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SHORT COMMUNICATION

Some pentafluorophenyl derivatives of lead

The chemistry of tetrakis(pentafluorophenyl) derivatives of the Group IV elements has recently been studied by a number of workers, *i.e.*, $(C_6F_5)_4M$ where M = Si[1,6], Ge[2,6,7,8], Sn[3,4,6,8,9], and Pb[5,6,7]. We have now examined the preparation of tetrakis(pentafluorophenyl)lead, improved the yields of this product, and prepared some other (pentafluorophenyl)lead derivatives.

In general tetraryllead compounds can be prepared by the reaction of either aryl Grignard reagents or aryllithium compounds with lead chloride. However several workers[5,6] have reported that tetrakis(pentafluorophenyl)lead is produced in poor yields (0–5%) by these methods, an observation confirmed by our results.

We have now found that addition of the stoichiometric amount of bromine required by the following equations results in yields of tetrakis(pentafluorophenyl)-lead of the order of 50% via either the Grignard or lithium derivative.

$$4\,C_6F_5MgBr + PbCl_2 + Br_2 \rightarrow (C_6F_5)_4Pb + 2\,MgBr_2 + 2\,MgBrCl$$

$$4\,C_6F_5Li + PbCl_2 + Br_2 \rightarrow (C_6F_5)_4Pb + 2\,LiBr + 2\,LiCl$$

The role of bromine in these reactions is not clear. It may facilitate the conversion of divalent lead into tetracovalent lead, a conversion which takes place spontaneously in the case of non-fluorinated derivatives, sometimes with concomitant formation of elemental lead. This view is supported by the facile synthesis of bis-(pentafluorophenyl)diphenyllead from pentafluorophenylmagnesium bromide and diphenyllead dichloride. On the other hand isolation of benzyltris(pentafluorophenyl)-lead from the reaction of pentafluorophenylmagnesium bromide, lead chloride, and benzyl chloride indicates that the presence of bromine is not essential.

$$3\,C_6F_5MgBr + PbCl_2 + C_6H_5CH_2Cl \rightarrow (C_6F_5)_3PbCH_2C_6H_5 + 3\,MgBrCl$$

The latter reaction may involve formation of an intermediate analogous to the triphenylleadmagnesium bromide described by Willemsens and Van der Kerk[10].

Experimental

All preparations were carried out under anhydrous argon using carefully dried reagents and solvents. Pentafluorobenzene and pentafluorobromobenzene from the Imperial Smelting Company, Avonmouth, England showed only one peak on GLC analysis. n-Butyllithium in hexane and methyllithium in diethyl ether were purchased from the Foote Mineral Company, Exton, Pennsylvania. Purification of the derivatives was controlled by thin-layer chromatography (TLC) on microscope slides and the spots were developed with iodine vapor. Melting points, uncorrected, were obtained with a Reichert–Kofler hot stage microscope, and infrared spectra were obtained with a Beckman Model IR-12 Spectrophotometer.

Preparation of tetrakis(pentafluorophenyl)lead from the Grignard reagent. Pentafluorophenylmagnesium bromide was prepared in diethyl ether (40 ml) from the reaction between magnesium (1.22 g, 0.05 g-atom) and pentafluorobromobenzene (12.3 g, 0.05 mole). The mixture was cooled to 0° and a suspension of lead chloride (6.95 g, 0.025 mole) in benzene (40 ml) was added with vigorous stirring. No metallic lead was apparent. After an hour, bromine (2.0 g, 0.0125 mole) in methylene chloride (15 ml) was run in slowly and the mixture was allowed to come to room temperature. The solvent was removed carefully under reduced pressure and the almost dry residue was extracted several times with boiling hexane. Tetrakis(pentafluorophenyl)-lead (5.6 g, 54%) was isolated from the hexane solution and recrystallized to m.p. 204° from hexane (lit.[7] m.p. 199–200°). (Found: C, 32.86; Pb, 23.60. $C_{24}F_{20}Pb$ calcd.: C, 32.94; Pb, 23.67%.)

