Journal of Organometallic Chemistry, 84 (1975) 1—15

Review

CYCLOPOLYARSINES

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(Received July 17th, 1974)

Contents

I. Introduction

The history of cyclopolyarsines dates back to at least 1881, when Michaelis and Schulte [1] synthesized "arsenobenzene" analogous to azobenzene, with

the proposed structure being PhAs=AsPh. The discovery [2] in 1907 that a derivative of "arsenobenzene", "3,3'-diamino-4,4'-dihydroxyarsenobenzene", otherwise known as Salvarsan or arsphenamine, had dramatic chemotherapeutic effects stimulated a vast amount of synthetic work in the early part of the century on derivatives of Salvarsan. Little characterization of these compounds was made, and the vogue of their use ended about 1930.

It is now known from X-ray crystallographic studies that "arsenobenzene" is actually a cyclic hexameric species [3, 4, 5], hexaphenylcyclohexaarsine $(PhAs)_6$, and likewise, "arsenomethane" is actually pentamethylcyclopentaarsine $(MeAs)_5$ [6]. It is not a necessary consequence of the cyclic nature of "arsenobenzene" that Salvarsan and its derivatives are also cyclic. In fact, it would appear that most of these derivatives are linear polymers, as argued by Kraft [3, 7]. The polymeric compounds tend to be colored, amorphous, and cannot be distilled or recrystallized. Using these criteria, all of the derivatives of arsenobenzene and Salvarsan, with the exception of $(p\text{-}CH_3C_6H_4As)_6$, $(m\text{-}CH_3C_6H_4As)_6$, and $(p\text{-}CH_3OC_6H_4As)_6$ appear to be polymers, not cyclopolyarsines, and will not be discussed in this review. There is an early, comprehensive tabulation of these polymers [8]. In support of the contention of the polymeric nature of these species is a recent crystallographic study [9, 10] of the purple-black modification of pentamethylcyclopentaarsine. The compound is a linear, ladder polymer, the structure of which may be pictured as stacked MeAs—AsMe units.

Although much of the work on cyclopolyarsines has paralleled cyclopolyphosphine studies, an attempt has been made in this review to minimize cross-references to cyclopolyphosphines. Several excellent recent reviews on cyclopolyphosphines have appeared [11, 12]. An attempt has been made in this article to give comprehensive coverage of the literature up to mid-1974.

II. Preparations

Cyclopolyarsines can be synthesized by a wide variety of reactions, and these are summarized below. The value for n, the ring size of cyclopolyarsines $(RAs)_n$, can be 4, 5 or 6, as indicated in Table 1. The factor or factors which are determinant of ring size are ill-understood. Successful prediction of the ring size of a new cyclopolyarsine $(RAs)_n$ has met with little success, and empiricism has prevailed, much as with cyclopolyphosphines [11, 12]. Tzschach and Kiesel have noted that in a series of alkylcyclopolyarsines, α-branched alkyl groups formed four-membered rings, whereas non α-branched alkyl groups produced five-membered rings [13]. There is only one modern reference to an attempt to produce a ring containing mixed substituents [14]. This is obviously an area needing much more study. It is, for example, possible that different preparative routes to a particular substituted ring $(RAs)_n$ might yield two different ring sizes, as in $(CF_3As)_4$ and $(CF_3As)_5$ [15, 16].

A. Reactions using arsonous dihalides

Substituted arsonous dihalides $RAsX_2$ have been used in a variety of ways to produce cyclopolyarsines. Commonly, an active metal or hypophosphorous acid is used as a reducing agent.

$RAsX_2 + M \rightarrow (RAs)_n$, where M = reducing agent

TABLE 1

PREPARATIONS OF CYCLOPOLYARSINES

Ring	B.p. (°C/mmHg)	M.p. (°C)	Preparation[a]	References
$(s\text{-BuAs})_4$		−1	c	13
$(t\text{-BuAs})_4$		145	c	13
$(c\text{-HexAs})_4$		195	f	13
$(CF_3As)_4$		98	c	15, 16
$(C_6F_5As)_4$		141	c	19, 20
$(MeAs)_5$	118/1.0		b	14, 26, 29
$(EtAs)_5$	125/0.2		b	14, 29
$(n\text{-PrAs})_5$	142/0.5		b	14, 30
$(n\text{-BuAs})_5$			c	13
$(i\text{-BuAs})_5$	70/0.1		c	13
$(CF_3As)_5$			c	15, 16
$(H_3GeAs)_5$			e	40
$(H_3SiAs)_5$			e	40
$(H_2CClAs)_5$			b	43
$(PhAs)_6$		212	a	1, 41
			b	14, 24-28
			c	17, 18
			d	21
$(p\text{-}CH_3C_6H_4As)_6$		216	a	41, 44
			b	27
			c	17
			d	21
$(m\text{-}CH_3C_6H_4As)_6$		169	a	44
			b	27
$(p\text{-}CH_3OC_6H_4As)_6$		230	a	44
			d	21

