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ORGANOTHALLIUM COMPOUNDS

XII* NMR SPECTRA OF SOME POLYFLUOROPHENYL-THALLIUM(III) COMPOUNDS

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SUMMARY

The PMR and ^{19}F NMR spectra of the complexes R_2TlBr (R = C_6F_5, o-HC_6F_4, m-HC_6F_4, p-HC_6F_4, 3,5-$H_2C_6F_3$, or 3,6-$H_2C_6F_3$) and $R_3Tl(diox)$ (R = C_6F_5, m-HC_6F_4, p-HC_6F_4, or 3,5-$H_2C_6F_3$; diox = 1,4-dioxan) have been recorded. Proton and fluorine chemical shifts, thallium-proton, thallium-fluorine, fluorine-fluorine, and fluorine-proton coupling constants, and thallium substituent chemical shifts are given and discussed.

INTRODUCTION

Although PMR spectra of arylthallium compounds have been extensively studied [2-5], little is known of the ^{19}F NMR spectra of polyfluorophenyl-thallium(III) compounds [6, 7]. Magnitudes and in some cases signs of both thallium-proton [2-5] and thallium-carbon [8-10] couplings have been reported for arylthallium(III) species, but there have been only two

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reports of thallium-fluorine couplings [8, 11] and the signs were not determined. Recent syntheses of tetrafluorophenyl- and trifluorophenylthallium(III) compounds [12] have greatly extended the available range of polyfluorophenylthallium(III) compounds, previously restricted [6, 13] to pentafluorophenyl derivatives, and provide the basis for a comprehensive NMR survey. Accordingly, we now report a study of the ^{19}F NMR and PMR spectra of polyfluorophenylthallium(III) compounds.

EXPERIMENTAL

The PMR (90 MHz) and ^{19}F NMR (84.66 MHz) spectra were recorded in PFT mode with a Bruker WH 90 spectrometer operating at ca. 306^{o}K. For the PMR spectra, spectral widths of 1.2 KHz and accumulation of 8 K data points resulted in resolution of 0.3 Hz per channel. Chemical shifts are given in p.p.m. downfield from internal tetramethylsilane. The ^{19}F NMR spectra were obtained using a spectral width of 25 KHz and accumulation of 16 K data points, resulting in resolution of 3 Hz/channel. These spectra were then re-recorded with much smaller spectral widths, typically 2.5 KHz to 7.5 KHz (resolution 0.3-0.9 Hz/channel) to allow accurate determination of the coupling constants. Chemical shifts are given in p.p.m. upfield from internal $CFCl_3$. In general, deutero solvent were used (see Tables below) and the deuterium resonance served for field frequency stabilization. Where 1,4-dioxan was used as solvent, a D_2O capillary was added to provide field frequency stabilization. For both proton and fluorine spectra, 50-1000 pulses were accumulated at acquisition times of 1-4 sec/pulse. Complete proton decoupling of the ^{19}F NMR spectra was achieved using a broad band signal modulated at 90 MHz. Selective decoupling was achieved by applying a single frequency at or near that measured in the proton spectrum.

Preparations of tris(polyfluorophenyl)thallium(III) and bromobis-(polyfluorophenyl)thallium(III) compounds have been given [12, 14]. The nitrato derivative $(3,5\text{-}H_2C_6F_3)_2TlNO_3$ was prepared by the method reported for $(C_6F_5)_2TlNO_3$ [14] and was used without purification.

