New Pb–Pb bonds: syntheses and molecular structures of hexabiphenyldiplumbane and tri(trisbiphenylplumbyl)plumbate

Yuzhong Wang, Brandon Quillian, Pingrong Wei, Xiao-Juan Yang and Gregory H. Robinson*

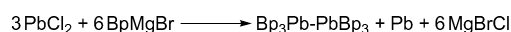*Department of Chemistry, The University of Georgia, Athens, Georgia, USA 30602-2556.
E-mail: robinson@chem.uga.edu*

Reaction of lead(II) chloride with biphenylmagnesium bromide yields $Bp_3Pb–PbBp_3$ and $[(THF)_3Mg(\mu\text{-}Cl)_3Mg(THF)_3]$-$[Pb(PbBp_3)_3]$ (Bp = biphenyl), which, upon single crystal X-ray crystallographic analysis, reveals an interesting variation of Pb–Pb bond distances.

Despite the once nearly ubiquitous, if now largely diminishing, utility of tetraethyllead as an "anti-knock" agent in motor fuels,[1,2] the organometallic chemistry of this heaviest member of group 14 has not developed in parallel with its lighter congeners. Indeed, while organometallic compounds containing double bonds, $R_2E=ER_2$ (E = C, Si,[3,4] Ge[5] and Sn[6]), of the lighter members of group 14 are now all well documented, the first unambiguous example of a compound containing a Pb=Pb double bond, tetrakis(2,4,6-triisopropylphenyl)diplumbene,[7] was only recently reported. Herein we report the syntheses and molecular structures of two new organolead compounds containing Pb–Pb bonds: a diplumbane with a short Pb–Pb bond, $Bp_3Pb–PbBp_3$ **1** and an ionic compound containing three Pb–Pb bonds, $[(THF)_3Mg(\mu\text{-}Cl)_3$-$Mg(THF)_3][Pb(PbBp_3)_3]$ **2** (Bp = biphenyl). The title compounds, isolated from reaction of lead(II) chloride with biphenylmagnesium bromide, are the first organolead compounds employing the biphenyl ligand. Moreover, **1** is significant as it is a rare example of a structurally characterized hexaaryldiplumbane while **2** may be added to a similarly small group of organometallic compounds containing multiple Pb–Pb single bonds.

The preparation of **1** begins with the addition of a 0.50 M THF solution of BpMgBr (12.5 mmol, 25.0 mL) to a suspension of $PbCl_2$ (6.25 mmol, 1.74 g) in a 40 mL THF–1,4-dioxane solvent mixture (7 : 1 ratio by volume) at −78 °C. Gradual warming of the system to room temperature resulted in a yellow-orange solution. The presence of elemental lead was observed. The solution was filtered and the solvent was reduced *in vacuo*. Cooling of the solution resulted in the formation of **1** as pale yellow crystals (Scheme 1 and Fig. 1).†

Structurally characterized hexaaryldiplumbanes, $(aryl)_3Pb–Pb(aryl)_3$, are quite rare. Aside from **1**, the literature reveals only hexaphenyldiplumbane, $Ph_3Pb–PbPh_3$ (isolated from the reaction of Ph_3PbCl with Ph_3SiLi in THF)[8] and $Ph_3Pb–Pb(p\text{-}tol)_3$ (isolated from the reaction of Ph_3PbLi with $(p\text{-}tol)_3PbCl$ in THF).[9] A number of points regarding structure and bonding in **1** are noteworthy. The two lead atoms reside in slightly distorted tetrahedral environments while the biphenyl ligands are arranged in a propeller fashion. The most prominent structural feature of **1**, the Pb–Pb single bond distance of 2.8697(10) Å, is slightly longer than that reported for $Ph_3Pb–PbPh_3$ (2.85 Å). However, perfectly consistent with the nature of organometallic compounds of the heavier main group elements, the Pb–Pb *single bond* distances in **1** and $Ph_3Pb–PbPh_3$ are substantially *shorter* than the *double bond* distance of 3.0515(3) Å reported for the $(i\text{-}Pr_3C_6H_2)_2Pb=Pb(i\text{-}Pr_3C_6H_2)_2$ diplumbene.[7]

