Journal of Organometallic Chemistry, 252 (1983) 1–27
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CARBON-13 AND PROTON NMR PARAMETERS OF MONO- AND DI-ORGANOTHALLIUM(III) DERIVATIVES

F. BRADY, R.W. MATTHEWS *, M.M. THAKUR,
School of Chemistry, The Polytechnic of North London, Holloway, London N7 8DB (Great Britain)

and D.G. GILLIES,
The Bourne Laboratory, Department of Chemistry, Royal Holloway College, University of London, Egham, Surrey TW20 OEX (Great Britain)

(Received January 20th, 1983)

Summary

Carbon-13 and proton coupling constants and chemical shifts are reported for di- and mono-organothallium(III) compounds of the types TlR_2X and $TlRX_2$ respectively (X = anionic species). The nature of R was varied over thirty acyclic alkyl, alicyclic alkyl and alkenyl groups. Series of related derivatives were studied to identify the major factors upon which the NMR parameters depend. Several new organothallium(III) derivatives have been synthesised. The effects of solvent and anion (X) changes on the NMR parameters are generally minor. The major factor influencing J(Tl–C) and J(Tl–H) is the number of R groups attached to thallium and the ratios of analogous couplings in TlR_2X and $TlRX_2$ are generally close to the value of 1/2.2 predicted on the assumption that the Fermi contact contribution dominates these coupling constants. Couplings to thallium for acyclic alkyl R groups depend on the degree of substitution in R and follow the patterns $|^1J| \gg |^3J| > |^2J| > |^4J|$, $\pm {}^1J$, $\mp {}^2J$, $\pm {}^3J$ for J(Tl–C) and, with few exceptions, $|^3J| > |^2J| > |^4J|$, $\mp {}^2J$, $\pm {}^3J$, $\pm {}^4J$ for J(Tl–H). Values of ^3J(Tl–H) for cyclopropyl derivatives are included with existing data to quantify Karplus-type stereochemical dependence. The values of ^3J(Tl–C) and ^3J(Tl–H) for TlR_2X (R = cyclohexyl) suggest a preference for equatorial substitution by thallium, and a similar conclusion seems reasonable for R = cyclopentyl. $|^nJ$(Tl–C)$|$ in alkenyl derivatives follows the same pattern as for R = acyclic alkyl, but in contrast to alkyl derivatives, ^1J and ^2J have the same sign. Thallium–proton couplings ^2J and ^3J also have the same sign for R = alkenyl. Compounds with α,β-unsaturated R groups have very large values of ^1J(Tl–C) compared to those with saturated R groups. These increases can be partly attributed to changes in hybridization at the α-carbon atom. The effects of the Cl substituent on ^1J(Tl–C), ^2J(Tl–H) and ^1J(C–H) for $Tl(ClCH_2)X_2$ are discussed in terms of the Fermi contact contribution to these coupling constants. Substituent effects on carbon-13 chemical shifts are reported.

Introduction

The crucial role which ^{13}C and proton NMR studies have played in determining geometric, dynamic and electronic features of organometallic compounds [1,2] has been particularly manifest when the metal has spin $I = 1/2$. Coupling to the metal then provides an additional structural probe. Carbon-13 and proton NMR spectra of organotin [3], -platinum [1,2,4], -mercury [5], and -lead [6–9] compounds have been extensively investigated, but only limited studies have been carried out for organo compounds of the other potentially useful spin 1/2 metals (i.e. Rh [1,2], Cd [10,11], Tl). The major omission for organothallium compounds is ^{13}C NMR data; proton NMR data are available for a wide variety of organothallium(III) compounds [12] but ^{13}C NMR studies have been limited to methyl [13–17], phenyl [18–21], neopentyl and trimethylsilylmethyl [22] derivatives, and to oxythallation products of norbornene derivatives [23–26] and D-galactal triacetate [27]. We report here the results of a systematic study of ^{13}C and proton coupling constants and chemical shifts in mono- and di-organothallium(III) compounds. Within synthetic, solubility and stability constraints, NMR parameters have been determined for series of related compounds in an effort to identify the major factors on which the parameters depend and hence to provide a detailed basis for future applications of ^{13}C and ^{1}H NMR to organothallium chemistry. Wherever possible, relative signs of spin–spin coupling constants have been determined. Several new organothallium(III) derivatives have been synthesized.

Results

Carbon-13 NMR chemical shifts and coupling constants for di- and mono-organothallium(III) compounds are given in Tables 1 and 2 respectively, and proton NMR parameters are shown in Tables 3 and 4. The compound numbering scheme is defined in Tables 1 and 2.

^{13}C NMR spectra

The doublet arising from carbon directly bonded to thallium was assigned in all cases as the largest coupling observed. In most cases, pairing of these components was obvious through observation of separate coupling to ^{205}Tl and ^{203}Tl. (^{205}Tl and ^{203}Tl have $I = 1/2$ and natural abundance 70.5 and 29.5% respectively; $\gamma(^{205}\mathrm{Tl})/\gamma(^{203}\mathrm{Tl}) = 1.0098$). Other signals were paired, where appropriate, and assigned on the basis of some or all of the following features: signal intensity, chemical shift, ^{13}C-{^{1}H} single frequency off-resonance decoupled (sford) spectra, and comparison of spectra obtained at different magnetic fields (20.1, 22.63, 45.28 MHz). Frequently, the spectra for a particular compound were completely assigned on the basis of experiment, and assignments for derivatives with different anion, or for solutions of the same compound in different solvents, were made by analogy with the properly determined compound. Assignments for some compounds were made by analogy with the spectra of compounds with related R groups. Thus assignments for carbons in R_2TlX ($R = CH_3(CH_2)_n$, $n = 3,4,5$) were facilitated by comparison with the parameters observed for $R = CH_3(CH_2)_2$. Other cases where assignments depend on comparison with completely determined spectra of similar compounds, or on other special factors, are: both alternative assignments for CH_3

groups in **10** are comparable with spectra for **3a**, **7a** and **8**; the spectra for **11** and **13** are assigned by analogy with those for **10** and **3a**, **7a**, **9a**, **14** respectively; signals for C(2) and C(3) in **14** are assigned by interpreting sford spectra on the assumption that ^3J(Tl–H) ≫ ^4J(Tl–H) (carbon shifts for C(2), C(3) and C(4) derived on this basis agree closely with those for $Sn(C_6H_{11})(CH_3)_3$ [29,30] and $Hg(C_6H_{11})(OAc)$ [31]); spectra for **15** and **21** were assigned by analogy with those for **14** and **17a**, **17b** respectively; the Ph carbon signals in **23** were assigned by comparison with those in **22**.

^{13}C NMR parameters for **20** (Table 1) are reported for the *trans,trans* isomer. Compound **20** was prepared from an equilibrium mixture of *cis-* and *trans*-propenyl bromide and the broad-band proton decoupled ^{205}Tl NMR spectrum of the product indicates the presence of at least two components [32]. The major component was identified as the *trans,trans* isomer on the basis of the proton coupled ^{205}Tl NMR spectrum [32], assuming $^3J(\mathrm{Tl{-}H})_{trans} > {}^3J(\mathrm{Tl{-}H})_{cis}$ as previously reported for these species [28]. The ^{13}C NMR spectrum showed sufficient signals to accommodate the presence of all three possible isomers, but only the spectrum of the major product could be assigned with confidence.

Relative signs of ^nJ(Tl–C) and ^{n+1}J(Tl–H) were determined for several compounds by ^{13}C-{^{1}H} experiments in which the high or low frequency components of thallium-coupled proton multiplets are selectively irradiated to produce differential decoupling effects in the ^{13}C NMR components defining ^nJ(Tl–C). This technique is feasible because of the generally large thallium–proton couplings which facilitate selective irradiation of the proton components. The method was first applied [28,33] to determination of relative signs of ^nJ(Tl–H) and ^{n+1}J(Tl–H) in organothallium(III) compounds by ^{1}H-{^{1}H} experiments and has since been applied to ^{13}C spectra of $TlAr(OCOCF_3)_2$ compounds [18]. Results of relative sign determinations are indicated in Tables 1 and 2 by placing ± or ∓ before the value of the coupling constant. The upper sign is preferred on the basis of taking ^1J(Tl–C) > 0 relative to ^1J(^{13}C–^{1}H) > 0 as found for $Tl(CH_3)_3$ and $Tl(CH_3)_2Br$ [13]. On this basis, the preferred sign for ^3J(Tl–H) is positive for all compounds examined, in accord with the earlier [28] assumption that vicinal Tl–H coupling constants are positive. Relative signs of thallium–carbon coupling constants for adjacent carbons were deduced using results of relative sign determinations for the appropriate thallium–proton couplings (e.g. for (8), ^{13}C-{^{1}H} experiments show that the signs of ^1J(Tl–C) and ^2J(Tl–H) are opposite, and that the signs of ^2J(Tl–C) and ^3J(Tl–H) are opposite; ^{1}H-{^{1}H} experiments yield opposite signs for ^2J(Tl–H) and ^3J(Tl–H), giving the relative signs ± ^1J(Tl–C), ∓ ^2J(Tl–H), ± ^3J(Tl–H), ∓ ^2J(Tl–C)).

With the exception of the methyl derivatives **1** and **25**, and the phenyl derivative **22**, the ^{13}C NMR chemical shifts and coupling constants for compounds with the R groups specified in Tables 1 and 2 are presented for the first time. The parameters for **22** are similar to those found for other Ph_2TlX derivatives [21], but, additionally, the results presented here include coupling constant signs. This is also the case for **1**.

^{1}H NMR spectra

Pairing of component signals arising from protons coupled to thallium was achieved using, as necessary, signal intensities, multiplicities, and ^{1}H-{^{1}H} experiments in which irradiation of one component causes the disappearance of the other component as a result of saturation transfer effects [34]. Coupling constants for **18**

(Continued on p. 9)

TABLE 1

^{13}C NMR PARAMETERS FOR DIORGANOTHALLIUM(III) COMPOUNDS R_2TlX AND $RR'TlX$[a]

Compound number	R	X	Solvent[b]	Concentration[c]	$^1J(^{205}Tl–C)$ (Hz) ($\delta(^{13}C)$, ppm)	$^2J(Tl–C)$ (Hz) ($\delta(^{13}C)$, ppm)	$^3J(Tl–C)$ (Hz) ($\delta(^{13}C)$, ppm)	$^4J(Tl–C)$ (Hz) ($\delta(^{13}C)$, ppm)
1	CH_3	NO_3[d]	Py	1.0	±3018 (22.5)			
2a	CH_3CH_2	Br	DMSO	0.3	2519 (40.8)	174 (12.6)		
			Py	0.2	2552 (39.5)	187 (13.9)		
2b		OAc[e]	DMSO	0.3	±2640 (37.7)	∓181 (11.9)		
2c		NO_3[f]						
3a	$CH_3(CH_2)_2$	Br	DMSO	0.3	2425 (51.1)	122 (20.8)	504 (18.6)	
			Py[g]	0.2	±2437 (49.8)	∓127 (22.4)	±498 (19.1)	
3b		NO_3[f]						
4	$CH_3(CH_2)_3$	Br	DMSO	0.3	2424 (48.5)	126 (29.4)	h	16 (13.6)
			Py	0.3	±2425 (47.4)	131 (31.0)	487 (27.7)	16 (13.7)
5a	$CH_3(CH_2)_4$	Br[i]	Py	0.2	2427 (47.4)	128 (28.4)	468 (36.9)	18 (22.5)
5b		NO_3[f]						
6a	$CH_3(CH_2)_5$	Br[j]	Py	0.1	2416 (47.5)	129 (28.8)	468 (34.4)	18 (31.6)
6b		NO_3[f]						
7a	$(CH_3)_2CH$	Cl	DMSO	0.2	2224 (55.2)	60 (22.5)		
			Py[k]	0.4	±2225 (55.1)	∓63 (23.7)		
7b		OAc[f]						

