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{(η^5,κN)-[(*tert*-Butylamido)dimethylsilyl]cyclopentadienyl}dichlorotitanium(IV)

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The crystal structure of the title compound, [Ti($C_{11}H_{19}$NSi)Cl_2], has been determined as part of a broad investigation of half-sandwich titanium complexes. Titanium has a pseudo-tetrahedral coordination formed by two Cl atoms [Ti—Cl = 2.2719 (4) and 2.2730 (4) Å], the N atom of the *N-tert*-butyl group [Ti—N = 1.9094 (12) Å] and the silyl-substituted Cp ligand [metal–Cp ring centroid distance = 2.0185 (9) Å]. The *tert*-butyl group was found to be disordered.

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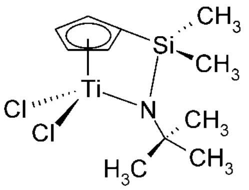
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
Disorder in main residue
R factor = 0.027
wR factor = 0.072
Data-to-parameter ratio = 21.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound, (I), is a precatalyst of α-olefin polymerization (Qian *et al.*, 2003). This paper reports its structure at 150 K. Previously, Carpenetti *et al.* (1996) mentioned the structural study of this compound at room temperature and published its crystal data as well as the value of one geometrical parameter, namely the Ti—N bond distance. However, full structural data for the title compound, to our knowledge, have neither been published nor submitted to the Cambridge Structural Database (Allen, 2002).



(I)

The title compound exhibits the expected pseudo-tetrahedral coordination geometry for Ti, consisting of a bifunctional η^1:η^5-cyclopentadienyl amide ligand and two Cl atoms (Fig. 1). The amide N atom exhibits sp^2-hybridization and a planar environment; the sum of the bond angles around atom N1 is 359.9°. The Ti1—N1 bond distance is 1.9094 (12) Å; the value reported by Carpenetti *et al.* (1996) was 1.901 (3) Å. The distance between the metal and the centre of the cyclopentadienyl ring [Ti1—Cg1 = 2.0185 (9) Å] is close to that in [Ti(η^5:η^1-$C_5H_4SiMe_2NPr^i$)Cl_2] [2.0168 (9) Å; Okuda *et al.*, 1997] and somewhat shorter than that in [Ti(η^5:η^1-$C_5Me_4SiMe_2NBu^t$)Cl_2] [2.033 (3) Å; Zemánek *et al.*, 2001]. The Ti1—Cl1 [2.2719 (4) Å] and Ti1—Cl2 [2.2730 (4) Å] bonds are slightly longer than the Ti—Cl bonds in the above-mentioned related complexes [2.266 Å (Okuda *et al.*, 1997) and 2.265 Å (Zemánek *et al.*, 2001)].

The Cg1—Ti1—Cl1 [115.01 (3)°], Cg1—Ti1—Cl2 [115.97 (3)°] and Ti1—N1—Si1 [105.53 (6)°] angles are significantly smaller (Table 1) than those in the corresponding isopropylamide derivative [118.61 (3) and 108.67 (13)°, respectively; Okuda *et al.*, 1997]. This observation reflects the bulkier character of the NBu^t group in comparison with the NPr^i group.

The tertiary butyl group exhibits rotational disorder, each of the three methyl C atoms having two positions, related by rotation around the N1—C8 bond by approximately 30°.

Experimental

The title compound was prepared following the procedure of Ciruelos *et al.* (1995). The crude product was purified by repeated vacuum sublimation, yielding 63% of an orange solid. Yellow crystals of (I) suitable for X-ray measurements were obtained by sublimation in a sealed ampoule at 10^{-3} Pa and 370 K.

Crystal data

$[Ti(C_{11}H_{19}NSi)Cl_2]$
$M_r = 312.16$
Triclinic, $P\bar{1}$
$a = 8.2900$ (2) Å
$b = 8.3810$ (2) Å
$c = 12.7950$ (3) Å
$\alpha = 73.8820$ (15)°
$\beta = 89.3720$ (14)°
$\gamma = 62.4650$ (13)°
$V = 750.07$ (3) Å^3

$Z = 2$
$D_x = 1.382$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3278 reflections
$\theta = 1$–27.5°
$\mu = 0.98$ mm^{-1}
$T = 150$ (2) K
Plate, yellow
0.45 × 0.4 × 0.37 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: none
13 385 measured reflections
3425 independent reflections

3171 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$
$\theta_{\rm max} = 27.5°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.072$
$S = 1.04$
3425 reflections
163 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0349P)^2 + 0.3748P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.46$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.43$ e Å^{-3}
Extinction correction: *SHELXL* (Sheldrick, 1997)
Extinction coefficient: 0.015 (3)

Table 1
Selected geometric parameters (Å, °).

Cg1—Ti1	2.0185 (9)	N1—Ti1	1.9093 (12)
Cl2—Ti1	2.2731 (6)	N1—Si1	1.7591 (14)
Cl1—Ti1	2.2719 (5)		
Cg1—Ti1—N1	107.12 (5)	Cl1—Ti1—Cl2	103.50 (2)
Cg1—Ti1—Cl1	115.01 (3)	Ti1—N1—Si1	105.53 (7)
Cg1—Ti1—Cl2	115.97 (3)	C1—Si1—N1	90.68 (7)

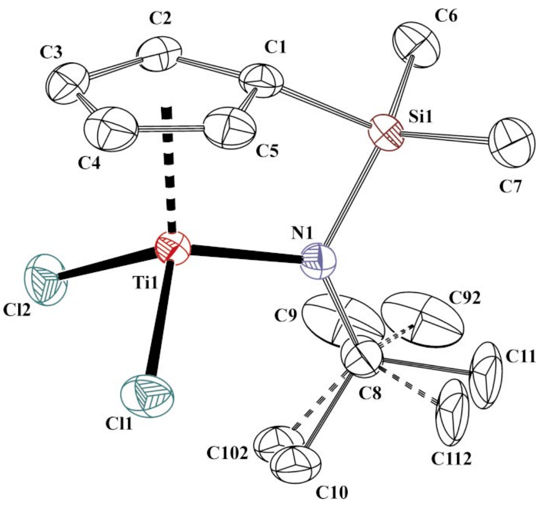


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity; atoms C9, C10 and C11 correspond to the major component of the disorder; atoms C92, C102 and C112 represent its minor component.

The tertiary butyl group is disordered over two distinct positions with partial occupancies (0.7:0.3) for methyl C atoms. The positions of atoms with high occupancy were supplied by direct methods; however the anisotropic displacement parameters of these atoms and three high residual maxima in a difference Fourier map with suitable geometry indicate the disorder. Therefore the occupancy factors were lowered until reasonable displacement parameters were obtained and the second position of the butyl moiety was included in the refinement. All H atoms were positioned geometrically and included in the refinement in the riding-model approximation, with C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for cyclopentadienyl H atoms, and C—H = 0.96 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for methyl H atoms.

Data collection: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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