Chapter 2: A homoleptic phosphine adduct of Tl(I)

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Credit should be given to the following people for their work that appears in this chapter. I. R. Shapiro first synthesized and structurally characterized [PhBP$_3$]Tl. J. C. Peters wrote much of the following text, that also appears in the above cited work. J. C. Thomas helped with the NMR characterization. My specific contributions included the synthesis as it appears in the experimental section and NMR characterization.

2.1 Introduction

Although hard donor ligands are known to stabilize simple molecular complexes of thallium-(I) and -(III),[1] well-defined examples of thallium supported by correspondingly soft donor ligands are relatively rare.[2] With respect to phosphine donors specifically, only two phosphine adducts have been structurally characterized: both of thallium(III).[3] To our knowledge, there are no well-characterized phosphine adducts for thallium(I). By comparison, there are numerous structurally characterized examples of thallium(I) supported by hard N-donor ligands, including the tripodal ligands [Tp] ([Tp] = tris(pyrazolyl)borate) and Me_3-tacn (tacn = triazacyclononane).[4,5]

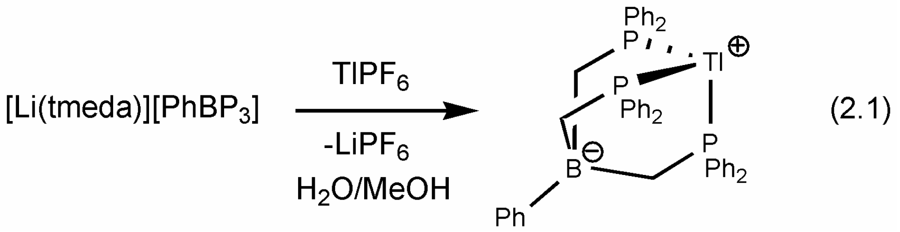
We set out to prepare a thallium adduct of the tris(phosphino)borate ligand, $[PhBP_3]$ ($[PhBP_3] = [PhB(CH_2PPh_2)_3]^-$),[6] for two reasons. We were surprised by the dearth of well-defined phosphine complexes of thallium and hoped that the anionic $[PhBP_3]$ ligand might support and stabilize a thallium(I) species. Additionally, the previously reported lithium salt of this ligand, $[Li(tmeda)][PhBP_3]$ (tmeda = tetramethylethylenediamine), is not a reagent of general synthetic utility for clean delivery of the $[PhBP_3]$ ligand to transition metals. A versatile thallium reagent of this ligand therefore seems highly desirable. Herein we report the isolation and structural characterization of a homoleptic phosphine adduct of thallium(I) stabilized by the $[PhBP_3]$ ligand.

2.2 Results and discussion

2.2.1 Synthesis and ^{31}P NMR characterization of $[PhBP_3]Tl$

It was convenient to prepare the target complex, $[PhBP_3]Tl$, **2.1**, by transmetallation of lithium for thallium upon addition of $TlPF_6$ to a methanolic solution of

[Li(tmeda)][PhBP$_3$] (Eq. 2.1). The reaction occurred rapidly and cleanly at ambient temperature as indicated by ^{31}P NMR spectroscopy. Following work-up, the light yellow product was isolated in reasonable yield (65%). It is worth noting that the entire reaction sequence can be executed in air without decomposition. Furthermore, the thallium salt itself is stable to moisture and oxygen for an extended period, both in solution and in the solid state.



(2.1)

Examination of the ^{31}P NMR spectrum of **2.1** (C_6D_6) showed two resonances (1 1 ratio) separated by more than 40 ppm, each resonance bearing a resolvable shoulder. This spectrum represents two separate doublets from a very strong $^{1}J_{\mathrm{TlP}}$ coupling interaction (5214, 5168 Hz) for each of the naturally occurring $S = ½$ thallium isotopes (^{205}Tl (70.5%), ^{203}Tl (29.5%), respectively). Notably, these coupling values are significantly larger than those reported for phosphine complexes of thallium(III) (approximately 1500 Hz).

