Hydrotris(7-*tert*-butylindazol-2-yl)borate: a super-hindered homoscorpionate ligand

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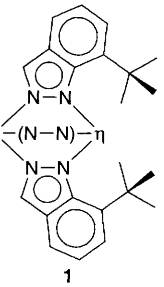
The super-hindered ligand hydrotris(7-*tert*-butylindazol-2-yl)borate is synthesized and shown to undergo rearrangement during the formation of a tetrahedral cobalt(II) complex.

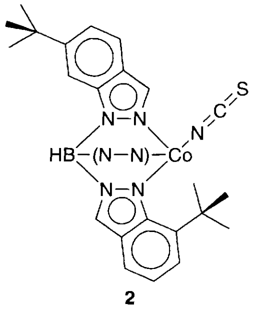
The coordination chemistry of homoscorpionates [tris(pyrazolylborates)] has provided a number of unique examples of stable complexes unavailable with any other ligand. These include stable monomeric organoalkyls of Be,[1] Mg,[2] Zn[3] and Cd,[4] their hydrides, and their monomeric hydroxides, all based on the sterically hindered homoscorpionates, mostly $\mathrm{Tp}^{\mathrm{Bu^t}}$ and $\mathrm{Tp}^{\mathrm{Bu^t,Me}}$.[5] The $\mathrm{Tp}^{\mathrm{Bu^t}}$ ligand was initially viewed as a 'tetrahedral enforcer' but, later on, examples of five-coordinate (though not six-coordinate) species based thereon were reported. We sought to create an even more hindered ligand, closer to the 'tetrahedral enforcer' concept, by aiming for a species similar to $\mathrm{Tp}^{\mathrm{Np}}$,[6] yet with the 'neopentyl' group rigidly fixed so that its *tert*-butyl group would be directed at the coordinated metal, thus precluding the large degree of rotational freedom around the pz-$\mathrm{CH_2}$ bond present in $\mathrm{Tp}^{\mathrm{Np}}$. These requirements were to be met by hydrotris(7-*tert*-butylindazol-2-yl)borate, as in **1**, where the rigidity of the fused benzo ring imparts a unique orientation to the *tert*-butyl group.

It had been shown earlier,[7] that indazole (benzopyrazole), and its 3-, 4-, 5- and 6-alkylated analogues, exhibit abnormal regiochemistry in the reaction with borohydride ion to form polyindazolylborates where the boron is bonded to the *more hindered* N(1), which contrasts with the behaviour of substituted pyrazoles, where B–N bonding always occurs at the *less hindered* N atom. This is probably for electronic reasons,[8] as N(1) has the highest electron density in indazoles.[9] Still, we expected the large bulk of the *tert*-butyl group to override electronic effects, since the presence of a 7-substituent derived from the adjacent =C–H of a fused benzo ring in the case of benzindazole,[10] led to the formation of a regioselectively pure ligand, $\mathrm{Tp^{a*}}$, in which boron was bonded exclusively to N(2), as one would have predicted on the basis of steric effects alone.

The starting indazole† was synthesized by catalytic dehydrogenation of its tetrahydro precursor, and the ligand $\mathrm{Tp}^{\mathrm{3Bo,Bu^t}}$ (Bo = benzo) was prepared in standard fashion from $\mathrm{KBH_4}$ and 7-*tert*-butylindazole, being characterized as its Tl salt, **1**.†



1
$[(\mathrm{Tp}^{\mathrm{3Bo,\,7Bu^t*}})\mathrm{Tl}]$



2
$[(\mathrm{Tp}^{\mathrm{3Bo,\,7Bu^t*}})\mathrm{Co(NCS)}]$

[-(N-N)- is the third, hidden, 7-*tert*-butylindazol-2-yl group]

Surprisingly, the NMR spectrum of **1**, while confirming the presence of a single regioisomer of C_{3v} symmetry, did not show any resolvable $^{13}\mathrm{C}$–$^{205}\mathrm{Tl}$ coupling, except for a modest broadening of the *tert*-butyl $^{13}\mathrm{C}$ (Me) peak. This was unusual, since the 7-Me analogue, $\mathrm{Tp}^{\mathrm{3Bo,7Me}}$, exhibited the largest $^{13}\mathrm{C}$–$^{205}\mathrm{Tl}$ coupling of any homoscorpionate known (J = 416 Hz) to the 7-Me carbon.† Nevertheless, an X-ray crystallographic study established the proposed structure, confirming that boron was bonded to the less hindered N(2).‡ Fig. 1 shows clearly the extent of the Tl ion being enveloped by the ligand. The lack of $^{205}\mathrm{Tl}$ coupling in the $^{13}\mathrm{C}$ NMR spectrum of **1** may be accounted for by the Tl–N bonding being weak due to the steric back-pressure, and the molecule becoming an ion pair in solution, beyond the range of Tl–C interaction.

