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Bis- and Tris(pyrazolyl)hydroborato Ligands with Bulky Triptycyl Substituents: The Synthesis and Structural Characterization of Tl[$\mathrm{Bp^{Trip}}$] and Tl[$\mathrm{Tp^{Trip}}$]

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Introduction

The poly(pyrazolyl)borate ligand system has found extensive use in areas as diverse as organometallic and bioinorganic chemistry.[1] Central to these studies is the use of a wide variety of substituents on the 3-position of the pyrazolyl ring to modify the steric and electronic environment around a metal center. For example, the [$\mathrm{Tp^{Bu^t}}$] ligand,[2,3] with bulky *tert*-butyl substituents in the 3-positions, has been used as a "tetrahedral enforcer"[4] with the intent of inhibiting the formation of six-coordinate sandwich complexes of the type [$\mathrm{Tp^{Bu^t}}$]$_2$M. However, although *tert*-butyl substituents do prevent the formation of six-coordinate [$\mathrm{Tp^{Bu^t}}$]$_2$M derivatives, their extreme bulk also results in an attenuation of the reactivity of four-coordinate [$\mathrm{Tp^{Bu^t}}$]MX complexes.[5] Incorporation of less sterically-demanding substituents would be expected to promote the reactivity [$\mathrm{Tp^{RR'}}$]MX complexes, but such species are often unstable with respect to ligand redistribution and the formation of [$\mathrm{Tp^{RR'}}$]$_2$M.[1] For example, simple aryl substituents do not prevent such complex formation, as illustrated by the manganese and iron complexes [$\mathrm{Tp^{Ph}}$]$_2$M (M = Mn, Fe).[6,7] In this paper, we describe the syntheses of bis- and tris(pyrazolyl)hydroborato ligands which incorporate the 9-triptycyl (triptycyl = 9,10-dihydro-9,10-*o*-benzenoanthryl) substituent, [$\mathrm{Bp^{Trip}}$] and [$\mathrm{Tp^{Trip}}$]. The intent is that such a ligand system will be of use in inhibiting the formation of [$\mathrm{Bp^{Trip}}$]$_2$M and [$\mathrm{Tp^{Trip}}$]$_2$M derivatives, while permitting greater access to the metal center than is afforded by *tert*-butyl substituents.

Results and Discussion

The aforementioned inability of an unsubstituted phenyl group to prevent the formation of six-coordinate [$\mathrm{Tp^{Ph}}$]$_2$M complexes is in part due to its ability to lie coplanar with the pyrazolyl moiety. Coplanarity may, however, be inhibited by incorporation of substituents into the *ortho* positions of the aryl group, as illustrated by the mesityl derivatives [$\mathrm{Tp^{Ms}}$]MX (Ms = mesityl).[8] More recently, we have described the use of the planar 9-anthryl substituent in the 3-position to provide a ligand system in which the aryl and pyrazolyl planes are strongly inhibited from adopting a coplanar orientation, as illustrated in Figure 1 for [$\mathrm{Tp^{Ant}}$]CoNCS.[9] However, although the 9-anthryl substituents of [$\mathrm{Tp^{Ant}}$]CoNCS are non-coplanar with the pyrazolyl groups, they are not completely orthogonal, with interplanar angles of *ca.* 41°, 65°, and 81°. Consequently, the 9-anthryl substituents of [$\mathrm{Tp^{Ant}}$]CoNCS adopt a chiral array (with idealized C_3 symmetry) such that lateral access to the metal center, is not completely blocked. As an extension of the latter study, we rationalized that a more symmetric array (with closer to C_{3v} symmetry) could be generated by the use of nonplanar 3-fold symmetric 9-triptycyl substituents. It was, therefore, anticipated that the 9-triptycyl substituents of the [$\mathrm{Tp^{Trip}}$] ligand would provide a relatively spacious conical pocket about a metal center, but that formation of six-coordinate sandwich complexes [$\mathrm{Tp^{Trip}}$]$_2$M would be inhibited due to the difficulty of meshing the 9-triptycyl groups on adjacent ligands.

