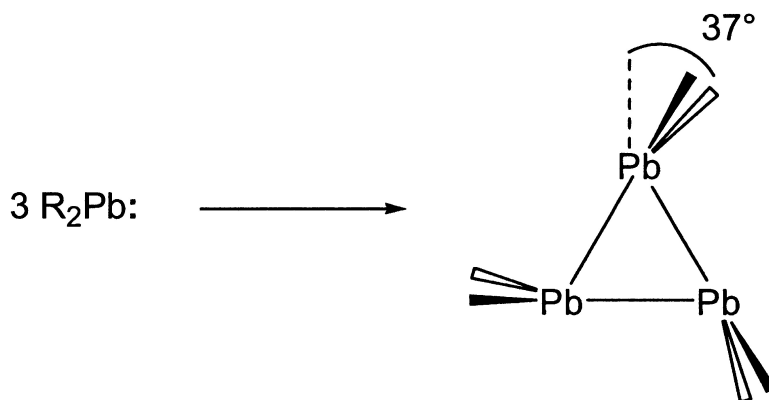


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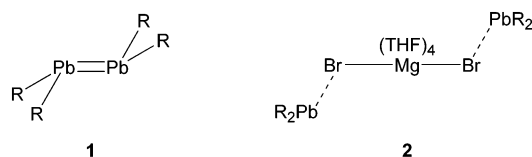
Hexaarylcyclotriplumbane: A Molecule with a Homonuclear Ring System of Lead

Frank Stabenow,[†] Wolfgang Saak,[†] Heinrich Marsmann,[‡] and Manfred Weidenbruch^{*†}

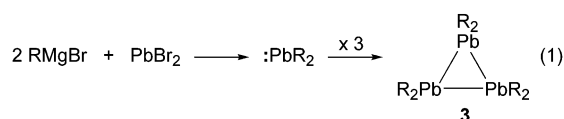
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The reactions of lead(II) halides with aryl Grignard reagents, RMgBr, depend not only on the spatial demands of the respective group R but also on how the reaction is performed. While the reaction with R = 2-*t*-Bu-4,5,6-Me₃C₆H furnishes a monomeric plumbylene,¹ the use of the only slightly smaller 2,4,6-triisopropylphenyl group affords the diplumbene **1** as the first example of a molecule with a lead/lead double bond.² A further reduction in the spatial requirements of the group to R = 2,4,6-triethylphenyl leads to the formation of the molecule **2** in which two plumbylene units are linked through MgBr₂.³ Finally, when R = mesityl, a plumbylene dimer in which the two lead atoms are each stabilized by a magnesium bromide molecule is obtained.⁴



To separate the MgBr₂(THF)₄ formed in the reaction between 2,4,6-triethylphenylmagnesium bromide and lead(II) bromide in THF and thus suppress the formation of **2**, we performed the reaction in the presence of dioxane. We then obtained in 34% isolated yield black crystals of the cyclotriplumbane **3** which can be heated to 80 °C without decomposition (eq 1).⁵



The thermal stability of **3** as well as the ²⁰⁷Pb NMR signal at 1160 ppm clearly demonstrate that the structural integrity of **3** in the solid state is also preserved in solution. This NMR shift differs substantially from those observed with typical plumblyenes that range from 3870 to 8888 ppm.^{1,6} The structure of compound **3** was confirmed by an X-ray crystallographic analysis⁷ that revealed some unusual structural parameters (Figure 1). With an average value of 3.184 Å, the Pb/Pb bond lengths are markedly longer than those of a typical diplumbane such as Ph₃Pb–PbPh₃ with 2.844(4) Å.⁸ They rather correspond to the Pb/Pb separation in the diplumbylene RPb–PbR where R = 2,6-Tip₂C₆H₃ (Tip = 2,4,6-triisopropylphenyl), determined by Power et al. as 3.1881(1) Å.⁹

Equally unusual is the orientation of the substituents at the lead atoms which are twisted by about 37° out of their ideal positions (Figure 2). The structural parameters observed here are in accord with those obtained from calculations on the parent compound,

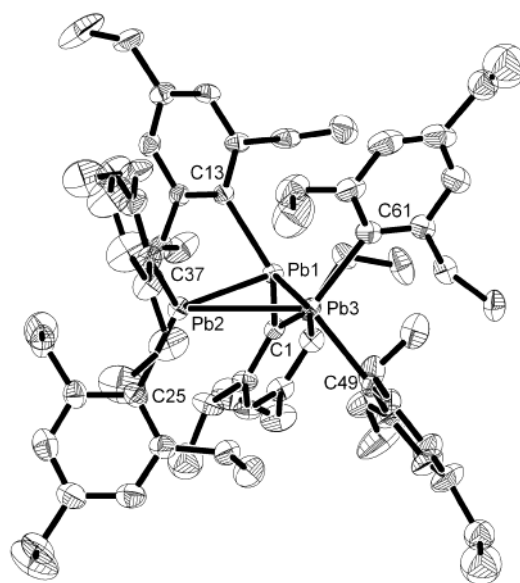


Figure 1. Molecule of **3** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Pb(1)–Pb(2) = 3.1812(3), Pb(2)–Pb(3) = 3.2014(2), Pb(1)–Pb(3) = 3.1727(3), Pb–C = 2.30 (average); Pb(3)–Pb(1)–Pb(2) = 60.510(6), Pb(2)–Pb(3)–Pb(1) = 59.876(6), Pb(1)–Pb(2)–Pb(3) = 59.614(6), C–Pb–C = 102.9 (average).

