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Fusing Triphenylphosphine with Tetraphenylborate: Introducing the 9-Phosphatriptycene-10-phenylborate (PTB) Anion

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Abstract

In a fusion of two ubiquitous organometallic reagents, triphenylphosphine (PPh_3) and tetraphenylborate (BPh_4^-), the 9-phosphatriptycene-10-phenylborate (PTB) anion has been prepared for the first time. This borato species has been fully characterized by a suite of spectroscopic methods, and initial reactivity studies introduce it as a competent ligand for transition metals, including Co(II) and Fe(II).

Graphical abstract

Owing to low-cost, high availability, and ease of synthesis and handling, triphenylphosphine (PPh_3) and tetraphenylborate (BPh_4^-) have evolved to become prevailing reagents in the synthetic chemist's toolbox. Congruent with interest in developing zwitterionic organometallic complexes for catalysis,¹ including examples from our group featuring *P,B*- and *N,B*-containing ligands,² we envisioned a tethering strategy between these two partners in the form of a triptycene. Some years ago, we explored the use of conceptually related 3- and 4-substituted acyclic diphenylphosphino(tetraphenyl)borates as electron-releasing ligands for coordination to platinum-group metals, along with some preliminary C-C cross coupling investigations (Chart 1A).^{2a,b} It is noteworthy that a host of other phosphine-containing ligands incorporating group 13 elements have also been reported.³

Since the early report of parent 9-phosphatriptycene in 1974 by Bickelhaupt *et al.* (Chart 1B),⁴ several research groups have reported related geometrically constrained compounds

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Experimental details including ^1H , ^{31}P , ^{11}B , and ^{13}C NMR spectra for all complexes as well as crystallographic data for $[\mathbf{3}][\text{NEt}_4]$, $[\mathbf{3}][\text{ASN}]$, $[\mathbf{4}][\text{ASN}]$, $[\mathbf{5}][\text{NEt}_4]_2$, $[\mathbf{7}][\text{NEt}_4]_2$, $[\mathbf{8}][\text{NEt}_4][\text{Na}(\text{THF})_4(\text{NCMe})_2]$, $[\mathbf{9}][\text{NEt}_4]$, and $[\mathbf{10}][\text{NEt}_4]_2$. CCDC 1824471–1824478 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

containing group 14 or 15 elements, though the synthesis of anionic group 13 analogues has not been achieved.⁵ In this work, we present the formal joining of PPh₃ and BPh₄[−] in the form of the 9-phosphatriptycene-10-phenylborate anion. To fully characterize this phosphino(borate), several derivatives, including *cis*-dimethylplatinum(II) and *pentakis*(carbonyl)tungsten(0) PTB complexes, have been prepared. We also show that the PTB anion can be employed for the synthesis of paramagnetic, Co(II) and Fe(II) complexes, serving roles as both σ -donating ligand and halide abstracting equivalent.

The route used to prepare the 9-phosphatriptycene-10-phenylborate (PTB) anion [**3**][−] is shown in Scheme 1. Treatment of *tris*(*o*-bromophenyl)phosphine^{5a} with ^tBuLi followed by slow addition of PhBCl₂ at −78 °C and careful warming to room temperature furnishes *tetrakis*(tetrahydrofuran) lithium 9-phosphatriptycene-10-phenylborate, [**3**][Li(THF)₄] as a white solid in 64% yield after work-up. The countercation of [**3**][−] is straightforwardly tailored by treatment of a CH₃OH solution of [**3**][Li(THF)₄] with [Y]Br (Y = ASN; ASN = 5-azoniaspiro[4.4]nonane or NEt₄) giving [**3**][ASN] or [**3**][NEt₄] as white solids in 97 and 87% yield, respectively.

