

A C_3 -symmetric chiral hexadentate podand ligand based on a tris(pyrazolyl)borate core

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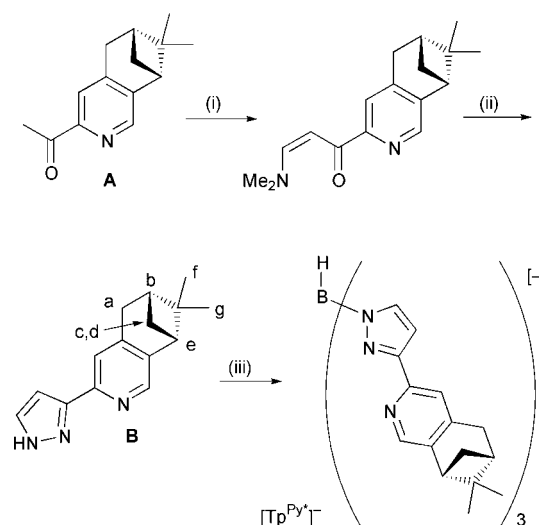
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A hexadentate podand ligand having C_3 symmetry has been prepared, consisting of a tris(pyrazolyl)borate core bearing pinene-functionalised 2-pyridyl units attached to the C^3 position of each pyrazolyl ring such that each arm is a chiral bidentate chelate; complexes with Tl(I) and Tb(III) have been prepared and structurally characterised.

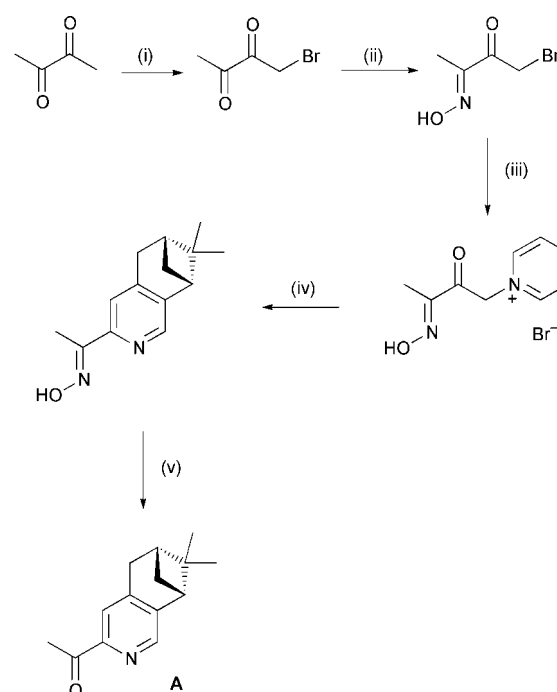
Chiral C_3 -symmetric ligands are of considerable interest for use in asymmetric catalysis and chiral recognition.¹ Amongst these, chiral derivatives of the well-known tris(pyrazolyl)borates² have been studied principally by Tolman and co-workers, who have investigated the synthesis and coordination behaviour of several chiral tris(pyrazolyl)borate (generically, Tp) derivatives^{3,4} and the use of their complexes in asymmetric catalysis.^{5,6} Also related to these are a few examples of chiral tris(pyrazolyl)phosphine oxides^{5,7} and a chiral tetrakis-(pyrazolyl)borate.⁸ All of the known chiral Tp ligands are potentially terdentate, with a chiral unit such as camphoryl or menthyl fused to two sites of the pyrazolyl ring, such that the coordination behaviour of the ligand is basically that of a conventional but sterically hindered Tp ligand.⁴

We describe here the first example of a C_3 -symmetric hexadentate tripodal ligand tris[3-(2-(pinene[4,5]pyridyl)-pyrazolyl)hydroborate (hereafter abbreviated as $[\text{Tp}^{\text{Py}^*}]^-$) based on a tris(pyrazolyl)borate core. The achiral hexadentate parent ligand $[\text{Tp}^{\text{Py}}]^-$ has been extensively studied by us,^{9–12} and the addition of 2-pyridyl substituents to the C^3 positions of the pyrazolyl rings, such that each arm of the ligand is now a bidentate chelate, results in completely different coordination behaviour from the simpler terdentate Tp ligands.² $[\text{Tp}^{\text{Py}}]^-$ can accommodate a single metal ion such as a lanthanide(III) ion⁹ or thallium(I)¹¹ in its hexadentate cavity, or can act as a trinucleating bridging ligand, with each bidentate arm coordinated to a different metal ion to afford tetrahedral cages such as $[\text{Mn}_4(\text{Tp}^{\text{Py}})_4]^{4+}$ in interesting self-assembly processes.¹⁰

