# Synthesis and Structure of Half-Sandwich Zincocenes

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Dedicated to Professor Alfonso Castañeiras on the Occasion of his 65th Birthday

**Abstract.** Half-sandwich zinc complexes ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)ZnR have been prepared for R= Me, 2; Et, 3; Mes, 4 and Ph, 5, by the conproportionation reaction of Zn(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub> and the corresponding ZnR<sub>2</sub> reagent. The new compounds have been fully characterized by spectroscopy and in the cases of 2 and 4 by X-ray crystallography. Since the reaction of Zn(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub> and ZnEt<sub>2</sub> yields 3, together with the known dizincocene Zn<sub>2</sub>( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>, the rearrangements of the

## Introduction

Organozinc reagents are an important family of organometallic compounds that find numerous applications in synthesis [1-3]. Alkyl and aryl zinc derivatives, in addition to possessing a distinguished history [4], are widely used as hydrocarbyl transfer reagents in a variety of transmetallation reactions [1]. Related derivatives containing cyclopentadienyl ligands, namely zincocenes ZnCp<sub>2</sub>' (Cp' stands as a general representation for C<sub>5</sub>H<sub>5</sub> or any substituted cyclopentadienyl group) exhibit interesting structural features since they contain almost parallel cyclopentadienyl groups with one  $\eta^5$ - and one  $\eta^1$ -Cp' rings, in the so-called slipped sandwich geometry [5]. It is therefore somewhat surprising that information on the corresponding half-sandwich structures  $(\eta^5$ -Cp')ZnR is sparse and dates back to about twenty to forty five years ago. Thus, the ethyl and phenyl derivatives were prepared in 1960 by the reaction of ZnCl<sub>2</sub> with  $Mg(C_2H_5)Br$  and  $C_5H_6$  [6] (an alternative, high-yield synthesis of  $(\eta^5-C_5H_5)Zn(C_2H_5)$ , consisting in the conproportionation of Zn(C5H5)2 and Zn(C2H5)2, was later provided [7]), while the related methyl compound ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)ZnCH<sub>3</sub> was obtained from Zn(CH<sub>3</sub>)I and NaC<sub>5</sub>H<sub>5</sub> [8].

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It appears that only the latter compound has been characterized by diffraction methods. In the crystal it is a polymer consisting of a puckered chain of zinc atoms [8] each bound to a terminal methyl group and to two bridging cyclopentadienyl units, with coordination between  $\eta^2$  and  $\eta^3$ . The compound is monomeric in benzene and also in the gas phase [9], with a relatively strong Zn–Me bond of 1.903(12) Å and weaker Zn- $\eta^5$ -C<sub>5</sub>H<sub>5</sub> interactions of *ca* 2.28 Å.

related zincocenes ZnCp<sub>2</sub>' and ZnEt<sub>2</sub> were investigated, with the

result that only the half-sandwich  $(\eta^5-Cp')ZnEt$  derivatives (Cp'=

 $C_5Me_4SiMe_3$  (6);  $C_5Me_4CMe_3$  (7) and  $C_5Me_4H$  (8)) were produced.

Keywords: Zinc; Metallocenes; Sandwich complexes; Solid-state

Following previous studies on the structural properties of zincocenes containing the bulky  $C_5Me_4CMe_3$ , and  $C_5Me_4SiMe_3$  ligands [10] we set out to prepare half-sandwich complexes of type ( $\eta^5$ -Cp')ZnR for different cyclopentadienyl groups. As discussed in detail somewhere else [11], attempts to obtain ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Zn(C<sub>2</sub>H<sub>5</sub>) led unexpectedly to a mixture of this product and Zn<sub>2</sub>( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>, the first compound with a Zn–Zn bond. Here we wish to report the synthesis and structural characterization of half-sandwich compounds ( $\eta^5$ -Cp')ZnR for various combinations of the cyclopentadienyl ligand (C<sub>5</sub>Me<sub>5</sub>, C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>, C<sub>5</sub>Me<sub>4</sub>CMe<sub>3</sub> and C<sub>5</sub>Me<sub>4</sub>H) and of the hydrocarbyl group R (Me, Et, Ph, Mes).

