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A new route to tris(pyrazolyl)borate ligands and new structural variations in TlTp complexes †

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Tris(pyrazolyl)borate ligands were synthesized by a new route from $MeBBr_2$ and pyrazole derivatives under very mild conditions at room temperature to give TlL complexes. For L = $[MeB(3,5\text{-}Me_2pz)_3]^-$ a bridging co-ordination of the ligand is found, interpreted as sterically enforced upon comparison with the structures for L = $[MeB(3\text{-}Mepz)_3]^-$ and $[HB(3,5\text{-}Me_2pz)_3]^-$.

Introduction

The tris(pyrazolyl)borate (Tp) ligand together with various substituted forms has developed into one of the most versatile tripodal auxiliary ligands in (bio)inorganic co-ordination chemistry.[1] The standard or so-called Trofimenko method of synthesis is the reaction of substituted pyrazoles with KBH_4 at elevated temperatures above 190 °C, eqn. (1) (Hpz′ = pyrazole

$$KBH_4 + 3\ Hpz' \xrightarrow{190\ °C} K[HB(pz')_3] + 3\ H_2 \quad (1)$$

or derivative).[2] However, this route fails in the case of thermally sensitive pyrazole derivatives.[3] A few other syntheses to tris(pyrazolyl)borates have been described. They start from monoorganylboron compounds and are given in eqns. (2)[4,5] (R = ^{i}Pr, ^{n}Bu, Ph or 4-BrC_6H_4) and (3) (pyrazole only).[4] The

$$RB(OH)_2 + Na(pz) + 2\ Hpz \xrightarrow{185\text{–}220\ °C} Na[RB(pz)_3] + 2\ H_2O \quad (2)$$

$$PhBCl_2 + 4\ pzH \xrightarrow{55\ °C} [H_2pz]^+[PhB(pz)_3]^- + 2\ HCl \quad (3)$$

route outlined in eqn. (2) also requires high temperatures. Neither of the synthetic schemes in eqns. (2) and (3) appears to have found widespread applications for the preparation of Tp ligands. In part, this may be due to the low yield of the products and the noted difficulty to crystallize the boron substituted Tp–metal complexes.[4,5] Here, we report the results of our search for yet another route to Tp ligands.

Results and discussion

Following a procedure to ferrocene-based Tp ligands by Wagner and co-workers,[6] we found that dibromo(methyl)borane, $MeBBr_2$,[7] reacts at room temperature with pyrazole derivatives in the presence of NEt_3 and thallium ethoxide to form methyltris(pyrazolyl)boratothallium complexes, eqn. (4). The reaction is demonstrated with pyrazole, 3,5-dimethylpyrazole and 3-methylpyrazole and can easily be extended to other pyrazole derivatives.

$$MeBBr_2 + 3\ Hpz' + 2\ NEt_3 + TlOEt \xrightarrow{\text{toluene, RT}} Tl[MeB(pz')_3] + 2\ [NHEt_3]Br + EtOH \quad (4)$$

1 pz′ = pz
2 pz′ = 3,5-Me_2pz
3 pz′ = 3-Mepz

The boratothallium complexes are obtained in good to high yield. Often, TlTp compounds are valued as a means of isolation and characterization of a (new) Tp ligand.[8] Moreover, just like cyclopentadienylthallium,[9] TlTp is also a milder (less reducing) and mostly more stable ligand transfer reagent in place of Tp alkali-metal salts. Hence, the initial KTp salt from the Trofimenko route, eqn. (1), is occasionally transformed into the TlTp complex for further reactions. Despite its toxicity, TlTp is a common reagent for Tp-ligand transfer and ligand characterization in the case of the more sterically demanding or so-called "second-generation Trofimenko ligands".[8] This is the basis of interest in TlTp structural chemistry.

