

Zinc Bis[μ -*N,N'*-chlorozinc-bis(*N*-trimethylsilylimino-diphenylphosphoranyl)-methanediide]: A Zinc Derivative of a Geminal Carbdianion

Tobias Bollwein,^{a,b} Matthias Westerhausen,^a and Arno Pfitzner^c

^a Department Chemie, Ludwig-Maximilians-University Munich Butenandtstr. 9, D-81377 Munich, Germany

^b Current address: Johnson & Johnson GmbH Heckinghauser Strasse 263, D-42289 Wuppertal, Germany

^c Institut für Anorganische Chemie, University of Regensburg Universitätsstr. 31, D-93040 Regensburg, Germany

Z. Naturforsch. **58b**, 493–495 (2003); received February 13, 2003

The trinuclear title compound, $C_{74}H_{88}Cl_2N_4P_4Si_4Zn_3$, is derived from a geminally substituted carbdianion. The central zinc atom shows a nearly linear coordination geometry with very short Zn-C bond lengths (average 191 pm). The peripheral metal centers of the chlorozinc moieties are chelated by the phosphanimine donors and hence are triply coordinated, thus forming a six-membered CP_2N_2Zn ring with Zn-N distances of 195 pm (average).

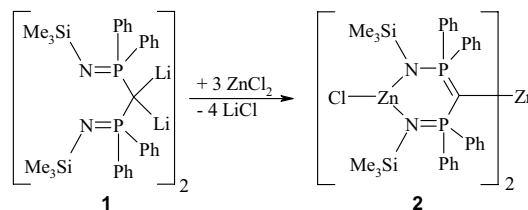
Key words: Geminal Carbdianions, Metathesis Reactions, Zinc

Geminally bis-zincated alkanes are already mentioned in the literature [1]. The insertion of zinc into the halogen carbon bonds of 1,1-dihalogenoalkanes yields compounds of the type $H_2C(ZnX)_2$ [2–4] and $RCH(ZnX)_2$ [5]. Activation of the zinc metal by lead or copper accelerates the reaction and gives higher yields [4]. However, the molecular structures of the products are unknown as of yet. The only structurally characterized geminal bis(alkylzinc) substituted alkane is the tetrameric compound [(2-pyridyl)(Me_3Si)CZn]₄ [6].

The metalation of bis(*N*-trimethylsilylimino-diphenylphosphoranyl)methane, $[Me_3SiN=P(Ph)_2]_2CH_2$, with alkyllithium and dimethylzinc gives the corresponding methanides [7,8]. The lithium derivative can be used as a synthon for metathesis reactions, for example with the trihalides of aluminium, gallium and indium; the MCl_2 moieties are bonded to the nitrogen bases and not to the anionic carbon atom [7]. The geminally double-deprotonated alkane is accessible by metalation of

bis(*N*-trimethylsilylimino-diphenylphosphoranyl)methane with tetrabenzylzirconium [9] or with two equivalents of alkyllithium [8,10]. The lithium derivative $[Me_3SiN=P(Ph)_2]_2CLi_2$ (**1**) crystallizes as a dimer with a central C_2Li_4 octahedron.

The metathesis reaction of the dilithium compound **1** with zinc dichloride in toluene yields the trinuclear complex zinc bis[μ -*N,N'*-chlorozinc-bis(*N*-trimethylsilylimino-diphenylphosphoranyl)methanediide], $\{ClZn[\mu-(Me_3Si)N=P(Ph)_2]_2C\}_2Zn$ (**2**), according to equation 1. In the product the formation of two geminal Zn-C bonds (average: 191 pm) is avoided by chelation of the chlorozinc fragments with the nitrogen bases. Although the ligands are sterically very demanding the central Zn-C bond lengths are very short even compared to dimethylzinc [11]. In $Ph-Zn-C(SiMe_3)_3$ a similar Zn-C distance was found [12]. This zinc atom is in a nearly linear coordination environment ($CZnC$ 178.6°) and shielded by the phenyl substituents. The average P-N bond length of 163 pm is larger than the value of 159 pm observed for $HC[P(Ph)_2N(SiMe_3)]ZnMe$ which shows the partial delocalization of the anionic charge within the six-membered CP_2N_2Zn cycle [7].



The triply coordinated zinc atoms in the outer sphere of the molecule are in a nearly trigonal planar environment. The six-membered CP_2N_2Zn rings with Zn-N distances of 195 pm show a boat conformation, with the P-C-P angles being 120°. The reason for this conformation could be the attraction between the positively charged chlorozinc fragments and the carbanions which leads to rather short transannular $Zn \cdots C$ contacts of 304.0 ($Zn2 \cdots C1$) and 305.3 pm ($Zn3 \cdots C1C2$). However, due to intramolecular repulsion between the chlorine atom and the phenyl substituents (see Fig. 1) this transannular contact is larger than in $HC[P(Ph)_2N(SiMe_3)]ZnMe$ [7].

