X-ray Structural Analysis of
# Hexakis[2-(3,5-di-*t*-butylphenyl)-2-methylpropyl]diplumbane

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Abstract: X-ray crystallographic analysis was performed for diplumbane Ar'_6Pb_2 (Ar'=2-(3,5-di-*t*-butylphenyl)-2-methylpropyl), prepared from the reaction of ArM (Ar=2,4,6-tri-*t*-butylphenyl, M=Li or MgBr) with $PbCl_2$, to show that it has the longest Pb-Pb distance (Pb1-Pb2=2.9448(6) Å) ever reported.

We have previously found that reactions of ArM (Ar=2,4,6-tri-*t*-butylphenyl, M=Li or MgBr) with $PbCl_2$ afforded unusual products which contained rearranged Ar' group (Ar'=2-(3,5-di-*t*-butylphenyl)-2-methyl-propyl).[1] Diplumbane Ar'_6Pb_2 (1), one of unexpected rearranged products, is especially interesting from a structural point of view. We report here the X-ray structure analysis for 1.

The chemistry of group 14 ethane congeners R_3X-YR_3 (X, Y=C, Si, Ge, Sn, or Pb) have been of great interest for long time. It involves structural discussions for sterically congested compounds such as phantom hexaphenylethane (HPE)[2] which actually exists as the methylenecyclohexadiene structure.[3] The lead
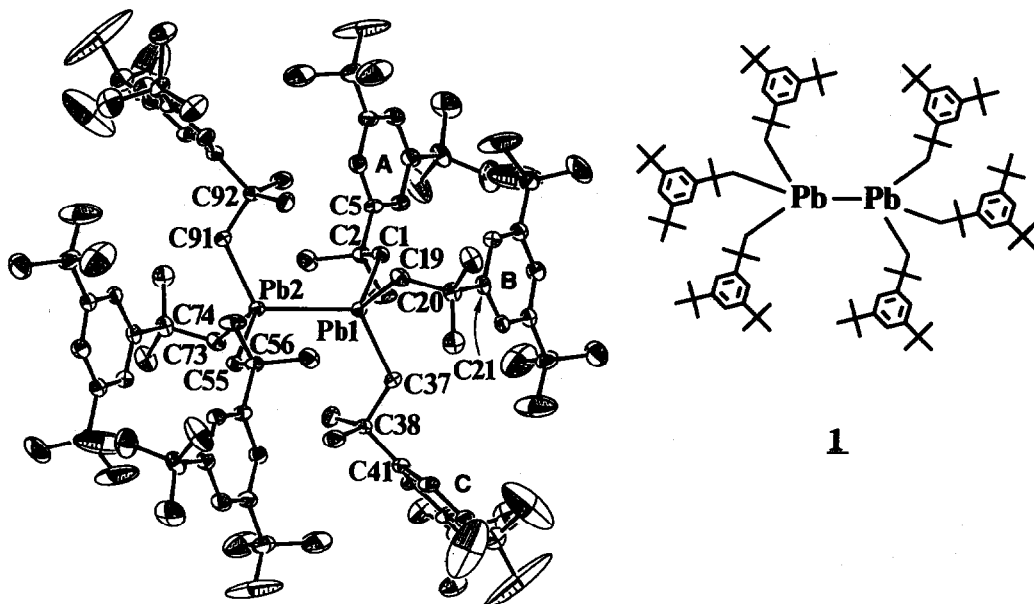
Figure 1. *ORTEP* drawing of Ar'_6Pb_2 (1). Selected bond lengths (Å) and angles (deg) ; Pb1-Pb2 2.9448(6), Pb1-C1 2.289(7), Pb1-C19 2.280(7), Pb1-C37 2.274(7), Pb2-Pb1-C1 115.5(2), Pb2-Pb1-C19 106.4, Pb2-Pb1-C37 118.4(2), C1-Pb1-C19 97.1(3), C19-Pb1-C37 107.0(3), Pb1-C1-C2 123.1(5), Pb1-C19-C20 120.4(5), Pb1-C37-C38 123.1(5). Selected tortion angles (deg) ; Pb1-Pb2-C55-C56 63.1(5), Pb1-Pb2-C73-C74 -150.7(5), Pb1-Pb2-C91-C92 -11.3(7), Pb1-C1-C2-C5 165.8(4), Pb1-C19-C20-C21 173.4(5), Pb1-C37-C38-C41 -177.1(5), C1-Pb1-Pb2-C73 73.5(3), C1-Pb1-Pb2-C91 -51.1(3), C19-Pb1-Pb2-C91 55.4(3). Dihedral angles between least squares planes (deg) ; A-B 1.03, A-C 121.61, B-C 121.43.

analogue of HPE, hexaphenylplumbane $Ph_3PbPbPh_3$ has been also investigated.[4,5] The discussions have focused on the structure in solution and in solid. Equilibriums such as $(R_3Pb)_2 \rightleftharpoons 2\ R_3Pb\cdot$ [4a,c] or $(R_3Pb)_2 \rightleftharpoons R_4Pb + R_2Pb$ [6] have been postulated, but it was proven that R_3PbPbR_3 was the appropriate structure for the description of the molecule.[7]

We became interested in the structure of the sterically crowded diplumbane Ar'_6Pb_2, and X-ray crystallographic analysis was performed (Figure 1).[8] Ar'_6Pb_2 (1) has a very long Pb-Pb distance (2.9448(6) Å) and this is the longest lead-lead single bond so far reported for diplumbanes; Me_6Pb_2 2.88(3) Å (electron diffraction[10]), Ph_6Pb_2 2.848(4) Å (X-ray[4d]), (p-tolyl)$_6Pb_2$ 2.851(1) Å (X-ray[11]), (cyclohexyl)$_6Pb_2$ 2.876(4) Å (X-ray[12]), (o-tolyl)$_6Pb_2$ 2.895(2) Å (X-ray[9]).

The Pb-Pb distance is apparently lengthened by the severe steric repulsion of Ar' groups on each lead atom. Three Ar' groups are not equivalent in the solid state, and the ring C lies nearly perpendicular to the rings A and B and in the space between the parallel rings A and B (see the plane-plane angle in Figure 1). Sebald and Harris[9] reported the ^{207}Pb CP MAS NMR of several sterically crowded diplumbanes, but among them the single crystal of $(Mes_3Pb)_2$ (Mes=mesityl), whose X-ray crystallographic data would be necessary for comparison, has been unavailable because of its limited solubility. Ar'_6Pb_2 would be useful to such CP MAS studies.

References and Notes

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8. *Crystallographic data* for 1: $C_{108}H_{174}Pb_2$, M=1886.96, monoclinic, a=10.250(2), b=28.194(3), c=17.870(2) Å, β=94.66(1) °, V= 5147(1) Å^3, Z= 2, space group $P2_1/n$, Dc= 1.217 gcm^{-3}, μ=33.32 cm^{-1}. The intensity data ($2\theta \leq 60$ °) were collected on a Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation (λ=0.71069 Å) and the structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 7621 observed reflections [I>3.0σ(I)] and 496 variable parameters with R(Rw)=0.047(0.046). Atomic coordinates, bond length, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
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