8	$(CH_3)_2CHCH_2$	Cl	DMSO	0.4	±2357 (60.6)	∓71 (27.4)		±370 (26.7)	
9a	$(CH_3)_2CH(CH_2)_2$	NO_3	DMSO	0.2	2431 (46.0)	*h*		524 (31.3)	< 5 (22.1)
			Py	0.3	±2472 (44.6)	∓143 (36.6)		518 (32.4)	< 5 (22.2)
9b		OAc[f]							
						(CH_3)	(CH_2)		
10	$CH_3CH_2(CH_3)CH$	Cl	DMSO	0.3	±2175 (64.1)	103 (19.5) 116[l] (19.8)	< 5 (29.0)	337 (14.9) 324[l] (14.6)	
11	$CH_3(CH_2)_2(CH_3)CH$	Cl	Py	0.2	2115 (62.0)	145 (20.6) 122[l] (21.1)	12 (39.8)	302 (25.1) 325[l] (24.5)	< 5 (14.1)
12a	$(CH_2)_2CH$	Br	DMSO[m]	0.3	±4496 (36.5)	∓138 (3.0)			
			Py	0.3	4552 (35.0)	150 (4.2)			
12b		$OCOCH(CH_3)_2$[f]							
13	$(CH_2)_4CH$	BF_4	DMSO	0.2	2380 (64.5)	18 (30.1)		394 (25.5)	
14	$(CH_2)_5CH$	BF_4	DMSO	0.2	±2047 (68.8)	71 (31.9)		458[n] (29.8)	49 (26.5)
			Py	0.3	1880[p] (70.0)	66 (33.4)		452 (30.6)	53 (26.8)
15	$(CH_2)_6CH$	Br	DMSO	0.2	1863 (70.0)	30 (30.6)		538 (29.9)	< 5 (27.4)
16	$(CH_2)_5CHCH_2$	Br	Py	0.2	±2303 (57.8)	∓75 (37.9)		366 (38.1)	41[q] (26.7)
17a	CH_2CH	BF_4[r]	DMSO	0.6	±4874 (162.6)	±55 (132.8)			
17b		OAc[s]	Py	0.5	5032 (160.6)	29 (133.2)			

TABLE 1 (continued)

Compound number	R	X	Solvent[b]	Concentration[c]	$^1J(^{205}Tl-C)$ (Hz) ($\delta(^{13}C)$, ppm)	$^2J(Tl-C)$ (Hz) ($\delta(^{13}C)$, ppm)		$^3J(Tl-C)$ (Hz) ($\delta(^{13}C)$, ppm)	$^4J(Tl-C)$ (Hz) ($\delta(^{13}C)$, ppm)
18	*trans*-ClHCCH	Cl	DMSO	0.3	±5828 (153.0)	±730 (130.2)			
			MeOH	0.3	5435[t] (151.2)	669 (134.4)			
						(CH_2)	(CH_3)		
19	$CH_2C(CH_3)$	Br	DMSO	0.2	4173 (174.8)	348 (124.4)	505[u] (28.4)		
			Py	0.3	4232 (173.4)	370 (125.6)	446 (28.6)		
20	*trans*-CH_3CHCH	NO_3[v]	Py		4971 (151.8)	158 (139.2)		770 (22.2)	
21	*trans*-PhCHCH	NO_3	DMSO	0.3	5223[u] (154.2)	175 (144.8)		759[w] (137.3)	
22	Ph	OAc[x]	DMSO	0.2	5293 (165.9)	±281 (136.7)		±433 (127.9)	85 (128.0)

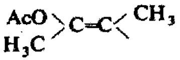
23	$ClCH_2$	Cl	DMSO	0.3	4646 (57.0)			
	R′ = Ph				y	335 (136.0)	491 (128.2)	94 (128.0)
24	$CH_3CH(OCH_3)CH_2$	OAc[z]		0.2	2754 (22.1)	158 (76.1)	309 (23.3)	7 (55.9)
	R′ = Me				3160 (52.9)			

---

[a] All spectra obtained at a temperature in the range 295–317 K. Coupling constants in Hz, errors ±3 Hz unless otherwise noted. Separate coupling to ^{203}Tl and ^{205}Tl was resolved only for $^1J(Tl{-}C)$ unless otherwise noted. Results of relative sign determinations are indicated by placing ± or ∓ before the value of $J(Tl{-}C)$; the upper sign is preferred on the basis of taking $^1J(Tl{-}C) > 0$ relative to $^1J(^{13}C{-}^1H) > 0$ (ref. 13). Chemical shifts (in parentheses) in ppm relative to internal $SiMe_4$ (up-frequency positive). Errors ±0.2 ppm unless otherwise noted. [b] Deuterated solvents were used. [c] In mol dm^{-3}. [d] $^1J(C{-}H)$ 137 Hz. [e] δ(OAc): CO, 176.6; CH_3, 25.2 ppm. Relative signs of ^1J and ^2J deduced by assuming that signs of $^2J(Tl{-}H)$ and $^3J(Tl{-}H)$ are opposite, as found for **2a** in DMSO (Table 3). [f] See Table 3 for ^1H NMR parameters. [g] Relative signs of ^1J, ^2J and ^3J deduced by assuming that sign of $^2J(Tl{-}H)$ is opposite to those of $^3J(Tl{-}H)$ and $^4J(Tl{-}H)$, as found for $Pr^n_2Tl^+$ (ref. 28). [h] Component masked by solvent signal. [i] $^5J(Tl{-}C) < 5$ Hz, $\delta(^{13}C)$ 14.2 ppm. [j] $^5J(Tl{-}C) < 5$ Hz, $\delta(^{13}C)$ 22.8 ppm; $^6J(Tl{-}C) < 5$ Hz, $\delta(^{13}C)$ 14.2 ppm. [k] Relative signs of ^1J and ^2J deduced by assuming that signs of $^2J(Tl{-}H)$ and $^3J(Tl{-}H)$ are opposite, as observed in DMSO solution (Table 3). [l] Possible alternative assignment. [m] Relative signs of ^1J and ^2J deduced by assuming that signs of $^2J(Tl{-}H)$ and $^3J(Tl{-}H)$ are the same, as observed for compound **12b** in pyridine solution (Table 3). Separate coupling to $^{205,203}Tl$ not observed for $^1J(Tl{-}C)$. [n] Component masked by solvent signal. Errors: ±15 Hz, ±0.7 ppm. [p] Component masked by solvent signal. Errors: ±10 Hz, ±0.5 ppm. [q] $^5J(Tl{-}C) < 5$, $\delta(^{13}C)$ 26.3 ppm; possible alternative assignment with ^4J and ^5J interchanged. [r] Relative signs of ^1J and ^2J deduced by assuming that signs of $^2J(Tl{-}H)$ and $^3J(Tl{-}H)_{cis,trans}$ are the same, as found for the ClO_4 derivative (ref. 28). $^1J(C{-}H)156 \pm 7$ Hz. [s] δ(OAc): CO, 178.9; CH_3, 25.5 ppm. [t] Separate coupling to ^{203}Tl and ^{205}Tl unresolved; errors ±5 Hz, ±0.3 ppm. [u] Component masked by solvent signal; errors ±50 Hz, ±2.0 ppm. [v] Results for *trans,trans* isomer in mixture with *cis,cis* and *cis,trans* isomers; total concentration 0.3 mol dm^{-3}. [w] Errors; ±20 Hz, ±1.5 ppm; other Ph carbons in range 130.7 to 124.4 ppm. [x] Positive signs for ^2J and ^3J deduced by assuming signs of $^2J(Tl{-}H)$ and $^3J(Tl{-}H)$ to be positive, as found for ClO_4 derivative in D_2O (ref. 28). δ(OAc): CO, 177.5; CH_3, 25.2 ppm. [y] Not detected. [z] δ(OAc): CO, 177.7; CH_3, 25.1 ppm.

TABLE 2

^{13}C NMR PARAMETERS FOR MONO-ORGANOTHALLIUM(III) COMPOUNDS, $RTlX_2$ [a]

Compound number	R	X	Solvent [b]	Concentration [c]	$^1J(^{205}Tl-C)$ (Hz) ($\delta(^{13}C)$, ppm)	$^2J(Tl-C)$ (Hz) ($\delta(^{13}C)$, ppm)
25	CH_3	OAc [d]	MeOH	1.0	5976 (17.7)	
26	CH_3CH_2	$OCOCH(CH_3)_2$ [e]	DMSO	1.3	±6108 (36.7)	281 (7.5)
27	$CH_3(CH_2)_2$	$OCOCH(CH_3)_2$ [f]				
28	$(CH_3)_2CHCH_2$	$OCOCH(CH_3)_2$ [f]				
29	$(CH_3)_2CH(CH_2)_2$	OAc [f]				
30	$(CH_2)_2CH$	$OCOCH(CH_3)_2$	DMSO	0.3	±9799 [g] (30.8)	∓318 [g] (2.6)
31	CH_2CH	Cl	MeOH	*h*	8715 (148.3)	100 (134.8)
32	*trans*-ClCHCH	Cl	MeOH	*h*	9185 (141.8)	1069 (133.6)
33		OAc [i]	DMSO	0.2	9551 (139.4)	1624 [j] (147.9)
34	$ClCH_2$	OAc [k]	MeOH	1.0	±8877 (51.7)	

[a] All spectra obtained at a temperature in the range 295–317 K. Coupling constants in Hz, errors ±5 Hz unless otherwise noted. Separate coupling to ^{203}Tl and ^{205}Tl was resolved only for $^1J(Tl-C)$ unless otherwise noted. Results of relative sign determinations are indicated by placing ± or ∓ before the value of $J(Tl-C)$; the upper sign is prefered on the basis of taking $^1J(Tl-C) > 0$ relative to $^1J(^{13}C-^1H) > 0$ (ref. 13). Chemical shifts (in parentheses) in ppm relative to internal $SiMe_4$ (up-frequency positive). Errors ±0.3 ppm unless otherwise noted. [b] Deuterated solvents were used. [c] In mol dm^{-3}. [d] From ref. 14. [e] $\delta(OCOCH(CH_3)_2)$: CO, 181.0; CH, 35.6; CH_3, 20.1 ppm. [f] See Table 4 for ^1H NMR parameters. [g] Relative signs of ^1J and ^2J deduced by assuming that signs of $^2J(Tl-H)$ and $^3J(Tl-H)$ are the same, as observed in pyridine solution (Table 4). [h] Compound not isolated, but formed in NMR tube by reaction of R_2TlX with TlX_3. [i] CH_3 carbons were not assigned because of overlap with solvent and anion signals. $\delta(OAc)$: CO, 175.9; CH_3, 22.3 ppm. $^4J(Tl-C)$ 118 Hz, $\delta(^{13}C)$ 167.9 ppm. [j] Alkene carbon. [k] $^1J(H-CHCl)$ 167 Hz. $\delta(OAc)$: CO, 179.1; CH_3, 21.5 ppm.

were determined from analysis of the ABX spin system using the LAOCOON 1968 spectral simulation programme. Assignments were generally straight-forward and unambiguous, although certain assumptions were necessary in some cases. The methine protons for **10** and **11** were assigned by analogy with spectra for **7a** and **7b**. Values of $^3J(H^\alpha-H)$ for **12b** in pyridine were revealed by $^1H-\{^1H\}$ experiments and their assignment on the basis of $^3J(H^\alpha-H)_{cis} > {}^3J(H^\alpha-H)_{trans}$ [35] allows distinction between vicinal couplings to thallium such that $^3J(Tl-H)_{cis} > {}^3J(Tl-H)_{trans}$. This assignment is assumed for other spectra of **12b**, and for **12a** and **30**. Spectra of **17a**, **17b** and **31** were assigned on the basis that $^3J(H-H)_{trans} > {}^3J(H-H)_{cis} > {}^2J(H-H)_{gem}$ [36], and alkene protons in **19** were assigned by analogy with **17a** and **17b**. The spectrum of **27** was assigned by analogy with that of **26** because the thallium-coupled components lacked diagnostically useful fine structure. Assignments for the bis-cycloalkyl derivatives **13–16** assume $^3J(Tl-H) \gg {}^nJ(Tl-H)$ where $n > 3$.

