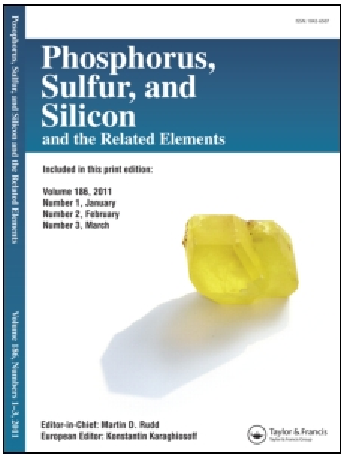


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis of New Main Group Ring and Cage Compounds

T. Chen[ab]; E. N. Duesler[ab]; R. T. Paine[ab]; H. Nöth[ab]
[a] Department of Chemistry, University of New Mexico, Albuquerque, NM, USA [b] Institut für Anorganische Chemie, Universität München, München, Germany

To cite this Article Chen, T. , Duesler, E. N. , Paine, R. T. and Nöth, H.(1994) 'Synthesis of New Main Group Ring and Cage Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 73 — 85
To link to this Article: DOI: 10.1080/10426509408021800
URL: http://dx.doi.org/10.1080/10426509408021800

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93–94, pp. 73–85
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS OF NEW MAIN GROUP RING AND CAGE COMPOUNDS

T. CHEN, E.N. DUESLER, R.T. PAINE*, AND H. NÖTH
Department of Chemistry, University of New Mexico, Albuquerque, NM 87131, USA and Institut für Anorganische Chemie, Universität München, 80333 München, Germany

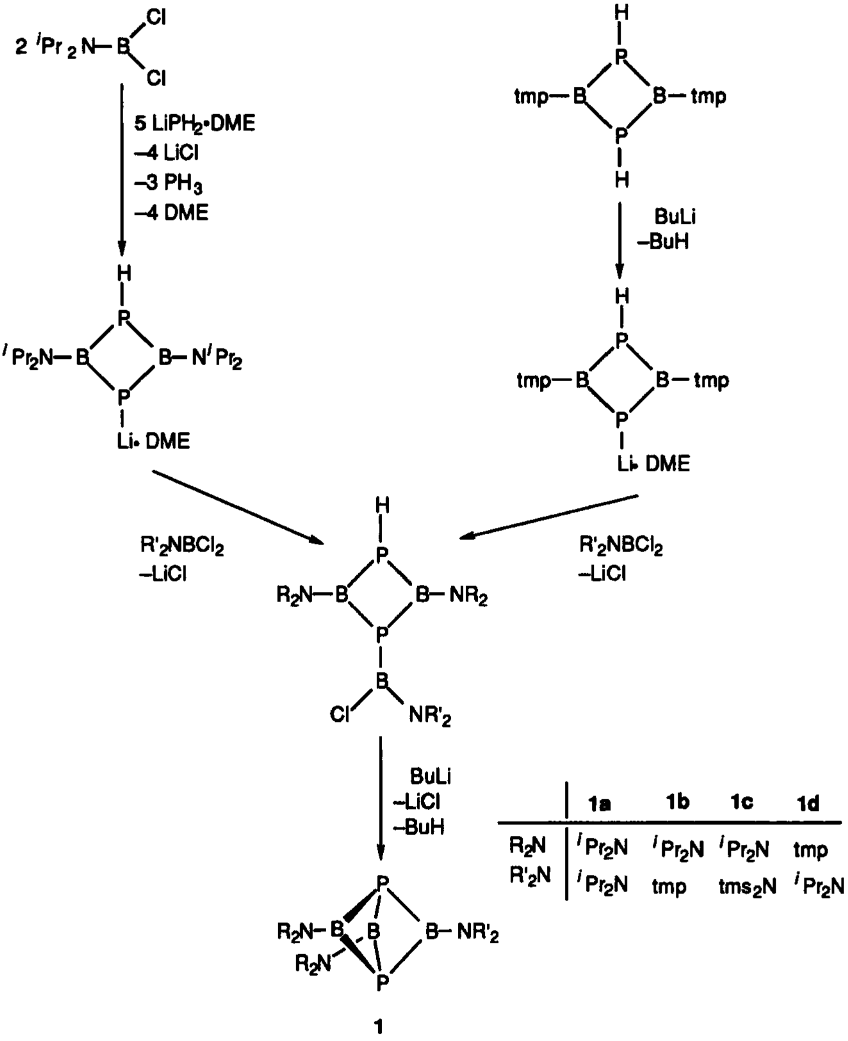
Abstract The reactions of 1-(lithio•DME) salts of two 1,3,2,4-diphosphadiboretanes with R_2ECl_2 reagents have been examined. Under most conditions, this chemistry provides precursors to novel cage compounds $P_2(BNR'_2)_2ER_2$, although in some cases soluble oligomers are formed when the intermediate species undergo dehydrohalogenation.

