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A doubly bridged isodicyclopentadienyl zirconium complex: bis{*N*-(3,5-dimethylphenyl)-*N*-[(η^5-isodicyclopentadien-2-yl)dimethylsilyl]amido-κN}zirconium(II) diethyl ether solvate

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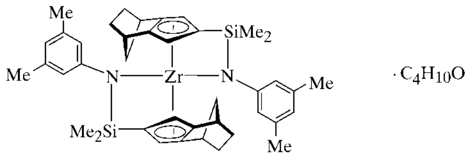
Transmetallation of the dilithium salt of (3,5-dimethyphenylamino)(isodicyclopentadienyl)dimethylsilane by treatment with zirconium tetrachloride in a 2:1 ratio leads to the substitution of all four chloride ligands. With the applied stoichiometry, the title complex, $[Zr(C_{20}H_{25}NSi)_2]\cdot C_4H_{10}O$, was obtained and crystallized from diethyl ether. X-ray diffraction characterization showed that both isodicyclopentadienyl ligands (alternatively called 4,5,6,7-tetrahydro-4,7-methano-1*H*-indene) are complexed to the metal on their *exo* face in a completely stereoselective manner and that they are η^5-bonded to the Zr atom.

Comment

'Constrained geometry' (CG) catalysts can be obtained *via* different methods. Group 4 ansa-monocyclopentadienyl–amido complexes can be synthesized with excellent results by the amine-elimination reaction (Hughes *et al.*, 1993; Herrmann & Morawietz, 1994; Carpenetti *et al.*, 1996). When use is made of the synthetic pathway first employed by Bercaw (Shapiro *et al.*, 1990, 1994) and then by Okuda (Okuda, 1990; Okuda *et al.*, 1995), the CG catalyst yield is strongly influenced by the degree of cyclopentadienyl (Cp) substitution. Unsubstituted Cp rings give ansa-Cp–amido complexes in very low yield, whereas reactions with substituted Cp rings are quite efficient. We have demonstrated previously that the classical half-sandwich synthetic strategy can be readily adapted to the preparation of isodicyclopentadienyl–amido–zirconium–dichloro complexes (Gentil *et al.*, 2000) by reaction with solid zirconium tetrachloride. In this paper, we report the preparation and structure of the complex bis{*N*-(3,5-dimethylphenyl)-*N*-[(η^5-isodicyclopentadien-2-yl)dimethylsilyl]amido-κN}zirconium(II) diethyl ether solvate, obtained by the use of high amido–dilithium salt concentrations relative to zirconium tetrachloride.



(I)

Complex (I) has approximate C_2 symmetry. The ligand has a constrained geometry, which is characterized by the small values of 94.46 (9) and 94.67 (9)°, respectively, for the N1—Si2—C3 and N2—Si1—C13 angles. Further evidence of the constrained nature of this ligand is seen in the displacement of each Si atom from its adjacent Cp ring; the angle between the Si1—C13 bond and its adjacent Cp ring is 25.8 (1)°, and the angle between the Si2—C3 bond and its adjacent Cp ring is 25.5 (1)°.

This Zr complex displays features characteristic of non-bridged isodicyclopentadienyl–zirconium complexes (Gallucci *et al.*, 1987; Gobley *et al.*, 1998). The *Cg*1—Zr—*Cg*2 angle of 134.17 (4)°, where *Cg*1 and *Cg*2 are the centroids of the C1–C5 and C11–C15 rings, respectively, is slightly larger than the corresponding angles in $(isodiCp)_2ZrCl_2$ (129.0°) and $(isodiCpPPh_2)_2ZrCl_2$ [129.02 (5)°], where isodiCp is isodicyclopentadienyl. The isodiCp ligands are found to be in a *gauche*-like configuration with respect to each other (Gobley *et al.*, 1998).

The metal–C_{ring} distances [2.461–2.623 (2) Å for atoms C1–C5 and 2.461–2.615 (2) Å for atoms C11–C15] are also larger than for the two above-mentioned isodicyclopentadienyl complexes. The shorter Zr—C_{ring} distances involve atoms C3 and C13, which are both bonded to Si atoms. These short distances are likely to be due to the constrained geometry of this ligand. To the best of our knowledge, the Zr—C1 and Zr—C15 distances of 2.623 (2) and 2.615 (2) Å, respectively, are the longest observed for Zr—C bonds in isodicyclopentadienyl complexes. Both the Cp—Zr—Cp angle and the Zr—C_{ring} distances are comparable with those in the doubly bridged amido spiro-metallocene $Zr[Cp\text{-}SiMe_2\text{-}NPh]_2$ reported by Herrmann *et al.* (1994).

