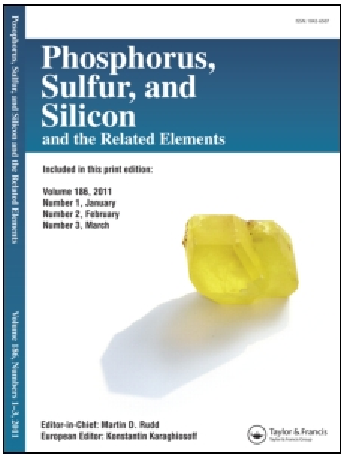

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The Chemical Properties of Alkali Metals Heptaphosphides

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*Trisodium heptaphosphide Na_3P_7 (**1**) reacts with alkyl tosylates with formation of sodium dialkylheptaphosphides (**2**) or trialkylheptaphosphines (**3**) depending on the stoichiometry. Sodium 1,2-diphosphacyclopentadienide is formed in the reaction of cyclopropenyl complexes of nickel with sodium polyphosphides.*

Keywords Alkyl tosylate; sodium 1,2-diphosphacyclopentadienide; sodium pentaphosphacyclopentadienide; trisodium heptaphosphide

INTRODUCTION

Homopolyatomic anionic clusters of phosphorus (polyphosphide anions) have stimulated the interest of scientists as possible intermediates in the transformation of elemental phosphorus into organophosphorus compounds,[1,2] and some alkali metal polyphosphides have been used as semiconductor systems.[3]

The numerous cagelike polyphosphide anions include P_7^{3-}, which has a nortricyclane structure[4] and is the only polyphosphide anion which exhibits valence tautomerism—a Cope rearrangement—in solution.[5] This is responsible for the greater stability of P_7^{3-} in comparison with other polyphosphides. Furthermore, the P_7 unit is a building block of numerous polyphosphides.[6,7,8]

The focus of our research is the investigation of the chemical properties of the P_7^{3-} anion in reactions with organic and organometallic

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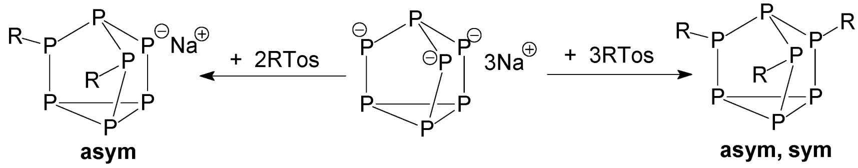
compounds, and comparison of the chemical properties of two different types of polyphosphides: aromatic (NaP_5) and cagelike [Na_3P_7 (**1**)].

The chemical properties of the P_7^{3-} anion are not well studied, and only two methods for preparation of organic derivatives thereof are known. First, the reaction of the P_7^{3-} anion with an excess of tetraalkylammonium salts leads to the formation of disubstituted heptaphosphides NaP_7R_2 (**2**).[9] Second, the reaction of **1** with various alkyl halides yields a mixture of di- and trisubstituted symmetrical and asymmetrical isomers of organylheptaphosphines.[10] Therefore, it was of interest to elaborate a method for the selective synthesis of di- and trisubstituted heptaphosphines as potential polydentate ligands. One possibility is the well-known reaction between alkali metal phosphides and alkyl or aryl tosylates,[11] which can be realized under mild conditions and gives good yields of the products.

We found that the reaction of **1** with two equivalents of alkyl tosylates results in the formation of the asymmetric isomer of sodium dialkylheptaphosphides (**2**) (Scheme 1).



2 **1** **3**

SCHEME 1

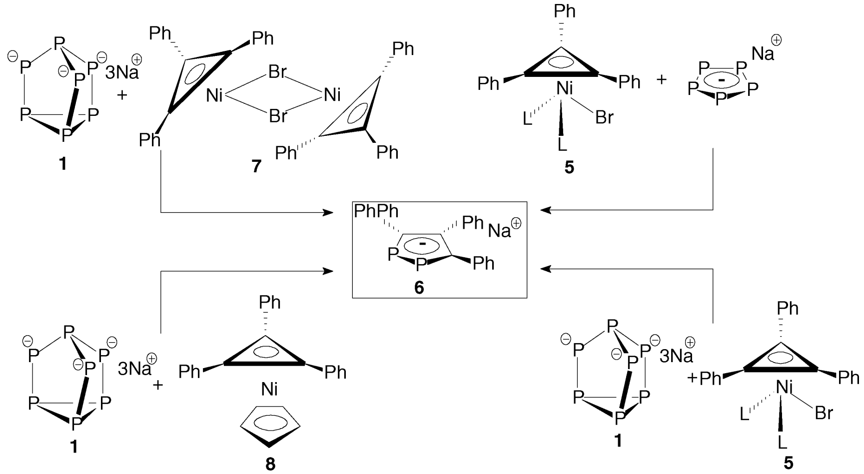
However, when **1** was treated with three equivalents of alkyl tosylate a mixture of symmetric and asymmetric isomers of trialkylheptaphosphines (**3**) was formed.[12]

Thus, the reactivity of the cagelike sodium polyphosphides toward alkyl halides or alkyl tosylates is clearly different from that of the aromatic P_5^- anion in NaP_5: NaP_5 reacts with alkyl halides to form a mixture of different alkylpolyphosphines with destruction of the P_5 ring.[13] However, the reaction of Na_3P_7 (**1**) with alkyl halides or alkyl tosylates leads to the formation of dialkylheptaphosphides (**2**) or trialkylheptaphosphines (**3**) with a nortricyclane phosphorus cage.

