Brief Communications

A new route for the metallation of trihydroheptaphosphine P_7H_3 with butyllithium

V. A. Milyukov,[a]★ A. V. Kataev,[a] O. G. Sinyashin,[a] and E. Hey-Hawkins[b]

[a]A. E. Arbuzov Institute of Organic and Physical Chemistry,
Kazan Research Center, Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.
Fax: +7 (843) 276 7424. E-mail: miluykov@iopc.knc.ru, oleg@iopc.knc.ru
[b]Institute of Inorganic Chemistry, University of Leipzig,
*29 Johannisallee, D-04103 Leipzig, Germany.**
Fax: +49 (0341) 973 9319. E-mail: hey@rz.uni-leipzig.de

A new route for the metallation of heptaphosphine P_7H_3 with BuLi, namely, decomposition of the nortricyclane P_7 unit to form dilithium hexadecaphosphide Li_2P_{16}, was found.

Key words: homopolyatomic clusters, polyphosphides, heptaphosphine, butyllithium.

Homopolyphosphorus clusters[1] play an important role for understanding of the mechanism of elemental phosphorus transformations into various organophosphorus derivatives[2] and for solving the problem of diagonal relationship between carbon and phosphorus.[3] In spite of the fact that many alkaline metal polyphosphides have been described,[4] the main method for their synthesis is the reaction of the corresponding metal with elemental phosphorus at high temperature[5,6] or in liquid ammonia.[7,8] To date processes of modification of known polyphosphorus compounds remain virtually unstudied, although they provide a possibility of selective synthesis of homopolyatomic clusters of alkaline metals.

Therefore, we paid attention to one of simplest polyphosphines: trihydroheptaphosphine P_7H_3 (**1**),[9] which is a potentially convenient reagent for preparing various alkaline metal polyphosphides. At the same time, chemical properties of this compound remain virtually unstudied so far. It is only known that its metallation with $LiPH_2$ occurs to form Li_3P_7 in ~100% yield.[10]

We found that the use of butyllithium as the metallating agent in this reaction makes it possible to accomplish a new route, namely, opening of the nortricyclane structure of the P_7 fragment resulting in the formation of several polyphosphorus products. From this mixture we have isolated dilithium hexadecaphosphide Li_2P_{16} (**2**)

* Institut für Anorganische Chemie der Universität Leipzig, Johannisallee 29, Leipzig, Germany.

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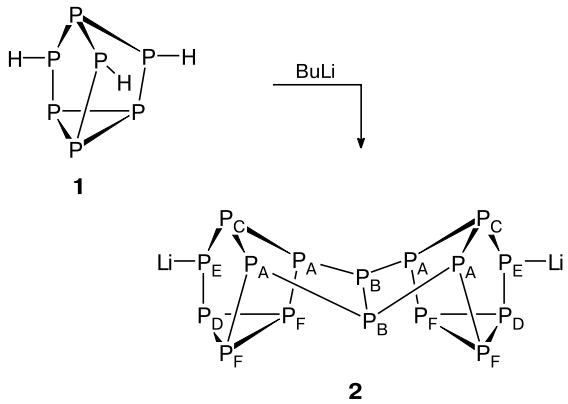
(Scheme 1), whose structure was proved by ^{31}P NMR spectroscopy and the composition was determined by mass spectrometry.

Scheme 1



1 **2**

The ^{31}P NMR spectrum exhibits six groups of signals corresponding to nonequivalent phosphorus atoms, which is rigidly consistent with the spectral pattern described earlier for similar systems.[11]

It should be mentioned that only two reactions of P_7 fragment transformation affording the hexadecaphosphide anion have been described to presently. When the metal atoms in trisodium heptaphosphide P_7Na_3 were replaced by tetraphenylphosphonium cations, the nortricyclane structure decomposed to form bis(tetraphenylphosphonium) hexadecaphosphide $(Ph_4P)_2P_{16}$ (see Ref. 12). The selective formation of dilithium hexadecaphosphide was also observed for the thermal decomposition of Li_2HP_7 (see Ref. 13). Probably, in the metallation of heptaphosphine **1** with BuLi, the hydrogen atoms are partially substituted for the metal cations to form the dilithium derivative of heptaphosphine, which is transformed into Li_2P_{16} (**2**) at room temperature.

Thus, we have shown for the first time that the reaction of heptaphosphine P_7H_3 (**1**) with butyllithium affords dilithium hexadecaphosphide Li_2P_{16} (**2**).

Experimental

All reactions were carried out in inert atmosphere using the standard Schlenk technique. Heptaphosphine P_7H_3 (**1**) was synthesized by a described procedure.[10] ^{31}P NMR spectra were recorded on a Bruker MSL-400 spectrometer with a working frequency of 121.7 MHz using 85% H_3PO_4 as external standard. Electron impact mass spectra were obtained on a Finnigan MAT-212 instrument with the energy of ionizing electrons 50 eV and current of the electron collector 0.5 mA. Precise mass values were determined by the superposition with reference peaks of perfluorokerosene.

Dilithium hexadecaphosphide (2). A 2.33 *M* solution (4.1 mL, 0.009 mol) of BuLi in hexane was added at −70 °C to a suspension of heptaphosphine P_7H_3 (**1**) (0.68 g, 0.003 mol) in THF (20 mL). The reaction mixture was stirred for 5 h at −70 °C and then for 6 h at ~20 °C. The filtration and concentration of the solution to one half of the volume resulted in the growth of red crystals of Li_2P_{16} (**2**) (0.29 g, 42%), which completed within a week. Mass spectrum, *m/z*: 509.612 $[M]^+$ (calculated 509.612 for Li_2P_{16}). ^{31}P NMR (ethylenediamine), δ: 60 (m, 4 P, P_A); 38 (m, 2 P, P_B); 6 (m, 2 P, P_C); −34 (m, 2 P, P_D); −134 (m, 2 P, P_E); −172 (m, 4 P, P_F).

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