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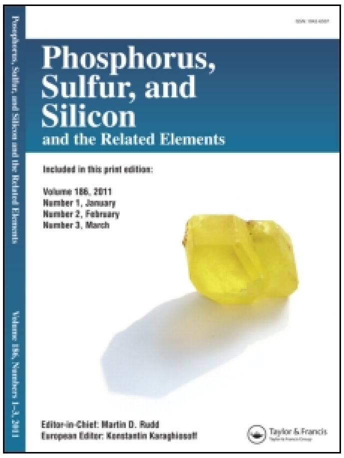

Phosphorus, Sulfur, and Silicon and the Related Elements

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New BP Cage Species

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Lectures

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NEW BP CAGE SPECIES

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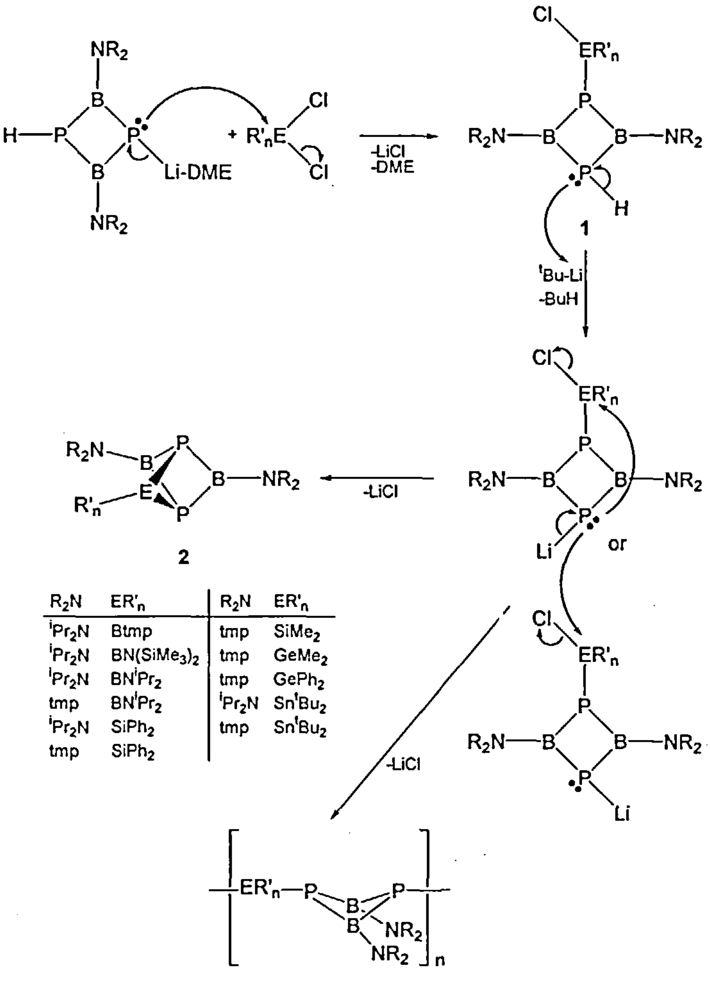
Continuing studies of cage compounds containing boron and phosphorus atoms have led to the discovery of new five-atom cages containing not only B and P atoms, but also Group 14 elements Si, Ge and Sn, as well as transition metal atoms Ni, Pd and Pt. The syntheses of these interesting compounds are summarized.

Keywords boron, phosphorus, rings, cages

INTRODUCTION

Our research groups have been interested in developing systematic approaches for the construction of new main group element cage compounds in particular ones containing boron and phosphorus atoms[1]. Two approaches have now been reported[2-8]. In the first, the addition of selected carbenoid, R_2E, fragments across the P-P bond in the bicyclic compound $[tmpBP]_2$ (tmp = 2,2,6,6-tetramethyl-piperidino) gives five vertex cage species $(tmpB)_2P_2ER_2$ with ER_2 = $Sn[CH(SiMe_3)_2]_2$, and $Pt(PPh_3)_2$. Unfortunately, at this time this route is limited by the number of appropriate bicyclic starting materials, as well as the reactivity of the carbene species. We have also developed a second method that is based upon sequential addition and elimination chemistry on small ring fragments and this process is outlined in a general fashion in Scheme 1[3-8]. For most cases, the intermediate species 1 may be isolated, and they are stable toward spontaneous dehydrohalogenation. Addition of a base such as ^{t}BuLi



