SYNTHESIS AND STRUCTURAL STUDIES ON FOUR- AND SIX-COORDINATED COMPLEXES OF (BUTYL/ETHYL)PHENYLTIN DICHLORIDES WITH ALKYL PYRUVATE AROYLHYDRAZONES

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Abstract

The synthesis and spectroscopic characterization of 4-and 6-coordinated diorganotin(IV) complexes of the type $RPhSn(L)_nCl_{2-n}$ where R = butyl or ethyl, n = 1 or 2, LH = methyl pyruvate benzoylhydrazone (MPBHyH), ethyl pyruvate benzoylhydrazone (EPBHyH), methyl pyruvate nicotinoylhydrazone (MPNHyH), ethyl pyruvate nicotinoylhydrazone (EPNHyH), methyl pyruvate isonicotinoylhydrazone (MPINHyH) and ethyl pyruvate isonicotinoylhydrazone (EPINHyH) are described.

Introduction

Organotin compounds have very good biocidal and pesticidal properties while their toxicity towards mammals is tolerable.¹ As a result, they have been put to a wide range of technical applications.^{2,4} Though a number of symmetrical organotin halides and their derivatives have been synthesised, very little attention has been paid to the study of unsymmetrical organotin compounds.^{5,7} As a part of our study on the synthesis and coordination mode in unsymmetrical organotin derivatives, we undertook a study of the reactions of $EtPhSnCl_2$ and $BuPhSnCl_2$ with alkyl pyruvate aroylhydrazones and found that whereas the ligands behaved as bidentate in ethylphenyltin complexes, they acted as monodentate in butylphenyltin complexes. The structure of alkyl pyruvate aroylhydrazones used is as follows.

where Ar = C_6H_5 , 3- NC_5H_4 , 4- NC_5H_4 and $R^1 = CH_3$, C_2H_5

Experimental

All manipulations were carried out in an inert atmosphere on vacuum lines using Schlenk tubes technique. Tetraethyltin (Aldrich), phenyltin trichloride (Aldrich) and butyltin trichloride (Aldrich) were used as such. Tin and chloride were estimated as described elsewhere.⁸ All the solvents were dried and distilled by reported methods. IR spectra were recorded in the range 4000-200 cm^{-1} on Perkin-Elmer 842 and Perkin-Elmer 631 spectrophotometer. 1H NMR spectra were recorded on Perkin-Elmer R-32, 90MHz spectrometer. ^{13}C NMR and ^{119}Sn NMR spectra were recorded on a Bruker 300 MHz instrument using TMS and Me_4Sn as standards respectively.

Synthesis

Ethylphenyltin dichloride was prepared by literature method.⁹ However, butylphenyltin dichloride was prepared by analogously to ethylphenyltin dichloride. Alkyl pyruvate aroylhydrazones were prepared by the condensation of the corresponding alkyl pyruvate with aroylhydrazine in equimolar ratios.¹⁰ The purity of these compounds was checked by elemental analysis, infrared, 1H , ^{13}C and ^{119}Sn NMR (in case of $BuPhSnCl_2$ and $EtPhSnCl_2$) spectral data.

Syntheses of Complexes

The syntheses of the complexes of $EtPhSnCl_2$ and $BuPhSnCl_2$ with alkyl pyruvate aroylhydrazones involved mixing of the reactants in tetrahydrofuran in the presence of triethylamine at room temperature. The mixture was stirred for 4-6h and the precipitate of $(C_2H_5)_3N.HCl$ so formed was filtered off and weighed to check the completion of the reaction. The solvent was removed in vacuo and the resulting product was recrystallised with THF/Hexane mixture and recrystallised product was washed with hexane. Satisfactory C, H, N, Sn and Cl elemental analysis have been obtained for all the complexes. Data are available from the authors upon request.

