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Coordinational Behavior of Solvent-Free Diorganylzinc Compounds: The Remarkable X-ray Structure of Dimeric Diphenylzinc

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The crystal structure of solvent-free diphenylzinc has been determined. Crystals of $[Ph_2Zn]_2$ are triclinic, space group $P\bar{1}$, with unit cell dimensions $a = 9.956$ (1) Å, $b = 10.024$ (2) Å, $c = 12.011$ (2) Å, $\alpha = 113.74$ (2)°, $\beta = 108.79$ (1)°, $\gamma = 97.68$ (2)°, and $Z = 2$. The structure refinement converged at $R_F = 0.042$. A remarkable $PhZn(\mu\text{-}Ph)_2ZnPh$ dimeric structure is found, in which the zinc atoms are tricoordinated. The structure confirms the ability of Zn to take part in multicenter bonding to carbon. It is unique not only in the sense that it is the first example of an arylzinc derivative but also because of the unsymmetrical orientation of the μ-phenyl groups: they retain the predominant bonding relation to one zinc atom, as the association of the two monomeric Ph_2Zn units only partially disturbs their original, linear geometry: the average Zn–C bond distances within one Ph_2Zn unit are 1.946 (5) Å (terminal) and 2.011 (5) Å (bridging), whereas the bridging Zn–C bond to the second Ph_2Zn unit is 2.403 (5) Å. In the crystal packing, two dimeric residues are weakly associated by interactions (3.0–3.7 Å) between the two zinc atoms of one dimer and one of the terminal phenyl groups of the other.

Introduction

The chemistry of organozinc compounds has a rather long history, in which many applications for this class of compounds have been found. They are used both as intermediates in organic synthesis and as mild alkylating (arylating) agents in the preparation of organometallic compounds. In order to obtain a deeper understanding of these reactions, detailed information about the structure and properties of the organozinc intermediates will be needed. Knowledge of the association and coordination of organozinc compounds, as derived from X-ray crystal structure measurements and gas-phase electron diffraction studies, can be useful to understand their physical behavior and chemical reactivity. In spite of these considerations, the structural characterization of organozinc compounds has until quite recently received relatively little attention.[1] Most published results deal with alkylzinc or cyclopentadienylzinc derivatives (see Table I). Information about arylzinc derivatives (even the parent compound diphenylzinc) is completely absent, which makes the structure presented here unique. At this moment, we are also investigating the complexation behavior of diphenylzinc toward ethers.

Table I. Structural Investigations of Simple Organozinc Compounds, As Found in the Literature

compd	characteristic data	ref
	(a) Gas-Phase Electron Diffraction	
$ZnMe_2$	C–Zn–C = 180°, Zn–C = 1.93 Å	2
$ZnEt_2$	C–Zn–C = 180°, Zn–C = 1.95 Å	2
$Zn(n\text{-}Pr)_2$	C–Zn–C = 180°, Zn–C = 1.95 Å	2
$(\eta^5\text{-}CpZn)Me^a$	Cp–Zn–C = 180°, Zn–C(Me) = 1.903 (12) Å, Zn–C(Cp) = 2.280 (9) Å	3
$(\eta^1,\eta^5\text{-}Me_3SiCp)_2Zn$	Cp–Zn–C = 180°, Zn–C(η^5) = 2.26 (3) Å, Zn–C(η^1) = 2.07 (10) Å, (η^1-Cp plane)–C–Zn = 53 (7)°	4c
$(\eta^1,\eta^5\text{-}Me_5Cp)_2Zn$	Cp*–Zn–C_σ = 180°, Zn–C(η^5) = 2.28 (2) Å, Zn–C(η^1) = 2.04 (6) Å, (η^1-Cp plane)–C–Zn = 84 (4)°	4a,b
	(b) Crystal Structure Determinations	
$(\eta^1,\eta^5\text{-}Cp)_2Zn$	polymeric structure, bridging and terminal Cp groups	4b
$(\eta^1,\eta^5\text{-}Me_3SiCp)_2Zn$	Zn–C(η^5) = 2.28 (2) Å, Zn–C(η^1) = 2.04 (6) Å, (η^1-Cp plane)–C–Zn = 84 (4)°	5
$[\eta^{2/3}\text{-}CpZnMe]_n$	polymeric structure, bridging Cp groups, terminal Me groups	6
$[EtZnI]_n$	polymeric structure, tri- and tetracoordinate Zn	7
$(\eta^1\text{-fluorenyl})_2Zn\cdot 2THF$	tetracoordinate Zn, Zn–C = 2.041 (5) and 2.053 (6) Å, Zn–O = 2.114 (5) and 2.095 (4) Å, C–Zn–C = 117.6 (2)°	8

