

Cyclopentadienyldimethylthallium

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IONIC cyclopentadiene derivatives of Tl^I are well known^{1a,b} but no cyclopentadiene derivatives of Tl^{III} have yet been reported. We have found that trimethylthallium reacts with a wide variety of compounds containing an acidic hydrogen to give methane and the corresponding dimethylthallium derivative.² Thus, trimethylthallium and cyclopentadiene react over 2 hr. at room temperature to give cyclopentadienyldimethylthallium as colourless crystals in quantitative yield. Good analytical data have been obtained.

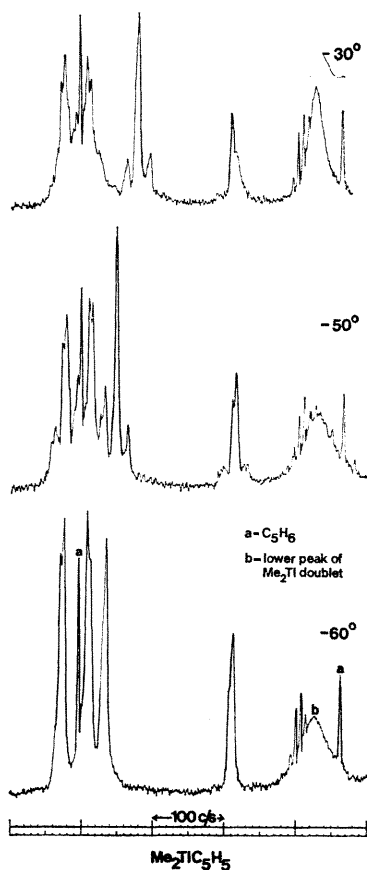
The n.m.r. spectrum of $Me_2TlC_5H_5$ in monoglyme at 39°

shows a single sharp peak at τ 4.24 assignable to the C_5H_5 protons, and a doublet, τ 9.58, J 372 c./sec., that can be assigned to the Me_2Tl group, with spin-spin coupling between the methyl protons and the two thallium isotopes, both of spin $I = \frac{1}{2}$. The methyl proton signals were broad at 39°, and on cooling the solution they became even broader. This has been observed to occur for solutions of dimeric dimethylthallium compounds^{2,3} and is probably due to a retarding of an exchange between monomeric and dimeric species (in the fast exchange limit of exchange of a group between two sites of different chemical shift). The

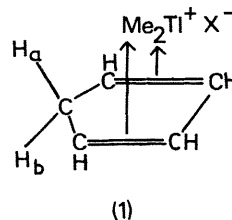
C_5H_5 peak remains unchanged on cooling a solution in trimethylamine or monoglyme to -60° .

The compound reacts with SO_2 to give a 1:1 adduct as a pale yellow solid. Sulphur dioxide has been shown to insert into a Tl-C bond in trimethylthallium but does not react with dimethylthallium chloride.³ It would seem that with $Me_2TlC_5H_5$ a 1:1 adduct is formed rather than an insertion product: the n.m.r. spectrum of $Me_2TlC_5H_5$ in liquid SO_2 shows no peak attributable to an $-SO_2Me$ group. This n.m.r. spectrum at -60° shows a broad doublet due to the Me_2Tl protons and three peaks at τ 3.26, 3.58, and 5.77, having relative areas approximately 2:2:1. As the

temperature of the solution is raised the three peaks collapse in a symmetrical manner to give a single peak. On cooling again to -60° , the original spectrum is obtained. The compound thus contains a covalently bound C_5H_5 group rather than an ionic one. As no splitting of the peaks due to the thallium could be seen even at -60° , rapid intermolecular exchange of the C_5H_5 groups must be occurring. The symmetrical collapse of the signals with increasing temperature implies that rotation of the C_5H_5 ring is now occurring by random shifts as it transfers from one thallium nucleus to another.



FIGURE



Cyclopentadienyldimethylthallium reacts with HI and HCl to give 1:1 adducts, as red and purple solids, respectively. These adducts dissociate in monoglyme solvent regenerating $Me_2TlC_5H_5$. The SO_2 adduct also gives a 1:1 adduct with HCl, as a pale pink solid. A solution of $Me_2TlC_5H_5$ in liquid SO_2 with a 6:1 excess of HCl shows a complex n.m.r. spectrum. $Me_2TlC_5H_5$ in liquid SO_2 with a slight excess of the highly protonating species H_2O, BF_3 shows a similar, but considerably stronger, spectrum (Figure). The spectrum shows a broad doublet due to the Me_2Tl protons and complex absorption in the region τ 3.2–3.7 and τ 5.7, associated with the olefinic and methylene protons of cyclopentadiene, respectively. At low temperatures it seems that the two methylene protons are non-equivalent, but that as the temperature increases, the two become more equivalent, suggesting that protonation to a species such as (1) has occurred. As the temperature increases, the C_5H_5 ring exchanges more rapidly from one thallium atom to another and protons H_a and H_b become more equivalent.

Similar results have been obtained for $Me_2TlC\equiv CPh$. Single-crystal X-ray studies on these compounds are to be performed.

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¹ (a) E. O. Fischer, *Angew. Chem.*, 1957, **69**, 207; (b) T. J. Katz and J. J. Mrowca, *J. Amer. Chem. Soc.*, 1967, **89**, 1105.

² A. G. Lee and G. M. Sheldrick, to be published.

³ A. G. Lee, *Chem. Comm.*, 1968, 1614.