CHEMISTRY A European Journal



Accepted Article Title: Synthesis and Identification of Aryl and Alkyl Gem-Dilithium Phosphido-Boranes: A Boost to the Chemistry of Phosphandiides Authors: Anne Harrison-Marchand, Jie Guang, Romain Duwald, Jacques Maddaluno, Hassan Oulyadi, Sami Lakhdar, and Annie-Claude Gaumont This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article. To be cited as: Chem. Eur. J. 10.1002/chem.201800742 Link to VoR: http://dx.doi.org/10.1002/chem.201800742

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Synthesis and Identification of Aryl and Alkyl Gem-Dilithium Phosphido-Boranes: A Boost to the Chemistry of Phosphandiides

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Abstract: The synthesis and identification of unprecedented gemdianionic phosphorus compounds, *i.e.* gem-dilithium phosphidoboranes Li₂[RP•BH₃], with R = Ph or Cy, are reported in THF solution. Those are obtained by double deprotonation of the corresponding primary phosphine-borane precursors RPH₂•BH₃. Their in-depth structural study, based on multinuclear (¹H, ⁶Li, ⁷Li, ¹¹B, ¹³C, ³¹P) mono- and bi-dimensional NMR analyses, indicates a strong influence of the phosphorus substituent on the structure of the gem-dianionic phosphorus structure: while a monomeric arrangement is obtained when R = phenyl, a cyclic oligomer is observed for R = cyclohexyl. These compounds represent a new type of common handy reagents, and their access certainly insufflates the long awaited dynamic to the concept of "RP synthons" likely to be the most flexible precursors of a multitude of varied phosphorus targets.

Due to the capacity of gem-dianions Y2- (Scheme 1) to deliver complex molecular structures within a minimum of chemical steps, an increasing interest has been devoted to these species this last decade.^[1-3] Among points raised in such studies is the understanding of how these compounds react and what their inherent advantages and limitations for practical reactions are.[1] Numerous carbon-centred gem-dianions, *i.e.* methandiides R₂C²⁻ (Scheme 1, left), have been examined,^[2] in contrast to the phosphorus analogues, i.e. phosphandiides RP2- (Scheme 1, right), that have received less attention.^[3] A main reason could be attributed to the weak stability of their precursors, primary phosphorus species, that easily oxidize or decompose under ambient reaction conditions.^[4] Our interest in phosphination reactions,^[5] which is another topic garnering attention in organic chemistry, led us to initiate a program to investigate the structures in solution of dianions derived from the bis deprotonation of primary phosphine derivatives. In this context, we report here the first structural identification in THF solution of two representative gem-dianionic phosphorus compounds, i.e. gem-dilithium phosphido-boranes Li₂[RP•BH₃] with R corresponding to a phenyl (R = Ph) or a cyclohexyl (R = Cy) group.

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The rare examples of phosphandiides, from which structural information has been obtained,^[3] refer to solid state data and are related to very specific R groups. The information brought by these studies indicates that the second deprotonation is very difficult and achieving effective stabilization of the final product requires the presence of a main-group metallic cation and an adjacent silicon atom to supply an empty d orbital. This constraint, in addition to the fact that the concerned RP²⁻ compounds are poorly soluble in common organic solvents, probably due to highly aggregated structures, narrows the scope of the R substituent and thus, limits synthetic applications. The complexation of a P-atom with a borane group being a general and easy strategy employed to stabilize phosphines,^[6] we decided to overpass the problems mentioned above by taking advantage of this to reach likely easier-to-handle primary phosphine-boranes (RPH₂•BH₃) and their corresponding dilithiated derivatives (Li₂[RP•BH₃]). Two RPH₂•BH₃, *i.e.* PhPH₂•BH₃ and CyPH₂•BH₃, have been selected to exemplify common aromatic and alkyl primary phosphine-boranes, respectively. Both species, seldom considered in literature, have nonetheless been easily prepared by mixing commercially available PhPH₂ or CyPH₂ with BH₃•SMe₂ at 0 °C for 30 minutes, respectively (pages 3S to 5S in SI).

