Non-arylic Diorganothallium Derivatives obtained by Metallation. Synthesis and Isolation of the First Diketonylthallium(III) Complexes

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Addition of trifluoroacetic or trifluoromethanesulfonic acid to solutions of thallium(III) trifluoroacetate in acetone results in formation of the compounds $[Tl\{CH_2C(O)Me\}_2X]$ (X = CF_3CO_2 **1a** or CF_3SO_3 **1b**. Compound **1b** reacts in a 1:1 ratio with LiCl or KBr giving the halogeno derivatives $[Tl\{CH_2C(O)Me\}_2Y]$ (Y = Cl **2a** or Br **2b**). Compound **2a** reacts with $[N(PPh_3)_2]Cl$ yielding the anionic complex $[N(PPh_3)_2][Tl\{CH_2C(O)Me\}_2Cl_2]$ **3**. The reaction of **1b** with 2,2'-bipyridine (bipy) gives $[\{Tl[CH_2C(O)Me]_2(\mu\text{-}CF_3SO_3)(bipy)\}_2]$ **4** in which each thallium atom has a distorted six-co-ordination with the acetonyl ligands in *trans* positions and two *cis* positions occupied by two bridging triflate anions.

Metallation reactions of organic compounds usually lead to monoorganometallic derivatives and, sometimes, to products resulting from polymetallation of the organic substrate. They seldom allow the isolation of a diorganometallic compound. As far as we are aware, there is only one example of the formation of a diorganothallium(III) compound by a thallation reaction (occurring at high temperatures) and only a few examples involving reaction of an organic substrate with a monoorganothallium(III) derivative.[1,2] In both cases the thallium compounds are aryl derivatives. In this paper we report the first example of the synthesis and isolation of non-arylic diorganothallium derivatives obtained by metallation.

Metallated ketones play a very important role in organic synthesis.[3] There are several ways to prepare them involving, for example, direct metallation of the ketone, oxidative-addition reactions (with α-halogenocarbonyl compounds or epoxides), and transmetallation reactions.[4]

The activation of aromatic and heteroaromatic C–H bonds by thallium(III) salts (thallation reactions) to give mono-arylthallium derivatives constitutes a well known process of interest in organic synthesis.[1] However, such reactions are unknown for other organic substrates with the exception of some ketones: the formation of thallium(III) monoketonyl species, $[Tl\{CH_2C(O)R\}X_2]$ (R = Me, CMe_3, CH=CH_2, Ph, 4-chlorophenyl, 4-methoxyphenyl, mesityl or 2-naphthyl; X = Cl, Br, CN, MeCO_2 or CF_3CO_2), in aqueous solution has been reported, some of them being isolated. Diketonyl species, $[Tl\{CH_2C(O)R\}_2X]$, (R = Me or Ph) were assumed to be formed in solution (based on NMR data) but were always accompanied by the corresponding monoorgano derivatives and were never isolated.[5]

During work on the synthesis of monoarylthallium compounds[6] we detected the compound $[\overline{Tl(C_6H_4N=NPh)}\{CH_2C(O)Me\}(CF_3CO_2)]$ on heating $[\overline{Tl(C_6H_4N=NPh)}(CF_3CO_2)_2]$ in acetone. Furthermore, we had previously obtained gold(III) acetonyl complexes by C–H activation of acetone with 2-(phenylazo)phenylgold(III) complexes.[7] All this encouraged us to seek suitable conditions for the formation and isolation of thallium(III) acetonyl compounds. Some preliminary results have been communicated.[8]