In addition to the usual spectroscopic methods, identification of compounds **2** and **3** was also based on X-ray crystallography. There is interest in thallium(I) structures because of their diversity and theoretical aspects of the in/active lone pair of electrons.[10,11] So far, TlTp compounds have shown little variation. All, but four, are clearly built up from molecular units with a trihapto, C_3-symmetrical metal co-ordination. The exceptions are $Tl[HB(3\text{-}C_3H_5pz)_3]$ (C_3H_5 = cyclopropyl)],[10] $Tl[HB\{3\text{-}(4\text{-}MeC_6H_4)pz\}_3]$,[12] $Tl[HB\{2,4\text{-}(MeO)_2pz\}_3]$[13] and $Tl[HB(pz)_3]$.[14] The first complex forms a stable tetramer with a perfect tetrahedron of Tl atoms. The next two are "dimeric" with Tl···Tl contacts of 3.86 and 3.995 Å, respectively. The last has metal–ligand strands based on eletrostatic thallium–pyrazolyl π interactions. Despite these differences in the molecular packing, every TlTp structure hitherto reported shows the expected threefold co-ordination of the Tp ligand to the metal.

The structure of compound **2** represents a remarkable exception to the above generalization. Fig. 1 illustrates that the ligand $[MeB(3,5\text{-}Me_2pz)_3]^-$ bridges between two thallium atoms. One thallium atom is co-ordinated by two pyrazolyl rings. The third pyrazolyl ring binds the adjacent symmetry related thallium center in a monodentate fashion. The plane of this ring assumes an angle of 81.3(4)° to the B–Me axis. The bridging

† *Supplementary data available*: IR data. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/3133/, otherwise available from BLDSC (No. SUP 57609, 2 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

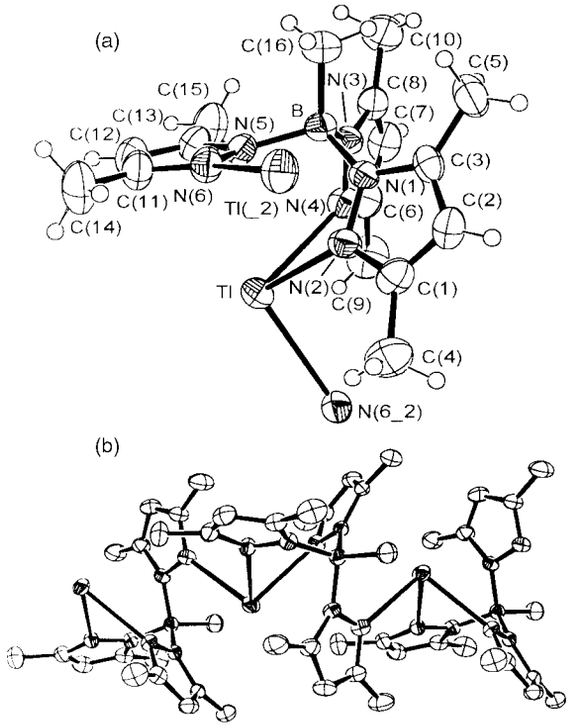

Fig. 1 (a) Repeat unit of $^{1}_{\infty}$Tl[MeB(3,5-Me$_2$pz)$_3$] **2** and (b) section of the 2_1-helicoidal co-ordination polymer. In (b) the hydrogen atoms have been omitted for clarity. Symmetry relation: _2 $0.5 - x$, $-0.5 + y$, $0.5 - z$.

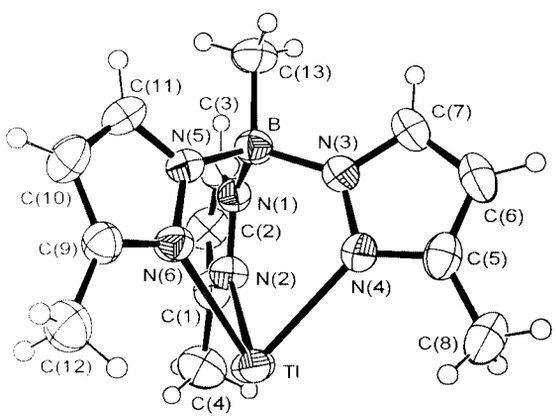

Fig. 2 Molecular structure of Tl[MeB(3-Mepz)$_3$] **3**.

