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Key indicators

Single-crystal X-ray study
T = 200 K
Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$
R factor = 0.071
wR factor = 0.162
Data-to-parameter ratio = 15.2For 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(2,4,6-tri-*tert*-butylphenolato)titanium toluene solvate**

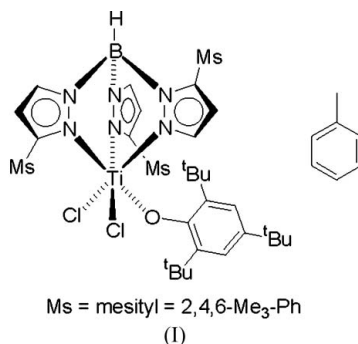
In the title complex, $[\text{Ti}(\text{C}_{18}\text{H}_{29}\text{O})\text{Cl}_2(\text{C}_{36}\text{H}_{40}\text{BN}_6)] \cdot \text{C}_7\text{H}_8$, the Ti atom is coordinated by three N atoms that are constrained to a *facial* arrangement by the Tp^{Ms^*} ligand [$\text{Tp}^{\text{Ms}^*} = \text{HB}(3\text{-mesitylpyrazolyl})_2(5\text{-mesitylpyrazolyl})$], two chloride ligands and the sterically bulky 2,4,6-*t*Bu₃-phenolate ligand in a distorted octahedral geometry.

Received 19 August 2006

Accepted 29 August 2006

Comment

Activation of group 4 metal Tp'/MCl_3 complexes ($M = \text{Ti}, \text{Zr}, \text{Hf}$) that contain sterically bulky tris(pyrazolyl)borate ligands (Tp') using methylalumoxane (MAO) generates ethylene polymerization catalysts with interesting properties, including the production of ultra-high molecular weight polyethylene and high 1-hexene incorporation in ethylene/hexene copolymerization (Murtuza *et al.* 2002; Michiue & Jordan, 2003, 2004; Gil *et al.* 2004; Lee & Jordan, 2005). 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 Tp^{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 particularly high activity. As part of a general investigation of sterically crowded $\text{Tp}^{\text{Ms}^*}\text{Ti}$ complexes, we have prepared and structurally characterized the title complex, $\text{Tp}^{\text{Ms}^*}\text{TiCl}_2(\text{O}-2,4,6\text{-}^t\text{Bu}_3\text{-Ph})$, (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, two chloride ligands and the sterically bulky 2,4,6-*t*Bu₃-phenolate ligand in a distorted octahedral geometry. The 2,4,6-*t*Bu₃-phenolate ligand is located *cis* to the 5-mesitylpyrazolyl ring, which minimizes steric crowding between the 2,4,6-*t*Bu₃-phenolate and Tp^{Ms^*} ligands. The N–Ti–N angles formed by the tridentate Tp^{Ms^*} ligand are acute. The N3–Ti1–N5 angle is larger than both the N1–Ti1–N3 angle and the N1–Ti1–

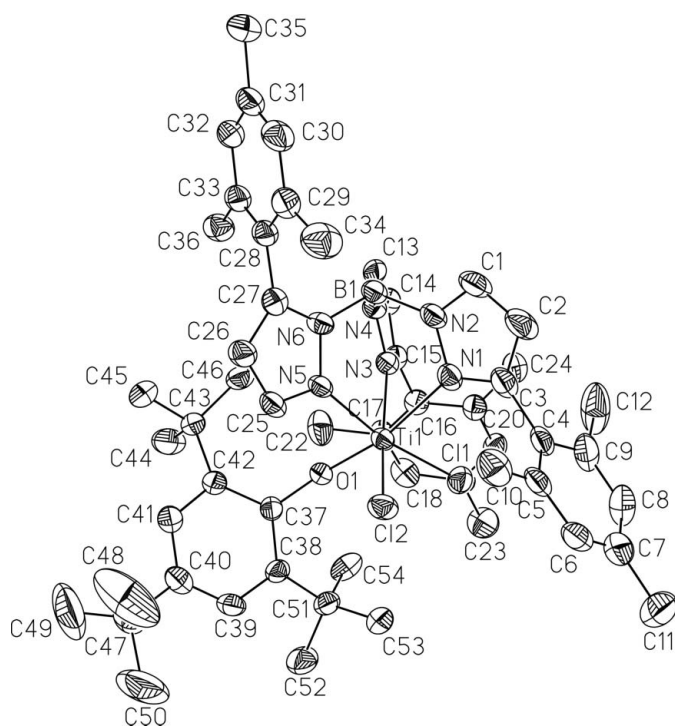


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms and the solvent molecule have been omitted.

