirmed by IR and ^{31}P NMR spectroscopy, as well as ES/MS. Infrared carbonyl vibrations for **19** were recorded at 2065 and 1925 cm^{-1}, whereas those for **20** were recorded at 2070 and 1942 cm^{-1}.[16,17] Both the high and low energy vibrations thus shift to lower energy in the anionic system **19**, likely reflecting an appreciable increase in electron-releasing character of anionic **5** versus neutral **9**.

Future work will examine the utility of these anionic phosphines in generating zwitterionic precursors for catalytic studies.

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Supporting Information Available: Experimental procedures (PDF), characterization data, additional Suzuki coupling data, and crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The phenyl substituted ligands **1**, **3**, and **4** were much less effective in the Suzuki coupling of aryl chlorides. Ligand **6** showed comparable activity to **5** in several model studies. Also, a point of concern pertains to whether the tetraarylborate unit of ligand **5** is transferred during the cross-coupling reactions. While we cannot rule-out this possibility altogether, we note that tolylboronic acids were also screened briefly and found to give comparable yields.

(16) Although three IR active vibrations are predicted, only the A_1^2 and E stretches are resolved. The A_1^1 stretch is weak and presumably coincident with the E vibration.

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