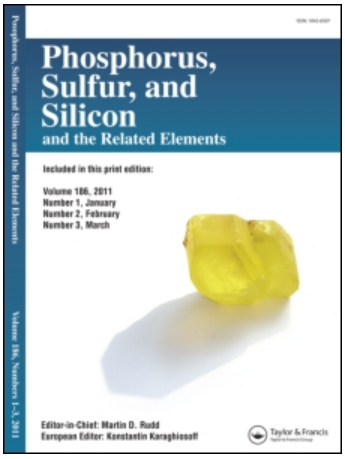

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Assembly of Cage Compounds Containing Boron, Phosphorus, and Silicon Atoms

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To cite this Article Chen, T. , Duesler, E. N. , Paine, R. T. and Nöth, H.(1994) 'Assembly of Cage Compounds Containing Boron, Phosphorus, and Silicon Atoms', Phosphorus, Sulfur, and Silicon and the Related Elements, 87: 1, 41 — 48
To link to this Article: DOI: 10.1080/10426509408037438
URL: http://dx.doi.org/10.1080/10426509408037438

Phosphorus, Sulfur, and Silicon, 1994, Vol. 87, pp. 41–48
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ASSEMBLY OF CAGE COMPOUNDS CONTAINING BORON, PHOSPHORUS, AND SILICON ATOMS

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A systematic synthetic route for the construction of two spirocyclic P_4B_4Si cage compounds is described, and spectroscopic data for the new compounds are presented. In addition, the molecular structures have been determined by single crystal X-ray diffraction analysis, and these data are compared with structural parameters for related bicyclic cage compounds.

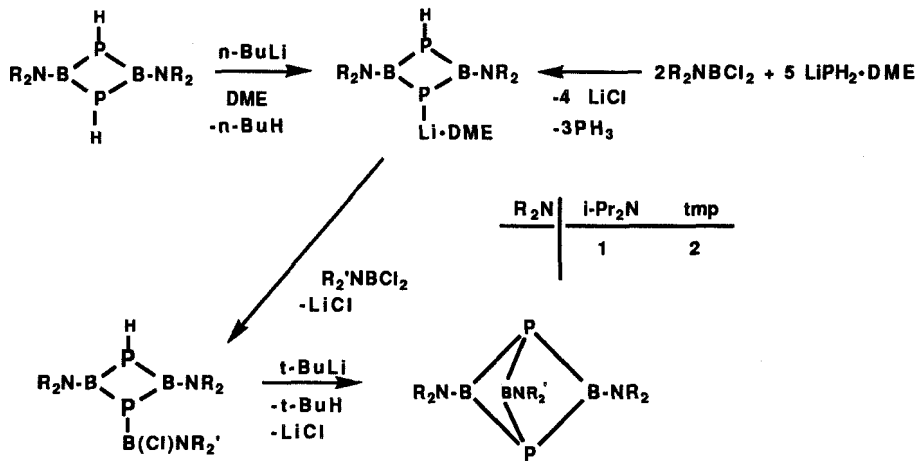
Key words: Aminophosphinoboranes, phosphinosilanes, spirocycles, spectroscopic and molecular structure studies.

INTRODUCTION

One of the highlights of modern inorganic chemistry is the discovery of cage and cluster structures containing boron. The last fifty years has seen the advent of a beautiful collection of polyhedral boron hydrides, carboranes, metalloboranes, and metallocarboranes for which much is known about their structures, bonding, and reactivity.[1] On the other hand, the development of cage and cluster compounds containing boron together with other main group elements is much less advanced. This is due, in part, to a lack of appropriate starting reagents and synthetic schemes, and it is not a result of inherent instability of the elemental compositions or structure types. Our groups have been attracted to this shortcoming, and we set out to establish molecular precursor chemistry that would provide a vehicle for the systematic construction of new cage species containing, in particular, boron, phosphorus, and silicon atoms. The effort was also stimulated by parallel interests in inorganic polymer

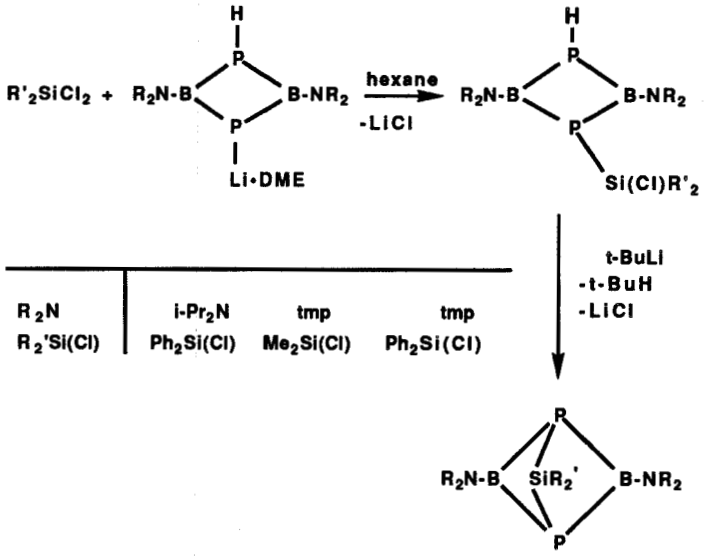
chemistry that should provide access to new solid state materials.

