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The unusual solid state structures of the pentasubstituted bis(cyclopentadienyl)zinc compounds bis(pentamethylcyclopentadienyl)zinc and bis(tetramethylphenylcyclopentadienyl)zinc

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Abstract

The replacement of all hydrogen atoms of $\text{Zn}(\text{C}_5\text{H}_5)_2$ by methyl groups causes a major change in the solid state structure. Whereas $\text{Zn}(\text{C}_5\text{H}_5)_2$ is polymeric in the solid state, an X-ray diffraction study of $\text{Zn}(\text{C}_5\text{Me}_5)_2$ has shown it to be a monomer, with one η^5 - and one η^1 -bonded ring. The crystals are monoclinic, space group $P2_1/n$ with unit cell a 8.70(4), b 7.88(5), c 14.64(8) Å, β 102.1(2)°, $Z = 2$. The structure is disordered.

The crystal structure of $\text{Zn}(\text{C}_5\text{Me}_4\text{Ph})_2$ has been studied in more detail. The compound crystallizes in the monoclinic space group $P2_1/a$, with unit cell a 8.086(1), b 17.640(2), c 8.823(1) Å, β 93.70(2)°, $Z = 2$. Anisotropic full-matrix least-squares refinement with 1693 observed reflections and 158 parameters converged at $R_F = 0.0621$. This compound is also monomeric. The zinc atom is disordered between two equivalent sites. In each site it is η^1 -bonded to one ring and η^5 to the other.

Introduction

We have recently reported the synthesis and crystal structure determinations of a number of cyclopentadienyl derivatives of the group 12 metals zinc, cadmium, and

mercury, viz. $\text{Zn}(\text{C}_5\text{H}_5)_2$ [1], $\text{Cd}(\text{C}_5\text{H}_5)_2 \cdot 2\text{py}$ [2], $\text{Hg}(\text{C}_5\text{H}_5)_2$ [3], and $\text{Zn}(\text{C}_{13}\text{H}_9)_2 \cdot 2\text{THF}$ [4] (C_{13}H_9 = fluorenyl). Together with Haaland we have studied the structure of $\text{Zn}(\text{C}_5\text{Me}_5)_2$ and $\text{Zn}(\text{C}_5\text{H}_4\text{SiMe}_3)_2$ in the gas phase [5].

The large differences between the chemistry of zinc and cadmium on the one hand and that of mercury on the other [6] are reflected in the cyclopentadienyl derivatives of these compounds. $\text{Zn}(\text{C}_5\text{H}_5)_2$ and $\text{Cd}(\text{C}_5\text{H}_5)_2$ form coordination polymers in the solid state and dissolve only in strongly coordinating solvents, forming stable coordination complexes. In these complexes, as well as in the pure compounds, the metal–cyclopentadienyl interaction is largely ionic. $\text{Hg}(\text{C}_5\text{H}_5)_2$, on the other hand, is monomeric in the solid. The crystal structure shows that the mercury–cyclopentadienyl interaction is covalent, and we have been unable to prepare stable coordination complexes of this compound.

The introduction of substituents into the cyclopentadienyl groups may change the situation. Although $\text{Zn}(\text{C}_5\text{H}_4\text{Me})_2$, $\text{Zn}(\text{C}_5\text{H}_4\text{-Bu})_2$, bis(indenyl)zinc [$\text{Zn}(\text{C}_9\text{H}_7)_2$], and bis(fluorenyl)zinc [$\text{Zn}(\text{C}_{13}\text{H}_9)_2$] are thought from their insolubility and involatility to be coordination polymers in the solid state [4,7], others, e.g. $\text{Zn}(\text{C}_5\text{H}_4\text{SiMe}_3)_2$ and $\text{Zn}(\text{C}_5\text{Me}_5)_2$, are sufficiently volatile to be sublimed and are soluble in apolar solvents [5]. Molecular weight measurements showed both compounds to be monomeric in benzene over a large concentration range.

The replacement of a cyclopentadienyl by a pentamethylcyclopentadienyl ligand gives rise to striking structural changes, particularly in the case of main group cyclopentadienyl compounds [8]. These changes arise from steric and electronic effects: the pentamethylcyclopentadienyl ligand is much larger, and the electron-releasing effects of the five methyl groups increase the electron density and hence the effective basicity of the filled ring MO's. Both effects generally stabilize the substituted with respect to the unsubstituted compound.

