Chapter 11

Recent Developments in Boron–Phosphorus Ring and Cage Chemistry

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The chemical and structural diversity of compounds containing Groups 13/15 element combinations continues to expand at a rapid pace. In this paper we outline some recent results from our groups that illustrate the continued evolution of boron-phosphorus ring and cage constructs.

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The molecular chemistry of boron-phosphorus Lewis acid-base compounds was initially developed in the 1960's; however, the area remained relatively dormant for the next twenty years as other topics in inorganic and organometallic chemistry evolved. Spurred by discoveries in the 1980's of main group element multiple bond conditions (*1*) and rational, low energy syntheses of solid state materials via main group precursors (*2*), attention to Group 13/15 molecular chemistry in general and boron/phosphorus chemistry in particular exploded. In 1995, we summarized the remarkable advances that had occurred in boron-phosphorus chemistry since 1985, and new areas ripe for development in synthesis, structure and reactivity were suggested (*3*). Since that review appeared, the field has continued to prosper in a number of research groups worldwide. No attempt will be made here to comprehensively review the many advances since 1995. Instead, some snapshots of several recent developments from our groups are presented that illustrate the continued excitement in the area.

Phosphine Borane Systems

Boron phosphide (BP), a little studied but potentially important optoelectronic material (*4*) is prepared as a bulk powder by using traditional metallurgical approaches. Several gas mixtures, including B_2H_6/PH_3 (*5*), have been employed to prepare BP films by using CVD methods, but all of the simple reagent mixtures suffer from one or more of the drawbacks common to this methodology. As a result, attention has been given to the development of single source precursor molecules for BP synthesis (*6*). Perhaps the simplest single source precursor to BP would be H_3BPH_3 which ideally could undergo inter- or intra-molecular elimination of H_2 that could be easily and cleanly removed from the preparative system. Although the adduct has been carefully studied and characterized in solid and molten states as well as in the gas phase at -60°C (*7*), it is unstable toward dissociation near 23°C and elimination products containing boron and phosphorus have not been fully characterized due in part to low solubility. Although this adduct may prove to be a suitable low temperature CVD precursor system, it is not particularly useful as a starting material for the synthesis of ring or cage condensation products that could be employed as solution phase precursors for nano-sized materials.

In 1959, Parshall and Lindsey (*8*) reported the formation of $H_3BP(SiMe_3)_3$ as a colorless, crystalline compound from B_2H_6 and $P(SiMe_3)_3$. This reaction system was subsequently studied by Leffler and Teach (*9*), and Nöth and Schrägle (*10*) and found to undergo stepwise Me_3SiH elimination. Products formed at 125°C and at 200°C were proposed to be $H_2BP(SiMe_3)_2$ and $[HBPSiMe_3]_n$, respectively. A reinvestigation of the system in our groups showed that the initial adduct indeed undergoes Me_3SiH elimination in solution even at 23°C and this elimination chemistry is influenced by the presence of either excess phosphine or borane (*11*). Further, the crystalline adduct slowly decomposed in a sealed tube held at 100°C, and the rate of Me_3SiH elimination significantly accelerated at 150°C and higher. Two crystalline compounds, **1** and **2**, were isolated from the thermolysis reactions at 150°C and single crystal x-ray diffraction analyses provided unambiguous assignments of the structures which are shown in Figures 1 and 2, respectively. Compound **1** is the trimer of the coordinatively unsaturated monomer $H_2BP(SiMe_3)_2$ originally proposed by Nöth and Schrägle. It is noteworthy that this six-membered ring containing four coordinate boron and phosphorus atoms is much flatter than the related cyclohexane-like chair shaped structures of $(H_2BPMe_2)_3$ (*12*) and $(H_2BPPh_2)_3$ (*13*). The second crystalline compound, **2**, $P[\mu\text{-}H\text{-}B_2H_2]\{(H_2B)_2P(SiMe_3)_2]_2\}_2$ displays a unique spirocyclic structure in which two B_3P_3 rings share a common P atom. Adjacent BH groups in the two rings are joined via a bridge B-H-B bond. The structure of this molecule suggests that elimination reactions in the B_2H_6 + $P(SiMe_3)_3$ system are not confined to processes that split out Me_3SiH, but may also include $P(SiMe_3)$ elimination. Subsequent gc-ms studies of the system confirmed that Me_3SiH, $P(SiMe_3)_3$ and H_2 are present in the gas phase over decomposing $H_3BP(SiMe_3)_3$. Furthermore, several additional non-crystalline intermediate compounds are also formed. As a consequence of the competing elimination processes, the thermal decomposition chemistry of bulk samples is complex. In fact, pyrolysis of gram-sized samples of the adduct at elevated temperatures (> 400°C) gives solid state materials that contain BP and SiC (identified by XRD) and carbon (identified by elemental analyses).

