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The Bis(cyclopentadienyl)thallate(I) Anion Isoelectronic with Stannocene**

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We have recently shown that a range of tri(cyclopentadienyl)stannate and -plumbate complexes consisting of discrete, "ion-separated" ion pairs and bridged, "contacted" ion pairs can be prepared by nucleophilic addition reactions of $[Cp_2Mg]$ and $[CpNa]$ to $[Cp_2E]$ ($Cp = C_5H_5$; $E = Sn, Pb$).

Pb).^[1–3] In all these derivatives the heavy p block metals behave as acceptors rather than donating their electron pairs. In the Pb complexes^[3] $[(\eta^5-Cp)_2Pb(\mu-\eta^5-Cp)Na \cdot PMDETA]$ [$PMDETA = (Me_2NCH_2CH_2)_2NMe$] and $[(\eta^3-Cp)Pb^-]_2 \cdot Mg(THF)_6^{2+}$, the $[Cp_3Pb]^-$ ions can be seen as extruded fragments of the polymeric zig-zag chain structure of orthorhombic $[Cp_2Pb]_x$.^[4] With this in mind, we have turned our attention to cyclopentadienyl complexes with elements of Group 13 ($E = Ga, In, Tl$). The solid-state structures of $[CpIn]$ and $[CpTl]$ are both known and display polymeric zig-zag chains, $[(\mu-\eta^5-Cp)E]_x$, in which the metal centers again behave as acceptors to the bridging Cp ligands.^[5] We wondered whether complexes containing $[Cp_2E]^-$ units could be prepared by addition of Cp^- to Group 13 metallocenes.

We report the syntheses and structures of the ion-separated complex **1** and of the contacted complex **2**.^[6] Both com-

plexes contain bent $[(\eta^5-Cp)_2Tl]^-$ ions which are isoelectronic and isostructural with the 14-electron complex stannocene.

Complex **1** is prepared by stirring a mixture of $[CpTl]$ and $[Cp_2Mg]$ (1:1 mol ratio) in THF. Addition of PMDETA (1 mol equiv) produces a colorless precipitate of **1** which is recrystallized from THF. Similar reaction of $[CpTl]$ and $[CpLi]$ (1:2 mol ratio) in THF, followed by addition of PMDETA (1 mol equiv), produces **2** (see Experimental Procedure).

An X-ray crystallographic study on complex **1**^[6] shows a structure with discrete ion pairs (Fig. 1). The unit cell con-

Fig. 1. Molecular structure of **1**. Hydrogen atoms have been omitted for clarity. Selected distances [Å]: Anion 1: $Tl(1)-C(1)$ 2.86(3), $Tl(1)-C(2)$ 2.91(3), $Tl(1)-C(3)$ 2.99(3), $Tl(1)-C(4)$ 3.07(4), $Tl(1)-C(5)$ 2.85(3), $Tl(1)-C(6)$ 3.05(3), $Tl(1)-C(7)$ 3.04(3), $Tl(1)-C(8)$ 2.94(2), $Tl(1)-C(9)$ 2.93(3), $Tl(1)-C(10)$ 2.88(3). Anion 2: $Tl(2)-C(11)$ 3.02(3), $Tl(2)-C(12)$ 2.94(3), $Tl(2)-C(13)$ 2.93(3), $Tl(2)-C(14)$ 2.98(3), $Tl(2)-C(15)$ 3.09(3), $Tl(2)-C(16)$ 2.93(3), $Tl(2)-C(17)$ 2.87(3), $Tl(2)-C(18)$ 2.92(3), $Tl(2)-C(19)$ 3.03(3), $Tl(2)-C(20)$ 3.03(3). Averages over all molecules in the unit cell: $Tl-Cp$ (centroid) 2.72, $Mg-N$ 2.20, $Mg-Cp$ (centroid) 2.08, Cp (centroid)- $Tl-Cp$ (centroid) 156.7°.

