

Chloro[hydridotris(3-*tert*-butyl-5-methylpyrazolyl)-borato]cobalt(II)Gregory M. Ferrence* and
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In the title complex, $[\text{Co}(\text{C}_{24}\text{H}_{40}\text{BN}_6)\text{Cl}]$, the Co atom is coordinated by three N atoms, arranged with the typical facial arrangement imposed by trispyrazolylborate ligands, and a chloride ligand in a distorted tetrahedral geometry. The molecule has mirror symmetry.

Received 21 October 2006
Accepted 16 November 2006

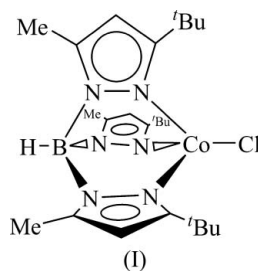
Key indicators

Single-crystal X-ray study
 $T = 193 \text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
Disorder in main residue
 R factor = 0.030
 wR factor = 0.070
Data-to-parameter ratio = 15.3

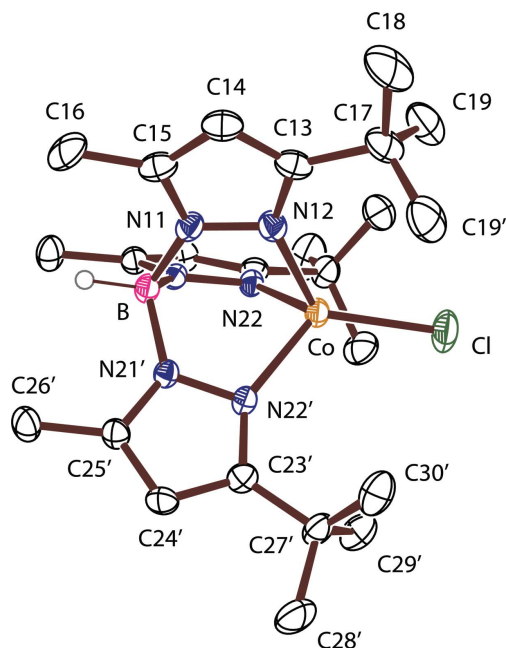
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Comment

The chemistry of scorpionate-supported transition-metal complexes has been the subject of intense research with in excess of 2000 papers published on polypyrazolylborate complexes spanning over 70 elements of the periodic table (Trofimenko, 2004, 1999, and references therein; Parkin, 2000; Vahrenkamp, 1999). The Cambridge Structural Database (Version 5.27, August 2006 update; Allen, 2002) includes data for over 2900 crystal structures of trispyrazolylborate (Tp) metal complexes, many with bulky derivatives, including 54 incorporating the tris(3-*tert*-butyl-5-methylpyrazolyl)borate ligand, $\text{Tp}^{\text{tBu,Me}}$. The coordination number of Tp-coordinated metals is strongly controlled by the steric properties of the substituents attached to the 3-pyrazolyl C atoms. Sterically demanding Tp ligands have been found to be well suited for the isolation of low-coordinate metal complexes; those with *tert*-butyl groups attached to the pyrazolyl 3-positions have been referred to as tetrahedral enforcers (Trofimenko *et al.* 1987). The title complex, $(\text{Tp}^{\text{tBu,Me}})\text{CoCl}$, (I), is consistent with this generalization.



The molecular structure of (I) is shown in Fig. 1, and selected bond distances and angles are presented in Table 1. Atoms Co, Cl, H1, B, C13–C18, H14, H18A and H16B all lie on a mirror plane. The Co atom is coordinated by three N atoms, with the typical facial arrangement imposed by trispyrazolylborato ligands, and a chloride ligand in a distorted tetrahedral geometry. $(\text{Tp}^{\text{tBu,Me}})\text{CoCl}$ is essentially isostructural with $(\text{Tp}^{\text{tBu}})\text{CoCl}$ (Gorrell & Parkin, 1990), with few bond distances or angles differing more than within experimental standard uncertainties. Beyond the obvious difference in the pyrazolyl 4-position substituent, none of the differences


Figure 1

The molecular structure of (I), showing the atom labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Primed atoms are related to the unlabeled atoms of the asymmetric unit by $\frac{1}{2} - x, y, z$.

are chemically significant. The N–Co–N angles formed by the tridentate $\text{Tp}^{\text{tBu,Me}}$ ligand are over 12° less than perfect tetrahedral angles because of the Tp-imposed bite angle. Correspondingly, the N–Co–Cl angles are over 11° more than perfect tetrahedral angles. The structure of (I) is similar to those of related complexes, including $(\text{Tp}^{\text{tBu}})\text{CoMe}$, $(\text{Tp}^{\text{tBu}})\text{CoH}$ (Jewson *et al.*, 1999), $(\text{Tp}^{\text{tBu}})\text{CoF}$ (Gorrell & Parkin, 1990), $(\text{Tp}^{\text{tBu}})\text{CoNCS}$ (Trofimenko *et al.*, 1987), and $(\text{Tp}^{\text{tBu,Me}})\text{CoOH}$ (Bergquist *et al.*, 2003).