action of the [MeB(3,5-Me$_2$pz)$_3$]$^-$ ligand leads to a 2_1-helicoidal chain. Why is there no triphapto metal co-ordination? A visual inspection of the structure suggests that the space requirements of the methyl groups on the boron and the pyrazolyl-C5 atoms do not allow the simultaneous trihapto co-ordination of all three rings to one thallium center. The thallium, boron and (B)carbon atom do not lie on a straight line but form an angle of 159.6°. Both, the thallium atom as well as the boron-bonded methyl group appear to be moved away from the imaginary axis. Only one of the chelating pyrazolyl rings [N(3)–N(4)] coincides with the B–Me axis, the other is tilted by 27.8(3)°. This interpretation of a methyl–methyl repulsion was tested with a structural investigation of Tl[MeB(3-Mepz)$_3$] **3** and of Tl[HB(3,5-Me$_2$pz)$_3$] **4**. The prototypical complex **4** with the Tp* ligand has been used as a ligand transfer reagent,[15] but has apparently never been characterized. Both these complexes lack a methyl group either on the pz 5 position or on the boron atom, so that there is no repulsive methyl–methyl interaction. Hence, the expected trihapto, C_3-symmetrical thallium co-ordination is found in their molecular structures (Figs. 2 and 3). Selected bond distances and angles are collected in Table 1.

Table 1 Selected bond lengths (Å) and angles (°) in compounds **2**–**4**

	2	**3**	**4**
Tl–N(2)	2.638(3)	2.547(4)	2.534(6)
Tl–N(4)	2.760(4)	2.504(4)	2.499(6)
Tl–N(6)	2.876(4)[a]	2.499(4)	2.515(6)
B–C	1.602(6)	1.587(7)	—
B–N	1.557(6)	1.555(7)	1.555(10)
	−1.577(6)	−1.654(7)	−1.566(10)
N(2)–Tl–N(4)	68.9(1)	75.4(1)	75.7(2)
N(2)–Tl–N(6)	96.5(1)[a]	74.4(1)	74.4(2)
N(4)–Tl–N(6)	96.6(1)[a]	73.9(1)	73.9(2)
N–B–N	106.5(3)	107.6(4)	109.2(6)
	−108.5(3)	−109.4(4)	−111.2(6)

[a] Symmetry related atom generated by the transformation $0.5 - x$, $-0.5 + y$, $0.5 - z$.

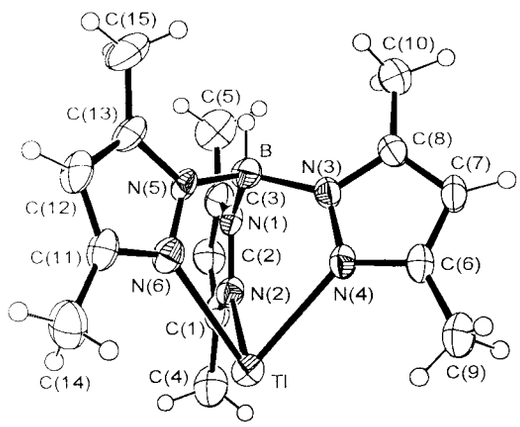

Fig. 3 Molecular structure of Tl[HB(3,5-Me$_2$pz)$_3$] **4**.

The Tl–N distances in **2** are longer than usual for TlTp compounds.[8]

It may be noted that the NMR spectra of the polymeric compound **2** are rather simple, suggesting a C_3 symmetrical structure in solution. They show that all three rings are equivalent in solution, since only one signal is observed for each type of proton or carbon atom. This is the typical NMR pattern for TlTp complexes and is also seen in the spectra of **1**, **3** and **4**. Of course, a C_{3v} symmetrical structure of a thallium–ligand complex **2** in solution would be a contradiction to the above argument on the solid-state arrangement. Here we note that the TlTp complexes are seldom retained intact in solution. Usually, very loose or solvent-separated cation–anion pairs are formed. If the TlTp complex is present in solution Tl–H and Tl–C coupling would be observed. Both natural thallium isotopes ^{205}Tl and ^{203}Tl have spin $\frac{1}{2}$. The absence of such coupling to thallium is indicative of either a predominantly ionic thallium–ring interaction or fast intermolecular exchange processes.[8] Then, the solution NMR spectra correspond to the more-or-less free and anionic Tp ligand. Even in view of the steric interactions in the free Tp ligand of **2**, a C_3 symmetrical structure can still be assumed in solution by having the three ring planes canted all in the same direction with respect to the B–Me bond. Fig. 4 presents a space-filling drawing of [MeB(3,5-Me$_2$pz)$_3$]$^-$ obtained from a molecular mechanics optimization.

