

SOME SPECTROSCOPIC PROPERTIES OF CYCLIC ORGANOLEAD COMPOUNDS I

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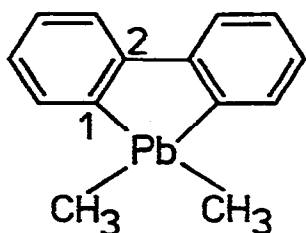
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ABSTRACT

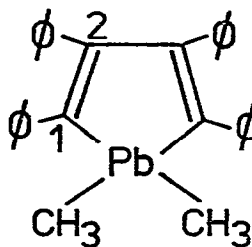
The nuclear magnetic resonance and infrared properties of two new cyclic organolead compounds are discussed.

INTRODUCTION

In recent years there has been a growing interest in the chemical and physical properties of cyclic Group IVA organometallics, but while much work has been done on such compounds of Si, Ge and Sn, there have been few studies of cyclic organolead compounds (1). We report here some spectroscopic investigations of two new compounds: 1,1-dimethyl-2,3,4,5-dibenzoplumbole (I) and 1,1-dimethyl-2,3,4,5-tetraphenylplumbole (II). Although the latter has been mentioned in a patent (2), nothing is known about its physical properties.



1,1-dimethyl-
2,3,4,5-dibenzoplumbole (I)



1,1-dimethyl-
2,3,4,5-tetraphenylplumbole (II)

RESULTS AND DISCUSSION

Nuclear magnetic resonance properties

Some $^1\text{H-NMR}$ data of the two cyclic lead compounds are listed in Table 1. Owing to the great number of magnetically inequivalent aromatic protons, the spectrum in the 6 to 8 ppm region is extremely complex. More information can be

TABLE 1

¹H-NMR data for cyclic dimethyllead compounds ^a.

	I	II	$\phi_2\text{Pb}(\text{CH}_3)_2$ ^b	$(\text{CH}_3)_4\text{Pb}$ ^b
$\delta(\text{CH}_3)$	1.22	1.26	1.09	0.74
$^2J(^{207}\text{Pb}-^1\text{H})$	75	66	65	61

^a δ in ppm (reference TMS), J in Hz; ^b see ref. (3).

obtained from the NMR data of the two methyl groups. It is readily seen from Table 1 that the resonances of the methyl protons in the cyclic compounds are shifted towards lower field compared with those in diphenyldimethyllead and tetramethyllead (3), indicating the deshielding effect of the two ring fragments. This cannot be solely attributed to the greater electronegativity of the ring fragments compared with the electronegativity of the phenyl groups in diphenyldimethyllead (vide infra). Steric factors may also be responsible.

It is now generally accepted (3-6) that the Fermi-contact term is the dominant factor in determining the magnitude of the M-X coupling constants. A simplified expression for this term is given by (1), in which C is a collection of constants,

$$J(\text{M-X}) = (C/\Delta) \cdot \alpha^2(\text{M}) \cdot \alpha^2(\text{X}) \cdot \psi^2(0)_{\text{ns}(\text{M})} \cdot \psi^2(0)_{\text{ns}(\text{X})} \quad (1)$$

Δ the mean excitation energy, α^2 the s-character of the hybrid orbital used to form the M-X bond and $\psi^2(0)_{\text{ns}}$ the valence s-electron density at the nucleus (3). It appears that the magnitude of $^2J(^{207}\text{Pb}-^1\text{H}(\text{CH}_3))$ depends on the nature of the ring fragment. The difference between the two coupling constants of the cyclic compounds indicates the greater electronegativity of the ring fragment of I compared with that of II.

The ¹³C-FT-NMR data (Table 2) support the conclusions from the ¹H-NMR spectra. The deshielding effect of the ring system in II is somewhat greater than that in I. The variation of the $J(^{207}\text{Pb}-^{13}\text{C})$ coupling constants is very interesting. In contrast with $^2J(^{207}\text{Pb}-^1\text{H})$, there is a great difference between $^1J(^{207}\text{Pb}-^{13}\text{C}(\text{CH}_3))$ for I and II, the coupling constant for the latter being even smaller than that in tetramethyllead (3). Along with a difference in the effective nuclear charge on the lead atom, which is related to $\psi^2(0)_{6s(\text{Pb})}$, there may be a substantial change in the hybridisation of the lead atom from the ideal sp^3 -case as in tetramethyllead, which affects $\alpha^2(\text{Pb})$ of the Fermi-contact term. This change may be attributed to internal strain in the plumbacyclopentadiene ring.

TABLE 2

¹³C-NMR data for cyclic dimethyllead compounds ^a.

compound	$\delta(C_1)$ [¹ J(²⁰⁷ Pb- ¹³ C ₁)]	$\delta(C_2)$ [² J(²⁰⁷ Pb- ¹³ C ₂)]	$\delta[C(CH_3)]$ [¹ J(²⁰⁷ Pb- ¹³ C(CH ₃))]
I	149.3 [344]	148.6 [107]	1.6 [300]
II	153.6 (290)	152.3 (146)	4.6 (222)
$\Phi_2Pb(CH_3)_2$ ^b			-1.0 (295)
$(CH_3)_4Pb$ ^b			-3.2 (251)

^a δ in ppm (reference TMS), J in Hz (in parentheses); ^b see ref. (3).