The ³¹P{¹H} NMR spectrum of [**3**][Li(THF)₄] (CD₃CN, 298 K) displays a singlet at δ = −43.7 ppm (d, ³J_{P-B} = 3.8 Hz), while ¹¹B{¹H} NMR spectroscopy provides a sharp resonance at δ = −8.75 ppm (d, ³J_{P-B} = 3.8 Hz); *c.f.* δ _B = −6.7 ppm for Li[BPh₄].⁶ Notably, this is a rare case where three-bond scalar coupling between phosphorus and boron (*I* = 3/2) is experimentally observed. Analogous NMR spectroscopic parameters are observed for [**3**][ASN] and [**3**][NEt₄] (see ESI) -all of which are significantly upfield-shifted compared to PPh₃ (δ _P = −3.1 ppm), but in the same range as **1** (δ _P = −64.8 ppm) and **2** (δ _P = −44.4 ppm). Additionally, the ⁷Li{¹H} NMR spectrum of [**3**][Li(THF)₄] provides a signal at δ _{Li} = −1.2 ppm.

Crystalline material of [**3**][Li(THF)₄] was obtained from a saturated THF solution at −35 °C, while crystals of [**3**][ASN] or [**3**][NEt₄] could be grown from a saturated CH₃OH solution at −35 °C. The crystal structure of [**3**][ASN] is shown in Scheme 1 and features a constrained phosphorus atom having an average <C-P-C bond angle of 96.5° *c.f.* 106.3° for PPh₃ (Table 1) and an average <C-B-C bond angle of 104.4°. The <C-P-C bond angle for [**3**][ASN] is the smallest reported among the known 9-phosphatriptycenes (<C-P-C = 98.0° for **1** and 99.3° for **2**; Table 1).

Having prepared PTBs [**3**][−], we next assessed phosphine s-character and σ -donating ability (Table 1 & Scheme 2). In agreement with incorporation of an insulated borate, the cyclic voltammogram of [**3**][NEt₄] shows an irreversible oxidative feature at 0.97 V that is cathodically-shifted compared to related phosphatriptycene **1** and PPh₃ (Figure 1A). Compound [**3**][−] was further evaluated based on the following characteristics: a) ¹J_{P,Se} = 746 Hz for the phosphine selenide, [**4**][ASN] (X-ray, Figure S30);⁷ b) ¹J_{Pt,C} = 597 Hz for the Pt(II) complex, *cis*-[Pt(CH₃)₂(PTB)₂][NEt₄]₂ ([**5**][NEt₄]₂; Figure 1B), and c) ν (CO) = 1943 cm^{−1} for the W(0) complex, [W(CO)₅(PTB)][Li(THF)₄] ([**6**][Li(THF)₄]). Despite having the smallest <C-P-C bond angle of the series, these data point toward [**3**][−] as having lower s-character and similar σ -donating ability when compared with **1** or **2**. Of note, oxidation of PTB to the phosphine selenide, [**4**][ASN], also results in increased pyramidalization at

phosphorus ($\angle(\text{C-P-C}) = 301.8^\circ$ (*c.f.* 289.4°)) and a decreased P(1)-B(1) distance of 2.911(5) Å (*c.f.* 3.020(2) Å) corresponding to a five-fold increase in $^3J_{\text{P-B}}$ to 19.3 Hz.

Protonation of $[\mathbf{3}][\text{NEt}_4]$ was also shown to be facile. Treatment of an MeCN solution of $[\mathbf{3}][\text{NEt}_4]$ with $[\text{H-OEt}_2][\text{BAR}^{\text{F}}_4]$ results in formation of the neutral zwitterion, PTB-H (**3-H**) along with $[\text{NEt}_4][\text{BAR}^{\text{F}}_4]$. Protonation is evidenced by ^{31}P NMR spectroscopy that shows a broad doublet at $\delta = -25.3$ ppm ($^1J_{\text{P-H}} = 512$ Hz), which collapses to a singlet on ^1H decoupling. Notably this value of $^1J_{\text{P-H}}$ is close to that observed for $[\text{H-PPh}_3]^+$ ($^1J_{\text{P-H}} = 510$ Hz) and lower than that observed for the $[\text{H-PH}_3]^+$ cation ($^1J_{\text{P-H}} = 548$ Hz), which is near ideally sp^3 -hybridized.⁸

