

SOME RECENT ADVANCES IN THE ORGANOMETALLIC CHEMISTRY OF THALLIUM(III)

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ABSTRACT

A summary, dealing mainly with the authors own work, of the preparations, reactions and structures of monoalkylthallium, alkylcyanothallium and unsymmetrical diorganothallium derivatives, is presented.

INTRODUCTION

Our review¹ 'Recent Advances in Organothallium Chemistry' included a list of 452 organothallium(III) and 26 thallium(I) organic derivatives which had been reported by the end of 1969. Other short reviews^{2, 3} have also been published.

Several triorganothalliums, R_3Tl , have been prepared since 1930. They all are hydrolysed readily by atmospheric moisture, and some of them are inflammable in air. It is frequently observed that one of the three organic groups of triorganothalliums is easily substituted with more electronegative groups, giving stable diorganothallium derivatives. Another notable feature of trialkylthalliums is that, although they are monomeric in solution, intermolecular alkyl exchange reactions occur easily.

Since the preparation of diethylthallium compounds in 1870, a large variety of diorganothallium compounds of the type R_2TlX have been synthesized and these are known to be among the most stable organometallic compounds. Most compounds of this type are thought to be salts of the diorganothallium cation which is isoelectronic with diorganomercurials, R_2Hg . It has been believed that the alkyl exchange reaction, which is often observed in trialkylthalliums, is difficult to occur in dialkylthallium compounds, because of the particular stability of the C-Tl-C group. We found that in some methylethylthallium derivatives, $CH_3(C_2H_5)TlX$, the exchange of the alkyl groups occurred under mild conditions to form redistribution products. Other interesting reactions found for $RR'TlX$ are alkyl replacement and dealkylation reactions.

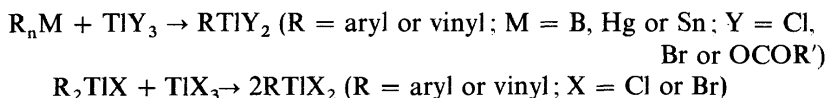
We isolated several novel monomethylthallium dicarboxylates for the first time in 1967 from the reaction of dimethylthallium carboxylate with mercuric dicarboxylate. We have also developed a convenient method for the preparation of monoalkylthallium derivatives from aqueous thallic acetate using some mild alkylating reagents, in the absence of chloride,

bromide or iodide anions. They are air stable but decompose slowly at room temperature.

In this lecture, the preparation, properties and some interesting reactions of monoalkylthallium and unsymmetrical diorganothallium derivatives will be described together with structural considerations by means of i.r. and ^1H n.m.r.

MONOALKYLTHALLIUM DERIVATIVES

Monoaryl- and monovinylthallium derivatives can be prepared by the reactions of thallic salts with corresponding organo-derivatives of boron⁴⁻⁷, mercury⁸⁻¹³ and tin¹⁴.



On the other hand, the history of preparation of lower monoalkyl compounds was not straightforward. Melnikov and Gratscheva reported¹⁵ that they first succeeded in preparing several monoalkylthallium dihalides, RTIX_2 ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ and $i\text{-C}_5\text{H}_{11}$). However, Sarrach¹⁶ as well as Hart and Ingold¹⁷ failed to confirm the results and suggested non-existence or instability of these compounds by carrying out some skillful experiments. We examined a reaction of $(\text{CH}_3)_2\text{TlOAc}$ with $\text{Tl}(\text{OAc})_3$ in water or in methanol, and found that the reaction did not occur at room temperature. At elevated temperature TlOAc and CH_3OAc were obtained. These seem to be the decomposition products of the expected compound, $\text{CH}_3\text{Tl}(\text{OAc})_2$.

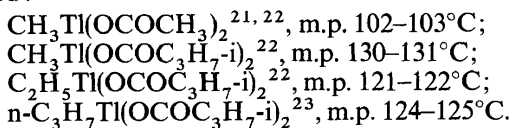
We have found¹⁸ the existence of the monomethylthallium species in considerable duration at room temperature by the analysis* of ^1H n.m.r. spectra of the reaction system (1) (where $\text{R} = \text{R}' = \text{CH}_3$).



