Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THALLIUM IN ORGANIC SYNTHESIS
XVIII*. SYNTHESIS AND SPECTROSCOPIC STUDIES OF $ArTlX_2$ AND Ar_2TlX COMPOUNDS

ALEXANDER McKILLOP AND JOHN D. HUNT
School of Chemical Sciences, University of East Anglia, Norwich, NOR88C (Great Britain)
EDWARD C. TAYLOR
Department of Chemistry, Princeton University, Princeton, N.J., 08540 (U.S.A.)

(Received March 4th, 1970)

SUMMARY

General procedures for the preparation of arylthallium dichlorides and difluorides via the readily available arylthallium bis(trifluoroacetates) are described. The latter compounds have been found to undergo symmetrisation to the corresponding diarylthallium trifluoroacetates in variable yields when heated with water or acetone. A much improved, general synthesis of diarylthallium trifluoroacetates has been discovered, however, consisting simply of treatment of arylthallium bis(trifluoroacetates) with trimethyl phosphite. NMR and IR data for $ArTlX_2$ and Ar_2TlX compounds are presented, and their application to structure determination discussed.

INTRODUCTION

Direct thallation of aromatic compounds with thallium(III) trifluoroacetate has been shown to lead to high yields of arylthallium bis(trifluoroacetates), the reaction proceeding under mild conditions[1]. Organothallium derivatives of the type $ArTlX_2$ are attractive intermediates for the synthesis of a wide range of organic and organometallic compounds; applications to the preparation of aromatic iodides[2a], nitriles [2b] and phenols[2b] have recently been described. Prior to the development of thallium(III) trifluoroacetate as a thallating reagent, $ArTlX_2$ compounds were available only by one of three rather restricted routes. The first of these, symmetrisation of a diarylthallium(III) compound with a thallium(III) halide [eqn. (1)], has been little investigated[3]. The remaining methods, both of which are limited by the relative accessibility of the requisite starting materials, are standard organometallic reactions involving the use of organoborane[4,5] [eqn. (2)] and organomercury[6] [eqn. (3)] derivatives. A number of classical procedures have been described for the preparation

$$Ar_2TlX + TlX_3 \rightarrow 2\,ArTlX_2 \qquad (1)$$

---

* For Part XVII see ref. 22.

of Ar_2TlX compounds, most of which proceed in satisfactory yield, and these methods have been reviewed[7,8].

$$ArB(OH)_2 + TlX_3 \rightarrow ArTlX_2 + BX(OH)_2 \quad (2)$$

$$Ar_2Hg + Tl[OOCCH(CH_3)_2]_3 \rightarrow ArTl[OOCCH(CH_3)_2]_2 + HgOOCCH(CH_3)_2 \quad (3)$$

RESULTS AND DISCUSSION

Organothallium derivatives of the type $ArTlX_2$ are normally regarded as being at least partially ionic in nature ($ArTlX^+ \cdot X^-$)[9,10] and this property has occasionally been utilised to alter the nature of X. Thus treatment with inorganic nucleophiles, Y^-, generally* leads to simple replacement, with formation of the corresponding $ArTlY_2$ derivative [eqn. (4)][4,5,11].

$$ArTlX_2 + 2\,Y^- \rightarrow ArTlY_2 + 2\,X^- \quad (4)$$

In our experience, the stability of $ArTlX_2$ compounds varies considerably and often erratically with the nature of X. We have therefore studied the reaction of arylthallium bis(trifluoroacetates) with inorganic halides, where a clear trend in the stability of the resulting $ArTlX_2$ derivatives exists. Thus treatment of arylthallium bis(trifluoroacetates) with aqueous potassium iodide leads directly to the corresponding aromatic iodide and thallium(I) iodide, presumably via formation of the unstable arylthallium diiodide [eqn. (5)][2a]. All attempts to isolate or intercept arylthallium diiodides in this process were unsuccessful, thus confirming Challenger's

$$ArTl(OOCCF_3)_2 + 2\,KI \rightarrow [ArTlI_2] \rightarrow ArI + TlI + 2\,K^{+\,-}OOCCF_3 \quad (5)$$

earlier observation on the instability of phenylthallium diiodide[4]. Addition of aqeuous potassium bromide to solutions of arylthallium bis(trifluoroacetates) at 0–5° results in rapid replacement of CF_3COO^- by Br^- and formation of the corresponding arylthallium dibromides. These compounds generally precipitate from solution but are very unstable, and undergo decomposition rapidly either on storage or on gentle heating. The major products of decomposition are the aromatic bromide and thallium(I) bromide, but small amounts of diarylthallium bromide are also produced (10–20%).

In contrast to the bromides and iodides, arylthallium difluorides and dichlorides are stable crystalline solids which show little tendency either to decompose or symmetrise under normal storage conditions. These compounds were prepared by addition of aqueous potassium fluoride or chloride to solutions of arylthallium bis(trifluoroacetates) in aqueous ethanol. This simple procedure normally proceeds in high yield, and is complete within a few minutes at room temperature. The overall sequence involving thallation followed by treatment with inorganic halide thus represents a valuable alternative to the previous methods for the synthesis of these compounds. Experimental data for typical conversions are summarized in Table 1.

The symmetrisation process shown in eqn. (6) is a well-known, if poorly under-

$$2\,ArTlX_2 \rightarrow Ar_2TlX + TlX_3 \quad (6)$$

---

* Simple replacement is not always straightforward, and in certain cases complex ions are produced; see refs. 5 and 23.