2.2.2 Solid-state structure of [PhBP$_3$]Tl

In order to corroborate the NMR assignment consistent with a structure resulting from symmetric, tridentate binding of the [PhBP$_3$] ligand to the thallium cation, we sought independent structural confirmation. Slow evaporation of a benzene solution of **2.1** afforded crystals suitable for an X-ray diffraction study. A structural representation of complex **2.1** is shown in Figure 2.1 (top view, 50% ellipsoids). The structure confirms our assignment of **2.1** as a homoleptic phosphine adduct of thallium. The anionic [PhBP$_3$]

ligand coordinates the thallium cation in the expected tridentate conformation (top view). The large ionic radius of the thallium(I) ion forces it to sit well above the basal plane (2.074 Å), defined by its three phosphine donor atoms. This structural feature affords a significant separation between the thallium ion and the molecule's anionic borate counteranion (Tl1–B distance = 4.253 Å). It is interesting to compare the intramolecular Tl–B distance found in a host of structurally characterized thallium(I) adducts of variously substituted [Tp] ligands. The Tl–B distance is much longer in **2.1** than in all related [Tp] adducts of thallium(I) (range = 3.46–3.90 Å) and is approximately 0.6 Å longer than the mean distance (3.65 Å) for the related [Tp] systems. The pronounced Tl–B distance in **2.1**, in conjunction with the absence of simple resonance contributors that delocalize the anionic charge from the borate counteranion to the Tl center, suggests that **2.1** may be represented as a simple zwitterion (Eq. 2.1). Although equivalent phosphorus nuclei are observed by ^{31}P NMR spectroscopy, the three phosphine donors are not symmetrically bound in the solid state. The Tl1–P3 distance, 2.880 Å, is appreciably shorter than the Tl1–P1 and Tl1–P2 distances (2.953 and 2.934 Å, respectively).