The double deprotonation of PhPH₂•BH₃ underwent quickly and quantitatively using *n*-BuLi at –78 °C in THF. It afforded Li₂[PhP•BH₃] fully soluble and stable for several hours, even at room temperature (pages 8S, 9S and 11S in SI). Reaching pure Li₂[CyP•BH₃] in THF proved more difficult, resulting in a mixture of Li[CyPH•BH₃], Li₂[CyP•BH₃] and *n*-BuLi, even after a longer time of contact (pages 10S and 11S in SI). Using stronger bases, such as sec-BuLi and *tert*-BuLi, was not considered since these reactants are likely to deprotonate the α-CH group, even at – 78 °C.^[6,7] While still using *n*-BuLi, we completed the deprotonation, however under ultrasound at room temperature for 15 min in toluene containing THF. Under these conditions, the final solution is homogeneous, showing a good solubility of Li₂[CyP•BH₃] in a 10:1 toluene/THF solution (page 12S in SI).

The structural investigations of the two dilithiated phosphidoborane Li₂[RP•BH₃] freshly prepared above were conducted on the basis of the lithium NMR data^[8] with the aim of locating the two lithium cations. Note that in the following, ⁷Li NMR is used by default, but we also resorted to ⁶Li NMR (deprotonating the phosphine-boranes with ⁶Li-labelled *n*-BuLi^[5a]) to either strengthen the conclusion derived from the observations *via* ⁷Li NMR or reduce the possibility of peak overlapping.^[9]

Previous work on the structure of a secondary lithium phosphido-borane (Li[Ph₂P•BH₃]^[5a]) showed that the lithium atom is exclusively next to the borane group. This has led to substantiating the dual reactivity observed for such species. We wondered if this sole BH₃---Li link remains within Li₂[RP•BH₃]. Starting with Li₂[PhP•BH₃] in THF, the ⁷Li NMR spectrum obtained at 20 °C shows a sole signal at $\delta_{7\text{Li}}$ 0.88 ppm (page 13S in SI). Studying the ⁶Li congener did not provide any change, nor did it when varying the temperature of the analysis from 20 °C to –90, however there was the expected change of the move of the chemical shift ($\delta_{6\text{Li}}$ 0.41 ppm, page 13S in SI), (Figure 1). Such observations put into evidence that the two lithium cations of Li₂[PhP•BH₃] are not distinguished by NMR in THF, even at very low temperature.



Figure 1. VT ⁶Li-NMR spectra of Li₂[PhP•BH₃] in THF-d₈

The fact that this Li signal corresponds to a singlet regardless of the temperature and the isotope suggests that Li₂[PhP•BH₃] would not comprise P-Li bonds. Nevertheless, the ⁶Li-¹H HOESY spectrum recorded at -40 °C (Figure 2) shows that the Li signal strongly correlates with the BH₃ group, a result similar with our previous observations on secondary phosphidoboranes.^[5a] and more modestly, but in a non-negligible way, also with the ortho protons of the phenyl appendage. If these results allow us to discard the option of a separated ion pair, two possible dispositions of the lithium cations with respect to the [PhP•BH₃] moiety are to be considered to fit with the absence of P-Li scalar coupling: i) the two Li atoms are equivalent, being in interaction with both the phenyl and the BH₃ groups (Figure 3, left); ii) one Li interacts with the phenyl and the other with the BH₃, and they undergo a rapid exchange process (Figure 3, left). At this stage, instrumental and technical limitations do not allow deciding between these two options.



Figure 2. ⁶Li-¹H HOESY spectrum of ⁶Li₂[PhP•BH₃] in THF-d₈ at -40 °C.



