Acc. Chem. Res. **1999,** *32,* 1017−1025

Multiple-Shell Clusters of Alkali Metal-Rich Phosphanides and Arsanides

MATTHIAS DRIESS*

Lehrstuhl für Anorganische Chemie I, Molekül- und
Koordinationschemie, Fakultät für Chemie der
Ruhr-Universität Bochum, Universitätstrasse 150,
D-44801 Bochum, Germany

Received July 8, 1999

Introduction

Understanding structure−reactivity relationships is an important prerequisite to recognizing general concepts and to refining synthetic methods in chemistry. The question of how to control regio- and stereoselectivity in reactions when ionogenic associates (e.g., organolithium reagents) are employed as nucleophilic (basic) reagents toward different electrophiles is an actual topic in molecular chemistry. Whereas this question has already been answered for many cases of organolithium compounds,[1] lithium amides, lithium imides, and related systems,[2] little is known about appropriate methods to control the reactivity pattern of respective metalated heavier homologues (e.g., silanides, phosphanides, and arsanides). However, metalated compounds of the heavier main group 5 elements (pnictogens) play an important role in organometallic synthesis. In particular, lithium derivatives deserve attention as key reagents for many pnictide transformation and acid−base reactions. In fact, molecular monometalated phosphanides and arsanides are valuable nucleophilic phosphorus- and arsenic-transfer reagents for the introduction of phosphaneyl and arsaneyl groups into diversely functionalized systems, but knowledge of their structure−selectivity relationships seems relatively scarce.[3] Even more unexplored is the state of metal-rich polyanionic systems. Structural insight into the chemistry of molecular main group dimetalated primary phosphanes and arsanes was not developed until 1996, when the first structures of dilithium derivatives of primary phosphanes and arsanes were reported.[4] The considerable interest generated by this fairly young class of compound cannot be denied: molecular dimetalated phosphanes and arsanes are among the most reactive nucleophilic phosphorus- and arsenic-transfer reagents, but, however, they are usually obtained in the form of amorphous, insoluble solids.[5−8] Their tendency to aggregate lies between those of monometalated derivatives and typical solid-state structures of binary main group metal pnictides (e.g., Li_3P).[3,9] Thus, they can be regarded as intermediates between molecular clusters and typical solid-state compounds in the pnictide series (Figure 1).

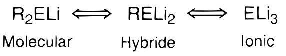

$R_2ELi \Longleftrightarrow RELi_2 \Longleftrightarrow ELi_3$

FIGURE 1.

In addition, discrete cluster compounds of the phosphandiide and arsandiide series are a new class of "container molecules" which can adopt a large variety of cluster shapes. Moreover, they represent one of the rare types of spherical molecules comprising an anionic framework of heavier main group elements.[10] The purpose of this Account is to present main structural features of spherical alkali metal-rich pnictide clusters which may help readers to understand the tremendously different reactivities of mono- versus dimetalated phosphanes and arsanes, respectively.

Structural Principles of Molecular Main Group Metal Pnictides

The ionic character of main group metal−pnictogen bonds with alkali and alkaline earth metals (groups 1 and 2) is relatively large (>90%) due to the huge differences in electronegativities, whereas groups 3 and 4 metals possess more covalent properties. The presence of lone pair electrons at the pnictogen atom adjacent to an coordinatively unsaturated metal center in monomeric metalated amines and their homologues strongly favors intermolecular head-to-tail oligomerization to give molecular aggregates. Such clustering is typically seen if electron-precise and electron-deficient centers are present in a molecule at the same time. While the ionicity of groups 1 and 2 amides, phosphanides, and their congeners determines primarily their structural chemistry, the oligomeric structures of molecular groups 3 and 4 pnictide compounds are more influenced by steric and strain effects incurred by the substituents. The resulting aggregates adopt the different types of cluster structures, **A**−**J**, depending on the nature of the metal (atom/ion size, partial charge, polarizability), steric demands of the substituents, and solvation of the metal centers, which has also been seen for other metal−heteroatom associates (Figure 2).[3] Extensive theoretical studies on aggregates of lithium compounds, which represent the most basic reagents in synthetic chemistry, witnessed the importance

---

Matthias Driess was born in 1961 in Eisenach, East Germany. He received his chemistry diploma and Ph.D. degree from the University of Heidelberg under the supervision of Professor Walter Siebert. After a one-year postdoctoral position with Professor Bob West in Madison, Wisconsin, he retured to Heidelberg and finished his habilitation in 1993. After two more intellectually exciting years as lecturer at the Inorganic Chemistry Devision in Heidelberg, he took up a chair of Inorganic Chemistry at the Ruhr-University Bochum in 1996. His research activities are presently devoted to polymetalated molecular main group element clusters, reactive intermediates in Group 14 (Si, Ge, Sn, Pb) and Group 15 element (P, As, Sb, Bi) chemistry (low-coordination states), design of polyphosphane ligands with a silicon−phosphorus backbone, and synthesis of metastabile multinary solids starting from fragile molecuar single-source precursors. He received a generous fellowship of the "Fonds der Chemischen Industrie" (1996) and the Chemistry Award of the Academy of Science at the University of Göttingen in 1997.

---

* E-mail: driess@ibm.anch.ruhr-uni-bochum.de.

10.1021/ar990038k CCC: $18.00

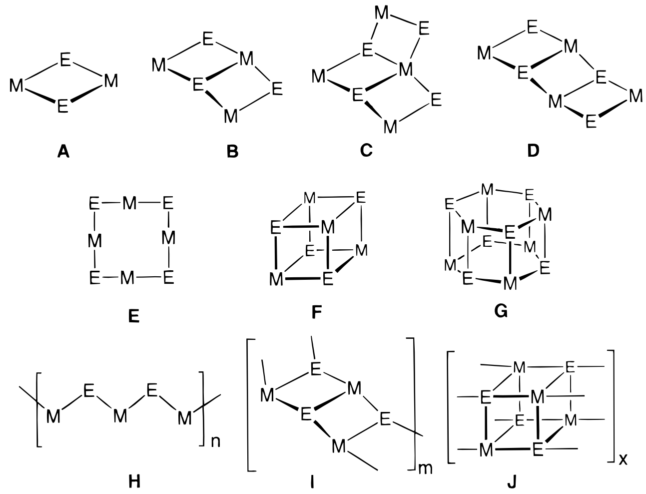


FIGURE 2.