To investigate how these effects would influence the structure and properties of zinc derivatives, we have studied the synthesis and the solid state and solution structures of $\text{Zn}(\text{C}_5\text{Me}_5)_2$ and $\text{Zn}(\text{C}_5\text{Me}_4\text{Ph})_2$.

Results and discussion

Bis(pentamethylcyclopentadienyl)zinc was prepared by a published method [5], involving the reaction of pentamethylcyclopentadienylpotassium, itself prepared from pentamethylcyclopentadiene and potassium in THF, with dry zinc chloride in THF. Bis(tetramethylphenylcyclopentadienyl)zinc was prepared in essentially the same way starting from phenyltetramethylcyclopentadiene.

In the gas phase bis(pentamethylcyclopentadienyl)zinc is monomeric [5]. The zinc is bonded to one pentamethylcyclopentadienyl ligand in an η^5 bonding mode and in an η^1 bonding mode to the other. The structure is best described as an open-faced sandwich, i.e. one derived from a ferrocene-type structure by translating one of the two rings sideways. The η^5 -bonded ring is symmetrically bonded to zinc. The monohapto bonded ring refined best with a diene structure of this ring. The angle of the ring plane with the C–Me bond of the carbon bonded to zinc is indicative of an sp^3 -character of that carbon atom and thus of a covalent zinc–ring interaction. This is, however, contradicted by the angle between the ring plane and the zinc–carbon bond, i.e. 84° . For covalent zinc–ring interaction a much smaller angle of 54° (half the value of a tetrahedral angle) would be expected [2,3].

Table 1

¹H^a and ¹³C NMR data of Zn(C₅Me₅)₂ and Zn(C₅Me₄Ph)₂

Zn(C ₅ Me ₅) ₂	¹ H	1.98(s, 15H)
	¹³ C ^b	11.05, 111.62
Zn(C ₅ Me ₄ Ph) ₂	¹ H	1.88(s, 6H) 1.98(s, 6H) ^c
	¹³ C ^d	10.04, 11.05 (methyl groups) 108.98(γ), 116.72(β), 118.16(α) (cyclopentadienyl ring) 124.85(p), 127.54(m), 129.87(o), 137.15(i) (phenyl ring)

^a Measured in C₆D₆ at 200 MHz at 298 K, δ in ppm relative to external SiMe₄. ^b Measured in toluene-*d*₈ at 125 MHz at 198 K, δ in ppm relative to external SiMe₄. ^c The aromatic protons give a complex pattern of multiplets between 7.31 and 7.93 ppm; s: singlet. ^d Measured in C₆D₆ at 50.32 MHz at 298 K, δ in ppm relative to external SiMe₄; α, β, γ: positions relative to the carbon atom bearing the phenyl substituent; p; *para*, m: *meta*, o: *ortho*, i: *ipso*.

In contrast to the parent compound Zn(C₅H₅)₂, bis(pentamethylcyclopentadienyl)zinc dissolves very well in apolar solvents and is monomeric. In apolar solvents it probably adopts an η⁵,η¹-structure, as in the gas phase and in the solid state (vide infra). Low temperature ¹H NMR spectra (200 MHz, -100 °C, toluene-*d*₈), showed one singlet, at 1.98 ppm, and the ¹³C NMR spectra (125 MHz, -100 °C, toluene-*d*₈) only two signals, at 11.05 and 111.62 ppm. In a static η⁵,η¹-structure at least 5 signals would be expected in the ¹H NMR spectrum, and the ¹³C NMR spectra should show at least 8 different signals. If we assume an η⁵,η¹-structure, as found in the solid state, then obviously two different fluxional processes, which are fast on the NMR timescale, render all ring atoms equal. The first is a fast 1,5-sigmatropic shift of the monohapto bonded ring, while the second probably involves a fast exchange between the η¹- and η⁵-hapticity of both rings. To slow down these exchanges we prepared Zn(C₅Me₄Ph)₂, since its lower symmetry might result in an increase in the activation energy for both processes, which might thus become detectable by NMR spectroscopy. Variable temperature NMR studies on this compound, however, gave the same result as found for Zn(C₅Me₅)₂ (NMR data are given in Table 1). This indicates that the energy barriers are very low indeed, probably of the order of 1–5 kJ/mole, as for several other substituted metallocenes [9].