Figure 3. The two possible locations of the Li cations of Li2[PhP•BH3]

We then completed our study resorting to a ¹H rDOSY experiment designed to evaluate the aggregation/solvation state of Li₂[PhP•BH₃] in THF at -40 °C.^[10] A diffusion coefficient-formula weight correlation analysis in the presence of four internal references (benzene = BEN, cyclooctene = OCT, tetradecene = TDE and squalene = SQU) led us to determine a molecular weight MW_{exp} of 473 (Table 1 and page 14S in SI). This value points toward either a penta-solvated monomer (MW_{th} 494, -4.4% error) or a tri-solvated dimer (MW_{th} 508, -7.0% error).

Table 1. ¹H Referenced DOSY: Theoretical (MW_{th}) and experimental (MW_{exp}) molecular weight (g.mol⁻¹) of internal references + putative Li₂[PhP•BH₃] monomer (MW_{th} = 134) and dimers (MW_{th} = 268) in THF- d_8 (MW_{th} = 80).

entry	Compound	MW_{th}	MW_{exp}	Err (%)
1	BEN	78.1	78.6	+1
2	OCT	110	111	+1
3	TDE	196	190	-3
4	SQU	410	418	+2
5	Li ₂ [PhP•BH ₃]+4THF Li ₂ [PhP•BH ₃]+5THF	414 <i>494</i>	473	+12.5 <i>-4.4</i>
6	{Li ₂ [PhP•BH ₃]} ₂ +2THF {Li ₂ [PhP•BH ₃]} ₂ +3THF	428 508		+9.5 -7.0

Considering that there are four Li⁺ in a dimeric structure, it seemed unlikely in the absence of significant steric hindrance, that three THF molecules could suffice to fully stabilize the four cations. Therefore, the penta-solvated monomer Li₂[PhP•BH₃]•5THF should be the most likely species in THF. Note that an accurate measurement of the solvation values by DOSY techniques is, as for other organolithium species,^[11] limited by the dynamic of Li-THF interactions.

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10.1002/chem.201800742

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With regards to the cyclohexyl congener, a VT ⁷Li-NMR experiment (Figure 4) was carried out first on Li₂[CyP•BH₃] in the 10:1 Tol-*d*₈/THF-*d*₈ solution. This time, two different Li peaks were identified below –20 °C with an integration ratio of one to one. Interestingly, the downfield signal is a triplet with a 46 Hz coupling constant. This value is consistent with the one-bond coupling between ⁷Li and ³¹P (¹J_{7Li-31P}) reported by Reich (≈ 43-48 Hz) in the case of lithium diphenylphosphide (Ph₂PLi).^[112] Thus, the structure of Li₂[CyP•BH₃] in 10:1 Tol-*d*₈/THF-*d*₈ would contain a P-Li bond observed for the first time in the context of such compounds. A ⁷Li-¹H HOESY spectra obtained at –30 °C (Figure 5) shows that the upfield peak (a singlet) exhibits through-space dipolar interactions with the BH₃ hydrides.



Figure 4. VT 7Li-NMR studies of Li2[CyP•BH3] in 10:1 Tol-d8/THF-d8



Figure 5. ⁷Li-¹H HOESY spectrum of Li₂[CyPH•BH₃] in 10:1 Tol-*d*₈/THF-*d*₈ at – 30 °C.

Unfortunately, the aggregation/solvation of $Li_2[CyP+BH_3]$ in 10:1 Tol- d_8 /THF- d_8 could not be examined running rDOSY experiments because all H peaks are upfield and overlap with

