Coordination of Pnictogenylboranes Towards Tl(I) Salts and a Tl- Mediated P—P Coupling

Robert Szlosek[+],[a] Matthias T. Ackermann[+],[a] Christian Marquardt,[a] Michael Seidl,[a] Alexey Y. Timoshkin,[b] and Manfred Scheer*[a]

Dedicated to Professor Sjoerd Harder on the occasion of his 60th birthday.

Abstract: The coordination chemistry of only Lewis-base (LB)-stabilized pnictogenylboranes $EH_2BH_2 \cdot NMe_3$ (E = P, As) towards Tl(I) salts has been studied. The reaction of $Tl[BAr^{Cl}]$ ($BAr^{Cl} = [B(3,5-C_6H_3Cl_2)_4]^-$) with the corresponding pnictogenylborane results in the formation of $[Tl(EH_2BH_2 \cdot NMe_3)][BAr^{Cl}]$ (**1a**: E = P; **1b**: E = As). Whereas the Tl ion in **1a/b** is monocoordinated, the exchange of the weakly coordinating anion (WCA) in the Tl(I) salt leads to the formation of a trigonal pyramidal coordination mode at the Tl atom by coordination of three equivalents of $EH_2BH_2 \cdot NMe_3$ in [Tl- $(EH_2BH_2 \cdot NMe_3)_3][WCA]$ (**2a**: E = P, WCA = TEF^{Cl}; **2b**: E = As, WCA = TEF) (TEF = $[Al\{OC(CF_3)_3\}_4]^-$, $TEF^{Cl} = [Al\{(OC-(CF_3)_2(CCl_3)\}_4]^-$). Furthermore, by using two equivalents of $PH_2BH_2 \cdot NMe_3$, a Tl(I)-mediated P—P coupling takes place in CH_2Cl_2 as solvent resulting in $[Me_3N \cdot BH_2PH_2PHBH_2 \cdot NMe_3][WCA]$ (WCA = TEF, **3a**; BAr^{Cl}, **3b**; TEF^{Cl}, **3c**). In contrast, for the arsenic derivatives **1b** and **2b**, no coupling reaction is observed. The underlying chemical processes are elucidated by quantum chemical computations.

Introduction

The very weak interactions of weakly coordinating anions (WCAs) with their corresponding cations allows to study the pseudo gas phase coordination chemistry of naked cations in the condensed phase, such as monocationic group 13 elements.[1] The first structurally characterized Tl(I)-arene complex was reported in 1985 by Schmidbauer and coworkers.[2] Following this discovery, Tl(I) coordination chemistry received little attention for almost 20 years during which rarely new developments were reported. The years after 2000 marked a turning point in this field of chemistry, as several new Tl(I) complexes were described by different groups. In 2005, Power and coworkers reported on $Tl_2[Ar_2P_4]$ complexes resulting from the reaction between P_4 and $[TlAr_2]$ (Ar = 2,6-

diisopropylphenyl).[3] Bochmann and coworkers reported on the first examples of Tl(I)-arene and Tl(I)-diethylether complexes in which no predominant bonding between the employed WCA $([H_2N-B(C_6F_5)_3]^-)$ and the complex cations $[Tl(arene)_n]^+$ and $[Tl(Et_2O)_4]^+$, respectively, exists.[4] Those missing interactions simplify investigations on the coordination chemistry of the Tl^+ ion. Additionally, the groups of Mindiola and Ozerov prepared a PNP pincer complex of Tl (Figure 1, **I**) by reaction of Li(PNP) with Tl(OTf).[5] Simultaneously, our group was able to report the first coordination compounds composed of organometallic polyphosphorus (P_n) complexes and Tl(I) (Figure 1, **II**).[6] Previous results have already demonstrated that organometallic P_n ligand complexes represent excellent building blocks for supramolecular assemblies.[7] Subsequently, by using the WCA

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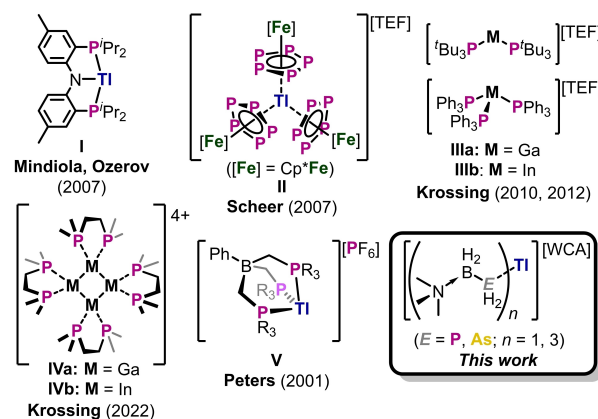**Figure 1.** Examples of phosphorus-based coordination compounds with low-valent group 13 salts of weakly coordinating anions.

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$[Al\{OC(CF_3)_3\}_4]^-$ (TEF),[8] our group was able to expand the coordination chemistry of P_n ligand complexes from monovalent transition metals (Cu, Ag) to monovalent group 13 metals (Ga, In, Tl).[9] Hereby, several coordination compounds as well as one-dimensional coordination polymers have been obtained.