INTRODUCTION

The ring and cage chemistry of the main-group elements is rich, diverse, and expanding rapidly[1]. There are many examples of these rings and cages that are composed of homocycles and even more compounds that are heterocycles. The substituents associated with these compounds are also varied. In some cases, they control the size and shape of the homo- and heterocycles formed, while in other cases they seem to have little influence on the structure. In nearly all cases, however, the substituents affect the eventual chemical reactivity of the mono- or polycyclic compounds. Stimulated in part by the progress made in defining boron hydride, carborane, metalloboranes, phosphonitriles, and polysilane rings and cages[1], our groups[2-21] in Albuquerque and München and Power and coworkers[22-29] have explored the possibilities of forming ring and cage compounds containing boron, phosphorus, and in some cases third elements, E. The search for such compounds has been very successful, and a number of unusual new mono- and polycyclic species have been derived.

For the formation of B_xP_y cage species, we have found it particularly fruitful to utilize a stepwise assembly approach that begins with the formation of

1,3,2,4-diphosphadiboretanes[11]. At this time, we have reported only on the cases that employ B-amino substituted (R_2N = $^iPr_2N$ and tmp) four-membered rings, and that chemistry is summarized in Scheme I. It is important to note that the final

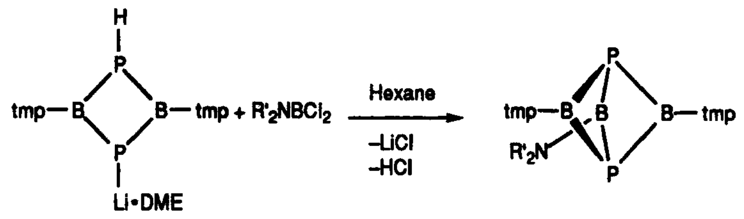


	1a	1b	1c	1d
R_2N	$^iPr_2N$	$^iPr_2N$	$^iPr_2N$	tmp
R'_2N	$^iPr_2N$	tmp	tms_2N	$^iPr_2N$

1

Scheme I

cage closure reactions that produce **1a-d** usually require addition of a strong base such as ^{t}BuLi, although in a few instances (eq.1) the dehydrohalogenation is spontaneous.



(1)

	1e	1f
R'₂N	tms₂N	tmp

The [1.1.0]bicyclo-pentane cage analogs have a trigonal bipyramidal structure. The structures of three of these compounds have been determined[3,12], and a full view and framework representation of **1a** are shown in Figure 1.