[a] Structures of cyclopentadienylzinc derivatives are reviewed in ref 5 and 9.

Experimental Section

Reactions and crystallizations were carried out in fully sealed glassware with use of high-vacuum techniques. Dry solvents were prepared by distillation from liquid Na/K alloy in sealed glassware, after predrying on NaOH. The starting materials di-

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phenylmercury (Merck) and zinc (Ventron, high-purity grade) were commercially available. Yields of the organozinc compound were determined by titration with HCl for "total base" and EDTA for "total Zn^{2+}" after hydrolysis. ^1H NMR spectra were measured on a Bruker WH 90 (90 MHz) or a Bruker WM 250 (250 MHz) spectrometer.

Diphenylzinc. Diphenylmercury (7.1 g, 20 mmol) was stirred with zinc (13 g, 200 mmol) for 2 weeks in diethyl ether (about 200 mL). The clear, light brown solution was decanted after settling of the zinc amalgam. An aliquot of this solution was titrated to check the complete conversion of the organomercury starting material. The expected concentrations of total base and Zn^{2+} were found in a ratio of 2.01:1. The solution was divided over several ampules containing 1-mmol samples (10 mL of Et_2O).

One of these was distilled to dryness with use of liquid nitrogen; a colorless, solid residue remained, from which the remaining solvent was removed by pumping on a high-vacuum line. A sample was dissolved in [D_8]THF for characterization by ^1H NMR spectroscopy (250 MHz; reference [D_7]THF, $\delta = 1.75$ ppm): δ 7.08 (tm, $^3J = 7$ Hz, 2 H, aryl H(4)), 7.15 (ddm, $^3J = 7$ Hz, $^3J = 7$ Hz, 4 H, aryl H(3,5)), 7.61 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 4 H, aryl H(2,6)). In the NMR spectrum, no impurities could be detected. Due to the very weak complexation of diphenylzinc with diethyl ether, only a trace amount of this solvent was present in the NMR solution.

Crystallization of Diphenylzinc. Diphenylzinc could be crystallized from *n*-heptane, but the crystals obtained in this way were of low quality. For this purpose, 0.5 mmol of diphenylzinc was isolated from the diethyl ether solution as a solid, high-vacuum pumped, and dissolved with heating (water bath) in 10 mL of *n*-hexane. On slow cooling to 5 °C, a finely divided crystalline material precipitated.

Good-quality crystals were obtained with use of high-vacuum sublimation. In this experiment, diphenylzinc (1 mmol) was isolated from the diethyl ether solution as a solid and purified by high-vacuum sublimation (from 50 °C/10^{-4} mbar to 90 °C/2 × 10^{-6} mbar). A second sublimation was performed under a static vacuum, i.e. after the glass apparatus was sealed off from the high-vacuum line. At a sublimation temperature of 90 °C, beautiful crystals grew in the cold parts of the glass assembly (room temperature). A sample of the crystals was hydrolyzed, to analyze the amounts of total base and total Zn^{2+} by titration. The expected 2:1 stoichiometry was found; the yield of diphenylzinc crystals was 67% after two sublimations.

