X-ray Crystal Structure Analysis of Bis[(dimethylisopropoxysilyl)methyl]zinc, a Diorganozinc Compound with an Oxygen-Coordinated Trigonal-Planar Zinc Atom in the Solid State

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Abstract: The structure of bis[(dimethylisopropoxysilyl)methyl]zinc (**1**) has been determined by X-ray diffraction analysis. **1** crystallizes in orthorhombic space group $P2_12_12_1$ (No. 19) with four molecules in a unit cell of dimensions $a = 8.071(2)$, $b = 11.672(2)$, and $c = 20.342(1)$ Å. The structure, which was refined to $R = 0.054$ ($R_w = 0.055$) for 2737 observed reflections and 135 variables, is characterized by an intermolecular coordination of an oxygen atom (O1') to the Zn atom, leading to a helical polymer. The Zn is coordinated in a trigonal-planar fashion and lies in a chiral plane with C11–Zn–C21, O1'–Zn–C11, and O1'–Zn–C21 angles of 152.3(3), 104.2(2), and 103.5(2)°, respectively, Zn–C bond distances of 1.953(7) and 1.988(6) Å, and a Zn–O1' bond distance of 2.252(4) Å. Semiempirical and ab initio calculations show that the bending of the C–Zn–C linkage is due to the coordination of the zinc atom by the oxygen atom. Conformations around the C11–Si1 and C21–Si2 bonds are antiperiplanar (O1–Si1–C11–Zn, 176.2-(3)°) and synperiplanar (O2–Si2–C21–Zn, 21.4(4)°), respectively, resulting in an intramolecular Zn–O2 distance of only 2.984(6) Å. **1** is the first example of a structurally characterized diorganozinc compound coordinated by one heteroatom donor in a trigonal-planar fashion in the solid state.

Introduction

Recent years have witnessed a renaissance of diorganozinc compounds. The main reason therefor is, besides the availability of highly functionalized dialkylzinc reagents,[1] their advantageous utilization instead of lithium or magnesium organyls in enantioselective addition to aldehydes[2] as well as in transition-metal-catalyzed cross-coupling.[3] Of crucial importance for the reactivity of diorganozinc reagents in some cases seems to be their weak and thus transient coordination by oxygen or nitrogen donors. For example, in enantioselective addition to aldehydes, which is catalyzed by chiral zinc[2a,b] or titanium[2c–e] alkoxides, bimetallic complexes between chiral zinc alkoxides and the diorganozinc reagents having a tricoordinate zinc atom with an

oxygen donor are proposed as reactive species.[4] Structurally defined complexes of diorganozinc compounds feature zinc atoms coordinated either by two oxygen,[5e–i,m,n,6b] two nitrogen,[5a–c,j,k] two sulfur,[5c] or two phosphorus[5d] donors in a pseudotetrahedral fashion.[7,8] Although complexes having a tricoordinate zinc atom such as Me$_2$Zn·OMe$_2$[9a] and Me$_2$Zn·NMe$_3$[9b] have been known for a long time,[10] structural information on the coordination of

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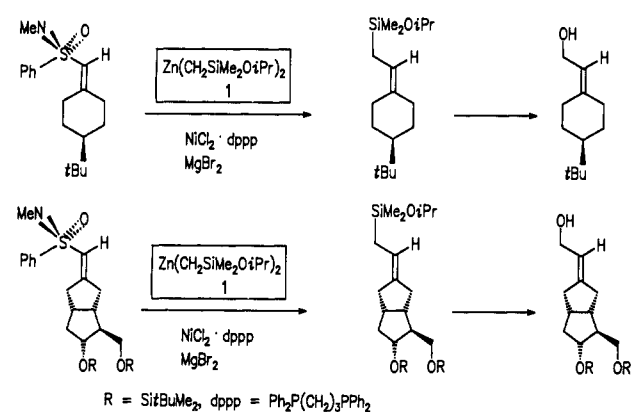
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Scheme I

R = Si*t*BuMe₂, dppp = Ph₂P(CH₂)₃PPh₂

the zinc atom of a diorganozinc compound by one heteroatom donor in the solid state or in the gas phase as revealed by, for example, X-ray crystal structure analysis or electron diffraction is as yet to the best of our knowledge not available.