The new ligand $[\text{Tp}^{\text{Py}^*}]^-$ mimics the donor set of $[\text{Tp}^{\text{Py}}]^-$ but is chiral by virtue of the pinene units fused to the C^4 and C^5 positions of each pyridyl ring. The synthesis is summarised in Scheme 1 and follows the same basic route as that for $[\text{Tp}^{\text{Py}}]^-$.[†] The key intermediate is the chiral 2-acetylpyridine derivative (–)-2-acetyl{pinene[4,5]pyridine} **A**, which is prepared in several steps starting from 2,3-butanedione: protection of one acetyl group as its oxime allows the other to be converted to a pyridine ring by a Kröhnke-type reaction with (–)-myrtenal in the presence of ammonium acetate. This synthesis is summarised in Scheme 2; full experimental details will be described elsewhere.¹³ Conversion of the acetyl group of **A** to a pyrazole is straightforward,⁹ and the pyrazole **B** was then converted to $[\text{Tp}^{\text{Py}^*}]^-$ by reaction with KBH_4 in 4-methylanisole at reflux,¹⁴ followed by isolation of the ligand as its Tl(I) complex to give $[\text{Tl}(\text{Tp}^{\text{Py}^*})]$.[†] The formulation of the complex was confirmed by ¹H and ¹¹B NMR spectroscopy, a FAB mass spectrum, and a crystal structure.



Scheme 1 Preparation of $[\text{Tp}^{\text{Py}^*}]^-$. (i) *N,N*-Dimethylformamide-dimethylacetal, reflux for 6 h; (ii) hydrazine hydrate, ethanol, 60 °C, 30 minutes; (iii) KBH_4 , 4-methylanisole, reflux, 24 h.



Scheme 2 Preparation of (–)-2-acetyl{pinene[4,5]pyridine} (**A**). (i) Br_2 , 0 °C; (ii) $\text{NH}_2\text{OH}\cdot\text{HCl}$, water, Na_2CO_3 , 0 °C; (iii) pyridine, Et_2O , rt; (iv) (–)-myrtenal, NH_4OAc , dmf, 80 °C; (v) aq. HCl, reflux.

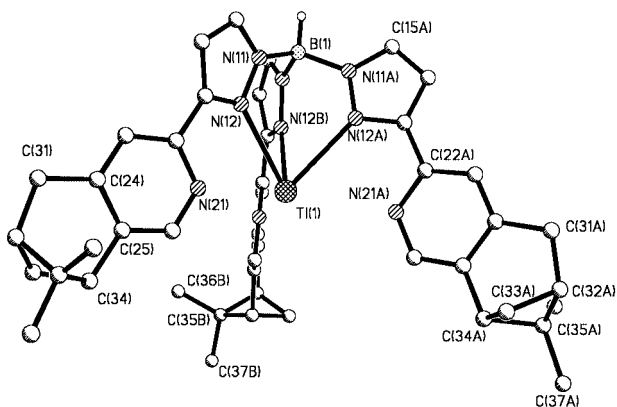


Fig. 1 Crystal structure of one of the independent complex molecules of $[\text{Ti}(\text{Tp}^{\text{Py}^*})]$. Selected bond distances (Å) (the corresponding values for the alternate independent molecule are given in brackets): $\text{Ti}(1)\text{--}\text{N}(12)$, 2.719(3) [$\text{Ti}(2)\text{--}\text{N}(42)$, 2.721(3)]; $\text{Ti}(1)\cdots\text{N}(21)$, 3.101(3) [$\text{Ti}(2)\cdots\text{N}(51)$, 3.131(3)].