Structure Determination and Refinement. A colorless block-shaped crystal mounted in a glovebox (Braun, Garsching, West Germany) under nitrogen in a Lindemann glass capillary was transferred to an Enraf-Nonius CAD4F diffractometer for data collection. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections with $10.6 < \theta < 17.5°$. The unit cell parameters were checked for the presence of higher lattice symmetry.[10] Data were corrected for Lp, for a small linear decay (0.6%) of the intensities during the 91 h of X-ray exposure time, and for absorption (DIFABS; correction range 0.61–1.42)[11] and averaged into an unique data set ($R_{av} = 0.024$). The structure was solved with Patterson methods (SHELXS86)[12] and subsequent difference Fourier syntheses. Refinement on F was carried out by full-matrix least-squares techniques. H atoms were introduced on calculated positions (C–H = 0.98 Å) and included in the refinement riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters; H atoms were refined with one common isotropic thermal parameter ($U = 0.064$ (3) Å^2). Weights were introduced in the final refinement cycles; convergence was reached at $R = 0.042$. Residual densities (Table II) in the final difference Fourier synthesis are localized within 1 Å from Zn and are interpreted as residual absorption artifacts.

Table II. Crystal Data and Details of the Structure Determination

	(a) Crystal Data
formula	$C_{24}H_{20}Zn_2$
mol wt	439.18
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, b, c, Å	9.956 (1), 10.024 (2), 12.011 (2)
α, β, γ, deg	113.74 (2), 108.79 (1), 97.68 (2)
V, Å^3	989.7 (3)
Z	2
D_{calc}, g cm^{-3}	1.474
$F(000)$	448
μ, cm^{-1}	24.9
cryst size, mm	0.42 × 0.30 × 0.18
	(b) Data Collection
temp, K	294
$\theta_{min}, \theta_{max}$, deg	2.04, 27.5
radiation	Mo Kα (Zr filtered), 0.71073 Å
scan type	$\omega/2\theta$
$\Delta\omega$, deg	$0.65 + 0.35 \tan \theta$
horiz and vert aperture, mm	3.0, 6.0
dist of cryst to detector, mm	173
ref rflns	–2,1,0, 0,–3,4
data set	h, –12 to +12; k, –13 to +11; l, 0 to +15
total no. of data	6421
total no. of unique data	4541
no. of obsd data	2981 ($I > 2.5\sigma(I)$)
	(c) Refinement
no. of refined params	236
weighting scheme	$w = 1.0/[\sigma^2(F) + 0.000397F^2]$
final R, R_w, S	0.042, 0.046, 0.81
$(\Delta/\sigma)_{av}$ in final cycle	0.035
min and max resid dens, e Å^{-3}	–0.38, 0.72

Table III. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for $C_{24}H_{20}Zn_2$

atom	x	y	z	U_{eq},[a] Å^2
Zn(1)	0.20542 (6)	0.37914 (6)	0.27543 (5)	0.0488 (2)
Zn(2)	0.22669 (6)	0.58920 (6)	0.19175 (4)	0.0476 (2)
C(1)	0.2027 (4)	0.6667 (5)	0.0636 (4)	0.042 (1)
C(2)	0.2610 (5)	0.8240 (5)	0.1149 (4)	0.049 (2)
C(3)	0.2451 (5)	0.8919 (5)	0.0333 (4)	0.054 (1)
C(4)	0.1716 (5)	0.8027 (5)	–0.1039 (4)	0.050 (2)
C(5)	0.1182 (4)	0.6473 (5)	–0.1575 (4)	0.047 (1)
C(6)	0.1332 (4)	0.5803 (5)	–0.0753 (4)	0.044 (1)
C(7)	0.2655 (5)	0.6574 (4)	0.3847 (3)	0.043 (1)
C(8)	0.4105 (5)	0.6960 (5)	0.4775 (4)	0.050 (2)
C(9)	0.4492 (5)	0.7753 (5)	0.6134 (4)	0.059 (2)
C(10)	0.3461 (5)	0.8189 (5)	0.6610 (4)	0.057 (2)
C(11)	0.2022 (5)	0.7827 (5)	0.5725 (4)	0.052 (2)
C(12)	0.1622 (5)	0.7036 (4)	0.4360 (4)	0.046 (1)
C(13)	0.1860 (4)	0.2905 (4)	0.3885 (4)	0.039 (1)
C(14)	0.1561 (5)	0.1346 (5)	0.3372 (4)	0.049 (2)
C(15)	0.1585 (5)	0.0635 (5)	0.4155 (5)	0.062 (2)
C(16)	0.1906 (5)	0.1499 (6)	0.5492 (5)	0.062 (2)
C(17)	0.2188 (5)	0.3048 (5)	0.6031 (4)	0.052 (2)
C(18)	0.2174 (4)	0.3758 (5)	0.5251 (4)	0.045 (1)
C(19)	0.2594 (5)	0.3438 (4)	0.1209 (4)	0.043 (1)
C(20)	0.1632 (5)	0.2429 (5)	–0.0122 (4)	0.048 (1)
C(21)	0.2145 (6)	0.1910 (5)	–0.1106 (4)	0.061 (2)
C(22)	0.3613 (6)	0.2375 (6)	–0.0809 (5)	0.069 (2)
C(23)	0.4614 (5)	0.3369 (6)	0.0497 (5)	0.069 (2)
C(24)	0.4090 (5)	0.3881 (5)	0.1470 (4)	0.055 (2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized **U** matrix.

Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table III. Crystal data and numerical details of the structure determination are given in Table II. Neutral-atom scattering factors were taken from Cromer et al. and corrected for anomalous dispersion.[13,14] All calculations were

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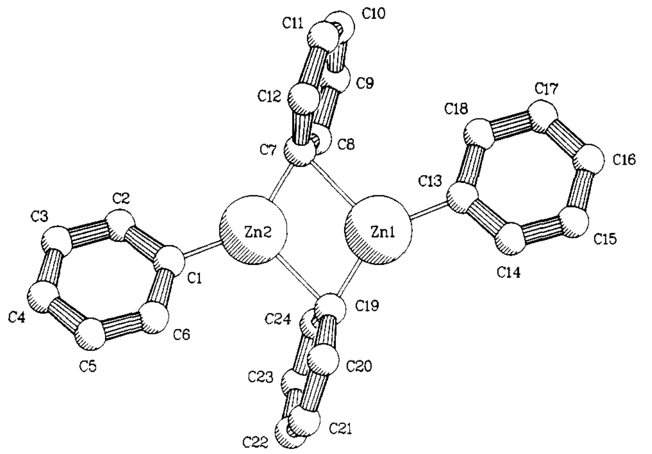

Figure 1. Drawing of the molecular structure of the dimeric unit $[Ph_2Zn]_2$, including the adopted numbering. Hydrogen atoms have been omitted for clarity.

performed with SHELX76[15] and the EUCLID package[16] (geometrical calculations and illustrations) on a MicroVAX cluster.

Results

Synthesis. The synthesis of diphenylzinc from anhydrous zinc chloride and phenyllithium has been reported,[17] a method which has the disadvantage of salt contamination of the product. For this reason, we have chosen the exchange reaction between diphenylmercury and zinc metal in dry diethyl ether.[18] By this reaction, a solution of analytically pure diphenylzinc is obtained. Because of the high reactivity of diphenylzinc with H_2O and O_2, this reaction and all further manipulations are carried out in fully sealed glass apparatus with use of a high-vacuum line. The complexation of diphenylzinc with the diethyl ether solvent is only weak. When the solvent is distilled off to dryness, decomplexation occurs, yielding solvent-free solid diphenylzinc. The purity of this product was checked by ^1H NMR spectroscopy (250 MHz, $[D_8]$-THF). Good-quality crystals of diphenylzinc (lit.[1] mp 107 °C, bp 280–285 °C/1 atm dec) were obtained after two high-vacuum sublimations. In the first sublimation step, which was performed in a glass apparatus connected to a high-vacuum line, traces of impurities and solvent were removed. The second (slow) sublimation, performed under a static vacuum, served to grow high-quality single crystals.