Moreover, for the first time, Krossing and coworkers introduced the synthesis of univalent gallium and indium phosphine complexes $[M(PR_3)_n]^+$ (M = Ga, In, Tl; Figure 1: **IIIa**, **IIIb**).[10,11] The obtained complexes reveal a trigonal-pyramidal coordination at the group 13 metal atom in the solid state for PPh₃, while the increased steric bulk of P^{t}Bu₃ leads to carbene-analogous bis-phosphine complexes. Very recently, Krossing and coworkers also reported on bis(dimethylphosphino)ethane-stabilized indium and gallium tetracationic salts (Figure 1, **IVa**, **IVb**).[12]

In contrast, no monovalent thallium phosphine complexes have been reported so far. Given the fact that Tl(I) can be considered a rather soft metal, it seems surprising that the number of Tl(I) phosphine adducts is very limited, despite phosphines being very suitable ligands in principle. The first structurally characterized homoleptic phosphine adduct of Tl(I) supported by a tris(phosphino)borate was reported in 2001 by Peters and Botley (Figure 1, **V**).[13] Since then, hardly any new Tl(I) phosphine adducts have been published to our knowledge.
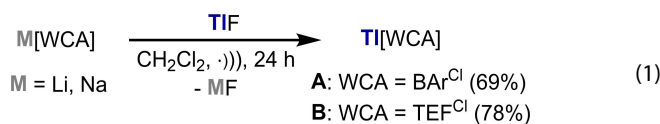
Our group has an interest in the synthesis and reactivity of only LB-stabilized 13/15 monomers such as pnictogenylboranes $EH_2BH_2 \cdot NMe_3$ (E = P, As),[14,15] which are excellent building blocks for the formation of group 13/15 oligomeric and polymeric compounds.[16] In addition, pnictogenylboranes turned out to be excellent donors for transition metal and main group Lewis-acids.[14,15,17–20] While cluster formation was observed for reactions with Cu(I) complexes,[18,20] coordination towards Au(I) centers afforded complexes with aurophilic interactions acting as blue-green light emitters.[19] The reaction of phosphanylborane with the early transition metal compound $[Cp_2Ti(btmsa)]$ (btmsa = bis(trimethylsilyl)acetylene) results in dehydrocoupling leading to oligomeric chains stabilized in the coordination sphere of titanium.[21] Therefore, the question arises whether coordination complexes of the main group element Tl(I) with pnictogenylboranes including unknown monocoordinated complexes are achievable and, if so, whether subsequent reactions will occur.

Herein, we report on the synthesis of new Tl(I) salts, the first pnictogenylborane Tl(I) coordination compounds and an unprecedented Tl(I)-mediated P–P coupling. Moreover, the synthesis of novel Tl[WCA] salts and an improved synthetic route of NMe₃-stabilized parent pnictogenylboranes are presented.

Results and Discussion

To start off our investigations, we evaluated suitable Tl[WCA] salts in the literature. Tl[TEF][22] synthesized earlier by Krossing and coworkers was considered to be an appropriate reagent for our purposes. However, we decided to introduce a larger variety in the substrate scope by having slightly more differences in

the steric and the electronic nature of the used WCA. Thus, we prepared Tl[BAr^{Cl}] (BAr^{Cl} = $[B(3,5-C_6H_3Cl_2)_4]^-$) and Tl[TEF^{Cl}] (TEF^{Cl} = $[Al\{(OC(CF_3)_2(CCl_3)\}_4]^-$) by sonication of a suspension of Na[BAr^{Cl}] or Li[TEF^{Cl}] with TlF in CH_2Cl_2 for 24 h [Eq. (1)]. After subsequent filtration of NaF/LiF, the Tl(I) salts can be isolated as microcrystalline powders and recrystallized for improved purity. Both compounds are obtained as colorless solids in good yields that can be stored under an inert atmosphere for months.

$$M[WCA] \xrightarrow[\substack{CH_2Cl_2,\ \cdot))),\ 24\ h \\ -\ MF}]{TlF} Tl[WCA] \quad (1)$$

M = Li, Na

A: WCA = BAr^{Cl} (69%)
B: WCA = TEF^{Cl} (78%)

Tl[BAr^{Cl}] (**A**) shows a sharp singlet in the $^{11}B\{^1H\}$ NMR spectrum at -6.39 ppm (CD₃CN) and Tl[TEF^{Cl}] (**B**) a sharp singlet in the $^{19}F\{^1H\}$ NMR spectrum at -68.6 ppm (CD₂Cl₂). **A** and **B** crystallize from CH_2Cl_2/n-hexane as colorless plates and blocks in the space groups $P2_1/n$ and $Pbcn$, respectively, and the molecular structures in the solid state were elucidated by single crystal X-ray diffraction (Figure 2). The asymmetric units show Tl$^+$ loosely coordinated to their respective WCA by weak interactions with either aryl groups or halide atoms. The ESI-MS spectra of **A** and **B** show intact [BAr^{Cl}]$^-$ and [TEF^{Cl}]$^-$ anions in the gas phase at $m/z = 594.8$ and 1164.5, respectively.

Then, we set out to react **A**, **B** and Tl[TEF] with Lewis base-stabilized phosphanyl and arsanylboranes $EH_2BH_2 \cdot NMe_3$ (E = P, As), which by themselves are usually obtained by salt metathesis of $(Me_3Si)_2ELi \cdot THF$ with $BH_2Cl \cdot NMe_3$ followed by treatment with MeOH. To avoid this time-consuming and expensive synthetic route, we devised a new, simpler and robust approach of these compounds. By directly employing $NaPH_2$ and $LiAsH_2 \cdot TMEDA$ in salt metathesis reactions with $BH_2I \cdot NMe_3$ [Eqs. (2) and (3)], both arsanyl- and phosphanylboranes $EH_2BH_2 \cdot NMe_3$ could conveniently be prepared in one-step reactions in yields of 57% (E = P) and 37% (E = As), respectively.

