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Synthesis and structural characterization of tris[3-trifluoromethyl-5-(2-thienyl)pyrazolyl]hydroborato thallium, Tl[Tp^{CF_3,Tn}]: a monovalent thallium complex with a highly solvent dependent $J_{Tl–F}$ coupling constant, ranging from 0 to 850 Hz

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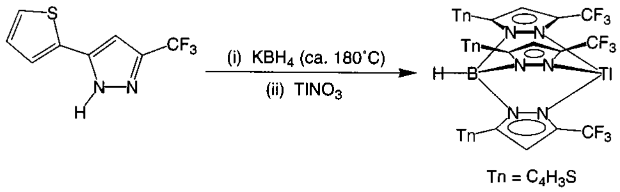
The tris[3-trifluoromethyl-5-(2-thienyl)pyrazolyl]hydroborato thallium complex, Tl[Tp^{CF_3,Tn}], has been prepared *via* the reaction of 3-trifluoromethyl-5-(2-thienyl)pyrazole with KBH_4 followed by metathesis with $TlNO_3$. Both ^{19}F and ^{203}Tl NMR spectroscopies reveal the presence of an exceptionally large 850 Hz four-bond $^4J_{Tl–F}$ coupling constant for Tl[Tp^{CF_3,Tn}] in chloroform at room temperature; however, the observed coupling constant is highly solvent dependent and is reduced to 0 Hz in methanol, acetonitrile and dimethyl sulfoxide. The molecular structure of Tl[Tp^{CF_3,Tn}] has been determined by X-ray diffraction: Tl[Tp^{CF_3,Tn}] is triclinic, $P\bar{1}$ (no. 2), a = 8.328(1), b = 11.432(2), c = 16.088(3) Å, α = 70.58(2), β = 82.90(2), γ = 77.54(2)°, U = 1408(1) Å^3, Z = 2.

An important feature of the tris(pyrazolyl)hydroborato [Tp$^{RR'}$] ligand system[1,2] is the ability to control the steric and electronic environment about a metal center by modification of the pyrazolyl substituents. For example, we have employed sterically demanding tris(pyrazolyl)hydroborato ligands with *tert*-butyl substituents in the 3-positions of the pyrazolyl groups to support a variety of uncommon types of complexes of the s- and p-block metals,[3] as exemplified by our recent report of the monomeric monovalent gallium complex Ga[Tp$^{Bu^t_2}$].[4] Likewise, electronic effects have been investigated with the syntheses of several perfluoroalkyl tris(pyrazolyl)hydroborato derivatives, including [Tp^{CF_3}],[5] [Tp$^{(CF_3)_2}$],[5,6] [Tp^{CF_3,Me}][7] and [Tp^{R_f}] (R_f = C_2F_5 or C_3F_7).[8,9] In this paper we describe the synthesis of a further member of the series of trifluoromethylated ligands, namely the 2-thienyl derivative [Tp^{CF_3,Tn}] (Tn = C_4H_3S). The latter complex is of particular interest since it is the first Tl[Tp^{CF_3,R}] derivative reported to exhibit a four-bond $^4J_{Tl–F}$ coupling; furthermore, this coupling is highly solvent dependent, ranging from 850 Hz in chloroform to 0 Hz in methanol, acetonitrile and dimethyl sulfoxide.

