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SYNTHESIS AND PROTON MAGNETIC RESONANCE STUDY OF SOME TETRAALKYLLEAD DERIVATIVES*

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In the absence of accurate theoretical predictions of spin–spin coupling constants their empirical correlations with molecular parameters are of great practical as well as theoretical importance. With the help of such correlations, coupling constants in unknown molecules can be predicted; and, on the theoretical side, they assist in understanding the mechanism of spin–spin interaction between nuclei.

Consequently, in the recent years, a considerable effort has been made to relate spin–spin coupling constants to structural parameters of molecules**. Our present investigation is of interest in this general context.

Recently, we reported[2] the first observation of long-range spin–spin coupling between magnetically active isotope of lead, ^{207}Pb (spin 1/2, 21.11 % natural abundance), and protons over four σ bonds (^{207}Pb–C–C–C–^{1}H). In continuation of our investigations of organolead chemistry, we have now prepared some alkylneopentyllead derivatives and have measured their proton magnetic resonance (PMR) spectra. Long-range ^{207}Pb–γ-H coupling and some interesting correlations of $J(^{207}\text{Pb}-\alpha\text{-H})$ with molecular parameters have been observed. The purpose of this paper is to report on these relationships.

PREPARATIVE AND STRUCTURAL ASPECTS

Several methods are known in literature for the preparation of tetraalkyllead compounds. For extensive reviews, see refs. 7–9. The most convenient method to prepare symmetrical tetraalkyllead compounds in laboratory is by the reaction of an appropriate Grignard reagent with lead chloride[10]. The reaction is believed to proceed via an unstable dialkyllead intermediate which disproportionates to hexaalkyldilead which, in turn, generally undergoes thermal disproportionation to give tetraalkyllead and metallic lead [*e.g.* eqns. (1), (2), and (3)][11].

$$PbCl_2 + 2\,RMgX \rightarrow R_2Pb + MgX_2 + MgCl_2 \qquad (1)$$

$$3\,R_2Pb \rightarrow R_3PbPbR_3 + Pb \qquad (2)$$

$$2\,R_3PbPbR_3 \rightarrow 3\,R_4Pb + Pb \qquad (3)$$

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** For a summary of literature, see ref. 3. Recently more work has been reported on this subject; for example, see refs. 4–6.

Thermal disproportionation of hexaalkyldileads to tetraalkyllead derivatives and metallic lead depends greatly on the nature of the alkyl groups[12]. For example, the lower members of the series such as hexamethyllead and hexaethyldilead disproportionate at room temperature to give tetramethyllead and tetraethyllead respectively. In contrast, sterically-hindered hexacyclohexyldilead is a stable compound[7] and decomposes (without melting) only at > 196°. Similar effect of large alkyl groups is noted in the case of hexaneopentyldilead. Hexaneopentyldilead is also a high-melting solid (202–203° dec.[2], 205–206° dec.[13]). It did not disproportionate to tetraneopentyllead even when its benzene solution was refluxed overnight.

Tetraneopentyllead, that could not be prepared by thermal decomposition of hexaneopentyldilead, was readily accessible in quantitative yield through the reaction of neopentylmagnesium chloride with trineopentyllead bromide. Alkyltrineopentyllead derivatives were also prepared by the reaction of Grignard reagents with trineopentyllead bromide (eqn. 4); however, these reactions were sometimes

$$[(CH_3)_3CCH_2]_3PbBr + RMgx \xrightarrow[\text{or THF}]{\text{Ether}} [(CH_3)_3CCH_2]_3PbR + \tfrac{1}{2}\,MgBr_2 + \tfrac{1}{2}\,MgX_2 \tag{4}$$

$$R = CH_3,\ CH_2CH_3,\ CH(CH_3)_2,\ C(CH_3)_3,\ \text{and}\ CH_2C(CH_3)_3$$

complicated by redistribution reaction products*. For example, during the reactions of methylmagnesium bromide and ethylmagnesium bromide with trineopentyllead bromide at 0°, besides methyltrineopentyllead and ethyltrineopentyllead, dimethyldineopentyllead and diethyldineopentyllead were also formed respectively.

