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Synthesis of an anionic tridentate phosphinoborate and its reaction chemistry with Sn(II)

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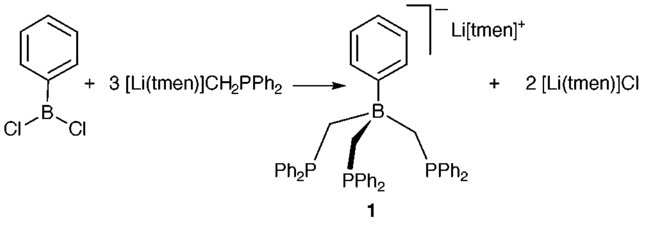
Dichlorophenylborane reacts smoothly with [Li(tmen)][CH_2PPh_2] in THF to afford, in good yields, the Li(tmen)$^+$ salt of a novel monoanionic tridentate phosphinoborate, tris(diphenylphosphinomethyl)phenylborate; reaction of the ligand with $SnCl_2$ produces tris(diphenylphosphinomethyl) phenylboratotin(II) chloride, which may be dehalogenated to give the η^3 compound, {[PhB(CH_2PPh_2)$_3$]Sn}PF_6, tris(diphenylphosphinomethyl)phenylboratotin(II) hexafluorophosphate.

By comparison to their neutral congeners,[1] tridentate anionic phosphines are rarely found within the coordination spheres of metal ions, emerging as viable ligands only recently in the preparation of water-soluble hydrogenation catalysts.[2] In these systems, an isolated anionic charge is introduced by sulfonylation of conventional phosphine ligands remote to the ligation site. With the desire of adding new, anionic six-electron donor ligands to the palette of coordination chemistry, we turned our attention to strategies that would permit the incorporation of a negative charge within the framework of a tridentate phosphine. As amply demonstrated in pyrazoylborate chemistry[3,4] and the recent synthesis of [PhB(CH_2SR)$_3$]$^-$ by Riordan and coworkers,[5] the borate bridgehead provides both the desired negative charge and a scaffold to support three ligating arms with a hybridization that sustains a *fac* conformation about a metal center. We now report the synthesis and characterization of the novel anion, tris(diphenylphosphinomethyl)phenylborate **1**. The ligand features a negative charge proximate to a highly polarizable six-electron phosphine donor set. Within the context of hard/soft treatments of acid/base properties, **1** should exhibit a propensity to associate to soft metals. Along these lines, we initially elaborate the chemistry of **1** with tin(II), reporting the X-ray characterization of tris(diphenylphosphinomethyl)phenylboratotin(II) chloride **2** and its structural changes upon replacement of the coordinating chloride with an outer sphere anion PF_6.

Addition of diphenylphosphinomethide to dichlorophenylborane yields a borate salt, which subsequently undergoes substitution of its chlorides by two additional equivalents of diphenylphosphinomethide to provide the tris(diphenylphosphinomethyl)phenylborate ligand in good yields (Scheme 1).† Work up should follow immediately after the addition is completed, as prolonged reaction times lead to lower isolated yields. The crude compound is a pale yellow solid that can be recovered in a purified form from CH_2Cl_2. The phenyl and methylene resonances of the phosphinoborate anion are readily discerned in the ^1H NMR spectrum at δ 6.8–7.6 and 1.07, respectively, as are the methyl and ethylene protons of the Li(tmen)$^+$ cation at δ 2.18 and 2.30.



Scheme 1

Anion **1** reacts with $SnCl_2$ in CH_2Cl_2 to give [PhB(CH_2PPh_2)$_3$]SnCl **2**, which was structurally characterized.‡ This is noteworthy in view of the small number of structurally characterized tin(II) phosphine complexes. The recent classification and analysis of structural data for > 500 tin coordination compounds[6] reveals *ca.* 200 to contain divalent tin. Of these, nitrogen and oxygen are the most common non-halogen atoms found to bond with Sn(II), with poly(pyrazolyl)borates figuring prominently within this classification.[7–9] However, structurally characterized monomeric compounds containing direct ligation of phosphorus to tin are few, and only a small number of these possess tin in its divalent oxidation state.[10–15] The solution of the single crystal X-ray structure of **2** now adds to this abbreviated list.

