250 *Inorg. Chem.* **2011**, *50*, 250–260
DOI: 10.1021/ic101884s

Inorganic Chemistry
Article

Ring-Closing Metathesis Reactions of Terminal Alkene-Derived Cyclic Phosphazenes

Dheeraj Kumar, Nem Singh, Karunesh Keshav, and Anil J. Elias*

Department of Chemistry, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi 110016, India

Received September 14, 2010

The first examples of ring-closing metathesis (RCM) reactions of a series of terminal alkene-derived cyclic phosphazenes have been carried out. The tetrakis-, hexakis-, and octakis(allyloxy)cyclophosphazenes $(NPPh_2)(NP(OCH_2CH{=}CH_2)_2)_2$ (**1**), $N_3P_3(OCH_2CH{=}CH_2)_6$ (**2**), and $N_4P_4(OCH_2CH{=}CH_2)_8$ (**3**) and the tetrakis(allyloxy)-*S*-phenylthionylphosphazene $(NS(O)Ph)[NP(OCH_2CH{=}CH_2)_2]_2$ (**4**) were prepared by the reactions of $CH_2{=}CHCH_2ONa$ with the cyclophosphazenes $(NPPh_2)(NPCl_2)_2$, $N_3P_3Cl_6$, and $N_4P_4Cl_8$ and the *S*-phenylthionylphosphazene $(NS(O)Ph)(NPCl_2)_2$. The reactions of **1**−**4** with Grubbs first-generation olefin metathesis catalyst $Cl_2Ru{=}CHPh(PCy_3)_2$ resulted in the selective formation of seven-membered di-, tri-, and tetraspirocyclic phosphazene compounds $(NPPh_2)[NP(OCH_2CH{=}CHCH_2O)]_2$ (**5**), $N_3P_3(OCH_2CH{=}CHCH_2O)_3$ (**6**), and $N_4P_4(OCH_2CH{=}CHCH_2O)_4$ (**7**) and the dispirocyclic *S*-phenylthionylphosphazene compound $(NS(O)Ph)[NP(OCH_2CH{=}CHCH_2O)]_2$ (**8**). X-ray structural studies of **5**−**8** indicated that the double bond of the spiro-substituted cycloalkene units is in the cis orientation in these compounds. In contrast to the reactions of **1**−**4**, RCM reactions of the homoallyloxy-derived cyclophosphazene and thionylphosphazene $(NPPh_2)[NP(OCH_2CH_2CH{=}CH_2)_2]_2$ (**9**) and $(NS(O)Ph)[NP(OCH_2CH_2CH{=}CH_2)_2]_2$ (**10**) with the same catalyst resulted in the formation of 11-membered diansa compounds $NPPh_2[NP(OCH_2CH_2CH{=}CHCH_2CH_2O)]_2$ (**11**) and $(NS(O)Ph)[NP(OCH_2CH_2CH{=}CHCH_2CH_2O)]_2$ (**13**) and the intermolecular doubly bridged ansa−dibino−ansa compounds **12** and **14**. The X-ray structural studies of compounds **11** and **13** indicated that the double bonds of the ansa-substituted cycloalkene units are in the trans orientation in these compounds. The geminal bis(homoallyloxy)tetraphenylcyclotriphosphazene $[NPPh_2]_2[NP(OCH_2CH_2CH{=}CH_2)_2]$ (**15**) upon RCM with Grubbs first- and second-generation catalysts gave the spirocyclic product $[NPPh_2]_2[NP(OCH_2CH_2CH{=}CHCH_2CH_2O)]$ (**16**) along with the geminal dibino-substituted dimeric compound $[NPPh_2]_2[NP(OCH_2CH_2CH{=}CHCH_2CH_2O)_2PN][NPPh_2]_2$ (**17**) as the major product. The dibino compound **17**, upon reaction with the Grubbs second-generation catalyst, was found to undergo a unique ring-opening metathesis reaction, opening up the bino bridges and partially converting to the spirocyclic compound **16**.

Introduction

The prospect of variety in substitution reactions on the reactive P−X bonds make cyclophosphazenes attractive for the preparation of a wide range of derivatives having diverse applications.[1−8] Numerous structural isomers and stereoisomers, unique to the cyclophosphazene ring skeleton are known, and many of these have been prepared by careful

*To whom correspondence should be addressed. E-mail: eliasanil@gmail.com.

(1) (a) Chandrasekhar, V.; Murugesapandian, B. *Acc. Chem. Res.* **2009**, *42*, 1047–1062. (b) Allcock, H. R. *Chemistry and Applications of Polyphosphazenes*; Wiley: Hoboken, NJ, 2003; p 1. (c) Chandrasekhar, V. *Inorganic and Organometallic Polymers*; Springer-Verlag: Heidelberg, Germany, 2005; p 82. (d) Allcock, H. R. *Phosphorus−nitrogen compounds; cyclic, linear, and high polymeric systems*; Academic Press: New York, 1972.

(2) (a) Chandrasekhar, V.; Thilagar, P.; Pandian, M. *Coord. Chem. Rev.* **2007**, *251*, 1045–1074. (b) Chandrasekhar, V.; Andavan, G. T. S.; Azhakar, R.; Pandian, B. M. *Inorg. Chem.* **2008**, *47*, 1922–1944. (c) Chandrasekhar, V.; Thilagar, P.; Krishnan, V.; Bickley, J. F.; Steiner, A. *Cryst. Growth Des.* **2007**, *7*, 668–675. (d) Chandrasekhar, V.; Pandian, B. M.; Azhakar, R. *Inorg. Chem.* **2006**, *45*, 3510–3518. (e) Chandrasekhar, V.; Krishnan, V.; Steiner, A.; Bickley, J. F. *Inorg. Chem.* **2004**, *43*, 166–172. (b) Chandrasekhar, V.; Krishnan, V. *Adv. Inorg. Chem.* **2002**, *53*, 159–173.

(3) (a) Boomishankar, R.; Richards, P. I.; Gupta, A. K.; Steiner, A. *Organometallics* **2010**, *29*, 2515–2520. (b) Richards, P. I.; Bickley, J. F.; Boomishankar, R.; Steiner, A. *Chem. Commun.* **2008**, 1656–1658. (b) Benson, M. A.; Ledger, J.; Steiner, A. *Chem. Commun.* **2007**, 3823–3825. (c) Boomishankar, R.; Ledger, J.; Guilbaud, J. B.; Campbell, N. L.; Bacsa, J.; Bonar-Law, R.; Khimyak, Y. Z.; K.; Steiner, A. *Chem. Commun.* **2007**, 5152–5154. (d) Benson, M. A.; Zacchini, S.; Boomishankar, R.; Chan, Y.; Steiner, A. *Inorg. Chem.* **2007**, *46*, 7097–7108. (e) Richards, P. I.; Steiner, A. *Inorg. Chem.* **2005**, *44*, 275–281. (f) Richards, P. I.; Steiner, A. *Inorg. Chem.* **2004**, *43*, 2810–2817.

(4) (a) Omotowa, B. A.; Phillips, B. S.; Zabinski, J. S.; Shreeve, J. M. *Inorg. Chem.* **2004**, *43*, 5466–5471. (b) Muralidharan, K.; Omotowa, B. A.; Twamley, B.; Piekarski, C.; Shreeve, J. M. *Chem. Commun.* **2005**, 5193–5195.

(5) (a) Carter, K. R.; Calichman, M.; Allen, C. W. *Inorg. Chem.* **2009**, *48*, 7476–7481. (b) Calichman, M.; Derecskei-Kovacs, A.; Allen., C. W. *Inorg. Chem.* **2007**, *46*, 2011–2016. (c) Bahadur, M.; Allen, C. W.; Geiger, W. E.; Bridges, A. *Can. J. Chem.* **2002**, *80*, 1393–1397. (d) Nataro, C.; Myer, C. N.; Cleaver, W. M.; Allen, C. W. *J. Organomet. Chem.* **2001**, *637*−*639*, 284–290. (e) Allen, C. W.; Bahadur, M. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1993**, *76*−*77*, 203–206. (f) Allen, C. W.; Bahadur, M. *J. Inorg. Organomet. Polym.* **1998**, *8*, 23–31.

 Published on Web 11/29/2010

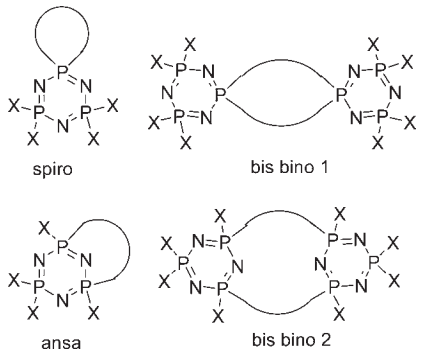


Figure 1. Types of intra- and intermolecular cyclic products possible from the reactions of halocyclophosphazenes with simple difunctional reagents.

reaction strategies.[1d,9−11] Among these, the reactions involving difunctional reagents with halogenated cyclophosphazenes have focused mostly on understanding the preferences in the formation of ansa- and spiro-substituted isomeric products, as well as in making the intermolecular bridged bino derivatives (Figure 1).[12,13] In general, the nature of the products formed in these reactions is controlled by a variety of factors such as the chain length of the difunctional reagents, the nature of the reacting functional groups, and their mode of activation.[14,15] We have earlier shown the possibility of conversion of many examples of ansa derivatives of fluorophosphazenes to their spiro analogues,[14] while Shaw and co-workers have shown the interconversion of a spiro-substituted cyclophosphazene to an ansa compound as well.[16]

While the ansa, spiro, and bino derivatives of cyclophosphazenes known so far have been prepared by the reactions of multifunctional reagents such as diols, diamines, pentaerythritol, etc., with halophosphazenes, no attempts have been made to see the selectivity in the formation of these structurally different derivatives if existing acyclic substituents on a cyclophosphazene scaffold are made to undergo ring formation. Olefin metathesis using Grubbs' and Schrock's catalysts has been one of the most sought-after reactions utilized in ring-closing reactions of terminal alkenes in recent times.[17] Although such reactions have been centered mostly on organic substrates, their usefulness in realizing metathesis products of main-group- and transition-metal-based alkenes has been steadily evolving.[18] In the area of phosphazene-based polymers, Allcock and co-workers have shown the utility of ADMET and ROMP polymerization methods using the Grubbs first-generation catalyst in the synthesis of novel phosphazene pendant polymers.[19] However, no olefin metathesis studies have been reported on cyclic phosphazenes specifically involving ring-closing metathesis (RCM) reactions. In this paper, we report the first study of RCM reactions on a series of terminal alkene-derived cyclophosphazenes using the Grubbs first-generation catalyst. The study, in addition to showing selectivity in the ansa, spiro, and bino ring formations (Figure 1), was also expected to generate novel cycloalkene-derived cyclophosphazenes, which can be utilized for further reactions centered on the alkene moiety. Details of the RCM reactions of allyloxy- and homoallyloxy-derived cyclophosphazenes and thionylphosphazenes and structural characterization of the new cycloalkene-derived phosphazene derivatives are described. The first ring-opening metathesis (ROM) reaction of a cycloalkene-based dibinocyclophosphazene dimer using

(6) (a) Carriedo, G. A.; Crochet, P.; Alonso, F. J. G.; Gimeno, J.; Persa-Soto, A. *Eur. J. Inorg. Chem.* **2004**, *18*, 3668–3674. (b) Carriedo, G. A.; Garcia-Alonso, F. J.; Garcia-Alvarez, J. L.; Pappalardo, G. C.; Punzo, F.; Rossi, P. *Eur. J. Inorg. Chem.* **2003**, *13*, 2413–2418. (c) Carriedo, G. A.; Alonso, F. J.; Elipe, P. G.; Brillas, E.; Julia, L. *Org. Lett.* **2001**, *3*, 1625–1628. (d) Ainscough, E. W.; Brodie, A. M.; Davidson, R. J.; Moubaraki, B.; Murray, K. S.; Otter, C. A.; Waterland, M. R. *Inorg. Chem.* **2008**, *47*, 9182–9192. (e) Ainscough, E. W.; Brodie, A. M.; Derwahl, A.; Kirk, S.; Otter, C. A. *Inorg. Chem.* **2007**, *46*, 9841–9852.