Results and Discussion

The tris[3-trifluoromethyl-5-(2-thienyl)pyrazolyl]hydroborato thallium complex Tl[Tp^{CF_3,Tn}] is readily synthesized by the reaction of 3-trifluoromethyl-5-(2-thienyl)pyrazole with KBH_4 at *ca.* 180 °C followed by metathesis with $TlNO_3$ (Scheme 1). The compound Tl[Tp^{CF_3,Tn}] has been characterized by ^1H, ^{13}C, ^{19}F and ^{203}Tl NMR spectroscopies, as summarized in Tables 1–3, and its molecular structure has been determined by X-ray diffraction. Two views of the structure of Tl[Tp^{CF_3,Tn}] are illustrated in Figs. 1 and 2, with selected bond lengths and angles being listed in Table 4. The view down the non-crystallographic C_3 axis (Fig. 2) indicates that the pyrazolyl groups are effectively coplanar with respect to the Tl···B vector, in common with other Tl[Tp$^{RR'}$] derivatives with sterically undemanding substituents in the 5-positions.[10] The co-ordination environment about thallium in Tl[Tp^{CF_3,Tn}] is comparable to that in other Tl[Tp$^{RR'}$] derivatives, as evidenced by the metrical data summarized in Table 5. Indeed, the average Tl–N bond length in Tl[Tp^{CF_3,Tn}] (2.62 Å) is close to the middle of the range observed for other Tl[Tp$^{RR'}$] complexes (2.50–2.74 Å); all of these bond lengths are, however, notably longer than the sum of the covalent radii (2.31 Å),[11] presumably due to the bonding between Tl and the tris(pyrazolyl)hydroborato ligand being composed of one normal covalent and two dative covalent interactions.[12] Of the complexes listed in Table 5, the most appropriate structural comparison of Tl[Tp^{CF_3,Tn}] is with Tl[Tp$^{(CF_3)_2}$], which has substantially longer Tl–N bond lengths: 2.675(10), 2.725(7) and 2.724(7) Å.[6a] The origin of the greater



Scheme 1

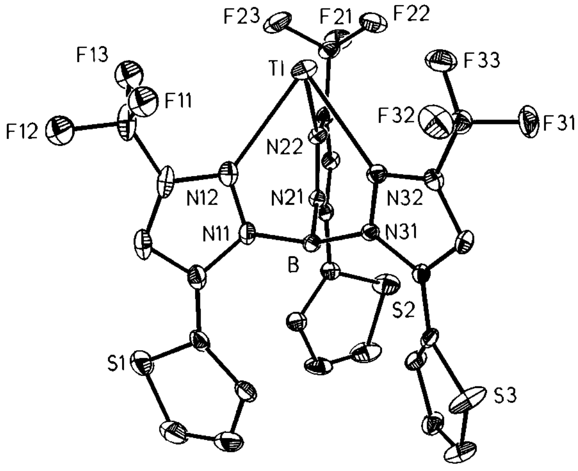


Fig. 1 Molecular structure of Tl[Tp^{CF_3,Tn}]

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Table 1 Proton and ^{13}C NMR spectroscopic data for $Tl[Tp^{CF_3,Tn}]$

Assignment	δ (ppm)	Multiplicity, coupling (Hz)
^1H NMR (200 MHz, $C_6D_5CD_3$)		
η^3-$HB\{C_3N_2H(CF_3)(C_4\mathit{H}_3S)\}_3$		
3H	6.40	dd, $^3J_{H-H} = 4$, $^4J_{H-H} = 1$
3H	6.53	dd, $^3J_{H-H} = 5$, $^3J_{H-H} = 4$
3H	6.79	dd, $^3J_{H-H} = 5$, $^4J_{H-H} = 1$
η^3-$HB\{C_3N_2\mathit{H}(CF_3)(C_4H_3S)\}_3$	6.33	d, $^4J_{Tl-H} = 4$
η^3-$\mathit{H}B\{C_3N_2H(CF_3)(C_4H_3S)\}_3$	Not observed	
^{13}C NMR (75 MHz, $CDCl_3$)		
η^3-$HB\{C_3N_2H(\mathit{C}F_3)(C_4H_3S)\}_3$	121.8	q, $^1J_{C-F} = 269$
η^3-$HB\{C_3N_2H(CF_3)(\mathit{C}_4H_3S)\}_3$		
3C	126.8	d, $^1J_{C-H} = 186$
3C	127.1	d, $^1J_{C-H} = 165$
3C	129.4	d, $^1J_{C-H} = 171$
3C	130.8	s
η^3-$HB\{\mathit{C}_3N_2H(CF_3)(C_4H_3S)\}_3$		
3C	105.8	dd, $^1J_{C-H} = 181$, $^3J_{Tl-C} = 19$
3C	142.6	m
3C	144.6	s