RESULTS AND DISCUSSION

1. PMR Spectra

Chemical shifts and thallium-proton coupling constants of R_2TlBr (R = o-HC_6F_4, m-HC_6F_4, p-HC_6F_4, 3,5-$H_2C_6F_3$, or 3,6-$H_2C_6F_3$) and R_3Tl(diox) (diox = 1,4-dioxan; R = m-HC_6F_4, p-HC_6F_4, or 3,5-$H_2C_6F_3$) complexes are given in Table 1. Proton-fluorine coupling is considered later [Section 2(b) and Table 3]. The trends in the coupling constants $^3J_{TlH} > {}^4J_{TlH} > {}^5J_{TlH}$ and $^nJ_{TlH(R_2TlBr)} > {}^nJ_{TlH(R_3Tl.diox)}$ (n = 3-5) are as previously observed for hydrocarbon arylthallium(III) compounds [3, 4]. Previous workers have shown that heavy atom-proton coupling is dominated by the Fermi contact interaction [3, 15-18]. On this basis, the increase in J_{TlH} from R_3Tl to R_2TlBr can be explained by an increase in the s character of the outer thallium electrons and an increase in the effective nuclear charge of thallium. Good agreement has been observed between the calculated $J_{TlH(R_3Tl)} : J_{TlH(R_2Tl^+)}$ ratio (1 : 1.8) and the observed ratios (1 : 1.7) [3] for hydrocarbon arylthallium(III) compounds. The $J_{TlH(R_3Tl.diox)} : J_{TlH(R_2TlBr)}$ ratio for the present compounds is 1 : 1.6 - 1.75. The values for $^nJ_{TlH}$ (n = 3-5) generally fall somewhat outside the ranges previously noted for these coupling constants [2-4]. Thus, for the diorganothallium compounds, $^3J_{TlH}$ and $^4J_{TlH}$ are somewhat larger than previous values (433-512 Hz and 104-208 Hz respectively [2-4]), whilst $^5J_{TlH}$ of (p-$HC_6F_4)_2TlBr$ is smaller than reported values (21-52 Hz [2-4]). For $^3J_{TlH}$ and $^4J_{TlH}$, the coupling is mainly transmitted via the σ-electrons, whereas for $^5J_{TlH}$ transmission via the π electrons is also considered to be important [3]. Fluorine is strongly inductively electron withdrawing (through σ-bonds) [19], hence multiple fluorine substitution could well markedly shift $^3J_{TlH}$ and $^4J_{TlH}$ from the usual value for hydrocarbon arylthallium(III) derivatives. By contrast, fluorine is electron donating by resonance effects (through π-bonds), hence multiple fluorine substitution could shift $^5J_{TlH}$ in the opposite direction from $^3J_{TlH}$ and $^4J_{TlH}$.

TABLE 1. PMR Data for the Compounds R_2TlX and $R_3Tl(diox)$ [a]

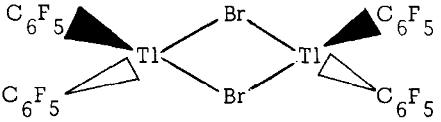
Compound	Solvent	δ	J_{TlH} [b]
$(o\text{-}HC_6F_4)_2TlBr$	$(CD_3)_2CO$	7.70	590
$(o\text{-}HC_6F_4)_2TlBr$	$(CD_3)_2SO$	7.70	601
$(m\text{-}HC_6F_4)_2TlBr$	$(CD_3)_2CO$	7.25	229
$(m\text{-}HC_6F_4)_2TlBr$	$(CD_3)_2SO$	7.42	237
$(p\text{-}HC_6F_4)_2TlBr$	$(CD_3)_2CO$	7.54	10
$(3,5\text{-}H_2C_6F_3)_2TlBr$	$(CD_3)_2CO$	7.00	176
$(3,5\text{-}H_2C_6F_3)_2TlBr$	$(CD_3)_2SO$	7.12	178
$(3,5\text{-}H_2C_6F_3)_2TlNO_3$	$(CD_3)_2SO$	7.32	197
$(3,6\text{-}H_2C_6F_3)_2TlBr$	$(CD_3)_2CO$	7.43 (H3)	269
		7.89 (H6)	557
$(3,6\text{-}H_2C_6F_3)_2TlBr$	$(CD_3)_2SO$	7.62 (H3)	270
		7.90 (H6)	564
$(m\text{-}HC_6F_4)_3Tl(diox)$	$(CD_3)_2SO$	7.37	143
$(p\text{-}HC_6F_4)_3Tl(diox)$	$(CD_3)_2SO$	7.70	~6 ± 2
$(3,5\text{-}H_2C_6F_3)_3Tl(diox)$	$(CD_3)_2SO$	7.02	112

[a] δ values ± 0.05 p.p.m. J values ± 1 Hz, except where indicated otherwise.