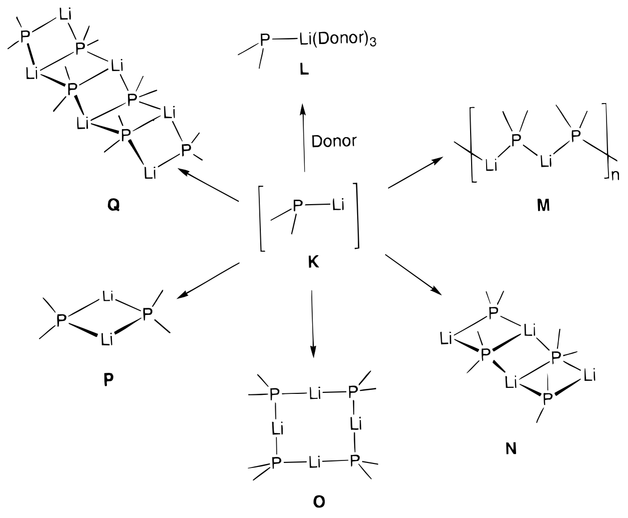
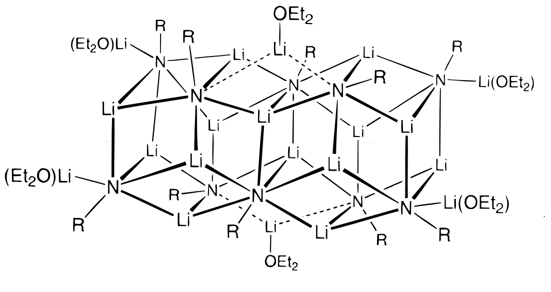


FIGURE 3.

of steric and electronic effects (e.g., nature of the pnictogen atom, solvation effects, etc.).[11]

Hitherto, no monometalated molecular pnictide exists without solvation of the main group metal atom. Therefore, the monomeric species **L** (Figure 3) can be stabilized only if the Li ion coordination sphere is enlargened through donor solvation. More importantly, the lithium phosphanides of type **K** undergo oligomerization processes to form dimeric, tetrameric, hexameric, and polymeric assemblies, **M**−**Q** (Figure 3), which dissociate in solution more easily than related amides.[3,12,13]

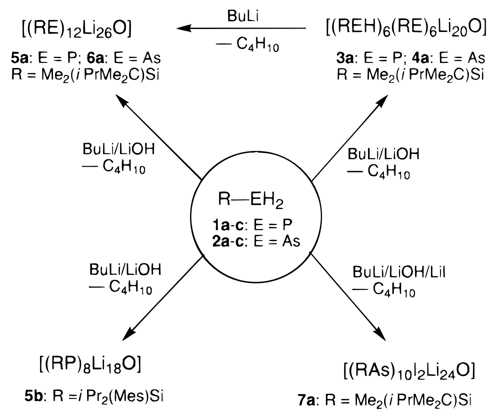
The aggregates of types **N** and **Q** possess ladder-like, two-dimensional structures of which the size is strongly dependent on the degree of solvation of the lithium center and the steric demand of the silyl group. Due to the lipophilicity of the trimethylsilyl ligands and other organosubstituted silyl groups, the degree of association and the solubility of the resulting clusters can be controlled in various ways. For topological reasons, self-assembly processes lead, in the case of bis- and tris(lithium pnictideyl) silanes or germanes, to aggregates which adopt, per se, three-dimensional, ladder-like skeletons.[14,15] The topology of such two- and three-dimensional clusters is the result of a close packing of anionic pnictide moieties with alkali metal ions, which maximizes ionic interactions. As expected, three-dimensional aggregates, possessing ladder-like closed structures, have also been formed for dimetalated amines and phosphanes and their congeners. However, only one dilithium derivative of a primary amine has been structurally elucidated thus far: the dilithium azandiide of α-naphthylamine furnishes in Et_2O the decameric form **R**, which consists of a $N_{10}Li_{14}$ cluster framework (Figure 4).[16] The latter framework can be described as being composed of two face-fused rhombic dodecahedra which coordinate to the remaining six exohedral $Li(OEt_2)$ groups. This clearly demonstrates that the "oligomer-laddering" model is retained as a basic structural principle even for multivalent molecular pnictides.



R = α-Naphthyl

FIGURE 4.

Scheme 1. Synthesis of E_nLi_mO Clusters (E = P, As)



Dilithiation and Disodiation of Primary Phosphanes and Arsanes

The considerably strong tendency of dimetalated group 1 metal derivatives of primary phosphanes and arsanes has been hampered by the lack of isolable crystalline material. Thus, dilithiation of the organophosphanes RPH_2 (R = Ph, cyclohexyl) with PhLi in Et_2O or other polar solvents has led to amorphous and insoluble $RPLi_2$.[5] Similarly, the same reaction with more lipophilic substituted phosphanes such as $MesPH_2$ (Mes = 2,4,6-$Me_3C_6H_2$)[17] or Mes^*PH_2 (Mes^* = 2,4,6-t-$Bu_3C_6H_2$)[18] has also resulted in unsatisfactory results. Only the employment of triorganosilyl groups at phosphorus and arsenic in respective silylphosphanes and silylarsanes solved this problem, due to the stronger E−H acidity (E = P, As) as well as the

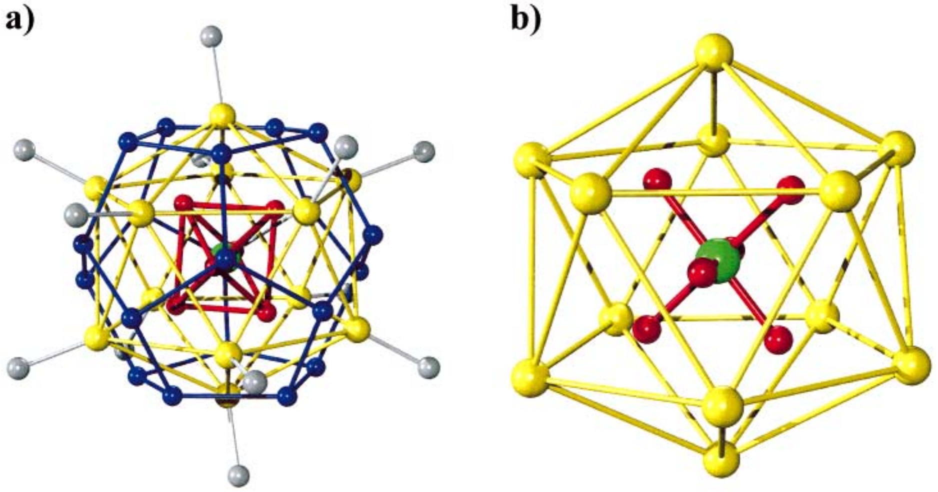


FIGURE 5. (a) Topological representation of the $E_{12}Li_{26}O$ cluster **5a** (E = P) and **6a** (E = As); E = yellow, Li = blue, red, O = green, Si = gray. Organic groups have been omitted for clarity. (b) Orientation of the Li_6O core within the E_{12} icosahedral shell (E = P, As).

higher solubility of the dimetalated derivatives in hydrocarbon and ethereal solvents.[4] However, only the corresponding complexes with Li_2O (Li_2O inclusion compounds) and redox reactions under partial H_2 elimination have been isolated. The latter led, for first time, to mixed-valent lithium-rich pnictides.[19]

(a) Spherical Clusters of Dilithium Derivatives with Li_2O Inclusion. Dilithiated primary phosphanes could be isolated in a reproducible crystalline form only if the lithiation of the phosphane with BuLi (ratio of 1:2) in toluene had been carried out in the presence of a trace amount of LiOH.[4] This is evident from the respective transformation of the silylphosphanes **1**, which furnished, depending on the steric demand of the silyl group, a dodecameric or an octameric associate (Scheme 1). Thus, reaction of **1a** with BuLi in the molar ratio of 1:2 led to the globular, Li_2O-filled cluster **5a**, whereas metalation of the bulkier substituted phosphane **1b** gave the Li_2O-filled octamer **5b**.