The thallium bis- and tris[3-(9-triptycyl)pyrazolyl]hydroborato complexes, Tl[$\mathrm{Bp^{Trip}}$] and Tl[$\mathrm{Tp^{Trip}}$], respectively, have been synthesized by the methods illustrated in Scheme 1. Thus, the bis[3-(9-triptycyl)pyrazolyl]hydroborato complex Tl[$\mathrm{Bp^{Trip}}$] is obtained by the reaction of 3-(9-triptycyl)pyrazole[10] with $\mathrm{LiBH_4}$, followed by treatment with $\mathrm{TlNO_3}$. In contrast to the synthetic method commonly used to prepare tris(pyrazolyl)hydroborato thallium complexes, *i.e.*, metathesis of an alkali metal derivative [$\mathrm{Tp^{RR'}}$]M with TlX (*e.g.*, X = $\mathrm{NO_3}$, OAc),[1] we have found that Tl[$\mathrm{Tp^{Trip}}$] may be conveniently obtained directly by heating a mixture of Tl[$\mathrm{Bp^{Trip}}$] and 3-(9-triptycyl)pyrazole at *ca.* 170 °C *in vacuo* (Scheme 1).

The molecular structures of Tl[$\mathrm{Bp^{Trip}}$] and Tl[$\mathrm{Tp^{Trip}}$] have been determined by X-ray diffraction, as illustrated in Figures 2−4. Selected bond lengths and angles are listed in Tables 1 and 2. A view of Tl[$\mathrm{Tp^{Trip}}$] down the Tl···B axis is shown in Figure 4, illustrating the approximately C_{3v} nature of the conical cavity about the metal center provided by the three triptycyl substituents. The average Tl−N bond length of 2.74 Å is slightly longer than the range previously established for Tl[$\mathrm{Tp^{RR'}}$] complexes (2.50−2.72 Å; mean = 2.59 Å),[11,12] which is presumably a consequence of the steric bulk associated with the triptycyl groups. Similarly, the average Tl−N bond length of 2.70 Å for Tl[$\mathrm{Bp^{Trip}}$] is slightly longer than the average values observed for the 3-*tert*-butyl-substituted derivatives Tl[$\mathrm{Bp^{Bu^t,Me}}$] (2.60 Å), Tl[$\mathrm{Bp^{Bu^t,Pr^i}}$] (2.65 Å), and Tl[$\mathrm{Bp^{Bu^t{}_2}}$] (2.64 Å).[13] The

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† On leave from C. N. R. S, France.

(1) For recent reviews, see: (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943−980. (b) Parkin, G. *Adv. Inorg. Chem.* **1995**, *42*, 291−393. (c) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 419−531. (d) Santos, I.; Marques, N. *New. J. Chem.* **1995**, *19*, 551−571. (e) Reger, D. L. *Coord. Chem. Rev.* **1996**, *147*, 571−595.

(2) Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507−1514.

(3) The abbreviations adopted here for bis- and tris(pyrazolyl)hydroborato ligands are based on those described by Trofimenko (ref 1a). Thus, the tris(pyrazolyl)hydroborato ligands are represented by the abbreviation [Tp] with the 3- and 5-alkyl substituents listed, respectively, as superscripts. Likewise, bis(pyrazolyl)hydroborato ligands are represented by the abbreviation [Bp] with the appropriate superscripts.

(4) The term "tetrahedral enforcer" mainly applies to elements of comparable size to those of the first transition series, see: Calabrese, J. C.; Domaille, P. J.; Trofimenko, S.; Long, G. J. *Inorg. Chem.* **1991**, *30*, 2795−2801.

(5) Parkin, G. Effect of Tris(pyrazolyl)hydroborato Ligation. In *Handbook of Grignard Reagents*; Silverman, G. S., Rakita, P. E., Eds.; Marcel Dekker: New York, 1996.

(6) Eichhorn, D. M.; Armstrong, W. H. *Inorg. Chem.* **1990**, *29*, 3607−3612.

(7) Interestingly, the potentially tridentate [$\mathrm{Tp^{Ph}}$] ligand acts only as a bidentate ligand in [$\mathrm{Tp^{Ph}}$]$_2$Zn so that the zinc center is four-coordinate and tetrahedral.[7a] However, the zinc centers in [Tp]$_2$Zn,[7b] [$\mathrm{Tp^{Me_2}}$]$_2$-Zn,[7c] and [$\mathrm{Tp^{4\text{-}Me}}$]$_2$Zn[7d] are six-coordinate and octahedral. (a) Hartmann, F.; Kläui, W.; Kremer-Aach, A.; Mootz, D.; Strerath, A.; Wunderlich, H. *Z. Anorg. Allg. Chem.* **1993**, *619*, 2071−2076. (b) Nakata, K.; Kawabata, S.; Ichikawa, K. *Acta Crystallogr.* **1995**, *C51*, 1092−1094. (c) Looney, A.; Han, R.; Gorrell, I. B.; Cornebise, M.; Yoon, K.; Parkin, G.; Rheingold, A. L. *Organometallics* **1995**, *14*, 274−288. (d) Lobbia, G. G.; Bovio, B. Santini, C.; Pettinari, C.; Marchetti, F. *Polyhedron* **1997**, *16*, 671−680.

