(EtZn)₄Zn₂(PSi₃Bu₃)₄ – a Homometallic Phosphanediide of Zinc with a Novel Zn₆P₄ Cage

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The metalation of tri(tert-butyl)silylphosphane with diethylzinc yields quantitatively the title compound tetraethyltetrakis(tert-butyl)phosphanediido)hexazinc (1) with a novel Zn₆P₄ cage with two Zn₂P₂ rings interconnected by two zinc atoms.

Key words: Cage Compounds, Geminal Dianions, Metalation, Phosphanediides, Zinc

Dialkylzinc is a mild metalating reagent and therefore, the deprotonation of anions such as amides is hardly possible. Nevertheless, there are reports on bis(alkylzinc) alkylimides as polymerization catalysts [1], however, these compounds are poorly characterized and more recent attempts to prepare (RZn)₂NR via zincation of primary alkylamines failed [2]. However, compounds of the type (MeZnNPR’₃)₄ with a central Zn₄N₄ heterocubane cage have been known for more than 35 years [3]. More recent investigations focussed on derivationisation and reactivity of such cage compounds [4].

For the preparation of phosphanediides several pathways have been explored. The reaction of P(SiMe₃)₃ with zinc(II) chloride in the presence of triisopropylphosphane gives Zn₁₀Cl₁₂(PSiMe₃)₄ and volatile chlorotrimethylsilane [5]. The central Zn₄P₄ heteroadamantane cage is embedded in a zinc(II) chloride matrix. A phosphanediide was obtained in the metathesis reaction of (Me₃Si)₃CZnCl with LiP(H)SiPr₃ [6]. Homoleptic compounds Zn{P(SiMe₃)₂}₂ are valuable precursors for the synthesis of semiconducting materials at high temperatures [7]. However, alkylzinc diorganylphosphanides are quite unreactive which makes possible the isolation of a diphenylphosphane complex of alkylzinc diphenylphosphanide [8]. The zinc-bonded phosphanediides prepared so far are shielded by bulky trimethylsilyl groups [6] or embedded in a matrix of zinc(II) chloride with additional trialkylphosphane ligands [5] or stabilized by a multidentate ligand [9]. Here we report the first example of a novel Zn₇P₅ cage built only by zinc atoms and phosphanediide substituents.

In order to obtain soluble cage compounds and to ensure high reactivity the primary tri(tert-butyl)silyl substituted phosphane was chosen, small alkyl substituents at the zinc atom ensure that the reactivity at this site is maintained. The reaction of diethylzinc with H₂P-Si₃Bu₃ in toluene at room temperature gives the title compound tetraethyltetraakis(tert-butyl)phosphanediido)hexazinc (1) according to equation 1 with a 86% yield. During this zincation the colorless solution turns yellow. (EtZn)₄Zn₂(PSi₃Bu₃)₄ (1), which crystallizes from a toluene solution as yellow plates, is thermally stable up to 220 °C, however, it is sensitive towards moisture and has to be handled in an inert gas atmosphere.

The molecular structure of the inner core of 1 is represented in Fig. 1. The molecule contains an inversion center, the atoms generated by this symmetry element are marked with an apostrophe. The molecule consists of two (EtZn)₂(PSi₃Bu₃)₂ rings with three-
coordinate metal atoms Zn1 and Zn2. These Zn2P2 cycles are connected by two-coordinate atoms Zn3 and Zn3'. The shielding of the cage by the demanding tri(tert-butyl)silyl groups is shown as a ball and stick representation in Fig. 2.

Due to the small coordination number and the high electrostatic attraction the Zn3-P2 bond length of 224.4 pm is nearly 20 pm smaller than endocyclic Zn1-P and Zn2-P with an average value of 242.0 pm. Comparable short Zn-P bonds were observed for [(Me3Si)3CZn]SiPr3 (223.2 pm [6]) and for [1,2-dipiryld-1,2-bis(tert-butyl)dihydroxysilyl]trizinc bis(trisopropylsilylphosphanediide) (224.2 pm [9]). The latter shows a P-Zn-P bond angle of 154.0° due to a rather strong ring strain. In I the two-coordinate metal atoms Zn3 show P2-Zn3-P1' values of 163.3°. The deviation from a linear coordination environment is the consequence of an intramolecular electrostatic repulsion between the zinc atoms Zn3 and Zn3' which also leads to a widening of the Zn3-P2-Zn1 angle (116.3°) whereas the other Zn3-P2-Zn2 (102.7°), Zn3'-P1-Zn1 (104.0°) and Zn3'-P1-Zn2 (90.0°) bond angles show smaller values. This feature leads to a slippage of the two Zn2P2 rings against each other and reduces the van der Waals contact of the P-bonded bulky tri(tert-butyl)silyl substituents.

The P-Si bonds with an average value of 227.6 pm are longer than those observed for P(SiMe3)3 (224.5 pm [10]) due to the higher coordination number of the phosphorus atoms and the steric strain induced by the bulky tBu3Si groups. The P-Si distances found in the cation [P(SiMe3)4]2+ (230.0 pm [11]) are even larger. The Zn2P2 rings show nearly rectangular angles at the zinc and phosphorus atoms.

Compound I is the first binary cage compound of zinc and phosphorus with only moderate stabilization by steric shielding of the reactive sites. The trialkylsi-
fore, secondary amines and phosphanes act as Lewis bases and bind to the metal centers rather than being deprotonated by the second zinc-bonded alkyl group. The Zn6P4 cage of 1 differs from cages of other divalent metals such as the alkaline earth metals and tin(II) which tend to build M4E4 heterocubane structures or M6E6 hexagonal prisms (M = divalent metal, E = N, P, As) [12].

**Experimental Section**

All manipulations were carried out in an anhydrous argon atmosphere. The solvents were thoroughly dried and distilled under argon. Diethylzinc in n-hexane (3 ml of a 1-molar solution) was dissolved in 15 ml of toluene. At r.t. 2 mmol of tri(tert-butyl)silylphosphane were added. This solution was stirred until its color turned yellow. Reduction of the volume to a few milliliters and cooling to 5 °C gave 0.61 g of yellow plates of 1 (0.43 mmol, 86%). Dec. above 270 °C without melting. – IR: 1477 vs, 1442 m, 1415 w, 1550 M. Westerhausen et al. (1967); H. Schmidbaur, G. Jonas, Chem. Ber. 129, 1621 (1996); M. Krieger, R. O. Gould, K. Harms, S. Parsons, K. Dehnicek, Chem. Ber. 129, 1621 (1996); M. Krieger, R. O. Gould, B. Neumüller, K. Harms, K. Dehnicek, Z. Anorg. Allg. Chem. 624, 1434 (1998).

Crystal data for 1: yellow plates, (C19H40P2Si2Zn3)2, M = 1430.04, orthorhombic, space group Pbca (no. 61), a = 1145.76(7), b = 2413.0(2), c = 2602.0(2) pm, V = 7.1936(9) nm3, ρcalcd = 1.32 g cm−3, μ(Mo-Kα) = 2.155 mm−1, Z = 4, 58067 reflections were collected on a STOE IPDS diffractometer at 173(2) K, 6916 independent reflections, 316 refined parameters, R1 = 0.0255 on 6022 reflections with I > 2σ(I), s = 1.020. Crystallographic data (excluding structure factors) for 1 has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-244907. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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