It seems clear that LiOH/Li_2O serves as a template during the formation of the closed clusters. This has been corroborated by the partial lithiation of **1a** with BuLi in the molar ratio of 2:3, which furnished colorless crystals of the intermediate **3a**. Complete lithiation of **3a** led to yellow crystals of **5a** in high yield. (Scheme 1).[19] The analogous intermediate **4a** has been accessible by the same procedure, starting from the corresponding arsane **2a**; complete lithiation furnished cluster **6a** in the form of pale orange crystals. The Li_2O-filled dodecameric clusters **5a** and **6a** are isotypic. There are obviously different possibilities to model the structures discussed above: first, by drawing (conventional) bonding lines which define attractive interactions between anionic E centers (E = P, As, O) and Li cations (three-dimensional globular laddering of the Li−E network), or second, by means of topological lines between identical anionic and cationic centers, respectively, resulting in a close packing of interpenetrating subshells (multiple shell description). The advantage of the latter model is that one can easily recognize the importance of close packing under internal symmetry relations. Therefore, the ionogenic aggregates are topologically best described as being composed of three closed (platonic) shells covered by lipophilic triorganosilyl groups (Figure 5a,b).[4,19] The E centers (E = P, As) constitute the anionic partial structure of the clusters and form a slightly distorted E_{12} icosahedron, in which each of the 20 triangular faces is capped by a Li center. The 20 Li centers thereby adopt a pentagonal dodecahedron as a dual polyhedron with approximately I_h point symmetry.

The remaining four Li centers are located in the void of the interpenetrating double shells $(E_{12}Li_{20})^{4-}$ (diameter ca. 8 Å). These Li centers are complexed by an encapsulated Li_2O molecule, leading to the formation of a $[Li_6O]^{4+}$ octahedral core. This core has approximately O_h symmetry and is tilted with respect to the orientation of the E_{12} icosahedron. The latter reflects symmetry "frustration", which is the result of the incompatibility between I_h and O_h point group symmetric bodies. Six-fold coordination of O^{2-} by metal ions in molecular compounds is relatively rare.[20] The Li centers of the inner Li_6O core are, as expected, still coordinated to E centers in close proximity. Therefore, their coordination numbers are 4 and 3, whereas the "external" 20 Li centers are three-coordinated. The related aggregates **3a** and **4a** crystallize in a different space group. Although they have a shell structure to those of **5a** and **6a** (Figure 6a), they merely possess a Li_2O core.

The "open" clusters **3a** and **4a** consist of a three-dimensional, wheel-like $E_{12}Li_{18}$ ladder framework whereby the Li_2O molecule in its void may be regarded as a "stabilizing axis" of the wheel. The remaining E−H hydrogen atoms are probably located on E atoms of the hexagonal E_3Li_3 holes (Figure 6b). Even larger triorganosilyl groups at phosphorus lead to aggregates with a smaller degree of association, as shown for the octameric phosphandiide cluster **5b** (Figure 7).[4] It also consists of three ionic shells which are wrapped by the lipophilic silyl "skin". The eight P atoms of the anionic shell comprise a severely distorted cube, which is surrounded by a Li_{12}

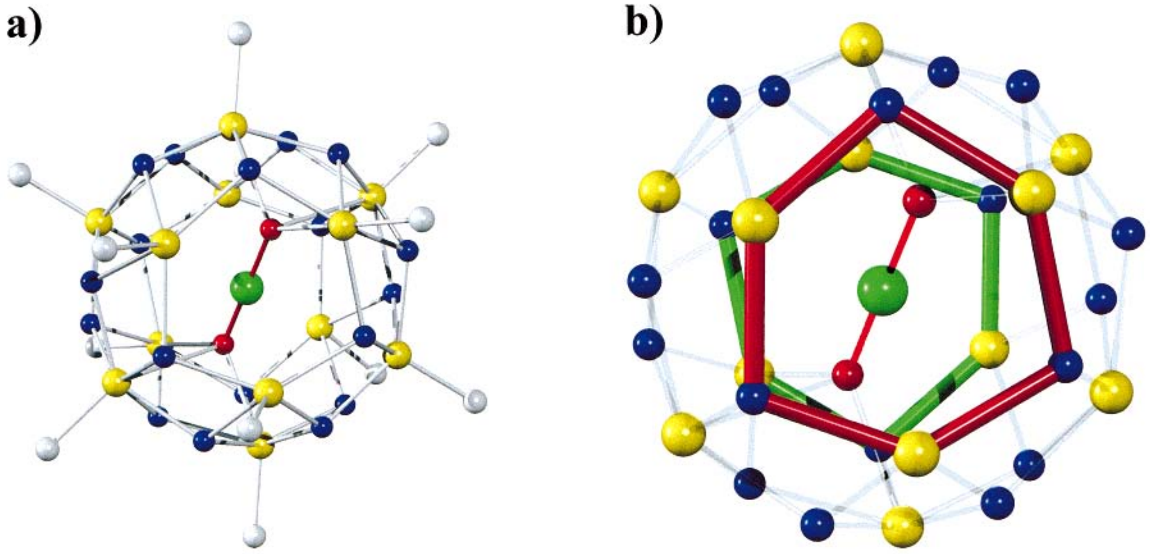


FIGURE 6. (a) Structure of **3a** (E = P) and **4a** (E = As); E = yellow; Li = blue, red, O = green, Si = gray. Organic groups have been omitted for clarity. (b) Structure of **3a** (E = P) and **4a** (E = As) along the hexagonal E_3Li_3 voids; E = yellow, Li = blue, red, O = green. Silyl groups at the E atoms have been omitted for clarity.

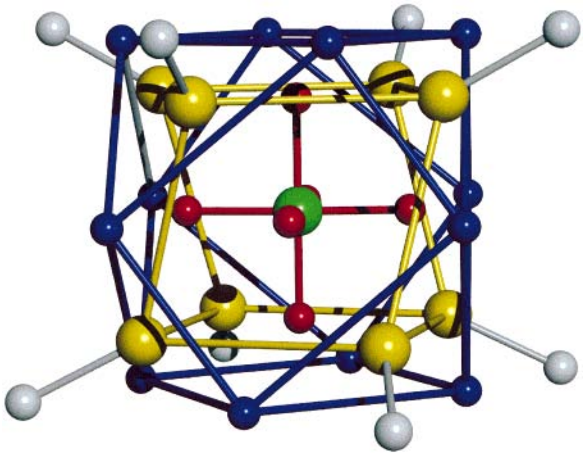


FIGURE 7. Structure of **5b**; P = yellow, Li = blue, red, O = green, Si = gray. Organic groups have been omitted for claritiy.

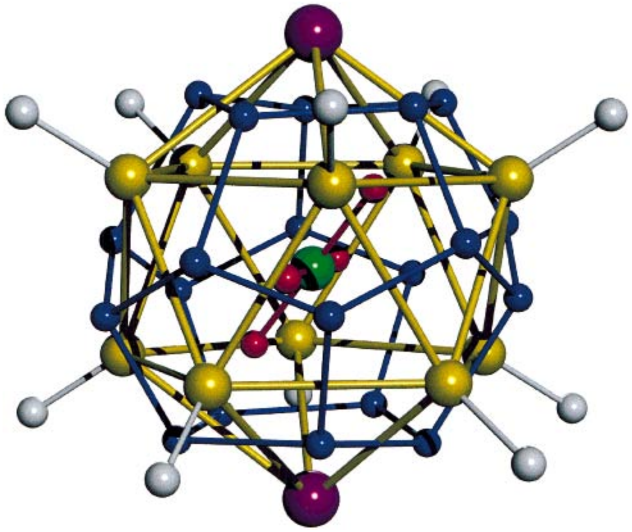


FIGURE 8. Structure of **7a**; As = yellow, I = ruby, Li = blue, red, O = green, Si = gray. Organic groups have been omitted for clarity.

cube-octahedron, which additionally surrounds a Li_6O octahedron.

