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# Synthesis and Structure of the Thallium(I) Salt of the Tetrakis{3,5-bis(trifluoromethyl)phenyl}borate Anion

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## Introduction

Weakly coordinating anions are important in the generation of reactive cationic complexes and catalysts.[1−4] The $TFPB^-$ (TFPB = tetrakis{3,5-bis(trifluoromethyl)phenyl}borate) anion has been recognized recently as an extremely useful member of the family of weakly coordinating counterions because of its stability toward oxidation and acidic media.[5] Recently, Brookhart and co-workers have reported the preparation of an acid form of this anion, $[H(OEt_2)_2]^+[TFPB]^-$, which protonates alkyl or olefin complexes to afford reactive cationic complexes.[6] A similar acid form of the tetrakis(pentafluorophenyl)borate anion, $B(C_6F_5)_4^-$,[7] and the trityl salt of the TFPB anion[8] have also been used for alkyl abstraction to afford cationic complexes with weakly coordinating anions. An alternative method for generating cationic complexes is by halide abstraction; silver or thallium reagents are commonly used for this purpose because the resultant metal halide is of low solubility, and its precipitation both drives the reaction to the product side and facilitates reaction workup. For example, silver and trityl salts of weakly coordinating carborane anions have been used for halide abstraction reactions.[9] The $Ag^+$ salt of the $TFPB^-$ anion was reported initially in a footnote by Golden[10] and in more detail in a report by Corey.[11] While it is reported to be useful in removing halides from boron[11] and other unspecified[10] centers, its preparation and storage require exclusion of light[10,11] and extensive drying over molecular sieves to achieve an anhydrous reagent.[11] In addition, extended periods *in vacuo* reportedly lead to decomposition.[10] We thought that the thallium(I) salt of the $TFPB^-$ anion might be more useful as a mild, stable reagent for halide abstraction, and here we report a convenient synthesis of this anhydrous, air and light stable salt, together with the solid-state structure of a methylene chloride solvate.

## Experimental Section

**General Considerations.** All reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of dinitrogen which had been deoxygenated over BASF catalyst and dried over Aquasorb, or in a Braun drybox. $^1H$ NMR (300 MHz) and $^{19}F$ NMR (282.2 MHz) were recorded on a Varian Unity Plus 300 FT spectrometer at 23 °C. $^1H$ NMR chemical shifts were recorded in $CD_2Cl_2$ as ppm downfield from tetramethylsilane, unless otherwise stated, and referenced to the solvent; coupling constants were recorded in Hz. $^{19}F$ NMR chemical shifts were recorded in $CD_2Cl_2$, unless otherwise stated, as ppm and internally referenced to $CFCl_3$. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

**Reagents.** Thallium ethoxide was purchased from Strem Chemical Inc. Brookhart's acid, $[H(OEt_2)_2]^+[TFPB]^-$, was prepared according to the literature method,[6] but an alternative drying procedure was used to remove water from the immediate precursor $Na^+TFPB^-$; azeotropic distillation with benzene in a Dean−Stark apparatus appears to be a more useful method of drying large quantities of this salt instead of using molecular sieves.[6] Hydrocarbon and ethereal solvents were distilled under dinitrogen from sodium or sodium/potassium alloy and benzophenone ketyl; halogenated solvents from calcium hydride. Deuterated solvents were purchased from ISOTEC Inc. or Cambridge Isotope Laboratories.

**Thallium(I) Tetrakis{3,5-bis(trifluoromethyl)phenyl}borate.** Thallium(I) ethoxide (0.254 g; 1.02 mmol) was dissolved in ether and added to an ethereal solution of $[H(OEt_2)_2]^+[TFPB]^-$ (1.00 g; 1.02 mmol) at room temperature. The reaction mixture was stirred for 15 min, and then the solvent was removed *in vacuo* to afford the desired product in 82% yield. Clear, colorless crystals used in the X-ray crystallographic analysis were grown from a methylene chloride−hexanes (ca. 1:1 v/v) mixture overnight at −20 °C. This material is shown by microanalysis and by NMR to contain 0.33 molecule of $CH_2Cl_2$ per formula unit. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 7.75 (br s, 8H), 7.59 (s, 4H), 5.33 (s, 0.66H, $CH_2Cl_2$). $^{19}F$ NMR ($CD_2Cl_2$): $\delta$ −62.7 (s, $CF_3$). Anal. Calcd for $C_{32}H_{12}BF_{24}Tl\cdot 0.33\ CH_2Cl_2$: C, 35.49; H, 1.16. Found: C, 35.96; H, 1.45. The complex shows moderate solubility in comon organic solvents such as methylene chloride, chloroform, and acetone. It is insoluble in hexane.

