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# One-Pot Synthesis of a 1,2-Diphospholide by Double C–H **Deprotonation**

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The relationship between phosphorus and carbon chemistry has been realized for many years. Phosphorus relatives of classical organic ligands (like cyclopentadienide, Cp<sup>-</sup>) in which carbon atoms have been substituted for phosphorus atoms are important classes of organometallic ligands, which are relevant to catalysis. Often, however, a limit to applying the phosphorus counterparts is the low-yielding and circuitous nature of their synthesis. A case in point is the 1,2-diphospholide ligand framework, an important analogue of the cyclopentadienyl ligand, which has only been obtained from

#### Introduction

The ability to tune the steric and electronic character of transition metal centers using different auxiliary ligand sets is an important and central theme in organo-transition metal chemistry and homogeneous catalysis.<sup>[1]</sup> For this reason, there has been increasing interest in new types of phosphorus-based ligands, particularly counterparts of classical organic ligands in which some or all of the carbon atoms are substituted for phosphorus atoms.<sup>[2]</sup> A developing class of phosphorus ligands are the oligophosphanediides of the form  $[PR]_n^{2-,[3]}$  These were first elucidated in landmark studies by Issleib.<sup>[4]</sup> The general method of synthesis (outlined in Scheme 1) has been used to prepare a series of oligophosphanediides through the coupling of dicholorophosphanes and subsequent reductive ring opening by further equivalents of alkali metal, either in a one- or two-step synthesis. More recent studies by Hey-Hawkins and Grützmacher have explored the structural properties and coordination chemistry of these compounds.<sup>[5,6]</sup> However, aside from transmetallations of the alkali metal salts of  $[PR]_n^{2-}$  with a range of transition and main group metal precursors, yielding metallocyclic and heterocyclic products in which the  $[RP]_n$  backbone is maintained, little investigation into the reactivity of the oligophosphanediides in their own right has been conducted.

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multistep syntheses. We report in this paper a high-yielding and direct route to this type of framework using a very simple approach. Treatment of MesPHLi (Mes = 2,4,6-trimethylphenyl) with Sb(NMe<sub>2</sub>)<sub>3</sub> generates the 5,7-dimethyl-1,2benzodiphosphol-1-ide anion (1), the first 1,2-diphospholide analogue of indenyl. Structural and NMR spectroscopic investigations suggest that this unique reaction, involving double C-H deprotonation of a CH3 group of the Mes ligand, occurs through the rearrangement of a tetraphospha-1,4-diide anion.



Scheme 1. General method for the preparation of oligophosphanediides. M = Na, K; R = tBu, Mes, Ph; n = 0, 1, 2; controlled by varying R, x and y.

Recently, we have been interested in the use of main group metals in the stoichiometric and catalytic dehydrocoupling of element-H bonds. Relevant to the current study is work that has shown that treatment of primary phosphanes (RPH<sub>2</sub>) with a redox-active superbase mixture of *n*-butyllithium and  $E(NMe_2)_3$  (E = As, Sb) results in the ultimate formation of cyclic phosphanes [RP]<sub>4</sub> and Zintl ions.<sup>[7]</sup> Intermediates in these reactions are the heterocyclic anions  $[(\mathbf{RP})_n\mathbf{E}]^-$ , the size of which depends on the steric demands of the R group (Scheme 2). In the sterically most demanding case, Mes\*PH<sub>2</sub> (Mes\* = 2,4,6-tri-tert-but-



Scheme 2. Products generated on the treatment of various lithiated primary phosphanes with  $As(NMe_2)_3$  (L,L' = Lewis base ligand).

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ylphenyl), the 1,3-diphospha-2-arsaallyl anion is produced, which is valance-isoelectronic with the carbon-based allyl anion.<sup>[8]</sup>

In studies initially aimed at extending this work to MesPH<sub>2</sub>, we found that the (5,7-dimethyl-1,2-benzodiphosphol-1-ide anion, the first 1,2-phospholide homologue of the indenyl ligand, can be obtained in a single, high-yielding step from the reaction of MesPH<sub>2</sub> (Mes = 2,4,6-trimethylphenyl) with *n*BuLi/Sb(NMe<sub>2</sub>)<sub>3</sub>. This reaction results from base-induced rearrangement of a tetraphospha-1,4-diide anion and is a unique example of double C–H deprotonation of a CH<sub>3</sub> group in main group chemistry.