Results

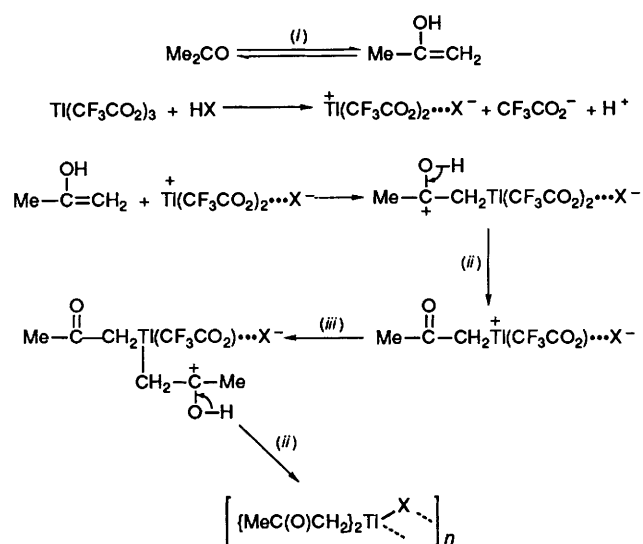*Synthesis.*—Addition of trifluoroacetic acid to brown acetone
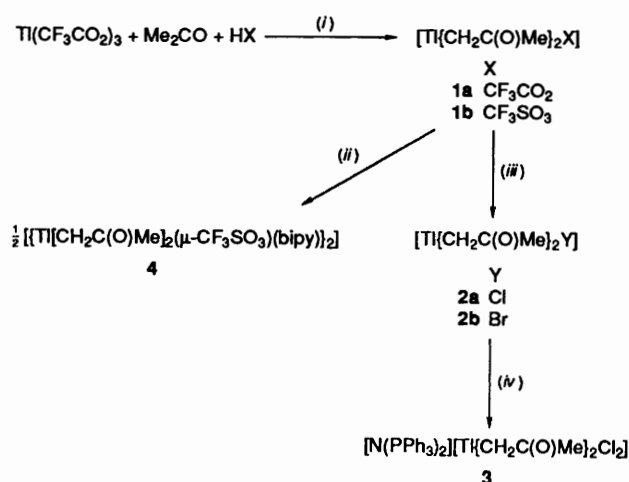
Scheme 1 (i) $-3CF_3CO_2H$; (ii) bipy; (iii) $+Y^-$, $-X^-$; (iv) $[N(PPh_3)_2]Cl$

solutions of $Tl(CF_3CO_2)_3$ (*ca.* 1:1) gives colourless solutions from which the compound $[Tl\{CH_2C(O)Me\}_2(CF_3CO_2)]$ **1a** could be isolated in moderate yield (35%). However, attempts to prepare derivatives of this compound failed because of the decomposition of the resulting compounds or the formation of intractable oils. However, on using the stronger trifluoromethanesulfonic acid instead of trifluoroacetic acid, the triflato ($CF_3SO_3^-$) analogue $[Tl\{CH_2C(O)Me\}_2(CF_3SO_3)]$ **1b** was obtained in good yield (76%) (Scheme 1). Similar reactions using MeC(O)Et, MeCHO, or MeC(O)R [R = $C_6H_2(OMe)_3$-3,4,5] do not form ketonyl compounds; the attempted metallation of MeCN using $Tl(CF_3CO_2)_3 + CF_3CO_2H$ was also unsuccessful.

The only diacetonyl compound of which we are aware is $[Hg\{CH_2C(O)Me\}_2]$, prepared by reaction of $[Hg\{N(SiMe_3)_2\}_2]$ with acetone.[9] The mercuration of acetone in aqueous solutions leads to a mixture of all possible mercuriated products from mono- to per-mercuriated acetone.[10]

By reaction of **1b** with LiCl or KBr the corresponding halogeno compounds $[Tl\{CH_2C(O)Me\}_2Y]$ (Y = Cl **2a** or Br **2b**) are easily isolated. They exhibit very low solubilities in most common solvents; however, when $[N(PPh_3)_2]Cl$ is added to **2a**

$$Me_2CO \xrightleftharpoons{(i)} Me-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2$$

$$Tl(CF_3CO_2)_3 + HX \longrightarrow \overset{+}{Tl}(CF_3CO_2)_2\cdots X^- + CF_3CO_2^- + H^+$$

$$Me-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2 + \overset{+}{Tl}(CF_3CO_2)_2\cdots X^- \longrightarrow Me-\overset{\overset{\displaystyle O\!-\!H}{|}}{\underset{+}{C}}-CH_2Tl(CF_3CO_2)_2\cdots X^-$$

$$\Bigg\downarrow (ii)$$

$$Me-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle O\!-\!H}{\underset{\displaystyle \|}{\overset{+}{C}-Me}}}{CH_2Tl(CF_3CO_2)}\cdots X^- \xleftarrow{(iii)} Me-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2\overset{+}{Tl}(CF_3CO_2)\cdots X^-$$

$$\Bigg\downarrow{\diagdown}{(ii)}$$

$$\left[\{MeC(O)CH_2\}_2Tl\diagdown\!\!\overset{X}{\underset{\cdots}{\diagdown}} \right]_n$$

Scheme 2 $X = CF_3SO_3$. (i) Catalytic H^+; (ii) $-CF_3CO_2^-$, $-H^+$; (iii) $+ MeC(OH)=CH_2$

(1:1) a solution is formed from which the anionic complex $[N(PPh_3)_2][Tl\{CH_2C(O)Me\}_2Cl_2]$ **3** can be isolated. The reaction of **1b** with KI gives a compound which, according to IR spectroscopy, could be $[Tl\{CH_2C(O)Me\}_2I]$. However, its solutions rapidly decompose to give TlI.

