Notes

Characterization of a Plumbylplumbylene: An Isomeric Form of a "Diplumbene"

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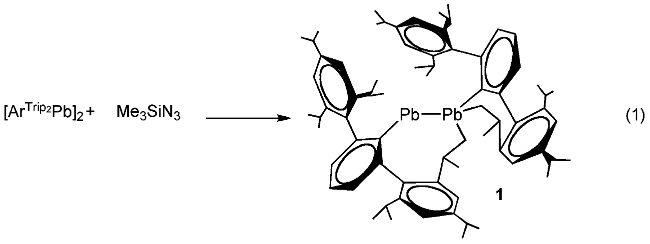
Summary: The synthesis and characterization of the first stable example of a substituted lead analogue of methylmethylene, a valence isomer of ethylene, are reported. The title compound features a bond between a divalent and a tetravalent lead center and is stabilized by the incorporation of the lead−lead bond into a stabilizing ring structure. It was synthesized fortuitously and in low yield by the "activation" of the diplumbyne [PbAr^{Trip_2}]$_2$, where Ar^{Trip_2} = −C$_6$H$_3$−2,6-(C$_6$H$_2$-2,4,6-^{i}Pr$_3$)$_2$, with trimethylsilyl azide, N$_3$SiMe$_3$, and it was characterized via NMR spectroscopy and by single-crystal X-ray crystallography.

Introduction

The stabilization of multiply bonded compounds of the heavier main group elements has been a major theme of organometallic chemistry for more than two decades.[1] However, it is becoming increasingly clear that, unlike their lighter congeners, many multiply bonded heavier element species lie close in energy to other isomeric forms that have greatly differing structures. In 1990, Trinquier calculated the structures and relative energies of various isomers of heavier group 14 analogues of ethylene, M$_2$H$_4$ (M = Si, Ge, Sn, Pb).[2] The relative stabilities of the most stable structures and the mixed valence isomers are illustrated in Figure 1. Unlike the planar ethylene, the disilene, Si$_2$H$_4$, and digermene, Ge$_2$H$_4$, have a trans-pyramidal geometry for their most stable configuration. In contrast, for Sn$_2$H$_4$ and Pb$_2$H$_4$, the most stable structure is a trans-doubly bridged isomer. However, the energy difference between the most stable arrangement and the unsymmetric isomers is small for germanium (2.4 kcal mol^{-1}) and tin (7.0 kcal mol^{-1}), whereas it is significantly greater for silicon (22.5 kcal mol^{-1}) and lead (17.8 kcal mol^{-1}). We have previously shown by studies on tin derivatives that the unsymmetric isomers, Ar^{Trip_2}SnSnMe$_2$Ar^{Trip_2} [3] and Ar^{Trip_2}-SnSnPh$_2$Ar^{Trip_2} [4] could be stabilized with the use of terphenyl ligands. In the case of germanium, a base-stabilized unsymmetric isomer, Ar^{Dipp_2}(H)$_2$GeGeAr^{Dipp_2}-(PMe$_3$), where Ar^{Dipp_2} = −C$_6$H$_3$-2,6-(C$_6$H$_2$-2,6-^{i}Pr$_2$)$_2$, could be isolated.[5] We now report the isolation and characterization of the first lead analogue of a substituted methylmethylene, an unsymmetric isomer of a diplumbene.

Results and Discussion

The reaction of the sterically encumbered terphenyl "diplumbylene" [PbAr^{Trip_2}]$_2$[6] with N$_3$SiMe$_3$ (eq 1) afforded the product **1** in low yield. It is formed by activation of two CH bonds, each from an isopropyl methyl substituent from different −C$_6$H$_3$-2,4,6-^{i}Pr$_3$ rings.



