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Notes

Synthesis and X-ray Crystal Structure of a Novel Zinc “Ate Complex”, $[Li(TMEDA)]_2\overline{Zn(CH_2SiMe_2SiMe_2C}H_2)_2$

Ralf Wyrwa and Hans-Otto Fröhlich*

Institut für Anorganische und Analytische Chemie der Friedrich-Schiller-Universität Jena,
August-Bebel-Strasse 2, 07743 Jena, Germany

Helmar Görls

Max-Planck-Gesellschaft, Arbeitsgruppe “CO_2-Chemie” an der Universität Jena,
Lessingstrasse 12, 07743 Jena, Germany

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*Summary: $[Li(TMEDA)]_2\overline{Zn(CH_2SiMe_2SiMe_2C}H_2)_2$ (**6**) (TMEDA = $(CH_3)_2NCH_2CH_2N(CH_3)_2$) was obtained in 70% yield by a one-pot reaction of $ClCH_2SiMe_2SiMe_2CH_2Cl$, $ZnCl_2$, and lithium sodium alloy in diethyl ether. DTA investigations of the complex showed that thermal decomposition takes place at 148 °C; the molecular structure of **6** has been established by X-ray structure analysis.*

Metallacycles are of great significance as intermediates of numerous catalytic reactions, such as the [2 + 2] cycloaddition of olefins,[1] the oligomerization of 1,2- and 1,3-dienes,[2] the isomerization of strained cyclic hydrocarbons,[3] olefin metathesis, and ring-opening metathesis polymerization (ROMP).[4,5] Especially mechanistic and structural investigations on metallacyclopentane complexes of the type $L_m\overline{M(CH_2CH_2CH_2C}H_2)$ (M = d-metal; L = neutral ligand) have considerably contributed to a better understanding of the catalytic behavior of such systems, and they also have shown the influence of the neutral ligand L on their structure, thermal stability, and reactivity.[6,7] Thus it was of interest to prepare metallacyclopentane compounds, in which exclusively butane-1,4-diyl ligands are bonded to the central atom.

Recently we have reported the synthesis of such new compounds without stabilizing neutral ligands bonded to the central atom of the type $[LiL'_x]_y\overline{M(CR_2CR_2CR_2C}R_2)_n$ (L′ = ether, amine; R = H, CH_3; M = Ni, Pd, Pt, Zn, Fe, Zr).[8] Most of these new “ate complexes” (for marking the new nonionic, mainly hydrocarbon-soluble complexes we use in this publication the term ate complex in quotation marks) are thermally very stable, and some of them are suitable synthons in organic chemistry.[9] These interesting results prompted us to synthesize complexes containing heteroatoms, for example silicon atoms, in the metallacyclopentane rings. The “ate complexes” are normally prepared by reaction of dilithium butanes with suitable d-block metal complexes. Attempts to prepare a corresponding platinum compound by use of $LiCH_2SiMe_2SiMe_2CH_2Li$ (**1**) failed, because the reaction of **1** and $(COD)PtCl_2$ (**2**) in the presence of $(CH_3)_2NCH_2CH_2N(CH_3)_2$ (TMEDA) gives the neutral complex $(COD)\overline{Pt(CH_2SiMe_2SiMe_2C}H_2)$ (**3**), whereas under the same conditions $LiCH_2CMe_2CMe_2CH_2Li$ (**4**) reacts with **2** in the presence of TMEDA to afford the “ate complex” $[Li(TMEDA)]_2\overline{Pt(CH_2CMe_2CMe_2C}H_2)_2$ (**5**).[10] This result indicates that **1** is a less reactive agent than **4** and that it would be more difficult to produce “ate complexes” from **4** and d-block metal complexes.

In this paper we report the preparation of $[Li(TMEDA)]_2\overline{Zn(CH_2SiMe_2SiMe_2C}H_2)_2$ (**6**) by using an unconventional method we recently applied to the preparation of $[Li(TMEDA)]_2\overline{Zn(CH_2CH_2CH_2CH_2C}H_2)_2$.[11] This compound is the first representative of a new type of “ate complexes” of B-group elements with two metalla-3,4-disilacyclopentane rings.

