

A Convenient Synthesis of 1,1,1,3,3,3-Hexaphenyldiplumbathiane and 1,1,1,3,3,3-Hexaphenyldiplumbaselenane

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Introduction

Hexaphenyldiplumbathiane has been synthesized by several methods which include mixing Ph_3PbCl and aqueous sodium sulfide in ethanol,¹ stirring $(\text{Ph}_3\text{Pb})_2$ with sulfur powder for several days,² and treating Ph_3PbCl with Ph_3PbSLi in tetrahydrofuran.³ Only one procedure has been reported for the synthesis of hexaphenyldiplumbaselenane, and it requires Ph_3PbCl and $\text{Ph}_3\text{-PbSeLi}$.³ Recently we reported new methods for making anhydrous sodium sulfide⁴ and sodium selenide⁵ and are now investigating their utility in the synthesis of group 14–group 16 organometallic compounds, which may be useful as precursors to group 14–group 16 binary semiconductor materials.^{6,7} We report here the usefulness of these reagents in the synthesis of $(\text{Ph}_3\text{Pb})_2\text{S}$ and $(\text{Ph}_3\text{Pb})_2\text{Se}$ by treating them with Ph_3PbCl or Ph_2PbCl_2 .

Experimental Section

Materials and General Procedures. Sodium sulfide and sodium selenide were prepared by combining sodium chips (prepared by cutting pellets) and sulfur or selenium powder. Tetraphenyllead⁸ and triphenyllead chloride⁹ were prepared by literature methods. Diphenyllead dichloride was obtained commercially (Alfa) and used without further purification or synthesized from tetraphenyllead.⁸ Tetrahydrofuran (THF) and diethyl ether were distilled from sodium/benzophenone ketyl just prior to use. Hexane was stirred over H_2SO_4 and distilled. Benzene was shaken with H_2SO_4 , dried by azeotropic removal of water, and distilled into a storage bottle containing 4-Å molecular sieves. All experiments were performed under a dry nitrogen atmosphere, and air-sensitive compounds were transferred in an argon-filled glovebox. The ^1H (270.17 MHz), ^{13}C (67.94 MHz), and ^{207}Pb (56.53 MHz) NMR spectra were obtained on a JEOL GSX270 spectrometer. ^{207}Pb NMR spectra were referenced relative to Me_4Pb (0 ppm). ^{77}Se (76.25 MHz) NMR spectra were obtained on a JEOL GSX400 spectrometer equipped with a variable-temperature accessory to control the temperature at 25 ± 0.5 °C with chemical shifts reported relative to Me_2Se (0 ppm). X-ray powder diffraction (XRD) patterns were recorded from ethanol slurry mounted samples on glass slides using a Philips automated diffractometer with $\text{Cu K}\alpha$ radiation and data reduction software from MDI, Inc. The diffractometer was calibrated with an NIST SRM 6406 silicon standard. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Mass spectra were obtained on a Hewlett-Packard 5988A mass spectrometer at 70 eV. Melting points were taken on a Thomas Hoover capillary melting point apparatus and are uncorrected.

Synthesis of Hexaphenyldiplumbathiane. A 50-mL three-necked round-bottomed flask fitted with a condenser/ N_2 inlet and two rubber septa was

charged with sodium chips (280 mg, 12 mmol), sulfur powder (193 mg, 6.0 mmol), naphthalene (150 mg, 1.2 mmol), and 20 mL of THF. A light gray suspension of Na_2S resulted after 10 h at reflux. Ph_2PbCl_2 (2.6 g, 6.0 mmol) was carefully added to the flask in 0.5-g portions over a 30-min period at room temperature. A black precipitate formed after a few minutes and remained constant after stirring at room temperature for an additional 14 h. At this point, air-sensitive manipulations were not required. The mixture was poured into 25 mL of water and gravity-filtered to remove the black precipitate (0.96 g), which was extracted with two 50-mL portions of ether. X-ray diffraction analysis of the black solid revealed only poorly crystalline PbS . Combustion analysis showed 12.23% carbon and 0.79% hydrogen. The ether layers were combined, and ether was removed by vacuum, leaving a light yellow solid. The solid was placed on a vacuum line for 30 min and recrystallized from benzene/hexane, giving 1.1 g of white, crystalline $(\text{Ph}_3\text{Pb})_2\text{S}$ (61% yield), mp 136–137 °C (lit.¹⁰ mp 139–140 °C). ^{207}Pb NMR (CDCl_3): δ 5.25. Anal. Calcd for $\text{C}_{36}\text{H}_{30}\text{Pb}_2\text{S}$: C, 47.56; H, 3.33. Found: C, 47.67, H, 3.46.

