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Synthesis and Characterization of Some Novel Triphenylarsenic(V) Derivatives of Monofunctional Bidentate 2,2-Disubstituted Benzothiazoline Ligands

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ABSTRACT: *A series of triphenylarsenic(V) derivatives $Ph_3As(OPr^i)[SC_6H_4N{:}C(R)CH_2C(O)R]$ have been synthesized by the reactions of triphenylarsenic(V)-isoproproxide, $Ph_3As(OPr^i)_2$ with the corresponding 2,2-disubstituted benzothiazolines of the type $HNC_6H_4SC(R)CH_2C(O)R'$ (where $R = CH_3$, $R' = CH_3$(**1**); $R = CH_3$, $R' = C_6H_5$(**2**); $R = CH_3$, $R' = 4\text{-}CH_3C_6H_4$(**3**); $R = CH_3$, $R' = 4\text{-}ClC_6H_4$(**4**); and $R = CF_3$, $R' = C_6H_5$(**5**)) in equimolar ratio in refluxing benzene solution. Molecular weight measurements of these complexes show their monomeric nature in solution. Characterization of these compounds using elemental analyses, molecular weight measurements, and spectral studies (IR as well as NMR (^1H and ^{13}C)) shows the monofunctional bidentate nature of the ligands and a hexacoordination around the central arsenic atom in these organoarsenic(V) derivatives.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:76–80, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20233

INTRODUCTION

Compounds containing heavier group 15 elements have attracted attention over the last decade because of their applications in heterogeneous catalysis [1–3] and as precursors for superconducting materials in MOCVD process [4,5]. The use of organoarsenic in medicines dates from the discovery in 1905 by H.W. Thomas after atoxyl cure hypsoniasis, i.e., sleeping sickness. In 1907, R.E. Rechard and A. Bertheins showed that atoxyl was sodium hydrogen-4-aminophenylarsonate [6]. Recently interest has also been renewed in low temperature ionic liquid technology using organoarsenic derivatives for electrodeposition of actinides of relevance to nuclear fuel processing [7]. In addition to these applications, these compounds also display structural diversity which, for various organoarsenic complexes, has been established ranging from monomeric complexes [8,9] to structures with infinite polymeric chains [10,11].

Benzothiazolines constitute an important class of multidentate ligands [12]. The use of these Lewis base functionalized ligands can be effective in increasing the coordination number of the group 15 center at the expense of benzothiazoline ring to the corresponding Schiff base leading to greater stability of the compounds. In view of the above and in continuation of our analogous studies on organoantimony(V) derivatives [13], we report herein the synthesis and characterization of triphenylarsenic(V) derivatives of these ligands.

RESULTS AND DISCUSSION

The reactions of $Ph_3As(OPr^i)_2$ with a number of benzothiazoline ligands of the type $H\,NC_6H_4SC(R)CH_2C(O)R'$ in 1:1 molar ratios in refluxing anhydrous

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benzene yielded the corresponding organoarsenic(V) derivatives 1–5 represented by the following equations:

(i) $2Pr^iOH + 2Na \longrightarrow 2NaOPr^i + H_2\uparrow$

(ii) $2NaOPr^i + Ph_3AsBr_2 \xrightarrow[\text{Reflux}]{C_6H_6} Ph_3As(OPr^i)_2 + 2NaBr\downarrow$

(iii) $Ph_3As(OPr^i)_2 + H\overline{NC_6H_4SC}(R)CH_2C(O)R' \xrightarrow[\text{Reflux}]{C_6H_6} Ph_3As(OPr^i)[SC_6H_4N{:}C(R)CH_2C(O)R'] + Pr^iOH$

where $R = CH_3$, $R' = CH_3$(**1**); $R = CH_3$, $R' = C_6H_5$(**2**); $R = CH_3$, $R' = 4\text{-}CH_3C_6H_4$(**3**); $R = CH_3$, $R' = 4\text{-}ClC_6H_4$(**4**), and $R = CF_3$, $R' = C_6H_5$(**5**).

