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Asymmetric bis(pyrazolyl)hydroborato ligands *via* direct synthesis: structural characterization of thallium and zinc complexes†

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Asymmetrically substituted bis(pyrazolyl)hydroborato ligands, *i.e.* $[H_2B(pz^{RR'})(pz^{Bu^t_2})]^-$, in which the two pyrazolyl groups possess different substituents, have been synthesized by the direct reaction of a *ca.* 1:1 molar mixture of the respective pyrazoles with $LiBH_4$.

While Trofimenko's poly(pyrazolyl)hydroborato ligand system has emerged as one of the most popular in modern coordination chemistry, the majority of studies have concentrated on the use of tris(pyrazolyl)hydroborato derivatives.[1] Indeed, tris(pyrazolyl)hydroborato ligands have been subject to a large variety of modifications, which include the incorporation of sterically demanding (*e.g. tert*-butyl), electron withdrawing (*e.g.* CF_3), and optically active substituents.[1] By comparison, bis(pyrazolyl)hydroborato ligands have received much less attention, although we have recently used such ligands as a framework for constructing tridentate [NNO] and [NNS] donor ligands.[2] In this paper, we report the syntheses of asymmetric bis(pyrazolyl)hydroborato ligands in which the two pyrazolyl groups incorporate different substituents, *i.e.* $[H_2B(pz^{RR'})(pz^{Bu^t_2})]^-$.

Since the first report in 1982, asymmetrically substituted bis(pyrazolyl)hydroborato ligands have been restricted to derivatives in which one of the pyrazolyl groups is methyl substituted in both the 3- and 5-positions, *i.e.* $[H_2B(pz^{Me_2})(pz^{R'R''})]^-$.[3] The principal reason for this restriction is due to the fact that the synthetic methods employed to incorporate two different pyrazolyl groups on boron have to date required the use of a pyrazole–borane reagent, $(Hpz^{RR'})(BH_3)$, of which only the 3,5-dimethylpyrazole adduct could be synthesized (Scheme 1).[4] It is, therefore, significant that we have discovered that a variety of asymmetrically substituted bis(pyrazolyl)hydroborato ligands may be constructed straightforwardly, by the direct reaction of $LiBH_4$ with a *ca.* 1:1 molar mixture of two different pyrazoles, as illustrated in Scheme 2. For example, a mixture of pyrazole and 3,5-di-*tert*-butylpyrazole reacts with $LiBH_4$ to give $[H_2B(pz)(pz^{Bu^t_2})]Li$.[5] Metathesis of the latter complex with TlOAc yields its thallium derivative $[H_2B(pz)(pz^{Bu^t_2})]Tl$, which has been structurally characterized by X-ray diffraction (Fig. 1).[6] Subsequent treatment of $[H_2B(pz)(pz^{Bu^t_2})]Tl$ with ZnI_2 gives $[H_2B(pz)(pz^{Bu^t_2})]ZnI$, which has been structurally characterized as the 3-*tert*-butyl-5-isopropylpyrazole adduct, $[H_2B(pz)(pz^{Bu^t_2})]ZnI(Hpz^{Bu^t,Pr^i})$ (Fig. 2). In addition to $[H_2B(pz)(pz^{Bu^t_2})]^-$, the synthetic method is also

