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Phenyl tris(3-*tert*-butylpyrazolyl)borato complexes of lithium and thallium, [PhTp$^{\mathrm{Bu^t}}$]M (M = Li, Tl): a novel structure for a monomeric tris(pyrazolyl)boratothallium complex and a study of its stereochemical nonrigidity by ^{1}H and ^{205}Tl NMR spectroscopy

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The syntheses and structures of the phenyl substituted tris(3-*tert*-butylpyrazolyl)borato complexes, [PhTp$^{\mathrm{Bu^t}}$]M (M = Li, Tl, H), are reported. In contrast to other monomeric [Tp$^{\mathrm{RR'}}$]Tl derivatives, which exhibit symmetric tridentate coordination of the tris(pyrazolyl)borate ligand, [PhTp$^{\mathrm{Bu^t}}$]Tl exhibits an unprecedented structure. Specifically, one of the *tert*-butylpyrazolyl groups is rotated by *ca.* 90° and the Tl interacts with the nitrogen attached directly to the boron *via* a p-orbital component of the aromatic π-system of the pyrazolyl nucleus. [PhTp$^{\mathrm{Bu^t}}$]Tl is stereochemically nonrigid on the NMR spectroscopic timescale in solution at room temperature, but cooling to *ca.* −80 °C slows down the dynamic processes sufficiently to allow "axial" and "equatorial" isomers to be identified, with the descriptors denoting the position of the pyrazolyl group relative to the boat configuration of the six-membered [$\mathrm{BN_4Tl}$] ring.

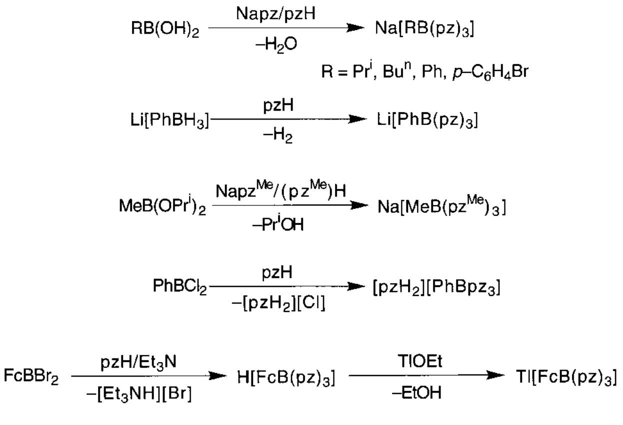
Introduction

The poly(pyrazolyl)borato ligand system is one of the most widely used in modern coordination chemistry.[1] Alkali metal and thallium[2] derivatives, in particular, have played a prominent role in the development of this chemistry by virtue of their use as ligand transfer agents. Other than their use as reagents, however, these complexes have received relatively little attention. To date, the majority of studies using tris(pyrazolyl)borato ligands have concentrated on [Tp$^{\mathrm{RR'}}$] derivatives in which the fourth site on boron is a hydride, with comparatively fewer studies having been reported for those with an alkyl or aryl substituent, [RTp$^{\mathrm{RR'}}$].[3] We are particularly interested in applying such [RTp$^{\mathrm{RR'}}$] ligands to situations in which the potential reactivity associated with the B–H bond may prove problematic.[4] In this paper, we report the syntheses and structures of the phenyl substituted tris(3-*tert*-butylpyrazolyl)borato complexes, [PhTp$^{\mathrm{Bu^t}}$]M (M = Li, Tl, H). Significantly, [PhTp$^{\mathrm{Bu^t}}$]Tl exhibits an unprecedented type of structure for monomeric tris(pyrazolyl)borato thallium derivatives.

Results and discussion

Syntheses of [PhTp$^{\mathrm{Bu^t}}$]Li, [PhTp$^{\mathrm{Bu^t}}$]Tl, and [PhTp$^{\mathrm{Bu^t}}$]H

Tris(pyrazolyl)borato ligands with alkyl or aryl substituents on boron, *i.e.* [RTp$^{\mathrm{RR'}}$], have been known for more than 30 years[5] and have been synthesized by a variety of methods, as illustrated in Scheme 1.[6–10] However, the majority of these [RTp$^{\mathrm{RR'}}$] ligands are derivatives of unsubstituted pyrazole, with relatively few examples incorporating bulky substituents in the 3-positions. For example, methyl is the bulkiest pyrazolyl substituent reported in the literature to have been incorporated into the [RTp$^{\mathrm{RR'}}$] ligand system; specifically, Na[MeTp$^{\mathrm{Me}}$] was obtained *via* the reaction of MeB(OPr$^{\mathrm{i}}$)$_2$ with a mixture of Na[pz$^{\mathrm{Me}}$] and Hpz$^{\mathrm{Me}}$.[11] In view of the important role that bulky substituents in the 3-positions of [Tp$^{\mathrm{RR'}}$] ligands has played in allowing isolation of certain reactive M–X functionalities,[12] we are particularly interested in the construction of related boron-substituted counterparts, [RTp$^{\mathrm{RR'}}$], with the notion that a more resistant ligand system will be obtained upon elimination of possible degradation reactions involving the B–H bond. Significantly, the phenyl tris(3-*tert*-butylpyrazolyl)borato ligand [PhTp$^{\mathrm{Bu^t}}$] may be constructed by heating a mixture of Li[PhBH$_3$][13] and 3-*tert*-butylpyrazole (*ca.* 3 equivalents) at *ca.* 220 °C (Scheme 2).[14] Subsequent metathesis of [PhTp$^{\mathrm{Bu^t}}$]Li with Tl(O$_2$CMe) yields the thallium derivative, [PhTp$^{\mathrm{Bu^t}}$]Tl, from which the acid form [PhTp$^{\mathrm{Bu^t}}$]H may be obtained by treatment with H$_2$S (Scheme 2). In contrast to the hydrated derivatives [Tp$^{\mathrm{RR'}}$]H·*n*(H$_2$O) that have been prepared by other methods,[15,16] the use of H$_2$S permits the synthesis of an anhydrous material.[17]



