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SYNTHESIS AND CHARACTERIZATION OF BIOLOGICALLY ACTIVE ORGANOTIN-PLATINUM-IMINE AND ORGANOTIN-PLATINUM-AMINE COMPLEXES

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^1H, ^{13}C and ^{31}P-chemical shifts are reported for the first time for new biologically active organotin-imine, organotin-amine ligand, and their complexes with platinum(II), complexes of the type *trans*-[$PtCl_2(PPh_3)$(imine)] and trans-[$PtCl_2(PPh_3)$(amine)], the imine ligand being derived from 3-[tri-n-butylstannyl)-benzaldehyde and primary amines; the amine ligand obtained by the reduction of the appropriate imine. The use of multinuclear spectroscopy provides strong evidence for structure determination of these complexes. Of interest is that both ^1H and ^{13}C resonances of CH=N and ^{13}C of R-carbon data (γ-protons and β-carbons to the platinum atom), exhibit large downfield shifts upon coordination of imine (or amine) with respect to free imine (or amine). In addition, ^1H, ^{13}C and ^{31}P-NMR spectra show that only a single rotamer exists.

INTRODUCTION

Organotin compounds are toxic to a variety of microorganisms and find widespread application in biocidal compositions. In the past 25 years, the triorganotin compounds of the R_3SnX-type, such as tributyltin chloride, tributyltin fluoride, triphenyltin chloride, and tributyltin oxides have become well known as environmentally compatible broad spectrum biocides, incorporated as toxic additives in marine biocidal paints, molluscicides, fungicides and other pesticide formulations[1]. It is noteworthy that trialkyltin compounds dealkylate in natural environments to harmless oxides of tin[2].

In spite of the interest in these organotin compounds, we report here the synthesis and characterization of some organotin-imine, organotin-amine, organotin-imine-platinum and organotin-amine-platinum complexes. The imine ligand being derived from 3-(tri-n-butylstannyl)-benzaldehyde and primary amines, in addition, amine ligand were obtained by reduction of the appropriate imine.

RESULTS AND DISCUSSION

^1H and ^{13}C-NMR Chemical Shifts of Imine Ligands

The imine (1–5) in the present work were obtained from the reaction of 3-(tri-n-butylstannyl)-benzaldehyde with the appropriate primary amines (Table 1).

The products were solids and the yields were reasonably high which indicates great reactivity of these carbonyl compounds. The sterochemistry of these imines was assigned using UV, IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. The UV spectra of imines have a characteristic absorption bands for the C=N group (*ca.* 255–268 nm in CH_2Cl_2). The infrared data show that the absorption of the C=N group for imines (1–5) occured in the region 1615–1650 cm^{-1} as one band for each imine. The UV and IR results are in good agreement with an earlier study of some imines derived from some thiophene derivatives which have been reported to exist exclusively in the E-forms[3,4].

The most valuable information came from the ^{1}H and ^{13}C-NMR spectra (Table1). The ^{1}H-NMR and ^{13}C-NMR chemical shifts show only one set of the N-alkyl signals and one set of the CH=N signals which indicate that only one diastereoisomer is present in solution for these imines (Table 1). Further support was obtained from the ^{13}C-NMR spectra of these imines. The ^{13}C-NMR chemical shift of imines (1–5) (Table 1) leads to precise stereochemical assignments of these imines. Inspection of the spectra shows that each carbon gave one signal in the complete decoupled spectra. No satellites or any other small singal which may be due to the minor isomer have been observed. The ^{13}C-NMR spectra of imine (1) has been chosen as a model in order to simplify the NMR spectra (Table 1). The quaternary carbons, C-1 and C-3 and the carbon of the imine group C=N are readily identified since they are less intense compared with other signals as a result of long relaxation times of the quaternary carbons[5,6]. The ^{13}C spectrum shows (in $CDCl_3$) singnals at δ 163.05 assigned to the C=N group and at δ 135.56 and δ 142.49 assigned to the C-1 and C-3 quaternary carbons and confirmed by using the NOE technique. N–CH_3 resonate at δ 48.34. Phenyl carbons C-2, C-4, C-5 and C-6 appear at δ 135.96, 138.73, 127.63 and 128.10 ppm, respectively. These values were confirmed by using the substituent chemical shift (SCS) effect of the $Sn(Bu)_3$ and of the imine group C=N on *o*, *m* and *p*-positions, long-range C–H coupling, and comparison with the parent benzaldehyde compound[7].