Table 2 Fluorine-19 NMR spectroscopic data (282 MHz) for $Tl[Tp^{CF_3,Tn}]$ (relative to $CFCl_3$)

Solvent	δ (ppm)	Multiplicity, $^4J_{Tl-F}$ (Hz)
$CDCl_3$	−60.6	d, 850
C_6D_6	−60.2	d, 810
$C_6D_5CD_3$	−60.3	d, 810
Et_2O	−61.9	d, 810
THF	−62.3	d, 710
Et_2O–DME*	−61.9	d (br), 620
DME	−58.4	s (br)
CD_3OD	−62.8	s
MeCN	−62.0	s
Me_2SO	−60.4	s

* *ca.* 90% Et_2O by volume.

Table 3 Thallium-203 NMR spectroscopic data (171 MHz) for $Tl[Tp^{CF_3,Tn}]$ (relative to $TlNO_3$ extrapolated to infinite dilution)

Solvent	δ (ppm)	Multiplicity*
$CDCl_3$	1131	dectet
$C_6D_5CD_3$	1001	dectet
Et_2O	1035	dectet
THF	771	dectet
DME	594	s, br
Me_2SO	368	s

* $^4J_{Tl-F}$ are within 10 Hz of those reported in Table 2.

Table 4 Selected bond lengths (Å) and angles (°) for $Tl[Tp^{CF_3,Tn}]$

Tl–N(12)	2.603(2)	Tl–N(22)	2.635(4)
Tl–N(32)	2.623(6)	B–N(11)	1.558(8)
B–N(21)	1.561(10)	B–N(31)	1.529(8)
B–H	1.09(7)		
N(12)–Tl–N(22)	72.6(2)	N(12)–Tl–N(32)	71.5(2)
N(22)–Tl–N(32)	71.0(2)	N(11)–B–N(21)	109.2(5)
N(11)–Tl–N(31)	110.8(4)	N(21)–B–N(21)	111.0(6)
N(11)–B–H	113(3)	N(21)–B–H	105(3)
N(31)–B–H	108(3)		

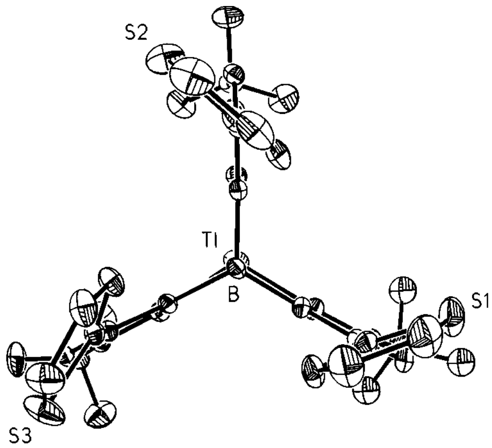

Fig. 2 View of $Tl[Tp^{CF_3,Tn}]$ down the Tl · · · B axis

Tl–N bond lengths for $Tl[Tp^{(CF_3)_2}]$ compared to $Tl[Tp^{CF_3,Tn}]$ is most likely attributed to an electronic influence, *i.e.* the presence of an additional electron-withdrawing CF_3 group in the 5-position reduces the donor capability of the tris(pyrazolyl)-hydroborato ligand.[13] In support of this suggestion, Dias *et al.*[14] have recently documented that incorporation of a CF_3 substituent at the 5-position of a tris(pyrazolyl)hydroborato ligand does exert a significant electronic influence upon a metal center.