The activation of the Pr^i−CH$_3$ groups results in the incorporation of the Pb(1)−Pb(2) unit into a Pb$_2$C$_6$ eight-membered ring, which, along with steric factors, is responsible for the stability of **1**. The mechanism of this transformation is currently unknown, but it may proceed through a radical pathway leading to an ortho-metalation of the isopropyl groups on the flanking aryls. However, the addition of α,α′-azobis(isobutyronitrile), AIBN (a radical initiator), to [PbAr^{Trip_2}]$_2$ led only to the recovery of unreacted [PbAr^{Trip_2}]$_2$. Nonetheless, the activation of the ortho-alkyl groups on flanking aryl rings of the terphenyl ligands has been observed in other reactions. For example, in the reduction of bulky terphenyl boron halides, the presumed boranediyl intermediate inserted[7] into C−C or C−H σ-bonds, while the reduction of a phosphorus chloride analogue led to phosphorus[8] insertion into a C−C bond of the isopropyl group on the flanking aryl. Furthermore, it is notable

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(1) (a) Weidenbruch, M. *Organometallics* **2003**, *22*, 4340. (b) Cowley, A. H. *J. Organomet. Chem.* **2000**, 600. (c) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463.

(2) Trinquier, G. *J. Am. Chem. Soc.* **1990**, *112*, 2130; **1991**, *113*, 144.

(3) Eichler, B. E.; Power, P. P. *Inorg. Chem.* **2000**, *39*, 5444.

(4) Phillips, A. D.; Hino, S.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 7520.

(5) Richards, A. F.; Phillips, A. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 3204.

(6) Pu, L.; Twamley, B.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 3524.

(7) Grigsby, W. J.; Power P. P. *J. Am. Chem. Soc.* **1996**, *118*, 7981.

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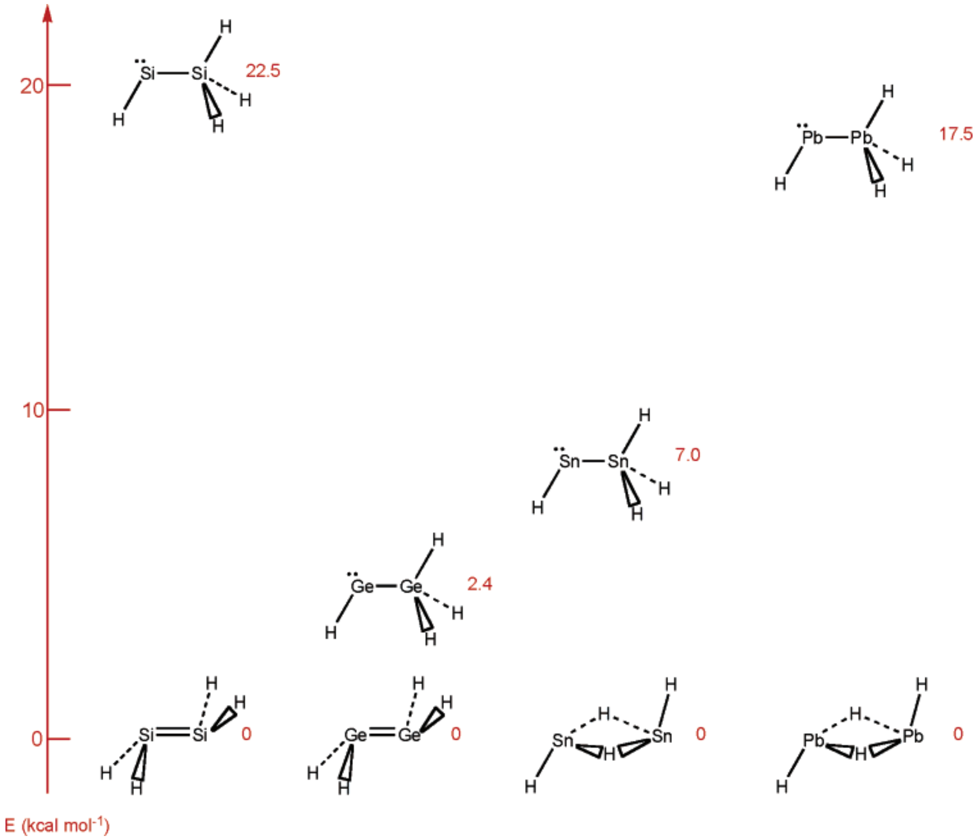