(7) (a) Asmafiliz, N.; Kılıç, Z.; Ozturk, A.; Hokelek, T.; Koc, L. Y.; Acik, L.; Kisa, O.; Albay, A.; Ustundag, Z.; Solak, A. O. *Inorg. Chem.* **2009**, *48*, 10102–10116. (b) Besli, S.; Coles, S. J.; Davies, D. B.; Erkovan, A. O.; Hursthouse, M. B.; Kılıç, A. *Inorg. Chem.* **2008**, *47*, 5042–5044. (c) Ilter, E. E.; Asmafiliz, N.; Kilic, Z.; Isiklan, M.; Hokelek, T.; Caylak, N.; Sahin, E. *Inorg. Chem.* **2007**, *46*, 9931–9944. (d) Bilge, S.; Demiriz, S.; Okumus, A.; Kilic, Z.; Tercan, B.; Hokelek, T.; Buyukgungor, O. *Inorg. Chem.* **2006**, *45*, 8755–8767.

(8) (a) Keshav, K.; Singh, N.; Elias, A. J. *Inorg. Chem.* **2010**, *49*, 5753–5765. (b) Kumar, M. S.; Gupta, R. P.; Elias, A. J. *Inorg. Chem.* **2008**, *47*, 3433–3441. (c) Kumar, M. S.; Upreti, S.; Elias, A. J. *Inorg. Chem.* **2006**, *45*, 7835–7842.

(9) Jung, J.-H.; Pomeroy, J. C.; Zhang, H.; Wisian-Neilson, P. *J. Am. Chem. Soc.* **2003**, *125*, 15537–15542. Wisian-Neilson, P.; Johnson, R. S.; Zhang, H.; Jung, J.-H.; Neilson, R. H.; Ji, J.; Watson, W. H.; Krawiec, M. *Inorg. Chem.* **2002**, *41*, 4775–4779. Jung, J.-H.; Zhang, H.; Wisian-Neilson, P. *Inorg. Chem.* **2002**, *41*, 6720–6725.

(10) (a) Isiklan, M.; Asmafiliz, N.; Ozalp, E. E.; Ilter, E. E.; Kilic, Z.; Cosut, B.; Yesilot, S.; Kilic, A.; Ozturk, A.; Hokelek, T.; Koc Bilir, L. T.; Acik, L.; Akyuz, E. *Inorg. Chem.* **2010**, *49*, 7057–7071. (b) Besli, S.; Coles, S. J.; Erkovan, A. O.; Hursthouse, M. B.; Kilic, A. *Polyhedron* **2009**, *28*, 3513–3599. (c) Uslu, A.; Coles, S. J.; Davies, D. B.; Eaton, R. J.; Hursthouse, M. B.; Kılıç, A.; Shaw, R. A. *Eur. J. Inorg. Chem.* **2005**, *6*, 1042–1047. (d) Kumar, N. N. B.; Swamy, K. C. K. *Chirality* **2008**, *20*, 781–789. (e) *Chirality*, **2005**, *17*, 438−443.

(11) Allen, C. W. *Chem. Rev.* **1991**, *91*, 119–135 and references cited therein.

(12) (a) Chandrasekhar, V.; Muralidhara, M. G.; Selvaraj, I. *Heterocycles* **1990**, *31*, 2231–2266. (b) Chandrasekhar, V.; Krishanan, V. *Adv. Inorg. Chem.* **2002**, *53*, 159–173.

(13) Elias, A. J.; Shreeve, J. M. *Adv. Inorg. Chem.* **2001**, *52*, 335–358 and references cited therein.

(14) (a) Muralidharan, K.; Venugopalan, P.; Elias, A. J. *Inorg. Chem.* **2003**, *42*, 3176–3182. (b) Muralidharan, K.; Elias, A. J. *Inorg. Chem.* **2003**, *42*, 7535–7543. (c) Muralidharan, K.; Reddy, N. D.; Elias, A. J. *Inorg. Chem.* **2000**, *39*, 3988–3994. (d) Muralidharan, K.; Elias, A. J. *Inorg. Chem. Commun.* **2003**, *6*, 584–588. (e) Elias, A. J.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1994**, *33*, 2727–2734.

(15) (a) Brandt, K.; Czomperlik, P. I.; Olejnik, A.; Shaw, R. A.; Davis, D. B.; Hursthouse, M. B.; Sykara, G. A. *J. Am. Chem. Soc.* **1996**, *118*, 4496–4497. (b) Brandt, K.; Czomperlik, P. I.; Siwy, M.; Kupka, T.; Shaw, R. A.; Davis, D. B.; Hursthouse, M. B.; Sykara, G. A. *J. Am. Chem. Soc.* **1997**, *119*, 12432–12440. (c) Brandt, K.; Czomperlik, P. I.; Siwy, M.; Kupka, T.; Shaw, R. A.; Davis, D. B.; Hursthouse, M. B.; Sykara, G. A. *J. Am. Chem. Soc.* **1997**, *119*, 1143–1144.

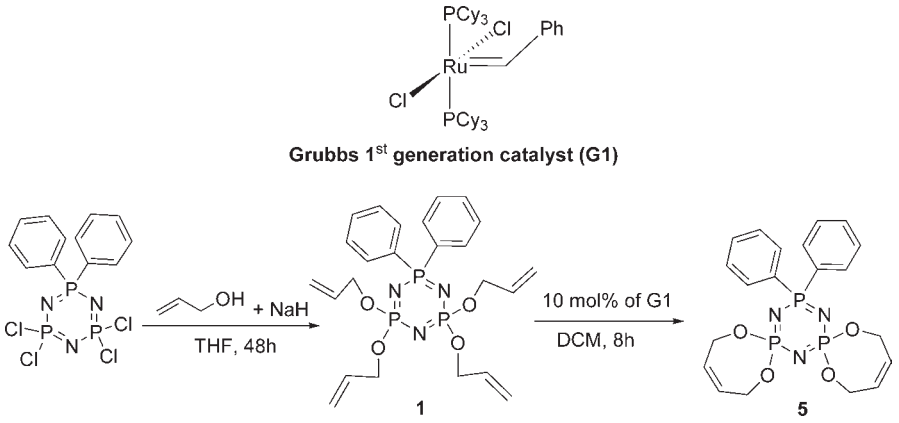
(16) Shaw, R. A.; Besli, S.; Coles, S. J.; Davies, D. B.; Hursthouse, M. B. *Dalton Trans.* **2007**, 2792–2801.

(17) (a) Deshmukh, P. H.; Blechert, S. *Dalton Trans.* **2007**, 2479–2491. (b) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18–29. (c) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543–6564. (d) Schrock, R. R.; Hoyeda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592–4633. (e) Grubbs, R. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 3760–3765. (f) Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748–3759. (g) Schrodi, Y.; Pederson, R. L. *Aldrichimica Acta* **2007**, *40*, 45–52. (h) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887–3897.

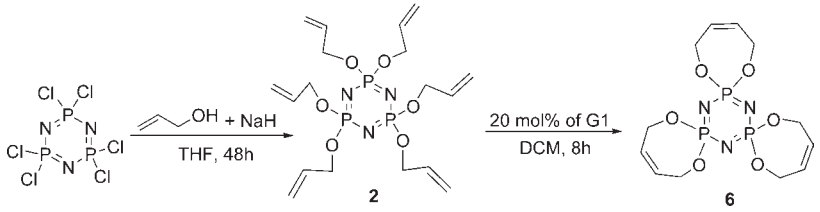
(18) (a) Han, J.; Deng, C.; Fang, R.; Zhao, D.; Wang, L.; Gladysz, J. A. *Organometallics* **2010**, *29*, 3231–3234. (b) Chambron, J. C.; Collin, J. P.; Heitz, V.; Jouvenot, D.; Kern, J. M.; Mobian, P.; Pomeranc, D.; Sauvage, J. P. *Eur. J. Org. Chem.* **2004**, 1627–1638. (c) Frey, J.; Kraus, T.; Heitz, V.; Sauvage, J. P. *Chem.—Eur. J.* **2007**, *13*, 7585–7592. (d) Hiraoka, S.; Yamauchi, Y.; Arakane, R.; Shionoya, M. *J. Am. Chem. Soc.* **2009**, *131*, 11646–11647. (e) McReynolds, M. D.; Dougherty, J. M.; Hanson, P. R. *Chem. Rev.* **2004**, *104*, 2239–2258. (f) Feher, F. J.; Eklund, A. G.; Wyndham, K. D. *Chem. Commun.* **1997**, 1185–1186. (g) Zak, P.; Pietraszuk, C.; Marciniec, B. *J. Mol. Catal., A: Chem.* **2008**, 1–8. (h) Matsuda, T.; Yamaguchi, Y.; Murakami, M. *Synlett* **2008**, *4*, 561–564.

(19) (a) Allcock, H. R.; Kellam, E. C.; Hofmann, M. A. *Macromolecules* **2001**, *34*, 5140–5146. (b) Allcock, H. R.; Laredo, W. R.; Kellam, E. C.; Morford, R. V. *Macromolecules* **2001**, *34*, 787–794. (c) Stone, D. A.; Allcock, H. R. *Macromolecules* **2006**, *39*, 4935–4937.

Scheme 1



Scheme 2



the Grubbs second-generation catalyst followed by ring closing, leading to a spiro-substituted derivative, is also reported.

Results and Discussion

Examples of cyclic phosphazenes and thionylphosphazenes with terminal alkene-derived acyclic substituents were prepared and RCM reactions carried out on them using the Grubbs first-generation catalyst. Allyloxy and homoallyloxy groups were chosen as the terminal alkene-containing moieties to observe the effect of the chain length on the nature of the products formed, and their cyclophosphazene derivatives, when prepared, were found to be viscous liquids. These phosphazene derivatives upon RCM resulted in intra- and intermolecular cycloalkene products, most of them as solids. The primary objective of the present study was to recognize any selectivity in the nature of the products formed from these reactions (ansa, spiro, and bino) and also to identify the factors responsible for the formation of the same.