(8) Rheingold, A. L.; White, C. B.; Trofimenko, S. *Inorg. Chem.* **1993**, *32*, 3471−3477.

(9) Han, R.; Parkin, G.; Trofimenko, S. *Polyhedron* **1995**, *14*, 387−391.

(10) Burckhardt, U.; Hintermann, L.; Schnyder, A.; Togni, A. *Organometallics* **1995**, *14*, 5415−5425.

(11) Cambridge Structural Database (Version 5.12, October 1996). Also see ref 1b.

(12) After Tl[$\mathrm{Tp^{Trip}}$], the complex with the next longest Tl−N bond lengths is Tl[$\mathrm{Tp^{(CF_3)_2}}$], with values of 2.675(10) and 2.725(7) Å, see: Renn, O.; Venanzi, L. M.; Marteletti, A.; Gramlich, V. *Helv. Chim. Acta* **1995**, *78*, 993−1000.

S0020-1669(97)00259-0 CCC: $14.00

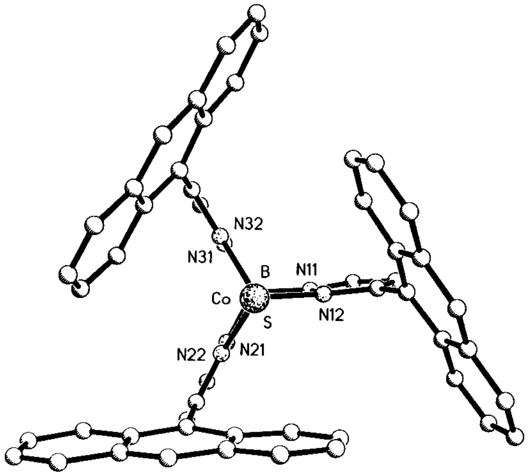


Figure 1. View of [Tp^{Ant}]CoNCS down the 3-fold axis.

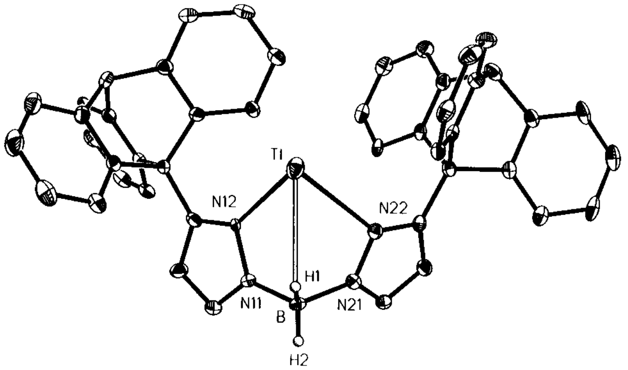
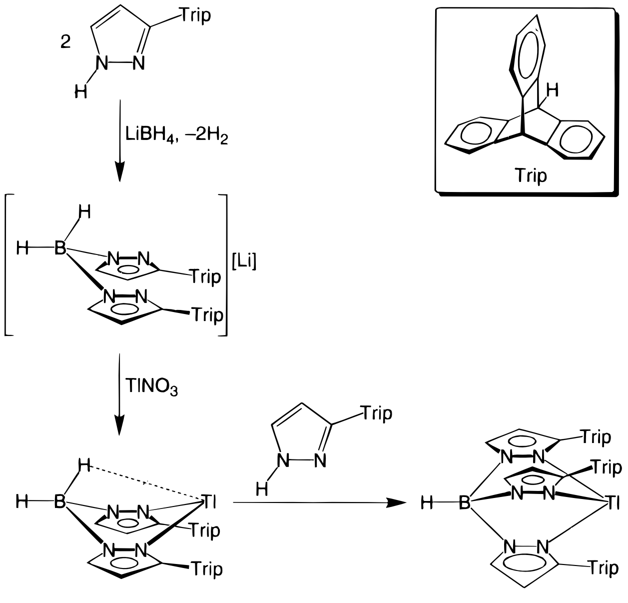


Figure 2. Molecular structure of Tl[Bp^{Trip}].

