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Key indicators

Single-crystal synchrotron study

T = 100 K

Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$

R factor = 0.052

wR factor = 0.130

Data-to-parameter ratio = 14.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**[Bis(3-mesitylpyrazol-1-yl)(5-mesitylpyrazol-1-yl)borohydrido]dichloro(5-mesitylpyrazole)-titanium(III) toluene solvate**

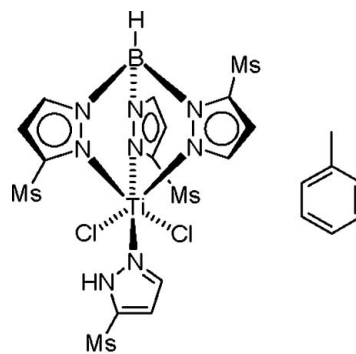
In the title Ti^{III} complex, $[\text{Ti}(\text{C}_{36}\text{H}_{40}\text{BN}_6)\text{Cl}_2(\text{C}_{12}\text{H}_{14}\text{N}_2)] \cdot \text{C}_7\text{H}_8$, the Ti atom is coordinated in a distorted octahedral geometry by three N atoms that are constrained to a facial arrangement by the Tp^{Ms^*} ligand [$\text{Tp}^{\text{Ms}^*} = \text{HB}(\text{3-mesitylpyrazolyl})_2(\text{5-mesitylpyrazolyl})$], by two mutually *cis* chloride ligands and by an N atom from a 5-mesitylpyrazole ligand.

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Comment

Group 4 metal d^0 trispyrazolylborate complexes of general formula $\text{Tp}'\text{M}^{\text{IV}}\text{Cl}_3$ ($\text{Tp}' =$ sterically bulky trispyrazolylborate ligand; $M = \text{Ti}, \text{Zr}$ or Hf) are activated by methylalumoxane (MAO) to generate highly active catalysts for ethylene polymerization and ethylene/hexene copolymerization (Gil *et al.* 2001, 2004; Gil & Casagrande 2004; Lee & Jordan 2005; Michiue & Jordan, 2004; Murtuza *et al.* 2002; Pires *et al.*, 2006). Interestingly, the olefin polymerization characteristics of the d^1 Ti^{III} complex $\text{K}[\text{Tp}^{\text{Ms}^*}\text{TiCl}_3]$ are distinctly different from those of the analogous d^0 Ti^{IV} complex $\text{Tp}^{\text{Ms}^*}\text{TiCl}_3$, and these differences were exploited in the synthesis of end-capped polyethylenes (Michiue & Jordan, 2003). As part of a general investigation of $\text{Tp}^{\text{Ms}^*}\text{Ti}^{\text{III}}$ catalysts aimed at understanding the influence of the metal oxidation state on polymerization properties, we report the structure of the Ti^{III} complex $\text{Tp}^{\text{Ms}^*}\text{TiCl}_2(\text{pz}^{\text{Ms}^*}\text{H}) \cdot \text{toluene}$ ($\text{pz}^{\text{Ms}^*}\text{H} = 5\text{-mesitylpyrazole}$), (I).

Ms = mesityl = 2,4,6-Me₃-Ph

(I)

The molecular structure of (I) is shown in Fig. 1, and selected bond distances and angles are presented in Table 1. The $\text{pz}^{\text{Ms}^*}\text{H}$ ligand is located *cis* to the 5-mesitylpyrazolyl unit of the Tp^{Ms^*} ligand, which minimizes steric crowding between these ligands. The N—Ti—N angles formed by the tridentate Tp^{Ms^*} ligand are acute [range 81.59 (9)–85.62 (8)°]. The N2—Ti1—N6 angle [81.59 (9)°] is smaller than the N2—Ti1—N4 [85.37 (10)°] and N4—Ti1—N6 [85.62 (8)°] angles due to steric

