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Aminoarsolanes. 1. Transamination and Ammonolysis Studies

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The compounds $\overline{\mathrm{OCH_2CH_2OAs}}\mathrm{NR_2}$ and $\overline{\mathrm{OC(CH_3)_2C(CH_3)_2OAs}}\mathrm{NR_2}$ ($\mathrm{R = CH_3, C_2H_5}$, n-$\mathrm{C_3H_7}$) readily undergo transamination in the presence of ammonia, primary amines, and secondary amines at room temperature. The high lability of the aminoarsolane arsenic–nitrogen bond in the presence of a species containing the weakly protonic N–H group and the equilibrium nature of this transamination reaction permit an easy synthetic route to a variety of aminoarsolanes in high yields. In the reaction of $\mathrm{NH_3}$ and $\mathrm{CH_3NH_2}$ with $\overline{\mathrm{OC(CH_3)_2C(CH_3)_2OAs}}\mathrm{NR_2}$, the novel diarsolanylamines are obtained. From the reactions of $\mathrm{NH_3}$ and n-$\mathrm{C_4H_9NH_2}$ with $\overline{\mathrm{OCH_2CH_2OAs}}\mathrm{NR_2}$, $\overline{\mathrm{OCH_2CH_2OAs}}\mathrm{O}\mathrm{CH_2CH_2O}\overline{\mathrm{AsOCH_2CH_2O}}$ and $\mathrm{As_4[N(}n\mathrm{-C_4H_9)]_6}$ are isolated, respectively. These results are discussed relative to a reaction pathway that includes Lewis acid–base interactions at the –O–AsN–H sites on arsolane derivatives. The mass spectral data, fragment ion identities, and fragmentation modes are given for the two series of aminoarsolanes. Molecular ion elimination of a dialkylamino group to yield the respective arsenium ion, $\overline{\mathrm{OCR_2CR_2OAs}}^{+}$, is observed in the electron impact induced fragmentation of the aminoarsolanes. Formation of the $\mathrm{R_2NAs^{+\bullet}}$ ion via aldehyde elimination processes is also an important route for the $\overline{\mathrm{OC(CH_3)_2C(CH_3)_2OAs}}\mathrm{NR_2}$ but not the $\overline{\mathrm{OCH_2CH_2OAs}}\mathrm{NR_2}$ compounds.

Introduction

During initial studies on the chloramination of 2-(dialkylamino)-1,3,2-dioxarsolanes, almost quantitative yields of triazanium chlorides were obtained.[1] This was in contrast to the significantly lower triazanium chloride yields obtained in the chloramination of aminophospholanes.[2,3] The latter reaction was postulated to proceed via an initial reaction of the aminophospholane with $\mathrm{NH_2Cl}$ and a subsequent cleavage of the P–N bond.[2,3] It could also proceed via a transamination of the initial chloramination product, amino(dialkylamino)-dioxaphospholanium chloride, to give a secondary amine that may be chloraminated to yield the triazanium compound.[4] Since aminoarsines are known to readily undergo transamination reactions,[5-10] the aminoarsolanes should be transaminated by ammonia to give a secondary amine.[11] The liberated secondary amine could then react with chloramine and ammonia to give the 1,1-dialkylhydrazine,[12] which would further react with chloramine and ammonia to yield the triazanium salt.[2] This high lability of the As–N bond toward ammonia could explain the increased triazanium yields.

The transamination reaction of aminoarsolanes was investigated to determine its overall importance in the chloramination process and to study this as an easy synthetic route to a variety of substituted aminoarsolanes. While this research was being completed, Kober and co-workers[13-17] published several articles on the synthesis and reactivity of dioxarsolanes, oxathiarsolanes, and dithiarsolanes. Adler and Kober[10] showed that 2-(dimethylamino)-1,3,2-dioxarsolane readily transaminates wiith secondary amines.

Mass spectral data and studies on arsenic–nitrogen-bonded compounds are relatively limited.[9,10,13,18-23] Most available information suggests that the arsenic–nitrogen bond is relatively labile under electron impact. Anderson and Cragg[20] reported that the mass spectra of $\overline{\mathrm{OCH_2CH_2OAs}}\mathrm{N(CH_3)_2}$ and $\overline{\mathrm{OCH_2CH_2OAs}}\mathrm{N(C_2H_5)_2}$ showed the arsenium ion $\overline{\mathrm{OCH_2CH_2OAs}}^{+}$ as one of the most intense peaks. Kober[21] made similar observations in the electron-impact and chemical ionization mass spectra of $\overline{\mathrm{OCH_2CH_2OAs}}\mathrm{N(CH_3)_2}$. The chemical ionization mass spectra of 2-(dimethylamino)-1,3,2-dioxarsolane, 2-(dimethylamino)-1,3,2-oxathiarsolane, and 2-(dimethylamino)-1,3,2-dithiarsolane show the presence of $[\mathrm{M_2 + H}]^+$ and $[\mathrm{M_2 - N(CH_3)_2}]^+$ species.[21] Such species are not observed in the electron-impact mass spectra or are of very low intensity, because of low ion source pressures. Dimeric species and associated fragments have been observed for other cyclic arsenious acid esters, which do not contain an arsenic–nitrogen bond.[22]

Other than the electron-impact studies of 2-substituted 1,3,2-dioxarsenanes,[24] the fragmentation mechanisms associated with these cyclic arsenious acid esters have received little attention. The fragmentation mechanisms have not been reported or confirmed for the aminoarsolanes, nor have elemental ion compositions been determined by high-resolution mass measurements for these compounds.

In this paper the low- and high-resolution mass spectra are reported on a series of 2-(dialkylamino)-1,3,2-dioxarsolanes and 2-(dialkylamino)-4,4,5,5-tetramethyl-1,3,2-dioxarsolanes in an attempt to ascertain fragment ion identities and fragmentation pathways.