Next, we studied the coordination chemistry and spectroscopic features of $[\mathbf{3}]^-$ with Co and Fe. Combination of two equiv. of $[\mathbf{3}][\text{NEt}_4]$ with CoBr_2 in CH_3CN at ambient temperature produced a dark turquoise solution (Scheme 3). Metalation of $[\mathbf{3}][\text{NEt}_4]$ was confirmed by ^1H NMR spectroscopy, which displayed paramagnetically shifted resonances, while no discernable signal was obtained by ^{31}P NMR spectroscopy (CD_3CN , 298 K). In an effort to provide material suitable for single crystal X-ray diffraction, cooling a CH_3CN solution of this reaction mixture to -35°C resulted in a color change from turquoise to forest green, while cooling a saturated THF solution caused no change in color, indicative of a solvent-dependent coordination equilibrium. This process was later studied by variable temperature UV-Visible spectroscopy (*vide infra*).

Ultimately, the identity of the constituent Co(II) species was obtained by layering the aforementioned CH_3CN solution with THF at -35°C , which gave three different crystal morphologies (ESI, Figure S26): i) thin blue sheets, ii) turquoise blocks, and iii) orange blocks (Figure 2). Analysis by single crystal X-ray diffraction confirmed the identity of each of these species to be: the *mono*(PTB) complex $[\text{Co}(\text{PTB})\text{Br}_3][\text{NEt}_4]_2$ (**[7]** $[\text{NEt}_4]_2$) and *bis*(PTB) complexes $[\text{Co}(\text{PTB})_2\text{Br}_2][\text{NEt}_4]_2$ (**[8]** $[\text{NEt}_4]_2$) and $[\text{Co}(\text{PTB})_2(\text{NCCH}_3)_2\text{Br}][\text{NEt}_4]$ (**[9]** $[\text{NEt}_4]$). The Co(1)-P(1) bond length for **[7]** $[\text{NEt}_4]_2$ [2.358(4) Å] and **[8]** $[\text{NEt}_4]_2$ [2.386(4)/2.383(5) Å] agree with those reported for $\text{Co}(\text{PPh}_3)_2\text{Br}_2$ [2.349(2) Å],⁹ while for the Co(II) zwitterion, **[9]** $[\text{NEt}_4]$, a shorter distance of 2.248(4) Å is noted. For the pseudo-tetrahedral complex **[8]** $[\text{NEt}_4]_2$, the angles, $\angle\text{Br}(1)\text{-Co}(1)\text{-Br}(2)$ ($117.54(9)^\circ$) and $\angle\text{P}(1)\text{-Co}(1)\text{-P}(2)$ ($121.1(2)^\circ$) are also in line with those reported for $\text{Co}(\text{PPh}_3)_2\text{Br}_2$ ($117.27(3)^\circ$ and $115.88(2)^\circ$). Finally, for the trigonal bipyramidal complex **[9]** $[\text{NEt}_4]$, the P(1)-Co(1)-P(2) bond angle (177.58°) is close to 180° , while the sum of angles in the equatorial plane is equal to 360° .