As observed in all structures involving an isodicyclopentadienyl ligand with *exo* complexation, there is a slight bending in this ligand in (I) about the bond common to the Cp ring and the norbornane fragment, and this bending is in the *endo* direction. The dihedral angle between the least-squares planes defined by atoms C1–C5 and C1/C5/C6/C9 is 10.6 (1)°, while the angle between the planes defined by atoms C11–C15 and C11/C15/C16/C19 is 11.0 (1)°. These values are midway between those for an isodiCp half-sandwich zirconium complex [9.5 (1)° for *exo*-$isodiCpSiMe_2N\text{-}^tBuZr(CH_2SiMe_3)_2$ (Gentil *et al.*, 2000)] and a bis(isodiCp)zirconium dichloride

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complex [13.0 (3) and 14.1 (4)° for $(\text{isodiCpPPh}_2)_2\text{ZrCl}_2$ (Gobley *et al.*, 1998)].

The Zr—N bond lengths of 2.143 (2) Å for N1 and 2.135 (2) Å for N2 are longer than the Zr—N bond length of 2.086 (1) Å in the *exo*-isodiCpSiMe$_2$N-^{t}BuZr(CH$_2$SiMe$_3$)$_2$ complex (Gentil *et al.*, 2000), but are comparable with the Zr—N bond lengths of 2.142 (2) and 2.143 (2) Å in (η^5-C$_5$H$_4$-CHMe-NPh-κN)$_2$Zr (Kunz *et al.*, 2002), and the values of 2.137 (2) and 2.127 (2) Å in [η^5-C$_5$H$_4$-Si(Me)$_2$-NPh-κN]$_2$Zr (Herrmann *et al.*, 1994). The sums of the bond angles at the two N atoms are essentially 360° (*viz.* 360.0° for N1 and 359.9° for N2), which is indicative of trigonal-planar N atoms.

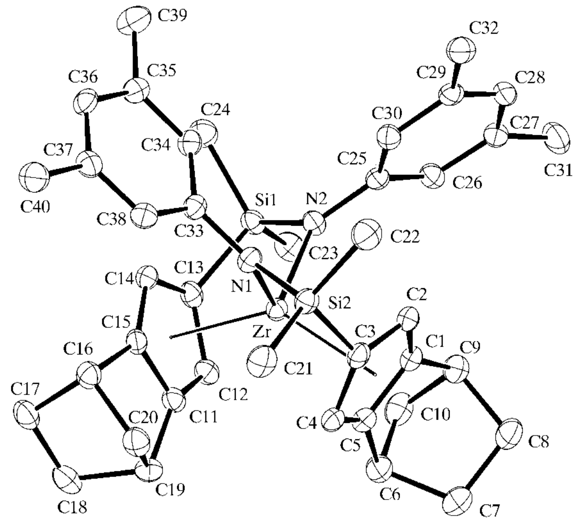

Figure 1

A view of the molecule of complex (I), with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

Experimental

All experiments were carried out under an argon atmosphere. The solvents were dried and distilled prior to use. (3,5-Dimethylphenylamino)(isodicyclopentadienyl)dimethylsilane was prepared according to published methods, using chloro(isodicyclopentadienyl)dimethylsilane (Gentil *et al.*, 2000) and solid lithium (3,5-dimethylphenyl)amine in diethyl ether. To a solution of (3,5-dimethylphenylamino)(isodicyclopentadienyl)dimethylsilane (3.04 mmol, 897 mg) in diethyl ether (15 ml) at 195 K was slowly added *n*-butyllithium (6.1 mmol, 3.8 ml of a 1.6 *M* solution in hexane). The mixture was allowed to warm to room temperature, after which it was refluxed overnight and then filtered. The pale-yellow precipitate was washed three times with diethyl ether and dried *in vacuo* (628 mg, 69%). The pale-yellow powder was then placed in diethyl ether (15 ml) and the suspension treated gradually with solid zirconium tetrachloride (1.05 mmol, 244 mg, 0.5 equivalents). The mixture was warmed to room temperature and stirred for 48 h; the resulting suspension was filtered off. Concentration of the filtrate and cooling to 253 K over a period of 2 d afforded colourless crystals of (I) (164 mg, 20% yield).

