metal-organic compounds

{*N*-[Dimethyl(η^5-2,3,4,6-tetramethyl-indenyl)silyl]cyclobutylamido-κN}-(η^4-1,4-diphenyl-1,3-butadiene)-titanium(II)

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The titanium metal center in the title compound, [Ti($C_{19}H_{27}N$-Si)($C_{16}H_{14}$)], is coordinated in a distorted tetrahedral geometry by a η^5-indenyl ligand, a dimethylsilyl-bridged *N*-cyclobutylamido ligand and an *s-cis*-η^4-1,4-diphenyl-1,3-butadiene ligand in a 'prone' π-fashion, revealing a formal divalent Ti center.

Comment

Constrained-geometry catalysts are a very important catalyst family which has had a major impact on homogeneous olefin polymerization technologies (Stevens *et al.*, 1991; McKnight & Waymouth, 1998). In this catalyst family, constrained-geometry titanium(II)–diene complexes, in particular, offer structural diversity and unique olefin polymerization activity (Devore *et al.*, 1995). A common procedure used for the preparation of a variety of constrained-geometry titanium–diene complexes is to react the corresponding dichloride precursor with two equivalents of ^{n}BuLi in the presence of excess diene. In the course of structure–activity studies of the constrained-geometry catalysts having ancilliary η^5:η^1-$C_5Me_4SiMe_2N^tBu$, we found that when replacing ^{t}Bu of the ^{t}BuN group in the ligand with less bulky secondary C atoms, such as cyclobutyl, the diene complex cannot be obtained using the common procedure. Considering the reactivity of the α-H atom of the *N*-cyclobutyl group, we found that the use of the milder ^{n}BuMgBr reagent instead of ^{n}BuLi successfully produced the desired titanium(II)–diene complex, *viz.* $Me_2Si(\eta^5$-2,3,4,6-$Me_4C_9H_2)(C_4H_7N)Ti(s$-*cis*-η^4-1,4-$Ph_2C_4H_4$), (I), the structure of which is reported here.

The molecular structure of the title compound is depicted in Fig. 1 and selected geometrical parameters are given in Table 1. The Ti metal center is coordinated in a distorted tetrahedral

geometry by a η^5-indenyl ligand, a dimethylsilyl-bridged *N*-cyclobutylamido ligand and a 1,4-diphenyl-1,3-butadiene ligand in a 'prone' π-fashion (Dahlmann *et al.*, 2000; Devore *et al.*, 1995; Erker *et al.*, 1985; Yasuda *et al.*, 1985). A Cp—Ti—N angle (Cp is the centroid of the indenyl five-membered ring) of 110.40 (8)° reflects the openness of the coordination sphere about Ti.
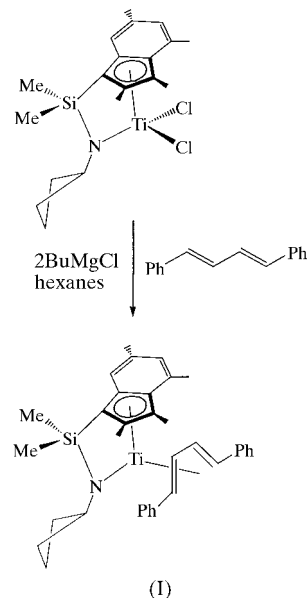
The 1,4-diphenyl-1,3-butadiene ligand adopts an *s-cis* orientation with the diene being bound to Ti in a π-fashion. The two Ti—C(terminal) diene distances [Ti—C20 = 2.217 (2) Å and Ti—C23 = 2.233 (2) Å] differ from the two Ti—C(internal) diene distances [Ti—C21 = 2.295 (2) Å and Ti—C22 = 2.295 (2) Å] by only 0.070 Å. The very small C—C distance differences [C20—C21 = 1.416 (3) Å, C21—C22 =
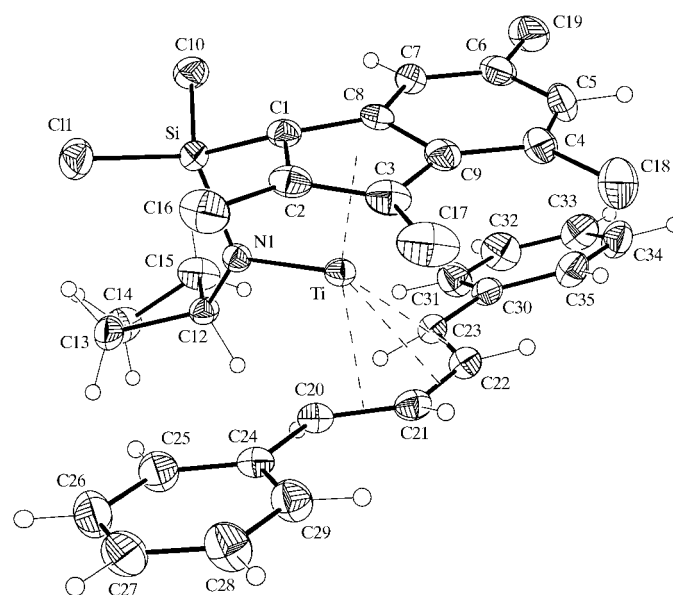

Figure 1
The molecular structure of (I) with 50% probability ellipsoids, showing the atom-numbering scheme.

