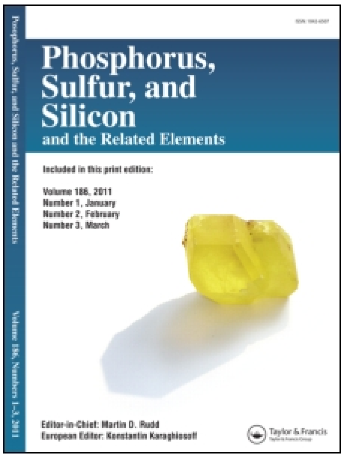

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Alkaline Earth Metal-Phosphorus Cages of the Type $M_{2n}P_{2m}$: Synthetic Approach and Topological Relations

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The metalation of triisopropylsilyl- and tri(tert-butyl)silylphosphane with alkaline earth metal bis[bis(trimethylsilyl)amides] yields the corresponding phosphanides. Depending on the stoichiometry, the dimeric and heteroleptic or homoleptic derivatives $[(Me_3Si)_2N]_nM_2[\mu\text{-}P(H)SiR_3]_{4-n}$ with n = 0, 1, and 2 are isolated and can be regarded as steps on the way to $M_{2n}P_{2m}$ cage compounds in which the ratio n/m can vary between 1/2 [metal bis(phosphanides)] and 1/1 (metal phosphandiides). The metalation of triisopropylsilyl- and tri(tert-butyl)silyl-phosphane with dibutylmagnesium gives $Mg_{2n}P_{2m}$ cages with n/m = 1/1, 2/3, and 4/5. The heavier alkaline earth metals form $M_{2n}P_{2m}$ cages with n/m = 1/2 and 3/4 (M = Ca, Sr, Ba) in which the ratio n/m = 1/2 represents the homoleptic dimeric alkaline earth metal bis(phosphanide). All these cages can be derived from a M_2P_2 cycle which appears dimeric (M_4P_4 heterocubane) or trimeric (hexagonal M_6P_6 prism) in which two opposite planes can be capped by alkaline earth metal bis(phosphanide) molecules.

Keywords: Alkaline Earth Metals; Cages; Metalations; Phosphandiides; Phosphorus

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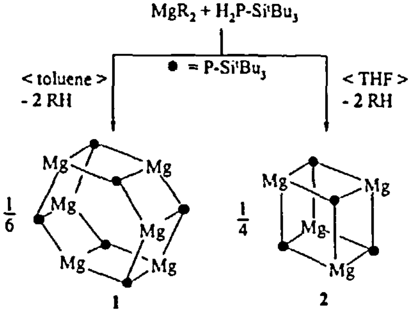
INTRODUCTION

Alkaline earth metal imides are well-known and structurally characterized for magnesium only. Power and coworkers were able to isolate hexameric magnesium phenyl- [1] and naphthylimide [2] with central hexagonal Mg_6N_6 prisms. A heteroleptic bromide containing magnesium imide with a Mg_6N_4 adamantane-like structure was isolated by the same research group [3]. The root compound CaPH was already published in 1942. Legoux metalated phosphane with calcium in liquid ammonia and decomposed the resulting $(H_3N)_2Ca(PH_2)_2$ at approximately 70°C [4].

Heterobimetallic cages of phosphorus, tin(II) and the heavier alkaline earth metals calcium, strontium, and barium are known and already summarized elsewhere [5]. The metalation of $HP(SiMe_3)_2$ with $M[N(SiMe_3)_2]_2$ in the presence of $Sn[N(SiMe_3)_2]_2$ yields M_3P_4 cages which can be described as two trigonal bipyramids interconnected by a common face. The metalation of $H_2PSi^tBu_3$ with $Ba[N(SiMe_3)_2]_2$ and $Sn[N(SiMe_3)_2]_2$ gives $(\eta^6\text{-toluene})BaSn_3[\mu_3\text{-}PSi^tBu_3]_4$ with a M_4P_4 heterocubane cage [6].