Crystal structures of Zn(C₅Me₅)₂ and Zn(C₅Me₄Ph)₂

Single crystals of Zn(C₅Me₅)₂ are easily obtained by either crystallization from apolar solvents or by slow vacuum sublimation. They are, however, extremely sensitive towards oxygen and moisture and readily deformed by mechanical forces. Manipulation of the crystals, necessary for sampling, usually made them amorphous. We were, however, able to isolate a single crystal of rather poor quality, and to conduct a crystal structure investigation.

The solution and refinement of the structure was hampered by two facts. The poor quality of the crystal allowed only a restricted number of reflections to be measured, and the total structure appeared to be disordered. The disorder of the zinc atom between two crystallographically equivalent sites results in a disorder in the cyclopentadienyl rings in such a way that the carbon atoms of one of the disordered molecules are placed exactly between those of a second molecule. Using a number of constraints, we succeeded in obtaining the overall molecular structure

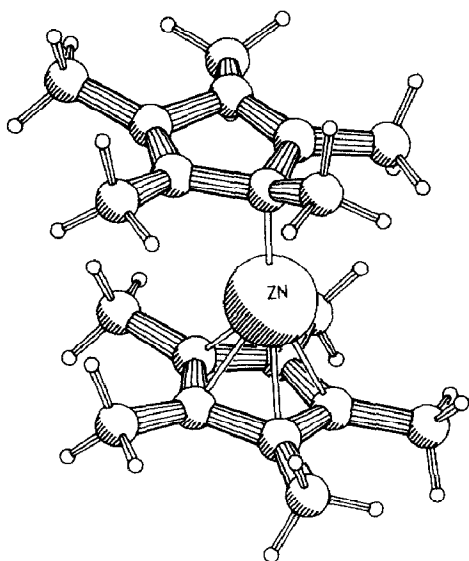


Fig. 1. View of the structure of $\text{Zn}(\text{C}_5\text{Me}_5)_2$. The molecule is disordered over a crystallographic inversion centre. Only one of the disordered molecules is shown.

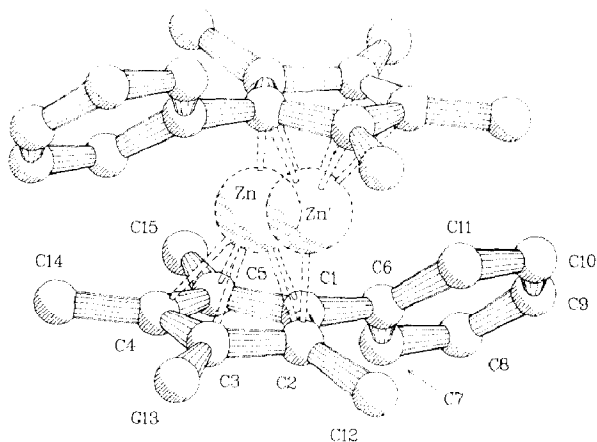


Fig. 2. View of the molecular structure of $\text{Zn}(\text{C}_5\text{Me}_4\text{Ph})_2$ with the adopted atom numbering. H atoms have been omitted for clarity. The zinc sites, indicated by dashed lines, are related by a crystallographic inversion centre.

presented in Fig. 1. In view of the above mentioned problems it is not possible to discuss the structure in detail. The η^5, η^1 -bonding mode of the pentamethylcyclopentadienyl rings is, however, unequivocal.

In order to study the bonding in $\text{Zn}(\text{C}_5\text{Me}_4\text{R})_2$ compounds in more detail we carried out an X-ray structural study of $\text{Zn}(\text{C}_5\text{Me}_4\text{Ph})_2$. It was expected that the induced asymmetry in the ring system would prevent the disorder found in $\text{Zn}(\text{C}_5\text{Me}_5)_2$. Good quality, rod-shaped single crystals were obtained by slow cooling of a hexane solution of $\text{Zn}(\text{C}_5\text{Me}_4\text{Ph})_2$.