Experimental Section

Materials. Pinacol and ethylene glycol were obtained from Eastman Kodak Co. and used as obtained. All solvents used were dried, distilled,

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(3) Utvary, K. *Monatsh. Chem.* **1968**, *99*, 1473.
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(19) Krannich, L. K.; Thewalt, U.; Cook, W. J.; Jain, S. R.; Sisler, H. H. *Inorg. Chem.* **1973**, *12*, 2304.
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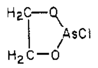
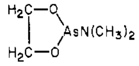
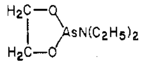
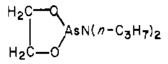
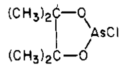
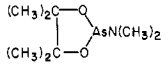
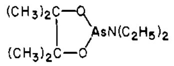
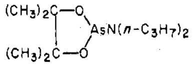
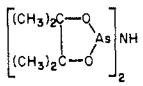
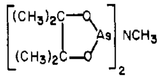
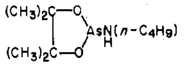
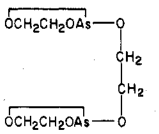
0020-1669/80/1319-3300$01.00/0

Table I. ^1H NMR Spectral Data[a] of Arsolanes

arsolane	δ	area ratio
	$CDCl_3$ solvent 4.33 (s)	
	CCl_4 solvent 4.13 (s)[b]	
	$CDCl_3$ solvent	
	CH_2CH_2: 4.33–3.75 (m)	
	$N(CH_3)_2$: 2.73 (s)	
	$CDCl_3$ solvent	
	CH_2CH_2: 4.33–3.75 (m)	1.0 (1.0)
	NCH_2: 3.23 (q), $J = 0.12$ Hz	1.0 (1)
	CH_3: 1.02 (t), $J = 0.12$ Hz	1.4 (1.5)
	CCl_4 solvent	
	CH_2CH_2: 3.55–4.25 (m)	1.0 (1.0)
	NCH_2: 2.98 (t), $J = 0.12$ Hz	1.0 (1)
	CH_2: 1.82–1.13 (m)	1.1 (1.0)
	CH_3: 85 (t), $J = 0.10$ Hz	1.5 (1.5)
	$CDCl_3$ solvent $(CH_3)_2CC(CH_3)_2$:[c] 1.40 (s), 1.32 (s)	
	CCl_4 solvent	
	$(CH_3)_2CC(CH_3)_2$: 1.20 (s), 1.17 (s)	2.0 (2.0)
	NCH_3: 2.75 (s)	1 (1)
	CCl_4 solvent	
	$(CH_3)_2CC(CH_3)_2$: 1.19 (s), 1.17 (s)	4.6 (4.5)
	CH_3: 1.08 (t), $J = 0.12$ Hz	
	NCH_2: 3.18 (q), $J = 0.12$ Hz	1 (1)
	CCl_4 solvent	
	$(CH_3)_2CC(CH_3)_2$: 1.20 (s), 1.19 (s)	4.1 (4.0)
	CH_2: 3.38–2.33 (m)	
	NCH_2: 3.06 (t), $J = 0.11$ Hz	1 (1)
	CH_3: 1.69 (t), $J = 0.11$ Hz	
	CCl_4 solvent	
	$(CH_3)_2CC(CH_3)_2$: 1.23 (s), 1.17 (s)	
	NH: 4.33 (br)	1 (1)
	C_6D_6 solvent 1.17 (s), 1.07 (s)	24 (24)
	CCl_4 solvent	
	$(CH_3)_2CC(CH_3)_2$: 1.23 (s), 1.18 (s)	8.0 (8.0)
	NCH_3: 2.83 (s)	1 (1)
	$CDCl_3$ solvent	
	NH, NCH_2: 3.38–2.72 (br)	1 (1)
	$CH_2CH_2CH_3$: 1.67–0.70 (m)	6.3 (6.4)
	$(CH_3)_2CC(CH_3)_2$: 1.26 (s), 1.22 (s)	
	Me_2SO-d_6 solvent	
	NH: 4.17 (br, t), $J_{HN-CH} = 0.12$ Hz	1 (1)
	NCH_2: 3.28–2.80 (m)	2 (2)
	$CH_2CH_2CH_3$: 1.58–0.55 (m)	20 (19)
	$(CH_3)_2CC(CH_3)_2$: 1.25, 1.18	
	$CDCl_3$ solvent	
	$\overline{OCH_2CH_2OAs}$: 4.33–3.83 (m)	1.8 (2)
	OCH_2CH_2O: 3.92 (s)	1 (1)
$As_4[N(n\text{-}C_4H_9)]_6$	$CDCl_3$ solvent	
	NCH_2: 3.17 (t), $J = 0.11$ Hz	1 (1)
	CH_2CH_2: 1.83–1.10 (m)	2 (2)
	CH_3: 0.93 (t), $J = 0.11$ Hz	1.5 (1.5)

[a] All values reported downfield of Me_4Si in ppm. Theoretical area ratio values are in parentheses. [b] Foster, R.; Fyfe, C. A. *Spectrochim. Acta* 1965, *21,* 1785.

and stored over calcium hydride. Ammonia, methylamine, and dimethylamine were obtained from Matheson and used as obtained. Diethylamine and di-*n*-propylamine were obtained from Baker Chemical Co. and used as obtained. Arsenic trichloride was obtained from Columbia Organic Chemicals and used as obtained.

All storing and transferring of arsenic-containing starting materials and experimental purification work were conducted in a dry nitrogen atmosphere in a Vacuum Atmospheres Model HE-43 Dri-Lab equipped with a Model HE-493 Dri-Train. Because of the high reactivity of the aminoarsolanes toward oxygen and water, all transamination reactions were carried out in an all-glass vacuum line.

Analyses. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. All molecular weight determinations were by the cryoscopic method. Melting points were determined by using the Thomas-Hoover capillary melting point apparatus with an uncorrected thermometer.

Infrared Spectra. Infrared spectra were recorded on a Beckman IR-20A spectrometer. The spectra were obtained on the solids in the form of Kel-F mulls by using KBr plates for the 4000–1330-cm^{-1} range and as Nujol mulls by using CsI plates for the 1330–500-cm^{-1} range. Previously unreported infrared absorption peaks of all compounds are listed in the supplementary material.

Nuclear Magnetic Resonance Spectra. The proton magnetic resonance spectra were recorded at 60 MHz with a Varian A-60A spectrometer. Tetramethylsilane was used as an internal standard for all spectra when CCl_4, $CDCl_3$, and C_6D_6 were the solvents. The sodium salt of 3-(trimethylsilyl)propanesulfonic acid was used as an internal standard when Me_2SO-d_6 was the solvent. NMR spectral data of all compounds are given in Table I.