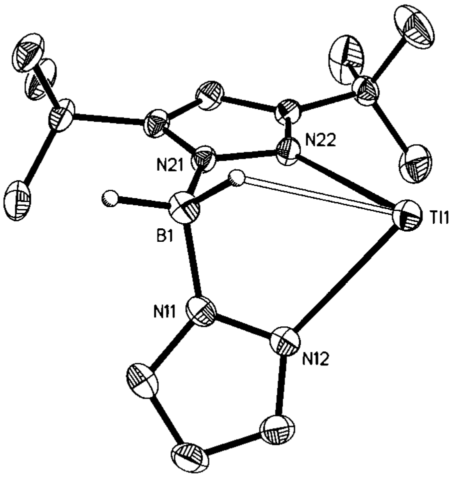
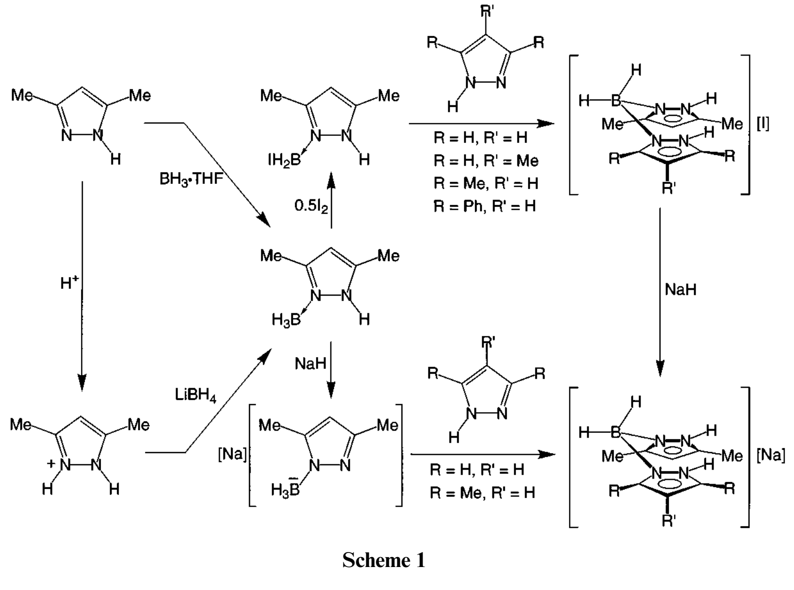


Fig. 1 Molecular structure of $[H_2B(pz)(pz^{Bu^t_2})]Tl$ (only one of the crystallographically independent molecules is shown). Selected bond lengths (Å) and angles (°): Tl(1)–N(12) 2.634(4), Tl(1)–N(22) 2.677(3), N(12)–Tl(1)–N(22) 72.87(10), Tl(2)–N(112) 2.658(4), Tl(2)–N(122) 2.680(3), N(112)–Tl(2)–N(122) 75.20(11).



Scheme 1

Table 1 Comparison of M–N bond lengths for asymmetric bis(pyrazolyl)hydroborato complexes

{[$H_2B(pz^1)(pz^2)$]M}	d(M–Npz^1)/Å [a]	d(M–Npz^2)/Å [a]	|Δd(M–N)|/Å	Ref.
$[H_2B(pz)(pz^{Bu^t_2})]Tl$	2.634(4), 2.658(4) [b]	2.677(3), 2.680(3) [b]	0.032	This work
$[H_2B(pz^{Trip})(pz^{Bu^t_2})]ZnI$	1.994(2)	1.994(2)	0.000	This work
$[H_2B(pz)(pz^{Bu^t_2})]ZnI(Hpz^{Bu^t,Pr^i})$ [c]	2.017(2)	2.011(2)	0.006	This work
$[H_2B(pz^{Me_2})(pz^{Bu^t_2})]ZnI(Hpz^{Bu^t_2})$ [d]	1.978(4)	2.017(3)	0.039	This work
$[H_2B(pz)(pz^{Me_2})]_2Ni$	1.883(3)	1.894(2)	0.011	7
$[H_2B(pz^{Me_2})(pz^{Ph_2})]_2Zn$	1.982(2), 1.982(2)	2.019(2), 2.010(2)	0.033	8

[a] pz^1 and pz^2 are the first and second pyrazolyl groups, respectively, in the compound formula. [b] Values for two crystallographically independent molecules. [c] d(Zn–$pz^{Bu^t,Pr^i}H$) = 2.038(2) Å. [e] d(Zn–$pz^{Bu^t_2}H$) = 2.090(3) Å.

