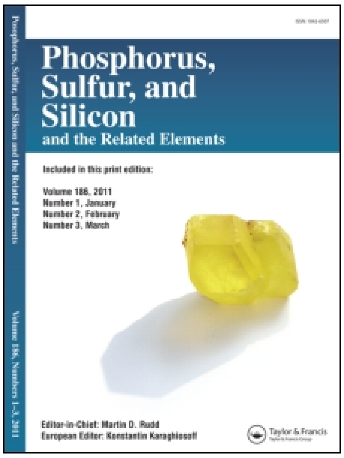

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A Facile Route to a New Class of Silicon- And Germaniumphosphorus Compounds: P_2Si_2-and Ge_2P_2- Bicyclo[1.1.0]Butanes-Synthesis and Inversion

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A FACILE ROUTE TO A NEW CLASS OF SILICON- AND GERMANIUM-PHOSPHORUS COMPOUNDS: P_2Si_2-AND Ge_2P_2-BICYCLO[1.1.0]BUTANES-SYNTHESIS AND INVERSION

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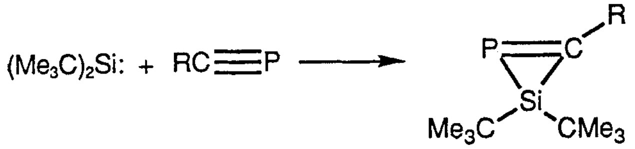
Abstract A new synthesis of 1,3-diphospha-2,4-disilabicyclo-[1.1.0]butanes and of the novel 1,3-digerma-2,4-diphosphabicyclo-[1.1.0]butane derivative as well as their exo,endo ——→ exo,exo-isomerization are discussed.

INTRODUCTION

In the past, a number of novel strained organosubstituted P-Si containing heterocycles have been prepared which are of theoretical and synthetic interest due to their molecular structure and high reactivity. Only recently, M.Weidenbruch et al. have characterized the phosphasilirene **1** which was synthezised by [2+1]-cycloaddition of $(Me_3C)_2Si$ to the PC-triple bond of a phosphaalkyne.[1] The x-ray crystal structure of the *P*-$W(CO)_5$ complex shows the smallest endocyclic angle (58.8°) at the Si-atom so far established in a CPSi-three-membered ring.[1] Furthermore, M.Baudler et al. achieved the synthesis of the first P_4Si_4 cubane-like derivative **2** in an elegant one-step procedure employing Me_3C-$SiCl_3$ and $LiAl(PH_2)_4$.[2]



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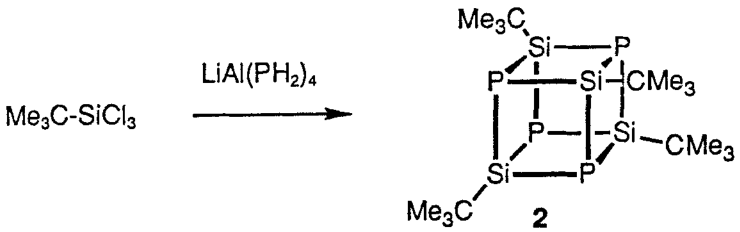
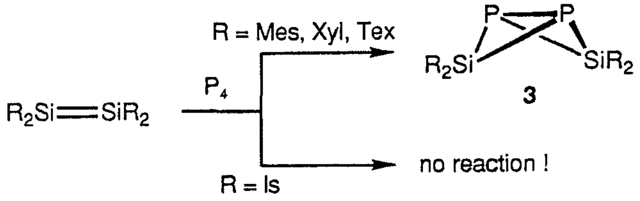


2

A x-ray crystal structure analysis of **2** as well as a PE spectrum prove that the cubane-cage is highly distorted due to strong sigma-bond interactions.[2-3]

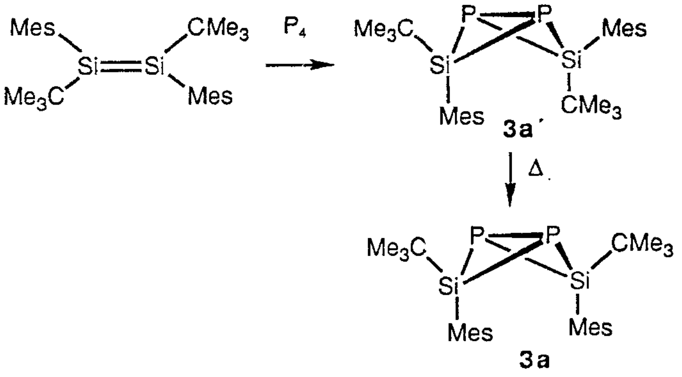
Another class of strained PSi-heterocycles are represented by 1,3-diphospha-2,4-disilabicyclo[1.1.0]butanes **3** which were isolated in 1989 by M.Driess, A.D.Fanta, D.Powell, and R.West.[4] Compounds of this type are produced in high yield by reacting kinetically stabilized tetraorganodisilenes with P_4.