In contrast to the “outer” Li shell in **5a**, the Li centers of the Li_{12} cube-octahedron are located on the edges of the P_8 framework, whereas the Li centers of the Li_6O core are each located over a face. This situation led to different coordination numbers (2 vs 4) for the two types of Li centers, implying much shorter Li−P bonds for the “external” ones (Δ ca. 0.2 Å). Some of the 12 As centers of the anionic icosahedral partial structure in **6a** can be replaced by other anions, which has only recently been demonstrated (Scheme 1).[21] Thus, **7a**, which can be prepared by dilithiation of the arsane **2a** with BuLi in the presence of trace LiOH and a molar excess of LiI, possesses a slightly distorted anionic icosahedral framework, which is identical to that observed for **6a**, but two of the $(AsR)^{2-}$ units are replaced by iodide centers. (Figure 8).

The O^{2-} center of the encapsulated Li_2O is only square-planar coordinated due to the lower lithium content. However, the four Li centers of the Li_4O core show dynamic disordering, even at −80 °C, whereas the Li centers of **3**−**6** are not dynamic in the solid state up to 50 °C. Bulkier substituted primary silylphosphanes than **1b** could not be transformed with BuLi in the presence of LiOH to a crystalline, Li_2O-containing dilithium derivative.[22] The multinuclear NMR spectra of the Li_2O-filled clusters **3a**, **4a**, **5a**, **5b**, and **6a** in toluene or THF suggest that the compounds possess a low tendency for dissociation in solution. The latter is proven by cryoscopic measurements in benzene with different concentrations. The remaining E−H protons (E = P, As) in the partially lithiated derivatives **3a** and **4a** were detected in the ^1H NMR spectra.[19] Correspondingly, the E−H streching frequencies for **3a** ($\nu = 1930$ cm^{-1}) and **4a** ($\nu = 1897$ cm^{-1}) clearly corroborate the presence of E−H moieties. The CP/MAS ^{29}Si solid-state NMR spectrum of **6a** proves the presence of six crystallographically (and chemically) dif-

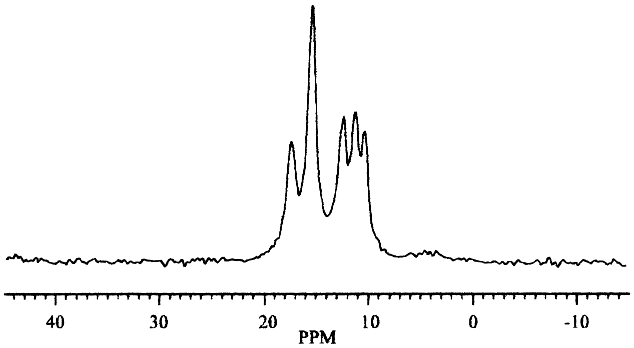


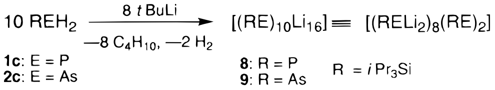
FIGURE 9. ^{29}Si-MAS solid-state NMR spectrum of **6a**.

ferent ^{29}Si nuclei, of which two sorts coincide (Figure 9). It is noteworthy that the ^{7}Li NMR spectrum of **6a** in solution (Figure 10) shows the expected distinction of four Li sorts: the two singlets at $\delta = 1.78$ and 1.56 correspond to the Li_{20} shell ("outer" Li centers), whereas the broad signal at $\delta = 0$ and the singlet at $\delta = -1.32$ has been assigned to the "inner" Li centers of the Li_6O core.[4]

(b) How To Change: Spherical Clusters without Li_2O Inclusion. Reaction of the phosphane **1a** and the arsane **2a** with freshly sublimed *t*-BuLi in the molar ratio of 1:2 in toluene at −80 °C led, surprisingly, to the decameric clusters **8** and **9** in high yield (Scheme 2).[19]

Remarkably, molecular hydrogen has been evolved concomitantly, implying the occurrence of a redox reaction during the lithiation. Indeed, **8** and **9** represent lithium-poor, mixed-valent phosphandiide and arsandiide clusters, having a Li:E ratio (E = P, As) of only 1.6:1. No remaining E−H bonds are left in **8** and **9**, which has subsequently been proven by ^{1}H NMR and IR spectroscopy. It is also noteworthy that the same clusters can been formed if **1c** and **2c** are added in molar deficiency to a solution of *t*-BuLi in toluene at −80 °C. Apparently, the formation of a closed cluster framework is favored, leading to an E−H activation of the endothermic E−H bonds[23] and reductive H_2 elimination during the lithiation process. The electrostatically favored cation (Li) and anion (RE) arrangement implies the presence of each two different E, Si, and Li sorts, which has been established by solution- and solid-state NMR spectroscopy. The electronic structures of the mixed-valent pnictides **8** and **9** have been described simply as electron-deficient clusters with delocalized framework electrons. Formally, the latter consists of two low-valent "anediyl" moieties RE: and eight "andiides" $(RE)^{2-}$ (E = P, As). The relatively large E−E distances of >4 Å exclude the occurrence of localized E−E bonds. However, delocalization of the cluster valence electrons is achieved without Li−Li bonds via Li-mediated multiple bonding. Evidence for this has been seen in the NMR spectra (^{31}P, ^{7}Li, ^{29}Si), which are in accordance with the electron delocalization model. The oval $E_{10}Li_{16}$ cluster skeleton (E = P, As) is topologically best described as a two-fold capped cubic antiprism (Archimedean antiprism) formed by the 10 E atoms, of which each of the 16 deltahedral faces is occupied by a lithium center (Figure 11).[19]

Scheme 2. Synthesis of the $E_{10}Li_{16}$ Clusters (E = P, As) 8 and 9



$$10\ REH_2 \xrightarrow[-8\ C_4H_{10},\ -2\ H_2]{8\ t\text{BuLi}} [(RE)_{10}Li_{16}] \equiv [(RELi_2)_8(RE)_2]$$