DISCUSSION

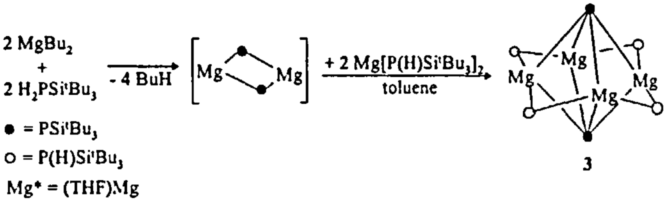


SCHEME 1. Dependency of the solvent on the size of the magnesium phosphorus cages during the magnesiation of tri(tert-butyl)silylphosphane.

The metalation of primary phosphanes yields phosphanides and/or phosphandiides. Their structures depend on the alkaline earth metal in which magnesium stabilizes different cages than the heavier metals.

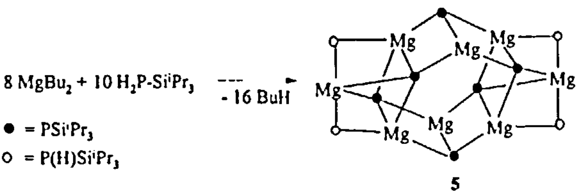
Magnesium-Phosphorus Cages

The magnesiation of $H_2PSi^tBu_3$ in toluene yields the hexameric solvent-free magnesium tri(tert-butyl)silylphosphandiide **1** with a central hexagonal Mg_6P_6 prism [7]. However, the performance of this reaction in THF leads to the formation of the tetramer $[(THF)Mg(\mu_3\text{-}PSi^tBu_3)]_4$ (**2**) due to the enhanced steric strain induced by intramolecular repulsion between the THF molecules and the trialkylsilyl substituents (Scheme 1) [8].



SCHEME 2. Magnesiation of $H_2PSi^tBu_3$ in toluene with a 4/6 stoichiometry and formation of **3**.

The metalation of $H_2PSi^tBu_3$ with dibutylmagnesium in toluene in a molar ratio of 4/6 yields a M_4P_2 octahedron with $Mg[P(H)Si^tBu_3]_2$ molecules above the Mg···Mg edges (**3**) as shown in Scheme 2.

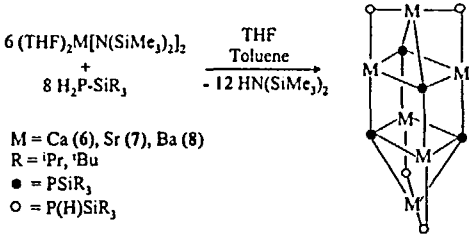


SCHEME 3. Magnesiation of triisopropylsilylphosphane in toluene and formation of **5**.

The magnesiation of the sterically less demanding triisopropylsilylphosphane in THF yields the similar THF complex $[(THF)MgPSi^iPr_3]_4$ (**4**) as described above for **2**, however, the choice of toluene as a solvent leads to the formation of a hexagonal Mg_6P_6 prism with two opposite planes capped by $Mg[P(H)Si^iPr_3]_2$ molecules (**5**) as shown in Scheme 3 [9].

Metal-Phosphorus Cages of Ca, Sr, and Ba

The metalation of triisopropyl- and tri(tert-butyl)silylphosphane with $(THF)_2M[N(SiMe_3)_2]_2$ (M = Ca, Sr, and Ba) in toluene or THF yields alkaline earth metal-phosphorus cages with M/P ratios of 6/8 as shown in Scheme 4 (M = Ca (**6**), Sr (**7**), Ba (**8**) [10]). The central fragment is a M_4P_4 heterocubane moiety with two opposite planes capped by $M[P(H)SiR_3]_2$ molecules.



SCHEME 4. Metalation of $H_2PSi^iPr_3$ and $H_2PSi^tBu_3$ in THF and toluene with alkaline earth metal bis[bis(trimethylsilyl)amides].

