80. High-Yield Syntheses of Sodium, Potassium, and Thallium Hydrotris[3,5-bis(trifluoromethyl)pyrazolyl]borates and the X-Ray Crystal Structure of {Hydrotris[3,5-bis(trifluoromethyl)pyrazolyl]borato}thallium(I)

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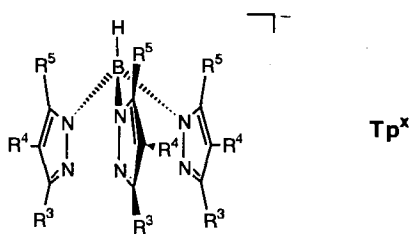
An improved synthesis of 3,5-bis(trifluoromethyl)pyrazole (**1**) is described. This compound was used for the high-yield syntheses of the tris(pyrazolyl)borates Na[HB(3,5-$(CF_3)_2$-pz)$_3$] (**2a**) and the corresponding potassium salt, **2b**, starting from **1** and $NaBH_4$ and KBH_4, respectively. A convenient route to the corresponding thallium(I) salt, **2c**, using thallium(I) acetate and either **2a** or **2b** in $CHCl_3$, is also described. The sodium (**3a**), potasium (**3b**), and thallium (**3c**) salts of bis(pyrazolyl)borate $[H_2B(3,5\text{-}(CF_3)_2\text{-pz})_2]^-$ were also prepared. The above pyrazolylborates were characterized by ^{1}H-, ^{13}C-, ^{19}F-, and ^{11}B-NMR spectroscopy. The X-ray crystal structure of the thallium derivative **2c** was determined. The compound crystallizes in the monoclinic space group $P2_1/m$ with $a = 8.248(9)$ Å, $b = 15.034(12)$ Å, $c = 9.243(8)$ Å, $\beta = 100.10(7)°$, $Z = 2$. The Tl-atom adopts a pyramidal geometry with respect to the three N-atoms. However, two Tl–N distances (2.725(7) Å) are longer than the third (2.675(10) Å).

Introduction. – The poly(pyrazolyl)borates are the most studied among the pyrazole-derived chelating agents. In particular, the donor properties of pyrazolylborate anions $[H_{4-n}B(pz)_n]^-$ (pz = pyrazole, $n = 2$–4), have been extensively investigated, as their steric and electronic properties can easily be modified by changing the number of pyrazolyl rings and the substituents thereon or at the B-center [1].

The tris(pyrazolyl)borates, Tp^x [1a], are the most widely used ligands of this family, as they form a wide range of complexes with metal ions throughout the Periodic Table [1]. Substituent changes on the C-centers of the pyrazolyl groups have strong effects on the nuclearity, geometry, spectroscopic properties, and reactivity of complexes containing those ligands.



Tp^x

Particularly reactive species important in organometallic [2], inorganic [3], and bioinorganic chemistry [4] have been produced using sterically hindered ligands derived from pyrazoles containing simple alkyl or aryl substituents at C(3). The incorporation of substituents at C(3) allows the control of the steric environment and thus the shapes of potential active sites on metal complexes containing such ligands, although they can also exert electronic effects.

The influence of substituents placed at C(4) is mainly electronic. In some cases, the tendency of the complexes to give crystalline materials is improved by substituting the H-atom at C(4) by Br [5].

Substituents at C(5) of a pyrazole ring, particularly in the tris(pyrazolyl)borates, exert a protecting function on the B–H groups against attack by electrophiles. Thus, while ligands with R=H at C(5) are especially sensitive towards hydrolysis, the presence of bulky groups at C(5) reduce their sensitivity towards attack by H_2O. This hydrolytic process has recently been documented by the X-ray structure study of a partially hydrolyzed Fe(pyrazolyl) borate [6].