On the other hand compound **1b** reacts with 2,2′-bipyridine (bipy) to give the dimer $[\{Tl[CH_2C(O)Me]_2(\mu\text{-}CF_3SO_3)\text{-}(bipy)\}_2]$ **4**. This compound and **1b** behave as 1:1 electrolytes in acetone solution (see Experimental section) probably because of the formation of solvento complexes $[Tl\{CH_2C(O)Me\}_2\text{-}(bipy)(Me_2CO)_n][CF_3SO_3]$ or $[Tl\{CH_2C(O)Me\}_2(Me_2\text{-}CO)_n][CF_3SO_3]$, respectively. However, acetone does not displace the CF_3CO_2 group in **1a** since this compound does not behave as an electrolyte.

Except for the above reactions the reactivity of compound **1b** is very low. Thus, it does not add neutral ligands such as pyridine, PPh_3, or dibenzo-18-crown-6(6,7,9,10,17,18,20,21-octahydrodibenzo[b,k][1,4,7,10,13,16]hexaoxacycloocta-decine), nor give condensation products with 4-nitrophenyl-hydrazine or 3,4,5-trimethoxyphenylaniline; nor does it oxidize Pd^0 in $[Pd(dba)_2 + 2PPh_3]$ (dba = dibenzylideneacetone) or Au^I in $[AuCl(PPh_3)]$.

Discussion

The facile formation of diacetonylthallium(III) compounds in neat acetone contrasts with previous results in aqueous solution in which the main species (and the only isolable ones) were monoacetonyl compounds. However, our results confirm some observations made in the acetone–water system, e.g. that increasing the acetone:Tl^{III} ratio and using poorly co-ordinating anions increases the concentration of diorgano-thallium compounds in solution.[5]

We assume a double role for the acid in this metallation process. As in aromatic thallations, the presence of a strong acid (corresponding conjugate base is a weak co-ordinating ligand) catalyses these reactions by increasing the concentration of the electrophilic species. In addition, in our case, the acid is a catalyst in the formation of the enol that undergoes electrophilic attack by the thallium salt.[1,5] The monoacetonyl derivative first formed should have enough electrophilic character to attack the enol, giving the diorganothallium(III) compound (see Scheme 2).

The use of CF_3SO_3H probably contributes to the good yields of diacetonylthallium complexes; thallium(III) triflate is the most powerful electrophilic thallating agent yet investigated,
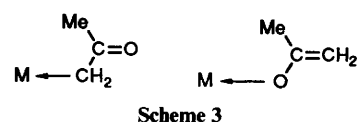
since it is capable of thallating polyfluorobenzenes, which are strongly deactivated towards electrophilic substitution and are not thallated by $Tl(CF_3CO_2)_3$.[1b,c] Our results suggest that a 1:1 mixture of $Tl(CF_3CO_2)_3$ and CF_3SO_3H is also a strong thallating agent. We assume in Scheme 2 that the electrophile responsible is the complex resulting from the displacement of CF_3CO_2H by the stronger acid CF_3SO_3H and formulated as $^+Tl(CF_3CO_2)_2\cdots(CF_3SO_3)^-$ to indicate that the triflato ligand is more weakly co-ordinated to thallium than is $CF_3CO_2^-$, thus rendering the intermediate more electrophilic than $Tl(CF_3CO_2)_3$.

Infrared Studies.—The solid-state IR spectra of compounds **1–4** show strong bands at *ca.* 1660 cm^{-1} (see Table 1) assignable to $\nu(CO)$ of the acetonyl groups. In the case of **1a** this band is masked by that due to $\nu_{asym}(CO_2)$ of the CF_3CO_2 group. The presence of the triflate anion in **1b** and **4** is confirmed by the appearance of bands at 1280–1285 $[\nu(SO_3)(E)]$ and 1025–1030 cm^{-1} $[\nu(SO_3)(A_1)]$.[11] The similar spectra of complexes **1b** and **4** suggests that the triflate ligand in **1b** acts as a bridging ligand, as in **4** (see below).