Wherever possible, relative signs of thallium-proton coupling constants were determined by $^1H-\{^1H\}$ experiments as previously described [28,33]. These experiments were commonly thwarted, however, by disadvantageous signal overlaps, although in some cases a change of solvent was sufficient to unmask the pertinent signals and allow determination of several signs (e.g. **9b** in benzene). Like signs for $^2J(Tl-H)$ and $^3J(Tl-H)$ in **18** were evident from the highly perturbed AB subspectra of the ABX spin system.

^1H spectra for some compounds were additionally obtained at 220 MHz. These were occasionally useful in pairing thallium-coupled components (e.g. for **12a** in DMSO) but the normal advantages resulting from spectral simplification at high field were generally outweighed by the broadness of the component signals. The increased linewidths arise from rapid ^{205}Tl spin-lattice relaxation dominated by the field dependent chemical shift anisotropy mechanism [37].

Values of $J(Tl-H)$ for $Tl(C_2H_5)_2X$ derivatives have been extensively reported and those for **2a**, **2b**, **2c** are within the previously recorded [28,33,38–42] ranges (^2J, 306–399 Hz; ^3J, 612–659 Hz). Thallium–proton coupling constants have also been reported for some of the other compounds included in Tables 3 and 4 (or for derivatives with the same organo-group but with different anion), i.e. **3** [28,39,40], **4**, **7**, **8**, **13**, **17**, **18** [28], **23** [43], **26** [41,44], **31** [28], **34** [43] (organo groups are denoted by the compound number only (Tables 1 and 2) and anion-designating letters are omitted). Taking into account the use of different anions and solvents, the $J(Tl-H)$ values for similar derivatives are in good agreement. The earlier reports frequently omitted proton chemical shift results. For compound **33**, the change of solvent from $CDCl_3$ [45] to DMSO (Table 4) revealed long range thallium coupling, $^6J(Tl-H)$, to the acetoxy group.

NMR spectra of non-isolated compounds

Since the published route [46] to CH_2CHTlX_2 derivatives from $(CH_2CH)_2TlX$ did not furnish pure products in our hands, the ^{13}C and ^1H NMR spectra were determined for products formed in situ in the NMR tube by mixing stoichiometric quantities of $(CH_2CH)_2TlCl$ and $TlCl_3$ in MeOH-d_4 (reaction ca. 90% complete). The widely differing coupling constants for $CH_2CHTlCl_2$ and $(CH_2CH)_2TlCl$ allowed easy separation of precursor from product signals. A similar procedure was

(Continued on p. 14)

TABLE 3

^{1}H NMR PARAMETERS FOR DIORGANOTHALLIUM(III) COMPOUNDS, R_2TlX AND RR′TlX [a]

Compound number	Solvent [b]	Concentration [c]	^2J(Tl–H) (Hz) (δ(^{1}H), ppm)	^3J(Tl–H) (Hz) (δ(^{1}H), ppm)	^3J(Tl–H) (Hz) (δ(^{1}H), ppm)	^3J(Tl–H) (Hz) (δ(^{1}H), ppm)	^4J(Tl–H) (Hz) (δ(^{1}H), ppm)
1	DMSO	0.2	449 [d] (0.70)				
	Py	1.0	∓437 [d] (1.44)				
2a	DMSO	0.3	∓370 [e,f] (1.62)	±637 [f] (1.54)			
	Py	0.2	∓336 [e,f] (2.07)	±631 [f] (1.74)			
2b	DMSO [g]	0.3	∓375 [f] (1.47)	626 [f] (1.44)			
2c	DMSO	0.3	392 [d] (1.37)	635 [d] (1.44)			
3a	DMSO	0.2	379 [f] (1.67)	477 [f] (1.97)			22 (0.96)
	Py	0.2	350 [f] (2.16)	480 [f] (2.16)			21 (0.98)
3b	DMSO	0.3	400 [d] (1.63)	436 [d] (1.93)			30 [d] (1.07)
4	DMSO [h]	0.2	385 (1.67)	456 (1.91)			
	Py [h]	0.2	355 (2.20)	462 (2.12)			
5b	DMSO [h]	0.3	392 [d] (2.00)	421 [d] (2.24)			
6a	Py [h]	saturated	352 [d] (2.18)	468 [d] (2.15)			
6b	DMSO [h]	0.3	396 [d] (1.67)	414 [d] (1.82)			
7a	DMSO	0.4	∓304 [i] (2.07)	±587 [f] (1.55)			

	Py	0.3	∓267 (2.51)	585^{f} (1.71)			
7b	MeOH^{j}	0.1	270 (2.28)	577^{f} (1.58)			
8	DMSO	0.2	∓404 (1.83)	±491^{k} (2.26)			±20 (0.96)
	Py	0.2	∓382^{l} (2.26)	±519 (2.67)			±18 (1.02)
	benzene	0.06	355 (2.51)	*m*			14 (0.95)
9a	DMSO^{h}	0.3	∓404^{d,n} (1.62)	±365^{d} (1.78)			
	Py^{h}	0.2	∓388^{d} (2.26)	±365^{d} (1.89)			
9b	DMSO^{g,h}	0.04	396^{d} (1.52)	418^{d} (1.70)			
	Py^{h,p}	0.3	377^{d} (1.93)	423^{k} (1.89)			
	Benzene^{h,j}	0.3	∓377^{n} (1.91)	±465^{d} (1.92)			∓50^{q} (1.0)
				(CH_3)	(H^a)	(H^b)	
10	DMSO	0.2	∓323^{d} (2.09)	±559 (1.59)	±705^{d} (2.05)	±513^{k} (2.01)	∓20 (0.97)
	Py	0.1	293^{d} (2.44)	548 (1.74)	730^{d} (2.16)	511^{q} (2.05)	22 (1.09)
	Benzene	0.01	*m*	582 (1.87)	*m*	*m*	25 (1.03)
11	DMSO^{h}	0.2	∓307^{k,r} (2.19)	±563 (1.64)	±716^{k} (2.02)	±474^{k} (1.99)	
	Py^{h}	0.1	268^{k} (2.68)	553 (1.79)	754^{k} (2.18)	465^{k} (2.12)	
	Benzene^{h}	0.06	295^{k} (2.79)	584 (1.93)	736^{k} (2.26)	538^{k} (2.26)	

TABLE 3 (continued)

Compound number	Solvent ^{b}	Concentration ^{c}	^{2}J(Tl–H) (Hz) (δ(^{1}H), ppm)	^{3}J(Tl–H) (Hz) (δ(^{1}H), ppm)	^{3}J(Tl–H) (Hz) (δ(^{1}H), ppm)	^{3}J(Tl–H) (Hz) (δ(^{1}H), ppm)	^{4}J(Tl–H) (Hz) (δ(^{1}H), ppm)
				(*cis*)	(*trans*)		
12a	DMSO	0.3	±318 ^{q} (0.91)	579 ^{k} (1.08)	344 ^{k} (0.75)		
	Py	0.3	409 ^{q} (1.37)	572 ^{k} (1.48)	345 ^{k} (0.93)		
12b	DMSO ^{s}	0.3	343 ^{q} (0.76)	571 ^{k} (0.93)	343 ^{k} (0.76)		
	Py ^{t}	0.3	±402 ^{k,u} (1.23)	±564 ^{k} (1.72)	±345 ^{k} (0.87)		
	MeOH ^{v}	0.2	338 ^{q} (0.92)	568 ^{k} (0.99)	338 ^{k} (0.92)		
13	DMSO ^{h}	0.2	268 ^{q} (2.05)	496 ^{d} (2.00)	268 ^{k} (2.05)		
	Py ^{h}	0.3	243 ^{k} (2.51)	483 ^{d} (2.08)	200 ^{k} (2.16)		
14	DMSO ^{h}	0.3	∓346 ^{q} (2.17)	346 ^{q} (2.17)	207 ^{d} (1.81)		
15	Py ^{h}	0.2	403 ^{k} (2.78)	598 ^{k} (2.55)	214 ^{k} (2.24)		

16	Py[h]	0.1	∓383 (0.89)	±453[k] (2.33)			
				(*trans*)	(*cis*)		
17a	DMSO[w]	0.8	±798[f] (6.80)	±1671[f] (6.10)	±800[f] (5.84)		
17b	DMSO[g,w]	0.5	±829[f,x] (6.76)	1590[f] (6.04)	±792[f] (5.75)		
18	DMSO	0.4	±459[y] (6.43)		±456[y] (6.69)		
19	py	0.3		1503[f] (5.88)	667 (5.59)	440 (2.36)	
23	DMSO[z]	0.3	256 (3.77)	478 (7.75)			148 (7.42)

---

[a] See Table 1 for labelling of compounds. All spectra obtained at 35 ± 1 °C. Coupling constants in Hz, errors ± 1 Hz unless otherwise noted. Separate coupling to ^{205}Tl and ^{203}Tl was unresolved unless otherwise noted. Results of relative sign determinations are indicated by placing ± or ∓ before the value of J(Tl–H); the upper sign is preferred on the basis of knowing the relative signs of ^1J(Tl–C) and ^2J(Tl–H) and taking ^1J(Tl–C) > 0 relative to $^1J(^{13}\mathrm{C}-^1\mathrm{H}) > 0$ (ref. 13). Chemical shifts (in parentheses) in ppm relative to internal $\mathrm{SiMe_4}$ (up-frequency positive). Errors ±0.02 ppm unless otherwise noted. [b] Deuterated solvents were used. [c] In mol dm^{-3}. [d] Errors: ±4 Hz, ±0.1 ppm. [e] Negative sign preferred by analogy with **2b** in DMSO. [f] $J(^{205}\mathrm{Tl}-\mathrm{H})$. [g] δ(OAc) 1.65[d] ppm. [h] Signals overlapped for omitted parameters. [i] Negative sign preferred by analogy with **7a** in pyridine. [j] δ(OAc) 1.89[d] ppm. [k] Errors: ± 10 Hz, ±0.2 ppm. [l] Negative sign preferred by analogy with **8** in DMSO. [m] Not detected because of low solubility. [n] Negative sign preferred by analogy with **9a** in pyridine. [p] δ(OAc) 2.14[d] ppm. [q] Errors: ± 15 Hz, ±0.3 ppm. [r] Negative sign preferred by analogy with **10** in DMSO. [s] δ($\mathrm{OCOCHMe_2}$): Me, 1.0 ppm; C*H* signal obscured. [t] δ($\mathrm{OCOCHMe_2}$): Me, 1.32; C*H* 2.64 ppm. $^3J(\mathrm{H}^a_\alpha-\mathrm{H})$: *cis*, 9; *trans*, 6 Hz. [u] Positive sign preferred by analogy with **12a** in DMSO. [v] δ($\mathrm{OCOCHMe_2}$): Me, 1.10, C*H*, 2.33 ppm. [w] ^3J(HH): *trans*, 19.3; *cis*, 12.0; *gem*, < 3 Hz. [x] Positive sign preferred by analogy with **17a** in DMSO. [y] Possible alternative assignment with ^2J and ^3J interchanged. [z] ^5J 55 Hz, δ 7.25 ppm.

