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CYCLIC ORGANOLEAD COMPOUNDS

III *. SYNTHESIS AND DYNAMIC BEHAVIOUR OF 10,10-DIMETHYLPHENOXAPLUMBIN AND A TWELVE MEMBERED HETEROCYCLIC ORGANOLEAD COMPOUND $C_{28}H_{28}O_2Pb_2$

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Summary

The synthesis of 10,10-dimethylphenoxaplumbin (II), a related twelve membered ring compound (III), and 2,2'-bis-(trimethyllead)diphenylether (IV) are reported. These compounds have been studied by NMR (^1H, ^{13}C and ^{207}Pb) and IR spectroscopy. The twelve membered cyclic organolead compound (III) exists in solution as an equilibrium mixture of different conformational isomers.

Introduction

There are few reports in the literature concerning six membered heterocyclic organolead compounds. Only two saturated plumbacyclohexanes have been described [2,3], while in the case of plumbines, compounds of the general type (a) in which E = CH_2, NR, O or S, the only previous example was 5-ethyl-10,10 diphenylphenazzaplumbin (b) [4].

We describe below the synthesis of 10,10-dimethylphenoxaplumbin and some related compounds. Two papers have been published on the synthesis of phenoxastannin derivatives; Kupchik et al. reported the synthesis of 10,10-dimethylphenoxastannin [5], but according to Meinema and Noltes this product is a twelve membered ring compound rather than the desired product [6].

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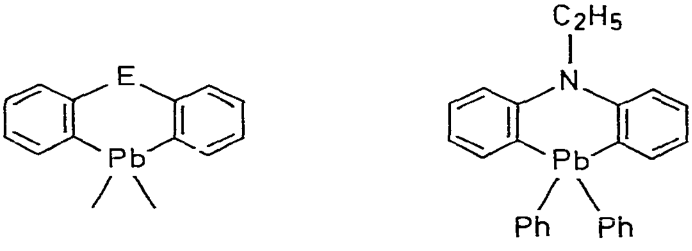
* For Part II: see ref. 1.



(a) (b)

Fig. 1.

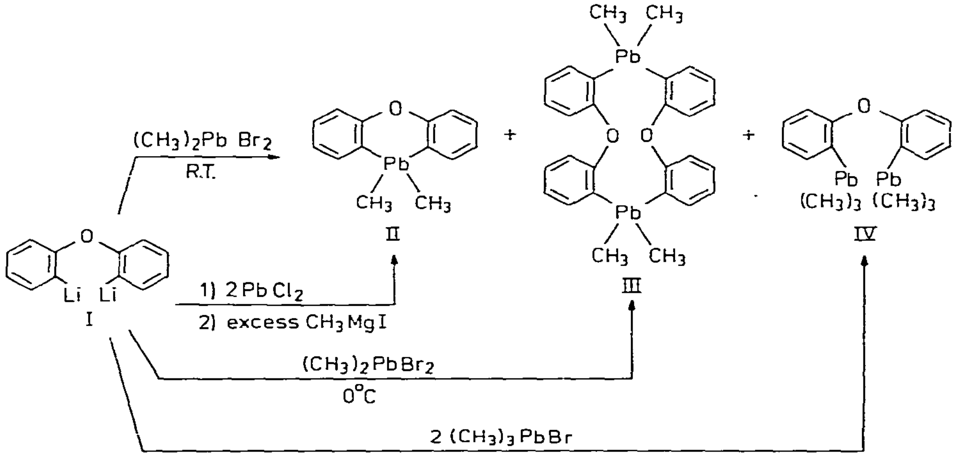
Results and discussion

a. Synthesis

The reactions leading to 10,10-dimethylphenoxaplumbin (II) are presented in Scheme 1. The starting material, 2,2'-dilithiodiphenylether I can be prepared