#### **Results and Discussion**

As mentioned briefly in the Introduction, a 1:1 mixture of  $Zn(C_5H_5)_2$  and  $ZnEt_2$  reacts at 60 °C to give almost pure  $(\eta^5-C_5H_5)ZnEt$  in quantitative yield [7]. In agreement with this result, the room temperature reaction of  $Zn(C_5Me_5)_2$  (1a), with  $ZnMe_2$  in  $Et_2O$  as the solvent proceeds in accord with Eq. (1), to give the expected complex  $(\eta^5-C_5Me_5)ZnMe$  (2), in almost quantitative yield (by <sup>1</sup>H NMR). At variance with this result, the analogous reaction

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Scheme 1 Reaction of 1a with  $ZnR_2$  in  $Et_2O$  which leads to a mixture of two compounds.

of **1a** with ZnEt<sub>2</sub>, which is also fast at room temperature, yields a mixture of two compounds, the expected half-sandwich derivative ( $\eta^{5}$ -C<sub>5</sub>Me<sub>5</sub>)ZnEt (**3**) and the unforeseen [11] dizincocene Zn<sub>2</sub>( $\eta^{5}$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub> (Scheme 1). The bis(mesityl) complex ZnMes<sub>2</sub> (Mes = 2,4,6-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>) behaves like ZnMe<sub>2</sub> and provides only the half-sandwich compound **4**, as shown in Eq. 1. However Zn(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> has behaviour akin to ZnEt<sub>2</sub> and provides also a mixture of the half-sandwich product **5** and the dizincocene Zn<sub>2</sub>( $\eta^{5}$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub> (Scheme 1).

$$Zn(C_5Me_5)_2 + ZnR_2 \rightarrow 2 (\eta^5 - C_5Me_5)ZnR$$
(1)  

$$1a \qquad 2 R = Me 
$$4 R = Mes$$$$

As discussed elsewhere [11], generation of the metalmetal bonded zincocene in the reactions of **1a** with ZnEt<sub>2</sub> and ZnPh<sub>2</sub> is competitive with formation of the respective half-sandwich products **3** and **5**, when ether solvents are employed. However, hydrocarbon solvents prevent formation of Zn<sub>2</sub>( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub> and direct the syntheses towards the half-sandwich compounds **3** and **5**. Thus, **1a** and ZnEt<sub>2</sub> combine in pentane at -60 °C to afford **3** as the exclusive reaction product. It is likely that the route leading to **2**–**5** involves the intermediacy of binuclear species similar to those that participate in Schlenk-type equilibria (Scheme 2).

To complete these studies the analogous reactions of  $Zn(C_5Me_4SiMe_3)_2$  (1b),  $Zn(C_5Me_4CMe_3)_2$  (1c) and  $Zn(C_5Me_4H)_2$  (1d) with  $ZnEt_2$ , have been investigated (Eq. (2)). Originally, these reactions were intended to ascertain if generation of dimetallocenes  $Zn_2(\eta^5-C_5Me_4R)_2$  derived from the above cyclopentadienyl ligands could be possible, but as shown in Eq. 2 only the half-sandwich products  $(\eta^5-C_5Me_4R)ZnEt$  were observed ( $C_5Me_4SiMe_3ZnEt$ , 6;  $C_5Me_4CMe_3ZnEt$ , 7;  $C_5Me_4HZnEt$ , 8).

$$Zn(C_5Me_4R)_2 + ZnEt_2 \xrightarrow{Pentane} 2 (\eta^5 - C_5Me_4R)ZnEt$$
(2)  

$$1b-1d \qquad 6 R = SiMe_3 
7 R = CMe_3$$

8 R = H

All new compounds are colourless or pale-yellow crystalline solids, very reactive toward oxygen and water, both in solution and in the solid state. They are soluble in common ether and hydrocarbon solvents and are fairly volatile. Thus, the methyl derivative **2** sublimes readily at 40 °C and 0.1 mbar, while the bulkier mesityl species **4** requires heating at 120 °C under high vacuum for sublimation  $(10^{-4} \text{ mbar})$ .