Tris(pyrazolyl)borates have been extensively used in this laboratory for the preparation of Rh^{I} [7] and Rh^{III} complexes [8], the latter being the precursors for polyhydrides such as $[RhH_2(H_2)\{HB(3,5\text{-}(CH_3)_2\text{-}pz)_3\}]$ [9]. The coordination of dihydrogen to Rh^{III} is attributed to the low electron density at the metal center and to the low *trans*-influence of the tris(pyrazolyl)borates. This is supported by the observation that a reduction of electron density on the pyrazole ring, resulting from the replacement of one CH_3 by a CF_3 group at C(3) of each ring (*i.e.*, in $[RhH_2(H_2)\{HB(3\text{-}CF_3\text{-}5\text{-}CH_3\text{-}pz)_3\}]$, increases the stability of the coordinated H_2 molecule [10]. Therefore, it is particularly interesting to synthesize the corresponding dihydrogen complexes with a tris(pyrazolyl)borate ligand with six strongly electron-withdrawing substituents, *i.e.*, $[HB(3,5\text{-}(CF_3)_2\text{-}pz)_3]^-$ (**2**).

The use of salts of **2** has been mentioned in the literature [11], but no details about their preparation have been reported. However, a low-yield synthesis of $Tp^{CF_3,CF_3}K$ appeared in print [12] after the work described here had been completed.

The preparation of the tris(pyrazolyl)borate anion **2** uses 3,5-bis(trifluoromethyl)-pyrazole (**1**). This compound was obtained *1*) by reacting 1,1,1,5,5,5-hexafluoropentane-2,4-dione with hydrazine hydrate under various conditions [13–15] and *2*) by dipolar cycloaddition of 2-diazo-1,1,1-trifluoroethane with 3,3,3-trifluoropropyne [16]. The former reaction was reinvestigated by *Threadgill et al.* [17] and an improved procedure of the synthesis of **1** is described here.

This paper also reports *1*) the synthesis and characterization of the sodium and potassium salts of the hydrotris[3,5-bis(trifluoromethyl)pyrazol-1-yl]borate anion, **2a** and **2b**, respectively, obtained by reacting either $NaBH_4$ or KBH_4 with an excess of 3,5-bis(trifluoromethyl)pyrazole (**1**), *2*) the preparation of the corresponding Tl^{I} salt, **2c**, using thallium(I) acetate and either **2a** or **2b**, and *3*) the reaction conditions for the synthesis of the corresponding bis(pyrazolyl)borates, **3**.

Tl^{I} salts of the tris(pyrazolyl)borates are increasingly used for the preparation of their transition-metal complexes because of good hydrolytic stability. Tl^{I} complexes are also interesting because their coordination numbers range from 2 to 12 [18] and may exhibit a stereoactive lone electron pair. It is found [19] that a Tl^{I} with a stereoactive electron pair will form short bonds and have a low coordination number and a pronounced asymmetry in the coordination polyhedron. 'Ionic' Tl^{I}, however, will show longer metal–donor atom

distances and have coordination numbers greater than 6. Thus, the structural features of the thallium salt of the anion **2** were of interest, and the X-ray crystal structure analysis of $Tp^{CF_3,CF_3}Tl$, **2c**, was carried out.

Experimental. – *General.* All operations involving air- and moisture-sensitive materials, *i.e.*, the pyrazole and alkali-metal salts of the tris(pyrazolyl)borate, were carried out under Ar using standard *Schlenk* techniques. All solvents and reagents were of '*purum*' or '*puriss*' grade, and the solvents used for the synthesis of the tris(pyrazolyl)borates were of '*puriss. p.a. absolute*' quality. The solvents, hexafluoroacetylacetate (1,1,1,5,5,5-hexafluoropentane-2,4-dione), CaH_2, KBH_4, $NaBH_4$, and thallium(I) acetate were purchased from *Fluka* and were used without further purification. Hydrazine hydrate was obtained from *Siegfried Handel*, Zofingen, Switzerland. Although 3,5-bis(trifluoromethyl)pyrazole is now available from *Aldrich*, for this study it was prepared as described below.

