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ORGANOLEAD CHEMISTRY

II*. ACCEPTOR PROPERTIES OF SOME ALKYNYLLEAD COMPOUNDS

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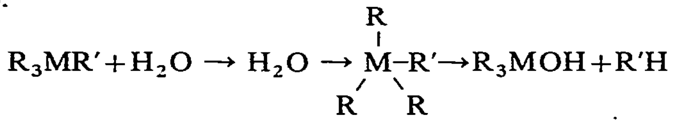
SUMMARY

Some alkynyllead compounds have been synthesised and their acceptor properties investigated by NMR spectroscopy. Addition reactions of trimethyllead methoxide and dimethylamide to hexafluoro-2-butyne, and a study of the modes of decomposition of hexamethyldilead are also described.

INTRODUCTION

There is considerable evidence from kinetic studies[2-4] that the base catalysed hydrolysis of tetraorgano-derivatives of the Group IV elements proceeds by way of five coordinate intermediates (eqn. (1), R = alkyl, R′ = aryl or alkynyl, M = Group IV metal).



$$R_3MR' + H_2O \rightarrow H_2O \rightarrow \overset{\displaystyle R}{\underset{\displaystyle R\quad R}{M}}\text{–}R' \rightarrow R_3MOH + R'H \qquad (1)$$

The reaction rate decreases in the order M = Pb > Sn > Ge > Si and increases with increasing electronegativity of R′, as expected for the reaction of eqn. (1). However, in no case is there direct evidence for formation of five- or six-coordinate complexes from these tetraorgano-derivatives, though such complexes of the organotin or organolead halides[5-9] are well known. For the latter compounds, the acceptor strength is known to increase as the number of electronegative groups increases, thus giving the acceptor strength sequence[10] $SnCl_4 > RSnCl_3 > R_2SnCl_2 > R_3SnCl > R_4Sn$.

Since the organolead compounds appear to have the greatest tendency to form compounds with coordination numbers greater than four[11], we have studied the acceptor properties of a series of methylalkynyllead compounds $(CH_3)_nPb(C{\equiv}CR)_{4-n}$ where $n = 4, 3, 2, 0$ and $R = CH_3$ or CF_3. It was hoped to correlate the acceptor properties of a particular compound with the reactivity of the alkynyllead bond in substitution[1,12] and addition[12] reactions.

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* For Part I see ref. 1.

RESULTS AND DISCUSSION

Preparation of the alkynyllead compounds

We usually prepared the alkynyllead compounds from trimethyllead chloride or dimethyllead dichloride with the appropriate alkynyl Grignard reagent or preferably the alkynyllithium reagent. The compounds $(CH_3)_3PbC{\equiv}CR$ were liquids and $(CH_3)_2Pb(C{\equiv}CR)_2$ were solids and were purified by vacuum distillation or sublimation. Analytical data and physical properties are given in Table 1.

TABLE 1

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF THE ALKYNYLLEAD COMPOUNDS

Compound	*B.p.* (°*C/mm*)	*M.p.* (°*C*)	*ν(CC)* (*cm*$^{-1}$)	*Analysis: Found (calcd.)* (%) *C*	*H*	*Pb*
$(CH_3)_3PbCCCH_3$	85(15)		2156	24.9 (24.7)	4.0 (4.2)	(71.1)
$(CH_3)_2Pb(CCCH_3)_2$	100(10^{-3})[a]	112	2148	30.35 (30.5)	3.8 (3.8)	67.2 (65.7)
$Pb(CCCH_3)_4$	90(10^{-3})[a]	136–138	2130	39.0 (39.7)	2.9 (3.3)	
$(CH_3)_3PbCCCF_3$	80(15)	13–14	2156	21.0 (20.9)	2.7 (2.6)	
$(CH_3)_2Pb(CCCF_3)_2$	100(10^{-3})	60–64	2174	22.6 (22.7)	1.6 (1.4)	
$Pb(CCCF_3)_4$		[b]	2110			

[a] Sublimation. [b] Compound not purified. See text.