Spectroscopic characterization of 2 - 8 relies on <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} 1D and 2D NMR experiments. NMR spectra are simple and allow unequivocal solution characterization, complemented by X-ray studies on single crystals of 2 and 4 (see below). Thus, the <sup>1</sup>H NMR spectrum of 2 recorded in  $C_6D_6$  shows signals at  $\delta$  1.96 and -0.65, with intensity ratio 5:1, due respectively to the cyclopentadienyl and zincbound methyl protons. Corresponding  ${}^{13}C{}^{1}H$  resonances appear at  $\delta$  9.8 and -25.8, and are complemented by another resonance at  $\delta$  107.8 which arises from the ring carbon nuclei. This is a very characteristic value, that can be taken as diagnostic for  $(\eta^5-C_5Me_5)Zn$  coordination. Indeed the ethyl complex analogue 3 exhibits identical chemical shift while the corresponding resonance for the aryl derivatives 4 and 5 centres around 108.5 ppm (see Experimental Section). The NMR spectra of the ethyl derivatives 6-8 are also simple. For example, compound 6, with a  $C_5Me_4SiMe_3$ ligand, exhibits (<sup>1</sup>H NMR) the expected quartet at  $\delta$  0.37  $(Zn-CH_2CH_3)$  and triplet at 1.19 ppm  $(Zn-CH_2CH_3)$ ;  ${}^{3}J_{\rm HH}$  = 8.1 Hz) for the zinc-bonded ethyl group, together with singlets at  $\delta$  0.34, 1.90 and 2.12 (relative intensity 3:2:2) due to the  $-SiMe_3$  and -Me substituents of the ring. <sup>13</sup>C{<sup>1</sup>H} resonances for the ring carbon atoms at  $\delta$  98.2 (*C*-SiMe<sub>3</sub>) and 115.1 and 117.6 can be taken as a clear indication of  $(\eta^5-C_5Me_4SiMe_3)$  coordination to zinc.

As mentioned above, confirmation of the proposed structures for 2 - 8 has been obtained by solid-state X-ray studies carried out with compounds 2 and 4. The structure of the mesityl derivative 4 exhibits disorder of the C<sub>5</sub>Me<sub>5</sub> ring over two sets of positions with refined occupancies of 0.67 and 0.33 (see Experimental Part). Since there are no relevant features in this structure it is not further discussed. Instead we concentrate on the structure of 2 (Figure 1) and in the comparison of the structural parameters of this complex with those of the parent ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)ZnMe (Figure 2), as obtained from gas electron diffraction [9].

The molecules of **2** feature in the solid state the expected  $(\eta^5-C_5Me_5)ZnMe$  structure, characterized by  $Zn-Cp^*_{centr.}$  and  $Zn-CH_3$  distances of 1.90 and 1.94 Å, respectively, and by a linear  $Cp^*_{centr.}-Zn-Me$  arrangement (177.4°). The Zn-C distances to the ring carbon atoms concentrate



Scheme 2 Possible mechanism for the formation of compounds 2-5.



**Figure 1** ORTEP drawing of compound **2**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity.



**Figure 2** Comparison between structures of  $(C_5H_5)ZnMe$  (a) determined by GED and  $(C_5Me_5)ZnMe$  (b) determined by XRD.

within the very narrow range of 2.24-2.27 Å, in marked contrast with corresponding  $Zn-C(\eta^5)$  distances to the  $\eta^5$ -ring of the slipped-sandwich  $(\eta^5-Cp')Zn(\eta^1-Cp')$  structures of known zincocenes [5]. For the latter complexes there are remarkable irregularities, as found for example in  $Zn(C_5Pr_4^{i}H)_2$ , where Zn-C distances vary between 1.99 and 2.51 Å [5d] and to a lesser extent in  $Zn(C_5Me_4Ph)_2$  (2.09 to 2.30 Å) [5c]. Even in  $Zn(C_5Me_4SiMe_3)_2$ , where the  $Zn(\eta^5-C_5Me_4SiMe_3)$  coordination is fairly regular, Zn-C distances vary between 2.15 and 2.32 Å [10].

