

COMPLEXES OF ORGANOMETALLIC COMPOUNDS XXV. STUDIES ON FIVE-COORDINATED DIORGANOLEAD(IV)

ROSARIO BOSCO AND ROSALBA CEFALÙ

Istituto di Chimica Generale ed Inorganica, Università di Palermo, 90123 Palermo (Italia)

(Received July 27th, 1970)

SUMMARY

A number of novel compounds of dimethyllead(IV) and diphenyllead(IV) moieties with ligands having a rigid geometry when coordinating, have been prepared and characterized.

The goal of the work was the building of model molecules for five-coordinated R_2Pb^{IV} , with known configuration of the C–Pb–C skeleton. From spectroscopic data it is inferred that the complexes under investigation have a distorted bipyramidal trigonal structure, with the C–Pb–C moiety allocated in the trigonal plane.

The configuration of the C–Pb–C moiety in five- and six-coordinated complexes of R_2Pb^{IV} with mono- and bidentate ligands cannot be straightforwardly assigned, there being (on principle) the possibility of a linear (*trans*) or bent (*cis*) structure. This alternative should not exist, at least as a prediction, in complexes of R_2Pb^{IV} with coordinating ligands having a rigid geometry such as the "planar" tridentate and tetradentate bases¹. We planned to investigate complexes of this type, in order to study model compounds containing five- and six-coordinated R_2Pb^{IV} with an unambiguous C–Pb–C skeletal configuration.

In this paper we report the synthesis of several new complexes R_2PbL ($R = Me$ or Ph ; L^{2-} = the dianion of "planar" tridentate ligands, with ONO and SNO donor atoms^{1,2}), and the related structural spectroscopic investigations.

The following "planar" ligands, H_2L , employed for the preparation of R_2PbL compounds, were used: 4-(2-benzothiazolinyl)-2-pentanone², from 2,4-pentanedione and *o*-aminomercaptobenzene, SNO donor atoms in the L^{2-} form, indicated in the following as H_2AAT ; 3-(*o*-hydroxyphenylamino) crotonophenone², from benzoylacetone and *o*-aminophenol, ONO, H_2BAH ; 2-(*o*-hydroxyphenyl)benzothiazoline², from salicylaldehyde and *o*-aminomercaptobenzene, SNO, H_2SAT ; 2,2'-methylidynenitrilodiphenol², from salicylaldehyde and *o*-aminophenol, ONO, H_2SAB .

The preparation of R_2PbL was performed as follows. A solution of the ligand (5 mmole in 15 ml of dry methanol) was mixed with sodium methoxide (10 mmole of Na in 4 ml of dry methanol). The resulting solution, containing the dianion ligand in form of the Schiff base², was added to a solution of R_2PbCl_2 (5 mmole in 15–25 ml of dry methanol). Immediate precipitation of the complex occurred; the crystals were

filtered off, washed and dried under vacuum. Incidental precipitation of sodium chloride occurred only after partial evaporation of the mother liquor. Attempts to prepare Me_2PbL with the SNO ligands were unsuccessful.

TABLE 1
ANALYTICAL DATA

Compound (colour)	M.p. (°C)	C (%) found (calcd.)	H (%) found (calcd.)	O (%) found (calcd.)	N (%) found (calcd.)	Pb (%) found (calcd.)	Mol.wt. found (calcd.)
$\text{Ph}_2\text{PbAAT}^a$ (yellow)	157–160	48.56 (48.74)	3.70 (3.73)	2.94 (2.82)	2.63 (2.47)	36.51 (36.56)	574 (566.698)
Me_2PbBAH (orange red)	193–195	44.33 (44.25)	4.15 (3.92)	6.74 (6.55)	3.10 (2.87)	42.11 (42.41)	^c
Ph_3PbBAH (orange yellow)	98–100	53.81 (54.88)	4.09 (3.78)	5.73 (5.22)	2.23 (2.29)	34.29 (33.82)	616 (612.704)
$\text{Ph}_2\text{PbSAT}^b$ (orange yellow)	179–180	50.70 (51.00)	3.09 (3.25)	2.77 (2.72)	2.46 (2.38)	34.90 (35.20)	596 (588.702)
Me_2PbSAB (orange yellow)	260 ^o (subl.)	40.12 (40.17)	3.32 (3.37)	7.21 (7.13)	3.20 (3.12)	46.30 (46.20)	454 (448.490)
Ph_2PbSAB (orange yellow)	232–235	52.27 (52.44)	3.51 (3.34)	5.51 (5.59)	2.31 (2.44)	36.15 (36.19)	576 (572.622)

^a S found 5.73, calcd. 5.66%. ^b S found 5.79, calcd. 5.44%. ^c Not taken owing to low solubility.

