Notes

Sterically Hindered Group IV-A Organometallics. V.[1a-d] Preparation and Properties of Certain Neopentyl- and Neophylleads[1e]

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Our investigations of the chemical behavior of sterically hindered group IV-A organometals have now been extended to include some organometals of lead.

The chemistry of the organoleads has been the subject of several reviews[2,3] and as is to be expected varies only in degree from that of the organotins. Perhaps the most striking difference of the organolead compounds involves the method of preparation. Owing to the instability of lead tetrachloride at room temperature and its fairly high oxidation potential, this material is not generally available and not suitable for the preparation of the tetraorganoleads. However, these compounds can be prepared from lead dichloride *via* the sequence of reactions shown in eq 1-3. There exists

$$2RMgCl + PbCl_2 \longrightarrow R_2Pb + 2MgCl_2 \qquad (1)$$

$$3R_2Pb \longrightarrow R_3PbPbR_3 + Pb \qquad (2)$$

$$2R_3PbPbR_3 \longrightarrow 3R_4Pb + Pb \qquad (3)$$

an alternate route to obtain tetrasubstituted lead organics which is represented by eq 4. Only the diphenyl- and ditolylleads have been reported. However, the product of reaction 2, the hexaorganodilead, is readily isolated by operating at low temperatures, while the tetraorganolead may be obtained simply by heating the reaction mixture.

$$R_3PbPbR_3 + X_2 \longrightarrow 2R_3PbX \xrightarrow{2RMgX} 2R_4Pb + 2MgX_2 \qquad (4)$$

As is to be expected from the increased covalent radius of lead, 1.54 A, compared with that of tin, 1.41 A,[4] the organoleads are influenced less by steric factors than are the corresponding tin compounds. The tetraisoalkylleads are reportedly prepared in good yields[5] and a number of unsymmetrical tetraorganoleads containing tertiary alkyl groups are known and are reported to be more stable than the corresponding primary or secondary butyl analogs.[2] The preparation of tetracyclohexyllead in 82% yield compared with 62% yield for the corresponding tin compound has been reported.[6]

Results and Discussion

Hexaneopentyldilead resulted from the reaction of neopentylmagnesium chloride and lead dichloride at less than −10° in fair yield. Solutions of the product slowly became turbid, apparently the result of a slow decomposition and oxidation of the resulting lead to lead oxide.

The preparation of tetraneopentyllead (I) was attempted by treating a benzene solution of hexaneopentyldilead with iodine until the yellow color of the lead compound had been discharged and treating the resulting trineopentyllead iodide solution with an excess of neopentylmagnesium chloride. The only product which could be isolated from the reaction mixture was hexaneopentyldilead, indicating that reduction had occurred in preference to coupling. In a second experiment designed to obtain a type-I compound, a solution of trineopentyllead iodide was treated with phenylmagnesium bromide, in an attempt to prepare phenyltrineopentyllead; however, the only isolated product again proved to be the dilead reduction product.

Hexaneophyldilead was prepared similarly to the hexaneopentyldilead. Heating a xylene solution of this material under reflux for several hours resulted in a slow degradation, so that only lead and unreacted hexaneophyldilead were recovered from the reaction mixture. Again no tetraneophyllead, which should have formed according to eq 3, could be found. It was prepared by treating a solution of trineophyllead iodide, prepared from the dilead compound as described above, with neophylmagnesium chloride.

It is difficult to attribute the results obtained in the attempted preparation of tetraneopentyllead to steric factors alone, since the tetraneophyllead could be prepared in good yield without difficulty and without the indication of the presence of a reduction product; *i.e.*, the reaction mixture was water-white after decomposition and filtration. We have previously observed the competition between the reduction and coupling reactions in the case of the organotin compounds.[1a] Similar preferences for reduction have previously been observed in the lead series in reactions in which the steric hindrance would be less. For example, the reaction of trimethyllead bromide with *t*-butylmagnesium chloride resulted in the formation of hexamethyldilead, whereas the use of the corresponding lead iodide yielded the desired product.[7] Reduction products were also obtained from the reaction of tri-

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(1) (a) Part IV: H. Zimmer, I. Hechenbleikner, O. A. Homberg, and M. Danzik, *J. Org. Chem.*, **29**, 2632 (1964). (b) Part III: J. D'Ans, H. Zimmer, and M. V. Brauchitzsch, *Ber.*, **88**, 1507 (1955). (c) Part II: H. Zimmer and H. W. Sparmann, *ibid.*, **87**, 645 (1954). (d) Part I: H. Zimmer and H. W. Sparmann, *Naturwissenschaften*, **40**, 220 (1953). (e) Neophyl = $C_6H_5\text{–}C(CH_3)_2\text{–}CH_2\text{–}$. (f) Taken in part from the doctoral dissertation of O. A. Homberg, University of Cincinnati, 1965.

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(3) L. C. Willemsens, "Organolead Chemistry," International Lead Zinc Research Organization, New York, N. Y., 1964.

(4) F. A. Cotton and G. Wilkenson, "Advanced Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1962, p 347.

(5) G. Grüttner and E. Krause, *Ber.*, **50**, 278, 574 (1917); *Ann.*, **415**, 338 (1918).

(6) G. Grüttner, *Ber.*, **47**, 3257 (1914).