[b] Separate ^{203}TlH and ^{205}TlH couplings not resolved.

2. ^{19}F NMR Spectra

(a) Thallium-fluorine coupling constants: Values of $^nJ_{TlF}$ (n = 3-5) are given in Table 2. Signs of the constants have been determined for R_2TlBr (R = $o\text{-}HC_6F_4$, $m\text{-}HC_6F_4$, $3,5\text{-}H_2C_6F_3$, and $3,6\text{-}H_2C_6F_3$) and are discuss below. The only previously reported values for J_{TlF} in organometallic species are $^3J = 799$, $^4J = 343$, and $^5J = 99$ Hz for $(C_6F_5)_2TlBr$ in an unspecified solvent [11], and $^5J = 112$ and ca. 230 Hz for $(p\text{-}FC_6H_4)_2TlO_2CCF_3$ and $p\text{-}FC_6H_4Tl(O_2CCF_3)_2$ respectively in various solvents [8]. Some unpublished data for $(C_6F_5)_2TlBr$ in solvents (pyridine and methanol) not used in the present study are available [20] and are included in Table 2. The increase in $^{3}J_{TlF}$ of $(C_6F_5)_2TlBr$ in the solvent sequence, pyridine, perdeuteroacetone, methanol, and perdeuterodimethyl sulphoxide can be attributed to increased solvent polarity in the same sequence. A similar trend, except for inversion of the values in pyridine and acetone, is observed for $^{2}J_{TlH}$ of Et_2TlClO_4 in the same solvents [21]. On the other hand, $^{2}J_{TlH}$ of Me_2TlClO_4 shows little change in the first three solvents, but is markedly larger in the last [21]. Bromobis(pentafluorophenyl)thallium(III) is monomeric in acetone and has very low conductances (essentially a non-electrolyte) in pyridine, acetone, and methanol [14]. Probably, the complex is monomeric in pyridine, methanol, and dimethyl sulphoxide, as well as in acetone. The very low conductances increase in the solvent series, pyridine $\leqslant$ acetone < methanol, consistent with increased solvent polarity in the same sequence. However, the large $^{3}J_{TlF}$ value for $(C_6F_5)_2TlBr$ (Table 2) in C_6D_6 cannot be correlated with solvent polarity. The compound is dimeric (A) in benzene [14] (and



(A)

probably also in the solid state [22]), hence the result in this solvent is not strictly comparable with the values in solvents where monomeric species are established or likely. There is no clear relationship between $^{n}J_{TlH}$ of dimers and $^{n}J_{TlH}$ of comparable simpler species. Thus $^{2}J_{TlH}$ of the dimeric complex $(Et_2TlNMe_2)_2$ in benzene (382 Hz) [23] is at the high end of values for diethylthallium(III) compounds [21, 24], whereas $^{2}J_{TlH}$ of $(Me_2TlNMe_2)_2$ in benzene (342 Hz) [23, 25] is a low value for dimethylthallium(III) species [21]. Although $(C_6F_5)_2TlBr$ in C_6D_6 is expected to give a complex spectrum based on a $[A(MM'RXX')_2]_2$ spin system (A = Tl; M,M' = *o*-F; R = *p*-F; X,X' = *m*-F) with three possible combinations of thallium isotopes, $^{205}Tl_2$, $^{203}Tl_2$, and $^{205}Tl^{203}Tl$ (see e.g. a discussion of the PMR spectrum of $(Me_2TlNMe_2)_2$ [25]), the observed spectrum has the same appearance (except for the size of the coupling constants) as the