In addition to the direct bonding interactions between thallium and nitrogen, there are several close contacts between thallium and the fluorine atoms of the trifluoromethyl substituents: specifically, the shortest Tl · · · F interaction is 3.03 Å, noticeably less than the value of 3.43 Å for the sum of the van der Waals radii of Tl and F.[15,16] Such interactions are not, however, uncommon.[17] For example, short Tl · · · F interactions less than the sum of the van der Waals radii have been observed in the $Tl[Tp^{(CF_3)_2}]$ analogue (3.12 Å)[6a] and a variety of other derivatives, *e.g.* $[CpMo(SC_6F_5)_2(CO)_2Tl]$ (3.09 Å),[18] $[CpMo(SC_6F_5)_4Tl]$ (2.98 Å),[18] $[Tl_2Zr\{OCH(CF_3)_2\}_6]$ (3.07 Å),[19] $[Tl\{OC_6H_2(CF_3)_3\}]_2$ (3.20 Å),[20] $[(p\text{-}HC_6F_4)_2TlCl(OPPh_3)]_2$ (3.14 Å),[21] $[Ph_2Tl(O_2CC_6F_5)(OPPh_3)]_2$ (3.09 Å),[22] $[Tl\{CF_3C(O)CHC(O)CF_3\}]$ (3.07 Å),[23] $[Bu_4N]_2[Tl\{Pt(C_6F_5)_4\}]$ (2.84 Å),[24] $[W(PMe_2Ph)_4Cl_2][Tl(OCH_2CF_3)]_4$ (3.12 Å),[25] $[Tl\{S(C_6H_2(CF_3)_3\}]$ (3.13 Å),[26] $(C_6F_5)_2TlOH$ (3.17 Å)[27] and $[Tl(C_6F_5)_2(acac)\{(O)Ph_2P(CH_2)PPh_2(O)\}]$ (3.22 Å) (Cp = η^5-C_5H_5, acac = acetylacetonate).[28]

One of the most interesting features of $Tl[Tp^{CF_3,Tn}]$ is the observation of a very large four-bond $^4J_{Tl-F}$ coupling constant.[29] Specifically, chloroform solutions of $Tl[Tp^{CF_3,Tn}]$ exhibit a substantial $^4J_{Tl-F}$ coupling of 850 Hz, as manifested by a doublet in the ^{19}F NMR spectrum (Fig. 3) and as a dectet in the ^{203}Tl NMR spectrum (Fig. 4).[30] For comparison purposes, data on $^nJ_{Tl-X}$ coupling constants for thallium(I) complexes are rather limited.[31] However, a significant body of data does exist for thallium(III) complexes, from which it is evident that $^nJ_{Tl-X}$ coupling constants are among the largest reported;[31] for example, the $^1J_{Tl-H}$ coupling constant in $[TlH_4]^-$ is 6144 Hz.[32] With respect to fluorine, the most extensive compilation of $^nJ_{Tl-F}$ coupling constants is for thallium(III) complexes, $(Ar_f)_2$-

Table 5 Selected metrical data for Tl[Tp$^{RR'}$] complexes[a]

Complex	d(Tl–N$_{av}$)/Å	N–Tl–N$_{av}$/°	Ref.
Tl[Tp^{CF_3,Tn}]	2.62(2)	72(1)	This work
Tl[Tp$^{(CF_3)_2}$]	2.71(3)	68(1)	T1
Tl[Tp$^{Bu^t}$]	2.59(1)	78(3)	T2
Tl[Tp$^{Bu^t,Me}$]	2.50(2)	78(1)	T3
Tl[Tp$^{Bu^t_2}$]	2.57(3)	78(3)	T4
Tl[Tp^{Menth}]	2.55(2)	76(4)	T5
Tl[Tp^{Mementh}]	2.56(4)	77(3)	T5
Tl[Tp$^{p\text{-}Tol}$]	2.58(1)	77(2)	T6
Tl[Tp^{In}]	2.53(2)	76(4)	T7
Tl[Tp^{Ar_2}]	2.61(5)	77(2)	T8
Tl[Tp^{Ant}]	2.68(3)[b]	66(1)[b]	T9
Tl[Tp^{Trip}]	2.74(7)	75(9)	T10
Tl[Tp$^{2\text{-}py}$]	2.67(3)	71(1)	T11

