# Synthesis and molecular structure of bis(pyrazolyl)(3,5-di-*tert*-butylpyrazolyl)hydroborato thallium: a hetero-tris(pyrazolyl)hydroborato ligand derived from two different pyrazoles

Letter

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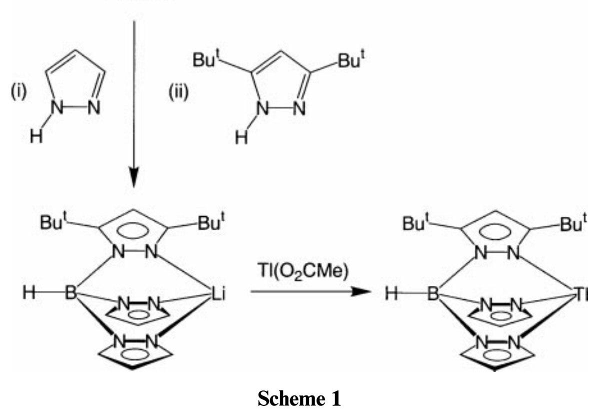
**The hetero-tris(pyrazolyl)hydroborato thallium complex $[HB(pz)_2(pz^{Bu^t_2})]Tl$, derived from two different pyrazoles, may be obtained by the reaction of $LiBH_4$ with a mixture of pyrazole and 3,5-di-*tert*-butylpyrazole, followed by treatment with $Tl(O_2CMe)$.**

Tris(pyrazolyl)hydroborato ligands are presently a prominent feature in coordination chemistry.[1] In part, the interest in such ligands derives from the facile ability to modify the steric and electronic properties by incorporation of a variety of different substituents. Without exception, however, structurally characterized tris(pyrazolyl)hydroborato ligands are presently restricted to derivatives in which all three pyrazolyl groups are derived from the same pyrazole.[2,3] In this paper, we report the synthesis and structure of a hetero-tris(pyrazolyl)hydroborato thallium complex that is derived from two differently substituted pyrazoles.

We have recently described that asymmetrically substituted hetero-bis(pyrazolyl)hydroborato ligands may be obtained by the direct reaction of $LiBH_4$ with a mixture of two different pyrazoles.[4] Ligands that have been constructed using this method include $[H_2B(pz)(pz^{Bu^t_2})]^-$, $[H_2B(pz^{Me_2})(pz^{Bu^t_2})]^-$ and $[H_2B(pz^{Trip})(pz^{Bu^t_2})]^-$. We now report that hetero-tris(pyrazolyl)hydroborato complexes derived from two different pyrazoles may also be obtained by this method. Specifically, the mixed bis(pyrazolyl)(3,5-di-*tert*-butylpyrazolyl)hydroborato complex $[HB(pz)_2(pz^{Bu^t_2})]Li$ may be synthesized by reaction of $LiBH_4$ with pyrazole followed by 3,5-di-*tert*-butylpyrazole (Scheme 1). Subsequent treatment of $[HB(pz)_2(pz^{Bu^t_2})]Li$ with $Tl(O_2CMe)$ yields the thallium complex $[HB(pz)_2(pz^{Bu^t_2})]Tl$, which has been structurally characterized by X-ray diffraction.

The molecular structure of $[HB(pz)_2(pz^{Bu^t_2})]Tl$ is shown in Fig. 1, with selected bond lengths and angles listed in Table 1. Inspection of Table 1 indicates that the pyrazolyl groups are not coordinated identically, with the Tl–N($pz^{Bu^t_2}$) bond length [2.741(4) Å] being considerably longer than those for the unsubstituted pyrazolyl groups [2.526(4) and 2.588(4) Å]. While such a difference may be attributed to steric factors, it is worthwhile noting that an *opposite* trend is observed for the homoleptic counterparts, $[Tp^{Bu^t_2}]Tl$[5] and [Tp]Tl[6] (Table 2).[7] Thus, the unsubstituted [Tp]Tl complex exhibits both a greater range of Tl–N bond lengths, and a greater average Tl–N bond length, than does $[Tp^{Bu^t_2}]Tl$.[8] On the other hand, the Tl–N bond lengths in the hetero-bis(pyrazolyl)hydroborato complex $[H_2B(pz)(pz^{Bu^t_2})]Tl$ are comparable: *d*[Tl–N(pz)] = 2.65 Å and *d*[Tl–N($pz^{Bu^t_2}$)] = 2.68 Å. It is, therefore, evident that the Tl–N bond lengths in these complexes must be influenced by rather subtle factors, one of which is likely to be "crystal packing effects",[9] especially since $[Tp^{RR'}]Tl$ derivatives are known to exhibit a variety of packing arrangements.[10] In this regard, the $[HB(pz)_2(pz^{Bu^t_2})]Tl$ molecules pack in the crystal such that each thallium atom exhibits weak interactions with four nitrogen atoms of the pyrazolyl groups of an adjacent molecule, as illustrated in Fig. 2. As would be