N5 angle owing to steric pressure from the bulky phenolate ligand. The Ti1–N1 distance of the pyrazolyl unit which is *trans* to the phenolate ligand is longer than the Ti1–N3 and Ti1–N5 distances involving the pyrazolyl units which are *trans* to the chloride ligands, because of the difference in the *trans* influence of the substituted phenoxy ligand and the Cl ligands. The Ti–O bond distance is normal and the Ti–O–C37 angle deviates from linearity. The structure of (I) is similar to those of the related complexes $\text{Tp}^{\text{Ms}^*}\text{TiCl}_3$ (Michiue & Jordan, 2003) and $[\text{HB}(3,5\text{-dimethylpyrazolyl})_3]\text{TiCl}_2\text{(O}^t\text{Bu)}$ (Murtuza *et al.*, 2002).

Experimental

An NMR tube was charged with $\text{Tp}^{\text{Ms}^*}\text{TiCl}_3$ (12 mg, 0.016 mmol) and $\text{K}[\text{O}-2,4,6\text{-}^t\text{Bu}_3\text{-Ph}]$ (5.0 mg, 0.016 mmol), and toluene was added by vacuum transfer. The tube was warmed to 293 K, which resulted in the formation of a blue suspension that gradually turned to a dark-brown suspension. The tube was stored for 21 days at 293 K, which resulted in the precipitation of crystals of the title compound.

Crystal data

$[\text{Ti}(\text{C}_{18}\text{H}_{29}\text{O})\text{Cl}_2(\text{C}_{36}\text{H}_{40}\text{BN}_6)]\cdot\text{C}_7\text{H}_8$	$V = 2888.2 (7) \text{ \AA}^3$
$M_r = 1039.90$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.196 \text{ Mg m}^{-3}$
$a = 9.9124 (15) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 13.656 (2) \text{ \AA}$	$\mu = 0.28 \text{ mm}^{-1}$
$c = 23.488 (3) \text{ \AA}$	$T = 200 (2) \text{ K}$
$\alpha = 74.082 (3)^\circ$	Needle, red
$\beta = 88.828 (3)^\circ$	$0.24 \times 0.08 \times 0.08 \text{ mm}$
$\gamma = 71.303 (3)^\circ$	

Data collection

Bruker SMART APEX CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{\text{min}} = 0.883$, $T_{\text{max}} = 0.978$

21142 measured reflections
 10192 independent reflections
 6885 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$
 $\theta_{\text{max}} = 25.1^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.071$
 $wR(F^2) = 0.162$
 $S = 1.06$
 10192 reflections
 672 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0655P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.038$
 $\Delta\rho_{\text{max}} = 0.63 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.45 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

B1–N6	1.525 (5)	N1–Ti1	2.302 (3)
B1–N2	1.529 (5)	N3–Ti1	2.196 (3)
B1–N4	1.535 (5)	N5–Ti1	2.171 (3)
Cl1–Ti1	2.2350 (12)	O1–Ti1	1.806 (2)
Cl2–Ti1	2.2719 (12)		
N2–N1–Ti1	116.5 (2)	O1–Ti1–Cl2	94.48 (8)
N4–N3–Ti1	118.8 (2)	N5–Ti1–Cl2	84.10 (8)
N6–N5–Ti1	124.3 (2)	N3–Ti1–Cl2	167.12 (8)
C37–O1–Ti1	144.4 (2)	Cl1–Ti1–Cl2	94.88 (4)
O1–Ti1–N5	90.95 (11)	O1–Ti1–N1	168.01 (11)
O1–Ti1–N3	95.71 (11)	N5–Ti1–N1	78.15 (11)
N5–Ti1–N3	87.86 (11)	N3–Ti1–N1	79.07 (11)
O1–Ti1–Cl1	102.11 (8)	Cl1–Ti1–N1	88.82 (9)
N5–Ti1–Cl1	166.94 (8)	Cl2–Ti1–N1	89.41 (8)
N3–Ti1–Cl1	90.67 (8)		

The atom H62 attached to B1 was located in a difference Fourier map, after which it was refined isotropically [$\text{B}–\text{H} = 1.08 (3) \text{ \AA}$]. All other H atoms were positioned geometrically ($\text{C}–\text{H} = 0.95$ and 0.98 \AA) and refined as riding, with $U_{\text{iso}}(\text{H})$ values of 1.2 or 1.5 times U_{eq} (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.

This work was supported by the US Department of Energy (DE-FG02-00ER15036).

References

- Bruker (2002). SMART (Version 5.628), SAINT-Plus (Version 6.02), SADABS (Version 2.03) and SHELXTL (Version 5.1). Bruker AXS Inc., Madison, Wisconsin, USA.
- Gil, M. P., dos Santos, J. H. Z. & Casagrande, O. L. Jr (2004). *J. Mol. Catal. A Chem.* **209**, 163–169.
- Lee, H. & Jordan, R. F. (2005). *J. Am. Chem. Soc.* **127**, 9384–9385.
- Michiue, K. & Jordan, R. F. (2003). *Macromolecules*, **36**, 9707–9709.
- Michiue, K. & Jordan, R. F. (2004). *Organometallics*, **23**, 460–470.
- Murtuza, S., Casagrande, O. L. & Jordan, R. F. (2002). *Organometallics*, **21**, 1882–1890.