The synthesis of **2** is straight-forward. However, this compound is nearly insoluble in hydrocarbons and crystallizes after its formation. The reactivity is extremely high and leads to an abstraction of

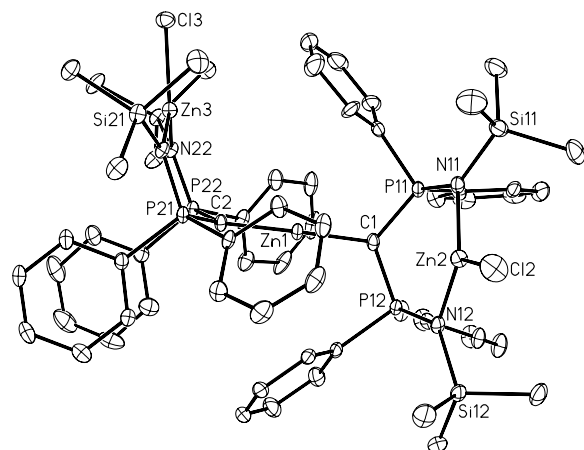


Fig. 1. Molecular structure of **2** with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The hydrogen atoms are omitted for clarity reasons.

hydrogen atoms from solvents after redissolving of **2** in common organic solvents such as ethers. Therefore, the far less reactive monozincated derivative is always formed and an analytically pure sample of **2** was not obtained. Similar observations were made by Linti *et al.* [13] for a geminally dilithiated 9,9-dilithiofluorene.

Table 1. Selected structural data for **2**.

<i>n</i>	1	2
Zn1-C(n)	190.8(3)	191.1(3)
Zn(n+1)-Cl(n+1)	218.57(9)	220.66(10)
Zn2/3-N(n1)	194.9(3)	196.0(3)
Zn2/3-N(n2)	194.0(3)	194.9(2)
C(n)-P(n1)	171.9(3)	172.6(3)
C(n)-P(n2)	171.8(4)	171.8(3)
P(n1)-N(n1)	163.5(2)	162.1(3)
P(n2)-N(n2)	163.3(2)	162.5(3)
N(n1)-Si(n1)	174.0(3)	174.8(3)
N(n2)-Si(n2)	174.8(3)	175.8(3)
C1-Zn(n)-C2	178.6(2)	
Cl(n+1)-Zn(n+1)-N(n1)	119.34(8)	118.32(8)
Cl(n+1)-Zn(n+1)-N(n2)	119.41(8)	121.51(9)
N(n1)-Zn(n+1)-N(n2)	121.09(10)	119.77(11)
P(n1)-C(n)-P(n2)	120.2(2)	119.9(2)
Zn1-C(n)-P(n1)	122.5(2)	120.9(2)
Zn1-C(n)-P(n2)	116.9(2)	117.7(2)
C(n)-P(n1)-N(n1)	113.9(1)	114.2(1)
C(n)-P(n2)-N(n2)	114.1(2)	113.7(1)
P(n1)-N(n1)-Si(n1)	131.0(2)	129.4(2)
P(n1)-N(n2)-Si(n2)	129.2(2)	129.5(2)

Experimental Section

All experiments were carried out under an argon atmosphere. The solvents were dried according to common procedures and distilled under argon, deuterated solvents were degassed and saturated with argon.

The dilithium salt **1** was prepared by lithiation of 8.95 mmol of $[\text{Me}_3\text{SiN}=\text{P}(\text{Ph})_2]_2\text{CH}_2$ [14] with two equivalents of *n*-butyllithium (8.95 mmol) in 20 ml of toluene. Zinc dichloride (1.22 g, 8.95 mmol) was added at 0 °C. Then the suspension was stirred for a few hours. The formation of **2** was followed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy ($\delta = +30.0$). The solid materials were removed at room temperature. Within several days, a few colorless crystals of **2** precipitated from the mother liquor.

X-ray data was collected on a STOE-IPDS diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 71.073$ pm) using oil-coated, rapidly cooled single crystals. Crystal data and structure refinement parameters for **2** are listed in Table 2. The structure was solved by direct meth-

Table 2. Crystal data and structure refinement parameters for **2**.