In agreement with the reports of Fenton and Massey[5] and Tamborski *et al.*[6], we were able to isolate only a small quantity of tetrakis(pentafluorophenyl)lead (5%) from the reaction of pentafluorophenylmagnesium bromide with lead dichloride in ether/benzene, ether/toluene, or tetrahydrofuran. The main product is a white material insoluble in water or organic solvents.

Reaction of lead chloride with pentafluorophenyllithium. Pentafluorobenzene (16.8 g, 0.1 mole) in ether (20 ml) was added slowly with vigorous stirring to n-butyllithium (0.1 mole) in hexane (80 ml) at −78°. The mixture was allowed to warm gradually (1–2 h) to −20°. Dry, finely ground, lead chloride (13.9, 0.05 mole) was added and the temperature was maintained at −20° for a further 1.5 h. No lead was deposited even when the reaction was stirred overnight at room temperature, or boiled under reflux. Bromine (4 g, 0.05 g-atom) in methylene chloride (15 ml) was added and the reaction mixture stirred for 2 h at room temperature. Hydrolysis with dilute hydrochloric acid, and filtration and evaporation of the organic layer gave a residue which was completely soluble in hexane. Tetrakis(pentafluorophenyl)lead 12 g, (49%) was the only product isolated, although trace amounts of a compound having the same R_f as tris(pentafluorophenyl)lead bromide* were detected by TLC. The reaction of lead chloride and pentafluorophenyllithium[6] in ether did not produce tetrakis(pentafluorophenyl)lead. No lead was deposited and hydrolysis gave a copious white precipitate, insoluble in water and organic solvents. Tetraphenyllead has been prepared in good yield from the reaction of lead dichloride with iodobenzene and phenyllithium[11], but the analogous reaction with pentafluoroiodobenzene did not give the desired products.

$$3\ C_6F_5Li + C_6F_5I + PbCl_2 \rightarrow (C_6F_5)_4Pb + 2\ LiCl + LiI$$

Again no lead was formed, and hydrolysis gave a white precipitate which suggested the presence of $(C_6F_5)_3PbLi$. A similar lithium complex was proposed by Glockling[12] in the preparation of the phenyl compound.

Preparation of benzyltris(pentafluorophenyl)lead. Lead chloride (3.47 g, 0.012 mole) was added to a Grignard reagent prepared from pentafluorobromobenzene (6.2 g) and magnesium (0.6 g) in ether at 0°. The mixture was allowed to come to room temperature and refluxed for an hour. Benzyl chloride (1.52 g, 0.012 mole) in benzene (75 ml) was added and the reaction was stirred overnight. Benzene (75 ml) was added

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* Authentic $(C_6F_5)_3PbBr$ obtained from E. W. Randall, Queen Mary College, London, England.

and the insoluble material was removed by filtration. The remaining solution was evaporated almost to dryness and the brown residue was extracted with hot hexane from which 4.0 g (43%) of pale yellow crystals of benzyltris(pentafluorophenyl)lead were obtained, m.p. 108°. This material decomposed slowly in the atmosphere. (Found: C, 38.39; H, 8.66; Pb, 25.59. $C_{25}F_{15}H_7Pb$ calcd.: C, 38.38; H, 8.93; Pb, 25.76%.)

Preparation of diphenylbis(pentafluorophenyl)lead. The Grignard reagent was prepared in the usual manner by treating pentafluorobromobenzene (6.2 g, 0.025 mole) with magnesium (0.6 g) at 0° in ether. Diphenyllead dichloride (5.33 g, 0.025 mole) was added and the mixture was stirred for 8 h and then refluxed for 1 h. Benzene was added to the ether solution and the ether was removed under vacuum. The mixture was filtered and the filtrate was evaporated. The residual brown solid was dissolved in hot alcohol, the brown color was removed by addition of charcoal, filtered and allowed to cool. White crystals precipitated out of solution. Recrystallization from a benzene/hexane solution gave 5.1 g of crystals with, m.p. 91°. (Found: C, 41.77; H, 1,41; Pb, 30.12. $C_{24}F_{10}H_{10}Pb$ calcd.: C, 41.45; H, 1.45; Pb, 29.78%.)

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