The structure consists of the packing of two molecules in a monoclinic unit cell. The molecular structure together with the numbering scheme is given in Fig. 2 and bonding distances and bond-angles in Table 2.

As in $\text{Zn}(\text{C}_5\text{Me}_5)_2$, the molecule is located over an inversion centre. The two parallel flat $\text{C}_5\text{Me}_4\text{Ph}$ rings in the molecule are crystallographically equivalent and enclose one disordered zinc atom that occupies two crystallographically equivalent sites. This places the zinc atom at positions corresponding to η^5 - and η^1 -coordination to both rings. The two phenyl groups are rotated $46.72(18)^\circ$ with respect to the cyclopentadienyl ring plane. The introduction of the phenyl groups did, indeed, inhibit disorder in the position of the cyclopentadienyl rings. Unfortunately, the disorder of the zinc atoms is still present and this means that the observed C–C bond distances in the cyclopentadienyl rings are the average of those in centrally bonded (η^5) and in peripherally bonded (η^1) rings. A similar type of disorder has been reported for $\text{Be}(\text{C}_5\text{H}_5)_2$ [10].

However, it is possible to estimate the true C–C bond distances in the mono-hapto-bonded ring of each $\text{Zn}(\text{C}_5\text{Me}_4\text{Ph})_2$ molecule. First we assume that the C–C

Table 2

Bond distances (Å) and angles (°) for the non-hydrogen atoms of $\text{Zn}(\text{C}_5\text{Me}_4\text{Ph})_2$

<i>Distances</i>			
Zn–C(1)	2.210(3)	C(3)–C(4)	1.411(4)
Zn–C(2)	2.093(3)	C(3)–C(13)	1.502(4)
Zn'–C(2)	2.094(3)	C(4)–C(5)	1.415(4)
Zn–C(3)	2.168(3)	C(4)–C(14)	1.514(4)
Zn–C(4)	2.268(3)	C(5)–C(15)	1.507(4)
Zn–C(5)	2.299(3)	C(6)–C(7)	1.389(5)
C(1)–C(2)	1.446(4)	C(6)–C(11)	1.400(5)
C(1)–C(5)	1.400(4)	C(7)–C(8)	1.410(6)
C(1)–C(6)	1.480(4)	C(8)–C(9)	1.361(7)
C(2)–C(3)	1.437(4)	C(9)–C(10)	1.360(7)
C(2)–C(12)	1.506(4)	C(10)–C(11)	1.388(5)
<i>Angles</i>			
C(1)–Zn–C(2)' ^a	149.4(1)	C(2)–C(3)–C(4)	107.6(2)
C(2)–Zn–C(2)'	151.7(1)	C(2)–C(3)–C(13)	124.7(3)
C(2)'–Zn–C(3)	146.4(1)	C(4)–C(3)–C(13)	127.6(3)
C(2)'–Zn–C(4)	141.7(1)	Zn–C(4)–C(3)	67.7(2)
C(2)'–Zn–C(5)	143.1(1)	Zn–C(4)–C(5)	73.1(2)
Zn–C(1)–C(2)	66.1(1)	Zn–C(4)–C(14)	125.9(2)
Zn–C(1)–C(5)	75.4(2)	C(3)–C(4)–C(5)	109.0(2)
Zn–C(1)–C(6)	125.5(2)	C(3)–C(4)–C(14)	126.3(3)
C(2)–C(1)–C(5)	108.3(2)	C(5)–C(4)–C(14)	124.6(3)
C(2)–C(1)–C(6)	124.8(3)	Zn–C(5)–C(1)	68.5(2)
C(5)–C(1)–C(6)	126.9(3)	Zn–C(5)–C(4)	70.8(2)
Zn–C(2)–C(1)	74.8(2)	Zn–C(5)–C(15)	123.5(2)
Zn–C(2)–C(3)	73.2(2)	C(1)–C(5)–C(4)	108.3(2)
Zn–C(2)–C(12)	135.0(2)	C(1)–C(5)–C(15)	126.6(3)
Zn'–C(2)–C(1)	92.3(2)	C(4)–C(5)–C(15)	125.0(3)
Zn'–C(2)–C(3)	88.5(2)	C(1)–C(6)–C(7)	120.6(3)
Zn'–C(2)–C(12)	106.7(2)	C(1)–C(6)–C(11)	120.9(3)
C(1)–C(2)–C(3)	106.8(2)	C(7)–C(6)–C(11)	118.5(3)
C(1)–C(2)–C(12)	125.7(3)	C(6)–C(7)–C(8)	119.7(4)
C(3)–C(2)–C(12)	123.7(2)	C(7)–C(8)–C(9)	119.6(4)
Zn–C(3)–C(2)	67.5(2)	C(8)–C(9)–C(10)	121.9(5)
Zn–C(3)–C(4)	75.4(2)	C(9)–C(10)–C(11)	119.2(4)
Zn–C(3)–C(13)	126.4(2)	C(6)–C(11)–C(10)	121.0(3)