SCHEME 1

REACTIONS LEADING TO 10,10-DIMETHYLPHENOXAPLUMBIN II AND RELATED COMPOUNDS

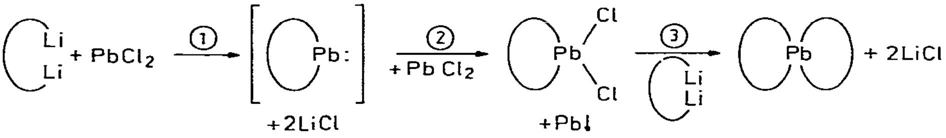


from diphenylether by direct metallation with n-butyllithium in a 1 : 1.3 mixture of THF and Et_2O (yield 50.5% [7]). Reaction of I with $(CH_3)_2PbBr_2$ at room temperature gave the desired six membered ring compound II in a yield of 26%. The product was isolated in a pure form by careful molecular distillation of the hydrolysed reaction mixture. As described earlier by Meinema and Noltes [6] for the corresponding organotin compounds, we also obtained a twelve membered cyclic organolead compound III. The yields of the two cyclic products were found to depend on the temperature used. Addition of I to $(CH_3)_2PbBr_2$ at 0°C gave III in a yield of 9%, while product II could not be isolated from the residue because of the severe bumping during the molecular distillation. When the reaction was performed at room temperature the yield of III was much lower (1%), but the desired 10,10-dimethylphenoxaplumbin (II) was obtained in a yield of 26%. From this reaction mixture however a third product could be isolated with a higher boiling point than II. Analysis showed it to be 2,2′-bis(trimethyllead)diphenylether (IV) (yield 14%). Evidently a rearrangement has occurred in situ to give $(CH_3)_3PbBr$. This rearrangement might be affected by the influence of unreacted n-butyllithium or dilithio compound I. We have observed similar rearrangements during several other syntheses [8]. Another route to compound IV involves the reaction between I and two equivalents of $(CH_3)_3PbBr$. The yield of this process was 36%.

We have also succeeded in synthesizing compound II using $PbCl_2$. It is known from the literature that $PbCl_2$ can be used in the synthesis of spirocyclic organolead compounds [1,9]. Although the mechanism of this reaction has not been investigated, it is likely to proceed by the route shown in Scheme 2. In this synthesis the $PbCl_2$ is added to the dilithio compound in a 1 : 1 ratio, and this results in the formation of a plumbylene derivative [10]. When a 2 : 1 ratio is used the reaction should stop after the second step and the cyclic dichloro organolead compound obtained should be able to undergo a reaction with an excess of Grignard compound, thus leading to a monocyclic tetraorganolead compound. In this way, by using methylmagnesium iodide, product II was obtained in a yield of 21%. This method seems promising for the synthesis of other cyclic organolead compounds. It is not necessary to synthesize any other organolead compound first because of the ready availability of $PbCl_2$.

SCHEME 2

MECHANISM OF THE FORMATION OF SPIROCYCLIC ORGANOLEAD COMPOUNDS



b. *Characterization*

The compounds were characterized by means of NMR and IR spectroscopy. The results are summarized in Tables 1 and 2 respectively. The NMR spectrum of compound II shows only one methyl proton signal down to −90°C (in CD_2Cl_2). This indicates a rapid equilibrium between the two butterfly-like conformers II_1 and II_2 (see Figure 2) on the NMR time scale.

As can be seen from Table 1, the ^1H as well as the ^{13}C NMR spectrum of compound III shows three different methyl signals, with different lead—proton and lead—carbon coupling constants. In the ^{207}Pb NMR spectrum two signals are observed for compound III in a ratio of 1 : 2. It was demonstrated in the elegant studies of Meinema and Noltes [6] that the corresponding tin compound exists in solution as an equilibrium mixture of conformational isomers. Obviously, an analogous situation holds for the twelve membered heterocyclic organolead compound. In the ^1H NMR spectrum in $CDCl_3$ (see Figure 3) the three methyl proton signals are observed in an integration ratio of about 1 : 1 : 1. The signal at 1.18 ppm can be attributed to an equilibrium mixture of conformers $IIIA_1$ and $IIIA_2$ (see Fig. 4). Since only one signal is observed from these conformers

TABLE 1

NUCLEAR MAGNETIC RESONANCE DATA FOR COMPOUNDS II, III AND IV [a]

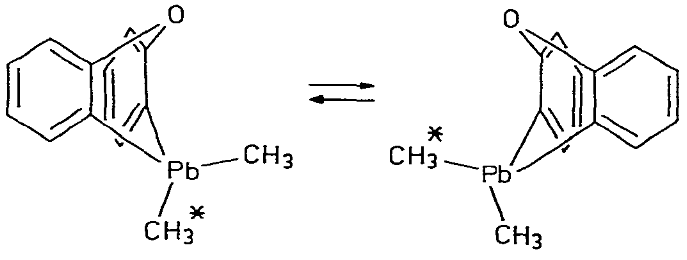
Compound	^{1}N NMR		^{13}C NMR								^{207}Pb NMR [c]
	CH_3	CH_3*	CH_3	CH_3*	C_1	C_2	C_3	C_4	C_5	C_6	
II	0.88 (67)		−1.6 (296)		139.7 (257)	160.7 (16)	118.1	129.3	124.2 (56)	137.3 (43)	−41.5
IIIA	1.18 (70)		0.5 (342)		140.1 (371)	161.2 (14)	116.9 (32)	129.1 (12)	123.3 (68)	136.8 (50)	−108.3 [b]
IIIB	1.13 (56)	0.96 (87)	2.5 (437)	−2.5 (275)	140.3 (342)	161.8 (18)	117.3 (31)	129.6 (12)	123.8 (64)	137.2 (45)	−101.7 [b]
IV	0.93 (66)		−1.4 (293)		138.7 (272)	162.3 (16)	117.5 (27)	129.3 (12)	123.5 (58)	137.0 (45)	−43.4