Unlike other homoscorpionate Tl complexes **1** did not react with $\mathrm{MX_2}$ salts in non-polar solvents at room temperature. Reaction took place only under forcing conditions, accompanied by rearrangement of the ligand to the less hindered $[\mathrm{HB}(3\text{-}tert\text{-butylindazol-2-yl})_2(3\text{-}tert\text{-butylindazol-1-yl})]$, $\mathrm{Tp}^{\mathrm{3Bo,7Bu^t*}}$, as was established by an X-ray crystallographic structure determination of the complex $\mathrm{Co}(\mathrm{Tp}^{\mathrm{3Bo,7Bu^t*}})(\mathrm{NCS})]\cdot 2\mathrm{C_6H_6}$, **2**.†‡ This is the first known instance of rearrangement of a symmetrical $\mathrm{Tp^x}$ ligand to an unsymmetrical one in a tetrahedral complex. Such rearrangements have so far been confined only to octahedral complexes of ligands such as $\mathrm{Tp}^{\mathrm{Pr^i}}$,[11] and $\mathrm{Tp}^{\mathrm{Np}}$.[6]

Since cone angles for homoscorpionate ligands are a function of the N–M bond length, we compared the cone angles in **1** and **2** with analogous isometallic complexes. The cone angle of the $\mathrm{TP}^{\mathrm{3Bo,7Bu^t}}$ ligand in **1** was 261°, and thus substantially higher than the 225° angle determined for the isometallic complex $[\mathrm{Tl}(\mathrm{Tp}^{\mathrm{Bu^t,Me}})]$.[12] In **2**, the cone angle, as determined from the two unrearranged 7-*tert*-butylindazolyl groups, was an awe-

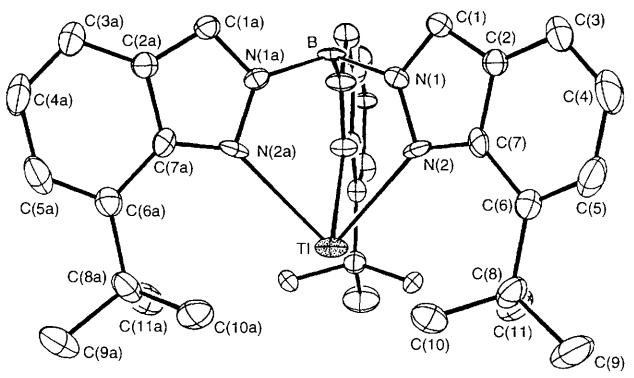


Fig. 1 ORTEP plot of the structure of **1** (ellipsoids are at the 30% probability levels). The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Tl–N(2) 2.6555, Tl–N(4) 2.656, Tl–N(2A) 2.655, N(1)–B 1.558, N(3)–B 1.552, N(1A)–B 1.558; N(2)–Tl–N(4) 78.6, N(2)–Tl–N(2a) 78.2, N(4)–Tl–N(2a) 78.6, N(1)–B–N(1a) 110.0, N(1)–B–N(3) 111.5, N(3)–B–N(1a) 111.5.

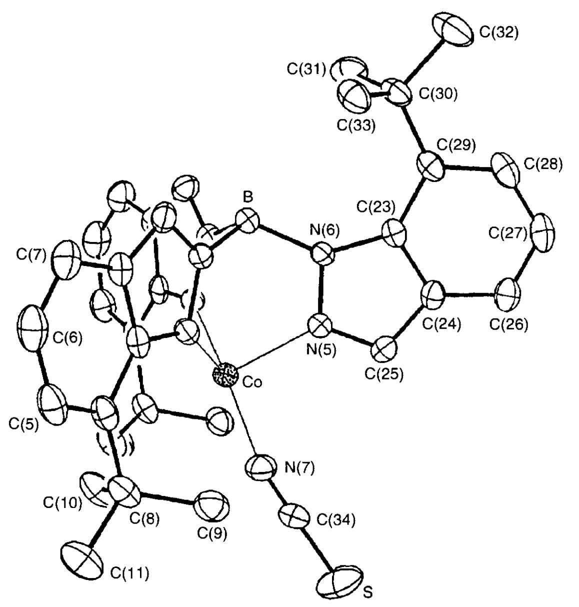


Fig. 2 ORTEP plot of the structure of **2** (ellipsoids are at the 30% probability level). The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co–N(1) 2.019, Co–N(3) 2.032, Co–N(5) 2.020, Co–N(7) 1.913, S–C(34) 1.593, B–N(2) 1.575, B–N(4) 1.562, B–N(6) 1.543; N(1)–Co–N(3) 98.9, N(1)–Co–N(5) 93.3, N(3)–Co–N(5) 90.8, N(1)–Co–N(7) 129.9, N(3)–Co–N(7) 129.7, N(5)–Co–N(7) 97.0, N(2)–B–N(4) 106.7, N(2)–B–N(6) 110.3.

some 305 °C. This greatly exceeds the 261° cone angle found in the related complex [Co(Tp$^{Bu^t}$)(NCS)].[13] The Co–NCS bond in **2** departs by 29° from co-linearity with the B–Co axis, as can be seen in Fig. 2, presumably being pushed away by the *tert*-butyl groups near the metal. The repulsive forces between the neighbouring *tert*-butyl groups spread the angle between the respective indazolyl planes to 127°, at the same time compressing the angles between the 7-*tert*-butylindazol-1-yl and the 7-*tert*-butylindazol-1-yl planes to 116.5°.