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sists of two independent $[(\eta^5\text{-Cp})_2\text{Tl}]^-$ ions and two independent $[(\eta^5\text{-Cp})\text{Mg}\cdot\text{PMDETA}^+]$ ions. The structure of **2** contains two independent contacted ion pairs in the solid state (Fig. 2), in which one Cp ligand bound to Tl is additionally involved with a Lewis base solvated Li^+ ion (av $\text{Li}-\text{Cp}(\text{b})_{\text{centroid}}$ 2.25 Å) as a $(\mu\text{-Cp})$ bridge.^[6] All the independent $[(\eta^5\text{-Cp})_2\text{Tl}]^-$ units of **1** and **2** are bent, with a mean Cp-Tl-Cp angle (from the centroids of the Cp ligands) of 156.7° in **1** and 153.3° in **2**. These angles can be compared to the average centroid Cp-E-Cp angle of 146° for the two independent bent molecules of $[\text{Cp}_2\text{Sn}]$ in the solid state^[10] and approximately 135° for $[\text{Cp}_2\text{Pb}]$ in the gas phase,^[11] with which the 14-electron thallate ions in **1** and **2** are isostructural and isoelectronic. The Cp-Tl-Cp angle in polymeric $[(\eta^5\text{-Cp})\text{Tl}]_x$ is significantly more acute (ca. 137°) than those observed in the $[(\eta^5\text{-Cp})_2\text{Tl}]^-$ ions of both complexes.^[15]

Fig. 2. Molecular structure of **2**. Hydrogen atoms have been omitted for clarity. Selected distances [Å]: Molecule 1: Tl(1)-C(11) 3.02(1), Tl(1)-C(12) 3.07(1), Tl(1)-C(13) 3.20(1), Tl(1)-C(14) 3.19(1), Tl(1)-C(15) 3.10(1), Tl(1)-C(16) 2.81(1), Tl(1)-C(17) 2.86(1), Tl(1)-C(18) 2.89(1), Tl(1)-C(19) 2.89(1), Tl(1)-C(12) 2.82(1), Li(1)-C(11) 2.69(2), Li(1)-C(12) 2.53(2), Li(1)-C(13) 2.34(2), Li(1)-C(14) 2.42(2), Li(1)-C(15) 2.62(2). Molecule 2: Tl(2)-C(21) 3.00(1), Tl(2)-C(22) 3.04(1), Tl(2)-C(23) 3.13(1), Tl(2)-C(24) 3.10(1), Tl(2)-C(25) 3.03(1), Tl(2)-C(26) 2.82(1), Tl(2)-C(27) 2.86(1), Tl(2)-C(28) 2.91(1), Tl(2)-C(29) 2.90(1), Tl(2)-C(30) 2.86(1), Li(2)-C(21) 2.68(2), Li(2)-C(22) 2.61(2), Li(2)-C(23) 2.45(2), Li(2)-C(24) 2.46(2), Li(2)-C(25) 2.59(2). Averages over all molecules in the unit cell: Tl-Cp(a) (centroid) 2.61, Tl-Cp(b) (centroid) 2.85, Li-Cp(b) (centroid) 2.25, Li-N 2.23, Cp(a) (centroid)-Tl-Cp(b) (centroid) 153.3° , Cp(a) (centroid)-Li-Cp(b) (centroid) 175.7° .

