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trans-Dichloro-*cis*-bis(3,6-dimethylcarbazolyl)-*cis*-bis(tetrahydrofuran)zirconium(IV) benzene sesquisolvate

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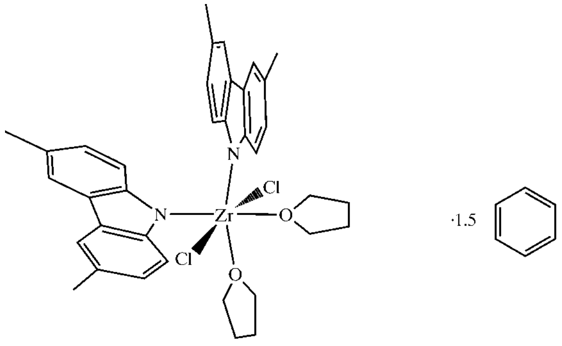
In the title compound, $[ZrCl_2(C_{14}H_{12}N)_2(C_4H_8O)_2]\cdot 1.5C_6H_6$, the Zr atom is pseudo-octahedral, with two Cl atoms in *trans* positions and two tetrahydrofuran molecules in *cis* positions. The two 3,6-dimethylcarbazolyl ligands are in *cis* positions and are canted with respect to one another. The two Zr—N distances are 2.1148 (18) and 2.1236 (18) Å, and the N—Zr—N angle is 95.08 (7)°. The title compound crystallizes as the benzene solvate, with one of the benzene molecules positioned on an inversion center.

Comment

Amide complexes of transition metals are known to display reactivity that is often unusual. This fact has been highlighted recently by the reduction of N_2 to NH_3 using a trisamide complex of Mo (Yandulov & Schrock, 2002, 2003). One of the major goals of inorganic chemistry has been attained with the application of the electronic properties of hard amide ligands, an area that has been reviewed recently (Cummins, 1998; Schrock, 1997*a*,*b*). In contrast, recent work by ourselves (Nygren *et al.*, 2003, 2004) and others (Riley *et al.*, 1998, 1999, 2001; Tanski & Parkin, 2003) has been based on the exploration of the chemistry of amide ligands in which the π interaction is uncertain with respect to the donation to the metal center. These amides with a lower π basicity (Tanski & Parkin, 2003) form a class of non-innocent ligands in coordination chemistry that differ from the non-innocent ligands described by Gray *et al.* (1967), in that the oxidation state is not uncertain, only the degree of electronic coupling between the π-donating ligating atom and the metal center. Although formally an *LX* ligand (Green, 1995), the carbazolyl ligand is related to the N-heterocyclic carbenes (Arduengo, 1999; Herrmann, 2002; Tulloch *et al.*, 2003), which are known to be almost pure σ donors, although in the case of carbazolyl there is some π basicity. In this structure report, we describe a neutral biscarbazolyl zirconium dichloride, *viz.* the title compound, (I), that will serve as a useful synthetic entrance into this area.

Carbazolyl complexes of transition metals that are σ-bound are rare (Lopez *et al.*, 2002); most of the known examples (Riley *et al.*, 1998, 1999, 2001) involve group 4B and 5B metals. A few biscarbazolyl structures are known for the group 4B metals (mostly containing titanium; Riley *et al.*, 2001). There are also a few known complexes for the group 5B metals (Riley *et al.*, 1999).



(I)

Recently, the crystal structures of (tetrahydrofuran)potassium *mer-trans*-tris(carbazolyl)dichloro(tetrahydrofuran)zirconate and tetrakis(tetrahydrofuran)lithium *mer-trans*-tris(carbazolyl)dichloro(tetrahydrofuran)zirconate have been reported (Nygren *et al.*, 2003, 2004).

The molecular structure of (I) (Fig. 1) consists of a pseudo-octahedral zirconium center bearing *trans* chloro ligands, *cis* carbazolyl moieties and *cis*-coordinated tetrahydrofuran (THF) molecules. Examination of the Cambridge Structural Database (Allen, 2002; Bruno *et al.*, 2002) reveals that this composition of the first coordination sphere, consisting of two

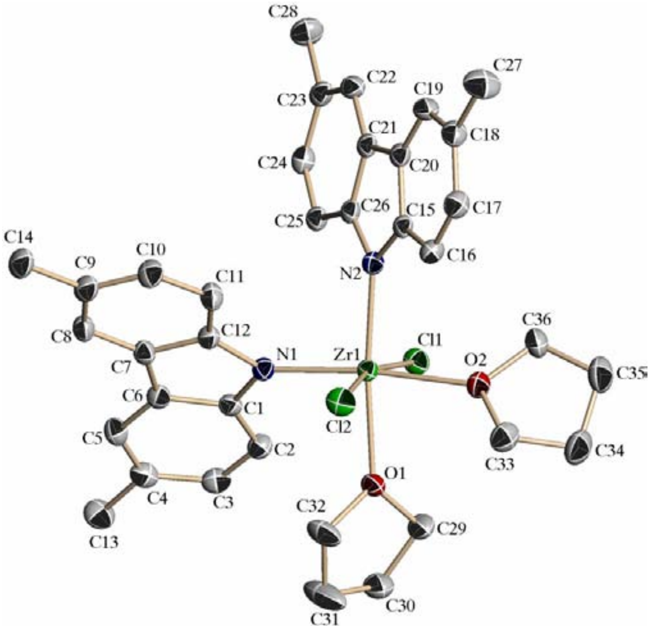


Figure 1
A view of the structure of (I), showing the atomic numbering scheme. All H atoms and solvent molecules have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