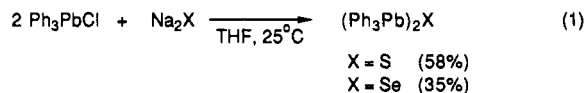
When a THF solution of Ph_3PbCl (3.4 g, 7.2 mmol) was added to a suspension of Na_2S (3.6 mmol) in 10 mL of THF using a similar procedure as described above, 1.92 g (58% yield) of $(\text{Ph}_3\text{Pb})_2\text{S}$ was isolated.

Synthesis of Hexaphenyldiplumbaselenane. A 50-mL reaction flask equipped with a condenser/ N_2 inlet and rubber septa was charged with sodium chips (372 mg, 16.2 mmol), selenium powder (640 mg, 8.1 mmol), naphthalene (200 mg, 1.6 mmol), and 20 mL of THF. To ensure complete consumption of sodium, the mixture was refluxed for 10 h, giving a white suspension of Na_2Se . (If a purple color persists at this point, small amounts of sodium can be added until the white end point is attained. For a green mixture, adding Se powder will eventually give the white suspension.) Ph_2PbCl_2 (3.5 g, 8.1 mmol) was added through a flask neck in 0.5-g quantities over a 30-min period, and the resulting black mixture was stirred at room temperature for 24 h. (At this point, the workup can be accomplished with the aqueous method described above or the following procedure.) THF was removed by vacuum, 40 mL of benzene was added, and the mixture was filtered until a clear yellow solution was obtained. Benzene was removed by vacuum, and the resulting yellow oil was rinsed with 5 mL of hexane, leaving a yellow solid, which was recrystallized from benzene/hexane to give 1.2 g (46% yield) of light yellow, crystalline $(\text{Ph}_3\text{Pb})_2\text{Se}$, mp 136–138 °C. ^{13}C NMR (CDCl_3): δ 128.7, 129.5, 137.7, 152.9 (Ph). ^{207}Pb NMR (CDCl_3): δ -112. ^{77}Se NMR (CDCl_3): δ -454 ($J_{\text{Pb-Se}} = 780$ Hz). MS (EI): m/e 439 (Ph_3Pb^+ , 40%), 208 (Pb^+ , 100%). Anal. Calcd for $\text{C}_{36}\text{H}_{30}\text{Pb}_2\text{Se}$: C, 45.23; H, 3.16. Found: C, 45.65; H, 3.35.

A THF solution of Ph_3PbCl (2.3 g, 4.8 mmol) added to Na_2Se (2.4 mmol) in 10 mL of THF produced 0.80 g (35% yield) of $(\text{Ph}_3\text{Pb})_2\text{Se}$.

Results and Discussion

When sodium, sulfur or selenium, and a catalytic amount of naphthalene are refluxed in THF, anhydrous Na_2S or Na_2Se can be generated.^{4,5} Reacting these suspensions with 2 equiv of $\text{Ph}_3\text{-PbCl}$ produced $(\text{Ph}_3\text{Pb})_2\text{S}$ or $(\text{Ph}_3\text{Pb})_2\text{Se}$ in 58% or 35% yield, respectively (eq 1). These reactions were accompanied by trace