The chloro compound **2a** shows no absorption in the 200–300 cm^{-1} region that might be assignable to $\nu(TlCl)$, which may indicate a di- or polymeric structure with chloro bridges, as usually observed in halogenodiorganothallium com-pounds.[1b] Complex **2b** could be similar. However, **3** shows a broad band at 225 cm^{-1} assignable to terminal Cl–Tl bonds, which would point to a monomeric structure.

NMR Studies.—The most common co-ordination mode of a deprotonated ketone anion to a metal is through the oxygen atom to give enolato complexes (see Scheme 3).[3] In our case, ^{1}H NMR spectra indicate that CH_2COMe^- co-ordinates through the methylenic carbon atom, since the CH_2 protons are equivalent and appear as a doublet due to H–Tl coupling $[^2J(H-Tl) = 600-700 \text{ Hz}]$.[5] Methyl resonances appear as broad singlets but for complex **3** they occur as a doublet $[^4J(H-Tl) = 5 \text{ Hz}]$.

Structure of Compound 4.—The co-ordination of the acetonyl group through C was confirmed for complex **4** by X-ray diffraction studies (see Fig. 1). Details are given in the preliminary communication.[8]

Experimental

Infrared spectra, the C, H and N analyses, conductance measurements, melting-point determinations and ^{1}H NMR spectra were performed as described elsewhere.[7] Reactions were carried out at room temperature with magnetic stirring and without special precautions against light or atmospheric moisture.

$[Tl\{CH_2C(O)Me\}_2(CF_3CO_2)]$ **1a.**—Trifluoroacetic acid (2 drops, *ca.* 1.15 mmol) was added at room temperature to a brown solution of $Tl(CF_3CO_2)_3$ (500 mg, 0.92 mmol) in acetone (8 cm^3). The solution was stirred at room temperature until the colour disappeared (*ca.* 1 h). The solvent was partially removed and diethyl ether added to precipitate compound **1a** as a white solid. Yield 142 mg, 35%. M.p. 161 °C (decomp.); $\Lambda_M = 6 \ \Omega^{-1}$ cm^2 mol^{-1} (Found: C, 22.55; H, 2.40. Calc. for $C_8H_{10}F_3O_4Tl$: C, 22.25; H, 2.35%).

$[Tl\{CH_2C(O)Me\}_2(CF_3SO_3)]$ **1b.**—Operating as described for compound **1a**, $Tl(CF_3CO_2)_3$ (500 mg, 0.92 mmol) and

Scheme 3

$$\underset{M \longleftarrow CH_2}{\overset{\overset{\displaystyle Me}{\diagdown}}{\underset{\diagup}{C}=O}} \qquad\qquad \underset{M \longleftarrow O}{\overset{\overset{\displaystyle Me}{\diagdown}}{\underset{\diagup}{C}=CH_2}}$$

Table 1 Relevant spectroscopic data for complexes 1–4

| | | ^{1}H NMR data (δ, J/Hz) | | |
Compound	IR data (cm^{-1}), v(CO)	δ(CH$_2$)	^2J(TlH)	δ(CH$_3$)
1a [Tl{CH$_2$C(O)Me}$_2$(CF$_3$CO$_2$)]	See text	3.00(d)^a	728	2.13(s)
1b [Tl{CH$_2$C(O)Me}$_2$(CF$_3$SO$_3$)]	1650, 1670	2.58(d)^b	756	2.12(s)
2a [Tl{CH$_2$C(O)Me}$_2$Cl]	1650	2.68(d)^b	729	2.14(s)
2b [Tl{CH$_2$C(O)Me}$_2$Br]	1645, 1675	2.60(d)^b	633	2.11(s)
3 [N(PPh$_3$)$_2$][Tl{CH$_2$C(O)Me}$_2$Cl$_2$]^c	1665	2.94(d)^d	654	2.31(d)
4 [{Tl[CH$_2$C(O)Me]$_2$(μ-CF$_3$SO$_3$)(bipy)}$_2$]	1655, 1675	2.99(d)^{d,e}	692	1.98(s)