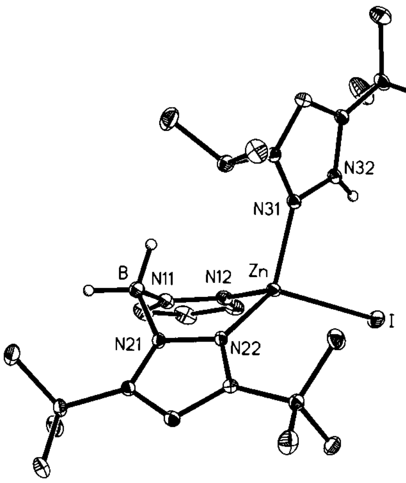
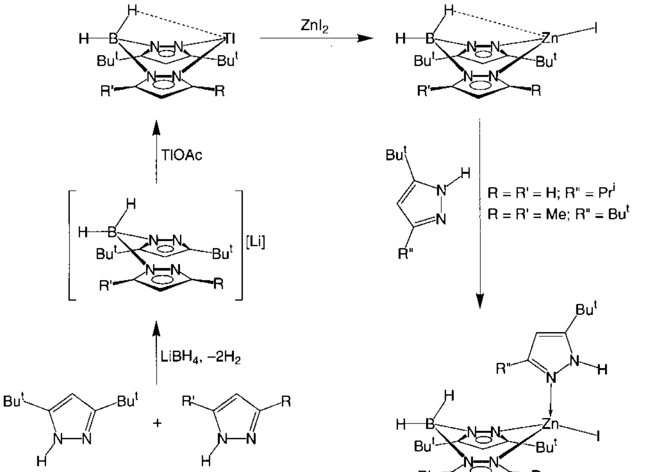


Fig. 2 Molecular structure of $[H_2B(pz)(pz^{Bu^t_2})]ZnI(Hpz^{Bu^t,Pr^i})$. Selected bond lengths (Å) and angles (°): Zn–N(22) 2.011(2), Zn–N(12) 2.017(2), Zn–N(31) 2.038(2), Zn–I 2.6150(3), N(22)–Zn–N(12) 98.71(8), N(22)–Zn–N(31) 117.83(8), N(12)–Zn–N(31) 113.43(8), N(22)–Zn–I 127.46(6), N(12)–Zn–I 100.62(6), N(31)–Zn–I 97.95(5).



Scheme 2

applicable for $[H_2B(pz^{Me_2})(pz^{Bu^t_2})]^-$ and $[H_2B(pz^{Trip})(pz^{Bu^t_2})]^-$ (Trip = triptycyl, 9,10-*o*-benzeno-9,10-dihydroanthracenyl) ligands, which have been structurally characterized as the zinc iodide derivatives, $[H_2B(pz^{Me_2})(pz^{Bu^t_2})]ZnI(Hpz^{Bu^t_2})$ (Fig. 3) and $[H_2B(pz^{Trip})(pz^{Bu^t_2})]ZnI$ (Fig. 4).

Other than the complexes described above, structurally authenticated asymmetric bis(pyrazolyl)hydroborato complexes are limited to the nickel and zinc complexes, $[H_2B(pz)(pz^{Me_2})]_2Ni$[7] and $[H_2B(pz^{Me_2})(pz^{Ph_2})]_2Zn$,[8] respectively. For comparison, the M–N bond lengths for all structurally characterized asymmetric bis(pyrazolyl)hydroborato ligands are summarized in Table 1. Interestingly, despite substantial differences in the size of the pyrazolyl substituents, there is little variation in the two M–N bond lengths for a given complex, *i.e.* Δd(M–N) ≈ 0.

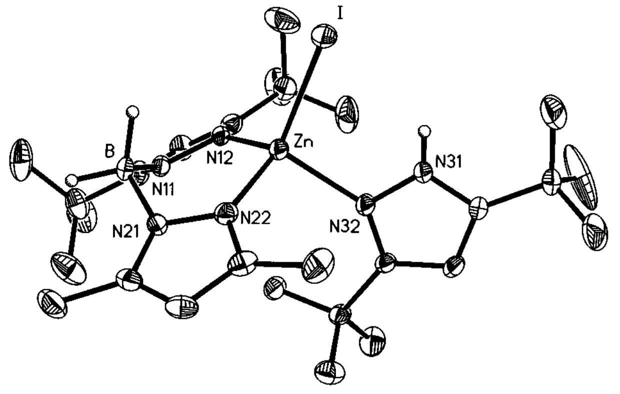


Fig. 3 Molecular structure of $[H_2B(pz^{Me_2})(pz^{Bu^t_2})]ZnI(Hpz^{Bu^t_2})$. Selected bond lengths (Å) and angles (°): Zn–N(22) 1.978(4), Zn–N(12) 2.017(3), Zn–N(32) 2.090(3), Zn–I 2.5864(6), N(22)–Zn–N(12) 105.4(2), N(22)–Zn–N(32) 101.8(2), N(12)–Zn–N(32) 115.31(13), N(22)–Zn–I 113.44(10), N(12)–Zn–I 116.31(10), N(32)–Zn–I 103.94(10).

