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Key indicators

Single-crystal X-ray study
 $T = 130$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
 R factor = 0.045
 wR factor = 0.120
Data-to-parameter ratio = 14.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

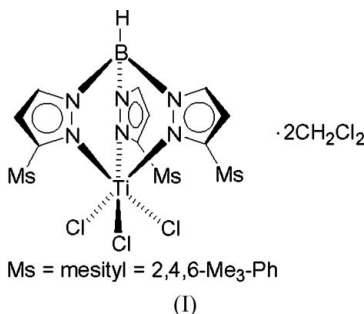
Trichloro[tris(3-mesitylpyrazol-1-yl)boro-hydrido]titanium dichloromethane disolvate

In the title complex, $[\text{Ti}(\text{C}_{36}\text{H}_{40}\text{BN}_6)\text{Cl}_3] \cdot 2\text{CH}_2\text{Cl}_2$, the Ti atom is coordinated by three N atoms that are constrained to a facial arrangement by the Tp^{Ms} ligand [$\text{Tp}^{\text{Ms}} = \text{HB}(3\text{-mesitylpyrazolyl})_3$] and three chloride ligands in a distorted octahedral geometry. The complex molecules are located on crystallographic mirror planes.

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Comment

Group 4 metal tris(pyrazolyl)borate complexes of general formula $\text{Tp}'\text{MCl}_3$ [$\text{Tp}' =$ generic tris(pyrazolyl)borate ligand; $M = \text{Ti}, \text{Zr},$ or Hf] can be activated by methylalumoxane (MAO) to generate active catalysts for ethylene polymerization and ethylene/hexene copolymerization (Murtuza *et al.*, 2002; Michiue & Jordan, 2003; Michiue & Jordan, 2004; Gil *et al.* 2004). The activity of $\text{Tp}'\text{MCl}_3/\text{MAO}$ catalysts is strongly influenced by the steric properties of the Tp' ligands, and catalysts that contain the sterically bulky Tp^{Ms} and $\text{Tp}^{\text{Ms}*}$ ligands [$\text{Tp}^{\text{Ms}} = \text{HB}(3\text{-mesitylpyrazolyl})_3$; $\text{Tp}^{\text{Ms}*} = \text{HB}(3\text{-mesitylpyrazolyl})_2(5\text{-mesitylpyrazolyl})$] exhibit very high activity.



As part of an ongoing investigation of the properties of these catalysts (Lee & Jordan, 2005), we have structurally characterized the title complex, $\text{Tp}^{\text{Ms}}\text{TiCl}_3$, (I). The molecular structure of (I) is shown in Fig. 1, and selected bond distances and angles are presented in Table 1. The Ti atom is coordinated by three N atoms that are constrained to a facial arrangement by the Tp^{Ms} ligand, and by three chloride ligands in a distorted octahedral geometry. The complex is located on a mirror plane. The core structure of (I) is typical for tris(pyrazolyl)borate titanium complexes. The N–Ti–N angles formed by the tridentate Tp^{Ms} ligand are acute [range 83.25 (8)–83.40 (12)°], the Cl–Ti–Cl angles are correspondingly larger [range 94.78 (5)–95.22 (3)°], and the Ti–Cl distances are normal [range 2.2417 (12)–2.2635 (9) Å]. Very similar values for these parameters were observed for $\text{Tp}^{\text{Ms}*}\text{TiCl}_3$ [(II); Michiue & Jordan, 2003], Tp^*TiCl_3 [(III); $\text{Tp}^* = \text{HB}(3,5\text{-Me}_2\text{-pyrazolyl})_3$] (Antiñolo *et al.*, 1999), $\text{Tp}^{\text{Np}}\text{TiCl}_3$ [(IV); $\text{Tp}^{\text{Np}} = \text{HB}(3\text{-neopentylpyrazolyl})_3$] (Gil &

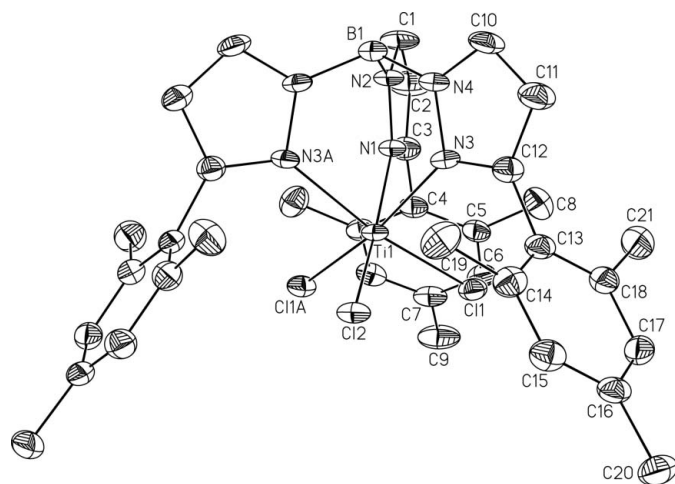


Figure 1
View of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted. Symmetry-equivalent atoms are generated by the (010) mirror. The suffix A corresponds to the symmetry position $(x, -y, z)$. The solvent molecules have been omitted.

