The Preparation and Reactions of Some Triphenyllead Derivatives

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Introduction

By taking advantage of the reducing properties of solutions of the alkali metals in liquid ammonia and related solvents, it is possible to prepare some types of organo-metallic compounds which elude preparation in any other way. The method has had striking success in studying the organo-metallic compounds of the elements in Group 4B of the periodic table.[1] Until very recently no work on lead compounds from this viewpoint had been reported,[2] and the purpose of this investigation was to extend the earlier studies to the triphenyllead derivatives.[3]

In all of their properties the triphenyllead derivatives are found to follow the trends observed with the corresponding derivatives of the other elements in Group 4B. In passing from lead to carbon, the strength of the bond between the phenyl group and the metallic element becomes continually greater and, except for carbon, the same is true of the metal-to-metal bond in the dimeric form of the "free group." The high degree of dissociation of hexaphenylethane is decidedly abnormal, but the apparent partial dissociation of hexaphenyldilead, $(C_6H_5)_3Pb$—$Pb(C_6H_5)_3$, observed in dilute benzene solutions, is not unexpected.

The halides of triphenyllead and triphenyltin are stable in liquid ammonia, but those of the germanium and silicon derivatives are irreversibly and completely ammonolyzed. Triphenylmethyl halides undergo partial ammonolysis, but the reaction is reversible and the compounds may be used in preparations in ammonia without much side reaction.

With all of the Group 4B elements, the alkali metal salts of the triphenyl derivatives are stable in liquid ammonia at $-33.4°$. There is, however, a marked deepening of the color of their solutions in proceeding from lead to carbon. A solution of sodium triphenylplumbide, $NaPb(C_6H_5)_3$, is colorless when dilute and pale yellow

when concentrated, but a solution of potassium triphenylmethide, $KC(C_6H_5)_3$, is an intense red even when dilute. The solutions of the corresponding salts of the intervening metals are intermediate in color. In these salts the triphenylmetal anion becomes progressively more electronegative in the same order When, for example, sodium triphenylgermanide is allowed to react with an ammonium salt, the anion, $(C_6H_5)_3$-Ge^{1-}, takes on a proton and triphenylgermane is precipitated. This reaction is characteristic of the entire group with the exception of the lead analog. No hydride is formed when ammonium bromide is added to a solution of sodium triphenylplumbide in ammonia, but the solution appears to contain ammonium triphenylplumbide as a highly ionized salt. Evidently the triphenylplumbide ion, $(C_6H_5)_3Pb^{1-}$, is not basic enough to remove the proton from the ammonium ion, and the normal group reaction is not observed, even in the presence of great excess of ammonium salt.

Experimental

Preparation of Tetraphenyllead.—The method followed was that of Gilman and Robinson,[4] in which carefully dried lead dichloride is allowed to react with phenylmagnesium bromide, but with the substitution of xylene for benzene to increase the temperature of refluxing. The yields were sometimes as high as 81% (based upon the amount of lead dichloride used) but the results were not uniform.

Preparation of Triphenyllead Chloride.—Dry hydrogen chloride was passed into a solution of tetraphenyllead in chloroform, according to the method of Gilman and Robinson,[5] and the yield of 75% of the theoretical agreed with their observations.

Preparation[6] and Purification of Triphenyllead Iodide.—The preparation of triphenyllead chloride is not entirely satisfactory, so the iodide was investigated. It was found that it could be made easily and in addition the iodide proved to be a superior reagent for the syntheses undertaken. A solution of iodine in chloroform was stirred vigorously into a suspension of an equivalent quantity of tetraphenyllead in chloroform. The solvent and the iodobenzene formed in the reaction were removed by vacuum distillation at 100°. The yellow crystalline residue was extracted with methyl alcohol to separate the product from the diphenyllead diiodide also formed and from the unreacted tetraphenyllead. Crude triphenyllead iodide

(1) A review of some of this work is given by Kraus. J. Chem. Ed., **8**, 2130 (1931).