[a] Abbreviations used: p-Tol = tolyl; ant = anthryl; trip = triptycyl; [Tp^{In}] = tris(1,4-dihydroindeno[1,2-c]pyrazol-1-yl)borato; Ar = p-C_6H_4-Bu^t. [b] The structure was performed on a compositionally disordered crystal, so that the derived metrical data is of limited accuracy. References: T1 O. Renn, L. M. Venanzi, A. Marteletti and V. Gramlich, *Helv. Chim. Acta*, 1995, **78**, 993. T2 A. H. Cowley, R. L. Geerts, C. M. Nunn and S. Trofimenko, *J. Organomet. Chem.*, 1989, **365**, 19. T3 K. Yoon and G. Parkin, *Polyhedron*, 1995, **14**, 811. T4 C. Dowling, D. Leslie, M. H. Chisholm and G. Parkin, *Main Group Chemistry*, 1995, **1**, 29. T5 D. D. LeCloux, C. J. Tokar, M. Osawa, R. P. Houser, M. C. Keyes and W. B. Tolman, *Organometallics*, 1994, **13**, 2855. T6 G. Ferguson, M. C. Jennings, F. J. Lalor and C. Shanahan, *Acta Crystallogr., Sect. C*, 1991, **47**, 2079. T7 A. L. Rheingold, R. L. Ostrander, B. S. Haggerty and S. Trofimenko, *Inorg. Chem.*, 1994, **33**, 3666. T8 E. Libertini, K. Yoon and G. Parkin, *Polyhedron*, 1993, **12**, 2539. T9 R. Han, G. Parkin and S. Trofimenko, *Polyhedron*, 1995, **14**, 387. T10 T. Fillebeen, T. Hascall and G. Parkin, *Inorg. Chem.*, 1997, **36**, 3787. T11 A. J. Amoroso, J. C. Jeffery, P. L. Jones, J. A. McCleverty, E. Psillakis and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1995, 1175.

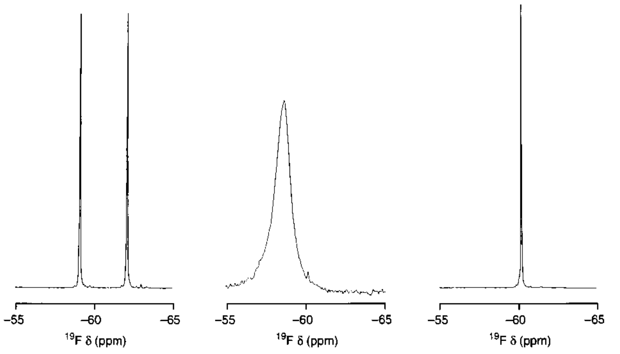

Fig. 3 Fluorine-19 NMR spectra of Tl[Tp^{CF_3,Tn}] in $CDCl_3$, MeOCH$_2$CH$_2$OMe and Me$_2$SO

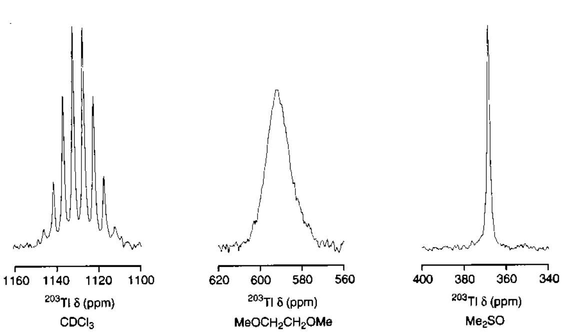

Fig. 4 Thallium-203 NMR spectra of Tl[Tp^{CF_3,Tn}] in $CDCl_3$, MeOCH$_2$CH$_2$OMe and Me$_2$SO