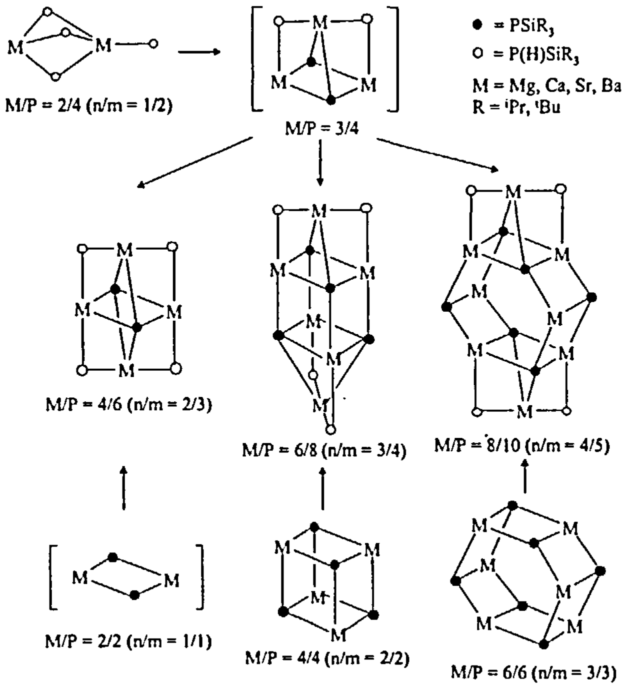
Topological Relations

Scheme 5 shows the topological relations between the alkaline earth metal-phosphorus cages of the type $M_{2n}P_{2m}$. The compounds drawn in square brackets are not isolated, however, $M_3(PR)_2(PHR)_2$ shown in the top row is well-known for some heterobimetallic cages with tin(II) [5].

Prospectives

A dimeric alkaline earth metal trialkylsilylphosphandiide as displayed in the bottom row of Scheme 5 is also thus far unknown. Attempts to isolate a dimer via the addition of a bidentate ether such as DME failed.

The isolated compound 9 is a tetramer with a central heterocubane fragment because this ether shows a monodentate coordination behavior as shown in Figure 1.



SCHEME 5. Topological relations between the alkaline earth metal-phosphorus cages of the type $M_{2n}P_{2m}$.

The reactivity of the magnesium trialkylsilylphosphandiides differs from that of the alkaline earth metal bis[bis(trialkylsilyl)phosphanides]. Contrary to the reaction of $M[P(SiMe_3)_2]_2$ with benzonitrile which yields the corresponding 1,3-bis(trimethylsilyl)-2-phenyl-1,3-azaphosphapropenides compound 1 trimerizes benzonitrile and 2,4,6-triphenyl-1,3,5-triazine as well as $[(Ph\text{-}CN)Mg]_4Mg_2[\mu_3\text{-}PSi^tBu_3]_6$ (10) are isolated. The molecular structure of the latter compound is shown in Figure 2, the hexagonal Mg_6P_6 prism is retained.

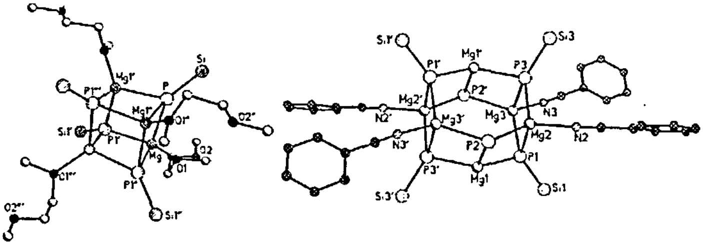


FIGURE 1. The molecular structures of $[(DME)MgPSi^iPr_3]_4$ (9) (left) and $[(Ph\text{-}CN)Mg]_4Mg_2[\mu_3\text{-}PSi^tBu_3]_6$ (10) (right). Silicon-bonded alkyl groups are omitted for clarity.

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