Mass Spectra. The low-resolution mass spectra were recorded with a Perkin-Elmer Hitachi RMU-6E mass spectrometer operating at 70 eV. The high-resolution spectra were recorded with an AEI MS-30 mass spectrometer operating at 70 eV and equipped with a DS-30 data system. Perfluorokerosene was used for the high-resolution reference standard. Samples were introduced, in both cases, through an all-glass, gas probe inlet system. The source temperature was kept near 70 °C. The mass spectral data were obtained for the aminoarsolanes $\overline{OCH_2CH_2OAs}NR_2$ and $\overline{OC(CH_3)_2C(CH_3)_2OAs}NR_2$ (R = CH_3, C_2H_5, and n-C_3H_7), and these data are given as supplementary material.

Preparation of 2-(Dialkylamino)-1,3,2-dioxarsolanes. These arsolanes were synthesized by reacting the appropriate amine with previously prepared 2-chloro-1,3,2-dioxarsolane[25] according to the procedure described in the literature.[26] The following synthesis

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(25) Kamai, G.; Khisamova, Z. L. *J. Gen. Chem. USSR (Engl. Transl.)* **1954**, *23*, 1387.

modification gave essentially quantitative yields of all the aminoarsolanes, whereas the literature preparations gave 26.7 and 58.0% yields for the dimethylamino and diethylamino compounds, respectively. The reactions were carried out on the vacuum line in a stainless-steel reaction vessel equipped with stainless fittings and a high-pressure valve. The amine was distilled onto the ether solution of the chloroarsolane at −76 °C and in vacuo. The reaction occurred as the mixture was slowly warmed to 0 °C. The filtrate was fractionally distilled. $OCH_2CH_2OAsN(n\text{-}C_3H_7)_2$ (bp 112 °C (30 torr)) is a clear colorless liquid, very soluble in C_6H_6, $CHCl_3$, CCl_4, and hexane.

Preparation of 2-(Dialkylamino)-4,4,5,5-tetramethyl-1,3,2-dioxarsolanes. These arsolanes were synthesized by reacting the appropriate amine with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxarsolane[27] according to the procedure described in the literature.[26] The modification described above also gave almost quantitative yields of all these aminoarsolanes. $OC(CH_3)_2C(CH_3)_2OAsN(n\text{-}C_3H_7)_2$ (bp 110–111 °C (14 torr)) is a clear colorless liquid, very soluble in C_6H_6, $CHCl_3$, CCl_4, and hexane.

Transamination Reactions of $OCH_2CH_2OAsNR_2$ and $OC(CH_3)_2C(CH_3)_2OAsNR_2$ with Secondary Amines. A typical experimental procedure is demonstrated in the reaction of $OCH_2CH_2OAsN(CH_3)_2$ with $(n\text{-}C_3H_7)_2NH$. 2-(Dimethylamino)-1,3,2-dioxarsolane, $OCH_2CH_2OAsN(CH_3)_2$ (3.6 g, 0.02 mol), was added to a pressure reaction flask which was attached to the vacuum line and degassed. $(n\text{-}C_3H_7)_2NH$ (10 mL) was distilled onto freshly cut sodium in a tube flask and stirred at 0 °C for 30 min. The dried amine was distilled into the reaction flask at −76 °C. The reaction mixture was then warmed to room temperature with constant stirring. After the mixture was stirred overnight at room temperature, all volatile compounds were distilled from the flask.

For those reactions that involved a liberated amine of volatility lower than that of the added amine, the above procedure was modified. A gaseous stream of the added dried amine with or without N_2 as a carrier gas was bubbled through the aminoarsolane in a dry nitrogen atmosphere. In some cases, yield data were obtained from the NMR spectra of the product mixtures.

The elemental analysis data of the newly synthesized compounds are as follows: Anal. Calcd for $OCH_2CH_2OAsN(n\text{-}C_3H_7)_2$: C, 40.84; H, 7.72; As, 31.87; N, 5.96. Found: C, 40.57; H, 7.74; As, 32.27; N, 5.79. Calcd for $OC(CH_3)_2C(CH_3)_2OAsN(C_2H_5)_2$: C, 45.6; H, 8.44; As, 28.46; N, 5.32. Found: C, 45.45; H, 8.49; As, 29.15; N, 5.40. Calcd for $OC(CH_3)_2C(CH_3)_2OAsN(C_3H_7)_2$: C, 49.46; H, 9.00; As, 25.73; N, 4.81. Found: C, 49.82; H, 9.18; As, 27.49; N, 4.87.

Reaction of NH_3 with $OCH_2CH_2OAsNR_2$ and $OC(CH_3)_2C(CH_3)_2OAsNR_2$. A typical reaction is as follows: 2-(Dimethylamino)-4,4,5,5-tetramethyl-1,3,2-dioxarsolane (1.30 g, 5.5 mmol) and diethyl ether (10 mL) were mixed. Liquid ammonia (5 mL) was dried over freshly cut sodium. The ammonia was warmed, and the dry, effluent NH_3 gas was bubbled through the constantly stirred ether solution. After all volatiles were distilled from the product solution in vacuo, a white solid [mp 65 °C (wet appearance), 75 °C (completely melted); bp 126–128 °C (0.05 torr); very soluble in hexane and CCl_4] remained. The yield was 1.02 g (94% of theory). Anal. Calcd for $[OC(CH_3)_2C(CH_3)_2OAs]_2NH$: C, 36.27; H, 6.35; N, 3.53; As, 37.73; mol wt 397. Found: C, 36.21; H, 6.35; N, 3.52; As, 37.80; mol wt 400. The NMR spectral data are given in Table I.

The reaction of $OCH_2CH_2OAsNR_2$ with NH_3 gave a product mixture—a white solid, a viscous oil, and a quantiative yield of the respective amine. All attempts to purify the white solid (insoluble in all common solvents) were unsuccessful. The viscous oil was distilled; bp 47 °C (10^{-3} torr). The crude yield was 91% of theory. Anal. Calcd for $C_6H_{12}As_2O_6$: C, 21.83; H, 3.67. Found: C, 21.52; H, 3.66. The infrared spectral data are given as supplementary material. The NMR spectral data are given in Table I.

All aminoarsolane reactions with ammonia are summarized in Table II.