TlX and (Ar$_f$)$_3$Tl (Ar$_f$ = fluorinated aryl group), for which the magnitudes of the $^nJ_{Tl\text{–}F}$ coupling constants typically decrease in the sequence $^3J_{Tl\text{–}F}$ (*ca.* 500–1200 Hz) > $^4J_{Tl\text{–}F}$ (*ca.* 150–500 Hz) > $^5J_{Tl\text{–}F}$ (*ca.* 10–100 Hz).[33,34] Thus, by comparison with these simple organic derivatives, the $^4J_{Tl\text{–}F}$ coupling constant of 850 Hz is particularly large. There are, however, several metal-containing Tl^I complexes that exhibit large $J_{Tl\text{–}F}$ coupling constants. A particularly noteworthy example is provided by the molybdenum complex [CpMo(SC$_6$F$_5$)$_2$(CO)$_2$Tl][18] for which the *ortho*-fluorine substituents are observed in the ^{19}F NMR spectrum as a doublet at −50 °C with $^4J_{Tl\text{–}C}$ coupling constant of 1905 Hz; interestingly, at −100 °C, rotation about the S–C$_6$F$_5$ bond is sufficiently slow that the proximal and distal *ortho*-fluorine substituents do not exchange and two doublet resonances with very distinct $^4J_{Tl\text{–}F}$ coupling constants of 3770 Hz and 70 Hz are observed. Likewise, at 18 °C the *ortho*-fluorine substituents of [CpMo(SC$_6$F$_5$)$_4$Tl] are observed as a doublet in the ^{19}F NMR spectrum with an averaged $^4J_{Tl\text{–}F}$ coupling constant of 1770 Hz, but at −79 °C two distinct resonances are observed, with $^4J_{Tl\text{–}F}$ coupling constants of 3630 Hz and 0 Hz. Despite the large magnitude of the $J_{Tl\text{–}F}$ coupling constants, and the close intramolecular contacts between Tl and F in [CpMo(SC$_6$F$_5$)$_2$(CO)$_2$Tl] (3.09 Å) and [CpMo(SC$_6$F$_5$)$_4$Tl] (2.98 Å), the interactions were considered to not represent a significant bonding interaction. In contrast, the $J_{Tl\text{–}F}$ coupling constant of 383 Hz for [Tl$_2$Zr{OCH(CF$_3$)$_2$}$_6$] (with the closest Tl···F separation of 3.07 Å) has been considered to be indicative of a significant interaction between Tl and F, a notion that has been supported by consideration of valence bond sums.[35,36] On this basis, the spectroscopic and structural data for Tl[Tp^{CF_3,Tn}] are also consistent with a direct interaction between Tl and F, but ascertaining the significance of this interaction awaits further studies and comparisons with related complexes.

The observation of a large $^4J_{Tl\text{–}F}$ coupling constant for Tl[Tp^{CF_3,Tn}] becomes even more significant when it is considered that no such coupling was reported for the closely related complex Tl[Tp$^{(CF_3)_2}$] in acetonitrile: the two chemically inequivalent CF$_3$ groups were observed as singlets at δ −59.6 and −60.8.[37] In view of this discrepancy, we were prompted to examine the solvent dependence of the $^4J_{Tl\text{–}F}$ coupling constant for Tl[Tp^{CF_3,Tn}], as summarized in Tables 2 and 3. Thus, the $^4J_{Tl\text{–}F}$ coupling constant was observed to be highly solvent dependent, ranging from 850 Hz in chloroform to 0 Hz in methanol, acetonitrile and dimethyl sulfoxide.[38] For example, the absence of an observable $^4J_{Tl\text{–}F}$ coupling for Tl[Tp^{CF_3,Tn}] in dimethyl sulfoxide is illustrated by the ^{19}F and ^{203}Tl NMR spectra shown in Figs. 3 and 4. In the case of dimethoxyethane (DME), an intermediate result is obtained with the observation of broad singlets in both ^{19}F and ^{203}Tl NMR spectra (Figs. 3 and 4). Similarly, in the mixed solvent system Et$_2$O–DME (*ca.* 90% Et$_2$O by volume) a broad doublet with a reduced coupling constant of 620 Hz is observed.

