The spectrum to be expected from the methylene protons of a molecule containing the atom sequence $XCH_2PbPbCH_2X$ in which $J(CH_2Pb^{207})$ and $J(CH_2PbPb^{207})$ are 19.6 and 12.1 cps, respectively, has been determined graphically and shown to correspond to the methylene portion of the observed spectrum of hexaneopentyldilead. The 21.11% natural abundance of Pb^{207} would result in a fractional distribution of 0.662 for $XCH_2PbPbCH_2X$, 0.344 for $XCH_2PbPb^{207}CH_2X$, and 0.044 for $XCH_2Pb^{207}Pb^{207}CH_2X$, from which it is possible to calculate the relative peak heights. The experimental and calculated spectra are shown in Figure 1.

Experimental Section

All melting points are uncorrected. Analyses were by A. Bernhardt, Microanalytical Laboratories, Mülheim/Ruhr, Germany.

Hexaneopentyldilead.—A Grignard solution prepared from 26.4 g (0.25 mole) of neopentyl chloride and 6.0 g (0.25 g-atom) of magnesium in 100 ml of ether was treated slowly below −10° with 27.8 g (0.1 mole) of lead chloride. When the addition was complete, the mixture was stirred at −10° for 0.5 hr, then warmed to room temperature and decomposed by pouring onto ice. The organic layer was separated and the aqueous layer was extracted twice with 50-ml portions of benzene. The combined organic layers were dried over magnesium sulfate and filtered, and the solvent was removed under reduced pressure to yield 10.5 g of crude product. Crystallization of the crude material from petroleum ether (bp 60–90°) yielded a pale yellow crystalline solid which melted with decomposition at 205–206°.

Anal. Calcd for $C_{30}H_{66}Pb_2$: C, 42.83; H, 7.91. Found: C, 43.11; H, 7.88.

Grignard Reactions of Trineopentyllead Iodide.—A solution of 4.2 g (0.005 mole) of hexaneopentyldilead in 50 ml of benzene was treated with 1.27 g (0.005 mole) of iodine. The resulting trineopentyllead iodide solution was added dropwise to a Grignard solution prepared from 5.3 g (0.05 mole) of neopentyl chloride and 1.22 g (0.05 g-atom) of magnesium in 50 ml of ether. The reaction mixture was heated under reflux for 1 hr and decomposed by pouring onto an ice–dilute hydrochloric acid solution mixture. The organic layer was separated and dried over magensium sulfate, and the solvent was removed under reduced pressure. The residue was crystallized from petroleum ether to yield 2.5 g of hexaneopentyldilead, mp 205°.

In a similar reaction using 2.5 g (0.003 mole) of hexaneopentyldilead, 0.76 g (0.003 mole) of iodine, 7.9 g (0.05 mole) of bromobenzene, and 1.22 g (0.05 g-atom) of magnesium, only a small amount of the hexaneopentyldilead could be isolated from the reaction mixture.

Hexaneophyldilead.—A Grignard reagent was prepared from 33.7 g (0.2 mole) of neophyl chloride and 4.86 g (0.2 g-atom) of magnesium in 50 ml of ether and treated with 27.8 g (0.1 mole) of lead chloride below −10°. After working up the reaction mixture as previously described, 6.8 g (17%) of hexaneophyldilead, mp 132–133°, was obtained.

Anal. Calcd for $C_{60}H_{78}Pb_2$: C, 59.36; H, 6.48. Found: C, 59.32; H, 6.50.

Thermal Decomposition of Hexaneophyldilead.—A soultion of 6.06 g (0.005 mole) of hexaneophyldilead in 50 ml of xylene was heated under reflux for 5 hr. The solution was filtered hot to remove the precipitated lead; the filtrate was stripped. The residue was crystallized from petroleum ether and yielded only 3.6 g of unreacted hexaneophyldilead.

Tetraneophyllead.—A Grignard solution prepared from 8.4 g (0.05 mole) of neophyl chloride and 1.2 g (0.05 g-atom) of magnesium in 50 ml of ether was treated with a solution of trineophyllead iodide prepared from 3.6 g (0.003 mole) of hexaneophyldilead and 0.76 g (0.003 mole) of iodine in benzene. After working up the reaction mixture in the usual manner, the residue remaining from removal of the solvent was crystallized from petroleum ether and yielded 3.0 g (68%) of tetraneophyllead, mp 88–89°.

Anal. Calcd for $C_{40}H_{52}Pb$: C, 64.92; H, 7.08. Found: C, 65.03; H, 7.14.

Acknowledgment.—The authors wish to acknowledge stimulating discussions with Dr. F. Kaplan.