Experimental

The NMR spectra were collected on a Bruker ARX200 spectrometer (200.1 MHz for ^{1}H, 50.3 MHz for ^{13}C) and calibrated against the solvent signal ($CDCl_3$, ^{1}H δ 7.26, ^{13}C δ 77.0), IR spectra on a Nicolet-Magna Spectrometer 750 as KBr disks (only major peaks are listed) and mass spectra with a Varian MAT 311 A/AMD spectrometer and electron-impact (EI)

Table 2 Crystal data for compounds **2**–**4**

	2	**3**	**4**
Formula	$C_{16}H_{24}BN_6Tl$	$C_{13}H_{18}BN_6Tl$	$C_{15}H_{22}BN_6Tl$
M	515.59	473.51	501.57
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$C2/c$
a/Å	11.4656(1)	8.1756(1)	30.6275(5)
b/Å	9.9676(1)	14.1921(1)	8.6168(1)
c/Å	17.0414(3)	13.9746(1)	15.6585(2)
β/°	96.125(1)	96.771(1)	119.812(1)
V/Å^3	1936.45(4)	1610.15(3)	3585.57(9)
Z	4	4	8
D_c/g cm^{-3}	1.769	1.953	1.858
$F(000)$	992	896	1920
μ/cm^{-1}	83.50	100.3	90.16
Measured reflections	14261	12008	13372
Unique reflections (R_{int})	4432 (0.0604)	3685 (0.0549)	4110 (0.0758)
Observed reflections [$I > 2\sigma(I)$]	3304	2800	2909
Parameters refined	225	194	214
$\Delta\rho$[a]/e Å^{-3}	0.651, −1.211	0.661, −0.974	1.350, −2.862
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0312, 0.0566	0.0311, 0.0617	0.0479, 0.0948
(all reflections)	0.0560, 0.0625	0.0502, 0.0688	0.0790, 0.1060

[a] Largest difference peak and hole.

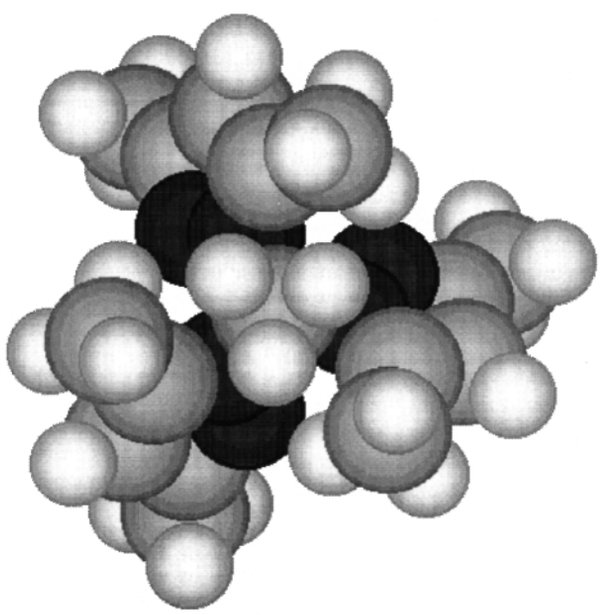

Fig. 4 Molecular mechanics optimized structure of free $[MeB(3,5\text{-}Me_2pz)_3]^-$ in complex **2** viewed along the Me–B bond; dark spheres are the nitrogen atoms.

sample ionization at 70 eV. Elemental analyses were done with a Perkin-Elmer 2400 Series II CHNS/O Analyzer. The reactions were carried out with Schlenk techniques using flame-dried glassware and argon as inert gas. The solvent CH_2Cl_2 was dried by refluxing over CaH_2 followed by distillation and storage under inert gas; $MeBBr_2$ was prepared according to ref. 7 and $K[HB(3,5\text{-}Me_2pz)_3]$ according to ref. 2. Pyrazoles and TlOEt were purchased from Aldrich.