In contrast to the preparation of **1**, addition of a 0.50 M THF solution of BpMgBr (12.5 mmol, 25 mL) to a neat THF suspension of $PbCl_2$ (6.25 mmol, 1.74 g) at −78 °C gives orange crystals of **2** (Fig. 2).‡
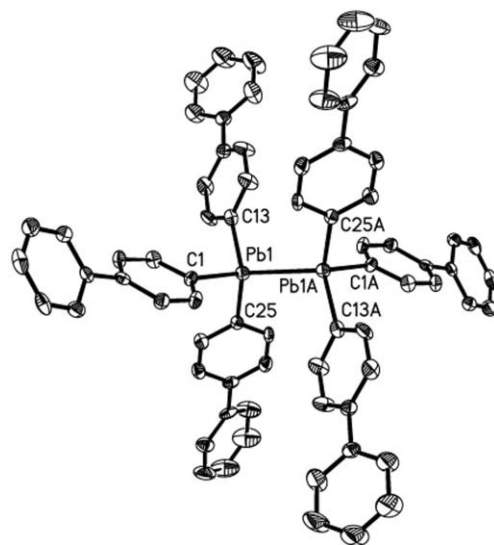
Generally, the number of reported organometallic compounds

Fig. 1 Molecular structure of **1** (30% probability ellipsoids, hydrogen atoms omitted). Selected bond distances (Å) and angles (°): Pb(1)–Pb(1A), 2.8697(10); Pb(1)–C(1), 2.193(11); Pb(1)–C(13), 2.193(11); Pb(1)–C(25), 2.223(9); C(1)–Pb(1)–C(13), 106.1(4); C(1)–Pb(1)–C(25), 108.4(4); C(13)–Pb(1)–C(25), 106.0(4).
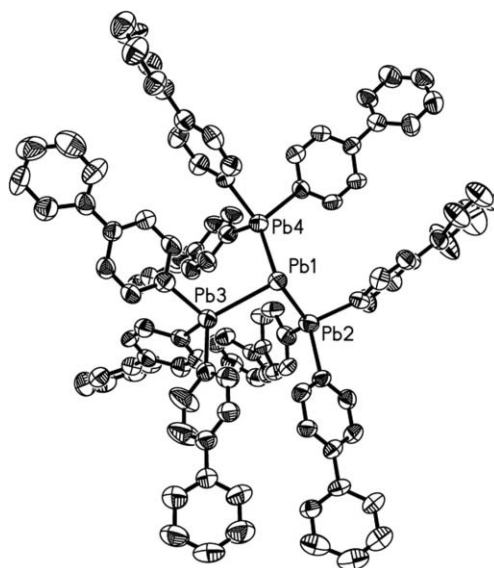

Fig. 2 Molecular structure of **2** (30% probability ellipsoids, hydrogen atoms omitted). Selected bond distances (Å) and angles (°): Pb(1)–Pb(2), 2.9461(8); Pb(1)–Pb(3), 2.9739(7); Pb(1)–Pb(4), 2.9698(8) Å; Pb(2)–Pb(1)–Pb(3), 93.17(2); Pb(2)–Pb(1)–Pb(4), 93.15(2); Pb(3)–Pb(1)–Pb(4), 95.887(19).

$$3\,PbCl_2 + 6\,BpMgBr \longrightarrow Bp_3Pb\text{-}PbBp_3 + Pb + 6\,MgBrCl$$

Scheme 1

containing more than one Pb–Pb bond is exceedingly small. Indeed, other than the tri(trisbiphenylplumbyl)plumbate anion **2** reported herein, the literature reveals only two other such species, both recently reported: (1) the novel hexaarylcyclotriplumbane containing a lead three-membered ring, $[(i\text{-}Pr_3C_6H_2)_2Pb]_3$;[10] and (2) the closely related tris(triphenylplumbyl)plumbate anion, $[Pb(PbPh_3)_3]^-$ (cation: $[(THF)_5MgBr]^+$).[11] The coordination of the central lead atom in both $[Pb(PbPh_3)_3]^-$ and **2** (Fig. 2) may be described as trigonal pyramidal with the lone pair of electrons residing at the apex. The mean Pb–Pb bond distance of 2.9633 Å for **2** compares well with the mean Pb–Pb bond distance of 2.9759 Å for $[Pb(PbPh_3)_3]^-$. The $[(THF)_3Mg(\mu\text{-}Cl)_3Mg(THF)_3]^+$ cation of **2** has been previously observed.[12]