^a (') Indicates symmetry operation: $1-x, -y, -z$.

distances in the pentahapto-bonded ring are all the same, and equal to the mean of the average C–C distances, i.e. 1.422(9) Å. The bond distances in the monohapto-bonded ring are then estimated by subtracting this mean value from twice the value of each individual C–C distance. The following bond lengths are then obtained: C(1)–C(2) 1.470, C(2)–C(3) 1.452, C(3)–C(4) 1.400, C(4)–C(5) 1.408, and C(5)–C(1) 1.378 Å. It appears that the longest C–C distances originate from C(2), indicating partial sp^3 character of this carbon atom as a result of its monohapto bonding to zinc. Both the observed and the estimated values deviate from those expected for a diene-like structure.

The interaction of Zn with the monohapto-bonded ring comprises two very long (non-bonding) Zn–C distances (3.112(3) and 3.066(3) Å), two intermediate (non-bonding) Zn–C distances (2.592(3) and 2.509(3) Å) and one short (bonding) Zn–C

distance of 2.094(3) Å. The latter distance compares very well with the Zn–C distances found for the η^1 -bonded cyclopentadienyl groups in $Zn_4Ni_2(C_5H_4R)_6$ clusters, viz. 2.08 Å (R = t-Bu) and 2.06 Å (R = SiMe₃) [7]. The two intermediate Zn–C distances can be regarded as originating from the molecular geometry, and do not imply a bonding interaction.

In $Zn(C_5Me_4Ph)_2$, the pentahapto-bonded ring has Zn–C distances in the range 2.093(3) to 2.299(3) Å; these are all bonding. This irregularity in the η^5 -bonding is also evident from a ring-slippage of 0.197 Å (The ring-slippage is defined as the distance between the ring centroid and the perpendicular projection of the metal atom on the least-squares plane).

The hybridization of the C(2) atom is neither pure sp^3 nor pure sp^2 . On one hand, the partial sp^3 character of C(2) is well illustrated by the deviations from the ring plane of the different substituents. C(14) lies in the ring plane while C(6), C(13), and C(15) deviate only little from this plane (angles between ring plane and C–C bonds: 3.0, 5.6, and 3.6°, respectively). The angle between the C(2)–C(12) bond and the ring plane, however, is 15.6° in the observed ring. So, in the imaginary isolated η^1 case it may be as large as 30°. On the other hand, the angle which the η^1 -Zn–C(2) bond makes with the plane of the ring indicates that C(2) has appreciable sp^2 character. The value of this angle (87.38(13)°) is close to the 90° expected for the interaction with the π -orbital of an sp^2 hybridized carbon atom.

These pentasubstituted bis(cyclopentadienyl)zinc compounds are the second example of metallocenes having one η^5 - and one η^1 -metal-bonded cyclopentadienyl ring. So far this bonding mode has only been observed for the first elements of groups 2 (Be) and 12 (Zn). A number of studies on main-group metallocenes has shown that metal–cyclopentadienyl interactions that are predominantly ionic, usually give rise to the formation of either polymeric structures or of regular sandwich compounds, whereas compounds with more covalently bonded cyclopentadienyl groups have either regular sandwich structures or structures with σ -bonded cyclopentadienyl groups [3,11–14]. The present η^5, η^1 -coordination can be regarded as intermediate between the above mentioned extreme forms, reflecting the balance between ionic and covalent zinc–cyclopentadienyl interactions. The monomeric nature of these species is most probably the result of the electronic and steric effects of the substituents, both of which render aggregation less favourable.

