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Preliminary communication

TRIMETHYLSILYLMETHYL DERIVATIVES OF THALLIUM(III)

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Summary

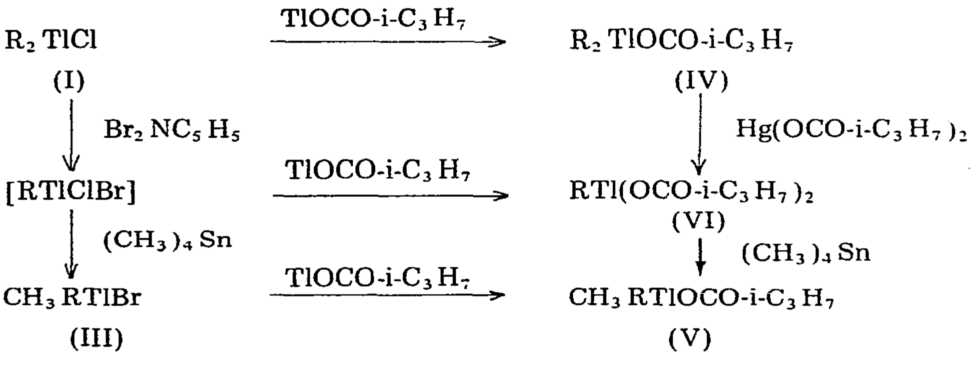
Some trimethylsilylmethyl derivatives of thallium(III) have higher stability and unusual coordination behavior in comparison with simple alkylthallium(III) analogs for steric reasons.

The trimethylsilylmethyl group, $(CH_3)_3SiCH_2$, is of current interest because of the kinetic stability of its bond to a metal. Among several interpretations for this enhanced stability over methyl-- and particularly ethyl-- transition metal bonds [1--3] are (1) the absence of a β-hydride elimination reaction, and (2) the bulkiness of the $(CH_3)_3SiCH_2$ group which makes approach of reactants unfavorable.

We now report that some trimethylsilylmethylthallium(III) derivatives also have higher stability and unusual coordination behavior compared to those of simple alkylthallium(III) analogs mainly for steric reasons.

Bis(trimethylsilylmethyl)thallium(III) chloride (I) or bromide (II) can be prepared by treatment of thallic chloride or thallous bromide with lithiomethyltrimethylsilane [4]. Other trimethylsilylmethylthallium(III) derivatives (III—VI) have been obtained according to Scheme 1.

SCHEME 1



R = $(CH_3)_3SiCH_2$

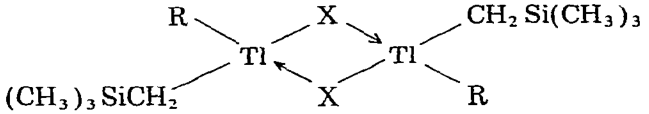
TABLE 1

MOLECULAR WEIGHT, RELEVANT INFRARED FREQUENCIES (in cm^{-1}) AND J(Tl—H) (in Hz) FOR TRIMETHYLSILYLMETHYLTHALLIUM(III) DERIVATIVES [a] R = $CH_2Si(CH_3)_3$

		Mol. Wt.		ν(Tl—C) [c]		J(Tl—H) [d]	
		Found [b] (Calcd)	Concs. mole (%)	*asym.*	*sym.*	Tl—CH_2	Tl—CH_3
R_2TlCl	I	824(414)	0.125	520 [e]	491 [e]	537	
R_2TlBr	II	920(459)	0.152	520	489	536	
$R(CH_3)TlBr$	III	751(386)	0.073	528	464	539	342
$R_2TlOCO\text{-}i\text{-}C_3H_7$	IV			514	478	566	
$R(CH_3)TlOCO\text{-}i\text{-}C_3H_7$	V			[f]	488	562	376
$RTl(OCO\text{-}i\text{-}C_3H_7)_2$	VI					1121	

[a] Satisfactory elemental analyses were obtained. [b] Measured in chloroform solution at 25° using a Mechrolab vapor pressure osmometer Model 302. [c] In nujol mulls. [d] In $CDCl_3$. [e] Same values were obtained in $CHCl_3$. [f] Obscured by the absorption due to the ligand.

Unlike simple diorganothallium(III) halides, all of the trimethylsilylmethylthallium(III) halides prepared in this study are very soluble in chloroform, benzene or alcohols, and were found to be dimeric in chloroform (Table 1). Furthermore, the IR spectra of I in the solid state and in solution (Table 1) clearly show both asymmetric and symmetric Tl—C stretching bands, indicating the presence of a non-linear C—Tl—C skeleton. A similar dimeric structure is proposed for II and III since the aspects of the IR spectra of these are very similar to those of I.



X = Cl, Br; R = $CH_2Si(CH_3)_3$, CH_3

This structure is in marked contrast to those of simple dialkylthallium(III) halides [5] which are polymeric in the solid state with a linear C—Tl—C unit, although the presence of chloro- or bromo-bridged dimeric structures was previously suggested for bis(pentafluorophenyl)thallium(III) halides [6] on the basis of molecular weight determinations and Tl—Cl or Tl—Br stretching frequencies. We believe a reason for a decrease in the degree of association in the case of I, II and III is possibly steric in nature rather than electronic, as will be described below.

As shown in Table 1, J(Tl—CH_2) and J(Tl—CH_3) values of V are almost the same as those of IV and dimethylthallium(III) isobutyrate (377 Hz) [7], respectively. Similarly, the J(Tl—CH_2) value of II is very close to that of III. This suggests a similarity in the electronic effect of $(CH_3)_3SiCH_2$ and CH_3 groups on the basis of the proposition that thallium—proton spin—spin coupling is dominated by the Fermi contact term [8]. Similar results were also reported [9] in that *trans* influences of the two groups are comparable in square planar platinum(II) compounds. It is not surprising, however, that the reaction of III with pyridinium perbromide in a 1/1 mole ratio gave a mono(trimethylsilylmethyl)thallium(III) species selectively as confirmed by

NMR spectra, since electrophilic substitution at the $(CH_3)_3SiCH_2$ group is sterically unfavorable compared to attack at the CH_3 group.

It is also of interest to note that VI is much more stable than its methyl or ethyl analogs [7]. Thus, for example, VI can be recovered unchanged from hot methanol, chloroform or dimethyl sulfoxide, while the latter two readily decomposed under similar conditions to give thallous isobutyrate and ROCO-i-C_3H_7 (R = CH_3, C_2H_5) in a way similar to that proposed for decomposition of an oxythallated intermediate in the reaction of olefins with thallic carboxylates [10]. It has been suggested [11] that a reductive decomposition of monoalkylthallium(III) species most probably proceeds through a bimolecular nucleophilic displacement at the carbon attached to the thallium atom and hence the bulkiness of the $(CH_3)_3SiCH_2$ group in VI may suppress such a decomposition path.

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