Preparation and Proton Magnetic Resonance of Some Neopentyl Derivatives of Lead. Long-Range Pb^{207}–H^1 Coupling

GURDIAL SINGH

Carothers Research Laboratory, Textile Fibers Department,
Experimental Station, E. I. du Pont de Nemours and Company,
Wilmington, Delaware 19898

Received October 18, 1965

Several studies on spin–spin coupling of protons with hetero nuclei such as fluorine[1] and phosphorus[2] over more than three consecutive single bonds have been reported. However, nothing seems to be known about the long-range interaction of protons with other heavier isotopes of spin $^1/_2$. Lead, a typical example of a heavy element, has 21.11% natural abundance of its isotope Pb^{207} of $^1/_2$ spin. With an objective to study coupling interaction between lead and γ-protons, we have prepared some model neopentyl derivatives of lead. An examination of their proton magnetic resonance has revealed that the protons couple rather strongly with lead over four σ bonds (Pb^{207}–C–C–C–H^1). The pertinent data are summarized in Table I and represented in Figure 1.

The compounds used in the present study were prepared by the general sequence of reactions given in eq 1 and 2.[3] It is well known that R_3PbCl is also

$$6RMgCl + 3PbCl_2 \longrightarrow R_3PbPbR_3 + Pb + 6MgCl_2 \quad (1)$$

$$R_3PbRbR_3 + Br_2 \longrightarrow 2R_3PbBr \quad (2)$$

formed along with the other products during the reaction of the Grignard reagent with lead chloride.[4] Actually, a mixture of hexaneopentyldilead and trineopentyllead chloride was isolated from reaction 1. However, they could be separated easily because of their solubility difference in petroleum ether (bp 30–60°). Hexaneopentyldilead was readily soluble in petroleum ether, while trineopentyllead chloride remained essentially undissolved.

Trineopentyllead bromide was prepared in quantitative yield by the action of bromine on hexaneopentyldilead in benzene solution (eq 2).

The contact contribution to spin–spin coupling between two nuclei is approximately related to their optical hyperfine structure constants.[5] The large values of $J_{Pb^{207}-H-\gamma}$ are not entirely unexpected because of the large hyperfine structure constant for the lead atom. However, the possibility of any contribution to γ coupling through space may not be excluded.

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TABLE I
PMR DATA

Compd	δ^a		J, cps	
	CH$_2$	C(CH$_3$)$_3$	Pb^{207}, H-α	Pb^{207}, H-γ
$[(H_3C)_3CCH_2]_3PbCl$	2.45	1.12	30.0 ± 0.2	8.0 ± 0.1
$[(H_3C)_3CCH_2]_3PbBr$	2.53	1.11	28.0 ± 0.2	8.0 ± 0.1
$[(H_3C)_3CCH_2]_3Pb{-}Pb[CH_2C(CH_3)_3]_3$[b,c]	2.01	1.03	19.8 ± 0.2	5.0 ± 0.1

[a] Chemical shifts are in parts per million downfield from an internal standard of tetramethylsilane and are accurate to 0.01 ppm. [b] Coupling between protons and lead through three bonds ($Pb^{207}{-}Pb{-}C{-}H^1$) was 12.0 ± 0.2 cps. [c] A low-intensity quartet expected from the system $Pb^{207}{-}Pb^{207}{-}CH_2$ could not be observed because of the poor signal-to-noise ratio.

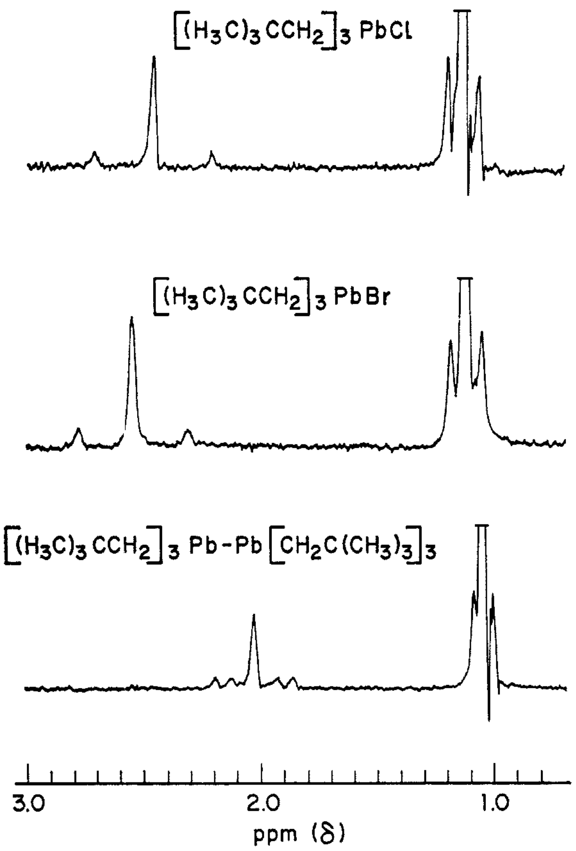


Figure 1.—Pmr spectra of trineopentyllead chloride, trineopentyllead bromide, and hexaneopentyldilead in deuteriochloroform solutions.