The ^{13}C-NMR chemical shift of other imines are listed in Table 1. It is worth noting that the ^{13}C chemical shift of both C-1 and the C=N carbons are sensitive to the groups attached to the C=N group (Table 1). It is worth noting that when the attached group is *t*-butyl, a considerable shift to high field occured for the C=N, which appear at δ 155.41 (Table 1, imine 5) compared with N-methyl group (Table 1, imine 1), which C=N, appear at δ 163.05. When imine (5), R=$(CH_3)_3$ C, R, donates more electrons to C=N (compared with R=CH_3, imine (1), Table 1). Thus, there is a decrease in the polarization of (C^+–N^-) in the imine bond and shift the carbon resonance to higher field for R=$(CH_3)_3$C group compared with R=CH_3. Assignment of the ^{13}C chemical shift of butyl carbon directly bonded to tin are straightforward and their ^{13}C-data are presents in Table 1.

^{1}H-NMR and ^{13}C-NMR Chemical Shifts of Amine Ligands

Amines were obtained by the reduction of the appropriate imine, (see experimental), and the ^{1}H and ^{13}C-NMR spectrum of amine (1), (Table 2), has been chosen as model in order to simplify the NMR spectra. The new CH_2–N and the

TABLE 1

^{1}H AND ^{13}C-NMR DATA OF ORGANOTIN-IMINE COMPOUNDS^A

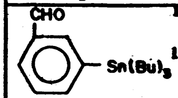
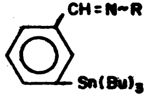
Compound		CH=N–	C-1	C-2	C-3	C-4	C-5	C-6	Sn–CH$_2$	CH$_2$CH$_2$	CH3	N–CH$_3$	CH	CH$_2$	CH$_3$	C
	^{1}H			7.70				7.20	1.60		0.80					
	^{13}C	192.17 (CHO)	135.60	137.68	143.55	142.61	128.40	129.45	29.07	27.39; 13.68	9.69					
	^{1}H	8.27(q) ^{4}J(1.75)		7.78				7.33	1.65		0.88	3.50(d) ^{4}J(1.75)	(E-form)			
1 R = CH$_3$	^{13}C	163.5	135.56	135.96	142.49	138.73	127.63	128.10	29.13	27.36; 13.68	9.63	48.34				
2 R = ^{i}P$_r$	^{1}H	8.29		7.74				7.36	1.59		0.88		3.53			
	^{13}C	158.69	135.91	136.55	142.25	138.55	127.39	128.04	29.13	27.37; 13.68	9.69		67.73		24.20	
3 R = ^{i}B$_u$	^{1}H	8.22		7.80				7.32	1.65		0.92			3.43d	0.85d	
	^{13}C	161.22	135.79	136.32	142.31	138.61	127.69	128.04	29.13	27.43; 13.68	9.09		29.72	69.95	20.73	
4 R = ^{S}B$_u$	^{1}H	8.26		7.75				7.31	1.65		0.78		3.23C	o	o	
	^{13}C	159.22	135.91	136.62	142.25	138.62	127.39	128.04	29.13	27.43; 13.68	9.70		68.42	22.32	30.78; 11.10	
5 R = ^{t}B$_u$	^{1}H	8.26		7.77				7.32	1.66		0.82				1.29S	
	^{13}C	155.41	137.08	136.44	142.08	138.32	127.16	127.98	29.13	27.37; 13.68	9.63				29.72	57.15