With respect to the Zn–Me moiety of compound 2 its length of 1.94 Å is comparable to that found in ZnMe<sub>2</sub> (1.930(2) Å by gas electron diffraction [9]; 1.945 Å, computed value from DFT calculations [12]). This bond length is significantly shorter than the Zn–C distance to the  $\eta^1$ ring of the slip-sandwich structures of zincocenes (formally this geometry may be considered as a half-sandwich structure), with the exception of Zn(C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>. The latter compound has a geometry close to  $\eta^5/\eta^1(\sigma)$  and it is characterized by a Zn-C distance of 1.953(3) Å, somewhat shorter than the Zn–C separations to the  $\eta^1$ -ring found in the slip-sandwich structures of Zn(C<sub>5</sub>Pr<sub>4</sub><sup>i</sup>H)<sub>2</sub> (1.99 Å, [5d] and Zn(C<sub>5</sub>Me<sub>4</sub>Ph)<sub>2</sub> (2.09 Å, [5c]).

As shown in Figure 2 the  $Zn-C(\eta^5)$  bond lengths have comparable values in  $(\eta^5-C_5H_5)ZnMe$  and  $(\eta^5-C_5Me_5)ZnMe$ , indicating that in these complexes substitution of the hydrogen atoms of  $C_5H_5$  by Me groups does not alter significantly the strength of the  $Zn-C(\eta^5)$  bonds. The same conclusion stems from the comparison of the  $Zn-Cp'_{centr.}$  distances of  $1.93(C_5H_5)$  and  $1.90 \text{ Å} (C_5Me_5)$ . The difference in both the  $Zn-C(\eta^5)$  and the  $Zn-Cp'_{centr.}$ distances just discussed, although too small to allow any conclusions to be drawn, point into the same direction, namely, somewhat stronger  $(\eta^5-Cp')-Zn$  interaction for the better electron-donor  $C_5Me_5$  ring.  $Zn-CH_3$  distances in the two compounds differ by 0.04 Å, being longer for compound **2** of the permethylated cyclopentadienyl ligand. This might indicate somewhat higher *trans* influence of  $C_5Me_5$ as compared with  $C_5H_5$ .

#### **Experimental Part**

#### General methods and instrumentation

All preparations and manipulations were carried out under oxygenfree argon using conventional Schlenk [13] and glovebox techniques. Solvents were rigorously dried and degassed before use [14].  $Zn(C_5Me_5)_2$ , [5c]  $ZnPh_2$  [15] and  $ZnMes_2$  [16] were prepared following the procedures described in the literature while  $Zn(C_5Me_4SiMe_3)_2$ ,  $Zn(C_5Me_4Bu^{t})_2$  and  $Zn(C_5Me_4H)_2$  were obtained as described [17]. Microanalyses were obtained at the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla). NMR spectra were recorded on Bruker DPX-300, DRX-400 and DRX-500 spectrometers. The <sup>1</sup>H and <sup>13</sup>C resonances of the solvent were used as the internal standard, and the chemical shifts are reported relative to TMS.

## **Syntheses**

Although all new compounds have been isolated as crystalline or microcrystalline solids of spectroscopic purity, due to their high reactivity toward oxygen and water obtaining sufficiently accurate microanalytical data has proved difficult in some instances. However, as discussed in the text, characterization by NMR is complete and furthermore, the structures of two of the new compounds (**2** and **4**) have been authenticated by X-ray crystallography.

 $(C_5Me_5)ZnMe$  (2): Over a solution of 500 mg (1.5 mmol) of  $Zn(C_5Me_5)_2$  in pentane (20 mL) 0.75 mL (1.5 mmol) of a 2.0 M solution of  $ZnMe_2$  in toluene were added. The mixture was stirred at room temperature for 1 hour and the solvent was removed under vacuum to yield a white solid which can be purified by sublimation  $(10^{-1} \text{ mbar}, 40 \text{ °C})$  yielding colourless crystals (325 mg; 50 %). *Elemental analysis*:  $C_{11}H_{18}Zn$  (215.6); C 60.8 (calc. 61.3); H 8.5 (8.4) %.

<sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): -0.65 (s, 3H, ZnCH<sub>3</sub>), 1.96 (s, 15H, C<sub>5</sub>Me<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): -25.8 (ZnCH<sub>3</sub>), 9.8 (C<sub>5</sub>Me<sub>5</sub>), 107.8 (C<sub>5</sub>Me<sub>5</sub>).

 $(C_5Me_5)ZnEt$  (3): Over a solution of 335 mg (1 mmol) of  $Zn(C_5Me_5)_2$  in pentane (20 mL) 1 mL (1 mmol) of a 1.0 M solution of  $ZnEt_2$  in hexane were added. The mixture was stirred at -10 °C for 1 hour and the solvent was removed under vacuum to yield a colourless solid with spectroscopical purity (138 mg; 60 %).

<sup>1</sup>H NMR (300 MHz,  $C_6D_6$ , 25 °C, ppm): 0.38 (q, 2H,  $J_{HH} = 8$  Hz,  $ZnCH_2CH_3$ ), 1.19 (t, 3H,  $J_{HH} = 8$  Hz,  $ZnCH_2CH_3$ ), 1.98 (s, 15H,  $C_5Me_5$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz,  $C_6D_6$ , 25 °C, ppm): -8.2 ( $ZnCH_2CH_3$ ), 9.8 ( $C_5Me_5$ ), 12.9 ( $ZnCH_2CH_3$ ), 107.8 ( $C_5Me_5$ ).

Table 1Selected bond distances /Å and angles /° for 2.

Zn-Cp' <sub>centr</sub>	1.904(4)	C1-C2	1.438(5)
Zn-C1	2.262(4)	C2-C3	1.429(5)
Zn-C2	2.245(4)	C3-C4	1.424(5)
Zn-C3	2.243(4)	C4-C5	1.433(5)
Zn-C4	2.274(4)	C5-C1	1.433(5)
Zn-C5	2.276(4)	Cp' <sub>centr</sub> -Zn-C11	177.40(2)
Zn-C11	1.943(5)		

 $(C_5Me_5)ZnMes$  (4): 200 mg (0.6 mmol) of  $Zn(C_5Me_5)_2$  and 182 mg (0.6 mmol) of  $ZnMes_2$  were dissolved in diethyl ether (20 mL). The mixture was stirred at room temperature for 3 hours and the solvent was removed under vacuum to yield a white solid which can be purified by sublimation (10<sup>-4</sup> mbar, 120 °C) yielding colourless crystals (171 mg; 80 %). *Elemental analysis*:  $C_{19}H_{26}Zn$  (277.72); C 71.3 (calc. 71.4); H 8.2 (8.2) %.

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): 1.99 (s, 15H, C<sub>5</sub>*Me*<sub>5</sub>), 2.18 (s, 3H, ArC*H*<sub>3,para</sub>), 2,20(s, 6H, ArC*H*<sub>3,ortho</sub>), 6.8(s, 2H, Ar*H*<sub>meta</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): 10.2 (C<sub>5</sub>*Me*<sub>5</sub>), 21.2 (ArCH<sub>3,para</sub>), 28.7 (Ar-CH<sub>3,ortho</sub>), 108.2 (*C*<sub>5</sub>Me<sub>5</sub>), 126.0 (CH<sub>meta</sub>), 137.0 (CH<sub>3,*ipso*</sub>), 141.5 (CH<sub>3,para</sub>), 145.8 (CH<sub>3,meta</sub>).

 $(C_5Me_5)ZnPh$  (5): 620 mg (1.85 mmol) of  $Zn(C_5Me_5)_2$  and 406 mg (1.85 mmol) of  $ZnPh_2$  were dissolved in toluene (10 mL). The mixture was stirred at -20 °C for 2 hours and the solvent was removed under vacuum to yield compound 5 as a yellow solid (410 mg; 40 %).

<sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): 1.98 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 7.12–7.15 (3H, H<sub>aryl</sub>), 7.30-7.34 (2H, H<sub>aryl</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): 10.9 (C<sub>5</sub>Me<sub>5</sub>), 108.6 (C<sub>5</sub>Me<sub>5</sub>), 127.5 (C<sub>ortho</sub>), 127.9 (C<sub>meta</sub>), 140.2 (C<sub>para</sub>).