TABLE 1

EXPERIMENTAL DATA FOR REPRESENTATIVE ARYLTHALLIUM DIFLUORIDES AND DICHLORIDES, $ArTlX_2$

Ar	X	Yield (%)	M.p. (°C)[a]	Molecular formula	Analysis found (calcd.) (%)	
					C	H
C_6H_5	F	95	>300	$C_6H_5F_2Tl$	22.32 (22.56)	1.96 (1.58)
	Cl	40	212–214	$C_6H_5Cl_2Tl$	20.69 (20.45)	1.76 (1.43)
4-ClC_6H_4[b]	F	61	>300	$C_6H_4ClF_2Tl$	20.02 (20.36)	1.40 (1.14)
	Cl	31	282–286	$C_6H_4Cl_3Tl$	18.69 (18.63)	1.08 (1.04)
2,4-$(CH_3)_2C_6H_3$	F	95	178–189	$C_8H_9F_2Tl$	28.14 (27.64)	2.56 (2.61)
	Cl	28	178–180	$C_8H_9Cl_2Tl$	25.34 (25.26)	2.48 (2.38)
2,5-$(CH_3)_2C_6H_3$	F	98	186–188	$C_8H_9F_2Tl$	27.85 (27.64)	2.75 (2.61)
	Cl	71	194–197	$C_8H_9Cl_2Tl$	25.42 (25.26)	2.48 (2.38)
3,4-$(CH_3)_2C_6H_3$	F	93	195–204	$C_8H_9F_2Tl$	27.85 (27.64)	2.68 (2.61)
	Cl	83	188–190	$C_8H_9Cl_2Tl$	25.56 (25.26)	2.59 (2.38)
2,4,6-$(CH_3)_3C_6H_2$	F	93	243–246	$C_9H_{11}F_2Tl$	30.00 (29.90)	3.20 (3.07)
	Cl	89	>300	$C_9H_{11}Cl_2Tl$	27.43 (27.40)	2.59 (2.81)
4-$CH_3OC_6H_4$[b]	F	51	>300	$C_7H_7F_2OTl$	23.80 (24.05)	2.43 (2.02)
	Cl	63	>300	$C_7H_7Cl_2OTl$	21.52 (21.98)	2.06 (1.85)

[a] All compounds melted with decomposition. [b] Probably contains small amounts of *ortho* and *para* isomers (see refs. 2a and 2b).

stood, phenomenon in organothallium chemistry[12], and one which we encountered early in our investigations into the chemistry of arylthallium bis(trifluoroacetates). Attempted recrystallisation of these latter compounds from water or acetone, for example, frequently resulted in partial symmetrisation to the corresponding diarylthallium trifluoroacetate [eqn. (6), $X = OOCCF_3$]. This process could be carried to completion by prolonged reflux of the solutions, but a much simpler procedure for effecting the same transformation was found to consist of treatment of the arylthallium bis(trifluoroacetate) with trimethylphosphite. Admixture of the two reagents results in a rapid, exothermic reaction, the mechanism of which is obscure. The diarylthallium trifluoroacetate is isolated by dilution of the reaction mixture with water and filtration. Experimental data for $Ar_2TlOOCCF_3$ compounds prepared in this way are summarised in Table 2.

Ar_2TlX compounds are highly ionic species $(Ar_2Tl^+ \cdot X^-)$[13] which rapidly and quantitatively undergo anion exchange with inorganic nucleophiles[14]. As a

TABLE 2

EXPERIMENTAL DATA FOR REPRESENTATIVE DIARYLTHALLIUM TRIFLUOROACETATES, $Ar_2TlOOCCF_3$

Ar	Yield (%)	M.p. (°C)	Molecular formula	Analysis found (calcd.) (%)	
				C	H
C_6H_5	67	258–264	$C_{14}H_{10}F_3O_2Tl$	35.58	2.38
				(35.65)	(2.14)
4-FC_6H_4[a]	83	268–270	$C_{14}H_8F_5O_2Tl$	32.89	2.09
				(33.13)	(1.89)
4-ClC_6H_4[a]	92	>300	$C_{14}H_8Cl_2F_3O_2Tl$	30.93	1.98
				(31.11)	(1.71)
4-$CH_3C_6H_4$[a]	87	261–264	$C_{16}H_{14}F_3O_2Tl$	38.33	2.89
				(38.46)	(2.82)
2,4-$(CH_3)_2C_6H_3$	99	265–267	$C_{18}H_{18}F_3O_2Tl$	40.52	3.38
				(40.97)	(3.44)
2,5-$(CH_3)_2C_6H_3$	98	260–264	$C_{18}H_{18}F_3O_2Tl$	40.48	3.43
				(40.97)	(3.44)
3,4-$(CH_3)_2C_6H_3$	98	223–226	$C_{18}H_{18}F_3O_2Tl$	40.93	3.70
				(40.97)	(3.44)
2,4,6-$(CH_3)_3C_6H_2$	71	196–198	$C_{20}H_{22}F_3O_2Tl$	43.09	4.05
				(43.22)	(3.99)

[a] Probably contains small amounts of *ortho* and *para* isomers (see refs. 2a and 2b).

consequence, symmetrisation of $ArTl(OOCCF_3)_2$ to $Ar_2TlOOCCF_3$, followed by treatment with X^- represents a general entry into Ar_2TlX compounds.