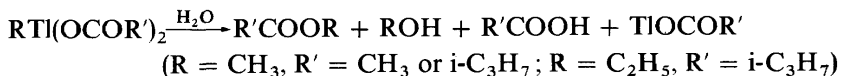
Preparation and properties

(i) Alkylthallium dicarboxylates

According to the reaction (1) in methanol, the following compounds have been isolated:



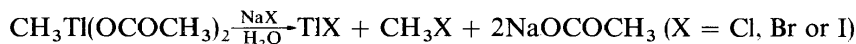
These monoalkylthallium dicarboxylates slowly decompose in aqueous solution even at room temperature according to the following scheme^{22, 24}.



* The ratio of $J(\text{Tl}-\text{CH}_3)$ for the monomethylthallium species to that for the dimethylthallium cation is almost similar to $J(\text{R}_2\text{Tl}^{2+}):J(\text{R}_2\text{Tl}^+)$ observed for the vinyl and aromatic series^{19, 20}.

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The decomposition reaction of methylthallium diacetate occurs immediately in aqueous sodium halide solutions as indicated below.



The amount of precipitated thallic halide was almost quantitative, and the methyl halide was detected as the gaseous product²².

Another interesting property of these compounds is their strong tendency to form stable diorganothallium compounds by the reactions with mild alkylating reagents. The reaction of monomethylthallium dicarboxylates with tetramethyltin gave $(\text{CH}_3)_2\text{TlOCOR}'$ and that with $\text{NaB}(\text{C}_6\text{H}_5)_4$ gave a phenylated product, $\text{CH}_3(\text{C}_6\text{H}_5)\text{Tl}[\text{B}(\text{C}_6\text{H}_5)_4]$. The formation of a fairly stable $\text{CH}_3(\text{CN})\text{TlOAc}$ in the reaction of $\text{CH}_3\text{Tl}(\text{OAc})_2$ with $(\text{CH}_3)_3\text{SnCN}$ ²⁵, in chloroform, may also be associated with this tendency.

(ii) *Alkylcyanothallium carboxylates*

We have found that the monomethylthallium species was produced in fairly good yield in the early stage of the alkylation reaction of $\text{Tl}(\text{OAc})_3$. The yield of dimethylthallium cation increased with time or when the mole ratio of $\text{CH}_3:\text{Tl}$ employed was greater than unity, as shown²⁶ in Table 1. These facts suggest that the methylation of thallium proceeds in two steps.

Table 1. Methylation of thallic acetate with some methyltin compounds

Methyltin Compound	Mole ratio (Sn:Tl)	Solvent	Product (%) after			
			3h		24h	
			$\text{CH}_3\text{Tl}^{2+}$	$(\text{CH}_3)_2\text{Tl}^+$	$\text{CH}_3\text{Tl}^{2+}$	$(\text{CH}_3)_2\text{Tl}^+$
$(\text{CH}_3)_4\text{Sn}$	1	CH_3OH	70	28	26	62
	1/4	CH_3OH	59	0		
$(\text{CH}_3)_3\text{SnOAc}$	1	CH_3OH	78	8	44	52
	1*	CH_3OH	—	—	57	9
	1/3	CH_3OH	61	0		
$(\text{CH}_3)_2\text{SnF}_2$	1	H_2O	56	8	0†	20†
	1/2	H_2O	43	0		

* In the presence of NaCN (mole ratio, Tl:CN = 1).

† Monomethylthallium species seems to decompose to CH_3OH and $\text{CH}_3\text{COOCH}_3$.

However, in the presence of NaCN further methylation of the monomethylthallium species is retarded. This is probably a consequence of the formation of the stable C-Tl-C configuration^{25, 27} in $\text{CH}_3(\text{CN})\text{TlOAc}$.

Methylation of $\text{Tl}(\text{OAc})_3$ to form $\text{CH}_3(\text{CN})\text{TlOAc}$ was also observed with ammonium methylpentafluorosilicate²⁸ in the presence of NaCN. Similarly the preparation of ethylcyanothallium acetate with tetraethyltin in methanol has been carried out²⁶.

Alkylcyanothallium acetates are thermally stable and useful starting materials for the alkylthallium derivatives. Alkylcyanothallium acetate, $\text{R}(\text{CN})\text{TlOAc}$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$), can be converted into RTlY_2 ($\text{Y} = \text{N}, \text{N}$ -dialkylthiocarbamate²⁹, oxinate or tropolonate) by the reaction with

excess KSSCNr_2 , oxine or tropolone. However, with an equivalent amount of oxine or tropolone, $\text{R}(\text{CN})\text{TlY}^{30}$ was the product.

