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Note

An examination of the effects of borate group proximity on phosphine donor power in anionic (phosphino)tetraphenylborate ligands

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The ligand electron-donating abilities are compared among a series of monodentate, anionic (phosphino) tetraphenylborate phosphines $[Ph_4P][Ph_2P\text{-}R\text{-}C_6H_4BPh_3]$ (R = $-C_6H_4-$, $-CH_2-$, $-CH_2CH_2-$ or none), and their neutral counterparts Ph_2PR (R = biphenyl, $-CH_2Ph$, $-CH_2CH_2Ph$ or Ph). Among the anionic ligands, the position of the tetraphenylborate group relative to the diphenylphosphino donor moiety was systematically varied in an effort to examine how its proximity impacts donor power. The donor power was determined by measuring the $^{31}P-^{77}Se$ coupling constant for the corresponding selenide of each phosphine ligand via ^{31}P NMR spectroscopy. The anionic ligands yield lower $^{31}P-^{77}Se$ coupling constants than those measured for their respective neutral counterparts. Moreover, the $^{31}P-^{77}Se$ coupling constants among the anionic ligands increase when the tetraphenylborate group is positioned further from the phosphorus centre.

Introduction

One of the most widely used strategies for synthesizing anionic phosphine ligands involves (at least conceptually) modifying the neutral parent phosphine's substituents through the installation of anionic groups, such as sulfonate or phosphonate groups [1]. This approach has been widely adapted to include covalently bound borate groups [2–10], which, when introduced into the general framework of the phosphine, also render it anionic. In addition, some anionic phosphine ligands modified in this way reportedly display enhanced donor powers over their neutral counterparts [2–4,6e,8i,11]. We recently reported on the synthesis of an anionic, tetraphenylborate-functionalized, [P,N]-hybrid phosphinobenzimidazole ligand [12]. While pursuing this work, we questioned the significance of the proximity of the borate group to the donor atoms, and wondered if there was a threshold distance beyond which the impact of the borate group became negligible. Indeed, it has been argued that one pathway by which the borate group's negative charge may be transmitted to the ligand's donor atom(s) is via the ligand framework [2,13], therefore the relative position of the borate group to the phosphorus donor atom(s) should be very important to the electron-donating ability of the anionic phosphine.

We report here on the synthesis of a series of monodentate, anionic (phosphino)tetraphenylborate ligands, all of which contain a diphenylphosphino moiety tethered to a tetraphenylborate group via different linkers. In order to gain some insight into the electron-donating abilities of these anionic phosphines, we have measured the $^{31}P-^{77}Se$ coupling constants of their corresponding selenides. For comparative purposes, the neutral counterparts of these ligands have also been included in this study.

Results and discussion

The neutral series (**1**–**4**) and anionic (**5**–**8**) series of phosphine ligands examined as part of this work are illustrated in Chart 1. The tetraphenylborate-functionalized variants of ligands **1**–**4** were prepared using either a slightly modified literature procedure [3] (**5** and **6**), or as shown in Scheme 1 (**7** and **8**). Conceptually, the anionic phosphines **5**–**8** may be viewed as being constructed from their respective neutral parent phosphines **1**–**4** by substitution of a proton at the 4-position of the phenyl (**1**), biphenyl (**2**), benzyl (**3**) or 2-phenylethyl (**4**) substituents for a BPh_3 group. In this way, the position of the tetraphenylborate group was systematically varied by inserting aryl or methylene spacers between it and the phosphorus atom of the diphenylphosphino moiety.