Compound	2
Empirical formula	$\text{C}_{74}\text{H}_{88}\text{Cl}_2\text{N}_4\text{P}_4\text{Si}_4\text{Zn}_3$
Formula weight (g mol^{-1})	1536.73
<i>T</i> (K)	193(2)
Crystal system	triclinic
Space group	<i>P1</i> (No. 1)
<i>a</i> (pm)	1202.95(13)
<i>b</i> (pm)	1229.91(13)
<i>c</i> (pm)	1466.01(14)
α (°)	71.271(12)
β (°)	70.905(12)
γ (°)	88.326(13)
<i>V</i> (nm^3)	1.9341(3)
<i>Z</i>	1
<i>d</i> _{ber} (g cm^{-3})	1.319
μ (mm^{-1})	1.179
<i>F</i> (000)	800
Scan range (°)	$5.2 < 2\theta < 55.7$
No. of data collected	16950
Flack-Parameter	-0.007(6)
Restraints	3
No. of parameters <i>N</i> _p	820
<i>wR</i> ₂ (on <i>F</i> ² , all data) ^a	0.0931
data <i>I</i> > 2 σ (<i>I</i>) ^a	15369
<i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>) ^a	0.0894
<i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>) ^a	0.0369
Goodness of fit ^b <i>s</i> on <i>F</i> ²	1.008
Residual density (e nm^{-3})	694/-961
CCDC- [15]	CCDC-203233

^a $R1 = (\sum||F_o| - |F_c||) / \sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$;

^b $s = \{\sum[w(F_o^2 - F_c^2)^2] / (N_o - N_p)\}^{1/2}$.

ods and refined with the software package SHELXL-97 [16]. Scattering factors for neutral atoms were taken for the heavy [17] as well as for the hydrogen atoms [18]. The non-hydrogen atoms were refined anisotropically. The H atoms were considered with a riding model under restriction to ideal symmetry at the corresponding carbon atoms. The unit cell of compound **2** contains two molecules of benzene.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft for generous financial support. T. B. is grateful to the Verband der Chemischen Industrie for a Ph. D. scholarship as well as to the Alexander-von-Humboldt-Foundation for an additional scholarship for a research year at the University of Auckland/New Zealand.

-
- [1] I. Marek, *Chem. Rev.* **100**, 2887 (2000).
[2] S. Miyano, T. Ohtake, H. Tokumaso, and H. Hachimoto, *Nippon Kagaku Kaishi* 381 (1973); *Chem. Abstr.* **78**, 159784 (1973).
[3] J. J. Eisch and A. Piotrowski, *Tetrahedron Lett.* **24**, 2043 (1983).
[4] K. Takai, T. Kakiuchi, Y. Kataoka, and K. Utimoto, *J. Org. Chem.* **59**, 2668 (1994).
[5] B. Martel and M. Varache, *J. Organomet. Chem.* **40**, C53 (1972).
[6] P. C. Andrews, C. L. Raston, B. W. Skelton, and A. H. White, *Organometallics* **17**, 779 (1998).
[7] a) C. M. Ong, P. McKarns, and D. W. Stephan, *Organometallics* **18**, 3775 (1999); b) C. M. Ong, P. McKarns, and D. W. Stephan, *Organometallics* **18**, 4197 (1999).
[8] C. M. Ong and D. W. Stephan, *J. Am. Chem. Soc.* **121**, 2939 (1999).
[9] R. P. Kamalesh Babu, R. McDonald, S. A. Decker, M. Klobukowski, and R. G. Cavell, *Organometallics* **18**, 4226 (1999).
[10] A. Kasani, R. P. Kamalesh Babu, R. McDonald, and R. G. Cavell, *Angew. Chem.* **111**, 1580 (1999); *Angew. Chem. Int. Ed.* **38**, 1483 (1999).
[11] A. Almenningen, T. U. Helgaker, A. Haaland, and S. Samdal, *Acta Chem. Scand.* **A36**, 159 (1982).
[12] M. Westerhausen, B. Rademacher, W. Schwarz, J. Weidlein, and S. Henkel, *J. Organomet. Chem.* **469**, 135 (1994).
[13] G. Linti, A. Rodig, and H. Pritzkow, *Angew. Chem.* **114**, 4685 (2002); *Angew. Chem. Int. Ed.* **41**, 4503 (2002).
[14] R. Appel and I. Ruppert, *Z. Anorg. Allg. Chem.* **406**, 131 (1974).
[15] Crystallographic data (excluding structure factors) for **2** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-203233. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E-mail: deposit@ccdc.cam.ac.uk].
[16] G. M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen (1997).
[17] D. T. Cromer and J. B. Mann, *Acta Crystallogr.* **24**, 321 (1968).
[18] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.* **42**, 3175 (1965).

Nachdruck – auch auszugsweise – nur mit schriftlicher Genehmigung des Verlages gestattet
Satz und Druck: AZ Druck und Datentechnik GmbH, Kempten