### **Results and Discussion**

The one-pot synthesis of the 1,2-diphospholide anion 1 was achieved by treatment of MesPH<sub>2</sub> with nBuLi/TMEDA (2 equiv./4 equiv.), followed by addition of Sb(NMe<sub>2</sub>)<sub>3</sub> (0.5 equiv.). The salt [Li(TMEDA)<sub>2</sub>][1] was isolated as a yellow solid in a yield of 72%, the reaction involves net oxidation of the MesPH<sub>2</sub> and reduction of Sb<sup>III</sup>. Although the complex is also formed in a high yield using 2 equiv. of TMEDA, the presence of an excess of the ligand avoids contamination of the solid product by LiNMe<sub>2</sub> (Scheme 3). The complex [Li(TMEDA)<sub>2</sub>][1] was initially characterized by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy. Diagnostic signals in the <sup>31</sup>P NMR spectrum at  $\delta$  = 221.3 (dd, <sup>1</sup>J<sub>PP</sub> = 447, <sup>2</sup>J<sub>PH</sub> = 38 Hz, 1 P) and 131.0 (d,  ${}^{1}J_{PP}$  = 447 Hz, 1P) ppm and in the <sup>1</sup>H NMR spectrum at  $\delta$  = 7.89 (d, <sup>2</sup>J<sub>PH</sub> = 38 Hz, 1 H) ppm were strongly indicative of double C-H deprotonation of an ortho-methyl group and the formation of a carbonphosphorus double bond (for spectra see the Supporting Information, Figures S1 and S2).



Scheme 3. Method for the synthesis of the 5,7-dimethyl-1,2-benzodiphosphol-1-ide anion (1). Complete conversion to 1 was observed by in situ <sup>31</sup>P NMR spectroscopy. Toluene solvent, (i) stirred at room temp. for 1 h, (ii) stirred at room temp. for 30 min, then heated under reflux for 1 h.

Further confirmation of the structure of **1** was provided by X-ray analysis (Figure 1). This allowed unequivocal assignment of atom connectivity; however, the poor quality of the data obtained renders an in depth discussion of bond lengths and angles meaningless.<sup>[9]</sup>

In comparison to this simple one-pot route, the few examples of the synthesis of 1,2-diphospholides found in the literature involve multistep syntheses, make use of highly hazardous reagents (white phosphorus, sodium metal) or are low-yielding.<sup>[10,11]</sup> A case in point is the 3,4,5-triphenyl-1,2-diphosphacyclopentadienide anion,  $[(PhC)_3P_2]^-$ , which has only been obtained by the reaction of an organometallic cyclopropenylium–Ni<sup>II</sup> complex with the P<sub>5</sub><sup>-</sup> anion.<sup>[10]</sup> It is also worthwhile noting that due to the lack of generality of



Figure 1. Molecular structure of 5,7-dimethyl-1,2-benzodiphosphol-1-ide (1); the Li(TMEDA)<sub>2</sub> counterion and all hydrogen atoms [except H(1)] are omitted for clarity.

these synthetic methods, there are no known syntheses of indenyl variants of 1,2-diphospholides, such as 1.

In situ <sup>31</sup>P NMR spectroscopy was utilized to probe intermediates formed during the reaction (Figure 2). These studies were carried out under the same conditions as in Scheme 3, except that 1 equiv. of *n*BuLi and 2 equiv. of TMEDA were used to deliberately limit the extent of reaction. Immediately after mixing the reactants, a number of intermediates can be identified, including the cyclic phosphanes *cyclo*-[MesP]<sub>3</sub> (A<sub>1</sub>) and *cyclo*-[MesP]<sub>4</sub> (A<sub>2</sub>) and the tetraphospha-1,4-diide [MesP]<sub>4</sub><sup>2-</sup> (B) (Figure 2a).<sup>[12]</sup> After heating to reflux for 1 h, the spectrum shows the formation of 1 and the build-up of an unidentified intermediate (C) characterized by doublets at  $\delta = 89.4$  and -101.6 (<sup>1</sup> $J_{PP} =$ 347 Hz) (Figure 2b) (see also Scheme 5). Extended heating of this reaction mixture led to no further reaction. However,



Figure 2. (a) <sup>31</sup>P NMR spectrum of the reaction residue obtained immediately after addition of 0.5 equiv. of Sb(NMe<sub>2</sub>)<sub>3</sub>;<sup>[12]</sup> (b) in situ <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the reaction mixture prepared after heating under reflux for 1 h; (c) in situ <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the reaction mixture with a further 0.5 equiv. of Sb(NMe<sub>2</sub>)<sub>3</sub> added and stirred at room temp. for 16 h. The region  $\delta = -10$  to 85 ppm (which shows no other species) has been omitted.

addition of further equivalents of base  $[Sb(NMe_2)_3 \text{ or } nBuLi/TMEDA]$  led to near quantitative conversion into 1 (Figure 2c), illustrating that the transformation of **C** to 1 is base-induced.

