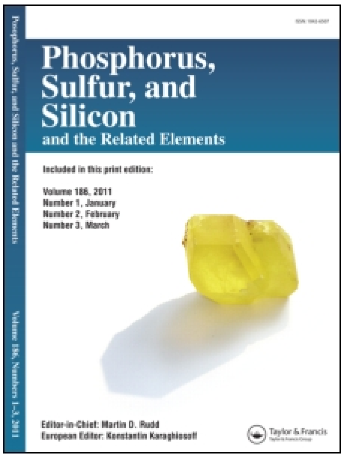

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Johnson, Stephen E. and Hawthorne, M. Frederick(1992) 'Rings Compounds of Boron and Phosphorus', Phosphorus, Sulfur, and Silicon and the Related Elements, 64: 1, 7 — 13
To link to this Article: DOI: 10.1080/10426509208041122
URL: http://dx.doi.org/10.1080/10426509208041122

Phosphorus, Sulfur, and Silicon, 1992, Vol. 64, pp. 7–13
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RINGS COMPOUNDS OF BORON AND PHOSPHORUS.

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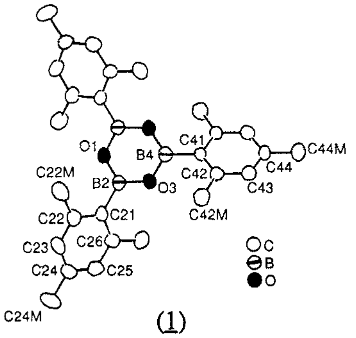
Abstract The synthesis and characterization of some ring systems of phosphorus and boron are described. Ring systems of boron such as boroxines, silylboranes, and diborabenzenes are considered. The structural and spectroscopic data for the ring derivatives support varying degrees of electron delocalization, depending on the size of the ring. Ring systems of phosphorus such as phosphenium ions and diphosphorus cations are outlined. The importance of P-C π-bonding interactions and the heterocyclic frameworks in the stabilization of these compounds are highlighted. Finally, new heterocyclic organoboranes are reported, which result from reductions of RBX_2 and with alkalai metals. All the rings and their respective derivatives have been characterized spectroscopically and the solid-state structures of some representative members were determined by X-ray crystallography. The degree of delocalization in the pertinent ring complexes are compared with theoretical models.

INTRODUCTION

Recently there has been renewed interest in ring systems of main group elements, particularly those sharing an isoelectronic relationship with phosphazene and borazine derivatives.[1] The "quasi-aromatic" boron-phosphorus[2] and germanium-nitrogen[3] ring systems have only recently been described. Structurally, these ring systems are analogous to aluminum-nitrogen[4] and boron-nitrogen[5] congeners. We reasoned a case could made for the inclusion of boroxines, based on previous structural studies[6] and our observation of facile B-C bond cleavage of R_2BF compounds in ethereal solvents.[7] We have observed silicon-boron rings systems of the type $(R_2SiBR')_3$, and while these compounds do not belong to the above category on the basis of electronic structure, they represent a new class of inorganic ring systems.[8] Attempts to generate diborabenzenes had remained unreported, until our sudies, though diboratabenzene derivatives had been reported within the last six years.[9] Formally, these may be considered as electron deficient analogues of borazine and boroxine. Our interest with regard to ring systems of phosphorus stemmed from investigations of phosphenium ions containing exclusively P-C bonds. The final aspect of work in this laboratory focuses on ring compounds of boron resulting from the reduction of RBX_2 derivatives.

RESULTS AND DISCUSSION

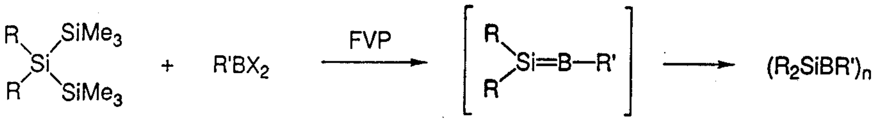
Boroxines Boroxines represent a fairly well characterized class of boron compounds in terms of structure, bonding, and reactivity.[10] The most widely used and successful means of producing boroxine derivatives involves dehydration of organoboronic acids.[11] Boroxines are, as well, undesired by-products in reactions of RBX_2 derivatives in ethereal solvents. We have observed, interestingly, that diorganoboronhalides react with silver salts in ethereal solutions to produce triorganoboroxines in high yield via B-C bond cleavage. The scope of the reaction appears to be general in nature as $(RBO)_3$ (R = *t*-Bu, Ph, Mes) derivatives have been observed in yield ranging from 79 - 88%. The molecular structure of the Mes derivative 1 was determined from a single-crystal X-ray diffraction study.[12] It is of interest to compare the structural parameters of 1 with X-ray data reported for $(PhBO)_3$.[13] Compared with the Ph derivative and other phenyl-substituted boroxine structures, the B-O, B-C bond distances and O-B-O bond angles are comparable within experimental error. The most distinctive structural parameter for 1 is the large torsional angles of the mesityl substituents. This is in sharp contrast to all three of the triphenylboroxine structures where the phenyl substituents are essentially coplanar with the B_3O_3 ring. This difference is reasonable in view of the larger steric requirements of the mesityl-substituents. The mechanism of this reaction is not fully understood, although formation of B-O bonds undoubtedly supply the driving force. Current work focuses on examining