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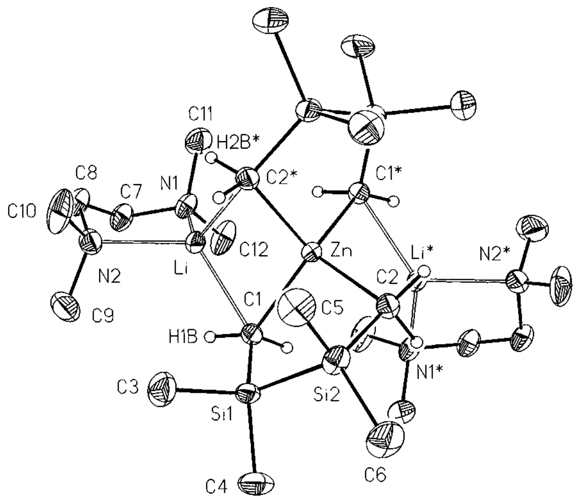

Figure 1. Molecular structure of complex **6**.

Results and Discussion

We found that a mixture of $\text{ClCH}_2\text{SiMe}_2\text{SiMe}_2\text{CH}_2\text{Cl}$[12] and ZnCl_2 (mol ratio 2.3:1) dissolved in Et_2O reactswith lithium sodium alloy (1% sodium) to give complex **6** in 70% yield (eq 1).

$$2\text{ClCH}_2\text{SiMe}_2\text{SiMe}_2\text{CH}_2\text{Cl} + \text{ZnCl}_2 + 8\text{Li} \xrightarrow[+(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]{\text{Et}_2\text{O},\ -6\text{LiCl}} [\text{Li}((\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)]_2\text{Zn}(\text{CH}_2\text{SiMe}_2\text{SiMe}_2\text{CH}_2)_2 \quad (1)$$

According to DTA studies the following decomposition temperature of the air- and moisture-sensitive compound **6** resulted: $T_{\text{dec}} = 148$ °C. The ^{1}H NMR spectrum of a C_6D_6 solution of **6** shows a broadened peak for the ZnCH_2 groups ($\delta = -1.34$ ppm) and singlets for the groups $\text{Si(CH}_3)_2$ ($\delta = 0.50$), NCH_2 ($\delta = 1.71$), and $\text{N(CH}_3)_2$ ($\delta = 1.93$). The ^{13}C NMR spectrum of **6** exhibits also four resonances at $\delta = -5.02$ ppm (br, ZnCH_2), $\delta = 2.45$ (s, $\text{Si(CH}_3)_2$), $\delta = 56.89$ (s, NCH_2), and $\delta = 46.26$ (s, $\text{N(CH}_3)_2$). The broad α-CH_2 resonances observed in both the ^{1}H and ^{13}C NMR spectra of **6** and also in the NMR spectra of the compounds $[\text{Li(TMEDA)}]_2\text{M}(\text{CH}_2\text{CMe}_2\text{CMe}_2\text{CH}_2)_2$ (M = Ni,[8a] Pt[10]) we recently described suggest the presence of Li−C or Li−H coupling or of some exchange phenomenon.[13] The ^{29}Si NMR spectrum shows a single resonance at $\delta = -24.48$ ppm.