Scheme 1



coordination of the Tl(I) center of Tl[Bp^{Trip}] is augmented by an intramolecular [Tl···H−B] interaction with a Tl···H separation of *ca.* 2.70 Å, which is intermediate between that of Tl−H in the gas phase (1.87 Å)[14,15] and the sum of their van der Waals radii (3.16 Å).[16,17] In accord with the notion of a weak [Tl···H−B] interaction, the nonbonded Tl···B separation in Tl[Bp^{Trip}] (3.31 Å) is less than that observed for the tris(pyrazolyl)-hydroborato derivative Tl[Tp^{Trip}] (3.63 Å).[18] The Tl···B separation in Tl[Bp^{Trip}] is not, however, as short as the separations in Tl[Bp$^{Bu^t,R}$] (3.12−3.18 Å), suggesting that the [Tl···H−B] interaction may be weaker in the former complex. In this regard, it is worth noting that the Tl center of Tl[Bp^{Trip}] also experiences a close intermolecular interaction with a molecule of toluene, as illustrated in Figure 5: specifically, the Tl···C separations

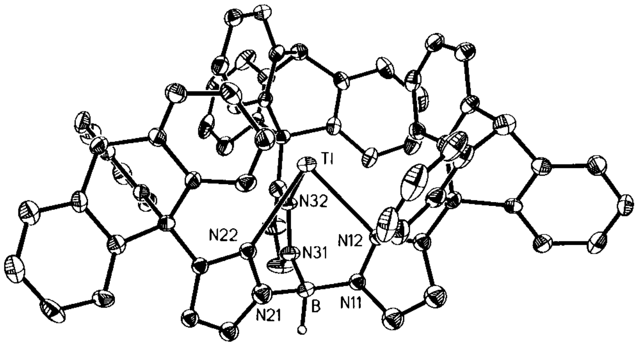


Figure 3. Molecular structure of Tl[Tp^{Trip}].

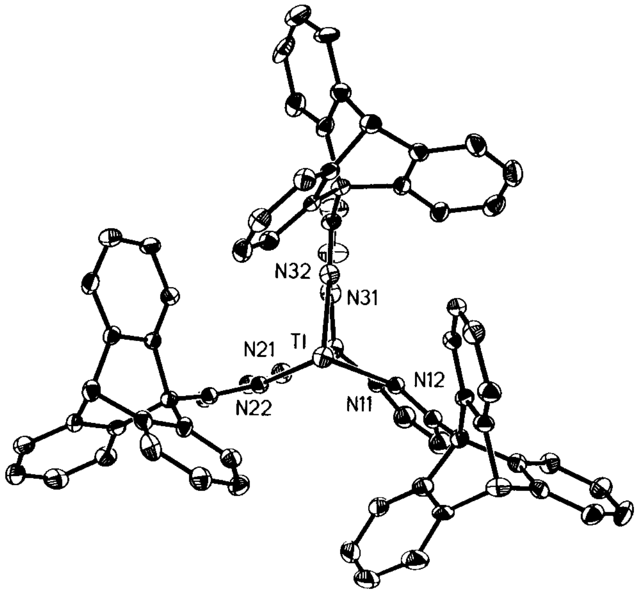


Figure 4. Molecular structure of Tl[Tp^{Trip}] viewed down the 3-fold axis.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Tl[Bp^{Trip}]

Tl−N(12)	2.704(6)	Tl−N(22)	2.696(6)
B−N(11)	1.537(14)	B−N(21)	1.553(12)
N(12)−Tl−N(22)	78.3(2)	N(11)−B−N(21)	110.4(6)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Tl[Tp^{Trip}][a]

Tl−N(12)	2.70(2)	Tl−N(12a)	2.67(2)
Tl−N(22)	2.72(2)	Tl−N(22a)	2.80(2)
Tl−N(32)	2.786(7)	B−N(11)	1.55(2)
B−N(11a)	1.53(2)	B−N(21)	1.53(2)
B−N(21a)	1.55(2)	B−N(31)	1.54(1)
N(12)−Tl−N(22)	80.3(6)	N(12)−Tl−N(32)	73.8(5)
N(22)−Tl−N(32)	73.9(4)	N(12a)−Tl−N(22a)	79.1(7)
N(12a)−Tl−N(32)	78.1(5)	N(22a)−Tl−N(32)	66.4(4)

[a] Site occupanies: N12, N22, N21, and N22 are 0.54; N12a, N22a, N21a, and N22a are 0.46; Tl, B, N31, and N32 are 1.0.

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(13) Dowling, C.; Ghosh, P.; Parkin, G. *Polyhedron*, in press.

(14) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979; p 652.

(15) The sum of the covalent radii of Tl (1.55 Å) and H (0.30 Å) is 1.85 Å, see: Pauling, L. *The Nature of The Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY 1960.

