

## Dichlorobis(dibenzylamino)bis(tetrahydrofuran)zirconium(IV) toluene hemisolvate

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Received 13 November 2000

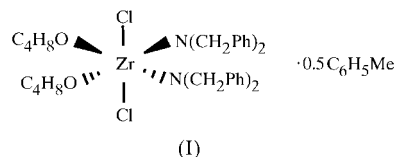
Accepted 21 February 2001

The title complex,  $[\text{ZrCl}_2(\text{C}_4\text{H}_8\text{O})_2(\text{C}_{14}\text{H}_{14}\text{N})_2] \cdot 0.5\text{C}_7\text{H}_8$ , was prepared in an unusual manner by utilizing  $[\text{Mg}\{\text{N}(\text{CH}_2\text{Ph})_2\}_2]$  as a ligand transfer reagent. The Zr atom lies in a distorted octahedral environment where steric repulsion from the large dibenzylamino ligands leads to a widening of the N—Zr—N angle  $[99.95(9)^\circ]$  and corresponding compression of other angles  $[\text{Cl—Zr—Cl } 160.95(3)^\circ$  and  $\text{O—Zr—O } 78.22(7)^\circ]$ . This distortion is compared with those found in the previously determined structures of the dimethylamino and diethylamino analogues.

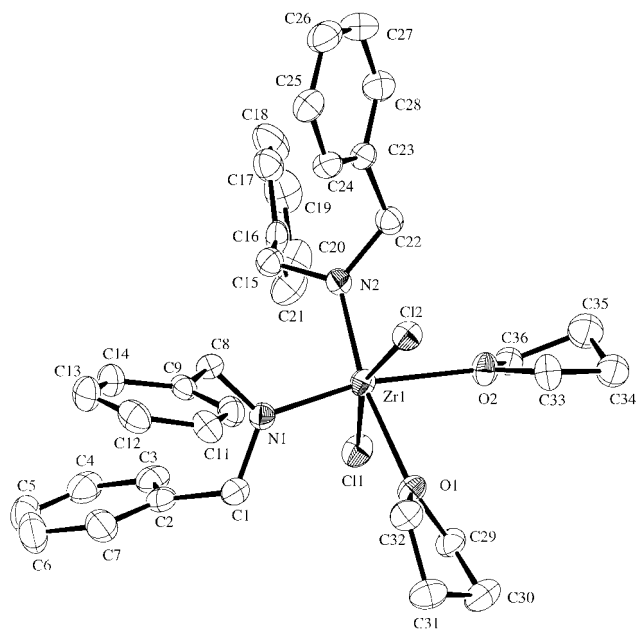
### Comment

Interest in zirconium complexes has risen in recent years due to their utility in a number of processes, most notably as catalysts in olefin polymerization (Gibson & Wass, 1999) and as precursors for chemical vapour deposition (Chiu & Huang, 1993). We have recently been interested in the ability of zirconium amides to catalyse ethylene polymerization (Armstrong *et al.*, 2000), and as part of this study, we have prepared and structurally characterized the complex  $[\{(\text{PhCH}_2)_2\text{N}\}_2\text{ZrCl}_2(\text{thf})_2]$ , (I) (thf is the tetrahydrofuran ligand), as a toluene hemisolvate. A search of the Cambridge Structural Database (Allen & Kennard, 1993) revealed only two complexes closely related to (I), namely  $[(\text{Me}_2\text{N})_2\text{ZrCl}_2(\text{thf})_2]$ , (II), and  $[(\text{Et}_2\text{N})_2\text{ZrCl}_2(\text{thf})_2]$ , (III) (Brenner *et al.*, 1995). Both of these complexes were formed by the ligand redistribution reaction of  $\text{ZrCl}_4$  with equimolar amounts of the appropriate tetraamide,  $\text{Zr}(\text{NR}_2)_4$ . In contrast, the synthesis of (I) was achieved by the treatment of  $\text{ZrCl}_4$  with the rather unusual reagent  $[\text{Mg}\{\text{N}(\text{CH}_2\text{Ph})_2\}_2]$  (Clegg *et al.*, 1997). Despite current interest in the ability of magnesium bis-amides to act as strong bases in deprotonation reactions (Henderson *et al.*, 2000; Allan *et al.*, 1999), this is, to our knowledge, the first example of using such compounds as ligand-transfer reagents.