SPECTROSCOPIC STUDIES*

High resolution IR spectroscopic studies of arylthallium compounds have been reported for only a few derivatives, and in most cases the assignments of C–Tl stretching vibrations were tentative. Beck and Schuierer[15], in a study of diphenylthallium bromide, reported strong absorptions at 452 and 410 cm^{-1} which they assigned to the asymmetric and symmetric C–Tl–C stretching frequencies respectively**.

There are no strong absorptions above 400 cm^{-1} in the spectra of diarylthallium trifluoroacetates which can be unambiguously assigned to C–Tl stretching vibrations. The spectra of arylthallium bis(trifluoroacetates), on the other hand, always show two medium intensity absorptions at about 500 and 580 cm^{-1}, and which we conclude are the C–Tl stretching vibrations. The most interesting region in the spectra of arylthallium bis(trifluoroacetates) and diarylthallium trifluoroacetates lies between 600 and 900 cm^{-1}. All of these compounds show three sets of absorptions at approximately 720, 800 and 835 cm^{-1} which are assignable respectively to the $C–CO_2$ in-plane bending, CF_3 symmetric stretching, and C–C stretching modes of the trifluoroacetate group[16,17]. For diarylthallium trifluoroacetates these

---

* A number of unsuccessful attempts were made to determine the Raman spectra of $ArTl(OOCCF_3)_2$ and $Ar_2TlOOCCF_3$ compounds. Failure here may have been due to the fine crystalline form of these compounds, which resulted in Rayleigh rather than Raman scattering. It is interesting to note, however, that Deacon and Green[24] were also unsuccessful in attempts to record the Raman spectrum of crystalline diphenylthallium bromide.

**The corresponding vibrations in the alkyl analogues are usually in the region 530 and 470 cm^{-1}; see refs. 24 and 25.

absorptions are sharp singlets, but for arylthallium bis(trifluoroacetates) they are *always* sharp doublets. Representative spectra, which illustrate this phenomenon and clearly establish the utility of IR spectroscopy in structure elucidation, are reproduced in Figs. 1–3. It is possible that the doublets observed in the spectra of the arylthallium bis(trifluoroacetates) originate from their ionic nature, which leads to two distinctly different trifluoroacetate entities ($ArTlOOCCF_3^+ \cdot CF_3COO^-$)*.

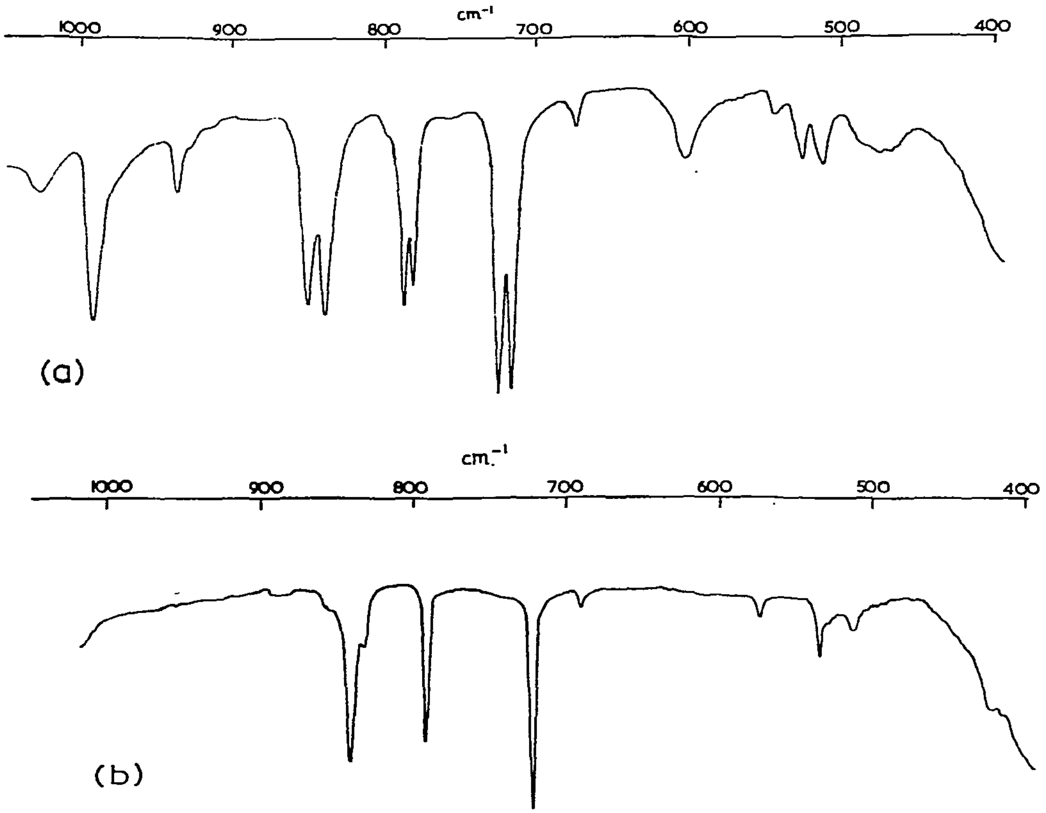

Fig. 1. IR spectra of (a) mesitylthallium bis(trifluoroacetate) and (b) dimesitylthallium trifluoroacetate.

