



## Review

## Phosphanides of calcium and their oxidation products

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## ABSTRACT

In this review phosphorus-containing anions and molecules acting as ligands at calcium cations are discussed. Limitation to calcium derivatives is justified on the basis of its advantageous properties, its electropositive character ensuring high reactivity, and particularly the tremendous recent interest in calcium-based organometallics. Detailed discussions focus on substance classes such as phosphanides, phosphane oxides, phosphinites, phosphinates, and phosphonates. Isoelectronic relationships based on Grimm's hydride displacement law (such as  $O/NH/CH_2$  and also  $O/N^-/CH^-/C^{2-}$ ) allow categorization of calcium derivatives with phosphorus-containing anionic and neutral ligands. Applications of these compounds in stoichiometric and catalytic reactions are presented including very recent developments in calcium-mediated intermolecular hydrophosphanylation of alkynes.

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## 1. Introduction: scope and limitations

Calcium represents an attractive element in many aspects due to diverse beneficial properties. It is non-toxic regardless of its concentration, inexpensive, and available worldwide. In common inorganic and organometallic chemistry this alkaline earth metal is divalent and not redox active thus making reaction mechanisms intelligible and reducing the danger of side reactions. Calcium and its heavier homologues advantageously show intermediate chemical behaviors between typical s-block elements (highly heteropolar bonds to non-metals, salt-like behavior, strong

electrostatic interactions) and early transition metals (Lewis acidic cations, catalytic activity, d-orbital participation). The organometallic chemistry of calcium is in the process of leaving its infancy. This fact, the diagonal relationship of carbon and phosphorus(III) in the periodic table, and diverse applications [1] justify an overview on calcium phosphanides and derivatives thereof. The development of the chemistry of calcium-based phosphanides happened in the shadow of calcium cyclopentadienides [2], organylcalcium complexes [3,4], and calcium compounds based on N-donor bases [4,5] which attracted much attention in the last decade and, hence, were already summarized in excellent reviews.

Phosphorus (in contrast to the s-block metals) offers a rich redox chemistry with phosphorus of the formal oxidation states from  $-3$  to  $+5$ . Starting from P-based compounds of the formal oxidation state (O.S.) of  $-3$  with the root compound being acidic  $PH_3$

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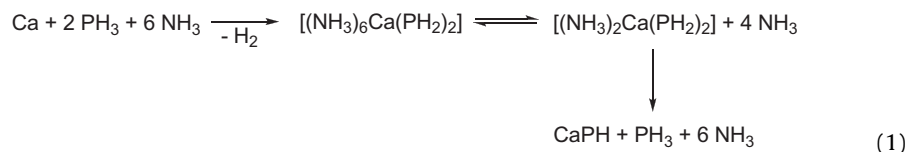
**Table 1**

The nomenclature and acidity of phosphorus-based molecules depend on the formal oxidation state (O.S., increasing from row to row) and on the coordination number (C.N.) of phosphorus. The acids with three-coordinate (front half) and four-coordinate P atoms (back half of the table) can be converted into one another by migration of an oxygen-bound hydrogen atom to the phosphorus center (tautomerism) without changing the oxidation state. Peroxoacids are neglected. Salts are deprotonated acids with the oxygen-bound H atoms being the most acidic ones; singly and doubly metalated phosphonium ions yield metal-phosphane complexes and metal phosphanides, respectively. Meta forms are generated by elimination of water from the acids but they commonly exist as oligomers or polymers of the given formula.

C.N. of P	3			4		
	Meta forms (anhydrides)	Salts	Acids	Acids	Salts	Meta forms (anhydrides)
-3		[PH <sub>2</sub> ] <sup>-</sup> Phosphanide	PH <sub>3</sub> Phosphane	PH <sub>4</sub> <sup>+</sup> Phosphonium		
-1	(H <sub>2</sub> P) <sub>2</sub> O	[H <sub>2</sub> P—O] <sup>-</sup> Phosphinite	H <sub>2</sub> P—OH Phosphinous acid	H <sub>2</sub> P(O) Phosphane oxide		
+1	[HP(OH)] <sub>2</sub> O HP=O	[HP(O—O)] <sub>2</sub> <sup>-</sup> Phosphonites	HP(OH) <sub>2</sub> Phosphonous acid	H <sub>2</sub> P(O)—OH Phosphinic acid	[H <sub>2</sub> P(O)—O] <sup>-</sup> Phosphinate	[H <sub>2</sub> P(O)] <sub>2</sub> O
+3	P(O)—OH, P <sub>4</sub> O <sub>6</sub>	[P(O—O)] <sub>3</sub> <sup>-</sup> Phosphites	P(OH) <sub>3</sub> Phosphorous acid	HP(O)(OH) <sub>2</sub> Phosphonic acid	[HP(O)(—O)] <sub>2</sub> <sup>-</sup> Phosphonates	[HP(O)(OH)] <sub>2</sub> O HP(O) <sub>2</sub>
+5				P(O)(OH) <sub>3</sub> Phosphoric acid	[P(O)(—O)] <sub>3</sub> <sup>-</sup> Phosphates	HO—P(O) <sub>2</sub> , P <sub>4</sub> O <sub>10</sub>