Cage polyhedra, of course, are composed of edge sharing small ring geometric elements having three to six vertices; therefore, our approach has been to assemble desired polyhedra by coupling small rings or by adding or removing small reactive fragments across ring faces or edges. For example, we have reported that combinations of the lithium salts of four membered cyclic diphosphadiboretanes with aminodichloroboranes produce P-borylated diphosphadiboretanes.[2] These compounds undergo spontaneous or base promoted dehydrohalogenation with subsequent cage closure. The resulting [1.1.1] bicyclo-pentane cage molecules, $P_2(BNR_2)_3$ and $P_2(BNR_2)_2(BNR'_2)$ have trigonal bipyramidal structures with apical phosphorus atoms. Some representative examples of this assembly process are summarized in Scheme I. This sequence should be general, and we are presently attempting to assemble larger propellane P_xB_y analogues.



Scheme I

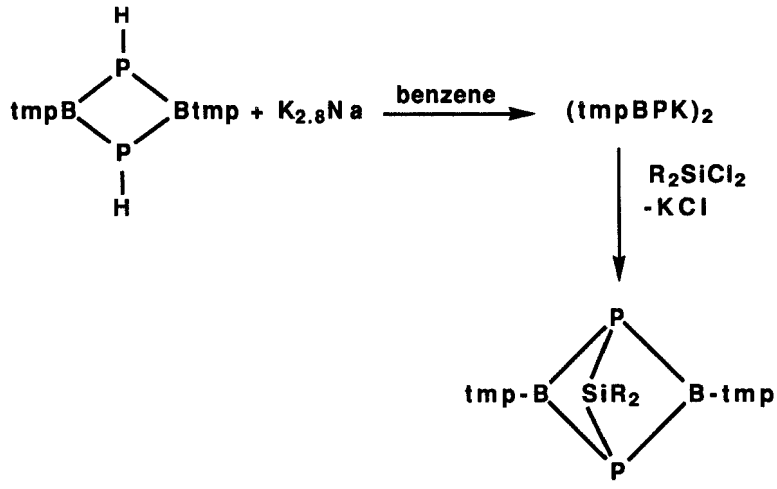
As noted above, we are also interested in preparing cage species that contain boron, phosphorus, and silicon atoms. Extending the chemistry in Scheme I, reactions of the lithium salts **1** and **2** with organosilicon dichlorides have been found to produce P-silylated diphosphadiboretanes.[3] Dehydrohalogenation of these compounds gives [1.1.1] bicyclo-pentane analogues $P_2(BNR_2)_2(SiR_2)$ that also have trigonal bipyramidal structures. This chemistry is summarized in Scheme II.



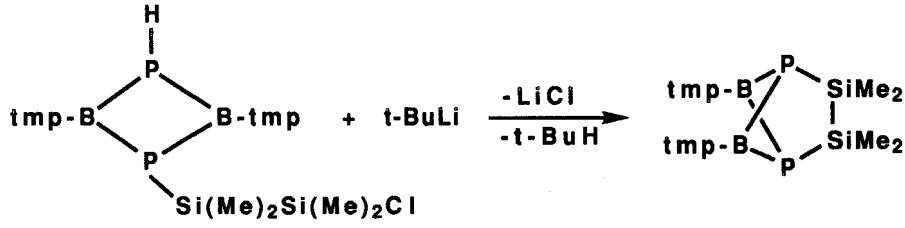
Scheme II

Some of the same cage compounds have also been prepared directly by reaction of R_2SiCl_2 with a species obtained from the reaction of $(tmpBPH)_2$ with $K_{2.8}Na$ as shown in Scheme III.[3] The search for larger $P_xB_ySi_y$ propellanes has also been realized by formation of P-disily-diphosphadiboretanes which undergo base promoted dehydrohalogenation with cage closure as summarized in Scheme IV.

These initial studies clearly indicate that stepwise assembly processes can be devised for the synthesis of polyhedral cage compounds rich in phosphorus, boron, and silicon. A host of related and new schemes are now under study that will greatly expand the field of possibilities and a number of interesting new species have recently been prepared. In the following section a direct extension of the chemistry shown in Scheme III is found to give new spirocyclic cage compounds.