Probing the sample by optical spectroscopy allowed for the study of complex speciation in CH_3CN as a function of temperature. At 25°C , the UV-Vis spectrum showed the presence of several bands between 600 and 700 nm [617, 642, 668, 681, and 696 nm] (Figure 3A). Related absorptions have been documented for the PPh_3 analogues, $[\text{Co}(\text{PPh}_3)\text{Br}_3][\text{NEt}_4]$ and $\text{Co}(\text{PPh}_3)_2\text{Br}_2$.¹⁰ Cooling the sample to -40°C , however, gradually revealed the formation of a new species, exhibiting clear isosbestic behavior with growth of bands at 310 and 376 nm. We posit that these data result from a low-temperature metathesis equilibrium of **[8]** $[\text{NEt}_4]_2$ (turquoise) to give the bis(acetonitrile) adduct **[9]** $[\text{NEt}_4]$ (orange) and $[\text{NEt}_4]\text{Br}$; these species account for the forest green color observed at low temperature. This

result highlights the ability of $[3]^-$ to undergo metathesis with an M-X (X = halide) bond, providing an entryway into coordinatively unsaturated metal complexes that can react with L-type donor ligands (*e.g.*, NCMe).

A related set of Fe(II) PTB complexes were also obtained with coordination being substantiated by NMR spectroscopy (Scheme 3). Layering of a CH_3CN solution with THF and cooling to -35°C gave colorless blocks – one of which was analyzed by X-ray diffraction as $[\text{Fe}(\text{PTB})\text{Br}_3][\text{NEt}_4]_2$, $[10][\text{NEt}_4]_2$ (X-ray, Figure S32). The Fe(1)-P(1) bond length for $[10][\text{NEt}_4]_2$ [2.4320(6) Å] is similar to that noted for $[\text{Fe}(\text{PPh}_3)\text{Br}_3][\text{HPr}]$ (HPr = 1,3-bis(2,6-diisopropylphenyl)imidazolium) [2.463(2) Å] and is otherwise comparable to the Co derivative $[7][\text{NEt}_4]$.¹¹

The ^{57}Fe Mössbauer spectrum of a frozen CH_3CN solution revealed the presence of three Fe-containing species with parameters suggesting the presence of two four- and one higher-coordinate Fe(II) centers (Figure 3B).¹² For the two major species, isomer shifts of $\delta = 0.87$ and 0.79 mm/s, with quadrupole splittings of $E_Q = 2.34$ and 2.87 mm/s, respectively were observed. These doublets are assigned to the four-coordinate species $[\text{Fe}(\text{PTB})\text{Br}_3][\text{NEt}_4]_2$ (43%, $[10][\text{NEt}_4]_2$) and $[\text{Fe}(\text{PTB})_2\text{Br}_2][\text{NEt}_4]_2$ (47%, $[11][\text{NEt}_4]_2$). For comparison, values of $\delta = 0.86$ and 0.83 mm/s and $E_Q = 2.10$ and 2.71 mm/s were reported for $[\text{Fe}(\text{quinoline})\text{Br}_3][\text{NEt}_4]$ and $\text{Fe}(\text{quinoline})_2\text{Br}_2$.¹³ A third species, accounting for the remaining 10% of the overall fit, displayed an unusually large isomer shift, $\delta = 1.72$ mm/s with $E_Q = 2.52$ mm/s. We presume this species to be a higher-coordinate $\text{Fe}(\text{PTB})_x\text{Br}_y(\text{NCCH}_3)_z$ complex, such as $[\text{Fe}(\text{PTB})_2(\text{NCCH}_3)_2\text{Br}][\text{NEt}_4]$, akin to $[9][\text{NEt}_4]$. Given the low known isomer shift for $[\text{Fe}(\text{PET}_3)_2(\text{NCCH}_3)_4]^{2+}$ ($\delta = 0.37$ mm/s), it is unlikely that this doublet results from the neutral zwitterion, $\text{Fe}(\text{PTB})_2(\text{NCCH}_3)_4$.¹⁴

Inspired by the success of PPh_3 and BPh_4^- as reagents of broad utility, we have provided here the first synthesis of the 9-phosphatriptycene-10-phenylborate anion. The s-character and σ -donating capability of this ligand have been assessed, and preliminary forays into coordination chemistry with Co and Fe demonstrate that this anion can be used to advantage as both a ligand and halide-abstracting agent. Future work will focus on the small-molecule reactivity of these and other PTB-ligated transition metal complexes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

A) The CV for $[3]^-$ with the oxidative feature highlighted (using an internal Fc/Fc^+ reference). **B)** Mercury depiction of the solid-state molecular structure for $[5][NEt_4]_2$ (50% ellipsoid probability, hydrogens and counterions omitted for clarity).