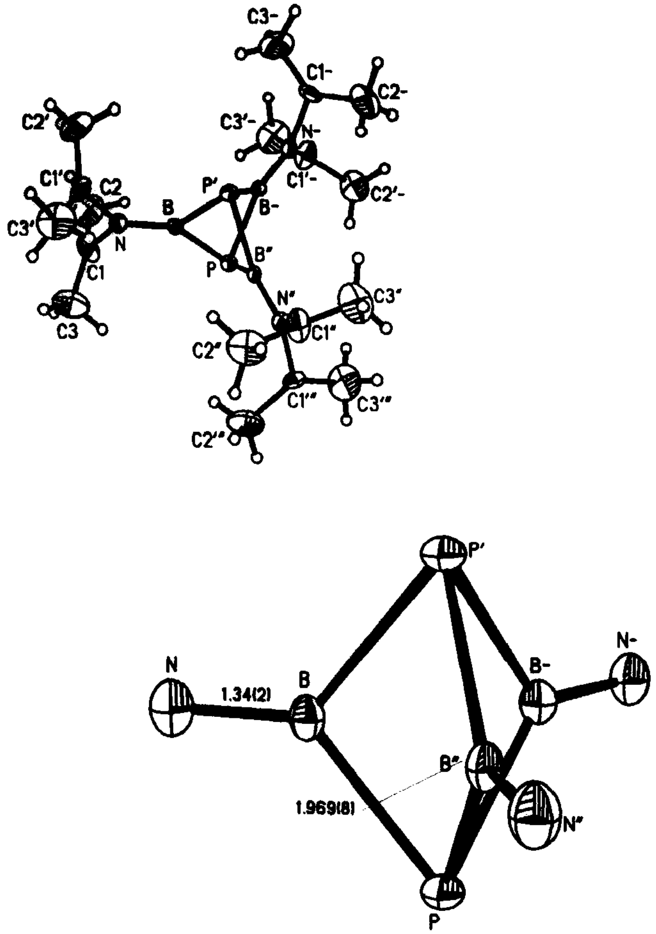
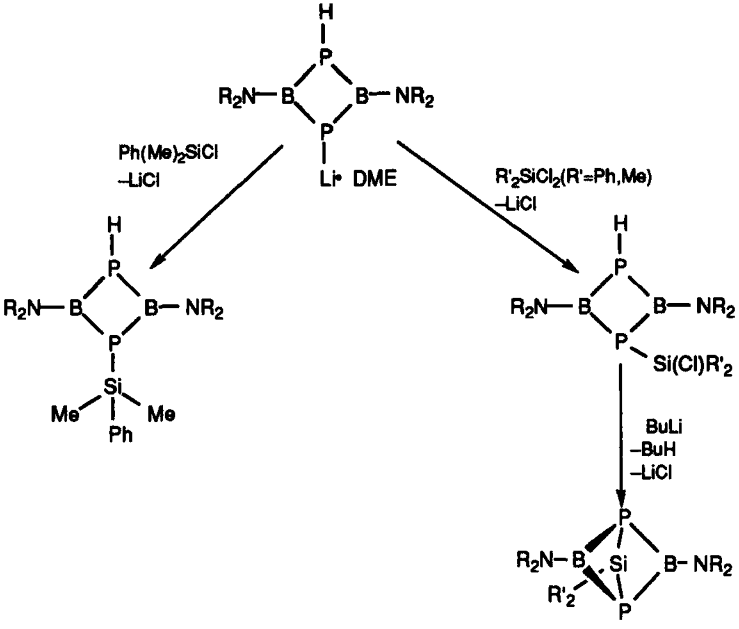


FIGURE 1 Molecular structure and framework for **1a**.

The simplicity of this assembly process suggested that it might be possible to prepare related five-membered bicyclic cages containing other heteroatoms. Indeed, reactions of the lithium salts of the 1,3,2,4-diphosphadiboretanes with diorganodihalosilanes R_2SiCl_2 produce bicycles **2**, as shown in Scheme II[18]. Like **1**, these compounds are quite stable in the absence of air. The molecular structures for two of these cages have been determined by X-ray diffraction techniques, and a full view and framework representation of **2a** are shown in Figure 2.