There has been considerable recent interest in the NMR spectra of organothallium compounds[18]. We have examined in detail the spectra of a large number of compounds of the types $ArTl(OOCCF_3)_2$ and $Ar_2TlOOCCF_3$. Both of the naturally occurring isotopes of thallium ($^{205}Tl/^{203}Tl$: 70/30) have nuclear spin values of one half; ^{205}Tl–H coupling constants are, however, only slightly larger than ^{203}Tl–H coupling constants ($^{205}\gamma/^{203}\gamma = 1.0098$)[19]. Hence separate signals due to the two isotopes are clearly distinguishable only in very simple molecules[20], and in the subsequent discussion quoted Tl–H coupling constants refer to average values, which are due primarily to ^{205}Tl–H spin–spin interactions.

In general, Tl–H coupling constants are numerically very large, and the magni-

---

* The IR spectrum of phenylthallium diacetate also shows absorptions due to two different acetoxy groups. These were similarly presumed to be a consequence of the ionic nature of the compound in the solid state; see ref. 26.

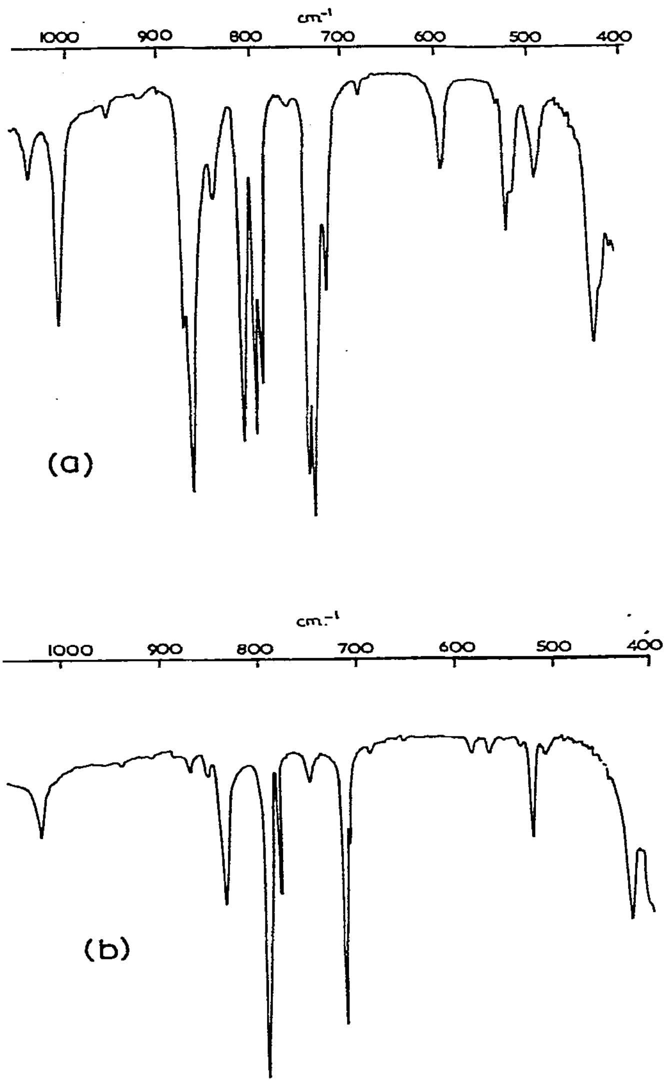

Fig. 2. IR spectra of (a) 2,4-xylylthallium bis(trifluoroacetate) and (b) di-2,4-xylylthallium trifluoroacetate.

tude of the values has been explained qualitatively on the basis of a Fermi contact interaction as a result of the large effective nuclear charge on the thallium atom[9,19]. In benzene and substituted benzenes, for example, Tl–H coupling constants are approximately 130 times greater than the corresponding H–H values. With respect to structure elucidation, moreover, two empirical observations made by Maher and Evans have proved invaluable in the present work. Firstly, the ratios of the Tl–H coupling constants for the series Ar_3Tl, Ar_2TlX and $ArTlX_2$ have been shown to be approximately 1/1.7/4 regardless of the nature of the Ar group[9,21]. Secondly, Maher and Evans[9] argued that coupling to *ortho* and *meta* positions is transmitted mainly via the σ-electrons, but that transmission via the π-electrons becomes important in coupling to the *para* position. This rationalisation then accounts reasonably for the