TABLE 4
^{1}H NMR PARAMETERS FOR MONO-ORGANOTHALLIUM(III) COMPOUNDS, $RTlX_2$ [a]

Compound number	Solvent [b]	Concentration [c]	^2J(Tl–H) (Hz) ($\delta(^1H)$, ppm)	^3J(Tl–H) (Hz) ($\delta(^1H)$, ppm)	^3J(Tl–H) (Hz) ($\delta(^1H)$, ppm)
25	MeOH [d]	1.0	939 (1.72)		
26	DMSO [e]	1.2	∓889 (2.29)	±1627 [f] (0.84)	
27	$CDCl_3$ [e,g]	0.7	812 [h] (2.81)	1515 [h] (1.96)	
28	MeOH [g]	i	835 [h] (2.73)	1722 [j] (2.41)	
29	MeOH [g]	i	∓898 [h,k] (2.68)	±1300 [h] (1.76)	
				(*cis*)	(*trans*)
30	Py [l]	0.5	±548 [h,m] (1.89)	±1280 [h] (1.20)	±776 [h] (0.84)
	MeOH [n]	0.1	603 [h] (1.73)	1350 [h] (0.99)	804 [h] (0.94)
				(*trans*)	(*cis*)
31	MeOH	*p*	±1882 [f,h,q] (6.55)	±3574 [f,j] (6.10)	±1707 [f,h] (5.82)
32	MeOH	*p*	±1040 [f,h,r,s] (6.63)		±807 [f,h,r] (6.77)
33	DMSO [t]	0.5		940 [f] (1.82)	
34	MeOH [u]	0.7	∓451 (4.27)		
	Py [v]	0.6	429 [f] (4.63)		
	D_2O [w]	0.7	438 [f] (4.31)		

[a] See Table 2 for labelling of compounds: see footnote (*a*) of Table 3. [b] Deuterated solvents were used. [c] In mol dm^{-3}. [d] From ref. 14. [e] $\delta(OCOCH(CH_3)_2)$: C*H*, 2.37±0.2; CH_3, 1.09±0.05 ppm. [f] $J(^{205}Tl–H)$. [g] Signals overlapped for omitted parameters. [h] Errors: ±10 Hz, ±0.2 ppm. [i] Compound not isolated, but formed in NMR tube by reaction of R_2TlX with HgX_2. [j] Errors: ±25 Hz, ±0.5 ppm. [k] Negative sign preferred by analogy with compound **26**. [l] $\delta(OCOCH(CH_3)_2)$: C*H*, 2.62; CH_3, 1.13 ppm. [m] Positive sign preferred by analogy with compound **30** in DMSO. [n] $\delta(OCOCH(CH_3)_2)$: C*H*, 2.51; CH_3, 1.15 ppm. [p] Compound not isolated, but formed in NMR tube by reaction of R_2TlX with TlX_3. [q] Positive sign preferred by analogy with compound **17a** (Table 3). $^3J(H–H)_{trans}$ 18.0, $^3J(H–H)_{cis}$ 9.5, $^2J(H–H)_{gem} < 2$ Hz. [r] Possible alternative assignment with ^2J and ^3J interchanged. [s] Positive sign preferred by analogy with compound **18** in DMSO (Table 3). ^3J(H–H) 14.6 Hz. [t] ^4J(Tl–H) 139 Hz. $\delta(^1H)$ 2.01 ppm, ^6J(Tl–H) 13 Hz, $\delta(^1H)$ 2.13, δ(OAc,anion) 1.87 ppm. [u] δ(OAc) 1.99 ppm. [v] δ(OAc) 2.14 ppm. [w] δ(OAc) 1.94 ppm.

also adopted to obtain spectra of new organothallium(III) compounds which we were unable to isolate (i.e. **28**, **29**, **32**).

Discussion

The various factors upon which ^{1}H and ^{13}C NMR parameters for $TlRX_2$ and TlR_2X depend will be discussed separately. The variations of chemical shifts and

TABLE 5

RATIOS OF ANALOGOUS THALLIUM-CARBON AND THALLIUM-PROTON COUPLING CONSTANTS (Hz) FOR $TlRX_2$ AND TlR_2X COMPOUNDS [a]

R	^1J(Tl–C)	^2J(Tl–C)	^3J(Tl–C)	^2J(Tl–H)	^3J(Tl–H)	^4J(Tl–H)
CH_3	2.4 [b]			2.3 [b]		
CH_3CH_2	2.4 ± 0.1 [c]	1.6 ± 0.1 [c]		2.5 ± 0.2 [d]	2.6 [d]	
$CH_3(CH_2)_2$				2.2 ± 0.2 [e]	3.4 ± 0.2 [e]	
$(CH_3)_2CHCH_2$				2.3 ± 0.2 [f]	3.4 ± 0.1 [f]	
$(CH_3)_2CH(CH_2)_2$				2.3 ± 0.1 [g]	3.2 ± 0.4 [g]	
$(CH_3)_3CCH_2$ [h]	2.2	12.0	2.1	1.8 ± 0.2		2.3 ± 0.1
$(CH_3)_3SiCH_2$ [h]	1.9 ± 0.1		1.9	2.0 ± 0.1		1.8 ± 0.1
$(CH_2)_2CH$	2.2 [i]	2.2 ± 0.1 [i]		1.6 ± 0.3 [j]	2.3 ± 0.1 [j,k]	
CH_2CH [l]	1.8 ± 0.1	2.6 ± 0.8		2.4 ± 0.1	2.2 ± 0.1 [k]	
trans-ClHCCH [m]	1.7 ± 0.1	1.6 ± 0.1		2.3	1.8	
Ph	2.02 [n]	1.9 [n]	2.4 [n]		2.1 [p]	2.6 [p]

[a] Ratios are $|^nJ(Tl-Y)|$ (for $TlRX_2$)/$|^nJ(Tl-Y)|$ for (TlR_2X), where Y = C, H. [b] From ref. 14. [c] **2a**, **2b** cf. [26]. [d] **2a**, **2b**, **2c** cf. [26]. [e] **3a**, **3b** cf. [27]. [f] **8** cf. [28]. [g] **9a**, **9b** cf. [29]. [h] From ref. 22. [i] **12a** cf. [30]. [j] **12a**, **12b** cf. [30]. [k] For both *cis* and *trans* coupling. [l] **17a**, **17b** cf. [31]. [m] **18** cf. [32]. [n] **22** cf. $TlPh(OCOCF_3)_2$ in DMSO (ref. 19). [p] From ref. 28.

spin–spin coupling constants with concentration were not investigated because preliminary experiments showed these effects to be negligible. Also, these parameters were previously [15] shown to have little or no dependence on concentration for dimethylthallium(III) derivatives.

Solvent and anion effects

Before discussing the dependence of NMR parameters on the number and nature of the organic groups attached to thallium, it is important to establish the magnitude of solvent- and anion-induced changes. Our investigation was not extensive with respect to solvent, being limited by solubility restrictions to mainly pyridine and DMSO and occasionally benzene, methanol and chloroform. Solubility requirements also limited the number of cases where anion effects could be measured, particularly for ^{13}C spectra. The available results indicate, however, that the effects of solvent and anion are generally insufficient to be important in the discussion of other effects. The situation for TlR_2X derivatives is summarized below.

Variations in ^nJ(Tl–C) (n = 1–4) with solvent (mainly Py and DMSO) are less than 14% which is less than the maximum change (25%) noted for $TlMe_2X$ derivatives [15]. Results for compounds **2a**, **2b**, and **22**, taken together with previous results [15,21,22] for TlR_2X derivatives, show that the variation of ^nJ(Tl–C) with anion is < 6%. Variations in ^nJ(Tl–H) (n = 2–4) with solvent (including derivatives where R = Me [14,15] $(CH_3)_3CCH_2$, $(CH_3)_3SiCH_2$ [22]) are < 16% with the exception of ^2J(Tl–H) for $Tl[(CH_2)_2CH]_2X$ (**12a**, 29%; **12b**, 19%) and ^3J(Tl–H) for **13** (34%). For $TlMe_2X$ compounds, it was noted [15] that $|^2J(Tl-H)|$ increases with solvent in the order non-polar solvent < pyridine < DMSO. The same trend is observed in this work (and for R = $(CH_3)_3CCH_2$, $(CH_3)_3SiCH_2$ [22]) although there are exceptions, i.e. **12a** and **12b** where the order for pyridine and DMSO is reversed. Anion effects on ^nJ(Tl–H) (n = 2–4) are small (this work and refs. 15, 21, 22), < 8%, with the exception of ^3J(Tl–H) for **9a**, **9b** (< 16%). The effects of solvent and anion on chemical shifts are also small; < 5 ppm for $\delta(^{13}C)$ and < 0.9 ppm for $\delta(^1H)$ (this work and refs. 14, 15, 21, 22).

There is insufficient data to reliably assess solvent and anion effects on ^{13}C and ^1H NMR parameters for mono-organothallium(III) derivatives, although the few results available here and elsewhere [14,22] indicate that the effects are likely to be similar to those noted above for the diorgano compounds.

Dependence of coupling on the number of R groups

$|J$(Tl–C)$|$ and $|J$(Tl–H)$|$ decrease from $TlRX_2$ to TlR_2X derivatives. The decrease is summarized in Table 5 which shows ratios of analogous couplings in $TlRX_2$ and TlR_2X for the results presented here and for other relevant cases. As noted above, the coupling constants are slightly solvent and anion dependent and in many cases this allows a choice of anion and/or solvent for the individual $TlRX_2$ and TlR_2X systems used to obtain the ratios. The ratios given in Table 5 are average values with uncertainties encompassing these variations. The decrease in J values from $TlRX_2$ to TlR_2X has previously been noted for $|J$(Tl–C)$|$ where R = methyl [14], neopentyl, trimethylsilylmethyl [22], and phenyl [21], and for $|J$(Tl–H)$|$ with these groups [14,22,28,41,47] and also R = ethyl [41] and vinyl [28]. These observations have been taken as support [14,28,47] for the assumption that the Fermi contact mechanism is the dominant contribution to coupling between thallium and carbon or hydrogen. On this assumption, J(Tl–C) and J(Tl–H) are expected to be proportional to $(Z_{eff})^3 \cdot \alpha^2(Tl)$ [14] (where Z_{eff} is the effective nuclear charge on the thallium atom, and $\alpha^2(Tl)$ represents the *s*-character of the hybrid orbital on thallium involved in bonding between thallium and the organo-group) giving a ratio [14] of 1/2.2 for analogous couplings in TlR_2X and $TlRX_2$ under similar conditions of anion and solvent. The argument is expected to have greatest validity when applied to one bond coupling, ^1J(Tl–C) [14], and the observed ratios for $|^1J$(Tl–C)$|$ are encouragingly close to 1/2.2 (Table 5). Ratios for $|^2J$(Tl–H)$|$, on the basis of which the explanation was first proposed [28], show poorer agreement (range, 1.3–2.7) with the predicted ratio, a result which is not unexpected for coupling between non-directly bonded atoms [14,28]. Ratios for the other multibond couplings span similar ranges (with the exception of $|^2J$(Tl–C)$|$ for R = neopentyl [22]) and provide a useful empirical generalization between couplings in mono- and di-organothallium(III) compounds.