Recently we described the use of bis[(dimethylisopropoxysilyl)-methyl]zinc (1) in nickel-catalyzed cross-coupling reactions with alkenylsulfoximines, yielding allylic silanes with complete retention of configuration (Scheme I).[3e,f] Subsequent oxidative cleavage of the allylic carbon–silicon bond of the silanes gave the allylic alcohols.

In view of the scarcity of structural information concerning donor complexes of diorganozinc compounds with a tricoordinate zinc atom,[10] the crystal structure of 1 warranted determination because of the possible existence of such an oxygen–zinc coordination in an intermolecular fashion. Since the oxygen atom in 1 is located in a γ-position, internal mono- or dicoordination as observed in diorganozinc compounds with donor atoms in a δ- or ε-position[5c,d,6b,10] was deemed to be less likely,[8c] albeit not impossible.[5b] Furthermore, X-ray crystal structure analyses of α-heteroatom-substituted dialkylzinc compounds are rare. The only examples known are the iodo derivative (1*S*,2*R*,3*S*)-dimethoxynorbornane-*O,O'*)bis(iodomethyl)zinc,[5i,n] and the silyl derivatives bis[tris(trimethylsilyl)methyl]zinc,[8d] bis[bis(trimethylsilyl)(methoxy-, hydroxy-, or (trifluoroacetato)dimethylsilyl)-methyl]zinc,[8c,e] and bis[2-(bis(trimethylsilyl)methyl)pyridyl-*C,N*]zinc,[5b] which all have trisubstituted α-carbon atoms.

Experimental Section

All manipulations were performed in an atmosphere of dry and oxygen-free argon or nitrogen, with normal Schlenk and syringe techniques in flame-dried glassware. Tetrahydrofuran and *n*-hexane were destilled from sodium/benzophenone, and deuteriochloroform was filtered through activated aluminum oxide prior to use. ¹H and ¹³C NMR spectra were recorded on a Bruker AM 400 instrument with Me₄Si as an internal standard.

Synthesis and Recrystallization of Bis[(dimethylisopropoxysilyl)methyl]-zinc (1). [(Dimethylisopropoxysilyl)methyl]magnesium chloride was prepared from magnesium (1.02 g, 42 mmol) and freshly destilled, commercially available (Aldrich) (chloromethyl)dimethylisopropoxysilane (7.20 mL, 40 mmol) in tetrahydrofuran (80 mL) in 90% yield.[11] To a magnetically stirred solution of [(dimethylisopropoxysilyl)methyl]-magnesium chloride (36 mmol) in tetrahydrofuran (80 mL) was added dropwise a solution of freshly melted (10⁻⁴ Torr) zinc chloride (2.45 g,

18 mmol) in tetrahydrofuran (40 mL) at room temperature. After the solution was stirred for 12 h, the tetrahydrofuran (80 mL) was removed through distillation at reduced pressure (1 Torr) and the residue diluted with *n*-hexane (40 mL). The resulting suspension was filtered through a filter funnel with a glass frit, and the filtrate was concentrated under high vacuum. The residue was distilled to give 1 (3.39 g, 52%) as a colorless oil, bp 78–80 °C/1.1 Torr, which crystallized in the freezer, mp 29–30 °C. ¹H NMR (400 MHz, CDCl₃): δ −0.41 (s, -ZnCH₂-, 2H), 0.10 (s, -Si*Me₂*O*i*Pr, 6H), 1.11 (d, *J* = 6.0 Hz, -OCH*Me₂*, 6H), 3.95 (sept, *J* = 6.0 Hz, -OC*H*Me₂, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 1.87 (-ZnCH₂-), 1.98 (-Si*Me₂*O*i*Pr), 26.08 (-OCH*Me₂*), 64.80 (-O*C*H-Me₂). *n*-Hexane (7 mL) was added to the crystalline 1 (3.0 g) at 0 °C. By gentle shaking of the suspension, the crystals were dissolved until only a few remained, and the thus formed solution was kept at −20 °C. Within several days 1 crystallized as fine colorless needles which turned into larger needles suitable for X-ray analysis within 2 weeks. At −15 °C the mother liquid was removed by syringe and the crystals were dried in vacuum (0.1 Torr) at −15 °C for 1 min.