1c: E = P
2c: E = As
8: R = P
9: R = As
R = *i* Pr_3Si

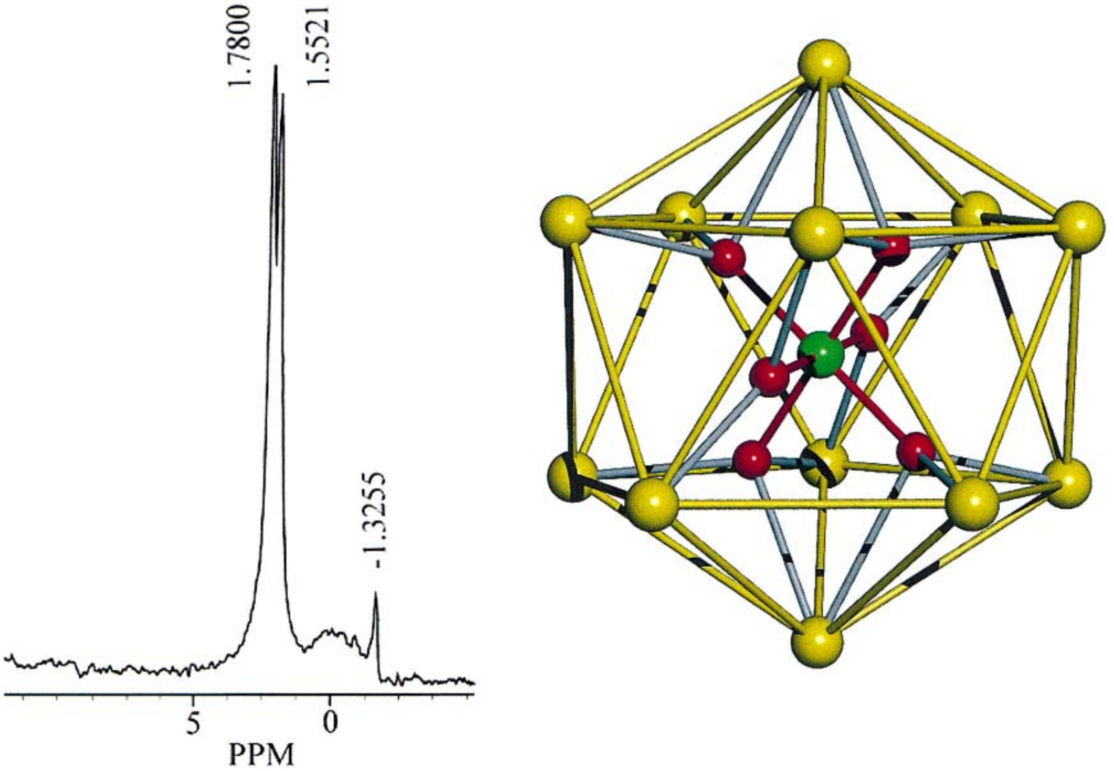


FIGURE 10. (Left) ^{7}Li NMR spectrum of **6a** in solution. (Right) Different coordination mode of the Li ions of the Li_6O core within the As_{12} icosahedron in **6a**; As = yellow, Li = red, O = green.

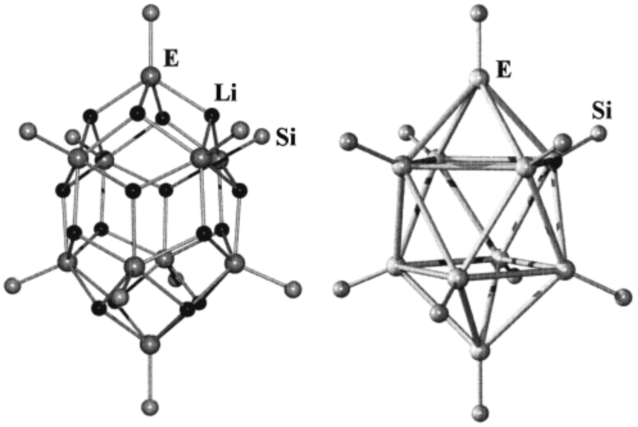


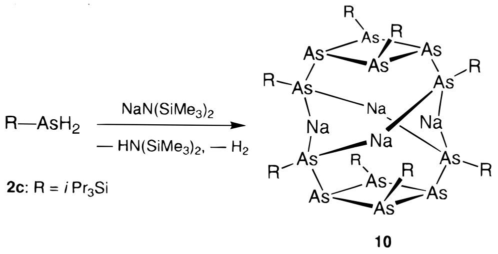
FIGURE 11. Structure of **8** (E = P) and **9** (E = As). Organic groups have been omitted for clarity.

Thereby, two of the E centers result in five-coordination, whereas the remaining eight are six-coordinated. However, the respective average Li−E, Si−E, and Li−Li distances are unremarkable with respect to the values in **3a**, **4a**, **5a**, and **6a**, and the Li−E distances differ only marginally.[4,19] All of the metal pnictide clusters discussed above are more strongly aggregated than their monometalated analogues. Thus, the NMR spectra of **8** and **9** show that the structures are retained in solution. Furthermore, the ^{31}P-decoupled CP/MAS ^{29}Si solid-state NMR spectrum of **8** shows two singlets at $\delta = 27.9$ and 29.0 in the ratio of 4:1, whereas the ^{7}Li{^{31}P} NMR spectrum exhibits two singlets at $\delta = 1.42$ and 1.65 in the expected ratio of 1:1.[24] Cryoscopic measurements have proven that the degree of aggregation of **8** is $n = 8$.[19]

(c) Disodium Derivatives with Li$_2$O Filling and a Tetrasodium Dication Cluster. The synthesis of crystalline disodium derivatives of primary phosphanes and arsanes turned out to be more difficult than that of dilithium compounds. The compounds NaN(SiMe$_3$)$_2$ and BuNa have been employed as sodiation reagents of choice. Metalation of the arsane **2c** led, as its lithiation with *t*-BuLi, under redox reaction (H$_2$ elimination, As−As bond formation) to the Na$_2$As$_6$ dimer **10** (Scheme 3, Figure 12).[25]

The latter represents the first aggregate of a solvent-free tetrasodium polyarsanide which has been elucidated by X-ray diffraction analysis. The centrosymmetric dimer consists of four sodium centers which are embedded between the two (As$_6$)$^{2-}$ ligands. Interestingly, the unusual two-coordinated Na ions are bonded only to the anionic, exocyclic arsaneyl As centers of the cyclotetraarsane-1,4-bis(silylarsanide-yl) ligands [(As$_6$)$^{2-}$]. The large Na−Na distances of 3.6−3.8 Å are mainly due to repulsive electrostatic interactions. The strong tendency of silylarsanes to undergo redox reactions with basic and nucleophilic reagents seems to be responsible for the reaction of sterically congested silyl(fluorosilyl)arsane **2d** with NaN(SiMe$_3$)$_2$ in toluene over several days, which led to the **6a** analogue dodecameric disodium salt **6d** (Scheme 4). The latter contains one molecule of Na$_2$O, which is incorporated in the void of the dodecamer, giving a distorted [Na$_6$O]$^{4+}$ core (Figure 13). Therefore, the yield of **6d** is enhanced through the presence of Na$_2$O.[25]

Scheme 3. Synthesis of the As$_{12}$Na$_4$ Cluster 10



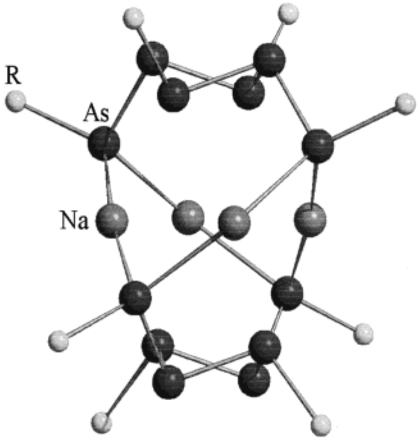
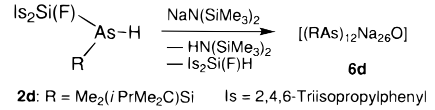


FIGURE 12. Solid-state structure of **10**. R = *i*-Pr$_3$Si.