The highly approximate nature of these considerations should be borne in mind. The approximations are illustrated by the seemingly favourable ratios for J(Tl–C) in the cyclopropyl derivatives. $Tl[(CH_2)_2CH]_2X$ is expected to contain an essentially linear C–Tl–C unit as found for a number of dialkylthallium(III) derivatives [22,48] hence lending some justification to the assumption of *sp* hybridization at thallium. The assumption that thallium uses only its *s*-orbital for bonding to the cyclopropyl group in the mono-cyclopropyl compound, **30**, has less validity because in the solid state the thallium atom in **30** shows a marked preference for a near-linear configuration (168°) involving a C–Tl–O unit [49]. The short Tl–O bond length (2.12 Å) in this unit compared to other Tl–O bonds (2.49–2.71 Å) in the same compound reflects the strength of this bond and it seems reasonable to assume that the solid state structure at least sets a precedent for the structure of **30** in solution.

The effects of chain length and branching on J(Tl–C) and J(Tl–H) for acyclic alkyl groups (R)

Values of ^1J(Tl–C) (taken as positive [13,50]) for TlR_2X derivatives (R = acyclic alkyl group, unsubstituted by heteroatoms) are in the range 2115–3018 Hz. The magnitudes of carbon–thallium couplings to more distant carbon atoms follow the pattern $^1J \gg {}^3J > {}^2J > {}^4J$ and, generalizing from the five cases where determinations have been possible, the relative signs of J(Tl–C) alternate: $\pm {}^1J$, $\mp {}^2J$, $\pm {}^3J$. A similar result was obtained for relative signs where R = $(CH_2)_2CH$ and $(CH_2)_5CHCH_2$, and also for $Tl[(CH_2)_2CH][OCOCH(CH_3)_2]_2$. The relative magnitudes of ^nJ(Tl–C) follow a similar pattern in $TlRX_2$ derivatives for R = $(CH_3)_3CCH_2$ [22] and C_2H_5.

The magnitudes of ^nJ(Tl–C) as a function of n thus follow the pattern already established for heavy metal–carbon coupling constants in acyclic alkyl derivatives of, for example, Cd (n = 1,2) [11], Hg [5,51], Sn [3,29,52–54], Pb (n = 1–3) [6–9]. It appears that in none of these cases was four-bond coupling to carbon detected whereas values of 16–18 Hz are observed for the thallium compounds **4**, **5a**, and **6a**. Observation of this longer range coupling to thallium is a manifestation of the generally larger values of coupling constants involving thallium [14], resulting in part from the particularly large magnetogyric ratio [55] of ^{205}Tl.

The relative sign determinations for ^nJ(Tl–C) reported here appear to be the most extensive hitherto available for metal–carbon couplings in acyclic alkyl derivatives. Thus comparable information is unavailable for Cd and Pb compounds, but by combining the results of sign determinations for HgR_2 (R = CH_3 [56], CH_3CH_2 [57], $CH_3(CH_2)_2$ [58]) it seems probable that the signs of $^1J(^{199}$Hg–C) and $^2J(^{199}$Hg–C) are positive and negative respectively. Petrosyan [3] has suggested that $^1J(^{119}$Sn–C) and $^2J(^{119}$Sn–C) are negative and positive respectively in $Sn(CH_3CH_2)_4$. The pattern of alternating signs with increasing n may therefore be general for ^nJ(M–C) (M = metal with spin $I = 1/2$) in alkyl derivatives. Assuming that the metal–carbon coupling constants are dominated by the Fermi contact contribution [59,60], these relative signs cannot be accounted for by the form of the theory which involves the mean excitation energy approximation (and hybrid orbital "*s*-character") [59,61]. At an earlier stage of approximation, however, the signs are determined by the mutual polarizabilities of the valence *s*-orbitals of the atoms involved in the coupling [59,61] and, indeed, recent calculations [62] of mutual polarizabilities for β-methoxyalkylmercury(II) complexes have reproduced the observed signs for $^nJ(^{199}$Hg–C) and $^{n+1}J(^{199}$Hg–H) (n = 1,2).

Values of $|^nJ$(Tl–C)$|$ for TlR_2X in DMSO and pyridine solutions also depend on the degree of substitution at the relevant carbon atom. Thus $|^1J$(Tl–C)$|$ values in the range 2897–3080 Hz for $Tl(CH_3)_2X$ [15] fall by ca. 400 Hz to those in $Tl(CH_3CH_2)_2X$ compounds and by ca. 200 Hz more for substitution at C(α) by alkyl groups larger than CH_3. Further replacement of protons at C(α) by methyl groups reduces $|^1J|$ by ca. 250 Hz. $|^2J|$ is also reduced by sucessive substitution at C(β) and also by substitution at C(α). Couplings to C(γ) also experience reductions on substitution at C(α), C(β), C(γ) (with the exception of R = isobutyl). Thallium-carbon coupling constants reported [22] for R = $(CH_3)_3CCH_2$ also conform to these patterns. For the positive one-bond couplings, where the expression [59] for the Fermi contact contribution is expected to have greatest validity, the reductions resulting from alkyl substitution at C(α) can be rationalized on the assumption that the increased inductive effect $(+I)$ of larger alkyl groups leads to a reduction in effective nuclear charge at the thallium atom and hence a reduced value for the $|\psi_{6s}(0)|^2$ term in the Fermi contact equation [59]. A similar relationship between $^1J(^{119}Sn{-}C)$ and the nature of R has been noted by Mitchell and Walter [54] for a closely related series of tetraalkyltin compounds, SnR_4. The linear correlation [54] between $^1J(^{119}Sn{-}C)$ and Taft σ^* constants of the alkyl groups does not, however, find precise analogy in the thallium case, possibly because of the unavoidable anion and solvent induced variations in $^1J(Tl{-}C)$.

The magnitudes of thallium–proton coupling also alternate with the number of intervening bonds for TlR_2X and $TlRX_2$ compounds (R = acyclic alkyl group, unsubstituted by heteroatoms) i.e. $^3J > {}^2J > {}^4J$. An exception occurs for R = $(CH_3)_2CH(CH_2)_2$ where a change of anions from OAc^- to NO_3^- reverses the relative magnitudes of $^2J(Tl{-}H)$ and $^3J(Tl{-}H)$. The relatively small changes in ^2J and ^3J necessary to effect this reversal reflects a general feature of these couplings, i.e. $(|^3J| - |^2J|)$ decreases substantially when the chain length exceeds two carbon atoms. Thus comparing results for compounds with similar anions and in similar solvents, $(|^3J| - |^2J|)$ for TlR_2X has values in the range 243–318 Hz for compounds **2**, **7** whereas for compounds **3**–**6**, **8**, and **9** (Table 3), the range is 137 to −39 Hz. The results presented in Tables 3 and 4 serve to generalise the previous observation [28] that $|^3J| > |^2J| > |^4J|$ for TlR_2X derivatives, and to extend the results to monoalkylthallium(III) compounds.

Values of $|^2J(Tl{-}H)|$ and $|^3J(Tl{-}H)|$ show some dependence on the degree of substitution at the α and β carbon atoms respectively. Limiting the comparison to TlR_2X compounds in DMSO and pyridine solutions, but without restriction on anion, substitution of a methyl proton at $C(\alpha)$ by an alkyl group reduces $|^2J|$ from ca. 400–450 Hz [15] to 336–404 Hz, and a further reduction to 267–323 Hz results from a second substitution at $C(\alpha)$ by a methyl group. $|^3J(Tl{-}H)|$ is reduced by ca. 200 Hz on substitution of an alkyl group for a proton of a $C(\beta)$ methyl group.

The relative signs of $^nJ(Tl{-}H)$ for TlR_2X (R = CH_3CH_2, $(CH_3)_2CHCH_2$) are in good agreement with those previously [28] determined for these alkylthallium compounds and thus confirm the sequence $\mp {}^2J$, $\pm {}^3J$, $\pm {}^4J$. Opposite signs for ^2J and ^3J are also found for monoalkyl compounds **26** and **29**, and in five other dialkyl derivatives, **7a**, **9a**, **9b**, **10**, and **11**. In contrast to the above pattern, however, the signs of ^4J in **9b** and **10** are negative. Presumably structural and medium effects combine to reverse the sign of these relatively small four-bond couplings.

The large differences (192–289 Hz) between $|^3J(Tl{-}H)|$ values for the non-equivalent methylene protons in compounds **10** and **11** are of the same order as those found in β-methoxy-β-phenylethylthallium(III) complexes [63]. As in the latter cases, these differences probably arise from unequal conformer populations and a dependence of vicinal coupling on dihedral angle (see below). In contrast to the β-methoxy compounds [63], however, the H^a and H^b component signals for **10** and **11** did not exhibit sufficiently well resolved fine structure from which the preferred conformations could be deduced. The relevant components of **10** and **11** (i.e. H^a, H^b and $H(\alpha)$) were complicated by additional three bond proton–proton coupling which is absent in the β-methoxycompounds. Also, in these and many other thallium-coupled proton components examined in this work, the signals were complicated by overlap of ^{205}Tl- and ^{203}Tl-coupled components and appeared intrinsically broad, possibly as a result of particularly efficient thallium relaxation dominated by the chemical shift anisotropy mechanism [37].

J(Tl–C) and J(Tl–H) for the alicyclic R-groups

Thallium–carbon coupling for the cyclohexyl derivative **14** follows the same pattern as for acyclic alkyl derivatives, i.e. $|^1J| \gg |^3J| > |^2J| > |^4J|$. Coupling in the cyclopropyl derivative **12a** also conforms to this pattern and reasonable spectral assignments are achieved for the cyclopentyl, **13**, and cycloheptyl, **15**, derivatives if their J(Tl–C) values are also assumed to conform. ^1J(Tl–C) decreases with increasing ring size for TlR_2X ($R = (CH_2)_nCH$; $n = 2, 4, 5, 6$), probably reflecting changes in hybridization at C(1) [64]. A similar trend has been noted for ^1J(C–H) in cycloalkanes where ^1J(C–H) shows a linear correlation with ring strain energy [65]. Such a clear trend is not found for cycloalkyl derivatives of tin [29] and lead [8] although steric factors may obscure the effect in these tetraorgano compounds.

All three thallium–proton couplings are positive in sign for both the di- and mono-cyclopropyl derivatives, **12b** and **30** respectively, in pyridine solution. This is in contrast to the opposite signs noted for ^2J and ^3J in acyclic derivatives. Uniformly positive signs for metal–proton coupling in cyclopropyl derivatives have also been derived from analysis of proton spectra of the tin, lead and mercury compounds [66].

The cyclopropylthallium compounds provide an opportunity to quantify the previously suggested [27,34] stereochemical dependence of vicinal proton–thallium coupling. Values of ^3J(Tl–H) are available [34] for norbornyl- and norbornenyl-thallium(III) compounds and like those reported here for cyclopropyl derivatives, they have been derived without assumption of ^3J(Tl–H) stereochemical dependence. These, the values for monocyclopropyl compounds, and values for other norbornyl derivatives [25] and a thallium derivative of D-galactal triacetate [27] (assignment bases not reported [25,27]) are shown plotted against dihedral angle (estimated from molecular models) in Fig. 1. All values of ^3J(Tl–H) are assumed positive, as demonstrated for the norbornyl [34] and cyclopropyl compounds. The curve shown in Fig. 1 was obtained by computer least squares fit of the results to the expression [67] $^3J(\text{Tl–H}) = A + B\cos\phi + C\cos 2\phi$ using a principal axis minimization routine [68]. Values of the fitting parameters are: $A = 7.7 \times 10^2$, $B = -3.2 \times 10^2$, $C = 8.3 \times 10^2$. Although the fit is poor (rms error 253.5), a Karplus-type relationship is indicated. Additional experimental points covering "missing" angles are needed for satisfactory definition of the relationship.