Experimental

All experiments were carried out under dry oxygen-free nitrogen by standard Schlenk techniques. Solvents were dried and distilled from sodium benzophenone ketyl prior to use. NMR spectra were recorded on Bruker AC 500 and AC 200P spectrometers. $Zn(C_5Me_5)_2$ was prepared by a published method [5], as was 2,3,4,5-tetramethylcyclopentene-2-one-1 [15].

$Zn(C_5Me_4Ph)_2$

1-Phenyl-2,3,4,5-tetramethylcyclopentadiene-1.3. To 650 ml of a 1.4 molar solution (190 mmol) of phenylmagnesium bromide in diethyl ether, kept at 0°C, was added during 3 h 84 g (610 mmol) of 2,3,4,5-tetramethylcyclopentene-2-one-1 in 200 ml of diethyl ether. After 8 h stirring at room temperature, the solution was boiled

under reflux for 3 h. The excess of the Grignard reagent was destroyed with 30 ml of isopropanol and the mixture was added to 500 ml of water. Concentrated hydrochloric acid was added until both layers were clear. The water layer was separated and extracted twice with 100 ml of diethyl ether. The combined ethereal layers were washed twice with 100 ml of water and dried over sodium sulphate. The solvent was removed in vacuo, and vacuum distillation of the residue yielded 72.5 g (360 mmol, 60% yield) of pale yellow, liquid C_5Me_4PhH (b.p. 75–77 °C, 0.2 torr).

1-Phenyl-2,3,4,5-tetramethylcyclopentadienylpotassium. A solution of 12 g (60 mmol) of phenyltetramethylcyclopentadiene in 30 ml of THF was added during 30 min to a warm (60 °C) suspension of 3.9 g (100 mmol) of finely divided potassium in 80 ml of THF. Stirring and heating were continued until the hydrogen evolution had ceased. The solution was decanted from the excess of potassium and evaporated to dryness in vacuo. The remaining solid was washed three times with 50 ml of pentane and the residue was dried in vacuo to yield 12.0 g of pure, white $K(C_5Me_4Ph)$ (51 mmol, 85% yield).

Bis(1-phenyl-2,3,4,5-tetramethylcyclopentadienyl)zinc. To a solution of 9.3 g (39 mmol) of $K(C_5Me_4Ph)$ in 50 ml of THF was slowly added 19.5 ml of a 1 molar solution of dry zinc chloride in diethyl ether. The mixture was stirred under reflux for 2 h and the potassium chloride then removed by means of centrifugation and washed twice with 25 ml of THF. The combined solutions were evaporated to dryness in vacuo. The solid residue was extracted with three 50 ml portions of hexane. The combined hexane solutions were evaporated to dryness to yield 7.3 g of pure, white $Zn(C_5Me_4Ph)_2$ (15.7 mmol, 80%). Single crystals were obtained by crystallisation from hexane. NMR data are given in Table 1, elemental analysis data: Found: C, 77.56; H, 7.46; Zn, 13.97. $C_{15}H_{17}Zn$ calcd.: C, 78.33; H, 7.45; Zn, 14.21%.

Structure determination and refinement of $Zn(C_5Me_4Ph)_2$

A colourless rod-shaped crystal suitable for an X-ray structure determination was mounted under nitrogen in a Lindemann-glass capillary and transferred to an Enraf–Nonius CAD-4F diffractometer for data collection. Crystal data and details of the structure determination are given in Table 1. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 12 reflections in the range $10.8 < \theta < 16^\circ$. The unit cell parameters were checked for the presence of higher lattice symmetry [16]. Data were corrected for Lp and a linear decay of 5.2% during the 132 h of X-ray exposure time and merged into a unique set with a consistency index (on F) of 3.25%. Standard deviations as obtained by counting statistics were increased according to an analysis of the excess variance of the three reference reflections: $\sigma^2(I) = \sigma_{cs}^2(I) + (0.042I)^2$ [17]. Space group $P2_1/a$ was determined from the systematic extinctions: $h0l$: $h = 2n + 1$ and $0k0$: $k = 2n + 1$. The structure was solved with direct methods (SHELXS86) [18], the solution with the best figure of merit showed the disordered Zn atom and most of the C atoms. The remaining non-H atoms were located from subsequent difference Fourier maps. Refinement on F was carried out by full matrix least squares techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. H-atoms were introduced at calculated positions (C–H 0.98 Å) and included in the refinement riding on their carrier atom. All H atoms were refined with one common isotropic thermal parameter (U 0.127(3) Å²). Weights were introduced in