Scheme 4. Synthesis of the As$_{12}$Na$_{26}$O Cluster 6d



Whereas the positions of the "outer" Na centers have been precisely located, the six "inner" Na centers can adopt 20 equivalent sites. This is probably due to the larger void of the As$_{12}$Na$_{20}$ double shells. However, the origin of this disorder (static and/or dynamic) is not yet known. In contrast, the same reaction between the bulkily substituted silyl(fluorosilyl)phosphane **1d** with NaN(SiMe$_3$)$_2$ underwent, surprisingly, a different course (Scheme 5). Its transformation in the molar ratio of 1:1 in toluene as solvent furnished the dimer **11**, whereas **1d** can be completely converted to **11** only if 2 molar equiv of sodium amide is employed, due to the initial formation of heteroaggregate intermediates.[26] Excess sodium amide has been recovered by fractional crystallization. However, if the reaction is performed at 60 °C during a prolonged reaction time (2 d), the unusual complex **12** is furnished as a side product in 8% yield (Scheme 5).[27]

Compound **12** is diamagnetic and represents the first tetrasodium−dication cluster which is stabilized by two sterically congested silyl(fluorosilyl)phosphanide counterions. It has been also independently synthesized through sodium consumption of **11** in the presence of styrene as catalyst in 24% yield. In contrast to the bonding situation in the dimeric tetrasodium salt **10**, Na−Na bonds are present in the case of the tetrasodium diphosphanide **12**. The centrosymmetric molecule comprises a rhomboidally distorted planar Na$_4$ cycle, which is the most interesting part of the aggregate (Figure 14).[27]

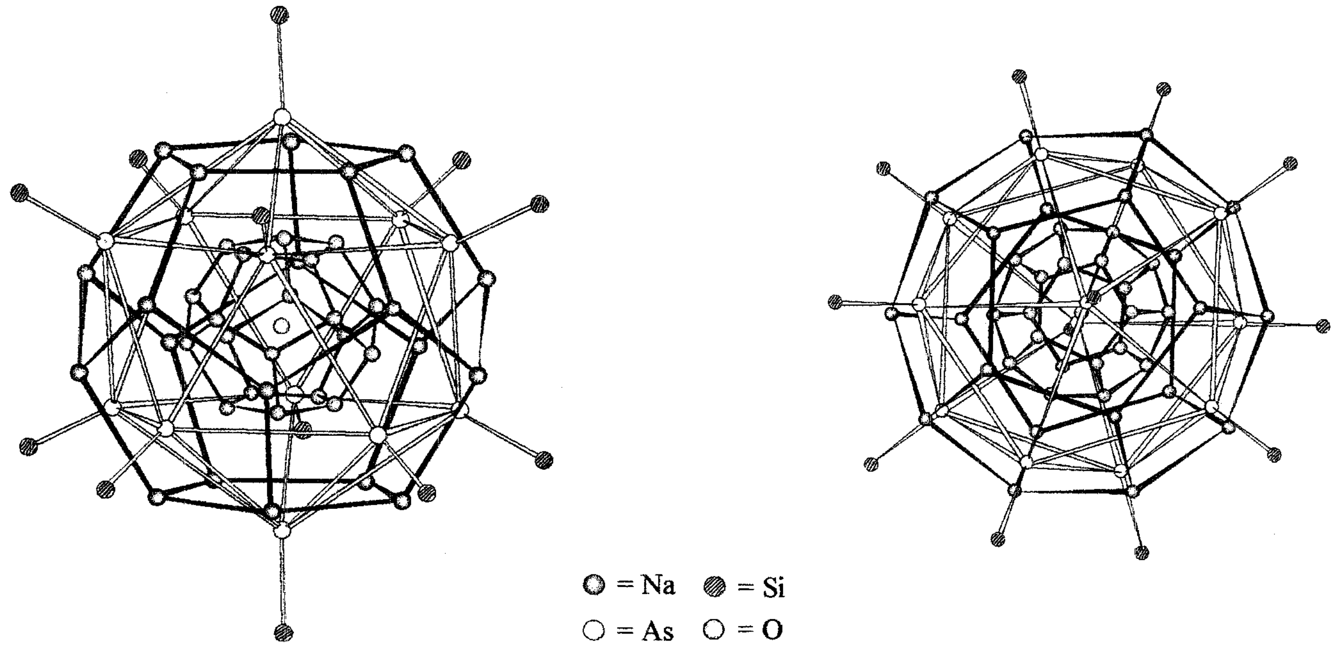
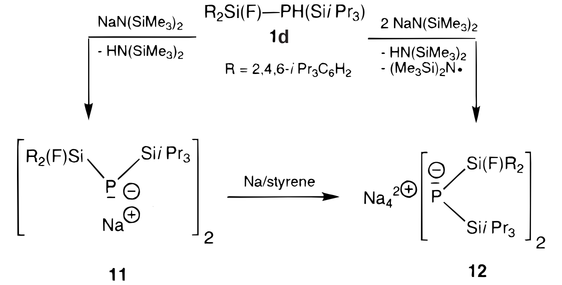
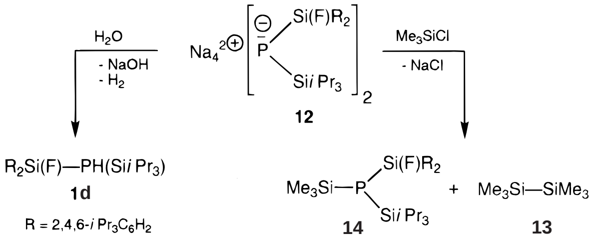


FIGURE 13. (Left) Topological representation of **6d**. (Right) View of **6d** along a C_5 axis.

Scheme 5. Synthesis of the Sodium/Phosphanide 11 and the Na_4^{2+} Salt 12



Scheme 6. Reactivity of 12



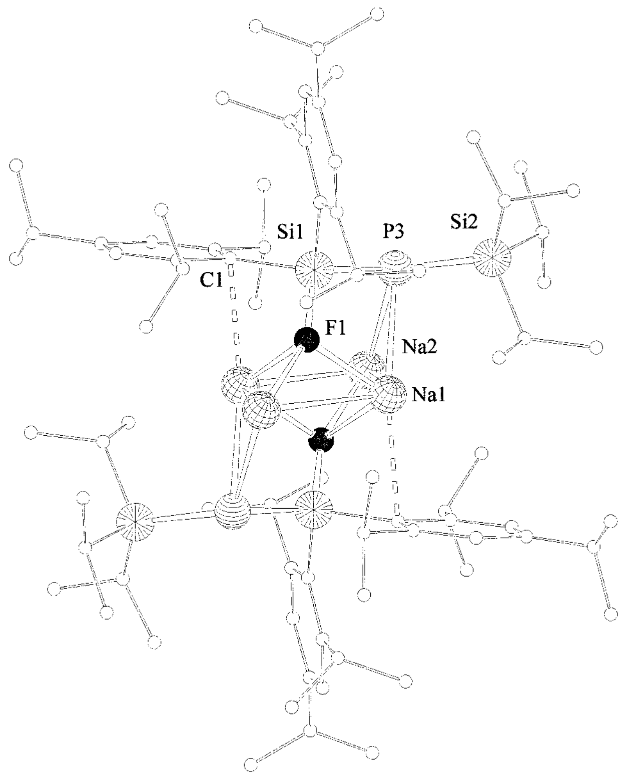
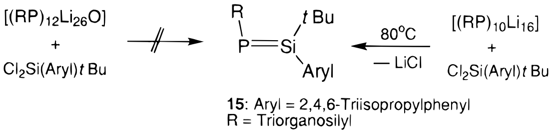


FIGURE 14. Structure of the Na_4^{2+} salt **12**.

