The Next Homologue of the Bis(cyclopentadienyl)thallate Anion; Synthesis and X-Ray Structure Determination of $[(\eta^5\text{-}C_5H_5)Tl(\mu\text{-}C_5H_5)Tl(\eta^5\text{-}C_5H_5)]^-[Li(12\text{-crown-}4)_2]^+\cdot$thf

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Reaction of $(C_5H_5)Li$ with $(\eta^5\text{-}C_5H_5)Tl$ (1.2 equiv.) in the presence of 12-crown-4 (2 equiv.) produces the ion-separated complex $[(\eta^5\text{-}C_5H_5)Tl(\mu\text{-}C_5H_5)Tl(\eta^5\text{-}C_5H_5)]^-[Li(12\text{-crown-}4)_2]^+\cdot$thf **1** which contains the first homometallic main group metal triple-decker sandwich as the anion; this anion can be viewed as the first homologue of the thallocene anion $[(\eta^5\text{-}C_5H_5)_2Tl]^-$ and is a molecular segment of the polymeric structure of $[(\eta^5\text{-}C_5H_5)Tl]_\infty$.

We recently reported that the archetypal group 13 and 14 cyclopentadienyl complexes $[(\eta^5\text{-}C_5H_5)E$, E = In, Tl; $(\eta^5\text{-}C_5H_5)_2E$, E = Sn, Pb] underwent nucleophilic addition with weak nucleophiles.[1–4] A range of ion-separated and ion-contacted cyclopentadienyl anion complexes are produced from their nucleophilic addition reactions with $(C_5H_5)^-$. The reaction of $[(\eta^5\text{-}C_5H_5)_2Pb]_\infty$ with $(\eta^5\text{-}C_5H_5)_2Mg$ (1 : 1 monomer equivalents) in THF as the solvent results in the ion-separated complex $2[(\eta^3\text{-}C_5H_5)_3Pb]^-[Mg(thf)_6]^{2+}$, containing an essentially planar 'paddle-wheel' tris(cyclopentadienyl)plumbate anion.[4] This can be viewed as a discrete fragment of the polymeric structure of the parent plumbocene $[(\eta^5\text{-}C_5H_5)_2Pb]_\infty$.[5] The similar reaction of $(\eta^5\text{-}C_5H_5)_2Mg$ with the polymeric $[(\eta^5\text{-}C_5H_5)Tl]_\infty$ and pmdeta [pmdeta = $(Me_2NCH_2CH_2)_2NMe$] gives the ion-separated complex $[(\eta^5\text{-}C_5H_5)_2Tl]^-[(\eta^5\text{-}C_5H_5)Mg(pmdeta)]^+$, the bent bis(cyclopentadienyl)thallate anion of which is isoelectronic and isostructural with 14e $(\eta^5\text{-}C_5H_5)_2Sn$.[3]

We report here the synthesis of $[(\eta^5\text{-}C_5H_5)Tl(\mu\text{-}C_5H_5)Tl(\eta^5\text{-}C_5H_5)]^-[Li(12\text{-crown-}4)_2]^+\cdot$thf **1** from the reaction of $[(\eta^5\text{-}C_5H_5)Tl]_\infty$ with $(C_5H_5)Li$ and 12-crown-4 (2 : 1 : 2 monomer equiv.).†

A low-temperature X-ray crystallographic study (Fig. 1) shows the structure to be an ion-separated complex $[(\eta^5\text{-}C_5H_5)Tl(\mu\text{-}C_5H_5)Tl(\eta^5\text{-}C_5H_5)]^-[Li(12\text{-crown-}4)_2]^+\cdot$thf **1**.‡ The cation contains an eight-coordinate Li centre complexed by two 12-crown-4 ligands. The same cation has been seen in the ion-separated complex $[Li(12\text{-crown-}4)_2]^+[Li\{N(SiMe_3)\}_2SPh]_2$.[6] In addition there is one thf molecule present within the lattice per formula unit of **1**. Although a few mixed-transition metal/main group metal multi-decker sandwich complexes have been structurally characterised, *e.g.* $[\{(\eta^5\text{-}C_5H_5)Co(\mu\text{-}1,3,4,5\text{-tetramethyl-}2,3\text{-dihydro-}1H\text{-}1,3\text{-diboroyl})\}Tl]$,[7] the $[(\eta^5\text{-}C_5H_5)Tl(\mu\text{-}C_5H_5)Tl(\eta^5\text{-}C_5H_5)]^-$ anion of **1** is the first example of a homometallic main group metal triple-decker sandwich complex and is the next homologue of the bis(cyclopentadienyl)thallate anion $[(\eta^5\text{-}C_5H_5)_2Tl]^-$.