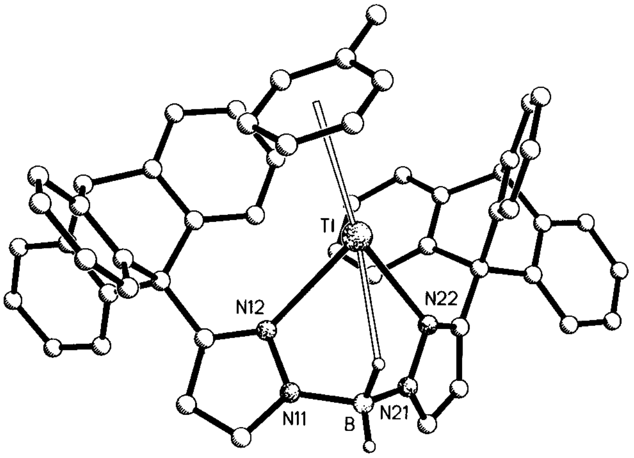

Figure 5. View of the intermolecular interaction between the Tl center of Tl[Bp^{Trip}] and lattice toluene.

Table 3. Tl–Arene Interactions

	d(Tl···centroid), Å	ref
Tl[Bp^{Trip}](C_6H_5Me)	3.22	this work
[($C_6H_3Me_3$)$_6$Tl$_4$][GaBr$_4$]$_4$	2.94, 3.01, 3.03	*a*
[($C_6H_3Me_3$)$_2$Tl(μ_3-AlCl$_4$)]$_2$	2.94, 2.98, 3.01, 3.03	*b*
[($C_6H_3Me_3$)$_2$Tl(μ-OTeF$_5$)]$_2$	2.99, 3.03, 3.08, 3.10	*c*,*d*
[($C_6H_3Me_3$)$_2$Tl][B(OTeF$_5$)$_4$]	2.85, 2.85	*c*,*d*
[(2,6-Pr$^i_2$C$_6$H$_3$(Me$_3$Si)NTl]$_4$	3.11	*e*

[a] Schmidbaur, H.; Bublak, W.; Riede, J.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 414–416. [b] Frank, W.; Korrell, G.; Reiss, G. J. *Z. Anorg. Allg. Chem.* **1995**, *621*, 765–770. [c] Noirot, M. D.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1987**, *26*, 2216–2223. [d] *d*(Tl···centroid) data taken from ref 2. [e] Waezsda, S. D.; Belgardt, T.; Noltemeyer, M.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1351–1352.

range from 3.42 to 3.58 Å (with a Tl···centroid separation of 3.22 Å), compared to a value of 3.66 Å for the sum of the van der Waals radii.[16] Although precedented, complexes with Tl–arene interactions are not very common, with the first structurally-characterized example, [($C_6H_3Me_3$)$_6$Tl$_4$][GaBr$_4$]$_4$, having been reported in 1985.[19] For comparison, the Tl···centroid interactions for other Tl–arene complexes are summarized in Table 3.[20] Thus, it is evident that the Tl–arene interaction in Tl[Bp^{Trip}](toluene) is comparable with, but not as significant as, the corresponding interactions in other derivatives.

Conclusion

In summary, 3-(9-triptycyl)pyrazole has been used to prepare the bis- and tris(pyrazolyl)hydroborato complexes Tl[Bp^{Trip}] and Tl[Tp^{Trip}]. As a result of the nonplanar 3-fold symmetry of the 9-triptycyl group, the [Tp^{Trip}] ligand offers potential in providing an environment in the direct vicinity of a metal center that is less sterically demanding than that created by, for example, the classic tetrahedral enforcer ligand, [Tp$^{Bu^t}$].[2,4] At the same time, however, it is anticipated that the [Tp^{Trip}] ligand will be incapable of forming a six-coordinate sandwich complex [Tp^{Trip}]$_2$M due to the difficulty of meshing the 9-triptycyl groups on adjacent ligands.

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques.[21] Solvents were purified and degassed by standard procedures. ^{1}H and ^{13}C NMR spectra were measured on Varian VXR 200, 300, and 400 and Bruker DMX 500 spectrometers. IR spectra were recorded as KBr pellets on a Perkin-Elmer 1600 FTIR spectrophotometer and are reported in cm^{-1}. Elemental analyses were measured using a Perkin-Elmer 2400 CHN Elemental Analyzer. 3-(9-Triptycyl)pyrazole was prepared as previously reported.[10]