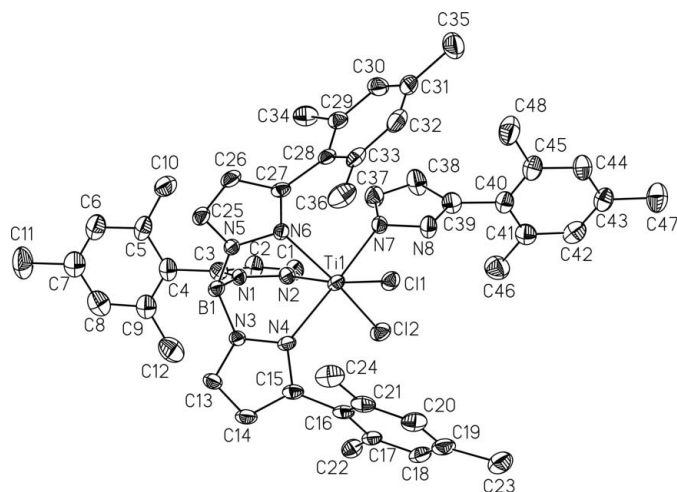


Figure 1
Perspective view of (I), with 50% probability displacement ellipsoids. H atoms and the toluene solvent molecule have been omitted.

pressure from the $\text{pz}^{\text{Me}}\text{H}$ ligand. The $\text{Ti1}-\text{N7}$ distance involving the $\text{pz}^{\text{Me}}\text{H}$ ligand [2.152 (2) Å] is shorter than the $\text{Ti}-\text{N}$ distances involving the Tp^{Me^*} ligand [range 2.183 (3)–2.218 (2) Å]. The $\text{Ti}-\text{Cl}$ distances in (I) [2.3153 (12) and 2.3523 (13) Å] are longer than those in the sterically similar Ti^{IV} complex $\text{Tp}^{\text{Me}^*}\text{TiCl}_3$ [range 2.1958 (12)–2.2561 (12) Å], as expected due to the difference in the Ti oxidation state (Michiue & Jordan, 2003). The structure of (I) is very similar to that of the analogous but less crowded Ti^{III} complex $\text{Tp}^*\text{TiCl}_2(\text{pz}^{\text{Me}^2}\text{H})$ ($\text{Tp}^* = \text{HB}(3,5\text{-Me}_2\text{-pyrazolyl})_3$, $\text{pz}^{\text{Me}^2}\text{H} = 3,5\text{-Me}_2\text{-pyrazole}$) (Hughes *et al.*, 1988). The $\text{Ti}-\text{N}$ distances are *ca* 0.02 Å longer and the $\text{Ti}-\text{Cl}$ distances *ca* 0.03 Å shorter in (I) compared to the corresponding distances in $\text{Tp}^*\text{TiCl}_2(\text{pz}^{\text{Me}^2}\text{H})$, due to the steric crowding associated with the bulky mesitylpyrazolyl units in (I). Comparison of the structures of (I) and $\text{K}[\text{Tp}^{\text{Me}^*}\text{TiCl}_3]$ is complicated by ion-pairing in the latter species.

Experimental

A mixture of $\text{Tp}^{\text{Me}^*}\text{TiCl}_3$ (1.00 g, 1.39 mmol) and $\text{K}[\text{O}^t\text{Bu}]$ (0.155 g, 1.39 mmol) in toluene (70 ml) was stirred at 293 K for 12 h. The volatiles were removed under vacuum to give a dark-green solid. The solid was taken up in hexanes (100 ml) and filtered to give a pale blue powder (414 mg, identified as $\text{K}[\text{Tp}^{\text{Me}^*}\text{TiCl}_3]$) and a dark yellow filtrate. The filtrate was taken to dryness under vacuum to give an ivory powder. The powder was dissolved in toluene (5 ml) and the resulting dark-green solution was layered with hexanes and stored at 236 K. Needle-like crystals of (I) slowly formed (yield 268 mg, 22.2% based on Ti).