The redistribution reactions depend on temperature and the nature of the alkyl groups. For example, when the above reactions between methyl- and ethylmagnesium bromides and trineopentyllead bromide were carried out at −30° to −40°, no detectable (by PMR) amounts of redistribution products were formed. The only products isolated were methyltrineopentyllead and ethyltrineopentyllead respectively. Whereas, isopropylmagnesium bromide and tert-butylmagnesium bromide reacted with trineopentyllead bromide at 0° to yield only the primary reaction products, *i.e.*, isopropyltrineopentyllead and tert-butyltrineopentyllead respectively; and at −30° to −40°, no reaction occurred.

Redistribution reaction also did not occur during the reaction of neopentylmagnesium chloride with trimethyllead bromide at 0°. Trimethylneopentyllead was obtained in high yield (82.5%).

The structures of organolead compounds prepared during the present study were established by C,H analysis and PMR spectra. In some cases, molecular weight determination and mass spectral analysis were also employed to further support their structures.

PROTON MAGNETIC RESONANCE SPECTRA

Results

The proton magnetic resonance spectra of tetraalkyllead derivatives reported

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* Redistribution reactions (alkyl–alkyl exchange) on lead are very facile and are catalyzed by alkyllead halides, metal halides, etc. An extensive study of these reactions has been carried out by Calingaert and coworkers[14], and recently reviewed by Moedritzer[15].

in this paper are relatively easy to interpret. Methyl, tert-butyl, and neopentyl groups bonded to lead give simple first-order spectra. Only the ethyl and isopropyl groups exhibit A_3B_2 and A_6B complex patterns respectively (Fig. 1)*. Actually, the ethyl protons in ethyltrineopentyllead appear as a sharp singlet. Hence, it is an extreme case of $A_3B_2 \rightarrow A_5$ type spectrum.

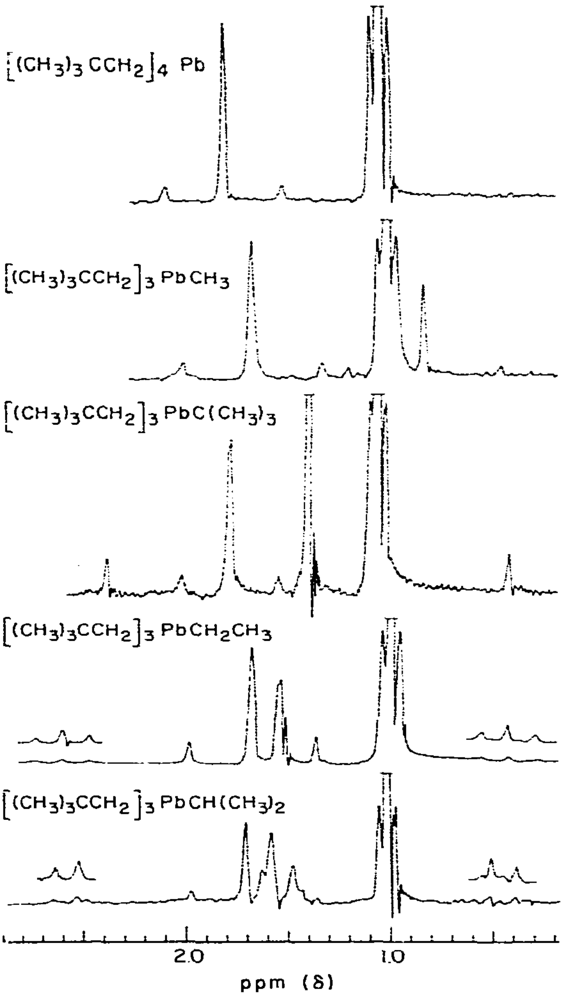

Fig. 1. PMR spectra of alkyltrineopentyllead derivatives.

The measurements of the spectral parameters of ethyl and isopropyl groups in ethyltrineopentyllead and isopropyllead respectively are made convenient by the large difference in the coupling constants of lead with α and β protons. The large value of $J(^{207}\text{Pb}\text{-}\beta\text{-H}) - J(^{207}\text{Pb}\text{-}\alpha\text{-H})$ results in the removal of the near-equivalence of

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* A similar A_3B_2 type spectrum has been observed for tetraethyllead by Baker[16], and has been attributed to the electronegativity value of ~1.7 for lead.