The 3,3,3-trifluoropropynyl derivatives were the more easily hydrolysed by atmospheric moisture. Thus trimethyl(3,3,3-trifluoropropynyl)lead fumed violently in air giving trimethyllead hydroxide and 3,3,3-trifluoropropyne, while trimethylpropynyllead could be handled briefly in air without appreciable hydrolysis. A similar difference in reactivity has been noted in the reactions of compounds $(CH_3)_2Pb(C{\equiv}CR)_2$, where $R = CH_3$ or CF_3, with alcohols[1].

The trimethylalkynyllead compounds could also be prepared by reaction of the acetylene with trimethyllead methoxide (eqn. 2).

$$(CH_3)_3PbOCH_3 + RC{\equiv}CH \rightarrow (CH_3)_3PbC{\equiv}CR + CH_3OH \qquad (2)$$

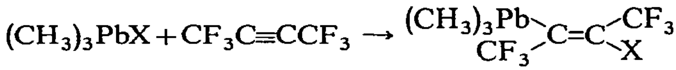
Thus when a suspension of trimethyllead methoxide in tetrahydrofuran was treated with propyne a clear solution was obtained as trimethylpropynyllead was formed. However on evaporation of the solvent the reaction was rapidly reversed as the propyne was preferentially evaporated. A good yield could be obtained by passing propyne through a suspension of the methoxide in boiling benzene so that methanol was evaporated as it formed[12].

With the stronger acid 3,3,3-trifluoropropyne, the latter procedure was not necessary and a yield of 55% of trimethyl(3,3,3-trifluoropropynyl)lead could be obtained by simple reaction, though some reversion to trimethyllead methoxide did take place and an uncharacterised by-product whose infrared spectrum contained a strong band at 1770 cm^{-1} was also formed.

It is possible that 3,3,3-trifluoropropyne could react with trimethyllead methoxide not by substitution but by addition (eqn. 3).

$$(CH_3)_3PbOCH_3 + CF_3C{\equiv}CH \rightarrow (CH_3)_3PbC(CF_3){=}CHOCH_3 \qquad (3)$$

Thus while we find that reaction of trimethyllead dimethylamide with 3,3,3-trifluoropropyne gives trimethyl(3,3,3-trifluoropropynyl)lead, it has been reported that the similar reaction using trimethyltin dimethylamide gives an unidentified product but no (3,3,3-trifluoropropynyl)tin compound[13]. In order to test the possibility that addition as well as substitution might take place, we have treated trimethyllead methoxide[14] and trimethyllead dimethylamide[15] with hexafluoro-2-butyne. In each case a rapid reaction took place giving the product of *trans*-addition across the triple bond (eqn. 4, $X = OCH_3$ or $N(CH_3)_2$).



$$(CH_3)_3PbX + CF_3C{\equiv}CCF_3 \rightarrow \begin{matrix}(CH_3)_3Pb \\ CF_3\end{matrix}\!\!>C{=}C<\!\!\begin{matrix}CF_3 \\ X\end{matrix} \qquad (4)$$

The formation of the *trans*-adduct only, as deduced from the NMR spectra[16], indicates an ionic mechanism of addition rather than a mechanism involving a four-centre transition state.

The C=C stretching frequency in the infrared spectra of these adducts was at 1627 cm^{-1} so that the by-product from the reaction with 3,3,3-trifluoropropyne is unlikely to be a simple addition product. We have independently shown that no addition reaction takes place between trimethyllead methoxide and trimethyl(3,3,3-trifluoropropynyl)lead.

NMR spectra of the alkynyllead compounds

The NMR spectra of the alkynyllead compounds and certain other reference compounds are given in Table 2. The spectra in the non-donor solvents benzene, chloroform or carbon disulphide were very similar and only the data for chloroform solvent is included. In the mixed methylalkynyllead compounds coupling of ^{207}Pb ($I = \frac{1}{2}$, natural abundance 23%) with both methyllead protons and alkynyllead protons* or fluorine atoms was observed, and the observed values of these coupling constants for chloroform solutions are collected in Table 3. These coupling constants are thought to be determined largely by the %*s* character in the lead orbitals involved in the Pb–C bonds. Previous studies have indicated that there is not a linear correlation of %*s* character with the coupling constant $^2J(^{207}Pb\text{–}CH_3)$ in methyllead compounds[20,21], and it seems unlikely that such a simple relationship would hold for the longer range coupling constant $^4J(CH_3\text{–}C{\equiv}C\text{–}^{207}Pb)$. Nevertheless changes in these coupling constants in different compounds do appear qualitatively to parallel changes in %*s* character in the lead orbitals involved in the relevant bonds. Thus, it is immediately apparent that in the mixed methylalkynyllead compounds the *s*-character in the lead orbitals is concentrated in the bonds to the less electronegative methyl groups. This effect is more marked in the (3,3,3-trifluoropropynyl)lead

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* Long range coupling constants from ^{207}Pb to alkynyl protons has been observed previously[18,19].

