Alkali Metal Phenylphosphandiides, [M$_2$P$_n$Ph$_n$] (M = Li, Na)

Daniel Stein[§], Jens Geier, Hartmut Schönberg, and Hansjörg Grützmacher*
[§]SCS Poster Prize Winner

Abstract: The reaction of phenyldichlorophosphane, PhPCl$_2$, a commercially important precursor for organophosphorus compounds, with lithium and sodium as reducing metals was re-investigated with the aim to well-characterize the resulting oligophosphandiides, [M$_2$(P$_n$Ph$_n$)(solv)$_x$] (M = Li, Na). Experimental conditions for the optimal formation of these compounds were found for both series with M = Li and M = Na and several of these were crystallized and characterized by X-ray diffraction studies. As a result, we find that sodium strongly prefers ion triple structures [M$_2$(P$_n$Ph$_n$)(solv)$_x$] over solvent-separated ion pairs, [M(solv)$_m$]$^+$[MP$_n$Ph$_n$(solv)$_n$]$^-$, which have a higher tendency to form with M = Li. Also, while [Na$_2$(P$_4$Ph$_4$)(solv)$_x$] retains its structure in thf solution, [Li$_2$(P$_4$Ph$_4$)(solv)$_x$] partially dissociates into the radical anion (Ph$_2$P$_2$)$^{\cdot-}$ which is detected by EPR spectroscopy. The knowledge about the structures and the behavior of the alkali metal diphosphandiides allows us to propose a reaction mechanism for their formation.

Keywords: Alkali metals · Ion triples · Phosphanes · Phosphorus · Radicals

1. Introduction

Phenyldichlorophosphane, PhPCl$_2$ (IUPAC: phenylphosphonous acid dichloride) is produced on large scale from PCl$_3$ and benzene [1] and is a versatile starting material in organophosphorus chemistry. Since the middle of the last century, the reaction of PhPCl$_2$ with alkali metals M has been intensively studied [2]. In collaboration with our industrial partner, Ciba Specialty Chemicals Inc, we became particularly interested in the question of whether a compound of the formula PhPM$_2$ may be prepared from the reaction of PhPCl$_2$ with metals as M = Li and Na. The use of sodium is of particular interest because of its availability and low price. Evidently, bismetallated phosphandiides, RPM$_2$, may serve as versatile reagents for the synthesis of a wide variety of functionalized phosphanes [3].

PhPM$_2$ (M = Li, Na, K) compounds have been postulated as products in the reductive bond cleavage (RBC) of cyclic oligo(phenylphosphanes), (PhP)$_n$ (n = 4, 5, 6) [4] (Eqn. (1), Scheme 1) or by deprotonation of phenylphosphane, PhPH$_2$, by organolithium reagents (Eqn. (2), Scheme 1) [5].

These compounds are, however, because of their very low solubility poorly characterized and neither conclusive spectroscopic data nor their structures have been reported. Only recently, a detailed characterization of some phosphandiides became possible. For example, Driess *et al.* were able to isolate and structurally characterize the ionic clusters [Li$_{16}$(P-SiR$_3$)$_{10}$] and [Li$_6$O⊂Li$_{20}$(P-SiR$_3$)$_{12}$] in the reactions of primary silylphosphanes, R$_3$Si-PH$_2$ (R = bulky alkyl group) with RLi (Eqn. (3), Scheme 1) [6]. The structures of these novel aggregates are schematically depicted in Fig. 1. In [Li$_{16}$(P-SiR$_3$)$_{10}$], the sixteen Li$^+$ ions form a closed polyhedron with eight pentagonal and two square planar faces. Remarkably, eight of the ten P-SiR$_3$ units can be considered as (P-SiR$_3$)$^{2-}$ dianions which two correspond to neutral P-SiR$_3$ phosphinidene fragments (likely capping the square planar faces on the top and bottom of the (Li$_{16}$)$^{16+}$ polyhedron shown in Fig. 1a). The [Li$_6$O⊂Li$_{20}$(P-SiR$_3$)$_{12}$] aggregate (Fig. 1b) represents a member of the so-called 'onion-cluster' where a [Li$_6$O]$^{4+}$-octahedron is fully encapsulated by a Li$_{20}$-dodecahedral shell

where each (P-SiR$_3$)$^{2-}$ unit caps a pentagonal face. These two examples show that complex redox reactions and fascinating structures will be part of the chemistry of RPM$_2$ compounds. (RP)$^{2-}$ dianions have also been characterized as [RPM]$_n$ aggregates with divalent main group element metals M = Mg^{2+} [7], Sn^{2+}; n = 6 [8] or with copper cations M = Cu$^+$, n = 12 [8]. In Fig. 1c we show schematically the structure of [Mg$_6${PSi(*i*Pr)$_3$}$_6$] which corresponds to a distorted hexagonal prism.

