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ARYLTHALLIUM TRIFLUOROACETATES

CARBON-13 AND FLUORINE-19 NUCLEAR MAGNETIC RESONANCE: THE SUBSTITUENT EFFECT OF THE BIS(TRIFLUOROACETATO)-THALLIUM(III) GROUP

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Summary

^{13}C NMR data for a series of arylthallium trifluoroacetates ($ArTlX_2$, X = $OCOCF_3$) are reported and assigned. The range of carbon—thallium couplings to be expected, the dependence on the disposition of coupled nuclei, and chemical shift effects are discussed. The $Tl(OCOCF_3)_2$ group is shown to be a powerful electron withdrawing group, from both the ^{13}C data and ^{19}F substituent chemical shifts of the *p*-fluorophenyl derivative.

Organothallium chemistry is currently an area of great interest [1, 2], but this renaissance has not included any ^{13}C NMR studies, which are of increasing importance in bonding and general constitutional aspects of organometallic chemistry. We report ^{13}C NMR studies of a series of arylthallium trifluoroacetates [1, 3], which indicate the range of carbon—thallium coupling constants to be expected, the dependence on disposition of the coupled nuclei, and chemical shift effects. ^{19}F substituent chemical shifts of *p*-fluorophenyl derivatives, and these ^{13}C data, explain an important characteristic of aromatic thallation by $Tl(OCOCF_3)_3$ in CF_3COOH viz. the absence of di- or poly-thallated products [4].

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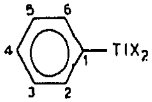
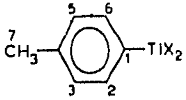
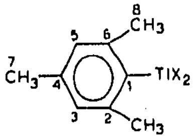
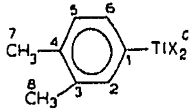
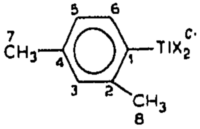
TABLE 1

^{13}C CHEMICAL SHIFTS AND ^{13}C—^{203,205}Tl COUPLING CONSTANTS

X = OCOCF$_3$. $>\underline{C}=O$ at 162.4 ppm [J(C—F) 41 Hz] and $\underline{C}F_3$ at 118.7 ppm [J(C—F) 287 Hz]

Entry	Compound	1	2	3	4	5	6	7	8
1		150 (9902) ^{b}	137.5 (676)	126.9 (878)	130.7 (183)	126.9 (878)	137.5 (676)		
2		143 (9756) ^{b}	137.4 (756)	127.0 (895)	141.0 (195)	127.0 (895)	137.4 (756)	20.4 (110)	
3		150.3 (8841) ^{b}	141.6 (512)	129.3 (968)	141.3 (166)	129.3 (968)	141.6 (512)	20.1 (107)	23.8 (459)
4		143.7 (9634) ^{b}	134.0 (565)	137.1 (800)	140.2 (183)	125.5 (820)	132.0 (~500)		19.7 (br)
5		146.3 (9329) ^{b}	140.9 (549)	126.9 (793)	d	123.4 (849)	137.1 (646)	21.0 (br)	23.9 (402)

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[a] Spectra were recorded in the FT mode for undegassed THF solutions at 22.6 MHz. The α-carbon of THF was taken as 67.0 ppm from TMS. Quoted values in ppm from TMS. Values in parentheses are coupling constants in Hz. [b] Broader peaks, due in part to partial resolution of coupling from ^{203}Tl and ^{205}Tl (γ ratio —1.0098). Other factors may also contribute. [c] Other than J_1, data here to be regarded as less precise, due to much signal overlapping. [d] C_4 doublet completely obscured but ca. 140 ppm.

The ^{13}C data are assembled in Table 1. C_1 (bearing thallium) was assigned on the basis of its large one-bond coupling (9—10 kHz) and large α-effect (downfield by $\approx$ 20 ppm) of the thallium group. With a pulse interval of 1 s, the *p*-tolyl derivative showed (besides signals for $\underline{C}_1$, CH_3 and $O\underline{C}O\underline{C}F_3$) two doublets of essentially equal intensity, with another doublet of ca. 1/5 the above intensity. This is consistent with the expectation of very similar T_1 values for protonated *ortho* (C_2, C_6) and *meta* (C_3, C_5) carbons (both T_1 much less than pulse spacing) and a longer T_1 (and much longer than pulse spacing) for C_4 (bearing the CH_3 group) resulting in some saturation and loss of intensity. The mesityl derivative [$ArTl(OCOCF_3)_2$; Ar = 2,4,6-trimethylphenyl] under the same conditions, showed one strong doublet (in the aryl region) which must be assigned to the protonated $C_{3,5}$, and two other doublets (with intensity ratio of ca. 2/1) assigned to $C_{2,6}$ and C_4 respectively, consistent with these methylated carbons having longer T_1 values (and comparable to pulse spacing) than $C_{3,5}$. On these bases, consistent patterns of chemical shifts and coupling constants emerged. In line with the above, examination of $Ar_2TlOCOCF_3$ (Ar = 2-deutero-4-methyl) confirmed $J(Tl—C_{meta}) > J(Tl—C_{ortho})$.