Nöth and Schrägle (*10a*) also reported on the reactions of the haloboranes BX_3 (X=Cl, Br, I) with $P(SiMe_3)_3$ in hexane solution where they noted formation of crystalline 1:1 adducts. In subsequent reinvestigations of these systems Lube and Wells (*14*) noted that additional products form. By using salt elimination chemistry between BX_3 and $LiP(SiMe_3)_2$, they isolated and structurally characterized $[X_2BP(SiMe_3)_2]_2$ (X=Cl, Br). The planar four membered $(BP)_2$ rings contain four coordinate B and P atoms. Pyrolyses of the 1:1 adducts and the dimeric elimination products were examined up to 500°C and, under the conditions utilized, none gave boron phosphide as a pure solid state material.

Based upon the prior work by Groshens and Johnson (*6b*) one would not anticipate that organyl phosphines would provide good single source precursors for electronic grade BP since the organyl groups typically provide a source for carbon under high temperature conditions. Nonetheless, reactions of B_2H_6 and H_3B-base adducts with organyl phosphines are of interest for comparison with the chemistry described above. Nöth and Schrägle (*10a*), for example, reported that the reaction of $(Me_3Si)_3P$ with $PhBCl_2$ gave a stable crystalline adduct $Ph(Cl)_2BP(SiMe_3)_3$ which upon heating to 150°C produced a golden polymeric

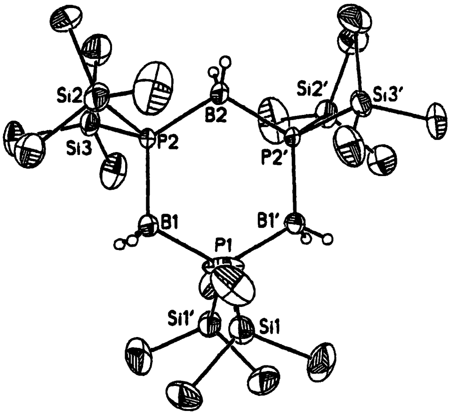


Figure 1. Molecular structures of [$H_2BP(SiMe_3)_2]_3$, 1.

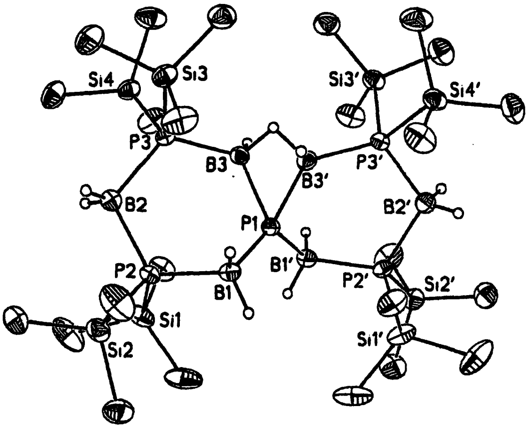


Figure 2. Molecular structure of $P[\mu\text{-}H\text{-}B_2H_2]\{(H_2B)_2P(SiMe_3)_2]_2\}_2$, 2.

