ELSEVIER

Journal of Organometallic Chemistry 650 (2002) 75–76

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

A new, tetragonal, helical phase of plumbocene, Cp_2Pb; variations on a molecular string ($Cp = C_5H_5$)

Richard A. Layfield [a,*], Carole A. Morrison [b], Dominic S. Wright [a,*]

[a] *Chemistry Department, University of Cambridge, Lensfield Road, Cambridge CB2 1EW UK*
[b] *Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK*

Received 8 November 2001; accepted 22 December 2001

Abstract

The isolation of a tetragonal, helical phase of plumbocene, Cp_2Pb, provides a rare example of a helical metallocene and the opportunity to shed light on the relationship between the modes of aggregation found in its various polymorphs.

Keywords: Lead; Metallocene; Plumbocene

1. Introduction

The structural flexibility of plumbocene, Cp_2Pb, is evident from recrystallization of pre-sublimed orthorhombic, zigzag Cp_2Pb from toluene at 5 °C; a toluene–solvated complex, $[(Cp_2Pb)_3{\cdot}C_6H_5CH_3]_\infty$, which adopts a sinusoidal, polymeric chain structure, and an unsolvated cyclic, hexagonal modification, $(Cp_2Pb)_6$, have also been structurally characterised [1]. Recently, the structure of the orthorhombic, zigzag phase of Cp_2Pb has been accurately redetermined using crystals grown from a toluene–THF mixture at 27 °C, allowing the space group ambiguity to be eliminated [2a].

As a part of our continuing studies into the effects of internal donor groups on the nature of aggregation of metallocene 'paddle-wheel' anions [3], we have treated Cp_2Pb (prepared according to a literature procedure [2b]) with $(Cp^{THF})_2Mg$ [2:1 equivalents, $Cp^{THF} = (C_5H_4)CH_2\text{-}2\text{-}C_4H_7O]$ in toluene solvent, but the envisaged product of nucleophilic addition, $[Cp_2PbCp^{THF}\text{-}MgCp^{THF}PbCp_2]$, was not formed. Instead, Cp_2Pb was itself crystallized from a toluene solution at − 15 °C over 72 h in a new polymeric, helical phase **1**. This polymorph adds a new dimension to the understanding of the nature of propagation in plumbocene and provides a key insight into the relationship between its different modifications.

The low-temperature X-ray crystallographic study of **1**[1] shows that the individual molecules of Cp_2Pb assemble into an infinite, polymeric structure where each Pb centre is bonded to two $\mu\text{-}\eta^5\text{-}C_5H_5$ ligands and one terminal $\eta^5\text{-}C_5H_5$ ligand (Fig. 1). This results in approximate trigonal planar coordination geometry around Pb [av. $Cp_{cent}\text{–}Pb\text{–}Cp_{cent} = 120.0$ °, range 117.0–122.3 ° (Cp_{cent} = centroid axis of the Cp ligand)], which is qualitatively very similar to the arrangement in the orthorhombic, zigzag form and the sinusoidal toluene solvate. Pb–C distances in **1** do not vary greatly {Pb–C[Cp(B)] 2.71–2.80 Å, av. 2.76 Å; Pb–C[Cp(A)] 2.95–3.06 Å, av. 3.01 Å; Pb–C[Cp(AA)] 2.92–3.02 Å, av. 2.98 Å} and the Pb-(μ-Cp)-Pb bridges deviate only slightly from linearity [av. Pb-(μ-Cp)-Pb 174.4 °, Fig. 1]. The pattern of Cp_{cent}–Pb distances in **1** is very similar to that found for the other characterised polymeric forms of Cp_2Pb, with short contacts to the terminal Cp ligands (Cp_{cent}–Pb 2.51 Å) and slightly

---

* Corresponding author. Tel.: + 44-1223-336343; fax: + 44-1223-336362.

E-mail address: ral34@hermes.cam.ac.uk (R.A. Layfield).

[1] X-ray data for **1**; $[C_{10}H_{10}Pb]_\infty$, yellow, air-sensitive crystals, M = 337.37, tetragonal, space group $I4_1/a$, $Z = 16$, $a = b = 16.5600(9)$ Å, $c = 14.8161(10)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 4063.1(4)$ Å, μ(Mo–K_α) = 16.548 mm^{-1}, $T = 180(2)$ K. Data were collected on a Nonius KappaCCD diffractometer. Of a total of 6301 reflections collected, 2284 were independent ($R_{int} = 0.0922$). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 [9]. $R_1 = 0.0475$ [$I > 4\sigma(I)$], $wR_2 = 0.1247$.