The Na−Na distances of 3.07 (Na1−Na2) and 3.20 Å (Na1−Na1′) reflect Na−Na bonds (3.82 Å in elemental Na), whereas the Na1−Na2′ distance of 3.53 Å suggests less attractive interactions in compound **10**. The Na_4−dication cluster is embedded between two silyl(fluorosilyl)phosphanide counterions. The relatively low-coordinated Na centers are stabilized remarkably by the μ_3-fluorine atoms and by multiple-center Na−Na−P and *ipso*-C atom interactions. The Na−P distances of ca. 2.91 Å resemble those values observed for other sodium phosphanides.[14,28] Further, it is intriguing that **12** is intensely yellow and not red or blue as observed for Na-loaded zeolites (e.g., Na_4^{3+} and related clusters),[29] which suggests that the residual metal electrons are probably much less delocalized. Dimer **10** undergoes dissociation when dissolved in ethereal solvents, which is corroborated by cryoscopic measurements and ^{23}Na NMR; however, the Na_4 cluster salt **12** cannot be dissolved in any common organic solvents without decomposition (^{31}P and ^{19}F NMR spectroscopy), and attempts to record a CP/MAS solid-state NMR spectrum (^{19}F, ^{31}P, ^{23}Na) failed due to the large line-broadening by the ^{23}Na ions ($I = {}^3/_2$) and strong spin−spin coupling. The electron reservoir of the Na_4^{2+} cluster can serve for reduction processes; that is, it reduces Me_3SiCl to hexamethyldisilane **13**, besides formation of the trisilylphos-

Scheme 7. Formation of the Phosphasilene 15 by Salt Metathesis Reaction



phane **14**, and reacts with water to form **1d** with evolution of H_2 (Scheme 6).

Li_2O-Filled and Empty Clusters: What About Reactivity?

One important question is the following: Can these andiide clusters, disscussed above, serve as soluble RE^{2-}-transfer sources which can be employed even under relatively gentle reaction conditions? Therefore, it is instructive to compare the reactivities of the Li_2O-filled alkali metal-rich clusters **5a**, **5b**, and **6a** with those of the related mixed-valent ("empty") pnictide clusters **8** and **9**, respectively. Since these compounds are well soluble dilithiated phosphandiide and arsandiide derivatives, they can serve as nucleophilic building blocks in metathesis reactions. A considerable challenge would be their employment as phosphorus- and arsenic-transfer reagents, as demonstrated in the synthesis of metastable phosphasilenes (i.e., compounds with a Si═P bond). The latter contain relatively fragile multiple bonds and deserve, therefore, mild phosphandiide-transfer reagents. Not unexpectedly, the reactivities of Li_2O-filled vs "empty" mixed-valent clusters toward the bulky substituted dichloro(aryl)-*tert*-butylsilanes are remarkably different. In fact, while **5a** reacts with dichloro(isityl)-*tert*-butylsilane (isityl = 2,4,6-i-$Pr_3C_6H_2$) in toluene only above 110 °C with the formation of several products (no Si═P compound survives under those reaction conditions), the same reaction with the mixed-valent cluster **8** led to the desired phosphasilene **15** at 80 °C in 55% yield (Scheme 7).[30]

The lower reactivity of **5a** versus **8** reflects the stronger close packing of the anionic and cationic centers than that in the electron-deficient cluster **8**. Similar relations have been observed for analogous arsenic compounds.[30]

Summary and Outlook

Apparently, the solubility and the degree of aggregation of dimetalated phosphanes and arsanes can be controlled by employing appropriate lipophilic substituents at phosphorus and arsenic. In particular, triorganosilyl substituents fulfill this requirement. The tendency of such clusters to undergo dissociation in solution is crucial for their reactivity, which is particularly important for "andiide"-transfer reactions with electrophiles. However, the tendency for dissociation is determined not only by the metal−pnictogen bond polarity but also by the ability of the aggregates to form inclusion compounds. The latter has been obtained for dilithium and disodium "andiides", which easily accommodate M_2O (M = Li, Na) in their voids. The latter act as templates and seem to control the cluster size (degree of association). In addition, the resulting multiple-shell clusters adopt structural principles which are related to other inorganic "host−guest complexes" (e.g., most prominent are polyoxometalates).[31] However, this issue also provides model compounds for the study of nucleation processes of ionogenic materials.[32] As pointed out, the structural principle of aggregation is based mainly on the model of three-dimensional ring-laddering, leading to globular or spherical cluster frameworks. However, "what are the buildup steps" and "how do template effects of larger templates other than Li_2O influence the degree of aggregation" are essential questions which cannot be answered yet. The formation of the mixed-valent pnictide clusters **8** and **9** and the isolation of the molecular Na_4^{2+} cluster compound **12** suggest a terra incognita of exciting new types of main group element clusters which are promising mild nucleophilic transfer reagents.

This paper is dedicated to Professor Heinrich Vahrenkamp on the occasion of his 60th birthday. The author is indebted to his fellow workers, Drs. S. Rell, K. Merz, S. Martin, H. Pritzkow, and Dipl. Chem. U. Hoffmanns. Financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Ministerium für Wissenschaft und Forschung, Nordrhein-Westfalen (Germany), is gratefully acknowledged.

References

(1) (a) Setzer, W. N.; Schleyer, P. v. R. X-Ray Structural Analysis of Organolithium Compounds. *Adv. Organomet. Chem.* **1985**, *24*, 353. (b) Maercker, A. Preparation and Reactions of Polylithiumorganic Compounds. In *Lithium Chemistry: A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P.v. R., Eds.; Wiley: New York, 1995; p 477. Dilithium alkandiide clusters have also been described: (c) Gais, H.-J.; Vollhardt, J.; Günther, H.; Moskau, D.; Linder, H. J.; Braun, S. Solid State and Solution Structure of Dilithium Trimethyl((phenylsulfonyl)methyl)silane, a True Dilithiomethane Derivative. *J. Am. Chem. Soc.* **1988**, *110*, 978. (d) Kasini, A.; Kamalesh Babu, R. P.; McDonald, R.; Cavell, R. G. $[Ph_2P(NSiMe_3)]_2CLi_2$: a Dianionic Dilithium Methanide Salt with Unusual Li_4C_2 Cluster Structure. *Angew. Chem.* **1999**, *111*, 1580; *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1438.

(2) Pauer, F.; Power, P. P. Structure of Lithium Salts of Heteroatom Compounds. In *Lithium Chemistry: A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley: New York, 1995; pp 324−361.

(3) Pauer, F.; Power, P. P. Structure of Lithium Salts of Heteroatom Compounds. In *Lithium Chemistry: A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley: New York, 1995; pp 361−373.

(4) Driess, M.; Pritzkow, H.; Martin, S.; Rell, S.; Fenske, D.; Baum, G. Molecular, Shell-Like Dilithium (Silyl)phosphandiide and Dilithium (Silyl)arsandiide Aggregates with an $(Li_6O)^{4+}$ Core. *Angew. Chem.* **1996**, *108*, 1064; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 986.

(5) Issleib, K.; Tzschach, A. Synthesis of Alkalimetal Phosphorus Compounds. *Chem. Ber.* **1959**, *92*, 1118.

(6) Parshall, G. W.; Lindsey, R. V. Synthesis of Alkylsilylphosphines. *J. Am. Chem. Soc.* **1959**, *81*, 6273.