Figure 1. Comparison of energies of M_2H_4 (M = Si, Ge, Sn, Pb) isomers. Only data for the most stable isomer and the mixed valence isomer are shown. Energy is reported in kcal mol^{-1} (in red).[2]

that the reaction of related extremely crowded salts such as LiMes* or BrMgMes* (Mes* = $-C_6H_2$-2,4,6-$Bu^t{}_3$) with $PbCl_2$ led to C−H activation and the isolation of hexakis[2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl]-diplumbane[9] and $Pb(CH_2CMe_2C_6H_3$-3,5-$Bu^t{}_2)Mes^*$.[10]

Green crystals of **1**·C_6H_6 were grown from benzene, and the molecular structure (Figure 2) was determined by X-ray crystallography.[11] It consists of noninteracting molecules of **1**, whose most prominent structural feature is the Pb(1)−Pb(2) bond, which links two-coordinate Pb(1) and four-coordinate Pb(2) lead centers that have the formal oxidation states of +1 and +3, respectively. The Pb(1)−Pb(2) bond length is 2.9928(3) Å, and the interligand angle at the divalent Pb(1) is 97.99(6)°. The Pb(2) atom is bound to the ipso carbon (C37) of the terphenyl ligand, to a methylene carbon (C(65)) from its terphenyl substituent, and to a methylene carbon (C(29)) from the terphenyl ligand bound to Pb(1).

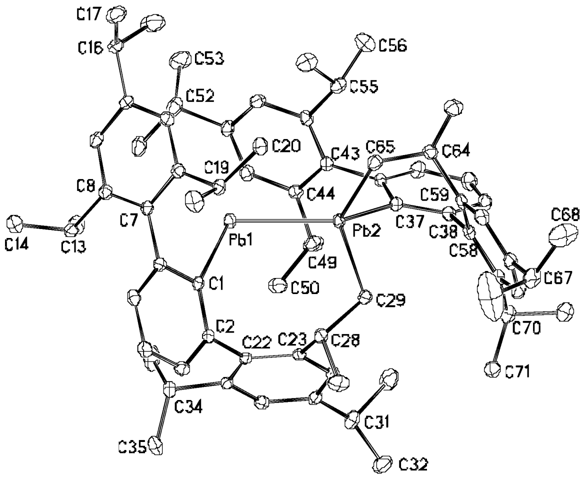

Figure 2. Thermal ellipsoidal (30%) plot of **1**. H atoms were omitted for clarity. Selected bond distance (Å) and angles (deg): Pb(1)−Pb(2) = 2.9928(3), C(1)−Pb(1) = 2.314(3), C(29)−Pb(2) =2.261(2), C(37)−Pb(2) = 2.269(3), C(65)−Pb(2) = 2.289(3), C(1)−Pb(1)−Pb(2) = 97.99(6), C(37)−Pb(2)−Pb(1) = 112.59(6), C(37)−Pb(2)−C(29) = 104.11(9), C(29)−Pb(2)−C(65) = 103.39(9), C(37)−Pb(2)−C(65) = 93.16(10).

The Pb−Pb bond distance (2.9928(3) Å) lies between the Pb−Pb bond distance in the diplumbylene, Ar^{Trip_2}-$PbPbAr^{Trip_2}$ (Pb−Pb = 3.1881(1) Å),[6] and the bond distances found in the diplumbanes (2.84−2.97 Å)[12] and is close to the ca. 2.98 Å recently reported for $[Pb(PbPh_3)_3]^-$.[13] The Pb−Pb bond in the diplumbylene is believed to be particularly long because it is composed of overlapped 6p orbitals, which have larger radii than

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(8) Twamley, B.; Sofield, C. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1999**, *121*, 3357.

(9) Shibata, K.; Tokitoh, N.; Okazaki, R. *Tetrahedron Lett.* **1993**, *34*, 1499.

(10) Stürmann, M.; Weidenbruch, M.; Klinkhammer, K. W.; Lissner, F.; Marsmann, H. *Organometallics* **1998**, *17*, 4425.