TABLE 2

^{1}H AND ^{13}C-NMR DATA OF ORGANOTIN-AMINE COMPOUNDS^{A}

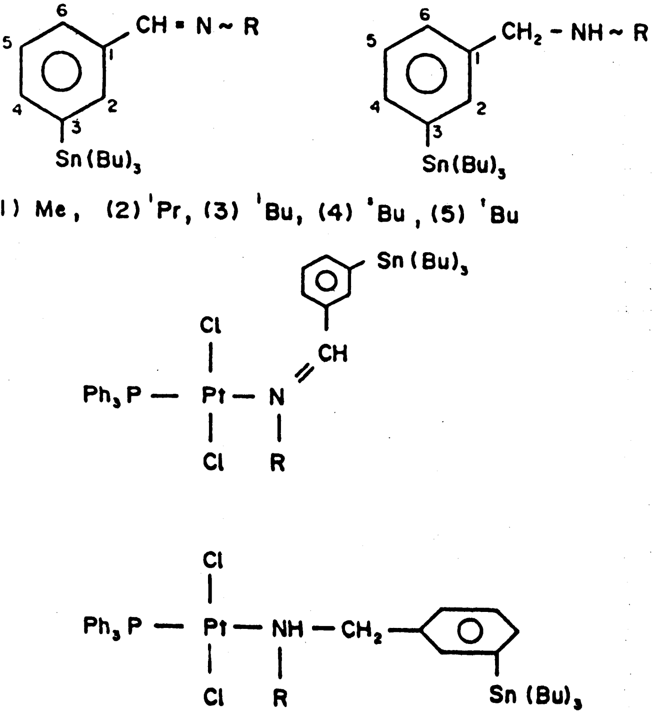
Compound		CH=N	C-1	C-2	C-3	C-4	C-5	C-6	C	$Sn-CH_2$	CH_2CH_2	CH_3	$HN-CH_3$	CH	CH_2	CH_3
1	^{1}H	3.70		7.38	—	—	—	7.21		2.42	—	0.81	2.42			
	^{13}C	56.33	139.26	135.14	141.90	136.26	127.92	127.92		29.13	27.37; 13.68	9.57	35.95			
2	^{1}H	3.75		7.39	—	—	—	7.19		1.60	—	0.82		2.90		1.06
	^{13}C	51.68	139.90	134.79	141.60	135.97	127.74	127.74		29.01	27.25; 13.51	9.39		47.87		22.79
3	^{1}H	3.76		7.40	—	—	—	7.22		1.65	—	0.82		1.40	2.44	0.90
	^{13}C	57.50	139.90	134.97	141.84	136.15	127.86	127.86		29.37	27.42; 13.68	9.57		28.37	54.27	20.67
4	^{1}H	3.77		7.40	—	—	—	7.21		1.65	—	0.82		2.64		1.10; 1.00
	^{13}C	53.80	140.14	134.90	141.90	136.15	127.86	127.86		29.13	27.37; 13.68	9.57		51.57	29.55	19.79 10.22
5	^{1}H	3.70		7.40	—	—	—	7.18		1.66	—	0.85				1.17
	^{13}C	50.75	140.61	134.97	141.91	136.38	127.98	127.98	47.46	29.13	27.43; 13.68	9.57				29.13

(A) δ ppm relative to TMS in $CDCl_3$; (Key; s,singlet; d,doublet; q,quartet; o,overlaps).

NH–CH_3 groups of this secondary amine resonate apart from each other in chloroform at 26°. The spectrum shows two singlets for CH_2–N at δ 3.70, and for NH–CH_3 at δ 2.42 (Table 2). The ^{1}H chemical shifts of other protons are simply identified and listed in Table 2. The ^{13}C chemical shifts for amines (1–5) are also given in Table 2. The quaternary carbons are readily identified since they are less intense and almost invarient in position. The ^{13}C chemical shift of the CH_2–N and $NHCH_3$ are readily identified and resonate at δ 56.33 and 35.95 respectively. These values were confirmed by using the NOE technique. The remaining carbons absorb as expected (Table 2).