TABLE 2. Thallium-Fluorine Coupling Constants for R_2TlX and $R_3Tl(diox)$ Compounds [a]

Compound	Solvent	$^3J_{TlF}$			$^4J_{TlF}$			$^5J_{TlF}$
		F2	F2,6	F6	F3	F3,5	F5	F4
$(C_6F_5)_2TlBr$	C_5H_5N [b]		768 ± 4			341 ± 6		80 ± 2
	$(CD_3)_2CO$		780 ± 2			339 ± 2		82 ± 2
	CH_3OH [b]		802 ± 3			340 ± 5		82 ± 1
	$(CD_3)_2SO$		813.2 ± 0.5			361.4 ± 0.5		84.8 ± 0.5
	C_6D_6		868 ± 1			345 ± 1		79 ± 1
$(\underline{o}\text{-}HC_6F_4)_2TlBr$	$(CD_3)_2CO$	+1188 ± 5			+525 ± 1		+205.4 ± 0.5	-93.5 ± 0.5
$(\underline{m}\text{-}HC_6F_4)_2TlBr$	$(CD_3)_2CO$	+792 ± 1		+709 ± 1	+282 ± 1			-67 ± 1
	$(CD_3)_2SO$	856 ± 1		775 ± 1	309 ± 1			74 ± 1
	C_6D_6	848 ± 1		856 ± 1	290 ± 1			67 ± 1
$(\underline{p}\text{-}HC_6F_4)_2TlBr$	$(CD_3)_2CO$		783 ± 1			369 ± 1		
$(3,5\text{-}H_2C_6F_3)_2TlBr$	$(CD_3)_2CO$		+785.8 ± 0.5 +778.7 ± 0.5 } [c]					-22.5 ± 0.5
	$(CD_3)_2SO$		813.9 ± 0.5					22.8 ± 0.5
	C_6D_6		838.1 ± 0.5 831.0 ± 0.5 } [c]					20.5 ± 0.5

TABLE 2 (Cont'd.)

Compound	Solvent		$^3J_{\mathrm{TlF}}$			$^4J_{\mathrm{TlF}}$		$^5J_{\mathrm{TlF}}$
		F2	F2,6	F6	F3	F3,5	F5	F4
$(3,5\text{-}H_2C_6F_3)_2TlNO_3$	$(CD_3)_2SO$ [d]		950.5 ± 0.5 [c]					26.3 ± 0.5
			938.5 ± 0.5 [c]					
	CH_3OH [e]		945 ± 2					28 ± 2
$(3,6\text{-}H_2C_6F_3)_2TlBr$	$(CD_3)_2CO$	+1087 ± 1					+141.5 ± 0.5	-48.2 ± 0.5
	$(CD_3)_2SO$	1091.3 ± 0.5					147.1 ± 0.5	48.2 ± 0.5
	C_6D_6	1170 ± 5					139 ± 2	45 ± 2
$(C_6F_5)_3Tl(\text{diox})$	diox		546 ± 8			217 ± 8		58 ± 1
$(\underline{m}\text{-}HC_6F_4)_3Tl(\text{diox})$	diox	530 ± 1		472 ± 1	175 ± 1			46 ± 1
$(\underline{p}\text{-}HC_6F_4)_3Tl(\text{diox})$	diox		529 ± 1			232 ± 1		
$(3,5\text{-}H_2C_6F_3)_2Tl(\text{diox})$	diox		497 ± 1					14.3 ± 0.5

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[a] Except where indicated otherwise, $^nJ_{\mathrm{TlF}}$ values are the average of $J(^{205}Tl-^{19}F)$ and $J(^{203}Tl-^{19}F)$, since separate resonances could not usually be resolved. [b] From Ref. [20]. [c] $J(^{205}Tl-^{19}F)$ (higher value) and $J(^{203}Tl-^{19}F)$ (lower value) distinguished using proton decoupled spectra. [d] At 346°K. [e] Measurement at 56 MHz.