$$BH_2I \cdot NMe_3 \begin{cases} \xrightarrow[\substack{THF,\ sonication, \\ r.t.,\ 2\ h}]{NaPH_2} PH_2BH_2 \cdot NMe_3 \ (57\%) \\ \xrightarrow[\substack{PhMe,\ r.t.,\ 18\ h}]{LiAsH_2 \cdot TMEDA} AsH_2BH_2 \cdot NMe_3 \ (37\%) \end{cases} \quad (2,3)$$
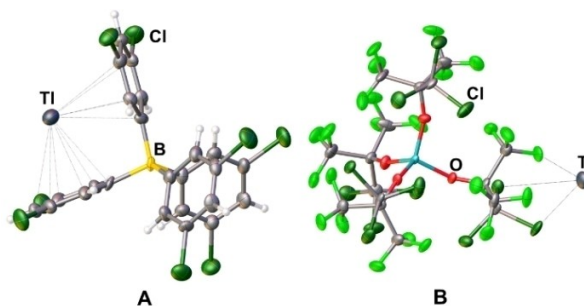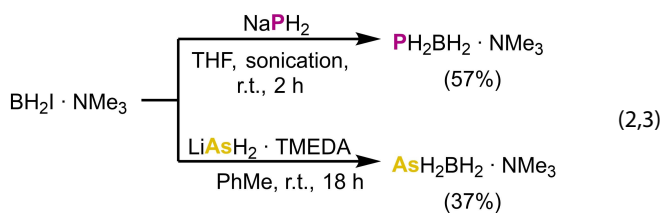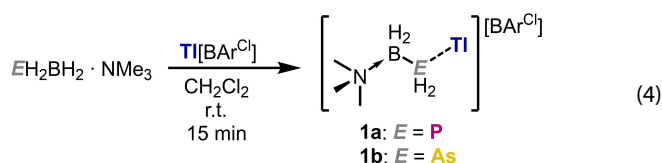

Figure 2. Molecular structures of **A** and **B** in the solid state. Anisotropic displacement ellipsoids are shown at 50% probability.

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With now plentiful starting material available, we performed coordination attempts with Tl[WCA] by adding the pnictogenylboranes either neat or in a solution of toluene to a solution (WCA = TEF, TEF^{Cl}) or suspension (WCA = BAr^{Cl}) of Tl[WCA] in dichloromethane.

$$E H_2 B H_2 \cdot N M e_3 \xrightarrow[\substack{CH_2Cl_2 \\ r.t. \\ 15\ min}]{Tl[BAr^{Cl}]} \left[\begin{array}{c} H_2 \\ N-B \\ \diagdown \quad E-Tl \\ H_2 \end{array} \right] [BAr^{Cl}] \qquad (4)$$

1a: E = **P**
1b: E = **As**

Reactions of **A** with the corresponding pnictogenylboranes $EH_2BH_2 \cdot NMe_3$ (E = P, As) in a stoichiometry of 1 : 1 lead to the monovalent coordination compounds [Tl($EH_2BH_2 \cdot NMe_3$)][BAr^{Cl}] (**1a**: E = P; **1b**: E = As) [Eq. (4)]. Even if the amount of pnictogenylborane was increased, the only isolable products are **1a** and **1b**. The products are obtained as colorless solids in yields of 80% (**1a**) and 72% (**1b**), respectively, that are stable under inert conditions at room temperature for months. In the ESI-MS spectrum, the molecular ion peaks of **1a** and **1b** were detected at $m/z = 310.1$ and 354.0, respectively. **1a** displays a significantly downfield shifted triplet in the ^{31}P NMR spectrum at -132.0 ppm ($^1J_{HP} = 175$ Hz, CD$_2$Cl$_2$) and a broadened triplet at -8.4 ppm ($^1J_{BH} = 100$ Hz) for the {BH$_2$} unit in the ^{11}B NMR spectrum, as well as a nonet at -7.1 ppm ($^1J_{BH} = 3$ Hz) from [BAr^{Cl}]$^-$. **1b** shows a broadened triplet at -6.3 ppm ($^1J_{BH} = 100$ Hz, CD$_2$Cl$_2$) and a nonet at -7.1 ppm ($^1J_{BH} = 3$ Hz) in the ^{11}B NMR spectrum. Both **1a** and **1b** crystallize in the monoclinic space group $P2_1/c$ as clear colorless needles and blocks, respectively, from CH$_2$Cl$_2$/n-hexane (Figures 3). The molecular structures show linear coordination modes of one molecule of a pnictogenylborane towards Tl$^+$ with a bond length of 3.0419(15) Å (E = P) or 3.1193(8) Å (E = As), respectively. The As–Tl distance is slightly elongated compared to the P–Tl bond, as the atomic radius of As is larger. The N–B [**1a**: 1.628(10) Å, **1b**: 1.616(11) Å] and B–E [**1a**: 1.960(8) Å, **1b**: 2.072(9) Å] bonds are within the range of classic single bonds.[14,15] In both compounds, the Tl$^+$ ion is loosely coordinated by the anion throughout simultaneous interaction with two aryl groups of [BAr^{Cl}]$^-$ in the solid state. These compounds represent the first monovalent phosphine Tl(I) complexes.

After the successful synthesis of **1a** and **1b**, we wondered if it is possible to coordinate several molecules of pnictogenylborane simultaneously to the Tl(I) ion. Therefore, we exchanged [BAr^{Cl}]$^-$ for the even weaker coordinating [TEF]$^-$ and [TEF^{Cl}]$^-$ anions to loosen the ion pair between Tl$^+$ and the WCA and hence facilitate the coordination of multiple ligands [Eq. (5)].