^{1}H, ^{13}C and ^{31}P-NMR Data of Organotin-Imine-Platinum(II) Complexes, Trans-[$PtCl_2(PPh_3)$(Imine)]

Previously we reported the synthesis and characterization of some platinum-imine-complexes of the type *trans*-[$PtCl_2(n^2C_2H_4)$(imine)] (the imine ligand being derived form 2-thienylketone and primary amines)[5,6]. We present here the synthesis and characterization of new imines in which tributyltin substituted in the *meta*-position of the imine group and of the type *trans*-[$PtCl_2(PPh_3)$(imine)]. The stoichiometry of the complexes was established by elemental analysis; in addition, ^{1}H, ^{13}C and ^{31}P-NMR spectra of freshly prepared solutions showed that in each case only a single rotamer exist. Thus the ^{1}H spectrum of complex 1 (Table 3), in $CDCl_3$, showed the presence of only one rotamer, the peaks arising from =N–CH_3, CH=N,



SCHEME 1

TABLE 3

^{13}C-NMR DATA OF ORGANOTIN-IMINE-PLATIMUN (II) COMPLEXES^{A}

Compound	CH=N	Sn–CH$_2$–	–CH$_2$CH$_2$–	CH3	N–CH$_3$	CH	CH2	CH$_3$	C$_{\text{-ipso}}$	c$_o$	C$_m$	C$_p$	C
1	175.00	29.07	27.37; 13.68	9.75	52.43				140.61; 142.66	134.67; 135.08	127,74; 128.21	130.74	
2	175.70	29.07	27.90, 13.63	9.69		70.10		27.37	140.60; 142.70	134.62; 135.03	127.63; 128.10	131.00	
3	175.00	29.13	27.43; 13.74	9.75		29.74	70.90	20.61	140.43; 142.60	134.74; 135.14	127.69; 128.14	130.68	
4	175.60	29.25	27.84; 13.57	8.75		68.42	26.84	30.13; 11.22	140.00; 142.30	134.67; 134.97	127.57; 128.98	131.27; 131.86	
5	175.40	27.80	26.84; 17.56	13.63				29.71; 31.95	140.10; 142.00	134.97; 135.57	127.68; 128.16	130.32	67.80

(A) δ ppm relative to TMS in CDCl$_3$ (C$_{\text{ipso}}$, C$_o$, C$_m$ and C$_p$ for PPh$_3$ ligand carbons).

TABLE 4

^{13}C-NMR DATA OF ORGANOTIN-AMINE-PLATIMUN (II) COMPLEXES^{A}

Compound	PH–CH_2	Sn–CH2–	–CH_2CH_2–	CH3	NH–CH_3	CH	CH_2	CH_3	Cipso	c_o	C_m	C_p	C
1	67.00	29.07	27.31; 13.63	9.69	37.24				140.10; 142.96	134.67; 135.09	127.68; 128.10	130.68	
2	64.79	29.13	27.37; 13.68	9.63		53.27			140.12; 142.82	134.56; 135.97	127.51; 127.98	130.45	
3	57.44	29.07	27.31; 13.68	9.69		26.72	56.38	20.85; 19.85 (ineqv.)	140.58; 142.32	134.64; 135.09	127.63; 128.10	130.74	
4	58.56	29.07	27.37; 13.68	9.63					140.15; 142.01	134.56; 134.97	127.51; 127.92	130.39	
5	O	29.13	27.37; 13.68	9.63					141.11; 142.01	134.61; 135.03	127.45; 127.86	130.01	72.97

(A) δ ppm relative to TMS in ODCl$_3$ (O, overlaps; ineqv., inequivalents).