A series of reactions was investigated using the reagent  $A_{s}(NMe_{2})_{3}$  in place of  $Sb(NMe_{2})_{3}$ , reasoning that the slower rates of the reactions, resulting from the lower basicity of the base, would allow us to deduce the order in which key intermediates are formed. Using the same stoichiometry and reaction conditions that were employed in the previous NMR spectroscopic study of the Sb system produced a final mixture composed of 1 and a new mixed As-P heterocycle (2) (Scheme 4).<sup>[13]</sup> The crystalline solid obtained from storage at 4 °C was found to have a bulk composition of [Li(TMEDA)<sub>2</sub>][1]<sub>0.6</sub>[2]<sub>0.4</sub> based on <sup>31</sup>P and <sup>1</sup>H NMR analyses (see the Supporting Information, Figures S4 and S5). The identity of **2** is further supported by X-ray analysis of a single crystal, which showed this to be the co-complex  $[\text{Li}(\text{TMEDA})_2][1]_{0.25}[2]_{0.75}$  (see the Supporting Information, Figure S6). We assume that the absence of the antimonybased analogue of 2 in the reaction with  $Sb(NMe_2)_3$  is due to its instability. We were also able to identify the previously reported Zintl compound [As7(Li·TMEDA)3] in the reaction mixture (see the Supporting Information, Figure S7). The isolation of this Zintl compound is consistent with the overall oxidation of MesPH<sub>2</sub> to 1 and 2 in the reaction (i.e., with accompanying reduction of  $As^{III}$  to the  $As_7^{3-}$  ion).



Scheme 4. Products isolated from reaction of  $MesPH_2$  with *n*BuLi/ 2TMEDA and As(NMe<sub>2</sub>)<sub>3</sub>. Toluene solvent, (i) stirred at room temp. for 1 h, (ii) stirred at room temp. for 30 min, then heated under reflux for 1 h.

The <sup>31</sup>P NMR spectrum of the reaction obtained after initial mixing of the reagents and brief heating shows the presence of the cyclic phosphanes [MesP]<sub>3</sub> ( $A_1$ ) and [MesP]<sub>4</sub> ( $A_2$ ) (see the Supporting Information, Figure S8).

After stirring at ambient temperature for 30 min, only  $[MesP]_4^{2-}$  (**B**) and the P/As heterocycle **2** are observed (Figure 3a). The formation of **B** was confirmed by X-ray analysis of the crystalline complex  $[{Li(TMEDA)_2} - {(MesP)_4Li(TMEDA)}]$  grown from this solution (Figure 4).<sup>[14]</sup> The addition of *n*BuLi (ca. 0.5 equiv.) and TMEDA (ca. 1 equiv.) to the mixture of **B** and **2** followed by heating under reflux for 1 h gave near complete conversion to **1** and **2** (Figure 3b). This illustrates that the

 $[MesP]_4^{2-}$  anion (**B**) is the precursor to **1** and that conver-



Figure 3. (a) <sup>31</sup>P NMR spectrum of a **B**/2 mixture in  $[D_8]$ THF. (b) <sup>31</sup>P NMR spectrum following treatment of the **B**/2 mixture in toluene with TMEDA (2 equiv.) and *n*BuLi (1 equiv.) and refluxing for 1 h ( $[D_8]$ THF).



Figure 4. Molecular structure of the singly chelated tetraphospha-1,4-diide,  $[Li(TMEDA)(MesP)_4]$ ; hydrogen atoms and the  $[Li(TMEDA)_2]^+$  counterion are omitted for clarity.<sup>[16]</sup>

Drawing together the observations made from both reaction systems involving Sb(NMe<sub>2</sub>)<sub>3</sub> and As(NMe<sub>2</sub>)<sub>3</sub>, allows the mapping of a partial mechanism for the reaction producing the diphospholide 1 (Scheme 5). The formation of cyclic phosphanes { $[MesP]_3$  (A<sub>1</sub>) and  $[MesP]_4$  (A<sub>2</sub>)} observed at the early stage of the reaction (STEP 1) is understandable in terms of previous work in this area, which has shown that a range of aliphatic and aromatic phosphanes undergo similar dehydrocoupling to cyclic phosphanes in the presence of E(NMe<sub>2</sub>)<sub>3</sub>/*n*BuLi, an oxidative coupling reaction that is accompanied by the reduction of  $E(NMe_2)_3$ to Zintl compounds  $(E_7^{3-})$ .<sup>[7]</sup> STEP 2 involves the reductive ring opening of  $A_1$  and  $A_2$  forming the tetraphospha-1,4diide  $[MesP]_4^{2-}$  (**B**). This process is well established for alkali metals, but is likely to be due here to the presence of the highly reducing Zintl ions in this system. What is strikDate: 30-03-15 12:34:37