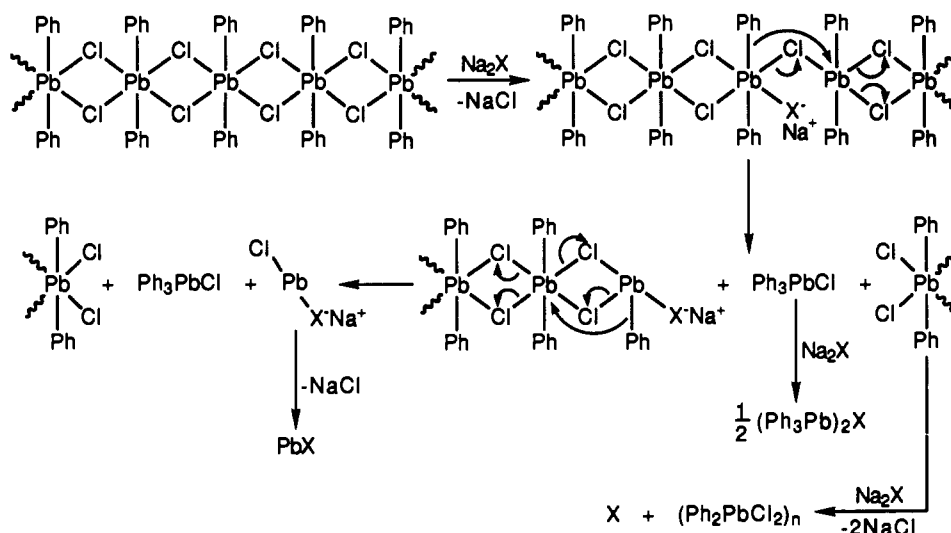
amounts of a black precipitate, presumably containing PbS or PbSe . This is an improved procedure compared to mixing $\text{Ph}_3\text{-PbCl}$ in aqueous Na_2S (25% yield)¹ or treating hexaphenyldiplumbane with sulfur powder (10 days, 59% yield)² and gives yields comparable to those obtained by treating Ph_3PbCl with Ph_3PbSLi or Ph_3PbSeLi (58% yield of $(\text{Ph}_3\text{Pb})_2\text{S}$; 40% yield of $(\text{Ph}_3\text{Pb})_2\text{Se}$).³ $(\text{Ph}_3\text{Pb})_2\text{S}$ displays a ^{207}Pb NMR signal at 5.25 ppm relative to Me_4Pb (0 ppm), while $(\text{Ph}_3\text{Pb})_2\text{Se}$ has a ^{207}Pb NMR resonance at -112 ppm and a ^{77}Se NMR signal 454 ppm upfield of Me_2Se with distinctive ^{207}Pb satellites at 780 Hz. Both compounds are stable toward air and moisture and are readily recrystallized from benzene/hexane solvent.

Previous results in our group have shown that the reaction of our anhydrous sodium chalcogenide with Ph_2SiCl_2 or Ph_2SnCl_2

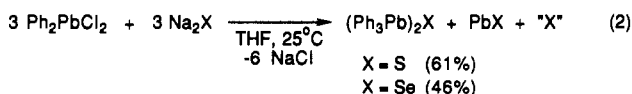
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Scheme I



leads to good yields of six-membered-ring compounds having the formula $(\text{Ph}_2\text{EX})_3$ ($\text{E} = \text{Si}, \text{Sn}; \text{X} = \text{S}, \text{Se}$).^{5,6b} Employing $\text{Ph}_2\text{-PbCl}_2$ in the same way gave surprisingly different results. Treatment of Na_2S or Na_2Se with 1 equivalent of Ph_2PbCl_2 gave $(\text{Ph}_3\text{Pb})_2\text{S}$ or $(\text{Ph}_3\text{Pb})_2\text{Se}$ in 61% or 46% yield, respectively (eq 2). These yields are calculated by assuming 3 equiv of Ph_2PbCl_2