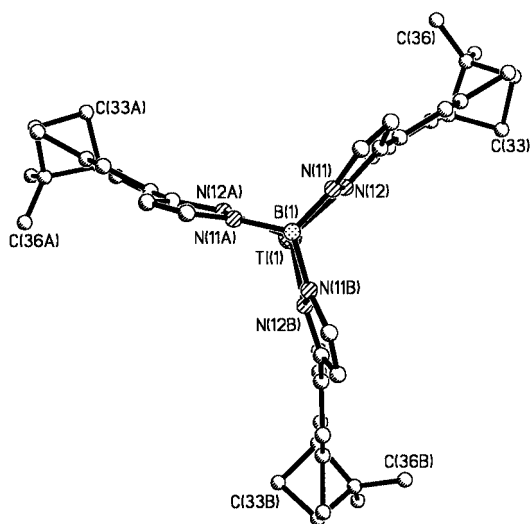


Fig. 2 Alternative view of $[\text{Ti}(\text{Tp}^{\text{Py}^*})]$ looking down the threefold $\text{Ti}\cdots\text{B}$ axis.

The crystal structure of $[\text{Ti}(\text{Tp}^{\text{Py}^*})]$ is shown in Figs. 1 and 2.† It is similar to that of the related non-chiral complex $[\text{Ti}(\text{Tp}^{\text{Py}})]$,¹¹ with the $\text{Ti}(\text{t})$ centre being coordinated principally by the three pyrazolyl N donors in a pyramidal arrangement [$\text{Ti}\text{--}\text{N}(\text{pyrazolyl})$ distances, 2.719(3) in one independent molecule and 2.721(3) Å in the other], and the fourth coordination site vacant. Fig. 2 is a view down the $\text{Ti}\cdots\text{B}$ axis which emphasises the C_3 symmetry. The $\text{Ti}\cdots\text{N}(\text{pyridyl})$ distances are too long for these interactions to be considered as full bonds [3.101(3) in one independent molecule and 3.131(3) Å in the other], nevertheless the presence of a weak interaction is shown by the fact that the pyridyl rings are oriented such that the lone pairs of the N atoms are pointing at the metal centre. We have observed similar weak $\text{Ti}\cdots\text{N}$ interactions in related complexes,¹⁵ and we note that the unusual structural properties of $\text{Ti}(\text{t})/\text{Tp}$ complexes in general continue to be a subject of current interest.¹⁶

Reaction of $[\text{Ti}(\text{Tp}^{\text{Py}^*})]$ with $\text{Tb}(\text{III})$ nitrate in MeOH afforded $[\text{Tb}(\text{Tp}^{\text{Py}^*})(\text{NO}_3)_2]$, whose identity was confirmed by its FAB mass spectrum.† The crystal structure (Fig. 3) is likewise similar to that of the achiral complexes $[\text{Ln}(\text{Tp}^{\text{Py}})(\text{NO}_3)_2]$ ($\text{Ln} = \text{Eu}, \text{Er}, \text{Pr}$),⁹ with a 10-coordinate metal ion arising from hexadentate coordination of the podand ligand and two bidentate nitrates. The presence of two nitrate ligands breaks the threefold symmetry that would otherwise be imposed by the ligand. Several lanthanide(III) complexes with substituted Tp derivatives have been reported by others recently.¹⁷

Together these structures confirm that attachment of the chiral pinene units to the C^4 and C^5 positions of the pyridyl

