Solvent directed aggregation of a metallocene; structures of $\{[Pb(\eta\text{-}C_5H_5)_2]_3{\cdot}C_6H_5Me\}_\infty$ and $[Pb(\eta\text{-}C_5H_5)_2]_6$

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The classic zigzagged chain structure of orthorhombic plumbocene, $[Pb(\eta\text{-}C_5H_5)_2]_\infty$, is obtained by crystal growth from the vapour phase; however, crystallisation from toluene results in modification of the conformation of the polymer chain, as observed in the solvate $[Pb(\eta\text{-}C_5H_5){\cdot}C_6H_5Me]_\infty$ 1, and cyclisation into hexamers, as seen in the new hexagonal phase $[Pb(\eta\text{-}C_5H_5)_2]_6$ 2.

We have recently observed that nucleophilic addition of the cyclopentadienide anion (C_5H_5) to plumbocene $\{[Pb(\eta\text{-}C_5H_5)_2]\}$ produces a variety of complexes containing mononuclear and linear extended anions of general formulae $[Pb_n(\eta\text{-}C_5H_5)_{2n+1}]^-$.[1] The chain length of the homologue formed depends on the size and nature of the counter cations, and therefore on the lattice energy involved. Accordingly, the reaction of $[Pb(\eta\text{-}C_5H_5)_2]$ with $[Mg(\eta\text{-}C_5H_5)_2]$ in thf produces $[Mg(thf)_6]^{2+}\{[Pb(\eta\text{-}C_5H_5)_3]^-\}_2$[1c] whereas the same reaction in the presence of 12-crown-4 gives the mixed anion complex $\{[Li(12\text{-crown-}4)_2]^+\}_2[Pb_2(\eta\text{-}C_5H_5)_5]^-[Pb_9(\eta\text{-}C_5H_5)_9]^-$.[1a] The formation of these anions points to the underlying structural flexibility of plumbocene itself. In this respect, two phases of plumbocene have been identified (triclinic and orthorhombic). However, only the orthorhombic polymeric phase $\{[Pb(\eta\text{-}C_5H_5)_2]_\infty\}$, grown from the vapour phase, has been structurally characterised.[2]

With the previous background in mind we have recently embarked on an investigation of the influence of solvation on the structure of plumbocene.[3] We report here that simple crystallisation of orthorhombic plumbocene from toluene solution results in major structural modification of the polymer chain. From such solutions two new complexes, the polymeric toluene solvate $\{[Pb(\eta\text{-}C_5H_5)_2]_3{\cdot}C_6H_5Me\}_\infty$ **1** and the cyclic molecular phase $[Pb(\eta\text{-}C_5H_5)_2]_6$ **2**, have been characterised.†

Complex **1** has an infinite polymer structure which is qualitatively similar to the orthorhombic form of plumbocene [Fig. 1(*a*)].‡ In both cases the association of the $[Pb(\eta\text{-}C_5H_5)_2]$ monomer units by bridging $\mu\text{-}C_5H_5$ ligands results in trigonal-planar metal environments {av. Cp–Pb–Cp 120.8° in **1**; *cf.* av. 120.0° in orthorhombic $[Pb(\eta\text{-}C_5H_5)_2]$;[2] Cp = centroid of cyclopentadienyl ring}. The pattern of C_5H_5–Pb bond lengths in **1** is also similar to that found in orthorhombic $[Pb(\eta\text{-}C_5H_5)_2]$, with a shorter interaction being made to the terminal C_5H_5 ligand (av. Pb–Cp 2.50 Å) and two longer interactions being made with the bridging ligands [av. Pb–(μ-Cp) 2.75 Å]. However, the presence of toluene solvation within the lattice has a marked effect on the conformation of the polymer chain of **1**. Rather than consisting of a simple two-dimensional zigzagged structure, as is observed in orthorhombic plumbocene, polymer strands of **1** adopt a sinusoidal pattern in order to avoid the interstitial toluene molecules [Fig. 1(*b*)].

Molecules of **2** are composed of six identical $[Pb(\eta\text{-}C_5H_5)_2]$ units which are linked together into a cyclic arrangement (Fig. 2).§ The mode of association of these units and the resulting environments of the metal centres are similar to those found in orthorhombic $[Pb(\eta\text{-}C_5H_5)_2]$ and **1**.[2] However, the monomers of **2** are less affected by their association than in either of the latter. The $[Pb(\eta\text{-}C_5H_5)_2]$ units resemble those found for monomeric plumbocene in the gas phase (Cp–Pb ≈ 2.50 Å and Cp–Pb–Cp 138°),[4] with the Pb centre of each monomer being bonded more closely to two of the C_5H_5 ligands [Cp(A)–Pb(1) 2.44 Å, Cp(B)–Pb(1) 2.53 Å and Cp(A)–Pb–Cp(B) 135.3°] than to the C_5H_5 ligand of the next monomer unit [Cp(B)···Pb(1b) 3.33 Å]. This pattern of C_5H_5–Pb interactions implies that the association of the monomers is extremely loose. The stacking of the $[Pb(\eta\text{-}C_5H_5)_2]_6$ rings results in infinite cylindrical channels through the crystal lattice.