Description of the Structure. In the crystal unit cell, two dimeric molecules related by an inversion center are found, having the chemical composition $PhZn(\mu\text{-}Ph)_2ZnPh$. The structure of this dimer is depicted in Figure 1; relevant data on the geometry can be found in Table IV. The zinc atoms are tricoordinated, with bonds to one terminal and two bridging phenyl groups. The bond lengths between zinc and the terminal phenyl groups are as expected (Zn(1)–C(13) = 1.941 (4) Å, Zn(2)–C(1) = 1.951 (5) Å; cf. Table IV). The Zn atoms are lying almost in the least-squares (LS) plane of these phenyl rings (C(13–18)–Zn(1) = 0.24 (1) Å, C(13–18)–Zn(2) = 0.29 (1) Å, C(1–6)–Zn(1) = 0.12 (2) Å, C(1–6)–Zn(2) = 0.08 (2) Å). The bridging phenyl group is in a remarkably unsymmetrical orientation, with short (Zn(1)–C(19) = 2.006 (5) Å and Zn(2)–C(7) = 2.016 (3) Å) and long (Zn(1)–C(7) = 2.442 (4) Å and Zn(2)–C(19) = 2.364 (5) Å) zinc–carbon distances. In this respect, the dimer can be regarded as composed of two associated monomeric molecules: C(1–6)–Zn(2)–C(7–12) and C(13–18)–Zn(1)–C(19–24). These monomers are connected by weak interactions of the phenyl π system via the ipso carbon with the zinc atom of the other residue. This interpretation is confirmed by other characteristics of the structure, the Ph–Zn–Ph angles and the positions of the zinc atoms with respect to the bridging phenyl groups. Among the Ph–Zn–Ph angles, two larger values (C(1)–Zn(2)–C(7) = 141.5 (2)°, C(13)–Zn(1)–C(19) = 142.2 (2)°) indicate sp^n hybridization ($1 < n < 2$), a moderate change from the normal sp hybridization of the zinc atom in monomeric R_2Zn species. The other angles are significantly smaller, ranging from about 100° (inside the four-membered ring) to 115° (outside the four-membered ring). The short-bonded zinc atoms are lying near the LS planes of the bridging phenyl groups (C(7–12)–Zn(2) = 0.45 (1) Å, C(19–24)–Zn(1) = 0.50 (1) Å) and are thus essentially σ-bonded, whereas the longer Zn–C_α (p orbital) interactions are more perpendicular to the LS plane of a bridging phenyl group (C(7–12)–Zn(1) = −2.11 (1) Å, C(19–24)–Zn(2) = −2.05 (1) Å).

The central four-membered ring is decidedly nonplanar, with a ring folding along the Zn(1)–Zn(2) axis of 27.8 (2)°. The Zn–Zn distance of 2.685 (1) Å indicates that some Zn–Zn bonding may exist (in metallic Zn, the interatomic distance is 2.669 (4) Å).[19] Inside the four-membered ring, the Zn–C–Zn angles are small (Zn(1)–C(7)–Zn(2) = 73.4 (1)°, Zn(1)–C(19)–Zn(2) = 75.3 (2)°), whereas the C–Zn–C angles (C(7)–Zn(1)–C(19) = 100.3 (2)°, C(7)–Zn(2)–C(19) = 102.6 (2)°) are larger.

In the crystal packing, a weak association over a crystallographic inversion center is discernible between two neighboring dimeric molecules (Figure 2). One of the terminal phenyl groups (C(1–6)) has short contacts of its carbon atoms with both zinc atoms of the adjacent molecule (3.00–3.75 Å; see Table IV); although the contacts between zinc and the hydrogens of the phenyl group (2.75–3.5 Å; see Table IV) are short as well, they are probably of lesser importance than the carbon contacts if one takes the van der Waals radii of hydrogen and carbon into account. The folding of the C_2Zn_2 four-membered ring is related to this by making the zinc atoms more accessible for these interactions. This phenomenon is probably electrostatic in nature, being an attraction between slightly anionic phenyl groups and zinc atoms with partial positive charge.