(2) Calingaert and Soroos, J. Org. Chem., **2**, 535 (1938).

(3) Many of the results reported here confirm the findings of Gilman and Bailie in a contribution which appeared after this manuscript was submitted to the Editor; THIS JOURNAL, **61**, 731 (1939).

(4) Gilman and Robinson, THIS JOURNAL, **49**, 2315 (1927).

(5) Gilman and Robinson, ibid., **51**, 3112 (1929).

(6) The preparation was carried out by H. I. Boynton as a part of a senior research problem, 1933.

was crystallized from the extract in an amount representing 97% of the theoretical yield. Even after several recrystallizations, the product still had a light yellow color, and melted over a range from 138° to 141°.[7] It was found that the colored impurity could be removed by dissolving the iodide in ether and allowing the solution to stand over metallic sodium or silver for two days. From the ether, pure white crystals of the iodide were recovered which melted sharply at 142° (uncorr.).[8]

Preparation of Hexaphenyldilead (Triphenyllead).— Krause and Reissaus[7b] (p. 894) prepared hexaphenyldilead by the reaction of phenylmagnesium bromide and lead dichloride in absolute ether, where it is an intermediate product in the formation of tetraphenyllead. Austin[9] reported that it is isolated as a by-product of the reaction between phenyllithium and lead dichloride, when the mixture is not heated to too high a temperature. It may be prepared most simply and practically quantitatively by reducing triphenyllead iodide by means of an equivalent amount of sodium in dry liquid ammonia. After the reaction is completed and the ammonia has evaporated, the residue is extracted with chloroform, filtered and concentrated by distillation until the solution is nearly saturated. Cold ethyl alcohol is added to precipitate the hexaphenyldilead. It is recrystallized in the same way, i. e., from chloroform solution by the addition of ethyl alcohol. The amount of the purified product is above 90% of the theoretical yield.

Use of Tetrasodium Nonaplumbide, Na₄Pb₉, as a Reducing Agent.—If triphenyllead chloride is used in place of the iodide in the preparation of triphenyllead, the reaction does not proceed so smoothly, evidently due to the lower solubility of the chloride in ammonia. It was found feasible, however, to carry out the reduction of the chloride by means of tetrasodium nonaplumbide, Na₄Pb₉,[10] which evidently is a much weaker reducing agent than sodium and permits the reduction to proceed without cleavage of phenyl groups from the triphenyllead radical. The equations for the reactions involved in the preparation of hexaphenyldilead by means of this reducing agent are

$$9PbCl_2 + 22Na = Na_4Pb_9 + 18NaCl$$
$$Na_4Pb_9 + 4(C_6H_5)_3PbCl = 2[(C_6H_5)_3Pb]_2 + 4NaCl + 9Pb$$
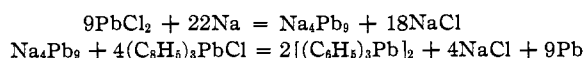
Lead dichloride is placed in a reaction tube immersed in a bath of liquid ammonia at −33.4°. When ammonia is condensed upon the lead halide, it swells tremendously, due to the formation of ammines,[11] and partly dissolves. Sodium is added in several pieces. The tetrasodium nonaplumbide formed is soluble and the solution is practically opaque. Triphenyllead chloride in powdered form is added slowly from an attached tube and hexaphenyldilead precipitates. The color of the solution disappears and a curdy mass (Pb) rapidly settles to the bottom of the tube. After the ammonia has evaporated, hexaphenyldilead is

(7) (a) Grüttner, Ber., **51**, 1301 (1918); (b) Krause and Reissaus, ibid., **55**, 897 (1922).

(8) The method was checked by M. A. Dicesaro, who obtained a yield of 87.7% of the purified product on a 10-g. run.

(9) Austin, THIS JOURNAL, **54**, 3726 (1932).

