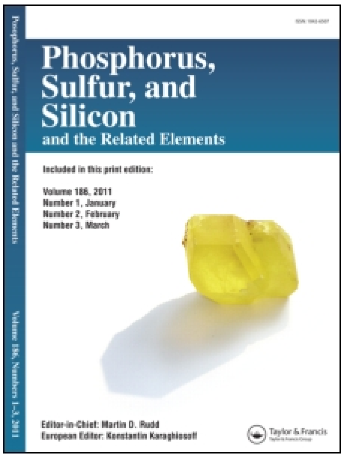

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SYNTHESIS AND REACTIONS OF NOVEL BORON-PHOSPHORUS COMPOUNDS

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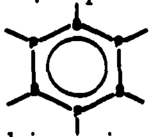
Abstract. Treatment of RBX_2 with two equivalents of LiPHR', has resulted in the isolation and characterization of boron-phosphorus analogues of borazine as illustrated.

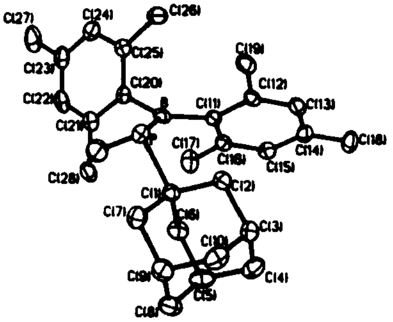
$2LiPHR' + RBX_2 \longrightarrow {}^1/_3$  $+ H_2PR' + 2LiX$

A range of these 6-membered rings involving various R and R' groups have been isolated and spectroscopic and structural studies show that they probably possess considerable aromatic character. In addition, larger R and R' substituents affords the anti-aromatic 4-membered cyclobutadiene analogs. Judicious choice of substituent also allows the isolation of boron phosphorus analogues of the allyl cation, anion and butadiene involving extremely short P-P single bonds.

INTRODUCTION

Since the discovery of borazine by Stock[1] in 1926 BN compounds have enjoyed continued popularity owing to the isoelectronic relationship of B-N and C-C. In contrast, boron-phosphorus compounds have not attracted the same degree of interest as their boron-nitrogen counterparts. However, recent developments in multiple bonding in the heavier main group elements and interest in main group III-V compounds as semiconductor precursors have awakened new interest in B-P compounds. In the past, development of BP chemistry has been hindered by the strong tendency of BP compounds to associate. Recent work has proved that this can be prevented by using bulky substituents on B and P or by use of π-donor ligands, for example, $-NR_2$ groups[2,3], on boron which reduce the Lewis acid character of the boron center. In this laboratory work has concentrated on the former approach. This is because the employment of ligands such as $-NR_2$ or -OR on boron interfere with, and generally overshadow, any interaction between the empty boron p-orbital and an adjacent phosphorus lone pair.

Initial work concentrated on compounds with only one boron and one phosphorus center. For example, Mes_2BPPh_2, **1**[4], and $Li(Et_2O)_2PRBMes_2$ (R = Ph, **2**; C_6H_{11}, **3**, or Mes, 4).[5] Structural and spectroscopic data showed that the phosphorus center in 1 had a flattened pyramidal geometry whereas in 2-4 it was planar. The P-B bonds, which ranged from 1.823(7)-1.859(3) Å, were considerably shorter than any previously observed and consistent with multiple bonding. The tendency toward planarity at the phosphorus centers was supported by spectroscopic evidence. For example, the ^1H and ^{31}P NMR of the compounds $HPRBMes_2$ (R = Ph, C_6H_{11}, Mes) were marked by increased P-H coupling constants (254-301 Hz). Attempts were made to correlate this coupling with the pyramidicity at phosphorus. Unfortunately, it has only been possible to crystallize one of the $HPRBMes_2$ compounds as illustrated by the structure[6] of $HP(1\text{-}Ad)BMes_2$, 1. In this compound the sum of the angles at P is 314.8° and the B-P distance is 1.897(3) Å. Reduction in the size of the substituents invariably results in dimerization, for example $[HP(t\text{-}Bu)BPh_2]_2$, 2.



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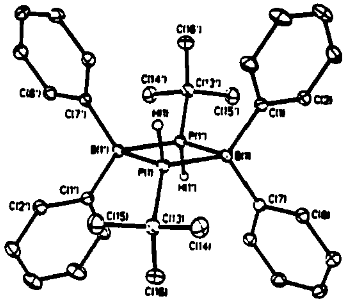
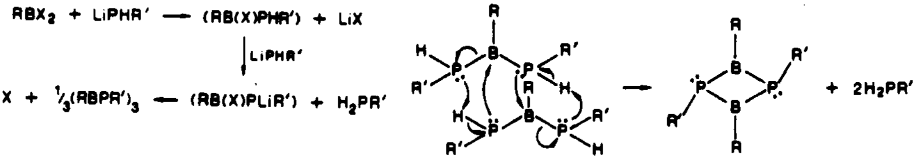
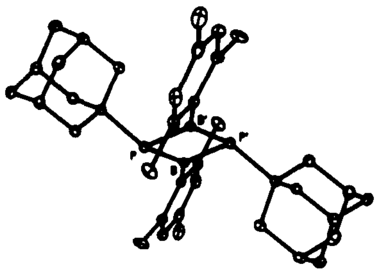