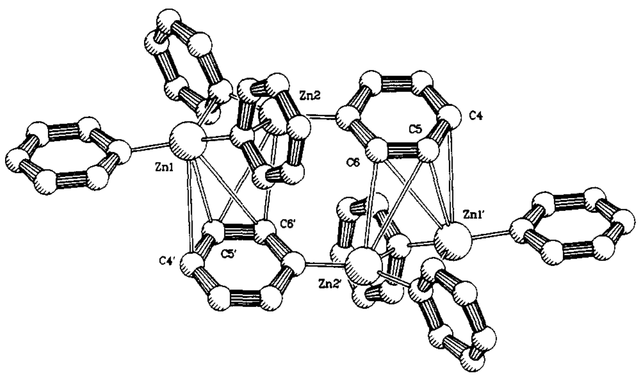

Figure 2. Association of two dimeric units $[Ph_2Zn]_2$ in the crystal packing. The hydrogen atoms have been omitted for clarity.

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Table IV. Bond Distances (Å), Short Intermolecular Distances (Å), and Bond Angles (deg) for $C_{24}H_{20}Zn_2$

Bond Distances

Zn(1)···Zn(2)	2.685 (1)	C(4)-C(5)	1.369 (7)	C(15)-C(16)	1.381 (7)
Zn(1)-C(7)	2.442 (4)	C(5)-C(6)	1.383 (7)	C(16)-C(17)	1.366 (8)
Zn(1)-C(13)	1.941 (4)	C(7)-C(8)	1.394 (6)	C(17)-C(18)	1.384 (7)
Zn(1)-C(19)	2.006 (5)	C(7)-C(12)	1.399 (7)	C(19)-C(20)	1.396 (6)
Zn(2)-C(1)	1.951 (5)	C(8)-C(9)	1.383 (6)	C(19)-C(24)	1.387 (7)
Zn(2)-C(7)	2.016 (3)	C(9)-C(10)	1.367 (7)	C(20)-C(21)	1.376 (7)
Zn(2)-C(19)	2.364 (5)	C(10)-C(11)	1.372 (7)	C(21)-C(22)	1.352 (9)
C(1)-C(2)	1.395 (7)	C(11)-C(12)	1.387 (6)	C(22)-C(23)	1.384 (7)
C(1)-C(6)	1.395 (6)	C(13)-C(14)	1.376 (7)	C(23)-C(24)	1.372 (7)
C(2)-C(3)	1.384 (7)	C(13)-C(18)	1.410 (6)		
C(3)-C(4)	1.383 (6)	C(14)-C(15)	1.387 (7)		

Short Intermolecular Distances[a]

C(4)···Zn(1)′	3.438 (5)	C(5)···Zn(2)′	3.703 (5)	C(6)···Zn(2)′	3.303 (5)
C(5)···Zn(1)′	2.998 (7)	C(6)···Zn(1)′	3.639 (5)	H(5)···Zn(1)′	2.752 (4)
H(4)···Zn(1)′	3.509 (5)	H(6)···Zn(1)′	2.926 (4)		