R_2N	ER'_n	R_2N	ER'_n
$^iPr_2N$	Btmp	tmp	$SiMe_2$
$^iPr_2N$	$BN(SiMe_3)_2$	tmp	$GeMe_2$
$^iPr_2N$	BN^iPr_2	tmp	$GePh_2$
tmp	BN^iPr_2	$^iPr_2N$	Sn^tBu_2
$^iPr_2N$	$SiPh_2$	tmp	Sn^tBu_2
tmp	$SiPh_2$		

ER'_2	NR_2
$GeMe_2$	N^iPr_2N
$GeMe_2$	tmp
$SnMe_2$	tmp

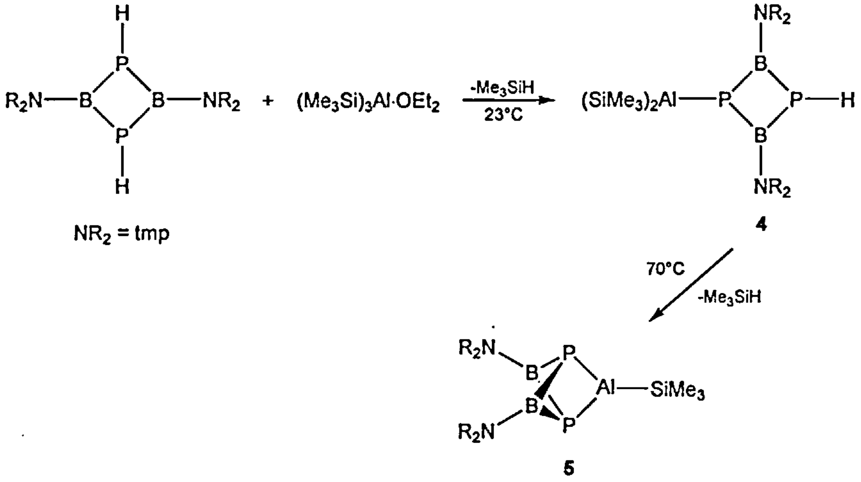
SCHEME 1

promotes HX elimination and with most combinations of substituent groups the five atom cages **2** are obtained in excellent yield. In those examples where **1** contains a large E element, e.g., Ge, Sn, with small substituents such as Me groups, the dehydrohalogenation produces oligomeric products **3**.

Our groups continue to explore extensions of this chemistry to larger cages, cages containing other heteroatoms, and cages with new substituent groups. Some recent findings are summarized below.

RECENT RESULTS

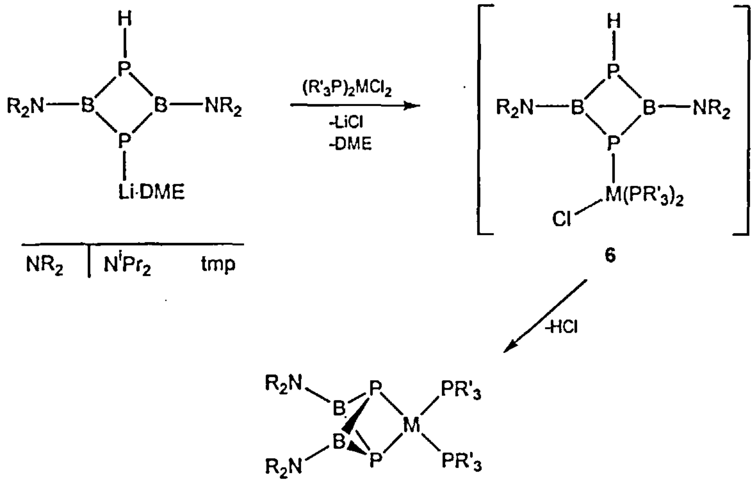
The reactions of various silyl main group element species with diphosphadiboretanes have been surveyed as another route to cage species. For example, the reaction of $(Me_3Si)_3Al$ with $(R_2NBPH)_2$ (R_2N = tmp) has been examined and the chemistry is summarized in Scheme 2. Me_3SiH gas evolution in both steps of the reaction was confirmed by ^1H NMR analysis of collected off-gases. Compound 4 was isolated in good yield and it was fully characterized. NMR spectra for the molecule are fully consistent with the proposed structure. The ^{31}P NMR spectrum shows two resonances at δ -125.5 and -128.4. The lower field resonance shows both $^1J_{PH}$ = 187 Hz and $^3J_{PP}$ = 25 Hz, while the upfield resonance shows $^3J_{PP}$ = 25 Hz. The ^{11}B NMR spectrum shows a single resonance at δ 41.9. The mass spectrum of 4 shows a parent ion envelope at m/e 539-536 and the