UNSYMMETRICAL DIORGANOTALLIUM DERIVATIVES

Unsymmetrical diarylthallium compounds, $(p\text{-CH}_3\text{C}_6\text{H}_4)$ $(\text{C}_6\text{H}_5)\text{TlX}^{5, 31}$ have been reported, but the attempts⁵ to obtain unsymmetrical dialkylthallium derivatives were unsuccessful. We succeeded in preparing these novel unsymmetrical compounds^{25, 32} through the reactions of monoalkylthallium compounds with appropriate organometallic reagents, as shown below.

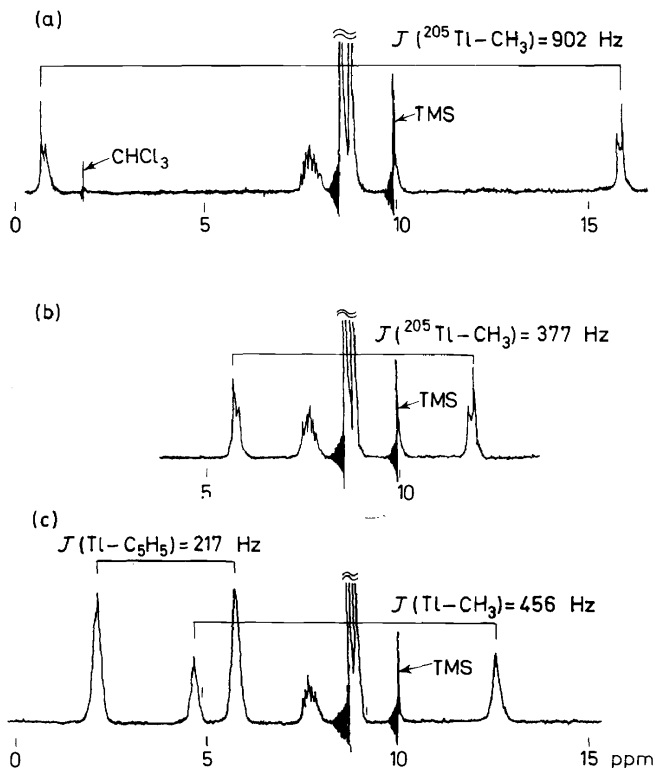
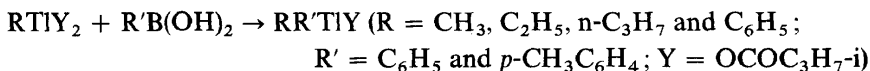


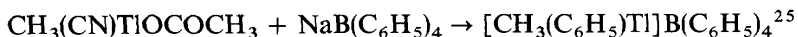
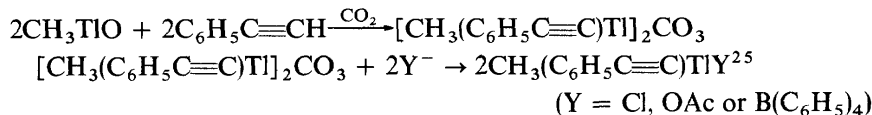
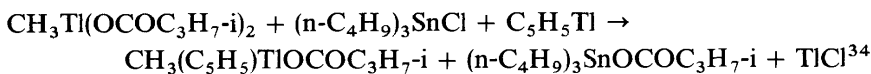
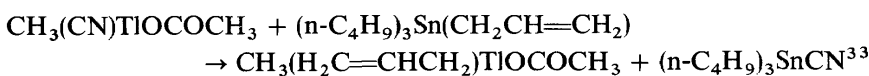
Figure 1. ^1H n.m.r. spectra in CDCl_3 at 60 MHz and 20°C .

(a) $\text{CH}_3\text{Tl}(\text{OCOC}_3\text{H}_7\text{-i})_2$

(b) $(\text{CH}_3)_2\text{TlOCOC}_3\text{H}_7\text{-i}$

(c) $\text{CH}_3(\text{C}_5\text{H}_5)\text{TlOCOC}_3\text{H}_7\text{-i}$ ($J(^{205}\text{Tl}-\text{CH}_3)$ and $J(^{203}\text{Tl}-\text{CH}_3)$ were not resolved.)

Other less common methods of preparation are as follows.