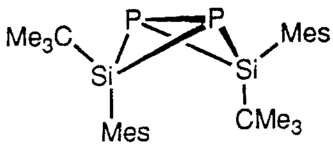
Mes = 2,4,6-trimethylphenyl, Xyl = 2,6-dimethylphenyl
Tex = 4-*tert*butyl-2,6-dimethylphenyl, Is = 2,4,6-tri-*iso*propylphenyl

SCHEME 1 Synthesis of P_2Si_2-bicyclo[1.1.0]butanes from disilenes and P_4.

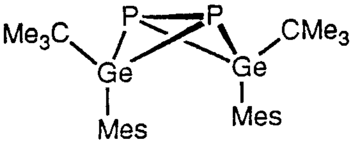
Surprisingly, the reaction of (E)-1,2-di-tert.butyl-1,2-dimesityldisilene with P_4 does not give the expected exo,endo-derivative **3a′**.[5] ^{31}P-NMR spectroscopic investigations of the reaction indicate that **3a′** is produced as a reactive intermediate which rearranges to **3a**. This would entail that an inversion at the silicon atom takes place, a process which has not been observed for such strained heterocyclosilanes.



To clarify in which way the organo groups at the Si-atom influence the silicon inversion a stereospecific method of synthesis without employing disilenes was established.[6] Using this route the exo,endo-derivative **3a′**could be synthesized and could also be characterized by ^{29}Si-NMR spectroscopy.[6] In analogy to **3a,** the 1,3-digerma-2,4-diphosphabicyclo[1.1.0]butane **4a** was also synthesized for the first time which results from **4a′**through a faster isomerization than in the case of **3a′** **3a.**[7]



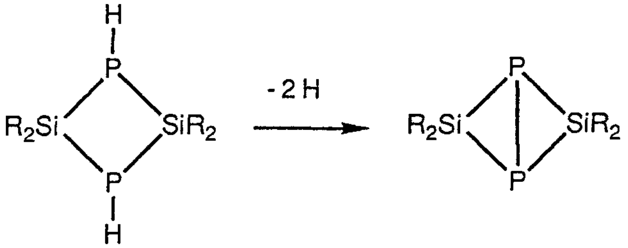
3a′



4a

SYNTHESIS OF 1,3-DIPHOSPHA-2,4-DISILABICYCLO[1.1.0]BUTANES AND A 1,3-DI-GERMA-2,4-DIPHOSPHABICYCLO[1.1.0]BUTANE

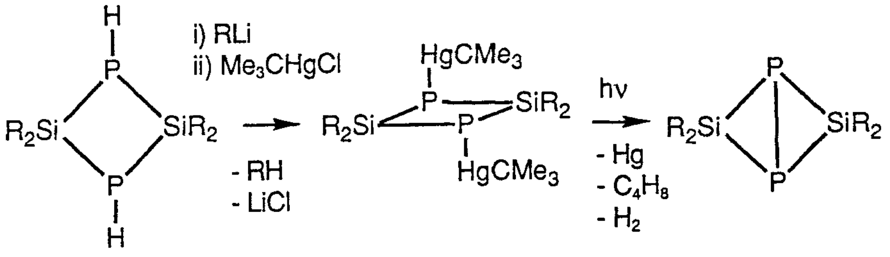
The basic concept to prepare new derivatives of **3** is the dehydrogenation of 1,3,2,4-diphosphadisiletanes **5**.



5 **3**

The dehydrogenation and P-P bond formation could not be carried out in one step, and therefore the route according to scheme 2 via Hg-P-substituted P_2Si_2-cyclobutanes **6** was chosen.

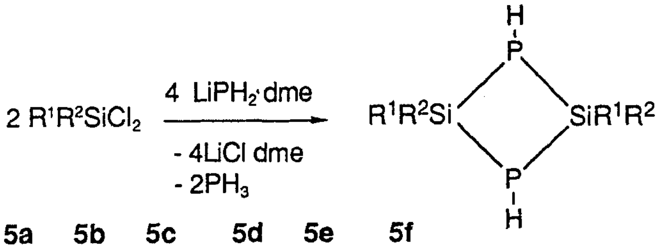
When irradiating derivatives of the type **6** with white light, compound **3**, mercury, isobutane, and H_2 are produced.



5 **6** **3**

SCHEME 2 Stepwise synthesis of **3** via **5** and **6**.