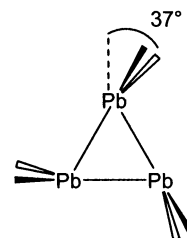


Figure 2. Details of the structure of **3**.

c-Pb₃H₆, for example, Pb/Pb bond lengths of 3.231 Å and displacement angles of 50° for the hydrogen atoms.^{10,11}

The calculated and observed structures clearly demonstrate that the Pb/Pb bonds in **3** are not classic single bonds but rather that the structure is held together by weak interactions between three singlet plumbylene molecules (Figure 3).¹⁰ This is in contrast to all other homonuclear ring systems of group 14 elements, which can be described as normal single bonds. The weakness of these interactions and the thus resulting widened bonds is probable due to the relativistic contraction¹² of the 6s orbital of one lead atom, which then only incompletely overlaps with the unoccupied 6p orbitals of the respective other lead atom. The Pb–C lengths and C–Pb–C angles, which do not differ substantially, are in the region typical for diarylplumblyenes.

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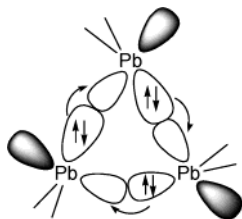


Figure 3. Interaction of three singlet plumbylenes R_2Pb .

The cyclotriplumbane **3** is the first compound of lead with a homocyclic ring system.¹³ This is worthy of note because the lighter homologues of group 14 form numerous ring systems. Although in the past few years a number of homo- and heteronuclear cluster compounds of lead have also been prepared,¹⁴ they contain bonding situations different from that in compound **3**.

Acknowledgment. Financial support for our work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic file for compound **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- All manipulations were carried out in oven-dried glassware under an atmosphere of dry argon. At $-110\text{ }^\circ\text{C}$, a solution of the Grignard compound $RMgBr$ in THF (35 mL), prepared in turn from 1-bromo-2,4,6-triethylbenzene (2.41 g, 10 mmol) and magnesium turnings (0.9 g, 37 mmol), was added dropwise to a suspension of lead(II) bromide (1.84 g, 5 mmol) in THF (10 mL) and dioxane (5 mL). The reaction mixture, which initially turned yellow, was allowed to warm to $0\text{ }^\circ\text{C}$ under constant stirring, and finally adopted a reddish-brown color. The solvents were removed under reduced pressure, the brownish residue was extracted with 30 mL of *n*-hexane, and the precipitate of magnesium salt was filtered off. Storing at $-30\text{ }^\circ\text{C}$ furnished 0.91 g (34% yield) of black crystals, dark red in thin layers. $^1\text{H NMR}$ (toluene- d_6): δ 1.55 (t, 18H, $^3J = 7.4$ Hz), 1.17, 1.19 (m, two overlapping signals, 36H), 2.50 (q, 24H, $^3J = 7.7$ Hz, *o*-CH₂), 2.70 (q, 12H, $^3J = 7.7$ Hz, *p*-CH₂), 7.22 (s, 12H, arom. H). $^{13}\text{C NMR}$ (toluene- d_6): 16.04 (C_p), 29.28 (C_s), 29.47 (C_s), 32.06 (C_p), 128.25 (C_{aromat}), 143.48 (C_{aromat}), 144.18 (C_{aromat}), 150.85 (C_{aromat}). $^{207}\text{Pb NMR}$ (toluene- d_6): 1152. UV-vis (*n*-hexane): λ (ϵ) 502 nm (1665).
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- Crystallographic data for **3** at 213 K with Mo $K\alpha$ ($\mu = 0.71073\text{ }^\circ\text{Å}^{-1}$) radiation, $a = 13.1218(6)\text{ }^\circ\text{Å}$, $b = 13.1291(5)\text{ }^\circ\text{Å}$, $c = 20.8767(11)\text{ }^\circ\text{Å}$, $\alpha = 94.223(5)^\circ$, $\beta = 98.564(6)^\circ$, $\gamma = 105.832(5)^\circ$; $V = 3396.8(3)\text{ }^\circ\text{Å}^3$; space group $P1$, $Z = 2$, $M = 1589.11\text{ g mol}^{-1}$; $\rho = 1.554\text{ g cm}^{-3}$. Data collection: Stoe IPDS. The structure was solved by direct phase determination and refined by full-matrix least-squares techniques against F^2 with the SHELXL-97 program system. R1/wR2 for 14 264 data = 0.0242/0.0534. The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC 211 375.
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