Reaction of CH_3NH_2 with $OC(CH_3)_2C(CH_3)_2OAsNR_2$. 2-(Diethylamino)-4,4,5,5-tetramethyl-1,3,2-dioxarsolane (2.0 g, 7.6 mmol) was added to a 100-mL, three-necked round-bottom flask equipped with a rubber serum plug, vacuum stopcock adapter, and glass stopper. The flask was connected to a nitrogen bypass line, and dry CH_3NH_2 was bubbled through the liquid, by means of a hypodermic needle inserted through the serum plug, until frothing of the liquid ceased (approximately 15 min). Distillation of the volatile fraction from the product solution at reduced pressure yielded a tacky white solid. Dissolution of the solid with hexane followed by evaporation of the hexane solution produced 1.57 g (100% of theory) of white solid. Recrystallization in cold hexane yielded 0.50 g (33% of theory) of white solid, mp 98–100°. The material was extremely soluble in hexane and all common organic solvents. Anal. Calcd for $[OC(CH_3)_2C(CH_3)_2OAs]_2NCH_3$: C, 37.95; H, 6.62; N, 3.41; As, 36.45; mol wt 411. Found: C, 38.61; H, 6.72; N, 3.24; As, 36.80; mol wt 410. NMR spectral data are given in Table I. Table II summarizes similar reactions.

Reaction of $n\text{-}C_4H_9NH_2$ with $OC(CH_3)_2C(CH_3)_2OAsCl$. The procedure described under the preparation of 2-(dialkylamino)-4,4,5,5-tetramethyl-1,3,2-dioxarsolane was used. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxarsolane, $OC(CH_3)_2C(CH_3)_2OAsCl$ (22.0 g, 97 mmol), and 14.6 g (0.2 mol) of $n\text{-}C_4H_9NH_2$ yielded 24.5 g of liquid (after distillation of the reaction filtrate on a falling-film molecular still at 25 °C and 0.01 torr). Anal. Calcd for $C_{36}H_{79}As_4N_3O_6$: C, 45.51; H, 8.39; As, 31.57; N, 4.42; mol wt 949. Found: C, 45.34; H, 8.32; As, 31.55; N, 4.27; mol wt 466 (in benzene).

Upon standing at room temperature and atmospheric pressure or in vacuo, this compound decomposed. One of the decomposition products was $n\text{-}C_4H_9NH_2$. The infrared spectrum of the liquid and the $n\text{-}C_4H_9NH_2$ confirmed this decomposition. A sample of this liquid (10 mL) was heated (150 °C) at 35 torr for 1 h and distilled on a spinning-band column at 0.02 torr. A clear colorless liquid (3 mL) (soluble in $CHCl_3$, CH_3CN, and diethyl ether) was obtained at 58–60 °C. Anal. Calcd for $OC(CH_3)_2C(CH_3)_2OAsN(H)(n\text{-}C_4H_9)$: C, 45.60; H, 8.43; As, 28.57; mol wt 263. Found: C, 45.07, H, 8.53; As, 28.50; mol wt 237. The NMR spectral data are given in Table I. Higher boiling fractions (up to 120 °C) with broad boiling point ranges were collected. All were very viscous, clear colorless liquids, and the NMR spectra of these materials showed peaks associated with $OC(CH_3)_2C(CH_3)_2O$ protons. The NMR spectra of the lower boiling fractions showed peaks (of low relative area ratios as compared with $OC(CH_3)_2C(CH_3)_2O$ peaks) associated with $n\text{-}C_4H_9N$ protons. No pure materials could be isolated from the higher boiling fractions.

Reaction of $n\text{-}C_4H_9NH_2$ with $OCH_2CH_2OAsNR_2$ and $OC(CH_3)_2C(CH_3)_2OAsNR_2$. The experimental procedure described under the transamination reactions was followed. In the reaction of $OC(CH_3)_2C(CH_3)_2OAsN(CH_3)_2$ (2.00 g, 8.5 mmol) with $n\text{-}C_4H_9NH_2$, a clear colorless liquid (2.12 g) and a quantitative yield of $(CH_3)_2NH_2$ were obtained. The infrared and NMR spectral data indicated that the liquid readily decomposed on standing and with mild heating. The liquid was distilled on a falling-film molecular still at 25 °C and 0.01 torr; yield 94% of theory. The infrared and NMR spectral data were identical with those of $OC(CH_3)_2C(CH_3)_2OAsN(H)(n\text{-}C_4H_9)$ isolated from the reaction of $OC(CH_3)_2C(CH_3)_2OAsCl$ with $n\text{-}C_4H_9NH_2$.

The reactions of $OCH_2CH_2OAsNR_2$ with $n\text{-}C_4H_9NH_2$ gave quantitative yields of the respective liberated amine and a clear colorless liquid that readily decomposed. No pure arsenic-containing products could be isolated from these reactions.