Bond Angles

Zn(2)-Zn(1)-C(7)	46.01 (8)	C(8)-C(7)-C(12)	116.7 (3)
Zn(2)-Zn(1)-C(13)	158.9 (1)	C(7)-C(8)-C(9)	121.3 (5)
Zn(2)-Zn(1)-C(19)	58.4 (1)	C(8)-C(9)-C(10)	120.9 (4)
C(7)-Zn(1)-C(13)	113.7 (2)	C(9)-C(10)-C(11)	119.4 (4)
C(7)-Zn(1)-C(19)	100.3 (2)	C(10)-C(11)-C(12)	120.2 (5)
C(13)-Zn(1)-C(19)	142.2 (2)	C(7)-C(12)-C(11)	121.5 (4)
Zn(1)-Zn(2)-C(1)	157.1 (1)	Zn(1)-C(13)-C(14)	118.1 (3)
Zn(1)-Zn(2)-C(7)	60.6 (1)	Zn(1)-C(13)-C(18)	124.5 (4)
Zn(1)-Zn(2)-C(19)	46.3 (1)	C(14)-C(13)-C(18)	116.9 (4)
C(1)-Zn(2)-C(7)	141.5 (2)	C(13)-C(14)-C(15)	122.1 (4)
C(1)-Zn(2)-C(19)	115.1 (2)	C(14)-C(15)-C(16)	119.8 (5)
C(7)-Zn(2)-C(19)	102.6 (2)	C(15)-C(16)-C(17)	119.7 (5)
Zn(2)-C(1)-C(2)	117.3 (3)	C(16)-C(17)-C(18)	120.5 (4)
Zn(2)-C(1)-C(6)	126.5 (4)	C(13)-C(18)-C(17)	121.1 (5)
C(2)-C(1)-C(6)	116.2 (4)	Zn(1)-C(19)-Zn(2)	75.3 (2)
C(1)-C(2)-C(3)	122.1 (4)	Zn(1)-C(19)-C(20)	123.8 (4)
C(2)-C(3)-C(4)	119.9 (5)	Zn(1)-C(19)-C(24)	118.1 (3)
C(3)-C(4)-C(5)	119.3 (5)	Zn(2)-C(19)-C(20)	112.1 (3)
C(4)-C(5)-C(6)	120.4 (4)	Zn(2)-C(19)-C(24)	97.6 (3)
C(1)-C(6)-C(5)	121.9 (5)	C(20)-C(19)-C(24)	115.8 (4)
Zn(1)-C(7)-Zn(2)	73.4 (1)	C(19)-C(20)-C(21)	121.8 (5)
Zn(1)-C(7)-C(8)	99.4 (3)	C(20)-C(21)-C(22)	120.6 (4)
Zn(1)-C(7)-C(12)	110.8 (3)	C(21)-C(22)-C(23)	119.9 (5)
Zn(2)-C(7)-C(8)	119.2 (4)	C(22)-C(23)-C(24)	119.0 (5)
Zn(2)-C(7)-C(12)	122.3 (3)	C(19)-C(24)-C(23)	123.0 (4)

[a] The prime indicates the symmetry operation $-x, 1 - y, -z$.

Discussion

Having a (Ar)$3d^{10}4s^2$ configuration, zinc may be expected to show a coordination behavior that is determined largely by electrostatic interactions. Due to the filled d^{10} shell, ligand field effects will be absent. In this sense, the situation is analogous to that of magnesium ((Ne)$2s^2$), an element which has much organometallic chemistry in common with zinc. Of course, large differences in chemical behavior between these elements will result because of their difference in electronegativity (1.65 for Zn vs 1.31 for Mg).[20] The zinc–carbon bond has a covalent, though polarized, character. Symmetric diorganylzinc compounds will therefore show a low tendency for association and complexation with ethers. For the unsolvated monomeric compounds, a linear structure is preferred, in which the zinc–carbon bonds make use of two equivalent sp-hybridized zinc orbitals. Bridging alkyl or aryl groups will be rather unlikely, due to the weak electron deficiency of the zinc atom.

Indeed, all investigations of simple diorganylzinc compounds fit this picture. A recent study[2] of the dialkylzinc compounds dimethylzinc, diethylzinc, and di-*n*-propylzinc by gas-phase electron diffraction proved their monomeric nature in the gas phase. The low melting points (−29, −28, and −81 to −84 °C, respectively[1]) and boiling points (46, 118, and 139 °C at 1 atm, respectively[1]) of these compounds suggest that monomeric structures are present in the solid phase and presumably in the liquid phase as well. The physical behavior of diarylzinc compounds also suggests that oligomerization does not occur. Their solubility in apolar solvents such as benzene is high, and melting points are moderate (diphenylzinc 107 °C, di-*o*-tolylzinc 70 °C, di-*m*-tolylzinc 53 °C, di-*p*-tolylzinc 168 °C, vs diphenylmercury 216 °C).[1,21,22] Although diarylzinc compounds in general[1] and diphenylzinc in benzene in particular[23] have been shown to be monomeric, we have determined the degree of association of diphenylzinc in *n*-hexane, as this solvent is the least likely one to compete with the presumably weak intermolecular forces between monomeric Ph_2Zn units. By the method of stationary isothermal distillation,[24] diphenylzinc was found to be monomeric ($i = [Ph_2Zn]_{formal}:[Ph_2Zn]_{osmometric} = 1.04 \pm 0.02$ at $[Ph_2Zn] = 0.001\text{–}0.005$ M; the solubility of diphenylzinc in *n*-hexane is 0.015 M). This illustrates that the inter-