 $(C_5Me_4R)ZnEt$  (6 - 8): To a solution of  $Zn(C_5Me_4R)_2$  in pentane, a 1.0 M solution of  $ZnEt_2$  in hexane was added to afford a 1:1 mixture of the reagents. The mixture was stirred at -10 °C for 2-4hours and the solvent was removed under vacuum to yield the corresponding compound.

**6**: 119 mg (0.26 mmol) of  $Zn(C_5Me_4SiMe_3)_2$  in 10 mL of pentane and 0.26 mL (0.26 mmol) of  $ZnEt_2$  (45 mg; 58 %).

<sup>1</sup>**H** NMR (400 MHz,  $C_6D_6$ , 25 °C, ppm): 0.34 (s, 9H, Si $Me_3$ ), 0.37 (q, 2H,  $J_{HH} = 8.1$  Hz,  $ZnCH_2CH_3$ ), 1.19 (t, 3H,  $J_{HH} = 8.1$  Hz,  $ZnCH_2CH_3$ ), 1.90 (s, 6H,  $2CpCH_3$ ), 2.12 (s, 6H,  $2CpCH_3$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz,  $C_6D_6$ , 25 °C, ppm): -8.3 ( $ZnCH_2CH_3$ ), 1.4 ( $SiMe_3$ ), 10.0 ( $2C_pCH_3$ ), 12.9 ( $2C_pCH_3$ ) and  $ZnCH_2CH_3$ ), 98.2 ( $C_qSiMe_3$ ), 115.1 ( $C_qCH_3$ ), 117.6 ( $C_qCH_3$ ).

7: 96 mg (0.23 mmol) of  $Zn(C_5Me_4CMe_3)_2$  in 10 mL of pentane and 0.23 mL (0.23 mmol) of  $ZnEt_2$  (40 mg; 65 %). *Elemental analysis*:  $C_{19}H_{26}Zn$  (215.67); C 61.4 (calc. 61.3); H 8.5 (8.4) %.

<sup>1</sup>**H NMR** (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): 0.40 (q, 2H, J<sub>HH</sub> = 8.1 Hz, ZnCH<sub>2</sub>CH<sub>3</sub>), 1.23 (t, 3H, J<sub>HH</sub> = 8.1 Hz, ZnCH<sub>2</sub>CH<sub>3</sub>), 1.42 (s, 9H, CCH<sub>3</sub>), 1.95 (s, 6H, 2CpCH<sub>3</sub>), 2.18 (s, 6H, 2CpCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} **NMR** (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): -8.4 (ZnCH<sub>2</sub>CH<sub>3</sub>), 10.1 (2C<sub>p</sub>CH<sub>3</sub>), 12.9 (2C<sub>p</sub>CH<sub>3</sub>), 13.6 (ZnCH<sub>2</sub>CH<sub>3</sub>), 32.2 (CMe<sub>3</sub>), 107.0 (C<sub>q</sub>CH<sub>3</sub>), 110.2(C<sub>q</sub>CH<sub>3</sub>), 119.8 (C<sub>q</sub>Bu<sup>t</sup>).

**8**: 30 mg (0.1 mmol) of  $Zn(C_5Me_4H)_2$  in 5 mL of pentane and 0.1 mL (0.1 mmol) of  $ZnEt_2$  (13 mg; 60 %).

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): -0.30 (q, 2H, J<sub>HH</sub> = 8 Hz, ZnCH<sub>2</sub>CH<sub>3</sub>), 1.19 (t, 3H, J<sub>HH</sub> = 8 Hz, ZnCH<sub>2</sub>CH<sub>3</sub>), 1.95 (s, 6H, 2CpCH<sub>3</sub>), 1.99 (s, 6H, 2CpCH<sub>3</sub>), 5.50 (s, 1H, Cp-H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): -8.3 (ZnCH<sub>2</sub>CH<sub>3</sub>), 9.8 (2C<sub>p</sub>CH<sub>3</sub>), 11.7 (2C<sub>p</sub>CH<sub>3</sub>), 12.9 (ZnCH<sub>2</sub>CH<sub>3</sub>), 95.9 (C<sub>p</sub>-H), 108.6 (C<sub>q</sub>CH<sub>3</sub>), 112.5 (C<sub>q</sub>CH<sub>3</sub>).