The molecular structure of compound **6** has been determined by an X-ray diffraction study (Figure 1). Selected bond lengths and angles are given in Table 1. The molecule of **6** exhibits C_2 symmetry. It is composed of a central $\text{Zn(CH}_2)_4$ core with distorted tetrahedral geometry [C2*−Zn−Cl = 108.18(9)°, C2*−Zn−C2 = 123.96(13)°, C2*−Zn−C1* = 98.90(9)°] connected to each of the two LiTMEDA fragments through two bridging CH_2 groups (Figure 1). Both five-membered metallacyclic rings (ZnCSiSiC) show an envelope structure. The dihedral angle of the planes C1,Zn,C2/C1,Si1,Si2,C2 of each of the two metallacyclic rings amounts to 47.5(2)°. The bite angles C−Zn−C (98.90(9)°) of the two chelate ligands CSiSiC are identical and significantly wider than the corresponding C−Zn−C angles (89.8°) in the complex $[\text{Li(TMEDA)}]_2\text{Zn}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_2$[8b] we recently described. The two identical $\text{ZnLi(CH}_2)_2$ moieties of **6** are folded in a butterfly conformation [C2*−Li−Zn−C1 = 146.5(1)°]. The angles subtended at the bridging carbon atoms [Zn−C1−Li = 69.56(12)°, Zn−C2*−Li = 68.94(12)°] are considerably narrow and, together with the short Zn−Li distances [Zn−Li = 2.544(4) Å], might suggest some extent of Zn−Li bonding interaction (the sum of the covalence radii of the two elements is 2.48 Å[14]). The Zn−C distances are elongated [Zn−C2* = 2.139(2) Å, Zn−C1* = 2.205(2) Å] with respect to the neutral compound $\text{Zn(CH}_3)_2$ [Zn−C = 1.93 Å][15] and are comparable to those found in the complexes $[\text{Li(TMEDA)}]_2\text{Zn}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_2$[8b] and $[\text{Li(TMEDA)}]_2\text{Zn}(\text{CH}_2(\text{CH}_2)_3\text{CH}_2)_2$.[11]

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 6

Zn−C1	2.205(2)	Si2−C2	1.848(2)
Zn−C2	2.139(2)	Si2−C6	1.891(3)
Zn−Li	2.544(4)	Si2−C5	1.889(3)
Si1−C1	1.854(2)	Li−C1	2.255(4)
Si1−C3	1.884(3)	Li−C2*	2.347(5)
Si1−C4	1.889(3)	Si1−Si2	2.345(1)
Li−H(2B*)	1.964(8)	Li−N1	2.172(5)
Li−H(1B)	2.055(8)	Li−N2	2.168(4)
C1*−Zn−C1	120.43(12)	C2*−Zn−Li*	149.18(11)
C2*−Zn−C2	123.96(13)	C1*−Zn−Li*	56.14(10)
C2*−Zn−C1	108.18(9)	C2*−Zn−Li	59.39(11)
C2*−Zn−C1*	98.90(9)	C1*−Zn−Li	100.80(11)
C1−Si1−C3	111.18(13)	C3−Si1−C4	105.3(2)
C1−Si1−C4	114.51(14)	C2−Si2−C6	115.47(14)
C2−Si2−C5	111.74(14)	C3−Si1−Si2	108.40(12)
C1−Si1−Si2	105.62(8)	C2−Si2−Si1	102.73(8)
C4−Si1−Si2	111.76(12)	C6−Si2−Si1	113.65(14)
C5−Si2−Si1	108.48(1)	Zn−C1−Li	69.56(12)
Li*−Zn−Li	136.3(2)	Si1−C1−Zn	104.05(11)
Zn−C2*−Li	68.94(12)	Si2−C2−Zn	100.92(11)
H(1A)−C1−H(1B)	105.6(2)	Si1−C1−H(1A)	106.9(2)
Si1−C1−H(1B)	110.4(2)	Zn−C1−H(1A)	97.1(2)
Zn−C1−H(1B)	130.3(2)	Li−H(1B)−C1	87.6(2)
Li−H(2B*)−C2*	93.4(1)	C2*−Li−Zn−C1	146.5(1)

The lithium atoms of **6** have a distorted tetrahedral geometry with the coordination tetrahedron defined by two carbon and two TMEDA nitrogen atoms [Li−C2* = 2.347(5) Å, Li−C1 = 2.255(4) Å, Li−N1 = 2.172(5) Å, Li−N2 = 2.168(4) Å]. The Li−C bond distances are comparable with those found in the tetrameric $(\text{LiCH}_3)_4$ (2.31 and 2.36 Å).[16]

The silicon and the two hydrogens of each bridging methylene group define a distorted tetrahedron centered on carbon with the fourth position occupied by zinc.