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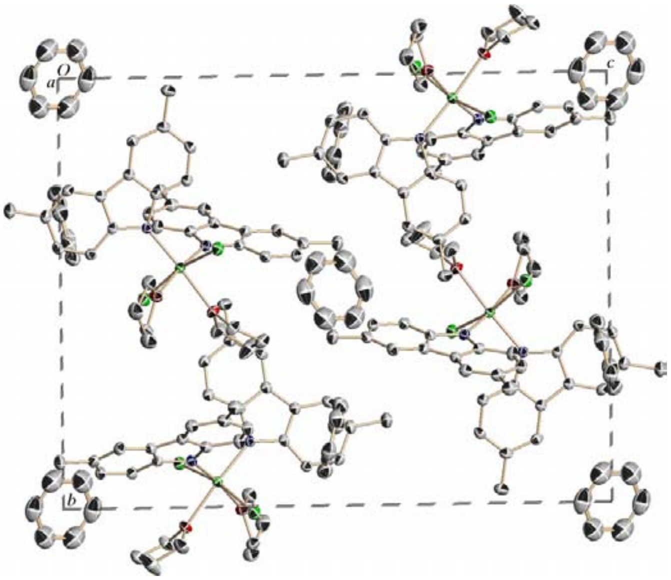

Figure 2
The crystal packing of (I), viewed along *a*. All H atoms have been omitted for clarity.

N atoms, two O atoms and two chloro ligands, is quite common for group 4B metals, and all bond lengths and angles in (I) (Table 1) are typical of those observed in zirconium complexes.

Examination of the intermolecular correlations reveals several interactions that are shorter than the sum of the van der Waals radii. Interestingly, the benzene molecules located at the cell corners do not participate in any of these short contacts, whereas the internal benzene molecules bridge the carbazolyl group of one molecule and the THF group coordinated to the Zr atom of another, *via* atoms H10, C38 and H35*A* (Fig. 2). Another long-range interaction pairs two molecules together through mutually *cis* interactions between atoms Cl2 and H27*B*. Although this does not constitute a strongly bonded dimer, these pairs of molecules then interact through shorter-range interactions between the coordinated THF group and the mutually *cis* aromatic systems of the carbazolyl moieties. A similar structural disposition is seen in tetrakis(tetrahydrofuran)lithium *mer-trans*-tris(carbazolyl)dichloro(tetrahydrofuran)zirconate (Nygren *et al.*, 2004). The final set of interactions occur between the methyl group (containing atom C14) and the aromatic ring of a neighboring molecule (atoms C21 and C26). The opposite methyl group on the same carbazolyl ligand is involved in a strong interaction with a carbazolyl ligand on a different zirconium center of a neighboring molecule [2.7420 (14) Å; Allen, 2002; Bruno *et al.*, 2002]. The range of distances for the intermolecular interactions is approximately 2.372–3.811 Å (Allen, 2002; Bruno *et al.*, 2002). Thus, a zigzag chain is formed in the *bc* plane throughout the extended lattice.

Experimental

Dropwise addition of dry THF to a mixture of $ZrCl_4$(s) (0.43 g, 0.0018 mol) and previously prepared carbazolyltetrahydrofuranlithium(s) (1.01 g, 0.0037 mol) at 195 K resulted in a slow reaction that, on warming to room temperature, afforded a yellow solution. After filtration, THF was evacuated and the product was washed with pentane. Benzene was added to the resulting compound, and large orange rectangular crystals formed spontaneously at room temperature over a period of one week. This compound was characterized by one- and two-dimensional ^{1}H and ^{13}C NMR spectroscopy at variable temperature in solution, and the spectroscopic data fully support formation of the title compound.

Crystal data

$[ZrCl_2(C_{14}H_{12}N)_2(C_4H_8O)_2]\cdot 1.5C_6H_6$
$M_r = 811.98$
Monoclinic, $P2_1/c$
$a = 10.200$ (3) Å
$b = 17.594$ (5) Å
$c = 22.760$ (7) Å
$\beta = 100.200$ (5)°
$V = 4020$ (2) Å^3
$Z = 4$
$D_x = 1.342$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 21 512 reflections
$\theta = 2.3$–26.5°
$\mu = 0.45$ mm^{-1}
$T = 173$ (2) K
Block, orange
0.30 × 0.18 × 0.17 mm

Data collection

Bruker SMART CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.891$, $T_{\max} = 0.927$
39 916 measured reflections
8342 independent reflections
6645 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 26.5°$
$h = -12 \rightarrow 12$
$k = -22 \rightarrow 22$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.085$
$S = 1.08$
8342 reflections
473 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0347P)^2 + 2.6992P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.041$
$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—Zr1	2.4473 (7)	N2—Zr1	2.1236 (18)
Cl2—Zr1	2.4413 (7)	O1—Zr1	2.2624 (15)
N1—Zr1	2.1148 (18)	O2—Zr1	2.2659 (15)
N1—Zr1—N2	95.08 (7)	Cl2—Zr1—Cl1	165.44 (2)
O1—Zr1—O2	82.83 (6)		

All H atoms were introduced at calculated positions and treated using a riding model [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C), and C—H = 0.98 (CH_3), 0.99 (CH_2) and 0.95 Å (aromatic)].

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1455). Services for accessing these data are described at the back of the journal.

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