Scheme 1

Molecular structures of [PhTp$^{\mathrm{Bu^t}}$]Li, [PhTp$^{\mathrm{Bu^t}}$]Tl, and [PhTp$^{\mathrm{Bu^t}}$]H

The molecular structures of [PhTp$^{\mathrm{Bu^t}}$]Li, [PhTp$^{\mathrm{Bu^t}}$]Tl, and [PhTp$^{\mathrm{Bu^t}}$]H, as determined by single crystal X-ray diffraction (Fig. 1–3), exhibit several interesting features. For example, the lithium complex is notable because there are no other structurally characterized [RTp$^{\mathrm{RR'}}$]Li (or even [Tp$^{\mathrm{RR'}}$]Li) complexes listed in the Cambridge Structural Database,[18] and it exists as a discrete mononuclear species with an uncommon trigonal coordination environment.[19] The average Li–N bond length of

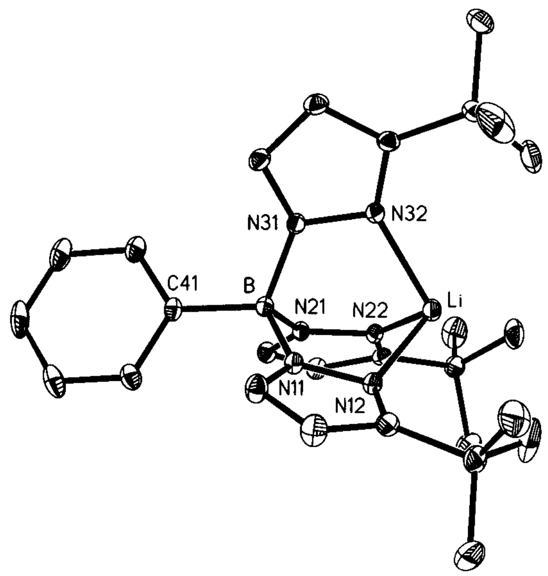
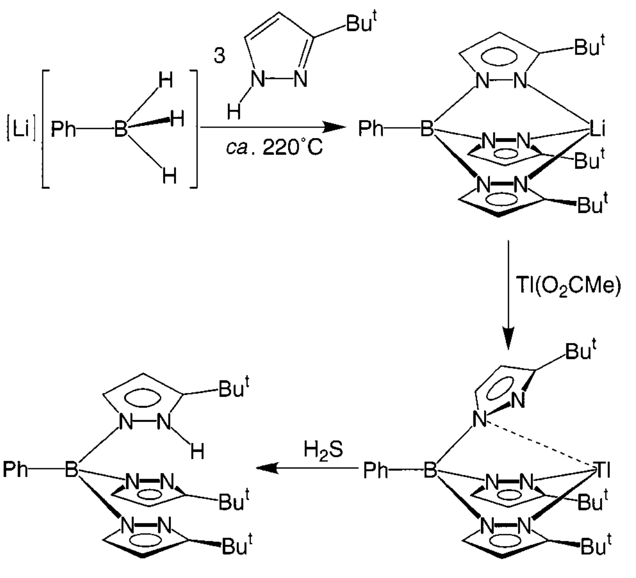


Fig. 1 Molecular structure of [PhTp$^{\mathrm{Bu^t}}$]Li.



Scheme 2

1.96 Å (Table 1) is comparable to, though marginally shorter than, the mean value of 2.08 Å for all complexes with Li–N bonds listed in the Cambridge Structural Database.[20] It is also shorter than the mean Li–N bond length of 2.06 Å in the tris(3,5-dimethylpyrazolyl)methane derivative, [HC(pz$^{\mathrm{Me_2}}$)$_3$]Li(η^3-H$_3$BH).[21]

Structurally characterized [Tp$^{\mathrm{RR'}}$]H derivatives are also rare, and the only examples of which we are aware are the tetrakis(pyrazolyl) complexes [pzTp]H·(H$_2$O)[16] and [(pz$^{\mathrm{Me_2}}$)Tp$^{\mathrm{Me_2}}$]H,[22] the latter of which was obtained as a decomposition product in the reaction of Cp$_2$TiCl$_2$ with [Tp$^{\mathrm{Me_2}}$]H. The structure of [PhTp$^{\mathrm{Bu^t}}$]H, as illustrated in Fig. 3, differs from that of the lithium derivative [PhTp$^{\mathrm{Bu^t}}$]Li in that the pyrazolyl groups of [PhTp$^{\mathrm{Bu^t}}$]H are not symmetrically disposed with C_{3v} symmetry. The [PhTp$^{\mathrm{Bu^t}}$]*H* hydrogen atom was both located and refined, and is localized on a single pyrazolyl nitrogen atom [N(12)] with a bond length of 0.84 Å; with a distance of 2.00 Å to the closest nitrogen atom [N(22)] on an adjacent pyrazolyl group, it is evident the N–H group does not participate in a significant hydrogen bonding interaction.

In contrast to the paucity of structurally characterized [RTp$^{\mathrm{RR'}}$]Li and [RTp$^{\mathrm{RR'}}$]H complexes, structurally characterized thallium derivatives are numerous.[23] Nevertheless, the structure of [PhTp$^{\mathrm{Bu^t}}$]Tl (Fig. 2) is unique amongst [RTp$^{\mathrm{RR'}}$]Tl derivatives. Specifically, whereas all other monomeric [RTp$^{\mathrm{RR'}}$]Tl complexes possess trigonally coordinated thallium, similar to that of the lithium derivative [PhTp$^{\mathrm{Bu^t}}$]Li, the thallium center of [PhTp$^{\mathrm{Bu^t}}$]Tl is principally coordinated to only *two* of the pyrazolyl groups: the third pyrazolyl group is effectively rotated by *ca.* 90° about the B–N bond. Despite the fact that one of the pyrazolyl groups is orthogonal to its position in other [RTp$^{\mathrm{RR'}}$]Tl derivatives, it is evident that there is still an interaction with the thallium center. The interaction is, however, of a fundamentally different nature to those in other [RTp$^{\mathrm{RR'}}$]Tl derivatives for two reasons: *(i)* the Tl interacts with the nitrogen atom attached directly to the boron, and *(ii)* the interaction is with the nitrogen p-orbital component of the aromatic π-system of the pyrazolyl nucleus. As a consequence, the unique Tl–N bond length [2.833(2) Å] is distinctly greater than those for the conventional bonds [2.528(3) Å and 2.585(3) Å], which are comparable to the average value in the counterpart without the phenyl substituent, [Tp$^{\mathrm{Bu^t}}$]Tl [2.59(1) Å].[24]