2. Results and Discussion

Firstly, we re-investigated the dehalogenation reaction of PhPCl$_2$ with reducing metals as the alkali metals Li–K, Mg, and Zn [9][10]. In our hands, this reaction gives the cyclic oligo(phenyl)phosphanes (PhP)$_n$ and the pentaphenylcyclopentaphosphane (n = 5) can be obtained in pure form in >90% yield after one re-crystallization of the crude reaction mixture. The best results were obtained with thermally activated zinc in thf as solvent (Scheme 2). Remarkably, while fresh solutions of highly pure (PhP)$_5$ (obtained by several crystallizations from acetonitrile or diethylether) only show the complex multiplet for a ABCDE spin-system in the ^{31}P NMR spectrum, the singlets for (PhP)$_6$ and (PhP)$_4$ were observed after keeping the C$_6$D$_6$ solutions for some hours at room temperature.

Correspondence: Prof. Dr. H. Grützmacher
Department for Chemistry and Applied Biosciences
ETH Hönggerberg, HCI H 131
CH-8093 Zürich
Tel: +41 1 632 28 55
Fax: +41 1 633 10 32
E-Mail: gruetzmacher@inorg.chem.ethz.ch
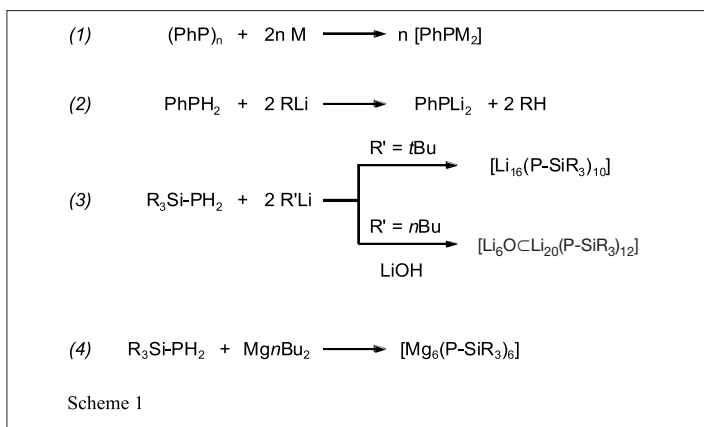
Scheme 1. Synthetic pathways leading to M_2PR and MPR compounds
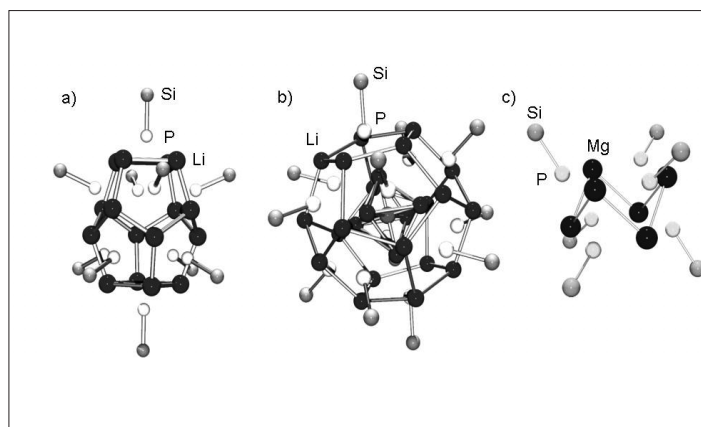
Fig. 1. a) $Li_{16}(P-SiR_3)_{10}$]; b) [$Li_6 \subset Li_{20}(P-SiR_3)_{12}$]; c) [$Mg_6\{PSi(iPr_3)\}_6$]. Only the metal (dark), the phosphorus (light), and silicon (grey) atoms are shown. The polyhedron formed by the metal atoms is highlighted.
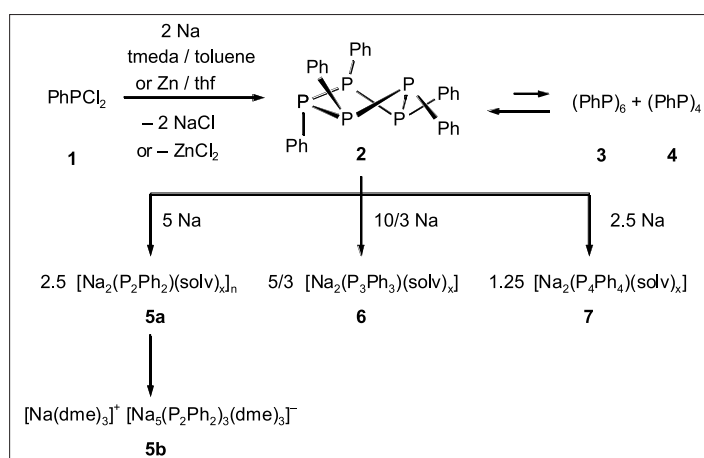
Scheme 2. Reductive bond formation (RPF) of $(PhP)_5$ using $PhPCl_2$ and reducing metals, and reductive bond cleavage (RBC) of $(PhP)_5$ leading to oligo(phosphandiides) [$Na_2(P_nPh_n)(solv)_x$]; x = unspecified number of solvent molecules
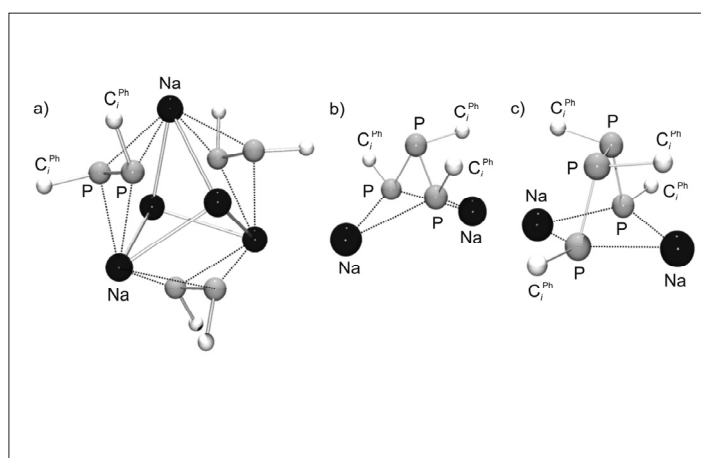
Fig. 2. a) Structure of the [$Na_5(P_2Ph_2)_3(dme)_3$] anion in **5b**. b) Structure of **6**. c) Structure of **7**. Only the Na, P, and *ipso*-carbon atoms of the phenyl groups are shown. The ion triple structures are indicated by dotted lines.

