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**Preliminary communication**

# Trimethylsilylcyclopentadienylthallium(I) complexes: syntheses and X-ray structures of the multidecker sandwich complexes $[Tl(\mu\text{-}\eta:\eta\text{-}C_5H_4SiMe_3)]_n$ and $[Tl\{\mu\text{-}\eta:\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}]_6$ (a "doughnut" molecule) *

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## Abstract

Crystalline trimethylsilylcyclopentadienylthallium(I) complexes $[Tl(\mu\text{-}\eta:\eta\text{-}C_5H_3RR')]_n$ (I: $R = SiMe_3$, $R' = H$, $n = \infty$; II: $R = SiMe_3 = R'$, $n = 6$) are obtained in high yield from TlOEt and $C_5H_4RR'$ in $C_6H_6$ at ca. 20 °C; single crystal X-ray data reveal I to be a chain polymer and II a cyclic hexamer (Tl atoms at the vertices of a regular hexagon), with Tl–C(cent) (C(cent) = centroid of $C_5$ ring) 2.71 and 2.84 Å for I and 2.74–2.78 Å for II. C(cent)–Tl–C(cent) 149° for I and 127–133° for II, and Tl–C(cent)–Tl 178° for I and 169–173° for II.

Cyclopentadienylthallium(I) compounds are key organometallic reagents, being widely employed as precursors of cyclopentadienyls of other metals [1]. Surprisingly, there is little structural information available on $(TlCp^x)_m$ [2], and some is misleading [3].

We now report (l) a convenient high yield synthesis (> 80% of pure crystalline material) of $Tl^I$ mono- and bis-(trimethylsilyl)cyclopentadienyls $[Tl(\mu\text{-}\eta:\eta\text{-}C_5H_3RR')]_n$ (I: $R = SiMe_3$, $R' = H$, and $n = \infty$; II: $R = SiMe_3 = R'$, $n = 6$) **,

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[*] Dedicated to Professor Jean Tirouflet in recognition of his important contributions to organometallic chemistry.

[**] M.p. I 115–116 °C (dec.) (Lit., 116 °C [3]), II (dec.) > 120 °C. Characterisation: (a) $^1H$ NMR at ca. 300 K ($C_6D_6$, external $SiMe_4$, 300 MHz): I: $\delta$ 0.28 (9H, s, $SiMe_3$), 6.25 (4H, m, CH); II 0.28 (18H, s, $SiMe_3$), 6.38 (2H, m, $H_{4,5}$), 6.43 (1H, m, $H_2$); (b) $^{13}C$ NMR ($C_6D_6$, 75.47 MHz): I: $\delta$ 1.53 ($SiMe_3$), 111.4 (C(3,4)), 114.8 (C(2,5)), 118.6 (C(1)-$SiMe_3$); II: 1.6 ($SiMe_3$), 117.6 (C(4,5)), 121.2 (C(2)), 122.2 (C(1,3)-$SiMe_3$): (c) $m/e$ I: 342 ($M^+$, 63), 327 [$(M-Me)^+$, 18], 205 ($Tl^+$, 100%); II: 414 ($M^+$, 16), 399 [$(M-Me)^+$, 11], 205 ($Tl^+$, 100%); (d) analytical data; (I): Found: C, 28.1; H, 3.75. $C_8H_{13}SiTl$ calcd.: C, 28.1; H, 3.84%; (II): Found: C, 31.8; H, 5.00. $C_{11}H_{21}Si_2Tl$ calcd.: C, 31.9; H, 5.11%.