α and β protons of these groups. Consequently, the split satellite peaks are clearly separated from the complex patterns of their spectra. The splitting of the satellite peaks is due to the coupling between α and β protons. The midpoints between the split satellite peaks determine the chemical shifts of the β protons.

An interesting feature of the PMR spectra of neopentyllead derivatives is the long-range spin–spin coupling between lead and γ protons. The spin–spin interaction is strong enough that the split proton peaks are clearly separated from the peak due to the unsplit protons.

Pertinent spectral data are presented in Table 1.

TABLE 1

PROTON MAGNETIC RESONANCE DATA

Compound		*δ (ppm)*[a]			*J(^{207}Pb–H) (cps)*		
		α-H	*β-H*	*γ-H*	*α-H*	*β-H*	*γ-H*[b]
$[(CH_3)_3CCH_2]_3PbCH_3$	CH_2	1.65			40.5±0.2		
	CH_3	0.81		0.98	44.2±0.1		5.5±0.1
$[(CH_3)_3CCH_2]_3PbCH_2CH_3$[c]	CH_2[d]	1.67			36.4±0.2		
	CH_3		1.53	1.00		129.0±0.2	5.5±0.1
$[(CH_3)_3CCH_2]_3PbCH(CH_3)_2$[e]	CH_2	1.68			32.5±0.2		
	CH_3		1.52	1.00		127.0±0.2	4.6±0.1
$[(CH_3)_3CCH_2]_3PbC(CH_3)_3$	CH_2	1.73			27.5±0.2		
	CH_3		1.35	1.02		115.0±0.1	4.6±0.1
$[(CH_3)_3CCH_2]_4Pb$	CH_2	1.78			33.8±0.2		
	CH_3	0.72		1.02			5.3±0.1
$[(CH_3)_3CCH_2]_2Pb(CH_3)_2$	CH_2	1.65			47.0±0.2		
	CH_3	0.73		0.98	49.5±0.2		5.8±0.1
$(CH_3)_3CCH_2Pb(CH_3)_3$	CH_2	1.70			54.5±0.2		
	CH_3	0.72		1.00	55.5±0.1		6.4±0.1
$Pb(CH_3)_4$	CH_3	0.74[f]			61.8±0.1[g]		

[a] Chemical shifts are downfield from TMS as an internal standard. [b] Measured at 100 cps sweep width. [c] J(α-H–β-H) 7.5 cps. [d] Of neopentyl groups. [e] J(α-H–β-H) 7.2 cps. [f] Ref. 17: 0.70 ppm (gas phase); ref. 18: 0.87 ppm (neat). [g] Ref. 18: 60.5 cps.

Discussion

J(^{207}Pb–α-H) vs. Taft's inductive σ constants.* In alkyltrineopentyllead derivatives, a linear relationship exists between the spin–spin coupling constants of lead with methylene protons of the neopentyl groups and the polar substituent constants (σ^* values) of the alkyl groups (Fig. 2). The σ^* value of the alkyl groups are from Table IV of Taft[19].

The importance of this relationship lies not only in that it offers a new spectral technique to determine inductive σ^* constants of alkyl groups but also in the elucidation of the mechanism of spin–spin coupling between lead and α protons.

In the recent years, considerable attention has been given to the mechanism of spin–spin coupling between magnetically active nuclei. Most of the work in this