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Results and Discussion

The Reactions of $RPhSnCl_2$ ($R = Bu$ or Et) with alkyl pyruvate aroylhydrazones in 1:1 and 1:2 molar ratios in dry THF in the presence of triethylamine are represented by the following general equations (where L represents the anion of corresponding alkyl pyruvate aroylhydrazone):

The complexes formed from butylphenyltin dichloride are viscous liquids while those from ethylphenyltin dichloride are solids. The complexes of ethylphenyltin dichloride are recrystallised from THF/hexane mixture. All the complexes are yellow and sensitive to hydrolysis. They are soluble in THF, DMSO, $CHCl_3$, DMF and acetone but insoluble in heptane, hexane and petroleum ether.

Spectral data

The IR spectra of the ligands reveal medium to strong intensity bands in the range $3280-3160\text{ cm}^{-1}$ which is due to ν (N-H). Strong bands in the range $1715-1710$, $1670-1665$, $1540-1535\text{ cm}^{-1}$ are assigned to ν (C=O) ester. ν (C=O) amide I, $[\nu$ (CN) + δ (NH)] amide II respectively.¹¹

The IR spectra of the complexes of $EtPhSnCl_2$ show no band in the range $3280-3160\text{ cm}^{-1}$ indicating that the -NH group has been deprotonated. The bands appearing at 1670 and 1540 cm^{-1} assignable to amide I and amide II respectively in the ligands are found to be absent in the complexes; instead a medium band at 1660 cm^{-1} appears which is due to ν (C=N) group which seems to have its origin in the conjugate system $>C=N-N=C<$.¹² Further, the observation of a band at 1710 cm^{-1} due to ν (C=O) suggests, non coordination of one of the carbonyl group (Table-1). A shift of 20 cm^{-1} is observed for amide II due to coordination through the azomethine nitrogen thereby suggesting the bidentate nature of the ligand. The bands between 540 and 420 cm^{-1} are due to ν (Sn-C) and ν (Sn-O) vibrations.¹³

The IR spectra of complexes of butylphenyltin dichloride also show the absence of the band in the range $3280-3160\text{ cm}^{-1}$ indicating deprotonation of the ligand. The strong band observed at 1720 cm^{-1} is due to ν (C=O). The band due to $>C=N-N=C<$ (observed at 1660 cm^{-1} in the complexes of $EtPhSnCl_2$) is not observed which suggests that both carbonyl groups are free and deprotonation is taking place through -NH having unidentate coordination. This has also been confirmed from ^{119}Sn NMR.

The ν (Sn-Cl) band in the case of the 1:1 derivatives of $EtPhSnCl_2$ as well as $BuPhSnCl_2$ show a slight upward shift of $10-20\text{ cm}^{-1}$ and is observed in the region $340-330\text{ cm}^{-1}$ indicating the coordination of the ligand.¹⁴ The bands due to phenyl, ethyl and butyl group appear at their usual positions.

The ^1H NMR spectra of the ligands show a broad singlet at δ 10.8-10.7 due to -NH protons. The phenyl group protons appear as a complex pattern in the range δ 8.1-7.2 in the alkyl pyruvate benzoylhydrazone while the protons of the pyridine moiety appear as complex pattern in the range δ 9.2-7.2 in the case of nicotinoylhydrazone, whereas in the case of isonicotinoylhydrazones, two doublets having equal coupling constants were observed at δ 8.7 and δ 7.8 assigned, to H_e and H_f protons respectively of the pyridine moiety of isonicotinoylhydrazones. The methyl protons attached to the azomethine group are observed as a singlet at δ 2.3-2.2. The methyl protons of the methoxy group of the methyl pyruvate aroylhydrazones appear as a singlet at δ 3.9-3.8 while the ethyl protons of the ethoxy groups of the ethyl pyruvate aroylhydrazones show a quartet and a triplet at δ 4.2 and δ 1.3 respectively.