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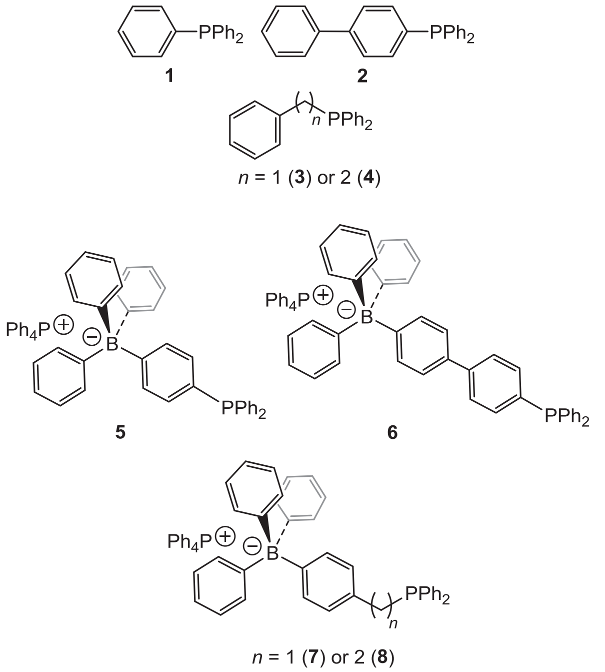


Chart 1. Ligands **1**–**8** investigated in this work.

Table 1
Selected structural (DFT) and experimental (NMR) data for ligands 1–8.

Ligand	d(P–C) (Å)[a]	∠C–P–C (°)[b]	^{31}P (ppm)/R$_3$P[c]	^{31}P (ppm)/R$_3$PSe[c]	$^1J_{PSe}$ (Hz)[c]
1	1.856	102.42	−5.31[d]	36.8[d]	729[d]
	1.856	102.42			
	1.856	102.42			
2	1.853	102.59	−6.11	34.8	730
	1.855	102.45			
	1.856	102.66			
3	1.892	101.71	−15.2[d]	35.2[d]	735[d]
	1.856	100.62			
	1.859	101.96			
4	1.877	101.45	−16.3	33.4	725
	1.860	102.33			
	1.854	100.51			
5	1.839	101.83	−5.86[e]	35.0	701
	1.860	102.77			
	1.861	104.00			
6	1.845	103.46	−6.14[e]	34.9	729
	1.858	102.02			
	1.858	102.57			
7	1.890	101.76	−11.9[e]	32.5	706
	1.857	101.15			
	1.859	102.67			
8	1.875	102.01	−13.7[e]	33.4	716
	1.857	99.88			
	1.861	103.87			

[a] For each Ph$_2$R′P and [Ph$_2$R′P]$^-$ ligand, the first bond distance listed represents the P-R′ distance.

[b] For each Ph$_2$R′P and [Ph$_2$R′P]$^-$ ligand, the first bond angle listed represents ∠C$_{Ph,ipso}$-P-C$_{Ph,ipso}$.

[c] Measured in CDCl$_3$.

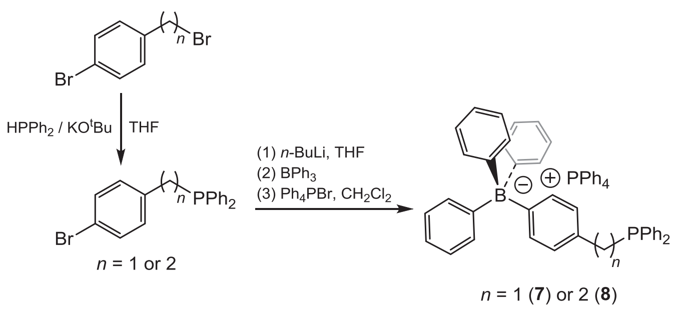
[d] Ref. [18f].

[e] The chemical shift of the anion of the ligand.

The ^{31}P{^{1}H} NMR chemical shifts of the anionic ligands (Table 1) are very close to their respective neutral parents. Among all four triarylphosphines compared in this investigation (*i.e.*, **1** *vs.* **5**, and **2** *vs.* **6**), a very narrow range in chemical shifts is observed. In fact, despite the anionicity of ligand **6**, its chemical shift is remarkably similar to that measured for the neutral parent ligand **2**, which perhaps is a reflection of the greater distance between the borate group and the phosphorus centre compared to **5**. The differences in chemical shifts observed between ligands **3** and **7**, and between ligands **4** and **8** are larger; however, we again observe that the greater separation between the tetraphenylborate group and the phosphorus centre of ligand **8** results in a smaller chemical shift difference with its neutral counterpart compared to **7** ($\Delta\delta_{\mathbf{4,8}} = 2.6$ ppm *vs.* $\Delta\delta_{\mathbf{3,7}} = 3.3$ ppm).