^{a} In (CD$_3$)CO. ^{b} In (CD$_3$)$_2$SO. ^{c} ^4J(TlH) 5 Hz. ^{d} In CDCl$_3$. ^{e} bipy resonances: δ 8.98 (H$^{3,3'}$, br d, $^3J_{HH}$ = 4.8 Hz), 8.2–8.0 (H$^{5,5'}$ + H$^{6,6'}$. m) and 7.64 (H$^{4,4'}$, br t).
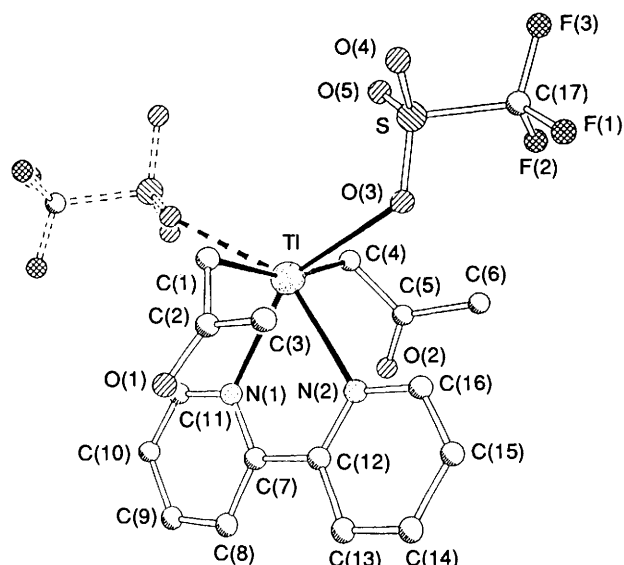
Fig. 1 The structure of compound 4. Radii are arbitrary; H atoms omitted for clarity. The co-ordination sphere at thallium is completed by a symmetry-generated triflate ion (indicated by dashed bonds)

CF$_3$SO$_3$H (2 drops, ca. 1.15 mmol) in acetone (8 cm^3) gave 1b as a white solid. Yield: 320 mg, 76%. M.p. 165 °C (decomp.); Λ_M = 103 Ω^{-1} cm^2 mol^{-1} (Found: C, 18.20; H, 2.25. Calc. for C$_7$H$_{10}$F$_3$O$_5$STl: C, 18.00; H, 2.15%).

[Tl{CH$_2$C(O)Me}$_2$Cl] **2a**.—Compound **1b** (75 mg, 0.16 mmol) was added to a solution of LiCl (7 mg, 0.16 mmol) in acetone (8 cm^3). After 15 min of stirring the white compound **2a** was filtered off and washed with acetone. Yield: 42 mg, 74%. M.p. 172 °C (decomp.) (Found: C, 20.70; H, 2.95. Calc. for C$_6$H$_{10}$ClO$_2$Tl: C, 20.35; H, 2.85%).

[Tl{CH$_2$C(O)Me}$_2$Br] **2b**.—Compound **1b** (50 mg, 0.11 mmol) and KBr (14 mg, 0.11 mmol) were mixed in acetone and stirred for 12 h. The white compound **2b** was filtered off and washed with acetone. Yield: 25 mg, 60%. M.p. 155 °C (decomp.) (Found: C, 18.00; H, 2.75. Calc. for C$_6$H$_{10}$BrO$_2$Tl: C, 18.10; H, 2.55%).

[N(PPh$_3$)$_2$][Tl{CH$_2$C(O)Me}$_2$Cl$_2$] **3**.—The salt [N-(PPh$_3$)$_2$]Cl (44 mg, 0.08 mmol) was added to a suspension of compound **2a** (27 mg, 0.08 mmol); most of the solid dissolved instantaneously. The mixture was filtered over Celite and the resulting solution partially evaporated. Addition of diethyl ether precipitated white compound **3**. Yield 49 mg, 70% M.p. 124 °C (decomp.); Λ_M = 103 Ω^{-1} cm^2 mol^{-1} (Found: C, 53.25; H, 4.80; N, 1.55. Calc. for C$_{42}$H$_{40}$Cl$_2$NO$_2$P$_2$Tl: C, 54.35; H, 4.35; N, 1.50%).

[{Tl[CH$_2$C(O)Me]$_2$(μ-CF$_3$SO$_3$)(bipy)}$_2$]   **4**.—Compound **1b** (75 mg, 0.16 mmol) and 2,2'-bipyridine (26 mg, 0.16 mmol) were allowed to react in acetone (8 cm^3) for 0.5 h. The solution was concentrated and diethyl ether added; compound **4** precipitated as a white solid. Yield 83 mg, 81%. M.p. 162 °C (decomp.); Λ_M = 98 Ω^{-1} cm^2 mol^{-1} (Found: C, 33.50; H, 3.25; N, 4.00. Calc. for C$_{17}$H$_{18}$F$_3$N$_2$O$_5$STl: C, 33.25; H, 2.95; N, 4.90%).

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