#### Structure Determination

Crystal data for **2**:  $C_{11}H_{18}Zn$ ,  $M_w = 215.62$ , a single crystal of suitable size, colourless prism (0.31 x 0.27 x 0.25 mm<sup>3</sup>) from subli-



**Figure 3** ORTEP drawing for compound 4. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity. The  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> ring was observed disordered in two positions with refined occupancy factors of 0.67 and 0.33, where the Cp' rings are rotated 36°; one of them is also omitted for clarity.

 Table 2
 Selected bond distances /Å and angles /° for compound 4.

mation, coated with dry perfluoropolyether was mounted on a glass fiber and fixed in a cold nitrogen stream, 100(2) K, to the goniometer head. Monoclinic, space group  $P2_1/c$  (no.14), a =12.0761(9) Å, b = 14.3625(9) Å, c = 12.4260(9) Å,  $\beta = 90.636(2)^{\circ}$ ,  $V = 2155.1(3) \text{ Å}^3$ , Z = 8,  $\rho_{calcd} = 1.329 \text{ gcm}^{-3}$ ,  $\lambda(\text{Mo } \text{K}_{\alpha 1}) =$  $0.71073 \text{ Å}, \text{ F}(000) = 912, \mu = 2.226 \text{ mm}^{-1}. 21767 \text{ Reflections were}$ collected from a Bruker-Nonius X8Apex-II CCD diffractometer in the range 3.38<20<61.86° and 6437 independent reflections [R(int) = 0.0514] were used in the structural analysis. The data were reduced (SAINT) and corrected for Lorentz polarisation effects and absorption by multiscan method applied by SADABS [18, 19]. The structure was solved by direct methods (SIR-2002) [20] and refined against all F<sup>2</sup> data by full-matrix least-squares techniques (SHELXL97) [21] converged to final  $R_1 = 0.0535 [I > 2\sigma(I)]$ , and  $wR_2 = 0.2457$  for all data, with a Goodness-of-fit on F<sup>2</sup>, S = 1.059 and 229 parameters. Crystal data for 4:  $C_{19}H_{26}Zn$ ,  $M_w =$ 

319.77, a single crystal of suitable size, colourless prism (0.28 x 0.26 x 0.12 mm<sup>3</sup>) from sublimation, coated with dry perfluoropolyether was mounted on a glass fiber and fixed in a cold nitrogen stream, 100(2) K, to the goniometer head. Monoclinic, space group  $P2_1/c$ (no.14), a = 15.2130(7) Å, b = 8.5525(4) Å, c = 13.3227(6) Å,  $\beta =$ 97.439(2)°, V = 1718.82(14) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.236$  gcm<sup>-3</sup>,  $\lambda$ (Mo  $K_{\alpha 1}$  = 0.71073 Å, F(000) = 680,  $\mu$  = 1.418 mm<sup>-1</sup>. 13378 Reflections were collected from a Bruker-Nonius X8Apex-II CCD diffractometer in the range  $6.12 < 2\theta < 57.58^{\circ}$  and 4163 independent reflections [R(int) = 0.0257] were used in the structural analysis. Data reduction, solving and refinement was performed likewise for **2** converged to final  $R_1 = 0.0467 [I > 2\sigma(I)]$ , and to  $wR_2 = 0.1240$ for all data, with a Goodness-of-fit on  $F^2$ , S = 1.057 and 232 parameters. As discussed in the text, the structure of 4 is disordered (see Fig. 3 and table 2 that contains selected bond distances and angles). Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre no. CCDC 643972 and 643973. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (44) 01223 336033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