One of the original intentions of this work was to compare the electronic properties among the two series of ligands. Therefore, for the anionic ligands **5**–**8**, it was imperative that any structural modifications resulting from the introduction of the bulky BPh$_3$ group be minimized, since the electronic properties of tertiary phosphines can be sensitive towards the steric environment (*i.e.*, the C–P–C intervalence bond angles) defined by the substituents attached to the phosphorus centre [14]. For example, strategically positioning the BPh$_3$ group specifically at the 4-position of the phenyl substituent in ligand **5** ensures it will exert the least impact on the steric environment about the phosphorus atom, thereby allowing us to isolate and observe any electronic changes that may arise as a result of the ligand's anionicity. As confirmation of this, the ranges in the three P–C bond distances and the three C–P–C bond angles derived from DFT (B3LYP) calculations on the optimized structures of ligand **1**, Ph$_3$P (1.856 Å; 102.42°), and ligand **5**, [Ph$_2$P(4-Ph$_3$BC$_6$H$_4$)]$^-$ (1.839–1.861 Å; 101.83–104.00°), compare well (Table 1), and are very similar to those distances and angles obtained from the X-ray crystallographic study of Ph$_3$P (1.824(2)–1.837(2) Å; 101.17(9)–102.68(9)°) [15]. The very similar P–C bond distances and C–P–C bond angles measured for the Ph$_3$P ligand in the complex [(η^6-*p*-cymene)RuCl$_2$(Ph$_3$P)] (1.824(2)–1.840(2) Å; 99.56(9)°–106.29(9)°) [16], and for the [Ph$_2$P(4-Ph$_3$BC$_6$H$_4$)]$^-$ ligand in the anion [(η^6-*p*-cymene)RuCl$_2${Ph$_2$P(4-Ph$_3$BC$_6$H$_4$)}]$^-$ (1.800(5)–1.826(5) Å; 99.7(2)°–106.4(2)°) [17] also provide further confirmation. Ligand **5**, then, may be viewed as a negatively charged, essentially isosteric variant of ligand **1**. For the remaining anionic ligands **6**–**8**, with the addition of aryl or methylene spacers, the increased separation between the tetraphenylborate group and the phosphorus centre presents less of a steric issue, and so they, too, represent anionic, isosteric variants of their neutral counterparts **2**–**4**, respectively (Table 1).

The primary objective of this work was to investigate the impact of the proximity of the tetraphenylborate group to the phosphorus centre by assessing and comparing the electronic properties of ligands **5**–**8**. As an entry into probing the relative donor powers of all of the ligands in this study, we synthesized the corresponding selenide for each of ligands **1**–**8** and measured their $^1J_{PSe}$ coupling constants in CDCl$_3$. The $^1J_{PSe}$ coupling constant of a phosphine selenide is related to the degree of *s*-character in the lone pair of the phosphorus atom, and thus provides a convenient means of