each other or with solvents. However, the low-field Li-signal is a triplet, signifying that this lithium atom is surrounded by two equivalent P-atoms. Such information is in favour of a {Li₂[CyP•BH₃]}_n cyclic oligomer (Figure 6), which is an hypothesis that is well-oriented to the general landscape of lithiated species into solution where cyclic dimers and trimers are commonplace.^[13] Again, instrumental limitations preclude verifying this hypothesis by performing a ⁷Li{³¹P} experiment.^[14] We therefore decided to repeat the VT experiment with a ⁶Lienriched Li₂[CyP•BH₃] sample (page 15S in SI) to assert, at least, that the lithium splitting pattern is really due to a Li-P coupling. Indeed, the ratio of ${}^{1}J_{7\text{Li}\cdot31\text{P}}$ to ${}^{1}J_{6\text{Li}\cdot31\text{P}}$ should be more or less equal to the quotient of the gyromagnetic ratio of ⁷Li to ⁶Li that is 2.64. We prepared ⁶Li₂[CyP•BH₃] by adding 0.5 equivalent of CyPH₂•BH₃ to n-Bu⁶Li in the same solvents mixture (10:1 Told₈/THF-d₈). Again, two broad peaks showed up in the ⁶Li NMR spectrum below -20 °C, the downfield peak becoming a sharp triplet at -110 °C (page 15S in SI).^[15] At this temperature, ¹J_{6Li}. _{31P} is found to be 17 Hz and thus, the ratio of ${}^{1}J_{7\text{Li-31P}} / {}^{1}J_{6\text{Li-31P}} =$ 2.70 is in fine agreement with our expectations. This further and strongly supports the hypothesis of a P-Li-P bridging. To check if the aggregation state would be influenced by the solvent, we repeated the ⁷Li VT experiment with a ⁷Li₂[CvP•BH₃] sample in pure THF- d_8 (page 16S in SI). Similarly, the down-field Li peak is a triplet with ${}^{1}J_{7\text{Li}\cdot31\text{P}} = 44$ Hz. Hence, Li₂[CyP•BH₃] forms a cyclic oligomer, even in pure THF (no monomer is observed while increasing the THF-concentration) at least at low temperature.



Figure 6. Speculated {Li₂[CyP•BH₃]}_n cyclic oligomer in THF.

To conclude, we investigated the structure in solution of dilithium phosphido-boranes Li₂[PhP•BH₃] and Li₂[CyP•BH₃]. This work shines light on an area of phosphorus chemistry that has been completely ignored to date, although it opens the door to a very promising key "RP synthon", *i.e.* RP²⁻ phosphandiides. The borane complexation of common RPH₂ primary phosphine precursors, with R = Ph and Cy, presents the double advantage of providing sufficient stability to the derived dianions so that they can be easily handled, and to allow these dianions to be fully soluble in the selected solvents. Structures in solution have been investigated for both dilithiated compounds thanks to NMR studies. Aromatic Li₂[PhP•BH₃] is identified as a pentasolvated monomer in THF while a cyclic oligomer would rather be formed for Li₂[CyP•BH₃] with a Li-P interaction observed for the first time for this class of lithium species. This structural study provides robust foundations for the chemistry of a novel class of phosphido-borane species that have synthetic potential in both organic and inorganic synthesis, and thus lays the foundations for new synthetic and theoretical investigations in phosphorus chemistry. Preliminary results obtained in this context by trapping the above Li₂[RP•BH₃] with MeI put into evidence i) a complete conversion of the lithiated starting material, and ii) intricated final mixtures, in which RPMe2•BH3 is spoted. The complexity of the results shows that, probably because of the strong electron density at the phosphorus atom.

phosphanediides do not behave as simple nucleophiles. Mechanistic studies, including EPR spectroscopy, laser flash photolysis and DFT calculations, are currently underway to confirm the *unique* reactivity of $Li_2[RP•BH_3]$.

Acknowledgements

The authors are thankful to the Labex SynOrg (ANR-11-LABX-0029) and the Région Normandie for having financed this project both in terms of wages (JG and RD) and material resources. Normandie Université (HO, ACG and AHM) and CNRS (JM and SL) are also thanked for financial support.

Keywords: primary phosphine • phosphandiide • phosphidoborane • RP-synthon • NMR structure

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Aryl and alkyl phosphandiides, stabilized by complexation with a borane group, are synthesised and their structure in THF-solution is reported. A monomer is identified for the gem-dilithium phosphido-boranes Li₂[PhP•BH₃] while Li₂[CyP•BH₃] arranges as a cyclic oligomer. This study highlights a new type of handy reagents and opens the door to a new concept of "RP synthons" likely to be the most flexible precursors of a multitude of tertiary phosphines.



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