[a] Solutions in $CDCl_3$; chemical shifts in ppm (^{1}H and ^{13}C NMR relative to internal TMS; ^{207}Pb NMR relative to external TML); $J(^{207}Pb—^1H)$ and $J(^{207}Pb—^{13}C)$ values in Hz (in parentheses); [b] Intensity IIIA:IIIB = 1:2, [c] Negative δ-values refer to high field shifts from TML.

down to −90°C in CD_2Cl_2 it must be concluded that this equilibrium is also rapid on the NMR time scale. The two methyl groups at 0.96 and 1.13 ppm with equal intensity arise from the conformers $IIIB_1$ and $IIIB_2$ (see Fig. 5). In this equilibrium mixture the two methyl groups are magnetically inequivalent. As can be seen from Figure 5, the CH_3*-groups are shielded by the aromatic rings a and b (in $IIIB_1$) and c and d (in $IIIB_2$). In both cases the CH_3-groups are directed outside the molecule, and this results in a lower field absorption than for the CH_3*-groups. Thus, no matter what the rate of this equilibrium process, in these conformers two pairs of magnetically inequivalent methyl groups are always present.

By analogy to the work of Meinema and Noltes [6], we carried some variable temperature ^{1}H NMR measurements on compound III. Upon heating in hexachlorobutadiene we observed a coalescence of the three methyl proton signals at about 200°C. However, at this temperature the twelve membered ring decomposed rather rapidly. Measurements at low temperature (−80°C) in CD_2Cl_2 showed that the signals at 0.96 and 1.13 ppm slowly disappeared, while a crystalline product precipitated from the solution. Probably compound III exists in the solid state in conformation IIIB.

The NMR data for compound IV are similar to those for compound II. This



II_1 II_2

Fig. 2. Conformational isomers of compound II.

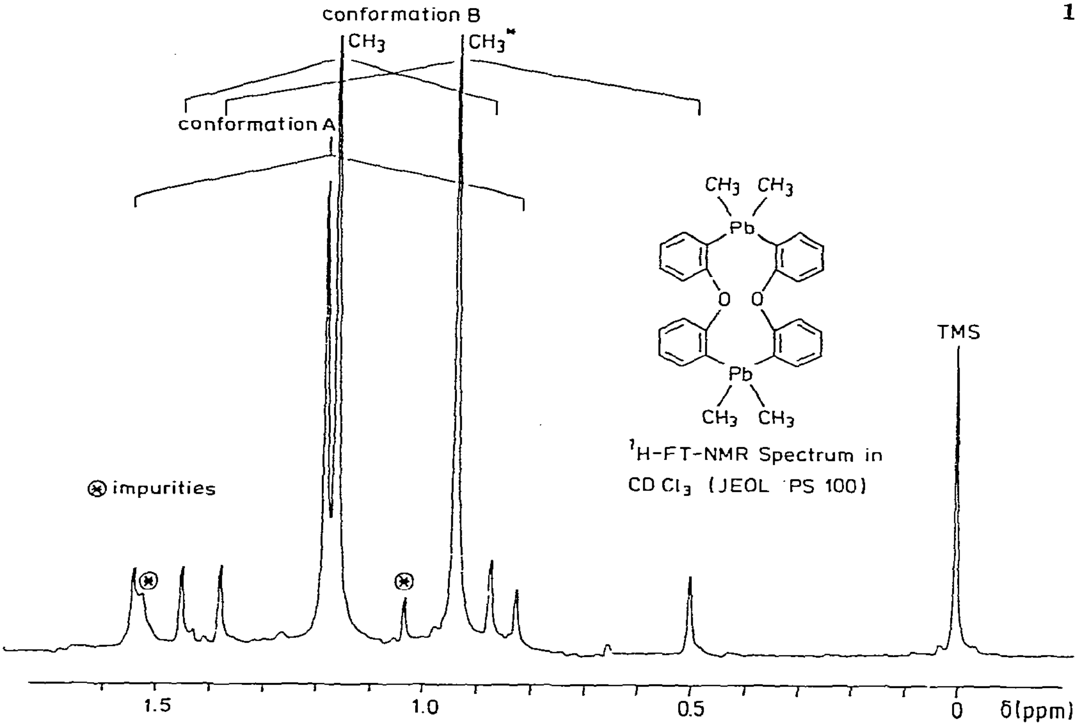
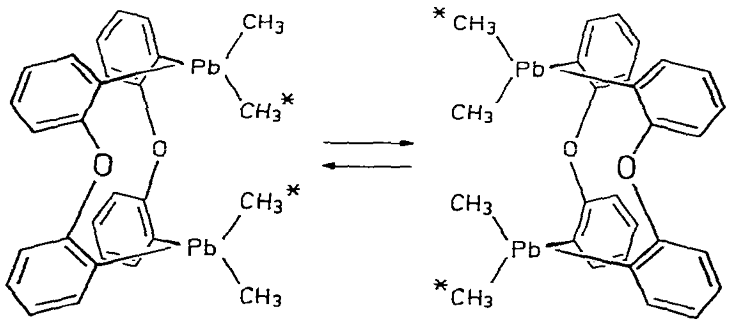
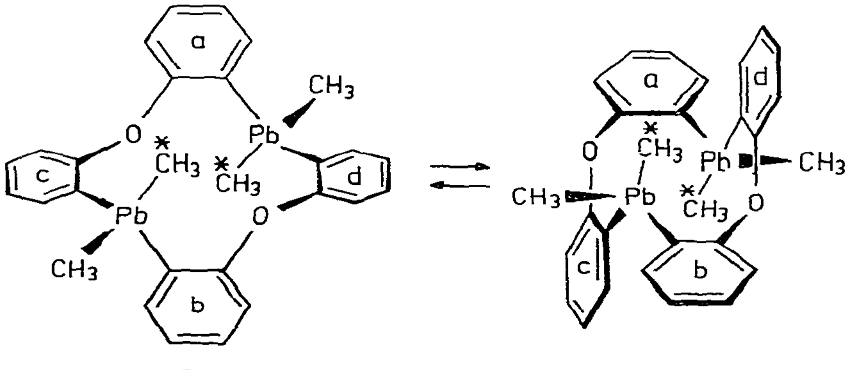


