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Amidobis[η^5-1,3-bis(trimethylsilyl)-cyclopentadienyl]titanium(III)

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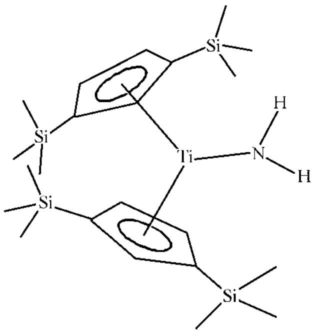
The title compound, $[Ti(C_{11}H_{21}Si_2)_2(NH_2)]$, crystallizes as a bent metallocene, with the NH_2 group oriented to maximize the π interaction between the N atom and the Ti^{III} center. The increased π bonding is reflected in a short Ti—N bond length of 1.933 (3) Å.

Comment

The title compound, $[Cp_2''Ti(NH_2)]$ [Cp″ is 1,3-bis(trimethylsilyl)cyclopentadienyl], (I), crystallizes in the primitive monoclinic space group $P2_1/n$ with four discrete molecules in the unit cell. Selected distances and angles are given in Table 1. Fig. 1 shows the molecular geometry and the atom-numbering scheme.



(I)

The Ti center is coordinated by two virtually planar cyclopentadienyl rings, in a staggered conformation relative to each other, and by an NH_2 group. The angle formed by the cyclopentadienyl ligands, *Cg*1—Ti—*Cg*2, is 137.90 (8)° (*Cg*1 and *Cg*2 are the centroids of the cyclopentadienyl rings C1–C5 and C6–C10, respectively). The distances between the Ti atom and *Cg*1 and *Cg*2 are 2.0611 (17) and 2.0623 (17) Å, respectively. These are comparable with values found for other Cp_2TiNR_2 derivatives (Brady *et al.*, 1995; Lukens *et al.*, 1996; Feldman & Calabrese, 1991).

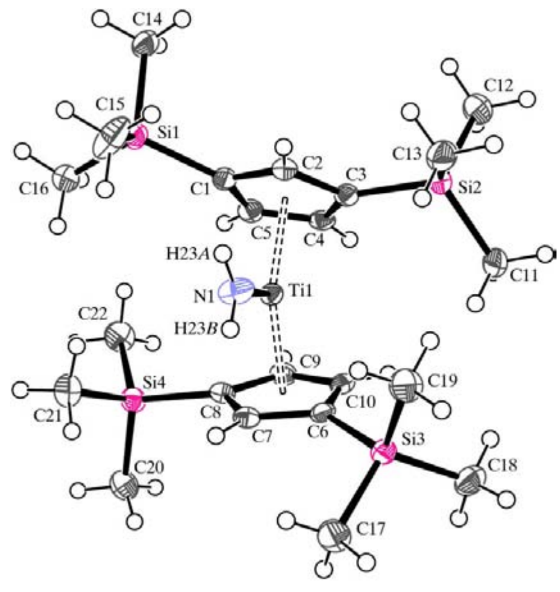


Figure 1
A view of the structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

The amide group is located within an open wedge formed by the sterically demanding trimethylsilyl groups, allowing the least steric bulk and a proper orientation for the filled *p* orbital to interact with the empty b_2 orbital of the $Cp_2''Ti$ fragment, enabling the NH_2 moiety to act as a π donor. This is also reflected in the small *Cg*—Ti—N—H torsion angle of 6.4° and the quite short Ti—N distance of 1.933 (3) Å. Similar N—*M* π bonding is also observed in $[(\eta^5-C_5Me_5)_2Ti(NH_2)]$ [Ti—N = 1.944 (2) Å; Brady *et al.*, 1995), $[(\eta^5-C_5Me_5)_2Ti(NHMe)]$ [Ti—N = 1.955 (2) Å; Lukens *et al.*, 1996] and $[(\eta^5-C_5Me_5)_2Hf(H)(NHMe)]$ [Hf—N = 2.027 (8) Å; Hillhouse *et al.*, 1988], as evidenced by a similar orientation of the amide groups as well as short (Ti,Hf)—N distances.