Casagrande, 2004), and $\text{Tp}^{\text{Menth}^*}\text{TiCl}_3$ [(V); $\text{Tp}^{\text{Menth}^*}$ = hydrotris[4,5,6,7-tetrahydro-4-methyl-7-(1-methylethyl)-2*H*-indazolato-N2]borate] (LeCloux *et al.*, 1994). The Ti–N distances in (I) [range 2.206 (2)–2.253 (3) Å] are similar to those in the isomeric complex (II) [range 2.172 (3)–2.239 (3) Å], which also contains bulky mesityl groups, but slightly longer than those in (III) [range 2.164 (2)–2.177 (2) Å], (IV) [range 2.162 (8)–2.167 (6) Å], and (V) [range 2.131 (7)–2.186 (6) Å], which contain sterically smaller Tp' ligands. In (I), the three mesityl rings lie roughly perpendicular to the pyrazolyl rings to which they are attached and together form a deep pocket that shields the three chloride ligands.

Experimental

The synthesis of (I) was carried out as described previously (Murtuza *et al.*, 2002). Crystals of (I) were grown from a saturated CH_2Cl_2 solution at 273 K.

Crystal data

| | |
|---|---|
| $[\text{Ti}(\text{C}_{36}\text{H}_{40}\text{BN}_6)\text{Cl}_3] \cdot 2\text{CH}_2\text{Cl}_2$ | $Z = 2$ |
| $M_r = 891.65$ | $D_x = 1.377 \text{ Mg m}^{-3}$ |
| Monoclinic, $P2_1/m$ | Mo $K\alpha$ radiation |
| $a = 7.964$ (3) Å | $\mu = 0.67 \text{ mm}^{-1}$ |
| $b = 22.940$ (7) Å | $T = 130$ (2) K |
| $c = 11.844$ (4) Å | Rod, red |
| $\beta = 96.484$ (5)° | $0.45 \times 0.15 \times 0.15 \text{ mm}$ |
| $V = 2149.9$ (12) Å ³ | |

Data collection

| | |
|--|--|
| Bruker SMART APEX CCD diffractometer | 16493 measured reflections |
| ω scans | 3894 independent reflections |
| Absorption correction: multi-scan (SADABS; Bruker, 2002) | 3026 reflections with $I > 2\sigma(I)$ |
| $T_{\min} = 0.670$, $T_{\max} = 0.90$ | $R_{\text{int}} = 0.047$ |
| | $\theta_{\text{max}} = 25.0^\circ$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 0.8057P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.045$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.120$ | $(\Delta/\sigma)_{\text{max}} = 0.002$ |
| $S = 1.05$ | $\Delta\rho_{\text{max}} = 0.92 \text{ e \AA}^{-3}$ |
| 3894 reflections | $\Delta\rho_{\text{min}} = -0.64 \text{ e \AA}^{-3}$ |
| 264 parameters | |
| H-atom parameters constrained | |

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-------------------------|-------------|--------------------------|-------------|
| Ti1–N1 | 2.253 (3) | Ti1–Cl1 | 2.2635 (9) |
| Ti1–N3 | 2.206 (2) | Ti1–Cl2 | 2.2417 (12) |
| B1–N2 | 1.539 (6) | B1–N4 | 1.541 (4) |
| N2–N1–Ti1 | 118.3 (2) | Cl2–Ti1–N1 | 172.53 (9) |
| N4–N3–Ti1 | 119.33 (17) | N3 ⁱ –Ti1–Cl1 | 171.27 (6) |
| N3–Ti1–N1 | 83.25 (8) | N3 ⁱ –Ti1–Cl2 | 91.19 (6) |
| N3 ⁱ –Ti1–N3 | 83.40 (12) | Cl1–Ti1–Cl1 ⁱ | 94.78 (5) |
| N3–Ti1–Cl1 | 90.53 (6) | Cl2–Ti1–Cl1 | 95.22 (3) |
| N1–Ti1–Cl1 | 89.83 (6) | N2–B1–N4 | 108.1 (2) |
| N3–Ti1–Cl2 | 91.19 (6) | N4 ⁱ –B1–N4 | 108.7 (3) |

Symmetry code: (i) $x, -y + \frac{1}{2}, z$.

Atom H22 attached to atom B1 was refined freely [B–H = 1.13 (4) Å]. All other H atoms were positioned geometrically (C–H = 0.95 and 0.98 Å) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2$ or 1.5 times $U_{\text{eq}}(\text{parent atom})$.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT-Plus (Bruker, 2002); data reduction: SADABS (Bruker, 2002); 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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