The synthetic and analytical data of these derivatives 1–5 are summarized in Table 1. All these reactions are quantitative and quite facile. Their progress and completion has been checked by estimating the isopropanol liberated azeotropically during the course of the reactions. The products obtained are hygroscopic, light to dark brown colored, viscous compounds, and soluble in common organic solvents. Ebullioscopic molecular weight measurements reveal their monomeric nature in the benzene solution.

IR SPECTRA

A comparison of the IR spectra of the complexes 1–5 with the IR spectra of corresponding free ligands show the following features: Disappearance of the broad stretching vibrations, observed at 3225–3335 cm^{-1} due to >N—H group in the spectra of the free ligands, suggesting the rearrangement of the benzothiazoline ring during complexation and the formation of the C=N bond. This rearrangement of the benzothiazoline ring is also supported by the appearance of three new bands at 1610–1622 cm^{-1}, 427–435 cm^{-1}, and 373–390 cm^{-1} due to ν(>C=N), ν(As←N) [14], and ν(As–S) [15] vibrations, respectively. No shift has been observed in the position (1720–1730 cm^{-1}) of the absorption band due to >C=O group on complexation, indicating that this group does not participate in bonding. The As–Ph vibrations (Y-mode) have been observed in the range 470–495 cm^{-1} [16].

^{1}H NMR SPECTRA

The characteristic signals in the ^{1}H NMR spectra of these derivatives are summarized in Table 2. The

TABLE 1 Synthetic and Analytical Data and Physical Properties of the Derivatives from 1 to 5

Complex	Reactants (g) (mmol)			Molecular Formula, Color, Physical State, and % Yield	Pr^iOH(g) Found (Calcd)	Analysis % Found (Calcd)				Molecular Weight Found (Calcd)
	Na	Ph_3AsBr_2	Ligand			As	N	S	OPr^i	
1. R = CH_3, R′ = CH_3	0.30 (13.05)	3.03 (6.50)	1.35 (6.51)	$C_{32}H_{34}NO_2SAs$, Light brown, viscous, 83	0.37 (0.39)	13.05 (13.11)	2.38 (2.45)	5.57 (5.61)	10.24 (10.34)	563 (571.60)
2. R = CH_3, R′ = 	0.29 (12.87)	3.00 (6.44)	1.73 (6.42)	$C_{37}H_{36}NO_2SAs$ Dark brown, viscous, 86	0.36 (0.39)	11.75 (11.82)	2.18 (2.21)	5.01 (5.06)	9.25 (9.32)	622 (633.67)
3. R = CH_3, R′ = 	0.31 (13.48)	3.15 (6.76)	1.91 (6.77)	$C_{38}H_{38}NO_2SAs$, Light brown, viscous, 85	0.37 (0.41)	11.50 (11.56)	2.12 (2.16)	4.88 (4.95)	9.04 (9.12)	635 (647.70)
4. R = CH_3, R′ = 	0.28 (12.18)	2.79 (5.99)	1.82 (5.99)	$C_{37}H_{35}ClNO_2SAs$, Black, viscous, 81	0.34 (0.36)	11.16 (11.21)	2.04 (2.10)	4.74 (4.80)	8.77 (8.84)	659 (668.12)
5. R = CF_3, R′ = 	0.26 (11.31)	2.62 (5.62)	1.82 (5.63)	$C_{37}H_{33}F_3NO_2SAs$, Dark brown, viscous, 88	0.31 (0.34)	10.85 (10.90)	1.98 (2.04)	4.57 (4.66)	8.51 (8.59)	680 (687.64)