Figure 2.

Mercury depiction of the solid-state molecular structure of the anions: [7]²⁻, [8]²⁻, and [9]¹⁻ (displacement ellipsoids are shown at the 50% probability, hydrogens and counterions omitted for clarity).

Figure 3.

A) Variable temperature UV-Visible absorbance data collected on a mixture of [7]²⁻, [8]²⁻, and [9]¹⁻ in CH₃CN. Inset shows expansion of 550 to 750 nm window and the frozen cuvette at -40 °C. Temperature increments are in 5 °C. **B)** Zero-field ⁵⁷Fe Mössbauer spectra of a mixture of [10]²⁻ (blue, 43%), [11]²⁻ (green, 47%), and an unknown species (yellow, 10%) as a frozen CH₃CN solution collected at 80 K.

Scheme 1.

Preparation of 9-phosphatriptycene-10-phenylborate and Mercury depiction of the solid-state molecular structure of **[3][ASN]** (displacement ellipsoids are shown at the 50% probability, hydrogens and ASN^+ counterion omitted for clarity). Selected bond lengths [$\text{\AA}$] and angles ($^{\circ}$). P(1)-C(1) 1.827(2), P(1)-C(3) 1.839(2), P(1)-C(5) 1.837(2), B(1)-C(2) 1.649(2), B(1)-C(4) 1.655(2), B(1)-C(6) 1.647(2), B(1)-P(1) 3.020(2), $\angle\text{C-P(1)-C}$ 96.5 (avg.), $\angle\text{C-B(1)-C}$ 104.4 (avg.), $\angle\text{C-P-C}$ 289.4.

Scheme 2. Assessing the s-character and σ -donating properties of **[3]⁻**.

Scheme 3.
Generation of Co(II) and Fe(II) PTB complexes

(A) *Related tetra(aryl)borate ligands prepared by the Peters group*

(B) *9-phosphatriptycene derivatives*

Chart 1.
 Representative borate ligands

Table 1

Characterizing the 9-phosphatriptycene-10-phenylborate (PTB) anion.

E_{ox}/V	Lone pair orbital ^c	$I_{\text{PSe}} \text{ (Hz)}$ Ar ₃ P–Se	$^1J_{\text{PtC}} \text{ (Hz)}$ <i>cis</i> -PtMe ₂ L ₂	$\nu(\text{CO}) \text{ (cm}^{-1}\text{)}$ W(CO) ₃ L	<C–P–C (°) by XRD ^b
PPh ₃	HOMO	736 ^d	616 ^d	1943 ^f	106.3
1	HMMO-5	828 ^d	--	1946 ^f	99.3
2	--	795 ^d	607 ^d	--	98.0
[3] [–]	HMMO-4	746 ^e	597 ^e	1943 ^g	96.5

^a Irreversible peak potential vs. Ag/Ag⁺ in CH₂Cl₂ with 0.1 M [N^{*n*}Bu₄][ClO₄].

^b Irreversible peak potential vs. Fc/Fc⁺ in CH₂Cl₂ with 0.1 M [N^{*n*}Bu₄][ClO₄] for NEt₄⁺ counterion.

^c Single-point calculations and geometry optimization were performed using DFT: B3LYP/6-311G(d) for P; and 6-31G(d) for all other atoms.

^d in CDCl₃.

^e in MeCN-d₃ for ASN⁺ counterion.

^f in hexane.

^g solid-state for Li(THF)₄⁺ counterion.

^h Average of three bonds.

Note: Data for PPh₃ and **1** are sourced from ref. 5c; data for **2** is sourced from ref. 5a.