

ansa-[(*tert*-Butylamino)(isodicyclopentadienyl)dimethylsilane]Zr(NMe₂)₂ prepared by an amine-elimination reaction

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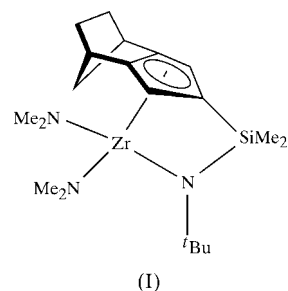
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An amine-elimination reaction was used to obtain the title compound, *i.e.* (*N-tert*-butyl-*N*-{[(1,2,3,3a,7a- η)-4,5,6,7-tetrahydro-4,7-methano-1*H*-inden-2-yl]dimethylsilyl}amido- κ *N*)-bis(*N*-methylmethanaminato- κ *N*)zirconium(IV) or [isodiCpSiMe₂N-*tert*-butyl]Zr(NMe₂)₂ (Cp is cyclopentadienyl), [Zr-(C₁₆H₂₅NSi)(C₂H₆N)₂], in very good yield. Treatment of isodiCpHSiMe₂NH-*tert*-butyl with Zr(NMe₂)₄ leads to the formation of a yellow solid that can be purified by sublimation. The single-crystal structure of the product shows the *exo* complexation of the isodicyclopentadienyl ligand to the Zr atom. The Cp portion of this ligand is bonded to the Zr atom in a η^5 manner, with a Zr–Cg (Cg is the ring centroid) distance of 2.2352 (10) Å. The isodiCpSiMe₂N-*tert*-butyl ligand has a constrained geometry, which is exhibited by the small angle of 95.55 (10)° for N–Si–C_{Cp}.

Comment

There is considerable industrial interest in group 4 half-sandwich complexes containing linked amido-cyclopentadienyl (Cp) ligands as catalysts for ethylene and propylene polymerization. The classical preparative route *via* amido dilithium salts and ZrCl₄ or TiCl₃(THF)₃ (THF is tetrahydrofuran) in combination leads to low isolated yields of product mixtures with non-substituted Cp ligands. Alternatively, such complexes can be prepared by an amine-elimination reaction with excellent efficiency (Hughes *et al.*, 1993; Herrmann & Morawietz, 1994; Carpenetti *et al.*, 1996; Leung *et al.*, 1999). We have previously demonstrated that the 'constrained geometry' complex [isodiCpSiMe₂N-*tert*-butyl]-ZrCl₂, where isodiCpSiMe₂N-*tert*-butyl is *N-tert*-butyl-*N*-{[(1,2,3,3a,7a- η)-4,5,6,7-tetrahydro-4,7-methano-1*H*-inden-2-

yl]dimethylsilyl}amido, can be synthesized by the classical metathesis route in 55% yield (Gentil *et al.*, 2000). In this paper, we report the high-yield 'one pot' formation of [isodiCpSiMe₂N-*tert*-butyl]Zr(NMe₂)₂, (I), and its X-ray structure. Complex (I) was obtained according to the amine-elimination pathway developed previously (Hughes *et al.*, 1993; Herrmann & Morawietz, 1994; Carpenetti *et al.*, 1996; Leung *et al.*, 1999), using Zr(NMe₂)₄ and the corresponding amine as starting materials.



As expected on the basis of experimental reaction conditions and prior results in this field (Paquette *et al.*, 1989; Sornay *et al.*, 1991; Zaegel *et al.*, 1995; Goblely *et al.*, 1998; Gentil *et al.*, 2000, 2002), the molecular structure of (I) indicates that *exo* complexation of the isodicyclopentadienyl ligand to Zr has occurred. This structure exhibits the classical half-sandwich pseudo-tetrahedral geometry about the Zr atom. Comparison with [isodiCpSiMe₂N-*tert*-butyl]Zr(CH₂SiMe₃)₂ (Gentil *et al.*, 2000) provides indications as to the structural changes due to the two –CH₂SiMe₃ substituents being replaced by dimethylamino groups. The presence of the –NMe₂ groups significantly increases both the Zr–Cg distance (Cg is the ring centroid for C1–C5) and the Zr–N1 bond length. The Zr–Cg distance is 2.2125 (8) Å and the Zr–N1 bond length is 2.0858 (14) Å for [isodiCpSiMe₂N-*tert*-butyl]Zr(CH₂SiMe₃)₂, whereas these values are 2.2352 (10)

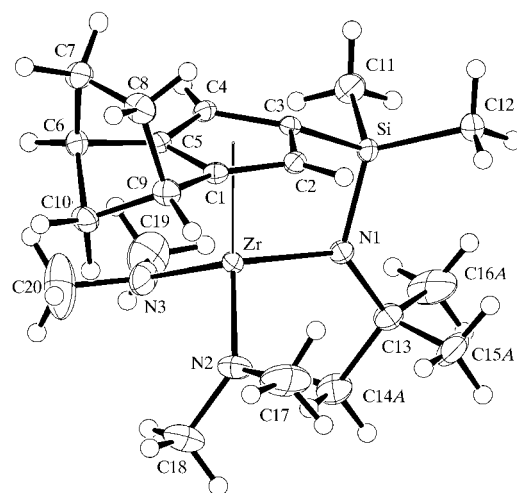


Figure 1

A view of the structure of (I), drawn with 40% probability displacement ellipsoids. For clarity, only the major component of the disordered *tert*-butyl group is shown. H atoms are shown as small spheres of arbitrary radii.

and 2.107 (2) Å, respectively, for (I). The values for this structure agree well with those in the analogous complex [C₅Me₄SiMe₂N-*tert*-butyl]Zr(NMe₂)₂ (Carpenetti *et al.*, 1996), where Zr–C_g is 2.233 (3) Å and Zr–N1 is 2.108 (4) Å.

