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Synthesis and Characterization of 2,6-Trip$_2$H$_3$C$_6$PbPbC$_6$H$_3$-2,6-Trip$_2$ (Trip = C$_6$H$_2$-2,4,6-*i*-Pr$_3$): A Stable Heavier Group 14 Element Analogue of an Alkyne

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The synthesis and isolation of compounds with multiple bonds between heavier main group elements have attracted widespread interest owing to their unusual properties, structures and bonding, which differ markedly from those of their lighter congeners.[1] Heavier element analogues of ethylene, $H_2C{=}CH_2$, have played a leading role in the development of the field, and a complete series of compounds of elements from the carbon group (group 14) of formula $R_2E{=}ER_2$ (E = Si,[2] Ge,[3,4] Sn,[4,5] or Pb,[6,7] R = bulky hydrocarbon group) has been isolated in the solid state by using various sterically crowding substituents. However, all currently known compounds of the formulas R_2SnSnR_2 and R_2PbPbR_2, as well as many R_2GeGeR_2 species, dissociate in solution to the monomers: ER_2 (E = Ge, Sn, or Pb) indicating that the bonding between these elements is weak.[8] The corresponding heavier element analogues of acetylene of formula REER (E = Si, Ge, Sn, or Pb) have not been stabilized, although theoretical data on the hypothetical silicon[9−11] and germanium[9,12] derivatives have described them as triple bonded. Experimental data on the physical properties or bonding of heavier group 14 acetylene analogues are limited to gas-phase spectroscopy on mono-[13] or di[14]-bridged isomers of Si_2H_2. In addition, recent attempts to synthesize ArEEAr (E = Ge and Sn) species via reduction of the halide E(Cl)Ar by alkali metals have led only to the isolation of reduced salts such as $[K(THF)_6][2,6\text{-}Trip_2H_3C_6\text{-}SnSnC_6H_3\text{-}2,6\text{-}Trip_2]$.[15] We now report the synthesis and characterization of the neutral lead species 2,6-Trip$_2$H$_3$C$_6$PbPbC$_6$H$_3$-2,6-Trip$_2$, which is the first formal heavier group 14 element analogue of a substituted acetylene molecule.

The title species **1** was synthesized[16] in ca. 10% yield by the reaction of $LiAlH_4$ with Pb(Br)C$_6$H$_3$-2,6-Trip$_2$. The mechanism of this reaction is currently unknown, but it may proceed through the hydride derivative Pb(H)C$_6$H$_3$-2,6-Trip$_2$ which may then condense to give the product 2,6-Trip$_2$H$_3$C$_6$PbPbC$_6$H$_3$-2,6-Trip$_2$ with hydrogen elimination as shown in eq 1:

$$2\text{Pb(Br)Ar} \xrightarrow{\text{LiAlH}_4} \underset{\text{Ar} = -\text{C}_6\text{H}_3\text{-2,6-Trip}_2}{2\text{Pb(H)Ar}} \xrightarrow{-\text{H}_2} \underset{\mathbf{1}}{\text{ArPbPbAr}} \qquad (1)$$

Dichroic, amber-green crystals of **1**·hexane were grown from hexane and the molecular structure (Figure 1) was determined by X-ray crystallography.[17] It consists of noninteracting 2,6-Trip$_2$H$_3$C$_6$PbPbC$_6$H$_3$-2,6-Trip$_2$ molecules which exist in a trans-bent rather than linear form. There is a center of symmetry midway along the Pb−Pb bond, as a result of which the two lead atoms and the two ipso carbons of the aryl groups all lie in the same plane. The central rings of the aryl ligands lie almost perpendicular to this plane. It can be seen from the space filling model (Figure 2) that the sterically crowding aryl ligands effectively surround the Pb−Pb moiety thereby ensuring its stability against decomposition.

The most important structural parameters of **1** are the Pb−Pb bond length, 3.1881(1) Å, and the Pb−Pb−C angle, 94.26(4)°. The Pb−Pb bond distance is significantly longer than typical values in diplumbanes such as $Ph_3PbPbPh_3$ (Pb−Pb = 2.844(4) Å)[18] although it is shorter than the interatomic distance of 3.49 Å in metallic lead.[19] The observed Pb−Pb−C angle, which is relatively close to 90°, indicates little hybridization[20] of the lead valence orbitals as well as the presence of a lone pair at each metal. In other words, each lead uses two of its 6p orbitals for bonding to the ipso-carbon and the other lead atom, the remaining 6p orbital is unoccupied, and the lone pair is thus accommodated in the lower energy 6s orbital. The use of almost pure p-orbitals instead of more hybridized orbitals and the presence of lone pairs at each lead may account for the length of the Pb−Pb bond.[21,22] In addition the relatively long Pb−C bond of 2.303(2) Å (cf. av. Pb−C = 2.22(2) Å in $Ph_3PbPbPh_3$)[18] is consistent with this view.