#### References

- (a) J. Boersma, in: Comprehensive Organometallic Chemistry, F. G. A. Stone, E. W. Abel, L. S. I. Hegedus (eds), Pergamon Press, Oxford 1982, Vol. 2. (b) P. O'Brien, in: Comprehensive Organometallic Chemistry, E. W. Abel, L. S. I. Hegedus, G. Wilkinson (eds), Pergamon Press, Oxford 1994, Vol. 3.
- [2] P. Knochel, P. Jones, Organozinc Reagents, Oxford Univ. Press, Oxford 1999.
- [3] (a) E. Negishi, N. F. Valente, M. Kobayashi, J. Am. Chem. Soc. 1980, 102, 3298. (b) H. Stadtmüller, R. Lentz, C. E. Turker, T. Stüdemann, W. Dörner, P. Knochel, J. Am. Chem. Soc. 1993, 115, 7027. (c) K. Yasui, Y. Goto, T. Yajima, Y. Tamiseki, K. Fugami, A. Tanaka, Y. Tamaru, Tetrahedron Lett. 1993, 34, 7691. (d) M. Yus, J. Gomis, Tetrahedron Lett. 2001, 42, 5721. (e) D.J. Ramón, M. Yus, Tetrahedron Lett. 1998, 39, 1239. (f) M. Yus, J. Gomis, Eur. J. Inorg. Chem. 2002, 1989.
- [4] E. Frankland, Annal. Chim. 1859, 111, 52.
- [5] (a) R. Blom, A. Haaland, J. Weidlein, J. Chem. Soc., Chem. Commun. 1985, 266. (b) R. Blom, J. Boersma, P. H. M. Bud-

zelaar, B. Fischer, A. Haaland, H. V. Volden, J. Weidlein, *Acta Chem. Scan.* **1986**, *A40*, 113. (c) B. Fischer, P. Wijkens, J. Boersma, G. van Koten, W. J. J. Smeets, A. L. Spek, P. H. M. Budzelaar, *J. Organomet. Chem.* **1989**, *376*, 223. (d) D. J. Burkey, T. P. Hanusa, *J. Organomet. Chem.* **1996**, *512*, 165.

- [6] W. Strohmeier, H. Ladsfeld, Z. Naturforsch. 1960, 15b, 332.
- [7] J. T. B. H. Jastrzebski, J. Boersma, G. van Koten, A. L. Spek, *Rec. Trav. Chim. Pais-Bas* 1988, 107, 263.
- [8] T. Aoyagi, H. M. M. Shearer, K. Wade, G. Whitehead, J. Organomet. Chem. 1978, 146, C29.
- [9] A. Haaland, S. Samdal, R. Seip, J. Organomet. Chem. 1978, 153, 187.
- [10] R. Fernandez, I. Resa, D. del Río, E. Carmona, E. Gutierrez-Puebla, A. Monge, *Organometallics* 2003, 22, 381.
- [11] (a) I. Resa, E. Carmona, E. Gutierrez-Puebla, A. Monge, *Science* 2004, 305, 1136. (b) A. Grirrane, I. Resa, A. Rodriguez, E. Carmona, E. Alvarez, E. Gutierrez-Puebla, A. Monge, A. Galindo, D. del Río, R. A. Andersen, *J. Am. Chem. Soc.* 2007, 129, 693.
- [12] A. Haaland, J. C. Green, G. S. McGrady, A. J. Downs, E. Gullo, M. J. Lyall, J. Timberlake, A. V. Tutukin, H. V. Volden, K. A. Ostby, *Dalton Trans.* 2003, 4356.
- [13] D. F. Shriver, *The Manipulation of Air-Sensitive Compounds*, Editorial Willey Interscience, **1986**.
- [14] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 2<sup>nd</sup> Edition; Pergamon Press: Oxford, **1980**.
- [15] D. K. Breitinger, W. A. Herrmann, Synthetic Methods of Organometallic and Inorganic Chemistry, Vol V, pag. 150, Thieme: New York, 1996.
- [16] (a) P. R. Sharp, D. Astruc, R. R. Schrock, J. Organomet. Chem. 1979, 182, 477. (b) W. Seidel, I. Bürger, Z. Anorg. Allg. Chem. 1981, 478, 166.
- [17] I. Resa, Ph D. Thesis, Univ. Sevilla 2006.
- [18] Bruker (2004). Apex 2, version 2.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- [19] Bruker (2001). SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- [20] M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, the program SIR2002. *J. Appl. Cryst.* 2003, *36*, 1103.
- [21] G. M. Sheldrick (1997) SHELXL97. University of Göttingen, Germany.