In the ^1H NMR spectra of the complexes, the absence of a band at δ 10.8 shows that the -NH group has been deprotonated. The other protons appear at their usual positions without any significant shift (Table 1).

^{13}C NMR proton decoupled spectra of the complexes show resonances of the aliphatic and aromatic carbon regions as expected. In the free ligand methyl pyruvate aroylhydrazone, the vinyl methyl carbon appears at δ 12.85 while the methoxy carbon resonates at δ 52.05. The aromatic and olefinic carbons absorb at δ 164.76, δ 132.98, δ 128.36 and δ 127.82.¹⁵ The signals in the complexes were very near to the values of ligands. In the spectra of the complexes of $EtPhSnCl_2$, there are two sets of signals for the carbonyl carbons (δ 150.7, δ 145.7). This suggests that the complexes probably exist as a mixture of two forms (a,b) as shown below (Fig. 1).¹⁶ Similar effect is also observed in complexes of ethyl pyruvate aroylhydrazones.

Table-1: Spectral Data of Alkyl Pyruvate Aroylhydrazone Derivatives of EtPhSnCl₂ and BuPhSnCl₂

Complex	IR(cm ⁻¹)		¹ H NMR δ (ppm)			¹¹⁹ Sn NMR δ (ppm)
	ν(C=O)	ν(C=N)	Aryl	-OOC-R	-CH ₃ of azomethine	
PhEtSnCl(MPBHy)	1710s	1660s	8.1-7.4m	3.7s	2.3s	-339.1
PhEtSn(MPBHy) ₂	1710s	1660s	8.1-7.4m	3.7s	2.3s	-340.3
PhEtSnCl(EPBHy)	1705s	1660s	7.9-7.2m	4.1q ^a , 1.2t ^e	2.2s	-339.6
PhEtSn(EPBHy) ₂	1710s	1665s	8.0-7.2m	4.2q ^a , 1.2t ^e	2.2s	-340.5
PhEtSnCl(MPNHy)	1705s	1660s	9.0s ^a , 8.6d ^b 8.2d ^c , 7.3t ^d	3.9s	2.3s	-339.8
PhEtSn(MPNHy) ₂	1705s	1660s	9.1s ^a , 8.6d ^b 8.2d ^c , 7.3t ^d	3.9s	2.3s	-339.7
PhEtSnCl(EPNHy)	1710s	1660s	9.1s ^a , 8.5d ^b 8.1d ^c , 7.3t ^d	4.2q ^a , 1.3t ^e	2.2s	-340.4
PhEtSn(EPNHy) ₂	1710s	1660s	9.0s ^a , 8.6d ^b 8.1d ^c , 7.3t ^d	4.2q ^a , 1.3t ^e	2.2s	-339.5
PhEtSnCl(MPINHy)	1705s	1665s	8.7d ^e , 7.8d ^f	3.7s	2.3s	-340.2
PhEtSn(MPINHy) ₂	1710s	1660s	8.6d ^e , 7.9d ^f	3.8s	2.3s	-339.3
PhEtSnCl(EPINHy)	1705s	1665s	8.6d ^e , 7.7d ^f	4.2q ^a , 1.3t ^e	2.2s	-340.4
PhEtSn(EPINHy) ₂	1710s	1660s	8.7d ^e , 7.8d ^f	4.2q ^a , 1.3t ^e	2.3s	-339.7
PhBuSnCl(MPBHy)	1720s	-	7.9-7.2m	3.7s	2.2s	-155.9
PhBuSn(MPBHy) ₂	1720s	-	8.0-7.1m	3.8s	2.3s	-156.1
PhBuSnCl(EPBHy)	1715s	-	7.9-7.3m	4.1q ^a , 1.2t ^e	2.3s	-156.3
PhBuSn(EPBHy) ₂	1720s	-	8.0-7.3m	4.2q ^a , 1.2t ^e	2.2s	-155.7
PhBuSnCl(MPNHy)	1720s	-	9.1s ^a , 8.7d ^b 8.2d ^c , 7.2t ^d	3.9s	2.3s	-155.3
PhBuSn(MPNHy) ₂	1715s	-	9.2s ^a , 8.6d ^b 8.1d ^c , 7.3t ^d	3.9s	2.2s	-156.2
PhBuSnCl(EPNHy)	1720s	-	9.1s ^a , 8.6d ^b 8.2d ^c , 7.3t ^d	4.2q ^a , 1.2t ^e	2.3s	-155.3
PhBuSn(EPNHy) ₂	1720s	-	9.0s ^a , 8.6d ^b 8.1d ^c , 7.3t ^d	4.2q ^a , 1.3t ^e	2.2s	-156.0
PhBuSnCl(MPINHy)	1715s	-	8.6d ^e , 7.8d ^f	3.7s	2.2s	-155.8
PhBuSn(MPINHy) ₂	1720s	-	8.7d ^e , 7.9d ^f	3.8s	2.3s	-155.9
PhBuSnCl(EPINHy)	1720s	-	8.6d ^e , 7.7d ^f	4.2q ^a , 1.3t ^e	2.3s	-155.7
PhBuSn(EPINHy) ₂	1720s	-	8.7d ^e , 7.8d ^f	4.2q ^a , 1.3t ^e	2.2s	-155.0