When three equivalents of $EH_2BH_2 \cdot NMe_3$ are added to a suspension of the Tl[WCA] salts in CH$_2$Cl$_2$, the threefold coordinated Tl(I) pnictogenylborane compounds [Tl-($EH_2BH_2 \cdot NMe_3$)$_3$][WCA] (**2a**: E = P, WCA = TEF^{Cl}; **2b**: E = As, WCA = TEF) are obtained as colorless solids in excellent yields between 74 and 80% [Eq. (5)]. In contrast to the reactions with the [BAr^{Cl}]$^-$ salts (see above), only intractable product mixtures were formed when one equivalent of $EH_2BH_2 \cdot NMe_3$ was added to the [TEF]$^-$ and [TEF^{Cl}]$^-$ Tl(I) salts. Both **2a** and **2b** can be
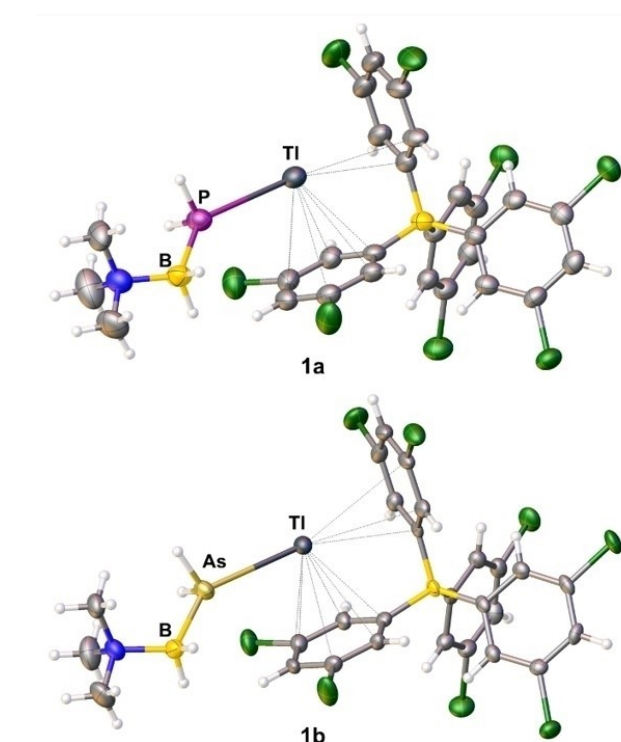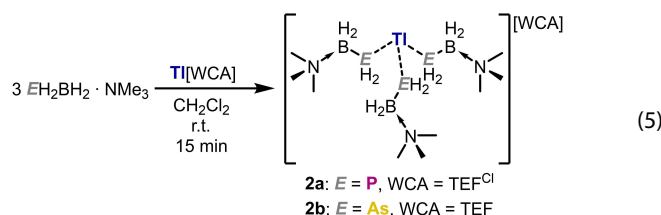

Figure 3. Molecular structures of **1a** and **1b** in the solid state. Anisotropic displacement ellipsoids are shown at 50% probability. Selected bond lengths [Å] and angles [°]: **1a**: N–B 1.628(10), B–P 1.960(8), P–Tl 3.0419(15), N–B–P 115.6(5), B–P–Tl 138.6(3). **1b**: N–B 1.616(11), B–As 2.072(9), As–Tl 3.1193(8), N–B–As 115.4(5), B–As–Tl1 143.4(3).

stored at room temperature under inert atmosphere for months. The ESI-MS spectra of **2a** and **2b** show fragment ion peaks of [Tl(PH$_2$BH$_2 \cdot$NMe$_3$)$_2$]$^+$/[Tl(PH$_2$BH$_2 \cdot$NMe$_3$)]$^+$ ($m/z = 415.1$, 310.0) and [Tl(AsH$_2$BH$_2 \cdot$NMe$_3$)]$^+$ ($m/z = 354.0$) instead of the molecular ion peaks for **2a** and **2b** due to fragmentation. **2a** displays a broadened triplet in the ^{31}P NMR spectrum at -166.7 ppm ($^1J_{HP} = 175$ Hz, CD$_2$Cl$_2$) and a strongly broadened triplet in the ^{11}B NMR spectrum at -8.0 ppm ($^1J_{HB} = 103$ Hz, CD$_2$Cl$_2$). Similarly, **2b** shows a broadened triplet in the ^{11}B NMR spectrum at -6.5 ppm ($^1J_{BH} = 111$ Hz, CD$_2$Cl$_2$).

$$3\, E H_2 B H_2 \cdot N M e_3 \xrightarrow[\substack{CH_2Cl_2 \\ r.t. \\ 15\ min}]{Tl[WCA]} \left[\begin{array}{c} H_2 \quad H_2 \\ N-B \quad Tl \quad B-N \\ \diagdown \ E \diagdown \ \diagup E \ \diagup \\ H_2 \quad \ E \ H_2 \\ H_2B \\ N- \end{array} \right] [WCA] \qquad (5)$$