While examples of bidentate [η^2-Tp$^{\mathrm{RR'}}$]MX derivatives are known, as summarized in Table 2, the two coordinate nature of monomeric [PhTp$^{\mathrm{Bu^t}}$]Tl is of particular interest because such a coordination motif is unknown for thallium in [Tp$^{\mathrm{RR'}}$]Tl complexes. Since all other monomeric [Tp$^{\mathrm{RR'}}$]Tl complexes with a hydrogen substituent on boron adopt a common trigonal (C_{3v}) η^3-coordination geometry, the unusual structure of [PhTp$^{\mathrm{Bu^t}}$]Tl

Table 1 Selected bond lengths (Å) and angles (°) for [PhTp$^{\mathrm{Bu^t}}$]Li, [PhTp$^{\mathrm{Bu^t}}$]Tl, and [PhTp$^{\mathrm{Bu^t}}$]H

	[PhTp$^{\mathrm{Bu^t}}$]Li	[PhTp$^{\mathrm{Bu^t}}$]Tl	[PhTp$^{\mathrm{Bu^t}}$]H
M–N(12)	1.977(3)	2.585(3)	—
M–N(22)	1.934(3)	2.528(3)	—
M–N(3X)[a]	1.979(3)	2.833(2)	—
B–N(11)	1.572(2)	1.560(4)	1.572(4)
B–N(21)	1.571(2)	1.554(4)	1.554(3)
B–N(31)	1.568(2)	1.558(4)	1.540(4)
B–C(41)	1.615(2)	1.610(4)	1.603(4)
N(12)–M–N(22)	96.1(2)	71.58(8)	—
N(22)–M–N(3X)[a]	97.6(2)	69.35(7)	—
N(12)–M–N(3X)[a]	98.1(2)	66.09(8)	—
N(11)–B–N(21)	109.3(2)	110.1(2)	107.6(2)
N(21)–B–N(31)	109.4(2)	107.7(2)	107.6(2)
N(11)–B–N(31)	104.5(2)	104.9(2)	106.0(2)
C(41)–B–N(11)	112.7(2)	110.6(2)	109.8(2)
C(41)–B–N(21)	107.0(2)	111.1(2)	111.6(2)
C(41)–B–N(31)	113.8(2)	112.3(2)	114.0(2)

[a] X = 2 for [PhTp$^{\mathrm{Bu^t}}$]Li and [PhTp$^{\mathrm{Bu^t}}$]H; X = 1 for [PhTp$^{\mathrm{Bu^t}}$]Tl.

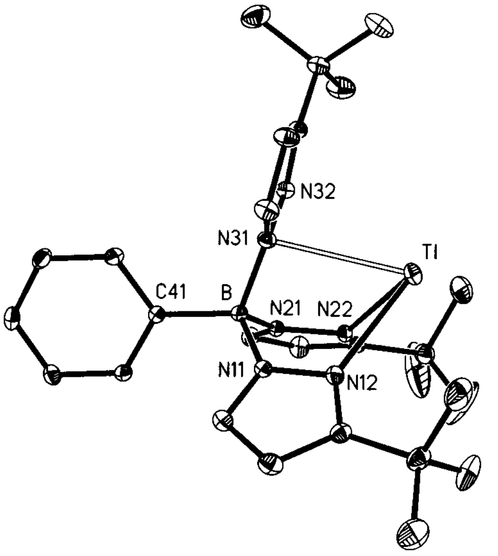


Fig. 2 Molecular structure of [PhTp$^{\mathrm{Bu^t}}$]Tl.

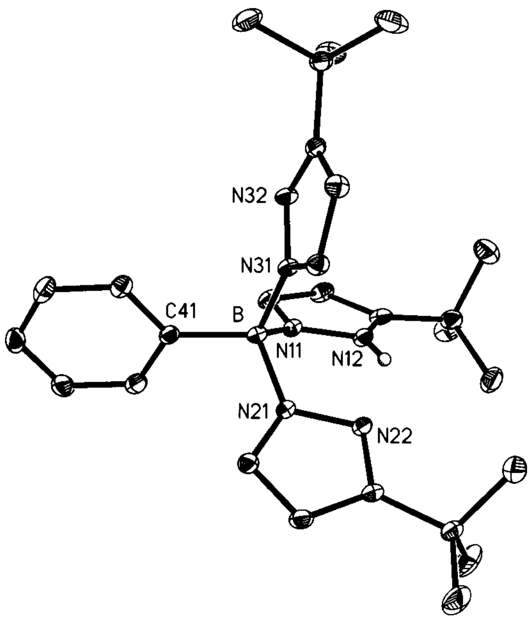


Fig. 3 Molecular structure of [PhTp$^{\mathrm{Bu^t}}$]H.