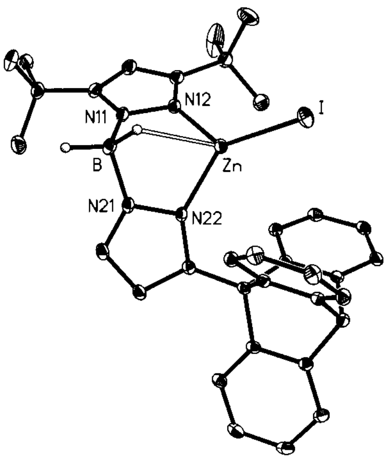


Fig. 4 Molecular structure of $[H_2B(pz^{Trip})(pz^{Bu^t_2})]ZnI$. Selected bond lengths (Å) and angles (°): Zn–N(22) 1.994(2), Zn–N(12) 1.994(2), Zn–H(1) 2.41(3), Zn–I 2.4651(3), N(22)–Zn–N(12) 99.92(8), N(22)–Zn–H(1) 72.4(7), N(12)–Zn–H(1) 71.2(7), N(22)–Zn–I 130.08(6), N(12)–Zn–I 129.91(6), H(1)–Zn–I 116.6(7).

In summary, a new method for the synthesis of asymmetrically substituted bis(pyrazolyl)hydroborato ligands is provided by the reactions of $LiBH_4$ with a *ca.* 1 : 1 molar mixture of two different pyrazoles. Ligands which have been constructed using this method include $[H_2B(pz)(pz^{Bu^t_2})]^-$, $[H_2B(pz^{Me_2})(pz^{Bu^t_2})]^-$ and $[H_2B(pz^{Trip})(pz^{Bu^t_2})]^-$. As such, this method is more convenient and potentially more general than previously reported procedures for the syntheses of asymmetrically substituted bis(pyrazolyl)hydroborato ligands.

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Notes and references

† *Supplementary data available*: experimental details and NMR data. For direct electronic access see http://www.rsc.org/suppdata/dt/1998/3355/, otherwise available from BLDSC (No. SUP 57435, 9 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (http://www.rsc.org/dalton).

1 For recent reviews, see: S. Trofimenko, *Chem. Rev.*, 1993, **93**, 943; G. Parkin, *Adv. Inorg. Chem.*, 1995, **42**, 291; N. Kitajima and W. B. Tolman, *Prog. Inorg. Chem.*, 1995, **43**, 419; I. Santos and N. Marques, *New. J. Chem.*, 1995, **19**, 551; D. L. Reger, *Coord. Chem. Rev.*, 1996, **147**, 571; M. Etienne, *Coord. Chem. Rev.*, 1997, **156**, 201; P. K. Byers, A. J. Canty and R. T. Honeyman, *Adv. Organomet. Chem.*, 1992, **34**, 1.

2 P. Ghosh and G. Parkin, *Chem. Commun.*, 1998, 413; C. Dowling and G. Parkin, *Polyhedron*, 1996, **15**, 2463; P. Ghosh and G. Parkin, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 2281.

3 E. Frauendorfer and G. Agrifoglio, *Inorg. Chem.*, 1982, **21**, 4122; G. Agrifoglio, *Inorg. Chim. Acta*, 1992, **197**, 159.

4 Specifically, attempts to synthesize the borane adduct of pyrazole, 4-nitropyrazole and diphenylpyrazole, resulted in elimination of H_2 and the formation of pyrazolyl bridged dimers, $[H_2B(pz^{RR'})_2BH_2]$. See ref. 3.