(11) Crystal data for **1** at 90 K with Mo Kα (λ = 0.71073 Å) radiation: **1**, triclinic, space group $P\bar{1}$, a = 12.2208(13) Å, b = 13.6627(14) Å, c = 22.913(2) Å, α = 75.798(2)°, β = 84.570(2)°, γ = 64.935(2)°, V = 3359.4(6) Å^3, Z = 2, R1 for 13 113 ($I > 2\sigma(I)$) data = 0.0220.

(12) (a) Mallela, S. P.; Geanangel, R. A. *Inorg. Chem.* **1994**, *33*, 6357. (b) Whittaker, S. M.; Cervantes-Lee, F.; Pannell, K. H. *Inorg. Chem.* **1994**, *33*, 6406. (c) Mallela, S. P.; Myrczek, J.; Bernal, I.; Geanangel, R. A. *J. Chem. Soc., Dalton Trans.* **1993**, *19*, 2891. (d) Okazaki, R.; Shibata, K.; Tokitoh, N. *Tetrahedron Lett.* **1991**, *32*, 6601. (e) Kleiner, N.; Draeger, M. *J. Organomet. Chem.* **1985**, *293*, 323.

(13) Stabenow, F.; Saak, W.; Weidenbruch, M., *Chem. Commun.*, **2003**, 2342.

the 6s orbitals. In Trinquier's calculated structure of the unsymmetric, C_s symmetry $\mathrm{HPb{-}PbH_3}$ species the Pb−Pb bond length is 2.96 Å.[2] The slightly longer (ca. 0.03 Å) bond distance in **1** can be attributed to the large size of the terphenyl substituents. The C(1)−Pb(1)−Pb(2) bond angle of 97.99(6)° (divalent) in **1** is similar to the bond angle determined for $[\mathrm{PbAr^{Trip_2}}]_2$ (94.26(4)°).[6] The Pb(1)−C(1) bond distance (2.314(3) Å) is somewhat longer than the average Pb(2)−C distance of 2.27(1) Å. This difference can be attributed to the greater 6p orbital character in bonding to the divalent lead. The coordination of Pb(2), whose interligand angles vary from 93.16(10)° to 126.15(6)°, is grossly distorted from idealized tetrahedral geometry. This is very probably due to the large differences in the sizes of the Pb(2) substituents and the unusual incorporation of this metal center into both seven- and eight-membered rings.

The ^{1}H NMR spectrum of **1** was complex, but consistent with the determined structure with complex overlapping multiplets in the alkyl region. The UV−vis spectrum displayed absorptions at 402 and 913 nm, which resemble those of $[\mathrm{PbAr^{Trip_2}}]_2$. A ^{207}Pb NMR signal could not be observed for **1**, which may be attributed to the large anisotropy associated with the lead environment[14] and relatively poor solubility of **1** in hydrocarbons. It is also notable that no ^{207}Pb or ^{119}Sn NMR signals could be detected for $[\mathrm{PbAr^{Trip_2}}]_2$[6] or its tin counterpart.[4]

In conclusion, the reaction of the diplumbylene, $[\mathrm{PbAr^{Trip_2}}]_2$, with $\mathrm{N_3SiMe_3}$ has led to the isolation of the plumbylplumbylene, **1**. Its unique structure features bonding between divalent and tetravalent lead. Earlier calculations[2] on simple model species had suggested that the unsymmetric isomer is among the least stable for the heavier group 14 elements relative to its symmetric counterpart, and previous attempts to synthesize such isomers by rational methods similar to those used for its tin analogue were unsuccessful.[15,16] Only monomeric diorganolead(II) species could be obtained from these reactions. However, the unanticipated activation of ligand substituents to produce **1** has permitted isolation of a divalent−tetravalent lead−lead bonded species in which stability has been induced by the incorporation of the two lead atoms into a ring that stabilizes the divalent−tetravalent metal−metal bond.

Experimental Section

General Considerations. All manipulations were carried out by using modified Schlenk techniques under an argon atmosphere or in a Vacuum Atmospheres HE-43 drybox. All solvents were distilled from Na/K alloy and degassed twice before use. $[\mathrm{Ar^*Pb}]_2$ was prepared according to a literature procedure.[6] Trimethylsilyl azide was purchased commercially and used as received. ^{1}H and ^{13}C NMR data were recorded on a Varian 300 MHz instrument and referenced to the deuterated solvent.