The ^1H-, ^{13}C-, and ^{19}F NMR spectra were recorded on a *Bruker AC 200* spectrometer operating at 200.13, 62.9, and 188.31 MHz for ^1H, ^{13}C, and ^{19}F, respectively. The ^{11}B-NMR spectra were recorded at 80.25 MHz on a *Bruker AC 250* spectrometer. The chemical shift scales are relative to internal TMS (^1H and ^{13}C), external $BF_3 \cdot Et_2O$ (^{11}B), and $CFCl_3$ (^{19}F). The IR spectra were recorded as KBr pellets on a *Perkin Elmer* model *833* spectrophotometer. The C, H, N, and F microanalyses were performed by the Microanalytical Laboratory of the ETH-Zürich.

3,5-Bis(trifluoromethyl)pyrazole (3,5-$(CF_3)_2$-pz, **1**). Hydrazine hydrate (10 ml, 205 mmol) was slowly added to 450 ml of EtOH. To this soln., 1,1,1,5,5,5-hexafluoropentane-2,4-dione (25 ml, 178 mmol) was slowly added through an dropping funnel and the mixture refluxed for 19 h. After cooling to r.t., EtOH was distilled off. The remaining yellow oil was transferred to a 25-ml, round-bottomed distillation flask connected to a *Vigreux* column pointing downward through a 120° bent glass adapter. A 250-ml *Schlenk* tube, cooled in an ice bath, was connected to the other end of the *Vigreux* column through a 60° bent adapter.

The oil bath was heated to 180° and the colorless product distilled off. It solidified on the walls of the bent adapter and was periodically removed with a heat gun. Most of the product then collected in the *Vigreux* column. This was subsequently warmed with the heat gun and the liquefied product condensed in the cooled *Schlenk* tube. Although the product is very volatile, it proved to be very difficult to remove it all from the round-bottomed flask by distillation under atmospheric pressure. Therefore, to increase the yield, a low vacuum was applied to the system through the *Schlenk* tube for less than 1 s, just long enough to allow the volatile product to solidify in the *Vigreux* column. If distillation is performed under reduced pressure for a longer time, the yield dramatically decreases, as the product does not condense in the cold trap. The distillation was stopped, when a solid orange material remained in the distillation flask. The glassware was thoroughly washed with CH_2Cl_2 to remove all 3,5-bis(trifluoromethyl)pyrazole, and the clear colorless soln. was dried overnight (Na_2SO_4), filtered, and the solvent removed by rotary evaporation. The colorless, crystalline product with a distinctive odor was stored at r.t. under Ar. Yield: 22.35 g (63%). ^1H-NMR ($CDCl_3(CD_3CN)$): 6.92 (7.12) (*s*, H–C(4)); 10.9–12.6 (br., NH). ^{19}F-NMR ($CDCl_3(CD_3CN)$): −62.1 (−61.7) (*s*, CF_3). ^{13}C-NMR (CD_3CN): 139.4 (*q*, $^2J(F,C) = 40$ CCF_3); 121.3 (*q*, $^1J(F,C) = 268$, CF_3); 105.4 (*s*, $^3J(F,C) = 2.2$, C(4)).

