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Complexation of diphenylzinc with simple ethers. Crystal structures of the complexes $Ph_2Zn \cdot$ glyme and $Ph_2Zn \cdot$ diglyme

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Abstract

The complexation behavior of diphenylzinc with a series of mono-, di- and tri-coordinating ethers has been investigated. Two stable crystalline 1:1 adducts, with ethyleneglycol dimethyl ether (glyme) (**1**) and diethyleneglycol dimethyl ether (diglyme) (**2**) were isolated and characterized by an X-ray diffraction study. Complex **1** has a normal tetra-coordinated zinc atom; **2** represents the first example of a complex penta-coordinated diorganozinc compound, and has a rather unusual geometry.

Introduction

The ability of diorganozinc compounds to form complexes with ethers has been known for more than a century [1]. As early as 1859 it was discovered that the synthesis of dimethylzinc from methyl iodide and zinc is accelerated by the addition of dimethyl ether or diethyl ether [2]. Distillation of pure dimethylzinc from a Me_2Zn/R_2O mixture proved to be impossible, in spite of a boiling point difference of 70°C in the case of dimethyl ether. Later, it was established that a dimethylzinc/dimethyl ether complex distils as such; though it is partially dissociated in the vapour phase [3]. Although coordination and association of organozinc compounds has attracted attention recently, many structural data are still lacking, in particular data for arylzinc compounds are especially scarce. The first structural data for an arylzinc compound were reported only recently, when we determined the crystal structure of solvent-free diphenylzinc, which is dimeric with two

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unsymmetrically bridging μ-phenyl groups [4]; we will present below the first structural data for an ether-complexed diphenylzinc.

Diorganozinc compounds generally have a low tendency to undergo association or complexation [1]. In the monomeric and unsolvated state, the two organic groups are usually bonded to the central *sp*-hybridized zinc atom in a linear fashion. Owing to the polarity of the Zn–C bond, the metal atom with its partially positive charge is able to form additional bonds to polarizable molecules such as ethers. As a consequence, rehybridization of the zinc atom must occur: the C–Zn–C bond angle decreases as the hybridization changes towards sp^2 and possibly even sp^3. The required rehybridization energy is furnished by the development of the coordinative interactions; they are mainly electrostatic of nature (polarization of the ether-oxygens) as the *d*-shell is filled ($3d^{10}$) and thus low lying orbitals for covalent coordination are not available.

The complexation of dimethylzinc may serve as an illustration of the general behaviour of diorganozinc compounds. Pure dimethylzinc is a colourless, volatile liquid ([1]: m.p. −29°C, b.p. 46°C); it is apparently monomeric in the solid, liquid and gaseous states. Being both thermodynamically and kinetically unstable towards hydrolysis and oxidation, it readily reacts when exposed to the air and is pyrophoric. When it is mixed with electron-donating solvents (ethers), exothermic complexation occurs. In most cases the complexes are liquids of undefined stoichiometry that dissociate upon distillation. It has been found that cyclic ethers (oxirane, oxetane, THF and tetrahydropyran) show an enhanced coordinating ability due to their lower steric requirements and their conformational freedom when compared with 'normal' ethers such as diethyl ether [3]. Preferred ligand: dimethylzinc stoichiometries of 1:1 and 2:1 were observed, suggesting tri- and tetra-coordinate zinc, respectively. The tetrahedral configuration, with two coordinating oxygen atoms, probably presents a state of coordinative saturation. The low melting and boiling points of the adducts prevented a detailed study of their coordination geometries by means of crystal structure determinations.

Compared with the mono-chelating ethers, di-chelating ethers tend to coordinate more strongly to dimethylzinc [5]. The complexes with 1,4-dioxane and 1,4-thioxane are crystalline solids (m.p. 66 and 23°C, respectively), with a well defined 1:1 stoichiometry. This may be attributed to a combination of entropically favourable di-chelation and the relatively low flexibility of the ligand (preorganization). In the case of 1,4-thioxane, the softness of the sulfur atom also gives a better match with the relatively soft character of zinc. More flexible di-chelates, like 1,2-dimethoxyethane (glyme) and 1,3-dimethoxypropane gave unstable liquid adducts with a 2:1 stoichiometry.

The results of thermochemical study [6] were consistent with the features mentioned above. The enthalpy of mixing dimethylzinc in a 1:1 ratio in benzene solution with a series of ligands was determined. The heats of reaction were found to increase in the sequence: diethyl ether < glyme < diglyme < 1,4-dioxane, with values of −7.95, −16.7, −26.4 and −40.6 kJ/mol, respectively. During the reaction of dimethylzinc with 1,4-dioxane a solid adduct separated from the solution. The 'softer' nitrogen-containing ligands tend to give even more exothermic heats of reaction, as can be seen from the examples of HMPT (a mixed N/O ligand; 57.7 kJ/mol), 2,2′-bipyridine (72.8 kJ/mol) and pyridine (2/1 ratio, 73.2 kJ/mol).