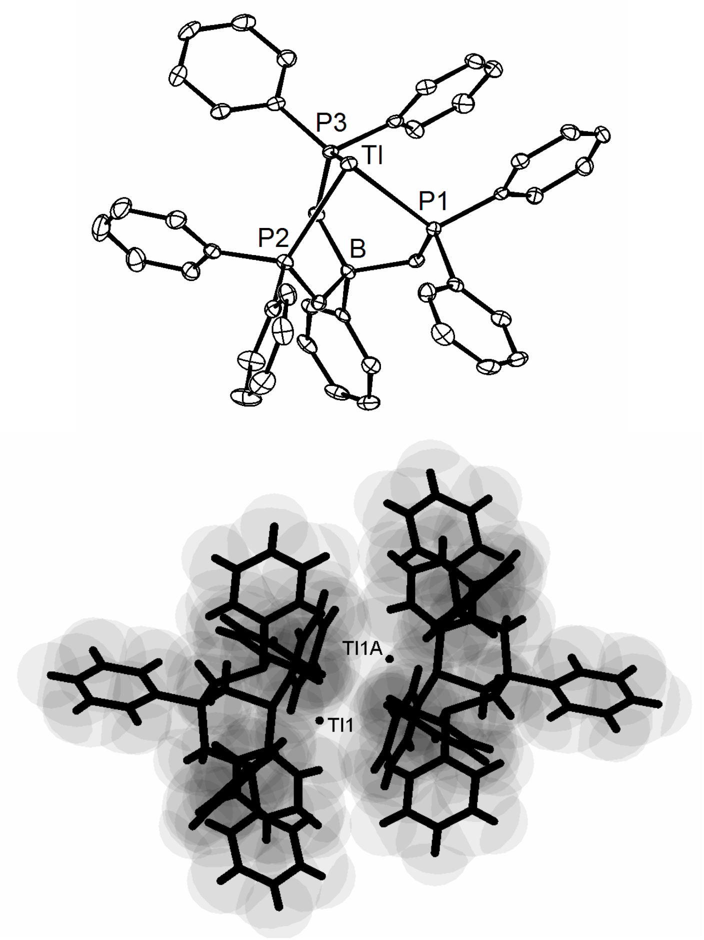


Figure 2.1. Displacement ellipsoid (50%) representation of [PhBP$_3$]Tl, **2.1**. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°): Tl1–P1 2.878, Tl1–P2 2.953, Tl1–P3 2.932, Tl1–B 4.254; P1–Tl1–P2 70.82, P1–Tl1–P3 76.78, and P2–Tl1–P3 77.46. The bottom view shows a transparent space-filling model of **2.1** depicted as a dimer [Tl1–Tl1A = 3.5652(2) Å]. The [PhBP$_3$] ligands are highlighted as bold stick figures, and the positions of the Tl nuclei are labeled.

The bottom view of Figure 2.1 shows a transparent space-filling model of **2.1** and its neighboring thallium adduct. The asymmetric unit of **2.1** contains a single thallium complex that is related to the neighboring thallium atom, Tl1A, by a center of symmetry. The distance between these thallium atoms is 3.5652(2) Å, which is considerably longer than twice the covalent radius (1.64 Å) of thallium, and is consistent with a thallium-thallium dimer resulting from weak interactions.

2.2.3 Evidence for a monomer of [PhBP$_3$]Tl in solution

Despite the solid state suggestion that **2.1** is a weak dimer in the solid state, the dimeric structure does not exist in solution. Direct evidence for assigning **2.1** as a monomer in solution is as follows: the ^{31}P NMR spectrum of **2.1** shows only $^{1}J_{\mathrm{TlP}}$ coupling. We would expect to observe a weaker $^{2}J_{\mathrm{TlP}}$ coupling to the neighboring Tl nucleus if the dimeric structure exists in solution. To buttress this argument, the ^{205}Tl NMR spectrum of **2.1** was obtained in C_6D_6:[7] a single resonance (2809 ppm) split into a quartet by the three equivalent phosphine donors was observed (Figure 2.2). There was no evidence for $^{1}J_{(205)\mathrm{Tl}(203)\mathrm{Tl}}$ coupling, ruling out Tl–Tl interactions in benzene solution. Finally, **2.1** was analyzed by electrospray mass spectroscopy (ESI/MS). The parent ion observed in positive mode (m/z = 891) was consistent with the protonated monomeric form of **2.1**. Thus, our data imply a monomeric formulation of **2.1** in solution.[8]

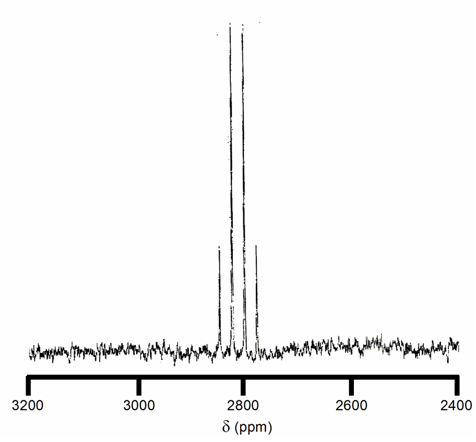


Figure 2.2. ^{205}Tl NMR for [PhBP$_3$]Tl (**2.1**) in C_6D_6.

2.2.4 Comparison to tris(thioether)borate

Regarding other soft, tripodal donor ligands supporting thallium(I), a good comparison to complex **2.1** comes from Riordan and co-workers, who recently reported a thallium(I) adduct of their second generation, anionic tris(thioether)borate ligand, [Tt$^{tert\text{-}butyl}$] ([Tt$^{tert\text{-}butyl}$] = [PhB(CH$_2$S^{t}Bu)$_3$]$^-$).[9] Notably, [Tt$^{tert\text{-}butyl}$] does not enforce a simple 1:1 complex between thallium(I) and the tris(thioether) ligand in the solid state. This is despite the fact that the [Tt$^{tert\text{-}butyl}$]Tl reagent enables access to monomeric, pseudotetrahedral geometries for simple divalent nickel and cobalt chlorides.