{Hydrotris[3,5-bis(trifluoromethyl)pyrazol-1-yl]borato}sodium (Na[HB(3,5-$(CF_3)_2$-pz)$_3$], $Tp^{CF_3,CF_3}Na$, **2a**). The anh. pyrazole required for this step was obtained as follows: 9.81 g (48.1 mmol) **1** was dissolved in 145 ml of benzene in a 250-ml round-bottomed flask. The soln. was refluxed under N_2 for 44 h and the distillate passed through a *Soxhlet* extractor whose timble was filled with CaH_2. Then, benzene was distilled off until a volume of 5–10 ml remained, and the residual yellow soln. of the anh. pyrazole used immediately. Its reaction with $NaBH_4$ was carried out in the same flask, equipped with a reflux condenser connected to a bubbler. The volume of H_2 developed was collected in a 1000-ml measuring cylinder filled with water, its opening being dipped into a plastic container also filled with water. The above soln. was cooled with an ice bath and, when solidified, 360 mg (9.51 mmol) of solid $NaBH_4$ were added. The stirred mixture was heated to 150° and kept at this temp. Temp. and H_2 volume were monitored every 5 min. After 80 min, the rate of H_2 evolution had apparently stopped. As it became clear later that at this stage the reaction was incomplete, the soln. was heated to 215° and kept at this temp. The 3,5-bis(trifluoromethyl)pyrazole, which sometimes solidified on the walls of the condenser, was transferred back into the reaction flask by warming the latter with a heat gun. During this period, the H_2 evolution occurred at a rate of *ca.* 2 ml every 10 min, the total amount being already more than 100% of the calculated volume (640 ml). However, the heating had to be continued for 5 h to insure the complete transformation of the bis(pyrazolyl)borate intermediate **3a** into the product **2a**. After this time, typically 130–140% of the calculated volume of gas was collected. The mixture was then cooled to r.t., the solvent removed on a rotary evaporator, the residual solid dried *in vacuo*, and then dissolved in 15 ml CH_2Cl_2. The soln. was filtered through *Celite*, the solvent removed on a rotary

evaporator, and the residual yellow oil was first dried under high vacuum for 30 h and then heated at 80° *in vacuo* for 1 h to remove the excess of pyrazole. After cooling to r.t., the product was dissolved in 10 ml MeCN, the soln. filtered through *Celite*, and the solvent removed on a rotary evaporator under reduced pressure at 60°. The slightly yellow solid was dried under high vacuum for 12 h and stored under Ar. Yield: 4.12 g (67%). IR: 2604 (B–H, str.). ^{1}H-NMR (CD_3CN): 7.04 (*s*, H–C(4)). ^{19}F-NMR (CD_3CN): −59.6, −61.5 (CF_3). ^{13}C-NMR (CD_3CN): 142.8 (*q*, ^2J(F,C) = 38, CCF_3); 138.3 (*q*, ^2J(F,C) = 39, CCF_3); 122.4 (*q*, ^1J(F,C) = 267, CF_3); 121.2 (*q*, ^1J(F,C) = 268, CF_3); 106.8 (C(4)). ^{11}B-NMR (CD_3CN): −3.9 (*d*, ^1J(B,H) = 116). Anal. calc. for $C_{15}H_4N_6BF_{18}Na \cdot 1.5\ CH_3CN$: C 29.8, H 1.2, N 14.9, F 48.5; found: C 29.9, H 1.2, N 14.5, F 48.8.

{Hydrotris[3,5-bis(trifluoromethyl)pyrazol-1-yl]borato}potassium ($K[HB(3,5\text{-}(CF_3)_2\text{-}pz)_3]$, $Tp^{CF_3,CF_3}K$, **2b**). This compound was prepared as described above using KBH_4 instead of $NaBH_4$. However, the reaction, although performed at 180° for 3 h, yielded a mixture of corresponding tris- and bis(pyrazolyl)borates, **2b** and **3b**, respectively, the latter being the major product. These products were not separated and the mixture used for the preparation of the corresponding Tl^I complexes. ^{1}H-NMR (CD_3CN): 7.05 (*s*, H–C(4)). ^{19}F-NMR (CD_3CN): −59.7, −61.6 (CF_3).