solid. We have returned to examine this reaction in greater detail. Indeed, combination of the reagents in a 1:1 ratio in hexane at -78°C leads to immediate formation of a white solid that crystallized from cold toluene. A molecular structure determination confirmed that this initially formed solid **3** is a 1:1 Lewis acid-base adduct with a P-B bond length of 2.059(4) Å as shown in Figure 3. Subsequent heating of a suspension of **3** in refluxing toluene for 3 days gave an orange solution which produced colorless crystals of **4** upon concentration. Single crystal x-ray analysis revealed that **4** is a planar, four-membered ring compound $[Ph(Cl)BP(SiMe_3)_2]_2$ with a *trans* orientation of the like substituents on the B atoms. The P-B bond lengths of 2.02(1) Å and 2.05(1) Å are similar to those reported by Wells for $[Cl_2BP(SiMe_3)_2]_2$, 2.025(3) Å and 2.024(3) Å, and for $[Br_2BrP(SiMe_3)_2]_2$, 2.03(1) Å. In **4** the single B-Cl bond length, 1.92(1) Å is significantly longer than those in $[Cl_2BP(SiMe_3)_2]_2$, 1.852(3) Å and 1.839(3) Å. Further reflux of the reaction mixture in toluene for several more days led to the formation of an orange colored crystalline compound **5**, $(PhB)_5P_5(SiMe_3)_4$. The molecular structure for **5** appears in Figure 5. The compound has a novel cage structure consisting of a tri-fold $(PhB)_3(PSiMe_3)_2P$ crown linked via two B-P bonds and a P-P bond to a $(PhB)_2(PSiMe_3)_2$ four-membered ring. The tri-fold crown has a B-B-B triangular base, with an average B-B bond length, 1.920 Å, and the average B-P bond lengths to the phosphorus atoms in the crown (P1, P2 and P3) is 1.974 Å. The upper B_2P_2 ring has an average B-P bond length, 2.005 Å. The two B-P bond lengths connecting the crown and four-membered ring fragments are P1-B4, 1.984(7) Å and P3-B5 1.992(7) Å. The connecting P2-P5 bond length is 2.175(7) Å. The cage is not configured as would be expected for a fragment from a cubic BP unit cell, but it can be considered to be on the way to such a state. Unfortunately, at this time, additional cage intermediates have not been isolated from the reaction mixture, but it can be anticipated that they exist (as evidenced by additional peaks in ^{31}P NMR spectra of the reaction mixture). Further studies will likely provide additional information on the growth of cage molecules from such reactions.

Additional Cage Assembly Chemistry

In prior reports from our group we have described efforts to develop systematic stepwise assembly routes for the formation of B_xP_y and $B_xP_yE_z$ cage molecules (*3, 15-20*). The syntheses have been based upon the use or transient existence of four-membered diphosphadiboretane ring compounds that undergo subsequent substitution and ring closure chemistry. For the known examples, the syntheses have been found to be highly efficient for formation of five and six-membered *closo* cages and several spirocyclic and chained cages. It has become

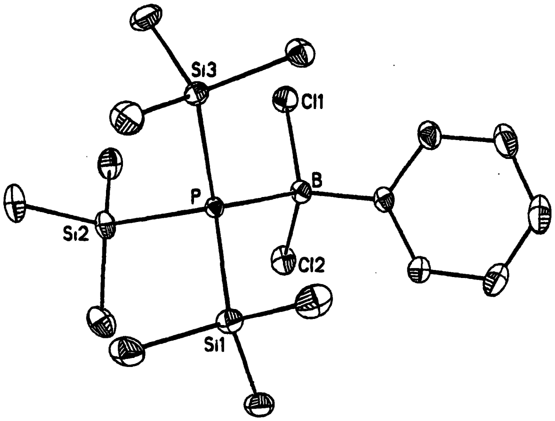


Figure 3. Molecular structure of PhB(Cl)$_2$P(SiMe$_3$)$_3$, 3.