Scheme 1

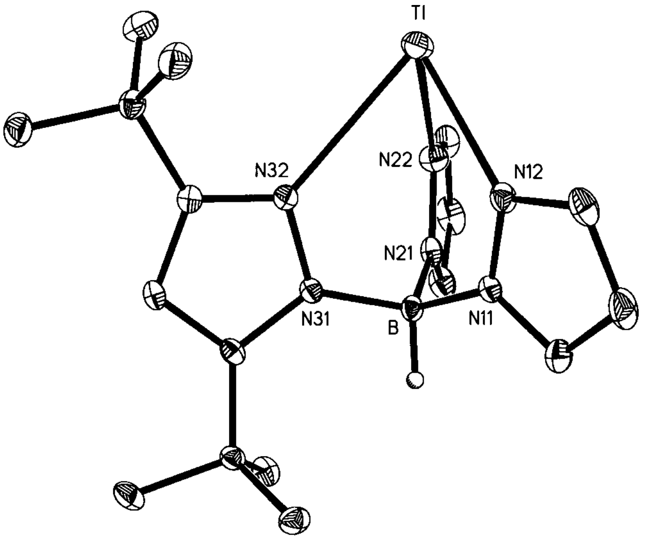


**Fig. 1** Molecular structure of $[HB(pz)_2(pz^{Bu^t_2})]Tl$.

**Table 1** Selected bond lengths (Å) and angles (°)

| | | | |
|---|---|---|---|
| Tl–N12 | 2.526(4) | N12–Tl–N22 | 77.7(1) |
| Tl–N22 | 2.588(4) | N12–Tl–N32 | 71.0(1) |
| Tl–N32 | 2.741(4) | N22–Tl–N32 | 71.1(1) |

Table 2 Comparison of Tl–N bond lengths in $[HB(pz)_2(pz^{Bu^t_2})]Tl$, [Tp]Tl and $[Tp^{Bu^t_2}]Tl$. The range is given in parentheses

| | $[HB(pz)_2(pz^{Bu^t_2})]Tl^a$ | $[Tp]Tl^b$ | $[Tp^{Bu^t_2}]Tl^c$ |
|---|---|---|---|
| d[Tl–N(pz)]/Å | 2.56 (2.53–2.59) | 2.63 (2.55–2.73) | |
| d[Tl–N($pz^{Bu^t_2}$)]/Å | 2.74 | | 2.57 (2.54–2.59) |

[a] This work. [b] Ref. 6. [c] Ref. 5.

expected, these intermolecular Tl···N interactions, which are in the range 3.65–3.85 Å, are considerably longer than the corresponding intramolecular bond lengths (2.53–2.74 Å).

In summary, a hetero-tris(pyrazolyl)hydroborato ligand derived from two different pyrazoles may be obtained by the direct reaction of $LiBH_4$ with a mixture of pyrazole and 3,5-di-*tert*-butylpyrazole. The ability to synthesize such ligands is noteworthy since it provides a means by which the steric environment about a metal center may be modulated in an asymmetric manner. Finally, it is likely that this approach may be adapted for other pyrazole derivatives.

## Experimental

All manipulations were performed using a combination of glovebox, high-vacuum and Schlenk techniques.[11] Solvents were purified and degassed by standard procedures. $^1H$ and $^{13}C$ chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity or the $^{13}C$ resonances, respectively. All coupling constants are reported in Hz. C, H, and N elemental analyses were measured using a Perkin-Elmer 2400 CHN Elemental Analyzer. Di-*tert*-butylpyrazole was prepared by the literature method.[12]

### Synthesis of $[HB(pz)_2(pz^{Bu^t_2})]Li$ and $[HB(pz)_2(pz^{Bu^t_2})]Tl$

A solution of $LiBH_4$ in THF (7.4 mL of 2M, 14.8 mmol) was added to a suspension of pyrazole (2.00 g, 29.4 mmol) and toluene (*ca.* 20 mL) in a large glass ampoule. The mixture was stirred overnight at room temperature, after which the volatile components were removed *in vacuo*. 3,5-Di-*tert*-butylpyrazole (2.65 g, 14.7 mmol) and toluene (*ca.* 30 mL) were added and the mixture was heated in the glass ampoule at *ca.* 120 °C overnight (**CARE! Pressures of several atmospheres may be generated**). The mixture was allowed to cool to room temperature, depositing crude $[HB(pz)_2(pz^{Bu^t_2})]Li$ as a white solid, which was isolated by filtration. The volatile components were removed from the filtrate and the residue obtained was washed with pentane, giving pure $[HB(pz)_2(pz^{Bu^t_2})]Li$ (0.30 g). $^1H$ NMR ($C_6D_6$, 400 MHz): 1.08 [s, 9H, $1C(CH_3)_3$], 1.54 [s, 9H, $1C(CH_3)_3$], 6.04 [br s, 1H, $C_3N_2HBu^t_2$], 6.10 [2H of $2C_3N_2H_3$], 7.69 [2H of $2C_3N_2H_3$] (2H of $2C_3N_2H_3$ obscured by solvent).