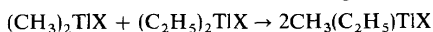
The ^1H n.m.r. spectra of representative methylthallium compounds are shown in *Figure 1*. The indirect spin-spin coupling constants between the methyl protons and the thallium nuclei for these unsymmetrical diorganothallium carboxylates, together with those of monomethylthallium carboxylates are shown in *Table 3*. The $J(\text{Tl}-\text{CH}_3)$ value increases with increasing electronegativity of R.

Reactions

(i) Redistribution³⁵

Methylethylthallium thiomethoxide and thiophenoxide were found to redistribute easily to dimethyl- and diethylthallium derivatives, in chloroform or benzene solution, even at room temperature. On the other hand, the oxinate, isobutylate and tropolonate, in which the ligands are bonded to thallium through oxygen and/or nitrogen, do not show any appreciable

Table 2. Redistribution reaction in refluxing toluene for 5 h



X	Initial concn. of (CH ₃) ₂ TlX (M)*	Conversion (%)
SCH ₃	0.053	53
SC ₆ H ₅	0.038	48
SSCN(CH ₃) ₂	0.026	0
Oxinate	0.025	47
Salicylaldehyde	0.030	28
Tropolonate	0.018	17
OCOC ₃ H ₇ -i	0.022	Trace

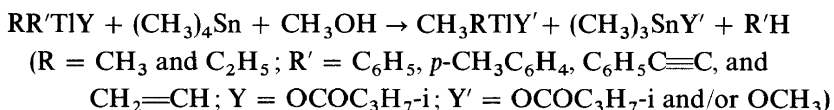
* Equimolar amounts of the dimethylthallium and diethylthallium compounds were used.

change after 10 hours in refluxing benzene. However, the redistribution reactions of these compounds were found to occur gradually in refluxing toluene, and the reverse reactions also proceed at this temperature, as shown in *Table 2*.

The extreme ease of the redistribution reactions of methylethylthallium thiomethoxide and thiophenoxide and their reverse reactions may be connected with the facts that the compounds have weak Tl—C bonds and are more or less associated in solution. On the other hand, monomeric methylethylthallium dithiocarbamate was found to be stable to the redistribution, although this compound has weak Tl—C bonds.

(ii) *Alkyl replacement and dealkylation*

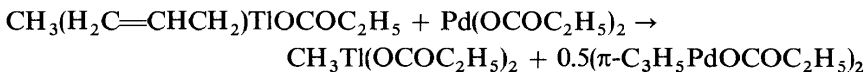
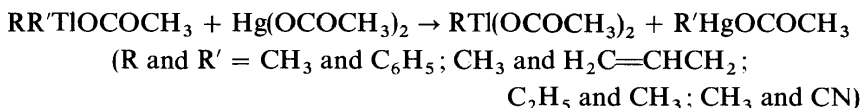
It was also found that tetramethyltin reacts with various unsymmetrical diorganothallium isobutylates causing a novel replacement reaction, as shown in the following equation^{2,3}.



Methylethylthallium isobutylate does not undergo this reaction. In these reactions, methanol is thought to act as a proton source for the formation of the hydrocarbon (R'H), since the reactions do not proceed in methylene chloride or in chloroform. It should be noted that in these unsymmetrical diorganothallium compounds, the more electronegative group (see *Table 3*) is replaced. In the above reaction, the methylation by tetramethyltin and the cleavage of the Tl—R' bond would be expected to take place simultaneously, in the sense of a concerted mechanism, without the formation of a $\text{CH}_3\text{RR'Tl}$ intermediate.

Recently we synthesized methyl(allyl)thallium carboxylates^{3,3}. In the replacement reaction of these compounds, in which the allyl group is 'frozen', the less electronegative allyl group is replaced in contrast to the trend of replacement of the more electronegative group.

Similarly, in the following reactions, the allyl group in the methyl(allyl)thallium derivatives is transferred preferentially.



From these results it is likely that the cleavage of the allyl–thallium bond in these reactions is due to a specific interaction between the π -electron system and an electrophilic reagent.