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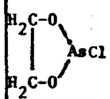
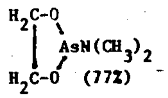
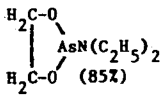
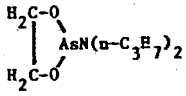
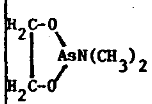
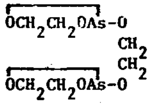
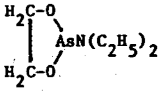
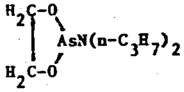
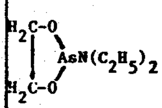
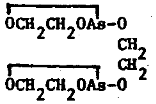
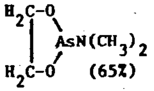
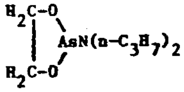
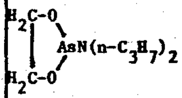
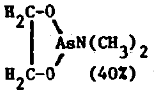
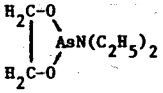
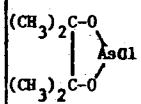
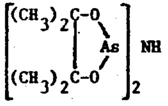
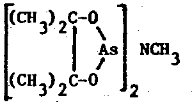
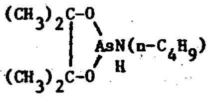
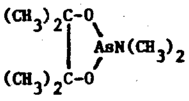
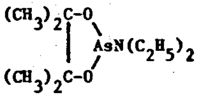
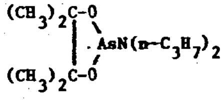
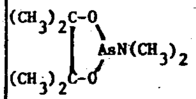
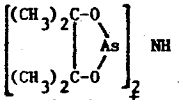
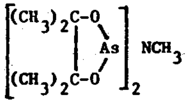
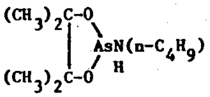
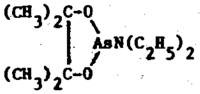
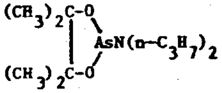
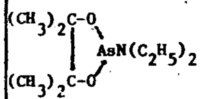
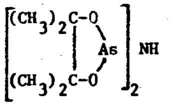
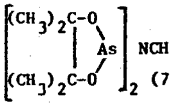
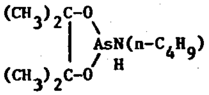
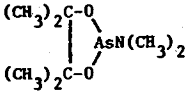
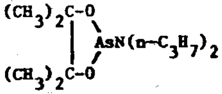
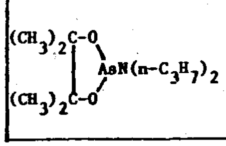
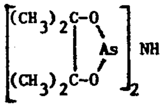
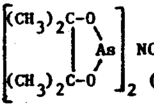
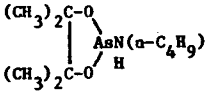
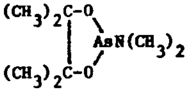
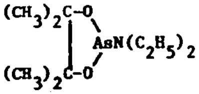
Table II. Summary of Transamination and Aminolysis Reactions

	NH_3	CH_3NH_2	$n\text{-}C_4H_9NH_2$	$(CH_3)_2NH$	$(C_2H_5)_2NH$	$(n\text{-}C_3H_7)_2NH$
			$As_4[N(n\text{-}C_4H_9)]_6$ (90%); mixture; and $C_4H_9NH_3^+Cl$	 (77%) and $(CH_3)_2NH_2^+Cl$	 (85%) and $(C_2H_5)_2NH_2^+Cl$	 and $(n\text{-}C_3H_7)_2NH_2^+Cl$
	 and $(CH_3)_2NH$		mixture and $(CH_3)_2NH$		 and $(CH_3)_2NH$	 and $(CH_3)_2NH$
	 and $(C_2H_5)_2NH$		mixture and $(CH_3)_2NH$	 (65%) and $(C_2H_5)_2NH$		 and $(C_2H_5)_2NH$
				 (40%) and $(n\text{-}C_3H_7)_2NH$	 and $(n\text{-}C_3H_7)_2NH$	
	 and NH_4Cl		 and $n\text{-}C_4H_9NH_3^+Cl$	 and $(CH_3)_2NH_2^+Cl$	 and $(C_2H_5)_2NH_2^+Cl$	 and $(n\text{-}C_3H_7)_2NH_2^+Cl$
	 and $(CH_3)_2NH_2^+Cl$	 and $(CH_3)_2NH$	 and $(CH_3)_2NH$		 and $(CH_3)_2NH$	 and $(CH_3)_2NH$
	 and $(C_2H_5)_2N_2^+Cl$	 (78%) and $(C_2H_5)_2NH$	 and $(C_2H_5)_2NH$	 and $(C_2H_5)_2NH$		 and $(C_2H_5)_2NH$
	 and $(n\text{-}C_3H_7)_2N_2^+Cl$	 (31%) $(n\text{-}C_3H_7)_2NH$	 and $(n\text{-}C_3H_7)_2NH$	 and $(n\text{-}C_3H_7)_2NH$	 and $(n\text{-}C_3H_7)_2NH$	

Reaction of n-$C_4H_9NH_2$ with $\overline{OCH_2CH_2OAs}Cl$. The modified experimental procedure described under the synthesis of (dialkylamino)-1,3,2-dioxarsolanes was used. When $\overline{OCH_2CH_2OAs}Cl$ (34 g, 0.2 mol) was reacted with a large excess of n-$C_4H_9NH_2$, a quantitative yield of n-$C_4H_9NH_3^+Cl^-$ and 38.1 g of a clear, slightly yellow liquid were obtained. Distillation of this liquid gave several fractions boiling up to 137 °C. A clear yellow oil (8.9 g, bp 137–139° C (10^{-5} torr)) was obtained. The yield was 90% on the basis of original postulated aminolysis product. Anal. Calcd for $As_4[N(n\text{-}C_4H_9)]_6$: C, 39.66; H, 7.50; As, 41.27; N, 11.57. Found: C, 38.14; H, 7.49; As, 41.73; N, 11.60. The NMR spectral data are given in Table I.

Discussion

Aminolysis and Transamination Studies of Aminoarsolanes. This study shows that the aminoarsolanes readily transaminate in the presence of ammonia, primary amines, and secondary amines at room temperature. The reaction occurs immediately upon the addition of ammonia or amine and no dependency of the direction or extent of reaction on amine base strength could be noted. The results of this study suggest that the mass action effect is the predominant factor in influencing the relative distribution of aminoarsolanes when the reaction is terminated. Whereas all the aminoarsolane reactions occur quantitatively at room temperature, analogous aminoarsine reactions occur at or above 120 °C.[8] Therefore, the arsenic–nitrogen bond in the aminoarsolanes is much more labile in the presence of the weakly protonic H–N< group than the arsenic–nitrogen bond in the aminoarsines.

The reactions of ammonia with all the aminoarsolanes give a quantitative yield of liberated amine and a condensed arsenic–nitrogen bonded product. The bis(4,4,5,5-tetramethyl-1,3,2-dioxarsolanyl)amine is one of the few known arsenic–nitrogen-bonded compounds that has a N–H bond on the nitrogen bonded to a tricoordinate arsenic.[19,33–36] Such compounds are usually very unstable with respect to intermolecular condensation reactions or intramolecular amine elimination followed by intermolecular cyclization.[7] Therefore, the initial unobserved transaminated species $\overline{OC(CH_3)_2C(CH_3)_2OAs}NH_2$ should immediately undergo an intermolecular condensation reaction to give $[\overline{OC(CH_3)_2C(CH_3)_2OAs}]_2NH$. Further condensation to a triarsolanylamine could be prohibited because of either steric considerations (although space-filling models do not show this) or the electron-withdrawing effects the oxygen atoms bound to arsenic in the diarsolanylamine system have on the basicity of the nitrogen. These electronic effects could also account for the occurrence of $(C_6H_5)_2AsNH_2$,[33] $(CF_3)_2AsNH_2$,[34,35] $[(CF_3)_2As]_2NH$,[34,35] $(CF_3)_2AsNHR$,[34] and $(CF_3)_2(NH)P(CF_3)_2$,[35] since all are compounds in which highly electron-withdrawing groups are bound to arsenic.