The molecular structure of (I) is similar to those of (II) and (III) in that the Zr atom exists in a distorted octahedral environment with mutually *trans* chloro ligands  $[\text{Cl1—Zr1—Cl2 } 160.95(3)^\circ]$ , mutually *cis* amides  $[\text{N1—Zr1—N2 } 99.95(9)^\circ]$  and mutually *cis* thf ligands  $[\text{O1—Zr1—O2 } 78.22(7)^\circ]$ . It is obvious from these angles, and the others given in Table 1, that the distortion from an octahedral



geometry is steric in nature, with the angles involving the bulky amide ligands widening and the angles between the smaller ligands being compressed to compensate. A comparison with the corresponding distortions found for the  $\text{NMe}_2$  and  $\text{NEt}_2$  analogues, (II) and (III), is interesting. The Cl—Zr—Cl, N—Zr—N and O—Zr—O angles in (II) are  $163.14(3)$ ,  $98.37(12)$  and  $81.45(8)^\circ$ , respectively. These are, as expected, all closer to ideal octahedral values than those found for the bulkier (I). However, the corresponding values for (III) are  $163.11(10)$ ,  $101.5(3)$  and  $76.8(2)^\circ$ , respectively. These much greater distortions from octahedral geometry than found in (II) were explained by Brenner *et al.* (1995) as being due to the increased steric bulk of ethyl over methyl. As (I) shows values intermediate between those of (II) and (III) (despite its greater steric requirements), this raises the possibility that the observed large differences between (II) and (III) are not solely due to considerations of size, but result from a combination of intra- and intermolecular interactions and the disorder present in all the organic parts of (III). This is



**Figure 1**  
ORTEP (Johnson, 1976) view of (I) with atoms represented as 50% probability ellipsoids. H atoms, the toluene solvate and one of the disordered components have been omitted for clarity.

further supported in that the Cl—Zr—Cl angle of (III), which is not directly affected by disorder, shows the expected smaller distortion from 180° than that found in (I). Although the Zr—O distances are slightly asymmetrical [Zr1—O1 2.3158 (17) Å, Zr1—O2 2.3391 (19) Å], all the bond lengths found in (I) are unexceptional and both the N and O atoms have essentially planar coordination geometries. There is some peripheral disorder present. The toluene solvate is disordered about a crystallographic inversion centre and atoms C34, C35 and C36 of one of the thf ligands are also modelled over two sets of sites, with refined site-occupation factors of 0.462 (12) and 0.538 (12).

## Experimental

All manipulations were carried out under a dry oxygen-free argon atmosphere using standard Schlenk techniques. ZrCl<sub>4</sub> was purchased from Lancaster and used as received. [Mg{N(CH<sub>2</sub>Ph)<sub>2</sub>}<sub>2</sub>] was prepared as previously described (Clegg *et al.*, 1997). Toluene and THF were distilled over sodium and used directly from the still. ZrCl<sub>4</sub> (1 mmol) and [Mg{N(CH<sub>2</sub>Ph)<sub>2</sub>}<sub>2</sub>] (1 mmol) were placed in a Schlenk tube and toluene (10 ml) added. The mixture was stirred at ambient temperature for 16 h, THF (2 ml) was then added to the mixture and the remaining white solid was removed by filtration. Crystals suitable for X-ray analysis were produced by layering the yellow solution with hexane and cooling the mixture to 250 K for several weeks. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.81 (*d*, 4H, *o*-H), 7.23 (*t*, 4H, *m*-H), 7.11 (*t*, 2H, *p*-H), 4.91 (*s*, 4H, CH<sub>2</sub>Ph), 3.91 (*m*, 4H, OCH<sub>2</sub>), 1.26 p.p.m. (*m*, 4H, CH<sub>2</sub>—CH<sub>2</sub>O); <sup>13</sup>C NMR: 141.63 (*i*-C, Ph), 130.58 (*m*-C, Ph), 128.10 (*o*-C, Ph), 126.27 (*p*-C, Ph), 72.48 (OCH<sub>2</sub>), 54.43 (CH<sub>2</sub>Ph), 26.09 p.p.m. (CH<sub>2</sub>CH<sub>2</sub>O).