Analytical data, melting points and molecular weights of the compounds prepared are listed in Table 1. The molecular weights were measured in acetone solution at 25° by a vapor pressure osmometer Mechrolab 301 A, and the melting points by a Leitz hot plate 350 microscope. The vibrational spectra were taken on nujol and hexachlorobutadiene mulls by a Perkin-Elmer Mod. 457 spectrometer. The electronic spectra were measured at 25° using Beckman DK 2A and DU spectrometers with 1 cm optical path cells and dry methanol as solvent. All the compounds obey Beer's law at all wavelengths, except Me_2PbBAH , which clearly decomposes on dilution. The results are listed in Table 2. The PMR spectra were recorded at 25° on a

TABLE 2
ELECTRONIC ABSORPTION SPECTRA OF DIORGANOLEAD(IV) COMPLEXES IN METHANOL SOLUTIONS
Wavelengths [λ (nm)] and absorptivities [a ($M^{-1}\cdot\text{cm}^2$)] refer to the band maxima and shoulders (sh).

Compound	λ	log a	λ	log a	λ	log a
Ph_2PbAAT	288	3.91	365	4.03		
Ph_2PbBAH	250	4.22	342	3.91	410	4.16
Ph_2PbSAT	241	4.47	286	4.30	306(sh)	4.12
	413	4.91				
Me_2PbSAB	246	4.26	283	3.96	305(sh)	3.86
	321(sh)	3.78	423*	4.16	429	4.13
Ph_2PbSAB	249	4.29	290	4.01		

JEOL C 60 spectrometer operating at 60 MHz using saturated CDCl_3 solutions with TMS as internal standard. The data obtained on compounds showing sufficient solubility are listed in Table 3.

TABLE 3

PMR SPECTRA OF DIORGANOLEAD(IV) COMPLEXES

Solvent CDCl_3 , $\delta(\text{TMS})$ 0

	(Pb)CH ₃ δ (ppm)	(C)CH ₃ δ (ppm)	(C)H δ (ppm)	Arom. δ (ppm)	$J(^{207}\text{PbCH})$ (Hz)
Ph ₂ PbAAT		2.05	5.05 ^a	6.6–8.0	
Me ₂ PbBAH	2.00	2.34	5.68 ^a	6.5–7.8	120
Ph ₂ PbBAH		2.32	5.67 ^a	6.2–8.0	
Ph ₂ PbSAT			8.12 ^b	6.3–8.0	
Me ₂ PbSAB	2.05		8.20 ^b	6.3–7.3	132
Ph ₂ PbSAB			8.25 ^b	6.2–8.0	

^a Vinyl signal. ^b Formimidoyl signal.

In the solid state, R_2PbL species appear to be stable and non-hygroscopic, which is a remarkable feature for compounds of the type $\text{Me}_2\text{Pb}^{\text{IV}}$. In fact $\text{Me}_2\text{PbHal}_2$ compounds undergo rapid photodecomposition³. The formation of complexes with the chelating agents here employed appears to stabilize the organometallic moiety.

The vibrational spectra of R_2PbL essentially coincide with those of R_2SnL^2 , apart from the bands characteristic for the $\text{R}_2\text{M}^{\text{IV}}$ moieties. For example, the spectra of Ph_2PbL possess a band around 440 cm^{-1} , which is associated with a Pb–Ph mode^{4,5}. The following more interesting features are discussed. Readers are referred to ref. 2 for a more comprehensive discussion.

The vibrational spectrum of Ph_2PbAAT does not show any band attributable to N–H and C=O stretching frequencies, which are present in the spectrum of H_2AAT^2 , while a band in the range $1580\text{--}1480\text{ cm}^{-1}$ appears, which can be ascribed to stretching vibrations of the C=N, C=C and C=O groups in the chelating AAT^{2-} . The vibrational spectra of R_2PbBAH and H_2BAH^2 are fundamentally alike, except for the disappearance of the band at 3050 cm^{-1} present in H_2BAH and ascribed to H-bonded groups². The stretching modes $\nu_s(\text{PbC}_2)$ and $\nu_{\text{as}}(\text{PbC}_2)$, which should occur in the $465\text{--}535\text{ cm}^{-1}$ region^{6,7,8}, could not be identified in the spectrum of Me_2PbBAH , owing to the presence in that frequency range of several bands of the free ligand². The IR spectra of the complexes Ph_2PbSAT and R_2PbSAB are similar, which suggests strictly related configurations of the coordinated ligands. The band ascribed to the N–H stretching frequency and those bands associated with the thiazoline ring vibrations in H_2SAT , as well as the bands ascribed to H-bonded groups in H_2SAT and H_2SAB^2 , disappear in the spectra of Ph_2PbSAT and R_2PbSAB . The stretching vibration $\nu(\text{C=N})$, occurring at 1630 cm^{-1} in H_2SAB^2 , is shifted to 1605 cm^{-1} in R_2PbSAB , so that one may infer that the band at 1605 cm^{-1} found in the Ph_2PbSAT spectrum is associated with the coordinated C=N group. In the lower frequency range the spectra of the complexes are similar². Again, owing to the complexity of the spectra, it was impossible to identify any $\nu(\text{PbC}_2)$ vibration concerning Me_2PbSAB .