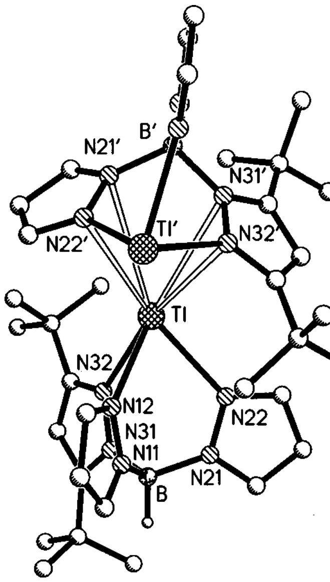


Fig. 2 Interaction of the Tl atom of $[HB(pz)_2(pz^{Bu^t_2})]Tl$ with an adjacent molecule. Selected separations (Å): Tl–N21′ 3.77, Tl–N22′ 3.85, Tl–N31′ 3.65 Å, Tl–N32′ 3.71 Å.

$Tl(O_2CMe)$ (3.87 g, 14.7 mmol) and THF (*ca.* 60 mL) were added to the crude $[HB(pz)_2(pz^{Bu^t_2})]Li$ obtained above and the mixture was stirred overnight at room temperature and filtered. The volatile components were removed *in vacuo* and the residue obtained was washed with pentane to give $[HB(pz)_2(pz^{Bu^t_2})]Tl$ as a white solid (1.30 g). Total yield of $[HB(pz)_2(pz^{Bu^t_2})]Li$ and $[HB(pz)_2(pz^{Bu^t_2})]Tl$: 25%. The thallium complex was also obtained by an analogous procedure, but reversing the order of addition of pyrazole and 3,5-di-*tert*-butylpyrazole. Anal. calcd for $C_{17}H_{26}N_6BTl$: C, 38.6%; H, 5.0%; N, 15.9%. Found: C, 37.7%; H, 4.7%; N, 15.9%. IR ($cm^{-1}$), KBr pellet: 2532 [ν(BH)]. $^1H$ NMR ($C_6D_6$, 300 MHz): 1.29 [s, 9H, $1C(CH_3)_3$], 1.49 [s, 9H, $1C(CH_3)_3$], 6.05 [s, 1H, $C_3N_2HBu^t_2$], 6.10 [t, $J = 2$, 2H of $2C_3N_2H_3$], 7.36 [d, $J = 1$,[13] 2H of $2C_3N_2H_3$], 7.69 [d, $J = 2$, 2H of $2C_3N_2H_3$]. $^{13}C$ NMR ($C_6D_6$, 125.76 MHz): 31.2 [q, $^1J_{CH} = 125$, $1C(CH_3)_3$], 32.1 [q, $^1J_{CH} = 125$, $1C(CH_3)_3$], 32.2 [s, $1C(CH_3)_3$], 32.3 [s, $1C(CH_3)_3$], 100.7 [d, $^1J_{CH} = 171$, 1C of $C_3N_2HBu^t_2$], 104.5 [d, $^1J_{CH} = 175$, 2C of $2C_3N_2H_3$], 136.3 [d, $^1J_{CH} = 184$, 2C of $2C_3N_2H_3$], 138.9 [d, $^1J_{CH} = 182$, 2C of $2C_3N_2H_3$], 156.8 [s, 1C of $C_3N_2HBu^t_2$], 161.2 [s, 1C of $C_3N_2HBu^t_2$].

### X-Ray structure determination

Crystal data, data collection and refinement parameters for $[HB(pz)_2(pz^{Bu^t_2})]Tl$ are summarized in Table 3. X-Ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector using graphite monochromated Mo-Kα X-radiation (λ = 0.710 73 Å). The struc-

Table 3 Crystal, intensity collection and refinement data for $[HB(pz)_2(pz^{Bu^t_2})]Tl$

| | |
|---|---|
| Formula | $C_{17}H_{26}BN_6Tl$ |
| Formula weight | 529.62 |
| Lattice | Monoclinic |
| Space group | $P2_1/n$ (no. 14) |
| $a$/Å | 10.300(3) |
| $b$/Å | 10.286(3) |
| $c$/Å | 18.917(5) |
| $\alpha$/° | 90 |
| $\beta$/° | 99.770(7) |
| $\gamma$/° | 90 |
| $U$/Å$^3$ | 1975(1) |
| $Z$ | 4 |
| $T$/K | 233 |
| μ(Mo-Kα)/mm$^{-1}$ | 8.189 |
| No. of data | 4224 |
| No. of parameters | 237 |
| $R_1$ [a] | 0.0375 |
| $wR_2$ [a] | 0.0849 |

[a] $R_1 = \Sigma\{\|F_o| - |F_c\|\}/\Sigma|F_o|$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ for $[I > 2\sigma(I)]$.

ture was solved using direct methods and standard difference map techniques, and was refined by full-matrix least-squares procedures using SHELXTL.[14] Hydrogen atoms on carbon were included in calculated positions, but the hydrogen attached to boron was freely refined. Systematic absences were consistent uniquely with $P2_1/n$ (no. 14).

CCDC reference number 440/139. See http://www.rsc.org/suppdata/nj/1999/961/ for crystallographic files in .cif format.

## Acknowledgements

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