[a] Methods used: a, $RAsO + H_3PO_3$; b, $RAsO(OH)_2$ or $RAsO(OM)_2 + H_3PO_2$; c, $RAsX_2 + M$; d, $RAsX_2 + H_3PO_2$; e, $R_3As + Me_2AsCl$; f, $RAsX_2 + RAsH_2$.

Sodium has commonly been used to reduce dichloroarsines [13, 17], while mercury has been the reducing agent of choice with diiodoarsines such as $PhAsI_2$ [18], or with perfluoro-substituted arsines such as CF_3AsI_2 [15, 16] and $C_6F_5AsCl_2$ [19, 20]. Hypophosphorous acid has also been used to reduce several dihaloarylarsines [21].

The reaction of a primary arsine $RAsH_2$ with a dihaloarsine has also been reported to yield cyclopolyarsines [13].

$$RAsH_2 + RAsX_2 \rightarrow (RAs)_n + 2HX$$

While this is a particularly clean procedure for producing cyclopolyarsines, it necessitates the synthesis of both the dihaloarsine and the appropriate primary arsine as precursors. This method has also been used in an attempt to produce mixed phosphorus—arsenic rings. Thus, dichlorophenylphosphine and phenylarsine were allowed to react, but only the disproportionation products of "arsenobenzene" and "phosphobenzene" were found [22]. The analogous reaction using dichlorophenylarsine and phenylphosphine also produced only disproportionation products [23].

B. Reactions using arsonic acids or their salts

The most widely used method for the preparation of cyclopolyarsines consists of the reduction of the appropriately substituted arsonic acid, $RAsO(OH)_2$ or its salt, with hypophosphorous acid.

$PhAsO(OH)_2 + H_3PO_2 \rightarrow (PhAs)_6$ [14, 24-28]

$MeAsO(ONa)_2 + H_3PO_2 \rightarrow (MeAs)_5$ [26, 29]

$n\text{-}PrAsO(O_2Mg) + H_3PO_2 \rightarrow (n\text{-}PrAs)_5$ [30]

An interesting variation of this reaction was used in an attempt to produce mixed methyl—phenyl-cyclopolyarsines, where sodium methylarsenate and phenylarsonic acid were simultaneously reduced with hypophosphorous acid [14].

C. Reactions using primary and secondary arsines

In addition to the reaction with arsonous dihalides already mentioned, primary arsines $RAsH_2$ have been reported to produce cyclopolyarsines with a number of other reagents: $PhAsH_2$ produces $(PhAs)_6$ by reaction with O_2 [31], Ph_2AsX [32], organotin and organolead compounds [33], or Ph(I)As—As(I)Ph [34, 35]; $MeAsH_2$ produces $(MeAs)_5$ by reaction with MeAsO [36] or $AsCl_3$ [36]; and $(EtAs)_5$ is the product of reaction of $EtAsH_2$ with $AsCl_3$ [36]. A compound reported to contain mixed substituents was made by the reaction of $PhAsH_2$ with EtAsO [37], but the structure of this compound is unknown.

Secondary arsines R_2AsH have also been used to produce cyclopolyarsines in some rather unusual reactions. The reaction of Me_2AsH with either O_2 [38] or As_2O_3 [36] produces $(MeAs)_5$, and $(PhAs)_6$ is a product of the reaction of Ph_2AsH with $PhAsCl_2$ [32].

D. Miscellaneous reactions

The chloramination of methyl- or phenyl-arsine with monochloroamine, dimethylchloroamine, or chlorine and triethylamine give $(MeAs)_5$ and $(PhAs)_6$, respectively [39].

Pentagermylcyclopentaarsine $(H_3GeAs)_5$ and pentasilylcyclopentaarsine $(H_3SiAs)_5$ have been prepared by the reaction of chlorodimethylarsine with $(H_3Ge)_3As$ and $(H_3Si)_3As$ [40].

$(H_3Ge)_3As + Me_2AsCl \rightarrow (H_3GeAs)_5$

$(H_3Si)_3\ As + Me_2AsCl \rightarrow (H_3SiAs)_5$

Another commonly used preparation of cyclopolyarsines utilizes the reduction of substituted arsinooxides RAsO with zinc [1], an acidic tin solution [1], sodium amalgam [1], or phosphorous acid [1, 41]. A reported reaction of little synthetic use which is, nevertheless, very interesting used methyl and ethyl free radicals with an arsenic mirror to give the $(MeAs)_5$ and $(EtAs)_5$ rings [42].