Structure Determination and Refinement of 1. A single crystal suitable for analysis was selected under a stream of argon with the aid of a thin glass rod tipped with high-vacuum grease. This crystal was transferred to an Enraf-Nonius CAD4 four-circle diffractometer under a stream of argon and mounted on top of a glass capillary tipped with high-vacuum grease in a stream of cold nitrogen (−10 °C). Cell constants were determined from 25 reflections in the range 15.05 ≤ θ ≤ 22.98°. The structure was solved by direct methods (SHELXS-86[12]), while the refinement was performed employing the facilities of the XTAL3.0 program package.[13] The data were corrected for Lorentz and polarization effects. An initial solution was obtained from a basis set collected with copper radiation. Although the data proved to be insufficient for a clean refinement of the structure, they provided a starting set of structural parameters for further refinement on basis of the Mo Kα intensities. Large displacement parameters of the atoms C24–C26 probably reveal disorder of this group. Since this disorder could not be resolved, atoms C24–C26 were treated as a rigid group and were refined isotropically with a common displacement parameter. Disorder in this part of the molecule might also affect the geometry of the adjacent O–Si moiety and thus account for the remarkable difference between the Si2–O2 and Si1–O1 bond lengths. In addition, all hydrogen atoms were calculated in idealized positions and kept fixed in the final full-matrix least-squares refinement process. All other structural parameters were refined anisotropically without constraints. Quantum chemical calculations were performed employing the MOPAC and GAMESS sets of routines.[14] All calculations were carried out on a local VAX 3100 workstation. Crystal data and technical details of the structure determination are listed in Table I, while selected interatomic distances and bond angles are compiled in Table II, and fractional atomic coordinates and equivalent isotropic displacement parameters are listed in Table III. Tables of final atomic positional parameters, anisotropic thermal parameters, bond lengths and angles, and torsion angles and a listing of observed and calculated structure factors for 1 are available as supplementary material. The structure of 1 in the solid state is plotted in Figure 1, while Figure 2 shows the monomeric unit and Figure 3 the coordination geometry as well as the shielding of the zinc atom in the crystal.

Results and Discussion

The solid-state structure of 1 (Figures 1 and 2) is distinctly different from that expected for the free molecule resulting from a semiempirical MNDO[15] calculation (vide infra). In addition

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Structure of Bis[(dimethylisopropoxysilyl)methyl]zinc

J. Am. Chem. Soc., Vol. 115, No. 16, 1993 7217

Table I. Crystal Data and Experimental Details of the Structure Determination of **1**

Crystal Data	
formula	$C_{12}H_{30}O_2Si_2Zn$
M_r	327.91
crystal system	orthorhombic
space group	$P2_12_12_1$ (No. 19)
Z	4
a, b, c, Å	8.071(2), 11.672(2), 20.342(1)
V, Å^3	1916.3
D_{calc}, g cm^{-1}	1.137
$F(000)$	704
μ, Mo Kα, cm^{-1}	14.27
Data Collection	
T, K	263
radiation, monochromator	Mo Kα (0.710 69 Å), graphite
scan mode	$\omega/2\theta$
horizontal aperture	$2.4 + 1.05\ (\tan(\theta))$
scan range	$1.0 + 0.35\ (\tan(\theta))$
ref rflcns	$-3,5,3; 2,-7,8; -5,-1,-5$
$\sin(\theta)/\lambda_{max}$	0.704
data set	$0 \le h \le 11, 0 \le k \le 16, 0 \le l \le 28$
total data	3301
total unique data	3172
observed data	$2737(I > 2\sigma(I))$
Refinement	
refined parameters	135
$R, R_w{}^a$	0.054, 0.055
U_H, Å^2	0.08
extinction, r^*	1.07×10^4
final shift/error	<0.0008
res. elect. density, e Å^{-3}	1.2