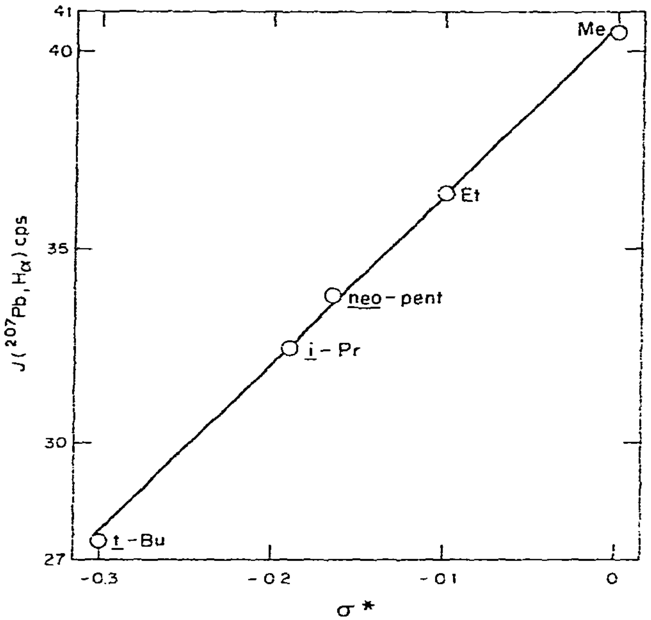

Fig. 2. Linear relationship between $J(^{207}$Pb–α-H) and the polar substituent constants (σ* values) of alkyl groups in alkyltrineopentyllead derivatives.

area has been done with directly bonded ^{13}C–^{1}H system. Generally, $J(^{13}$C–^{1}H) is related to the *s* character of the hydrogen-bonding orbital of carbon, and polarity is neglected to a first approximation[20–26]. However, recently, the effect of polarity on NMR coupling constants has been emphasized[27–30]. For example, Grant and Litchman[27] have shown that most of the variations in $J(^{13}$C–^{1}H) in halomethanes can be accounted for by the changes in the effective nuclear charge on carbon, calculated from dipole moments, and that large changes in the hybridization parameters are not necessary. As a support for this argument, Huheey[28] has obtained similar results by employing partial charge on carbon atom calculated from orbital electronegativities. Our present results also seem to strengthen this argument.

Polar substituent constant, σ*, is a reaction parameter and is linearly related to the charge induced at the reaction center[31]. Hence, it is tempting to conclude from the linear relationship represented in Fig. 1 that the effective nuclear charge (Z_{eff}) on lead atom has a very significant effect on the spin–spin coupling between lead and α-protons.

It may, however, be stated here that a redistribution of *s* character in the carbon-bonding hybridized orbitals of lead should also be expected depending upon the nature of the alkyl groups; and, consequently, affect $J(^{207}$Pb–α-H) through Fermi contact. But, that *s* character is not the sole contributor to ^{207}Pb–α-H spin–spin coupling is shown by the relation in Fig. 1 and also by the attempted calculations (see below) of % *s* character in lead orbitals involved in Pb–C bonds.

The question of percent s character in metal–carbon bond. Holmes and Kaesz[32] suggested an empirical method to calculate percent *s* character of the hybridized atomic orbitals of tin bonding to carbon. The method is based on the assumption that the contact term makes the dominant contribution to $J(^{119}$Sn–C–^{1}H), and consists of drawing a line from the origin to a point representing the observed $^{119}Sn{-}C{-}^{1}H$ coupling constant in tetramethyllead and 25% *s* character. The rehybridization of tin atom in various methyltin derivatives is then calculated by placing the respective values of $J(^{119}Sn{-}C{-}^{1}H)$ on this line.

In view of the above discussion concerning the role of effective nuclear charge in determining $J(^{207}Pb{-}\alpha{-}H)$, it was felt necessary to test the empirical validity of the method of Holmes and Kaesz. During the present study, we have synthesized mixed methylneopentyllead derivatives and have calculated % *s* character in the hybridized orbitals of lead by this method taking symmetrical tetramethyllead and tetraneopentyllead as representing 25% *s* character*. The results are compared in Table 2. On the basis of these results, it is suggested that caution should be exercised

TABLE 2

COMPARISON OF % *s* CHARACTER IN LEAD ORBITALS OF Pb–C BONDS[a]

Compound	*Pb–CH₃*		*Pb–CH₂*	
	TML	*TNL*	*TML*	*TNL*
$[(CH_3)_3CCH_2]_3PbCH_3$	17.8	10.0	27.4	30.0
$[(CH_3)_3CCH_2]_2Pb(CH_3)_2$	20.0	15.4	30.0	34.6
$(CH_3)_3CCH_2Pb(CH_3)_3$	22.5	19.9	32.5	40.3

[a] Calculated from tetramethyllead (TML) and tetraneopentyllead (TNL) as references representing 25% *s* character.

