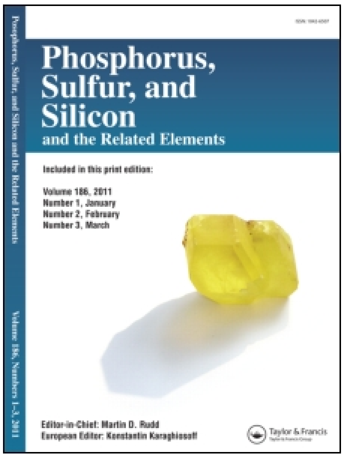

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OLIGODENTATE SILYLPHOSPHANIDES AND RELATED SYSTEMS: A NEW CLASS OF MOLECULAR AGGREGATES

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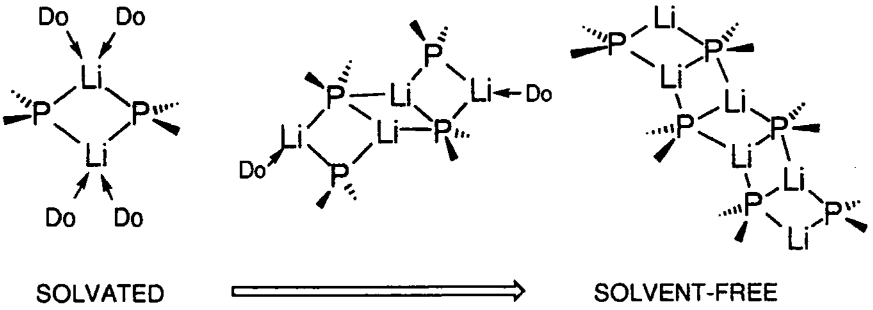
Abstract The structures of the self-assembled, solvent-free dipodal diphosphandiide [Is(*t*Bu)Si(PRLi)$_2$ LiCl](Is = 2,4,6-*i*Pr$_3$C$_6$H$_2$; R = H, SiPh$_3$), and of the tripodal systems EtSi[P(Si*i*Pr$_3$)M]$_3$ (M = Li,Na) are presented.

INTRODUCTION

The stucture principles of aggregation of alkalimetal main-group element compounds are a matter of fundamental interest. Due to their importance in preparative organometal chemistry, particularly lithium main-group compounds like lithium alkanides, phenylides, and amides have been studied.[1] The use of mono- and difunctional amides as precursors for transmetallated main-group element amides[2] has offered some insight into structure-reactivity relationship.

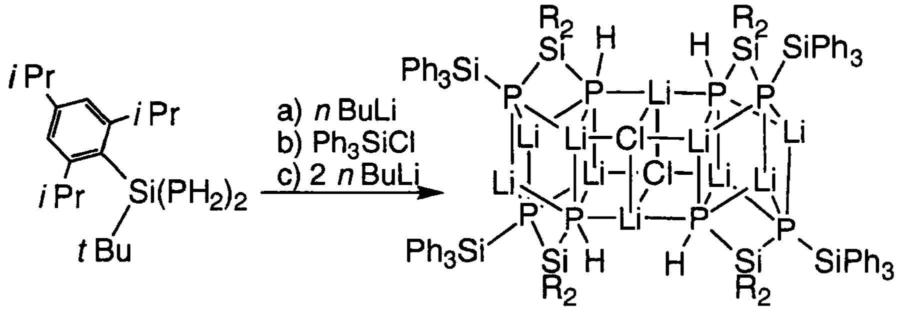


Scheme 1: Self-aggregation of LiPR$_2$ compounds

Most developed in the serie of heavier pnictides, the structures of some lithium diorgano- and disilylphosphanides[3] have been studied by means of X-ray crystallography. Their aggregation stage is depending on the number of donor molecules (scheme 1). According to the "laddering principle" as observed for amides, a hexameric aggregate of $LiP(SiMe_3)_2$ with ladder-like structure has been established.[3] In the course of our investigations of donor solvent-poor and -free alkalimetal mono-, bis-, and tris(phosphanido)-silanes $R_nSi[P(SiR_3)M]_{4-n}$ (n = 1-3; M = Li, Na, K, Rb, Cs), we isolated some new polycyclic aggrgates having unprecedented structures. We report here on three examples.