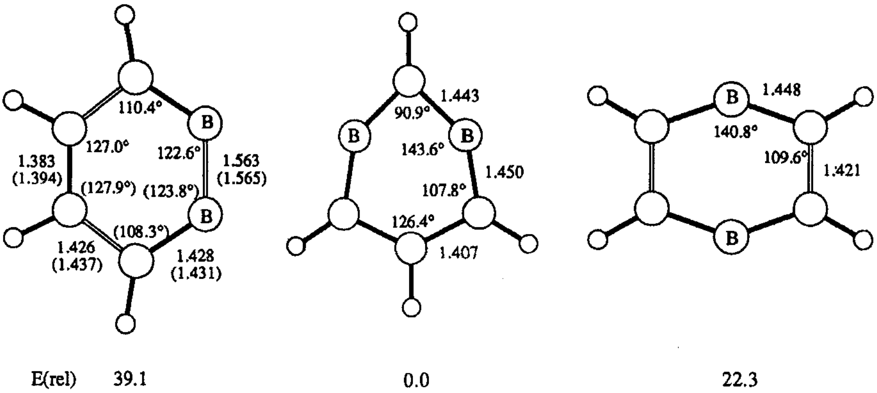
(1)

the optical properties of a variety of substituted aromatic boroxines.

Silylboranes This new class of ring system resulted from studies aimed at the generation of low-coordinate boron-silicon derivatives.[7] Dehydrohalogenation of $R_2Si(H)$-$B(Cl)R'$compounds (R = Ph, *t*-Bu, Mes; R' = Ph) or co-thermolysis of R_2SiX_2 (X = F, Cl, $SiMe_3$) with $R'BX_2$ derivatives give rise to ring systems of the type $(R_2SiBR')_n$ (n = 3). On the basis of ^1H, ^{13}C, ^{29}Si, ^{11}B NMR and MS data, we propose trimeric structures for these compounds. It is not unreasonable to expect that low-coordinate silylborylenes are likely intermediates. Attempts to isolate and structurally characterize dimeric and monomeric species are cuurently in progress.



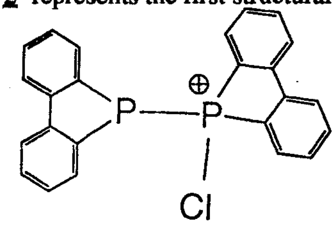
Diborabenzenes Unasaturated boron-carbon compounds represent an interesting class of boron compounds from an experimental[15] and theoretical[16] point of view in terms of structure, bonding, and reactivity. Despite the variety of structures no diborabenzene molecules have been reported in the literature.[17] In fact no examples of dicoordinate boron species possessing a formal boron-boron double bond have been observed experimentally. The only experimental relatives of diborabenzene are the amido-substituted diboratabenzenes.[9,18] The molecular structure of the dilithium salt of a 1,2-diboratabenzene has been determined and the bonding pattern in the planar B_2C_4 ring is consistent with that of a 6π-electron sysytem.[9] Our interest in the synthesis and characterization of low-coordinate boron derivatives prompted a theoretical and experimental examination of the the isomers of diborabenzene.[19] The fully optimized structures of diborabenzenes are shown. The six-membered ring frameworks of diborabenzenes are distorted significantly from a regular heaxagonal shape, with the bond angles ranging from 91° (B-C-B) to 142° (C-B-C). The C-B-C bond angle is very similar to that in borabenzene.[17] Nevertheless, all isomers have delocalized 6π-electron structures, with two vacant boron orbitals lying in the plane of the framework. The 1,3-isomer is predicted to be most stable, while the 1,2-isomer is least stable. Although it is higher in energy, it is a closed-shell system with a boron-boron double bond. Experimentally, *o,o'*-dichloro-*o,o'*-biphenyldiboron gives rise to a teraboron cluster upon Na/K reduction. Such an observation has been made for compounds of the type *t*-Bu(Cl)B-B(Cl)Bu-*t* [20] and it is not unreasonable that such a multiply bonded boron compound could be an intermediate.