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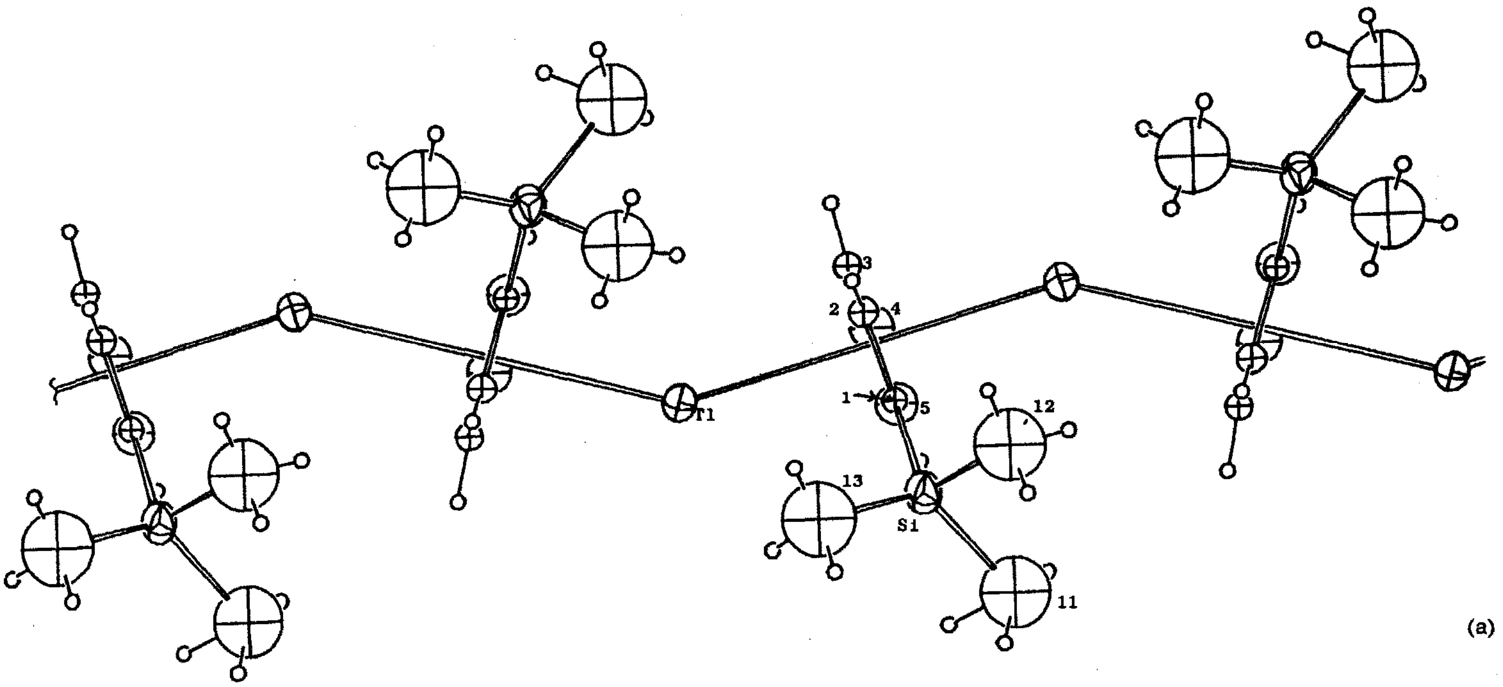

Fig. 1. The X-ray structure ((a) at right angles to the $C_5$ planes and (b) along a Tl–C(cent) vector; C(cent) represents the centroid of each $C_5$ ring), and atom labelling scheme, for crystalline $[Tl(\mu\text{-}\eta:\eta\text{-}C_5H_4SiMe_3)]_\infty$ (I), showing 20% thermal ellipsoids for the non-hydrogen atoms; for relevant dimensions, see Table 1.

