

Phenylarsenic(III) Derivatives of Schiff Bases; Synthesis and Characterization

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Research Article

Abstract: Complexes having the general formula $\text{Ph As} [\text{OC}(\text{R})\text{CHC}(\text{R}')\text{NC}_6\text{H}_5]_n \text{Cl}_{2-n}$ where $n=1$ or 2 ; $\text{R}=\text{R}'=\text{CH}_3, \text{C}_6\text{H}_5$; $\text{R}=\text{CH}_3, \text{R}'=\text{C}_6\text{H}_5$ have been synthesized by the reactions of phenyl arsenic(III) dichloride with the sodium salts of $[\text{RC}(\text{O})\text{CHC}(\text{R}')\text{N}(\text{C}_6\text{H}_5)]\text{Na}^+$ in 1:1 and 1:2 molar ratios in anhydrous benzene. These compounds have been characterized by elemental analyses; molecular weight determinations and their tentative structure have been proposed on the basis of spectral (I.R, ^1H and ^{13}C NMR) studies.

Key words: Phenylarsenic(III)dichloride ,elemental analyses, spectral studies ,Pseudo octahedral and Trigonal bipyramidal geometry.

Introduction

Arsenic in both form i.e. organic & inorganic, is of great interest today due to their wide occurrence in the environment & its health impact[1].Arsenic compounds are used as effective antibacterial drugs[2],[3] to treat a variety of diseases including syphilis & cancer[4]. Organoarsenic compounds are also known to possess significant biological activity[5]-[7]. Interest in the chemistry of these compounds is growing continuously because of structural variations[8],[9] synthetic challenges & wide ranging applications in biological activities[10]-[12]. The trivalent compounds of organoarsenic show considerable structural diversity which is extended by the presence of a stereo chemically active lone pair of electrons[8]. The geometry can also be influenced by the presence of lone pair of electrons[13] which may be either stereo chemically active or inactive & also by subtle change in the nature of groups attached to metal atom. In continuation of our previous work on some mixed ligand derivatives of phenyl arsenic (III) [14] & organoantimony (III) & (V) derivatives of Schiff bases, we report here the synthesis & characterization of phenyl arsenic (III) derivatives of Schiff bases.

Materials and Methods :

All the reactions were carried out under anhydrous conditions and solvents were dried by standard procedure. Phenylarsenic(III) dichloride[15] and Schiff bases[16] were synthesized from reagent grade chemicals by reported methods.The elements arsenic nitrogen and

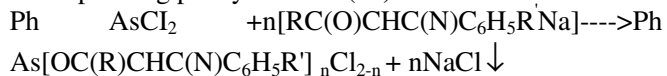
chlorine were estimated[17] by standard methods. I.R. spectra of these compounds have been recorded as nujol mull using KBr cells on FTIR spectrophotometer model 8400 Shimadzu in the range of $4000-400 \text{ cm}^{-1}$. The NMR ^1H and ^{13}C spectra have been recorded on JEOL FTAL300NMR spectrometer at 300MHz. Molecular weight of these complexes were determined cryoscopically using Beckmann's thermometer. Since similar methods have been used to synthesize these compounds, the preparative detail of one representative compound is given in detail. Synthetic and analytical data of the other analogous compounds are summarized in Table-1.

Synthesis of $\text{PhAs}[\text{OC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NC}_6\text{H}_5]_2$

A benzene solution of $\text{CH}_3\text{C}(\text{O})\text{CHC}(\text{CH}_3)\text{N}(\text{C}_6\text{H}_5)\text{H}$ (0.81gm 4.62mM) was added to the sodium methoxide solution obtained by the interaction of sodium(0.10gm 4.34Mm) with methanol and the reaction was refluxed for about 3 hours. The benzene solution of PhAsCl_2 (0.48gm 2.15mM) was added to the above reaction mixture after cooling. The reaction mixture was refluxed for about 4 hours and the precipitated NaCl was filtered off. The removal of volatile component from the filtrate under reduced pressure yield a dark brown viscous liquid, which was purified by benzene n-hexane mixture.