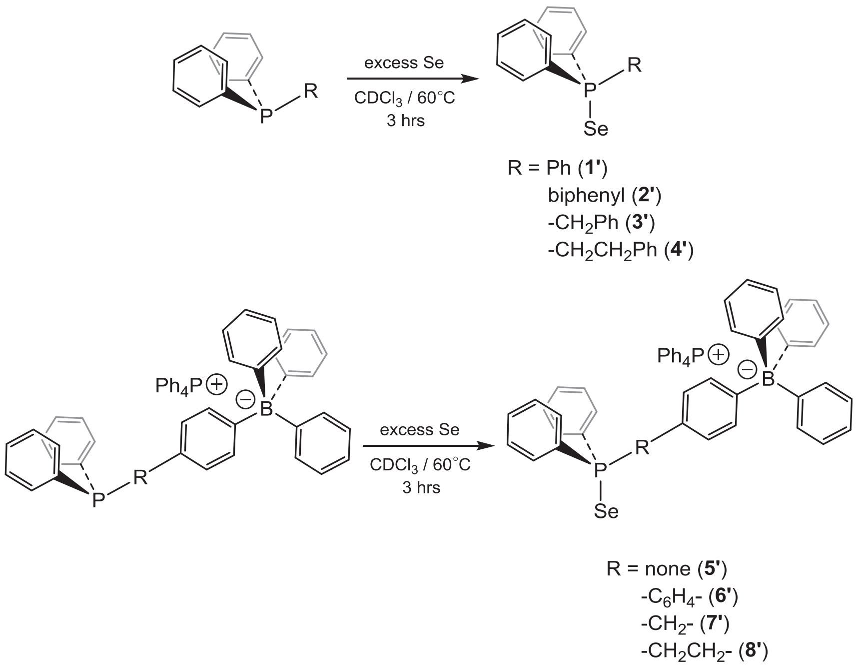
Scheme 1. Synthesis of ligands **7** and **8**.

assessing the σ-donating properties of the parent phosphine [18]. The magnitude of the $^1J_{PSe}$ coupling constant is sensitive to the steric and electronic nature of the substituents attached to the phosphorus centre. In general, phosphine selenides of more strongly σ-donating phosphines display smaller $^1J_{PSe}$ coupling constants than the corresponding selenides of weaker σ-donor phosphines.

The $^{31}P\{^1H\}$ chemical shifts and $^1J_{PSe}$ coupling constants for the selenides of ligands **1**–**8** (correspondingly identified as **1′**–**8′** in Scheme 2) are given in Table 1. Unlike the parent phosphines themselves, the selenides fall within a narrow range of chemical shifts regardless of substituent or overall phosphine charge. In contrast, the changes in the phosphorus–selenium coupling constants among **1′**–**8′** are less uniform. The difference in the $^1J_{PSe}$ coupling constants measured for the selenides of the neutral ligands **1** and **2** (**1′**, 729 Hz [18f]; **2′**, 730 Hz) is negligible. Compared to **2′**, the selenides of $Ph_2P(4\text{-}MeOC_6H_4)$ and $Ph_2P(4\text{-tolyl})$ yield lower $^1J_{PSe}$ coupling constants in the same solvent (722 Hz [18d] and 726 Hz [18e], respectively), reflecting the electron-releasing properties of the 4-methyl and 4-methoxy groups, and further revealing the sensitivity of the ^{31}P–^{77}Se coupling to even distant modifications. Among the neutral phosphine selenides containing methylene spacers, the selenide **4′** yields a lower $^1J_{PSe}$ coupling constant (725 Hz) compared to **1′** and **2′**, which is consistent with the substitution of an aryl substituent (*i.e.*, $Ph_2P–C(sp^2)$ linkage) for an alkyl substituent (*i.e.*, $Ph_2P–C(sp^3)$ linkage) [19]. However, the $^1J_{PSe}$ coupling constant for the selenide **3′** is larger (735 Hz) [18f] compared to **1′** and **2′**. Interestingly, a recent kinetic study [18f] on the oxidative addition of $[SeCN]^-$ to a series of tertiary phosphines revealed slower rates of selenide formation for Ph_2PCH_2Ph than for Ph_3P, thus suggesting the former is a weaker σ-donor phosphine as a result of the presence of the benzyl substituent, which is consistent with the relatively larger $^1J_{PSe}$ coupling constant.