The most striking feature of the ORTEP diagram shown in Fig. 1 is that one of the phosphine arms of the ligand coordinates the metal center only weakly. The bond distance between Sn(1) and the two phosphorus atoms P(1) and P(3) are d[Sn(1)–P(3)] = 2.6746(14) Å and d[Sn(1)–P(1)] = 2.690(2) Å, respectively. These distances are slightly longer than those found in the limited data set for Sn–P bond lengths.[10,11,15–17] In contrast, the weakly bonded phosphorus, P(2), is situated far from the metal, d[Sn(1)–P(2)] = 3.036(2) Å, slightly beyond the standard covalent bonding distances for tin and phosphorus.[18] This coordination of **2** is distinguished from the analogous tin(II) pyrazoylborate complex insofar as the long Sn–N bond is well within the standard covalent bonding distance for a formal Sn–N bond. Nevertheless, the distorted trigonal bipyramidal coordination geometry about the metal, as is often observed for tin(II) pyrazolylborate complexes, is completed by a Sn(1)–

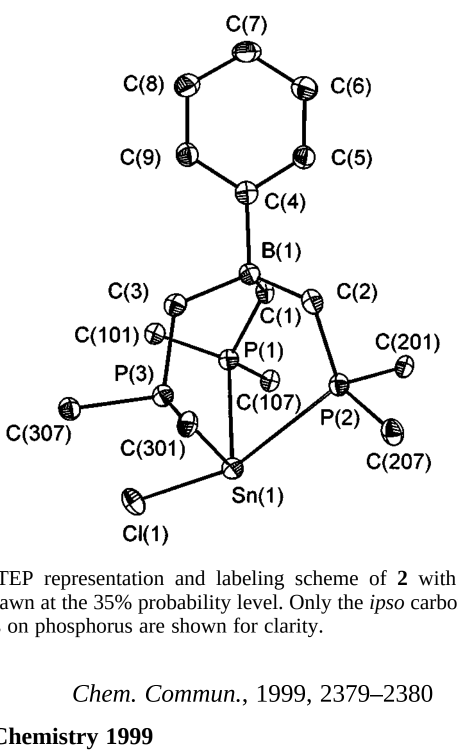


Fig. 1. ORTEP representation and labeling scheme of **2** with thermal ellipsoids drawn at the 35% probability level. Only the *ipso* carbons of the phenyl rings on phosphorus are shown for clarity.

Cl(1) bond, which is long at 2.599(2) Å, and the stereochemically active tin(II) lone pair. The intraligand P(1)–Sn(1)–P(3) bond angle of 81.76(4)° is markedly contracted relative to P–Sn–Cl angles of 87.57(4) and 95.18(5)°. Finally, the local geometry around the boron atom is approximately tetrahedral.

That all three phosphines are capable of bonding to the metal is revealed by the solution ^{31}P{^{1}H} NMR spectrum of **2**, which shows only a single broad peak, centered at δ −5.1. Similar results are observed for anionic bidentate phosphine[19] and poly(pyrazolyl)borate[7] complexes of tin(II) as well. With one coordination site of **2** occupied by chloride, the ligation of only two phosphines is consistent with the stereochemical influence exerted by the electron lone pair present on the tin(II) center. Accordingly, the removal of chloride from **2** would be expected to open a coordination site, thus allowing the dangling phosphine to strongly associate with the metal center. This contention is supported by the reaction chemistry of **2** with $TlPF_6$. Reaction of **2** with one equivalent of thallium hexafluorophosphate yields $\{[PhB(CH_2PPh_2)_3]Sn\}PF_6$ **3**. In contrast to **2**, the ^{31}P{^{1}H} NMR spectrum of **3** shows a single sharp resonance at δ +5.1 that is flanked by tin satellites. Coupling of three equivalent phosphorus atoms to ^{117}Sn (7.68%) and ^{119}Sn (8.59%) isotopes are clearly observed [^{1}J($^{117/119}$Sn–^{31}P) = 1330, 1270 Hz], consistent with the coordination of all three phosphines to the metal center.

Considering the rich coordination chemistry of the related tris(pyrazolyl)borate anion, a similarly diverse chemistry of **1** may be expected. The ligand is distinguished by its negative charge and ability of **1** to adopt four- and six-electron coordination modes about a highly polarizable metal center. The combination of these properties in a singular ligand system should find utility in the design of novel compounds and new metal-based catalytic schemes. Along these lines, the recent preparation of $[PhB(CH_2PPh_2)_3](H)Ir(\eta^3\text{-}C_8H_{13})$ and its reaction with H_2SiMes_2 to produce an iridium silylene[20] illustrates the unique reactivity engendered by this tridentate phosphinoborate ligand.