(a) Appears as a singlet due to H-2 of the nicotinoyl moiety. (b) Appears as a doublet (J = 7.5) assigned to H-6 of the nicotinoyl moiety. (c) Appears as a doublet (J = 7.3) assigned to the nicotinoyl moiety. (d) Appears as a doublet of doublets (J = 7.5) thereby appearing as a pseudo-triplet assigned to H-5 of the nicotinoyl moiety. (e) Appears as a doublet (J = 10.6) assigned to H-2,6 of the isonicotinoyl moiety. (f) Appears as a doublet (J = 10.6 assigned to H-3,5 of the isonicotinoyl moiety .

^{119}Sn NMR spectrum¹⁷ of EtPhSnCl_2 shows a sharp singlet at δ 102.32 and a broad peak at δ –244.15 that is probably due to presence of two forms, (i) tetracoordinated, (ii) penta-coordinated. However in the solid state, it exists as a trigonal bipyramid with distorted trans geometry as evident from its Mossbauer spectrum of EtPhSnCl_2 which shows quadrupole splitting (QS) at 3.24mm/s. The ratio $\rho = (\text{QS/IS}) = 2.10$ substantiate the ^{119}Sn NMR spectra of pentacoordination.¹⁸ ^{119}Sn NMR spectrum of BuPhSnCl_2 show singlets at δ 158.01 which is due to tetracoordinated Sn-Atom.

The ^{119}Sn NMR spectra of the complexes of EtPhSnCl_2 show singlets at δ –340, which suggests hexa-coordination of Sn atom (Fig. 2). The complexes of BuPhSnCl_2 show singlet at δ –156.3 to δ –155.0 (Table-1) thereby suggesting tetra-coordinated Sn atom.

FIG. 1

FIG. 2

The molecular weight determination of some of the complexes of EtPhSnCl_2 by isopiestic method in benzene suggest dimeric nature.

On the basis of elemental analysis, spectral data viz. IR, ^1H NMR, ^{13}C and ^{119}Sn NMR and molecular weight determination 6- and 4- coordinated structures have been proposed to the complexes of EtPhSnCl_2 and BuPhSnCl_2 respectively.

Conclusion

It may be concluded that alkyl pyruvate aroylhydrazones behave as bidentate ligands with EtPhSnCl_2 and as monodentate ligands with BuPhSnCl_2 as evident from spectral data. This may be attributed to the steric effect of alkyl group which may play a decisive role in deciding the coordination of tin atom. The existence of two distinct types of coordination involving the aroyl and ester carbonyls has been evident from ^{13}C NMR spectra.

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