While the Tl center of the discrete $[(\eta^5\text{-Cp})_2\text{Tl}]^-$ ion in **1** is attached almost equivalently to the two $\eta^5\text{-Cp}$ ligands (av $\text{Tl}-\text{Cp}_{\text{centroid}}$ 2.72 Å), in **2** the terminal $\eta^5\text{-Cp}$ contact (av $\text{Tl}-\text{Cp}(\text{a})_{\text{centroid}}$ 2.60 Å) is significantly shorter than that made with the Li^+ -bridging $\mu\text{-Cp}$ ligand (av $\text{Tl}-\text{Cp}(\text{b})_{\text{centroid}}$ 2.85 Å). In **2**, the Li^+ ion competes with Tl for the electron density on the bridging Cp ligand. The Cp ligand is “dragged” away from the Tl center, and there is a compensatory enhancement in the interaction between the terminal $\eta^5\text{-Cp}$ ligand and Tl; the $\text{Tl}-\text{Cp}(\text{a})_{\text{centroid}}$ distance approaches that found in the gas-phase structure of monomeric $[(\eta^5\text{-Cp})\text{Tl}]$ (ca. 2.41 Å).^[12] Similarly to the bridging $\mu\text{-}\eta^5\text{-Cp}$ ligand found in $[(\eta^5\text{-Cp})_2\text{E}(\mu\text{-}\eta^5\text{-Cp})\text{Na}\cdot\text{PMDETA}]$ (E = Sn, Pb), the $\mu\text{-Cp}$ bridge of **2** is bent (av $\text{Tl}-\text{Cp}(\text{b})_{\text{centroid}}\text{-Li}$ 175.2° , cf. ca. 172° in $[(\eta^5\text{-Cp})_2\text{E}(\mu\text{-}\eta^5\text{-Cp})\text{Na}\cdot\text{PMDETA}]$).^[1-3]

Complexes **1** and **2** are only the second examples of monomeric Cp thallium(I) species characterized in the solid state; the only other known monomeric complex is $[\text{Tl}(\text{C}_5(\text{CH}_2\text{Ph})_5)]$.^[13] Almost all structurally characterized Cp-based derivatives of thallium so far have had polymeric

structures akin to that of $[(\eta^5\text{-Cp})\text{Tl}]_x$.^[15] Additionally, **1** and **2** are the only structurally characterized unsubstituted Cp derivatives apart from $[(\eta^5\text{-Cp})\text{Tl}]_x$. The closest structural analogue to **1** and **2** is the dimeric ring complex $[\{\text{TlAu}(\text{C}_5\text{H}_4\text{PPh}_2)_2\}_2]$, in which essentially linear $[\text{C}_5\text{H}_4\text{PPh}_2\text{-Au-C}_5\text{H}_4\text{PPh}_2]$ units are linked together through $\eta^5\text{-Cp}$ contacts to Tl^+ ($\text{Cp}_{\text{centroid}}\text{-Tl-Cp}_{\text{centroid}}$ ca. 135°).^[14] In view of our results this complex can be reinterpreted as an ion-contacted gold thallate complex rather than the implied Tl-contacted gold diphosphide, although there is some ambiguity as to the charge distribution in the ligand.

To our knowledge, $[(\eta^5\text{-Cp})\text{Mg}\cdot\text{PMDETA}]^+$ of **1** is the first example of a mononuclear cationic fragment derived from $[\text{Cp}_2\text{Mg}]$.^[15] It is interesting to note that, although its bonding is largely ionic, the cation is formally isoelectronic with the 12-electron compound $[\text{Cp}_2\text{Mg}]$.

Ab initio MO calculations were performed on various isomers of the discrete $[\text{Cp}_2\text{Tl}]^-$ ion in **1** at the Hartree-Fock level and with electron correlation.^[16, 17] Initially minimum basis set (MBS) calculations were performed on different Cp ring conformations, to assess the relative stabilities of the “linear” and “bent” models. The most stable bent C_s conformer (**I**), the same as that observed for the $[\text{Cp}_2\text{Tl}]^-$ ion in **1** in the solid state, and the most stable linear D_{5d} conformer (**II**) were then optimized using the ECP-DZ basis set. Their geometries and that of monomeric $[\text{CpTl}]$ (**III**) are shown in Figure 3. The

Fig. 3. Optimized geometries (DZ basis set) of the $[\text{Cp}_2\text{Tl}]^-$ ion—the bent structure with C_s symmetry (**I**) and the linear structure with D_{5d} symmetry (**II**)—and that of monomeric $[\text{CpTl}]$ (**III**).