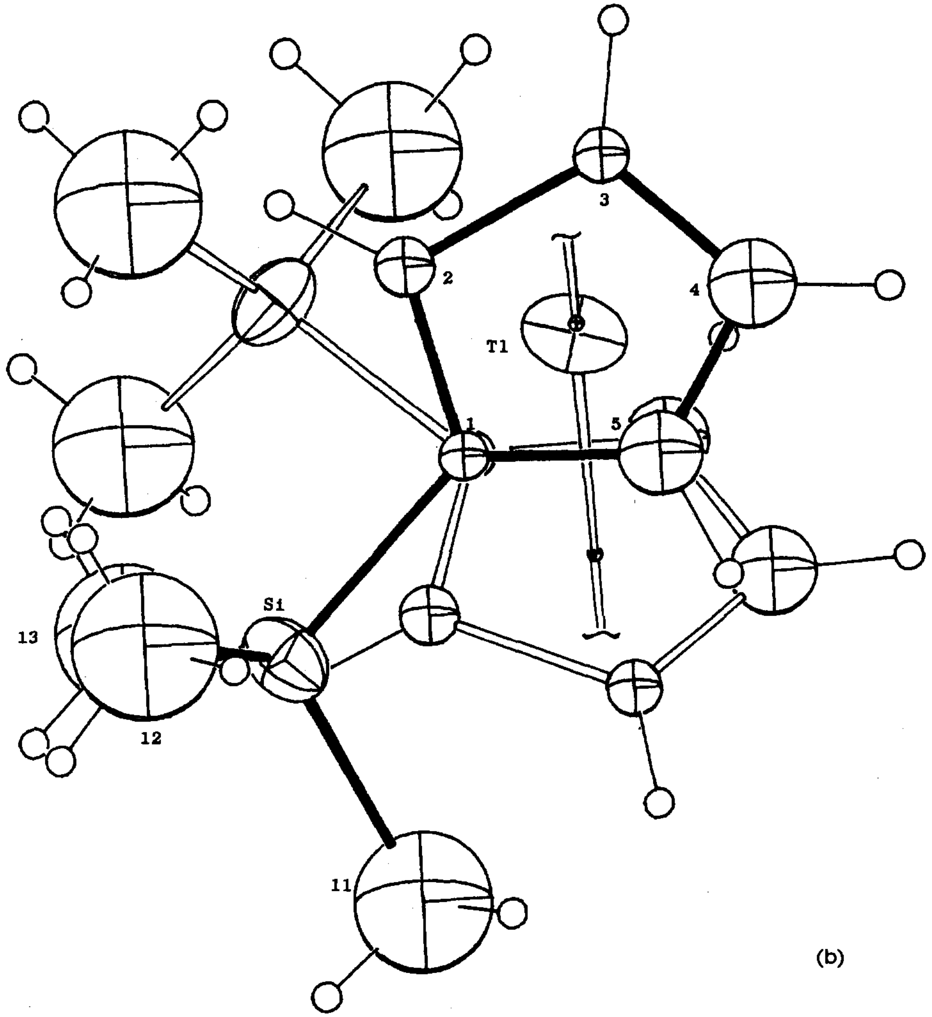

Fig. 1 (continued).

from the readily available $\mathrm{Tl^I}$ ethoxide (eq. 1), a method which appears to have some generality (see also ref. 1) (e.g., for $(\mathrm{TlCp^x})_m$ with $\mathrm{Cp^x} = C_5H_5$ or $C_5Me_5$); (ii) the X-ray structures of crystalline complexes I (Fig. 1) and II (Fig. 2) *; and (iii) their high field $^1$H and $^{13}$C NMR spectra **, which show no evidence for $SiMe_3$

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* Crystal data and structure solutions for $[\mathrm{Tl}(\mu\text{-}\eta:\eta\text{-}C_5H_4SiMe_3)]_\infty$ (I) and in square brackets for $[\mathrm{Tl}\{\mu\text{-}\eta:\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}]_6$ (II). $C_8H_{13}SiTl$ $[C_{66}H_{126}Si_{12}Tl_6]$, orthorhombic [tetragonal], space group *Pcab* $[I4_1/a]$, $a$ 24.12(2) [22.09(1)], $b$ 10.701(7), $c$ 8.216(5) [40.40(2)] Å, $Z = 8$ [8], $D_c$ 2.14 [1.67] g cm$^{-3}$, 552 [2165] "observed" reflections $\{I > 3\sigma(I)\}$, $2\theta_{max}$ 45 [50]°, $R = 0.072$ [0.083], $R_w = 0.063$ [0.099]; Mo-$K_\alpha$ radiation [$T$ 295 K] using a Syntex $P2_1$ diffractometer.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain).