$^a\ R = (\sum\|F_o\| - \|F_c\|)/\sum\|F_o\|;\ R_w = (\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2)^{0.5};\ w = 1/\sigma^2(F_o).$

Table II. Selected Bond Distances (Å) and Angles (deg) with esds in Parentheses for **1**

	Bond Distances		
Zn–C21	1.953(7)	Si2–C23	1.84(1)
Zn–C11	1.988(6)	O1–C14	1.456(8)
Si1–O1	1.675(4)	O2–C24	1.43(1)
Si1–C11	1.811(6)	C14–C16	1.46(1)
Si1–C12	1.830(8)	C14–C15	1.53(1)
Si1–C13	1.872(7)	Si2–O2	1.623(6)
Si2–C21	1.817(7)	Si2–C22	1.815(9)
C24–C26	1.44(2)	C24–C25	1.45(2)
Zn–O1′	2.252(4)	Zn–O2	2.984(6)
	Bond Angles		
C21–Zn–C11	152.3(3)	O1–Si1–C12	106.6(3)
O1–Si1–C11	108.9(3)	C11–Si1–C12	112.2(3)
O1–Si1–C13	107.6(3)	C12–Si1–C13	109.9(4)
C11–Si1–C13	111.4(3)	O2–Si2–C21	105.0(3)
O2–Si2–C22	108.8(4)	O2–Si2–C23	109.1(4)
C22–Si2–C21	113.4(4)	C22–Si2–C23	105.5(5)
C21–Si2–C23	114.9(5)	C14–O1–Si1	120.7(4)
C24–O2–Si2	123.1(6)	Si1–C11–Zn	111.1(3)
O1–C14–C16	110.7(6)	O1–C14–C15	106.9(5)
C16–C14–C15	114.4(6)	Si2–C21–Zn	110.0(4)
O2–C24–C26	106(1)	O2–C24–C25	110(1)
C26–C24–C25	107(1)	C11–Zn–O1′	104.2(2)
C21–Zn–O1′	103.5(2)		

Table III. Fractional Atomic Coordinates, Equivalent Isotropic Displacement Parameters ($U_{eq}{}^a$), and Their esds in Parentheses for **1**

atom	x/a	y/b	z/c	U_{eq}/Å^2
Zn	−0.874 56(9)	−0.336 95(6)	−0.566 34(4)	0.0428(2)
Si1	−0.6436(2)	−0.1219(1)	−0.556 31(9)	0.0444(5)
Si2	−0.8807(3)	−0.4578(2)	−0.701 39(9)	0.0584(7)
O1	−0.4997(5)	−0.0553(3)	−0.5110(2)	0.042(1)
O2	−0.7421(7)	−0.5185(5)	−0.6553(2)	0.086(2)
C11	−0.6933(7)	−0.2578(5)	−0.5182(3)	0.047(2)
C12	−0.555(1)	−0.1397(7)	−0.6385(4)	0.085(3)
C13	−0.8293(8)	−0.0260(6)	−0.5604(4)	0.078(3)
C14	−0.4495(8)	0.0616(6)	−0.5262(4)	0.052(2)
C15	−0.2628(9)	0.0592(7)	−0.5381(4)	0.082(4)
C16	−0.502(1)	0.1402(5)	−0.4742(4)	0.080(3)
C21	−1.0020(9)	−0.3694(5)	−0.6458(3)	0.056(2)
C22	−0.776(1)	−0.3763(7)	−0.7651(4)	0.114(4)
C23	−0.999(1)	−0.5690(9)	−0.7449(6)	0.133(5)
C24	−0.617(2)	−0.593(1)	−0.6804(6)	0.185(3)
C25	−0.645(3)	−0.708(1)	−0.6566(7)	0.185(3)
C26	−0.464(2)	−0.555(2)	−0.6521(7)	0.185(3)