(iii) *Miscellaneous*

The reaction products of the unsymmetrical methylorganothallium carboxylates, CH_3RTlY , together with those of monomethylthallium carboxylates, CH_3TlY_2 and $\text{CH}_3(\text{CN})\text{TlY}$, with some reagents such as Cl^- , $\text{B}(\text{C}_6\text{H}_5)_4^-$ and $\text{SSCN}(\text{CH}_3)_2^-$, are summarized in *Table 3*. From *Table 3*, it is clear that the compounds ($\text{R} = \text{C}_2\text{H}_5$, $\text{H}_2\text{C}=\text{CHCH}_2$, CH_3 , $\text{CH}_2=\text{CH}$ and C_6H_5) with the $J(\text{Tl}-\text{CH}_3)$ value comparable to that of the

Table 3. $J(\text{Tl}-\text{CH}_3)$ values (at 20°C) for $\text{CH}_3\text{R}(\text{TiOCOR})'$ and reaction products with Cl^- , $\text{B}(\text{C}_6\text{H}_5)_4^-$ and $\text{SSCN}(\text{CH}_3)_2^-$

R	R'	Solvent	$J(\text{Tl}-\text{CH}_3)$ (Hz)	Cl^-	$\text{B}(\text{C}_6\text{H}_5)_4^-$	$\text{SSCN}(\text{CH}_3)_2^- (= \text{dtc})$
C_2H_5	$\text{C}_3\text{H}_7\text{-i}$	CDCl_3	331 ³⁵	$\text{CH}_3(\text{C}_2\text{H}_5)\text{TlCl}^{32}$	$\text{CH}_3(\text{C}_2\text{H}_5)\text{TlB}(\text{C}_6\text{H}_5)_4$	$\text{CH}_3(\text{C}_2\text{H}_5)\text{Tl}(\text{dtc})^{35}$
$\text{CH}_2=\text{CHCH}_2$	$\text{C}_3\text{H}_7\text{-i}$	CDCl_3	365 ³³	$\text{CH}_3(\text{CH}_2=\text{CHCH}_2)\text{TlCl}^{33}$	$\text{CH}_3(\text{CH}_2=\text{CHCH}_2)\text{TlB}(\text{C}_6\text{H}_5)_4$	$\text{CH}_3(\text{CH}_2=\text{CHCH}_2)\text{Tl}(\text{dtc})^{33}$
CH_3	$\text{C}_3\text{H}_7\text{-i}$	CDCl_3	377 ³⁶	$(\text{CH}_3)_2\text{TlCl}^{36}$	$(\text{CH}_3)_2\text{TlB}(\text{C}_6\text{H}_5)_4$	$(\text{CH}_3)_2\text{Tl}(\text{dtc})$
$\text{CH}_2=\text{CH}$	$\text{C}_3\text{H}_7\text{-i}$	CDCl_3	412 ³⁶	$\text{CH}_3(\text{CH}_2=\text{CH})\text{TlCl}^{23}$	$\text{CH}_3(\text{CH}_2=\text{CH})\text{TlB}(\text{C}_6\text{H}_5)_4$	$\text{CH}_3(\text{CH}_2=\text{CH})\text{Tl}(\text{dtc})$
C_6H_5	$\text{C}_3\text{H}_7\text{-i}$	CDCl_3	426 ³⁶	$\text{CH}_3(\text{C}_6\text{H}_5)\text{TlCl}^{32}$	$\text{CH}_3(\text{C}_6\text{H}_5)\text{TlB}(\text{C}_6\text{H}_5)_4^{25}$	$\text{CH}_3(\text{C}_6\text{H}_5)\text{Tl}(\text{dtc})$
C_3H_5	$\text{C}_3\text{H}_7\text{-i}$	CDCl_3	456 ³⁴	TlCl^{34}	$\text{CH}_3(\text{C}_6\text{H}_5)\text{TlB}(\text{C}_6\text{H}_5)_4^{25}$	$\text{CH}_3\text{Tl}(\text{dtc})^{34}$
$\text{C}_6\text{H}_5\text{C}\equiv\text{C}$	CH_3	D_2O	672 ²⁵	$\text{CH}_3(\text{C}_6\text{H}_5\text{C}\equiv\text{C})\text{TlCl}^{25}$	$\text{CH}_3(\text{C}_6\text{H}_5\text{C}\equiv\text{C})\text{TlB}(\text{C}_6\text{H}_5)_4^{25}$	$\text{CH}_3\text{Tl}(\text{dtc})^{36}$
CN	CH_3	D_2O	828 ²⁵	TlCl^{36}	$\text{CH}_3(\text{C}_6\text{H}_5)\text{TlB}(\text{C}_6\text{H}_5)_4^{25}$	$\text{CH}_3\text{Tl}(\text{dtc})^{26}$
	$(\text{C}_3\text{H}_7\text{-i})_2$	CHCl_3	902 ²⁵	TlCl^{22}	$\text{CH}_3(\text{C}_6\text{H}_5)\text{TlB}(\text{C}_6\text{H}_5)_4^{25}$	$\text{CH}_3\text{Tl}(\text{dtc})^{29}$