While the disproportionation of lead(II) chloride in the presence of a Grignard reagent to give neutral diplumbanes, elemental lead, and magnesium salt (Scheme 1) may be considered a general process,[13] the mechanism of formation affording **2** remains intriguing. Focus is drawn to the presence, or absence, of a small amount of 1,4-dioxane—the essential experimental difference between **1** and **2**. Could the considerable difference in the nature of reaction products **1** and **2** be traced to a neat THF solvent system *versus* a THF–1,4-dioxane mixed solvent system? While the mechanism of formation of **2**, as Weidenbruch suggested for $[(THF)_5MgBr][Pb(PbPh_3)_3]$,[11] remains unclear, we agree with these workers that reactions of lead(II) halides with Grignard reagents would appear to be more complicated than one would initially suspect.

Notes and references

† *Crystal data* for **1**: $C_{78}H_{66}Pb_2O_3$. $M = 1465.69$, crystal dimensions $0.45 \times 0.40 \times 0.20$ mm^3, triclinic, space group $P\bar{1}$, $a = 11.9430(19)$, $b = 14.431(2)$, $c = 19.402(3)$ Å, $\alpha = 89.378(3)$, $\beta = 89.819(4)°$, $\gamma = 70.374(3)$, $V = 3149.5(9)$ Å^3, $Z = 2$, $D_a = 1.546$ g cm^{-3}, $\lambda(MoK\alpha) = 0.71073$ Å, at room temperature, unique reflections 10140, observed $[I > 2\sigma(I)]$ 6348, parameters 703. The data were corrected for Lorentz and polarization effects and processed using the SAINT, SADABS and XPREP processing packages. The structure was solved by direct methods (SHELXTL 5.1) and refined by full-matrix least squares techniques against F^2. In the final cycles of each refinement, the non-hydrogen atoms were refined anisotropically except for the 1.5 1,4-dioxane molecules. The three atoms O(1), C(73) and C(74) in the half 1,4-dioxane molecule in the asymmetric unit are disordered at their adjacent positions with half occupancies of each. Hydrogen atoms were placed in the calculated positions (assuming a C–H bond length of 0.95 Å) except for the solvent molecules. For the observed reflections, $R = 0.0589$, $wR2 = 0.1070$. The goodness-of-fit indicator for all data is 1.082. Peaks on the final difference map ranged from 1.077 to -1.719 e Å^{-3}. CCDC 241498. See http://www.rsc.org/suppdata/cc/b4/b408860n/ for crystallographic data in .cif format.

‡ *Crystal data* for **2**: $C_{148}H_{147}Pb_4O_7Mg_2Cl_3$. $M = 3021.39$, crystal dimensions $0.40 \times 0.30 \times 0.20$ mm^3, triclinic, space group $P\bar{1}$, $a = 19.222(3)$, $b = 19.329(3)$, $c = 20.958(3)$ Å, $\alpha = 77.520(4)$, $\beta = 85.906(4)°$, $\gamma = 67.523(3)$, $V = 7024.5(18)$ Å^3, $Z = 2$, $D_a = 1.428$ g cm^{-3}, $\lambda(MoK\alpha) = 0.71073$ Å, at room temperature, unique reflections 22212, observed $[I > 2\sigma(I)]$ 10962, parameters 1332. The data were corrected for Lorentz and polarization effects and processed using the SAINT, SADABS and XPREP processing packages. The structure was solved by direct methods (SHELXTL 5.1) and refined by full-matrix least squares techniques against F^2. In the final cycles of each refinement, the non-hydrogen atoms were refined anisotropically except for the carbon atoms of six coordinated THF molecules and non-hydrogen atoms of one discrete THF molecule. Hydrogen atoms were placed in the calculated positions (assuming a C–H bond length of 0.95 Å). For the observed reflections, $R = 0.0564$, $wR2 = 0.1231$. The goodness-of-fit indicator for all data is 1.017. Peaks on the final difference map ranged from 0.952 to -0.641 e Å^{-3}. CCDC 241499. See http://www.rsc.org/suppdata/cc/b4/b408860n/ for crystallographic data in .cif format.

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