The initial reactions were carried out on the *gem*-diphenyl-substituted cyclophosphazene, 1,1-$Ph_2N_3P_3Cl_4$ because, unlike $N_3P_3Cl_6$, the extent of substitution and ring formation on this phosphazene ring by allyloxy units can be easily monitored by NMR studies and the rigidity provided by the Ph_2P moiety often helps in realizing crystalline products, which are essential in differentiating isomeric products by X-ray structural studies. Sodium allyloxide was prepared by reacting allyl alcohol with NaH, and it was reacted with 1, 1-$Ph_2N_3P_3Cl_4$ to give the tetrakis(allyloxy) derivative **1** as a yellowish viscous liquid.[20] RCM, when carried out on **1** using 10 mol % of the Grubbs first-generation catalyst (G1; Scheme 1), resulted in the exclusive formation of the dispirocyclic compound **5** as a white crystalline solid. Compound **5** was purified by column chromatography and structurally characterized.

Hexakis(allyloxy)cyclotriphosphazene **2** was prepared in a manner similar to the synthesis of **1**.[21] When RCM was carried out on **2** using 10 mol % of the G1 catalyst, formation of a monospirocyclic compound was observed, which was identified using ^{1}H NMR spectral studies. However, when this reaction was carried out with 20 mol % of the G1 catalyst, the trispirocyclic compound **6** was obtained exclusively as colorless crystals (Scheme 2).

Because reactions carried out on the six-membered cyclotriphosphazene scaffold were giving exclusively the spirocyclic derivatives, we were keen to observe the nature of products formed on a larger phosphazene scaffold, which is significantly puckered. Structural studies on tetrameric phosphazene $N_4P_4Cl_8$ and its derivatives have indicated that they have, in general, a puckered (tub-shaped) structure.[22] The allyloxy substituents on such a ring can have proximities that are different from those of their trimeric analogues. The octakis(allyloxy)cyclotetraphosphazatetraene **3** was therefore prepared in a manner similar to the synthesis of **2**, and its RCM was carried out using the G1 catalyst. It was observed that the reaction was quite similar to that of the hexaallyloxy trimer **2** and yielded exclusively the tetraspirocyclic cyclotetraphosphazatetraene **7** (Scheme 3).

Thionylphosphazenes, although similar in many ways to cyclophosphazenes, have sometimes showed reaction chemistry different from that of the latter.[23] With a view to see if

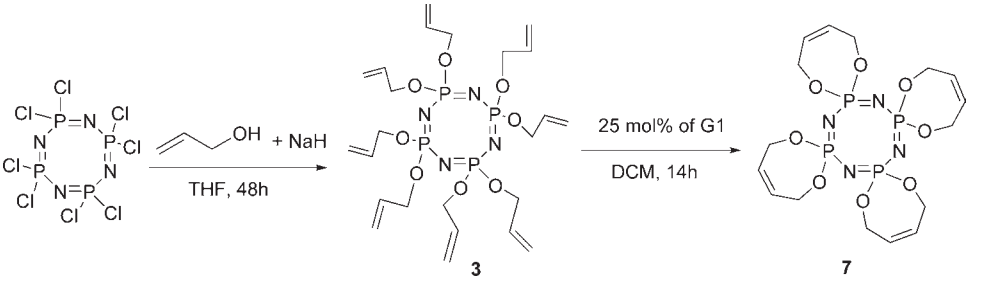
(20) Detlef, J.; Alfred, W.; Wiss, D. A. *Plaste Kautsch.* **1966**, *13*, 643–645.

(21) Fumiaki, Y.; Massaki, Y. *Kogakuin Daigaku Kenkyu Hokoku* **1959**, *7*, 62–66.

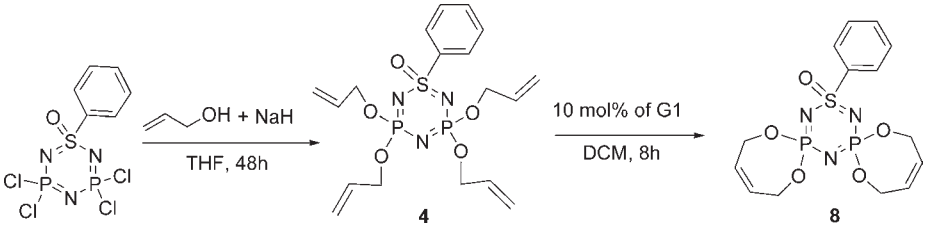
(22) Elias, A. J.; Twamley, B.; Haist, R.; Oberhammer, H.; Henkel, G.; Krebs, B.; Lork, E.; Mews, R.; Shreeve, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 10299–10303.

(23) (a) Elias, A. J.; Twamley, B.; Shreeve, J. M. *Inorg. Chem.* **2001**, *40*, 2120–2126. (b) Ramakrishna, T. V. V.; Elias, A. J. *J. Organomet. Chem.* **2001**, *637*−*639*, 382–389. (c) Gates, D. P.; Park, P.; Liang, M.; Edwards, M.; Angelakos, C.; Liable-sands, L. M.; Rheingold, A. L.; Manners, I. *Inorg. Chem.* **1996**, *35*, 4301–4309. (d) McWilliams, A. R.; Gates, D. P.; Edwards, M.; Liable-sands, L. M.; Guzei, I.; Rheingold, A. L.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 8848–8855.

Scheme 3



Scheme 4



similar chemistry can be extended to these inorganic heterocycles, we have prepared the tetrakis(allyloxy)-substituted *S*-phenylthionyldiphosphatriazene **4** (Scheme 4). Upon treatment with the G1 catalyst, this compound was also found to give a dispiro derivative **8** similar to **5**.

Because RCM on all of the allyloxy-derived cyclophosphazenes and thionylphosphazenes, irrespective of the ring size and the presence of hetero ring substituents on the cyclophosphazene, yielded only the spirocyclic derivatives, we were keen to observe the nature of RCM products formed when the chain length of the acyclic substituents are increased. To see the effect of an increase in the chain length of the alkene on the nature of the products in RCM, tetrakis(homoallyloxy) derivatives $(NPPh_2)[NP(OCH_2CH_2CH{=}CH_2)_2]_2$ (**9**) and $(NS(O)Ph)[NP(OCH_2CH_2CH{=}CH_2)_2]_2$ (**10**) were prepared by the reaction of a sodium salt of homoallyl alcohol with $(NPPh_2)(NPCl_2)_2$ and $(NS(O)Ph)(NPCl_2)_2$, respectively. These acyclic cyclophosphazene derivatives were subject to cyclization using the G1 catalyst. The reactions were found to give two major products in both cases, and mass spectral studies indicated that the molecular weight of the second compound was twice that of the first compound and indicated the presence of two phosphazene/thionylphosphazene units. The RCM reaction of **9**, in principle, can give six kinds of cyclized products (Figure 2). In addition to these compounds, the possibility of stereoisomers arising from the presence of different stereochemical configurations of phosphorus atoms also exists (e.g., ansa structures with cis and trans annulated rings for the ansa−dibino−ansa case).

The first compound crystallized in both cases (compounds **11** and **13**), and X-ray structural studies confirmed them to be diansa compounds. Quite interestingly, these compounds were found to have the alkene units of the ansa rings in the trans orientation, which was in contrast to the spiro compounds **4**−**8**, where the alkene units were in the cis orientation. The compound **12** with molecular weight 1034.11 was found to be a viscous liquid that could have either a spiro−dibino−spiro, an ansa−dibino−ansa, or an ansa−dibino−spiro structure. The ^{31}P NMR spectrum of a spiro−dibino−spiro structure should give three peaks for the three different phosphorus units, and that of an ansa−dibino−ansa compound should give only two peaks. The ^{31}P NMR spectrum of compound **12** gave two sets of peaks around δ 21.34 and 15.86 in a doublet−triplet pattern, and therefore it was assigned the ansa−dibino−ansa structure (Scheme 5). The possibility of **12** being the unsymmetrical ansa−dibino−spiro isomer was ruled out because it should have given five peaks in the ^{31}P NMR spectrum. The minor possibility of a tetrabino structural isomer for **12** (Figure 2) was also ruled out by the fact that the ^{1}H NMR spectrum of **12** gave two different signals for the alkene protons at δ 5.39 and 5.05, corresponding to the ansa and bino double bonds, respectively.

Analysis of the products of the RCM reaction of the tetrakis(homoallyloxy)-*S*-phenylthionylphosphazene **10** indicated them to be more complex compared to **9** because of the lower symmetry of the thionylphosphazene ring. In this reaction, also a diansa compound **13** similar to **11** was found to form as one of the main products, whose identity was confirmed by X-ray structural analysis. Mass spectral analysis indicated that the second major fraction in the reaction mixture has a molecular weight twice that of **13**. Compound **14** with a molecular weight of 914.19 was found to be a low-melting solid, which could have either a spiro−dibino−spiro, an ansa−dibino−ansa, or an ansa−dibino−spiro structure, similar to the product obtained in the case of **9**. The ^{31}P NMR spectrum of compound **14** gave only a singlet at δ 11.01, and therefore it was assigned the ansa−dibino−ansa structure because, for the spiro−dibino−spiro structure, two ^{31}P NMR signals and, for ansa−dibino−spiro, three ^{31}P NMR signals are expected (Scheme 6). ^{31}P NMR spectral analysis of the reaction mixtures in the RCM reactions of both **9** and **10** (Schemes 5 and 6) indicated the presence of more compounds in minor amounts in addition to compounds **11**−**14**, which, however, could not be obtained in isolable amounts and characterized. It was also not possible to clearly identify the orientation of the alkene double bonds present in semisolids **12** and **14** because of their multiplicity and the absence of crystal structure data.

To reduce the complexity in the product formation and also to see if the formation of compounds with intermolecular bridged