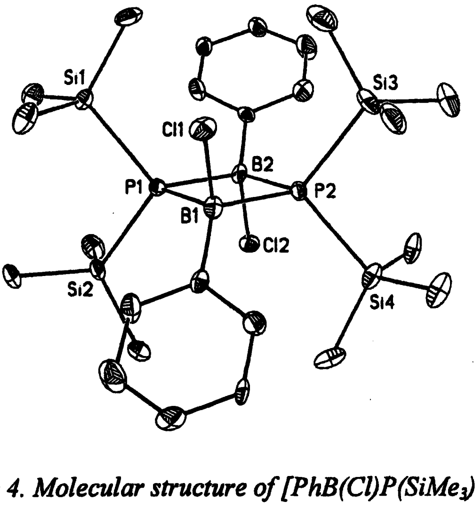


Figure 4. Molecular structure of [PhB(Cl)P(SiMe$_3$)$_2$]$_2$, 4.

clear, however, that these smaller cages represent thermodynamic "sinks" that acyclic systems have a tendency to descend to. In order to obtain larger cages it will likely be necessary to prepare larger building blocks than the four-membered diphosphadiboretanes. Several avenues are understudy and one involves the proposed assembly shown in Scheme 1.

The formation of **6** is known from our prior work, and the existence of **7** also has been substantiated. The subsequent dimerization of **7** to give the eight-membered ring compound **8** has not been confirmed although NMR spectra are consistent with its formation. The subsequent reduction and intramolecular P-P coupling reaction is validated by the isolation of (THF)(DME)P_2[(i-$Pr_2NB)_2PH]_2$. The molecular structure of **9** is shown in Figure 6. The P1-P2 bond length, 2.165(8) Å, in the edge-sharing bicyclic structure is normal for P-P single bonds. The average B-P bond length, 2.00 Å involving P1 and P2, however, is longer than those associated with P3 and P4, 1.84 Å. The P1 atom is coordinated to a lithium which is, in turn, bonded to DME and THF molecules. The reaction of **8** with BuLi was performed in an effort to make the lithiated derivative for subsequent additions of boryl phosphane fragments. Clearly deprotonation occurs, but this is accompanied by P-P bond formation. At the present time, the utilization of **8** and **9** as building units for larger cages remains to be explored, and both molecules provide attractive construction possibilities.

Diborane (4) Building Blocks

Power and coworkers (*21*) have examined the 2:1 reaction of $LiPPh_2$ with the diborane(4) species $(Me_2N)(Br)BB(Br)(NMe_2)$. They isolated the 1,2-diphosphinodiborane(4), $(Me_2N)(Ph_2P)BB(PPh_2)(NMe_2)$ and reported the formation of chelate complexes with the $Cr(CO)_4$ fragment. The diborane(4) fragment should also serve as a useful construct for B-P ring and cage compounds of interest to our groups. The entry point for these studies is 1,2-dichloro-1,2-bis-(dimethylamino)diborane(4) which was combined, in a 1:2 ratio with $LiP(SiMe_3)_2{\bullet}(thf)_x$, $LiP(SnMe_3)_2{\bullet}(thf)_x$ and $LiPH_2{\bullet}(thf)_x$. In the combinations with $LiP(SiMe_3)_2$, and $LiP(SnMe_3)_2$ crystalline products, $\{[(Me_3Si)_2P](Me_2N)B\}_2$ (**10**) and $\{[(Me_3Sn)_2P](Me_2N)B\}_2$ **11** were isolated, and the molecular structure of **11** was determined by single crystal x-ray diffraction methods. A view of the molecule is shown in Figure 7. Both **10** and **11** are moderately stable in hexane but, dissolved in thf, the compounds slowly evolve $P(SiMe_3)_3$ and $P(SnMe_3)_3$, respectively. In each case at least two condensation products are also formed, but they have not been isolated in a pure form and characterized.