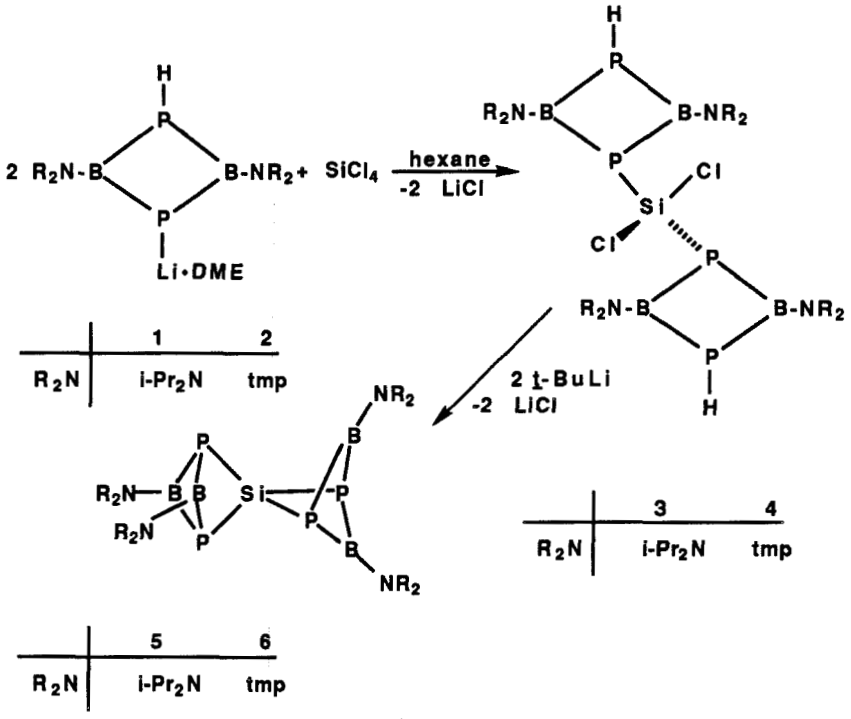
Scheme III



Scheme IV

RECENT RESULTS

The quest to find additional examples of $P_2B_2E_n$ compositions led us to examine the reactions of the lithium salts **1** and **2** with $SiCl_4$. When these reagents are combined in a 2:1 ratio in hexane at low temperature and then allowed to react at room temperature for 15 hours, solutions containing bis(diphosphadiboretanyl)dichlorosilanes, **3** and **4**, are obtained. Addition of two equivalents of t-BuLi in pentane to these solutions promotes dehydrohalogenation, and the spirocycles **5** and **6** are isolated as crystalline solids. This chemistry is summarized in Scheme V. The crystalline



Scheme V

compounds are remarkably stable in air and do not melt up to 150°C. The mass spectra of the compounds are dominated by the parent ion: **5** (HREIMS, 70 ev) 595.3630 M^+, 100% Calcd for $C_{24}H_{56}B_4N_4P_4Si$ 595.36398, dev-0.5 ppm; **6** (LREIMS, 30eV) 756 m^+, 100%. The $^{31}P\{^1H\}$ NMR spectra each display a single resonance: **5**, δ -6.5 and **6**, δ 38.9. These data compare favorably with shifts for the P_2B_2Si bicyclo-pentanes[3] $P_2[B(Ni\text{-}Pr_2)]_2SiPh_2$ **7** δ -18.4, $P_2[Btmp]_2SiMe_2$ **8** δ 31.3 and $P_2[Btmp]_2SiPh_2$ **9** δ 32.2. The $^{11}B\{^1H\}$ NMR spectra show a single resonance: **5** δ 45.7 and **6** δ 48.6, and these data are comparable with the shifts found for P_2B_2Si bicyclo-pentanes **7** δ 45.4, **8** δ 49.2 and **9** δ 48.2. The ^1H and ^{13}C NMR data for both new compounds are consistent with the proposed spirocyclic structures.

The spirocyclic molecular structures of **5** and **6** are confirmed by single crystal X-ray diffraction techniques, and views of the molecules are shown in Figures 1 and 2. The structures of **5** and **6** (two independent molecules in the unit cell) consist of two P_2B_2Si bicyclic cages joined at a common trigonal plane vertex site occupied by the single Si atom. The individual P_2B_2Si cores in **5** and **6** closely