Table 1

The intramolecular coordination in X–[(CH$_2$)$_n$]$_2$Zn

n	X	Method [a]	Bond lengths (Å)		Bond angles (deg)		Reference
3	OMe	GED	Zn–C	1.974(4)	C–Zn–C	175.00(20)	14
			Zn–O	2.37(3)	O–Zn–O	111.00(20)	
4	OMe	GED	Zn–C	1.984(6)	C–Zn–C	158.00(13)	14
			Zn–O	2.38(5)	O–Zn–O	92.00(10)	
3	SMe	GED	Zn–C	1.966(6)	C–Zn–C	163.00(15)	12
			Zn–S	2.732(12)	S–Zn–S	173.00(12)	
3	N(Me)$_2$	GED	Zn–C	1.991(5)	C–Zn–C	152.00(8)	12
			Zn–N	2.392(15)	N–Zn–N	117.00(4)	
3	N(Me)$_2$	X-ray	Zn–C	1.984(5)	C–Zn–C	156.4(2)	12
			Zn–N	2.307(4)	N–Zn–N	109.7(1)	
3	P(Ph)$_2$	X-ray	Zn–C	2.00(1)	C–Zn–C	147.1(4)	11
				2.02(1)	P–Zn–P	105.72(9)	
			Zn–P	2.572(3)			
				2.598(3)			

[a] GED: gas phase electron diffraction; X-ray: X-ray crystal structure determination.

Owing to the low melting points and ease of dissociation of intermolecular diorganozinc-ether complexes, there have been few structural characterizations. Recently, the crystal structure of the bis(9-fluorenyl)zinc · bis(tetrahydrofuran) complex was published [7]. This compound can be regarded as representative of the normal pseudo-tetrahedral, saturated coordination in a diorganozinc–ether complex. The zinc atom in this complex is surrounded by the η^1-bonded fluorenyl ligands (C–Zn 2.041(5) and 2.053(6) Å, C–Zn–C 117.6(2)° and two THF molecules (Zn–O 2.114(5) and 2.095(4) Å, O–Zn–O 89.3(2)°). The O–Zn–C angles range from 107.6(2) to 116.0(2)°. Another recently published crystal structure is that of diethylzinc · 18-crown-6, which provides the first example of a poly-coordinated diorganozinc complex (six rather long Zn–O bonds between 2.837(3) and 2.890(3) Å [8]. In this structure, the 'natural' linear C–Zn–C angle may be retained since rehybridization is not needed for complexation. The C–Zn bond length (1.950(2) Å) is identical with that in the linear diethylzinc (1.95(1) Å in the gas phase [9].

Relative to intermolecular complexes, intramolecular complexes generally are more stable owing to steric and entropic stabilization. This effect has been demonstrated for interaction of dialkylzinc compounds with various heteroatoms. A series of ω,ω'-functionalized zinc compounds ([X(CH$_2$)$_n$]$_2$Zn; $n = 3$ or 4) has been synthesized bearing OMe, SMe, N(Me)$_2$ or P(Ph)$_3$ as coordinating groups [10–16]. In some cases solid state X-ray [13–15] or gas phase electron diffraction studies [14–16] were possible. All structures show a tetra-coordinated zinc atom; relevant data (bond angles and distances) are listed in Table 1. The gas phase structures of two intramolecularly ROMe-coordinated dialkylzinc compounds show average Zn–C and Zn–O distances of 1.979 and 2.37 Å, respectively, and a tendency towards large C–Zn–C angles [16].

Compared with dialkylzinc compounds, little is known about the coordination of diarylzinc compounds. So far, no structural characterization of any diarylzinc complex has been reported. Stable crystalline adducts analogous to those from dimethylzinc were reported for various diarylzinc derivatives with the bidentate

Table 2

Isolated 1,4-dioxane complexes of diorganylzinc compounds

Diorganylzinc (R_2Zn)	M.p. (°C)		Reference
	($R_2Zn \cdot L$)	(R_2Zn)	
Dimethylzinc	66	−29	4
Diphenylzinc	113	105	15
Di(*p*-tolyl)zinc	144–145	169–170	15
Di(*p*-biphenylyl)zinc	60 (dec.)	100 (dec.)	15
Di(α-thienyl)zinc	150	> 150 (dec.)	15
Dibenzylzinc	–	–	15
Bis(1-naphthyl)zinc	–	> 200 (dec.)	16

ligand 1,4-dioxane (Table 2), but no structural characterizations were performed [17,18]. The complexation ability of diarylzinc derivatives towards simple (monodentate) ethers has not been thoroughly investigated. In the present work we isolated and characterized crystalline complexes of diphenylzinc with the open polydentate ligands glyme (ethyleneglycol dimethyl ether, bidentate) and diglyme (diethyleneglycol dimethyl ether, tridentate), in which the zinc atom is coordinated by two and three oxygen atoms, respectively. Tetrahydrofuran and 1,3-dimethoxypropane gave only liquid adducts.