1.397 (3) Å and C22—C23 = 1.419 (3) Å] in the diene ligand also support the assignment of a predominantly π-bound diene ligand (Dahlmann *et al.*, 2000; Devore *et al.*, 1995). A C20—C21—C22—C23 torsion angle of −0.6 (4)° reflects the coplanarity of these atoms.

The Ti—N distance of 1.963 (2) Å compares well with those in typical ^{t}BuN constrained-geometry Ti^{II} complexes (Dahlmann *et al.*, 2000; Devore *et al.*, 1995), but is considerably longer than in typical Ti^{IV}–amide complexes (Lappert *et al.*, 1980).

Experimental

Me$_2$Si(η^5-2,3,4,6-Me$_4$C$_9$H$_2$)(C$_4$H$_7$N)Ti(1,4-Ph$_2$C$_4$H$_4$) was prepared from the reaction of Me$_2$Si(η^5-2,3,4,6-Me$_4$C$_9$H$_2$)(C$_4$H$_7$N)TiCl$_2$ with two equivalents of ^{n}BuMgBr in the presence of one equivalent of *trans*-1,4-diphenyl-1,3-butadiene in hexanes under inert atomospheric conditions, using a similar procedure to that described previously by Devore *et al.* (1995). The resulting dark-red solution was stored at 238 K in a glove-box for 5 d, after which time dark crystals of the title complex had formed. The selected crystal was immersed in Paratone N oil and mounted on a thin glass fiber in a glove-box.

Crystal data

[Ti(C$_{19}$H$_{27}$NSi)(C$_{16}$H$_{14}$)]
$M_r = 551.68$
Monoclinic, $P2_1/n$
$a = 11.0726$ (6) Å
$b = 20.509$ (1) Å
$c = 13.9311$ (8) Å
$\beta = 112.020$ (1)°
$V = 2932.9$ (3) Å^3
$Z = 4$

$D_x = 1.249$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4542 reflections
$\theta = 2.0$–27.5°
$\mu = 0.36$ mm^{-1}
$T = 173$ (2) K
Needle, black
$0.19 \times 0.15 \times 0.09$ mm

Data collection

Bruker SMART diffractometer
ω scans
Absorption correction: analytical, integration based on measured indexed faces (*SHELXTL*; Sheldrick, 1998)
$T_{min} = 0.931$, $T_{max} = 0.973$
20 107 measured reflections

6740 independent reflections
4070 reflections with $I > 2\sigma(I)$
$R_{int} = 0.055$
$\theta_{max} = 27.5°$
$h = -14 \rightarrow 13$
$k = -26 \rightarrow 15$
$l = -17 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.103$
$S = 0.96$
6740 reflections
383 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0458P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.007$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

C—H distances of 0.98 and 0.99 Å were used for methyl and secondary H atoms, respectively. A distance of 0.95 Å was used for H atoms on Csp^2 atoms. The H-atom displacement parameters were set at 1.2U_{eq} (1.5U_{eq} for methyl H atoms) of the parent C atom. The H

Table 1
Selected geometric parameters (Å, °).

Cp is the centroid of the indenyl five-membered ring.

Ti—N1	1.963 (2)	Ti—C21	2.295 (2)
Ti—C1	2.242 (2)	Ti—C22	2.295 (2)
Ti—C2	2.355 (2)	Ti—C23	2.233 (2)
Ti—C3	2.476 (2)	C20—C21	1.416 (3)
Ti—C8	2.334 (2)	C21—C22	1.397 (3)
Ti—C9	2.490 (2)	C22—C23	1.419 (3)
Ti—C20	2.217 (2)		
Cp—Ti—N1	110.40 (8)	C20—Ti—C23	86.82 (8)
N1—Ti—C20	99.09 (8)	C20—C21—C22	125.7 (2)
N1—Ti—C23	99.33 (8)	C21—C22—C23	126.1 (2)
C12—C13—C14—C15	−20.5 (2)	C20—C21—C22—C23	−0.6 (4)

atoms on atoms C20–C23, as well as the methyl H atoms on C10 and C11, were obtained from a difference Fourier map and refined without constraints [C—H = 0.93 (2)–1.02 (3) Å]. Full data collection details are in the relevant _special_details section of the archived CIF and have also been reported elsewhere (Abboud *et al.*, 1997).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART* and *SAINT* (Bruker, 1998); data reduction: *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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