The above results suggest that the Tp$^{3Bo,7Bu^t}$ ligand may indeed be regarded as a 'tetrahedral enforcer', and this may also apply to its rearranged isomer, Tp$^{3Bo,7Bu^t*}$. Indeed, the steric restrictiveness of these ligands may be approaching the limit for effective coordination in homoscorpionates.

Footnotes

† All the new compounds gave satisfactory elemental analyses. 7-*tert*-butylindazole was synthesized *via* formylation of 2-*tert*-butylcyclohexanone, followed by reaction with hydrazine hydrate, with subsequent catalytic dehydrogenation over Pd/C at 280–290 °C of the tetrahydro precursor. The product, mp 127–128 °C (from heptane) was obtained in 56% yield. ^{1}H NMR δ 11.5 (br, 1 H, NH), 8.12 (s, 1 H, H^3), 7.63 (d, 1 H, H^4), 7.28 (d, 1 H, H^6), 7.11 (t, 1 H, H^5), 1.54 (s, 9 H, Me) ^{13}C NMR δ 30.1 (CCH_3), 34.6 (CCH_3), 118.7, 121.1, 122.7, 124.1, 133.3, 134.7, 138.3.

Compound **1** was prepared by refluxing 7-*tert*-butylindazole with KBH_4 (3.6 : 1 mol ratio) in 4-methylanisole until the theoretical amount of hydrogen was evolved. After distilling out the solvent *in vacuo*, the residue was converted to the Tl salt. Mp 265–266 °C; IR: ν(BH) 2457 cm^{-1}; ^{1}H NMR δ 8.42 (s, 3 H, H^3), 7.60 (d, 3 H, H^4), 7.13 (d, 3 H, H^6), 6.97 (t, 3 H, H^5), 1.60 (s, 27 H, Me), BH (1 H) by integration in the range δ 6.0–4.4; ^{13}C NMR δ 30.7 (br), 35.6, 119.6, 121.2, 122.1, 123.9 (C^4), 132.4, 138.9 (C^5) and 149.4 (C^3).

2: A large excess of anhydrous [Co(NCS)$_2$] was stirred and refluxed with **1** in xylene overnight. The slurry was filtered, and evaporation of the filtrate yielded the product as a green solid. Mp 266–269 °C; IR: ν(BH) 2601, ν(NCS) 2072 cm^{-1}. [Tl(Tp^{3Bo,7Me})] was prepared by the same method as **1**, starting with 7-methylindazole. Mp 226–228 °C; IR: ν(BH) 2455 cm^{-1}; ^{1}H NMR δ 8.36 (s, 3 H, H^3), 7.51 (d, 3 H, H^4), 7.03 (d, 3 H, H^6), 6.91 (t, 3 H, H^5), 2.78 (s, 9 H, Me), BH (1 H) discernible by integration in the range δ 5–6; ^{13}C NMR δ (d, *J* 416 Hz) 20.8, 118.7 (vs), 121.1 (vs), 121.5 (d, *J* 65 Hz), 125.4 (s), 126.4 (s), 131.5 (s), 150.8 (d, *J* 59 Hz).

‡ *Crystallographic data*: for **1**; $C_{33}H_{40}BN_6Tl$, M_r = 735.9, orthorhombic, space group $Pmn2_1$, a = 16.910(6), b = 10.155(3), c = 9.098(3) Å, U = 1562.3(9) Å^3, Z = 2. Data collected at 298 K with a Siemens P4 diffractometer (Mo-Kα radiation, λ = 0.71073 Å), graphite monochromator; $R(F)$ = 0.0360 for 1348 independent reflections ($4 \leq 2\theta \leq 45°$). Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein–Leopoldshafen (Germany), on quoting the depository number CSD-404560.

For **2**; $C_{46}H_{52}BCoN_7S{\cdot}2C_6H_6$, M_r = 804.7, triclinic, space group $P\bar{1}$, a = 10.617(2), b = 12.438(3), c = 16.196(5) Å, α = 99.84(2), β = 104.44(2), γ = 95.81(2)°, U = 2180(1) Å^3, Z = 2. Data collected at 270 K with a Siemens P4 diffractometer (Mo-Kα radiation, λ = 0.71073 Å), graphite monochromator; $R(F)$ = 5.86% for 5438 independent reflections ($4 \leq 2\theta \leq 50°$). Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-404561. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/49.

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