2.3 Conclusion

In summary, we have isolated and structurally characterized a rare example of a simple phosphine adduct of thallium(I). It has been found that complex **2.1** displays a signature $^1J_{\mathrm{TlP}}$ coupling constant of 5214 Hz. In addition to exposing new possibilities for thallium coordination chemistry within a phosphine donor sphere, complex **2.1** promises to be an important reagent for delivering the relatively unexplored [PhBP$_3$] ligand to transition metals.

2.4 Experimental section

2.4.1 General considerations

All manipulations were carried out using standard Schlenk or glovebox techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thorough sparging with N$_2$ gas, followed by passage through an activated alumina column. Diethyl ether, tetrahydrofuran, petroleum ether, benzene, and toluene were periodically tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran to confirm that oxygen and moisture had been effectively removed. Elemental analyses were performed by Desert Analytics, Tucson, AZ. A Varian Mercury-300 NMR spectrometer, a Varian Inova-500 NMR spectrometer, or a Joel 400 MHz was used to record ^{1}H, ^{13}C, ^{31}P, ^{11}B, and ^{19}F NMR spectra at ambient temperature. ^{1}H and ^{13}C chemical shifts were referenced to residual solvent. ^{31}P NMR chemical shifts are referenced to an external standard of H_3PO_4 with the ^{31}P signal being set at 0 ppm. ^{11}B NMR chemical shifts are referenced to an external standard of neat $BF_3{\cdot}Et_2O$ with the ^{11}B signal being set at 0 ppm. ^{19}F NMR chemical shifts are referenced to an external standard of neat hexafluorobenzene with the ^{19}F signal being set at -163 ppm. Deuterated toluene, benzene, and tetrahydrofuran were purchased from Cambridge Isotope Laboratories, Inc. and were degassed and dried over activated 3 Å molecular sieves prior to use. MS data were obtained by injection of a solution onto a Hewlett-Packard 1100MSD mass spectrometer (ESI/MS) or an Agilent 5973 mass selective detector (GC/MS). X-ray diffraction studies were carried out in the Beckman Institute Crystallographic Facility on a Bruker Smart 1000 CCD diffractometer.

2.4.2 Starting materials and reagents

$[PhBP_3][Li(tmeda)]$ and $Ph_2PCH_2Li(tmeda)$[10] were prepared by literature methods. $PhBCl_2$ and $TlPF_6$ were purchased from commercial vendors and used without any further purification.

2.4.3 Synthesis of compounds

Synthesis of $[PhBP_3]Tl$, 2.1. This synthesis can be performed outside of a glovebox. Solid $[PhBP_3][Li(tmeda)]$ (7.1 g, 8.6 mmol) was suspended in methanol (60 mL). To this stirring suspension was added an aqueous solution (30 mL) of $TlPF_6$ (3.00 g, 8.6 mmol) over a period of 5 min. A cloudy white suspension resulted, which was stirred for an additional 5 min, followed by extraction with dichloromethane (2 × 150 mL). Drying the organic extract in vacuo afforded a light yellow powder that was subsequently washed with hexanes and Et_2O (40 mL each). The remaining powder was extracted into benzene, stirred over $MgSO_4$, and dried thoroughly in vacuo to afford the thallium adduct **2.1** as a fine yellow powder (5.00 g, 65%). ^{1}H NMR (C_6D_6, 300 MHz, 25 °C): δ 8.13 (d, *J* = 6.6 Hz, 2H), 7.67 (m, *J* = 7.5 Hz, 2H), 7.42 (tt, *J* = 6.6, 1.2 Hz, 1H), 7.18–7.11 (m, 12H), 6.80–6.77 (m, 18H), 1.96 (br m, 6H). ^{31}P NMR (C_6D_6, 121.4 MHz, 25 °C): δ 21.6 [d, $^1J_{\mathrm{TlP}}$ = 5214 Hz for ^{205}Tl (70.5% abundance), $^1J_{\mathrm{TlP}}$ = 5168 Hz for ^{203}Tl (29.5% abundance)]. ^{205}Tl NMR (C_6D_6, 231.31 MHz, 25 °C): δ 2810 (q, $^1J_{\mathrm{TlP}}$ = 5204 ± 116 Hz). ^{13}C NMR (C_6D_6, 125.7 MHz, 25 °C): δ 139.8, 132.5, 128.8–129.1 (overlapping resonances), 124.6, 17.0 (br). ^{11}B NMR (C_6D_6, 128.3 MHz, 25 °C): δ -10.96. ESI/MS (m/z): 891 (**2.1** + H^+). Anal. Calcd for $C_{47}H_{48}BP_3Tl$: C, 60.73; H, 4.64. Found: C, 61.75; H, 4.76%.