III. Structural studies

A. Molecular weight determinations

The lack of consistent molecular weight data for phenylcyclopolyarsine

caused its true structure to be unknown until 1960 when the first X-ray crystal studies were completed [3-5]. Michaelis and Schäfer [41] determined the molecular weight of "arsenobenzene" ebullioscopically to be 399.8 in benzene and from this data assigned the azo-structure PhAs=AsPh (mol. wt. 304). Palmer and Scott [26] found the molecular weight cryoscopically to be 642 in naphthalene and 402 in benzene, and 334 in carbon disulfide by the ebullioscopic method. This led them to report that arsenobenzene has the "azo-type structure, PhAs=AsPh, in a non-associating solvent, but to be distinctly associated in benzene and naphthalene solutions". Blicke and Smith [21] determined more accurate molecular weights (895, 915, 867 [35]), but this was again reported to be due to association in the dissolved state. Lyon and Mann [17] obtained molecular weights consistent with those of Blicke and Smith and attempted, with little success, to determine the actual structure of "arsenobenzene". Kraft and coworkers [3] were the first to interpret Blicke and Smith's molecular weight data as being consistent with the six-membered ring (mol. wt. 912). They also assumed that the molecular weight data obtained by Blicke and Smith were accurate for "*p*-arsenotoluene" (810, 832) and "*p*-arsenoanisole" (1081, 1270), and that these were also six-membered rings. The calculated values for the six-membered rings are 996 and 1092, respectively.

The use of molecular weights to determine the structure of cyclopolyarsines met with more success in the case of methylcyclopolyarsine and n-propylcyclopolyarsine. Auger [29] obtained cryoscopic molecular weight values ranging from 300 to 340 for "arsenomethane" in benzene. Steinkopf, Schmidt and Smie [34], however, found molecular weights in benzene ranging from 428 to 469, with intermediate values in nitrobenzene. From these results they assigned to "arsenomethane" the formula $(MeAs)_5$, with a molecular weight of 450. Their work was confirmed by Palmer and Scott [26] who obtained an average ebullioscopic molecular weight in carbon disulfide of 474. From molecular weight data, Steinkopf and Dudek [30] assigned n-propylcyclopolyarsine the formula $(n\text{-}PrAs)_5$.

Recently Tzschash and Kiesel [13] assigned ring sizes to $(t\text{-}BuAs)_4$, $(s\text{-}BuAs)_4$, $(i\text{-}BuAs)_5$, and $(n\text{-}BuAs)_5$ from molecular weight data obtained cryoscopically in benzene. Molecular weight data were also used to assign structures to $(H_3GeAs)_5$ [40], $(H_3SiAs)_6$ [40], $(CF_3As)_4$ [15], $(C_6F_5As)_4$ [19].

Mass spectrometry has also been used with some success in the determination of molecular weights for cyclopolyarsines (see Section III. B).

It would appear that the unreliable molecular weights reported by early investigators, particularly in the case of "arsenobenzene", arose from the extreme solution air-sensitivity of the cyclic arsines. Almost without exception, recent determinations, where proper methods allow rigorous exclusion of oxygen, have given what appear to be reliable and accurate molecular weights.

B. Mass spectral studies

The molecular weights of several cyclopolyarsines have been determined by mass spectrometric methods. Parent *m/e* peaks have been reported for $(MeAs)_5$ [14, 39, 43, 45-47], $(EtAs)_5$ [14], $(n\text{-}PrAs)_5$ [14], $(c\text{-}HexAs)_4$ [13], $(t\text{-}BuAs)_4$ [13], $(PhAs)_6$ [14], $(CF_3As)_4$ [15, 48], $(CF_3As)_5$ [48], and $(C_6F_5As)_4$ [19, 20].

As with cyclopolyphosphines [49], the determination of molecular

weights by use of mass spectrometry must be carried out with some care. The fragmentation of cyclopolyarsines is apparently very sensitive to such variables as compound purity, as well as inlet temperature and ionizing voltage of the spectrometer. For example, West et al. [14] reported that the spectrum of $(PhAs)_6$ showed peaks corresponding only to $(PhAs)_5^+$ and $(PhAs)_3^+$ at 5 eV, whereas at 70 eV, peaks corresponding to $(PhAs)_6^+$ and other expected fragments were apparent. Sisler [39] observed major peaks corresponding to only Ph^+ (77) and $PhAs^+$ (152) for the mass spectrum of $(PhAs)_6$, although no conditions were cited. No parent peak was found for the compound $(H_2CClAs)_5$ [43], with the highest *m/e* value corresponding to $(H_2CCl_2)_2As_3^+$.