Results and discussion

The interaction of phenyl arsenic(III) dichloride with sodium salts of Schiff base in benzene solution in 1:1 & 1:2 molar ratios, respectively leads to the formation of the corresponding phenyl arsenic (III) derivatives.



$\text{R}=\text{R}'=\text{CH}_3, \text{C}_6\text{H}_5$; $\text{R}=\text{CH}_3, \text{R}'=\text{C}_6\text{H}_5$

where $n=1$ or 2

Precipitated sodium chloride was filtered off and the solvent removed under reduced pressure yield dark brown viscous liquids. These derivatives are soluble in common organic solvents and are purified by benzene n-hexane

mixture. The molecular weight determinations indicate the monomeric nature of these compounds.

I.R. Spectra

The appearance of a new band in the range $405\text{--}413\text{ cm}^{-1}$ ($\nu\text{As-N}$)[18] indicates, the NH deprotonation and the formation of an arsenic - nitrogen bond. The intense absorption bands observed in the spectra of the free ligand in the region $1600\text{--}1610\text{ cm}^{-1}$ ($\nu\text{C=N}$) and $1560\text{--}1570\text{ cm}^{-1}$ ($\nu\text{C=O}$) are shifted to lower wave number in the spectra of their corresponding phenyl arsenic(III) compounds. This indicates the involvement of these groups in the bonding. The presence of another band in the region $520\text{--}535\text{ cm}^{-1}$ due to $\nu\text{As-O}$ [19] confirmed the chelation.

^1H NMR Spectra

Absence of NH/OH signal from the spectra of complexes (Table-2) indicates the complexation of arsenic with Schiff base through As-N bond. A small downfield shift in the position of methyl and methine proton signal may be due to the delocalization[20] of electron in quasiaromatic chelate ring. The phenyl protons are observed as complex pattern in the range $7.10\text{--}8.42\text{ ppm}$.

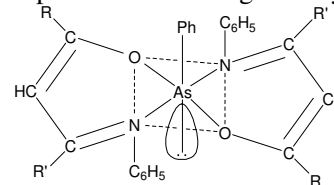
^{13}C NMR Spectra

^{13}C NMR spectra of the complexes (Table-3) confirm the delocalization of electrons in the chelate ring, which is indicated by the small downfield shift in the position of $\text{CH}_3, \text{CH}, \text{C=O}$ and C=N carbon as compared to their position in the corresponding ligands. The signals for phenyl carbons were observed in the range $128.2\text{--}151.8\text{ ppm}$. The corrected chemical shift value (δ') and Hammett constant (σR^0)[21] are found to be negative in the range -1.6 to -3.0 ppm and -0.06 to -0.15 ppm ,

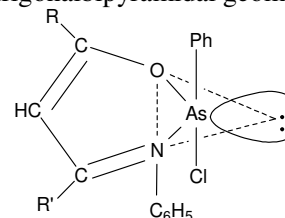
respectively. Negative values of δ' as well as σR^0 indicate $d\pi\text{-}p\pi$ conjugation with poor electron shift from arsenic to phenyl group in these complexes.

Conclusion

In view of the monomeric nature of these complexes and of the bidentate behaviour of the ligand, the following structure is being proposed in which the central arsenic atom acquires a pseudooctahedral geometry:



In view of the presence of a bidentate ligand, a chloro group, phenyl group in the chloroderivatives of phenylarsenic(III), keeping in mind bent rule the following structure may be proposed in which arsenic atom acquires trigonalbipyramidal geometry:



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Table 1: Synthetic & Analytical data of phenylarsenic (III) complexes of Schiff bases