THE "DIMER OF DIMERS" $[Is(tBu)Si(PRLi)_2\ LiCl]_2$
($Is = 2,4,6\text{-}iPr_3C_6H_2$; R = H, $SiPh_3$)

Sterically demanding substituents at silicon are mostly responsible for the high stability of the diphosphinosilane **1**, which can be destilled at 110°C (10^{-3} Torr) without decomposition. Remarkably, **1** is transformed into the "dimer of dimers" **2** by an one-pot reaction.[4]



1 **2**

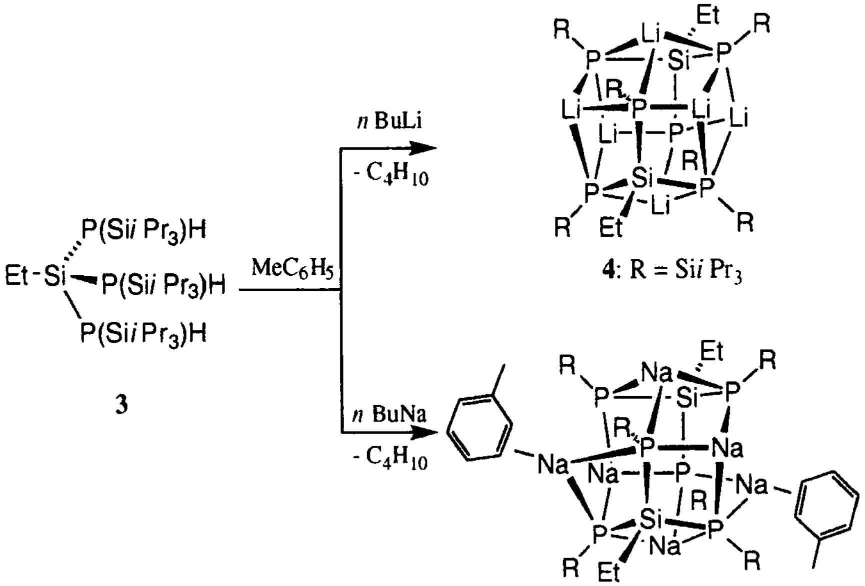
Monolithiation of **1**, subsquent silylation with Ph_3SiCl and partial deprotonation of phosphorus with two equivalents *n*BuLi gives colorless crystals of **2** in 52% yield.

Its structure has been determined by X-ray crystallography.[4] The $Si_2P_4Li_6Cl_2$-skeleton of **2** can be best regarded as a double aggrgate of two $Si_2P_4Li_4$- pseudo antiprisms which are held together by the $(LiCl)_2$ molecule as "aggregate glue".

The phosphorus atoms are five- and six-fold coordinated, whereas the lithium centres are distorted tetrahedral surrounded. Several phenyl groups of the $SiPh_3$ substituents have π interactions with the lithium centres Li1 close by (η^2 fashion). The chlorine centres, however, are pseudo trigonal bipyramidal coordinated as expected for their electronic situation (VSEPR model). The Si–P (2.237-2.252(2) Å) and Li–P distances (2.55-2.67(3) Å) obtained in this structure lie within the normal range of lithiumsilylphosphanides.

TRIPODAL TRIS(SILYLPHOSPHANIDYL)SILANES WITH Li AND Na CENTRES AT PHOSPHORUS

Silylation of $Et{-}Si(PH_2)_3$ with $iPr_3Si{-}OTf$ (OTf = Triflat) in the presence of $LiNiPr_2$ as an auxiliary base leads to the tris(silylphosphino)silane **3**. Metalation of the phosphorus atoms in **3** with *n*BuLi and *n*BuNa in toluene gives the colorless crystalline compounds **4** and **5**.[5]



3

4: R = Si*i*Pr₃

5: R = Si*i*Pr₃

The molecular structures of **4** and **5** were determined by X-ray crystallography. Compound **4** has a $Si_2P_6Li_6$ molecular framework with a center of symmetry; this novel structure motife for phosphanides has the topology of a distorted rhombododecahedron. Compared with that, **5** possess surprisingly a open polyhedral $Si_2P_6Na_6$ framework structure, in which two sodium centres are η^2 coordinated with two toluene molecules (Fig.1).

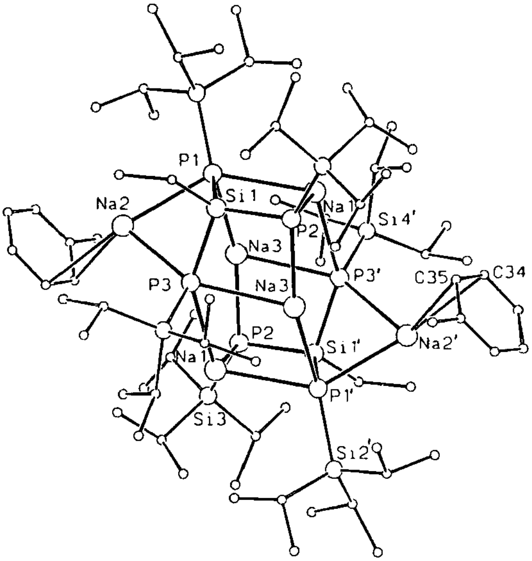


Figure 1: Solid state structure of **5**

Both compounds are dimers of the metalated tris(silylphosphanidyl)silane **3**, that is, they are self-assembled metal-phosphorus aggregates. The bonding situation in **4** and **5** can be described by metal-phosphorus multicenter bonds in the sense of clusters.

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