{Hydrotris[3,5-bis(trifluoromethyl)pyrazol-1-yl]borato}thallium(I) ($Tl[HB(3,5\text{-}(CF_3)_2\text{-}pz)_3]$, $Tp^{CF_3,CF_3}Tl$, **2c**). Compound **2a** (4.38 g, 6.80 mmol) was dissolved in 100 ml of $CHCl_3$ and 1.79 g (6.80 mmol) of solid thallium(I) acetate was added. The suspension was refluxed for 45 min. Upon cooling to r.t., a colorless precipitate formed. This was filtered off through a glass frit and proved to be NaOAc. The soln. was evaporated to dryness and 20 ml of CH_2Cl_2 added to the yellowish residue. The yellow soln., which contained some product as a whitish residue, was stored at −2° for 12 h. The solid was then rapidly filtered at low temp., as it is somewhat soluble in CH_2Cl_2 and then immediately dissolved in $CHCl_3$. The soln. was evaporated to dryness under reduced pressure and the white crystalline product dried *in vacuo*. Yield: 5.61 g (90%). IR: 2627 (B–H, str.). ^{1}H-NMR (CD_3CN): 7.16 (*s*, H–C(4)). ^{19}F-NMR (CD_3CN): −59.6, −60.8 (CF_3). ^{13}C-NMR (CD_3CN): 143.4 (*q*, ^2J(F,C) = 38, CCF_3); 139.2 (*q*, ^2J(F,C) = 40, CCF_3); 121.9 (*q*, ^1J(F,C) = 268, CF_3); 120.5 (*q*, ^1J(F,C) = 269, CF_3); 107.2 (C(4)). Anal. calc. for $C_{15}H_4N_6BF_{18}Tl$: C 21.83, H 0.49, N 10.18, F 41.43; found: C 22.08, H 0.59, N 10.42, F 41.68.

{Dihydrobis[3,5-bis(trifluoromethyl)pyrazol-1-yl]borato}sodium ($Na[H_2B(3,5\text{-}(CF_3)_2\text{-}pz)_2]$, **3a**). The reaction was carried out as described for **2a**, using a pyrazole $NaBH_4$ ratio of 4:1. A temp. of 180°, and the reaction time of 2 h were used. The mixture was worked up as described above. However, in this case, extraction of the final product **3a** with MeCN left a large amount of a white precipitate, which was filtered off. This precipitate did not contain the product and was not investigated further. IR: 2497, 2449 (B–H, str.). ^{1}H-NMR (CD_3CN): 6.92 (*s*, H–C(4)). ^{19}F-NMR (CD_3CN): −58.9, −61.4 (CF_3). ^{13}C-NMR (CD_3CN): 142.0 (*q*, ^2J(F,C) = 37, CCF_3); 138.1 (*q*, ^2J(F,C) = 39, CCF_3); 122.8 (*q*, ^1J(F,C) = 267, CF_3); 121.6 (*q*, ^1J(F,C) = 268, CF_3); 105.6 (C(4)). ^{11}B-NMR (CD_3CN): −8.2 (*t*, poorly resolved). Anal. calc. for $C_{10}H_4N_4BF_{12}Na$: C 27.2, H 0.9, N 12.7; found: C 27.9, H 1.2, N 13.0.

{Dihydrobis[3,5-bis(trifluoromethyl)pyrazol-1-yl]borato}potassium ($K[H_2B(3,5\text{-}(CF_3)_2\text{-}pz)_2]$, **3b**). It was obtained as side product during the attempted synthesis of **2b** (see above). No attempts were made to obtain it in pure form. It was only characterized spectroscopically. ^{1}H-NMR (CD_3CN): 6.90 (*s*, H–C(4)). ^{19}F-NMR (CD_3CN): −58.9, −61.3 (CF_3).

{Dihydrobis[3,5-bis(trifluoromethyl)pyrazol-1-yl]borato}thallium(I) ($Tl[H_2B(3,5\text{-}(CF_3)_2\text{-}pz)_2]$, **3c**). It was obtained, together with **2c**, when a mixture of **2a** and **3a** was used. No attempts were made to obtain it in pure form and was only characterized spectroscopically. ^{1}H-NMR (CD_3CN): 6.99 (*s*, H–C(4)). ^{19}F-NMR (CD_3CN): −58.9, −61.1 (CF_3).

