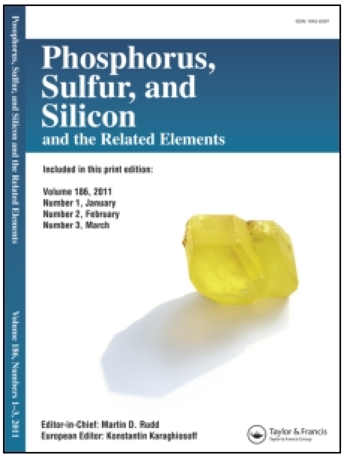

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# Synthesis and Reactivity of Borylphosphanes

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# SYNTHESIS AND REACTIVITY OF BORYLPHOSPHANES

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ABSTRACT Elimination reactions involving aminochloroboranes and borylphosphanes or borylphosphide salts provide access to a variety of new phosphaboretane ring and PB cage compounds. The evolution of the synthetic and structural chemistry of these species is described.

## INTRODUCTION

The syntheses of phosphinoborane compounds, $R_2P\text{-}BX_2$, from hydrogen halide elimination reactions between organophosphanes, $R_2PH$, or organosilylphosphanes, $R_2PSiMe_3$, and boron halides have been practiced for many years. For the most part, the products isolated have been four- and six-membered phosphaboretane ring compounds.[1] Some of this chemistry has recently been reexamined in efforts to obtain monomeric borophosphenes that contain a formal -B=P- double bond.[2] Our group has contributed to this chemistry by undertaking a systematic study of the reactions of $LiPH_2$ with aminochloroboranes. Some results of that study are outlined here.

## RESULTS

In general, it has been found that a 1:1 combination of $LiPH_2 \bullet DME$[3] with aminodichloroboranes produces primarily the single substitution product, $R_2NB(Cl)PH_2$ (eq. 1).[4,5] Combining the

$$R_2NBCl_2 + LiPH_2 \bullet DME \xrightarrow{-LiCl} \underset{\mathbf{1}}{R_2NB(Cl)PH_2} \qquad (1)$$

$$R_2NBCl_2 + 2LiPH_2 \bullet DME \xrightarrow{-2LiCl} R_2NB(PH_2)_2 \xrightarrow{-PH_3} 1/n\ (R_2NBPH)_n \qquad (2)$$

same reagents in a 2:1 reactant ratio leads to the bis-$PH_2$ substitution products, $R_2NB(PH_2)_2$, which are subject to expulsion of $PH_3$ and condensation of presumed borophosphene, $R_2NB{=}PH$, intermediates (eq. 2). The condensation products are a series of diphosphadiboretane, $(R_2NBPH)_2$, and triphosphatriboretane, $(R_2NBPH)_3$, ring compounds in which the ring size appears to be governed primarily by the steric bulk of the amino fragment (large amino groups favoring four-membered rings). One exception to this trend is found in the six-membered ring structure adopted when $R_2N = (Me_3Si)_2N$.

The subsequent reaction chemistry of the phosphaboretane ring compounds has proven to be interesting. For example, the donor ability of the phosphorus centers is retained, and a series of metal carbonyl adducts have been produced, as illustrated by one example (eq. 3). The latent acidity of the P-H groups in these

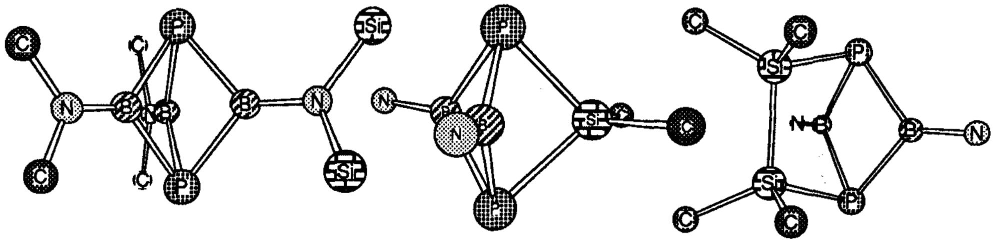
$$(tmpBPH)_2 + Cr(CO)_5\bullet NMe_3 \longrightarrow tmp\overline{BP(H)B(tmp)P}(H)Cr(CO)_5 \qquad (3)$$

compounds is demonstrated by their reactions with n-BuLi and t-BuLi (eq. 4). It is also convenient to prepare these lithium

$$(tmpBPH)_2 + BuLi \longrightarrow [tmp\overline{BP(H)B(tmp)P}^-][Li\bullet DME^+] \qquad (4)$$

phosphides by combining $R_2NBCl_2$ with excess $LiPH_2\bullet DME$. The products, $[R_2N\overline{BP(H)B(R_2N)P}^-][Li\bullet DME^+]$, are crystalline solids that are extremely useful synthons for constructing more complicated borylphosphanes. For example, the phosphides may be borylated (eq. 5) or silylated, and if the resulting molecules are arranged appropriately, they undergo dehydrohalogenation with formation of novel $P_2(BNR_2)_3$, $P_2(BNR_2)_2(SiR_2)$, and $P_2(BNR_2)_2(Si_2R_4)$ cage compounds, as illustrated below. Additional studies indicate that a broad family of cage compounds may be systematically assembled in this fashion.

$$[R_2N\overline{BP(H)B(R_2N)P}^-][Li\bullet DME^+] + R_2NBCl_2 \xrightarrow{-LiCl} R_2N\overline{BP(H)B(R_2N)P}B(Cl)NR_2 \qquad (5)$$



## CONCLUSIONS

The chemistry of simple borylphosphanes recently examined in our group demonstrates that these reagents have attractive reactivity patterns useful for the construction of more complex molecules. We expect that continued efforts in this field will provide a variety of new structural environments for boron-phosphorus compounds.

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3. Abbreviations used in the text include DME = ethylene glycol dimethyl ester, Me = methyl, i-Pr = isopropyl, Bu = n-butyl or t-butyl, tmp = 2,2,6,6-tetramethylpiperidino.
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