Regarding coupling constants, the one-bond coupling of 9—10 kHz is noteworthy and probably associated with the high effective nuclear charge on thallium as well as the large gyromagnetic ratio. The sequence $J(Tl—C_{meta}) > J(Tl—C_{ortho}) > J(Tl—C_{para})$ concurs with data for phenyl derivatives of other heavy metals (e.g. Hg, Sn, Pb) [5, 6] * with the *meta*-carbon and metal defining a strictly *trans* planar array**. Methyl substitution, particularly *ortho* or *para* to thallium, decreases the one-bond coupling significantly. Comparisons of coupling in alkyl and aryl derivatives of other metals (e.g. Sn, Hg) [6, 8] * lead to the suggestion that the *J* values reported herein will be a guide to couplings in alkylthallium compounds, and where a strong angular dependence of vicinal coupling is anticipated [9, 10] ***.

Compared with the parent hydrocarbon [12], C_1 and *ortho* carbons experience substantial downfield shifts (α and β effects) of 18—23 ppm and 5—9 ppm respectively, while *meta*-carbons in the main, experience upfield (γ) effects of 0—2 ppm‡. A significant trend is discerned in the substituent chemical shift (SCS) values‡‡ of C_4 (*para* to Tl) in entries 1—3 of Table 1 where values of +2.3, +3.2 and +3.7 ppm are observed, and imply substantial electron-withdrawal by $Tl(OCOCF_3)_2$.

Examination of the ^{19}F spectra of *p*-$FC_6H_4Tl(OCOCF_3)_2$ in a number of solvents confirms the above effect (Table 2). The SCS value‡‡ of —9.3 ppm for CF_3COOH solvent can be compared with SCS values of ca. —5 and —10 ppm for *p*-CF_3 and *p*-NO_2 respectively [12]. This powerful electron-withdrawal

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* For Hg, Sn and Pb this sequence is proven by deuteration (unpublished results).

** For proton—thallium coupling [$J(H—Tl)$] the sequence $J_{ortho} > J_{meta} > J_{para}$ exists [3] as it does in phenylmercury compounds. See ref. 7.

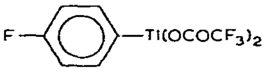
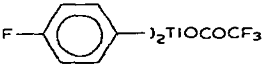
*** A pronounced "Karplus type" dependence of vicinal $^{199}Hg—^{13}C$ coupling has been demonstrated (ref. 10).

‡ These trends are manifested in phenyl type derivatives of other heavy metals, e.g., in phenyltrimethyllead, α, β, γ effects [of the $Pb(CH_3)_3$ group] of +20, +8.0 and —0.1 ppm, respectively.

‡‡ ^{13}C substituent chemical shift of the substituted compound and that of the appropriate carbon in the parent hydrocarbon.

TABLE 2

^{19}F SUBSTITUENT CHEMICAL SHIFTS OF *para*-FLUOROPHENYLTHALLIUM SYSTEMS [a]

Compound	Solvent	SCS(ppm) [b]	J(Tl—F)
	CF_3COOH	—9.3	240
	Pyridine	—2.4	230
	DMSO	—2.1	240
	THF	—4.1	233
	Dioxan	—4.5	226
	$CHCl_3$ [c]	—6.0	
	Pyridine	—1.0	113
	THF	—1.8	112

[a] Spectra were recorded for ca. 10—12 weight/volume percent solutions at 56.44 MHz (no ^{1}H decoupling) using tetrafluorotetrachlorocyclobutane as a lock. Chemical shifts were initially measured from added *p*-fluorotoluene and then converted to SCS values (i.e. from fluorobenzene) by subtracting 5.5 ppm.
[b] Minus sign indicates to lower field. [c] While the doublet signals varied in sharpness for other solvents, one broad resonance was observed for $CHCl_3$. On addition of a small amount of THF, the broad "hump" separated into a doublet. This behaviour could indicate transfer of *p*-fluorophenyl groups in this solvent (erased Tl—F coupling) but more studies are required.

probably accounts for the absence of dithallation*. There is the anticipated reduction in the SCS as the donor action of solvent improves, while the reduced SCS and J(Tl—F) values for $(p\text{-}FC_6H_4)_2TlOCOCF_3$ are associated with less electron deficiency at the metal.

This, and other chemical and spectroscopic information on thallation and oxythallation, will be discussed in detail at a later date.

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* For other discussions of the substituent effects of metal-containing groups (by ^{19}F resonance) see ref. 13.