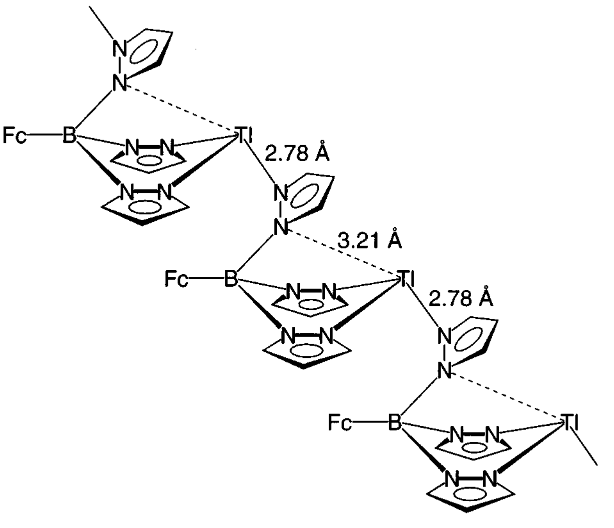


Fig. 4 Schematic representation of the polymeric nature of the ferrocynyl derivative {[FcTp]Tl}$_x$.

is most likely a consequence of the increased steric demands of the phenyl group. Thus, steric interactions between the 5-H substituents and the phenyl group would be expected to destabilize symmetric η^3-coordination.[25] Rotation about the B–N bond relieves such non-bonding interactions, but at the expense of the Tl–N interaction. The observed structure is, therefore, a compromise of maximizing Tl–N interactions and minimizing steric interactions with the phenyl substituent. Evidently, for [PhTp$^{\mathrm{Bu^t}}$]Tl, the steric interactions must be the dominant component. In contrast, the conventional η^3-coordination geometry of the lithium complex [PhTp$^{\mathrm{Bu^t}}$]Li is presumably a result of the Li–N interactions providing the dominant influence. Such a difference between [PhTp$^{\mathrm{Bu^t}}$]Tl and [PhTp$^{\mathrm{Bu^t}}$]Li is not unreasonable in view of the fact that two-coordinate thallium complexes, and especially [Bp$^{\mathrm{RR'}}$]Tl derivatives,[26] are well known. In contrast, two coordination is not common for lithium.[27]

The novel coordination geometry of [PhTp$^{\mathrm{Bu^t}}$]Tl has a specific feature in common with *polymeric* {[FcTp]Tl}$_x$,[10] namely that one of the pyrazolyl groups in {[FcTp]Tl}$_x$ is also orthogonal to its conventional position; however, in this case the 2-N coordinates to the thallium center of another molecule, thereby resulting in a polymeric structure (Fig. 4). The "intermolecular" Tl–N bond length of 2.780(5) Å in {[FcTp]Tl}$_x$ is only slightly greater than the intramolecular bond lengths [2.638(5) and 2.676(5) Å], but is distinctly shorter than the value of 3.21 Å for the intramolecular interaction involving 1-N from the orthogonal pyrazolyl group (Fig. 4). The latter value for {[FcTp]Tl}$_x$ is significantly greater than the corresponding bond length in [PhTp$^{\mathrm{Bu^t}}$]Tl [2.833(2) Å], which therefore provides a good indication that the unconventional interaction between thallium and the orthogonal pyrazolyl group in [PhTp$^{\mathrm{Bu^t}}$]Tl is structurally significant. It is also important to note that for [PhTp$^{\mathrm{Bu^t}}$]Tl the closest intermolecular Tl···N interaction is 5.67 Å; thus, the orthogonal pyrazolyl group of [PhTp$^{\mathrm{Bu^t}}$]Tl exhibits no significant interaction with adjacent molecules, and the strictly monomeric nature is presumably a consequence of the bulky *tert*-butyl substituents.[28]

Table 2 Representative examples of structurally characterized complexes with bidentate [RTp$^{\mathrm{RR'}}$] ligands

Compound	Ref.
[η^2-Tp$^{\mathrm{Bu^t}}$]AlEt$_2$	T1
[η^2-Tp$^{\mathrm{Me_2}}$]Ga(Me)X (X = Me, Cl)	T2
[η^2-pzTp][pzTp]GaMe	T2
[η^2-Tp$^{\mathrm{Me_2}}$][Tp$^{\mathrm{Me_2}}$]Sn	T3
[η^2-Tp$^{\mathrm{Me_2}}$]V(O)Cl$_2$	T4
[η^2-Tp$^{\mathrm{Me_2}}$]Rh(CNR)$_2$ (R = 2,6-Me$_2$C$_6$H$_3$, CH$_2$CMe$_3$)	T5
[η^2-Tp$^{\mathrm{Me_2}}$]Rh(CO)(PMe$_3$)	T6
[η^2-Tp]$_2$Pd	T7
[η^2-Tp]Pt(Me)CO	T8
{[η^2-Tp$^{\mathrm{Me_2}}$]PtMe$_2$}{PPN}	T9
[η^2-pzTp]Cu(PPh$_3$)$_2$	T10
[η^2-Tp$^{\mathrm{Ph_2}}$]$_2$Zn	T11
[η^2-pzTp]$_2$Pb	T12
[η^2-pzTp]HgSMe	T13
[η^2-Tp][Tp]$_2$Yb	T14

T1 M. H. Chisholm, N. W. Eilerts and J. C. Huffman, *Inorg. Chem.*, 1996, **35**, 445.
T2 D. L. Reger and Y. Ding, *Organometallics*, 1993, **12**, 4485.
T3 A. H. Cowley, R. L. Geerts, C. M. Nunn and C. J. Carrano, *J. Organomet. Chem.*, 1988, **341**, C27.
T4 E. Kime-Hunt, K. Spartalian, M. DeRusha, C. M. Nunn and C. J. Carrano, *Inorg. Chem.*, 1989, **28**, 4392.
T5 W. D. Jones and E. T. Hessel, *Inorg. Chem.*, 1991, **30**, 778.
T6 V. Chauby, C. S. Le Berre, P. Kalck, J.-C, Daran and G. Commenges, *Inorg. Chem.*, 1996, **35**, 6354.
T7 A. J. Canty, N. J. Minchin, L. M. Engelhardt, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1986, 645.
T8 P. E. Rush and J. D. Oliver, *J. Chem. Soc., Chem. Commun.*, 1974, 996.
T9 D. D. Wick and K. I. Goldberg, *J. Am. Chem. Soc.*, 1997, **119**, 10235.
T10 P. Cecchi, B. Bovio, G. G. Lobbia, C. Pettinari and D. Leonesi, *Polyhedron*, 1995, **14**, 2441.
T11 F. Hartmann, W. Klaüi, A. Kremer-Aach, D. Mootz, A. Strerath and H. Z. Wunderlich, *Z. Anorg. Allg. Chem.*, 1993, **619**, 2071.
T12 D. L. Reger, M. F. Huff, A. L. Rheingold and B. S. Haggerty, *Inorg. Chem.*, 1992, **114**, 579.
T13 S. Aime, G. Digilio, R. Gobetto, P. Cecchi, G. G. Lobbia and M. Camalli, *Polyhedron*, 1994, **13**, 2695.
T14 M. V. R. Stainer and J. Takats, *Inorg. Chem.*, 1982, **21**, 4050.