## Results and Discussion

Clean acid−base reaction of $[H(OEt_2)_2]^+[TFPB]^-$ with thallium ethoxide in ether affords the anhydrous thallium(I) salt of $TFPB^-$ in excellent yield. $Tl^+TFPB^-$ is air and light stable, is soluble in acetone, ether, methylene chloride and methanol, is slightly soluble in tetrahydrofuran, and is insoluble in hexanes and water. It crystallizes as clear, colorless crystals from a methylene chloride−hexanes (ca. 1:1 v/v) mixture at −20 °C as a $CH_2Cl_2$ solvate, which by NMR integration and microanalysis contains 0.33 molecules of $CH_2Cl_2$ per formula unit. These crystals were subjected to an X-ray crystallographic analysis.[12] An ORTEP is shown in Figure 1, and a packing diagram in Figure 2. The structure of the $TFPB^-$ anion is tetrahedral at boron consistent with other structures of the anion[4,13] but, unlike the structure of $LiTFPB\cdot H_2O$, shows no disorder in the $CF_3$ groups. Thallium rests on a 4-fold rotation

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(12) Crystal data for $C_{32.96}H_{12}BF_{24}Tl$: $M = 1079$, $0.1 \times 0.2 \times 0.2$ mm, tetragonal, $P4/ncc$, $a = 13.959(2)$ Å, $b = c = 19.208(4)$ Å, $V = 3743(1)$ Å$^3$, $Z = 4$, $\rho_{calc} = 1.895$ g/cm$^3$, $2\theta_{max} = 45°$, Mo Kα radiation, $\lambda = 0.710\ 73$ Å, $\omega$ scan mode, $T = 298$ K, 2894 measured reflections, 1197 independent, 836 reflections with $F_o > 4\sigma$, $\mu = 0.04$ cm$^{-1}$, $R(F) = 0.056$, $R(wF^2) = 0.139$. The thallium ion is located on a 4-fold rotation axis. The borate anion is located on a 4-fold rotoinversion axis. Attempts to model four residual peaks in the difference map, associated with each other and 2.4 Å away from the thallium ion, as a chemically recognizable, disordered solvent molecule, were unsuccessful. The apparent solvent molecule is encompassed by a spheroid void space of 1.7 Å radius which is described by the thallium ion and the fluorine atoms of the anion. All non-hydrogen atoms, excluding the apparent solvent atoms, were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions. All software and sources of scattering factors are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI).

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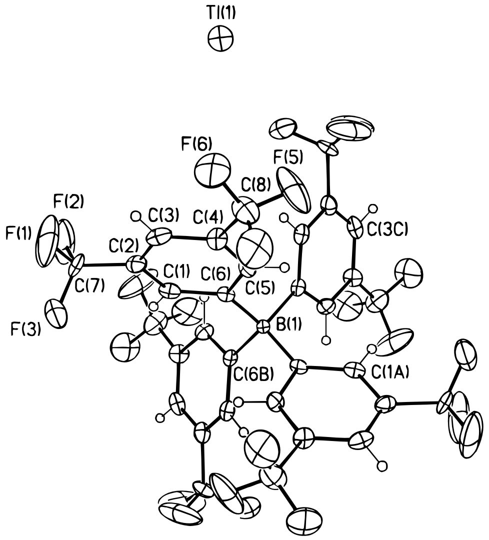

**Figure 1.** ORTEP drawing and labeling scheme for thallium(I) tetrakis-{3,5-bis(trifluoromethyl)phenyl}borate). Ellipsoids are drawn at 35% probability. Hydrogen atoms and the apparently disordered solvent molecule have been omitted for clarity.