The strongly bent geometry of **1** indicates that it exists in the unique dimethylene form (b) instead of the acetylene like

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(16) (a) All manipulations were carried out using modified Schlenk techniques under an atmosphere of N_2 or in a Vacuum Atmosphere HE-43 drybox. $LiAlH_4$ (0.053 g, 1.41 mmol) in diethyl ether (10 mL) was slowly added to a pale orange solution of Pb(Br){C$_6$H$_3$-2,6-Trip$_2$} (2.80 mmol synthesized by the addition of (Et$_2$O)LiC$_6$H$_3$-2,6-Trip$_2$[16b] (1.58 g, 2.8 mmol) to a diethyl ether suspension of $PbBr_2$ (1.03 g, 2.8 mmol)) in diethyl ether (25 mL) at ca. −78 °C with constant stirring. The reaction mixture, which had assumed a light green color, was stirred for a further 1 h after which it was allowed to come to room temperature. The ether was removed under reduced pressure, and the light green-black residue was extracted with hexane (40 mL). The solution was separated from the green-black precipitate by decanting it to another flask. The volume of the yellowish green solution was reduced to incipient crystallization and stored in a ca. 6 °C freezer to give the product as amber-green dichroic crystals. Yield 0.38 g, 9.8%. Mp 183−185 °C. ^{1}H NMR (C_6D_6): δ 1.18 (mult, 48H, o-CH(C*H*$_3$)$_2$), 1.32 (d, 24H, *p*-CH(C*H*$_3$)$_2$, J_{HH} = 6.8 Hz), 2.95 (sept, 4H, *p*-C*H*(CH$_3$)$_2$, J_{HH} = 6.8 Hz), 3.25 (sept, 8H, *o*-C*H*(CH$_3$)$_2$, J_{HH} = 6.8 Hz), 6.19 (t, 2H, *p*-C$_6$H$_3$, J_{HH} = 7.2 Hz), 7.00 (s, 4H, *m*-Trip), 7.10 (s, 4H, *m*-Trip), 7.68 (d, 4H, *p*-C$_6$H$_3$, J_{HH} = 7.2 Hz). ^{13}C{^{1}H}(C_6H_6): δ 25.10 (*o*-CH(*C*H$_3$)$_2$), 26.66 (*o*-CH(*C*H$_3$)$_2$), 32.99 (*p*-CH(*C*H$_3$)$_2$), 33.70 (*o*-*C*H(CH$_3$)$_2$), 34.80 (*p*-*C*H(CH$_3$)$_2$), 123.28 (*m*-Trip), 128.65 (*m*-C$_6$H$_3$), 129.36 (*p*-C$_6$H$_3$), 136.36 (*i*-Trip), 148.17 (*p*-Trip), 148.74 (*o*-Trip), 153.32 (*o*-C$_6$H$_3$), 198.65 (*i*-C$_6$H$_3$). IR (Nujol mull): 1915(vw), 1850(vw), 1755(vw), 1600(s), 1560(m), 1550(m), 1360(s), 1315(m), 1185(w), 1165(w), 1150(w), 1092(w), 1975(w), 1065(w), 1050(vw), 1020(w), 1005(w), 935(w), 920(vw), 890(vw), 875(s), 850(vw), 835(vw), 820(vw), 795(s), 770(m), 730(s), 690(vw), 645(m), 580(vw), 525(vw), 485(vw), 460(vw), 240(m). UV−vis (hexane): 719 nm, (5200); 397 nm, (29000); (b) Schiemenz, B.; Power, P. P. *Organometallics* **1996**, *15*, 958.

(17) Crystallographic data for **1**·hexane at 93 K with Mo Kα (μ = 0.71073 Å) radiation: a = 13.3312(3) Å, b = 15.9539(4) Å, c = 16.8793(4) Å, β = 103.720(1)°; V = 3487.53(14) Å^3; space group $P2_1/c$; Z = 4; M = 1464.06 g mol^{-1}; ρ_{calc} = 1.394 g cm^{-3}, $F(000)$ = 1488. Equipment: Bruker SMART 1000. Data processing software: solution, XS, Bruker SHELXTL v. 5.10; refinement (XL, Bruker SHELXTL) v. 5.10; full-matrix least squares on F^2; $R1/wR2$ for 9721 ($I > 2\sigma(I)$) data = 0.0206/0.0536.

