1,2,4-Tris(trimethylsilyl)cyclopentadienylthallium: Covalency by Silylation

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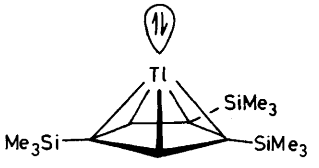
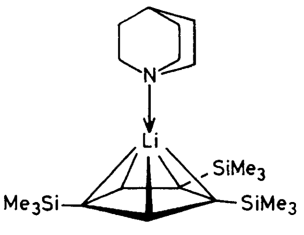
The introduction of three trimethylsilyl groups alters the nature of cyclopentadienyl–thallium interactions towards a situation where covalency is dominant and gives rise to a drastic change in the physical properties.

While cyclopentadienylthallium is a monomeric half-sandwich in the gas phase,[1] it forms a polymeric chain structure in the solid state, where a markedly longer cyclopentadienyl–metal bond indicates highly ionic character.[2,3] This type of bonding in the solid state is visualized by the low solubility of the compound in non-polar aprotic solvents. However, the addition of three trimethylsilyl groups to the cyclopentadienyl (cp) ring changes its nature significantly: tris(trimethylsilyl) cyclopentadienylthallium (**1**) is a monomeric species in solution, in the gas phase, and presumably also in the solid state.

Reaction of tris(trimethylsilyl)cyclopentadienyl-lithium



(1)



(2)

with thallium(I) chloride yielded the title compound (**1**), which was obtained upon repeated sublimation as a colourless microcrystalline solid, equation (1).†

$$(\mathrm{Me_3Si})_3\mathrm{C_5H_2Li} + \mathrm{TlCl} \xrightarrow{-\mathrm{LiCl}} \underset{(\mathbf{1})}{(\mathrm{Me_3Si})_3\mathrm{C_5H_2Tl}} \qquad (1)$$

The air-stable compound is fairly soluble in aromatic solvents. Cryoscopic molecular weight determinations confirm it to be monomeric in benzene. The presence of a compound with a covalent cp–thallium interaction follows from n.m.r. spectroscopic investigations. In contrast to unsubstituted and monosilylated cyclopentadienylthallium[4] ^{1}H and ^{13}C n.m.r. spectra show $^{(203)205}$Tl-atom couplings to the cyclopentadienyl protons, as well as to the hydrogen and carbon atoms of the methyl groups.‡ It can be anticipated that the thallium compound (**1**) has a *nido*-structure similar to gaseous C_5H_5Tl and the isoelectronic monomeric adduct (**2**) of tris(trimethylsilyl)cyclopentadienyl-lithium with quinuclidine.[5]

Summarizing all present data, the introduction of three trimethylsilyl groups at the cyclopentadienyl ring has the overall§ effect of enforcing covalency and therefore changing the physical properties considerably. Recent observations in potassium chemistry show[6] that this phenomenon appears to be general.

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† Preparation of (**1**): a suspension of thallium(I) chloride (1.78 g, 7.44 mmol) in light petroleum (30 ml) was added to a solution of tris(trimethylsilyl)cyclopentadienyl-lithium (7.44 mmol) in light petroleum (50 ml). Evaporation of the solvent and sublimation of the product from the residue (100—120 °C/0.01 mm Hg) followed by repeated resublimation yielded 2.17 g (60%) of (**1**). Unfortunately no single crystals have been obtained.

‡ *Spectroscopic data* for (**1**): ^{1}H n.m.r. (C_6D_6) δ 0.26 [d, 9H, SiMe$_3$, ^4J(TlH) 2.8 Hz], 0.35 [d, 18H, 2 SiMe$_3$, ^4J (TlH) 3.0 Hz], and 6.69 [d, 2H, ring-H, ^2J(TlH) 75.5 Hz]; ^{13}C n.m.r. (C_6D_6) δ 1.50 [d, SiMe$_3$, ^3J(TlC) 20 Hz] and 2.84 [d, SiMe$_3$, ^3J(TlC) 20 Hz]; carbon atoms of the C_5 ring were not clearly observed; *m/z* 486 (M^+, 23.2), 471 (M^+–Me, 15.0), 205 (Tl^+, 100%).

§ The main effects of the SiMe$_3$ groups are (i) to reduce intermolecular interactions and therefore decrease the tendency for aggregation, (ii) to delocalize negative charge in the cp ring and therefore influence the cp–Tl bonding, and (iii) to enhance the lipophilicity.