Fig. 3. ^{1}H NMR spectrum of compound III.



III A$_1$

III A$_2$



III B$_1$

III B$_2$

Figs. 4 and 5. Conformational isomers of compound III.

indicates that the presence of a heterocyclic lead atom in compound II does not give rise to any special chemical shift of coupling constant changes compared to the open chain analogue IV. This is indicated particularly by the value of $\delta(^{207}Pb)$, which is usually very sensitive to small changes at the environment of the lead atom [11].

Details of the IR spectrum are presented in Table 2 along with some tentative assignments. Several characteristic absorptions can be distinguished. The absorptions of the methyl groups on the lead atom are similar to those of tetramethyl-

TABLE 2

INFRARED DATA FOR COMPOUNDS II, III AND IV [a]

Compound II	Compound III	Compound IV	$(CH_3)_4Pb$ [b]	Assignment
3060m	3055m	3065m		$\nu(C—H)_{arom}$
3040m				
3000w	2995m	2990m	3000vs	$\nu(C—H)_{methyl}$
2925m	2920m	2920m	2920vs	
		1600m (sh)		$\nu(C{=}C)_{arom}$
1590s		1593m		
1585s (sh)				
1568s	1566vs	1567s		
1489vs	1490w	1491s		
		1461m (sh)		
1457s	1455s	1455s	1448vs	CH_3 asym def.
1432vs	1429vs	1430s		$\nu(C{=}C)_{arom}$
1332w				
1285m	1290w	1280w		
	1265m			
1255m (sh)	1255s	1255m		
1230vs (br)		1228s		$\nu(C—O)_{arom\ ether}$
	1201vs (br)	1203vs		
1192m				
1165m	1163s	1166m		$\beta(C—H)$
1155m (sh)	1154s	1155m	1148s	CH_3 sym def.
1109m	1111s	1110m		(C—H)
1073m		1074w		
1045m	1049s	1047m		
1024m	1025m	1025w		
940vw	945w	940w	930w	
905w (sh)				
875m	882m	878m		
868m	871s	865m (sh)		
	860m (sh)			
799m	800s	802s		
770m (sh)	775s (sh)	770s (br)	765vs	CH_3 rocking
750vs	754vs (br)	754vs		4H wag
713m	719s	715s		Ph(C—C) ring bend
692s		691m		
	643w	640vw		
	623w			
600w (br)				
	529vw			
500m				
480m	495m	478s	485vs	$\nu(Pb—C)$
	490m		478vs	
	480s		470vs	
432m	439s	432m		