The reductive bond cleavage (RBC) reactions of $(PhP)_n$ were first investigated using sodium as reducing metal and different solvents and solvent mixtures. Especially, reactions performed in tetramethylethylenediamine (tmeda)/ toluene gave clean products. Depending on the stoichiometric ratio $(PhP)_5$/ Na, we obtained [$Na_2(P_2Ph_2)(tmeda)_{0.5}$]$_n$ (**5a**), [$Na_2(P_3Ph_3)(tmeda)_3$] (**6**), or [$Na_2(P_4Ph_4)(tmeda)_2$] (**7**) as products. Crystallization of **5a** from dimethoxy ethane (dme) gave [$Na(dme)_3$]$^+$ [$Na_5(P_2Ph_2)_3(dme)_3$]$^-$ as crystalline compound. The structures of **5b**, **6** and **7** were determined by X-ray diffraction and sketches are shown in Fig. 2 [11]. While the structures of **6** and **7** have been previously proposed on the basis of ^{31}P NMR data [12], the structure of **5b** is without precedence [1c][12a][13]. More recently, Hey-Hawkins *et al.* investigated [$Na_2(P_4Ph_4)(thf)_5$], [$Na_2(P_4tBu_4)(thf)_4$] which have structures similar to **7**, and [$Na_2(P_4Mes_4)(thf)_4$] and [$K_2(P_4Mes_4)(thf)_6$] which have slightly

different structures [14]. However, in all structures the two alkali cations and the oligophosphandiide dianion, $(P_nPh_n)^{2-}$ form *ion triples* [15]. Our NMR investigations show that **5b** and **6** retain the solid-state structures in solution. For **7** we have indications that an equilibrium involving the solvent separated ion pair **8** is involved (Scheme 3). Under the assumption that the five-membered NaP_4-ring in the anion [$Na(P_4Ph_4)(solv)_x$] has a (puckered) envelope structure, the observed ^{31}P NMR pattern for a ABCD spin system can be explained (x stands for an unspecified number of solvent molecules).