2

	2a	2b	2c
R_2N	$^iPr_2N$	tmp	tmp
R'_2Si	Ph_2Si	Me_2Si	Ph_2Si

Scheme II

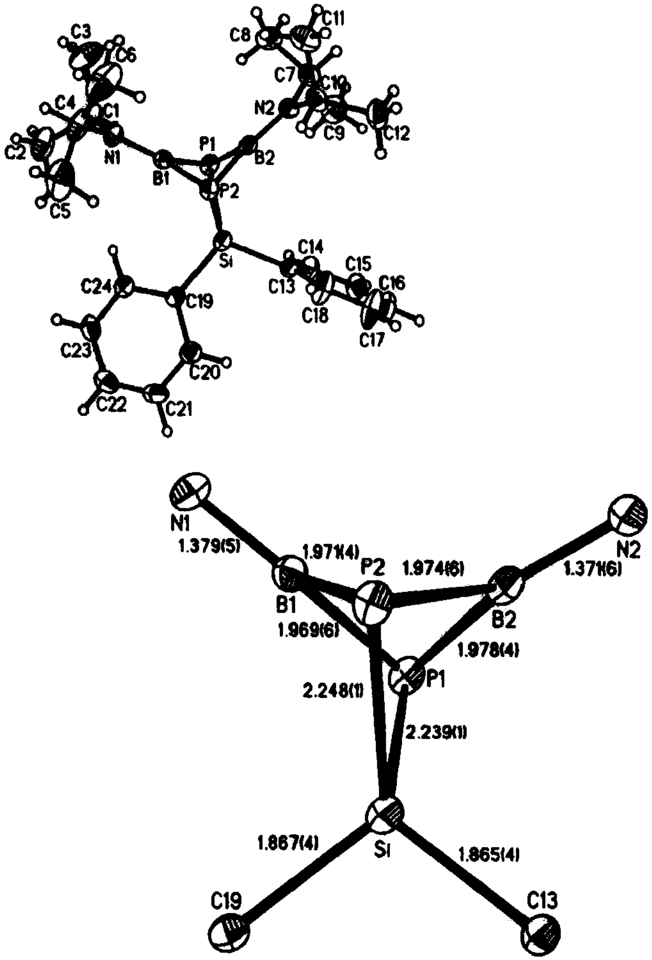
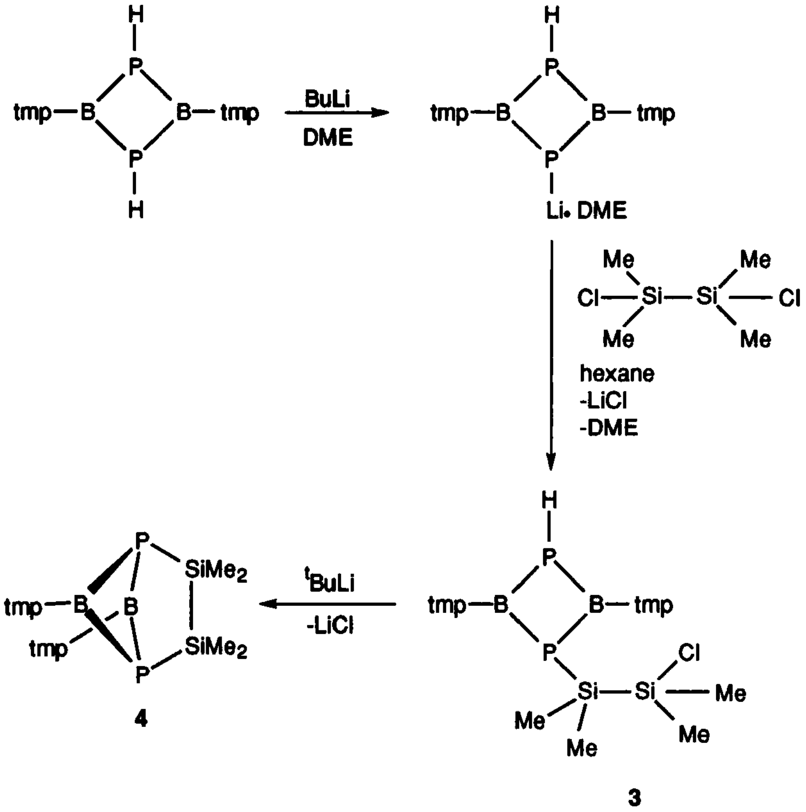


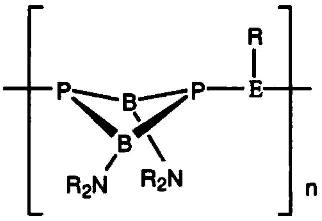
FIGURE 2 Molecular structure and framework for **2a**.

Seeking to expand on this theme, we then set out to construct larger and/or more complex cage species. Our approach involved the synthesis of 1-disilyl-1,3,2,4-diphosphadiboretanes **3**, one of which is shown in Scheme III. Subsequent base-promoted dehydrohalogenation with ^{t}BuLi gave the six-membered bicycle **4**, which has been fully characterized[18].