appearing as two multiplets at δ 3.80 (doublet), 8.40 (quartet) respectively with broad platinum satellites. The rest of ^{1}H chemical shifts are of the same as in the starting imine compound. Thus, the ^{1}H resonances of N–CH_3, CH=N, undergoes a considerable downfield shift upon coordination. ^{13}C–NMR data were also considered with the ^{1}H-NMR data showing only one set of ^{13}C resonance signals. The CH=N signal appears at δ 175.00 (complex 1, Table 3) and N–CH_3 signal appearsat δ 52.42, C(CH_3) signal appear at δ 67.80. The ^{13}C resonances of CH=N, N–CH_3, C–$(CH_3)_3$ undergoes a considerable downfield shift upon coordination and showed the existence of only one isomers in the solution (Table 3). The ^{13}C chemical shifts of the substituted benzene ring and Sn-alkyl group carbons, resonates at the same position as in the free ligand (Table 3).

However in the present work we report the isolation and characterization of stable platinum(II)-imine in which the imine molecules consists of only one σ N, and is monodentate bonded, *trans* to the phosphorus ligand (Scheme 1), and analogous to the platinum olefin complexes[8,9].

^{13}P data for imine complexes are presented in Table 5. The ^{31}P NMR spectrum of complex 1 (Table 5) R=CH_3, consists of a single peak with platinum satellites at δ 2.43 ppm, ^{1}J(^{195}Pt-^{31}P), 3568 Hz. Comparing of the ^{31}P spectra of the new compounds, with analogous, *trans*-[$PtCl_2(Ph_3P)$(imine)] (imine derived from cyclopropyl–2-thienylketone and primary amines[9]), the Pt is four-coordinate and the ^{31}P and the platinum-phosphorus coupling in agreement with the result reported here. Small difference in both δ and J value from the results reported here, this is because of the difference in the *trans*-imine ligand. However, the magnitude of ^{1}J (^{195}Pt–^{31}P) for all of our compounds is not unusual and suggest that the *trans*-influence of the N=, ligands is similar to amine ligands[10,11]

TABLE 5

^{31}P-NMR DATA OF ORGANOTIN-IMINE AND AMINE-PLATINUM (II) COMPLEXES

Compound	Imine Complexes		Amine Complexes	
	δ ppm	^{1}J (^{195}pt–^{13}P) Hz	δ ppm	^{1}J (^{195}pt–^{13}P) Hz
1	+ 2.43	3568	+ 4.36	3557
2	+ 1.95	3588	+ 4.66	3643
3	+ 2.24	3582	+ 4.12	3582
4	+ 1.99	3580	+ 3.64	3648
5	+ 0.90	3622	+ 3.21	3670

(a) δ ppm relative to 85% H_3PO_4.

^{1}H, ^{13}C and ^{31}P-NMR Data of Organotion-Amine Complexes; Trans-[$PtCl_2(PPh_3)$ (Amine)]

The ^{1}H and ^{13}C–NMR spectra of complex of *trans*-[$PtCl_2(PPh_3)$(amine)] amine was obtained by the reduction of the appropriate imine, Table 1), are in good agreement with those complexes prepared from imine or from available commercial amines, *i.e.*, Me_2NH, Et_2NH[8,9,12,13]. The ^{31}P-NMR data for amine complexes are presented in Table 5. The ^{31}P-NMR spectrum of comples (1), $R=CH_3$, consist of a single peak with platinum satellites at δ 4.36, $^1J(^{195}Pt-^{31}P)$, 3557 Hz. This is in agreement with the result reported for analogous amine complexes, *i.e.*, trans-$[PtCl_2(PPh_3)(BuNH_2)]$, δ 5.90, $^1J\ (^{195}Pt-^{31}P)$, 3540 Hz[14].