S.No.	Reactants (gm)			Molecular Formula Physical state & (yield %)	% Analysis Found(calcd)			Mol wt found (Calcd)
	Na	LH	Ph AsCl ₂		As	N	Cl	
1.	0.10	R=R ¹ =CH ₃ 0.81	0.48	PhAsL ₂ ; C ₂₈ H ₂₉ AsO ₂ N ₂ Brown Viscous(83)	14.23 (15.0)	5.00 (5.60)	-	490 (500)
2.	0.08	0.65	0.77	PhAsLCl; C ₁₇ H ₁₇ AsNOCl Yellow solid (85)	19.32 (20.74)	3.12 (3.87)	9.10 (9.82)	350 (361.5)
3.	0.11	R=R ¹ =C ₆ H ₅ 1.41	0.5	PhAsL ₂ ; C ₄₈ H ₃₇ AsO ₂ N ₂ Brown sticky(80)	9.30 (10.02)	3.00 (3.74)	-	730 (748)
4.	0.08	1.02	0.77	PhAsLCl; C ₂₇ H ₂₁ AsONCl Brown solid(82)	14.32 (15.44)	2.01 (2.88)	7.01 (7.31)	470 (485.5)
5.	0.09	R=CH ₃ ; R ¹ =C ₆ H ₅ 0.92	0.43	PhAsL ₂ ; C ₃₈ H ₃₃ AsO ₂ N ₂ Yellow Viscous(85)	11.32 (12.00)	4.12 (4.48)	-	600 (624)
6.	0.07	0.72	0.67	PhAsLCl; C ₂₂ H ₁₉ AsONCl Yellow solid (80)	17.00 (17.69)	2.98 (3.30)	8.22 (8.37)	400 (423.5)

Table 2: ¹H NMR data (in δ) of phenylarsenic (III) complexes of Schiff bases

S.No	Complexes	CH	CH ₃	Phenyl
1	a b Ph As[OC(CH ₃)CHC(CH ₃)NC ₆ H ₅] ₂	5.05(s)	a,2.01(s) b 1.96(s)	7.10-7.91(m)
2	a b Ph As[OC(CH ₃)CHC(CH ₃)NC ₆ H ₅]Cl	5.05(s)	a,2.05(s) b,1.87(s)	7.28-7.77(m)
3	Ph As[OC(C ₆ H ₅)CHC(C ₆ H ₅)NC ₆ H ₅] ₂	5.82(s)	-	7.28-7.40(m)
4	Ph As[OC(C ₆ H ₅)CHC(C ₆ H ₅)NC ₆ H ₅]Cl	5.62(s)	-	7.20-8.42(m)
5	Ph As[OC(CH ₃)CHC(C ₆ H ₅)NC ₆ H ₅] ₂	4.98(s)	2.01(s)	7.28-7.78(m)
6	Ph As[OC(CH ₃)CHC(C ₆ H ₅)NC ₆ H ₅]Cl	5.06(s)	2.12(s)	7.14-7.77(m)

Table 3: ¹³C NMR data (in δ) of phenylarsenic(III) complexes of Schiff bases

S. No.	Complexes	CH	CH ₃	C=O	C=N	C ₆ H ₅ *				δ'	σR^0
						C(i)	C(O)	C(m)	C(p)		
1.	a b Ph As[OC(CH ₃)CHC(CH ₃)NC ₆ H ₅] ₂	95.0	a,21.3 b,19.2	187.2	165.3	146.3	144.8	129.8	128.2	-1.6	-.06
2.	a b Ph As[OC(CH ₃)CHC(CH ₃)NC ₆ H ₅]Cl	94.0	a,22.3 b,20.1	189.3	166.2	150.3	141.3	129.7	127.3	-2.4	-.10
3.	PhAs[OC(C ₆ H ₅)CHC(C ₆ H ₅)NC ₆ H ₅] ₂	95.2	-	190.2	165.2	148.2	141.3	129.8	127.6	-2.2	-.09
4.	Ph As[OC(C ₆ H ₅)CHC(C ₆ H ₅)NC ₆ H ₅]Cl	94.8	-	192.1	166.2	151.8	142.7	130.8	127.2	-3.6	-.15
5.	Ph As[OC(CH ₃)CHC(C ₆ H ₅)NC ₆ H ₅] ₂	96.2	23.2	190.2	165.3	148.3	136.8	129.4	126.8	-2.6	-.11
6.	Ph As[OC(CH ₃)CHC(C ₆ H ₅)NC ₆ H ₅]Cl	95.4	23.8	187.2	166.2	149.3	136.9	129.9	126.9	-3.0	-.13

* = Values are given in order of ipso, ortho, meta, para, respectively.

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