The chemical behavior of alkali metal polyphosphides toward transition metal complexes is another example of the differences between aromatic and cagelike polyphosphides. Thus, NaP_5 reacts with numerous transition metal compounds to give sandwich complexes with an intact P_5 ring[13,14,15]or a tetraphosphabutadienide fragment.[16] On the other hand, Na_3P_7 reacts with transition metal complexes to form complexes either with an intact P_7 nortricyclane-like structure[17] or with transformation of the nortricyclane structure into a norbornadiene-like structure.[18,19]

We have found that both NaP_5[20] and Na_3P_7[21] react with nickel cyclopropenyl complexes **5** to give sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (**6**) independent of the kind of nickel cyclopropenyl complex employed (i.e., bimetallic (**7**) or sandwich (**8**) complexes) (Scheme 2).

Therefore, we assume that the first stage of the formation of sodium 1,2-diphosphacyclopentadienide (**6**) in the reaction of sodium polyphosphides with cyclopropenyl complexes of nickel is nucleophilic attack of the polyphosphide anion on a carbon atom of the aromatic cyclopropenyl ring, which has a positive charge according to Hückel's rules.



SCHEME 2

In summary, we have observed that, depending on the stoichiometry of the starting materials, the reaction between the heptaphosphide trianion and alkyl tosylates leads either to the asymmetric dialkylheptaphosphides (**2**) or to a mixture of symmetric and asymmetric isomers of trialkylheptaphosphines (**3**). Both types of polyphosphides, i.e., aromatic NaP_5 and cagelike Na_3P_7, react with cyclopropenyl complexes of nickel with formation of sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (**6**).

REFERENCES

[1] M. Ehses, A. Romerosa, and M. Peruzzini, *Top. Curr. Chem.*, **220,** 107 (2002).

[2] V. Miluykov, Y. Budnikova, and O. Sinyashin, *Russ. Chem. Rev.*, **74,** 781 (2005).

[3] R. Schachter, C. G. Michel, M. A. Kuck, J. A. Baumann, D. J. Olego, L. G. Polgar, P. M. Raccah, and W. E. Spicer, *Appl. Phys. Lett.*, **45,** 277 (1984).

[4] W. Hönle and H. G. von Schnering, *Z. Anorg. Allg. Chem.*, **440,** 171 (1978).

[5] M. Baudler, H. Ternberger, W. Faber, and J. Hahn, *Z. Naturforsch. B*, **34,** 1690 (1979).

[6] N. Korber, *Phosphorus, Sulfur, Silicon*, **124/125,** 339 (1997).

[7] H.-G. von Schering, V. Manriquez, and W. Hönle, *Angew. Chem.*, **93,** 606 (1981); *Angew. Chem. Int. Ed. Engl.*, **20,** 594 (1981).

[8] G. Fritz, H.-W. Scheider, W. Hönle, and H.-G. von Schering, *Z. Naturforsch. B*, **43,** 561 (1988).

[9] S. Charles, J. C. Fettinger, and B. W. Eichhorn, *J. Am. Chem. Soc.,* **117,** 5303 (1995).

[10] M. Baudler and K. Glinka, *Chem. Rev.* , **93,** 1623 (1993).

[11] A. M. R. Gonsalves, J. C. Bayon, M. E. S. Serra, and J. P. R. Pereira, *J. Organomet. Chem.*, **553,** 199 (1998).

[12] V. Miluykov, A. Kataev, O. Sinyashin, and E. Hey-Hawkins, *Russ. Chem. Bull.* in press, 2007.

[13] M. Baudler, S. Akpapoglou, D. Ouzounis, F. Wasgestian, B. Meinigke, H. Budzikiewicz, and H. Münster, *Angew. Chem.*, **100,** 288 (1988); *Angew. Chem. Int. Ed. Engl.,* **27,** 280 (1988).

[14] M. Baudler and T. Etzbach, *Angew. Chem.* **103,** 590 (1991); *Angew. Chem. Int. Ed. Engl.* **30,** 580 (1991).

[15] V. Miluykov, O. Sinyashin, O. Scherer, and E. Hey-Hawkins, *Mendeleev Commun.*, 1 (2002).

[16] V. Miluykov, O. Sinyashin, P. Lonnecke, and E. Hey-Hawkins, *Mendeleev Commun.*, 212 (2003).

[17] R. Ahlrich, D. Fenske, K. Fromm, H. Krautscheid, U. Krautscheid, and O. Treutler, *Chem. Eur. J.*, **2,** 238 (1996).

[18] S. Charles, B. W. Eichhorn, A. I. Rheingold, and S. G. Bott, *J. Am. Chem. Soc.,* **116,** 8077 (1994).

[19] S. Charles, J. C. Fettinger, S. G. Bott, and B. W. Eichhorn, *J. Am. Chem. Soc.*, **118,** 4713 (1996).

[20] V. Miluykov, O. Sinyashin, A. Kataev, P. Lönnecke, and E. Hey-Hawkins, *Organometallics*, **24,** 2233 (2005).

[21] V. Miluykov, O. Sinyashin, A. Kataev, P. Lönnecke, and E. Hey-Hawkins, *Russ. Chem. Bull.*, **56,** 304 (2007).