It may be reasonably concluded that, at the solid state, R_2PbL compounds

contain a chelating ligand L^{2-} , so that the Pb^{IV} atom would be five-coordinate.

As far as the complexes in solution are concerned, inspection of their electronic spectra shows the appearance of bands at longer wavelengths (Table 2) in comparison with the bands displayed by the spectra of the free ligands². This feature demonstrates that chelation has taken place². The formation of chelate compounds accounts for our PMR spectroscopic data (Table 3). The Ph_2PbAAT spectrum does not show any signal at 4.90δ and $3.05\text{--}3.27 \delta$ [assigned respectively to (N)H and methylene protons in H_2AAT^2], while a new signal appears at 5.05δ which can be ascribed to a vinyl hydrogen². The spectra of R_2PbBAH no longer show the signal at 12.3δ assigned to (N)H or (O)H in H_2BAH^2 . These data demonstrates that R_2PbL species occur in solution.

The coupling constants $J(^{207}PbCH)$ for the compounds Me_2PbBAH and Me_2PbSAB (Table 3) can be used to advance hypotheses on the structure of the CPbC skeleton in solution. A linear relationship between J and percentage s character of the metal orbitals involved in the metal-carbon bonds, such as that concerning organotin(IV) compounds⁹, does not exist for organolead(IV)^{10,11} compounds. Inspection of $J(^{207}PbCH)$ for several organolead(IV) compounds^{6,11-13} shows that it is a function of the molecular configuration, having values around 70 Hz for tetrahedral species, and around 150 Hz for hexacoordinated species. Moreover, the J value of a given derivative, e.g. Me_3PbCl , appears to increase as the donor character of the solvent increases, probably because of the increased tendency to form penta-coordinated solvated species. The $J(^{207}PbCH)$ values for Me_2PbL reported in Table 3 are intermediate between those discussed above. It may therefore be reasonably assumed that the CPbC skeleton is bent in Me_2PbL .

In conclusion we advance a (quasi) trigonal bipyramidal structure for R_2PbL , where the bent CPbC moiety is allocated to the trigonal plane, analogous to the structure assumed for R_2SnL^2 .

ACKNOWLEDGEMENTS

The authors wish to acknowledge financial support from NATO (Grant No. 301) and from Consiglio Nazionale delle Ricerche (Roma).

REFERENCES

- 1 H. A. GOODWIN, in F. P. DWYER AND D. P. MELLOR (Eds.), *Chelating Agents and Metal Chelates*, Academic Press, New York, 1964, p. 143.
- 2 R. CEFALÙ, R. BOSCO, F. BONATI, F. MAGGIO AND R. BARBIERI, *Z. Anorg. Allg. Chem.*, 376 (1970) 180, and references therein.
- 3 G. GRUTTNER AND E. KRAUSE, *Ber. Deut. Chem. Ges.*, 49 (1916) 1415.
- 4 R. J. H. CLARK, A. G. DAVIES AND R. J. PUDDEPHATT, *Inorg. Chem.*, 8 (1969) 457.
- 5 A. L. SMITH, *Spectrochim. Acta, Part A*, 24 (1968) 695.
- 6 G. D. SHIER AND R. S. DRAGO, *J. Organometal. Chem.*, 6 (1966) 359.
- 7 R. J. H. CLARK, A. G. DAVIES AND R. J. PUDDEPHATT, *J. Amer. Chem. Soc.*, 90 (1968) 6923.
- 8 T. TANAKA, *Organometal. Chem. Rev., Sect. A*, 5 (1970) 1.
- 9 J. R. HOLMES AND H. D. KAESZ, *J. Amer. Chem. Soc.*, 83 (1961) 3909.
- 10 G. SINGH, *J. Organometal. Chem.*, 11 (1968) 133.
- 11 Y. KAWASAKI, *J. Organometal. Chem.*, 9 (1967) 549.
- 12 W. KITCHING AND V. G. KUMAR DAS, *Aust. J. Chem.*, 21 (1968) 2401.
- 13 V. G. KUMAR DAS AND W. KITCHING, *J. Organometal. Chem.*, 13 (1968) 523.