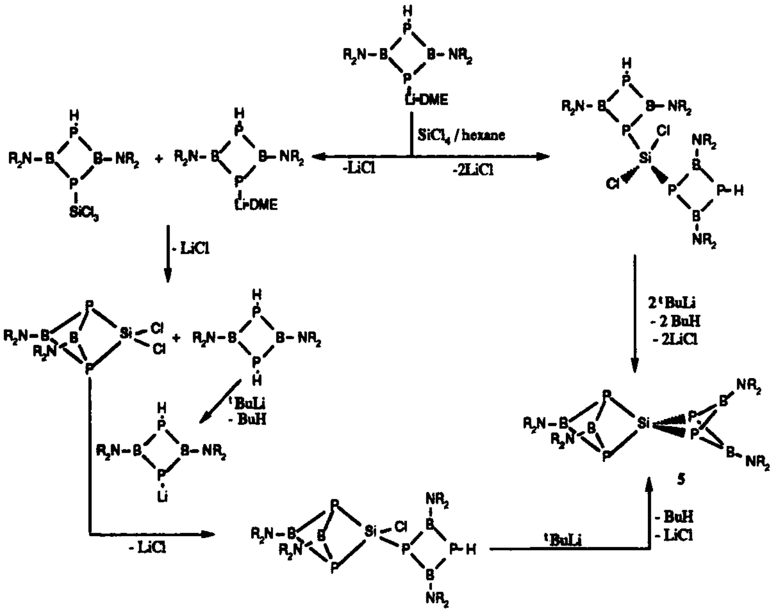


Scheme III

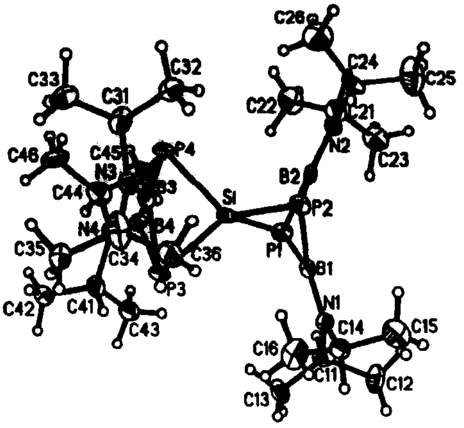
None of the systems described above showed any evidence of the formation of oligomeric products that might arise from intermolecular, as opposed to intramolecular, coupling of the 1-substituted-1,3,2,4-diphosphadiboretanes. Such a species is schematically represented below. It is still of interest to determine if



conditions can be found that will encourage intermolecular elimination that would produce linear oligomers or alternatively larger cages. With regard to the formation of more complex cages, we have recently found that the reactions of $SiCl_4$ with 1-(lithio•DME)-1,3,2,4-diphosphadiboretanes followed by dehydrohalogenation produce the "double ring closure" intramolecular reaction product **5**, as shown in Scheme IV[19]. The mechanism for this reaction has not yet been fully elucidated, but two possibilities for the assembly process are shown. No evidence for oligomeric products was obtained. The compounds **5** have been fully characterized, and the



Scheme IV



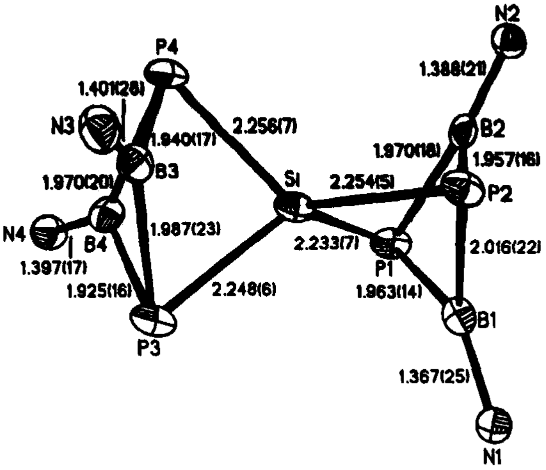
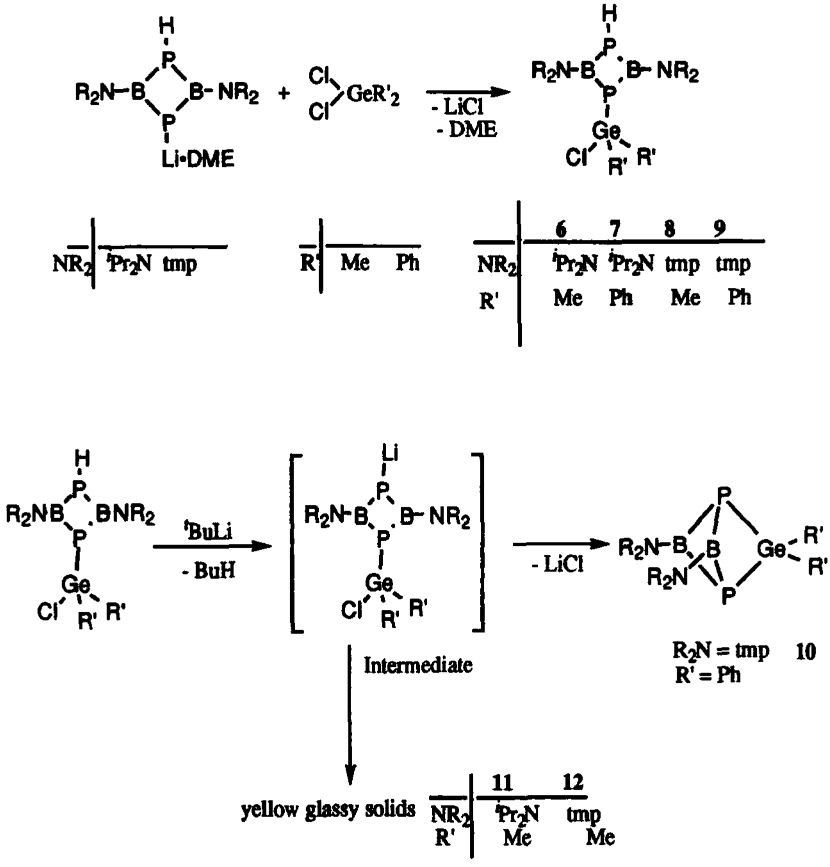