TABLE 2

^{1}H AND ^{19}F NMR SPECTRA OF THE ALKYNYLLEAD COMPOUNDS

Compound	*Solvent*	$\delta(CH_3Pb)$	$\delta(X_3CCCPb)^a$	$^2J(CH_3Pb)$	$^4J(X_3CCCPb)^a$
$(CH_3)_4Pb$				62[d]	
$(CH_3)_3PbCl$	$CHCl_3$	−1.1		70[e]	
	C_5H_5N[b]			81	
	DMSO[c]			83	
$(CH_3)_3PbCCCH_3$	$CHCl_3$	−1.1	−2.4	76	10
	C_5H_5N[b]	−0.6	−1.5	77	10
	DMSO[c]	−1.2	−2.1	80	10
$(CH_3)_3PbCCCF_3$	$CHCl_3$	−1.4	49.9	76	7.5
	C_5H_5N[b]	−1.1	48.8	80	<2
	DMSO[c]	−1.2	48.5	84	<2
$(CH_3)_2Pb(CCCH_3)_2$	$CHCl_3$	−1.7	−2.3	101	12
	C_5H_5N[b]	−0.9	−2.5	107	12
	DMSO[c]	−1.3	−2.6	112	11
$(CH_3)_2PbCl_2$	DMSO[c]			154.5[c]	
$(CH_3)_2Pb(CCCF_3)_2$	$CHCl_3$	−1.7	50.8	105	8.5
	C_5H_5N[b]	−1.8	49.6	125	<3
	DMSO[c]	−1.7	48.9	138	<2
$Pb(CCCH_3)_4$	$CHCl_3$		−1.3		28
	C_5H_5N[b]		−1.5		28
	DMSO[c]		−2.3		28
$Pb(CCCF_3)_4$	$CHCl_3$		48.3		35

[a] X=H or F. [b] C_5H_5N=pyridine. [c] DMSO=dimethylsulphoxide [d] Ref. 17. [e] Ref. 8.

TABLE 3

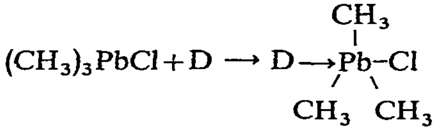
COUPLING CONSTANTS FOR THE ALKYNYLLEAD COMPOUNDS (CHLOROFORM SOLUTION)

Compound	*X=H*		*X=F*	
	$^2J(HC^{207}Pb)$	$^4J(XCCC^{207}Pb)$	$^2J(HC^{207}Pb)$	$^4J(XCCC^{207}Pb)$
$(CH_3)_4Pb$	62		62	
$(CH_3)_3PbCCCX_3$	76	10	76	7.5
$(CH_3)_2Pb(CCCX_3)_2$	101	12	105	8.5
$Pb(CCCX_3)_4$		28		35

compounds than in the propynyllead compounds as expected from the higher electronegativity of the 3,3,3-trifluoropropynyl group. Thus in the mixed compounds the coupling constant $^2J(CH_3\text{–}^{207}Pb)$ is greater than in tetramethyllead while $^4J(X_3C\text{–}C{\equiv}C\text{–}^{207}Pb)$ X=H or F, is smaller than in the tetrakis(alkynyl)lead, the difference being greater for the 3,3,3-trifluoropropynyl derivatives. A related effect has been noticed previously in some mixed methyl(neopentyl)lead compounds where *s*-

character in the lead orbitals was concentrated in the bonds to the less electronegative neo-pentyl groups[21].