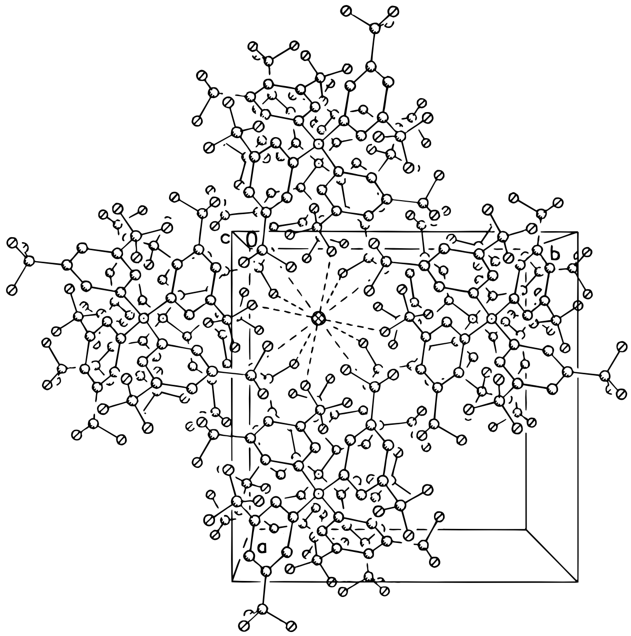

**Figure 2.** Packing diagram viewed along the *c*-axis. Hydrogen atoms and the apparently disordered solvent molecule have been omitted for clarity.

axis surrounded by fluorine atoms which appear to show a weak interaction with thallium. Three different thallium−fluoride distances are observed, (Tl(1)⋯F(1) = 3.86(6) Å, Tl(1)⋯F(3) = 3.18(6) Å, Tl(1)⋯F(6) = 3.05(6) Å), the first of which is longer than the sum of the van der Waals radii for thallium and fluorine, 3.35−3.50 Å.[13,14] Although the other two contacts are within bonding distance, the carbon−fluorine bond lengths are not perturbed. Other weakly coordinating fluorine-containing anions show similar interactions with thallium. For instance, the four closest thallium−fluorine contacts in [Tl(mesitylene)$_2$][B(OTeF$_5$)$_4$][15] are 3.17(1), 3.25(1), 3.47(1), and 3.83(1) Å; in [Tl(1,2-C$_2$H$_4$Cl$_2$)] [B(OTeF$_5$)$_4$][16] the distances range from 2.950(5) Å to 3.981(8) Å, and in Tl$_2$Zr[OCH(CF$_3$)]$_6$[17] close contacts range from 3.068(8) to 3.287(11) Å. In comparison, the thallium−fluorine distances in TlF range from 2.25(2) to 3.90(2) Å.[4,18]

In contrast to the lithium[10,19] or sodium[5] derivatives, Tl$^+$TFPB$^-$ is prepared in anhydrous form as confirmed by both NMR spectra and its solid-state structure. This presumably results from the larger ionic radius of the thallium cation compared to lithium (1.49 Å vs 0.60 Å),[10] which allows for more efficient crystal packing without solvation of the cation. However, while water is indeed excluded from the crystal lattice, the $^1$H NMR spectrum confirms the presence of 0.33 molecules of CH$_2$Cl$_2$ per molecular formula unit in the crystals. Unfortunately the solvent molecule could not be unambiguously located from the X-ray data; attempts to model four residual peaks in the difference map, associated with each other and 2.4 Å away from thallium, as a disordered solvent molecule were unsuccessful. There is a 1.7 Å radius void space in the lattice, described by thallium and fluorine atoms of the anion. Since the solvent molecule could not be located, the presence of weak thallium−chlorine interactions, similar to those observed in [Tl(1,2-C$_2$H$_4$-Cl$_2$)][B(OTeF$_5$)$_4$][16], cannot be discounted.

The solution data and elemental analysis support the solid-state structure. The $^1$H NMR spectrum (CD$_2$Cl$_2$) shows two peaks at 7.75 and 7.59 ppm in an 8:4 ratio, and at 5.33 ppm a peak corresponding to CH$_2$Cl$_2$ (0.33 equiv) is present. The $^{19}$F NMR spectrum consists of one peak at −62.7 ppm which does not show coupling to thallium.

In summary, Tl$^+$TFPB$^-$ is easily prepared from Brookhart's acid and is an excellent anhydrous source of the TFPB$^-$ anion. The thallium complex has been used in our laboratories as a reagent for facile halide abstractions to generate cationic complexes of Co(III) and Rh(III).[20]

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**Supporting Information Available:** Tables of crystallographic data, fractional atomic coordinates and *U* values, bond lengths and angles, anisotropic displacement parameters, and H coordinates and isotropic displacement coefficients (6 pages). Ordering information is given on any current masthead page.

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