The J(Tl–H) values for the biscyclopropylthallium(III) derivatives provide a further test of the reported [66] correlation between J(M–H) (M = Sn, Hg, Pb, Tl) for vicinal and geminal couplings. The empirical relationship $^nJ(\text{M–H}) = A[^nJ(\text{M}'\text{–H})] + B$ ($n = 2, 3$; A and B are constants for a particular choice of metals M and M′) correlates couplings in similar molecular systems. Calculation of $^3J(\text{Tl–H})_{cis}$ for $Tl[CH(CH_2)_2]_2X$ by this method yields 573 Hz, in excellent agreement with experiment, i.e. 564–579 Hz. Predictions are less satisfactory for $^3J(\text{Tl–H})_{trans}$ (calc., 282; found, 338–345 Hz), and for $^2J(\text{Tl–H})_{gem}$ (calc., 233, found, 318–409 Hz).

A preference for equatorial substitution by thallium in the cyclohexyl derivative, **14**, can be suggested on the basis of the value of ^3J(Tl–C) (452–458 Hz at ambient temperature). The dicyclohexylthallium(III) compound can exist in three conformations depending on the equatorial (e) or axial (a) position of thallium, i.e. (e,e), (a,a), and (a,e). Although a mixture of all three conformers might be characterized by four values of ^3J(Tl–C) corresponding to ^3J(axial) in (a,a) and (a,e) and ^3J(equatorial) in (e,e) and (a,e), consideration of results for dicyclohexylmercury(II)

[31] suggests that ^3J(equatorial) in (e,e) and (a,e) would have similar values. Assuming that ^3J(axial) would also remain unaffected by the conformation of the second cyclohexyl group in (a,a) and (a,e), the mixture would then be characterised by just two vicinal couplings, ^3J(axial) and ^3J(equatorial). ^{13}C NMR studies of norbornylthallium(III) derivatives [23–25], $TlRX_2$, provide evidence for an angular dependence of vicinal thallium–carbon coupling; values of ^3J(Tl–C) for pathways not involving oxygen substituents [23–25] are 3–169 Hz for ϕ (dihedral angle) ca. 85° and 1057–1303 Hz for ϕ ca. 170°. (Dihedral angles were estimated from molecular models). The single value of ^3J(Tl–C) observed for **14** might represent an average of ^3J(axial) and ^3J(equatorial) arising from one or more rapidly "flipping" conformers, or it might imply the presence of only rigid conformers (e,e) or (a,a). In either case, the observed value (after multiplication by ca. 2 (Table 5) to estimate the coupling in the monocyclohexyl derivative; i.e. ca. 900 Hz) indicates a distinct preference for equatorial (ϕ ca. 180°) rather than axial (ϕ ca. 60°) thallium substitution. This argument neglects the signs of the relevant couplings, but they are likely to be uniformly positive. Poor solubility precluded variable temperature experiments. The proton spectrum of **14** is also consistent with a preponderance of equatorially substituted conformer. Again assuming that the conformation of one ring has negligible effect on coupling in the other ring, four values of ^3J(Tl–H) are possible, arising from axially substituted thallium (^3J(Tla–Ha), ^3J(Tla–He)), and equatorially substituted thallium (^3J(Tle–Ha), ^3J(Tle–He)). Doubling the observed values of ^3J(Tl–H) to estimate values for $[Tl(CH_2)_5CH]^{2+}$ (i.e. ca. 700 and ca. 400 Hz), and using the angular dependence of ^3J(Tl–H) (Fig. 1), allows exclusion of a major contribution from the axially substituted conformation where the dihedral angle (ca. 180°) for ^3J(Tla–Ha) would be expected to produce a much larger coupling than either of these estimated values. This result contrasts with the axial substitution for thallium observed in the oxythalliation product of tri-O-acetyl-D-galactal [27], where steric factors undoubtedly influence thalliation of the highly substituted carbohydrate. NMR studies have indicated both equatorial and axial preferences for cyclohexyl derivatives of mercury [31] and equatorial preference for tin and lead compounds [30].

The ^{13}C NMR results can be usefully extended to consider conformation in the cyclopentyl derivative, **13**. Two puckered conformations of cyclopentane (the envelope and half-chair forms) have been recognized as representing probable energy minima, and models indicate that interactions with adjacent CH_2 groups would be minimised by substitution in axial or equatorial positions rather than in quasiaxial, quasiequatorial or bisectional positions [69]. Estimated dihedral angles (using molecular models) for vicinal thallium-carbon units with axial and equatorial thallium substitution are in the ranges 80–100° and 140–150° respectively. Again using the dependence of ^3J(Tl–C) on dihedral angle [23–25] the observed value of ^3J(Tl–C) (394 Hz) for **13** can, after allowance for the previously noted differences between values for TlR_2X and $TlRX_2$, be used to suggest a preference for equatorial substitution.

J(Tl–C) and J(Tl–H) for unsaturated R groups

Thallium–carbon coupling in alkenyl- and phenyl-thallium(III) [19,21] derivatives follows the same pattern as in alkylthallium(III) compounds, i.e. $|^1J| \gg |^3J| > |^2J|$, but unlike the alkyl case, ^2J has the same sign as ^1J in alkenyl compounds, and ^3J in phenyl derivatives [18], i.e. positive. A similar contrast occurs for ^{2}J(Tl–H) and ^{3}J(Tl–H) between the alkenyl compounds (^{2}J and ^{3}J both positive) and the alkyl compounds (^{2}J negative and ^{3}J positive). The former pattern is observed for cyclopropyl derivatives, **12b** and **30**, and this may reflect the partial olefinic character of the cyclopropane ring [70].

The most striking feature of the coupling in compounds with unsaturated R groups is the very large value of ^{1}J(Tl–C) compared to unsaturated derivatives. Thus ^{1}J(Tl–C) ranges are: for TlR_2X, alkyl [22] (excluding R = Me) 1863–2640 Hz, alkenyl 4173–5223 Hz, phenyl [21] 4996–5359 Hz; for $TlRX_2$, alkyl [22] 5002–6108 Hz, alkenyl 8715 Hz, phenyl [19] 10718 Hz. These increases can be partly attributed to hybridization changes at the α-carbon atom which affect the Fermi contact contribution through the $\alpha^2(C)$ term [14]. Equating $\alpha^2(C)$ with the square of the coefficient of the α-carbon 2*s* orbital, the ratio of ^{1}J(Tl–C) in the alkyl and unsaturated compounds should be 1/1.32. A contribution which might be expected to bring this ratio nearer to the experimental observed value (ca. 1/2) arises from changes in the effective nuclear charge at thallium [14] due to the nature of the organogroup. It is interesting that, alone amongst the alkyl derivatives, ^{1}J(Tl–C) values for the cyclopropyl compounds fall into the unsaturated group range, presumably again reflecting olefinic character.

Values of ^{3}J(Tl–H) for alkenyl derivatives are highly stereospecific and it is worth noting that the results for the monovinyl compound (**31**) (^{3}J(*trans*), 3574 Hz; ^{3}J(*cis*), 1707 Hz) and for $TlPh(OCOCF_3)_2$(^{3}J, 1035 Hz) [19] qualitatively follow the Karplus-type dependence illustrated in Fig. 1.

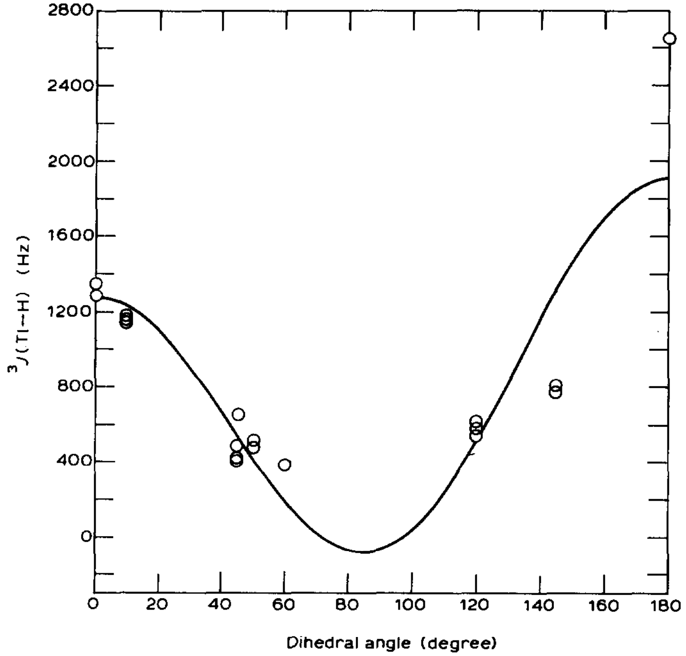


Fig. 1. Dependence of ^{3}J(Tl–H) on dihedral angle for $TlRX_2$ derivatives (see text). Dihedral angles were estimated from molecular models (Dreiding). The continuous curve represents the best fit to a Karplus-type expression.

Effect on J(Tl–C) and J(Tl–H) of substituent Cl

The effect of an electronegative substituent on ^1J(Tl–C), ^2J(Tl–H), and ^1J(C–H) has been investigated for the relatively simple case of TlR(OAc)$_2$ in MeOH (R = CH$_3$ (**25**), ClCH$_2$ (**34**)). The signs of the coupling constants and the value of ^1J(C–H) (137 Hz) determined for the dimethyl derivative, **1**, are assumed to apply also to **25**. Assuming that the Fermi contact contribution dominates all three couplings, the increase in ^1J(Tl–C) and ^1J(C–H) on substitution of Cl for H can be rationalized on the basis of Bent's postulate [71] that the *s*-character of an atom (carbon in this case) tends to concentrate in orbitals directed towards the more electropositive elements. However, as mentioned above, the approximation for the Fermi contact interaction which involves hybrid orbital "*s*-character" cannot accommodate the negative sign of ^2J(Tl–H). Thus the increase in ^2J(Tl–H) from −939 Hz in **25** to −451 Hz in **34** may be better considered in terms of the theory involving mutual polarizability [59,61]. The increase could then be attributed to an increase in either or both the mutual polarizability and the valence *s*-electron densities at the coupled nuclei. The effective nuclear charges and hence the latter terms would certainly be increased by the presence of Cl. The opposite effect is expected for substitution of carbon with the more electropositive (CH$_3$)$_3$Si group in Tl[(CH$_3$)$_3$CCH$_2$]$_2$Cl [22], and this is indeed observed; ^2J(Tl–H) decreases from −415 Hz to −556 Hz [22].

Results for other pairs of compounds (cf. **17** with **18**, **31** with **32**, and **1** with **23**) show that chlorine substitution increases coupling to the carbon of attachment.

Carbon-13 chemical shifts

The effects of substituting thallium for hydrogen on the carbon-13 chemical shifts of the parent hydrocarbons [72] are remarkably uniform over the wide range of organogroups studied. Summarizing the results for TlR$_2$X compounds, substitution by thallium causes downfield shifts in the range 24.6 to 43.2 ppm for C(α), and 1.2 to 10.4 ppm for C(β), and variations in the ranges −0.8 to 3.0 and −1.5 to 1.3 ppm are observed for C(γ) and C(δ) respectively. Analogous substituent effects for the TlRX$_2$ compounds fall within, or close to, these ranges. The ranges encompass variations of anion, X, solvent and, in the case of TlR$_2$X derivatives, the fact that the actual substituent is TlR and thus varied with R. The magnitude and direction of the α-, β-, and γ-substituent effects induced by thallium closely resemble those noted for organo-mercury [51] and -lead [6,7] compounds. The pattern of carbon shifts for organotin compounds is highly dependent on the nature of other substituents on tin and only approaches the pattern observed for thallium, mercury and lead derivatives for monoorganotin compounds [29,53].