Stereochemical nonrigidity of [PhTp$^{\mathrm{Bu^t}}$]Tl

Whereas the asymmetric nature of [PhTp$^{\mathrm{Bu^t}}$]Tl in the solid state is certain, the question remains as to how the ligand coordinates in solution. At room temperature, the ^{1}H NMR spectrum of [PhTp$^{\mathrm{Bu^t}}$]Tl reveals only one set of resonances attributable to the *tert*-butylpyrazolyl moiety. Such an observation is consistent with at least two common possibilities for the solution structure: *(i)* [PhTp$^{\mathrm{Bu^t}}$]Tl exists as a static symmetric C_{3v} tridentate structure, or *(ii)* [PhTp$^{\mathrm{Bu^t}}$]Tl exists with the asymmetric structure shown in Fig. 2, but the molecule is stereochemically nonrigid on the NMR spectroscopic timescale. In order to

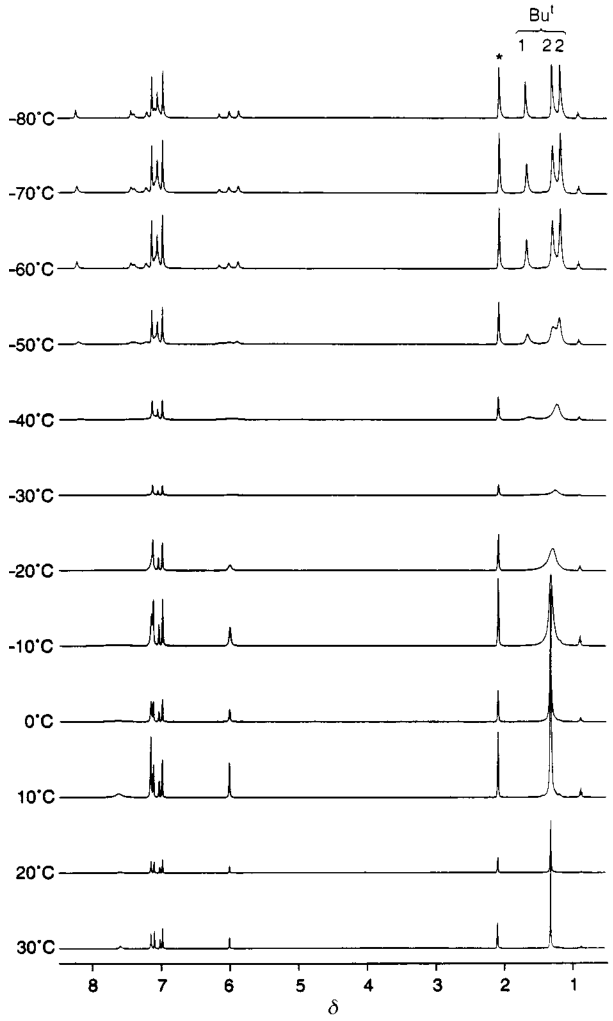


Fig. 5 Variable temperature ^{1}H NMR spectra of [PhTp$^{Bu^t}$]Tl in toluene (* = residual protio solvent).

address these possibilities, variable temperature ^{1}H NMR spectroscopic studies were conducted. Significantly, upon lowering the temperature to −80 °C, decoalescence was observed (Fig. 5), giving rise to three sets of resonances in the ratio *ca.* 2 : 2 : 1 (as most clearly seen by examination of the *tert*-butyl region). This pattern, however, is not consistent with the solid state structure of [PhTp$^{Bu^t}$]Tl, which would result in three sets of resonances in the ratio 1 : 1 : 1 corresponding to the three inequivalent *tert*-butylpyrazolyl groups (note that the two coordinated pyrazolyl groups of a static structure are not chemically equivalent, but are diastereotopically related). Alternatively, if the chemical shifts of the diastereotopically related pyrazolyl groups are coincidentally the same, or a mechanism exists which allows for their facile interconversion, then a 2 : 1 pattern of pyrazolyl groups would be expected. It is, therefore, evident that the experimentally observed 2 : 2 : 1 pattern is not consistent with the presence of a single chemical species at low temperature; the presence of a second species is thus required to generate the observed low temperature ^{1}H NMR spectrum.

Excellent support for the presence of a second species is provided by ^{205}Tl NMR spectroscopy: specifically, at low temperature (*ca.* −70 °C), the ^{205}Tl NMR spectrum exhibits two resonances (Fig. 6). Furthermore, these two signals coalesce upon warming to room temperature, clearly indicating that the two species are isomers of each other. The 2 : 2 : 1 distribution of pyrazolyl groups in the ^{1}H NMR spectrum can, therefore, be rationalized in terms of two species, $A_{3:0}$ and $B_{2:1}$ (Scheme 3), which possess equivalent and inequivalent (in the ratio 2 : 1) sets of pyrazolyl groups, respectively. Thus, if the ratio of $A_{3:0}$ to $B_{2:1}$ is 2 : 3,[29] the composite ^{1}H NMR spectrum would show pyrazolyl groups in the ratio 6 : [6 : 3], *i.e.* 2 : 2 : 1. Assuming this hypothesis to be correct, the important issue is concerned with identifying the nature of $A_{3:0}$ and $B_{2:1}$. At least two possible scenarios emerge.