TABLE 2 ^{1}H NMR Spectral Data (δ ppm) of the Derivatives 1–5

		Schiff Base Moiety				*Isopropoxy Moiety*		
	Complex	*R*	*R′*	*—CH_2—*	*—NC_6H_4S—*	*—OCH*	*—CH_3*	*Phenyl (Ph-Sb) Moiety*
1.	R = CH_3, R′ = CH_3	2.19(s)	1.82(s)	2.83(s)	7.13–7.70(m)	3.72(sept)	1.04 (d)	7.74–8.04(m)
2.	R = CH_3, R′ = 	2.55(s)	7.20–7.78(m)	2.75(s)	7.20–7.78(m)	3.67(sept)	1.09 (d)	7.82–8.08(m)
3.	R = CH_3, [a]R′ = 	2.62(s)	6.97–7.70(m)	2.61(s)	6.97–7.70(m)	3.70(sept)	1.03 (d)	7.78–8.12(m)
4.	R = CH_3, R′ = 	2.40(s)	6.91–7.64(m)	2.43(s)	6.91–7.64(m)	3.71(sept)	0.96 (d)	7.68–8.03(m)
5.	R = CF_3, R′ = 	–	7.26–7.78(m)	2.49(s)	7.26–7.78(m)	3.70(sept)	1.02 (d)	7.82–8.11(m)

(s) = singlet; (d) = doublet; t = triplet; (m) = multiplet; (sept) = septet.
[a]A singlet for –CH_3 protons has been observed at δ 2.40 ppm.

broad signal observed at δ 4.53–6.46 ppm, due to the NH group resonance in the spectra of benzothiazolines, is found to be absent in the corresponding triphenylarsenic(V) derivatives indicating the deprotonation of NH proton and rearrangement of the benzothiazoline ring during the complex formation. A sharp singlet observed at δ 2.43–2.83 ppm has been assigned to CH_2 protons. The absence of =CH as well as —C—OH signals and the presence of CH_2 signal in the spectra of both ligands and their corresponding complexes indicate the absence of enolization of >C=O group in these ligands, i.e., these ligands do not behave as bifunctional moieties in these derivatives, as reported by earlier workers in the case of Al [17], Ga and In [18]. Different R and R′ protons have been observed at their expected positions with small downfield shifts as compared to their positions in corresponding free ligands. Phenyl (directly attached to As) protons appear as a complex pattern in the range δ 7.68–8.12 ppm.

^{13}C NMR SPECTRA

Some useful information about the complexation behavior of benzothiazolines with central As atom and the geometry of these derivatives have been obtained from ^{13}C NMR spectral data summarized in Table 3. The signal observed for >C=N group carbon at δ 161.39–165.74 ppm in the spectra of free benzothiazolines (present as C—N) have been observed at δ 165.18–167.26 ppm in the spectra of these derivatives. This small downfield shifting (~2–4 ppm) in the position of >C=N group signal suggests the participation of this group in bonding with rearrangement of the benzothiazoline ring on complexation followed by the formation of As←N and As–S bonds. The signals for various R, R′, and CH_2 carbons show a small shift in comparison to their positions in free ligands.

The presence of the —CH_2— signal instead of the =CH signal indicates that enolization does not take place in these ligands. Appearance of >C=O signal at δ 195.93–198.57 in the spectra of ligand also rules out the possibility of the enolization in these ligands. This resonance signal does not show any shift in its position indicating that oxygen is not coordinated to the central atom. The presence of >CH(OPr^i) and —CH_3(OPr^i) resonances at δ 79.30–81.12 and δ 19.67–25.94 ppm, respectively, indicates the monofunctional behavior of these ligands. It is clear from the above facts that, in contrast to the earlier [17,18], these ligands behave as monofunctional bidentate moiety in these derivatives. The phenyl carbons appear in the region δ 128.25–155.85 ppm.

On the basis of these results, the plausible structure (Fig. 1) may be proposed for these

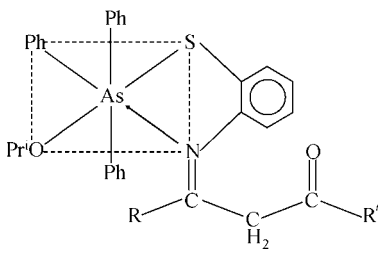

FIGURE 1 Proposed structure of the derivatives 1–5.