The anion contains two Tl^I centres bridged almost symmetrically by a bent $\mu\text{-}C_5H_5$ bridge [av. $Tl(1,2)\text{–}(C_5H_5)(B)_{\text{centroid}}$ 2.83 Å, $Tl(1)\text{–}(C_5H_5)(B)_{\text{centroid}}\text{–}Tl(2)$ 175.0°]. The terminal (C_5H_5) ligands are bonded more closely to the Tl centres [av. $Tl(1,2)\text{–}(C_5H_5)(A,C)$ 2.64 Å] and adopt a transoid orientation with respect to each other, with a dihedral angle of 161.4° between the centroids of the two terminal (C_5H_5) ligands and the Tl centres. The $(\mu\text{-}C_5H_5)\text{–}Tl$ contacts in **1** are longer than those seen in either the gas-phase structure of monomeric $[(\eta^5\text{-}C_5H_5)Tl]$ (2.41 Å)[8] or in the solid-state structure of the ion-separated bis(cyclopentadienyl)thallate anion of $[(\eta^5\text{-}C_5H_5)_2Tl]^-[(\eta^5\text{-}C_5H_5)Mg\cdot pmdeta]^+$ (av. 2.72 Å).[3] The $\mu\text{-}C_5H_5$ bridge bonding in the $[(\eta^5\text{-}C_5H_5)Tl(\mu\text{-}C_5H_5)Tl(\eta^5\text{-}C_5H_5)]^-$ anion appears to be comparable to that occurring in the ion-contacted bis(cyclopentadienyl)thallate of $[(\eta^5\text{-}C_5H_5)Tl(\mu\text{-}C_5H_5)Li\cdot pmdeta]$,[3] where similar terminal $(\eta^5\text{-}C_5H_5)_{\text{centroid}}\text{–}Tl$ (av. 2.60 Å) and bridging $(\mu\text{-}C_5H_5)_{\text{centroid}}\text{–}Tl$ (av. 2.85 Å) distances are observed.

$$2[(\eta^5\text{-}C_5H_5)Tl] + [(\eta^5\text{-}C_5H_5)Li] \xrightarrow[2(12\text{-crown-}4)]{\text{hexane–THF}} [(\eta^5\text{-}C_5H_5)Tl(\mu\text{-}C_5H_5)Tl(\eta^5\text{-}C_5H_5)]^-[Li(12\text{-crown-}4)_2]^+$$

1

Scheme 1

Many polymeric or oligomeric forms of substituted cyclopentadienyl derivatives of $[(C_5H_5)Tl]_n$ have been reported. In these compounds, varying the steric bulk has been used to modify the structures of the compounds compared to the parent $[(\eta^5\text{-}C_5H_5)Tl]_\infty$. When substituted with groups possessing