oxidation can formally be achieved by insertion of oxygen atoms into the P—H bonds (Table 1). A tautomeric equilibrium allows the conversion of these molecules with three-coordinate phosphorus atoms into derivatives with four-coordinate P-centers via a hydrogen shift from the oxo group to phosphorus. The acidic behavior is caused by the OH groups whereas P-bound H atoms show a much weaker acidity with the phosphonium ion being an exception. Deprotonation of the phosphonium ion PH<sub>4</sub><sup>+</sup> (i.e. substitution of a proton by a metal cation) yields phosphane (PH<sub>3</sub>) and then phosphanide (PH<sub>2</sub><sup>-</sup>) bound at a cation. In addition to the substantial redox chemistry, characterization and detection can advantageously be performed with <sup>31</sup>P NMR experiments.

phosphonic, and finally phosphoric acid). Phosphane itself attracted much attention due to its importance for the synthesis of organophosphorus compounds [9] but it acts as a rather poor ligand to calcium ions. Theoretical investigations showed that the bond between calcium ions and hard bases such as ammonia and water is favored compared to those between Ca<sup>2+</sup> and phosphane PH<sub>3</sub> and sulfane H<sub>2</sub>S [10]. Due to this fact many coordination compounds of calcium ions with ether and amine ligands exist but phosphane containing complexes are quite rare. Calcium bis(phosphanide) was prepared as an ammonia adduct via calcination of PH<sub>3</sub> with calcium in liquid ammonia (Eq. (1)). This complex decomposed at higher temperatures with liberation of ammonia leading to the formation of CaPH and PH<sub>3</sub> and finally to binary calcium phosphides [11] which can also be prepared from the elements [12].



Some of the derivatives shown in Table 1 cannot be isolated in pure form or even represent transient species. Substitution with alkyl and aryl groups generally leads to enhanced stabilization of the molecules. For example, phosphane oxide H<sub>3</sub>P=O can be characterized only in an argon matrix [6] (generated via photolysis of a PH<sub>3</sub>/O<sub>3</sub> mixture) or as a transient species in the gaseous phase [7] (produced via glow discharge in a mixture of PH<sub>3</sub>, CO<sub>2</sub>, and H<sub>2</sub>) whereas triphenylphosphane oxide resembles a stable and commercially available compound. Phosphorus strongly favors tetrahedral environments and, hence, acids with four-coordinate P atoms represent the major tautomer in the equilibria shown in Table 1. The wide spread utilization of phosphanes and phosphane oxides initiated considerable studies of the bonding situations verifying only very minor d-orbital participation at P [8].

Phosphane PH<sub>3</sub> represents the root compound that can be protonated and deprotonated yielding phosphonium (PH<sub>4</sub><sup>+</sup>) and phosphanide ions (PH<sub>2</sub><sup>-</sup>) shown in the upper row of Table 1. Within a column the formal insertion of an oxygen atom into the P—H bonds leads to acids with an increasing number of P—OH units (the first formal insertion product of PH<sub>4</sub><sup>+</sup> is [H<sub>3</sub>P—OH]<sup>+</sup> that eliminates a proton giving phosphane oxide H<sub>3</sub>PO; all subsequent oxygen insertion steps adhere to the outlined concept affording phosphinic,

According to Grimm's hydride displacement law and the isoelectronic relationship of O, NH/N<sup>-</sup>, CH<sub>2</sub>/CH<sup>-</sup>/C<sup>2-</sup> on the one hand and O<sup>-</sup>, NH<sup>-</sup>/N<sup>2-</sup>, CH<sub>2</sub><sup>-</sup>/CH<sup>2-</sup> on the other allow to widen the discussion beyond the classical P-containing acids and their salts. In this review we limit the discussion to calcium complexes and, hence, to phosphorus-based ligands and anions. The overview is structured according to the oxidation state of the phosphorus atom, starting with O.S. = -3 (i.e. phosphane complexes and phosphanides). In this review, structural principles of phosphorus-based anions, general preparative procedures, as well as exemplified applications in stoichiometric and catalytic processes are presented. In addition, the discussion is limited to calcium derivatives due to the advantageous and fascinating properties of this cation (non-toxicity, world-wide availability, inexpensiveness, moderate Lewis acidity, d-orbital accessibility). However, a complete coverage of the literature is not intended and the focus of this overview is centered on more recent studies.

## 2. Phosphane and phosphanide complexes of calcium

Phosphanes are very weak Brønsted acids and formally the oxidation state (O.S.) of P is considered to be -3 (in analogy to N in

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