spectra in solvents in which the compound is probably monomeric. Such a simplification requires <u>either</u> small values for $^{2}J_{TlTl}$ and $^{5}J_{TlF}$ (the long range <u>ortho</u> coupling), <u>or</u> fast exchange between the dimer and a low concentration of monomer effectively reducing $^{2}J_{TlTl}$ and $^{5}J_{TlF}$ to zero. Since $^{2}J_{TlTl}$ is unlikely to be small ($^{2}J_{TlTl}$ of $(Me_2TlNMe_2)_2$ is 536.2 Hz [25]), rapid exchange is the more likely explanation. Solubility limitations and the high freezing point of the solvent prevented investigation of the spectrum at low temperatures. Monomer $\rightleftharpoons$ dimer exchange has been studied for $(Me_2TlNMe_2)_2$ [25] .

Where investigated, the spectra of the other R_2TlBr derivatives showed a solvent dependence similar to that of $(C_6F_5)_2TlBr$ (Table 2). The couplin constants $^{n}J_{TlF}$ of R_2TlBr and $R_3Tl(diox)$ (R = <u>m</u>-HC_6F_4, <u>p</u>-HC_6F_4, or 3,5-$H_2C_6F_3$) are of similar magnitude to the corresponding constants of $(C_6F_5)_2TlBr$ and $(C_6F_5)_3Tl(diox)$ respectively. However, the presence of an <u>ortho</u> hydrogen leads to greatly enhanced values of $^{3}J_{TlF}$ in (<u>o</u>-$HC_6F_4)_2TlBr$ and (3,6-$H_2C_6F_3)_2TlBr$ and of $^{4}J_{TlF3}$ (F3 ortho to two fluorines) in the former, and greatly reduced values of $^{4}J_{TlF5}$ (F5 ortho to fluorine and hydrogen) in both compounds. Increased coupling constants for (3,5-$H_2C_6F_3)_2TlX$ on changing from X = Br to X = NO_3 can be attributed to increased ionic character in the Tl-X bonds. Conductances of $(C_6F_5)_2TlNO_3$ are higher than those of $(C_6F_5)_2TlBr$ [14] . The general pattern of thallium-fluorine coupling constants $^{3}J_{TlF} > {}^{4}J_{TlF} > {}^{5}J_{TlF}$ and $^{n}J_{TlF(R_2TlBr)} > {}^{n}J_{TlF(R_3Tl.diox)}$ (R = C_6F_5, <u>m</u>-HC_6F_4, <u>p</u>-HC_6F_4, or 3,5-$H_2C_6F_3$) parallels the behaviour of the $^{n}J_{TlH}$ constants.