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Each lithium atom is placed side-on and perpendicularly with respect to one of the two C−H bonds of each of the two bridging CH_2 groups [Li−H(2B*)−C2* = 93.4(1)°, Li−H(1B)−C1 = 87.6(2)°], forming considerably short Li···H distances [Li−H(2B*) = 1.964(8) Å, Li−H(1B) = 2.055(8) Å], typical of Li−H agostic interactions. Comparable Li−H agostic interactions have been observed in $[Li(TMEDA)_2]_2CrMe_4$.[17]

Experimental Section

General Considerations. All operations were carried out in an inert atmosphere (argon) with standard Schlenk techniques. Solvents were carefully dried and distilled from sodium/benzophenone prior to use. The starting compound 1,2-bis(chloromethyl)-1,1,2,2-tetramethyldisilane was prepared according to literature procedures.[12] ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on Bruker AC-200 F or AMX 400 spectrometers.

$[Li(TMEDA)]_2\overline{Zn(CH_2SiMe_2SiMe_2C}H_2)_2$ (6). A solution of 3.09 g (22.7 mmol) of $ZnCl_2$ and 11.4 g (53 mmol) of 1,2-bis(chloromethyl)-1,1,2,2-tetramethylsilane in 50 mL of diethyl ether was added dropwise at 0 °C to a stirred suspension of 4 g (571 mmol) of finely divided lithium sodium alloy (1% sodium). After the reaction started, the remaining part of the $ZnCl_2/ClCH_2SiMe_2SiMe_2CH_2Cl$ solution was added at −20 °C. The reaction mixture was stirred for 3 h and than filtered. Now 5 mL of $(CH_3)_2NCH_2CH_2N(CH_3)_2$ was added to the solution, and by evaporation under vacuum half of the diethyl ether was removed. After addition of 30 mL of hexane the mixture was cooled to −20 °C to give a crystalline colorless solid, which was characterized as **6** (9.5 g, 70% yield). Anal. Calcd for $C_{24}H_{64}Li_2N_4Si_4Zn$ (**6**): Li, 2.31; Zn, 10.89. Found: Li, 2.3; Zn, 10.76. ^1H NMR (C_6D_6): δ −1.34 (br, 8 H, $ZnCH_2$), 0.50 (s, 24 H, $Si(CH_3)_2$), 1.71 (s, 8 H, NCH_2), 1.93 (s, 24 H, $N(CH_3)_2$). ^{13}C NMR (C_6D_6): δ −5.02 (br, $ZnCH_2$), 2.45 (s, $Si(CH_3)_2$), 46.26 (s, $N(CH_3)_2$), 56.89 (s, NCH_2).

X-ray Crystallographic Study of 6. Diffraction data of a colorless cuboid single crystal of **6** were collected at 183(2) K on a CAD4 diffractometer using Mo Kα radiation (λ = 0.710 73 Å, graphite monochromator). The structure was solved by direct methods (Sheldrick, G. M. SHELXS-86, Göttingen, Germany, 1986) and refined by full-matrix least-square techniques against F^2 (Sheldrick, G. M. SHELXL-93, Göttingen, Germany, 1993): structural representation (Sheldrick, G. M. SHELXTL/PC, Siemens Analytical X-ray Instruments, Inc., Madison WI, 1992); molecular weight 600.41 g mol^{-1}; crystal system orthorhombic; space group *Pbcn* (No. 60); $a = 12.069(2)$ Å, $b = 14.981(3)$ Å, $c = 20.890(4)$ Å, $V = 3777.0(12)$ $Å^3$, crystal dimensions 0.40 × 0.40 × 0.38 mm^3, $D_c = 1.06$ g cm^{-3}, $\mu = 7.94$ cm^{-1}, $\theta_{max} = 29.96°$; number of collected data 5484; number of observed data with $I > 2\sigma(I)$ 3876; hydrogen atoms included at all calculated positions; non-hydrogen atoms refined anisotropically; number of variables 287; $R_1 = 0.0390$, $wR_2 = 0.0921$; residual electron density 0.341 e $Å^{-3}$; goodness of fit = 1.236.

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Supporting Information Available: Tables of complete positional and thermal parameters, anisotropic thermal parameters, and bond distances and angles and ORTEP structures (8 pages). Ordering information is given on any current masthead page.

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