Acceptor properties. The coupling constant ${}^2J({}^{207}Pb\text{-}CH_3)$ in methyllead compounds is dependent not only on the electronegativity of the other groups bonded to lead but also on the stereochemistry at lead. Thus the coupling constant ${}^2J({}^{207}Pb\text{-}CH_3)$ of 62 Hz for tetramethyllead increases to 70 Hz for trimethyllead chloride in chloroform solution and to 83 Hz for trimethyllead chloride in the donor solvent dimethyl sulphoxide[8] when the geometry about lead is probably trigonal bipyramidal (eqn. 5, D=donor).

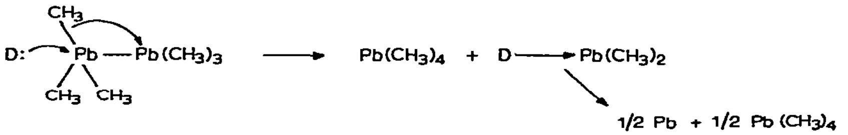


$$(CH_3)_3PbCl + D \longrightarrow D \longrightarrow \underset{CH_3\quad CH_3}{\overset{CH_3}{Pb}}\text{-}Cl \qquad (5)$$

Here the lead orbitals involved in bonding to the methyl groups are thought to be sp^2 hybridised, with the two axial bonds being essentially electrostatic and perhaps involving a p or pd hybrid orbital at lead. Other studies have shown that the magnitude of such changes in coupling constant in donor solvents is a measure of the strength of the Lewis acid–Lewis base interaction[8,22].

In order to assess the relative acceptor properties we have recorded the NMR spectra of the alkynyllead compounds in the donor solvents pyridine and dimethyl sulphoxide. The results are shown in Table 2.

Tetramethyllead and hexamethyldilead. The coupling constant ${}^2J({}^{207}Pb\text{-}CH_3)$ for tetramethyllead[17] and for hexamethyldilead[23] was independent of solvent donor strength, consistent with their having no acceptor properties. However, hexamethyldilead decomposed very rapidly to lead and tetramethyllead when dissolved in strong donor solvents. Decomposition as studied by changes in the NMR spectrum was slow in benzene or acetone but much faster in donor solvents, being half complete in 35 min in pyridine, 5 min in dimethylformamide, 3 min in dimethyl sulphoxide and was immeasurably fast in hexamethylphosphoramide. This data is consistent with the decomposition mechanism shown in eqn. (6) (D=donor).



(6)

We had hoped that the dimethyllead(II) might be sufficiently stabilised by the donor solvents to allow its characterisation by NMR spectroscopy. However although the characteristic green colour of dimethyllead was present in the solutions, no NMR signals attributable to this species could be detected.

Some support for the mechanism proposed above comes from the slow reaction of hexamethyldilead with methanol when the products are tetramethyllead and lead(II) dimethoxide. The latter product is presumably formed by methanolysis of the intermediate dimethyllead (eqn. 7).

$$Pb(CH_3)_2 + 2\,CH_3OH \longrightarrow Pb(OCH_3)_2 + 2\,CH_4 \qquad (7)$$

In a similar reaction hexaphenyldilead is known to react with sodium ethoxide in ethanol to give triphenyllead ethoxide and lead diethoxide[24].

Alkynyllead compounds. The NMR spectra clearly indicated that complex formation occurred when the alkynyllead compounds were dissolved in donor solvents. If the strength of the interaction is measured by ΔJ[8] where $\Delta J = [{}^2J({}^{207}\text{Pb–CH}_3)$ in donor solvent $- {}^2J({}^{207}\text{Pb–CH}_3)$ in chloroform$]$, the following series in order of ability to form adducts with Lewis bases is defined: $(CH_3)_3PbCl > (CH_3)_3PbCCCF_3 > (CH_3)_3PbCCCH_3 > (CH_3)_4Pb$ and $(CH_3)_2PbCl_2 > (CH_3)_2Pb(CCCF_3)_2 > (CH_3)_2Pb(CCCH_3)_2$.

For the 3,3,3-trifluoropropynyl derivatives the increases in ${}^2J({}^{207}\text{Pb–CH}_3)$ were accompanied by decreases in ${}^4J({}^{207}\text{Pb–C}{\equiv}\text{C–CF}_3)$ in donor solvents as predicted in terms of the theory mentioned previously, but this effect was not observed for the propynyl derivatives (Table 2).