The influence of substituents on the structures of p-block metallocenes is now well established. Increased substitution of the C_5H_5 rings with sterically demanding groups generally leads to the formation of oligomeric rather than polymeric species. For example, whereas $[E(\eta\text{-}C_5H_5)]_\infty$ (E = In, Tl)[5] have polymeric structures in the solid state, $[E\{C_5(CH_2Ph)_5\}]$[6] are essentially monomeric. The structural flexibility and subtle influence of the substituents are seen particularly in $[In(\eta\text{-}C_5Me_5)]_6$, which forms loosely associated In···In bonded octahedra in the solid state,[7] and $[Tl\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}]_6$, containing $Tl\text{–}\{\mu\text{-}\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}\text{–}Tl$ linked cyclic molecules related to **2**.[8] Despite its similarity with the structure of the latter, the oligomeric structure of **2** is unique for any unfunctionalised main group metallocene.

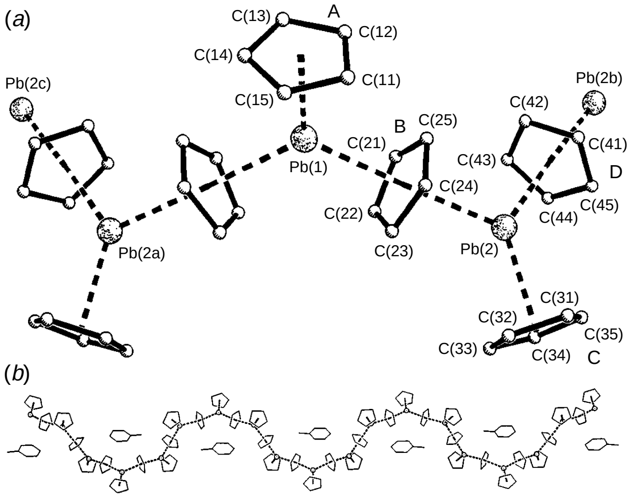

Fig. 1 (*a*) Asymmetric unit of **1**. Hydrogen atoms have been omitted for clarity. Key bond lengths (Å) and angles (°): Pb(1)–C(11) 2.74(7), Pb(1)–C(12) 2.73(7), Pb(1)–C(13) 2.76(6), Pb(1)–C(14) 2.79(7), Pb(1)–C(15) 2.79(5), Cp(A)–Pb(1) 2.48, Pb(1)–C(21) 3.03(7), Pb(1)–C(22) 3.05(7), Pb(1)–C(23) 2.96(7), Pb(1)–C(24) 2.93(7), Pb(1)–C(25) 2.98(7), Cp(B)–Pb(1) 2.73, Pb(2)–C(21) 3.08(7), Pb(2)–C(22) 3.11(7), Pb(2)–C(23) 3.03(7), Pb(2)–C(24) 2.95(7), Pb(2)–C(25) 2.98(7), Cp(B)–Pb(2) 2.78, Pb(2)–C(31) 2.74(3), Pb(2)–C(32) 2.79(3), Pb(2)–C(33) 2.85(3), Pb(2)–C(34) 2.84(3), Pb(2)–C(35) 2.77(3), Cp(C)–Pb(2) 2.53, Pb(2)–C(41) 3.00(7), Pb(2)–C(42) 3.02(7), Pb(2)–C(43) 3.01(7), Pb(2)–C(44) 2.97(7), Pb(2)–C(45) 2.97(7); Cp(D)–Pb(2) 2.74, av. Cp–Pb–Cp 120.8°, av. Pb–Cp–Pb 175.1, Cp(C)–Pb···Pb–Cp(A) (dihedral) 74.3; Cp represents centroid of $\eta\text{-}C_5H_5$ ring. (*b*) Polymer structure of **1**.