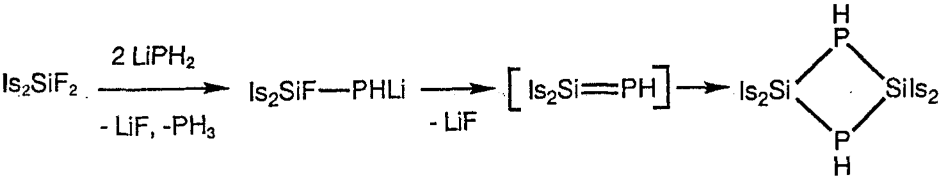
The P_2Si_2-cyclobutanes **5** were synthesized from dichlorodiorganosilanes and $LiPH_2$ according to published procedures.[8-9] The derivatives **5a-f** of 1,3,2,4-diphosphadisiletanes were isolated as colorless crystals.



	5a	5b	5c	5d	5e	5f
R^1	CMe$_3$	Mes	Mes	Mes	Mes	CMe$_3$
R^2	Mes	Mes	OCMe$_3$	Xyl	CHEtMe	Is

5

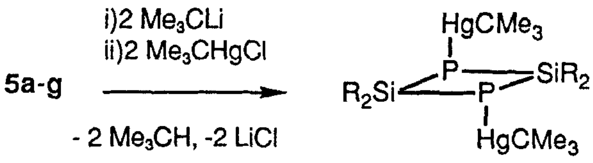
Their structures in the solid state show that they are comprised of non-planar four-membered rings with a *cis* configuration of the H-atoms at the phosphorus. The synthesis of the extremely steric hindered P_2Si_2-cyclobutane **5g** (isityl groups at silicon, Is = 2,4,6-triisopropylphenyl) is achieved starting from Is_2SiF_2 and $LiPH_2$ dme in a molar ratio of 1:2. At first, the Is_2SiF-PHLi molecule is produced which is then presumably converted in to the phosphasilene [Is_2Si=PH] in hexane solution and finally "head-to-tail" dimerization of [Is_2Si=PH] to **5g** occurs.



5g

The reaction of Is_2SiF_2 with $LiPH_2$·dme to yield **5g** was carried out at -30°C since at higher temperature the disubstitutional product $Is_2Si(PH_2)_2$ is formed.[9]

The P_2Si_2-cyclobutanes **5c**-**e** are isolated as mixtures of diastereomers (with regard to the organo groups at the Si-atom) whereas only the isomers with *trans* configuration of the organo substituents at silicon are produced in the case of **5a**, **5f**. Lithiation of **5a**-**g** at phosphorus with two equivalents of Me_3CLi gives the corresponding 1,3-dilithio derivatives which reacts with Me_3C-HgCl to yield the 1,3-dimercurio compounds **6a**-**g** as sole products.



6a-g

The single crystal x-ray structure analysis of **6b** shows that the Me_3C-Hg group at phosphorus occupy trans configuration.[6]

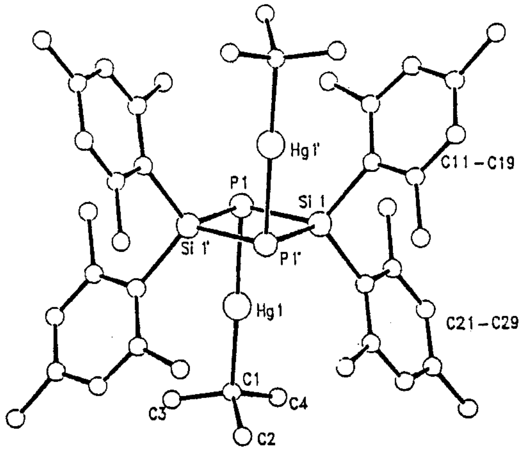


FIGURE 1 Solid state structure of **6b**.

Photolysis of dilute solutions (<0.05M) of the 1,3-dimercurio derivatives **6a-f** in toluene with visible light yields the corresponding P_2Si_2-bicyclo 1.1.0 butanes **3a-f**.[6] A larger concentration increases the formation of by-products due to a high concentration of radicals.

The route to 1,3-diphospha-2,4-disilabicyclo[1.1.0]butanes described herein allows the stereospecific synthesis of the exo,endo isomer **3a'** from **6a** although the ^{31}P-and ^{29}Si-NMR studies have clarified that **3a'** is kinetically labile under these conditions and rearranges quantitatively to **3a** (exo,exo isomer). The isomerization is caused by an unfavourable interaction of the endo substituents.

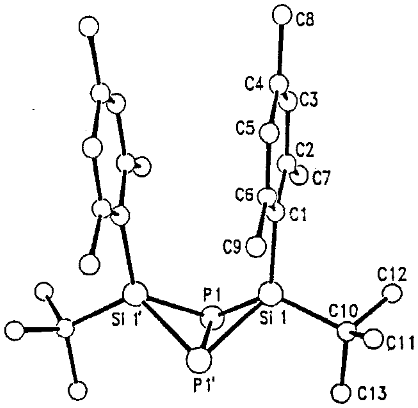
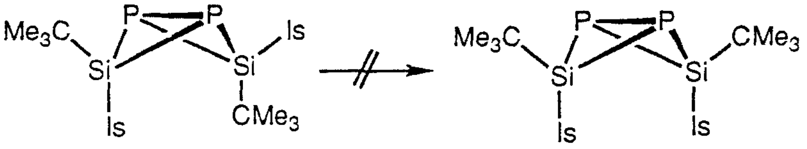


FIGURE 2 X-ray structure analysis of **3a**.