Of the alkynyllead compounds studied dimethylbis(3,3,3-trifluoropropynyl)-lead showed the strongest acceptor properties and we have attempted to isolate its complexes with Lewis bases. With 2,2'-bipyridyl an unstable 1/1 adduct could be crystallised from pentane, but this readily decomposed to its constituents. No other adducts could be isolated. Thus it is clear that the ability of alkynyllead compounds to form adducts with Lewis bases is considerably lower than that of the corresponding organolead halides.

The ${}^1H$ NMR spectrum of tetrapropynyllead was independent of the donor strength of the solvent (Table 2), though a study of the ${}^{207}Pb$ NMR spectra shows that it interacts more strongly with Lewis bases than does dimethyldipropynyllead[25]. This then is a further illustration of the insensitivity of the coupling constant ${}^4J(\text{Pb–C}{\equiv}\text{C–CH}_3)$ to changes in stereochemistry.

If a chelating ligand such as 2,2'-bipyridyl complexes with tetrapropynyllead, two propynyllead peaks in the ${}^1H$ NMR spectrum should be observed due to non-equivalent propynyl groups. The NMR spectrum in dichloromethane of tetrapropynyllead and 2,2'-dipyridyl contained only a single propynyllead peak even at −50°, so that a rapid exchange process involving the chelating ligand must take place even at low temperature.

Unfortunately tetrakis(3,3,3-trifluoropropynyl)lead was not sufficiently stable to allow a detailed investigation of its properties. It could be prepared in solution but decomposed rapidly by polymerising to a black solid.

CONCLUSION

We have shown by NMR spectroscopy that alkynyllead compounds form adducts with Lewis bases, though the adducts are generally too unstable to be isolated. The (3,3,3-trifluoropropynyl)lead compounds have higher acceptor properties than the propynyllead compounds and are also more reactive towards hydrolysis and alcoholysis reactions. These observations are interpreted in terms of the five-coordinate intermediate in hydrolysis (eqn. 1) being more stable for (3,3,3-trifluoropropynyl)lead compounds, though the fact that the 3,3,3-trifluoropropynyl group is a better leaving group compared with the propynyl group is probably also important[2-4].

EXPERIMENTAL SECTION

General techniques have been described previously[1]. ^{19}F NMR spectra were recorded using a Varian A60 NMR spectrometer at 56.4 MHz with $CFCl_3$ as internal standard.

Tetrapropynyllead was prepared by the method of Pant, Davidsohn and Henry[26]. We find, in contrast to these authors, that the product can be sublimed without mishaps, $90°/10^{-3}$ mm, if the bath temperature is kept below 100°.

Trimethyl(3,3,3-*trifluoropropynyl*)*lead* was prepared by treating $(CH_3)_3PbCl$ (5.0 g, 17.4 mmol) in tetrahydrofuran (50 ml) with (3,3,3-trifluoropropynyl)magnesium bromide [from C_2H_5MgBr (20 mmol) and 3,3,3-trifluoropropyne (28 mmol)] in tetrahydrofuran (50 ml). After stirring for 2 h at room temperature, the solvent was evaporated and the product extracted with pentane (100 ml). After evaporation of the pentane the product was purified by vacuum distillation (2.5 g, 50%).

This product was also obtained by stirring a suspension of trimethyllead methoxide (1.5 g) in tetrahydrofuran (10 ml) under an atmosphere of CF_3CCH until no more gas was consumed (5 min). The solvent was evaporated under vacuum and the product purified as above (55%). A second fraction was obtained b.p. 120°/15 mm (0.4 g) having a strong infrared absorption at 1770 cm^{-1} as well as peaks characteristic of $-CF_3$ and CH_3-Pb groups.

Tetrakis(3,3,3-*trifluoropropynyl*) *lead*, K_2PbCl_6 (11.8 g, 23.7 mmol)[27] was added to a solution of CF_3CCLi (105 mmol) in tetrahydrofuran (100 ml) at −78°. The solution was allowed to warm to room temperature. After an induction period of about 10 min an exothermic reaction took place and the flask was cooled in ice-salt. After stirring for 2 h, the solvent was evaporated under vacuum and the residue was extracted with benzene (100 ml). Evaporation of the benzene gave the product as an oil which blackened rapidly (2.7 g). The oil could not be sublimed or crystallised. In another experiment the initial reaction was violently exothermic and none of the desired product could be extracted.