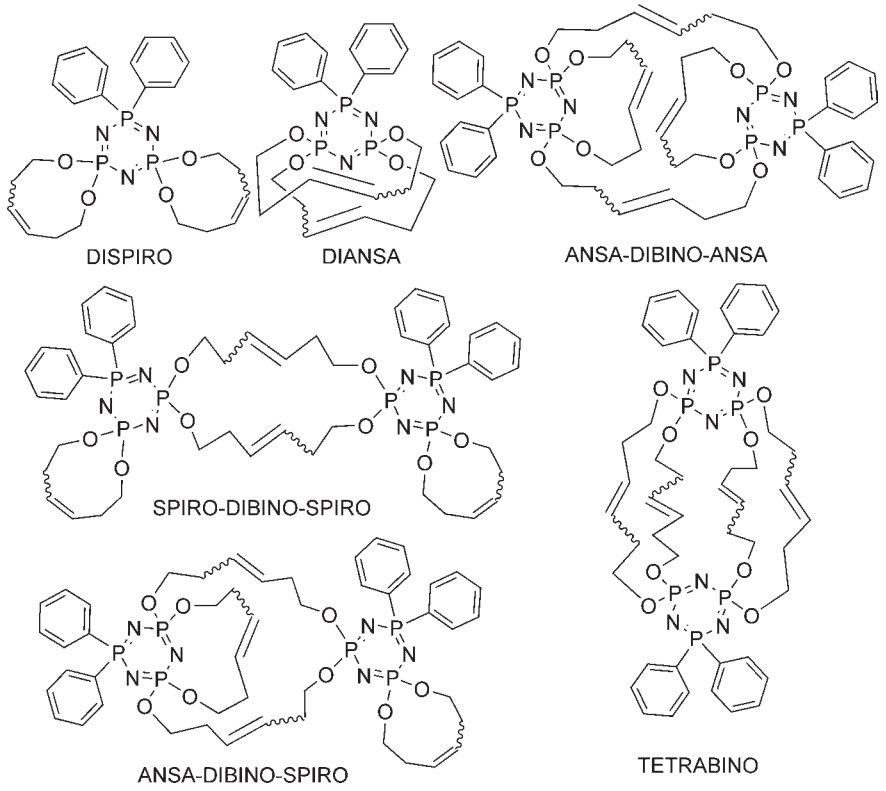
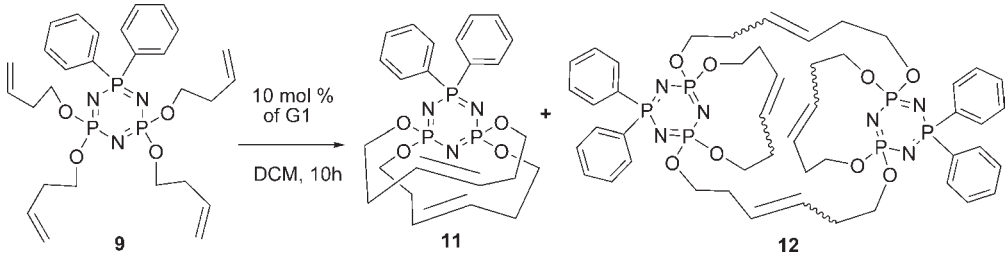
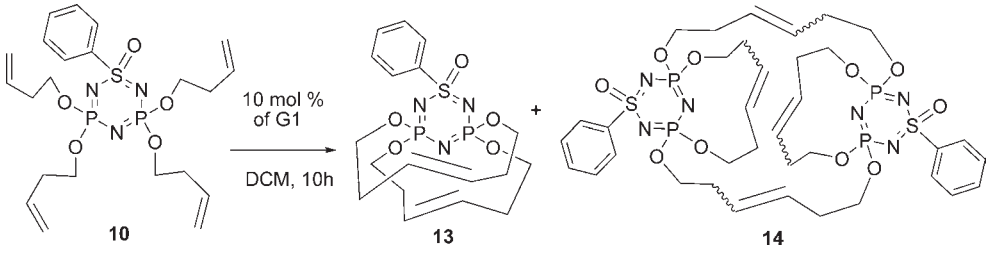


Figure 2. Possible cyclized products from the RCM reaction of **9**.

Scheme 5

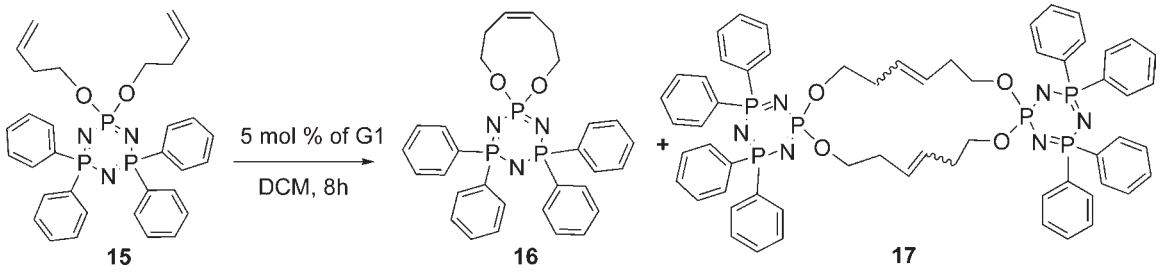


Scheme 6

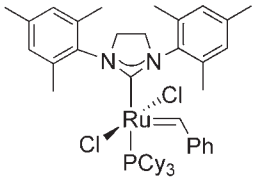


dibino units is a feature of RCM of long-chain terminal alkenes such as the homoallyloxy units, geminal bis(homoallyloxy) compound $(NPPh_2)_2[NP(OCH_2CH_2CH{=}CH_2)_2]$ (**15**), a derivative of the tetraphenyl-substituted cyclophosphazene $(NPPh_2)_2NPCl_2$, was prepared. Because in this case there is no possibility of realizing ansa-substituted compounds, a spirocyclic cycloalkene-derived phosphazene was expected upon RCM. When RCM of **15** was carried using 5 mol % of the G1 catalyst, the expected nine-membered monospirocyclic compound $[NPPh_2]_2[NP(OCH_2CH_2CH{=}CHCH_2CH_2O)]$ (**16**) was obtained, but interestingly, along with it, the 18-membered geminal dibino-substituted dimeric compound $[NPPh_2]_2[NP(OCH_2CH_2CH{=}CHCH_2CH_2O)_2PN][NPPh_2]_2$ (**17**) was obtained as the major product (Scheme 7). To the best of our knowledge, this is the first example of a geminal dibino derivative in cyclophosphazene chemistry. The identity of compound **16** was confirmed by X-ray structural analysis, and similar to the spirocyclic compounds **4**−**8**, the double bond of the cycloalkene unit of compound **16** was found to be cis, whereas compound **17**, as indicated by ^{31}P NMR, was obtained as an inseparable mixture of cis/trans isomers, which is quite common in RCM involving

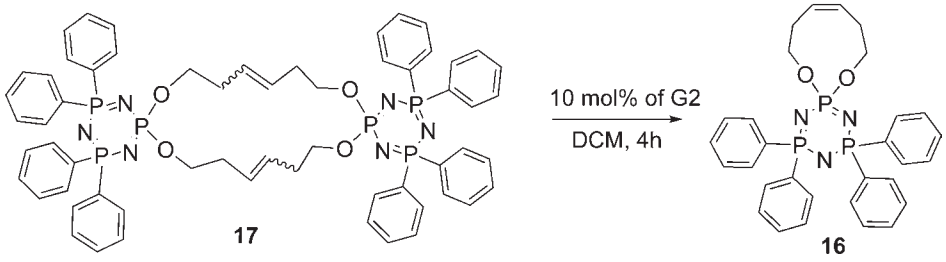
Scheme 7



Scheme 8



Grubbs 2nd generation catalyst (G2)



larger rings. While the ^{31}P NMR spectra of **17** indicated the presence of two very closely spaced sets of doublets and triplets, attempts to separate these isomers were found to be unsuccessful.

It has been reported that, unlike the Grubbs first-generation catalyst, the use of the Grubbs second-generation catalyst in macrocyclic RCM reactions provides better selectivity and a higher *E*/*Z* ratio of the alkene formed. This has been attributed to secondary metathesis reactions that happen in the presence of the Grubbs second-generation catalyst, which isomerizes the cyclized products further.[24] Because the dibino products obtained in this study were macrocyclic in nature, we were keen to see the effect, if any, of the Grubbs second-generation catalyst on them. When compound **17** (a mixture of cis/trans isomers) was reacted with 10 mol % of the Grubbs second-generation catalyst in refluxing dichloromethane, it showed an interesting partial transformation to compound **16** in 26% yield (Scheme 8). Although ansa-to-spiro and spiro-to-ansa transformations had been reported earlier, this is the first example of a dibino-to-spiro transformation in cyclophosphazene chemistry. The simplicity of the ^{13}C NMR spectra of **17** clearly indicated that the mixture contains only two symmetrical compounds (both cis and both trans), with signals for two double-bond carbons appearing at δ 128.55 and 128.39. After conversion, the ^{13}C NMR spectrum of the remaining fraction of **17** indicated that the relative intensity of the peak at δ 128.55 has considerably decreased, possibly indicating that the isomer with both double bonds in the cis configuration has undergone further metathesis, leading to compound **16** and also to more of the isomer with both double bonds in the trans configuration of **17**. This change in the *E*/*Z* ratio of **17** is in conformity with the observation of Grubbs and co-workers on secondary metathesis involving cycloalkenes of large ring sizes.[24] Analysis by ^{31}P NMR spectroscopy of the dibino compound **17** before and after partial conversion to **16** indicated that, among the two closely spaced set of peaks [δ 20.02, 19.97 (both doublets) and δ 10.15, 9.88 (both triplets)], the intensity of one set (δ 19.97 and 10.15) has reduced (from 45:55 to 36:64), further supporting the above observation. RCM of **15** carried out using the G2 catalyst instead of the G1 catalyst was found to give the spiro and dibino compounds **16** and **17** in 28 and 49% yields, respectively, and compound **17** was obtained as a 37:63 mixture of cis/trans isomers. This indicates that the Grubbs second-generation catalyst brings about a better *E*/*Z* ratio of cyclic alkene products of large rings with better yields of products compared to the first-generation catalyst.

Spectral Studies of Compounds 1−17. Compounds **1**−**17** have been characterized by IR, NMR (^{1}H, ^{13}C, and ^{31}P), and mass spectral studies. Cyclization of compounds **1**−**4**, **9**, **10**, and **15** can be easily monitored by the absence of a terminal $=CH_2$ peak in the ^{1}H NMR spectra of compounds **5**−**8**, **11**−**14**, **16**, and **17**. The terminal $=CH_2$ chemical shifts were found to be in the range of δ 5.10−5.50 for the allyloxy compounds **1**−**4** and δ 4.91−5.18 for the homoallyloxy compounds **9**, **10**, and **15**. The chemical shifts of −CH= protons were found to be in the range of δ 5.83−6.01 for compounds **1**−**4**, which showed a slight upfield shift of around δ 0.2 after cyclization in compounds **5**−**8**. A similar trend was also observed for compounds **9** and **10**. Contrary to the above, compound **15** showed a slight downfield shift in the chemical shift of −CH= protons after

(24) Lee, C. W.; Grubbs, R. H. *Org. Lett.* **2000**, *2*, 2145–2147.

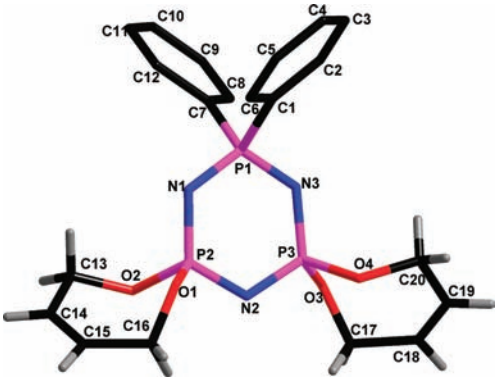


Figure 3. X-ray crystal structure of compound **5** (phenyl hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): P1−N1 1.598(3), P1−C7 1.801(3), P2−O1 1.575(3), O1−C16 1.447(4), C13−C14 1.476(5), C14−C15 1.309(5); N1−P1−N3 116.6(1), N1−P2−N2 118.3(1), C7−P1−C1 104.9(1), O1−P2−O2 102.7(1), C13−C14−C15 127.3(3).