When four extremely bulky organic groups are placed at the silicon atom the exo,endo→exo,exo rearrangment does not occur. Therefore, **3f'** is quite stabil under conditions of photolysis and also when heated at 140°C for several days.

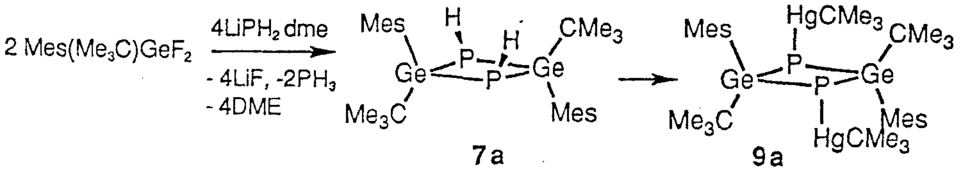


3f' **3f**

The steric control of the Si-inversion process is further demonstrated by experiments with mixtures of exo,exo and exo,endo isomers of the P_2Si_2-bicyclo[1.1.0]butanes **3d**, **3d'**generated by photolysis of a mixture of diastereomers of **6d**. When two different, yet sterically less demanding groups are placed at the silicon atom as in **6d** (R^1 = Mes, R^2 = Xyl; mixture of diastereomers) both isomers (exo,exo; exo,endo) are produced after irradiation. These however cannot be converted into each other by thermal or photochemical means!

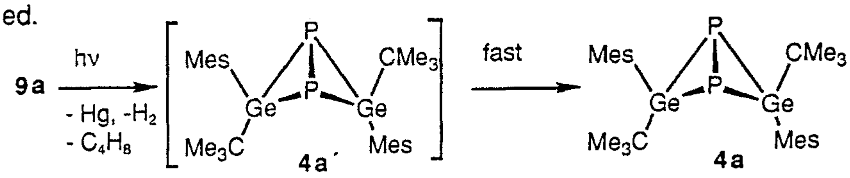
The method described above can also be used for the synthesis of **3g** which can- not be prepared from tetraisityldisilene and white phosphorus.

Furthermore, it was of interest to investigate whether the germanium analogue Ge_2P_2-bicyclo[1.1.0]butane **4a'**(exo,endo) could be synthesized using this route and also whether **4a'**would convert to **4a** (exo,exo). For this purpose the corresponding 1,3,2,4-digermadiphosphetane **7a** was synthesized from Mes(Me_3C)GeF_2 and $LiPH_2$. The NMR-spectra and a x-ray structure analysis of **7a** show that just as in the Si-analogue the Me_3C-groups at germanium exhibit a trans configuration. In solution at 25°C the derivative **7a** exists as a 1:1 mixture of cis and trans isomers (with regard to the H-atoms at phosphorus) which interchange rapidly. When removing the H-atoms at phosphorus from **7a** with Me_3CLi the 1,3-dilithio derivative **8a** is produced quantitatively which reacts with Me_3C-HgCl to form the 1,3-dimercurio compound **9a**.



7a 9a

The photolysis of a 0.025 M solution of **9a** results in a light yellow solution with the precipitation of mercury and shows a new signal at -367 ppm in the ^{31}P-NMR spectrum. The proton NMR spectrum and a x-ray structure analysis of this isolated product prove that the exo,exo configurated isomer **4a** is formed.



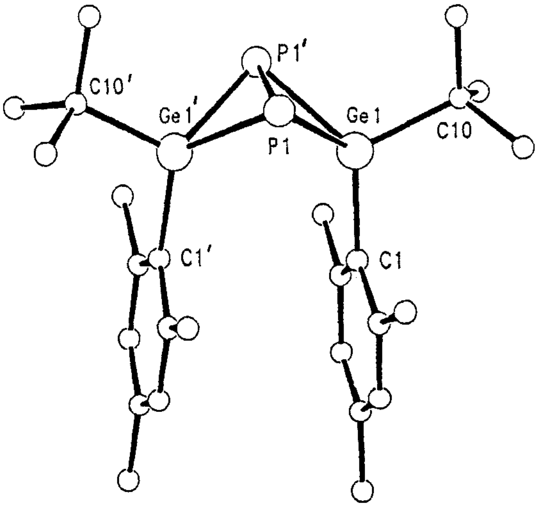


FIGURE 3 Solid state structure of **4a**.

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