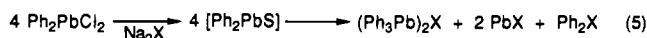


is necessary to produce 1 equiv of $(\text{Ph}_3\text{Pb})_2\text{X}$ ($\text{X} = \text{S}, \text{Se}$). A significant amount of a black solid was formed as a byproduct of the redistribution process and contained poorly crystalline PbS or PbSe , as determined by X-ray diffraction analysis. Combustion analysis of the black powder from a $\text{Ph}_2\text{PbCl}_2/\text{Na}_2\text{S}$ reaction showed a carbon content of 12.2% with 0.79% hydrogen. This C/H ratio is approximately the same as that for a phenyl group, suggesting that the PbS may also contain some type of phenylated lead-sulfur species and possibly some unreacted Ph_2PbCl_2 . The oxidized compound shown in eq 2, "X", is most likely elemental sulfur or selenium although there were no assignable peaks for these compounds in the X-ray diffraction pattern of the black solid.

The six-membered ring $(\text{Ph}_2\text{PbS})_3$ has been synthesized from diphenyllead diacetate and hydrogen sulfide.¹¹ It is stable to 90 °C and is resistant to air and moisture. This stability suggests that $(\text{Ph}_2\text{PbS})_3$ never forms and that redistribution is the dominant pathway. Similar redistribution reactions have been reported in the attempted preparation of diphenyllead bis(thiolates), $\text{Ph}_2\text{-Pb}(\text{SR})_2$. The product from the reaction of Ph_2PbCl_2 and a lead(II) thiolate was usually the triphenyllead thiolate, $\text{Ph}_3\text{Pb}(\text{SR})$, except in a few cases where $\text{Ph}_2\text{Pb}(\text{SR})_2$ was obtained through careful control of the reaction conditions.¹²

One possible reaction pathway to explain the formation of $(\text{Ph}_3\text{Pb})_2\text{X}$ is derived from the known thermal redistribution of Ph_2PbCl_2 (eq 3) followed by reductive elimination of chloroben-

zene (eq 4).¹³ Sodium chalcogenide could then react with $\text{Ph}_3\text{-PbCl}$ and PbCl_2 , producing $(\text{Ph}_3\text{Pb})_2\text{X}$ and PbX . However, chlorobenzene was not identified by GC analysis in any $\text{Ph}_2\text{-PbCl}_2/\text{Na}_2\text{X}$ reaction, suggesting that this is an unlikely explanation. Equation 5 shows $(\text{Ph}_3\text{Pb})_2\text{X}$ formation from some type of diphenyllead chalcogenide intermediate. This case is also not probable, since Ph_2X was not detected by GC analysis. There was also no evidence for evolution of chlorine gas as the oxidized product. A mechanism involving phenyl radicals is also unlikely,



since no biphenyl was identified in any $\text{Ph}_2\text{PbCl}_2/\text{Na}_2\text{X}$ reaction. Absence of these products leaves sulfur or selenium as the most likely oxidation products. However, we were unable to detect either element under our reaction conditions.

When an excess of either Ph_2PbCl_2 or Na_2S was employed, the amount of diplumbathiane formed was significantly reduced (<20% isolated yield). A 2/1 mixture of $\text{Ph}_2\text{PbCl}_2/\text{Na}_2\text{S}$ gave unreacted Ph_2PbCl_2 and a mixture of products, including PbS , $(\text{Ph}_3\text{Pb})_2\text{S}$ (<10% yield), and Ph_3PbCl , identified from its ²⁰⁷Pb NMR signal at 33.7 ppm (lit.¹⁴ δ 33). The presence of Ph_3PbCl suggests it is the predominant intermediate in the eventual formation of diplumbathiane or diplumbaselenane. A mechanism consistent with the product distribution is shown in Scheme I. Ph_2PbCl_2 appears to be insoluble in THF, so it probably retains the solid-state structure of polymeric chains with octahedral coordination at lead.¹⁵ In this mechanism, the sulfide anion causes phenyl migrations to adjacent lead centers bridged by chlorine atoms. Each Na_2S attack eventually leads to degradation of the polymeric structure and to extrusion of two molecules of $\text{Ph}_3\text{-PbCl}$ and one PbS molecule. The $\text{Pb}(\text{VI})$ species formed can react with Na_2X to yield elemental sulfur or selenium and $\text{Ph}_2\text{-PbCl}_2$.

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