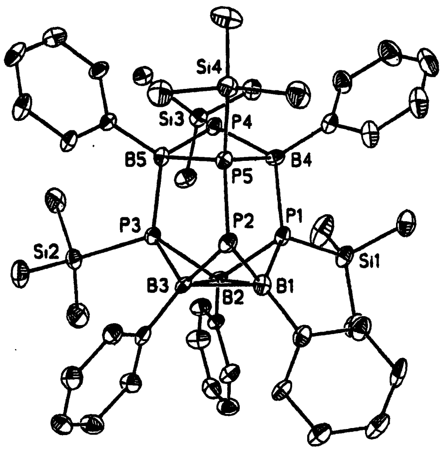
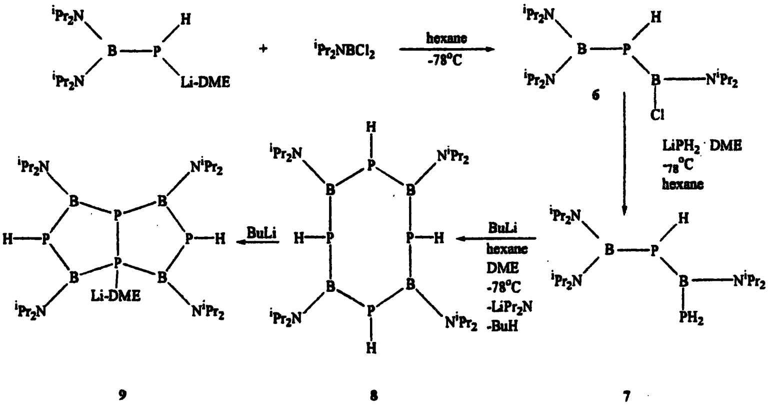


Figure 5. Molecular structure of $(PhB)_5P_5(SiMe_3)_4$, 5.



Scheme 1.

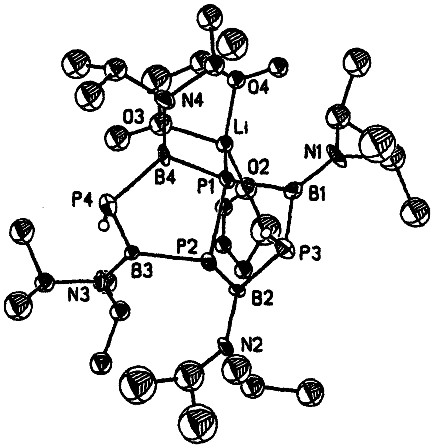


Figure 6. Molecular structure of $[(THF)(DME)Li]P_2[(i\text{-}Pr_2NB)_2PH]_2$.

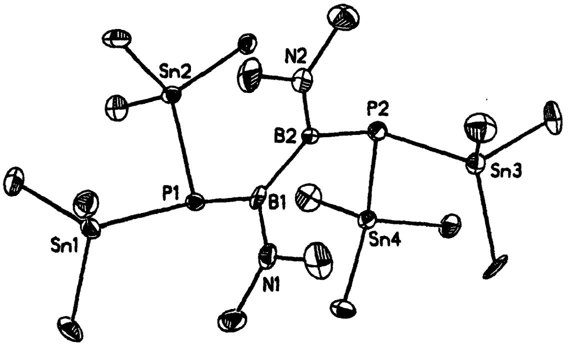
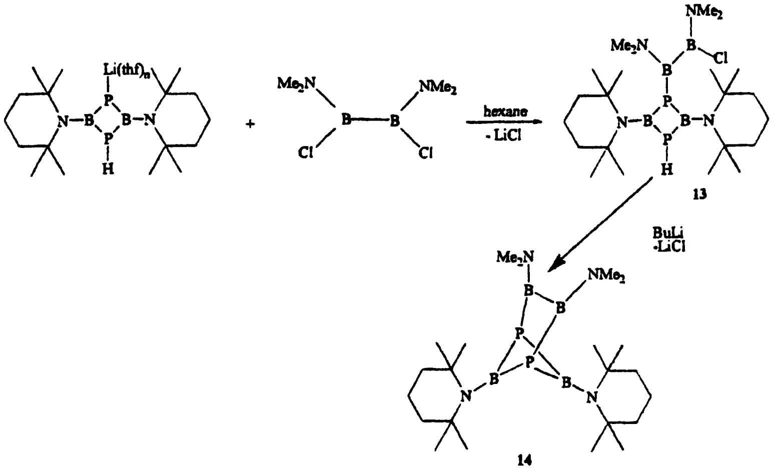


Figure 7. Molecular structure of $\{[(Me_3Sn)_2P](Me_2N)B\}_2$, 11.