FIGURE 3 The molecular structure and framework of **5** ($R_2N = {}^iPr_2N$).

molecular structure of **5** with $R_2N = {}^iPr_2N$ is shown in Figure 3. The compounds have spirocyclic structures in which one Si atom occupies a single basal position in the linked pair of trigonal bipyramids.

RECENT RESULTS

In our continuing quest to define additional cage species as well as new main-group oligomer systems, we recently examined the 1:1 reactions of 1-(lithio•DME)-1,3,2,4-diphosphadiboretanes with organohalogermanes. The outcome of some of that chemistry is summarized in Scheme V. The compounds **6**, **8**, and **9** are colorless to light yellow solids and **7** is a viscous oil. Compounds **6**, **8**, and **9** were purified and fully characterized by analytical and spectroscopic methods, but compound **7** is difficult to purify and has been characterized only by ^{31}P NMR spectroscopy.



NR2	iPr2N	tmp

R'	Me	Ph

	6	7	8	9
NR2	iPr2N	iPr2N	tmp	tmp
R'	Me	Ph	Me	Ph

R_2N = tmp 10
R' = Ph

	11	12
NR2	iPr2N	tmp
R'	Me	Me

Scheme V

The dehydrohalogenation chemistry of **6**, **8**, and **9** with t-BuLi in hexane was examined. Compound **8** was converted to the cage compound **10**, which was isolated in about 44% yield. The compound forms as a light yellow crystalline solid (mpt 196-198°C) that gives satisfactory elemental analysis and a parent ion cluster of peaks (m/e=596-587). The compound shows single resonances in the ^{11}B and ^{31}P NMR spectra at δ 47.3 and δ 49.8, respectively. The molecular structure of **10** was determined by single crystal X-ray diffraction techniques and a view is shown in Figure 4. The structure is quite similar in its general features to that found for the related molecule containing the $SiPh_2$ fragment.