However, when both sodium cations are removed by complexation with [2.2.2]cryptand (C222), the resulting 'naked' tetraphosphandiide chain $(Ph_4P_4)^{2-}$ decomposes partially into the diphosphene radical anion $(Ph_2P_2)^{•-}$ [16]. Note that in all the structurally characterized [$M_2(P_4Ph_4)$]-ion triples, the two internal phosphorus centers have $2R,3R/2S,3S$-configurations, *i.e.* the ion triple are obtained as racemic

mixtures of the chiral threo-isomers. Upon rapid crystallization, red and yellow crystals of [$Na(C222)$]$^+_2$ $(Ph_4P_4)^{2-}$ were obtained. While the yellow crystals contain the $2R,3R/2S,3S$-configured diastereomer, remarkably, the red ones consist of the meso-isomer $2R,3R$-$(Ph_4P_4)^{2-}$ which has the phenyl substituents sterically favorably arranged.

The evolution of the disodium(oligo-phosphandiides), [$Na_2(P_nPh_n)$] in the reaction of $(PhP)_5$ with sodium in thf was qualitatively followed by ^{31}P NMR spectroscopy (Fig. 3). Interestingly, as $(PhP)_5$ is consumed (black columns), the tetraphosphandiide [$Na_2(P_4Ph_4)(thf)_x$] (**7**) is formed (white columns). After a certain time, the ionic cluster [$Na(thf)_6$]$^+$ [$Na_5(P_2Ph_2)_3(thf)_x$]$^-$ (**5**) (striped columns) starts to form. At the same time, the triphosphandiide [$Na_2(P_3Ph_3)(thf)_x$] (**6**) (grey columns) starts to build up; however, its concentration remains low at all times. In a separate experiment, [$Na(dme)_3$]$^+$ [$Na_5(P_2Ph_2)_3(dme)_3$]$^-$ (**5b**) was reacted
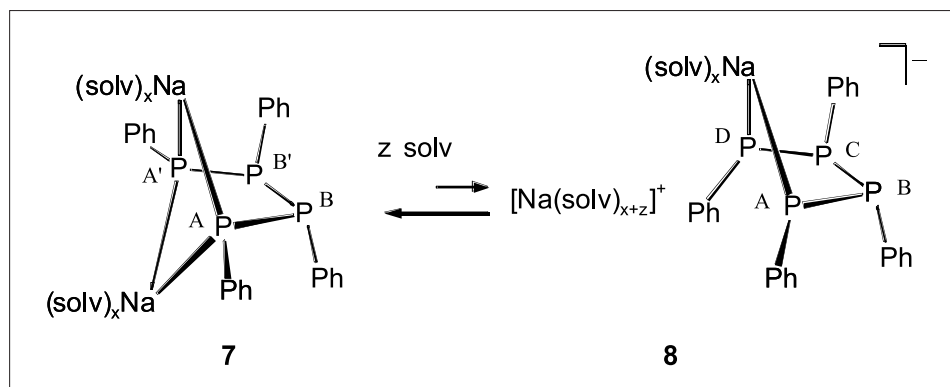
Scheme 3. Possible equilibrium between the ion triple **7** and solvent separated ion pair **8**

with $[Na_2(P_4Ph_4)(thf)_x]$ and indeed in a slow reaction **6** is obtained as the major product.