X-Ray Crystallography. A colorless needle of **2c**, of size 0.3 × 0.3 × 0.5 mm, obtained from an MeCN soln., which was held at −2° overnight, was used for the structure determination. Details of the X-ray data collection are as follows: $C_{15}H_4BF_{18}N_6Tl$, M = 825.4, monoclinic, space group $P2_1/m$, a = 8.248(9), b = 15.304(12), c = 9.243(8) Å, β = 100.10(7)°, V = 1149(2) Å^3, Z = 2, μ = 7.196 mm^{-1}, T = 293 K, $F(000)$ = 768, D_c = 2.387 Mgm^{-3}; *Picker-STOE* diffractometer, graphite crystal monochromated MoK_α radiation (0.71073 Å) and ω-scan mode. Accurate unit-cell parameters were obtained by least-square fits of the 2Θ values of the high order reflections. A total of 1124 reflections ($3.0° < 2\Theta < 40.0°$) were collected, of which 1118 were independent, with index ranges $-7 \le h \le 7$, $0 \le k \le 14$ and $0 \le l \le 8$. These gave 1066 observed ($F > 4.0\sigma(F)$) reflections. No absorption correction was applied.

The structure was solved by *Patterson* [20] and refined by full-matrix least-squares (204 parameters, the function minimized was $[\Sigma w(F_o\text{–}F_c)^2]$) methods, with anisotropic thermal ellipsoids for all non-H-atoms. Extinction corrections was deemed to be unnecessary. The H-atoms were introduced into the calculated positions with a riding model with fixed isotropic U. The final values R (observed data) = 5.69, R_w = 6.81, GOF = 1.15 for 204

variables, with weighting scheme $w^{-1} = \sigma^2(F) + 0.0040\ (F)^2$ were obtained. Maximum and minimum peaks were 3.32 (located on Tl) and -2.09 e Å^{-3}; largest and mean $\Delta/\sigma = 0.394$ and 0.029. The final coordinates and U_{eq} values and more details of the structure determination are available from the authors upon request.

Results and Discussion. – 1. *Synthesis of 3,5-Bis(trifluoromethyl)pyrazole* (**1**). The syntheses of **1**, reported by *Claire et al.* [15] and by *Threadgill et al.* [17], differ only in the reaction time, 5 *vs.* 18 h, and in the procedure used to isolate the product, *i.e.*, a crystallization from petroleum ether in one case and a distillation in the other. As the yield reported by *Claire et al.* is 77%, while that of *Threadgill et al.* is 25%, in this study attempts were made to prepare **1** using the procedure described by *Claire et al.* However, only mixtures of partial condensation products were obtained. These proved to be the diastereoisomeric pyrazolidines 3,5-dihydroxy-3,5-(trifluoromethyl)pyrazolidine, described by *Elguero* and *Yranzo* [21]. Usually, intermediates of this type are so unstable that they can only be characterized by NMR using special stop-flow techniques [22]. Thus, the electron-attracting CF_3 groups must hinder the heterolytic removal of the OH group [23] and, consequently, the carbinolamines are sufficiently stable to be isolated. However, pyrazole **1** was formed, when these partial condensation products were dehydrated by melting the reaction mixture.

Therefore, **1** was prepared as described by *Threadgill et al.* [17]. However, it was noted during this work that the purity of the product was generally higher, when the reaction residue was distilled, although the yield strongly depends on the distillation procedure. Despite the extraordinary volatility of **1**, it was impossible to distill it off completely at atmospheric pressure, even when the mixture was heated up to 200°. On the other hand, when the distillation was performed under reduced pressure, most of the product was lost, even when a cold trap is used. However, using the distillation apparatus and the conditions described in the *Experimental*, yields up to 70% were obtained.

2. *Syntheses of the Sodium and Potassium Salts,* **2a** *and* **2b**, *Respectively, of the Hydrotris[3,5-bis(trifluoromethyl)pyrazol-1-yl]borate Anion* **2**. Anion **2** was prepared essentially as described in the literature for related tris(pyrazolyl)borates [1] [24], *i.e.*, either by heating a borohydride with an excess of the appropriate molten pyrazole or by refluxing the borohydride with an excess of pyrazole in kerosene [8a], *N*,*N*-dimethylacetamide, or anisole [25]. The reaction was monitored by measuring the volume of H_2 evolved.