(7) Fritz, G.; Schäfer, H.; Hölderich, W. Metalation of the PH_2 Group in Silylphosphines. *Z. Anorg. Allg. Chem.* **1974**, *407*, 266.

(8) Appel, R.; Geisler, K. Facile Synthesis of Organosilylphosphines. *J. Organomet. Chem.* **1976**, *112*, 61.

(9) v. Schnering, H.; Hönle, W. Bridging Chasms with Polyphosphides. *Chem. Rev.* **1988**, *88*, 243.

(10) Atwood, J. L.; MacGillivray, L. R. Structural Classification of Spherical Molecular Hosts and General Principles for Their Design. *Angew. Chem.* **1999**, *111*, 1081; *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1018.

(11) Sapse, A.-M.; Jain, D. C.; Raghavachari, K. Theoretical Studies of Aggregates of Lithium Compounds. In *Lithium Chemistry: A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley: New York, 1995; pp 324−361.

(12) Becker, G.; Eschbach, B.; Käshammer, D.; Mundt, O. Metal Derivatives of Molecular Compounds. VII. Bis(1,2-bis(dimethylamino)ethane-N, N‘)lithium Disilylphosphanide- Synthesis and Structure. *Z. Anorg. Allg. Chem.* **1994**, *620*, 29.

(13) Driess, M.; Pritzkow, H. Molecular Aggregates of Donorsolvent-Free Lithium Silylphosphanides with the Triphenylsilyl- and Triisopropylsilyl-Substituent at Phosphorus. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1524.

(14) Driess, M.; Huttner, G.; Knopf, N.; Pritzkow, H.; Zsolnai, L. Novel Alkalimetal Phosphanide Aggregates. *Angew. Chem.* **1995**, *107*, 354; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 316.

(15) Zsolnai, L.; Huttner, G.; Driess, M. The Dimeric Tris(lithioarsino)germane $t\text{BuGe[As(Si}i\text{Pr}_3\text{)Li]}_3$: A Self-Assembled, Solvent-Free Lithium-Main Group Element Aggregate with a $Ge_2As_6Li_6$ Rhombodoecahedral Framework. *Angew. Chem.* **1993**, *105*, 1549; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1439.

(16) Armstrong, D. R.; Barr, D.; Clegg, W.; Drake, S. R.; Singer, R. J.; Snaith, R.; Stalke, D.; Wright, D. S. Dilithiation of a Primary Amine: Synthesis and Structure of $[(\alpha\text{-Naphthyl-NLi}_2)_{10}\ (Et_2O)_6)\ Et_2O$, an Paramagnetic $N_{10}Li_{20}$ Aggregate. *Angew. Chem.* **1991**, *103*, 1702; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1707.

(17) Niedieck, K,; Neumüller, B. Synthesis and Characterization of Organolithium Phosphides. The Crystal Structure of [Li(THF)(TMEDA)P(H)Mes]. *Z. Anorg. Allg. Chem.* **1993**, *619*, 385.

(18) Cowley, A. H.; Kilduff, J. E.; Newman, T. H.; Pakulski, M. Diphosphenes (RP═PR). Synthesis and NMR Characterization. *J. Am. Chem. Soc.* **1982**, *104*, 5820.

(19) Driess, M.; Hoffmanns, U.; Martin, S.; Merz, K.; Pritzkow, H. Lithiated Cluster of Primary Silylphosphanes and Silylarsanes: Spherical Bodies with and without Li_2O−Filling. *Angew. Chem.* **1999**, *111*, 2906; *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2733. Driess, M.; Rell, S. Pritzkow, H.; Janoschek, R. *Chem. Commun.* **1996**, 305.

(20) (a) Chivers, T.; Downard, A.; Yap G. P. A. A Sandwich Complex of Lithium Oxide: $[Li(BuC(NBu^t)_2)]_4\ Li_2O$. *J. Chem. Soc., Dalton Trans.* **1998**, 2603. (b) Kennedy, A. R.; Mulvey, R. E.; Rowlings, R. B. Reactions of Heterodimetal Amides with Molecular Oxygen: Cationic $(NMNMg)_2$ Cycles (M = Li, Na) with Central Anionic Oxo and Peroxo Groups. *Angew. Chem.* **1998**, *110*, 3321; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3180.

(21) Driess, M.; Kuntz, S.; Merz, K. Unpublished results.

(22) Driess, M.; Rell, S.; Pritzkow, H.; Janoschek, R. $[R{-}PLi_2(F{-}R)]_2$ $(R = SiPr^i_2(C_6H_2Pr^i_3\text{-}2,4,6))$ the First Structural Characterization of a Dilithium Phosphandiide in the Form of a Fluorosilane Complex. *Chem. Commun.* **1996**, 305.

(23) Hollemann−Wiberg. *Lehrbuch der Anorganischen Chemie*, 100th ed.; de Gruyter: Berlin−New York, 1985; p 277, Table 35.

(24) Driess, M.; Martin, S.; Pritzkow, H.; Skipinski, M.; Baum, G.; Fenske, D. Unpublished results.

(25) Driess, M.; Schaller, T.; Sebald, A. ^{29}Si CP/MAS NMR of Phosphorus-Bearing Organosilicon Compounds. *Solid State Nucl. Magn. Reson.* **1997**, *9*, 219.

(26) Driess, M.; Pritzkow, H.; Skipinski, M., Winkler, U. Synthesis and Solid State Structure of Sterically Congested Sodium and Cesium Silyl(fluorosilyl)phosphanide Aggregates and Structural Characterization of the Trimeric Sodium Bis(trimethylsilyl)amide. *Organometallics* **1997**, *16*, 5108.

(27) Driess, M.; Pritzkow, H.; Skipinski, M.; Winkler, U. Intriguing Tetrasodium Dication Cluster Na_4^{2+} Stabilized Between Two Silyl(fluorosilyl)phosphanide Shells. *J. Am. Chem. Soc.* **1998**, *120*, 10774.

(28) (a) Adrianarison, M.; Stalke, D.; Klingebiel, U. Cyclic Sodium and Potassium (Fluorosilyl)phosphides—Synthesis and Crystal Structures. *Chem. Ber.* **1990**, *123*, 71. (b) Koutsantonis, G. A.; Andrews, P. C.; Raston, C. L. Authentication of a Sodium Primary Phosphide: Synthesis and Crystal Structure of $[Na(PH(C_6H_{11})(pmdeta)]_2$ (pmdeta = N, N, N′, N″, N‴-pentamethyldiethylenetriamine). *J. Chem. Soc., Chem. Commun.* **1995**, 47.

(29) Edwards, P. P.; Anderson, P. A.; Thomas, J. M Dissolved Alkali Metals in Zeolites. *Acc. Chem. Res.* **1996**, *29*, 23.

(30) Driess, M. From Molecular Aggregates to Novel Organosilicon Phosphorus/Arsenic Compounds. *Pure Appl. Chem.* **1999**, *71*, 437.

(31) Müller, A.; Peters, F.; Pope, M. T.; Gatteschi, A. Polyoxometalates: Very Large Clusters-Nanoscale Magnets. *Chem. Rev.* **1998**, *98*, 239.

(32) Ohtaki, H. Molecular Aspects on the Dissolution and Nucleation of Ionic Crystals in Water. *Adv. Inorg. Chem.* **1992**, *39*, 401.

AR990038K