$^a\ U_{eq} = {}^1/_3 \sum_i \sum_j U_{ij} a_i{}^* a_j{}^* \mathbf{a}_i \mathbf{a}_j.$
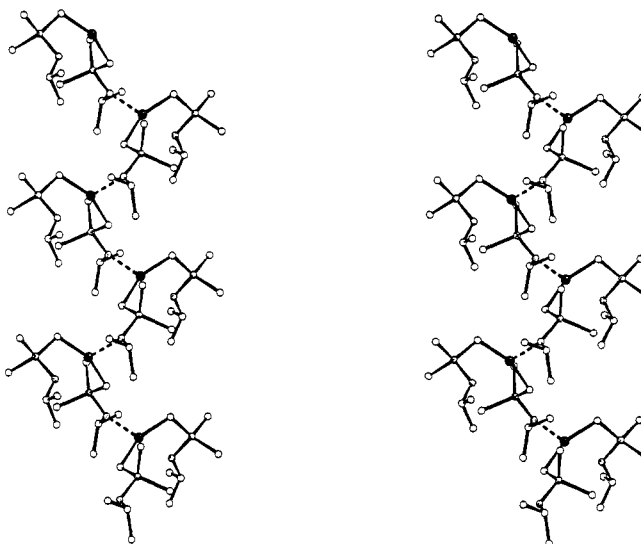

Figure 1. SCHAKAL drawing (stereoview) of the molecular structure of **1** in the crystal. Hydrogen atoms have been omitted for clarity.
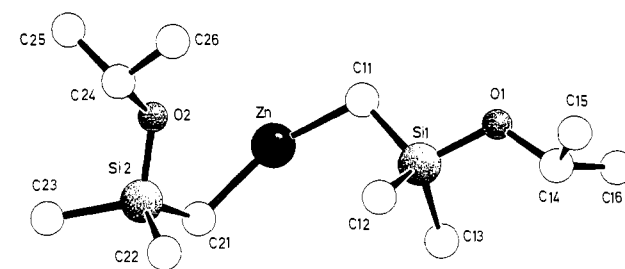
Figure 2. SCHAKAL drawing of the molecular structure of the monomeric unit of **1** in the crystal including the adopted numbering. Hydrogen atoms have been omitted for clarity.

to its two covalently bonded carbon atoms, the Zn atom is coordinated by an additional oxygen atom (O1′) belonging to a neighboring molecule. As a result, the C–Zn–C linkage is significantly bent, enclosing a bond angle of 152.3(3)°, and the molecules are arranged in helices perpendicular to the *bc* plane (Figure 1). In respect to the bending in **1**, it is interesting to note that in, for example, (diethyl[*N,N'*-ethylenebis(salicylideneaminato)-*O,O,O',O',N,N'*]nickel)zinc,[5e] where the zinc atom is coordinated by two oxygen atoms, the observed C–Zn–C angle of 147.9° is very similar. The zinc atom of **1** is coordinated in a trigonal-planar fashion, as revealed by the sum (360°) of its bond angles (Table II) and lies in a chiral plane (C11–Zn–C21–Si2, 72.9(6); C21–Zn–C11–Si1, 27.2(7); and O2–Si2–C21–Zn,