energy for the association of Cp^- and $[\text{CpTl}]$ is reasonably favorable ($-6.38 \text{ kcal mol}^{-1}$ to give the most stable bent structure **I**).^[17] Although the Cp-Tl contacts are significantly elongated in **I** and **II** compared to the Cp-Tl distance in **III**, there is little difference either in the charge carried by the Cp ring atoms or in the charge on the Tl center. Bending of the linear structure **II** producing **I** slightly enhances the Cp-Tl interactions but has only a marginal effect on the charge distribution within the molecule. However, whereas in **II** the Cp ligands are symmetrically attached to Tl ($\text{Cp}_{\text{centroid}}\text{-Tl}$ 2.918 Å), in **I** one of the Cp ligands is closer to the metal than the other is ($\text{Cp}_{\text{centroid}}\text{-Tl}$ 2.846 and 2.903 Å).

The optimized geometries (DZ basis set) of the linear and bent isomers of $[\text{Cp}_2\text{Tl}]^-$ were employed in a series of calculations with electron correlation. The results (MP2, MP3, MP4) confirm that the bent geometry is only slightly more stable than its linear counterpart; at the MP4 level the difference in energy is $0.82 \text{ kcal mol}^{-1}$.^[17] This finding is contrary

to that calculated for the 14-electron complex $[\text{Cp}_2\text{Ge}]$ and to the general consensus concerning $[\text{Cp}_2\text{Sn}]$,^[18–20] which proposes that bent structures are preferred on electronic grounds since bending presumably stabilizes the lone pair in the antibonding a_{1g}^* molecular orbital as a consequence of the admixing of this orbital with the metal p_x atomic orbital. Overall, the calculations on $[\text{Cp}_2\text{Tl}]^-$ indicate that the geometry of the thalocene anion is highly flexible. Orbital admixing appears to be ineffective here and a largely spherical lone pair orbital is present. This feature is illustrated in Figure 4 where, in addition, it can be seen that there is a constriction in the electron density between Tl and the more weakly attached Cp ligand.

Fig. 4. One of the isosurfaces of electron density for the bent structure of $[\text{Cp}_2\text{Tl}]^-$ having C_s symmetry (geometry optimization with the DZ basis set).

Experimental Procedure

1: $[\text{CpTl}]$ (0.538 g, 2.0 mmol) was stirred with $[\text{Cp}_2\text{Mg}]$ (0.308 g, 2 mmol) in 10 mL THF. The reactants dissolved giving a golden brown solution. On addition of PMDETA (0.42 mL, 2 mmol) a pink solid precipitated, which dissolved on heating the reaction mixture to reflux. The reaction mixture was filtered and cooled slowly (12 h at 20 °C) to give air-sensitive, light-pink crystals of **1**. Yield 0.360 g (30%) over two batches; decomp 120 °C to black solid; IR (Nujol) $\tilde{\nu}=3059\text{ cm}^{-1}$ (Cp-H); $^1\text{H NMR}$ (+25 °C, 400 MHz, $[\text{D}_8]\text{ THF}$): $\delta=5.66$ (s, 15 H; CpH), 2.41 (s, 3 H; $(\text{CH}_3)_2\text{N}$), 2.34 (s, 12 H; $(\text{CH}_3)_2\text{N}$), 2.11 (s, 8 H; $(\text{CH}_2)_2$); $^{13}\text{C NMR}$ (+25 °C, 100.6 MHz, $[\text{D}_8]\text{ THF}$): $\delta=107.0$ (C_5H_5), 55.0–59.0 (CH_3N and $(\text{CH}_2)_2\text{N}$), 46.0–49.0 ($(\text{CH}_2)_2$); correct C, H, N analysis.

2: $[\text{CpTl}]$ (0.538 g, 2.0 mmol) was stirred with $[\text{CpLi}]$ (0.288 g, 4 mmol) in 10 mL THF. The solid dissolved giving a yellow solution which was filtered before PMDETA (0.42 mL, 2 mmol) was added. Cooling of the resulting solution (2 d at –35 °C) gave air-sensitive, colorless crystals of **2**. The crystals melt and/or redissolve below 0 °C, and all attempts to isolate them were unsuccessful. **2** could only be characterized by low-temperature X-ray crystallography [7].

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