2a: E = **P**, WCA = TEF^{Cl}
2b: E = **As**, WCA = TEF

Single crystals of **2a** and **2b** suitable for diffraction experiments were grown by layering CH$_2$Cl$_2$ solutions with n-hexane (Figure 4). For both compounds, the cation directly resides on a threefold screw axis parallel to the c axis in the crystal lattice, resulting in the three coordination arms at Tl$^+$ to be symmetry-equivalent. The interactions between Tl$^+$ and the WCAs as seen in **1a** and **1b** are not present in this case. **2a** crystallizes in the trigonal space group $R3c$ as clear colorless needles. The
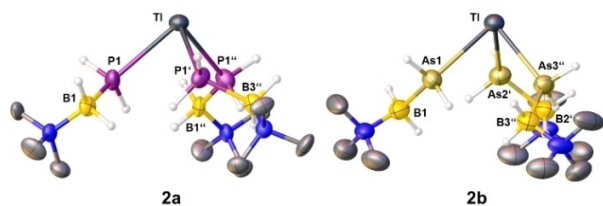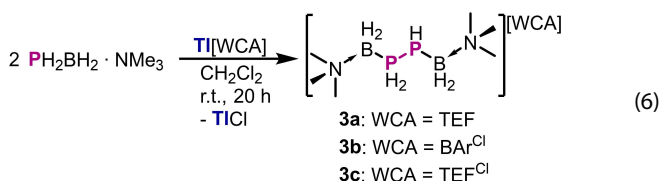
Figure 4. Molecular structures of **2a** and **2b** in the solid state. Anisotropic displacement ellipsoids are shown at 50% probability level. Counter ions and hydrogen atoms bound to carbon are omitted for clarity. Selected bond lengths [Å] and angles [°] ('/'' indicate symmetry-generated parts): **2a:** Tl–P1 2.989(4), P1–B1 1.961(18), P1–Tl–P1' 84.23(5). **2b:** Tl–As1 3.1158(12), As1–B1 2.084(12), As1–Tl–As1' 125.8(4).

molecular structure shows a trigonal pyramidal coordination mode of three phosphanylborane molecules to Tl$^+$ (Figure 4, left). The P–Tl bonds are equidistant with 3.002(3) Å and are close to the P–In bonds in [In(PPh$_3$)$_3$]$^+$ [2.9645(12)–3.0314(11) Å] due to similar atomic radii (In: 1.67 Å, Tl: 1.70 Å).[23] They are also slightly elongated compared to [PhB(CH$_2$P^{i}Pr$_2$)$_3$Tl]$^+$ [2.8936(8)–2.9206(9) Å]. The P–B bond length of 1.961(18) Å resembles a classic P–B single bond [cf. PH$_2$BH$_2$·NMe$_3$: 1.976(2) Å].[15] The P–Tl–P bond angles lie between 82.24(12)° and 86.13(11)° and are considerably smaller than in [In(PPh$_3$)$_3$]$^+$ [92.11(3)–95.72(3)°][10] owing to the more pronounced inert pair effect of thallium compared to indium. The P–Tl–P bond angles are also larger in comparison to [PhB(CH$_2$PPh$_2$)$_3$Tl]$^+$ [75.25(2)–77.72(2)°], as the scorpionate ligand introduces a higher steric strain in the backbone of the complex.

2b crystallizes in the trigonal space group *P*31*c* as clear colorless blocks (Figure 4, right). The molecular structure reveals a trigonal pyramidal coordination mode of the three arsanylborane molecules to Tl$^+$. The As–Tl bonds are equidistant with 3.1158(12) Å, which are elongated compared to **2a** due to the increased atomic radius of As. This is also accompanied by identical As–Tl–As angles of 81.51(4)°, which are slightly shorter than the P–Tl–P angles within **2a**. Accompanying DFT studies (M06-2X/def2-TZVPP, cf. Supporting Information)[24–26] show that the formation of all these complexes is exothermic and exergonic for both phosphanyl- and arsanylborane. The formation of a tight ion pair of [Tl(EH$_2$BH$_2$·NMe$_3$)]$^+$ with [BAr^{Cl}]$^-$ is exothermic by 317 kJ mol^{-1} (E=P) and 321 kJ mol^{-1} (E=As), respectively.

$$2\,\textbf{PH}_2\text{BH}_2\cdot\text{NMe}_3 \xrightarrow[\substack{\text{CH}_2\text{Cl}_2 \\ \text{r.t., 20 h} \\ -\,\textbf{Tl}\text{Cl}}]{\textbf{Tl}[\text{WCA}]} \left[\text{Me}_3\text{N}\cdot\text{BH}_2\text{PH}_2\text{PHBH}_2\cdot\text{NMe}_3\right][\text{WCA}] \quad (6)$$

3a: WCA = TEF
3b: WCA = BAr^{Cl}
3c: WCA = TEF^{Cl}

Although **2b** is stable in solution, according to NMR spectroscopy, **2a** is prone to a side reaction by involvement of CH$_2$Cl$_2$ as solvent, which then was investigated thoroughly. The combination of two equivalents of PH$_2$BH$_2$·NMe$_3$ and a solution of Tl[TEF] in CH$_2$Cl$_2$, leads to a white solid which precipitates out of the reaction mixture after stirring overnight [Eq. (6)]. The

powder was separated by filtration and identified as TlCl by X-ray powder diffraction (cf. Supporting Information). The soluble product was identified as [Me$_3$N·BH$_2$PH$_2$PHBH$_2$·NMe$_3$][TEF] (**3a**) by multinuclear NMR spectroscopy, featuring a Tl(I)-mediated P–P bond formation. Although Tl(I) salts were used as promotors in Suzuki cross couplings previously, a similar Tl(I) coupling reaction with solvent involvement (see below) has not yet been reported to our knowledge.[27] The ^{31}P{^{1}H} NMR spectrum (Figure 5) of **3a** shows a broadened doublet of multiplets at −91.3 ppm (^{31}P NMR: broadened and super-imposed doublet of triplets, $^1J_{PH} \approx 357$ Hz) and a doublet −199.6 ppm (^{31}P NMR: broadened and overlain doublet of doublets, $^1J_{PH} \approx 228$ Hz) with coupling constants of $^1J_{PP} = 255$ Hz and $^1J_{BP} = 32$ Hz which overall correspond to a {PH$_2$-PH} structure motif. Furthermore, the coupling between the two signals in the ^{31}P{^{1}H} spectrum was confirmed by ^{31}P,^{31}P COSY NMR (Figure 6). The ^{11}B{^{1}H} NMR spectrum of **3a** shows two broadened doublets at −10.7 ppm ($^1J_{BP} = 55$ Hz) and −6.5 ppm ($^1J_{BP} = 32$ Hz). These signals are split up upon proton coupling into a very broad triplet ($^1J_{BH} = 120$ Hz) and a triplet of doublets ($^1J_{BH} = 127$ Hz), respectively, thus confirming two separated {BH$_2$} moieties bound to one P atom each. The ESI-MS spectrum of a solution of **3a** shows the molecular ion peak at $m/z = 209$ for [Me$_3$N·BH$_2$PH$_2$PHBH$_2$·NMe$_3$]$^+$ and several fragment peaks at $m/z = 149$ ([Me$_3$N·H$_2$BH$_2$P–PHBH$_2$]$^+$), 135 ([Me$_3$N·H$_2$BH$_2$P–PH]$^+$) and 104 ([Me$_3$N·H$_2$BPH]$^+$).