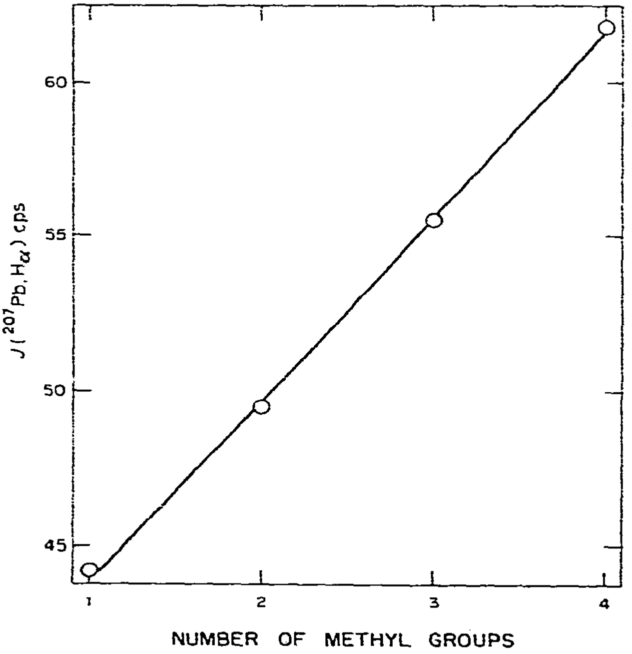

Fig. 3. $J(^{207}Pb{-}methyl{-}H)$ *vs.* the number of methyl groups in mixed methylneopentyllead compounds.

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* Both tin and lead are sp^3-hybridized in their tetrasubstituted compounds. Hence, the application of the method of Holmes and Kaesz[32] in the present case is justified.

to calculate percent *s* character in chemical bonds purely from spin–spin coupling constants.

Additivity relationship for $J(^{207}Pb\text{–}\alpha\text{-}H)$. Additivity relationships exist for $J(^{207}\mathrm{Pb}\text{–}\alpha\text{-H})$ in mixed methylneopentyllead derivatives (Figs. 3 and 4). In view of the additive nature of inductive σ^* parameters[19], these relationships are well in line with the linear relationship shown in Fig. 2. Based on these relations, it is possible to derive an expression to calculate $J(^{207}\mathrm{Pb}\text{–}\alpha\text{-H})$ in an unknown tetraalkyllead compound from the σ^* values of alkyl groups, if the corresponding coupling constant, $J_{\mathrm{ref}}(^{207}\mathrm{Pb}\text{–}\alpha\text{-H})$, for the same alkyl group is known in a reference tetraalkyllead derivative:

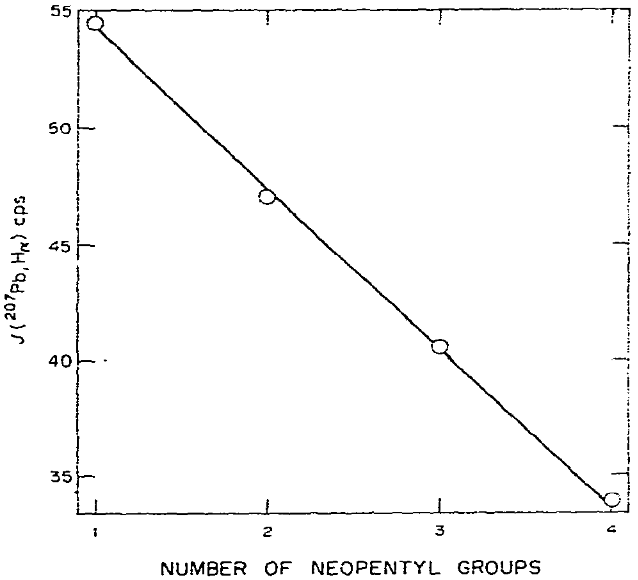

Fig. 4. $J(^{207}\mathrm{Pb}\text{–methylene-H})$ *vs.* the number of neopentyl groups in mixed methylneopentyllead compounds.

$$J(^{207}\mathrm{Pb}\text{–}\alpha\text{-H}) = J_{\mathrm{ref}}(^{207}\mathrm{Pb}\text{–}\alpha\text{-H}) - 42.14\,(\Sigma_{\mathrm{ref}}\sigma^*_{\mathrm{Alk}} - \Sigma\sigma^*_{\mathrm{Alk}})$$

obtained by the method of least squares (standard deviation 0.41). Tetraalkyllead compounds here represent both mixed and unmixed alkyl derivatives.