Experimental

Preparations

All preparations involving Grignard or organolithium reagents were carried out in dry solvents under argon, and organo-halides were distilled prior to use and stored over molecular sieves (4A). Solvents were dried by standard procedures. The following compounds were prepared by published methods: **1** [38], **2a** [73], **3a** [73], **4** [73], **5a** [73], **6a** [73], **12a** [49], **12b** [49], **18** [74], **22** [75], **23** [43,76], **24** [63], **26** [41], **27** [77], **30** [49], **33** [45], **34** [43,76]. Satisfactory analyses (C, H) were obtained for these compounds with the exception of **5a** and **6a** where ^{1}H NMR spectra showed no impurities.

It was found necessary to modify published methods for the preparation of the following compounds:

7a [78]: The mixture from reaction of isopropylmagnesium chloride and $TlCl_3$ was hydrolysed with aqueous (5%) ammonium chloride solution. The product was filtered off, washed with water and diethyl ether, dried over P_2O_5, and then stirred with absolute ethanol, (ca. 200 cm^3 ethanol per 5 g of product). After filtration, the solution was evaporated at 25°C on the rotary evaporator. Recrystallisation from ethanol gave the product as colourless needles. Found: C, 22.0; H, 4.4. $C_6H_{14}TlCl$ calcd.: C, 22.1; H, 4.3%.

8 [78]: The diethyl ether layer, present after hydrolysis of the reaction mixture, was removed by evaporation because the product was found to be soluble in it. The remaining aqueous suspension was filtered and the white product was washed with water and dried over P_2O_5. Recrystallisation from diethyl ether gave colourless needles. Satisfactory analyses (C, H) could not be obtained, but proton NMR spectra of a freshly prepared sample showed no impurities. The product was found to be unstable at room temperature (^{1}H NMR spectra indicate ca. 50% decomposition within 48 h) and was therefore stored at 0°C.

10 [78]: This compound was obtained as colourless, light sensitive needles by the modification described above for **8**. The product slowly decomposed at room temperature. Found: C, 26.0; H, 5.0. $C_8H_{18}TlCl$ calcd.: C, 27.1; H, 5.1%.

19 [79]: The organolithium reagent was treated with $TlBr_3$ in THF and the reaction mixture was hydrolysed with aqueous HBr (1%) at -10°C. Filtration gave a grey solid which was recrystallised from methanol to give a white, light sensitive solid. The compound slowly decomposed at room temperature. Found: C, 22.0; H, 2.9. $C_6H_{10}TlBr$ calcd.: C, 19.7; H, 2.7%.

31 [46]: Equimolar amounts of $Tl(CH_2CH)_2Cl$ [46] and $TlCl_3$ were mixed in MeOH-d_4 in an NMR tube. The product was not isolated but ^{1}H and ^{13}C NMR spectra were recorded using the reaction mixture.

Several previously unreported compounds were prepared by replacing the halide anion of a known compound with another anion, X. Generally, stoichiometric quantities of the halide derivative and AgX were stirred together in methanol for several hours. Silver halide was removed by filtration and the product was obtained by evaporating the filtrate at room temperature, followed by recrystallization from methanol. Compounds prepared in this way are: **7b** from **7a**, (^{1}H NMR showed no impurities); **9a** from $Tl[(CH_3)_2CH(CH_2)_2]_2Cl$ [78] (Found: C, 29.2; H, 5.4. $C_{10}H_{22}TlNO_3$ calcd.: C, 29.4; H, 5.4%); **9b** from $Tl[(CH_3)_2CH(CH_2)_2]_2Cl$ [78] (Found: C, 35.6; H, 6.2. $C_{12}H_{27}TlO_2$ calcd.: C, 35.5; H, 6.2%); **13** from $Tl[(CH_2)_4CH]_2Cl$ (prepared by a method analogous to that reported for $Tl[(CH_2)_5CH]_2Cl$ [78] (Found: C, 27.8; H, 4.1. $C_{10}H_{18}TlBF_4$ calcd.: C, 27.9, H, 4.2%); **14** from $Tl[(CH_2)_5CH]_2Cl$ [78] (Found: C, 31.2; H, 4.7. $C_{12}H_{22}TlBF_4$ calcd.: C, 31.5; H, 4.8%); **17a** from $Tl(CH_2CH)_2Cl$ [46] (^{1}H NMR showed no impurities); **17b** from $Tl(CH_2CH)_2Cl$ [46] (Found: C, 22.3; H, 2.8. $C_6H_9O_2Tl$ calcd.: C, 22.6; H, 3.4%); **20**, and *cis,cis*/*trans,cis* isomers, from Tl(*trans*-$CH_3CHCH)_2Cl$ (see below) (Found: C, 20.5; H, 2.8, N, 3.9. $C_6H_{10}TlNO_3$ calcd.: C, 20.7; H, 2.9, N, 4.0%); **21** from Tl(*trans*-$PhCHCH)_2Br$ (see below) (Found: C, 40.9; H, 2.7. $C_{16}H_{14}TlNO_3$ calcd.: C, 40.7; H, 2.9%). **2b** was prepared in a similar way from **2a** using H_2O as solvent (Found: C, 23.5; H, 4.3. $C_6H_{13}TlO_2$ calcd.: C, 22.4; H, 4.1%). A similar method, using $TlNO_3$ in pyridine, followed by recrystallization from pyridine/H_2O (1/4 v/v), was used to prepare **5b** from **5a** (Found: C, 29.3; H, 5.3; N, 3.4. $C_{10}H_{22}TlNO_3$ calcd.: C, 29.4; H, 5.4; N, 3.4%) and **6b** from **6a** (Found: C, 33.1; H, 6.1; N, 3.3. $C_{12}H_{26}TlNO_3$ calcd.: C, 33.0; H, 6.0; N, 3.2%). Metathesis of **2a** with $TlNO_3$ in H_2O followed by recrystallisation from water gave **2c** (Found: C, 14.9; H, 3.2; N, 4.4. $C_4H_{10}TlNO_3$ calcd.: C, 14.8; H, 3.1; N, 4.3%). **3b** was prepared from **3a** in an analogous way to **2c** (^1H NMR showed no impurities).

Several new compounds were synthesized as detailed below.

Compound 11. A solution of $Mg[CH_3(CH_2)_2(CH_3)CH]Br$ (0.13 mol), prepared from equimolar quantities of $CH_3(CH_2)_2(CH_3)CHBr$ and magnesium in Et_2O (100 cm^3), was added during 1 h to a solution of $TlCl_3$ (0.06 mol) in Et_2O (50 cm^3) at $-20°C$. Hydrolysis of the mixture at 0°C with aqu. HCl (50 cm^3, 2 mol dm^{-3}), followed by evaporation of the ether layer gave **11** as a pale yellow solid which was isolated by filtration. The crude product was dried over concentrated H_2SO_4 and recrystallized from Et_2O to yield colourless needles (2%) which were light sensitive and which decomposed slowly at room temperature. (Found: C, 30.9; H, 5.5 $C_{10}H_{24}TlCl$ calcd.: C, 31.4; H, 5.8%).

Compounds 15 and 16. Reaction of $Mg[(CH_2)_6CH]Br$ or $Mg[(CH_2)_5CHCH_2]Br$ in Et_2O with freshly prepared $TlBr_3$ in THF in a manner analogous to that described for **12a** [49] yielded **15** (14%) (Found: C, 37.0; H, 5.4. $C_{14}H_{26}TlBr$ calcd.: C, 35.1; H, 5.6%) or **16** (82%) (Found: C, 34.2; H, 5.3. $C_{14}H_{26}TlBr$ calcd.: C, 35.1, H, 5.4%), respectively.

Compounds 28, 29 and 32. Equimolar amounts of $Tl[(CH_3)_2CHCH_2]_2(OCOCHMe_2)$ (obtained from reaction of **8** with $AgOCOCHMe_2$ by a method similar to that described for **7a**, or **9b**, and $Hg(OCOCHMe_2)_2$, or $Hg(OAc)_2$, respectively, were mixed in MeOH-d_4 in an NMR tube. These solutions were used for NMR studies which also indicated that the reactions proceeded to ca. 60% completion and that the products decomposed in the reaction mixture within a few hours. **32** was similarly prepared, without isolation, from **18** and $TlCl_3$ in MeOH-d_4 (reaction ca. 70% complete).

The compound Tl(*trans*-$CH_3CHCH)_2Cl$, used as a precursor for **20**, was prepared as a mixture of *trans,trans*, *trans,cis* and *cis,cis* isomers by a method similar to that reported [80] for the isomerically pure bromide derivatives but using instead a freshly distilled mixture of *cis*- and *trans*-propenylbromide to prepare the lithium reagent which was reacted with $TlCl_3$, (Found: C, 22.2; H, 4.1. $C_6H_{10}TlCl$ calcd.: C, 22.4; H, 3.1%). The precursor for **21**, Tl(*trans*-$PhCHCH)_2Br$, was prepared using an organolithium reagent instead of by the previously reported reaction of $TlBr_3$ with β-styrylboronic acid [81]. A solution of β-styryllithium was prepared from β-styrylbromide (ca. 85% *trans* isomer; Koch-Light Ltd. 0.1 mol) and lithium (0.2 mol) in diethyl ether (100 cm^3) at $-5°C$. A solution of $TlBr_3$ (0.06 mol), prepared by mixing TlBr (0.06 mol) and Br_2 (0.06 mol) in THF (100 cm^3), was added at 0°C with vigorous stirring over one hour to the solution of β-styryllithium. After stirring for a further 20 min, the reaction mixture was filtered and the grey solid washed with water and diethyl ether. The product was obtained as a white solid by recrystallization from pyridine. (Found: C, 38.9; H, 2.9. $C_{16}H_{14}TlBr$ calcd.: C, 39.2; H, 2.9%).

Trichlorothallium(III) was prepared as reported by Meyer [82] with the modification that the product was dried over P_2O_5 under vacuum until the IR spectrum showed the absence of water (3 days). Other thallium, silver and mercury compounds used were commercially available with the exception of HgX_2 and AgX ($X = OCOCHMe_2$). $Hg(OCOCHMe_2)_2$ was prepared by adding freshly prepared orange mercuric oxide [83] (0.02 mol) in small portions to hot (ca. 150°C) isobutyric acid (10 cm^3). The resulting clear solution yielded the product (90%) as colourless plates on cooling. The product was filtered off, washed with diethyl ether and dried in vacuo over KOH. Isobutyratosilver(I) was prepared by heating isobutyric acid (150 cm^3) to ca 150°C and adding Ag_2O (0.09 mol) in small portions during 30 min. A further 20 cm^3 of isobutyric acid was added to the thick greyish suspension and the mixture heated for a further 2 h. A colourless crystalline solid was obtained on cooling. After standing overnight the product (90%) was filtered and washed with several portions of diethyl ether and then dried under vacuum. Commercially available organic substrates were used, with the exception of $(CH_3)_2CH(CH_2)_2Cl$ which was prepared from $(CH_3)_2CH(CH_2)_2OH$ by a standard method [84].

NMR spectra. Proton NMR spectra were obtained on a Perkin–Elmer R12B spectrometer at 60 MHz operating in lock mode. Signal positions were measured in 100 Hz expansions using a Racal digital frequency counter, and ^1H-$\{^1H\}$ experiments were performed using the Perkin–Elmer Double Resonance Accessory. Some spectra were obtained at 220 MHz on a Perkin–Elmer R34 spectrometer. Carbon-13 NMR spectra were obtained variously at 20.1, 22.63 and 45.28 MHz on WP80, HX 90E, and WH 180 WB Bruker spectrometers, respectively.

Acknowledgement

We thank the S.R.C. for a Studentship (to F.B.), a Technicianship (M.M.T.), and for use of the P.C.M.U. ^{13}C facility. We are particularly grateful to Dr. I. Stenhouse and Mr. M. Cooper at P.C.M.U. for their patient cooperation and helpful advice.