dimethylthallium compound gave the reaction products maintaining the $\text{CH}_3\text{-Tl-R}$ moiety. As far as the reaction products are concerned, the cyclopentadienyl compound behaves just like the monomethyl compound, in spite of the fact that its J value (456) is close to that of the phenyl compound (426). This may be associated with the fluxional behavior of the cyclopentadienyl group bonded to the thallium atom, as indicated from the spectroscopic data³⁴.

COORDINATION CHEMISTRY OF MONOALKYLTHALLIUM COMPOUNDS

From the i.r. and u.v. spectra, it was deduced that the monomeric monoalkylthallium chelate compounds, such as bisoxinate, bistropolonate or bisdithiocarbamate have a penta-coordinate thallium atom, similar to the reported monophenylthallium compounds, $\text{C}_6\text{H}_5\text{Tl}(\text{oxinate})_2$ ³⁷ and $[\text{C}_6\text{H}_5\text{TlCl}_4]^{2-}$ ^{38,39}. The penta-coordinate thallium was also suggested to exist in $\text{RTl}(\text{OCOC}_3\text{H}_7\text{-i})_2$ ($\text{R} = \text{CH}_3$ or C_2H_5) in non-polar solvents, from the molecular weight and i.r. measurements²². The results of the far-infrared spectra of $\text{RTl}(\text{Y})\text{OAc}$ ($\text{R} = \text{CH}_3$ or C_6H_5 ; $\text{Y} = \text{OAc}$ or CN) in the solid state showed that in these compounds the alkyl group and one ligand (Y) interact strongly with the thallium atom²⁷, as in RHgY . This conclusion is also supported by the similar study of monophenylthallium dicarboxylates⁴⁰.

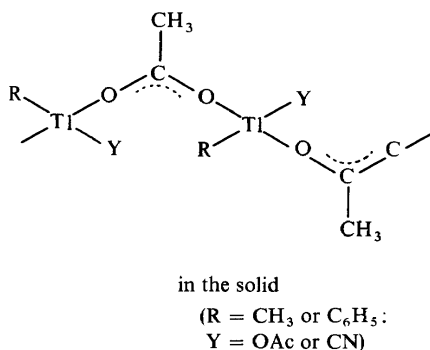
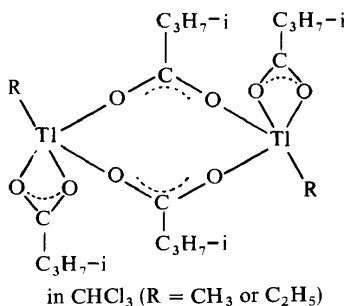


Table 4. $J(\text{Tl-CH}_3)$, $\rho(\text{Tl-CH}_3)$ and $\nu(\text{Tl-CH}_3)$ for some CH_3TlX_2

X	$J(\text{Tl-CH}_3)^*$ (Hz)	$\rho(\text{Tl-CH}_3)^\dagger$ (cm^{-1})	$\nu(\text{Tl-CH}_3)^\ddagger$ (cm^{-1})
$\text{OCOC}_3\text{H}_7\text{-i}$	902	813 (s)	‡
OCOCH_3	892	810 (s)	527 (m)
tropolonate	835	806 (s)	510 (m)
oxinate	790	‡	514 (m)
$\text{SSCN}(\text{CH}_3)_2$	678	781 (s)	487 (m)
$\text{SSCN}(\text{C}_2\text{H}_5)_2$	675	778 (s)	485 (m)

* In CDCl_3 solutions (5 wt %).

† In Nujol mulls.

‡ Obscured by the strong absorptions due to the ligand.

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From the spectral parameters for several monoalkylthallium derivatives (Table 4) it was found that the thallium atom interacts more strongly with the sulphur atom than the oxygen and/or nitrogen atoms²⁹.

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