21.4(4)°) (Figures 2 and 3). In the crystal of **1** investigated, the helices and the chiral planes, respectively, were of the same configuration. According to a Hamilton test,[17,18] the absolute configuration shown in Figure 1 is most likely correct. With 1.953(7) and 1.988(6) Å, the zinc-carbon bond distances fall into the range usually found for organozinc compounds.[5,6,8] The Zn–O1′ bond distance of 2.252(4) Å is slightly shorter than the average zinc-oxygen bond length in some diphenylzinc-crown ether adducts (2.292 Å),[5m] while it clearly exceeds the Zn–O distance in tetrameric methylzinc methoxide (2.039(14)–2.114(15) Å).[19]
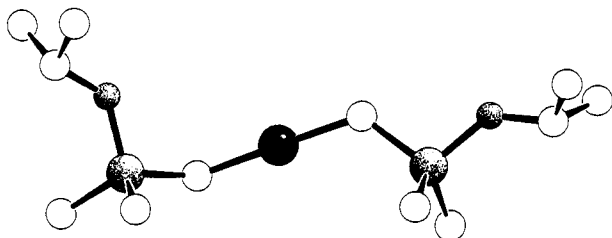
(17) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.
(18) Rogers, D. *Acta Crystallogr.* **1981**, *A37*, 734.
(19) Shearer, H. M. M.; Spencer, C. B. *Acta Crystallogr.* **1980**, *B36*, 2046.
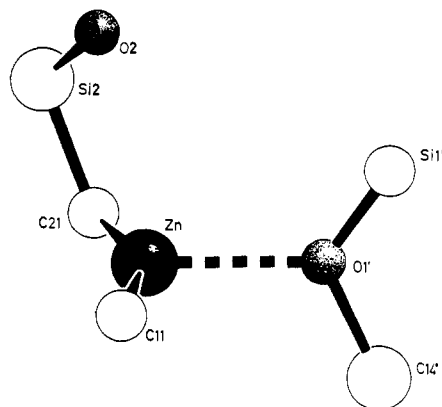
Figure 3. SCHAKAL drawing of the structure (in part) of **1** in the crystal showing the coordination geometry and the shielding of the zinc atom.

Figure 4. MNDO-optimized structure of the monomeric unit of **1**. Hydrogen atoms have been omitted for clarity.

Moreover, it is significantly longer than the zinc-oxygen bonds in bis(fluorenyl)bis(tetrahydrofuran)zinc (2.114(5)–2.095(4) Å)[5h] and those in bis(tetrahydrofuran)bis(pentafluorophenyl)-zinc (2.093(2)–2.113(3) Å),[5g] while it is shorter than the average Zn–O bond distance reported for (diethyl[*N,N'*-ethylenebis-(salicylideneaminato)-*O,O,O',O',N,N'*]nickel)zinc (2.321(6) Å).[5e] Whereas the conformation around the C11–Si1 bond is anti (O1–Si1–C11–Zn, 176.2(3)°), that around the C21–Si2 bond is approximately syn (O2–Si2–C21–Zn, 21.4(4)°). This results, in the latter case, in an approach of O2 to the zinc atom as close as 2.984(6) Å and in a shielding of the zinc atom (Figure 3). This distance is approximately equal to the sum of the van der Waals radius of oxygen and the radius of Zn in the nonbonded state.[20] Thus Zn and O2 should be considered as being in contact rather than being engaged in a bond. The reason for this C21–Si2 conformation is not apparent yet. A seemingly related situation is found in bis[bis(trimethylsilyl)(methoxydimethylsilyl)methyl]-zinc,[8c] where the methoxy groups are also bent toward the metal atom, resulting in an interatomic distance of 2.932(4) Å. The C–Zn–C linkage there, however, is linear, and the orientation of the methoxy groups may reflect minimization of steric strain in this crowded molecule.[8c] In monomeric diethylzinc–18-crown-6, which is a rotaxane with a linear C–Zn–C linkage and a zinc atom surrounded by the six crown oxygens, the zinc-oxygen distances are in the range of 2.837(3)–2.890(3) Å.[5f]

For unsolvated monomeric dialkylzinc compounds, a linear structure is preferred[5e,6a,8c–e] generally.[7] To substantiate the assumption that bending of the C–Zn–C linkage in **1** is indeed due to the presence of the third ligand, we performed quantum chemical calculations with the semiempirical MNDO method.[15] Starting from the experimentally found solid-state structure of **1**, we modeled the neighboring unit by a water molecule and optimized all structural parameters. In this way a C–Zn–C angle of 143.7° for **1·H₂O** was obtained, while reoptimization, in absence of the coordinating water molecule under otherwise identical conditions, resulted in an angle of 175.6° in **1** (Figure 4).