Synthesis of Tl[Bp^{Trip}]. A mixture of 3-(9-triptycyl)pyrazole (3.5 g, 10.9 mmol) and LiBH$_4$ (460 mg, 21.1 mmol)[22] in toluene (40 mL) was heated at 110 °C until evolution of H$_2$ ceased (*ca.* 2 h). The mixture was filtered, and the volatile components were removed under reduced pressure. THF (20 mL) and TlNO$_3$ (3.0 g, 11.3 mmol) were added, and the mixture was heated at 55 °C for 30 min. The mixture was allowed to cool to room temperature and was filtered, and the solvent was removed under reduced pressure. Tl[Bp^{Trip}] was obtained as a white crystalline solid by addition of MeOH to a toluene solution (1.8 g, 39%). ^{1}H NMR (C_6D_6): δ 5.15 (s, 2 H of $H_2B\{C_3N_2H_2[C(C_6H_4)_3C\mathit{H}]\}_2$), 6.37 (t, $^3J_{H-H} = 7$ Hz, 6H of $H_2B\{C_3N_2H_2[C(C_6\mathit{H}_4)_3CH]\}_2$), 6.69 (t, $^3J_{H-H} = 7$ Hz, 6H of $H_2B\{C_3N_2H_2[C(C_6\mathit{H}_4)_3CH]\}_2$), 6.78 (d, $^3J_{H-H} = 2$ Hz, 2H of $H_2B\{C_3N_2\mathit{H}_2[C(C_6H_4)_3CH]\}_2$), 7.13 (d, $^3J_{H-H} = 7$ Hz, 6H of $H_2B\{C_3N_2H_2[C(C_6\mathit{H}_4)_3CH]\}_2$), 7.43 (d, $^3J_{H-H} = 7$ Hz, 6H of $H_2B\{C_3N_2H_2[C(C_6\mathit{H}_4)_3CH]\}_2$), 8.07 (d, $^3J_{H-H} = 2$ Hz, 2H of $H_2B\{C_3N_2\mathit{H}_2[C(C_6H_4)_3CH]\}_2$), not observed [$\mathit{H}_2B\{C_3N_2H_2[C(C_6H_4)_3CH]\}_2$]. ^{13}C NMR (CDCl$_3$): δ 54.6 (d, $^1J_{C-H} = 142$ Hz, 2C of $H_2B\{C_3N_2H_2[C(C_6H_4)_3\mathit{C}H]\}_2$), 56.8 (s, 2C of $H_2B\{C_3N_2H_2[\mathit{C}(C_6H_4)_3CH]\}_2$), 107.1 (dd, $^1J_{C-H} = 175$ Hz, $^2J_{C-H} = 9$ Hz, 2C of $H_2B\{\mathit{C}_3N_2H_2[C(C_6H_4)_3CH]\}_2$), 123.6 (d, $^1J_{C-H} = 159$ Hz, 6C of $H_2B\{C_3N_2H_2[C(\mathit{C}_6H_4)_3CH]\}_2$), 124.1 (d, $^1J_{C-H} = 151$ Hz, 6C of $H_2B\{C_3N_2H_2[C(\mathit{C}_6H_4)_3CH]\}_2$), 125.0 (d, $^1J_{C-H} = 159$ Hz, 6C of $H_2B\{C_3N_2H_2[C(\mathit{C}_6H_4)_3CH]\}_2$), 125.2 (dd, $^1J_{C-H} = 159$ Hz, $^2J_{C-H} = 7$ Hz, 2C of $H_2B\{C_3N_2H_2[C(\mathit{C}_6H_4)_3CH]\}_2$), 137.2 (dd, $^1J_{C-H} = 185$ Hz, $^2J_{C-H} = 6$ Hz, 2C of $H_2B\{\mathit{C}_3N_2H_2[C(C_6H_4)_3CH]\}_2$), 146.1 (s, 6C of $H_2B\{C_3N_2H_2[C(\mathit{C}_6H_4)_3CH]\}_2$), 146.7 (s, 6C of $H_2B\{C_3N_2H_2[C(\mathit{C}_6H_4)_3CH\}_2$), 148.8 (s, 2C of $H_2B\{\mathit{C}_3N_2H_2[C(C_6H_4)_3CH\}_2$). IR (cm^{-1}): 2405–2247 (ν_{B-H}). Anal. Calcd for Tl[Bp^{Trip}]·toluene: C, 67.1; H, 4.3; N, 5.9. Found: C, 67.2; H, 4.3; N, 5.8.