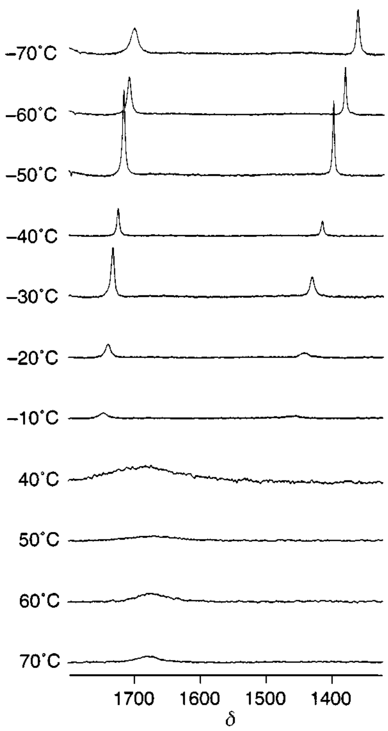
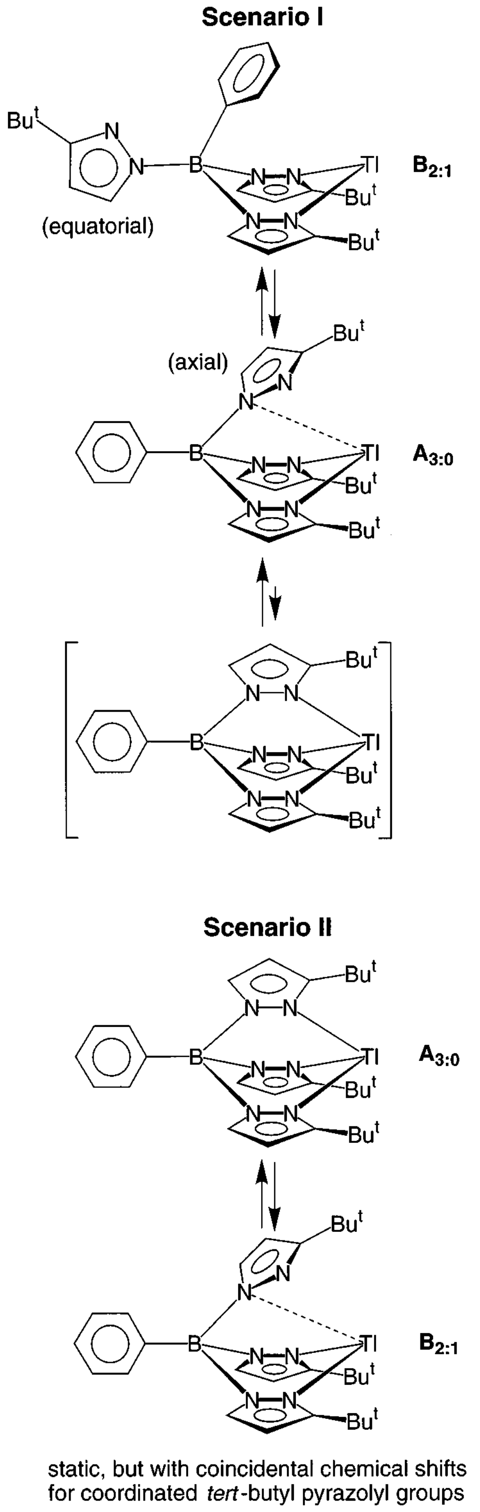


Fig. 6 Variable temperature ^{205}Tl NMR spectra of [PhTp$^{Bu^t}$]Tl in toluene.

(a) Scenario I. $A_{3:0}$ and $B_{2:1}$ correspond to isomers related by interchange of the uncoordinated pyrazolyl and phenyl substituents (Scheme 3). These isomers may be described as "axial" and "equatorial", with the descriptors denoting the position of the pyrazolyl group relative to the boat configuration of the six-membered [BN_4Tl] ring. Of these two structures, the axial isomer may be identified as $A_{3:0}$ and the equatorial isomer as $B_{2:1}$. The rationale for these assignments is based on the notion that the axial isomer is more likely to exhibit equivalent pyrazolyl groups on the NMR spectroscopic timescale than is the equatorial isomer. Specifically, rotation about the B–N bond of the axial isomer allows access to a symmetric tridentate species, thereby enabling facile exchange of all three pyrazolyl groups. In contrast, rotation about the B–N bond in the equatorial isomer ($B_{2:1}$) does not result in chemical exchange of the pyrazolyl groups, which therefore retain a 2 : 1 pattern. For this scenario, the interchange of axial ($A_{3:0}$) and equatorial ($B_{2:1}$) isomers corresponds to flipping the boat configuration of the six-membered [BN_4Tl] ring.

(b) Scenario II. A second possibility is that $A_{3:0}$ corresponds to a symmetric η^3-structure, and $B_{2:1}$ corresponds to the η^2-axial isomer as observed in the solid state.[30] The principal difference between the structure corresponding to $B_{2:1}$ in Scenario II and that of $A_{3:0}$ in Scenario I is that in Scenario I it is highly fluxional.