SCHEME 2

infrared spectrum shows a split ν_{PH} vibration at 2203 and 2182 cm^{-1}. Heating this compound leads to elimination of additional Me_3SiH. It appears that **5** is formed along with $(tmpBP)_2$ and perhaps another compound. Attempts have been made to solve the crystal structure of **5**, but at this time disorder in the $SiMe_3$ methyl groups has prevented full anisotropic refinement. The five atom cage core and tmp groups, however, appear properly accounted for. Additional studies of other E(TMS) eliminations are in progress.

Following another avenue, we have sought to prepare cage compounds containing one or more metal centers. In this regard we have completed the chemistry summarized in Scheme 3. No attempt was made to isolate the intermediates **6**. Each cage compound is obtained as a crystalline solid in moderate yield although isolation of the compounds in pure form results in reduced yield due to their high solubility in organic solvents. The spectroscopic data are fully consistent with the proposed five vertex polyhedral structure. In particular, the compounds display a parent ion in the HRFAB-MS with excellent agreement between the observed and calculated masses.



NR₂	N^{i}Pr₂	tmp

	7	**8**	**9**	**10**	**11**	**12**
NR₂	tmp	N^{i}Pr₂	tmp	N^{i}Pr₂	N^{i}Pr₂	tmp
M(PR'₃)₂	$Ni(PEt_3)_2$	$Pd(PEt_3)_2$	$Pd(PEt_3)_2$	$Pt(PEt_3)_2$	$Pt(PPh_3)_2$	$Pt(PPh_3)_2$

SCHEME 3

The ^{31}P NMR spectra in each case show a AA'XX' resonance pattern with the AA' portion (δ 6.3 to -68.1 ppm) assigned to the cage P atoms and the XX' portion (δ 9.9 to 24.9 ppm) identified with the PR_3 ligands. The full extent of the expected second order coupling is not resolved in these spectra. The molecular structures of four of the compounds **8**, **9**, **10** and **12**[2] have been determined and full details of the structures will be reported separately. A view of the core of **10** is shown in Figure 1.

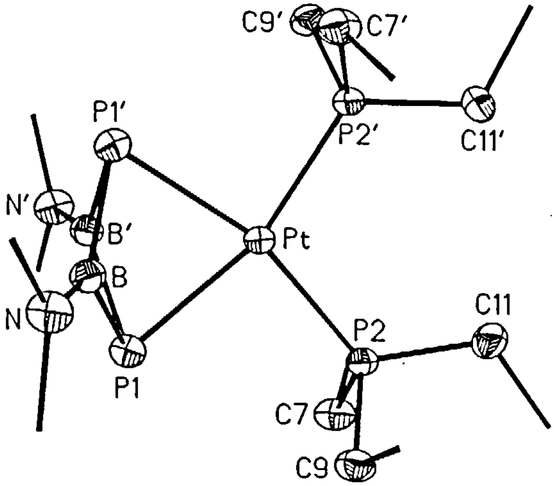


FIGURE 1

CONCLUSION

These new results indicate that cage construction chemistry for boron-phosphorus compounds is potentially rich and we anticipate that this area will continue to grow as new synthetic pathways are derived.

Acknowledgment

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