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A homoleptic phosphine adduct of Tl(I)†

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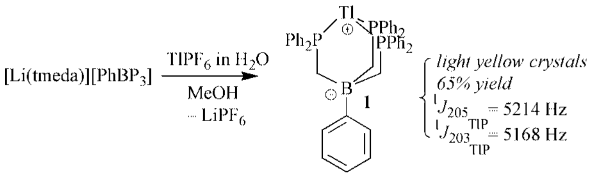
A homoleptic phosphine adduct of thallium(I) supported by a tris(phosphino)borate ligand has been isolated and structurally characterized.

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] Regarding 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]

Our group is developing transition metal chemistry utilizing anionic tris- and bis-(phosphino)borate ligands.[6] We have set out to prepare a thallium adduct of the tris(phosphino)borate ligand, [$PhBP_3$] ($PhBP_3$ = $PhB(CH_2PPh_2)_3$),[7] 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.

It was convenient to prepare the target complex, [$PhBP_3$]Tl, **1**, by transmetallation of lithium for thallium upon addition of $TlPF_6$ to a methanolic solution of [Li(tmeda)][$PhBP_3$] (Scheme 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.

Examination of the ^{31}P NMR spectrum of **1** (C_6D_6) showed two resonances (1 : 1 ratio) separated by more than 40 ppm, each resonance bearing a resolvable shoulder (ESI†). This spectrum represents two separate doublets from a very strong $^1J_{TlP}$ coupling interaction (5214, 5168 Hz) for each of the naturally occurring spin 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).[3]



Scheme 1

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 **1** afforded crystals suitable for an X-ray diffraction study. A structural representation of complex **1** is shown in Fig. 1 (top view, 50% ellipsoids).[8] The structure confirms our assignment of **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 counter-anion (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 **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.[4] The pronounced Tl–B distance in **1**, in conjunction with the absence of simple resonance contributors

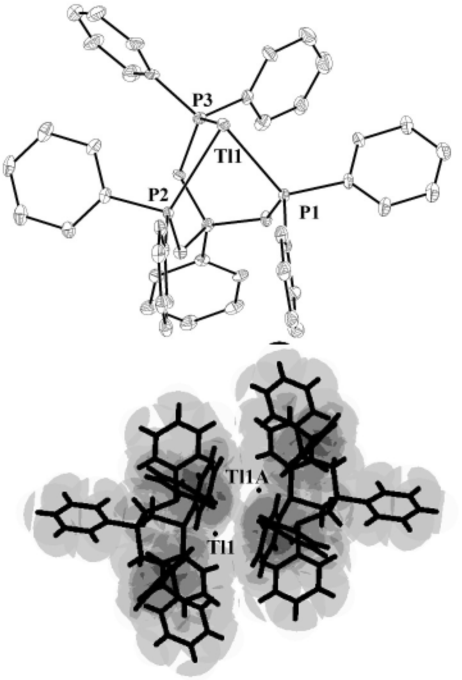


Fig. 1 Displacement ellipsoid (50%) representation of Tl[$PhBP_3$], **1**. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°): Tl1–P1 2.878, Tl1–P2 2.953, Tl1–P3 2.932, Tl1–B 4.254; P1–Tl1–P2 70.82, P1–Tl1–P3 76.78, P2–Tl1–P3 77.46. The bottom view shows a transparent space-filling model of **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 labelled.

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† Electronic supplementary information (ESI) available: ^{31}P and ^{205}Tl NMR spectra of [$PhBP_3$]Tl in C_6D_6. See http://www.rsc.org/suppdata/cc/b1/b104447h/

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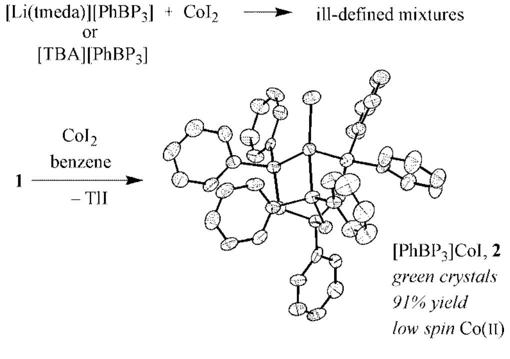
that delocalize the anionic charge from the borate counter-anion to the Tl center, suggests that **1** may be represented as a simple zwitterion (Scheme 1). Although equivalent phosphorus nuclei are observed by ^{31}P NMR spectroscopy, the three phosphine donors are not symmetrically bound in the solid 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).

The bottom view of Fig. 1 shows a transparent space-filling model of **1** and its neighboring thallium adduct. The asymmetric unit of **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. This dimeric structure does not exist in solution. Direct evidence for assigning **1** as a monomer in solution is as follows: the ^{31}P NMR spectrum of **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 **1** was obtained in C_6D_6:[9] a single resonance (2809 ppm) split into a quartet by the three equivalent phosphine donors was observed (ESI†). There was no evidence for $^{1}J_{(205)\mathrm{Tl}(203)\mathrm{Tl}}$ coupling, ruling out Tl–Tl interactions in benzene solution. Finally, **1** was analyzed by electrospray mass spectroscopy (ESI/MS). The parent ion observed in positive mode (891) was consistent with the protonated monomeric form of **1**. Thus, our data imply a monomeric formulation of **1** in solution,[10] consistent with its readiness to undergo thallium loss by transmetallation chemistry (*vide infra*).