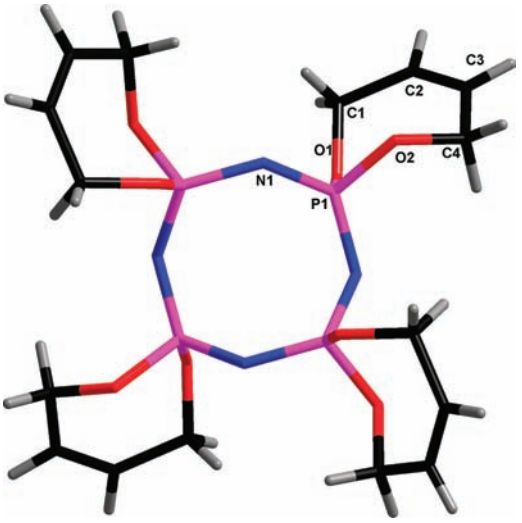


Figure 4. X-ray crystal structure of compound **7**. Selected bond lengths (Å) and angles (deg): P1−N1 1.564(2), P1−O1 1.577(2), C1−C2 1.485(4), C2−C3 1.306(4); N1−P1−N1 120.5(2), O1−P1−O2 103.5(1), O1−C1−C2 112.3(3), C3−C2−C1 127.7(3).

cyclization. The $-OCH_2-$ protons of compounds **1**−**4**, **9**, **10**, and **15** were found to be more shielded compared to the $-OCH_2-$ protons of their cyclized analogues. The ^1H NMR spectra of thionylphosphazene compounds **4** and **10** were found to be more complex because of the unsymmetrical nature of the thionylphosphazene ring. In these two compounds, two sets of signals were obtained for all types of protons, one corresponding to the allyloxy/homoallyloxy group pointing toward the phenyl ring and the other toward the S═O bond. Allyloxy/homoallyloxy groups pointing toward the S═O bond were deshielded compared to those directed toward the phenyl ring. In general, ^1H NMR studies on the cis and trans double bonds of the cycloalkene units indicated that the CH of the cis double bond is deshielded compared to the CH of the trans double bond. The CH hydrogen atoms of cyclized compounds **5**−**8** and **16** (all cis isomers) were found to be in the range of δ 5.69−5.74, while for compounds **11** and **13** (both trans isomers), they were found to be in the range of δ 5.38−5.71.

The ^{31}P NMR spectra of all of the compounds excluding **5** (which belong to an AB_2 spin system) were identified

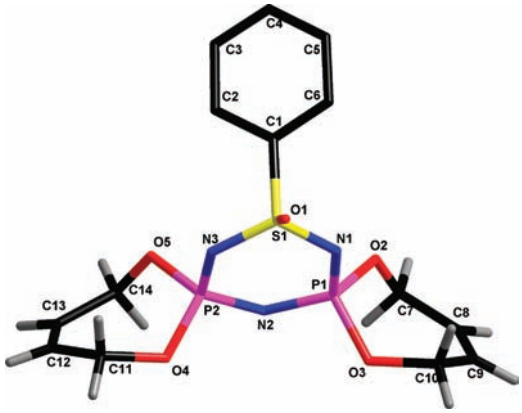


Figure 5. X-ray crystal structure of compound **8** (phenyl hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): S1−O1 1.427(4), S1−N3 1.552(5), S1−C1 1.766(5), P1−N2 1.562(5), P1−O2 1.567(4), O2−C7 1.445(7), C7−C8 1.465(9), C8−C9 1.297(9); O1−S1−N3 111.9(2), N3−S1−N1 113.7(2), O2−P1−O3 104.8(2), N2−P1−N1 116.0(2).

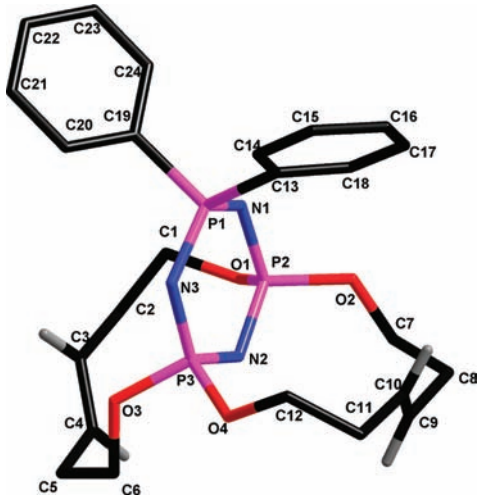


Figure 6. X-ray crystal structure of compound **11** (only double-bond hydrogen atoms have been shown for clarity). Selected bond lengths (Å) and angles (deg): P1−N1 1.601(2), P1−C13 1.808(3), P2−O2 1.580(2), O2−C7 1.445(4), C7−C8 1.505(5), C8−C9 1.506(5), C9−C10 1.299(5); N1−P1−N3 117.2(1), C19−P1−C13 104.6(1), O2−P2−O1 100.2(1), N3−P3−N2 117.5(1), C3−C2−C1 112.5(3), C4−C3−C2 125.3(4), C3−C4−C5 125.4(4).

to fit into a simple AX_2 spin system. A comparison of the ^{31}P NMR data of the allyloxy derivative **1**−**4** with the spirocyclic products **5**−**8** indicates that, upon ring formation, there is a systematic downfield shift in the δ values to the extent of δ 4−5. In contrast, no significant changes in the ^{31}P NMR chemical shifts were observed in a comparison of the acyclic homoallyloxy derivatives with their cyclized products. ^{31}P NMR and mass spectral studies also helped in the identification of dibino compounds **12**, **14**, and **17**, which has been discussed above.

X-ray Structures of Compounds 5−8, 11, 13, and 16. The crystal structures of compounds **5**, **7**, **8**, **11**, and **13** are given in Figures 3−7, and those of compounds **6** and **16** are given in the Supporting Information. Crystallographic data, data collection parameters, and tables of bond lengths and angles for compounds **5**−**8**, **11**, **13**, and **16** are given in the Supporting Information. The phosphazene ring was found to be almost planar in **5** because

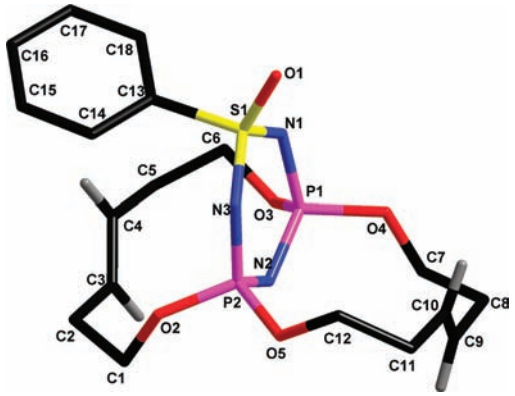


Figure 7. X-ray crystal structure of compound **13** (only double-bond hydrogen atoms have been shown for clarity). Selected bond lengths (Å) and angles (deg): S1−O1 1.434(3), S1−N3 1.544(4), S1−C13 1.780(4), P1−O2 1.567(4), P1−N2 1.575(4), P1−N1 1.591(4), C3−C4 1.292(7), C4−C5 1.497(7), C5−C6 1.499(7); O1−S1−N3 111.8(2), N3−S1−N1 114.5(2), O1−S1−C13 105.8(2), O3−P1−O4 102.4(2), N2−P1−N1 116.7(2), S1−N1−P1 123.5(2), C1−C2−C3 114.0(4), C4−C3−C2 127.8(5), C4−C5−C6 113.0(4).

the phosphorus atom bearing the *gem*-diphenyl group and the opposite ring nitrogen atom do not deviate significantly from the mean plane defined by the other four atoms of the phosphazene ring. The conformation of the N_3P_3 ring of **6** was more like a half-chair because the P1 and N2 atoms are deviating from the mean plane defined by the other four atoms by −0.318(1) and +0.017(4) Å, respectively. The half-chair conformation of **6** was also supported by the fact that the angle between the mean planes through N1−P2−P3−N3 and N3−P1−N1 is 22.4(2)°, whereas the analogous angle between the mean planes through N1−P2−P3−N3 and P3−N2−P2 is only 1.4(2)°. In compound **8**, the thionylphosphazene ring was found to be in a boat conformation because the S1 and N2 atoms are deviating from the mean plane defined by the other four atoms by −0.217(1) and −0.102(5) Å, respectively. In contrast, the N_4P_4 ring of compound **7** was found to be tub-shaped. The seven-membered spirocyclic rings in compounds **5**−**8** were found to be significantly puckered because the angle between the mean planes through the four carbon atoms of the spiro rings (which are in same plane) and the other three atoms of the same spiro ring (i.e., one phosphorus and two oxygen atoms) are found to be in the range of 34.2(2)−40.9(2)°. All of the spirocyclic compounds were found to have the cis configuration around the double bonds.

In contrast to the spirocyclic compound **5**, where the phosphazene ring was almost planar, the phosphazene ring of the ansa compound **11** was found to be in a half-chair conformation because the phosphorus atom bearing the *gem*-diphenyl group and the opposite nitrogen atom N2 were deviating from the mean plane defined by the other four atoms by −0.205(1) and −0.013(4) Å, respectively. Additional support for this conformation was obtained from the fact that the angle between the mean planes through N1−P2−P3−N3 and N3−P1−N1 is 14.7(1)°, while the angle between the mean planes through N1−P2−P3−N3 and P3−N2−P2 is 1.0(2)°. Unlike the two *gem*-diphenylphosphazene compounds **5** and **11**, the *S*-phenylthionylphosphazene **13** was found to have the N_3P_2S ring in a boat conformation similar to its dispiro compound **8**. In compound **13**, S1 and N2 were found to be deviating from the mean plane defined by the other four atoms by −0.197(1) and −0.100(4) Å, respectively. In both compounds **11** and **13**, the 11-membered ansa rings were found to be significantly puckered. Both diansa compounds **11** and **13** were found to have trans configuration around the double bond. Unlike the spiro compounds **4**−**8**, the two C=C bond distances of the ansa compounds varied significantly. They were found to be 1.321(6) and 1.299(6) Å for compound **11** and 1.294(7) and 1.225(9) Å for compound **13**.

Similar to the spiro compound **5**, the phosphazene ring was found to be in an almost planar geometry in **16** because the phosphorus atom bearing the *gem*-diphenyl group and the opposite ring nitrogen atoms do not deviate significantly from the mean plane defined by the other four atoms of the phosphazene rings. The nine-membered spiro ring is once again significantly puckered, and the configuration around the double bond was found to be cis, which is in agreement with compounds **5**−**8**.

Experimental Procedures

Preparation of $(NPPh_2)[(CH_2{=}CHCH_2O)_2PN]_2$ (1). Allyl alcohol (0.34 mL, 4.98 mmol) was dissolved in 10 mL of tetrahydrofuran (THF) and added to a suspension of NaH (0.22 g, 4.98 mmol) in 20 mL of THF. After the resulting suspension was stirred for 1 h at room temperature, a solution of $N_3P_3Cl_4Ph_2$ (0.50 g, 1.16 mmol) in 10 mL of THF was added to it. The resulting mixture was stirred at room temperature for 24 h, before refluxing for 6 h. The reaction was monitored using thin-layer chromatography and ^{31}P NMR spectroscopy. Afterward, the solvent was removed under vacuum and the resulting crude product chromatographed on an acidic alumina column and eluted with a hexane/ethyl acetate mixture. Compound **1** came out as a yellowish viscous liquid while using a 5% ethyl acetate/hexane mixture as the eluent. Yield: 0.48 g (80%). IR (ν, cm^{-1}): 3080 w, 2993 w, 1647 w, 1432 m, 1210 vs, 1112 m, 1025 vs. ^1H NMR: δ 7.80−7.87 (m, 4H, C_6H_5), 7.26−7.46 (m, 6H, C_6H_5), 5.840−5.96 (m, 4H, =C*H*−), 5.25 [d (J = 17 Hz), 4H, trans −CH=CH_2], 5.11 [d (J = 10.5 Hz), 4H, cis −CH=CH_2], 4.41−4.42 (m, 8H, −CH_2−). $^{13}C\{^1H\}$ NMR: δ 136.63, 130.83, 130.31, 127.99 [Ph*C*], 133.23 [=*C*H−], 116.76 [=*C*H_2], 66.15 [−*C*H_2−]. $^{31}P\{^1H\}$ NMR: δ 21.17 [t (J = 34 Hz), $P(C_6H_5)_2$], 15.95 [d (J = 34 Hz), $P(OCH_2CH{=}CH_2)_2$]. MS (ES) [m/e (species)]: 518.18 $[M + 1]^+$.