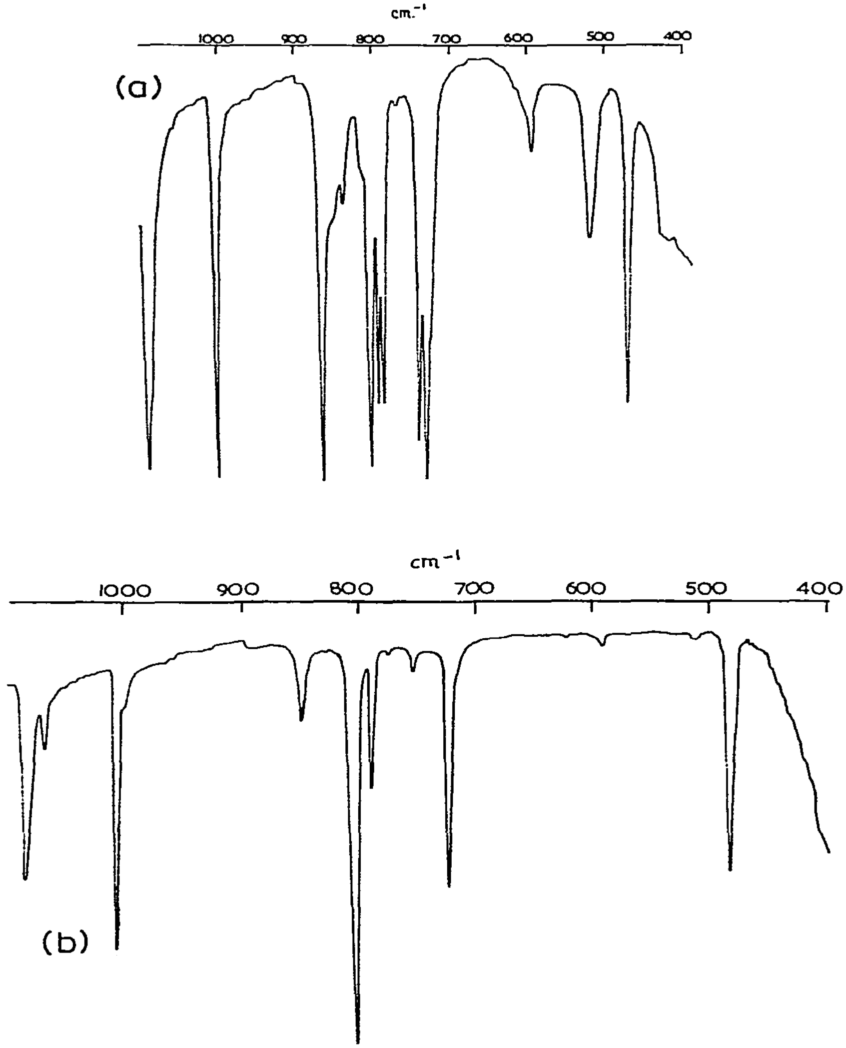

Fig. 3. IR spectra of (a) (*p*-chlorophenyl)thallium bis(trifluoroacetate) and (b) bis(*p*-chlorophenyl)thallium trifluoroacetate.

experimental observation that $J[\text{Tl–H}(p\text{-CH}_3)]$ is larger than $J[\text{Tl–H}(m\text{-CH}_3)]$.

The results of our studies are in complete agreement with those of Maher and Evans. Typical pairs of spectra are reproduced in Figs. 4–6, and coupling data are listed in Tables 3 and 4. In Table 5, the ratios for the coupling constants of $ArTl(OOCCF_3)_2$ and $Ar_2TlOOCCF_3$ are presented; the correlation of these figures with the value of 2.35 estimated by Maher and Evans in most cases is excellent.

From the above discussion it is evident that NMR spectroscopy offers an unambiguous method not only for distinguishing between Ar_2TlX and $ArTlX_2$ compounds, but also for determination of the orientation of the carbon–thallium bond.

(*continued* p. 87)