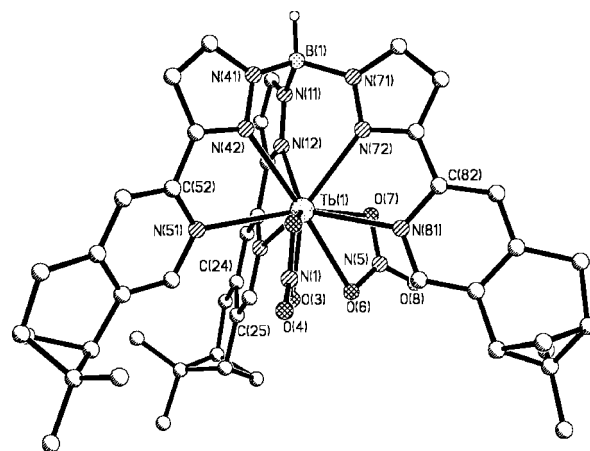


Fig. 3 Crystal structure of the complex molecule of $[\text{Tb}(\text{Tp}^{\text{Py}^*})(\text{NO}_3)_2]\cdot(\text{CH}_2\text{Cl}_2)$. Selected bond distances (Å): $\text{Tb}(1)\text{--}\text{N}(72)$, 2.477(3); $\text{Tb}(1)\text{--}\text{O}(3)$, 2.491(3); $\text{Tb}(1)\text{--}\text{N}(12)$, 2.491(3); $\text{Tb}(1)\text{--}\text{O}(7)$, 2.506(3); $\text{Tb}(1)\text{--}\text{O}(2)$, 2.519(3); $\text{Tb}(1)\text{--}\text{N}(42)$, 2.523(4); $\text{Tb}(1)\text{--}\text{O}(6)$, 2.571(3); $\text{Tb}(1)\text{--}\text{N}(81)$, 2.642(3); $\text{Tb}(1)\text{--}\text{N}(21)$, 2.643(4); $\text{Tb}(1)\text{--}\text{N}(51)$, 2.735(4); $\text{B}(1)\text{--}\text{N}(41)$, 1.539(7); $\text{B}(1)\text{--}\text{N}(11)$, 1.543(7); $\text{B}(1)\text{--}\text{N}(71)$, 1.551(6).

rings has, as we wanted, preserved the basic coordination behaviour of the podand ligand. Attachment of substituents at the pyridyl C^6 position would bring the chiral groups closer to the metal centre, but at the expense of a substantial degree of steric crowding which would completely change the coordination behaviour.¹⁸ Obvious avenues for investigation with the lanthanide complexes include (i) the possibility of chiral quenching with the different enantiomers of $[\text{Ru}(\text{bipy})_3]^{2+}$ $\{^*\text{Tb}(\text{III})\rightarrow\text{Ru}$ photoinduced energy transfer¹⁹ and $^*\text{Ru}\rightarrow\text{Eu}(\text{III})$ photoinduced electron-transfer²⁰ with $[\text{Ru}(\text{bipy})_3]^{2+}$ are both known), and (ii) their use as Lewis-acid catalysts for *e.g.* Diels–Alder reactions,²¹ since dissociation of the nitrate ions in a polar solvent⁹ will allow direct access of substrates to the primary coordination sphere of the metal in a C_3 -symmetric environment. It will also be of interest to investigate the use of $[\text{Tp}^{\text{Py}^*}]^-$ in the diastereoselective assembly²² of tetrahedral cages (*cf.* $[\text{Mn}_4(\text{Tp}^{\text{Py}})_4]^{4+}$) which are inherently chiral because of the presence of four tris-chelate metal centres which all have the same configuration.¹⁰

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Notes and references

† Preparation of $[\text{Ti}(\text{Tp}^{\text{Py}^*})]$: (–)-2-Acetyl{pinene[4,5]pyridine} (**A**) (ref. 13) was converted to the corresponding pyrazole (**B**) by the two-step procedure we have described before (refs. 9 and 18), and was fully characterised by NMR and mass spectrometry as well as X-ray crystallography; full details will be reported in due course. A mixture of **B** (2.09 g, 8.75 mmol) and KBH_4 (0.14 g, 2.5 mmol) dissolved in 4-methylanisole was heated to reflux for 24 h under N_2 , and the solvent was then distilled off *in vacuo*. The remaining brown oil was dissolved in thf (10 cm^3), and to this was added a solution of TiNO_3 (1 equiv. per hexadentate ligand) in water (10 cm^3). The resulting solution was extracted with several portions of CH_2Cl_2 which were combined, dried over MgSO_4 , and evaporated to dryness to give a brown oil which, on trituration with diethyl ether and treatment with ultrasound, crystallised to an off-white solid of $[\text{Ti}(\text{Tp}^{\text{Py}^*})]$ (30% yield). Found: C, 57.5; H, 4.8; N, 13.9. $\text{C}_{45}\text{H}_{49}\text{BN}_6\text{Ti}$ requires C, 58.1; H, 5.3; N, 13.5%. X-Ray quality crystals were grown by slow evaporation from CDCl_3 in an NMR tube. $^1\text{H-NMR}$ (270 MHz, CDCl_3): δ 8.13 (1H, s; pyridyl H⁶), 7.73 (1H, d, $J = 1.6$; pyrazolyl H⁵), 7.47 (1H, s; pyridyl H³), 6.59 (1H, d, $J = 1.5$; pyrazolyl H⁴), 2.96 (2H, d, $J = 2.4$; pinene H^a), 2.80 (1H, t, $J = 5.5$; pinene H^c), 2.67 (1H, m; pinene H^d), 2.27 (1H, m; pinene H^b), 1.39 (3H, s; pinene H^f), 1.19 (1H, d, $J = 9.5$ Hz; pinene H^e), 0.61 (3H, s; pinene H^g) (for the labelling scheme used for the pinene fragment, see Scheme 1). $^{11}\text{B-NMR}$: (300 MHz, CDCl_3) δ –3.51 (s) [this is characteristic of the BH unit of a tris(pyrazolyl)borate: there was no sign of a resonance corresponding to a bis(pyrazolyl)borate at between –8 and –10 ppm, or a tetrakis(pyrazolyl)borate at between +1 and +2 ppm]. FAB-MS: m/z 694 [100%, M^+ – one bidentate arm (**B**)].