Preparations

[Methyltris(pyrazol-1-yl)borato]thallium(I), Tl[MeB(pz)$_3$] 1. The compound $MeBBr_2$ (1.67 g, 9.0 mmol) was added to a solution of pyrazole (1.83 g, 20.9 mmol) in toluene (20 ml). After stirring for 1 h, NEt_3 (1.82 g, 18.0 mmol) was added and stirring continued for 12 h. A white precipitate was removed by filtration. The filtrate was cooled to −78 °C and TlOEt (2.24 g, 9.0 mmol) added. The mixture was stirred for 4 h at room temperature, the solvent then removed in vacuum and the residue extracted in a Soxhlet apparatus with CH_2Cl_2. Removal of CH_2Cl_2 in vacuum left the product as a white powder (yield 1.82 g, 47%). ^{1}H NMR ($CDCl_3$): δ 1.09 (s, 3 H, B-CH_3), 6.30 (s, 3 H, H4), 7.58 (s, 3 H, H5) and 7.82 (s, 3 H, H3). ^{13}C NMR ($CDCl_3$): δ 4.16 (B-CH_3), 103.84 (C4), 133.10 (C5) and 138.76 (C3). MS (65 °C): m/z 432 (2) $[M]^{+\bullet}$; 417 (43), $[M - Me]^+$; 365 (16), $[M - pz]^+$; 350 (2), $[M - Me - pz]^+$; and 205 (100%), $[Tl]^+$. Calc. for $C_{10}H_{12}BN_6Tl$: C, 27.84; H, 2.80; N, 19.48. Found: C, 28.01; H, 2.57; N, 19.38%.

[Tris(3,5-dimethylpyrazol-1-yl)methylborato]thallium(I), Tl[MeB(3,5-Me$_2$pz)$_3$] 2. The compound $MeBBr_2$ (1.84 g, 9.9 mmol) was added to a solution of 3,5-dimethylpyrazole (2.86 g, 29.7 mmol) in toluene (40 ml). After stirring for 1 h, NEt_3 (2.00 g, 19.8 mmol) was added and stirring continued for 12 h. A white precipitate was removed by filtration, TlOEt (1.70 g, 6.8 mmol) added and the reaction mixture stirred for 4 h. The solvent was removed in vacuum and the residue extracted in a Soxhlet apparatus with CH_2Cl_2. Removal of CH_2Cl_2 in vacuum left the product as a white powder (yield 2.71 g, 53%). A crystalline sample was obtained from CH_2Cl_2, mp 232 °C. ^{1}H NMR ($CDCl_3$): δ 0.83 (s, 3 H, B-CH_3), 2.17 (s, 9 H, pz 5-CH_3), 2.23 (s, 9 H, pz 3-CH_3) and 5.87 (s, 3 H, H4). ^{13}C NMR ($CDCl_3$): δ 1.01 (B-CH_3), 13.36 (pz 5-CH_3), 14.14 (pz 3-CH_3), 107.56 (C4), 146.15 (C5) and 147.62 (C3). MS (119 °C): m/z 516 (14), $[M]^{+\bullet}$; 501 (56), $[M - Me]^+$; 421 (100), $[M - Me_2pz]^+$; and 205 (42%), $[Tl]^+$. IR (strong signals only): 3061, 2738, 2520, 2420, 2359, 2290, 2236, 2129, 1105, 1057, 766, 760, 748, 703, 671, 655, 605, 593, 590, 513, 452 and 440 cm^{-1}. Calc. for $C_{16}H_{24}BN_6Tl$: C, 37.27; H, 4.69; N, 16.30. Found: C, 36.91; H, 3.96; N, 16.27%.