Preparation of $(NPPh_2)[NP(OCH_2CH{=}CHCH_2O)]_2$ (5). Compound **1** (0.50 g, 0.96 mmol) was dissolved in 20 mL of dry dichloromethane and transferred to a 100 mL flask (covered with aluminum foil) containing the Grubbs first-generation catalyst (80 mg, 0.09 mmol, 10 mol %) dissolved in 20 mL of dichloromethane. An additional 40 mL of dichloromethane was added to the same flask, and the resulting solution was refluxed for about 8 h. The reaction was monitored using thin-layer chromatography and ^{31}P NMR spectroscopy. Afterward, the solvent was removed under vacuum and the resulting crude product chromatographed on an acidic alumina column and eluted with a hexane/ethyl acetate mixture. The dispirocyclic compound **5** came out as a white crystalline solid while using a 25% ethyl acetate/hexane mixture as the eluent. Yield: 0.27 g (60%). Mp: 155−158 °C. IR (ν, cm^{-1}): 3042 w, 2924 s, 2874 m, 1736 w, 1591 w, 1458 m, 1231 vs, 1070 vs. ^1H NMR ($CDCl_3$, ppm): δ 7.76−7.83 (m, 4H, C_6H_5), 7.26−7.46 (m, 6H, C_6H_5), 5.72 (s, 4H, =C*H*), 4.67−4.73 (m, 8H, −CH_2−). $^{13}C\{^1H\}$ NMR: δ 136.19, 130.94, 130.57, 128.10 [Ph*C*], 127.16 [−*C*H=], 62.85 [−*C*H_2−]. $^{31}P\{^1H\}$ NMR: δ 22.4 [t (J = 35 Hz), $P(C_6H_5)_2$], 20.62 [d (J = 3 4.6 Hz), spirocyclic *P*]. MS (ES) [m/e (species)]: 462.09 $[M + 1]^+$. Anal. Calcd for $C_{20}H_{22}N_3O_4P_3$: C, 52.07; H, 4.81; N, 9.11. Found: C, 51.29; H, 4.97; N, 9.08.

Preparation of $[(CH_2{=}CHCH_2O)_2PN]_3$ (2). The reaction of allyl alcohol (3.13 mL, 46.02 mmol), NaH (2.00 g, 46.02 mmol), and $N_3P_3Cl_6$ (2.00 g, 5.75 mmol) was carried out and worked up in a manner similar to that of compound **1**, with stirring at room temperature for 24 h followed by refluxing for 8 h. Compound **2** came out as a yellowish viscous liquid while using a 3% ethyl acetate/hexane mixture as the eluent. Yield: 2.10 g (78%). IR (ν, cm^{-1}): 3085 s, 2935 s, 2879 s, 2734 w, 2879 s, 2073 w, 1954 m, 1875 m, 1648 s, 1457 s, 1419 s, 13661 m, 1228 vs, 1160 m, 1028 vs. ^1H NMR ($CDCl_3$, ppm): δ 5.88−6.00 (m, 6H, =C*H*−), 5.34 [d (J = 17 Hz), 6H, trans −CH=CH_2], 5.19 [d (J = 10.5 Hz), 6H, cis −CH=CH_2], 4.46 (s, 12H, −CH_2−). $^{13}C\{^1H\}$ NMR: δ 132.86 [=*C*H−], 116.82 [CH_2=], 66.18 [−*C*H_2−]. $^{31}P\{^1H\}$ NMR: δ 17.85 [s, $P(OCH_2CH{=}CH_2)_2$]. MS (ES) [m/e (species)]: 478.10 $[M + 1]^+$.

Preparation of $N_3P_3(OCH_2CH{=}CHCH_2O)_3$ (6). The reaction of **2** (0.65 g, 1.46 mmol) and the Grubbs first-generation catalyst (0.24 g, 0.29 mmol, 20 mol %) was carried out and worked up in a manner similar to that of compound **5** with refluxing for 12 h. Trispirocyclic compound **6** came out as a white crystalline solid while using a 45% ethyl acetate/hexane mixture as the eluent. Yield: 0.35 g (65%). Mp (dec): 135−138 °C. IR (ν, cm^{-1}): 3036 w, 2958 m, 2925 m, 2877 m, 2360 w, 2104 w, 1734 m, 1628 m, 1461 s, 1244 vs, 1047 vs, 1007 s. ^1H NMR ($CDCl_3$, ppm): δ 5.74 (s, 6H, =C*H*), 4.71−4.73 (m, 12H, −CH_2−). $^{13}C\{^1H\}$ NMR: δ 127.00 [−*C*H=], 63.14 [−*C*H_2−]. $^{31}P\{^1H\}$ NMR: δ 22.99 [s, spiro *P*]. MS (ES) [m/e (species)]: 394.02 $[M + 1]^+$. Anal. Calcd for $C_{12}H_{18}N_3O_6P_3$: C, 36.65; H, 4.61; N, 10.69. Found: C, 37.10; H, 4.65; N, 10.41.

Preparation of $[(CH_2{=}CHCH_2O)_2PN]_4$ (3). The reaction of allyl alcohol (1.46 mL, 21.57 mmol), NaH (0.94 g, 21.57 mmol), and $N_4P_4Cl_8$ (1.00 g, 2.15 mmol) was carried out and worked up in a manner similar to that of compound **1**, stirring at room temperature for 24 h followed by refluxing for 6 h. Compound **3** came out as a yellowish viscous liquid while using a 2% ethyl acetate/hexane mixture as the eluent. Yield: 1.00 g (73%). IR (ν, cm^{-1}): 3084 m, 2934 m, 2879 m, 2362 w, 1868 w, 1647 m, 1456 m, 1325 s, 1102 s, 1030 vs. ^1H NMR ($CDCl_3$, ppm): δ 5.87−6.00 (m, 6H, =C*H*−), 5.31 [d (J = 17 Hz), 8H, trans −CH=CH_2], 5.16 [d (J = 10.2 Hz), 8H, cis −CH=CH_2], 4.47 (s, 16H, −CH_2−). $^{13}C\{^1H\}$ NMR: δ 133.77 [=*C*H−], 116.72 [=*C*H_2], 66.84 [−*C*H_2−]. $^{31}P\{^1H\}$ NMR: δ 0.41 [s, $P(OCH_2CH{=}CH_2)_2$]. MS (ES) [m/e (species)]: 637.17 $[M + 1]^+$.

Preparation of $N_4P_4(OCH_2CH{=}CHCH_2O)_4$ (7). The reaction of **3** (0.50 g, 0.78 mmol) and the Grubbs first-generation catalyst (0.16 g, 0.19 mmol, 25 mol %) was carried out and worked up in a manner similar to that of compound **5** with refluxing carried out for 14 h. Tetraspirocyclic compound **7** came out as a white crystalline solid while using a 55% ethyl acetate/hexane mixture as the eluent. Yield: 0.30 g (73%). Mp: 165−168 °C. IR (ν, cm^{-1}): 3036 m, 2922 s, 2866 s, 1947 w, 1731 m, 1454 m, 1323 s, 1259 vs, 1220 w, 1042 vs. ^1H NMR ($CDCl_3$, ppm): δ 5.69 (s, 8H, =C*H*), 4.62 (m, 16H, −CH_2−). $^{13}C\{^1H\}$ NMR: δ 127.42 [−*C*H=], 63.32 [−*C*H_2−]. $^{31}P\{^1H\}$ NMR: δ 7.16 [s, spiro *P*]. MS (ES) [m/e (species)]: 525.08 $[M + 1]^+$. Anal. Calcd for $C_{16}H_{24}N_4O_8P_4$: C, 36.65; H, 4.61; N, 10.69. Found: C, 36.82; H, 4.53; N, 10.65.

Preparation of $[PhS(O)N][(CH_2{=}CHCH_2O)_2PN]_2$ (4). The reaction of allyl alcohol (1.01 mL, 14.80 mmol), NaH (0.65 g, 14.80 mmol), and *S*-phenylthionylphosphazene (NS(O)Ph)$(NPCl_2)_2$ (1.10 g, 2.96 mmol) was carried out and worked up in a manner similar to that of compound **1**, with stirring at room temperature for 24 h. Compound **4** came out as a yellow viscous liquid, while using a 8% ethyl acetate/hexane mixture as the eluent. Yield: 1.10 g (89%). IR (ν, cm^{-1}): 3083 m, 2930 s, 2357 m, 2108 w, 1887 w, 1741 w, 1647 m, 1454 m, 1367 w, 1234 vs, 1178 s, 1100 vs, 1026 vs. ^1H NMR ($CDCl_3$, ppm): δ 7.91−7.95 (m, 2H, C_6H_5), 7.41−7.48 (m, 3H, C_6H_5), 5.87−6.00 [m, 2H, =C*H*− (toward S=O)], 5.68−5.85 [m, 2H, =C*H*− (toward Ph)], 5.39 [d (J = 17 Hz), 2H, trans CH_2=CH− (toward S=O)], 5.25 [d (J = 9.6 Hz), 2H, cis CH_2=CH− (toward S=O)], 4.87−5.26 [m, 4H, CH_2= (toward Ph)], 4.57 [s, 4H, −CH_2− (toward S=O)], 4.40 [s, 4H, −CH_2− (toward Ph)]. $^{13}C\{^1H\}$ NMR: δ 146.55, 131.46, 128.58, 125.09 [Ph*C*], 132.21 [=*C*H−], 118.00 and 118.27 [*C*H_2=], 67.54 [−*C*H_2−]. $^{31}P\{^1H\}$ NMR: δ 11.37 [s, $P(OCH_2CH{=}CH_2)_2$]. MS (ES) [m/e (species)]: 458.08 $[M + 1]^+$.

Preparation of $(NS(O)Ph)[NP(OCH_2CH{=}CHCH_2O)]_2$ (8). The reaction of **4** (0.80 g, 1.74 mmol) and the Grubbs first-generation catalyst (0.14 g, 0.014 mmol, 10 mol %) was carried out and worked up in a manner similar to that of compound **5**, with refluxing for 8 h. The dispirocyclic compound **8** came out as a white crystalline solid while using a 20% ethyl acetate/hexane mixture as the eluent. Yield: 0.40 g (60%). Mp: 123−125 °C. IR (ν, cm^{-1}): 2926 m, 2356 w, 1731 w, 1634 w, 1453 s, 1253 vs, 1181 vs, 1077 s, 1039 vs, 1001 vs. ^1H NMR ($CDCl_3$, ppm): δ 7.90−7.93 (m, 2H, C_6H_5), 7.41−7.50 (m, 3H, C_6H_5), 5.74 (s, 4H, =C*H*), 4.54−4.93 (m, 8H, −CH_2−). $^{13}C\{^1H\}$ NMR: δ 146.52, 131.37, 128.61, 125.06 [Ph*C*], 127.04 and 126.31 [−*C*H=], 63.63 and 63.90 [−*C*H_2−]. $^{31}P\{^1H\}$ NMR: δ 17.12 [s, spiro *P*]. MS (ES) [m/e (species)]: 402.04 $[M + 1]^+$. Anal. Calcd for $C_{20}H_{22}N_3O_4P_3$: C, 41.90; H, 4.27; N, 10.47. Found: C, 42.30; H, 4.84; N, 10.02.