Preparation of [Tb(Tp^{Py*})(NO₃)₂]: [Tl(Tp^{Py*})] (0.050 g, 0.05 mmol) and Tb(NO₃)₃·5H₂O (0.024 g, 0.05 mmol) were dissolved in MeOH (10 cm³) and the solution was stirred for 24 hours. The solution was then reduced *in vacuo* to ca. 2 cm³ and refrigerated. The resultant precipitate was collected by filtration, washed with H₂O, and dried *in vacuo* to give an off-white solid of [Tb(Tp^{Py*})(NO₃)₂] (67% yield). Found: C, 52.4; H, 5.0; N, 13.3. C₄₅H₄₉BN₁₁O₆Tb requires C, 53.5; H, 4.9; N, 15.3%. Low C and N values are common for lanthanide tris(pyrazolyl)borate complexes (see ref. 9). X-Ray quality crystals were grown from CH₂Cl₂–hexane. FAB-MS: *m/z* 948 [100%, M⁺ – NO₃]. Satisfactory analytical data were obtained for the new complexes.

‡ Crystal data for [Tl(Tp^{Py*})]₂: C₄₅H₄₉BN₁₁O₆Tl, *M* = 931.11, rhombohedral (hexagonal setting), space group *R*3̄, *a* = *b* = 20.3970(18), *c* = 17.347(3) Å, *U* = 6250.1(12) Å³, *Z* = 6, *D*_c = 1.484 Mg m⁻³, μ(Mo-Kα) = 3.920 mm⁻¹, *F*(000) = 2808, *T* = 173 K, 6361 independent reflections (*R*_{int} = 0.0345) with 2θ < 55°. Refinement of 358 parameters converged at final *R*1 [for selected data with *I* > 2σ(*I*)] = 0.0261, *wR*2 (all data) = 0.0502. The Flack parameter was –0.008(5). The asymmetric unit contains two independent units which each constitute one-third of a complex molecule, *i.e.* an entire bidentate ligand 'arm' with one-third of the associated B and Tl atoms which lie on C₃ axes. There are accordingly two crystallographically independent but very similar complex molecules in the crystal, each lying on a C₃ axis.

Crystal data for [Tb(Tp^{Py*})(NO₃)₂](CH₂Cl₂)₂: C₄₈H₅₅BCl₆N₁₁O₆Tb, *M* = 1264.46, orthorhombic, space group *P*2₁2₁2₁, *a* = 12.6126(17), *b* = 17.623(2), *c* = 24.975(4) Å, *U* = 5551.3(13) Å³, *Z* = 4, *D*_c = 1.513 Mg m⁻³, μ(Mo-Kα) = 1.619 mm⁻¹, *F*(000) = 2560, *T* = 173 K, 12704 independent reflections (*R*_{int} = 0.0475) with 2θ < 55°. Refinement of 677 parameters converged at final *R*1 [for selected data with *I* > 2σ(*I*)] = 0.0357, *wR*2 (all data) = 0.1155. The Flack parameter was 0.001(7).

X-Ray measurements were made using a Bruker SMART CCD area-detector diffractometer; structure solution and refinement was with the SHELXTL program system.²³ CCDC reference numbers xxx. See <http://www.rsc.org/suppdata/dt/b1/b102295b/> for crystallographic data in CIF or other electronic format.

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