References

1 B.E. Mann, Adv. Organomet. Chem., 12 (1974) 135.
2 M.H. Chisholm and S. Godleski, Prog. Inorg. Chem., 20 (1976) 299;
P.W.N.M. van Leeuwen and K. Vrieze, ibid., 14 (1971) 1;
H.D. Kaesz, M.L. Maddox, and S.L. Stafford, Adv. Organomet. Chem., 3 (1965) 1.
3 V.S. Petrosyan, Progress in NMR Spectroscopy, 11 (1977) 115.
4 T.G. Appleton, H.C. Clark and L.E. Manzer, Coord. Chem. Rev., 10 (1973) 335.
5 V.S. Petrosyan and O.A. Reutov, J. Organomet. Chem., 76 (1974) 123.
6 R.H. Cox, J. Magn. Reson., 33 (1979) 61.
7 J. Gmehling, F. Huber, and T.N. Mitchell, J. Chem. Soc. Dalton, (1978) 960.
8 D.C. Van Beelen, A.E.J. van Kampen, and J. Wolters, J. Organomet. Chem., 187 (1980) 43.
9 D.C. van Beelen, G.J.M. Bots, L.J. van Doorn, D. de Vos, and J. Wolters, Inorg. Nucl. Chem. Lett., 12 (1976) 581.
10 C.J. Turner and R.F.M. White, J. Magn. Reson., 26 (1977) 1;
H. Dreeskamp and K. Hildenbrand, Z. Naturforsch. A, 23 (1968) 940.
11 W. Erb, H. Muller, L. Rosch, and R. Zeisberg, J. Organomet. Chem., 140 (1977) C17.
12 R.W. Briggs and J.F. Hinton in R.K. Harris and B.E. Mann (Eds.), NMR and the Periodic Table, Academic Press, 1979, pp. 288.
13 H. Dreeskamp and K. Hildenbrand, Z. Phys. Chem., 69 (1970) 171.
14 D.G. Gillies, C.S. Hoad, R.W. Matthews and M.M. Thakur, J. Organomet. Chem., 124 (1977) C31.
15 P.J. Burke, D.G. Gillies, and R.W. Matthews, J. Organomet. Chem., 118 (1976) 129.
16 P.J. Burke, D.G. Gillies, L.A. Gray, P.J.C. Hayward, R.W. Matthews, and M. McPartlin, J. Organomet. Chem., 136 (1977) C7.

17 K. Henrick, R.W. Matthews, and P.A. Tasker, Inorg. Chem., 16 (1977) 3293; P.J. Burke, D.G. Gillies and R.W. Matthews, J. Chem. Res., (S), (1981) 124; C. Schramm and J.I. Zink, J. Magn. Reson., 26 (1977) 513; H.J. Fuller, F.H. Kohler, and H. Schmidbaur, J. Organomet. Chem., 99 (1975) 353; A.T.T. Hsieh, C.A. Rogers, and B.O. West, Australian J. Chem., 29 (1976) 49; S. Bauer, B. Walther, and A. Zschunke, Z. Anorg. Allg. Chem., 450 (1979) 70.

18 L. Ernst, J. Organomet. Chem., 82 (1974) 319.

19 M. Duteil and J.Y. Lallemand, Organic Magn. Reson., 8 (1976) 328.

20 W. Adcock, D. Doddrell, W. Kitching, C.J. Moore, and D. Praeger, J. Organomet. Chem., 70 (1974) 339; W. Adcock, D. Doddrell, W. Kitching, and C.J. Moore, ibid., 94 (1975) 469; L. Ernst, Organic Magn. Reson., 6 (1974) 540.

21 R.T. Griffin, K. Henrick, R.W. Matthews and M. McPartlin, J. Chem. Soc. Dalton, (1980) 1550.

22 F. Brady, D.G. Gillies, K. Henrick, and R.W. Matthews, J. Organomet. Chem., 193 (1980) 21.

23 P.F. Barron, D. Doddrell, and W. Kitching, J. Organomet. Chem., 132 (1977) 351.

24 T. Inubushi, H. Miyoshi, I. Morishima, and S. Uemura, J. Amer. Chem. Soc., 100 (1978) 354.

25 T. Inubushi, H. Miyoshi, I. Morishima, M. Okano, and S. Uemura, J. Organomet. Chem., 165 (1979) 9.

26 F. Brady, K. Henrick, and R.W. Matthews, J. Organomet. Chem., 210 (1981) 281.

27 V.G. Gibb and L.D. Hall, Carbohydrate Res., 63 (1978) C1.

28 D.F. Evans and J.P. Maher, J. Chem. Soc., (1965) 637.

29 J.L. Considine, H.G. Kuivila, R.J. Mynott, and R.H. Sarma, J. Organomet. Chem., 111 (1976) 179.

30 D. Doddrell, J.B. Grutzner, and W. Kitching, J. Organomet. Chem., 107 (1976) C5.

31 P.F. Barron, D. Doddrell, and W. Kitching, J. Organomet. Chem., 139 (1977) 361.

32 F. Brady, D.G. Gillies, and R.W. Matthews, unpublished work.

33 D.W. Turner, J. Chem. Soc., (1962) 847.

34 F.A.L. Anet, Tetrahedron Letts., 46 (1964) 3399.

35 H. Booth, Progress in NMR Spectroscopy, 5 (1969) 149.

36 J.A. Pople, W.G. Schneider, and H.J. Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill, New York 1959, p. 242.

37 F. Brady, M.J. Forster, D.G. Gillies and R.W. Matthews, J. Inorg. Nucl. Chem. Letters, 17 (1981) 155; Chemical Communications, (1981) 911.

38 R.S. Drago and G.D. Shier, J. Organomet. Chem., 5 (1966) 330.

39 B. Adler, S. Bauer, A. Kolbe, B. Walther, and A. Zschunke, Z. Anorg. Allg. Chem., 427 (1976) 137.

40 J. Dallorso, G. Hoffman, H. Koppel, and B. Walther, Z. Anorg. Allg. Chem., 427 (1976) 24.

41 H. Kurosawa and R. Okawara, J. Organomet. Chem., 10 (1967) 211.

42 J.V. Hatton, J. Chem. Phys., 40 (1964) 933.

43 T. Abe and R. Okawara, J. Organomet. Chem., 43 (1972) 117.

44 H. Kurosawa and R. Okawara, J. Organomet. Chem., 14 (1968) 225.

45 N.H. Fellers and R.K. Sharma, J. Organomet. Chem., 49 (1973) C69.

46 A.E. Borisov, E.I. Golubeva, A.N. Nesmeyanov, and I.S. Savel'eva, Izvest. Akad. Nauk, SSSR, Otdel. Khim. Nauk, (1958) 1490.

47 J.P. Oliver and A.T. Weibel, J. Organomet. Chem., 74 (1974) 155.

48 K. Henrick, R.W. Matthews, and P.A. Tasker, Acta Cryst. B, 34 (1978) 935; 1347; S.K. Seale and J.L. Atwood, J. Organomet. Chem., 64 (1974) 57; D. Britton and Y.M. Chow, Acta Cryst. B, 31 (1975) 1922; 1929; 1934; T.L. Blundell and H.M. Powell, Proc. Roy. Soc. A, 331 (1972) 161; H.-D. Hausen, E. Veigel, and H.-J. Gudner, Z. Naturforsch. B, 29 (1974) 269; G.H.W. Milburn and M.R. Truter, J. Chem. Soc., A, (1967) 648; G. Mann, W. Schwarz, and J. Weidlein, J. Organomet. Chem., 122 (1976) 303.

49 F. Brady, K. Henrick, and R.W. Matthews, J. Organomet. Chem., 165 (1979) 21.

50 H.S. Gutowsky and C.J. Jameson, J. Chem. Phys., 51 (1969) 2790.

51 J. Casanova, H.R. Rogers, and K.L. Servis, Organic Magn. Res., 7 (1975) 57.

52 B. Barbe, M. Pereyre, M. Petraud, and A. Rahm, J. Organomet. Chem., 139 (1977) 49; G. Domazetis, B.D. James, and R.J. Magee, J. Organomet. Chem., 148 (1978) 339.

53 T.N. Mitchell, Organic Magn. Reson., 8 (1976) 34.

54 T.N. Mitchell and G. Walter, J. Organomet. Chem., 121 (1976) 177.

55 R.K. Harris and B.E. Mann, Eds., NMR and the Periodic Table, Academic Press, London, 1978.

56 P.R. Dean, and W. McFarlane, Mol. Phys., 13 (1967) 343; K.A. McLauchlan, L.W. Reeves and D.H. Whiffen, Mol. Phys., 10 (1966) 131.

57 P.T. Narasimhan and M.T. Rogers, J. Chem. Phys., 31 (1959) 1430.
58 J.D. Roberts and F.J. Weigert, Inorg. Chem., 12 (1973) 313.
59 J.A. Pople and D.P. Santry, Mol. Phys., 8 (1964) 1.
60 H.M. McConnell, J. Chem. Phys., 24 (1956) 460.
61 W. McFarlane, Quart. Rev., 23 (1969) 187.
62 T. Ibusuki, T. Iwayanagi, and Y. Saito, J. Organomet. Chem., 128 (1977) 145.
63 R. Kitano, H. Kurosawa and T. Sasaki, J. Chem. Soc. Dalton, (1978) 234.
64 F.J. McQuillin, Alicyclic Chemistry, Cambridge University Press, Cambridge, 1972, p. 12.
65 S. Kondo, K. Tokita, and M. Takeda, J. Chem. Res. (S), (1980) 63.
66 J.P. Oliver and P.A. Scherr, J. Amer. Chem. Soc., 94 (1972) 8026.
67 M. Karplus, J. Amer. Chem. Soc., 85 (1963) 2870.
68 D. Hyatt and R.W. Matthews, unpublished work.
69 M. Hanack, Conformational Theory, Academic Press, New York, 1965, Cht. 3.
70 M. Charton, Olefinic Properties of Cyclopropanes, in J. Zabicky (Ed.), The Chemistry of Alkenes, Vol. 2, Interscience, London, 1970.
71 H.A. Bent, J. Inorg. Nucl. Chem., 19 (1961) 43.
72 J.B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press, New York, 1972.
73 L.F. Elson, A. McKillop, and E.C. Taylor, J. Organomet. Chem., 15 (1968) 500.
74 R.K. Freidlina, A.K. Kochetkov, and A.N. Nesmeyanov, Izvest. Akad. Nauk. SSSR, Otdel. Khim. Nauk, (1948), 445.
75 A.E. Goddard and D. Goddard, J. Chem. Soc., (1922) 482.
76 F. Challenger and B. Parker, J. Chem. Soc., (1931) 1462; A.I. Vogel, A Textbook of Practical Organic Chemistry, 3rd ed., Longmans, London, 1964, p. 843.
77 H. Kurosawa, R. Okawara, and M. Tanaka, J. Organomet. Chem., 18 (1969) 49.
78 A. von Grosse and E. Krause, Ber., 58 (1925) 1933.
79 A.E. Borisov, A.N. Nesmeyanov, and N.V. Novikova, Doklady Akad. Nauk. SSSR, 96 (1954) 289.
80 A.E. Borisov, A.N. Nesmeyanov, and N.V. Novikova, Izvest. Akad. Nauk. SSSR. Otdel. Khim. Nauk, (1959) 1216.
81 N.Ya Kronrod and V.A. Sazonova, Zhur. Obsche. Khim., 26 (1956) 1876.
82 R.J. Meyer, Z. Anorg. Allg. Chem., 24 (1900) 325.
83 W.G. Palmer, Experimental Inorganic Chemistry, Cambridge Univ. Press, London, 1965, p. 182.
84 A.I. Vogel, A Textbook of Practical Organic Chemistry, 3rd ed., Longmans, London, 1964, p. 276.