### Crystal data

[ZrCl <sub>2</sub> (C <sub>7</sub> H <sub>8</sub> O) <sub>2</sub> (C <sub>14</sub> H <sub>14</sub> N) <sub>2</sub> ] ·0.5C <sub>7</sub> H <sub>8</sub>	$D_x = 1.305 \text{ Mg m}^{-3}$
$M_r = 744.92$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 12920 reflections
$a = 29.2399 (4) \text{ \AA}$	$\theta = 2.9\text{--}27.5^\circ$
$b = 12.5188 (2) \text{ \AA}$	$\mu = 0.47 \text{ mm}^{-1}$
$c = 23.8447 (4) \text{ \AA}$	$T = 150 (2) \text{ K}$
$\beta = 119.6495 (6)^\circ$	Block, colourless
$V = 7585.5 (2) \text{ \AA}^3$	$0.20 \times 0.15 \times 0.12 \text{ mm}$
$Z = 8$	

### Data collection

Nonius KappaCCD diffractometer	5092 reflections with $I > 2\sigma(I)$
$\varphi$ and $\omega$ scans to fill Ewald sphere	$R_{\text{int}} = 0.054$
Absorption correction: multi-scan (Blessing, 1997)	$\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.910$ , $T_{\text{max}} = 0.946$	$h = -37 \rightarrow 37$
19 143 measured reflections	$k = -16 \rightarrow 16$
8596 independent reflections	$l = -30 \rightarrow 30$

### Refinement

Refinement on $F^2$	H atoms constrained
$R[F^2 > 2\sigma(F^2)] = 0.050$	$w = 1/[\sigma^2(F_o^2) + (0.0360P)^2]$
$wR(F^2) = 0.106$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.97$	$(\Delta/\sigma)_{\text{max}} = 0.001$
8596 reflections	$\Delta\rho_{\text{max}} = 0.52 \text{ e \AA}^{-3}$
406 parameters	$\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Zr1—N1	2.041 (2)	Zr1—O2	2.3391 (19)
Zr1—N2	2.047 (2)	Zr1—Cl2	2.4853 (8)
Zr1—O1	2.3158 (17)	Zr1—Cl1	2.5027 (8)
N1—Zr1—N2	99.95 (9)	O1—Zr1—Cl2	81.92 (5)
N1—Zr1—O1	90.25 (8)	O2—Zr1—Cl2	82.17 (5)
N2—Zr1—O1	169.26 (8)	N1—Zr1—Cl1	93.70 (7)
N1—Zr1—O2	168.22 (8)	N2—Zr1—Cl1	98.85 (7)
N2—Zr1—O2	91.70 (8)	O1—Zr1—Cl1	83.69 (5)
O1—Zr1—O2	78.22 (7)	O2—Zr1—Cl1	82.73 (5)
N1—Zr1—Cl2	98.76 (7)	Cl2—Zr1—Cl1	160.95 (3)
N2—Zr1—Cl2	93.15 (7)		

All H atoms were placed in calculated positions and were refined in riding mode. The C atoms of the toluene molecule and the C34—C35—C36 fragment of a tetrahydrofuran ligand were disordered over two sites and were refined isotropically. The H atoms of the methyl group of the toluene solvate were not included and indeed there is evidence that this methyl group is further disordered over at least two more sites. However, this has not been included in the model.

Data collection: DENZO (Otwinowski & Minor, 1997) and COLLECT (Hooft & Nonius, 1988); cell refinement: DENZO and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); software used to prepare material for publication: SHELXL97.

We thank the EPSRC National Crystallography Service at the University of Southampton for data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1128). Services for accessing these data are described at the back of the journal.

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