Results and discussion

Diphenylzinc can be synthesized from phenylmagnesium bromide and zinc dichloride [17,18]. In order to obtain a completely salt-free diphenylzinc solution we used the exchange reaction between diphenylmercury and zinc metal in diethyl ether. In diethyl ether solution, diphenylzinc is probably weakly solvated, since decomplexation readily occurred on evaporation of the solution to dryness; solvent-free solid diphenylzinc was obtained by removal of the last traces of diethyl ether by pumping. This solid was treated with an equimolar amount of the relevant ligand in *n*-hexane; upon mixing of the reagents and gentle warming, a colourless solution was obtained. Slow cooling and concentration of this solution sometimes gave a crystalline adduct. When this was successful, the crystallization was repeated in order to give single crystals suitable for a structure determination. Crystals were analyzed by ^1H NMR spectroscopy (250 MHz, toluene-d_8) to determine their composition (see Experimental).

As ligands, we used potentially mono-coordinating (THF), di-chelating (glyme, 1,3-dimethoxypropane) and tri-chelating (diglyme) ethers. Crystalline products were isolated only in the case of the complexes **1** and **2** with glyme and diglyme, respectively. They were shown from their ^1H NMR spectra to be 1 : 1 adducts (see Experimental) and the subsequent X-ray crystal structure determinations (*vide infra*) confirmed this composition. The liquid adducts formed from THF and 1,3-dimethoxypropane were not further examined. The analogy with dimethylzinc (*vide supra*) is obvious; in both cases, THF (mono-coordinating) and 1,3-dimethoxypropane (flexible) do not give crystalline adducts.

Complex **1** has the expected tetra-coordinated $R_2Zn \cdot L_2$ structure (Fig. 1), with both oxygens coordinating to the zinc atom. This coordination geometry seems to

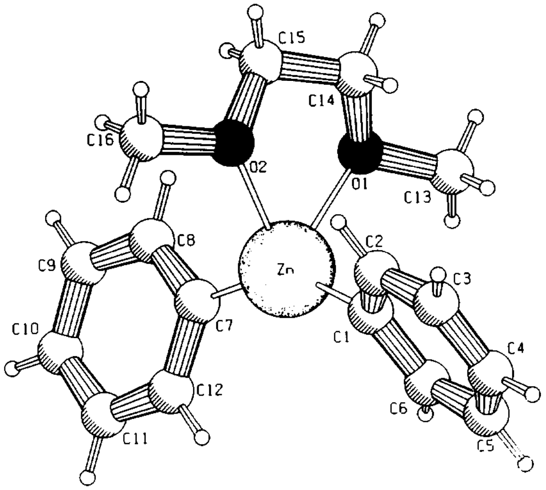

Fig. 1. PLUTON drawing of the structure of **1**, with the adopted numbering of the atoms.

be present both in solution and the solid state. The coordination of the zinc atom is pseudo-tetrahedral (Table 3), with a large C–Zn–C angle (146.6(2)°) and a small O–Zn–O angle (72.2(1)°); the latter is a consequence of the coordinative five-

Table 3

Bond distances (Å) and bond angles (deg) for **1**

Zn–O(1)	2.287(4)	C(3)–C(4)	1.346(10)
Zn–O(2)	2.259(4)	C(4)–C(5)	1.355(12)
Zn–C(1)	1.969(5)	C(5)–C(6)	1.385(8)
Zn–C(7)	1.958(5)	C(7)–C(8)	1.380(7)
O(1)–C(13)	1.421(7)	C(7)–C(12)	1.402(7)
O(1)–C(14)	1.437(8)	C(8)–C(9)	1.384(8)
O(2)–C(15)	1.408(7)	C(9)–C(10)	1.368(8)
O(2)–C(16)	1.403(8)	C(10)–C(11)	1.354(9)
C(1)–C(2)	1.392(8)	C(11)–C(12)	1.377(8)
C(1)–C(6)	1.378(8)	C(14)–C(15)	1.457(8)
C(2)–C(3)	1.385(9)		
O(1)–Zn–O(2)	72.16(14)	C(1)–C(2)–C(3)	122.6(6)
O(1)–Zn–C(1)	102.44(18)	C(2)–C(3)–C(4)	120.0(7)
O(1)–Zn–C(7)	104.81(18)	C(3)–C(4)–C(5)	119.7(6)
O(2)–Zn–C(1)	103.25(19)	C(4)–C(5)–C(6)	120.3(6)
O(2)–Zn–C(7)	103.14(17)	C(1)–C(6)–C(5)	122.4(6)
C(1)–Zn–C(7)	146.6(2)	Zn–C(7)–C(8)	124.0(4)
Zn–O(1)–C(13)	113.4(4)	Zn–C(7)–C(12)	121.8(4)
Zn–O(1)–C(14)	109.6(3)	C(8)–C(7)–C(12)	114.2(5)
C(13)–O(1)–C(14)	112.2(4)	C(7)–C(8)–C(9)	123.4(5)
Zn–O(2)–C(15)	114.6(3)	C(8)–C(9)–C(10)	119.8(5)
Zn–O(2)–C(16)	121.1(4)	C(9)–C(10)–C(11)	119.3(5)
C(15)–O(2)–C(16)	113.5(5)	C(10)–C(11)–C(12)	120.3(5)
Zn–C(1)–C(2)	122.7(4)	C(7)–C(12)–C(11)	123.0(5)
Zn–C(1)–C(6)	122.3(4)	O(1)–C(14)–C(15)	107.7(5)
C(2)–C(1)–C(6)	115.0(5)	O(2)–C(15)–C(14)	108.3(5)

