

# The Double Base Impact in the Dehydrochlorination of 1,2-Bis[bis(trimethylsilyl)methylchlorophosphino]ethane

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**ABSTRACT:** 1,2-Bis[bis(trimethylsilyl)methylchlorophosphino]ethane was prepared by the reaction of 1,2-bis(dichlorophosphino)ethane and the Grignard reagent of bis(trimethylsilyl)chloromethane. It adds DBN (1,5-diazabicyclo[4.3.0]non-5-ene) in a 1:2 ratio. Subsequent treatment with *t*-BuLi converts the adduct to a condensation product, which in its enamine form reacts with  $MgCl_2$  (still present from the preparation of **1**) to give the cyclic magnesium diamide **2**. By additional coordination of the two phosphine sites of the condensation product, **2** attains a tricyclic structure. An unchanged DBN molecule completes the pentacoordination of the magnesium atom. The structure of product **2** has been determined by single crystal X-ray diffraction. © 2003 Wiley Periodicals, Inc. *Heteroatom Chem* 14:197–199, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10122

## INTRODUCTION

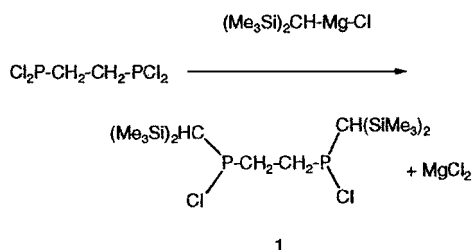
1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) as well as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were used extensively for the purpose of creating double bonds between heavier *sp*-elements by dehydrohalogenation reactions including phosphabutadienes [1–3].

*t*-BuLi was employed as a dehydrohalogenating agent to produce carbon–phosphorus multiple bonds [4,5].

DBN and DBU behaved as nonnucleophilic strong bases in the majority of applications [6]. However, there is an increasing number of reports [7–11] where the above highly popular bases act as nucleophiles. The subject of this communication is devoted to the same issue in the dehydrohalogenation of 1,2-bis[bis(trimethylsilyl)methylchlorophosphino]ethane in an attempt to synthesize the sterically less crowded 1,4-diphospha-1,3-butadienes suitable as novel ligands in catalytic chemistry.

## RESULTS AND DISCUSSION

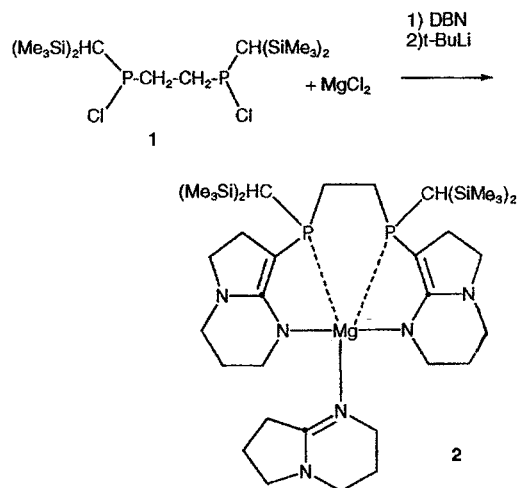
The reaction of the Grignard reagent, prepared from bis(trimethylsilyl)chloromethane and magnesium turning in THF [12,13], with commercially available 1,2-bis(dichlorophosphino)ethane led to the desired 1,2-bis(bis(trimethylsilyl)methylchlorophosphino)ethane (**1**).