The complete loss of $^4J_{Tl\text{–}F}$ coupling in methanol, acetonitrile and dimethyl sulfoxide is most probably a consequence of Tl$^+$ dissociation from Tl[Tp^{CF_3,Tn}] [equation (1)]. Specifically, loss

$$\mathrm{Tl[Tp^{CF_3,Tn}]} \rightleftharpoons \mathrm{Tl^+} + \mathrm{[Tp^{CF_3,Tn}]^-} \tag{1}$$

of coupling would be expected if either (*i*) Tl[Tp^{CF_3,Tn}] were to be fully dissociated so that [Tp^{CF_3,Tn}]$^-$ were the major component, or (*ii*) reversible dissociation of Tl$^+$ was sufficiently fast on the NMR time-scale to effect decoupling of the Tl nucleus from the ligand resonances.[39] Presumably, both of these effects would be promoted by methanol, acetonitrile and dimethyl sulfoxide (as compared with, for example, chloroform and benzene) due to their ability to stabilize the ionic species, Tl$^+$ and [Tp^{CF_3,Tn}]$^-$. Supporting this suggestion, the Tl chemical shift of Tl[Tp^{CF_3,Tn}] in Me$_2$SO (δ 368) is identical within experimental error to that reported for the Tl$^+$ ion in Me$_2$SO (δ 369).[40] Furthermore, it should be noted that the observed ^{203}Tl linewidth ($\Delta\nu_{\frac{1}{2}}$ < 200 Hz) precludes a mechanism involving only partial dissociation (*i.e.* η^3- to η^2-interconversion), since even in the fast exchange limit the observed $J_{Tl\text{–}F}$ coupling constant would be expected to be >550 Hz.[41]

Claramunt and co-workers have also commented that apparent $^{n}J_{\text{Tl–C}}$ and $^{n}J_{\text{Tl–H}}$ coupling constants for Tl[Tp$^{\text{RR}'}$] complexes are dependent on the nature of the solvent, being observable in $CDCl_3$ but not in dimethyl sulfoxide.[42] Likewise, whereas we do observe a $^{3}J_{\text{Tl–C}}$ coupling of 19 Hz and a $^{4}J_{\text{Tl–H}}$ coupling of 7 Hz with the [CH] group of the pyrazolyl fragment in $CDCl_3$,[43] no such coupling is observed in dimethyl sulfoxide.

Conclusion

In summary, the tris[3-trifluoromethyl-5-(2-thienyl)pyrazolyl]hydroborato thallium complex, Tl[Tp$^{\text{CF}_3\text{,Tn}}$], has been synthesized and structurally characterized by X-ray diffraction. Of most significance, both ^{19}F and ^{203}Tl NMR spectroscopies reveal the presence of an exceptionally large 850 Hz four-bond $^{4}J_{\text{Tl–F}}$ coupling constant for Tl[Tp$^{\text{CF}_3\text{,Tn}}$] in chloroform, which is also the first report of such a coupling for Tl[Tp$^{\text{CF}_3\text{,R}}$] complexes. The observed coupling constant is, however, highly solvent dependent and is reduced to zero in solvents which promote dissociation, such as methanol, acetonitrile and dimethyl sulfoxide.

Experimental

General considerations

3-(Trifluoromethyl)-5-(2-thienyl)pyrazole was prepared by reaction of thenoyltrifluoroacetone [4,4,4-trifluoro-1-(2-thienyl)-butane-1,3-dione] (Aldrich) with hydrazine by the literature method.[44] Elemental analyses were carried out by Microanalysis, Inc. of Wilmington, DE. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 1600 FTIR spectrophotometer and are reported in cm^{-1}. Proton NMR spectra were recorded on a Varian VXR 200 spectrometer and are referenced relative to $SiMe_4$, using residual protio solvent signals as an internal calibrant. Carbon-13 NMR spectra were recorded on a Varian VXR 300 spectrometer operating at 75.429 MHz and are referenced relative to $SiMe_4$, using solvent signals as an internal calibrant. Fluorine-19 NMR spectra were recorded on a Bruker Avance DRX 300 spectrometer operating at 282.404 MHz and are relative to $CFCl_3$ (δ 0.00), using external $PhCF_3$ (δ −63.72) as a calibrant.[45] Thallium-203 NMR spectra were recorded on a Bruker Avance DRX 300 spectrometer operating at 171.440 MHz and are relative to aqueous $TlNO_3$ (extrapolated to infinite dilution; δ 0.00),[40] using an external solution of aqueous TlOAc as calibrant.