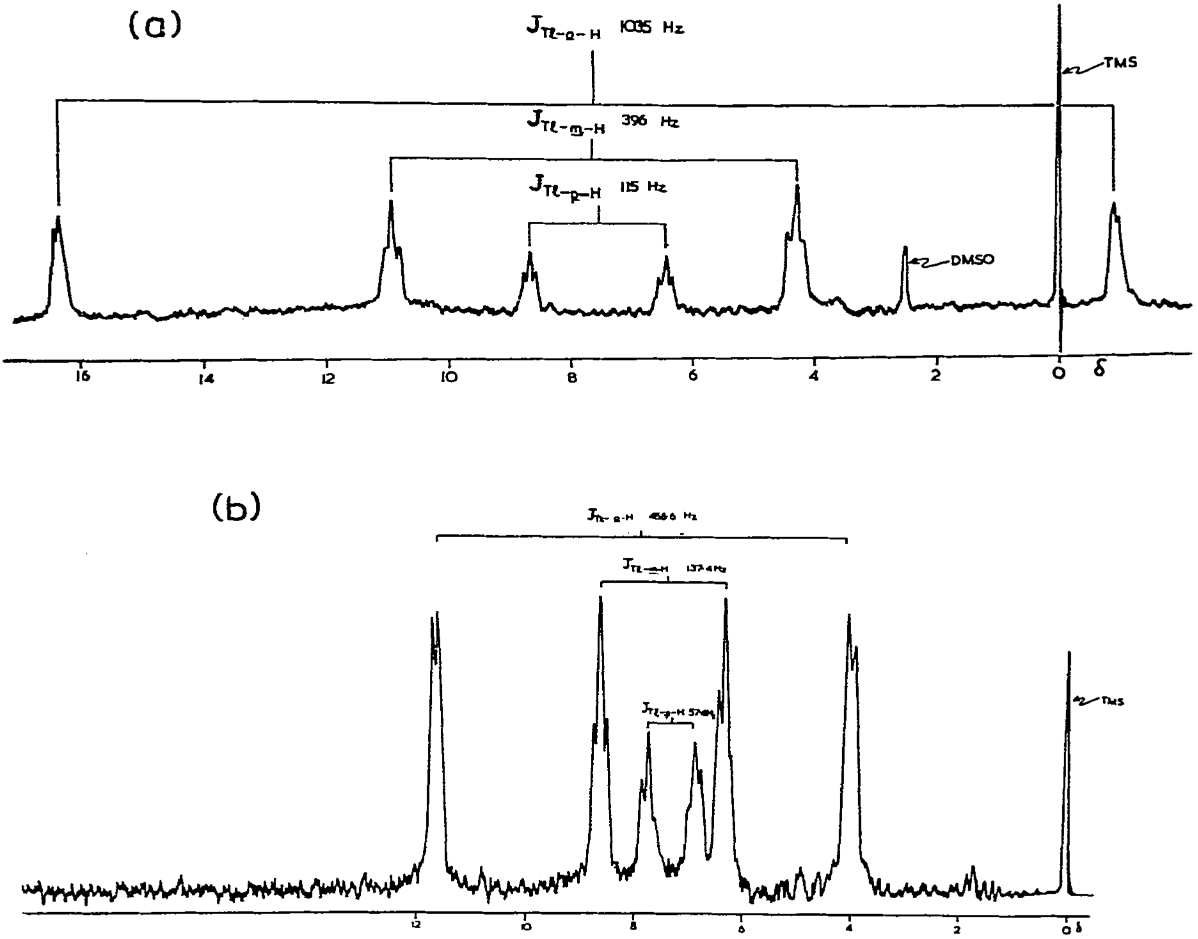

Fig. 4. NMR spectra of (a) phenylthallium bis(trifluoroacetate) and (b) diphenylthallium trifluoroacetate.

TABLE 3

Tl–H COUPLING CONSTANTS (Hz) FOR ARYLTHALLIUM BIS(TRIFLUOROACETATES), $ArTl(OOCCF_3)_2$

Ar	*o*-H	*m*-H	*p*-H	*o*-CH_3	*m*-CH_3	*p*-CH_3
C_6H_5	1035	396	115			
$4-FC_6H_4$	960	280				
$4-ClC_6H_4$	965	296				
$4-CH_3C_6H_4$	1025	376				66
$2,4-(CH_3)_2C_6H_3$	1065	496		111		65
$2,5-(CH_3)_2C_6H_3$	1109	559	115	113	55	
$3,4-(CH_3)_2C_6H_3$	1040	420			60	66
$2,4,6-(CH_3)_3C_6H_2$		460		114		64
$4-CH_3CH_2C_6H_4$	1059	394				(49)
$2-COOHC_6H_4$	1010	430	124			

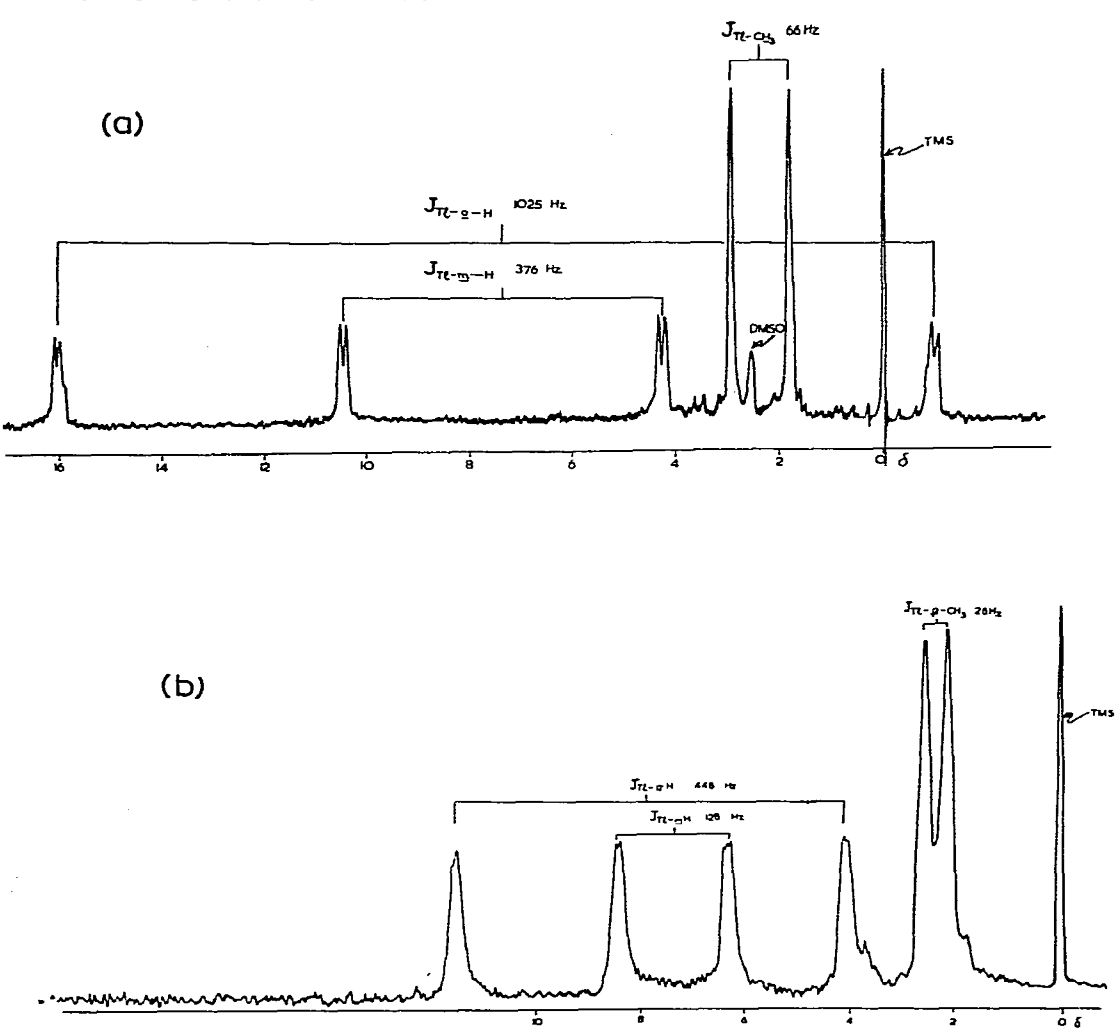

Fig. 5. NMR spectra of (a) *p*-tolylthallium bis(trifluoroacetate) and (b) di-*p*-tolylthallium trifluoroacetate.