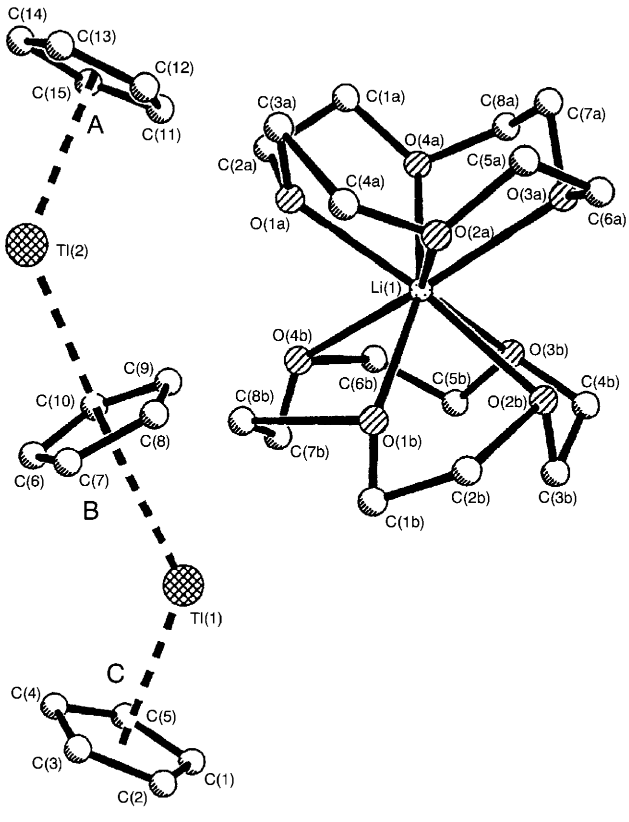

Fig. 1 Molecular structure of **1**. Hydrogen atoms and lattice bound thf solvation have been omitted for clarity. Selected distances (Å): Tl(1)–C(1) 2.97(1), Tl(1)–C(2) 2.92(1), Tl(1)–C(3) 2.83(1), Tl(1)–C(4) 2.83(1), Tl(1)–C(5) 2.90(1), $(C_5H_5)(A)_{\text{centroid}}$–Tl(1) 2.63, Tl(1)–C(6) 3.01(1), Tl(1)–C(7) 3.07(1), Tl(1)–C(8) 3.11(1), Tl(1)–C(9) 3.10(1), Tl(1)–C(10) 3.03(1), $(C_5H_5)(B)_{\text{centroid}}$–Tl(1) 2.83, Tl(2)–C(11) 2.83(2), Tl(2)–C(12) 2.85(2), Tl(2)–C(13) 2.91(2), Tl(2)–C(14) 2.95(2), Tl(2)–C(15) 2.91(2), $(C_5H_5)(C)_{\text{centroid}}$–Tl(2) 2.64, Tl(2)–C(6) 3.14(2), Tl(2)–C(7) 3.15(2), Tl(2)–C(8) 3.04(2), Tl(2)–C(9) 2.96(2), Tl(2)–C(10) 3.00(2), $(C_5H_5)(B)_{\text{centroid}}$–Tl(2) 2.83, dihedral$(C_5H_5)(A)_{\text{centroid}}$–Tl(1)···Tl(2)–$(C_5H_5)(C)_{\text{centroid}}$ 161.4, $(C_5H_5)(A)_{\text{centroid}}$–Tl(1)–$(C_5H_5)(B)_{\text{centroid}}$ 135.0, $(C_5H_5)(C)_{\text{centroid}}$–Tl(2)–$(C_5H_5)(B)_{\text{centroid}}$ 133.4, Tl(1)–$(C_5H_5)(C)_{\text{centroid}}$–Tl(2) 175.0.

relatively low steric bulk, the complexes remain polymeric like the parent $[(\eta^5\text{-}C_5H_5)Tl]_\infty$ such as in $[(C_5Me_5)Tl]_\infty$,[9] $[(C_5H_4SiMe_3)Tl]_\infty$,[10] $[\{C_5Me_4(SiMe_2Ph)\}Tl]_\infty$[11] and $[\{C_5Me_4(SiMe_2CH_2Ph)\}Tl]_\infty$.[11] Increasing the steric bulk on the cyclopentadienyl ring produces discrete oligomers, as in the hexameric (doughnut) $[\{C_5H_3(SiMe_3)_2\}Tl]_6$.[10] Only when extremes of steric bulk are introduced, as in $[\{C_5(CH_2Ph)_5\}Tl]$[12] and $[Tl\{Bu^t{}_2H_2C_5\text{–}C_5H_2Bu^t{}_2)Tl]$,[13] are simple monomers (or a pseudo-dimer in the case of $[\{C_5(CH_2Ph)_5\}Tl]$) obtained. In contrast to all the latter, structural modification in the anion homologues $[(C_5H_5)_2Tl]^-$ and $[(C_5H_5)_3Tl_2]^-$ is achieved by changing both the stoichiometry of the reagents and by altering the size of the cation.

An intriguing feature of the structure of **1** is that of the rather acute angles subtended by the centroids of the (C_5H_5) rings at the Tl atoms [av. (C_5H_5)(A,C)–Tl(1,2)–(C_5H_5)(B) 134.2°]. This angle is far lower than that seen in the structures of the ion-separated or ion-contacted $[(\eta^5\text{-}C_5H_5)_2Tl]^-$ anion (av. 156.7 and 153.3°, respectively).[3] The angles at the Tl centres of **1** are extremely similar to that observed in the polymeric structure of $[(\eta^5\text{-}C_5H_5)Tl]_\infty$ (137°),[14] implying that the steric and electronic environments of their Tl centres are similar.