In the NMR spectrum in benzene of the diarsolanylamine the two equally intense peaks at 1.17 and 1.07 ppm correspond to the two chemically nonequivalent groups of methyl protons on the arsolane rings. These are only shifted slightly from their positions in the chloro and dialkylamino derivatives. Therefore, the two arsolane rings are chemically equivalent in the bis compound. This suggests that free rotation about both arsenic–nitrogen bonds in this compound is unhindered at 32 °C. Such is not the case in the $\overline{OCH_2CH_2OAs}NR_2$ and $\overline{OC(CH_3)_2C(CH_3)_2OAs}NR_2$ species.[37]

The diarsolanylamine analogue could not be isolated from the reaction of NH_3 with $\overline{OCH_2CH_2OAs}NR_2$. Instead, the 1,2-bis(1,3,2-dioxarsolanyloxy)ethane was obtained in high yield. This compound has been previously reported by Kober[16] as a product from the alcoholysis of $\overline{OCH_2CH_2OAs}N(CH_3)_2$. The infrared spectrum of the insoluble, uncharacterized solid from the reaction of NH_3 with $\overline{OCH_2CH_2OAs}NR_2$ was analogous with that observed for the insoluble, uncharacterized solid obtained from the transamination of $As[N(CH_3)_2]_3$ with ammonia—a few peaks in the C–H region and a very broad and intense band of peaks in the 850–450-cm^{-1} region. These results suggest the formation of a polymeric arsenic–nitrogen-bonded compound containing some residual $\overline{OCH_2CH_2OAs}$ groups. This is not unexpected, considering all the possible inter- and intramolecular interactions and condensation reactions that could occur for the postulated species present during the course of the reaction. Uncharacterized polymeric arsenic–nitrogen-bonded species are always obtained in reactions that might yield the unknown compound $As(NH_2)_3$.[33,38–42]

These ammonolysis reactions suggest that the O–As–N–H region of the initially expected transamination product is a very reactive area for Lewis acid–base interactions between neighboring molecules and that steric considerations at the carbon bound to oxygen influence the ultimate course of the total reaction. For $\overline{OCH_2CH_2OAs}NR_2$ species where the oxygens are readily available, interactions at the –O–As– and –As–N– sites on neighboring molecules can account for the final product $\overline{OCH_2CH_2OAs}OCH_2CH_2O\overline{AsOCH_2CH_2O}$. For the $\overline{OC(CH_3)_2C(CH_3)_2OAs}NR_2$ species, the oxygen atoms are partially blocked, and the interactions at the As–N–H sites on neighboring molecules can account for the final product $[\overline{OC(CH_3)_2C(CH_3)_2OAs}]_2NH$.

The experimental data for the n-$C_4H_9NH_2$ reaction with $\overline{OC(CH_3)_2C(CH_3)_2OAs}NR_2$ suggest that $\overline{OC(CH_3)_2C(CH_3)_2OAs}N(H)(n\text{-}C_4H_9)$ and a mixture of high-boiling liquids and oils with broad boiling point range fractions of varying composition are produced. NMR spectra suggest that opening of the arsolane ring occurs upon decomposition of the initial reaction product. The reaction with $\overline{OCH_2CH_2OAs}NR_2$ gave arsenic-containing products whose NMR spectra also indicate arsolane ring opening and intermolecular condensation. The highest boiling fraction (137–139° C, 10^{-5} torr), $As_4[N(n\text{-}C_4H_9)]_6$, has previously been synthesized from the reaction of n-$C_4H_9NH_2$ with $AsCl_3$ and $As[N(CH_3)_2]_3$[6] and should be the final arsenic–nitrogen bond containing product that would arise from the condensation of unstable $As[N(H)(n\text{-}C_4H_9)]_3$. Analytical and NMR data suggest that the lower boiling fractions are mixtures of >As–N< compounds. Ayed et al.[36] have noted the synthesis of $\overline{OCH_2CH_2OAs}N(H)(n\text{-}C_4H_9)$ as part of their IR study of the doublet observed for the N–H vibration in >As–N–H systems, although no physical or complete spectroscopic data were reported for the compound.

The above results demonstrate the high lability of the aminoarsolane arsenic–nitrogen bond in the presence of ammonia and primary and secondary amines. The relative distribution

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Table III. Relative Abundances and Abundance Ratios of Common Ions in Spectra

amino-arsolane	$[M]^+$	$[M - NR_2]^+$	$[M - NR_2]^+/[M]^+$	$[M - OCR_2'CR_2'O]^+$	$[NR_2]^+$	$[HN(=CH_2)CH_2R]^+$	$[HN(=CH_2)CH_2R]^+/[NR_2]^+$	$[M - (\beta\text{-cleavage fragment})]^+$	$[M - (\beta\text{-cleavage fragment})]^+/[M]^+$
I	37.5	100	2.7[a]	96	84.2				
II	0.9	8.7	9.6[b]	1.4	17.5	100	5.7	2.5	2.8
III	3.8	100	26.3	15.1	3.2	63.8	19.9	50.3	13.2
IV	10.3	4.1	0.4	100	29.0				
V	10.4	42.6	4.1	100	24.7	20.5	0.8	16.6	1.6
VI	9.5	27.0	54	13.7	5.0	100	20.0	11.2	22.4

[a] Literature[20] value was 2.3. [b] Literature[20] value was 7.7.

and types of products and reactants in the product mixture appear to depend on a mass action effect, the types of Lewis acid–base interactions occurring between the –O–As–N–H sites on reacting aminoarsolane derivatives, and steric considerations involving the arsolanyl ring. The reactions provide an easy synthetic route to numerous substituted aminoarsolanes. Undoubtedly, the transamination process involving ammonia plays a very important role in the chloramination of aminoarsolanes in the presence of ammonia. Presently, detailed magnetic resonance dynamical studies of these systems are being carried out.