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ing about the proceeding reaction of **B** is that it exclusively yields the 1,2-diphospholide **1**, showing that both of the P<sub>2</sub> "halves" of **B** convert to **1**. A schematic for this conversion is shown in *STEP 3* and *STEP 4*, both of which are baseinduced. An interesting possibility is that the net reduction occurring in these steps (– 2 e<sup>-</sup>, *STEP 3*) could be coupled to the oxidation in the previous step (+ 2 e<sup>-</sup>, *STEP 2*), through oxidative and reduction of  $E_{7^{3-}}$  Zintl ions.<sup>[17]</sup> The absence of a signal arising from [MesP]<sub>2</sub><sup>2-</sup> in the <sup>31</sup>P NMR spectrum shown in Figure 3(b) suggests that if this species is formed during *STEP 3*, it is short-lived and undergoes conversion to **1**. The observed insertion of a phosphorus atom involved in the transformation of MesPH<sub>2</sub> to **1** is reminiscent of the formation of the 1,2,3-triphospholide

 $[C_6H_4P_3]^-$  from 1,2-(PH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>.<sup>[18]</sup> However, the mechanism of formation of **1** is clearly different from the triphospholide analogue and does not involve the sacrifice of a phosphorus-containing by-product.



Scheme 5. Proposed schematic for the formation of  $1\ \text{from}\ \text{MesPH}_2.$ 

## Conclusions

A novel 1,2-diphospholide, 1, analogous to the indenyl anion, is formed in a high-yielding, one-pot reaction directly from MesPH<sub>2</sub>. Detailed NMR spectroscopic and structural investigations show that the formation of 1 involves based-initiated rearrangement of a tetraphospha-1,4-diide anion. The deprotonation of two H atoms of the *or*-*tho*-methyl group of MesPH<sub>2</sub> to give 1 can be regarded as a double C–H/P–H dehydrocoupling reaction and is unprecedented for a main group reagent. Further studies are underway to extend this work to intermolecular P–C bond formation and to a range of other difficult to prepare heterocyclic systems.

## **Experimental Section**

Synthesis of Li(TMEDA)<sub>2</sub>[1]: The synthesis and all manipulations were carried out under dry, O<sub>2</sub>-free nitrogen and in anhydrous, degassed solvents. A solution of MesPH<sub>2</sub> (0.22 g, 1.4 mmol) and TMEDA (0.87 mL, 5.8 mmol) in toluene (7 mL) was cooled to

-78 °C and treated with 1.6 м n-butyllithium in hexane (2.0 mL, 3.2 mmol). The resultant yellow solution was warmed to room temp. and stirred for a further 1 h to give an orange suspension of MesPHLi. This suspension was cooled again to -78 °C and treated with 2.0 M Sb(NMe<sub>2</sub>)<sub>3</sub> in toluene (0.36 mL, 0.7 mmol) before being warmed to room temp. The now brown/black suspension was stirred for 30 min before being heated under reflux for 1 h. The volume of the reaction was reduced in vacuo to ca. 4 mL and the resultant mixture stored at -15 °C overnight. Crystals of Li(TMEDA)<sub>2</sub>[1] were isolated by filtration, before being washed with n-pentane (10 mL). The finely divided, almost colloidal Sb metal present does not settle and is removed with the washing solvent at this stage. The remaining yellow solid was dried under reduced pressure. Yield 0.21 g (72%). <sup>1</sup>H NMR (500 MHz, [D<sub>8</sub>] THF):  $\delta$  = 7.92 [d, <sup>2</sup>J<sub>PH</sub> = 38 Hz, 1 H, P(CH)C], 7.34 [s, 1 H, C(CH)C], 6.32 [s, 1 H, C(CH)C], 2.64 (s, 3 H, CH<sub>3</sub>, A), 2.33 (s, 8 H, CH<sub>2</sub>, TMEDA), 2.33 (s, 3 H, CH<sub>3</sub>, A), 2.18 (s, 24 H, CH<sub>3</sub>,  $^{31}\mathbf{P}$ TMEDA) NMR ppm. (202 MHz,  $[D_8]$ THF):  $\delta$  = 222.0 (dd,  ${}^1J_{PP}$  = 448,  ${}^2J_{PH}$  = 38 Hz, 1 P, PPCH), 132.1 (d,  ${}^{1}J_{PP}$  = 448 Hz, 1 P, *P*PCH) ppm.