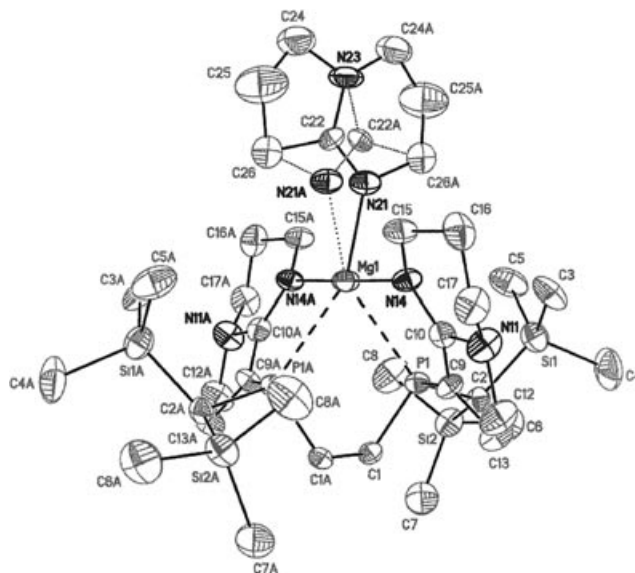
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The reaction mixture of **1** contains only two signals in the  $^{31}\text{P}$  NMR spectrum at  $\delta = 138.6$  and  $139.7$  with a 1:1 ratio corresponding to the isomers of 1,2-bis-[bis(trimethylsilyl)methylchlorophosphino]ethane. Because of thermal stability concern [12] of the chloro(trimethylsilyl)phosphine **1**, the product was not distilled and was used together with magnesium chloride in the next step. DBN reacted readily with compound **1** at  $-78^\circ\text{C}$ . The  $^{31}\text{P}$  NMR spectra signals of the starting compound disappeared and only one signal at  $\delta = 92.2$  ppm was detected. This intermediate was quite stable and did not undergo dehydrohalogenation when stirred at room temperature for 3 weeks or when refluxed in THF for 5 days. However, it did react with methanol. The product had chemical shifts at  $\delta = 152.2$  and  $153.4$  ppm with a 1:1 ratio in the  $^{31}\text{P}$  NMR spectra. This could be tentatively assigned to the change from N–P bonds in the onio-intermediate with DBN [9] to the O–P bonds of the methylate. To further prove the structure and accomplish the dehydrohalogenation, the reaction mixture was divided into 2 equal portions. The first half of the reaction was refluxed in *ortho*-dichlorobenzene after the removal of THF in order to carry out the dehydrohalogenation at a higher temperature. This approach did not result in the formation of the 1,4-diphospha-1,3-butadienes. We did not record any downfield signals in  $^{31}\text{P}$  NMR spectra between 100 and 350 ppm, which could be attributed to such structures. The other half of the reaction mixture was treated with a second base (*t*-BuLi) at a low temperature.



The  $^{31}\text{P}$  NMR spectra of the reaction mixture with *t*-BuLi contained one major new signal at  $\delta = -46.7$  ppm with about 85% intensity and no signal of the starting compound at  $\delta = 92.2$ . The new compound **2** was purified by extraction into the pentane



**FIGURE 1** ORTEP drawing of polycyclic compound **2**. [Thermal ellipsoids are drawn to the 50% probability level. Hydrogen atoms are omitted for clarity.] Compound **2** sits on a crystallographic twofold axis bisecting the magnesium atom. The DBN ligand is disordered across the twofold axis. Atoms N21a and C22a are shown with thin dotted bonds to represent the opposite ordering. There is a weak interaction between the magnesium and phosphorus atoms as shown with dashed lines. The Mg1–P1 distance is 2.737(2) Å.

and by the recrystallization at  $-35^\circ\text{C}$ . The structure of **2** was proved ultimately by X-ray analysis and its ORTEP is shown in Fig. 1. CCDC contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)). The deposition number is CCDC 192828.

The detailed mechanism of the formation of **2** has not been investigated yet. However the above transformation is a curious example where one base (DBN) chooses to act as a nucleophile and another base (*t*-BuLi) caused the final dehydrochlorination.

## EXPERIMENTAL

### Magnesium Diamide **2**

The Grignard reagent was prepared from 5.043 g (0.0259 mol) of bis(trimethylsilyl)chloromethane and 1.24 g (0.052 mol) of magnesium turnings in 50 ml of THF. 1,2-Bis(dichlorophosphino)ethane (2.5 g, 0.0108 mol) in 10 ml of THF was added to the solution at  $-78^\circ\text{C}$ . After warming the reaction mixture to room temperature, 9.6 g (0.077 mol) of DBN

was added and the reaction mixture was stirred for 3 weeks at room temperature. Half of the reaction mixture was separated and treated with THF and at  $-78^{\circ}\text{C}$  with excess of 1.7 M pentane solution of *t*-BuLi (5 ml). At this step, the resulted reaction mixture was stripped of the solvent under vacuum, redissolved in 20 ml of pentane, and filtered. The clear crystals of **2** were collected after storage of the pentane solution at  $-35^{\circ}\text{C}$ . The yield of **2** is 0.78 g (18% on half of the 1,2-bis(dichlorophosphino)ethane) with a mp with decomposition at  $139.3^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  = 0.01 (s, 36H,  $\text{Me}_3\text{Si}$ ), 0.89–3.50 (unresolved multiplets, 38H, DBN,  $\text{P}-\text{CH}_2$ , and  $\text{CH}-\text{Si}$  protons).  $^{31}\text{P}$  NMR ( $\text{THF}-d_8$ )  $\delta$  =  $-46.65$ . Anal. Calcd(%) for  $\text{C}_{37}\text{H}_{74}\text{MgN}_6\text{P}_2\text{Si}_4$ : C, 55.44; H, 9.30; N, 10.48; P, 7.73. Found: C, 55.21; H, 9.44; N, 10.39; P, 7.54.

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