Synthesis of Tl[Tp$^{\text{CF}_3\text{,Tn}}$]

A mixture of 3-(trifluoromethyl)-5-(2-thienyl)pyrazole (130 g, 0.60 mol) and KBH_4 (5.4 g, 0.10 mol) was heated to *ca.* 180 °C until evolution of H_2 ceased. Unreacted pyrazole was removed by sublimation at *ca.* 170 °C (1 Torr, 133.322 Pa). The residue was dissolved in tetrahydrofuran (THF) (500 ml) and treated with a solution of $TlNO_3$ in water (300 ml, 0.37 M). The mixture was diluted with water (1 l) and was extracted into CH_2Cl_2 (1 l). The CH_2Cl_2 extract was filtered through alumina. The volatile components were removed *in vacuo* and the residue was washed with methanol (3 × 300 ml) giving Tl[Tp$^{\text{CF}_3\text{,Tn}}$] as a white solid (48 g, 55%). Recrystallization from toluene gave a material with a melting point of 225–227 °C (Found: C, 32.8; H, 1.5; N, 9.4. Calc. for $C_{24}H_{13}BF_9N_6S_3Tl$: C, 33.2; H, 1.5; N, 9.7%). IR data: 2660w cm^{-1} ν(B–H). NMR spectroscopic data are presented in Tables 1–3.

Crystal-structure determination of Tl[Tp$^{\text{CF}_3\text{,Tn}}$]

Crystal data, data collection and refinement parameters for Tl[Tp$^{\text{CF}_3\text{,Tn}}$] are summarized in Table 6. A single crystal of Tl[Tp$^{\text{CF}_3\text{,Tn}}$] grown from CH_2Cl_2 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 (λ = 0.710 73 Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly (<1% decay) and corrected for Lorentz, polarization and absorption effects. The structure was solved using Patterson and standard difference map techniques on a Data General NOVA 4 computer using SHELXTL.[46] One of the trifluoromethyl groups (F31–F33) was disordered over two sites and was refined with occupancies of 0.78(1) and 0.22(1). Of the two possible space groups, *P*1 (no. 1) and $P\bar{1}$ (no. 2), a satisfactory solution was obtained in the centrosymmetric alternative, $P\bar{1}$ (no. 2). Hydrogen atoms on carbon were included in calculated positions. The hydrogen atom attached to boron was located in a difference map and its position was refined. Selected bond lengths and angles are listed in Table 4.

Table 6 Crystal, intensity collection and refinement data

Formula	$C_{24}H_{13}BF_9N_6S_3Tl$
M	867.8
Color	Colorless
Lattice	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	8.328(1)
b/Å	11.432(2)
c/Å	16.088(3)
α/°	70.58(2)
β/°	82.90(2)
γ/°	77.54(2)
U/Å^3	1408(1)
Z	2
F(000)	828
λ/Å	0.710 73 (Mo-Kα, graphite monochromator)
2θ range/°	3–49
ρ_c/g cm^{-3}	2.05
μ(Mo-Kα)/cm^{-1}	60.9
Octants collected	$h,\pm k,\pm l$
Number of reflections measured	4775
Number of independent reflections	4428
Number of reflections with $F > 6\sigma(F)$	3574
Number of parameters varied	411
Goodness of fit	1.26
*R**	0.0348
*R′**	0.0422
Final residual electron density/e Å^{-3}	0.79
Largest and mean Δ/σ	0.013, 0.003

* $R = \Sigma|F_o - F_c|/\Sigma|F_o|$; $R' = \Sigma w^{\frac{1}{2}}|F_o - F_c|/\Sigma w^{\frac{1}{2}}|F_o|$; $w = [\sigma^2(F) + 0.000\,51F^2]^{-1}$.

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