(10) Smyth, THIS JOURNAL, **39**, 1299 (1917); Kraus, ibid., **44**, 1229 (1922); Zintl, Goubeau and Dullenkopf, Z. physik. Chem., **154**, 1 (1931); Zintl and Harder, ibid., **154**, 47 (1931).

(11) Biltz and Fischer, Z. anorg. allgem. Chem., **124**, 230 (1922).

extracted from the residue and recrystallized. The yield of the purified product is above 90% of the theoretical.

Properties of Hexaphenyldilead. (a) Stability.—Krause and Reissaus[7b] report that when it is heated, hexaphenyldilead decomposes at 155° with the deposition of lead and finally melts at 225°, the melting point of tetraphenyllead. We have observed that different samples vary in their behavior. One exploded at 173°, turned black and melted at 225°. Frequently the blackening appears at 170°. If the determination is carried out very slowly in an open sample tube, no blackening is observed, due to the oxidation of the deposited lead, but melting occurs invariably at 225°. If the sample tube is evacuated, decomposition may occur from 5 to 10° below 170° but the blackening is always observed. The characteristic pyrolytic behavior may be used in confirming the identity of the material.

Hexaphenyldilead becomes yellow and infusible when kept for six months in a loosely corked, colorless bottle in the normal illumination of the laboratory, but samples have been kept for five years in the dark without change. From a solution of hexaphenyldilead in alcohol, kept for two months in the dark, the substance was recovered without change in its properties, but when it was dissolved in benzene, it underwent reaction, especially if the solution was kept warm. These observations are not entirely compatible with those of Krause and Reissaus, and may explain the anomalous molecular weight data discussed in a later section.

(b) Solubility.—Hexaphenyldilead is very soluble in carbon tetrachloride and chloroform, moderately soluble in benzene and acetone, and very slightly soluble in liquid ammonia, methyl and ethyl alcohols, ethyl ether and petroleum ether. It is insoluble in water.

(c) Molecular Weight.—Krause and Reissaus[7b] present evidence to show that hexaphenyldilead is highly dissociated into the monomeric form in dilute solutions in benzene. Three cryoscopic determinations made at different concentrations confirm their findings. At the concentrations stated below, expressed in grams of hexaphenyldilead per 1000 g. of benzene, the apparent molecular weight is seen to be less than 876, the theoretical value for the dimer: 9.53 g., 768; 18.71 g., 773; and 29.94 g., 791. While in both these results and those of Krause and Reissaus there is a steady rise in molecular weight with concentration increase, no mass action constant could be calculated for either set of data. At present it is not possible to offer any explanation for the observations.

Preparation of Sodium Triphenylplumbide.—This substance may be made in ammonia solution by reducing triphenyllead chloride or iodide or hexaphenyldilead by means of sodium or tetrasodium nonaplumbide. To prepare the pure salt, however, the reaction between sodium and hexaphenyldilead must be adopted. Due to side reactions, finely divided lead may appear as a precipitate, but if great care is exercised to prevent the concentration of sodium from becoming high at any time, not enough lead is formed to lower the yield appreciably. If the temperature is allowed to rise as the ammonia evaporates ammonolysis occurs, yielding unknown products. By removing the ammonia under reduced pressure at −33.4° or lower, the salt crystallizes from a faintly yellow saturated solution as a solid with a rather intense lemon-yellow color. The color

fades as the residual ammonia is withdrawn, and the dry, cream-colored salt formed is stable at room temperature.

