Journal of Organometallic Chemistry, 82 (1974) 155—158

COMPLEXES OF ORGANOMETALLIC COMPOUNDS

XLII. SPECTROSCOPIC STUDIES OF *N,N'*-ETHYLENEBIS(ACETYLACETONEIMINE) AND *N,N'*-ETHYLENEBIS(SALICYLIDENEIMINE) ADDUCTS OF ORGANOLEAD(IV) AND ORGANOTHALLIUM(III)

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(Received June 27th, 1974)

Summary

The nature of the 1/1 adducts formed from the ligands *N,N'*-ethylenebis(acetylacetoneimine) and *N,N'*-ethylenebis(salicylideneimine) with Ph_2PbCl_2 and $PhTlCl_2$ was investigated in the solid state and in methanol solution by IR, electronic and PMR spectroscopy, and by osmometry and conductivity. The adducts exist only in the solid state and dissociate fully into the parent compounds in solution. Polymeric structures are proposed for the solids, in which bis-monodentate ligands bridge the organometallic moieties.

Introduction

It has recently been determined that the potentially tetradentate ligands *N,N'*-ethylenebis(acetylacetoneimine) (H_2Acen) and *N,N'*-ethylenebis(salicylideneimine) (H_2Salen) form 1/1 adducts with metal ions as well as organometallic salts, where the ligand very probably acts as a neutral bridging bis-monodentate base, producing solid state polymers which are fully dissociated in solution (monomeric species, with the ligand behaving in a bidentate manner, were also advanced) [1-7]. Solid derivatives of this type, formed by Ph_2PbCl_2 and $PhTlCl_2$ with H_2Acen, have already been reported [4]. The interaction of the latter organometallics with H_2Acen and H_2Salen was further investigated in the solid state and in solution by IR, electronic and PMR spectroscopy, as well as by osmometry and conductivity, in order to enlarge our knowledge of this new class of compound, and these studies are reported in the present paper.

Experimental

Throughout this work analytical grade reagents and solvents were used and were purified and/or dried, when needed, following standard procedures. The com-

TABLE 1

PMR SPECTRA OF H_2Acen, H_2Salen AND THEIR DIPHENYLLEAD(IV) AND MONOPHENYLTHALLIUM(III) DICHLORIDE ADDUCTS

$T = 25^{\circ}$; δ in ppm; δ (TMS) = 0 ppm; solvent CD_3OD

Compound	$C(CH_3)$	$-CH_2-$	$-CH$	Aromatic
H_2Acen	1.93	3.48	5.00	7.30-8.25
$Ph_2PbCl_2 \cdot H_2$Acen	1 90	3.45	4.98	7.30-8.25
$PhTlCl_2 \cdot H_2$Acen [a]	1.92, 1.98	3.73, 3.43, 3.40	5.01	7.10-7.70
$PhTlCl_2 \cdot H_2$Acen	1.93	3.43	4.90	7.50-8.50
H_2Salen		3.90	8.43	6.50-7.60
$Ph_2PbCl_2 \cdot H_2$Salen		3.92	8.43	6.50-7.60

[a] Solvent $CDCl_3$, at 100 MHz with a Varian XL-100 instrument.

pound Ph_2PbCl_2 was a gift from DAP, Marienberg (Germany), while the ligands H_2Acen and H_2Salen and the adducts of Ph_2PbCl_2 and $PhTlCl_2$ with H_2Acen were obtained as previously described [1, 8-10].

The compound $Ph_2PbCl_2 \cdot H_2$Salen was prepared by mixing methanol solutions of Ph_2PbCl_2 and H_2Salen (2mmol in 100 ml) at room temperature. A crystalline solid was obtained, m.p. 220° (dec.). (Found: C, 48.10; H, 3.63; Cl, 10.14; N, 3.91; O, 4.62; Pb, 29.80. $C_{28}H_{26}Cl_2N_2O_2Pb$ calcd.: C, 48.14; H, 3.46; Cl, 10.15; N, 4.01; O, 4.58; Pb, 29.66%.) Despite many attempts we did not succeed in preparing the $PhTlCl_2 \cdot H_2$Salen adduct in either polar or non-polar organic solvents.