Since the signs of the thallium-proton coupling constants have been determined in diphenylthallium(III) compounds [2,3] , it was possible to obtain the signs of the thallium-fluorine coupling constants in the R_2TlBr (R = <u>o</u>-HC_6F_4, <u>m</u>-HC_6F_4, 3,5-$H_2C_6F_3$, or 3,6-$H_2C_6F_3$) derivatives by selective proton decoupling. Each proton signal consisted of two multiplets, separation J_{TlH}, corresponding to the α and β spins of the thallium atom. In all cases, recording the ^{19}F NMR spectrum whilst irradiating at or near the high field proton multiplet caused the high field multiplets of the ortho and the meta fluorines and the low field multiplet of the para fluorines to collapse. Thus, $^{3}J_{TlF}$ and $^{4}J_{TlF}$ have the same signs as $^{3}J_{TlH}$ and $^{4}J_{TlH}$ respectively and $^{5}J_{TlF}$ has the opposite sign to $^{5}J_{TlH}$. Since all thallium-proton coupling constants of Ph_2TlCl have positive signs [2,3], $^{3}J_{TlF}$ and $^{4}J_{TlF}$ are positive and $^{5}J_{TlF}$ is negative. Since the increase in thallium-fluorine coupling constants from R_3Tl(diox) to R_2TlBr (R = C_6F_5, p-HC_6F_4, m-HC_6F_4, or 3,5-$H_2C_6F_3$) is approximately the same for $^{3}J_{TlF}$, $^{4}J_{TlF}$, and $^{5}J_{TlF}$ [$^{n}J_{TlF(R_2TlBr)} : {}^{n}J_{TlF(R_3Tl.diox)}$ = 1.4-1.6 with $(CD_3)_2CO$ and dioxan as solvents for R_2TlBr and R_3Tl(diox) respectively, and 1.5-1.7 with $(CD_3)_2SO$ and dioxan as solvents], the coupling is probably dominated by a single mechanism, presumably the Fermi contact interaction, as has been argued on similar grounds for $^{4}J_{HgF}$ and $^{5}J_{HgF}$ of $(C_6F_5)_2Hg$ and $C_6F_5HgO_2CCH_3$ [17].* A similar increase (1.6-1.75) is observed for $^{n}J_{TlH}$ (n = 3-5), where the Fermi contact interaction is probably predominant (Section 1). However, the observation of a change in sign for $^{5}J_{TlF}$ of R_2TlBr raises the possibility of a modification of mechanism. Alternatively, if coupling to a para fluorine is transmitted via both σ and π electrons (as is coupling to a para hydrogen [3]) and if these effects are opposed, the net result could be the small negative coupling observed for $^{5}J_{TlF}$ or the small positive coupling observed [17] for $^{5}J_{HgF}$ of $(C_6F_5)_2Hg$.

(b) Fluorine-fluorine and proton-fluorine coupling constants

The values for fluorine-fluorine and proton-fluorine coupling constants are given in Table 3. For all the compounds studied, the resonances of

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* $^{n}J_{HgF(C_6F_5HgO_2CCH_3)} : {}^{n}J_{HgF[(C_6F_5)_2Hg]} \simeq 2.0$ for n = 4 or 5, whereas the ratio is $\simeq$1.3 for n = 3, suggesting two mechanisms contribute to the coupling [17].

TABLE 3. Fluorine-Fluorine and Proton-Fluorine Coupling Constants of R_2TlBr Compounds [a]

R	J_{23}	J_{24}	J_{25}	J_{26}	J_{34}	J_{35}	J_{36}	J_{45}	J_{46}	J_{56}
C_6F_5	[b]	~0	[b]	[b]	19.1	[b]	[b]	19.1	~0	[b]
o-HC_6F_4	26.8	2.4	13.6	[b]	19.3	~1.5	~2	19.7	8.2	8.6
m-HC_6F_4	25	7	~2	[b]	19	7	11	11	4	7
p-HC_6F_4	[b]	7.1	[b]	[b]	9.8	[b]	[b]	9.8	7.1	[b]
3,5-$H_2C_6F_3$	±7.0	8.2	∓1.5	0[c]	9.1	3.6[c]	∓1.5	9.1	8.2	±7.0
3,6-$H_2C_6F_3$	5.4	4.7	15.5	2.4	10.4	5.8	~0	20.1	9.7	9.3

[a] Values ± 0.5 Hz, except for (m-$HC_6F_4)_2TlBr$ (± 1 Hz) and cases where approximate values are indicated. The numbering of the substituents is as in the systematic names of the compounds.

[b] In all cases the resonances due to o-F and o-H were broad and this precluded determination of some of the couplings involving these nuclei.