Preparation of $(NPPh_2)[NP(OCH_2CH_2CH{=}CH_2)_2]_2$ (9). The reaction of homoallyl alcohol (1.49 mL, 17.40 mmol), NaH (0.76 g, 17.40 mmol), and $N_3P_3Cl_4Ph_2$ (1.50 g, 3.48 mmol) was carried out and worked up in a manner similar to that of compound **1**, with stirring at room temperature for 24 h. Compound **9** came out as a yellowish viscous liquid while using a 2% ethyl acetate/hexane mixture as the eluent. Yield: 1.40 g (70%). IR (ν, cm^{-1}): 3075 s, 2954 s, 2895 s, 1908 w, 1834 w, 1641 s, 1593 w, 1474 s, 1436 s, 1384 m, 1207 vs, 1122 vs, 1026 vs. ^1H NMR ($CDCl_3$, ppm): δ 7.80−7.87 (m, 4H, C_6H_5), 7.34−7.46 (m, 6H, C_6H_5), 5.66−5.80 (m, 4H, =C*H*−), 4.98−5.05 (m, 8H, =CH_2], 3.85−3.97 (m, 8H, −OCH_2−), 2.36 [q (J = 6.9 Hz), 8H, −CH_2−]. $^{13}C\{^1H\}$ NMR: δ 136.97, 130.88, 130.49, 128.08 [Ph*C*], 134.08 [=*C*H−], 116.88 [=*C*H_2], 64.82 [−O*C*H_2−], 34.57 [−*C*H_2]. $^{31}P\{^1H\}$ NMR: δ 20.87 [t (J = 33.65 Hz), $P(C_6H_5)_2$], 15.54 [d (J = 33.65 Hz), $P(OCH_2CH_2CH{=}CH_2)_2$]. MS (ES) [m/e (species)]: 574.21 $[M + 1]^+$.

Preparation of $(NS(O)Ph)[NP(OCH_2CH_2CH{=}CH_2)_2]_2$ (10). The reaction of homoallyl alcohol (1.52 mL, 17.80 mmol), NaH (0.85 g, 17.80 mmol), and *S*-phenylthionylphosphazene (NS(O)Ph)-$(NPCl_2)_2$ (1.10 g, 2.96 mmol) was carried out and worked up in a manner similar to that of compound **1**, with stirring at room temperature for 24 h. Compound **10** came out as a yellow viscous liquid while using a 3% ethyl acetate/hexane mixture as the eluent. Yield: 0.85 g (56%). IR (ν, cm^{-1}): 3076 m, 2960 s, 2925 s, 2856 m, 1731 w, 1641 m, 1471 m, 1439 m, 1234 vs, 1180 vs, 1024 vs. ^1H NMR ($CDCl_3$, ppm): δ 7.91−7.95 (m, 2H, C_6H_5), 7.40−7.51 (m, 3H, C_6H_5), 5.72−5.88 [m, 2H, =C*H*− (toward S=O)], 5.60−5.72 [m, 2H, =C*H*− (toward Ph)], 5.01−5.18 (m, 8H, CH_2=), 4.02−4.16 [m, 4H, −OCH_2− (toward S=O)], 3.87−3.94 [m, 4H, −OCH_2− (toward Ph)], 2.48 [q (J = 6.6 Hz), 4H, −CH_2− (toward S=O)], 2.33 [q (J = 6.6 Hz), 4H, −CH_2− (toward Ph)]. $^{13}C\{^1H\}$ NMR: δ 146.45, 131.36, 128.53, 125.09 [Ph*C*], 133.44 and 133.32 [=*C*H−], 117.50 and 117.61 [=*C*H_2], 66.07 and 66.11 [−O*C*H_2−], 34.28 [−*C*H_2]. $^{31}P\{^1H\}$ NMR: δ 10.93 [s, $P(OCH_2CH_2CH{=}CH_2)_2$]. MS (ES) [m/e (species)]: 514.16 $[M + 1]^+$.

Reaction of Compound 9 with 10 mol % of the Grubbs First-Generation Catalyst. The reaction of **9** (0.50 g, 0.87 mmol) and the Grubbs first-generation catalyst (71 mg, 0.08 mmol, 10 mol %) was carried out and worked up in a manner similar to that of compound **5**, with refluxing for 10 h. The diansa compound $NPPh_2[NP(OCH_2CH_2CH{=}CHCH_2CH_2O)]_2$ (**11**) came out as a white crystalline solid while using a 5% ethyl acetate/hexane mixture as the eluent. Yield: 0.11 g (24%). IR (ν, cm^{-1}): 3046 m, 2956 s, 2901 s, 1730 m, 1596 w, 1436 s, 1222 vs, 1124 s, 1070 vs, 1038 vs, 1003 vs. ^1H NMR ($CDCl_3$, ppm): δ 7.86−7.93 (m, 4H, C_6H_5), 7.44 (m, 6H, C_6H_5), 5.34−5.38 (s, 4H, =C*H*), 4.04−4.06 (m, 8H, −OCH_2−), 2.25 (s, 4H, −CH_2−), 2.14 (s, 4H, −CH_2−). $^{13}C\{^1H\}$ NMR: δ 137.05, 130.94, 130.65, 128.14 [Ph*C*], 129.85

[−*C*H═], 66.16 [−O*C*H$_2$−], 33.44 [−*C*H$_2$−]. ^{31}P{^{1}H} NMR: δ 22.15 [t (J = 80 Hz), *P*(C$_6$H$_5$)$_2$], 15.46 [d (J = 81 Hz), ansacyclic *P*]. MS (ES) [*m*/*e* (species)]: 518.16 [M + 1]$^+$. Anal. Calcd for $C_{24}H_{30}N_3O_4P_3$: C, 55.71; H, 5.84; N, 8.12. Found: C, 55.80; H, 5.69; N, 8.11. Further elution with a 36% ethyl acetate/hexane mixture gave the second fraction, which came out as a sticky solid and was characterized as a cis/trans mixture of the ansa−dibino−ansa compound **12**. Yield: 0.10 g (22%). IR (ν, cm^{-1}): 2925 s, 2855 s, 2355 w, 1729 m, 1633 m, 1438 s, 1380 s, 1210 vs, 1124 s, 1021 vs. ^{1}H NMR ($CDCl_3$, ppm): δ 7.81−7.85 (m, 8H, C$_6$*H*$_5$), 7.41 (m, 12H, C$_6$*H*$_5$), 5.39 (s, 4H, ansa ═C*H*), 4.96−5.14 (m, 4H, dibino ═C*H*), 4.04−4.15 (m, 8H, −OC*H*$_2$−), 3.77−3.96 (m, 8H, −OC*H*$_2$−), 2.22 (s, 16H, −C*H*$_2$−). ^{31}P{^{1}H} NMR: δ 21.34 [t (J = 82 Hz), *P*(C$_6$H$_5$)$_2$], 15.86 [d (J = 83 Hz), ansa−bino *P*]. MS (ES) [*m*/*e* (species)]: 1035.11 [M + 1]$^+$.

Reaction of Compound 10 with 10 mol % of the Grubbs First-Generation Catalyst. The reaction of **10** (0.65 g, 1.26 mmol) and the Grubbs first-generation catalyst (0.11 g, 0.012 mmol, 10 mol %) was carried out and worked up in a manner similar to that of compound **5**, with refluxing for 10 h. The disansa compound **13** came out as a white crystalline solid while using a 10% ethyl acetate/hexane mixture as the eluent. Yield: 0.11 g (19%). IR (ν, cm^{-1}): 2959 m, 2908 m, 2852 w, 2361 s, 1736 w, 1643 w, 1468 m, 1436 m, 1382 m, 1257 vs, 1230 vs, 1178 vs, 1128 m, 1043 vs. ^{1}H NMR ($CDCl_3$, ppm): δ 8.01−8.04 (m, 2H, C$_6$*H*$_5$), 7.46−7.49 (m, 3H, C$_6$*H*$_5$), 5.71 [t (J = 3.8 Hz), 2H, ═C*H* (toward S═O)], 5.35 [t (J = 3.9 Hz), 2H, ═C*H* (toward Ph)], 4.37−4.43 (m, 2H, −OC*H*$_2$−), 4.17−4.20 (m, 2H, −OC*H*$_2$−), 4.05−4.10 (m, 2H, −OC*H*$_2$−), 3.83−3.88 (m, 2H, −OC*H*$_2$−), 2.35−2.37 (m, 4H, −C*H*$_2$−), 2.14−2.29 (m, 4H, −C*H*$_2$−). ^{13}C{^{1}H} NMR: δ 146.57, 131.38, 128.49, 125.34 [Ph*C*], 130.14 and 129.87 [−*C*H═], 68.38 and 66.77 [−O*C*H$_2$−], 33.35 and 33.07 [−*C*H$_2$−]. ^{31}P{^{1}H} NMR: δ 10.85 (s, ansa *P*). MS (ES) [*m*/*e* (species)]: 458.11 [M + 1]$^+$. Anal. Calcd for $C_{18}H_{25}N_3O_5P_2S$: C, 47.26; H, 5.51; N, 9.19. Found: C, 47.41; H, 5.32; N, 9.41. Further elution with a 30% ethyl acetate/hexane mixture gave the second fraction, which came out as a sticky solid and was characterized as a cis/trans isomer mixture of intermolecular compound, i.e., ansa−dibino−ansa compound **14**. Yield: 0.11 g (19%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.91−7.93 (m, 4H, C$_6$*H*$_5$), 7.48−7.51 (m, 6H, C$_6$*H*$_5$), 5.67 (s, 4H, ansa ═C*H*), 5.12−5.43 (m, 4H, dibino ═C*H*), 4.33−4.36 (m, 4H, −OC*H*$_2$−), 4.17−4.22 (m, 4H, −OC*H*$_2$−), 3.73−3.85 (m, 8H, −OC*H*$_2$−), 2.30−2.35 (m, 8H, −C*H*$_2$−), 2.18−2.24 (m, 8H, −C*H*$_2$−). ^{31}P{^{1}H} NMR: δ 11.01 (s, ansa−bino *P*). MS (ES) [*m*/*e* (species)]: 915.00 [M + 1]$^+$.