TABLE 4

TI–H COUPLING CONSTANTS (Hz) FOR DIARYLTHALLIUM TRIFLUOROACETATES, $Ar_2TlOOCCF_3$

Ar	*o*-H	*m*-H	*p*-H	*o*-CH_3	*m*-CH_3	*p*-CH_3
C_6H_5	455	117	515			
4-FC_6H_4	448	104				
4-ClC_6H_4	456	113				
4-BrC_6H_4	455	115				
4-$CH_3C_6H_4$	448	128				24
2,4-$(CH_3)_2C_6H_3$	441	206		46.7		25.3
2,5-$(CH_3)_2C_6H_3$	454	208	40	48	17.6	
3,4-$(CH_3)_2C_6H_3$	456	141.2			23	27.6
2,4,6-$(CH_3)_3C_6H_2$		168		49		36
4-$CH_3OC_6H_4$	433	106				
4-$CH_3CH_2C_6H_4$	445	128				(21)

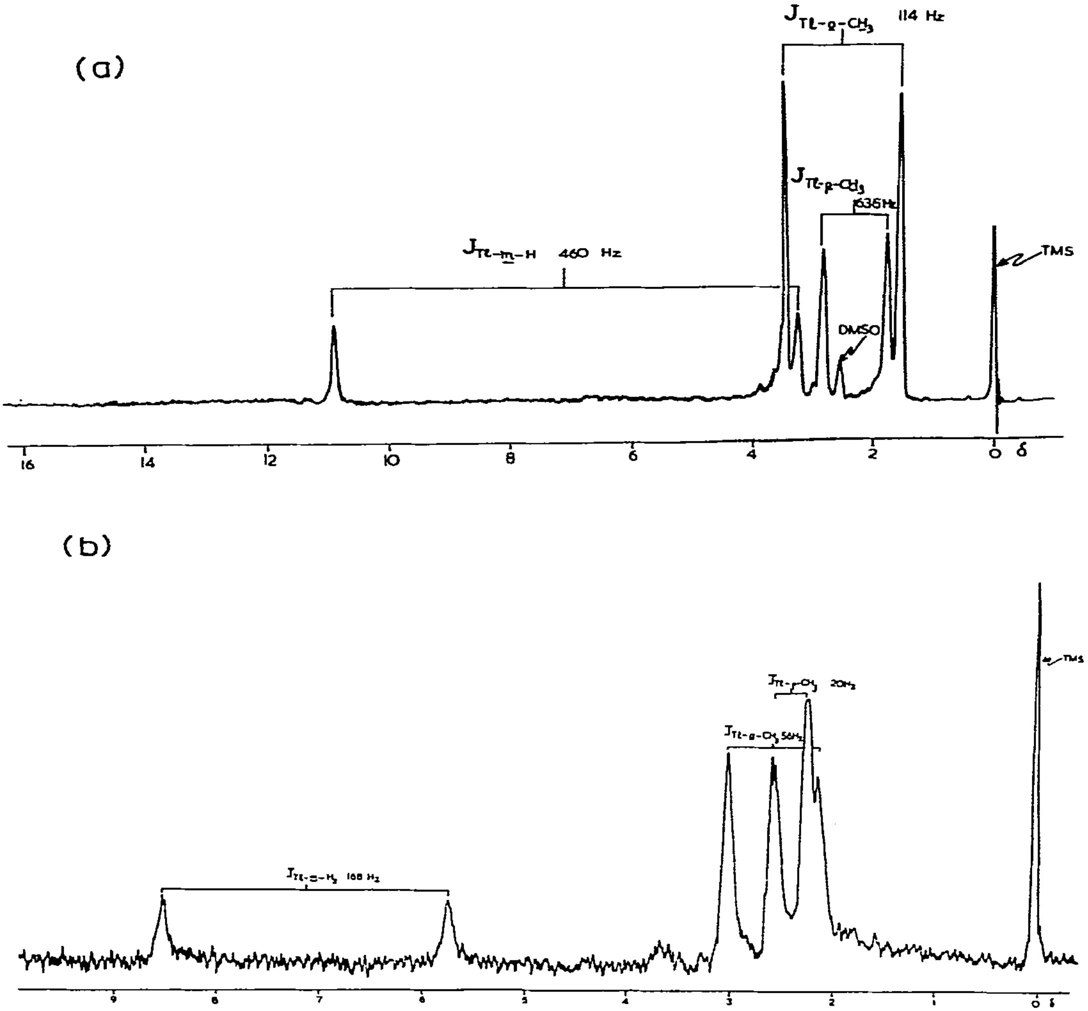

Fig. 6. NMR spectra of (a) mesitylthallium bis(trifluoroacetate) and (b) dimesitylthallium trifluoroacetate.