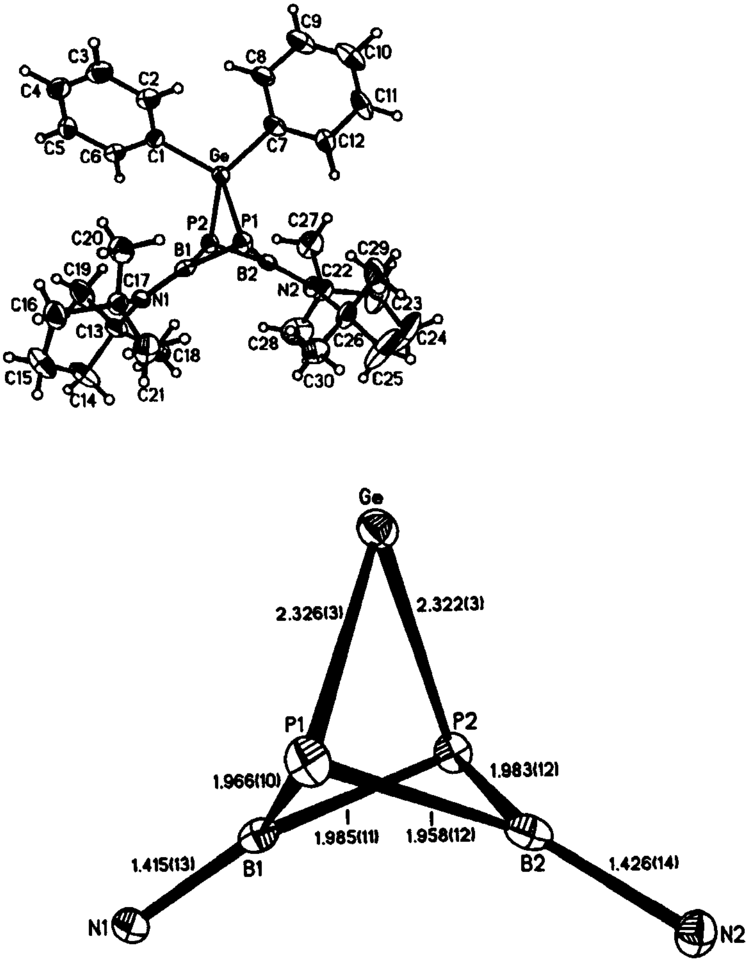


FIGURE 4 The molecular structure and framework of $P_2(tmpB)_2GePh_2$

The chemistry of **10** has been partially explored. In particular, the molecule combines with $(CO)_5Cr{\bullet}NMe_3$ and forms a monometallic coordination complex $(CO)Cr{\bullet}P_2(tmpB)_2GePh_2$. The molecular structure of the complex is shown in Figure 5. At this time, there is no evidence for the formation of bis coordination complexes or oligomeric metal complexes.

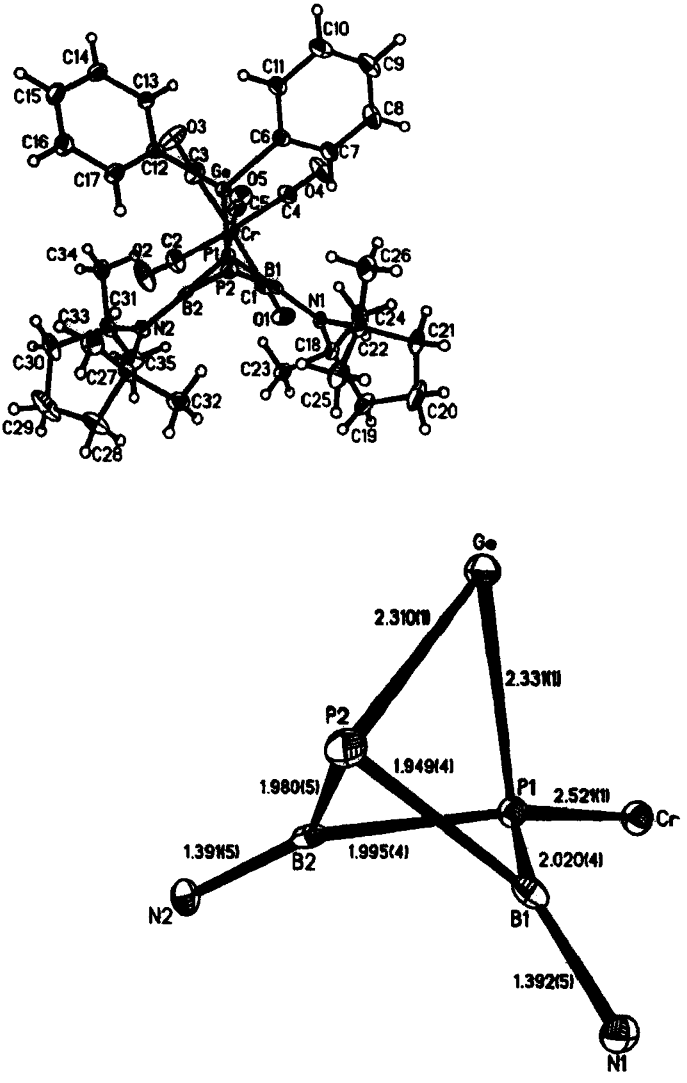


FIGURE 5 The molecular structure and framework of $(CO)_5Cr{\bullet}P_2(tmpB)_2GePh_2$

It is interesting that reaction of 6 and 8 with t-BuLi did not produce the anticipated cage derivatives. Instead, yellow glassy solids are isolated that so far have failed to yield pure samples. The characteristics of these compounds suggest that they may be oligomeric. If this proves to be the case, it suggests that we have reached a set of necessary conditions, e.g., E atom size and substituent group size that encourage the intermolecular reaction pathway over the intramolecular route. Further work on these and related systems is in progress to clarify this point.