Much more notably, we observed that the $^1J_{PSe}$ coupling constants for the anionic phosphine selenides **5′**–**8′** are all lower than those observed for their neutral counterparts **1′**–**4′**, suggesting the introduction of the borate group in each case has an additive effect on the σ-donor power of the phosphine. The greatest differences were observed between **1′** and **5′** ($\Delta^1J_{PSe} = 28$ Hz), and between **3′** and **7′** ($\Delta^1J_{PSe} = 29$ Hz). In comparison, the $^1J_{PSe}$ coupling constants of the selenides of Ph_2PCy (726 Hz) and Ph_2P^tBu (717 Hz) are larger [18e], suggesting the borate charges of the 4-substituted phenyl substituent in **5**, and the 4-substituted benzyl substituent of **7**, have a greater impact on enhancing the σ-donor power of the phosphine than some of the strongest electron-releasing alkyl groups. The insertion of a second methylene spacer upon moving from ligand **7** to ligand **8** leads to an increase in the magnitude of the $^1J_{PSe}$ coupling constant of the corresponding selenide (**7′** → **8′**, $\Delta^1J_{PSe} = 10$ Hz), and consequently to a decrease in σ-donor power. In comparison, the insertion of an aryl spacer in **5′** to give ligand **6′** leads to a substantial increase in the $^1J_{PSe}$ coupling constant (**5′** → **6′**, $\Delta^1J_{PSe} = 28$ Hz). In fact, the negligible difference in phosphorus–selenium couplings between **2′** and **6′** suggests that the location of the tetraphenylborate group in **6′** (or perhaps even its very presence) has no effect on the σ-donor power of the phosphine. Interestingly, the counterion of the anionic phosphines appears to exert little influence on the phosphorus–selenium coupling constant, despite the argument that the dipolar form $R_3P^+\text{-}Se^-$ of a phosphine selenide is the dominant contributor to the phosphorus–selenium bond rather than the double-bonded canonical form $R_3P{=}Se$ [20]. For example, the $^1J_{PSe}$ coupling constant measured for the selenide of the Bu_4N^+ salt [3] of ligand **5** (700 Hz) is almost identical to that observed for the Ph_4P^+ salt.

The trends in phosphorus–selenium coupling data observed among the phosphine selenides were corroborated by the results obtained from an IR spectroscopic analysis of the CO ligand vibrations in the complexes *cis*-$Mo(CO)_4L_2$ and $[Ph_4P]_2[$*cis*-$Mo(CO)_4L_2]$. For example, the A_1 ν(CO) vibration [21] observed in the IR spectrum of *cis*-$Mo(CO)_4(\mathbf{1})_2$ is higher than that observed for $[Ph_4P]_2[$*cis*-$Mo(CO)_4(\mathbf{5})_2]$ (2025 cm^{-1} *vs.* 2015 cm^{-1}, respectively; $\Delta\nu(CO) = 10\ cm^{-1}$), consistent with the relatively stronger σ-donor power of ligand **5** compared to **1**. Furthermore, the IR data confirm that the impact of the borate group decreases as it is positioned



Scheme 2. Synthesis of the selenides **1′**–**8′**.

further from the phosphorus centre. Thus, the A_1 ν(CO) vibration observed in the IR spectrum of *cis*-$Mo(CO)_4(\mathbf{4})_2$ (2017 cm^{-1}) is only 4 cm^{-1} higher than that observed for $[Ph_4P]_2[cis\text{-}Mo(CO)_4(\mathbf{8})_2]$ (2013 cm^{-1}).

Summary

We have prepared a series of (phosphino)tetraphenylborate ligands, where the position of the tetraphenylborate group was systematically varied by inserting aryl or methylene spacers between it and the phosphorus atom of a diphenylphosphino moiety. The direct ^{31}P—^{77}Se coupling constants of the corresponding selenides of the anionic ligands are all lower than those measured for their respective neutral counterparts, which suggests the borate group has an additive effect on the σ-donor power of the phosphine. The $^1J_{PSe}$ coupling constant data also reveal that the proximity of the tetraphenylborate group to the phosphorus centre is important to the magnitude of the enhancement in σ-donor power. Tethering the tetraphenylborate group directly to the diphenylphosphino moiety leads to the greatest enhancement in σ-donor power of the phosphine, however the insertion of an aryl group reduces its effects substantially.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.10.048.

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