resemble those reported recently for **7** and **9**.[3] The silicon atoms display a distorted tetrahedral geometry with the average internal P-Si-P angles (e.g., P(1)-Si(1)-P(2)) being very acute compared to the average external P-Si-P angles: **5** 85.0° and 123.0°; **6** (molecule 1) 83.9° and 123.7°. The apical phosphorus atoms are pyramidal, and the average angles about the phosphorus atoms also are acute: **5** 70.7°; **6** (molecule 1) 72.3°. These features are similar to the parameters found in **7** and **9** although the B-P-B angles and B-P-Si angles are slightly smaller and larger, respectively in **7** and **9**. The boron and nitrogen atoms in each compound have trigonal planar geometries as expected. The P-Si bond distances are identical in the two spirocycles: **5** avg 2.248 Å (range 2.233-2.256 Å); **6** avg (molecule 1) 2.243 Å (range 2.230-2.263 Å), and they are comparable to the average distances in **7** 2.244 Å, **9** 2.243 Å and $P_4(Me_2Si)_6$ 2.244 Å.[4] These distances are longer than the average distance in $(t\text{-BuP})_2Si(Pt\text{-Bu})_2$ 2.201 Å.[5] The last compound has a spirocyclic $(RP)_4Si$ structure which is probably more strained than found for **5** and **6** as indicated by the average P-Si-P bond angle of 61.6°. The average P-B bond distances in **5**, 1.966 Å and **6** (molecule 1) 1.922 Å are similar to those in **7**, 1.973 Å and **9**, 1.992 Å. Similarly, the average B-N bond distances in **5**, 1.388 Å and **6** (molecule 1) 1.377 Å are comparable with the distances in **7**, 1.375 Å and **9**, 1.384 Å.

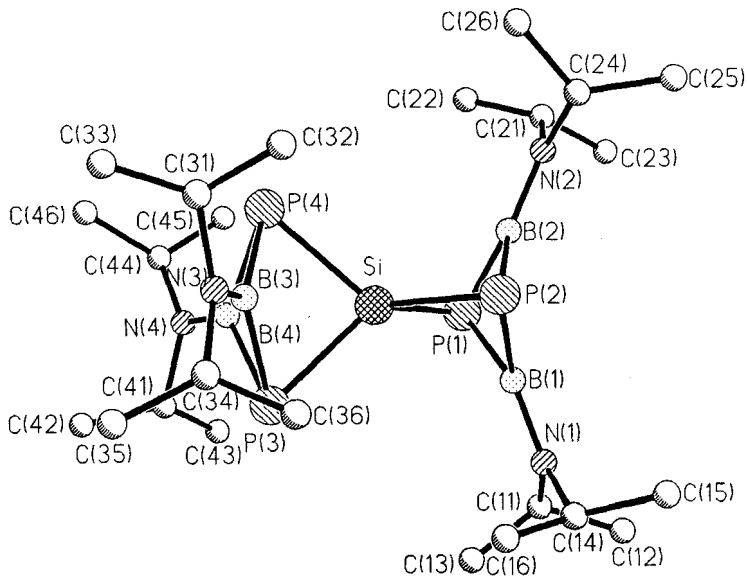


Figure 1. The molecular structure of $[P_2(i\text{-}Pr_2NB)_2]_2Si$

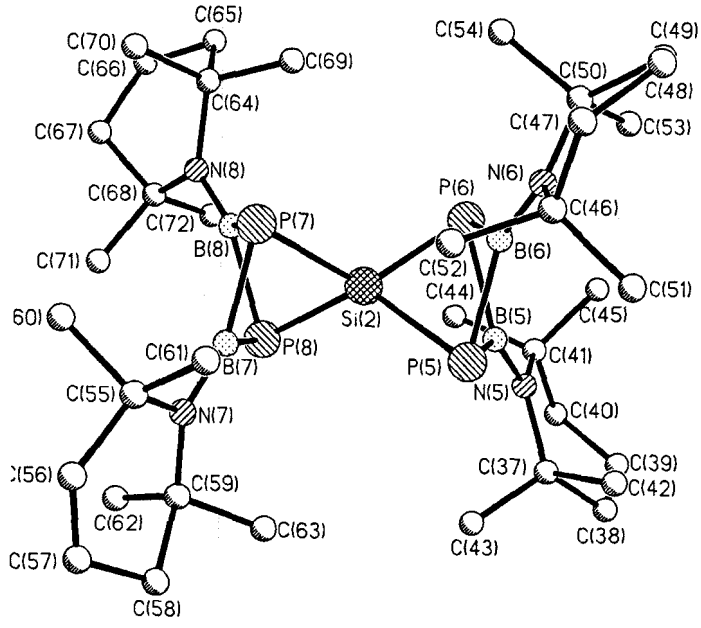


Figure 2. The molecular structure of $[P_2(tmpB)_2]_2Si$

CONCLUSION

We have previously shown that a stepwise synthesis approach can be used to prepare new families of bicyclic cage compounds containing boron and phosphorus atoms. We have now extended this chemistry to include the formation of spirocyclic "double cage" compounds wherein two cages are coupled via a shared vertex occupied by a Si atom. The potential extensions of this approach are many and additional examples are being defined in our groups at this time.

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