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

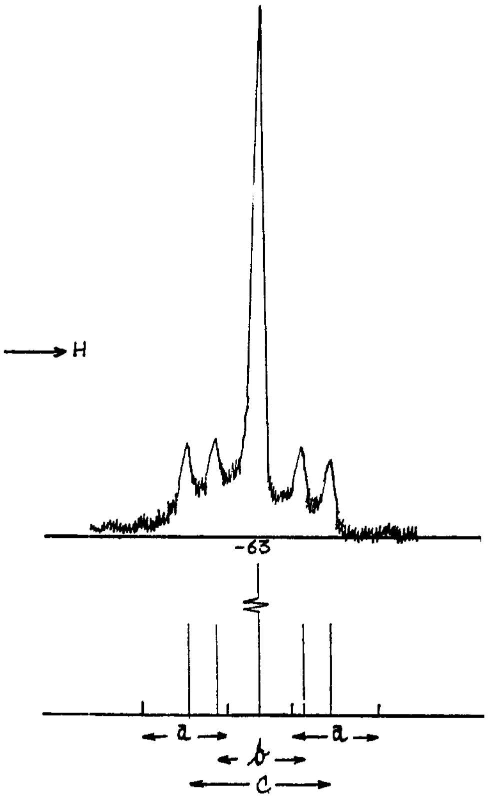

Figure 1.—The observed and calculated pmr spectra for a molecule containing $XCH_2PbPbCH_2X$: a, $J(XCH_2Pb^{207}Pb^{207})$, b, $J(XCH_2PbPb^{207})$, and c, $J(XCH_2Pb^{207})$.

phenyllead chloride[8] and triethyllead iodide[9] with the *t*-butyl Grignard reagent. In attempts to prepare different R_3PbPbR_3 compounds,[10] it was reported that the α-naphthyl Grignard compound yielded only 5.8% of the desired species. The corresponding lithium derivative gave a yield of 10% of the dilead compound. There was no mention of the formation of tetra-1-naphthyllead. The less hindered tetra-2-naphthyltin could be prepared in fair yield.[11] Similarly, tetrafluorenyltin has been prepared in fair yield,[1c,d] whereas attempted preparation of tetrafluorenyllead resulted only in the formation of metallic lead and difluorenyl.[1b]

A possible explanation of the difference in behavior could be found if one were to consider the polarities of the bonds involved. Thus, it was postulated[1f] for the neoalkyltins that the course of the reaction is also governed by the per cent ionic character of the metal to halogen bond of trialkyltin halide which must be a precursor of the tetraalkyltin. In the case of trineopentyltin halides it was observed that the chloride yielded almost exclusively the reduction product, while the bromide gave a quantitative yield of the coupling product. The per cent ionic character of the tin to chloride bond, based on dipole moment measurements of various organotin chlorides is reported to be 27%, while the lead to iodine bond is reported to have a 25% ionic character.[12] Thus it might be expected that, where all other factors are equal, the lead to iodine bond would react similarly to the tin to chlorine bond, as has been observed in their reactions with neopentyl and phenyl Grignard reagents.

The ionic character of the metal to halogen bonds would be increased by the inductive effect of the methyl groups and likewise decreased by the electrophilic nature of the phenyl group, so that for trineophyllead iodide, the ionic character of the lead to iodine bond is sufficiently decreased to permit isolation of a fair yield of tetraneophyllead. There still exists another possibility for explaining the improved yield of tetraneophyllead. It could be due to an increased thermodynamic stability.

As was observed in the case of the corresponding tin compounds,[1c] the chemical and physical properties of the neopentyl- and neophyllead compounds parallel those of the arylleads rather than those of the alkylleads. They are relatively high-melting crystalline solids. The dileads form pale yellow crystals and intensely yellow solutions. Hexaneopentyldilead melted with decomposition at 206°, while the hexaneophyldilead compound melted at 132–133° and decomposed only at 160–170°, depending on the rate of heating. The dilead compounds are sparingly soluble in ether, more soluble in benzene, and most soluble in chlorinated solvents.

Proton Magnetic Resonance Spectra.—The proton magnetic resonance spectra were recorded at 42° on a Varian A-60 spectrometer. Peak positions were determined by bracketing peaks with audio side bands generated by a Hewlett Packard 200CD wide-band oscillator and calibrated by a Hewlett Packard 521D electronic counter. Proton resonance peaks were compared to an internal tetramethylsilane reference. The compounds were investigated in deuteriochloroform solution.

The compounds yielded the expected A_9B_2X and $A_2B_2CM_6N_2X$ patterns for the neopentyl and neophyl compounds, respectively. The peak areas were in the ratio of 9:2 for the neopentyl compounds and 5:6:2 for the neophyl compounds, the various phenyl protons (A, B, and C) not being resolved.

Table I contains a tabulation of the observed chemical shifts and spin–spin coupling constants, both reported in cycles per second, of the various protons studied. It is interesting that no methyl proton to metal coupling could be observed in these compounds, whereas a methyl proton to metal coupling was readily discernible in the corresponding tin compounds.[1b]

TABLE I

Compound	Group	δ^a	$J(^{207}PbH)^b$	$J(CH_2Pb^{207}Pb)^b$	$J(^{13}C\text{–}H)$
(Neopentyl$_3$-Pb)$_2$	CH_3	−62.9	...	...	124.0
	CH_2	−121.6	19.6	12.1	...
(Neophyl$_3$-Pb)$_2$	CH_3	−74.8	...	...	125.7
	CH_2	−112.2	33.1	9.4	...
	C_6H_5	−430.7	...	...	...
Neophyl$_4$-Pb	CH_3	−83.2	...	...	125.2
	CH_2	−68.8	20.4	...	...
	C_6H_5	−427.6	...	...	...

[a] In cycles per second from TMS at 60 Mc. [b] In cycles per second.

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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.

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

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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

$$6RMgCl + 3PbCl_2 \longrightarrow R_3PbPbR_3 + Pb + 6MgCl_2 \tag{1}$$

$$R_3PbRbR_3 + Br_2 \longrightarrow 2R_3PbBr \tag{2}$$

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 $J_{Pb^{207}-H\text{-}\gamma}$ 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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