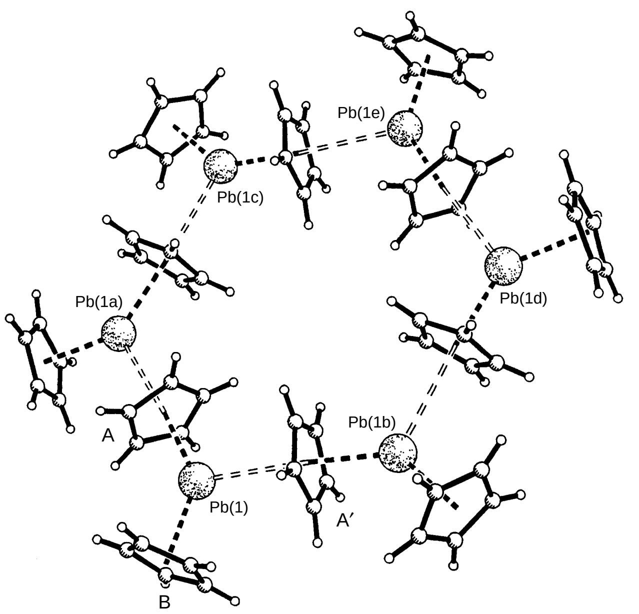

Fig. 2 Molecular structure of **2** in the solid state. Hydrogen atoms have been omitted for clarity. Key bond lengths (Å) and angles (°): Pb(1)–C(1) 2.76(1), Pb(1)–C(2) 2.86(1), Pb(1)–C(3) 2.88(1), Pb(1)–C(4) 2.79(1), Pb(1)–C(5) 2.71(1), Cp(A)–Pb(1) 2.53, Pb(1)–C(6) 2.79(1), Pb(1)–C(7) 2.78(1), Pb(1)–C(8) 2.69(1), Pb(1)–C(9) 2.64(1), Pb(1)–C(10) 2.71(1), Cp(B)–Pb(1) 2.44, Pb(1)–C(1a,2a,3a,4a,5a) 3.53(2), Cp(A)–Pb(1b) 3.33, Cp(A)–Pb(1)–Cp(B) 135.3, Cp(B)–Pb(1)–Cp(A′) 116.2, Cp(A)–Pb(1)–Cp(A′) 108.5, Pb(1)···Cp(A)–Pb(1b) 179.2, Pb···Pb 5.56, Pb···Pb···Pb 120.0.

The characterisation of **1** and **2** illustrates, for the first time, that non-coordinating solvent interactions can have profound consequences on the conformation and overall structure adopted by a main group metallocene. Similar observations may well be expected for group 13 metallocenes {[E(η-C_5H_5)]; E = In, Tl}, for which polymeric structures have been determined for crystals grown from the vapour phase.[5]

Footnotes

† Orthorhombic $[Pb(\eta\text{-}C_5H_5)_2]_\infty$ was prepared in the manner described in the literature and purified by sublimation (140 °C, 0.1 atm). Crystallisation from toluene at 5 °C gives a mixture of **1** and **2**. Owing to the composition of this mixture, elemental analysis (C, H) and ^1H NMR spectroscopy indicate that there is *ca.* toluene molecule to each $[Pb(\eta\text{-}C_5H_5)_2]$ monomer unit (*i.e.* consistent with largely **1**).

‡ *Crystal data*: **1**, $C_{37}H_{38}Pb_3$, M = 1104.24, orthorhombic space group $Pnma$, a = 16.421(3), b = 24.375(5), c = 8.234(2) Å, U = 3296(1) Å^3, Z = 4, λ = 0.710 73 Å, T = 153(2) K, D_c = 2.225 Mg m^{-3}, μ(Mo-Kα) = 15.311 mm^{-1}. Data were collected on a Siemens-Stoe AED diffractometer using an oil-coated crystal[9] of dimensions 0.3 × 0.2 × 0.2 mm using the θ–ω method ($8.32 \leqslant 2\theta \leqslant 45.06°$). Of a total of 2284 reflections collected 2199 were independent. A semi-empirical absorption correction based on ψ-scans was applied (max., min. transmission = 0.981, 0.149). The structure was solved by direct methods and refined by full-matrix least squares on F^2 to final values of R_1 = 0.102 (for 2195 data with $F > 4\sigma F$) and wR_2 = 0.231 (all data) $[R_1 = \Sigma|F_o - F_c|/\Sigma|F_o|, wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma w F_o^4\}^{0.5}, w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP], P = (F_o^2/3)]$.[10] Largest peak and hole in the final difference map = 2.968 and −2.958 e Å^{-3}. The C atoms were refined isotropically. The C_5H_5 rings and toluene molecules were refined as rigid groups. C_5H_5(A) is disordered on an inversion centre and C_5H_5(D) is disordered on a mirror plane. Hydrogen atoms were set geometrically.

2, $C_{60}H_{60}Pb_6$, M = 2024.22, hexagonal, space group $P6cc$, a = 18.058(2), c = 10.219(2) Å, U = 2885.9(7) Å^3, Z = 2, λ = 0.710 73 Å, T = 153(2) K, D_c = 2.329 Mg m^{-3}, μ(Mo-Kα) = 17.473 mm^{-1}. Data were collected on a Siemens-Stoe AED diffractometer using an oil-coated crystal[9] of dimensions 0.15 × 0.24 × 0.24 mm using the θ–ω method ($8.40 \leqslant 2\theta \leqslant 44.98°$). Of a total of 4906 reflections collected 1268 were independent. A semiempirical absorption correction based on ψ-scans was applied (max., min. transmission = 0.953, 0.476). The structure was solved as for **1** to final values of R_1 = 0.041 (for 1261 data with $F > 4\sigma F$) and wR_2 = 0.124 (all data). Largest peak and hole in the final difference map = 3.118 and −0.749 e Å^{-3}. C atoms were refined isotropically and the C_5H_5 rings as rigid groups. Hydrogen atoms were set geometrically.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/319.

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