5 For example, $[H_2B(pz)(pz^{Bu^t_2})]M$ ($M = Li$ and Tl) are synthesized as follows. A solution of $LiBH_4$ in THF (35 mL of 2 M, 70.0 mmol), diluted with toluene (*ca.* 35 mL), was added to a mixture of pyrazole (4.8 g, 70.5 mmol) and 3,5-di-*tert*-butylpyrazole (13.2 g, 73.2 mmol) and stirred overnight at room temperature. The solvent was removed *in vacuo*, toluene (*ca.* 40 mL) was added, and the resulting mixture was refluxed for one day. The solution was concentrated to *ca.* 20 mL, at which point the mixture became turbid and white solid started to precipitate. Pentane (*ca.* 50 mL) was added to complete precipitation and the mixture was filtered. The filtrate was allowed to stand at room temperature overnight, over which period colorless crystals of $[H_2B(pz)(pz^{Bu^t_2})]Li$ were deposited (5.5 g, 30%). $[H_2B(pz)(pz^{Bu^t_2})]Li$ was treated with TlOAc (8.2 g, 31.1 mmol) and THF (*ca.* 60 mL) and the mixture was stirred overnight at room temperature. The mixture was filtered and the residue was further extracted with pentane (*ca.* 50 mL). The THF and pentane extracts were combined and the solvent removed *in vacuo* to give $[H_2B(pz)(pz^{Bu^t_2})]Tl$ as a white solid which was washed with pentane (7.4 g, 77%). $[H_2B(pz^{Me_2})(pz^{Bu^t_2})]Tl$ is synthesized similarly, with the exception that the lithium derivative was converted to the potassium complex prior to metathesis with TlOAc.

6 $[H_2B(pz)(pz^{Bu^t_2})]Tl$ is monoclinic, $P2_1/c$ (no. 14), $C_{14}H_{24}BN_4Tl$, $M = 463.55$, $a = 10.2116(5)$, $b = 26.000(1)$, $c = 14.1494(7)$ Å, $\beta = 106.872(1)°$, $U = 3596.7(3)$ Å^3, $Z = 8$, $T = 293$ K, $\mu = 8.977$ mm^{-1}, 8222 independent reflections, $R1 = 0.0362$ $[I > 2\sigma(I)]$. $[H_2B(pz)(pz^{Bu^t_2})]ZnI(Hpz^{Bu^t,Pr^i})$ is monoclinic, $P2_1/n$ (no. 14), $C_{24}H_{42}BIN_6Zn$, $M = 617.72$, $a = 15.4692(8)$, $b = 12.2119(6)$, $c = 16.4996(8)$ Å, $\beta = 110.910(1)°$, $U = 2911.6(3)$ Å^3, $Z = 4$, $T = 203$ K, $\mu = 1.926$ mm^{-1}, 6641 independent reflections, $R_1 = 0.0321$ $[I > 2\sigma(I)]$. $[H_2B(pz^{Trip})(pz^{Bu^t_2})]ZnI$ is triclinic $P\bar{1}$ (no. 2), $C_{34}H_{36}BIN_4Zn$, $M = 703.75$, $a = 9.9469(5)$, $b = 11.9592(5)$, $c = 13.9733(6)$ Å, $\alpha = 90.085(1)$, $\beta = 96.387(1)$, $\gamma = 103.157(1)°$, $U = 1607.9(1)$ Å^3, $Z = 2$, $T = 203$ K, $\mu = 1.752$ mm^{-1}, 6874 independent reflections, $R_1 = 0.0327$ $[I > 2\sigma(I)]$. $[H_2B(pz^{Me_2})(pz^{Bu^t_2})]ZnI(Hpz^{Bu^t_2})$ is monoclinic, $P2_1/n$ (no. 14), $C_{27}H_{48}BIN_6Zn$, $M = 659.79$, $a = 17.701(1)$, $b = 9.5135(6)$, $c = 21.543(2)$ Å, $\beta = 113.781(2)°$, $U = 3319.7(4)$ Å^3, $Z = 4$, $T = 293$ K, $\mu = 1.693$ mm^{-1}, 5797 independent reflections, $R_1 = 0.0444$ $[I > 2\sigma(I)]$. CCDC number 186/1142.

7 H. Kokusen, Y. Sohrin, M. Matsui, Y. Hata and H. Hasegawa, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 195.

8 M. V. Capparelli and G. Agrifoglio, *J. Crystallogr. Spectrosc. Res.*, 1992, **22**, 651.

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