Although the compound could be crystallized by solvent diffusion, crystallographic characterization was unsuccessful, as
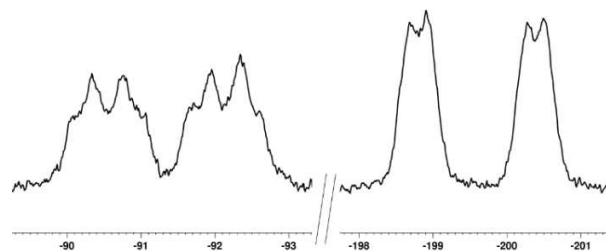

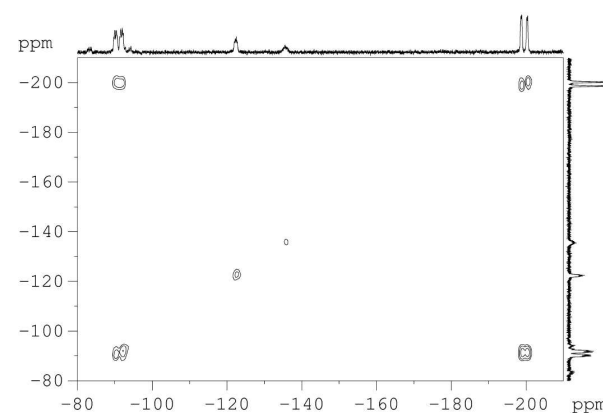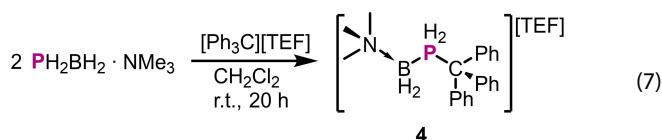**Figure 5.** Sections of the ^{31}P{^{1}H} NMR spectrum of **3a** (298 K, CD$_2$Cl$_2$).

Figure 6. ^{31}P, ^{31}P COSY NMR spectrum of **3a** highlighting the coupling between the two signals (298 K, CD$_2$Cl$_2$).

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only the anion of **3a** can be refined properly. Analogous reactions [Eq. (6)] with **A** and **B** led to the same results (**3b**, **3c**) as could easily be confirmed by NMR spectroscopy. Still, even with different WCAs, the crystallographic determination of the solid state structure of $[Me_3N \cdot BH_2PH_2\text{-}PHBH_2 \cdot NMe_3]^+$ was unfortunately not possible. To further investigate the influence of the solvent, CH_2Cl_2 was exchanged for 1,2-difluorobenzene and the reaction was repeated. No precipitate was observed in this case after prolonged stirring. According to $^{31}P\{^1H\}$ NMR spectroscopy data, the P–P coupling was indeed prevented and instead a highly broadened singlet at -143.0 ppm ($w_{1/2} = 69$ Hz) was found. As the chemical shift for this species lies in between **1a** (-132.0 ppm) and **2a** (-166.3 ppm), it seems likely that the twofold coordinated compound $[Tl(PH_2BH_2 \cdot NMe_3)_2]^+$ was formed. Unfortunately, the structure determination by X-ray crystallography was not possible due to the poor diffraction of any grown crystalline samples. The ESI-MS spectrum of this solution shows the coordination compounds $[Tl(PH_2BH_2 \cdot NMe_3)]^+$ ($m/z = 310.09$) and $[Tl(PH_2BH_2 \cdot NMe_3)_2]^+$ ($m/z = 415.2$). Interestingly, the molecular ion peak of the coupling product **3a** can also be detected at $m/z = 209.20$, which is probably a result of fragmentation and recombination in the mass spectrometer as no sign of **3a** was detected in the NMR spectra. Other test reactions with different Tl^+ salts (e.g., $Tl[PF_6]$) were unsuccessful, highlighting the importance of the employed WCAs in this coupling reaction.

In this context, we wondered if it might be possible to induce the P–P coupling with an abstracting agent other than Tl^+. Thus, we exposed two equivalents of phosphanylborane to $[Ph_3C][TEF]^{[28]}$ in CH_2Cl_2 [Eq. (7)]. The ^{31}P NMR spectrum of the reaction mixture shows several broadened signals, including unreacted $Me_3N \cdot BH_2PH_2$, the known cationic 13/15/13 chain compound $[Me_3N \cdot BH_2PH_2BH_2 \cdot NMe_3]^+$ (135.5 ppm, t, $^1J_{HP} = 354$ Hz)$^{[29]}$ and a very sharp triplet at -70.0 ppm ($^1J_{HP} = 192$ Hz), which is very likely caused by a $\{PH_2\}$ moiety that is not bound to a boron nucleus such as Ph_3CPH_2.