TABLE 3 ^{13}C NMR Spectral Data (δ, ppm) of the Derivatives 1–5

		Schiff Base Moiety						*Isopropoxy Moiety*		
	Complex	*R*	*R′*	*—CH_2—*	*—NC_6H_4S—*	*>C=O*	*>C=N*	*—OCH*	*—CH_3*	*Phenyl (Ph-Sb) Moiety*
1.	R = CH_3 R′ = CH_3	24.38	19.64	42.25	152.34,136.76, 134.70,131.18, 127.43, 122.16	195.93	165.18	79.67	25.94	154.17 (i) 135.26 (o) 128.97 (m) 128.43 (p)
2.	R = CH_3 R′ = 	26.64	135.20 133.09 130.26 129.65	40.32	151.78, 135.19, 133.50,130.68, 127.13,122.85	197.85	166.79	79.30	19.67	155.85 (i) 133.75 (o) 128.78 (m) 128.29 (p)
3.	R = CH_3 [a]R′ = 	26.10	132.78 131.98 130.29 129.35	41.86	151.98,135,77, 143.14,130.87, 127.64,122.88	198.15	166.40	80.35	25.16	154.76 (i) 133.40 (o) 128.72 (m) 128.25 (p)
4.	R = CH_3 R′ = 	26.53	135.18 133.04 128.51 129.93	40.82	154.09,135.23, 133.15,130.64, 127.34,122.13	198.57	165.78	81.12	25.40	154.73 (i) 136.75 (o) 129.04 (m) 128.43 (p)
5.	R = CF_3 R′ = 	108.12	134.13 132.25 128.87 130.92	40.26	152.69,135.18, 133.03,130.54, 127.35,122.86	197.35	167.26	79.96	24.16	155.27 (i) 136.37 (o) 128.98 (m) 130.29 (p)

[a] ^{13}C signal for $-CH_3$ group has been observed at δ 27.64 ppm.

triphenylarsenic(V) derivatives in which central arsenic atom adopts an octahedral geometry.

EXPERIMENTAL

Moisture was carefully excluded throughout the experimental manipulations. All the chemicals used were of reagent grade. Solvents (E. Merck) were carefully dried by standard methods before use. The benzothiazoline ligands were prepared [12] by equimolar condensation reactions of 2-aminothiophenol with corresponding β-diketones in refluxing benzene solution and were purified by distillation under vacuum before use. Ph_3AsBr_2 was prepared by the literature method [19]. Triphenylarsenic(V) isopropoxide was prepared by the reaction of Ph_3AsBr_2 with sodium isopropoxide [20]. Arsenic was estimated iodometrically [21]. Nitrogen and sulfur were estimated by Kjeldahl's and Messenger's methods, respectively [21]. Isopropanol and isopropoxide were estimated by the chromate oxidimetric method [22].

Molecular weight measurements were carried out by ebullioscopic method in the benzene solution using a Beckmann's thermometer. The IR spectra were recorded on a Nicolet DX FTIR spectrophotometer in the range 4000–200 cm^{-1} on a CsI cell. ^1H and ^{13}C NMR spectra were recorded in DMSO-d_6 solution on a JEOL-FX-90Q or Brucker DPX-300 MHz NMR spectrometer, using TMS as an internal and external reference, respectively.