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Notes and references

† *Experimental procedures*: reactions were carried out under the nitrogen atmosphere of a dry box, which was capable of supporting a variety of standard synthetic methodologies. Solvents were freshly prepared for synthesis by their distillation from appropriate drying agents and by subsequently degassing prior to use. ^{1}H, ^{31}P and ^{11}B NMR spectra were recorded on Varian Unity 300 and Mercury 300 spectrometers. Chemical shifts for ^{1}H, ^{31}P, and ^{11}B NMR are reported in ppm *vs.* TMS, H_3PO_4 (85%) and BF_3•Et_2O, respectively.

1: $[Li(tmen)]CH_2PPh_2$[21] (3 g, 9.31 mmol), dissolved in 100 mL of THF, was added slowly with stirring over 1.5 h to a 25 mL THF solution of dichlorophenylborane (0.49 g, 3.1 mmol) maintained at 0 °C. The mixture was stirred an additional 30 min whereupon the solvent was removed *in vacuo* to leave an oily residue. The borate was dissolved in CH_2Cl_2 and the solution was filtered to remove LiCl. Solvent removal gave **1** as a microcrystalline solid and the product was dried *in vacuo* overnight (2.36 g, 82% yield). $C_{51}H_{57}BLiN_2P_3$; found: C, 75.5; H, 7.18; N, 3.66; P, 11.09; requires: C, 75.75; H, 7.10; N, 3.46; P, 11.49%. ^{1}H NMR (CD_3CN): δ 6.8–7.6 (m, 35H), 2.3 (s, 4H), 2.18 (s, 12H), 1.07 (br, 6H) ^{31}P{^{1}H} NMR: δ −10.2 [q, ^{2}J (^{11}B–^{31}P) 9.16 Hz], ^{11}B{^{1}H} NMR: δ −15.45 [q, ^{2}J (^{31}P–^{11}B) 9.16 Hz)].

2: a 50-mL CH_2Cl_2 solution of **1** (0.4 g, 0.5 mmol) was added to a mol equivalent of $SnCl_2$ (0.094 g) dissolved in 10 mL of CH_2Cl_2. The resulting solution was stirred overnight. A residue remained upon the vacuum evaporation of CH_2Cl_2. The product was extracted away from unreacted $SnCl_2$ with benzene, and the resulting solution was filtered and concentrated to a third of its original volume. Purified product was obtained by layering the benzene filtrate with an equal volume of pentane. Compound **2** formed over 2–3 days, after which the clear crystals were collected and dried (0.31 g, 74%). $C_{45}H_{41}BClP_3Sn$; found: C, 64.01; H, 5.03; P, 10.98; requires: C, 64.37; H, 4.92; P, 11.07%. ^{1}H NMR (C_6D_6): δ 6.7–7.8 (m, 35H), 1.9 (br, 6H); ^{31}P{^{1}H} NMR (C_6D_6): δ −5.1 (br); ^{11}B{^{1}H} NMR (C_6D_6): δ −13.23 (br).

3: the chloride ligand was removed from **2** by dissolving 0.25 g (0.30 mmol) of the compound in 50 mL of acetonitrile, followed by the addition of a mol equivalent (0.104 g) of $TlPF_6$. The reaction mixture was stirred overnight and then filtered to remove TlCl as a white solid. The filtrate was removed *in vacuo* to afford the product, which was dried *in vacuo* overnight (0.250 g, 89%). $C_{45}H_{41}BF_6P_4Sn$; found: C, 56.96; H, 4.55; P, 13.17; requires: C, 56.94; H, 4.35; P, 13.05%. ^{1}H NMR ($CDCl_3$), δ 6.7–7.8 (m, 35H), 1.9 (br, 6H); ^{31}P{^{1}H} NMR ($CDCl_3$), δ 5.1 [s, ^{1}J($^{117/119}$Sn–^{31}P) 1331.8, 1272.8 Hz]; δ −142.9 [sept,^{1}J(^{31}P–^{19}F) 708.42 Hz]; ^{11}B{^{1}H} NMR($CDCl_3$); δ –11.9 (br).

‡ *Crystal data* for **2**: $C_{45}H_{41}BClP_3Sn$, M = 839.64, monoclinic, space group $P2_1/c$, a = 12.099(4), b = 19.699(4), c = 17.215(6), β = 103.818(10)°, U = 3984(2) Å^3, Z = 4, D_c = 1.400 g cm^{-3}, T = 183(2) K, μ = 0.860 mm^{-1}, $wR2$ = 0.0992 (5698 independent reflections), $R1$ = 0.0408 [$I > 2\sigma(I)$]. CCDC 182/1450.

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