Table 3
Crystal data and details of the structure determination

<i>(a) Crystal data</i>		
Formula	Zn(C ₅ Me ₄ Ph) ₂	Zn(C ₅ Me ₅) ₂
Mol. wt.	459.98	335.84
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>a</i> (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.086(1), 17.640(2), 8.823(1)	8.70(4), 7.88(5), 14.64(8)
β (°)	93.70(2)	102.1(2)
<i>V</i> (Å ³)	1255.8(3)	981(9)
<i>Z</i>	2	2
<i>D</i> _(calc) (g cm ⁻³)	1.216	1.137
<i>F</i> (000)	488	360
μ (cm ⁻¹)	14.3 (Cu <i>K</i> _α)	12.7 (Mo <i>K</i> _α)
Crystal size (mm)	0.42 × 0.16 × 0.13	0.25 × 0.30 × 0.10
<i>(b) Data collection</i>		
θ_{\min} , θ_{\max} (°)	2.5, 70.0	1.4, 20.0
Radiation	Cu <i>K</i> _α (Ni-filtered), 1.54184 Å	Mo <i>K</i> _α (Zr-filtered), 0.71073 Å
Scan type	$\omega/2\theta$	ω
$\Delta\omega$ (°)	0.50 + 0.35 tan θ	0.60 + 0.35 tan θ
Hor. and vert. aperture (mm)	3.0, 4.0	2.0, 3.0
Dist. cryst. to detector (mm)	173	173
Reference reflections	132, 1 $\bar{5}$ 0, 1 $\bar{3}$ 1	0 $\bar{1}$ 1, 00 $\bar{2}$, 01 $\bar{1}$, 002
Data set	<i>h</i> - 9 : 9; <i>k</i> - 21 : 21; <i>l</i> - 10 : 10	<i>h</i> - 8 : 8; <i>k</i> - 7 : 0; <i>l</i> 0 : 14
Total data	9360	1012
Total unique data	2374	917
Observed data	1693 (<i>I</i> > 2.5 σ (<i>I</i>))	373 (<i>I</i> > 2.0 σ (<i>I</i>))
<i>(c) Refinement</i>		
No. of refined parameters	158	50
Weighting scheme	$w = 1.0/\sigma^2(F)$	$w = 1$
Final <i>R</i> , <i>wR</i> , <i>S</i>	0.0621, 0.0515, 0.65	0.16, 0.17, 3.69
(Δ/σ) _{max} in final cycle	0.044	0.04
min., max. resd. dens. e/Å ³	-0.31, 0.21	-0.43, 0.40

the final refinement cycles, convergence was reached at $R = 0.0621$. Five low order reflections with $F_o \ll F_c$ were excluded from the final refinement calculations. A final difference Fourier synthesis reveals residual densities between 0.21 and -0.31 e/Å³ indicating the absence of disorder within the ligands. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 4.

Structure determination of Zn(C₅Me₅)₂

X-ray data were collected on an Enraf-Nonius CAD-4F diffractometer for a transparent colourless crystal mounted under nitrogen in a Lindemann glass capillary. The crystal reflected poorly and showed structured reflection profiles. Crystal data and details of the structure determination are given in Table 3. Unit cell parameters were determined from the θ -values of 15 reflections with $4 < \theta < 7^\circ$. The space group, *P*2₁/*n*, was determined from the observed systematic extinctions. Data were corrected for Lp and for a linear decay of 8% during 13 h of X-ray exposure time. The structure was solved by Patterson and Fourier methods and