[a] Compounds II and IV between CsI discs, compound III in KBr; [b] see ref. 12.

lead [12]. An indication of the different methyl groups in compound III can be found in the three different values of ν(Pb—C) at about 490 cm^{-1}, while the compounds II and IV show only one absorption in this region. The value of ν(C—O) of the six membered ring II at 1230 cm^{-1} differs significantly from those of the other two products (1210 and 1203 cm^{-1}). Other characteristic absorptions are found in the 700—800 cm^{-1} region: the rocking of the methyl group (ca. 770 cm^{-1}), the 4 H wag of the *ortho* disubstituted phenyl ring (ca. 750 cm^{-1}) and the aromatic ring bend (ca. 715 cm^{-1}).

Experimental

All reactions were carried out under dry nitrogen. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from $LiAlH_4$ before use.

The ^1H and ^{13}C NMR spectra were recorded on a JEOL-PS-100 NMR spectrometer, the ^{207}Pb NMR spectra on a Bruker WH 90 Multinuclear NMR spectrometer. A Model 580 Perkin Elmer Infrared spectrophotometer was used to record the infrared spectra.

Synthesis of 10,10-dimethylphenoxaplumbin II (i) and compound III

To a stirred solution of 10.0 g diphenylether (0.059 mol) in 45 ml THF and 59 ml Et_2O, which was cooled on an ice bath, was added 51.25 g of a 15% w/v solution of n-butyllithium in hexane (contains 0.12 mol n-BuLi). After the addition was complete, the orange-yellow solution was refluxed for 4 h. After cooling, the resulting red-brown solution was transferred to a dropping funnel and added to a stirred suspension of 23.4 g dimethyllead dibromide (0.059 Mol) [13] in 150 ml Et_2O at room temperature. The resulting mixture was stirred for 18 h and hydrolysed with 200 ml H_2O. After separation of the ether layer, the water layer was extracted with 100 ml Et_2O. The combined organic layers were dried over anhydrous $MgSO_4$. Filtration and distillation of the solvents left a yellow oil, to which 100 ml pentane was added. Cooling at —78°C during 2 h in a dry ice/alcohol bath resulted in the precipitation of a solid, which was isolated by filtration of the cold mixture. This procedure was repeated, giving a total yield of compound III of 0.25 g (1%). After recrystallisation from chloroform/ethanol the melting point was 242—244°C.

From the remaining filtrate the pentane was evacuated, the resulting yellow oil was transferred to a molecular pot still [14] and carefully degassed by means of an oil pump. At a pressure of 10^{-5} Torr the oil was slowly distilled. The following fractions were isolated (partly as mixtures): 3.82 g diphenylether (pot temperature ca. 80°C), 6.28 g 10,10-dimethylphenoxaplumbin II (26%; pot temperature ca. 120°C) and 5.40 g 2,2'-bis(trimethyllead)diphenylether IV (14%; pot temperature ca. 140°C).

When the dilithio compound I was added to the dimethyllead dibromide suspension at 0°C, a total yield of 2.23 g of compound III (9%) was isolated. From the remaining brown oil no further products could be isolated during the molecular distillation due to severe bumping.

Synthesis of 10,10-dimethylphenoxaplumbin II (ii)

A solution of 2,2'-dilithiodiphenylether I was prepared. After cooling at

0°C the stirred solution was diluted with 50 ml Et_2O and 35 ml THF, after which 32.8 g powdered $PbCl_2$ (0.118 mol) was added. The mixture immediately turned via yellow to orange-red, while a black precipitate of Pb was formed. The mixture was stirred at 0°C for 1 h and an excess of CH_3MgI, prepared from 28.4 g CH_3I (0.2 mol) and 4.86 g Mg (0.2 mol) in 150 ml Et_2O was added dropwise. After the addition was complete stirring was continued for 1 h at room temperature and the mixture was worked up. Molecular distillation afforded 5.0 g diphenylether and 5.1 g 10,10-dimethylphenoxaplumbin II (21%; n_D^{20} = 1.6069).

Synthesis of 2,2'-bis(trimethyllead)diphenylether IV

A solution of 2,2'-dilithiodiphenylether I was added dropwise to a stirred suspension of 39.9 g trimethyllead bromide [15], which was cooled on an ice bath. Stirring was continued for 18 h at room temperature, after which the mixture was worked up. Molecular distillation gave 4.8 g diphenylether and 14.5 g 2,2'-bis(trimethyllead)diphenylether IV (36%; n_D^{20} = 1.6258).

Acknowledgements

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