SHORT COMMUNICATION

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- [9] Crystal data: [Li(TMEDA)<sub>2</sub>][1], C<sub>21</sub>H<sub>41</sub>Li<sub>1</sub>N<sub>4</sub>P<sub>2</sub>, M = 418.46, triclinic, space group  $P\overline{1}$ , Z = 6, a = 16.5529(8), b = 16.7980(8), c = 17.6254(9) Å, a = 68.605(2),  $\beta = 69.828(2)$ ,  $\gamma = 61.803(2)^{\circ}$ , V = 3931.8(3) Å<sup>3</sup>,  $\mu$ (Cu- $K_a$ ) = 1.582 mm<sup>-1</sup>,  $\rho_{calcd.} = 1.060$  Mg m<sup>-3</sup>, T = 180(2) K. Total reflections 27302, unique 5699 ( $R_{int} = 0.0317$ ). R1 = 0.0864 [ $I > 2\sigma(I$ ]) and wR2 = 0.2440 (all data). Data were refined by full-matrix least squares on  $F^2$  (G. M. Sheldrick, *SHELX-2014/6*, Göttingen, **2014**). CCDC-1037634 contains the supplementary crystallographic data for [Li(TMEDA)<sub>2</sub>][1]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.
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- [12] In order to halt the reaction immediately, solvent was removed after addition of  $Sb(NMe_2)_3$  and the solid residue washed with *n*-pentane, removing *n*BuLi and TMEDA. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the *n*-pentane washings shows the presence of the cyclic phosphanes  $A_1$  and  $A_2$  (see the Supporting Information, Figure S3).
- [13] The mechanism of formation of 2 is not understood at this stage; however, <sup>31</sup>P NMR studies suggest that the tetraphospha-1,4-diide B is also the immediate precursor (see the Supporting Information, Figures S9 and S10).
- [14] After addition of As(NMe<sub>2</sub>)<sub>3</sub>, the reaction mixture was stirred at room temp. for 30 min, before being stored at 4 °C for 5 d to afford a batch of crystals containing B, 2 and [As<sub>7</sub>][Li•TMEDA]<sub>3</sub>.
- [15] Conversion to the neutral cyclic phosphanes  $A_1$  and  $A_2$  is observed on heating the B/2 mixture to reflux in toluene for 1 h in the absence of base, suggesting that the reductive ring opening from  $A_1/A_2$  to B is reversible under the reaction conditions.
- [16] Crystal data:  $[\text{Li}(\text{TMEDA})_2][(\text{MesP})_4 \cdot \text{Li}(\text{TMEDA})] \cdot (C_7 H_8), C_{61}H_{100}\text{Li}_2\text{N}_6\text{P}_4, M = 1055.23, monoclinic, space group <math>P2/n$ ,

Z = 2, a = 16.1229(7), b = 12.2196(6), c = 17.0599(8) Å, a = 90,  $\beta = 102.869(2)$ ,  $\gamma = 90^\circ$ , V = 3276.6(3) Å<sup>3</sup>,  $\mu$ (Mo- $K_a$ ) = 0.154 mm<sup>-1</sup>,  $\rho_{calcd.} = 1.070$  Mgm<sup>-3</sup>, T = 240(2) K. Total reflections 15328, unique 4215 ( $R_{int} = 0.0529$ ). R1 = 0.0947 [ $I > 2\sigma(I)$ ] and wR2 = 0.2772 (all data). Data were refined by full matrix least-squares on  $F^2$  (G. M. Sheldrick, SHELX-97, Göttingen, **1997**). CCDC-1037635 contains the supplementary crystallographic data for [Li(TMEDA)\_2][(MesP)\_4·Li(TMEDA)]·(C<sub>7</sub>H<sub>8</sub>). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. This structure is similar to those reported previously containing [RP]\_4<sup>2-</sup> anions (see ref.<sup>[5,6]</sup>).

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### Diphospholides

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One-Pot Synthesis of a 1,2-Diphospholide by Double C–H Deprotonation

**Keywords:** C–H deprotonation / Dehydrocoupling / 1,2-Diphospholide / Phosphorus / Phosphorus heterocycles



Almost "In-denyl": 5,7-Dimethyl-1,2benzodiphosphol-1-ide (1), a species valence-isoelectronic with the indenyl anion, is simply prepared in a one-pot synthesis by treatment of MesPH<sub>2</sub> with *n*BuLi and Sb(NMe<sub>2</sub>)<sub>3</sub>. This transformation involves an unprecedented double C–H deprotonation of a CH<sub>3</sub> group by a redox-active main group base.