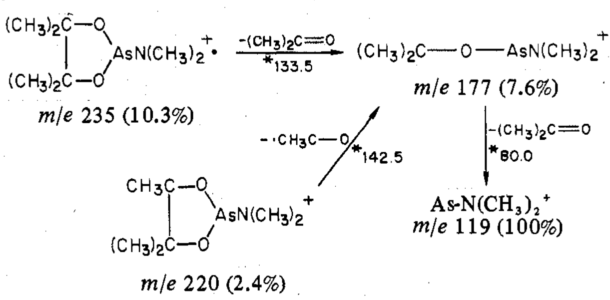
Mass Spectra Studies of the Aminoarsolanes. The mass spectra of $\overline{\text{OCH}_2\text{CH}_2\text{OAs}}\text{N(CH}_3)_2$ and $\overline{\text{OCH}_2\text{CH}_2\text{OAs}}\text{N(C}_3\text{H}_7)_2$ exhibit the arsenium ion $\overline{\text{OCH}_2\text{CH}_2\text{OAs}}^+$ as the base peak. This agrees with the results of previous investigations of $\overline{\text{OCH}_2\text{CH}_2\text{OAs}}\text{N(CH}_3)_2$.[20,21] The metastable at *m/e* 101.7, observed in the spectrum of $\overline{\text{OCH}_2\text{CH}_2\text{OAs}}\text{N(CH}_3)_2$, substantiates the formation of the arsenium ion through the loss of the dimethylamino group by the parent ion The spectra

$$\underset{m/e\ 178.9926}{\overline{\text{OCH}_2\text{CH}_2\text{OAs}}\text{N(CH}_3)_2{}^{+\cdot}} \xrightarrow[*101.7]{-[\cdot\text{N(CH}_3)_2]} \underset{m/e\ 134.9426}{\overline{\text{OCH}_2\text{CH}_2\text{OAs}}{}^{+}} \qquad (1)$$

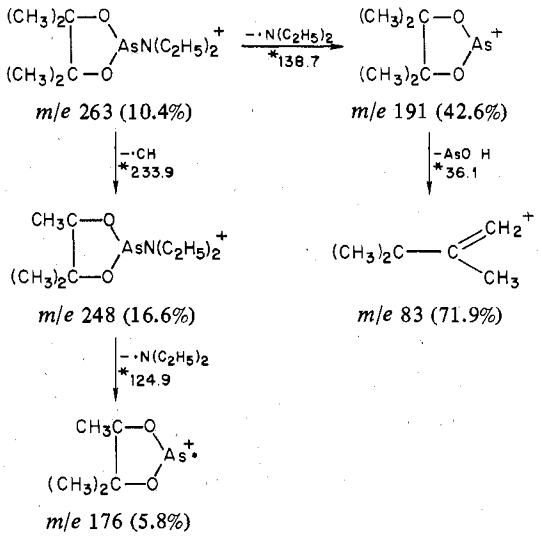
of both these compounds exhibit a number of peaks of appreciable intensity that correspond to species containing an arsenic–nitrogen bond and no arsenic–oxygen bonds. Loss of a dimethylamino group is no more favorable than the loss of $C_2H_4O_2$ in the electron-impact-induced fragmentation of the methyl compound. For the propyl derivative, the loss of $(C_3H_7)_2N\cdot$ or $C_3H_7N{=}CH_2$ is more favorable than the fragmentation of the arsolane ring.

The composition of the base peaks and the relative intensity of the arsenium ion $\overline{\text{OC(CH}_3)_2\text{C(CH}_3)_2\text{OAs}}^+$ in the spectra of $\overline{\text{OC(CH}_3)_2\text{C(CH}_3)_2\text{OAs}}\text{N(CH}_3)_2$ and $\overline{\text{OC(CH}_3)_2\text{C(CH}_3)_2\text{OAs}}\text{N(C}_2\text{H}_5)_2$ suggest that amino group elmination is not as highly favored a pathway for fragmentation of these compounds as observed for $\overline{\text{OCH}_2\text{CH}_2\text{OAs}}\text{N(CH}_3)_2$ and $\overline{\text{OCH}_2\text{CH}_2\text{OAs}}\text{N(}n\text{-C}_3\text{H}_7)_2$. It is, though, a common mode of fragmentation for all the aminoarsolanes. The tetramethyl-substituted arsenium ion decomposes to the stable allylcarbonium ion, $(CH_3)_2C^+C(CH_3)({=}CH_2)$ (*m/e* 83.0858), with a loss of AsO_2H as suggested by the metastable *m/e* at 36.1 in the spectra of the methyl and ethyl dialkylamino derivatives. The intensity of this species—*m/e* 37.0, 71.9, and 37.6 for the methyl, ethyl, and propyl dialkylamino derivatives, respectively—implies that its formation is an important process in the fragmentation mode of these compounds. Suggested fragmentation pathways of the methyl and ethyl compounds are indicated in Schemes I and II. In each case, observed metastables correspond to the indicated mode. The spectrum of $\overline{\text{OC(CH}_3)_2\text{C(CH}_3)_2\text{OAs}}\text{N(}n\text{-C}_3\text{H}_7)_2$ contained no metastables that could be used to indicate fragmentation modes for this species.

Scheme I



Scheme II



A comparison of the relative abundance ratios—$[M - NR_2]^+/[M]^+$—(Table III) suggests increasing stability of the $[M - NR_2]^+$ species relative to the $[M]^+$ species when going from methyl to ethyl to propyl substitution on the nitrogen in each homologous series of aminoarsolanes. This corresponds to the enhanced decomposition of M^+ that results from an increasing stability of the $NR_2\cdot$ radicals with R going from methyl to ethyl to propyl.

Another major fragment in several spectra was the $R_2NAs^{+\cdot}$ ion—$[M - OCR_2CR_2O]^{+\cdot}$. A comparison of $[M - OCR_2CR_2O]^+/[M]^+$ ratios (Table III) suggests no apparent trend with respect to the substituents on the nitrogen but does indicate a dependence on arsolane ring substitution. The replacement of the four hydrogens by four methyl groups tends to favor the formation of the $R_2NAs^{+\cdot}$ ion. Since the fragmentation modes (Scheme I) to this ion involve a breakdown of the arsolane ring species, this influence of methyl substitution on ring stability is consistent with that observed for arsenium ion stability.