** See footnote p. C1.

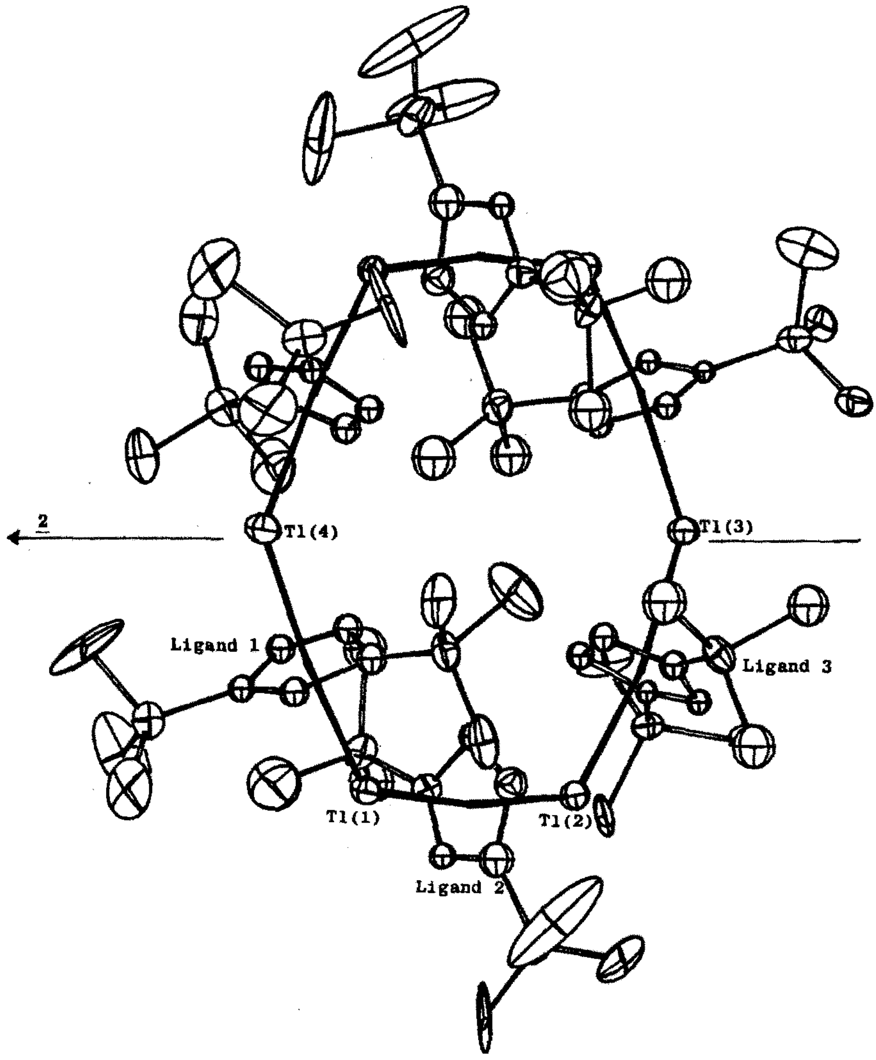


Fig. 2. The X-ray structure, and atom labelling scheme, for crystalline $[\mathrm{Tl}\{\mu\text{-}\eta:\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}]_6$ (II), showing 20% thermal ellipsoids for the non-hydrogen atoms; for relevant dimensions, see Table 1.

ring-whizzing in $C_6D_6$ at ambient temperature (cf. [3], the contrary assertion for I, made on the basis of the observation of a singlet ring proton signal at low field).

$$\mathrm{TlOEt} + C_5H_4RR' \xrightarrow[\text{ca. } 20\,^\circ\mathrm{C}]{C_6H_6} \frac{1}{n}\left[\mathrm{Tl}(\mu\text{-}\eta:\eta\text{-}C_5H_3RR')\right]_n\downarrow + \mathrm{EtOH} \qquad (1)$$

$$\begin{array}{l}(\mathrm{I}: R = SiMe_3,\ R' = H, n = \infty;\\ \mathrm{II}: R = SiMe_3 = R',\ n = 6)\end{array}$$

Compounds I and II are sparingly soluble in cold $C_6H_6$ (ca. 2.5 g $l^{-1}$; cf., the pentane-soluble $[\mathrm{Tl}(\mu\text{-}\eta:\eta\text{-}C_5Me_5)]_\infty$) [4]) but, unlike $[\mathrm{Tl}(C_5H_5)]_\infty$, have good solubility in hot benzene or toluene (from which single crystals were grown). They are probably monomers in the gas phase (mass spectrometry *), and hence are