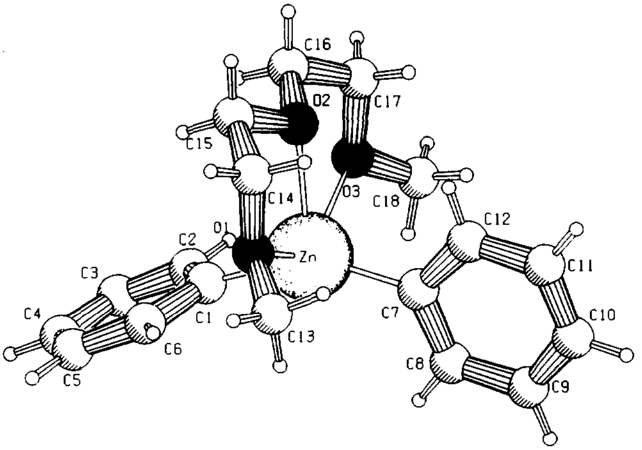

Fig. 2. PLUTON drawing of the structure of **2**, with the adopted numbering of the atoms.

membered ring. The O–Zn–C angles range from 102.4(2)° for C(1)–Zn–O(1) to 104.8(2)° for C(7)–Zn–O(1). The Zn–C distances (Zn–C(1) 1.969(5), Zn–C(7) 1.958(5) Å) are almost equal, and the Zn–O distances (Zn–O(1) 2.287(4), Zn–O(2) 2.259(4) Å) clearly shorter (about 0.1 Å) than those shown in Table 1. This suggests that the coordinative bonds in $(MeO(CH_2)_n)_2Zn$ ($n = 3$ or 4) are relatively weak; clearly, their thermodynamic stability is due more to entropy than to enthalpy. In bis(fluorenyl)zinc · $(THF)_2$ [7], the Zn–C bond is more polar, as indicated by the longer Zn–C distances (2.041(5) and 2.053(6) Å), shorter Zn–O distances (2.114(5) and 2.095(4) Å), and the smaller C–Zn–C angle (117.6(2)°), in spite of the larger size of the carbon ligand.

In complex **2**, the central zinc atom is penta-coordinate, all three oxygen atoms of the ligand being involved in the complexation (Fig. 2); this is the first $R_2Zn \cdot L_3$ structure to be reported. The ability of the diglyme ligand to induce higher coordination states was foreshadowed by thermochemical results obtained with Me_2Zn [6]. The heat of complexation of Me_2Zn with the di-chelating glyme was −16.7 kJ/mol, that of the tri-chelating diglyme −26.4 kJ/mol (i.e. for both ethers roughly −8.5 kJ/mol per coordinating ether oxygen).

Compared with those in **1**, the Zn–O bonds in **2** are significantly weaker (Zn–O(1) 2.483(5), Zn–O(2) 2.330(5), Zn–O(3) 2.509(6) Å), the central oxygen bond being stronger than the other two (Table 4). It is noteworthy that in spite of the differences in the oxygen coordination, the diphenylzinc moieties in **1** and **2** are practically identical, as evidenced by the large C–Zn–C angle (in **2**: 149.7(3)°) and the Zn–C bond distances (in **2**: Zn–C(1) 1.970(8), Zn–C(7) 1.969(8) Å). In this context it should be pointed out that the penta-coordinate zinc atom in **2** has a rather unusual configuration, which is neither a trigonal bipyramid (or at best a highly distorted one) nor a square planar pyramid, nor, for that matter, a configuration lying on the Berry pseudo-rotation path between the two. Obviously, the geometrical constraints of the complex components generate this uncommon arrangement.