Experimental Section

Melting points are uncorrected. The proton magnetic resonance spectra were recorded on 0.2 *M* solutions in deuteriochloroform, using a Varian Associates A-60 spectrometer. Tetrahydrofuran was distilled from calcium hydride before use. Experiments involving preparation and reaction of neopentylmagnesium chloride were carried out under an atmosphere of prepurified nitrogen.

Reaction of Neopentylmagnesium Chloride with Lead Chloride.—To a stirred solution of 13.90 g (0.05 mole) of lead chloride in 200 ml of tetrahydrofuran at 0° was added dropwise over a period of 30 min a solution of neopentylmagnesium chloride, prepared from 2.92 g (0.12 g-atom) of magnesium and 10.66 g (0.1 mole) of neopentyl chloride in 100 ml of tetrahydrofuran. The resulting dark black mixture was refluxed for 1 hr and then filtered while hot. Tetrahydrofuran was removed from the filtrate *in vacuo* and the residue was extracted with 600 ml of boiling 95% aqueous ethanol. On cooling the extract a yellow crystalline solid, 4.5 g, separated.

The yellow solid was stirred with 100 ml of petroleum ether (bp 30–60°). Filtration gave 2.7 g of a white solid which was identified as trineopentyllead chloride. Removal of solvent from the filtrate *in vacuo* gave 1.8 g of hexaneopentyldilead as shiny yellow crystals.

Trineopentyllead Chloride.—Recrystallization of trineopentyllead chloride from absolute ethanol furnished an analytically pure sample, mp 207–208°.

Anal. Calcd for $C_{15}H_{33}ClPb$: C, 39.51; H, 7.24; Cl, 7.80. Found: C, 39.47; H, 7.16; Cl, 7.88.

Hexaneopentyldilead.—Hexaneopentyldilead obtained above was analytically pure, mp 202–203° dec.

Anal. Calcd for $C_{30}H_{66}Pb_2$: C, 42.84; H, 7.85. Found: C, 42.83; H, 7.64.

Its infrared spectrum (KBr pellet), determined using a Perkin-Elmer 221 spectrometer equipped with sodium chloride optics, showed absorptions at 2950 (s), 2902 (s), 2865 (s), 1440 (m), 1350 (m), 1230 (s), 1092 (s), 995 (w), and 700 (s) cm^{-1}.

Trineopentyllead Bromide.—To a stirred solution of 0.8404 g (0.001 mole) of hexaneopentyldilead in 20 ml of benzene was added 1% bromine solution in benzene till the yellow color of the lead compound was discharged. Benzene was then removed *in vacuo*. Trineopentyllead bromide was left behind as white solid in almost quantitative yield. Its analytical sample was prepared by recrystallization from absolute ethanol, mp 166°.

Anal. Calcd for $C_{15}H_{33}BrPb$: C, 36.00; H, 6.60; Br, 16.00. Found: C, 36.32; H, 6.42; Br, 15.58.

Acknowledgment.—The author is grateful to Professor Dietmar Seyferth of Massachusetts Institute of Technology for advice and encouragement.

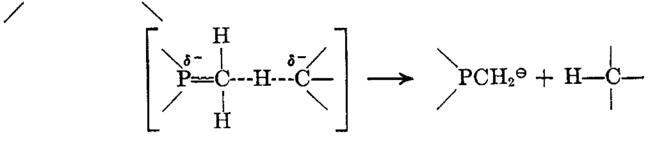
3d-Orbital Resonance in Trivalent Organophosphines. II. Additions of Organolithium Compounds to Vinylphosphines[1]

DONALD J. PETERSON

The Procter and Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239

Received September 22, 1965

In the first paper of this series, the selective methyl metalations of methyldiphenylphosphine, dimethylphenylphosphine, and di-*n*-hexylmethylphosphine were described.[1b] Also, it was reported that dimethyldodecylphosphine was metalated approximately 15 times as rapidly as dimethyldodecylamine. The selective methyl metalation of the methylphenylphosphines and the enhanced rate of metalation of dimethyldodecylphosphine, relative to the analogous amine, were regarded as evidence for d-orbital resonance stabilization of the incipient α-carbanions by trivalent phosphorus in the transition state.



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[1] (a) Presented in part at the 149th Meeting of the American Chemical Society, April 1965, Detroit, Mich. (b) Part I: D. J. Peterson and H. R. Hays, *J. Org. Chem.*, **30**, 1939 (1965).