In the case of **1**, the reaction of $NaBH_4$ with an excess of the molten pyrazole did not give **2a**. This could be due either to the loss of the volatile pyrazole **1** during the reaction or the presence of water H-bonded to **1**, as pyrazoles containing CF_3 groups are hygroscopic. Thus, **1** was dried chemically before use by refluxing it in benzene under Ar. However, benzene must not be completely removed prior to the addition of $NaBH_4$ to the suspension of **1**.

The critical step proved to be the formation of **2a**. The bis(pyrazolyl)borate **3a** was the only product, when the reaction was stopped after the calculated volume of H_2 had evolved. Increasing the reaction time 3–5 h still gave mixtures of **2a** and **3a** (or **2b** and **3b**, when KBH_4 was used).

The best method to obtain **2a** was to heat the reaction mixture to 150°, until the rate of H_2 evolution was almost zero (*ca.* 80 min) and then heat the solution to 215° and keep it at this temperature for another 5 h. Although the H_2 evolution during this period was less than 2 ml every 10 min, the reaction had to be continued to complete the transformation

of **3a** into **2a**. After this time, typically 130–140% of the calculated volume of gas was apparently collected and the reaction mixture contained only **3a**, which could be isolated in yields up to 70%.

Although monitoring the volume of H_2 with a wet-test meter generally give a reliable estimates of the reaction course, it is possible that in this case the pyrazole, dried as described above, still contained H_2O which reacted with BH_4^- forming additional H_2. Another source of error could be the volume change of the gas in the apparatus with temperature during the reaction; due to the small scale of the reaction and the relatively small H_2 volume evolved, this cannot be neglected.

3. *Synthesis of {Hydrotris[3,5-bis(trifluoromethyl)pyrazol-1-yl]borato}thallium* (**2c**). In addition to the sodium and potassium salts, the thallium derivatives are also useful reagents for the synthesis of tris(pyrazolyl)borate complexes, the latter having the advantages of good solubility in hydrocarbon solvents and of being more resistant towards hydrolysis. While the known thallium tris(pyrazolyl)borates are usually synthesized from the corresponding sodium or potassium salts by addition of $TlNO_3$ and extraction into the organic layer from a THF/H_2O solution [5] [26–29], another method was employed here, using organic solvents to avoid the possible loss of material due to hydrolysis. Compound **2a** was dissolved in $CHCl_3$, a stochiometric amount of thallium(I) acetate added, the mixture refluxed for 45 min and cooled to room temperature. The sodium acetate precipitate was filtered off, leaving **2c** in solution.

Interestingly, this procedure provided a simple method to separate mixtures of **2a** and **3a** (or **2b** and **3b**) as the corresponding thallium(I) salts **2c** and **3c**, as the former is soluble in CH_2Cl_2, and the latter is not. The thallium salt **2c** is air-stable, and easy to handle and store, whereas the sodium salt **2a**, although not extremely sensitive towards air and moisture, should be stored under N_2.

The Tp^xTl compounds often show ^{205}Tl coupling in the ^1H- and ^{13}C-NMR spectra. Thus, in $Tp^{tbu}Tl$ these couplings were attributed to the covalent character of the Tl–N bonds in this complex [26]. Furthermore, a significant broadening of the resonances in $Tp^{pTol}Tl$ was ascribed to unresolved coupling with ^{205}Tl [27]. However, no splittings due to this isotope were reported for $Tp^{(4tBuPh)2}Tl$ [28] and Tp^aTl (Tp^a = hydrotris(2*H*-benz[*g*]-4,5-dihydroindazol-2-yl)borate) [29].

The ^1H- and ^{13}C-NMR spectra of complex **2c** did not show ^{205}Tl couplings, these resonances were sharp. This may be in agreement with the expectation that the Tl–N bonds in **2c** are predominantly ionic, as the Tl–N bond lengths (2.675(10) to 2.725(7) Å) are significantly longer than the sum of the covalent radii of these two atoms (2.31 Å) [30] (see later).