Synthesis of Tl[Tp^{Trip}]. A mixture of 3-(9-triptycyl)pyrazole (5 g, 15.6 mmol) and LiBH$_4$ (115 mg, 5.3 mmol) in toluene (50 mL) was heated at 110 °C until H$_2$ evolution ceased (*ca.* 2 h). The volatile components were removed under reduced pressure, and THF (30 mL) and TlNO$_3$ (5 g, 18.8 mmol) were added. The mixture was heated at 55 °C for 30 min and filtered. The solvent was removed under reduced pressure, and the residue so obtained (which essentially consists of a mixture of Tl[Bp^{Trip}] and 3-(9-triptycyl)pyrazole, with small quantities of Tl[Tp^{Trip}]) was heated at *ca.* 170 °C under vacuum for 3 h. The resulting residue was crystallized from hot toluene (with methanol being added to complete the crystallization) giving Tl[Tp^{Trip}] as a white solid (3.6 g, 59% yield). Crystals suitable for X-ray diffraction analysis were obtained by vapor diffusion of Et$_2$O into a solution of Tl[Tp^{Trip}] in CH$_2$Cl$_2$. ^{1}H NMR (C_6D_6): δ 5.09 (s, 3H of $HB\{C_3N_2H_2[C(C_6H_4)_3C\mathit{H}]\}_3$), 6.07 (t, $^3J_{H-H} = 7$ Hz, 9H of $HB\{C_3N_2H_2[C(C_6\mathit{H}_4)_3CH]\}_3$), 6.57 (t, $^3J_{H-H} = 7$ Hz, 9H of $HB\{C_3N_2H_2[C(C_6\mathit{H}_4)_3CH]\}_3$), 6.85 (br, 3H of $HB\{C_3N_2\mathit{H}_2[C(C_6H_4)_3CH]\}_3$), 7.06 (d, $^3J_{H-H} = 7$ Hz, 9H of $HB\{C_3N_2H_2[C(C_6\mathit{H}_4)_3CH]\}_3$), 7.52 (br, 9H of $HB\{C_3N_2H_2[C(C_6\mathit{H}_4)_3CH]\}_3$), 8.32 (d, $^3J_{H-H} = 2.0$ Hz, 3H of $HB\{C_3N_2\mathit{H}_2[C(C_6H_4)_3CH]\}_3$), not observed [$\mathit{H}B\{C_3N_2H_2[C(C_6H_4)_3CH]\}_3$]. ^{13}C NMR (CDCl$_3$): δ 54.6 (d, $^1J_{C-H} = 140$ Hz, 3C of $HB\{C_3N_2H_2[C(C_6H_4)_3\mathit{C}H]\}_3$), 57.0 (s, 3C of $HB\{C_3N_2H_2[\mathit{C}(C_6H_4)_3CH]\}_3$), 108.2 (d, $^1J_{C-H} = 172$ Hz, 3C of $HB\{\mathit{C}_3N_2H_2[C(C_6H_4)_3CH]\}_3$), 123.3 (d, $^1J_{C-H} = 156$ Hz, 9C of $HB\{C_3N_2H_2[C(\mathit{C}_6H_4)_3CH]\}_3$), 123.7 (d, $^1J_{C-H} = 158$ Hz, 9C of HB-

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(16) The van der Waals radii of H, C, N, and Tl are 1.20, 1.70, 1.55, and 1.96 Å, respectively, see: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.

(17) The The Tl···H separations in Tl[Bp$^{Bu^t,Me}$] and Tl[Bp$^{Bu^t,Pr^i}$] are 2.44 and 2.26 Å, respectively. See ref 13.

(18) Although a shorter Tl···B separation for Tl[Bp^{Trip}] is consistent with a [Tl···H–B] interaction, it should be recognized that the greater Tl···B separation for Tl[Tp^{Trip}] may merely be a consequence of strain introduced by incorporation of a third pyrazolyl group.

(19) Schmidbaur, H.; Bublak, W.; Riede, J.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 414–416.

(20) For the structure of a [2.2]paracyclophane derivative (p-$C_6H_4CH_2CH_2$)$_2$Tl(GaCl$_4$), see: Schmidbaur, H.; Bublak, W.; Huber, B.; Hofmann, J.; Müller, G. *Chem. Ber.* **1989**, *122*, 265–270.

(21) (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. *ACS Symp. Ser.* **1987**, *357*, 6–23. (b) Burger, B. J.; Bercaw, J. E. *ACS Symp. Ser.* **1987**, *357*, 79–97.

(22) Excess LiBH$_4$ is used since these conditions minimize formation of the tris(pyrazolyl)hydroborato derivative Li[Tp^{Trip}].

