(EtZn)$_4$Zn$_2$(PSitBu$_3$)$_4$ – a Homometallic Phosphanediide of Zinc with a Novel Zn$_6$P$_4$ Cage

Matthias Westerhausen[a,*], Gerhard Sapelza[a], Manfred Zabel[b], and Arno Pfitzner[b]

[a] Department of Chemistry and Biochemistry, Ludwig-Maximilians-Universität, D-81377 München, Germany
[b] Institute for Inorganic Chemistry, University of Regensburg, D-93040 Regensburg, Germany

Reprint requests to Dr. Westerhausen. Fax: +49 89 2180-77867. Tel: +49 89 2180-77481.
E-mail: maw@cup.uni-muenchen.de

Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

The metalation of tri(*tert*-butyl)silylphosphane with diethylzinc yields quantitatively the title compound tetraethyltetrakis(tri(*tert*-butyl)silylphosphanediido)hexazinc (**1**) with a novel Zn$_6$P$_4$ cage with two Zn$_2$P$_2$ 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)$_2$NR' *via* zincation of primary alkylamines failed [2]. However, compounds of the type (MeZnNPR'$_3$)$_4$ with a central Zn$_4$N$_4$ heterocubane cage have been known for more than 35 years [3]. More recent investigations focussed on derivatisation and reactivity of such cage compounds [4].
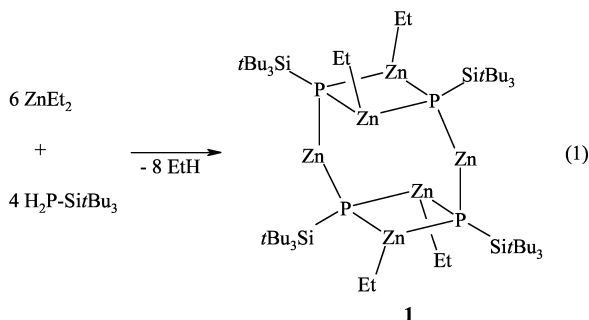
For the preparation of phosphanediides several pathways have been explored. The reaction of P(SiMe$_3$)$_3$ with zinc(II) chloride in the presence of triisopropylphosphane gives Zn$_{10}$Cl$_{12}$(PSiMe$_3$)$_4$ and volatile chlorotrimethylsilane [5]. The central Zn$_6$P$_4$ heteroadamantane cage is embedded in a zinc(II) chloride matrix. A phosphanediide was obtained in the metathesis reaction of (Me$_3$Si)$_3$CZnCl with LiP(H)SiiPr$_3$ [6]. Homoleptic compounds Zn{P(SiMe$_3$)$_2$}$_2$ 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 complexe of alkylzinc diphenylphosphanide [8]. The zinc-bonded phosphanediides prepared so far are shielded by bulky tris(trimethylsilyl)methyl 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 Zn$_n$P$_m$ 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 H$_2$P-SitBu$_3$ in toluene at room temperature gives the title compound tetraethyltetrakis[tri(*tert*-butyl)silylphosphanediido]hexazinc (1) according to equation 1 with a 86% yield. During this zincation the colorless solution turns yellow. (EtZn)$_4$Zn$_2$(PSitBu$_3$)$_4$ (**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)$_2$(PSitBu$_3$)$_2$ rings with three-

coordinate metal atoms Zn1 and Zn2. These Zn$_2$P$_2$ 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 [(Me$_3$Si)$_3$CZn]PSi*i*Pr$_3$ (223.2 pm [6]) and for [1,2-dipyridyl-1,2-bis(*tert*-but-yldimethylsilylamido)ethane]trizinc bis(triisopropyl-silylphosphanediide) (224.2 pm [9]). The latter shows a P-Zn-P bond angle of 154.0° due to a rather strong ring strain. In **1** 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 Zn$_2$P$_2$ rings against each other and reduces the van der Waals contact of the P-bonded bulky tri(*tert*-butyl)silylsilyl substituents.