4. *The X-Ray Crystal Structure of* **2c**. The structure of **2c** was determined by X-ray diffraction, and an ORTEP view of the molecule is shown in the *Figure*. The coordination geometry around the Tl-atom is similar to that found in the related complexes $Tp^{tBu}Tl$ [26], $Tp^{pTol}Tl$ [27], $Tp^{(4tBuPh)2}Tl$ [28], and Tp^aTl [29], the Tl-atom adopting a pyramidal geometry with respect to the three bound N-donors N(1a), N(1aa), and N(1b). The molecule contains a mirror plane, the two symmetry-related Tl–N distances Tl(1)–N(1a) (2.724(7) Å and Tl–N(1aa) (2.725(7) Å) being significantly shorter than the third Tl(1)–N(1b) (2.675(10) Å). Furthermore, these bond lengths are longer than those in the related complexes, the average Tl–N bond lengths there being 2.56–2.59 Å, although in the case of $Tp^{(4tBuPh)2}Tl$ one Tl–N bond is 2.66 Å [28]. Additionally, the

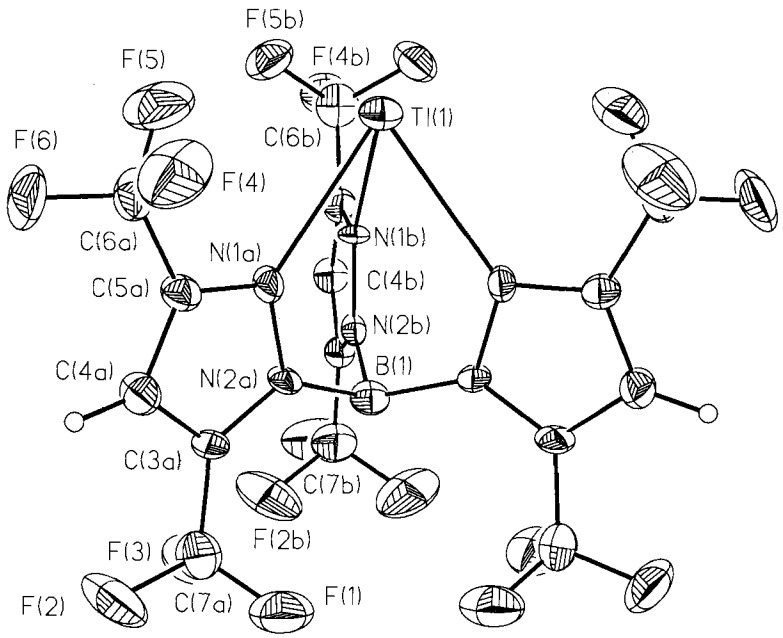


Figure. *An ORTEP plot of* **2c**. The thermal ellipsoids are drawn at the 30% level. Selected bond lengths [Å] and angles [°]: Tl(1)–N(1a): 2.724(7), Tl(1)–N(1aa): 2.725(7), Tl(1)–N(1b): 2.675(10), B(1)–N(2b): 1.590(15), B(1)–N(2a): 1.539(11), B(1)–N(2aa): 1.539(11), N(1a)–Tl(1)–N(1b): 67.9(2), N(1b)–Tl(1)–N(1aa): 67.9(2), N(1a)–Tl(1)–N(1aa): 68.7(3).

N–Tl–N bond angles in **2c** are smaller than those in the other complexes (72.3–79.4°), reflecting the longer Tl–N bonds.

No Tl···Tl contacts are observed and, apart from the three coordinating N-atoms, there are no other contacts that could be interpreted in terms of bonds. The shortest intra- and intermolecular contacts are the nine Tl(1)–F distances ranging from 3.116 to 3.941 Å which, therefore, are certainly too long to be considered as arising from bonding interactions. Finally, the presence of two different Tl(1)–N bonds cannot be taken as an indication of a stereoactive lone pair.

The CF_3 groups at C(3) of each pyrazole ring are oriented in such a way as to shield the B–H and B–N bonds from electrophilic attack. Interestingly, as may be expected from this structural feature, the complex **2c** is remarkably stable: its solution in H_2O/acetone 1:1 does not show any decomposition after several weeks.

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