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Phenylarsenic(III) Complexes of 2-(2-Hydroxyphenyl)benzothiazolines

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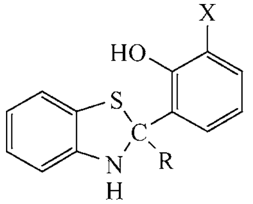
ABSTRACT: *Equimolar reactions of $PhAs(OMe)_2$ (prepared in situ) and 2-(2-hydroxyphenyl)benzothiazolines LH_2 give the addition products $PhAs(OMe)_2$-LH_2, while equimolar reactions of $PhAsCl_2$ with Na_2L yield substitution products PhAsL. All these derivatives have been characterized by elemental analyses and their plausible structures have been established on the basis of physico-chemical, IR, and NMR (^1H and ^{13}C) spectral studies.* © 2003 Wiley Periodicals, Inc. Heteroatom Chem 15:92–96, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10220

INTRODUCTION

Benzothiazoline ring opening is induced by metal ions with the formation of chelates [1,2]. However, in certain cases the benzothiazolines form addition products. For example, $AsCl_3$ [3], $SbCl_3$ [3], and $BiCl_3$ [3], and benzothiazoline yield addition products and the benzothiazoline ring does not open. However, with $Me_3Sn(OH)$ [4] and $Me_3Sn(OEt)$ [4], substitution products are formed with the opening of the benzothiazoline ring.

In view of the varying behavior of benzothiazoline as ligand, we have investigated the reactions of $PhAsCl_2$ with NaOMe and three 2-(2-hydroxyphenyl)benzothiazolines LH_2 in two ways differing in the sequence of combinations. The results are described and discussed in this communication.



	LH_2	R	X
a	L^1H_2	H	H
b	L^2H_2	Me	H
c	L^3H_2	H	OMe

RESULTS AND DISCUSSION

Equimolar amounts of $PhAs(OMe)_2$ (prepared in situ) and the benzothiazolines LH_2 yield 1:1 addition products.

$$PhAsCl_2 + 2NaOMe \rightarrow PhAs(OMe)_2 + 2NaCl$$

$$PhAs(OMe)_2 + LH_2 \rightarrow PhAs(OMe)_2LH_2$$

1a–c

However, the equimolar reaction of $PhAsCl_2$ with the sodium salts of the benzothiazolines, Na_2L, in benzene solution proceed with the rearrangement of benzothiazoline ring and the formation of As—S and

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As—O bonds yielding the substituted products.

$$LH_2 + 2NaOMe \rightarrow Na_2L + 2MeOH$$

$$PhAsCl_2 + Na_2L \rightarrow PhAsL + 2NaCl$$

2a–c

After removing the solvent under reduced pressure, colored viscous complexes soluble in common organic solvents like benzene, chloroform, etc., are obtained. These complexes are found to be monomeric in benzene solution. Their solubility decreases on ageing.

SPECTROSCOPIC STUDIES

IR Spectra

Absence of νSH mode (~2540 cm^{-1}) and the presence of νNH mode in the range 3260–3390 cm^{-1} in the spectra of ligands indicates the presence of benzothiazoline ring in the ligands. In the spectra of complexes (**1a–c**), the νNH band appears with a lowering of 25–30 cm^{-1} in its position. This indicates the participation of NH group in bonding. This is further supported by the appearance of a new band in the region 425–442 cm^{-1} which has been assigned to As ← N [5] stretching vibration. No significant shift has been observed in the position of phenolic OH band on complexation indicating that this group does not participate in bonding.

A comparative study of the IR spectra of complexes (**2a–c**) with the corresponding ligands shows the disappearance of —NH and phenolic —OH stretching bands, which were observed at 3260–3390 cm^{-1} and 3251–3427 cm^{-1} respectively. Bands observed in the region 1619–1645, 428–441, 366–380, and 427–485 cm^{-1} have been assigned to νC=N, νAs ← N [5], νAs-S [6], and νAs—O [7] modes of vibrations respectively. This may be interpreted in term of the opening of the benzothiazoline ring and the formation of Schiff base complexes. The νAs—C [8,9] band has been observed at 442–454 cm^{-1}.