Trimethyllead methoxide with hexafluoro-2-butyne

Trimethyllead methoxide (2.0 g, 7.1 mmol) in tetrahydrofuran (10 ml) was stirred under an atmosphere of hexafluoro-2-butyne until no more gas was absorbed (10 min). The solvent was evaporated and the product purified by vacuum distillation giving $(CH'_3)_3PbC(CF^1_3)=C(CF^2_3)OCH_3$ as a colourless liquid. B.p. 60–65° (bath)/0.1 mm. $\nu(C=C)$ 1627 cm^{-1} (s). NMR in CCl_4: $\delta(CH'_3Pb)$ −1.10 ppm, $^2J(^{207}PbH')$ 69.2 Hz, $^5J(F^1H')={}^6J(F^2H')=0.6$ Hz; $\delta(CH_3O)$ −3.70 ppm; $\delta(CF^1_3)$ 65.2 ppm, ^3J-(^{207}PbF) 22.5 Hz; $\delta(CF^2_3)$ 53.1 ppm. (Found: C, 21.7; H, 2.9. $C_8H_{12}F_6OPb$ calcd.: C, 21.6; H, 2.65%.) A similar reaction in benzene gave the same product.

Trimethyllead dimethylamide with hexafluoro-2-butyne

A similar reaction between trimethyllead dimethylamide[15] and hexafluoro-2-butyne gave $(CH_3)_3PbC(CF^1_3)=C(CF^2_3)N(CH_3)_2$ as a colourless liquid (55%) b.p. 60–70° (bath)/10^{-2} mm. NMR in CCl_4: $\delta(CH_3Pb)$ −1.00 ppm, $^2J(^{207}PbH)$ 68.6 Hz; $\delta(CH_3N)$ −2.63 ppm; $\delta(CF^1_3)$ 63.2 ppm, $^3J(^{207}PbF)$ 24 Hz; $\delta(CF^2_3)$ 53.2 ppm. (Found: C, 24.1; H, 3.5. $C_9H_{15}F_6NPb$ calcd.: C, 23.6; H, 3.3%.)

Dimethylbis(3,3,3-trifluoropropynyl)lead with 2,2'-dipyridyl

A solution of $(CH_3)_2Pb(CCCF_3)_2$ (0.39 g, 0.92 mmol) and 2,2'-dipyridyl (0.14 g, 0.90 mmol) in pentane (15 ml) was cooled to −20°. A white solid slowly crystallised. The solvent was decanted off, and the precipitate washed with pentane (15 ml, −20°) and then dried under vacuum (yield 0.35 g); m.p. 65–72°; $\nu(C{\equiv}C)$ 2176 cm^{-1}, $\nu(PbCH_3)$ 522 (s), 504 (sh), 476 (vw) *cf.* $(CH_3)_2Pb(CCCF_3)_2$, $\nu(PbCH_3)$ 524 (s), 508 (m), 475 (ms). NMR in CCl_4: $\delta(CH_3Pb)$ −1.3 ppm, $^2J(PbCH_3)$ 104 Hz, integration found CH_3Pb/Bipy=6/7.7 (calcd. 6/8). (Found: C, 37.7; H, 2.6; Pb 34.8. $C_{18}H_{14}F_6N_2Pb$ calcd.: C, 37.3; H, 2.4; Pb, 35.7%.) After a further crystallisation from pentane the product gave Pb 34.4%, m.p. 64–70°.

Hexamethyldilead with methanol

$(CH_3)_6Pb_2$ (0.4 g) was dissolved in dry methanol (0.5 ml) in an NMR tube. The characteristic NMR peak of hexamethyldilead slowly decayed and a new peak due to tetramethyllead appeared. After three days the reaction was complete and the white precipitate of lead dimethoxide (0.05 g) was filtered off, dried under vacuum and identified by its characteristic infrared spectrum[1,28].

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