Table 4. Crystal and Intensity Collection Data for Tl[Bp$^{\mathrm{Trip}}$] and Tl[Tp$^{\mathrm{Trip}}$]

	Tl[Bp$^{\mathrm{Trip}}$]·PhMe	Tl[Tp$^{\mathrm{Trip}}$]·Et_2O
formula	$C_{53}H_{40}N_4BTl$	$C_{73}H_{56}BN_6OTl$
fw	948.1	1248.2
lattice	triclinic	monoclinic
cell constants		
a, Å	11.677(2)	18.012(3)
b, Å	12.420(2)	16.036(5)
c, Å	15.420(3)	20.917(3)
α, deg	78.35(2)	90.0
β, deg	70.78(2)	108.92(1)
γ, deg	89.18(2)	90.0
V, Å^3	2065(1)	5715(2)
Z	2	4
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
space group	$P\bar{1}$ (No. 2)	$P21/c$ (No. 14)
ρ (calcd), g cm^{-3}	1.525	1.451
μ (Mo Kα), cm^{-1}	39.54	28.79
T, °C	23	23
R^a	0.0442	0.0484
$R_w{}^b$ or w$R_2{}^c$	0.0505	0.0966

[a] $R = \{\sum||F_o| - |F_c||\}/\sum|F_o|$ for $F_o > 4\sigma(F_o)$. [b] $R_w = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|$ for $F_o > 4\sigma(F_o)$. [c] $wR_2 = [\sum[w(F_o{}^2 - F_c{}^2)^2/\sum[w(F_o{}^2)^2]^{1/2}$ for $I > 2\sigma(I)$.

$\{C_3N_2H_2[C(C_6H_4)_3CH]\}_3$), 124.7 (d, $^1J_{C-H} = 167$ Hz, 9C of HB$\{C_3N_2H_2[C(C_6H_4)_3CH]\}_3$), 125.1 (d, $^1J_{C-H} = 159$ Hz, 9C of HB$\{C_3N_2H_2[C(C_6H_4)_3CH]\}_3$), 137.8 (d, $^1J_{C-H} = 186$ Hz, 3C of HB$\{C_3N_2H_2[C(C_6H_4)_3CH]\}_3$), 146.1 (s, 9C of HB$\{C_3N_2H_2[C(C_6H_4)_3CH]\}_3$), 146.6 (s, 9C of HB$\{C_3N_2H_2[C(C_6H_4)_3CH]\}_3$), 150.0 (s, 3C of HB$\{C_3N_2H_2[C(C_6H_4)_3CH]\}_3$). IR (cm^{-1}): 2430 ($\nu_{B-H}$). Anal. Calcd for Tl[Tp$^{\mathrm{Trip}}$]·toluene: C, 72.1; H, 4.3; N, 6.6. Found: C, 72.2; H, 4.3; N, 6.6.

X-ray Structure Determinations. Crystal data, data collection, and refinement parameters for Tl[Bp$^{\mathrm{Trip}}$] and Tl[Tp$^{\mathrm{Trip}}$] are summarized in Table 4. A single crystal of Tl[Bp$^{\mathrm{Trip}}$]·PhMe grown from toluene was mounted in a glass capillary and placed on a Nicolet R3m diffractometer. The unit cell was determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Intensity data were collected using graphite-monochromated Mo Kα X-radiation ($\lambda = 0.710\ 73$ Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects. The structure was solved using direct methods and standard difference map techniques and was refined by full-matrix least-squares procedures on F using SHELXTL PC. Systematic absences 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). Hydrogen atoms on carbon were included in calculated positions.

A single crystal of Tl[Tp$^{\mathrm{Trip}}$]·Et_2O grown by vapor diffusion of Et_2O into a solution of Tl[Tp$^{\mathrm{Trip}}$] in CH_2Cl_2 was mounted in a glass capillary and placed on a Siemens P4 diffractometer. The unit cell was determined by the automatic indexing of centered reflections and confirmed by examination of the axial photographs. Intensity data were collected using graphite-monochromated Mo Kα X-radiation ($\lambda = 0.710\ 73$ Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects. The structure was solved using direct methods and standard difference map techniques and was refined by full-matrix least-squares procedures on F^2 using SHELXTL 93 (version 5.0). Systematic absences were consistent uniquely with $P2_1/c$ (No. 14). Two of the pyrazolyl groups (but not their triptycyl substituents) were rotationally disordered over two orientations and were modeled accordingly. A badly disordered Et_2O molecule of crystallization was located and modeled with two orientations. Hydrogen atoms on carbon were included in calculated positions.

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Supporting Information Available: Tables of crystal and intensity collection data, atomic coordinates, bond lengths, bond angles, anisotropic displacement coordinates, and H-atom coordinates and ORTEP diagrams for Tl[Bp$^{\mathrm{Trip}}$] and Tl[Tp$^{\mathrm{Trip}}$] (23 pages). Ordering information is given on any current masthead page.

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