Preparation of (NPPh$_2$)$_2$[NP(OCH$_2$CH$_2$CH═CH$_2$)Cl] and (NPPh$_2$)$_2$[NP(OCH$_2$CH$_2$CH═CH$_2$)$_2$] (15). The reaction of homoallyl alcohol (0.60 mL, 6.99 mmol), NaH (0.34 g, 6.99 mmol), and $N_3P_3Cl_2Ph_4$ (1.20 g, 2.33 mmol) was carried out and worked up in a manner similar to that of compound **1**, with stirring at room temperature for 24 h followed by refluxing for 24 h. The first fraction, which came out while using a 1% ethyl acetate/hexane mixture as the eluent, was identified as (NPPh$_2$)$_2$[NP(OCH$_2$CH$_2$CH═CH$_2$)Cl]. Yield: 0.40 g (31%). Mp: 85−88 °C. IR (ν, cm^{-1}): 3056 s, 2955 s, 2362 m, 1965 w, 1897 w, 1821 w, 1643 s, 1586 w, 1479 s, 1436 s, 1384 m, 1217 vs, 1121 vs, 1034 vs. ^{1}H NMR ($CDCl_3$, ppm): δ 7.73−7.84 (m, 8H, C$_6$*H*$_5$), 7.32−7.46 (m, 12H, C$_6$*H*$_5$), 5.70−5.80 (m, 1H, ═C*H*−), 4.99−5.09 (m, 2H, ═C*H*$_2$], 4.20 [q (J = 6.9 Hz), 2H, −OC*H*$_2$−], 2.46 [q (J = 6.9 Hz), 2H, −C*H*$_2$−)]. ^{13}C{^{1}H} NMR: δ 136.20, 130.89, 130.46, 127.97 [Ph*C*], 133.42 [═*C*H−], 117.23 [═*C*H$_2$], 66.12 [−O*C*H$_2$−], 34.07 [−*C*H$_2$]. ^{31}P{^{1}H} NMR: δ 20.01 [d (J = 18.83 Hz), *P*(C$_6$H$_5$)$_2$], 17.84 [t (J = 18.83 Hz), *P*(OCH$_2$CH$_2$CH═CH$_2$)Cl]. MS (ES) [*m*/*e* (species)]: 550.14 [M + 1]$^+$. Anal. Calcd for $C_{28}H_{27}ClN_3OP_3$: C, 61.16; H, 4.95; N, 7.64. Found: C, 60.88; H, 4.98; N, 8.08. Further elution with the same 1% ethyl acetate/hexane mixture as the eluent gave the second fraction, which was identified as **15**. Yield: 0.51 g (37%). Mp: 95−98 °C. IR (ν, cm^{-1}): 3052 s, 2957 s, 1897 w, 1823 w, 1643 s, 1478 s, 1435 s, 1385 m, 1201 vs, 1121 vs, 1067 vs, 1028 vs. ^{1}H NMR ($CDCl_3$, ppm): δ 7.78−7.85 (m, 8H, C$_6$*H*$_5$), 7.34−7.40 (m, 12H, C$_6$*H*$_5$), 5.58−5.71 (m, 2H, ═C*H*−), 4.91−4.96 (m, 4H, ═C*H*$_2$], 3.82 [q (J = 7.4 Hz), 4H, −OC*H*$_2$−], 2.29 [q (J = 6.9 Hz), 4H, −C*H*$_2$−)]. ^{13}C{^{1}H} NMR: δ 137.57, 130.59, 130.56, 127.97 [Ph*C*], 134.24 [═*C*H−], 116.66 [═*C*H$_2$], 64.52 [−O*C*H$_2$−], 34.58 [−*C*H$_2$]. ^{31}P{^{1}H} NMR: δ 20.30 [d (J = 24.05 Hz), *P*(C$_6$H$_5$)$_2$], 10.57 [t (J = 24.54 Hz), *P*(OCH$_2$CH$_2$CH═CH$_2$)$_2$]. MS (ES) [*m*/*e* (species)]: 586.21 [M + 1]$^+$. Anal. Calcd for $C_{32}H_{34}N_3O_2P_3$: C, 65.64; H, 5.85; N, 7.18. Found: C, 65.69; H, 5.84; N, 7.60.

Reaction of Compound 15 with 5 mol % of the Grubbs First-Generation Catalyst. The reaction of **15** (0.54 g, 0.92 mmol) and the Grubbs first-generation catalyst (38 mg, 0.04 mmol, 5 mol %) was carried out and worked up in a manner similar to that of compound **5**, with refluxing for 8 h. The monospiro compound **16** came out as a white crystalline solid while using a 2% ethyl acetate/hexane mixture as the eluent. Yield: 0.11 g (23%). Mp: 190−192 °C. IR (ν, cm^{-1}): 3049 s, 3013 s, 2952 s, 2903 s, 2850 m, 2706 w, 1962 m, 1897 m, 1818 m, 1771 w, 1737 w, 1660 w, 1586 w, 1479 s, 1437 s, 1220 vs, 1071 vs, 1037 vs. ^{1}H NMR ($CDCl_3$, ppm): δ 7.74−7.81 (m, 8H, C$_6$*H*$_5$), 7.32−7.37 (m, 12H, C$_6$*H*$_5$), 5.76 [t (J = 5.55 Hz), 2H, ═C*H*], 4.11−4.19 (m, 4H, −OC*H*$_2$−), 2.47−2.48 (m, 4H, −C*H*$_2$−). ^{13}C-{^{1}H} NMR: δ 137.73, 130.66, 130.58, 127.90 [Ph*C*], 129.50 [−*C*H═], 64.65 [−O*C*H$_2$−], 28.62 [−*C*H$_2$−]. ^{31}P{^{1}H} NMR: δ 19.70 [d (J = 26.48 Hz), *P*(C$_6$H$_5$)$_2$], 9.12 [t (J = 26.60 Hz), spiro *P*]. MS (ES) [*m*/*e* (species)]: 558.11 [M + 1]$^+$. Anal. Calcd for $C_{30}H_{30}N_3O_2P_3$: C, 64.63; H, 5.42; N, 7.54. Found: C, 64.46; H, 5.62; N, 7.48. Further elution with a 14% ethyl acetate/hexane mixture as the eluent gave the second fraction, which was identified as geminal dibino-substituted dimeric compound [NPPh$_2$]$_2$[NP(OCH$_2$CH$_2$ CH═CHCH$_2$CH$_2$O)$_2$PN][NPPh$_2$]$_2$ (**17**). Yield: 0.19 g (40%). IR (ν, cm^{-1}): 2924 vs, 2854 s, 1740 m, 1461 m, 1437 s, 1200 vs, 1120 s, 1067 s, 1017 s. ^{1}H NMR ($CDCl_3$, ppm): δ 7.79−7.85 (m, 16H, C$_6$*H*$_5$), 7.33−7.36 (m, 24H, C$_6$*H*$_5$), 5.53 (m, 2H, ═C*H*), 5.49 (m, 2H, ═C*H*), 3.83−3.86 (m, 8H, −OC*H*$_2$−), 2.26 (s, 8H, −C*H*$_2$−). ^{31}P{^{1}H} NMR: δ 20.02 [d (J = 25.03 Hz), *P*(C$_6$H$_5$)$_2$], 19.97 [d (J = 24.78 Hz), *P*(C$_6$H$_5$)$_2$], 10.15 [t (J = 24.66 Hz), spiro−dibino−spiro *P*], 9.88 [t (J = 24.66 Hz), spiro−dibino−spiro *P*]. MS (ES) [*m*/*e* (species)]: 1115.20 [M + 1]$^+$.

Reaction of Compound 15 with 5 mol % of the Grubbs Second-Generation Catalyst. Compound **15** (0.30 g, 0.51 mmol) was dissolved in 10 mL of dry dichloromethane and transferred to a 100 mL flask containing the Grubbs second-generation catalyst (22 mg, 2.56 × 10^{-2} mmol, 5 mol %) dissolved in 10 mL of dichloromethane. An additional 20 mL of dichloromethane was added to the same flask, and the resulting solution was refluxed for 12 h. The reaction was monitored with thin-layer chromatography and ^{31}P NMR spectroscopy. Afterward, the solvent was removed under vacuum and the resulting crude product chromatographed on an acidic alumina column and eluted with a hexane/ethyl acetate mixture. The monospiro compound **16** came out as a white crystalline solid while using a 3% ethyl acetate/hexane mixture as the eluent. Yield: 80 mg (28%). Further elution with a 20% ethyl acetate/hexane mixture as the eluent gave the second fraction, which was identified as geminal dibino-substituted dimeric compound **17**. Yield: 0.14 g (49%).

Reaction of Compound 17 with 10 mol % of a Grubbs Second-Generation Catalyst. Compound **17** (66 mg, 5.91 × 10^{-2} mmol) was dissolved in 10 mL of dry dichloromethane and transferred to a 100 mL flask containing the Grubbs second generation catalyst (5 mg, 5.91 × 10^{-3} mmol, 10 mol %) dissolved in 10 mL of dichloromethane. An additional 10 mL of dichloromethane was added to the same flask, and the resulting solution was refluxed for 4 h. The reaction was monitored with thin-layer chromatography and ^{31}P NMR spectroscopy. Afterward, the solvent was removed under vacuum and the resulting crude product chromatographed on an acidic alumina column using a hexane/ethyl acetate mixture. The monospiro compound **16** came out as a white crystalline solid while using a 4% ethyl

acetate/hexane mixture. Yield: 17 mg (26%). Further elution with a 20% ethyl acetate/hexane mixture gave the second fraction, which was identified as a cis/trans isomer mixture of starting compound **17**. Yield: 38 mg (58%).

Conclusion

The first examples of RCM reactions on allyloxy- and homoallyloxy-substituted cyclophosphazenes and *S*-phenylthionylphosphazenes has been carried out. The metathesis reactions proceed readily in the presence of the Grubbs first-generation catalyst, resulting in ring-closed cycloalkene products. Multi-allyloxy-substituted trimeric and tetrameric cyclophosphazenes as well as thionylphosphazenes have been found to exclusively form seven-membered spirocyclic products upon RCM. Interestingly, upon replacement of all of the allyloxy groups on diphenyltetrakis(allyloxy)cyclophosphazene and *S*-phenylthionylphosphazene by homoallyloxy units, a tendency to form intramolecular ansa and intermolecular ansa−dibino−ansa ring-closed metathesis products was observed. Structural studies on the new spiro and ansa cycloalkene compounds indicated that the alkene double bonds in the spiro derivatives are in the cis orientation, while those present on the ansa-substituted derivatives are in the trans orientation. The 18-membered geminal dibino-substituted dimeric compound **17**, obtained as the major product in the RCM of $(NPPh_2)_2[NP(OCH_2CH_2CH{=}CH_2)_2]$ upon reaction with the Grubbs second-generation catalyst was found to undergo a novel ROM reaction, converting partially to the nine-membered spirocyclic compound $[NPPh_2]_2[NP(OCH_2CH_2CH{=}CHCH_2CH_2O)]$ as well as undergoing secondary metathesis reactions, leading to a higher *E*/*Z* ratio. The study opens up a fresh avenue in the ansa, spiro, and bino substitution reactions of cyclophosphazenes, and we are currently exploring the utility of ring closing and ROM reactions in the design of novel alkene-derived cyclophosphazene derivatives and the use of such compounds as cross-linking units in polymer synthesis.

Acknowledgment. The authors thank the Department of Science and Technology (DST), India, for financial assistance in the form of a research grant to A.J.E. (Grant DST SR/S1/IC-31/2007). We thank DST-FIST and IITD for funding of the single-crystal X-ray diffraction facility at IIT Delhi. We thank Dr. N. G. Ramesh (Department of Chemistry, IIT Delhi) for fruitful discussions. Thanks are due to SAIF, CDRI, Lucknow, for providing analytical data.

Supporting Information Available: General experimental methods and instrumentation used for the synthesis and characterization of compounds and X-ray crystallographic information, figures of X-ray crystal structures of compounds **6** and **16**, tables of selected bond lengths and angles and X-ray structural parameters, and crystallographic information files (CIF) for compounds **5**−**8**, **11**, **13**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.