We are currently investigating the scope and the limitations of this relation.

EXPERIMENTAL SECTION

General

All melting and boiling points are uncorrected. Experiments involving preparation and reactions of Grignard reagents were carried out in an atmosphere of prepurified nitrogen. PMR spectra were measured on 0.5 *M* solutions in deuteriochloroform at 30±0.5° using a Varian Associates A-60 spectrometer. Infrared spectra were obtained on a Perkin–Elmer 221 spectrometer equipped with sodium chloride optics. Mass spectra were determined using a Consolidated Electrodynamics Corporation Model 21-103C mass spectrometer operating at an ionizing current of 10.5 μa, and an ionization energy of 70 ev. The inlet and ionization chamber temperatures were 125° and 250° respectively.

Preparation of starting materials

Trineopentyllead bromide was prepared as described elsewhere[2]. Neopentylmagnesium chloride was prepared from freshly distilled neopentyl chloride in tetrahydrofuran, which was distilled from calcium hydride before use.

Tetraneopentyllead

To a stirred suspension of trineopentyllead bromide (5.0 g, 0.01 mole) in 70 ml of anhydrous ether was added dropwise over 15 min a solution of neopentylmagnesium chloride prepared from 3.5 g (0.03 mole) of neopentyl chloride in 60 ml of tetrahydrofuran. After the addition of the Grignard solution was complete, the reaction mixture was stirred for 10 additional min and then decomposed with 50 ml of cold water. The organic layer was separated and dried over anhydrous sodium sulfate. Volatiles were removed by trap-to-trap distillation *in vacuo*. The light yellow residue on sublimation (100°/0.5 mm) gave white crystals of tetraneopentyllead in almost quantitative yield, m.p. 139–141°. (Found: C, 48.80; H, 8.88; mol.wt. cryoscopic in benzene, 489. $C_{20}H_{44}Pb$ calcd.: C, 48.86; H, 8.96%; mol.wt., 491.)

The infrared spectrum (KBr) showed 2950 s, 2905 s, 2870 s, 1450 w, 1350 m, 1230 s, 1110 m, 1000 w, and 725 s cm^{-1}.

Reaction of methylmagnesium bromide with trineopentyllead bromide

To an ice-cold, stirred suspension of 5.0 g (0.01 mole) of trineopentyllead bromide in 100 ml of anhydrous ether was added 10 ml (0.03 mole) of 3 *M* solution of methylmagnesium bromide in ether over 5 min. The reaction mixture was stirred for 10 more min and then decomposed with 50 ml of ice-cold water. The ether layer was separated and dried over anydrous sodium sulfate. Ether was allowed to evaporate at room temperature under nitrogen and the remaining light yellow liquid was distilled under vacuum. The fraction boiling at 70–95°/1.0 mm (2.5 g) was collected. Its PMR spectrum ($CDCl_3$) showed that methyltrineopentyllead and dimethyldineopentyllead were present in *ca.* 2:1 ratio. Their separation was affected by preparative GLPC (20% General Electric Company XE-60 silicon gum on 60–80 mesh acid washed fire brick).

Methyltrineopentyllead. n_D^{25} 1.4980. (Found: C, 43.90; H, 8.18. $C_{16}H_{36}Pb$ calcd.: C, 44.12; H, 8.27%.) The mass spectrum showed no peak corresponding to the molecular ion. The major peak was at *m/e* 365.245 due to $[(CH_3)_3CCH_2]_2Pb^+$-CH_3 ion. The infrared spectrum (neat) showed 2955 s, 2905 s, 2870 s, 1450 w, 1350 m, 1230 m, 1110 m, 1000 w, and 720 m cm^{-1}.