Of these two scenarios, we consider the first to be the more reasonable since it makes no assumptions concerning coincidental chemical shifts of the diastereotopic pyrazolyl groups for $B_{2:1}$. Thus, as summarized in Scheme 3, the proposed identity of $B_{2:1}$ is the equatorial bidentate isomer, while $A_{3:0}$ is the axial isomer in rapid equilibrium with the tridentate species. Precedent for this suggestion is provided by Venanzi's study of stereochemical nonrigidity within complexes of the types [Tp$^{RR'}$]Rh(CO)$_2$ and [Tp$^{RR'}$]Rh(L_2) (L_2 = cyclooctadiene, nor-



Scheme 3

bornadiene), each of which exhibits magnetically equivalent pyrazolyl groups at room temperature.[31] IR spectroscopic studies on the carbonyl complexes demonstrated that the solutions consisted of three different species: *(i)* two four-coordinate complexes with bidentate $[\mathrm{Tp}^{\mathrm{RR'}}]$ ligands, differing according to whether the uncoordinated pyrazolyl group was in an axial or equatorial position, and *(ii)* a five-coordinate complex with tridentate $[\mathrm{Tp}^{\mathrm{RR'}}]$ coordination. The relative amounts of these three species depended upon both the nature of the $[\mathrm{Tp}^{\mathrm{RR'}}]$ ligand and the solvent. In one specific example, $[\mathrm{Tp}^{3\text{-}\mathrm{Pr^i},4\text{-}\mathrm{Br}}]\mathrm{Rh(CO)_2}$ was observed to decoalesce to a "symmetric" and asymmetric species. IR spectroscopy demonstrated that both species were four coordinate, so that the "symmetric" species was proposed to be stereochemically nonrigid and bidentate rather than a complex with tridentate coordination. As a further illustration that magnetic equivalence of the three pyrazolyl groups in $[\eta^2\text{-}\mathrm{Tp}^{\mathrm{RR'}}]\mathrm{MX}$ complexes does not require species with tridentate coordination to be present in detectable concentrations, Jones reported that the equivalence of the pyrazolyl groups in $[\eta^2\text{-}\mathrm{Tp}^{\mathrm{Me_2}}]\mathrm{Rh(CNR)}$ ($R = 2,6\text{-}Me_2C_6H_3$, CH_2CMe_3) is a consequence of facile chemical exchange of coordinated and uncoordinated pyrazolyl groups, with a symmetric tridentate species having no detectable concentration as determined by IR spectroscopy.[32]

Conclusions

In summary, the phenyl substituted tris(3-*tert*-butylpyrazolyl)borato complexes, $[\mathrm{PhTp}^{\mathrm{Bu^t}}]\mathrm{M}$ (M = Li, Tl, H) have been synthesized and structurally characterized by X-ray diffraction. In contrast to other monomeric $[\mathrm{Tp}^{\mathrm{RR'}}]\mathrm{Tl}$ derivatives, which exhibit symmetric tridentate coordination of the tris(pyrazolyl)borate ligand, $[\mathrm{PhTp}^{\mathrm{Bu^t}}]\mathrm{Tl}$ exhibits an unprecedented structure in which one of the *tert*-butylpyrazolyl groups is rotated by *ca.* 90° and the Tl interacts with the nitrogen attached directly to the boron *via* a p-orbital component of the aromatic π-system of the pyrazolyl nucleus. $[\mathrm{PhTp}^{\mathrm{Bu^t}}]\mathrm{Tl}$ is stereochemically nonrigid on the NMR spectroscopic timescale in solution at room temperature, equilibrating between isomers which differ according to whether the uncoordinated pyrazolyl group is located axially or equatorially relative to the six-membered $[\mathrm{BN_4Tl}]$ ring.

Experimental

General considerations

All manipulations were performed using a combination of glovebox, high-vacuum or Schlenk techniques.[33] Solvents were purified and degassed by standard procedures. Commercially available reagents were not further purified. All glassware was oven dried prior to use. NMR spectra were recorded on Bruker Avance 300wb DRX, Bruker Avance 400 DRX, and Bruker Avance 500 DMX spectrometers. ^{1}H 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; ^{205}Tl NMR spectra were recorded on a Bruker Avance 300wb DRX (173.393 Hz) instrument and are referenced relative to aqueous $TlNO_3$ (extrapolated to infinite dilution; $\delta = 0.00$),[34,35] using an external solution of aqueous $Tl(O_2CMe)$ as calibrant. All coupling constants are reported in Hz. C, H, and N elemental analyses were measured using a Perkin-Elmer 2400 CHN Elemental Analyzer.

Synthesis of $[\mathrm{PhTp}^{\mathrm{Bu^t}}]\mathrm{Li}$

A rapidly stirred mixture of $\mathrm{Li[PhBH_3]}$ (5.82 g, 59.5 mmol) and $\mathrm{Hpz}^{\mathrm{Bu^t}}$(22.2 g, 0.18 mol) was heated at *ca.* 220 °C under N_2 until evolution of H_2 ceased (*ca.* 1 h). The product was allowed to cool to room temperature and extracted into pentane (*ca.* 200 mL). The mixture was filtered and the volatile components removed *in vacuo* giving $[\mathrm{PhTp}^{\mathrm{Bu^t}}]\mathrm{Li}$ as a white solid (27.0 g, 98%). The product may be crystallized from pentane at −18 °C over a period of several days (Calc. for $[\mathrm{PhTp}^{\mathrm{Bu^t}}]\mathrm{Li}$: C, 69.8; H, 8.3; N, 18.1. Found: C, 69.6; H, 9.5; N, 18.9). NMR spectroscopic data are listed in Table 3.

Synthesis of $[\mathrm{PhTp}^{\mathrm{Bu^t}}]\mathrm{Tl}$

A mixture of $[\mathrm{PhTp}^{\mathrm{Bu^t}}]\mathrm{Li}$ (9.5 g, 20 mmol) and $\mathrm{Tl(O_2CMe)}$ (8.1 g, 31 mmol) in THF (50 mL) was stirred at room temperature for 1 day. After this period, the mixture was filtered and the volatile components were removed *in vacuo* giving $[\mathrm{PhTp}^{\mathrm{Bu^t}}]\mathrm{Tl}$ as an off-white solid (5.97 g, 45%). Pure $[\mathrm{PhTp}^{\mathrm{Bu^t}}]\mathrm{Tl}$ was

Table 3 NMR spectroscopic data for [ThTp$^{\mathrm{Bu^t}}$]Li, [PhTp$^{\mathrm{Bu^t}}$]Tl, and [PhTp$^{\mathrm{Bu^t}}$]H