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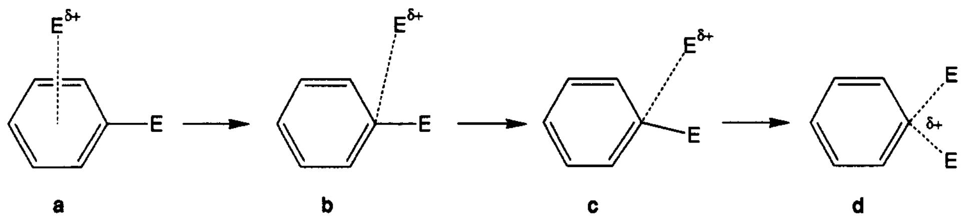

Figure 3. Successive stages in aryl bridging.

action between the two Ph_2Zn units is very weak indeed and is confined to the solid state. So far, multicenter bonding between zinc and carbon in diorganylzinc compounds has only been found in crystal structures of some cyclopentadienyl derivatives.[5,9]

Against this background, our dimeric structure for diphenylzinc is quite surprising. Clearly, generalizations from known structures are dangerous: the phenyl group in $[Ph_2Zn]_2$ bridges in a special manner that is facilitated by the aromatic sp^2 π hybridization of the ipso carbon. This carbon atom is bonded in a normal way to one of the zinc atoms by σ bonding, the angle between the Zn–C bond and the plane of the aromatic ring being rather small. The other zinc atom interacts from a direction nearly perpendicular to the aromatic plane, like an attacking electrophile, with the p orbital of the ipso carbon. This type of aryl group bridging was found earlier in compounds with heterometallic M–(μ-Ar)–M′ bridges (M′ = lithium, M = less electropositive metal). In these anionic complexes, M is σ-bonded to the ipso carbon close to its normal sp^2 position; the strongly electrophilic lithium atoms interact mainly with the aromatic π orbital at the ipso carbon. Two relevant examples are $Li(\mu\text{-}Ph)_2Mg(\mu\text{-}Ph)_2Mg(\mu\text{-}Ph)_2Li\cdot 2TMEDA$[25] and $Au_2Li_2[C_6H_4CH_2NMe_2]_4$;[26] the former also has a central homometallic Mg_2Ph_2 ring, which is only slightly asymmetric (Mg–ipso carbon distances of 2.286 (3) and 2.329 (3) Å). Homometallic M–(μ-Ph)–M complexes, as known for organoaluminum compounds (e.g. Al_2Ph_6)[27] and many organolithium compounds,[28] normally display symmetric phenyl bridges. At present, we are investigating the structures of simple oligomeric diarylmagnesium compounds, and in the future, we hope to discuss their aryl group bridging behavior.

As pointed out above, the unsymmetrical bridging of the μ-phenyl group has certain elements in common with an electrophilic aromatic substitution, although it must be pointed out that an essential difference is the fact that the bridging phenyl group *does not* show any signs of the bond distortion expected for a Wheland intermediate. Nevertheless, it would be of interest to investigate the influence of para substituents on the degree of bridging unsymmetry. In our $[Ph_2Zn]_2$ dimer, we encounter an early stage (Figure 3b) en route to the fully symmetrical μ-bridging mode (Figure 3d). Electron-donating substituents may be expected to shift the structure toward an intermediate situation (Figure 3c). In view of the recent availability of MNDO and AM1 parameters for zinc,[29,30] this problem is also accessible to theoretical investigation.

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Registry No. Ph_2Hg, 587-85-9; $[Ph_2Zn]_2$, 127398-99-6; Ph_2Zn, 1078-58-6.

Supplementary Material Available: Tables of anisotropic thermal parameters, all H atom parameters, bond lengths, bond angles, and torsion angles (5 pages); a listing of observed and calculated structure factor amplitudes (28 pages). Ordering information is given on any current masthead page.

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