^{1}H NMR Spectra

The ^{1}H NMR spectra of **1a–c** (Table 1) show a downfield shift of NH signal. This supports the formation of As←N bond during complexation. A signal for phenolic —OH has been observed in the range δ 12.20–12.82 ppm. No appreciable shift has been observed in the position of phenolic —OH signal on complexation indicating that this group does not participate in bonding.

However, the spectra of **2a–c** show the disappearance of NH signal and downfield shifting of C(R)—N proton signal. This supports the opening of benzothiazoline ring with no protonation of S and the formation of As—S bond. Absence of phenolic —OH signal (observed at δ 12.20–12.82 ppm in parent ligands) in the spectra of **2a–c** reveals the deprotonation of —OH group, due to bonding and the formation of an As—O bond.

^{13}C NMR Spectra

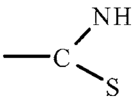
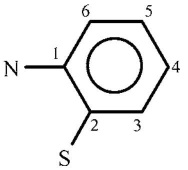
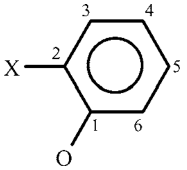
A comparative study of ^{13}C NMR spectra of the benzothiazoline ligands with their monophenylarsenic(III) complexes provides useful informations about the mode of bonding in these complexes. The spectra of complexes **1a–c** (Table 2) show a small shift in the position of $>$C(R)—N signal as compared to their position in free ligands. This indicates the involvement of nitrogen atom of the benzothiazoline in bonding. No appreciable shift has been observed in the position of $>$C—O(H) group carbon on complexation indicating that this group does not participate in the bonding. However, in the spectra of complexes **2a–c** (Table 2) a downfield shift of C—N carbon signal which appear at δ 164.02–166.72 ppm, confirms the formation of $>$C=N → As bond by rearrangement of benzothiazoline ring and no protonation of —S during the complexation. A downfield shift in the position of C—O group on complexation indicates deprotonation of phenolic —OH group and the formation of an As—O bond. The substituted phenyl ring carbons are observed in the range δ 122.01–171.92

TABLE 1 δ ^{1}H (ppm) of **1a–c** and **2a–c**

	R	*OMe*	*Aromatic*	*OH*	*NH*	*C_6H_5—As*
1a	8.72	3.37	6.88–7.41	12.69	8.29	7.86–8.12
1b	2.33	3.40	6.37–7.75	12.22	4.12	7.79–8.14
1c[a]	8.04	3.46	6.78–7.85	12.83	7.98	7.94–8.20
2a	–	–	6.92–7.43	–	–	7.88–8.14
2b	–	–	6.47–7.77	–	–	7.79–8.16
2c[a]	–	–	6.80–7.91	–	–	7.98–8.31

[a] OCH_3 Signal for **1c** and **2c** has been observed as singlet at δ 3.91 ppm.