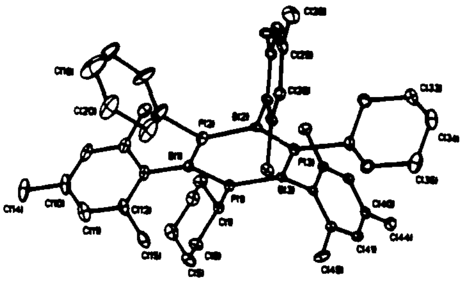
2

Work then proceeded to the synthesis of the species $RB(PR'H)_2$ as precursors to BP ring compounds. It was thought that if these could be metallated, as in $RB(PR'Li)_2$, further reaction with various dihalides such as $RBCl_2$, $RPCl_2$, R_2SiCl_2, etc. would lead to novel four-membered ring compounds. However, the unexpected products obtained[7] involved either four or six-membered BP rings depending on the size of the R and R' substituents. Apparently, $RB(PR'H)_2$ compounds, if they exist, are unstable with respect to elimination of $R'PH_2$. However, it is quite possible that there are two distinct pathways to the cyclic products as shown by the scheme.





$[MesBP(1\text{-}Ad)]_2$, **3**



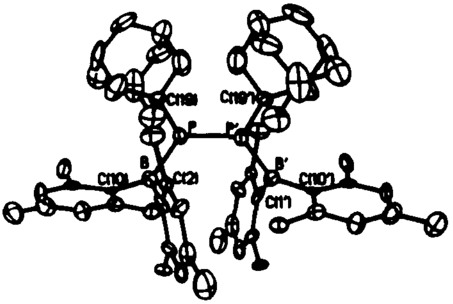
$(MesBPC_6H_{11})_3$, **4**

The structures of the six-membered ring consists of a planar $B_3P_3C_6$ array, **4**, with equal BP bonds that are about 1.84 Å in length whereas in the four-membered $B_2P_2C_4$ rings the BP bonds are about 1.9 Å long and the phosphorus centers are non-planar. These data, together with ^1H, ^{11}B and ^{31}P NMR studies, indicate that the six-membered ring is quasi aromatic. On the other hand, the four-membered ring compounds are BP analogues of cyclobutadiene and, in effect, anti-aromatic. The structures of $(ThexylBPMes)_2$[7] and $[MesBP(1\text{-}Ad)]_2$, **3**[6], support this comparison by displaying a much lowered tendency to delocalize as manifested by the pyramidal phosphorus centers and longer B-P bonds.

It is also possible to prepare[8] other "unsaturated" B-P acyclic compounds. The oxidation, under mild conditions, of $LiPRBMes_2$ compounds affords the BP butadiene analogue as shown

$$LiPRBMes_2 + CrCl_3 \rightarrow LiCl + CrCl_2 + {}^1/_2\, Mes_2B(R)P\text{-}P(R)BMes_2$$

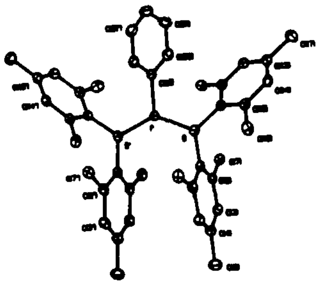
R = 1-Adamantyl or Mesityl



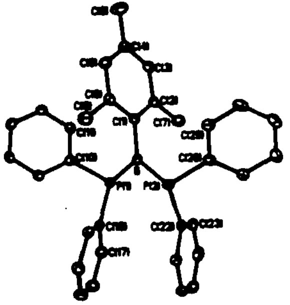
P - P' = 2.109(4) Å

In this case the B and P centers are planar with a high ~(70°) dihedral angle between the phosphorus planes. The P-P bond length is ca. 2.1 Å. This value is extremely short for a single bond which are normally 2.22 Å. One explanation for the short P-P bonds is that they involve the overlap of approximately sp^2 hybridized orbitals whereas in normal diphosphanes they involve orbitals that are much closer to purely p-character. If this hypothesis is correct then it follows that about 50% of the difference in length between a P-P single bond (2.22 Å) and a P-P double bond (2.02 Å) is attributable to rehybridization, the remainder being due to side on p-p π-overlap. These figures may be contrasted with the case of carbon where only 25-30% of the contraction is thought to be due to rehybridization.

Other acyclic BP compounds that have been recently prepared are the B-P analogs of the allyl cation and anion.[9] The allyl cation analog $PhP(BMes_2)_2$ possesses a planar $CP(BC_2)_2$ core and shortened (1.87 Å) BP bonds as illustrated by **5**.



5



6

The allyl anion analog $MesB(PPh_2)_2$, **6**, possesses two additional electrons in the allyl π-orbitals which occupy a non-bonding level. The B-P bond lengths are increased slightly (1.89 Å) and the phosphorus centers become non-planar. These changes are consistent with greater electron-electron repulsion and calculations on the carbon analogs.

Recent studies have concerned transition metal phosphine complexes with boryl substituents at the phosphorus center. For example, it is possible to synthesize[10] the unusual complex $[Ph_2B\{PH_2Cr(CO)_5\}_2]^-$ as its NEt_4^+ salt by the reaction of Ph_2BCl with $Cr(CO)_5PH_2Li$. This possesses B-P bonds which are about 2 Å long, in sharp contrast to **5** and **6**. This is consistent with the four coordinate nature of both B and P. Larger substituents at either boron or phosphorus will obviously be required to prevent bridging by the boron center in these complexes.

ACKNOWLEDGMENT

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