TABLE 5

OBSERVED $ArTl^{2+}/Ar_2Tl^+$ Tl–H COUPLING CONSTANTS FOR ARYLTHALLIUM BIS(TRIFLUOROACETATES) AND DIARYLTHALLIUM TRIFLUOROACETATES

Ar	*o*-H	*m*-H	*p*-H	*o*-CH_3	*m*-CH_3	*p*-CH_3
C_6H_5	2.27	3.38	2.23			
4-FC_6H_4	2.14	2.69				
4-ClC_6H_4	2.12	2.62				
4-$CH_3C_6H_4$	2.29	2.94				2.75
2,4-$(CH_3)_2C_6H_3$	2.41	2.40		2.38		2.57
2,5-$(CH_3)_2C_6H_3$	2.44	2.69	2.88	2.35	3.12	
3,4-$(CH_3)_2C_6H_3$	2.28	2.97			2.61	2.39
2,4,6-$(CH_3)_3C_6H_2$		2.74		2.33		1.78
4-$CH_3CH_2C_6H_4$	2.38	3.07				2.33

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage microscope melting point apparatus and are uncorrected. Microanalyses were performed by Mr. A. R. Saunders of the University of East Anglia. IR spectra were recorded on a Perkin–Elmer Model 125 Grating IR Spectrophotometer using the normal Nujol mull and potassium bromide pellet techniques. NMR spectra were recorded in DMSO-d_6 solution on a Perkin–Elmer R12 60 MHz Spectrometer.

General procedure for the preparation of arylthallium difluorides and dichlorides

An aqueous solution of the appropriate potassium halide (5 molar excess) was added to a stirred solution of the arylthallium bis(trifluoroacetate) in 50% aqueous ethanol. The arylthallium dihalide precipitated immediately and was collected by filtration after 5 min. The solid was washed with aqueous ethanol and dried. Experimental data for representative arylthallium difluorides and dichlorides are summarised in Table 1.

General procedure for the preparation of diarylthallium trifluoroacetates

Solid arylthallium bis(trifluoroacetate) (4 mmoles) was added with stirring to 3 ml of trimethyl phosphite. After the initial exothermic reaction had subsided the reaction mixture was cooled to room temperature and 3 ml of water was added. A second exothermic reaction ensued and, after the reaction mixture had again cooled to room temperature, a further 5 ml of water was added. The crystalline diarylthallium trifluoroacetate was collected by filtration, washed well with water, and dried. Representative compounds prepared in this way are listed in Table 2.

ACKNOWLEDGEMENT

We gratefully acknowledge the financial support of this work by the Smith Kline and French Laboratories, Philadelphia, Pa.

REFERENCES

1 A. McKillop, J. S. Fowler, M. J. Zelesko, J. D. Hunt, E. C. Taylor and G. McGillivray, *Tetrahedron Lett.*, (1969) 2423.
2 (a) A. McKillop, J. S. Fowler, M. J. Zelesko, J. D. Hunt, E. C. Taylor and G. McGillivray, *Tetrahedron Lett.*, (1969) 2427;
(b) E. C. Taylor, H. W. Altland, R. H. Danforth, G. McGillivray and A. McKillop, *J. Amer. Chem Soc.*, in press.
3 D. Sarrach, *Z. Anorg. Allg. Chem.*, 319 (1962) 16.
4 F. Challenger and B. Parker, *J. Chem. Soc.*, (1931) 1462.
5 F. Challenger and O. V. Richards, *J. Chem. Soc.*, (1934) 405.
6 V. P. Glushkova and K. A. Kocheshkov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1957) 1193.
7 A. N. Nesmeyanov and R. A. Sokolik, *Methods of Elemento-Organic Chemistry, Vol. 1. The Organic Compounds of Boron, Aluminium, Gallium, Indium and Thallium*, North-Holland Publishing Company, Amsterdam, 1967.
8 K. Yasuda and R. Okawara, *Organometal. Chem. Rev.*, 2 (1967) 255.
9 J. P. Maher and D. F. Evans, *J. Chem. Soc.*, (1965) 637.
10 C. R. Hart and C. K. Ingold, *J. Chem. Soc.*, (1964) 4372.
11 V. P. Glushkova and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, 116 (1957) 233.

12 See ref. 7, pp. 581–584.
13 G. E. Coates and K. Wade, *Organometallic Compounds*, Vol. 1. *The Main Group Elements*, Methuen, London, 1967, p. 363.
14 H. M. Powell and D. M. Crowfoot, *Z. Kristallogr.*, 87 (1934) 370.
15 W. Beck and E. Schuierer, *J. Organometal. Chem.*, 3 (1965) 55.
16 M. J. Baillie, D. H. Brown, K. C. Moss and D. W. A. Sharpe, *J. Chem. Soc.*, (1968) 3110.
17 R. E. Kagarise, *J. Chem. Phys.*, 27 (1957) 519.
18 J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Vol. 2, Pergamon, London, 1966, pp. 1088–1092.
19 J. V. Hatton, *J. Chem. Phys.*, 40 (1964) 933.
20 J. P. Maher and D. F. Evans, *J. Chem. Soc.*, (1963) 5534.
21 J. P. Maher and D. F. Evans, *Proc. Chem. Soc.*, (1963) 176.
22 A. McKillop, L. F. Elsom and E. C. Taylor, *Tetrahedron*, in press.
23 G. Faraglio, L. R. Fiorani, B. C. L. Pepe and R. Barbieri, *Inorg. Nucl. Chem. Lett.*, 3 (1967) 277.
24 G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A*, 24 (1968) 885.
25 G. D. Shier and R. S. Drago, *J. Organometal. Chem.*, 5 (1966) 300.
26 H. Kurosawa and R. Okawara, *J. Organometal. Chem.*, 19 (1969) 253.