Qualitatively, the same kind of observations are made when $(PhP)_5$ is reacted with lithium pieces in thf. Firstly, $[Li_2(P_4Ph_4)(thf)_x]$ is formed at the expense of the cyclo(pentaphosphane). After complete conversion, the formation of $[Li_2(P_2Ph_2)(thf)_x]$ is observed while only minor concentrations of $[Li_2(P_3Ph_3)(thf)_x]$ are seen. Interestingly, almost quantitative formation of the latter compound is obtained when the reaction is carried out in dme where $[Li_2(P_3Ph_3)(dme)_3]$ is sparingly soluble. The main differences in the reactions of $(PhP)_5$ (or $PhPCl_2$) with lithium compared to those with sodium are:

i) The reactions with lithium are considerably faster.
ii) The ion triples $[Li_2(P_nPh_n)(solv)_x]$ with n = 3, 4 show a higher tendency to dissociate into solvent-separated ion pairs $[Li(solv)_x]^+$ $[Li(P_nPh_n)(solv)_x]^-$ because of the higher solvation energies of lithium in organic solvents.

iii) While thf solutions of $[Na_2(P_4Ph_4)(thf)_x]$ are EPR-silent, solutions of the lithium analogue clearly show the typical EPR signal for the $(Ph_2P_2)^{\cdot-}$ radical anion. That is, complexation of the lithium ions in thf is sufficiently strong to generate small amounts of the 'naked' $(Ph_4P_4)^{2-}$ chains (not detected) which subsequently decompose.

These observations lead us to propose a qualitative scheme for the formation of oligo(phosphandiides) from $PhPCl_2$ and lithium or sodium as reducing metal: Reduction of $(PPh)_5$ by the alkali metal M = Li, Na to give a short lived $[M(PPh)_5^{\cdot-}(solv)_x]$ radical anion (not detected by EPR indicating a life time t < 10^{-9} s) which may rapidly dimerize and decompose to give $[M_2(P_4Ph_4)(solv)_x]$ as the first detectable product. Note, that we have no indications for longer chain dianions. We assume that $[M_2(P_4Ph_4)(solv)_x]$ partially dissociates to give very small amounts of the radical ion pair $[Na^+(solv)_x(P_2Ph)_2^{\cdot-}]$ which can be detected for M = Li. It is reasonable to assume that this species with its energetically

low-lying SOMO is reduced in a very fast single electron transfer reaction to give the $[M_2(P_2Ph_2)(solv)_x]$. This mechanism takes into account that at no time of the reaction, larger amounts of the tri(phosphandiide) $[M_2(P_3Ph_3)(solv)_x]$ are observed.

Remarkably with respect to the intention of this work, we have no indications for the formation of compounds of formula $[M_2PPh]_n$. These remain elusive and likely are not formed in a reductive bond cleavage reaction of oligo(phosphanes). A reason for this may be the high stability of the ion triples $[M_2(P_2Ph_2)(solv)_x]$ which are not further reduced neither degraded by phosphorus nucleophiles.

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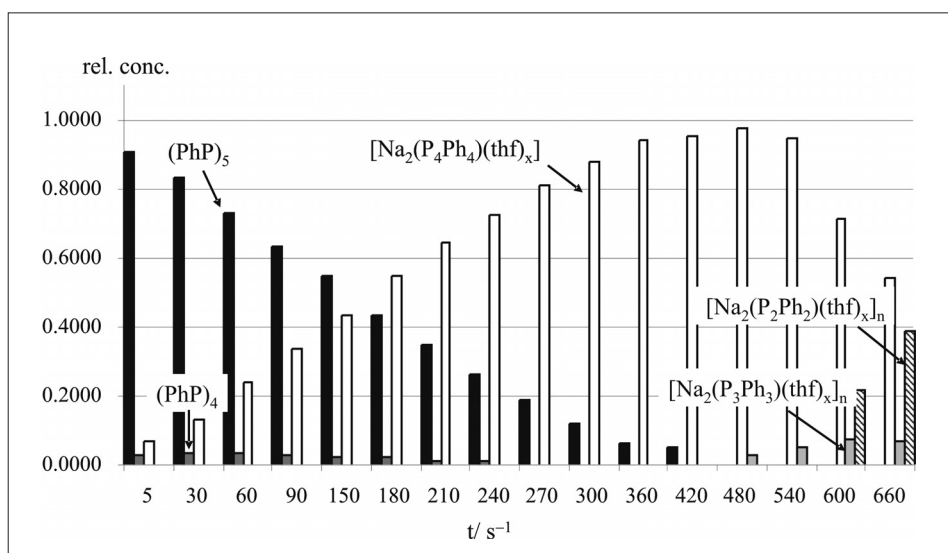
Fig. 3. Evolution of the consumption of $(PhP)_5$ and formation of $[Na_2(P_nPh_n)(solv)_x]$ (n = 4, 2) in the reaction of $(PhP)_5$ with sodium metal in thf

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