Crystal data

$[\text{Ti}(\text{C}_{36}\text{H}_{40}\text{BN}_6)\text{Cl}_2(\text{C}_{12}\text{H}_{14}\text{N}_2)] \cdot \text{C}_7\text{H}_8$	$Z = 4$
$M_r = 964.74$	$D_x = 1.217 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Synchrotron radiation
$a = 13.137$ (7) Å	$\lambda = 0.5500$ Å
$b = 17.277$ (10) Å	$\mu = 0.17 \text{ mm}^{-1}$
$c = 24.824$ (11) Å	$T = 100$ (2) K
$\beta = 110.82$ (3)°	Rod, colourless
$V = 5266$ (5) Å ³	$0.10 \times 0.02 \times 0.02 \text{ mm}$

Data collection

Huber diffractometer	50912 measured reflections
φ scans	9087 independent reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2002)	6036 reflections with $I > 2\sigma(I)$
$T_{\text{min}} = 0.984$, $T_{\text{max}} = 0.997$	$R_{\text{int}} = 0.159$
	$\theta_{\text{max}} = 19.1^\circ$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.052$	$wR(F^2) = 0.130$
$S = 0.97$	$w = 1/[\sigma^2(F_o^2) + (0.0684P)^2]$
9087 reflections	where $P = (F_o^2 + 2F_c^2)/3$
621 parameters	$(\Delta/\sigma)_{\text{max}} = 0.001$
	$\Delta\rho_{\text{max}} = 0.52 \text{ e } \text{Å}^{-3}$
	$\Delta\rho_{\text{min}} = -0.47 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

$\text{Ti1}-\text{N2}$	2.183 (3)	$\text{Ti1}-\text{Cl2}$	2.3153 (12)
$\text{Ti1}-\text{N4}$	2.203 (2)	$\text{N1}-\text{B1}$	1.567 (4)
$\text{Ti1}-\text{N6}$	2.218 (2)	$\text{N3}-\text{B1}$	1.535 (4)
$\text{Ti1}-\text{N7}$	2.152 (2)	$\text{N5}-\text{B1}$	1.534 (4)
$\text{Ti1}-\text{Cl1}$	2.3523 (13)		
$\text{N2}-\text{Ti1}-\text{N4}$	85.37 (10)	$\text{N6}-\text{Ti1}-\text{N7}$	93.86 (9)
$\text{N2}-\text{Ti1}-\text{N6}$	81.59 (9)	$\text{N6}-\text{Ti1}-\text{Cl1}$	92.37 (7)
$\text{N2}-\text{Ti1}-\text{N7}$	90.50 (10)	$\text{N6}-\text{Ti1}-\text{Cl2}$	168.05 (6)
$\text{N2}-\text{Ti1}-\text{Cl1}$	173.14 (7)	$\text{N7}-\text{Ti1}-\text{Cl1}$	86.63 (8)
$\text{N2}-\text{Ti1}-\text{Cl2}$	86.45 (7)	$\text{N7}-\text{Ti1}-\text{Cl2}$	86.00 (7)
$\text{N4}-\text{Ti1}-\text{N6}$	85.62 (8)	$\text{Cl1}-\text{Ti1}-\text{Cl2}$	99.55 (4)
$\text{N4}-\text{Ti1}-\text{N7}$	175.87 (9)	$\text{N5}-\text{B1}-\text{N3}$	109.1 (2)
$\text{N4}-\text{Ti1}-\text{Cl1}$	97.48 (8)	$\text{N5}-\text{B1}-\text{N1}$	107.9 (2)
$\text{N4}-\text{Ti1}-\text{Cl2}$	93.66 (7)	$\text{N3}-\text{B1}-\text{N1}$	108.7 (2)

Atom H56 attached to B1 was located in a difference Fourier synthesis, after which it was refined freely. All other H atoms were positioned geometrically ($\text{C}-\text{H} = 0.95$ and 0.98 Å) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5U_{\text{eq}}(\text{parent atom})$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT-Plus* (Bruker, 2002); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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