Assignment	[PhTp$^{\mathrm{Bu^t}}$]Li^a	[PhTp$^{\mathrm{Bu^t}}$]Tl	[PhTp$^{\mathrm{Bu^t}}$]H
^{1}H (C_6D_6)			
$C(CH_3)_3$	1.31, s	1.32, s	1.24, s
$C_3N_2H_2$	5.91, d, $^3J_{H-H} = 2$	6.04, d, $^3J_{H-H} = 2$	5.94, d, $^3J_{H-H} = 2$
	7.96, br	7.66, br	7.29, d, $^3J_{H-H} = 2$
C_6H_5	7.24–7.55	7.12–7.20	7.20–7.25
N*H*	—	—	Not observed
^{13}C (C_6D_6)			
$C(CH_3)_3$	31.0, q, $^1J_{C-H} = 126$	31.7, q, $^1J_{C-H} = 126$	30.6, q, $^1J_{C-H} = 126$
$C(CH_3)_3$	32.1, s	32.4, s	32.0, s
$C_3N_2H_2$	100.3, d, $^1J_{C-H} = 173$	101.4, d, $^1J_{C-H} = 172$	101.5, d, $^1J_{C-H} = 174$
	136.5, d, $^1J_{C-H} = 181$	137.2, d, $^1J_{C-H} = 184$	136.6, $^1J_{C-H} = 186$
	161.8, s	163.7, s	161.1, s
BC_6H_5	128.0, d, $^1J_{C-H} = 158$ (3C)	128.6, d, $^1J_{C-H} = 162$ (3C)^b	127.7, d, $^1J_{C-H} = 156$ (3C)^b
	135.6, $^1J_{C-H} = 159$ (2C)	135.4, d, $^1J_{C-H} = 157$ (2C)	133.2, d, $^1J_{C-H} = 156$ (2C)
	(C_{ipso} not observed)	148.5, br (C_{ipso})	(C_{ipso} not observed)

^{a} The NMR signals in the presence of additional *tert*-butylpyrazole are perturbed from the values listed here, presumably due to the formation of an adduct. ^{b} An HMQC experiment indicates that the *meta* and *para* resonances are coincident with each other.

Table 4 Crystal, intensity collection and refinement data.

	[PhTp$^{\mathrm{Bu^t}}$]Li	[PhTp$^{\mathrm{Bu^t}}$]Tl	[PhTp$^{\mathrm{Bu^t}}$]H
Lattice	Monoclinic	Monoclinic	Triclinic
Formula	$C_{27}H_{38}BN_6Li$	$C_{27}H_{38}BN_6Tl$	$C_{27}H_{39}BN_6$
Formula weight	464.38	661.81	458.45
Space group	*C*2/*c* (no. 15)	*P*2$_1$/*c* (no. 14)	$P\bar{1}$ (no. 2)
a/Å	18.6329(10)	15.2499(7)	11.6639(8)
b/Å	16.1563(9)	13.8902(7)	12.1658(8)
c/Å	18.7233(10)	15.3951(7)	12.2480(8)
α/°			114.003(1)
β/°	90.454(1)	117.055(1)	101.409(1)
γ/°			109.440(1)
V/Å^3	5636.3(5)	2904.2(2)	1380.7(2)
Z	8	4	2
T/K	203	203	173
λ/Å	0.71073	0.71073	0.71073
ρ_{calc}/g cm^{-3}	1.095	1.514	1.103
μ(Mo-Kα)/mm^{-1}	0.065	5.586	0.066
θ max/°	28.3	28.3	28.3
No. of data	6413	6600	5727
No. of parameters	326	326	321
R_1^{a}	0.0518	0.0279	0.0740
wR_2^{a}	0.1185	0.0585	0.1610
S	1.045	1.044	1.070

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

obtained as colorless crystals by repeated crystallization from pentane at −15 °C (Calc. for [PhTp$^{\mathrm{Bu^t}}$]Tl: C, 49.0; H, 5.8; N, 12.7. Found: C, 49.3; H, 5.7; N, 13.4). NMR spectroscopic data are listed in Table 3.

Synthesis of [PhTp$^{\mathrm{Bu^t}}$]H

A solution of [PhTp$^{\mathrm{Bu^t}}$]Tl (220 mg, 0.33 mmol) in benzene was treated with H_2S resulting in the formation of a black precipitate. The mixture was filtered and the volatile components were removed *in vacuo* giving [PhTp$^{\mathrm{Bu^t}}$]H as a white powder, from which colorless crystals were obtained by crystallization from pentane (*ca.* 1 mL) at −15 °C (66 mg, 43%) (Calc. for [PhTp$^{\mathrm{Bu^t}}$]H: C, 70.7; H, 8.6; N, 18.3. Found: C, 71.0; H, 8.4; N, 17.4). NMR spectroscopic data are listed in Table 3.

Crystal structure determinations

Crystal data, data collection and refinement parameters for [PhTp$^{\mathrm{Bu^t}}$]Li, [PhTp$^{\mathrm{Bu^t}}$]Tl, and [PhTp$^{\mathrm{Bu^t}}$]H are summarized in Table 4. X-Ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures using SHELXTL.[36] Hydrogen atoms on carbon were included in calculated positions. Systematic absences for [PhTp$^{\mathrm{Bu^t}}$]Li were consistent with *Cc* (no. 9) and *C*2/*c* (no. 15), of which a satisfactory solution was obtained in the centrosymmetric alternative *C*2/*c* (no. 15). Systematic absences for [PhTp$^{\mathrm{Bu^t}}$]Tl were consistent uniquely with *P*2$_1$/*c* (no. 14). Systematic absences for [PhTp$^{\mathrm{Bu^t}}$]H were consistent with *P1* (no. 1) and $P\bar{1}$ (no. 2), of which a satisfactory solution was obtained in the centrosymmetric alternative, $P\bar{1}$ (no. 2).

CCDC reference number 186/1440.

See http://www.rsc.org/suppdata/dt/1999/1929/ for crystallographic files in .cif format.

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