Infrared spectra were recorded with a Perkin—Elmer model 457 spectrometer, in the 4000-250 cm^{-1} region, on Nujol and hexachlorobutadiene mulls between CsI windows. Electronic spectra were measured with a Beckman DK-2A

TABLE 2

OSMOMETRIC (37°) AND CONDUCTOMETRIC (25°) DATA FOR ORGANOMETALLIC DICHLORIDES AND THEIR H_2Acen AND H_2Salen ADDUCTS IN METHANOL SOLUTION

Compound	i [a]	M ($\times 10^3$)	Λ_M ($Ohm^{-1} cm^2 mol^{-1}$)	M ($\times 10^5$)
$PhTlCl_2$	[b]		27.1	287
			74.0	28.7
			299.0	2.87
$PhTlCl_2 \cdot H_2$Acen	[b]		26.5	340
			74.7	34
			271.0	3.4
Ph_2PbCl_2	1.87	4 70	13.1	320
	1.26	5.98	52.0	32
	0.83	7.38	269.0	3.2
$Ph_2PbCl_2 \cdot H_2$Acen	2.12	5.10	10.7	428
	2.02	6.60	50.0	42.8
	2.12	9.45	201.0	4.28
$Ph_2PbCl_2 \cdot H_2$Salen	[b]		51.7	92.2
			217.0	9.22

[a] Van 't Hoff factor [b] Not determined owing to low solubility in CH_3OH.

spectrophotometer at 25° in anhydrous methanol (the solute concentrations ranging between 1×10^{-5} and $3 \times 10^{-5}\,M$), 10 mm optical path cells. PMR spectra were taken in nearly saturated CD_3OD solutions at room temperature with TMS as the internal standard, using Jeol C60 and Varian XL-100 spectrometers. The results are reported in Table 1. Osmometric data were obtained at 37° using a Mechrolab 301A vapor pressure osmometer, and molar conductivity values at 25° using an LKB 5300 B conductolyzer. Both sets of data relate to anhydrous methanol solutions and are summarized in Table 2.

Discussion

The IR spectra of the solids $Ph_2PbCl_2 \cdot H_2Acen$, $PhTlCl_2 \cdot H_2Acen$ and $Ph_2PbCl_2 \cdot H_2Salen$ show broad bands around 3000 cm^{-1} [ν(OH), or ν(NH)] and at 1600-1480 cm^{-1} [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$, $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$] which correspond strictly to analogous bands exhibited by organotin(IV) adducts and suggest the retention of the free ligand configuration with intramolecular OH···N bonding also in these compounds [1, 5-7]. Some of the most intense monosubstituted phenyl bands were observed (in Ph_2Pb^{IV} and $PhTl^{III}$), while metal—ligand and metal—chloride vibrations were not identified, owing to the complexity of the spectra and the fact that some of these modes may well occur below 250 cm^{-1} [11-14].

As far as the solution phase is concerned, the electronic spectra in anhydrous methanol of H_2Acen adducts show two band maxima at 304 nm (log a 4.53) (a = absorptivity M^{-1} cm^2) and at 322 nm (log a 4.55), while those of H_2Salen exhibit two band maxima at 317 nm (log a 3.98) and 405 nm (log a 3.18), which correspond essentially to those of the free ligands, agreeing with findings concerning organotin(IV) adducts [2, 5]. Analogous results were obtained for benzene solutions. Rigorously anhydrous solvents must be employed in measuring the spectra of H_2Salen and its adduct because hydrolytic cleavage of the C=N bond [15] of H_2Salen occurs readily in aqueous media.

The PMR spectra of H_2Acen and H_2Salen adducts in CD_3OD solutions (Table 1) do not significantly differ from those of free H_2Acen [16] and H_2Salen, which is again consistent with previous reports [2, 5] on the presence of uncoordinated ligands, with their usual H-bonded configurations, in solutions of this type of compound. Complete dissociation into the ligand and the organometallic moiety is also strongly indicated by molar conductivities and Van 't Hoff "i" factors of the organometal dichlorides and their H_2Acen and H_2Salen adducts.

It is concluded that the compounds considered here behave essentially like the related organotin(IV) derivatives; in particular, they occur only in the solid state, where they very likely assume polymeric configurations similar to those of $Me_2SnCl_2 \cdot H_2Salen$ [6, 7], $R_nSnHal_{4-n} \cdot H_2Acen$ and $\cdot H_2Salen$ [1, 6], with the metal atom probably six- and five-coordinated in the Ph_2Pb^{IV} and $PhTl^{III}$ derivatives, respectively.

Acknowledgements

Financial support by CNR (Roma) is gratefully acknowledged.

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