EXPERIMENTAL

Benzaldehyde, tributyltin chloride, $NaBH_4$, primary amines and other reagents were obtained from Fluka and Aldrich and were used without any further purification. $[Pt_2Cl_4(PPh_3)_2]$ dimer was prepared by the standard method[15]. Tertiary phosphine-imine, amine complexes were prepared by adding 2 mol equivalents of appropriate imine or amine to a chloroform solution of platinum dimer. The mixture was stirred for 1 hr then the solution was evaporated in vacuo. The yellow precipitate which separated out was washed with cold pentane, and dried in vacuo. The complexes recrystallized from a $CHCl_3$: pentane mixture. Secondary amine used were obtained by reduction of the imine ligand by $NaBH_4$ in absolute methanol similar to the reported procedure[16]. The Schiff bases (imine ligands) were prepared by the reaction of 3-(tri-n-butylstannyl)-benzaldehyde and appropriate primary amines in 20 ml methanol at room temperature or by refluxing the resulting solution for 1/2hr, following by concentration the methonal solution. The chelating ligands were not isolated, the above solutions being used directly for the subsequent reactions. For ^1H, ^{13}C–NMR analysis, the yellow solution were evaporated to dryness, the remaining yellow liquid was fractionally distilled at reduced pressure to give the imine.

3-(Tri-n-butylstannyl)-benzaldehydes were prepared from 2-[3-(tri-n-butylstannyl)phenyl]-1,3-dioxalane using the following procedure:

Preparation of 2-[3-(Tri-n-Butylstannyl)Phenyl]-1,3 Dioxalane[17]:

A suspension of magnesium turnings 2.5g (0.1 g-atom) in THF is heated under gentle reflux, and several drops of 1,2 dibromoethane was added to start the reaction then 22 g (0.09 mole) of 2-(3-bromophenyl)]-1,2-dioxalane was gradully added. To this solution of the Grignard reagent a THF soltuion of 24.5 g (0.07 mole) tri-n-butyltin chloride was added gradully and refluxed for several hrs. After cooling to room temperature and pouring over ice the organic layer was separated, washed with water and dried over $MgSO_4$. The solvent was stripped off and the remaining liquid was fractionally distilled two times. The yield of the product obtained reaches up to 73% b.pt. (145–147°C/0.2 mmHg). Preparation of 3-[tri-n-butylstannyl)-benzaldehyde.

This was prepared by dissolving 2-[3-(tri-n-butylstannyl)] 1,3-dioxalane in 100 ml THF, 50 ml of water and one gram of p-toluensulfonic acid. This solution was gently refluxed under an inert atmosphere. After 48 hrs, the organic layer was separated and the aqueous layer was extracted twice with 50 ml portions of benzene and the combined organic layers were dried over $MgSO_4$. The solvent were stripped off and the remaining liquid was fractionally distilled at reduced pressure to give up to 93% yield b.pt. 140-142°C/0.07 mmHg.

C, H, N analysis for organotin-imine-platinum complexes (Table 3), complex 1, (Found, % C, 48.8; H, 5.3; N, 1.5; $C_{38}H_{50}$ $NPCl_2SnPt$; Requires, % C, 48.7; H, 5.3; N, 1.5), complex 2 (Found, % C, 50.0; H, 5.6; N, 1.5, $C_{40}H_{54}NPCl_2SnPt$; Requires, % 49.99; H, 5.6; N, 1.5), complex 3 (Found, % C, 50.2; H, 5.7; N, 1.4, $C_{41}H_{56}NPCl_2SnPt$; Requires, %, C, 50.3; H, 5.7; N, 1.4), complex 4 and 5 have the same analysis as complex 3. C, H, N analysis for organotin-amine-platinum complexes (Table 4), complex 1, (Found, % C, 48.6; H, 5.3; N, 1.5; $C_{38}H_{52}NPCl_2SnPt$; Required, % C, 48.6; H, 5.3; N, 1.5), complex 2 (Found, % C, 49.7; H, 5.6; N, 1.4; $C_{40}H_{56}NPCl_2SnPt$; Required, % C, 49.7; H, 5.6; N, 1.4; complex 3 (Found, % C, 50.2; H, 5.7; N, 1.4; $C_{41}H_{58}NPCl_2Pt$; Required, % C, 50.2; H, 5.7; N, 1.4), complex 4 and 5 have the same analysis as complex 3.

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