The P-Si bonds with an average value of 227.6 pm are longer than those observed for P(SiMe$_3$)$_3$ (224.5 pm [10]) due to the higher coordination number of the phosphorus atoms and the steric strain induced by the bulky *t*Bu$_3$Si groups. The P-Si distances found in the cation [P(SiMe$_3$)$_4$]$^+$ (230.0 pm [11]) are even larger. The Zn$_2$P$_2$ rings show nearly rectangular angles at the zinc and phosphorus atoms.

Compound **1** is the first binary cage compound of zinc and phosphorus with only moderate stabilization by steric shielding of the reactive sites. The trialkylsi-
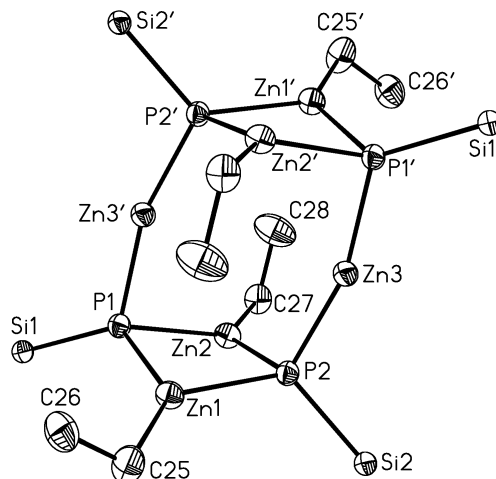
Fig. 1. Molecular structure of the inner core of (EtZn)$_4$Zn$_2$(PSi*t*Bu$_3$)$_4$. Symmetry-related atoms ($-x + 1$, $-y$, $-z + 2$) are marked with an apostrophe. The ellipsoids represent a probability of 30%, the *tert*-butyl groups at the silicon atoms as well as the hydrogen atoms of the ethyl groups are omitted for clarity reasons.
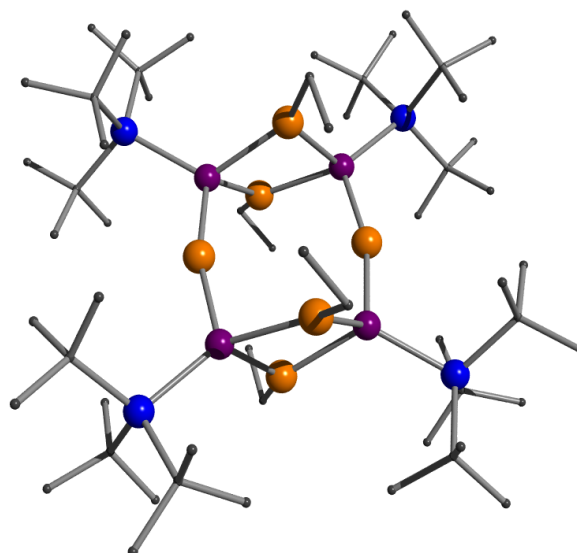

Fig. 2. Molecular structure of (EtZn)$_4$Zn$_2$(PSi*t*Bu$_3$)$_4$ showing the shielding by the tri(*tert*-butyl)silyl substituents. The atoms Zn, P and Si are drawn with radii of 37, 32 and 33 pm, respectively. For clarity reasons the carbon atoms are drawn with arbitrary small radii of 10 pm and the H atoms are not shown.

lyl substituent is necessary in order to enable a double deprotonation under mild reaction conditions. In het-eroleptic compounds of the type R-Zn-X (R = alkyl, X = NR'$_2$ [2], PPh$_2$ [8]) the metalation power of the zinc-bonded alkyl group is strongly reduced and there-