$$2\ \mathbf{P}H_2BH_2 \cdot NMe_3 \xrightarrow[\substack{CH_2Cl_2 \\ \text{r.t., 20 h}}]{[Ph_3C][TEF]} \left[\begin{array}{c} \text{Me}_3N\text{—}BH_2\text{—}\mathbf{P}H_2\text{—}CPh_3 \end{array} \right][TEF] \quad (7)$$

4

After work-up and crystallization from CH_2Cl_2/n-hexane, a clean inseparable mixture of the compound $[Me_3N \cdot BH_2PH_2BH_2 \cdot NMe_3]^+$ and another ionic product remained, which could be identified as $[Me_3N \cdot BH_2PH_2CPh_3][TEF]$ (**4**) by X-ray structure analysis (see below). The NMR data of the crystals also show that **4** represents the minor part of the crystalline product ($\sim 34\%$), which is less than in the reaction mixture ($\sim 71\%$). Overall, these observations indicate that **4** decomposes slowly in solution in the presence of an excess of phosphanylborane to give in situ $[Me_3N \cdot BH_2][TEF]$, which is easily attacked by $Me_3N \cdot BH_2PH_2$. Hence, the P–P coupling observed previously remains unique to reactions with Tl[WCA], so far. The ESI-MS spectrum of the crystals of **4** shows the molecular ion peaks of $[Me_3N \cdot BH_2PH_2CPh_3]^+$ ($m/z = 348.2$), $[Ph_3C]^+$ ($m/z = 243.1$) and $[Me_3N \cdot BH_2PH_2BH_2 \cdot NMe_3]^+$ ($m/z = 177.2$). Single crystals of **4**

suitable for single crystal X-ray diffraction experiments were grown by layering a solution of **4** in CH_2Cl_2 with n-hexane at $8\,°C$ (Figure 7). The compound crystallizes as large clear colorless prisms in the monoclinic space group $C2/c$. The CPBN chain adopts a zigzag geometry with all bond distances (cf. Figure 7) within regular single bond lengths for the respective interelement bonding and a CP–BN torsion angle of $-155.7365(7)°$. The substituents on the core motif are arranged in regular tetrahedral geometries.

To gain insight into this reaction behavior, quantum chemical calculations on possible reaction pathways were performed (M06-2X/def2-TZVPP).$^{[24–26]}$ Initially, a stepwise mechanism was considered starting with proton abstraction from $PH_2BH_2 \cdot NMe_3$ by for example $[CH_2Cl]^+$, potentially leading to in situ formed $[PHBH_2 \cdot NMe_3]^+$ or $[PH_2BH \cdot NMe_3]^+$ which could then undergo addition to a second molecule of phosphanylborane (Scheme 1, black pathway).

Upon geometry optimization, the structures of $[EHBH_2 \cdot NMe_3]^+$ ($E = P$, As, C_S point group) turned out to be transition states with respect to the H atom transfer from B to the P center. Optimization without symmetry constraints results in asymmetric $[EH_2BH \cdot NMe_3]^+$ cations which are by 148 kJ mol^{-1} ($E = P$) and 84 kJ mol^{-1} ($E = As$) lower in energy than corresponding $[EHBH_2 \cdot NMe_3]^{+\ddagger}$ transition states. Therefore, two types of addition products were considered: one containing an E–E bond, formally originating from the nucleophilic attack of $EH_2BH_2 \cdot NMe_3$ at the $[EHBH_2 \cdot NMe_3]^{+\ddagger}$ cation and the alternative isomer with a second E–B bond, originating from the nucleophilic attack at the $[EH_2BH \cdot NMe_3]^+$ cation.

Optimized structures and relative energies of isomers are given in the Supporting Information. It turned out that both isomers (indicated as EE-isomer and EB-isomer) are true minima on the potential energy surface and, in case of $E = P$, the PB-isomer is by 6.3 kJ mol^{-1} lower in energy than the PP-isomer. In contrast, for $E = As$, the AsAs-isomer is by 15.8 kJ mol^{-1} lower in energy than the AsB-isomer due to the weaker donor ability of As compared to P. The calculated results for a stepwise mechanism oppose the experimental findings, as exclusively the PP-isomer was observed and the coupling did not take place in case of $AsH_2BH_2 \cdot NMe_3$, even though the process is
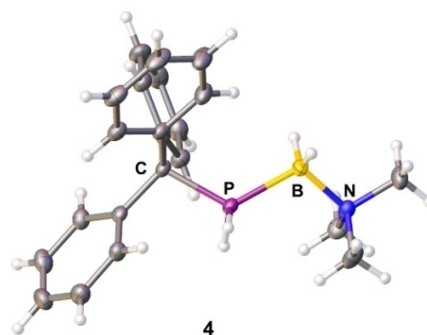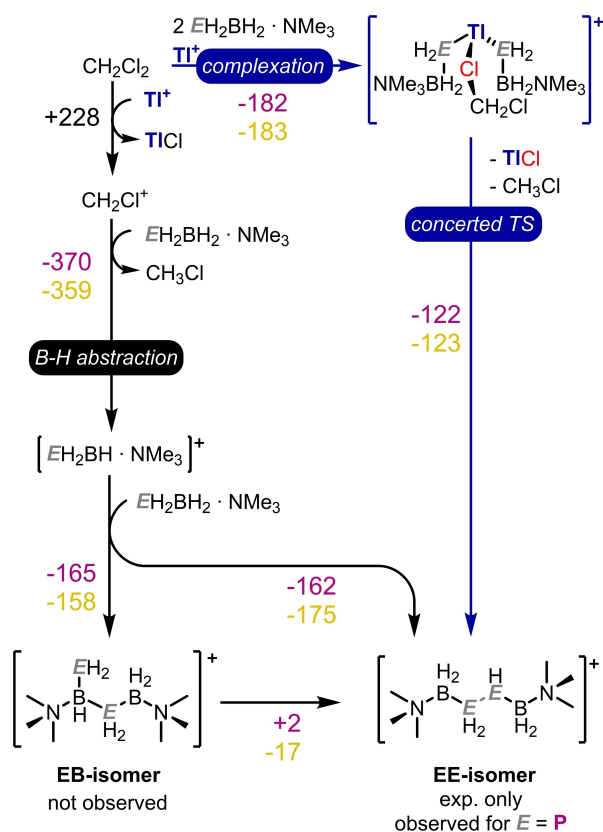