TABLE 2 δ ^{13}C (ppm) of **1a–c** and **2a–c**

	CH_3	OMe	>C=N				As–Ph[a]	δ' ($\sigma R°$)
1a	–	47.86	–	161.92	149.48(1), 137.82(2), 134.09(3), 128.41(4), 124.92(5), 122.31(6)	169.18(1), 124.62(2), 133.41(3), 118.02(4), 134.42 (5), 122.01(6)	152.36 135.71 126.98 124.27	−2.71 (−0.12)
1b	25.75	52.06	–	161.96	149.25(1), 137.65(2), 134.12(3), 128.96(4), 125.01(5), 123.11(6)	169.30(1), 128.12(2), 134.32(3), 118.81(4), 133.92(5), 122.32 (6)	152.48 135.96 126.82 124.21	−2.61 (−0.11)
1c	–	53.92	–	160.99	149.36(1), 137.91(2), 134.36(3), 128.99(4), 125.11(5), 122.16(6)	169.17(1), 125.01(2), 134.65(3), 119.01(4), 134.55(5), 122.44(6)	152.77 135.84 126.47 123.77	−2.70 (−0.12)
2a	–	–	166.72	–	148.97(1), 138.81(2), 134.12(3), 128.45(4), 125.61(5), 123.04(6)	171.86(1), 126.21(2), 135.04(3), 119.22(4), 134.96(5), 123.02(6)	154.92 136.81 129.42 126.81	−2.61 (−0.11)
2b	25.96	–	164.02		149.28(1), 139.01(2), 134.49(3), 128.96(4), 125.91(5), 122.33(6)	171.92(1), 128.12(2), 134.96(3), 119.01(4), 134.88(5), 123.99(6)	154.86 136.93 129.55 126.84	−2.71 (−0.12)
2c	–	–	166.26	–	149.91(1), 139.59(2), 134.91(3), 128.65(4), 125.77(5), 123.92(6)	171.89(1), 124.92(2), 135.02(3), 119.14(4), 134.12(5), 123.29(6)	154.79 136.96 129.96 126.91	−2.71 (−0.12)

[a] Phenylarsenic carbon values are given in order C(i), C(o), C(m), and C(p), respectively.

ppm. The —NC_6H_4S carbon signals are observed in the range δ 122.31–149.97 ppm. A new set of four signals observed in the range δ 123.77–152.77 ppm (**1a–c**) and δ 126.81–154.92 ppm (**2a–c**) have been assigned to phenyl ring carbons attached to arsenic atom.

In view of the possibility of dπ–pπ conjugation between As—Ph the corrected chemical shift value δ' [10] have been calculated by the relation $\delta' = \delta$ C(p) − δC(m) (where δC(p) and δC(m) are the chemical shift values of para and meta carbons of the ring). The δ' values are found to be negative in range −2.61 to −2.71 ppm. The Hammet-Taft constant [11] [$\sigma R^\circ = \delta'/22.06$] is also found to be negative in these complexes. Negative values of δ' as well as σR° indicate dπ–pπ conjugation with poor electron shift from arsenic to phenyl group in these complexes.

In view of the monomeric nature of these derivatives and monodentate (**1a–c**) and tridentate (**2a–c**) behavior of ligand moieties in the complexes as evident from observed IR and NMR spectral data, the following structures (Fig. 1) in which the central arsenic atom acquires trigonal bipyramidal coordination appear to be highly plausible.

EXPERIMENTAL

All the reactions were carried out under anhydrous conditions. The chemicals used were of

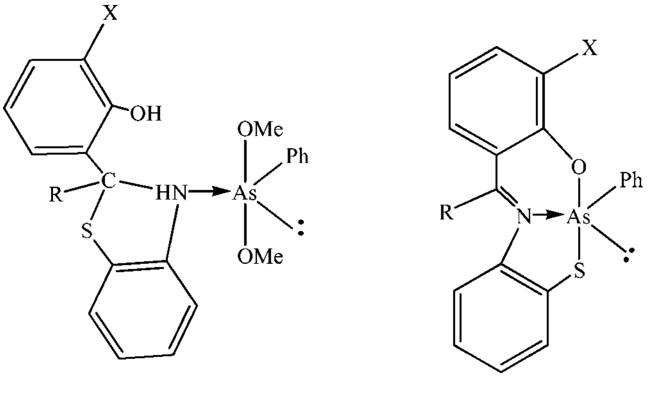


FIGURE 1 Suggested structures of **1** and **2**.