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 Zn$_6$P$_4$ cage of **1** differs from cages of other divalent metals such as the alkaline earth metals and tin(II) which tend to build M$_4$E$_4$ heterocubane structures or M$_6$E$_6$ 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 220 °C without melting. – IR: 1477 vs, 1442 m, 1415 w, 1386 s, 1361 m, 1356 m, 1250 m, 1212 w, 1178 m, 1159 w, 1098 w, 1029 m, 1011 vs, 985 m, 969 m, 952 w, 932 s, 910 w, 879 m, 839 m, 816 vs, 624 m, 606 s, 560 s, 499 vs, 458 m, 430 m, 387 w, 323 w, 289 w cm^{-1}. – ^{1}H NMR: $\delta = 0.57$ (q, CH$_2$), 1.16 (t, CH$_3$, ^3J(H, H) = 7.0 Hz), 1.26 (s, *t*Bu). – ^{13}C{^{1}H} NMR: $\delta = 32.0$ (SiC*Me*$_3$), 23.9 (Si*C*Me$_3$), 5.4 (ZnCH$_2$*CH*$_3$), 1.0 (Zn*CH*$_2$CH$_3$). – ^{29}Si{^{1}H} NMR: $\delta = 28.8$. – ^{31}P{^{1}H} NMR: $\delta = -252.5$. – C$_{56}$H$_{128}$P$_4$Si$_4$Zn$_6$ (1430.20): calcd. C 47.23, H 9.03; found C 47.02, H 9.20.

Crystal data for **1**: yellow plates, (C$_{28}$H$_{64}$P$_2$Si$_2$Zn$_3$)$_2$, $M = 1430.04$, orthorhombic, space group *Pbca* (no. 61), $a = 1145.76(7)$, $b = 2413.0(2)$, $c = 2602.0(2)$ pm, $V = 7.1936(9)$ nm^3, $\rho_{\text{calcd.}} = 1.32$ g cm^{-3}, μ(Mo-K$_\alpha$) = 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, w$R_2 = 0.0673$ (on F^2), $R1 = 0.0255$ on 6022 reflections with $I > 2\sigma(I)$, $s = 1.020$. 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).

[1] H. Tani, N. Oguni, Polym. Lett. **7**, 769 (1969); N. Oguni, H. Tani, J. Polym. Sci. **11**, 573 (1973).

[2] M. M. Olmstead, W. J. Grigsby, D. R. Chacon, T. Hascall, P. P. Power, Inorg. Chim. Acta **251**, 273 (1996); M. Westerhausen, T. Bollwein, A. Pfitzner, T. Nilges, H.-J. Deiseroth, Inorg. Chim. Acta **312**, 239 (2001).

[3] H. Schmidbaur, G. Jonas, Angew. Chem. Int. Ed. Engl. **6**, 449 (1967); H. Schmidbaur, G. Jonas, Chem. Ber. **101**, 1271 (1968).

[4] M. Krieger, R. O. Gould, K. Harms, S. Parsons, K. Dehnicke, Chem. Ber. **129**, 1621 (1996); M. Krieger, R. O. Gould, B. Neumüller, K. Harms, K. Dehnicke, Z. Anorg. Allg. Chem. **624**, 1434 (1998).

[5] O. Fuhr, D. Fenske, Z. Anorg. Allg. Chem. **625**, 1229 (1999).

[6] M. Westerhausen, M. Wieneke, K. Doderer, W. Schwarz, Z. Naturforsch. **51b**, 1439 (1996).

[7] S. C. Goel, M. Y. Chiang, W. E. Buhro, J. Am. Chem. Soc. **112**, 5636 (1990); S. C. Goel, M. Y. Chiang, D. J. Rauscher, W. E. Buhro, J. Am. Chem. Soc. **115**, 160 (1993); S. C. Goel, W. E. Buhro, N. L. Adolphi, M. S. Conradi, J. Organomet. Chem. **449**, 9 (1993).

[8] M. G. Davidson, A. J. Edwards, M. A. Paver, P. R. Raithby, C. A. Russell, A. Steiner, K. L. Verhorevoort, D. S. Wright, J. Chem. Soc., Chem Commun. 1989 (1995).

[9] M. Westerhausen, T. Bollwein, M. Warchhold, H. Nöth, Z. Anorg. Allg. Chem. **627**, 1141 (2001).

[10] J. Bruckmann, C. Krüger, Acta Crystallogr. **C51**, 1152 (1995).

[11] M. Driess, R. Barmeyer, C. Monsé, K. Merz, Angew. Chem. **113**, 2366 (2001); Angew. Chem. Int. Ed. **40**, 2308 (2001).

[12] M. Driess, R. E. Mulvey, M. Westerhausen, in M. Driess, H. Nöth (eds): Molecular Clusters of the Main Group Elements, p. 391 – 424, Wiley-VCH, Weinheim (2004).