All of the arsenic-containing ions in these aminoarsolanes can be assigned structures in which arsenic is monovalent/divalent or divalent/trivalent. No major peaks in the spectra can be assigned structures containing the As=O bond or trivalent/tetravalent arsenic. Such results are in agreement with those of Frøyen and Møller[24,43] for 2-substituted 1,3,2-dioxarsenanes and esters of arsenious acid and may be related to the thermodynamic stability of the As=O bond.[43]

Frøyen and Møller[24] observed that the main fragmentation route for the $[M - R]^+$ ion in the substituted 1,3,2-dioxarsenanes was caused by the loss of CH_2O and that, in some cases, the molecular ion directly eliminated aldehyde. Such elimination is not observed for $\overline{OCH_2CH_2OAs}N(C_2H_5)_2$ and $\overline{OCH_2CH_2OAs}N(n\text{-}C_3H_7)_2$ but appears to be an important process in the fragmentation of the methyl and ethyl derivatives of the 2-(dialkylamino)-4,4,5,5-tetramethyl-1,3,2-dioxarsolanes.

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Registry No. $\overline{OCH_2CH_2OAs}Cl$, 3741-33-1; $\overline{OCH_2CH_2OAs}N(CH_3)_2$, 27262-85-7; $\overline{OCH_2CH_2OAs}N(C_2H_5)_2$, 34713-88-7; $\overline{OCH_2CH_2OAs}N(n\text{-}C_3H_7)_2$, 74466-67-4; $\overline{OC(CH_3)_2C(CH_3)_2OAs}Cl$, 54128-06-2; $\overline{OC(CH_3)_2C(CH_3)_2OAs}N(CH_3)_2$, 57938-74-6; $\overline{OC(CH_3)_2C(CH_3)_2OAs}N(C_2H_5)_2$, 74466-68-5; $\overline{OC(CH_3)_2C(CH_3)_2OAs}N(n\text{-}C_3H_7)_2$, 74466-69-6; $[\overline{OC(CH_3)_2C(CH_3)_2OAs}]_2NH$, 74466-70-9; $[\overline{OC(CH_3)_2C(CH_3)_2OAs}]_2NCH_3$, 74466-71-0; $\overline{OC(CH_3)_2C(CH_3)_2OAs}NH(n\text{-}C_4H_9)$, 74466-72-1; $\overline{OCH_2CH_2OAs}OCH_2CH_2O\overline{AsOCH_2CH_2O}$, 14849-23-1; $As_4[N(n\text{-}C_4H_9)]_6$, 3690-32-2; $(n\text{-}C_3H_7)_2NH$, 142-84-7; $n\text{-}C_4H_9NH_2$, 109-73-9; CH_3NH_2, 74-89-5; NH_3, 7664-41-7.

Supplementary Material Available: A listing of infrared and mass spectral data (4 pages). Ordering information is given on any current masthead page.

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Metal Complexes of Diiminodiphosphines. Structural and Reactivity Patterns

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The coordination chemistries of *N,N'*-bis[*o*-(diphenylphosphino)benzylidene]ethylenediamine ($en{=}P_2$) and the corresponding 1,3-diaminopropane derivative ($tn{=}P_2$) have been explored for the metals nickel, copper, and silver, and these results provide fundamental information on this novel class of metal complexes. The ligands function as tetradentate chelating agents for these metal ions as inferred from spectroscopic data and proven by the X-ray structure of $[Cu(en{=}P_2)]ClO_4{\cdot}CH_2Cl_2$, the first iminophosphine chelate thus characterized. The crystals are triclinic, of space group $P\bar{1}$, with $a = 14.140$ (3) Å, $b = 24.926$ (5) Å, $c = 11.430$ (3) Å, $\alpha = 94.45$ (1)°, $\beta = 81.91$ (1)°, $\gamma = 97.42$ (1)°, and $Z = 4$. The complex adopts a severely distorted tetrahedral geometry, and this strain is manifested in its reactivity. The four-coordinate complexes $M(en{=}P_2)^z$ (M = Cu or Ag, z = 1+; M = Ni, z = 2+) all react with additional ligands L (M = Ag or Cu, L = *tert*-butyl isocyanide (*t*-BuNC); M = Ni, L = Br^-), affording five-coordinate adducts in the case of Ni(II) and Ag(I). Crystals of the derivative $[Cu(en{=}P_2)(t\text{-}BuNC)]ClO_4$, examined by X-ray methods show the metal to be tetrahedrally coordinated. The first coordination sphere contains only one imine functionality in addition to the isocyanide and the two phosphine moieties. The crystals are orthorhombic, of space group $P222$, with $a = 30.232$ (9) Å, $b = 16.144$ (4) Å, $c = 8.450$ (2) Å, and $Z = 4$. The complex is a unique example of a nine-membered chelate ring bound to a tetrahedral complex and is formed by the displacement of an internal donor of the chelate. All complexes are dynamic on the NMR time scale (−80 to 35 °C), and mechanisms consistent with the spectroscopic and X-ray data are presented. The electrochemical behavior of the complexes demonstrate the interconvertability of the $[M(en{=}P_2)]^z$ unit containing the metal ion in the d^8, d^9, and d^{10} configurations for M = Ni or Cu. The impact of the additional methylene group in the $tn{=}P_2$ complexes vs. the $en{=}P_2$ analogues is assessed chemically and electrochemically.

Introduction

A characteristic of the coordination chemistry of chelating bis(tertiary phosphines and arsines) is their distinctive ability to stabilize metal ions in a variety of uncommon oxidation states and geometries.[1] The adaptive nature of these ligands is a desirable attribute, from both theoretical[2] and applied (e.g., catalysis[3]) perspectives. Imino ligands, particularly the 1,2-diimines,[4] are also known to stabilize metal ions in a variety of low and high oxidation states, and their metal complexes are powerful catalysts in both biological (e.g., corrins, porphyrins) and industrial roles (e.g., phthalocyanins). Being a fusion of these ligand types, the iminophosphines hold promise to provide a new and readily available source of ligands which retain many of the aforementioned properties of imines and phosphines. A variety of iminophosphines[5-9] and iminoarsines[10]

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