TABLE 3 Synthetic and Analytical Data of **1a–c** and **2a–c**

	Reactants[a] (g)			*Molecular Formula,*	*% Analysis[b] Found*			*M. Wt.[b]*
	Na	*LH_2*	*$PhAsCl_2$*	*Color, and Yield (%)*	*As*	*S*	*N*	*Found*
1a	0.24	1.22	1.18	$C_{21}H_{22}AsNO_3S$,	16.58	7.02	2.29	440
	(10.6)	(5.30)	(5.30)	brown viscous, 83	(16.89)	(7.23)	(3.16)	(443.4)
1b	0.20	1.14	0.98	$C_{22}H_{24}AsNO_3S$,	16.21	6.89	2.89	452
	(8.78)	(4.39)	(4.39)	brown viscous, 85	(16.38)	(7.01)	(3.06)	(457.4)
1c	0.16	0.88	0.76	$C_{22}H_{24}AsNO_4S$,	15.68	6.54	2.62	469
	(6.82)	(3.41)	(3.41)	greenish brown viscous, 84	(18.53)	(6.77)	(2.96)	(473.4)
2a	0.19	0.99	0.96	$C_{19}H_{14}AsNOS$,	19.21	8.34	3.54	374
	(8.62)	(4.31)	(4.31)	brown viscous, 87	(19.75)	(8.45)	(3.69)	(379.3)
2b	0.18	0.95	0.87	$C_{20}H_{16}AsNOS$,	18.92	8.01	3.39	389
	(7.80)	(3.90)	(3.90)	brown viscous, 84	(19.05)	(8.15)	(3.56)	(393.4)
2c	0.17	0.98	0.85	$C_{20}H_{16}AsNO_2S$,	18.22	7.54	3.23	402
	(7.62)	(3.81)	(3.81)	greenish brown viscous, 86	(18.30)	(7.83)	(3.42)	(409.4)

[a] The values given in parentheses are given in millimoles.
[b] The values given in parentheses are calculated values.

reagent grade. Solvents (E-merck) were purified and dried by standard procedures [12]. Monophenylarsenic(III)dichloride was prepared by the literature method [13]. The benzothiazolines LH_2 [4] were prepared by the equimolar condensation reaction of 2-aminothiophenol and $HOC_6H_3XC(R)=O$. Arsenic was estimated iodometrically [14]. Sulphur and nitrogen were estimated by Messanger's and Kjeldahl's methods [14] respectively. Molecular weights of these complexes were determined ebullioscopically in benzene solution, using Beckmann's thermometer. IR spectra are recorded on a Nicolet DX FT IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL-FX-90 Q (90 MHz) and Bruker DPX (300 MHz) NMR in $CDCl_3$, using TMS as an internal reference.

As the synthetic procedures for **1a–c** as well as for **2a–c** are the same, the preparative details are given only for one complex of each type and are summarized in Table 3.

Synthesis of **1b**

A weighed amount of sodium metal (0.20 g, 8.79 mmol) was added to ∼15 ml of dried methanol with constant stirring for ∼30 min, and a benzene suspension of $PhAsCl_2$ (0.98 g, 4.39 mmol) was added to it. The contents were heated for about 30 min. A benzene solution (∼20 ml) of L^2H_2 (1.07 g, 4.39 mmol) was then added to the above and the reaction mixture was refluxed for ∼4 h. NaCl (0.51 g, 8.79 mmol) thus formed was filtered off and the solvent from the filtrate was removed under reduced pressure. For the purification, the viscous compound was dissolved in a small amount of $CHCl_3$ (∼15 ml), and *n*-hexane was slowly added to it till a viscous compound begins to separate. The solution was kept overnight at −10°C. The solvent was decanted and the compound was dried under vacuum.

Synthesis of **2b**

A weighed amount of sodium metal (0.18 g, 7.80 mmol) was added to ∼15 ml dried methanol with constant stirring for ∼30 min and a benzene solution of (0.95 g, 3.90 mmol) was added to it. The contents were heated for about 1 h. A benzene suspension of $PhAsCl_2$ (0.87 g, 3.90 mmol) was then mixed to it and the reaction mixture was further refluxed for ∼4 h. After the completion of the reaction, precipitated NaCl was filtered off and the excess solvent was removed from the filtrate under reduced pressure. The viscous compound thus obtained was then purified by dissolving it in a small amount of $CHCl_3$ (∼15 ml), and *n*-hexane slowly added till a viscous compound begin to separate out. The solution was kept overnight at −10°C. The solvent was decanted and the compound was dried under vacuum.

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