CONCLUSION

As shown by this brief summary, the construction of boron-phosphorus cage chemistry continues to develop along several fronts. In particular, it is now possible to prepare $P_2(R_2NB)_2ER'_2$ species that contain Group 14 fragments. The germanium compounds reported here are similar to the silicon analogs reported earlier, with two exceptions. In these cases, oligomeric species are obtained that suggest methods for the synthesis of additional polymeric species.

REFERENCES

1. I. Haiduc, D. B. Sowerby, The Chemistry of Inorganic Homo- and Heterocycles, Academic Press: New York, (1987).
2. P. Kölle, H. Nöth, R. T. Paine, Chem. Ber., 119, 2681 (1986).
3. G. L. Wood, E. N. Duesler, C. K. Narula, R. T. Paine, H. Nöth, J. Chem. Soc. Chem. Commun., 496 (1987).
4. P. Kölle,G. Linti, H. Nöth, G.L. Wood, C.K. Narula, R.T. Paine, Chem. Ber., 121, 871 (1988).
5. P. Kölle, G. Linti, H. Nöth, K. Polborn, J. Organomet. Chem., 355, 7 (1988).
6. P. Kölle, H. Nöth, R. T. Paine, W. Rattay, Z. Naturforsch., 43b, 1439 (1988).
7. P. Kölle, H. Nöth, R. T. Paine, Chem. Ber., 122, 423 (1989).
8. G. L. Wood, E. N. Duesler, R. T. Paine, H. Nöth, Phosphorus, Sulfur and Silicon, 41, 267 (1989).
9. G. Linti, H. Nöth, K. Polborn, R. T. Paine, Angew. Chem. Intl. Ed. Engl., 29, 682 (1990).
10. G. L. Wood, D. Dou, C.K. Narula, E.N. Duesler, R.T. Paine, H. Nöth, Chem. Ber., 123, 1455 (1990).
11. D. Dou, M. Westerhausen, G.L. Wood, G. Linti, E.N. Duesler, H. Nöth, R.T. Paine, Chem. Ber., 126, 379 (1993).
12. D. Dou, G.L. Wood, E.N. Duesler, R.T. Paine, H. Nöth, Inorg. Chem.., 31, 3756 (1992).
13. D. Dou, E. N. Duesler, R. T. Paine, H. Nöth, J. Am. Chem. Soc., 114, 9691 (1992).
14. R. T. Paine, D. Dou, M. Westerhausen, E.N. Duesler, G. Linti, H. Nöth, Phosphorus, Sulfur and Silicon, 77, 61 (1993).
15. G. Linti, H. Nöth, R. T. Paine, Chem. Ber., 126, 875 (1993).
16. H. Nöth, S. Staude, M. Thomann, R. T. Paine, Chem. Ber., 126, 611 (1993).
17. G. Linti, H. Nöth, Z. Anorg. Allgem. Chem., 593, 124 (1991).
18. D. Dou, B. Kaufmann, E.N. Duesler, T. Chen, R.T. Paine, H. Nöth, Inorg. Chem., 32, 3056 (1993).
19. D. Dou, M. Fan, E. N. Duesler, H. Nöth, R. T. Paine, Inorg. Chem., 33, 2151 (1994).
20. T. Chen, E. N. Duesler, R. T. Paine, H. Nöth, Phosphorus Sulfur and Silicon, 87, 41 (1994).
21. D. Dou, G. L. Wood, E. N. Duesler, R. T. Paine, H. Nöth, Inorg. Chem., 31, 1695 (1992).
22. H. V. Rasika Dias, P. P. Power, Angew. Chem. Intl. Ed., 26, 1270 (1987).

23. H. V. Rasika Dias, P. P. Power, J. Am. Chem. Soc., 111, 144 (1989).
24. R. A. Bartlett, H. V. Rasika Dias, X. Feng, P. P. Power, J. Am. Chem. Soc., 111, 1306 (1989).
25. H. V. Rasika Diaz, D. C. Pestana, M. Petrie, P. P. Power, Phosphorus Sulfur and Silicon, 51/52, 87 (1990).
26. P. P. Power, Angew. Chem. Intl. Ed. Engl., 29, 449 (1990).
27. P. P. Power, A. Moezzi, D.C. Pestana, M.A. Petrie, S.C. Shoner, K.M. Waggoner, Pure Appl. Chem., 63, 859 (1991).
28. P.P. Power, J. Organometal. Chem., 400, 49 (1990).
29. D. C. Pestana, P. P. Power, J. Am. Chem. Soc., 113, 8426 (1991).