[Methyltris(3-methylpyrazol-1-yl)borato]thallium(I), Tl[MeB(3-Mepz)$_3$] 3. The compound $MeBBr_2$ (1.27 g, 6.8 mmol) was added to a solution of 3-methylpyrazole (1.68 g, 20.5 mmol) in toluene (20 ml). After stirring for 1 h, NEt_3 (1.38 g, 13.6 mmol) was added and stirring continued for 12 h. The white precipitate was removed by filtration, TlOEt (1.70 g, 6.8 mmol) added and the reaction mixture stirred for 12 h. The solvent was removed to leave the product as a white powder (yield 2.95 g, 91%). A crystalline sample was obtained from CH_2Cl_2. ^{1}H NMR ($CDCl_3$): δ 0.97 (s, 3 H, B-CH_3), 2.43 (s, 9 H, pz CH_3), 5.98 (s, 3 H, H4) and 7.62 (s, 3 H, H5). ^{13}C NMR ($CDCl_3$): δ 5.16 (B-CH_3), 13.20 (pz CH_3), 104.11 (C4), 133.61 (C5) and 148.25 (C3). MS (104 °C): m/z 474 (4), $[M]^{+\bullet}$; 459

(100), $[M - Me]^+$; 393 (56), $[M - Mepz]^+$; 295 (28), $[M - Me - 2(Mepz) - 2H]^+$; and 205 (48%), $[Tl]^+$. IR (strong signals only): 3141, 2855, 1094, 884, 855, 846, 835, 520, 253, 207, 197 and 192 cm^{-1}. Calc. for $C_{13}H_{18}BN_6Tl$: C, 32.98; H, 3.83; N, 17.75. Found: C, 32.77; H, 3.43; N, 17.85%.

[Tris(3,5-dimethylpyrazol-1-yl)hydroborato]thallium(I), Tl[HB(3,5-Me$_2$pz)$_3$] 4. The compound K[HB(3,5-$Me_2pz)_3$] (5.00 g, 14.9 mmol) and $TlNO_3$ (3.96 g, 14.9 mmol) were stirred in CH_2Cl_2 (20 ml) for 6 h. The precipitate was separated by filtration to give a clear, colorless solution. Removal of the solvent in vacuum left a white solid (4.58 g, 61.4%). Free 3,5-dimethylpyrazole which had been formed during the reaction has to be removed by sublimation. The residue was dissolved again in CH_2Cl_2 and filtered. Cooling of the solution together with slow concentration gave clear crystals, Mp >240 °C. ^{1}H NMR ($CDCl_3$): δ 2.31 (s, 9 H, pz 3-CH_3), 2.39 (s, 9 H, pz 5-CH_3) and 5.76 (s, 3 H, H4). ^{13}C NMR ($CDCl_3$): δ 12.85 (3,5-CH_3), 105.15 (C4), 144.36 (C5) and 147.43 (C3). MS (125 °C): *m*/*z* 502 (22), $[M]^{+\bullet}$, 407 (100), $[M - 3,5Me_2pz]^+$; and 205 (55%), $[Tl]^+$. IR (strong peaks only): 2812, 2729, 2646, 2512 [ν(BH)], 2372, 2356, 2237, 1139, 858, 811 and 456 cm^{-1}. Calc. for $C_{15}H_{22}BN_6Tl$: C, 35.92; H, 4.42; N, 16.76; Found: C, 36.12; H, 4.49; N, 16.26%.

Structure determinations

Data were collected by the ω-scan method with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$) at 293 K on a Siemens Smart CCD diffractometer. Structure solution was by direct methods (SHELXS 97)[16] and refined by full-matrix least squares on F^2 (SHELXL 97);[16] all non-hydrogen positions were found and refined with anisotropic thermal parameters. Crystal data are listed in Table 2. Graphics were obtained with ORTEP 3 for Windows.[17]

CCDC reference number 186/1561.

See http://www.rsc.org/suppdata/dt/1999/3133/ for crystallographic files in .cif format.

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