Figure 7. Molecular structure of **4** in the solid state. Anisotropic displacement ellipsoids are shown at 50% probability level. The counter ion is omitted for clarity. Selected bond lengths [Å] and angles [°]: N–B 1.603(3), B–P 1.977(2), P–C 1.8842(19), N–B–P 110.80(14), B–P–C 120.87(9).

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Scheme 1. Schematic representation of possible mechanisms towards the coupling of pnictogenylboranes by H-atom abstraction (black arrows) or complexation (blue arrows) (M06-2X/def2-TZVPP). Values represent calculated reaction Gibbs free energies $\Delta_R G^{\circ}_{298}$ in kJ mol^{-1} (yellow: E=As, purple: E=P).

monovalent complexes [Tl(EH$_2$BH$_2 \cdot$NMe$_3$)][BAr^{Cl}] (**1a**: E=P; **1b**: E=As) were obtained and fully characterized, which represent unprecedented examples of monovalent Tl(I) phosphine/arsine complexes. By variation of the anion towards even looser interactions with the cation, we were also able to isolate and characterize the threefold coordinated Tl(I) compounds [Tl-(EH$_2$BH$_2 \cdot$NMe$_3$)$_3$][WCA] (**2a**: E=P, WCA=TEF^{Cl}; **2b**: E=As, WCA=TEF).

Surprisingly, when two equivalents of phosphanylborane were used for those reactions, an intriguing coupling reaction involving CH$_2$Cl$_2$ took place under elimination of TlCl, leading to [Me$_3$N$\cdot$BH$_2$PH$_2$PHBH$_2 \cdot$NMe$_3$][WCA] (WCA=TEF, **3a**; BAr^{Cl}, **3b**; TEF^{Cl}, **3c**) as characterized by multinuclear NMR spectroscopy. The coupling reaction itself does not take place when CH$_2$Cl$_2$ as solvent is replaced with a different solvent such as 1,2-difluorobenzene. Reaction with the H-atom abstractor [Ph$_3$C][TEF] exclusively led to the coordination compound [Me$_3$N$\cdot$BH$_2$PH$_2$CPh$_3$][TEF] (**4**), representing a unique cationic 13/15/14 chain compound. Computational studies on the P–P coupling reaction show that, very likely, a sophisticated concerted mechanism takes place, as stepwise H-atom abstraction would rather lead to a different isomer with the formation of an additional P–B bond.

During these investigations, the synthesis of novel Tl[WCA] salts Tl[BAr^{Cl}] (**A**) and Tl[TEF^{Cl}] (**B**) was developed and the synthetic approach towards the Lewis base-stabilized pnictogenylboranes EH$_2$BH$_2 \cdot$NMe$_3$ (E=P, As) was further improved by using reactions of NaPH$_2$ and LiAsH$_2 \cdot$TMEDA with IBH$_2 \cdot$NMe$_3$, enabling future investigations on the reactivity of these compounds on a much broader scale.

Experimental Section

Experimental procedures for the synthesis of all compounds, analytical data, quantum chemical calculations and X-ray crystallography are described in the Supporting Information.

Deposition numbers 2194092 (**A**), 2194093 (**B**), 2194094 (**1a**), 2194095 (**1b**), 2194096 (**2a**), 2194097 (**2b**) and 2194098 (**4**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

exergonic. This finding suggests that more likely a complex, concerted mechanism at the Tl$^+$ ion takes place rather than the calculated stepwise formation. One possibility is the simultaneous coordination in situ of two pnictogenylboranes and one molecule of CH$_2$Cl$_2$ (Scheme 1, blue pathway), forming the complex [Tl(EH$_2$BH$_2 \cdot$NMe$_3$)(CH$_2$Cl$_2$)]$^+$ which then undergoes the coupling reaction in case of E=P. And indeed, the formation of [Tl(EH$_2$BH$_2 \cdot$NMe$_3$)(CH$_2$Cl$_2$)]$^+$ is exergonic in both cases. Even the pathway leading to the coupling products is predicted to be highly exergonic at room temperature. Although it was not possible to locate the corresponding transition states, it is likely that the activation barrier for the P–P coupling is low enough to proceed smoothly, while any As–As coupling is kinetically hindered in contrast. Moreover, the formation of [Tl-(EH$_2$BH$_2 \cdot$NMe$_3$)(CH$_2$Cl$_2$)]$^+$ is likely to be prevented when a stronger coordinating anion such as [PF$_6$]$^-$ is used, which could explain the absence of the P–P coupling in this case.[30]

Conclusion

In summary, we were able to synthesize unprecedented coordination products of pnictogenylboranes and Tl(I) salts of weakly coordinating anions. At a stoichiometry of 1:1, the

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supporting material of this article.

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[30] A different pathway to the P–P coupling could potentially proceed via β-hydrogen elimination from [Tl(PH$_2$BH$_2$·NMe$_3$)$_2$][WCA] leading to in situ formed TlH(PH$_2$BH$_2$·NMe$_3$). Subsequent reactivity with PH$_2$BH$_2$·NMe$_3$ could then lead to **3a-3c**.