As observed in previous structures containing an isodicyclopentadienyl ligand with *exo* complexation, there is a small amount of bending in this ligand about the bond common to the Cp ring and the norbornane fragment. The dihedral angle between the least-squares planes defined by C1–C5 and C1/C5/C6/C9 is 8.1 (2)°, and this bending is in the *endo* direction.

The isodiCpSiMe₂N-*tert*-butyl ligand in (I) has a constrained geometry, characterized by the small angle of 95.55 (10)° for N1–Si–C3 and by the displacement of the Si atom from its adjacent Cp ring, measured by the angle of 27.4 (1)° between the Si–C3 bond and the plane of the Cp ring. The sum of the angles about atom N1 is 359.9 (3)°, indicative of *sp*² hybridization.

Experimental

All experiments were conducted under an argon atmosphere. The solvents were dried and distilled prior to use. IsodiCpHSiMe₂NH-*tert*-butyl and Zr(NMe₂)₄ (Diamond *et al.*, 1995; Gentil *et al.*, 2000) were prepared according to published methods. IsodiCpHSiMe₂NH-*tert*-butyl (3.74 mmol, 977 mg) was added to Zr(NMe₂)₄ (1.00 g, 3.74 mmol) without any solvent. The reaction mixture was heated at 423 K for 12 h. Me₂NH was removed from the flask by periodic evacuation. The resulting product was collected by sublimation at 433 K in a yield of 86%. Dissolution of the solid in a toluene/pentane (1:5) solution and cooling at 243 K for 2 d afforded colourless crystals of (I) suitable for X-ray analysis.

Crystal data

[Zr(C ₁₆ H ₂₅ NSi)(C ₂ H ₆ N) ₂]	Mo K α radiation
<i>M_r</i> = 438.84	Cell parameters from 4545 reflections
Orthorhombic, <i>Pbca</i>	θ = 2.0–25.0°
<i>a</i> = 10.593 (1) Å	μ = 0.54 mm ^{−1}
<i>b</i> = 15.134 (2) Å	<i>T</i> = 150 (2) K
<i>c</i> = 28.592 (3) Å	Rectangular block, colourless
<i>V</i> = 4583.7 (9) Å ³	0.35 × 0.31 × 0.19 mm
<i>Z</i> = 8	
<i>D_x</i> = 1.272 Mg m ^{−3}	

Data collection

Nonius Kappa CCD area-detector diffractometer	4038 independent reflections
ϕ and ω scans	3443 reflections with <i>I</i> > 2 σ (<i>I</i>)
Absorption correction: multi-scan (<i>HKL SCALEPACK</i> ;	<i>R</i> _{int} = 0.038
Otwinowski & Minor, 1997)	θ _{max} = 25°
<i>T</i> _{min} = 0.849, <i>T</i> _{max} = 0.902	<i>h</i> = −12 → 12
41 422 measured reflections	<i>k</i> = −18 → 18
	<i>l</i> = −34 → 34

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 6.0948P]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.080$	$(\Delta/\sigma)_{\max} = 0.010$
<i>S</i> = 1.04	$\Delta\rho_{\max} = 0.80 \text{ e \AA}^{-3}$
4038 reflections	$\Delta\rho_{\min} = -0.41 \text{ e \AA}^{-3}$
251 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Zr–N3	2.048 (2)	N1–C13	1.478 (3)
Zr–N2	2.059 (2)	N2–C17	1.433 (4)
Zr–N1	2.107 (2)	N2–C18	1.452 (4)
Si–N1	1.727 (2)	N3–C20	1.410 (4)
Si–C3	1.864 (2)	N3–C19	1.506 (5)
N3–Zr–N2	106.42 (10)	C17–N2–Zr	125.0 (2)
N3–Zr–N1	104.71 (9)	C18–N2–Zr	125.1 (2)
N2–Zr–N1	110.00 (9)	C20–N3–C19	107.4 (3)
N1–Si–C3	95.55 (10)	C20–N3–Zr	123.1 (2)
C13–N1–Si	127.19 (17)	C19–N3–Zr	126.5 (2)
C13–N1–Zr	128.52 (16)	C2–C3–C4	106.5 (2)
Si–N1–Zr	104.21 (9)	C2–C3–Si	120.33 (17)
C17–N2–C18	109.9 (3)	C4–C3–Si	125.17 (18)

Table 2
Selected geometric parameters (Å) involving the Zr atom and the ring centroid.

<i>C_g</i> is the ring centroid of the C1–C5 cyclopentadienyl ring.			
Zr– <i>C_g</i>	2.2352 (10)		
<i>C_g</i> –Zr–N1	100.26 (6)	<i>C_g</i> –Zr–N3	116.26 (8)
<i>C_g</i> –Zr–N2	118.16 (7)		

The *tert*-butyl group is disordered over two orientations. The occupancy factor for the major orientation (atom labels C14A, C15A and C16A) refined to 0.821 (6) and this set of atoms was refined anisotropically. The minor orientation (atom labels C14B, C15B and C16B) was kept isotropic with an occupancy factor of 0.179 (6). A SADI restraint (*SHELXL97*; Sheldrick, 1997) was used for the minor component to restrain the three C–C bonds to be equal. Methyl H atoms were added at calculated positions using a riding model, with C–H distances of 0.98 Å and *U*_{iso}(H) = 1.5*U*_{eq}(C). For each methyl group, the torsion angle which defines the orientation about the Si–C, N–C or C–C bond was refined. The remaining H atoms were included in the model at calculated positions using a riding model, with C–H distances in the range 0.95–1.00 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C).

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1410). Services for accessing these data are described at the back of the journal.

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