Crystal data

$[\text{Zr}(\text{C}_{20}\text{H}_{25}\text{NSi})_2]\cdot\text{C}_4\text{H}_{10}\text{O}$
$M_r = 780.34$
Triclinic, $P\overline{1}$
$a = 10.7036$ (2) Å
$b = 11.6479$ (2) Å
$c = 17.4618$ (3) Å
$\alpha = 70.848$ (1)°
$\beta = 78.069$ (1)°
$\gamma = 84.194$ (1)°
$V = 2010.81$ (6) Å^3
$Z = 2$
$D_x = 1.289$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9071 reflections
$\theta = 2.0$–27.5°
$\mu = 0.37$ mm^{-1}
$T = 150$ (2) K
Square plate, colourless
0.35 × 0.35 × 0.04 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
50 007 measured reflections
9121 independent reflections
7028 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.051$
$\theta_{\text{max}} = 27.5°$
$h = 0 \rightarrow 13$
$k = -14 \rightarrow 15$
$l = -21 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.077$
$S = 1.06$
9118 reflections
461 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2 + 1.2411P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} = 0.037$
$\Delta\rho_{\text{max}} = 0.51$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.33$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Zr—N2	2.135 (2)	C2—C3	1.435 (3)
Zr—N1	2.143 (2)	C3—C4	1.435 (3)
Zr—C13	2.461 (2)	C4—C5	1.417 (3)
Zr—C3	2.461 (2)	C5—C6	1.515 (3)
Zr—C4	2.499 (2)	C6—C7	1.556 (3)
Zr—C12	2.502 (2)	C6—C10	1.557 (3)
Zr—C14	2.544 (2)	C7—C8	1.551 (3)
Zr—C2	2.549 (2)	C8—C9	1.554 (3)
Zr—C5	2.575 (2)	C9—C10	1.542 (3)
Zr—C11	2.579 (2)	C11—C12	1.413 (3)
Zr—C15	2.615 (2)	C11—C15	1.413 (3)
Zr—C1	2.623 (2)	C11—C19	1.514 (3)
Si1—N2	1.733 (2)	C12—C13	1.440 (3)
Si1—C13	1.869 (2)	C13—C14	1.431 (3)
Si2—N1	1.728 (2)	C14—C15	1.401 (3)
Si2—C3	1.867 (2)	C15—C16	1.511 (3)
N1—C33	1.412 (3)	C16—C20	1.545 (3)
N2—C25	1.418 (3)	C16—C17	1.555 (3)
C1—C2	1.404 (3)	C17—C18	1.556 (3)
C1—C5	1.414 (3)	C18—C19	1.559 (3)
C1—C9	1.512 (3)	C19—C20	1.549 (3)
N2—Zr—N1	106.64 (7)	C9—C10—C6	95.5 (2)
N2—Si1—C13	94.67 (9)	C12—C11—C15	108.3 (2)
N1—Si2—C3	94.46 (9)	C12—C11—C19	143.2 (2)
C2—C1—C5	108.3 (2)	C15—C11—C19	106.6 (2)
C2—C1—C9	143.2 (2)	C11—C12—C13	108.0 (2)
C5—C1—C9	107.0 (2)	C14—C13—C12	106.4 (2)
C1—C2—C3	108.9 (2)	C15—C14—C13	108.7 (2)
C2—C3—C4	106.4 (2)	C14—C15—C11	108.5 (2)
C5—C4—C3	108.2 (2)	C14—C15—C16	142.6 (2)
C1—C5—C4	108.2 (2)	C11—C15—C16	107.4 (2)
C1—C5—C6	106.8 (2)	C15—C16—C20	100.3 (2)
C4—C5—C6	143.1 (2)	C15—C16—C17	104.4 (2)
C5—C6—C7	105.0 (2)	C20—C16—C17	99.8 (2)
C5—C6—C10	99.9 (2)	C16—C17—C18	103.5 (2)
C7—C6—C10	99.5 (2)	C17—C18—C19	104.1 (2)
C8—C7—C6	103.8 (2)	C11—C19—C20	100.4 (2)
C7—C8—C9	103.9 (2)	C11—C19—C18	104.9 (2)
C1—C9—C10	100.1 (2)	C20—C19—C18	99.1 (2)
C1—C9—C8	105.3 (2)	C16—C20—C19	95.8 (2)
C10—C9—C8	99.8 (2)		

Table 2
Selected geometric parameters (Å, °) involving Zr and the ring centroids.

*Cg*1 and *Cg*2 are the centroids of the C1–C5 and C11–C15 rings, respectively.

*Cg*1—Zr	2.2361 (10)	*Cg*2—Zr	2.2352 (10)
*Cg*1—Zr—*Cg*2	134.17 (4)	*Cg*2—Zr—N1	107.47 (6)
*Cg*1—Zr—N1	99.06 (6)	*Cg*2—Zr—N2	99.44 (6)
*Cg*1—Zr—N2	107.96 (6)		

Besides the Zr complex, the asymmetric unit of (I) contains a diethyl ether solvent molecule. The methyl group H atoms were added at calculated positions using a riding model, with $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(C). For each methyl group, the torsion angle which defines the orientation about the Si—C or C—C bond was refined. The remaining H atoms were included at calculated positions using a riding model, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C). Data integration was performed with *DENZO* (Otwinowski & Minor, 1997). Scaling and merging of the data were performed with *SCALEPACK* (Otwinowski & Minor, 1997); application of an absorption correction is inherent in this treatment and is reflected in the scale-factor range of 9.93–11.54 for the frames. *PLATON* (Spek, 1990) was used to calculate some metric parameters.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1005). Services for accessing these data are described at the back of the journal.

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