1 2 3

Figure 1. The HF/6-31G* optimized geometries of 1,2-diborabenzene (1), 1,3-diborabenzene (2) and 1,4-diborabenzene (3). The MP2/6-31G* results are shown in parenthesis. Bond lengths are in Ångstrom, bond angles are in degree. Relative energies at the HF/6-31G* level are in kcal/mol.

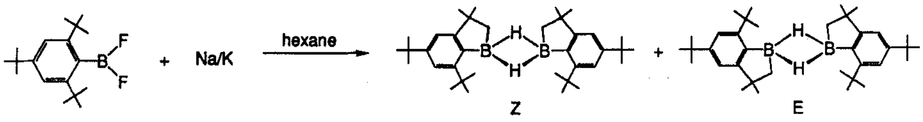
Phosphenium ions and Diphosphorus Cations Dicoordinate phosphorus cations and related diphosphorus cations represent relatively new and interesting classes of phosphorus compounds in terms of structure, bonding and reactivity.[21] While examples of both types of ions stabilized through N-P[21] and S-P[22] pπ–pπ interactions are well documented, there is little information regarding phosphorus cations having only P-C bonds.[23] Diphosphorus cations are derived from nucleophilic addition of phosphines with phosphenium ions. We have observed that reaction of dialkylchlorophosphines with equivalent amounts (or excess) of aluminum chloride gives rise to phosphonium rather than phosphenium ions, as confirmed from ^{31}P NMR and X-ray structural analysis of the *t* -Bu derivative.[24] Diphosphorus cations are observed, however, only as a minor products. In contrast, 5-chlorodibenzophosphole under similar conditions gives rise to an unusual tetraorganodiphosphorus cation 2 which is accompanied by the rare heptachloroaluminate ion. The synthesis and X-ray crystal structure analysis of 2 represents the first structural characterization of this class of phosphorus cations.



$[Al_2Cl_7]^{\ominus}$ (2)

The ionic nature of 2 in solution and in the solid-state is evident from ^{31}P, ^{27}Al NMR and IR spectra. The ^{31}P NMR spectrum of the diphosphorus cation consists of two sets of doublets, characteristic of P^{III} and P^{IV} sites, respectively. The IR and ^{27}Al NMR spectra were not characteristic of $AlCl_4^-$, but they were consistent with an $Al_2Cl_7^-$ species both in the solid-state and in solution. The results discussed above imply that the ability of a particular substituent to stabilize the phosphenium ion influences the reaction pathway. In this case formation of the intermediate dibenzophosphenium ion is stabilized through P-C π-bonding interactions. Theoretical calculations support the view of dispersal of positive charge into the aromatic system.[25] Attempts to structurally characterize the phosphenium ion have so far been unsucessful. It is interesting to note, however, that phosphenium ions of dialkyl- and diarylchlorophosphines can be stabilized as the organometallic derivatives. These results suggest that phosphenium ions can be stabilized through P-C pπ bonding interactions. Future work focuses on the derivative chemistry of 2 and the stabilization of other phosphenium ions containing exclusively P-C bonds.

Clusters and Rings of Boron and Aluminum We have reported a convenient procedure the synthesis of RBX_2 (R = sMes, Trip, Trpp; X = F, Cl, Br, $SiMe_3$, $SnMe_3$) in good yields.[26] We reasoned these precursors would provide the possibility of gaining access to new low-coordinate boron compounds. The reduction $(Me_3Si)_3CBCl_2$ had been reported to afford a heterocyclic diborane compound.[27] We observe as well the reduction of $sMesBF_2$ with Na/K alloy gives rise to 3 as isomers.[26] In the former case, intramolecular addition of C-H bond to the borylene is suggested to occur. We would suggest that H-abstraction coupled with radical generation could also account for formation of these boron heterocycles. We also observe as minor products coupled at the methyl portion of the *t*-Bu group in reductions of $sMesBF_2$.



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ACKNOWLEDGMENTS

The authors thank the National Science Foundation for generous support of this research. S. E. J. thanks the NSF post-doctoral Fellowship Program for support (CHE 90-01819).

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