Alternative synthesis of [$PhBP_3$][Li(tmeda)]. The lithiophosphine reagent Ph_2PCH_2Li(tmeda) (12.55 g, 0.0390 mol) is added to a 250 mL filter flask and dissolved in 90 mL of toluene. This solution is stirred until the reagent is completely dissolved. The borane $PhBCl_2$ (2.00 g, 0.0126 mol) is diluted in 10 mL of toluene and added dropwise to the flask over 20 min. The reaction is allowed to continue for 90 min. The flask is then placed under dynamic vacuum to remove toluene. The vacuum is released as soon as precipitate starts to form (approximately 20 min). The filter flask is then stored at -35 °C for 16 h to achieve full precipitation of product. The solid precipitate is collected on a medium frit and washed with petroleum ether (2 x 20 mL). The white powder is dried and is spectroscopically pure (8.46 g, 83% yield).

Alternative synthesis of [PhBP$_3$]Tl, 2.1. [PhBP$_3$][Li(tmeda)] (5.66 g, 0.00700 mol) is dissolved in a 250 mL Erlenmeyer flask in 120 mL of dried and degassed ethanol. The reagent is stirred until a homogenous solution is obtained. A THF (10 mL) solution of TlPF$_6$ (2.44 g, 0.00700 mol) is prepared, and this is added to the stirring ethanol solution over 10 min. The reaction is stirred for an additional 30 min as the product crashes out of solution as a fine light yellow powder. The product is collected on a medium frit and washed with petroleum ether (2 x 20 mL). The product is dried and is spectroscopically pure (4.90 g, 78% yield).

2.4.4 X-ray experimental information

A crystal of **2.1** was mounted on a glass fiber with Paratone-N oil. Crystallographic data was 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). All structural representations were produced using the Diamond software program.

X-ray structure analysis for **2.1**: Data for $C_{45}H_{41}BP_3Tl$, pale yellow rhombohedral plate, formula weight (g mol^{-1}) = 889.87, T (°C) = -175, monoclinic space group $P2_1/n$, λ (Å) = 0.71073, a = 13.7449(7) Å, b = 13.5812(7) Å, c = 20.5487(10) Å, β = 94.536(1)°, V = 3823.9(3) Å^3, Z = 4, D$_{calcd}$ (g cm^{-3})= 1.430, μ (cm^{-1}) = 43.81 R_1 = 0.0221 [$I > 2\sigma(I)$], wR_2 = 0.0381 [$I > 2\sigma(I)$] GOF = 1.308. CCDC reference number 162229.

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7) Dr. Todd Alam from Sandia National Laboratory is acknowledged for obtaining the ^{205}Tl NMR spectrum of [PhBP$_3$]Tl (**2.1**).

8) Attempts to obtain a solution molecular weight estimate for [PhBP$_3$]Tl (**2.1**) by the Signer method have thus far been inconclusive due to its tendency to precipitate from solution on prolonged standing.

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