The O–Zn–O angles inside the five-membered coordinative rings of **2** are very small (O(1)–Zn–O(2) 68.7(2), O(2)–Zn–O(3) 69.3(2)°); C–Zn–O angles range

Table 4

Bond distances (Å) and bond angles (deg) for **2**

Zn–O(1)	2.483(5)	C(2)–C(3)	1.388(12)
Zn–O(2)	2.330(5)	C(3)–C(4)	1.346(14)
Zn–O(3)	2.509(6)	C(4)–C(5)	1.372(15)
Zn–C(1)	1.970(8)	C(5)–C(6)	1.391(12)
Zn–C(7)	1.969(8)	C(7)–C(8)	1.377(12)
O(1)–C(13)	1.403(11)	C(7)–C(12)	1.379(12)
O(1)–C(14)	1.399(10)	C(8)–C(9)	1.397(14)
O(2)–C(15)	1.438(9)	C(9)–C(10)	1.354(16)
O(2)–C(16)	1.426(11)	C(10)–C(11)	1.332(15)
O(3)–C(17)	1.406(10)	C(11)–C(12)	1.379(14)
O(3)–C(18)	1.419(13)	C(14)–C(15)	1.487(12)
C(1)–C(2)	1.391(11)	C(16)–C(17)	1.487(14)
C(1)–C(6)	1.387(11)		
O(1)–Zn–O(2)	68.73(19)	Zn–C(1)–C(6)	120.9(6)
O(1)–Zn–O(3)	137.99(19)	C(2)–C(1)–C(6)	115.4(7)
O(1)–Zn–C(1)	94.4(3)	C(1)–C(2)–C(3)	121.9(8)
O(1)–Zn–C(7)	95.2(3)	C(2)–C(3)–C(4)	121.0(9)
O(2)–Zn–O(3)	69.30(18)	C(3)–C(4)–C(5)	119.3(9)
O(2)–Zn–C(1)	106.1(3)	C(4)–C(5)–C(6)	119.7(8)
O(2)–Zn–C(7)	104.2(3)	C(1)–C(6)–C(5)	122.5(8)
O(3)–Zn–C(1)	95.2(3)	Zn–C(7)–C(8)	122.2(6)
O(3)–Zn–C(7)	96.6(3)	Zn–C(7)–C(12)	123.6(6)
C(1)–Zn–C(7)	149.7(3)	C(8)–C(7)–C(12)	114.2(7)
Zn–O(1)–C(13)	121.1(5)	C(7)–C(8)–C(9)	122.5(8)
Zn–O(1)–C(14)	113.3(4)	C(8)–C(9)–C(10)	120.2(9)
C(13)–O(1)–C(14)	113.0(7)	C(9)–C(10)–C(11)	119.1(10)
Zn–O(2)–C(15)	110.9(4)	C(10)–C(11)–C(12)	120.6(10)
Zn–O(2)–C(16)	111.3(5)	C(7)–C(12)–C(11)	123.5(8)
C(15)–O(2)–C(16)	113.0(6)	O(1)–C(14)–C(15)	107.1(6)
Zn–O(3)–C(17)	110.1(5)	O(2)–C(15)–C(14)	108.2(7)
Zn–O(3)–C(18)	118.4(5)	O(2)–C(16)–C(17)	107.7(7)
C(17)–O(3)–C(18)	113.6(7)	O(3)–C(17)–C(16)	107.4(7)
Zn–C(1)–C(2)	123.5(6)		

from 94.4(3)° (C(1)–Zn–O(1)) to 106.1(3)° (C(1)–Zn–O(2)). The zinc atom and the three oxygen atoms lie (within the standard deviation) in a perfect plane; the complex has almost a mirror plane through C(1)–C(7)–O(2). The conformation of the diglyme ligand is therefore symmetrical about its centre O(2) (t-g-t-t-g′-t). The phenyl group Ph(2) [C(7)–C(12)] is almost perpendicular (89.5(4)°) to the other phenyl group Ph(1) [C(1)–C(6)] and to the ZnO_3 plane (86.7(4)°).

Conclusion

The structures described here demonstrate that simple diorganozinc compounds can form complexes with ethers. The tetracoordination around zinc in **1** is probably typical of most adducts of R_2Zn compounds with ethers (which have so far not been obtained in crystalline form). Complex **2** shows that higher coordination states (> 4) can under special conditions occur in organozinc compounds and are not restricted to inorganic zinc compounds. The structural details for complexes **1** and **2**, in particular the C–Zn–C bond angles may be of use in the parametrization of semiempirical calculations [20,21].