Experimental

The synthesis of $(\text{Tp}^{\text{tBu,Me}})\text{CoCl}$ was reported previously (Egan *et al.*, 1990; Trofimenko *et al.*, 1987). The title compound was prepared by a similar procedure. Specifically, $\text{K}(\text{Tp}^{\text{tBu,Me}})$ (1.000 g, 2.16 mmol) and CoCl_2 (0.259 g, 2.00 mmol) were mixed and dissolved in approximately 30 ml of dichloromethane. After stirring for 1 h, the solution was filtered through a coarse glass frit, washed with dichloromethane, and the filtrate was evaporated to dryness. The residue was dissolved in a minimal amount of dichloromethane and centrifuged to remove residual KCl. The decantate was transferred to a small Erlenmeyer flask and mixed with acetonitrile (2:1 ratio of dichloromethane to acetonitrile). Slow evaporation produced 0.591 g (1.14 mmol, 57%) of $(\text{Tp}^{\text{tBu,Me}})\text{CoCl}$ from which an X-ray quality crystal was selected.

Crystal data

$[\text{Co}(\text{C}_{24}\text{H}_{40}\text{BN}_6)\text{Cl}]$	$Z = 4$
$M_r = 517.81$	$D_x = 1.229 \text{ Mg m}^{-3}$
Orthorhombic, <i>Ama2</i>	Mo $K\alpha$ radiation
$a = 16.429 (2) \text{ \AA}$	$\mu = 0.73 \text{ mm}^{-1}$
$b = 16.035 (2) \text{ \AA}$	$T = 193 (2) \text{ K}$
$c = 10.6255 (14) \text{ \AA}$	Plate, blue
$V = 2799.1 (6) \text{ \AA}^3$	$0.62 \times 0.4 \times 0.09 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	6423 measured reflections
φ and ω scans	2791 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2594 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.660, T_{\max} = 0.937$	$R_{\text{int}} = 0.032$
	$\theta_{\max} = 26.4^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0311P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.07$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.05$	$\Delta\rho_{\max} = 0.29 \text{ e \AA}^{-3}$
2791 reflections	$\Delta\rho_{\min} = -0.21 \text{ e \AA}^{-3}$
183 parameters	Absolute structure: Flack (1983),
H atoms treated by a mixture of independent and constrained refinement	1228 Friedel pairs
	Flack parameter: 0.004 (14)

Table 1

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

Co–Cl	2.2076 (9)	C13–C14	1.386 (5)
Co–N12	2.023 (3)	C14–C15	1.370 (5)
Co–N22	2.0364 (15)	C15–N11	1.342 (4)
N11–N12	1.375 (3)	N22–C23	1.341 (3)
N21–N22	1.385 (3)	C23–C24	1.395 (3)
B–N11	1.554 (4)	C24–C25	1.373 (3)
B–N21	1.540 (2)	C25–N21	1.351 (3)
N12–C13	1.340 (4)		
N11–N12–Co	109.91 (18)	N11–N12–C13	107.0 (3)
N21–N22–Co	109.28 (12)	N12–C13–C14	108.9 (3)
N12–Co–N22	95.03 (8)	C13–C14–C15	106.9 (3)
N22 ⁱ –Co–N22	96.83 (8)	C14–C15–N11	107.7 (3)
N12–Co–Cl	121.33 (8)	C15–N11–N12	109.5 (2)
N22–Co–Cl	121.09 (6)	N21–N22–C23	106.77 (15)
N12–N11–B	120.7 (2)	N22–C23–C24	109.20 (19)
N22–N21–B	120.93 (18)	C23–C24–C25	106.85 (18)
N21 ⁱ –B–N21	110.3 (2)	C24–C25–N21	107.66 (18)
N21–B–N11	109.49 (17)	C25–N21–N22	109.52 (16)

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

H atoms attached to atoms C16, C18 and B were identified through difference Fourier synthesis and refined with isotropic displacement parameters. All other H atoms were included in the refinement in the riding-model approximation, with isotropic displacement parameters fixed at $1.2U_{\text{eq}}$ of the parent atom ($\text{C–H} = 0.95$ and 0.98 \AA). Atom C26 was refined as an idealized disordered methyl group with H atoms included using the HFIX 123 instruction in *SHELXL97*.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

GMF thanks Research Corporation for financial support, and Dr Robert McDonald and the University of Alberta Structure Determination Laboratory for collecting the low-temperature CCD X-ray data.

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