Table 4

Fractional atom coordinates and equivalent isotropic thermal parameters with esd's in parentheses for $\text{Zn}(\text{C}_5\text{Me}_4\text{Ph})_2$. The Zn atom is disordered over two equivalent positions related by the symmetry operation $1-x, -y, -z$.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a (Å ²)
Zn	0.5132(1)	0.02225(6)	0.0360(1)	0.0725(5)
C(1)	0.7180(3)	-0.0274(2)	0.1814(3)	0.050(1)
C(2)	0.7414(3)	-0.0323(2)	0.0206(3)	0.055(1)
C(3)	0.7616(3)	0.0440(2)	-0.0324(3)	0.058(1)
C(4)	0.7433(3)	0.0930(2)	0.0917(4)	0.058(1)
C(5)	0.7166(3)	0.0492(2)	0.2222(3)	0.054(1)
C(6)	0.7038(4)	-0.0934(2)	0.2834(4)	0.059(1)
C(7)	0.7960(5)	-0.0967(2)	0.4217(4)	0.080(2)
C(8)	0.7793(6)	-0.1596(3)	0.5181(5)	0.104(2)
C(9)	0.6764(7)	-0.2175(3)	0.4729(6)	0.117(3)
C(10)	0.5856(6)	-0.2161(2)	0.3377(6)	0.104(2)
C(11)	0.5998(4)	-0.1544(2)	0.2418(4)	0.076(2)
C(12)	0.7998(4)	-0.1013(2)	-0.0612(4)	0.076(1)
C(13)	0.8088(4)	0.0648(2)	-0.1890(3)	0.083(2)
C(14)	0.7523(5)	0.1787(2)	0.0890(4)	0.086(2)
C(15)	0.6819(5)	0.0811(2)	0.3754(3)	0.078(1)

$$^a U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

Table 5

Final coordinates and equivalent isotropic thermal parameters and their esd's in parentheses for $\text{C}_{20}\text{H}_{30}\text{Zn}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} or U (Å ²)
Zn	0.059(2)	0.072(2)	0.019(1)	0.113(6)
C(10)	0.239(4)	-0.219(5)	0.139(2)	0.12(1)
C(11)	0.313(4)	0.044(5)	0.051(2)	0.070(8)
C(12)	0.277(4)	0.104(5)	-0.043(2)	0.070(8)
C(13)	0.174(4)	-0.015(5)	-0.097(2)	0.070(8)
C(14)	0.147(4)	-0.149(5)	-0.037(2)	0.070(8)
C(15)	0.233(4)	-0.112(5)	0.054(2)	0.070(8)
C(16)	0.418(4)	0.131(5)	0.132(2)	0.12(1)
C(17)	0.336(4)	0.265(5)	-0.078(2)	0.12(1)
C(18)	0.106(4)	-0.002(5)	-0.200(2)	0.12(1)
C(19)	0.046(4)	-0.302(5)	-0.066(2)	0.12(1)
C(20)	-0.19(1)	0.310(7)	-0.095(4)	0.12(1)
C(21)	-0.321(7)	0.028(5)	-0.071(2)	0.070(8)
C(22)	-0.291(6)	-0.097(6)	0.004(3)	0.070(8)
C(23)	-0.200(9)	-0.024(7)	0.080(3)	0.070(8)
C(24)	-0.148(3)	0.146(5)	0.059(3)	0.070(8)
C(25)	-0.224(8)	0.159(6)	-0.040(3)	0.070(8)
C(26)	-0.38(1)	-0.028(8)	-0.170(3)	0.12(1)
C(27)	-0.396(9)	-0.248(7)	0.001(4)	0.12(1)
C(28)	-0.17(1)	-0.081(8)	0.180(3)	0.12(1)
C(29)	-0.13(1)	0.298(8)	0.122(5)	0.12(1)

found to be disordered over an inversion centre. The structure was refined with a group constraint on the $\eta^5\text{-C}_5\text{Me}_5$ ligand and soft bond constraints on the $\eta^1\text{-C}_5\text{Me}_5$ ligand in order to avoid unreasonable ring geometries. Hydrogen atoms were introduced at calculated positions. Only the Zn atom was refined with anisotropic thermal parameters, all other atoms with three additional common isotropic thermal parameters. Final refined parameters are given in the supplementary material.

Neutral atom scattering factors were taken from ref. 19 and corrected for anomalous dispersion [20]. All calculations performed with SHELX76 [21] and the EUCLID package [22] (geometrical calculations and illustrations) on a MicroVAX-II computer.

The fractional and final atom coordinates are given in Tables 4 and 5. Supplementary data (all positional and thermal parameters, bond lengths, bond angles, and a listing of structure factors) are available from A.L.S.

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