Dimethyldineopentyllead. n_D^{25} 1.4973. (Found: C, 38.18; H, 7.38. $C_{12}H_{28}Pb$ calcd.: C, 37.97; H, 7.38%.) The mass spectrum showed no parent peak. The major peak was at *m/e* 309.147 corresponding to $(CH_3)_3CCH_2Pb^+(CH_3)_2$ ion.

When the above experiment was carried out at −30° to −40°, methyltrineopentyllead (92%, determined by GLPC) was the only product formed.

Reaction of ethylmagnesium bromide with trineopentyllead bromide

To an ice-cold suspension of trineopentyllead bromide (5.0 g, 0.01 mole) in 100 ml of anhydrous ether was added dropwise over 2 min and during vigorous stirring a solution of ethylmagnesium bromide, prepared from 3.27 g (0.03 mole) of freshly distilled ethyl bromide in ether. The reaction mixture was stirred for 5 additional min and then decomposed with 30 ml of ice-cold water. Ether layer was separated and dried over anhydrous sodium sulfate. Ether was allowed to evaporate at room temperature under nitrogen. The remaining liquid was distilled under reduced pressure, 87–97°/0.6 mm (4.0 g). The distillate was analyzed by GLPC (20% Dow Corning 710 silicon fluid on 60–80 mesh on Chromosorb P). It was established that a mixture of ethyltrineopentyllead and diethyldineopentyllead had been formed. Both were isolated as colorless liquids by preparative GLPC and were characterized.

Ethyltrineopentyllead. n_D^{25} 1.5030. (Found: C, 45.58; H, 8.28. $C_{17}H_{38}Pb$ calcd.: C, 45.41; H, 8.46%.) The infrared spectrum (neat) showed 2960 s, 2905 s, 2870 s, 1450 w, 1350 m, 1230 m, 1110 w, 1000 w, and 735 s cm^{-1}.

Diethyldineopentyllead. n_D^{25} 1.4994. (Found: C, 41.20; H, 7.58. $C_{14}H_{32}Pb$ calcd.: C, 41.26; H, 7.86%.) The infrared spectrum (neat) showed 2955 s, 2905 s, 2868 s, 1450 m, 1350 m, 1225 s, 1145 w, 1108 m, 1002 m, 947 w, and 714 s cm^{-1}.

When the above reaction was carried out at −30° to −40°, ethyltrineopentyllead was formed in 90% yield (determined by GLPC) and no diethyldineopentyllead was formed.

Isopropyltrineopentyllead

To an ice-cold, stirred suspension of trineopentyllead bromide (5.0 g, 0.01 mole) in 100 ml of anhydrous ether was added dropwise over 3 min a solution of isopropyl bromide, prepared from 3.69 g (0.03 mole) of freshly distilled isopropyl bromide in 50 ml of ether. After the addition of Grignard solution was complete, the reaction mixture was stirred for 5 min and then decomposed with 50 ml of ice-cold water. The ether layer was separated and dried over anhydrous sodium sulfate. Ether was then removed by trap-to-trap distillation *in vacuo* and the remaining liquid was distilled at 94–98°/0.2 mm to afford 3.9 g (84.2%) of isopropyltrineopentyllead as a colorless liquid. An analytical sample was obtained by GLPC (10% General Electric Company XE-60 silicon gum nitrile on 60–80 mesh acid washed fire brick), n_D^{25} 1.5065. (Found: C, 46.46; H, 8.45. $C_{18}H_{40}Pb$ calcd.: C, 46.63; H, 8.65%.) The infrared spectrum (neat) showed 2956 s, 2905 s, 2860 s, 1440 w, 1350 m, 1230 s, 1170 w, 1130 w, 1100 s, 1000 w, 965 w, and 710 s cm^{-1}.