Experimental

General

The synthesis of diphenylzinc and its complexation reactions with several ethers were carried out in fully-sealed glassware by use of high vacuum techniques. Dry solvents were prepared by distillation from liquid Na/K alloy in sealed glassware, after predrying over NaOH. The polydentate ether ligands (glyme, diglyme, 1,3-dimethoxypropane) were predried over molecular sieve 4 Å, and distilled from sodium chips in an evacuated wholly glass apparatus. The starting materials diphenylmercury (Merck), zinc (Ventron, high purity grade), glyme (Janssen) and diglyme (Janssen) were commercially available. 1,3-Dimethoxypropane was available in our laboratory. Organozinc compounds were analysed by hydrolysis, followed by titration with HCl ('total base') and EDTA (Zn^{2+}). The ^1H NMR spectra were recorded on a Bruker WH 90 or a Bruker WM 250 spectrometer.

Synthesis of diphenylzinc

Diphenylmercury (7.1 g, 20 mmol) was stirred with zinc (13 g, 200 mmol) for two weeks in diethyl ether (about 200 mL). The clear light-brown solution was decanted from the zinc amalgam. An aliquot of this solution was titrated, and the expected concentrations of 'total base' and 'Zn^{2+}' were found to be in a ratio of 2.01/1. The solution was divided between several ampoules (1 mmol Ph_2Zn in 10 mL Et_2O). The samples were distilled to dryness to leave a colourless, solid residue. The last traces of solvent were removed by high vacuum pumping. The remaining solid was analysed by ^1H NMR spectroscopy (250 MHz, THF-d_8, ref. THF-d_7 $\delta = 1.75$ ppm) δ 7.08 (t, ^3J 7 Hz, 2H, aryl-H(4)), 7.15 (dd, $2 \times {}^3J$ 7 Hz, 4H, aryl-H(3,5)), 7.61 (dd, ^3J 7, ^4J 2 Hz, 4H, aryl-H(2,6)). In the spectrum, only a trace of diethyl ether ($< 1\%$), and no other impurities were discernible.

Complexation with THF

Solid diphenylzinc (1.0 mmol), n-hexane (10 mL) and THF (2.0 mmol = 162 μL) were mixed to give a clear solution. Concentration and cooling led to separation of a colourless oil, which crystallized at low temperatures (−80°C). These crystals melted upon slight warming and could therefore not be isolated for study.

Complexation with glyme ($Ph_2Zn \cdot CH_3OCH_2CH_2OCH_3$) (1)

Solid diphenylzinc (1.0 mmol), n-hexane (10 mL), and glyme (1.0 mmol = 110 μL) were mixed. Heating (hot water bath) gave a clear solution. This was slowly cooled to room temperature, and high quality crystals were formed after several days at that temperature. They were separated from the mother liquor and divided into several samples. The crystals were characterized as pure, solvent free 1:1 complex **1** by ^1H NMR spectroscopy (250 MHz, toluene-d_8, ref. $C_6D_5CD_2H$ $\delta = 2.32$ ppm) δ 3.06 (s, 6H, OMe), 3.18 (s, 4H, C_2H_4), 7.52 (tm, ^3J 7 Hz, 2H, phenyl-H(4)), 7.61 (ddm, ^3J 7, ^3J 7 Hz, 4H, phenyl-H(3,5)), 7.70 (dm, ^3J 7 Hz, 4H, phenyl-H(2,6)). A sample of crystalline material was transferred to a dry glovebox (Braun, Garching, Germany) for selection of crystals. The remaining crystals were hydrolysed and the solution titrated; a 'total base' to Zn^{2+} ratio of 2/1 was found. Another sample was subjected to vacuum sublimation ('static' vacuum, $< 10^{-5}$ mbar, 70°C) but the crystals melted and an oily distillate was obtained; this did not solidify.

Complexation with 1,3-dimethoxypropane

Mixing of solid diphenylzinc (1.0 mmol) with 1,3-dimethoxypropane (1.0 mmol = 120 μL) in n-hexane (10 mL) gave a clear solution. Upon cooling or concentration of this solution an oil separated. Even at low temperatures (−80°C) crystals were not obtained. The reaction was repeated but with 2.0 mmol of diphenylzinc. Upon cooling of the solution (−20°C) some colourless crystals were formed. These were isolated and shown by ^1H NMR spectroscopy (250 MHz, toluene-d_8, ref. $C_6D_5CD_2H$ $\delta = 2.32$ ppm) to be pure uncomplexed diphenylzinc: δ 7.42–7.50 (m, 10H, aryl-H).