Regarding other soft, tripodal donor ligands supporting thallium(I), a good comparison to complex **1** comes from Riordan and coworkers, who recently reported a thallium(I) adduct of their second generation, anionic tris(thioether)borate ligand, $[\mathrm{PhTt}^{t\text{-Bu}}]$.[11] Notably, $[\mathrm{PhTt}^{t\text{-Bu}}]$ 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 $\mathrm{Tl}[\mathrm{PhTt}^{t\text{-Bu}}]$ reagent enables access to monomeric, pseudo-tetrahedral geometries for simple divalent nickel and cobalt chlorides.

To highlight the synthetic utility of the thallium reagent **1**, we examined its reactivity with CoI_2. The previously prepared Li(tmeda) adduct of $[PhBP_3]$, in addition to its related ammonium salt $[^{n}Bu_4N][PhBP_3]$, afforded ill-defined mixtures of paramagnetic products on attempted metathesis with CoI_2 in benzene and other solvents.[6] By contrast, the softer and presumably less-reducing thallium reagent **1** reacted cleanly with CoI_2 in benzene to afford the bright green, low spin cobalt iodide complex $[PhBP_3]CoI$, **2**, in good yield (91%).§ Complex **2** was structurally characterized and adopts the expected pseudo-tetrahedral geometry in the solid state (Scheme 2).[8]

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 **1** displays a signature $^{1}J_{\mathrm{TlP}}$ coupling constant of 5214 Hz. In addition to exposing new possibilities for thallium coordination chemistry within a phosphine donor sphere, complex **1** promises to be an important reagent for delivering the relatively unexplored $[PhBP_3]$ ligand to transition metals.



Scheme 2

We thank the Dreyfus Foundation, Caltech, and the NSF for financial support of this work.

Notes and references

‡ *Synthesis* of $[PhBP_3]Tl$, **1**: solid $[Li(tmeda)][PhBP_3]$ (7.1 g, 8.6 mmol), generated as previously described,[7] 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 **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, $^{1}J_{\mathrm{TlP}}$ = 5214 Hz for ^{205}Tl (70.5% abundance), $^{1}J_{\mathrm{TlP}}$ = 5168 Hz for ^{203}Tl (29.5% abundance)]. ^{205}Tl NMR (C_6D_6, 231.31 MHz, 25 °C): δ 2810 (q, $^{1}J_{\mathrm{TlP}}$ = 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. Anal. Calc. for $C_{47}H_{48}BP_3Tl$: C, 60.73; H, 4.64. Found: C, 61.75; H, 4.76%.

§ *Synthesis* of $[PhBP_3]CoI$, **2**: a benzene solution (50 mL) of the thallium reagent **1** (0.356 g, 0.40 mmol) was added to a stirring suspension of CoI_2 (0.250 g, 0.80 mmol) in benzene (20 mL). After stirring at ambient temperature for 24 h, the resulting green solution was filtered through Celite, concentrated *in vacuo* (50%) and filtered through Celite once again. Vapor diffusion of petroleum ether into the resulting green filtrate afforded a good yield of the desired crystalline product (0.317 g, 91.1% yield). ^{1}H NMR (C_6D_6, 300 MHz, 25 °C): δ 22.2 (br s), 15.8 (s), 10.8 (s), 7.7 (s), 7.5 (s), 4.3 (br s), 2.2 (s), −8.5 (s). IR (ν/cm^{-1}): 1433 (s), 1091 (b), 739 (s). μ_{eff} = 2.60 μ_B (SQUID). UV–vis (C_6H_6): 638 nm (ε = 1112), 738 nm (ε = 627). Anal. Calc. for $C_{45}H_{41}BCoIP_3$: C, 62.03; H, 4.74. Found: C, 61.76; H, 4.75%.

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8 *Crystal data* for **1**: $C_{45}H_{41}BP_3Tl$, M = 889.87, pale yellow rhombohedral plate, T = 98 K, monoclinic, space group $P2_1/n$, a = 13.7449(7), b = 13.5812(7), c = 20.5487(10) Å, β = 94.536(1)°, V = 3823.9(3) Å^3, Z = 4, R_1 = 0.0221 [$I > 2\sigma(I)$], GOF = 1.308. For **2**: ($C_{45}H_{41}BCoIP_3$), M = 910.38, dark green blade, T = 98 K, monoclinic, space group $P2_1/c$, a = 22.5443(17), b = 12.7044(9), c = 29.526(2) Å, β = 90.230(2)°, V = 8456.6(11) Å^3, Z = 8, R_1 = 0.0476 [$I > 2\sigma(I)$], GOF = 1.137. CCDC reference numbers 160107 and 162229. See http://www.rsc.org/suppdata/cc/b1/b104447h/ for crystallographic data in CIF or other electronic format.

9 Dr Todd Alam from Sandia National Laboratory is acknowledged for obtaining the ^{205}Tl NMR spectrum of **1**.

10 Attempts to obtain a solution molecular weight estimate for **1** by the Signer method have thus far been inconclusive due its tendency to precipitate from solution on prolonged standing.

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