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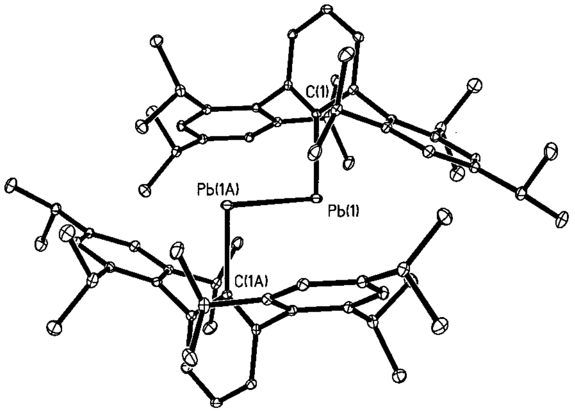

Figure 1. Thermal ellipsoidal (30%) plot of **1**. H atoms are not shown for clarity. Selected bond distances (Å) and angles (deg): Pb(1)−Pb(1A) = 3.1881(1), Pb(1)−C(1) = 2.303(2), C(1)−C(2) = 1.411(2), C(1)C(6) = 1.406(2), C(1)−Pb(1)−Pb(1A) = 94.26(4), C(2)−C(1)−Pb(1) = 114.02(11), C(6)−C(1)−Pb(1) = 127.69(12), C(2)−C(1)−C(6) = 118.17(15).

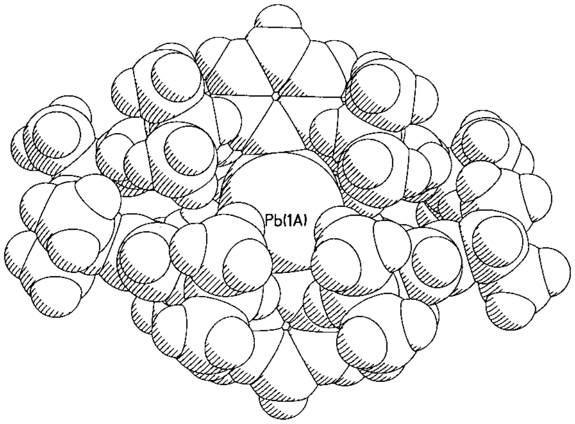

Figure 2. Space filling model of **1** (viewed almost along the Pb−Pb axis) illustrating the high steric protection of the Pb−Pb moiety.

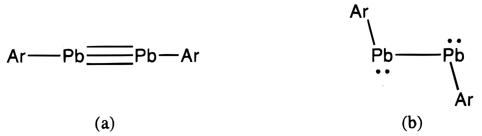

Figure 3. Linear and bent electronic forms of **1**.

dimethylyne form (a) as shown in Figure 3. The fact that (b) can be derived from (a) by the conversion of two bond pairs in (a) to two lone-pairs in (b) does not necessarily imply weakness of the Pb−Pb π-bonds, however. Indeed, it has been shown recently[23] that π-bonding involving 6p orbitals can be quite important, as in the doubly bonded species TbtBi=BiTbt (Tbt = C_6H_2-2,4,6-{CH(SiMe$_3$)$_2$}$_3$), which involves the neighboring element bismuth. Thus, the preference for the valence isomer (b) is a consequence of the decreased hybridization of the s and p orbitals in heavier main group elements[24] which in the case of lead is further diminished by relativistic effects.[25]

The unique structure of **1**, which has an essentially empty 6p-orbital and a lone pair at each lead, leads to the expectation that it could behave as both a Lewis acid and base. Investigation of this chemistry as well as attempts to synthesize germanium and tin analogues of **1** are in hand.

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Supporting Information Available: Tables of data collection parameters, atom coordinates, bond distances, angles, anisotropic thermal parameters, and hydrogen coordinates (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[22] Another explanation for the length of the Pb−Pb bond is that the structure involves bridging or terminal hydrogens as in {Pb(μ-H)C_6H_3-2,6-Trip$_2$}$_2$ or {Pb(H)C_6H_3-2,6-Trip$_2$}$_2$, compounds which would also be of significant interest. We think that the hydride is unlikely for a number of reasons: (a) the ^{1}H NMR displays no peak attributable to Pb−H hydrogens; (b) reduction of Pb(Br)C_6H_3-2,6-Trip$_2$ with $LiAlD_4$ affords a product that has an identical ^{1}H NMR spectrum to that of **1**; (c) the ^{2}H NMR spectrum of the $LiAlD_4$ reduction product displayed no resonances other than those of solvent C_6D_6; (d) the IR spectra of **1** and the product from the reduction with $LiAlD_4$ are essentially identical; (e) a cyclic voltammogram of **1** displays a quasireversible reduction peak consistent with the presence of empty p orbitals in **1**; (f) no stable compounds containing the Pb−H moiety are known to be stable at present. In addition, a ^{207}Pb NMR signal could not be detected in solution−possibly as a result of large anisotropies in the chemical shift tensor. The authors acknowledge that this evidence is largely of a negative character and that the definitive experiment would be a neutron diffraction study of **1**. Attempts to grow sufficiently large crystals for this experiment are in progress.

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