Complexation with diglyme ($Ph_2Zn \cdot CH_3O(CH_2CH_2O)_2CH_3$) (2)

Diphenylzinc (1.0 mmol), diglyme (1.0 mmol = 136 μL) and n-hexane (10 mL) were mixed to give a clear solution. Upon concentration of this solution, a

Table 5

Crystal data and details of the structure determination for 1

Crystal data	
Empirical formula	$C_{16}H_{20}O_2Zn$
Formula weight	309.71
Crystal system	Orthorhombic
Space group	*Pbca* (No. 61)
a, b, c (Å)	12.5540(10), 14.0620(10), 18.2880(10)
V (Å^3)	3228.5(4)
Z	8
D_{calc} (g/cm^3)	1.274
$F(000)$ (electrons)	1296
μ(Mo-K_α) (cm^{-1})	15.5
Crystal size (mm)	0.25 × 0.50 × 0.50
Data collection	
Temperature (K)	295
Radiation (Å)	Mo-K_α (Zr) 0.71073
$\theta_{min-max}$ (deg)	1.12, 27.5
Scan type	$\omega/2\theta$
Scan $\Delta(\omega)$ (deg)	$0.65 + 0.35 \tan(\theta)$
Horiz. and vert. aperture (mm)	3.00, 6.00
Reference reflection(s)	302; 420; 024
Dataset	0: 16; 0: 18; 0: 23
Tot., uniq. data	4439, 3700
Observed data [$I > 2.5\,\sigma(I)$]	1445
Refinement	
N_{ref}, N_{par}	1445, 171
R, wR, S	0.045, 0.044, 1.43
Weighting scheme	$w = 1/\sigma^2(F)$
Max. and av. shift/error	0.19, 0.02
Min. and max. resd. dens. (e/Å^3)	−0.27, 0.30

colourless oil separated. Crystallization was induced by cooling with liquid nitrogen. The solvent was poured back and the mixture warmed until almost all of the solid had dissolved. Cooling to room temperature gave, after several hours, high quality crystals. The crystalline material was separated from the mother liquor. Some crystals were used for ^1H NMR spectroscopy and the product was shown to be the expected solvent-free 1:1 complex: ^1H NMR (250 MHz, toluene-d_8, ref. $C_6D_5CD_2H$ $\delta = 2.32$ ppm) δ 3.08 (s, 6H, OMe), 3.23–3.27 and 3.29–3.33 (m(A_2B_2), 8H, C_2H_4), 7.53 (tt, ^3J 7, ^4J 2 Hz, 2H, phenyl-H(4)), 7.63 (ddm, ^3J 7, ^3J 7 Hz, 4H, phenyl-H(3,5)), 8.04 (dd, ^3J 7, ^4J 2 Hz, 4H, phenyl-H(2,6)). The ^1H NMR spectrum suggests a symmetrical coordination of the diglyme ligand on the NMR timescale. A reference spectrum of free diglyme was recorded under identical conditions: δ 3.35 (s, 6H, OMe), 3.53–3.57 and 3.65–3.69 (m(A_2B_2), 8H, C_2H_4). Upon complexation, the ligand signals are shielded by 0.3–0.4 ppm. Some of the crystals were introduced into the glovebox for selection. The remaining crystals were analysed by titration to check the 'total base' to Zn^{2+} ratio, which was 2/1.

Table 6

Crystal data and details of the structure determination for **2**

Crystal data	
Empirical formula	$C_{18}H_{24}O_3Zn$
Formula weight	353.77
Crystal system	Orthorhombic
Space group	*Pcab* (No. 61)
a, b, c (Å)	12.2840(10), 16.278(2), 18.595(2)
V (Å^3)	3718.2(7)
Z	8
$D_{calc.}$ (g/cm^3)	1.264
$F(000)$ (electrons)	1488
μ(Mo-K_α) (cm^{-1})	13.6
Crystal size (mm)	0.25 × 0.25 × 0.80
Data collection	
Temperature (K)	295
Radiation (Å)	Mo-K_α(Zr) 0.71073
$\theta_{min-max}$ (deg)	1.1, 27.5
Scan type	$\omega/2\theta$
Scan (deg)	$0.60 + 0.35 \tan(\theta)$
Horiz. and vert. aperture (mm)	3.00, 5.00
Reference reflection(s)	202; 120; 032
Dataset	0: 15; 0: 21; 0: 24
Tot., uniq. data	7138, 4247
Observed data [$I > 2.5\ \sigma(I)$]	1364
Refinement	
N_{ref}, N_{par}	1364, 208
R, wR, S	0.055, 0.044, 2.15
Weighting scheme	$w = 1/\sigma^2(F)$
Max. and av. shift/error	0.44, 0.02
Min. and max. resd. dens. (e/Å^3)	−0.38, 0.34