The influence of steric bulk *versus* electronic effects is demonstrated in bis(pentamethylcyclopentadienyl)titanium(III) *N*-methyl-*N*-phenylamide (Feldman & Calabrese, 1991), in which the amide ligand adopts a perpendicular orientation with respect to the plane formed by the Ti atom and the two cyclopentadienyl ring centroids, preventing the *p* orbital from interacting with the b_2 orbital of the $[(\eta^5-C_5Me_5)_2Ti]$ fragment. Therefore, the Ti—N distance [2.054 (2) Å] is elongated compared with that of (I).

Experimental

The title compound was synthesized from $Cp_2''TiMe$ and dry NH_3 in *n*-hexane in a manner similar to that used for the preparation of $(C_5Me_5)_2Ti(NH_2)$ (Brady *et al.*, 1995). Dichroic (green and brown) crystals were grown by slow cooling of a saturated hexane solution to 193 K. The crystal was handled under a nitrogen atmosphere, mounted on a glass fiber with Paratone-N hydrocarbon oil and cooled to 133 (2) K for data collection.

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Crystal data

$[Ti(C_{11}H_{21}Si_2)_2(NH_2)]$
$M_r = 482.84$
Monoclinic, $P2_1/n$
$a = 13.0945\ (3)$ Å
$b = 16.5699\ (3)$ Å
$c = 13.1869\ (2)$ Å
$\beta = 96.488\ (1)^\circ$
$V = 2842.90\ (9)$ Å^3
$Z = 4$
$D_x = 1.128$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5983 reflections
$\theta = 2$–51.2°
$\mu = 0.48$ mm^{-1}
$T = 133\ (2)$ K
Block, dichroic (green–brown)
0.38 × 0.32 × 0.18 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.839$, $T_{\max} = 0.919$
13 362 measured reflections
5071 independent reflections
3874 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.059$
$\theta_{\max} = 26.1^\circ$
$h = -16 \rightarrow 13$
$k = -20 \rightarrow 18$
$l = -15 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.113$
$S = 1.13$
5071 reflections
273 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0201P)^2 + 5.0672P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

*Cg*1 is the centroid of the C1–C5 ring and *Cg*2 is the centroid of the C6–C10 ring.

Ti1—C1	2.426 (3)	Ti1—C8	2.366 (3)
Ti1—C2	2.376 (3)	Ti1—C9	2.382 (3)
Ti1—C3	2.377 (3)	Ti1—C10	2.399 (3)
Ti1—C4	2.364 (3)	Ti1—N1	1.933 (3)
Ti1—C5	2.393 (3)	Ti1—*Cg*1	2.0611 (17)
Ti1—C6	2.430 (3)	Ti1—*Cg*2	2.0623 (17)
Ti1—C7	2.372 (3)		
Ti1—N1—H23*A*	128 (3)	*Cg*1—Ti1—*Cg*2	137.90 (8)
Ti1—N1—H23*B*	127 (3)	*Cg*1—Ti1—N1	111.13 (12)
H23*A*—N1—H23*B*	105 (4)	*Cg*2—Ti1—N1	110.97 (12)

Methyl H atoms of the trimethylsilyl groups, as well as H atoms of the cyclopentadienyl rings, were included in calculated positions, with C—H distances of 0.98 (CH_3) and 0.95 Å (CH), and were refined using a riding model, with $U_{\rm iso}(H) = 1.5U_{\rm eq}(C)$ for the methyl H atoms and $1.2U_{\rm eq}(C)$ for the cyclopentadienyl H atoms. The amide H atoms (H23*A* and H23*B*) were located using standard difference Fourier techniques and were refined isotropically; the N—H distances are 0.85 (4) and 0.87 (5) Å.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 2002); 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: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1076). Services for accessing these data are described at the back of the journal.

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