Synthesis of 1. The compound $[\mathrm{Ar^*Pb}]_2$ (0.746 g, 0.541 mmol) was dissolved in toluene (25 mL) and cooled to ca. −78 °C with constant stirring. Upon cooling, 0.60 mL (4.48 mmol) of $\mathrm{Me_3SiN_3}$ was added via syringe. The reaction was allowed to warm to room temperature and stirred overnight to afford a dark green solution with some black precipitate. The precipitate was allowed to settle, and the supernatant liquid was decanted. The toluene was removed, and the residue was redissolved in benzene. The volume of the dark green filtrate was reduced to 2 mL to incipient crystallization and stored in a ca. 5 °C refrigeration for 5 days to give product $\mathbf{1}\cdot\mathrm{C_6H_6}$ as green crystals (0.0224 g, 3%); mp 174−176 °C. Anal. Calcd for $\mathrm{C_{72}H_{96}Pb}$: C, 62.85; H, 7.03. Found: C, 63.14; H, 7.26. ^{1}H NMR ($\mathrm{C_6D_6}$, 300 K): δ 1.04 (d, $J_{\mathrm{HH}} = 6.9$ Hz, o-$\mathrm{CH(CH_3)_2}$); 1.16 (mult, o-$\mathrm{CH(CH_2)(CH_3)}$; 1.26 (mult, o-$\mathrm{CH(CH_2)(CH_3)}$); 1.32 (d, $J_{\mathrm{HH}} = 6.9$ Hz, p-$\mathrm{CH(CH_3)_2}$; 2.82 (mult, o-$\mathrm{CH(CH_2)(CH_3)}$); 2.86 (mult, p-$\mathrm{CH(CH_3)_2}$); 2.87 (sept, $J_{\mathrm{HH}} = 6.9$ Hz, o-$\mathrm{CH(CH_3)_2}$); 2.93 (mult, o-$\mathrm{CH(CH_3)_2}$); 3.04 (sept, $J_{\mathrm{HH}} = 6.9$ Hz, o-$\mathrm{CH(CH_3)_2}$); 7.11 (t, $J_{\mathrm{HH}} = 7.5$ Hz, p-$\mathrm{C_6H_3}$); 7.16 (s, m-Trip); 7.17 (s, m-Trip); 7.18 (s, m-Trip); 7.80 (d, $J_{\mathrm{HH}} = 7.5$ Hz, m-$\mathrm{C_6H_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 300 K): δ 1.37 ($\mathrm{CH(}\mathit{C}\mathrm{H_2)(CH_3)}$)); 23.37 ($\mathrm{CH(}\mathit{C}\mathrm{H_2)(CH_3)}$)); 24.47 ($\mathit{C}\mathrm{H(CH_2)(CH_3)}$)); 24.55 (o-$\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$); 26.19 (o-$\mathit{C}\mathrm{H(CH_3)_2}$); 30.82 (p-$\mathit{C}\mathrm{H(CH_3)_2}$); 120.72 (m-Trip); 121.49 (m-Trip); 126.11 (m−$\mathrm{C_6H_3}$); 131.95 (p-$\mathrm{C_6H_3}$); 135.38 (i-Trip); 136.97 (i-Trip); 146.82 (p-Trip); 147.38 (p-Trip); 148.01 (o-Trip); 148.38 (o-Trip); 148.75 (o-$\mathrm{C_6H_3}$); 177.58 (i-$\mathrm{C_6H_3}$)/ UV−vis (hexane) nm (ϵ mol $\mathrm{L^{-1}}$ cm): 402 (3400), 713 (350).

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Supporting Information Available: Crystallographic data for **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] Eichler, B. E.; Phillips, B. L.; Power, P. P.; Augustine, M. P. *Inorg. Chem.* **2000**, *39*, 5450.

[15] Pu, L.; Twamley, B.; Power, P. P. *Organometallics* **2000**, *19*, 2874.

[16] Hino, S.; Olmstead, M. M.; Phillips, A. D.; Wright, R. J.; Power, P. P. *Inorg. Chem.* **2004**, *43*, 7346.