PII: S0022-328X(02)01178-6

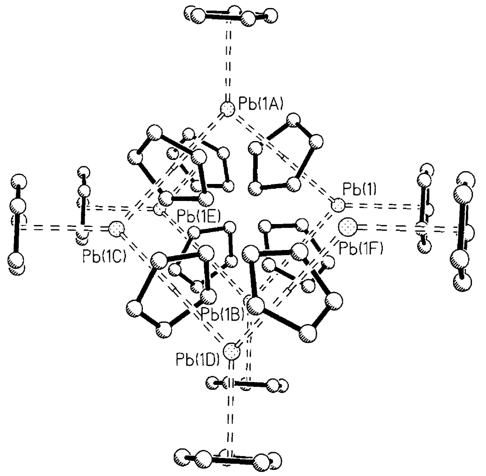

Fig. 1. Molecular structure of **1** viewed along the 4_1 screw axis.

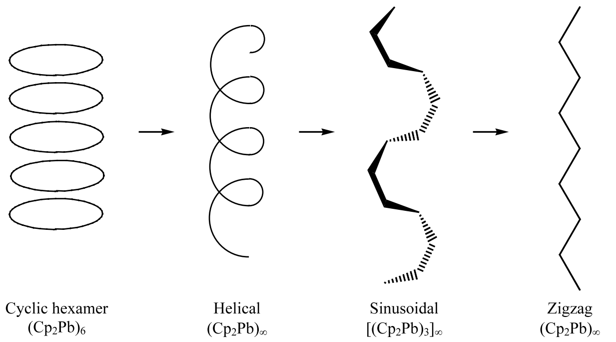

Fig. 2. The inter-relation between the known polymorphs of Cp_2Pb.

longer contacts to the bridging Cp ligands (Cp_{cent}–Pb 2.76 Å). In contrast to the previously determined structures of Cp_2Pb [1,2], the polymeric strands of **1** are non-planar. Indeed, fragments of $[Cp_2Pb]$ in **1** propagate in the form of an α-helix about a 4_1 screw axis, where one complete turn of the helix comprises four $[Cp_2Pb]$ units, with a pitch of 14.82 Å [corresponding to the Pb(1)–Pb(1F) distance]. Both the right-handed and the left-handed enantiomorphs are found in the crystal lattice of **1**.

Organometallic polymorphism is a well-documented phenomenon [4]; for plumbocene, in light of the sensitive and flexible nature of the metal–ligand bonding, and given the apparent differences and similarities between the various isomorphs, a conceptual scheme to illustrate the inter-relation that may exist between them can be proposed (Fig. 2). Viewed in this way, plumbocene may be regarded as a 'molecular string' being drawn out from a coiled, helical conformation to a sharp, zigzag conformation.

Observation of the helical structural motif is established for many transition metals, particularly in the case of classical, Werner-type coordination complexes of Group 11 [5]. For main group organometallic compounds, however, the occurrence of helical oligomers or polymers is extremely rare, $[\{Na[C_5H_4B(NMe_2)_2]\}\cdot C_5H_{10}O]_\infty$ [6], $[Me_3SnCl\cdot AlCl_3]_\infty$ [7] and [*R*-ethylmethylphenyltelluronium (1*S*)-camphor-10-sulphonate]$_\infty$ [8] being among the very few structurally characterised examples. The closest analogue to **1** is the solvated sodium borylcyclopentadienide $[\{Na[C_5H_4B(NMe_2)_2]\}\cdot C_5H_{10}O]$, the two compounds qualitatively sharing a number of structural properties. However, the molecular structure of **1** is unique in being the first unfunctionalized, helical, main group organometallic.

2. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 173672 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We gratefully acknowledge the EPSRC (R.A.L., D.S.W.), The Isaac Newton Trust (R.A.L.), Electron Industries Ltd., U.K. (R.A.L.), Clare College, Cambridge (Denman Baynes Senior Research Studentship for R.A.L.). We also thank Dr J.E. Davies for collecting the X-ray diffraction data on **1**.

References

[1] M.A. Beswick, C. Lopez-Casideo, M.A. Paver, P.R. Raithby, C.A. Russell, A. Steiner, D.S. Wright, J. Chem. Soc. Chem. Commun. (1997) 109.

[2] (a) J.S. Overby, T.P. Hanusa, V.G. Young Jr., Inorg. Chem. 37 (1998) 163;
(b) C. Panattoni, G. Bombieri, U. Croatto, Acta Crystallogr. 21 (1966) 823.

[3] N. Feeder, A.D. Hopkins, R.A. Layfield, D.S. Wright, J. Chem. Soc. Dalton Trans. (2000) 2247.

[4] D. Braga, F. Grepioni, Chem. Soc. Rev. 29 (2000) 229.

[5] M. Munakata, L.P. Wu, T. Kuroda-Sowa, Adv. Inorg. Chem. 46 (1998) 174.

[6] G.E. Herberich, A. Fischer, Organometallics 15 (1996) 58.

[7] J.J. Eisch, K. Mackenzie, H. Windisch, C. Krüger, Eur. J. Inorg. Chem. (1999) 153.

[8] T. Shimizu, T. Urakubo, S. Kitagawa, J. Organomet. Chem. 539 (1997) 171.

[9] SHELXTL PC version 5.03, Siemens Analytical Instruments, Madison, WI, 1994.