Preparation of Triphenylethyllead.—Since the properties of triphenylethyllead had been established previously,[12] its preparation was undertaken to demonstrate the existence of the triphenylplumbide ion in the ammonia solution of the sodium salt. An excess of ethyl bromide was admitted to the reaction vessel and white crystals of triphenylethyllead were precipitated. A pure product was obtained by dissolving the crude material in a small quantity of ethyl ether, adding about twice the quantity of methyl alcohol and evaporating the solution *in vacuo* at room temperature. The material precipitated in white curds, which when dried *in vacuo* formed a fine white powder. The melting point was 39° and molecular weight determinations and analyses for lead identified it as triphenylethyllead. It is very soluble in ether, acetone, carbon tetrachloride and petroleum ether, less soluble in methyl alcohol and only very slightly soluble in ammonia.

Ammonium Triphenylplumbide.—When an ammonium salt,[13] in equivalent amount, is added to a liquid ammonia solution of sodium triphenylplumbide, no reaction is observed. If a small excess is added, no change in appearance of the solution is apparent, but in the presence of great excess, complete destruction of the triphenylplumbide radical results, accompanied by the separation of metallic lead in large, heavy, black curds and the production of benzene.

When the solution containing sodium and ammonium triphenylplumbides is evaporated at low temperatures under reduced pressure, crystals do not appear until it has become very concentrated and no indication of reaction between the ammonium ion and the triphenylplumbide ion is detectable. If ethyl bromide is added to the

dilute solution, a white precipitate of triphenylethyllead separates, indicating that the triphenylplumbide ion remains unchanged. Ammonium triphenylplumbide appears to be stable and very soluble in liquid ammonia at −33.4°.

Reaction of Sodium Triphenylplumbide with Methylene Chloride.—Sodium triphenylplumbide, freed of ammonia at −33.4°, was allowed to react with an excess of dry methylene chloride. The salt dissolved at first to form a yellow solution, but the color gradually faded, due presumably to reaction. A soft, waxy solid of indefinite melting point and soluble in petroleum ether was isolated from the product. A single molecular weight determination gave a value of 640, suggesting that the product might contain two triphenyllead radicals, comparable to the product of the reaction of sodium triphenylgermanide with methylene chloride.[14] No similar product was detected, however, when the reaction was carried out in liquid ammonia solution. Since no pure, well characterized product could be obtained, this reaction was not investigated further.

Summary

1. Methods for the preparation of tetraphenyllead, triphenyllead iodide, hexaphenyldilead, sodium triphenylplumbide and triphenylethyllead are described and some of the reactions and properties of these compounds are recorded.

2. Use is made of tetrasodium nonaplumbide, Na_4Pb_9, as a mild reducing agent in liquid ammonia solutions.

3. The existence of ammonium triphenylplumbide as a fairly stable and soluble salt in liquid ammonia has been indicated, but triphenylplumbane does not appear to be formed.

(12) Krause and Schmitz, *Ber.*, **52**, 2150 (1919); Krause and Schlöttig, *ibid.*, **58**, 430 (1925).

(13) Compressed tablets (5 grain) of ammonium bromide, supplied by Burroughs, Wellcome and Co., New York, serve as a very satisfactory source of ammonium ions.

(14) Kraus and Nutting, THIS JOURNAL, **54**, 1622 (1932).

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Ammino Compounds of Triphenyllead Chloride

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When ammonia is condensed upon crystalline triphenyllead chloride at the boiling point of liquid ammonia, the volume of the solid increases greatly, indicating that a reaction occurs. It has been shown that a series of ammino compounds exists, none of which is stable at room temperature. Two methods have been employed in an attempt to establish the composition of the solid phases: in the first, method I, which was entirely volumetric, the amount of ammonia which was added or withdrawn from the reaction chamber was measured by means of a gas buret; and in the second, method II, the gas buret was used to

make small, definite adjustments in the amount of ammonia in the system, but the composition of the phase under investigation was determined by decomposing it and absorbing and weighing the ammonia evolved. Method I was found to be useful for a preliminary exploration of the system, but since the errors in the volume measurements were cumulative, it did not prove to be entirely satisfactory. Method II was used in determining the composition of the highest ammino compound only, and had the advantage that it was much more rapid.

Using the volumetric method (I), two runs