Table 7

Fractional coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for 1

Atom	x	y	z	U_{eq} (Å^2) [a]
Zn	0.63178(5)	0.09438(4)	0.29838(3)	0.0732(3)
O(1)	0.4706(3)	0.1186(3)	0.35366(19)	0.0787(14)
O(2)	0.5212(3)	−0.0235(3)	0.2626(2)	0.0863(16)
C(1)	0.7159(4)	0.0349(4)	0.3769(3)	0.065(2)
C(2)	0.7109(5)	−0.0619(4)	0.3925(3)	0.090(3)
C(3)	0.7708(5)	−0.1038(5)	0.4474(4)	0.107(3)
C(4)	0.8374(5)	−0.0503(6)	0.4879(3)	0.103(3)
C(5)	0.8461(4)	0.0441(6)	0.4743(3)	0.092(3)
C(6)	0.7859(4)	0.0860(4)	0.4196(3)	0.077(2)
C(7)	0.6319(4)	0.1806(3)	0.2143(3)	0.0640(17)
C(8)	0.5432(4)	0.2001(4)	0.1723(3)	0.075(2)
C(9)	0.5460(4)	0.2559(4)	0.1100(3)	0.082(3)
C(10)	0.6400(5)	0.2961(4)	0.0881(3)	0.080(3)
C(11)	0.7290(5)	0.2814(4)	0.1284(3)	0.080(2)
C(12)	0.7253(4)	0.2252(4)	0.1900(3)	0.078(2)
C(13)	0.4789(6)	0.1628(5)	0.4233(3)	0.114(3)
C(14)	0.4130(5)	0.0304(5)	0.3569(3)	0.097(3)
C(15)	0.4143(5)	−0.0114(4)	0.2840(3)	0.0920(18)
C(16)	0.5326(6)	−0.0670(5)	0.1940(4)	0.139(3)

[a] $U_{eq} = 1/3$ of the trace of the orthogonalized U.

Table 8

Fractional coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for 2

Atom	x	y	z	U_{eq} (Å^2) [a]
Zn	0.59759(7)	−0.12012(5)	0.33078(5)	0.0674(3)
O(1)	0.5824(5)	0.0167(3)	0.2726(3)	0.074(2)
O(2)	0.4294(4)	−0.0597(3)	0.3545(3)	0.065(2)
O(3)	0.4856(4)	−0.2100(4)	0.4117(3)	0.077(2)
C(1)	0.6966(6)	−0.0818(5)	0.4071(4)	0.057(3)
C(2)	0.7112(6)	−0.1229(5)	0.4720(4)	0.066(3)
C(3)	0.7883(8)	−0.0980(6)	0.5220(5)	0.078(4)
C(4)	0.8530(7)	−0.0329(7)	0.5093(5)	0.087(5)
C(5)	0.8402(6)	0.0109(6)	0.4468(6)	0.081(4)
C(6)	0.7630(6)	−0.0139(5)	0.3966(4)	0.069(3)
C(7)	0.5733(7)	−0.1833(5)	0.2419(4)	0.059(3)
C(8)	0.6524(7)	−0.2329(5)	0.2125(5)	0.077(4)
C(9)	0.6363(9)	−0.2768(6)	0.1488(6)	0.092(5)
C(10)	0.5407(10)	−0.2707(6)	0.1130(5)	0.091(5)
C(11)	0.4619(9)	−0.2237(6)	0.1399(6)	0.091(5)
C(12)	0.4777(7)	−0.1810(5)	0.2031(5)	0.079(4)
C(13)	0.6302(9)	0.0320(7)	0.2054(5)	0.122(5)
C(14)	0.4791(7)	0.0520(5)	0.2797(4)	0.074(4)
C(15)	0.4370(7)	0.0284(5)	0.3518(5)	0.079(4)
C(16)	0.3844(7)	−0.0892(6)	0.4203(5)	0.084(4)
C(17)	0.3783(7)	−0.1803(6)	0.4155(5)	0.082(4)
C(18)	0.4921(9)	−0.2964(7)	0.4026(6)	0.130(6)

[a] $U_{eq} = 1/3$ of the trace of the orthogonalized U.

Crystal structure determination of 1 and 2

Crystal data and some details of the structure determination are given in Tables 5 and 6. X-ray data were collected on an Enraf–Nonius CAD4 diffractometer from colourless, transparent crystals sealed under nitrogen in Lindemann glass capillaries. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections in the range of $10 < \theta < 15°$. Data were corrected for Lp and absorption (DIFABS; [22]). The structures were solved with Patterson and subsequent Fourier methods (SHELXS86; [23]) and refined on F by full matrix least-squares techniques (SHELX76; [24]). Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms with common isotropic thermal parameters. Final atomic coordinates are given in Tables 7 and 8. Neutral scattering factors were taken from [25] and corrected for anomalous dispersion [26]. All calculations were performed with SHELX76 and the programs PLATON and PLUTON (Geometrical calculations and illustrations; [27]) on a Microvax cluster.

Supplementary material available. Anisotropic thermal parameters, H-atom parameters, list of bond lengths, bond angles, and lists of observed and calculated structure factor amplitudes for **1** and **2** (59 pages) are available from A.L.S.

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