In the case of the product obtained by addition of $LiPH_2$ to $[(Me_2N)(Cl)B]_2$, the bis-phosphine was not isolated. Instead a mixture of three products was obtained, one of which, $[(Me_2N)B\text{-}B(NMe_2)PH]_2$, (**12**) has been isolated and structurally characterized by single crystal x-ray diffraction methods. A view of the molecule is shown in Figure 8. It appears that $[(H_2P)(Me_2N)B]_2$ likely forms in the initial metathesis reaction and this compound must undergo intermolecular PH_3 elimination with dimerization giving the six-membered ring. This ring system should be useful for further cage construction reactions although the synthesis must be improved so that **12** is obtained in high yield as a single product without impurities.

In previous work, we have used the 1,2,3,4-diphosphadiboretane $(tmp BPH)_2$ as a building unit to produce five and six vertex *closo* cage compounds. We have attempted to extend that approach as shown in Scheme 2. The yellow, crystalline 1-borylated intermediate $(tmpB)_2[PB(NMe_2)B(Cl)(NMe_2)]PH$, **13** was isolated and characterized. The ^{31}P NMR spectrum is consistent with the formation of the compound as two equal intensity resonances centered at δ -110 and -104 ppm are observed. The former is a doublet of doublets (J_{PH} = 172 Hz, J_{PP} = 60 Hz) and the latter is a doublet (J_{PP} = 60 Hz). Single crystal x-ray diffraction analysis for **13** confirms the structure of the molecule and a view is shown in Figure 9. The orientation of the B-Cl bond near the P-H group suggests that HCl elimination should provide the *closo* six atom cage molecule, **14**. The intramolecuolar HCl elimination process has been examined with and without base promotion. Compound **13** in hexane appears to be stable toward elimination at 23°C; however, addition of BuLi gives an orange solution and



Scheme 2.

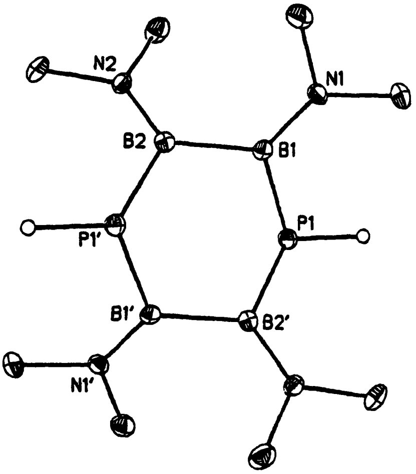


Figure 8. Molecular structure of* $[(Me_2N)B\text{-}B(NMe_2)PH]_2$*, 12.

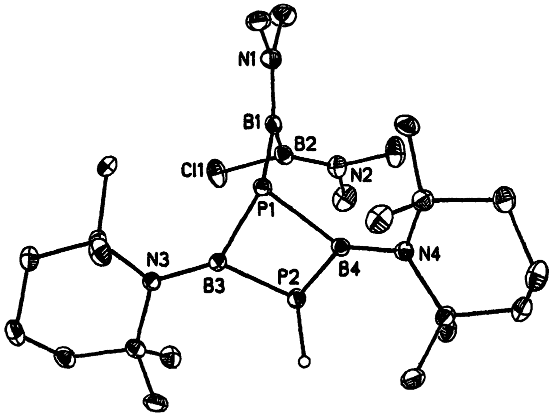


Figure 9. Molecular structure of* $(tmpB)_2[PB(NMe_2)B(Cl)(NMe_2)]PH$*, 13.

LiCl. Evaporation of the hexane leaves an orange oil which so far has not yielded single crystals. The ^{31}P NMR spectrum contains a strong, high field resonance at δ 7.7 which falls in the general region observed for $P_2(BNR_2)_3$ five vertex cage compounds. The spectrum also contains resonances at δ 46 and 51 which have not been assigned to a known product.

Conclusion

As pointed out in our 1995 review, molecular boron-phosphorus chemistry still contains many exciting frontiers. The snapshot summaries presented here provide some glimpses at targets under recent study in our groups in Albuquerque and München. Other groups are exploring alternative approaches to B-P ring, cage and oligomer systems including catalyzed dehydrocoupling reactions (*22*). Others are involved in the generation of novel radical molecules (*23*) and "heavy atom" ring and cage analogs containing aluminum, gallium and indium (*24*). We look forward to the continued development of the novel structural and electronic properties of boron-phosphorus ring and cage compounds.

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