Synthesis of **1**

A weighed amount of sodium metal (0.30 g, 13.05 mmol) was added to ~20 mL of anhydrous isopropanol, and the mixture was stirred for ~1 h. A benzene solution of Ph_3AsBr_2 (3.03 g, 6.50 mmol) was added to it, and the reaction mixture was refluxed for about 4 h. The NaBr thus precipitated was filtered off, and the excess solvent from the filtrate was removed under the reduced pressure to give viscous triphenylarsenic (V) isopropoxide. A benzene solution of the ligand $HNC_6H_4SC(CH_3)CH_2C(CH_3)$ (1.35 g, 6.51 mmol) was added in the above $Ph_3As(OPr^i)_2$, and the mixture was refluxed for ~5 h under a fractionating column. The progress as well as the completion of the reaction was checked by estimating the liberated isopropanol in the azeotrope. After the completion of the reaction, the excess solvent was distilled off and traces of solvent were removed under reduced pressure to give a viscous product. This product was purified by dissolving it in a small amount of anhydrous benzene and then adding into it well-dried petroleum ether (40–60°C) until the compound began to separate. This solution was kept overnight at –10°C. After decanting off

the solvent, the compound was dried under vacuum (yield 83%, (3.72g)).

Similar procedure was adopted for the synthesis of all other complexes. Their synthesis and analytical data are summarized in Table 1.

REFERENCES

[1] Boisselier, V. Le; Dunach, E.; Postel, E. J Organomet Chem 1994, 482, 119.
[2] Luo, S. G.; Tan, M. H.; Zhang, J. G.; Wu, Y. J.; Pei, F. K.; Meng, X. H. J Appl Polym Sci 1997, 65, 1217.
[3] Roux, C. Le; Ciliberti, L.; Laurent-Robert, H.; Laporterie, A.; Dubac, J. Synlett 1998, 1249.
[4] Cowley, A. H.; Jones, R.A. Angew Chem, Int Ed 1989, 28, 1208.
[5] Higa, K. T.; George , C. Organometallics 1990, 9, 275.
[6] Greenwood, N. N. Chemistry of Elements; Pergamon Press: London, 1984; p. 694.
[7] Bhatt, A. I.; May, I.; Volkovich, V. A.; Hetherington, M. E.; Lewin, B.; Thied, R. C.; Ertok, N. J Chem Soc, Dalton Trans 2002, 4532.
[8] Gupta, A.; Sharma, R. K.; Bohra, R.; Jain, V. K.; Drake, J. E.; Hursthouse, M. B.; Light, M. E. J Organomet Chem 2003, 667, 61.
[9] Jain, V. K.; Bohra, R.; Mehrotra, R. C. Indian J Chem 1986, 25A, 768.
[10] Levason, W.; Reid, G. J Chem Soc, Dalton Trans 2001, 2953.
[11] Hunter, G.; Weakley, T. J. R. J Chem Soc, Dalton Trans 1983, 1067.
[12] Saraswat, B. S.; Srivastava, G.; Mehrotra, R. C. J Organomet Chem 1977, 137, 301.
[13] Sharma, P. K.; Sharma, R. K.; Rai, A. K.; Singh, Y. P. Main Group Met Chem 2004, 27, 51.
[14] Goyal, R. G.; Maslowsky, E., Jr.; Senoff, C. R. Inorg Chem 1971, 10, 2572.
[15] Chremos, G. N.; Zingaro, R. A. J Organomet Chem 1970, 22, 647.
[16] Maslowsky, E., Jr. J Organomet Chem 1974, 70, 153.
[17] Agrawal, M.; Tandon, J. P.; Mehrotra, R. C. Synth React Inorg Met Org Chem 1980, 10, 9.
[18] Agrawal, M.; Tandon, J. P.; Mehrotra, R. C. J Inorg Nucl Chem 1981, 43, 1070.
[19] Beveridge, A. D.; Harris, G. S.; Inglis, F. J Chem Soc A 1966, 520.
[20] McEwen, W. E.; Briles, G. H.; Giddings, B. E. J Am Chem Soc 1969, 91, 7079.
[21] Vogel, A. I. A Text Book of Quantitative Inorganic Analysis; Longman: London, 1989.
[22] Bradley, D. C.; Mehrotra, R. C.; Abd-el-Halim, F. M. J Chem Soc 1952, 4609.