We are continuing these studies by an investigation of the possible formation of higher anion homologues of $(\eta^5\text{-}C_5H_5)_2E$ (E = Sn, Pb) [*e.g.*$(\eta^5\text{-}C_5H_5)_5E_2{}^-$] and of mixed-metal multidecker sandwich complexes. We are also examining the thermodynamics of the formation of higher anion homologues by *ab initio* MO calculations.

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Footnotes

† To a stirred suspension of $(\eta^5\text{-}C_5H_5)Tl$ (Aldrich, 0.539 g, 2.0 mmol) in THF (10 ml) was added a freshly prepared solution of $(\eta^5\text{-}C_5H_5)Li$ (1.0 mol l^{-1} in THF; 0.1 ml, 1.0 mmol) under argon at *ca.* 0 °C. An orange-yellow solution was produced. To this was added 12-crown-4 (0.35 g, 2 mmol) and the resulting mauve solution was filtered (porosity 3, Celite). The solution was reduced under vacuum (*ca.* 5 ml) and hexane (2 ml) was added. This resulted in the formation of a white precipitate which redissolved upon heating. Storage at −35 °C (24 h) gave pink blocks of **1**. The lattice bound THF solvation in **1** is lost upon placing the complex under vacuum (*ca.* 15 min, 10^{-1} atm.). The following analytical and spectroscopic data refer to the dry amorphous powder produced; yield 0.24 g, 25%; decomp. gradually up to 180 °C to a brown oil; IR (Nujol), ν/cm^{-1} 3076 $[(C_5H_5)]$; ^1H NMR ($[^2H_8]$THF), δ 5.99 (15H, C_5H_5), 3.60 (32H, 12-crown-4); small amounts of $[(\eta^5\text{-}C_5H_5)Tl]_\infty$ are always isolated (as colourless needles) along with **1**, leading to slightly lower percentage C and H than expected for **1**.

‡ *Crystal data* for **1**: $C_{35}H_{55}LiO_9Tl_2$, M = 1035.47, monoclinic, space group $P2_1/c$, a = 10.411(2), b = 23.759(5), c = 16.021(3) Å, β = 105.56(3)°, V = 3817.6(13) Å^3, Z = 4, D_c = 1.802 Mg m^{-3}, λ = 0.71073 Å, T = −120 °C, μ(Mo-Kα) = 8.480 mm^{-1}. Data were collected on a Siemens-Stoe AED diffractometer using an oil-coated rapidly-cooled crystal of dimensions 0.26 × 0.25 × 0.19 mm in an oil drop (T. Kottke and D. Stalke, *J. Appl. Crystallogr.*, 1993, **26**, 615) by the θ/ω method ($7.36° \leq 2\theta \leq 45.00°$). Of a total of 6656 collected reflections, 4958 were independent (R_{int} = 0.0343). The data were corrected for absorption by a semi-empirical method based on Ψ-scans. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 (G. M. Sheldrick, SHELXL-92, Göttingen, 1992) to final values of $R1[F > 4\sigma(F)]$ = 0.054 and $wR2$ = 0.134 and $R1$ = 0.075 and $wR2$ = 0.156 (all data) $\{R1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{0.5}\}$; largest peak and hole in the final difference map 1.596 and −2.957 e Å^{-3}.

The two 12-crown-4 ligands which complex the eight-coordinate Li cation exhibit disorder, in which there are secondary positions for each oxygen atom and alternate carbon atoms. The partial occupancies for the disordered atoms in each of the 12-crown-4 ligands were refined freely. The first 12-crown-4 ligand refines with a partial occupancy of 64.78% for atoms O(1) to O(4), C(1), C(3), C(5), C(7) and 35.25% for atoms O(1) to O(4), C(1), C(3), C(5), C(7). Atoms C(2), C(4), C(6), C(8), were refined with full occupancies. The second 12-crown-4 ligand refined with a partial occupancy of 52.43% for atoms O(1) to O(4), C(1), C(3), C(5), C(7) and 47.56% for atoms O(1′) to O(4′), C(1′), C(3′), C(5′), C(7′). Atoms C(2), C(4), C(6), C(8) were refined with full occupancies. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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