When the above reaction was attempted at −30° to −40°, trineopentyllead bromide was recovered quantitatively.

tert-Butyltrineopentyllead

A solution of tert-butylmagnesium bromide, prepared from 2.74 g (0.02 mole) of tert-butyl bromide in 50 ml of anhydrous ether, was added dropwise to an ice-cold, stirred suspension of 5.0 g (0.01 mole) of trineopentyllead bromide in 100 ml of anhydrous ether. The reaction mixture was stirred for an additional h and then decomposed with 30 ml of ice-cold water. The ether layer was separated and dried over anhydrous sodium sulfate. Evaporation of ether *in vacuo* afforded 3.70 g of a light yellow solid. Its PMR spectrum ($CDCl_3$) showed that tert-butyltrineopentyllead (75 %) and unreacted trineopentyllead bromide (25 %) were present. The mixture was chromatographed (acid washed alumina, methylene chloride). tert-Butyltrineopentyllead was obtained as a soapy solid, and was analytically pure, m.p. 75–7°. (Found: C, 47.72; H, 8.66. $C_{19}H_{42}Pb$ calcd.: C, 47.78; H, 8.80 %.) The infrared spectrum (KBr) showed 2945–2840 s, 1450 w, 1350 m, 1230 s, 1090 s, 1010 m, 795 m, and 710 s cm^{-1}.

Preparation of trimethyllead bromide

A mixture of tetramethyllead, toluene, and methylene chloride (66 %, 14 %, and 20 % by weight; kindly supplied by Dr. J. D. Sterling) containing 26.7 g (0.1 mole) of tetramethyllead was diluted with 200 ml of anhydrous ether. The mixture was cooled to *ca.* −70°, and a solution of 16.0 g (0.1 mole) of bromine in 50 ml of carbon tetrachloride was added during stirring over 1 h. A white solid separated. The reaction mixture was allowed to warm up to room temperature. Volatile contents were removed by trap-to-trap distillation *in vacuo* and the remaining solid was sublimed (100°/1.0 mm). White crystals of trimethyllead bromide, m.p. 126–7° (lit.[33] m.p. 133°), were obtained in 95 % yield.

Trimethylneopentyllead

To an ice-cold, stirred suspension of trimethyllead bromide (9.97 g, 0.03 mole) in 100 ml of anhydrous ether was added dropwise a solution of neopentylmagnesium chloride prepared from 9.6 g (0.09 mole) of neopentyl chloride in 50 ml of anhydrous tetrahydrofuran. The reaction mixture was then decomposed with 50 ml of ice-cold water. The organic layer was separated and dried over anhydrous sodium sulfate. Ether and tetrahydrofuran were removed by distillation and the remaining light yellow liquid was distilled under reduced pressure. Trimethylneopentyllead distilled at 32.5°/2.1 mm as colorless liquid, 8.0 g (82.5 %), n_D^{25} 1.4990. (Found: C, 29.80; H, 6.19. $C_8H_{20}Pb$ calcd.: C, 29.70; H, 6.19 %.) The infrared spectrum (neat) showed 3000–2860 s, 1465 s, 1366 m, 1240 s, 1125 s, 1000 w, and 760 s cm^{-1}.

Preparation of tetramethyllead

A 3 *M* solution of methylmagnesium bromide (20 ml, 0.06 mole) in ether was added dropwise to a well-stirred solution of lead chloride (8.3 g, 0.03 mole) at 0°. The reaction mixture was then decomposed with 20 ml of ice-cold water. The ether layer was separated and dried over anhydrous sodium sulfate. Ether was removed *in vacuo* and the residue (~4.0 g), hexamethyldilead, when allowed to stand at room temperature under nitrogen for 4 days, decomposed to lead and tetramethyllead. Trap-to-trap distillation *in vacuo* gave tetramethyllead as a colorless liquid.

SUMMARY

Some neopentyl derivatives of lead have been synthesized and their proton magnetic resonance spectra studied. Long-range spin–spin coupling between magnetically active isotope of lead (^{207}Pb) and protons has been observed over four σ bonds. In alkyltrineopentyllead derivatives (Alk = Me, Et, iso-Pr, tert-Bu, and neo-Pent), a linear relationship exists between $J(^{207}Pb–\alpha\text{-}H)$ and the polar substituent constants (σ^* values) of the alkyl groups. In mixed methylneopentyllead derivatives, additivity relationships exist for $J(^{207}Pb-\alpha\text{-}H)$. The results are interpreted that the effective nuclear charge (Z_{eff}) on lead contributes significantly to the spin–spin coupling between lead and α protons. An expression is derived to calculate $J(^{207}Pb-\alpha\text{-}H)$ in unknown tetraalkyllead compounds. The question of percent *s* character in metal–carbon bond is discussed.

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