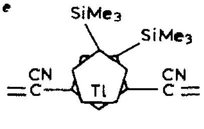
Table 1

Comparative X-ray data for crystalline $[Tl(\mu\text{-}\eta:\eta\text{-}C_5H_3RR')]_n$ and $[Tl(\mu\text{-}\eta:\eta\text{-}C_5Me_5)]_n$

| R, R′ | $n$ | Tl–C(cent) [a] (Å) | Tl–C(cent) –Tl (°) | C(cent)–Tl–C(cent) (°) | Rel. conformation of R(R′) substituents | Ref. |
|---|---|---|---|---|---|---|
| H, H | ∞ | 3.19 | 137 (0.5) | ca. 100 | – | 6 [b] |
| H, $C(CN)=C(CN)_2$ | ∞ | 3.01, 3.06 | 149 | 113.6 | Staggered, *trans*(III) [e] | 7 |
| H, $SiMe_3$ | ∞ | 2.71, 2.84 | 178 | 149 | Gauche (III) [e] | This work |
| $SiMe_3$, $SiMe_3$ | 6 | 2.74, 2.78 | 163, 169 | 127, 133 | (see Fig. 2) | This work |
| $[Tl(\mu\text{-}\eta:\eta\text{-}C_5Me_5)]_n$ | ∞ | 2.91, 2.99 | [c] | [c] | Staggered [d] | 4 |

[a] C(cent) refers to the centroid of the $C_5$ ring. [b] An early 2-dimensional study. [c] Tl–Tl′–Tl″ 142.8(1), 148.2(1)°. [d] Uncertainty, due to crystal decomposition in X-ray beam.

[e]



(III)

volatile, b.p. ca. 30 °C/$10^{-1}$ Torr, cf., also refs. 3 and 4. That the degree of polymerisation $n$ of crystalline $[Tl(\mu\text{-}\eta:\eta\text{-}C_5H_3RR')]_n$ is now shown to fall with increasing $SiMe_3$ substitution in the $C_5$-ring neatly illustrates the general principle that lipophilicity and volatility (or covalent character, as judged also by decreased tendency for molecular aggregation) for cyclopentadienylmetal complexes increases with increasing $SiMe_3$ substitution [5]. (For this reason, the ligands $(\eta\text{-}C_5H_4SiMe_3)^-$, and especially $(\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3)^-$ [5], already have a distinctive role in organometallic chemistry, complementary to $(\eta\text{-}C_5Me_5)^-$.) Indeed, the trisubstituted derivative $Tl(\eta\text{-}C_5H_2R_3\text{-}1,2,4)$ ($R = SiMe_3$) is monomeric in cold $C_6H_6$ (cryoscopy) and, unlike I or II *, shows $^{203,205}Tl\text{-}^1H$ ($^2J$ and $^4J$) and $^{203,205}Tl\text{-}^{13}C$ ($^3J$) coupling in $C_6D_6$ in its $^1H$ and $^{13}C$ NMR spectra [6] (in $[Tl(\mu\text{-}\eta:\eta\text{-}C_5Me_5)]_\infty$, $^3J(TlH)$ and $^{2\text{ and }4}J(TlC)$ were found [4]); the $^{13}C$ signals of the ring C's were not clearly observed, a further contrast with I or II *.

Although a polymeric structure for a cyclopentadienylthallium(I) complex $Tl(\mu\text{-}\eta:\eta\text{-}C_5H_4R)]_n$ has two precedents, there are notable differences between that for $R = SiMe_3$ (I) (Fig. 1) and $R = H$ [7] (an early-2-dimensional study, the In analogue was isostructural) or $R = C(CN)=C(CN)_2$ [8], Table 1. The "doughnut"-shaped hexameric complex II (Fig. 2) may arise from a preference for each Tl centre in this essentially covalent molecule to employ approximately $sp^2$-hybrid σ-orbitals (including one occupied by a stereochemically active non-bonding pair of electrons). There is an interesting contrast between the structure of the hexamer II and $[In(\eta\text{-}C_5Me_5)]_6$ [9]; the six metal atoms are arranged in a regular hexagon in the former, but an octahedron in the latter. A preliminary microwave examination of gaseous $Tl(\eta\text{-}C_5H_5)$ (fine structure not observed) was consistent with a monomeric $C_{5v}$ molecule and Tl–C(cent) ca. 2.4 Å, assuming $C_5H_5$ coplanar [10].

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