TABLE 3

Infrared data for cyclic dimethyllead compounds ^a.

I	II	$(CH_3)_4Pb$ ^b	assignment
1580 s	1595 s		} $\nu(C=C)$
	1570 m		
1465 m	1490 s		
1440 s	1445 s	1448 vs	} $\beta(C-H)$
1395 m	1390 m	1400 s	
1170 s	1163 m	1166 sh	
1157 s	1153 m	1148 s	
	1073 m		
	1025 m		
754 vs	764 s	765 vs	4H wag
749 vs			
	710 vs		} $\phi(C-C)$
	700 vs		
491 s	483 m	485 vs	$\nu_{asym}(Pb-C)$
474 s	471 m	478 vs	} $\nu_{sym}(Pb-C)$
		470 vs	

^a Nujol mulls / KBr discs; ^b see ref. (7).

The coupling constants $J(^{207}\text{Pb}-^{13}\text{C})$ for the ring carbon atoms have also been determined. As can be seen from Table 2, $^1J(^{207}\text{Pb}-^{13}\text{C}_1(\text{ring}))$ in I is greater than in II, while this sequence is reversed for $^2J(^{207}\text{Pb}-^{13}\text{C}_2(\text{ring}))$. It is clear that this behaviour must be explained in terms of the two factors $\alpha^2(X)$ and $\psi^2(O)_{ns(X)}$ of the Fermi-contact term. Because of the differing substituents on the plumbacyclopentadiene ring, these factors obviously differ between the two cyclic lead compounds.*

Infrared spectroscopy

Some IR absorptions are presented in Table 3. The spectra of these cyclic compounds consist of two fairly independent regions: one section arising from the two methyl substituents on the lead atom, which can be compared with the IR spectrum of tetramethyllead (7), and the other section arising from the remaining ring fragment. There is a close agreement between the wave numbers of the absorptions which are attributed to the methyl substituents for the two cyclic lead compounds, and this agreement also holds for the tetramethyllead absorptions. Of the other absorptions there are some which appear to be characteristic for classes of cyclic organolead compounds (8). Thus, all dibenzoplumboles show an absorption at about 750 cm^{-1} , due to the 4H wag of the two benzo substituents (9), while the tetraphenylplumboles characteristically absorb at about 1075 and 1025 cm^{-1} , associated with $\delta(\text{C-H})$ of the monosubstituted phenyl groups, and at about 700 cm^{-1} , associated with the out of plane ring bend of the phenyl groups (see also (10)).

EXPERIMENTAL

The NMR spectra were recorded on a JEOL-PS-100 NMR spectrometer as saturated CDCl_3 solutions. The IR spectra were recorded on a UNICAM-SP-1200 infrared spectrophotometer.

The reactions were carried out under dried, oxygen-free nitrogen. Diethyl ether and tetrahydrofuran were distilled from LiAlH_4 before use.

Synthesis of 1,1-dimethyl-2,3,4,5-dibenzoplumbole (I) (11)

6.24 g of 2,2'-dibromobiphenyl (0.02 Mol) was lithiated in 300 ml diethyl ether with n-butyllithium (0.04 Mol). The solution of the dilithio compound was slowly added to a stirred suspension of 7.94 g of dimethyllead dibromide (0.02 Mol) in 300 ml diethyl ether, while the flask was cooled in an ice bath. After the addition was complete, the mixture was stirred for 1 h at room temperature and for 0.5 h at reflux temperature.

The mixture was hydrolysed with 300 ml 5% HCl , the ether layer was separated

*: Further studies on the interpretation of the NMR properties of series of organolead compounds are being carried out.

and the water layer was hydrolysed with two 50 ml portions of diethyl ether. The combined ether layers were dried over Na_2SO_4 . Distillation of the diethyl ether left a yellow oil, and addition of 100 ml light petroleum (b.p. $40-60^\circ\text{C}$) gave the white product I. The yield was 4.05 gram (52%). After recrystallisation from chloroform/ethanol the m.p. was $142-143^\circ\text{C}$ (dec.).

Synthesis of 1,1-dimethyl-2,3,4,5-tetraphenylplumbola (II) [12]

10.69 g of diphenylacetylene (0.06 Mol) was stirred for 4 h in 30 ml of diethyl ether with 0.7 g (0.1 Mol) freshly cut lithium wire. A red solution was formed and a yellow solid precipitated. The slurry was rapidly added through a Büchner funnel to a stirred suspension of 11.91 g of dimethyllead dibromide (0.03 Mol) in 200 ml tetrahydrofuran. An additional 100 ml diethyl ether was used to transfer the dilithio compound to the suspension, which was cooled in an ice bath during the addition. The mixture was stirred for 2 h at room temperature, after which the ether layers were distilled off. Dichloromethane (250 ml) was added to the residue, and the resulting suspension was filtered through Hyflo. After concentration to about 50 ml, 100 ml absolute ethanol was added, whereupon the yellow product (II) crystallised. The yield was 12.50 gram (70%). Recrystallisation from dichloromethane/absolute ethanol resulted in a m.p. of $195-197^\circ\text{C}$ (dec.).

Both compounds are crystalline solids with remarkably high melting points. In contrast to saturated cyclic lead compounds [1], they are stable towards oxygen, light and moisture.

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