[c] These assignments could possibly be reversed.

the *ortho* fluorines and *ortho* protons were broad, and this prevented determination of meaningful values of some constants. This may be caused by incomplete resolution of peaks associated with ^{205}Tl and ^{203}Tl nuclei. The difference between ^{205}Tl-X and ^{203}Tl-X (X = H or F) couplings should be *ca.* 1% [18], i.e. *ca.* 8 Hz when J_{TlX} is *ca.* 800 Hz (see e.g. Table 2). All the resonances of the R_3Tl(diox) complexes are broad and only $^{n}J_{TlH}$ and $^{n}J_{TlF}$ could be obtained from these spectra. Decreased resolution with increased number of pentafluorophenyl substituents has previously been observed for organogermanes [6], and is considered to arise *either* from restricted rotation which prevents averaging out of dipole-dipole interactions *or* from increased inter-ring F-F coupling. The values for J_{FF} and J_{HF} (Table 3) generally fall within the ranges reported for these couplings [6,7,17,26]. The largest values of $^{3}J_{FF}$ are obtained when one of the fluorines is *ortho* to thallium. This has previously been seen for other heavy metal pentafluorophenyl derivatives [6,7,17]. Analysis of the PMR spectrum of $(3,5\text{-}H_2C_6F_3)_2TlBr$ showed that $J_{23}(^3J_{FH})$ and $J_{25}(^5J_{FH})$ have opposite signs, though the absolute signs were not determined. Usually, $^3J_{FH}$ and $^4J_{FH}$ are positive and $^5J_{FH}$ is negative [27].

(c) Chemical Shifts

The ^{19}F NMR chemical shifts for the compounds R_2TlBr and R_3Tl(diox) are given in Table 4, and are similar to those of corresponding mercurials where they are known [17,28]. As observed for other heavy metal substituents [6,7], the *ortho* fluorines are markedly shifted to low field by thallium atoms. An explanation of this effect has been given [6,17,26]. Substituent chemical shifts relative to hexafluorobenzene (162.9 p.p.m. upfield from $CFCl_3$ [26]) calculated from the data of Table 4 are (- 40) — (- 46) p.p.m. for an *ortho* thallium, (- 4.0) — (+ 4.0) p.p.m. for a *meta* thallium, and (- 7) — (- 11.5) for a *para* thallium substituent. Observation of some variation between the compounds is hardly surprising

TABLE 4. ^{19}F Chemical Shifts for R_2TlBr and R_3Tl(diox) Complexes [a]

Compound	δ (F2)	δ (F3)	δ (F4)	δ (F5)	δ (F6)
$(C_6F_5)_2TlBr$	119.7	160.4	152.5	160.4	119.7
(*o*-$HC_6F_4)_2TlBr$	117.8	154.9	154.3	138.2	
(*m*-$HC_6F_4)_2TlBr$	114.2	165.5	131.2		94.4
(*p*-$HC_6F_4)_2TlBr$	120.7	137.8		137.8	120.7
$(3,5\text{-}H_2C_6F_3)_2TlBr$	88.7		106.8		88.7
$(3,5\text{-}H_2C_6F_3)_2TlNO_3$	89.4		104.8		89.4
$(3,6\text{-}H_2C_6F_3)_2TlBr$	94.7		131.9	142.6	
$(C_6F_5)_3Tl$(diox)	118.1	159.3	151.5	159.3	118.1
(*m*-$HC_6F_4)_3Tl$(diox)	112.1	165.2	131.8		93.4
(*p*-$HC_6F_4)_3Tl$(diox)	119.3	137.6		137.6	119.3
$(3,5\text{-}H_2C_6F_3)_3Tl$(diox)	86.8		108.5		86.8

[a] In $(CD_3)_2CO$ (R_2TlBr), 1,4-dioxan (R_3Tl.diox), or $(CD_3)_2SO$ (R_2TlNO_3). Values ± 0.1 p.p.m.

since it is the effect of R_2Tl- and RTlBr- substituents that is being assessed and not the effect of isolated thallium substituents. Thus changes in R must cause some modification of the substituent effects. In any case, reported substituent chemical shifts [26] have errors (± 3 p.p.m.) giving ranges of values comparable to those in the present study. The effects of the thallium substituents are comparable to those of iodine [26] or mercury [28] .

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