Although at a highly precise level interatomic distances in the solid state and calculated bond length are not directly comparable

(20) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

to each other unless they are brought to a common basis, a rough comparison is permissible. Thus, calculated Zn–C bond lengths in water-complexed **1·H₂O** (average value 1.923 Å) are not too different from the experimentally determined solid-state data, and a similar agreement is obtained between the observed (2.252-(4) Å) and calculated (2.105 Å) Zn–O' distance. Removing the complexing water molecule results in slight reduction of the Zn–C bond lengths, yielding an average value of 1.890 Å. This result is quite similar to the corresponding MNDO values for some simple diorganozinc compounds (Me_2Zn, 1.89 Å; Et_2Zn, 1.91 Å; n-Pr_2Zn, 1.91 Å[15c]). From the calculated heats of formation for **1** (–202.29 kcal/mol), **1·H₂O** (–265.79 kcal/mol), and H_2O (–60.94 kcal/mol), we calculated a value of –2.56 kcal/mol for the heat of complexation. This surprisingly low value is in keeping with the results of Dekker et al.,[5c] who found that even Me_2-$Zn·NMe_3$, a complex with a strong ligand, completely dissociates in the gas phase. The authors conclude that the energies of complexation are in a range where they might easily be outbalanced by the increase of entropy gained upon dissociation. In the case of internal complexation, however, low energies may suffice to maintain a bond between the donor ligand and the metal.[5c] To further substantiate the influence of a complexing oxygen atom on the geometry of the C–Zn–C segment, we performed ab initio calculations on Me_2Zn[5k,6a,21] and $Me_2Zn·H_2O$ employing the 3-21G[22] and a triple-ζ valence (tzv)[23] basis set. At the 3-21G level we obtained a C–Zn–C bond angle of 142.3° and a C–Zn bond length of 1.982 Å for $Me_2Zn·H_2O$ (E_{tot} = –1923.574 21 au), while the Zn–O' distance is 1.992 Å. The corresponding C–Zn distance in free dimethyl zinc with a linear C–Zn–C moiety (E_{tot} = –1847.943 13 au) is 1.944 Å. Geometry optimization with the tzv basis set results in a C–Zn–C angle of 160.6° for $Me_2Zn·H_2O$ (E_{tot} = –1933.009 76 au), and the lengths of the Zn–C and Zn–O' bonds are 2.008 and 2.262 Å, respectively. Employing the same basis set, we calculated a C–Zn bond distance of 1.982 Å for linear uncomplexed Me_2Zn (E_{tot} = –1856.972 45 au).

Conclusion

The X-ray crystal structure analysis of **1** revealed the yet unobserved intermolecular coordination of the zinc atom of a diorganozinc compound in a planar-trigonal fashion by a heteroatom donor in the solid state. Semiempirical and ab initio calculations support the notion that bending of the C–Zn–C linkage is due to the coordination of the zinc atom by the oxygen atom. Semiempirical calculations on **1** and **1·H₂O** indicate that this coordination in solid **1** should be regarded as weak, which is in accordance with earlier observations on donor complexes of diorganozinc compounds. One might speculate that such a weak Zn–O interaction in combination with a flat potential energy surface for distortions of the coordination geometry of the zinc atom is a key factor for the asymmetric induction observed in the addition of diorganozinc reagents to aldehydes catalyzed by chiral alkoxides. The structure of **1** in the solid state may serve as a model for the intermediates formed thereby.

Supplementary Material Available: Structural data and diagrams; tables of final atomic positional parameters, anisotropic thermal parameters, bond lengths and angles, and torsion angles (18 pages); listing of observed and calculated structural factors for **1** (13 pages). Ordering information is given on any current masthead page.

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(23) This basis set is a modified version of the one described in Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033. For further details, see: *GAMESS User's Guide* for the *GAMESS* version described in ref 14b.