Mass spectrometry has been used most extensively to investigate $(MeAs)_5$. Elmes, Middleton and West [14] found a relatively intense pentameric parent ion $(MeAs)_5^+$, with no evidence under a wide variety of temperatures (30 to 200°) and ionizing energies (5 to 70 eV) of any peaks at higher mass. Other investigators [43, 46, 47] have seen weak peaks at higher mass, however. A fragmentation pattern was proposed which included some evidence for the neutral trimer $(MeAs)_3$. Similarly, the mass spectra of $(EtAs)_5$, $(n\text{-}PrAs)_5$, and $(PhAs)_6$ [14] indicated the possible existence of neutral trimers. The authors concluded, however, that the trimers were derived from fragmentation of the parent pentamer or hexamer rather than existing as impurities in the original compound. Knoll, Marsman and Van Wazer [46] found, contrary to the results of West [14], that the mass spectrum of the vapor removed from the liquid phase of $(MeAs)_5$ indicated trace amounts of hexamer $(MeAs)_6$ and heptamer $(MeAs)_7$ rings were present in the predominantly pentameric liquid, with perhaps some trimer $(MeAs)_3$, but no tetramer $(MeAs)_4$. They also interpreted their mass spectrometric data as indicating that in a dilute gas-phase sample of $(MeAs)_5$, there are appreciable amounts of trimeric and tetrameric species, but no larger rings. An alternate explanation for the lack of larger rings would be if the hexameric and heptameric species arose from mass spectrometric collisions, then the absence of these peaks in a dilute gas sample could be explained by the lower pressure, thus effectively reducing the number of collisions within the spectrometer.

Parent *m/e* peaks are reported for the perfluoromethyl compounds $(CF_3As)_4$ [15, 48] and $(CF_3As)_5$ [48]. The fragmentation patterns of these compounds have been interpreted [48] as being consonant with the production of CF_2 and CF_3 radicals.

Mass spectral data have been used to support the contention [14] of unsymmetrical cyclopolyarsines. Mixed methyl—phenyl rings were reported to produce peaks corresponding to $MePh_5As_6^+$ and $Me_2Ph_4As_6^+$. The possibility that these ions arose from recombination of fragmentation species from a mixture of $(PhAs)_6$ and $(MeAs)_5$ was not apparently considered, however.

Mass spectral data have also been reported for some transition metal complexes of cyclopolyarsines. These are discussed in Section V.

C. NMR spectroscopy

Proton NMR data have been reported for $(MeAs)_5$ [14, 47, 50], $(EtAs)_5$ [14], $(n\text{-}PrAs)_5$ [14], $(H_2CClAs)_5$ [43], $(PhAs)_6$ [14], $(H_3GeAs)_5$ [40], and $(H_3SiAs)_5$ [40], and ^{19}F NMR data for $(C_6F_5As)_4$ [19, 20], $(CF_3As)_4$ [47] and $(CF_3As)_5$ [47]. The data are tabulated in Table 2.

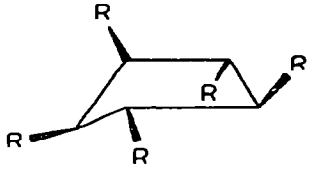
TABLE 2

NMR SPECTRA OF CYCLOPOLYARSINES

Compound	Nuclei	Shift (ppm)	Relative intensity	Solvent	Refs.
$(MeAs)_5$	^1H	−1.66[a]	2	$CDCl_3$	14
		−1.63	2		
		−1.62	1		
$(H_2CClAs)_5$	^1H	−4.09[b]	2	neat	43
		−3.96	2		
		−3.95	1		
$(PhAs)_6$	^1H	−7.59[a]		CS_2	14
		−7.25			
		−7.14			
		−6.96			
$(H_3GeAs)_5$	^1H	−4.49[b]	2		40
		−4.47	2		
		−4.41	1		
$(H_3SiAs)_5$	^1H	−4.50[b]			40
$(CF_3As)_5$	^{19}F	35.7[c]	2	neat	47
		38.3	2		
		38.8	1		
$(CF_3As)_4$	^{19}F	42.5[d]		$(CF_3As)_5$	47
$(C_6F_5As)_4$	^{19}F	125.9[d]	2	$CHCl_3$	19, 20
		161.8	2		
		152.1	1		

[a] Relative to internal TMS. [b] Relative to external TMS. [c] Relative to internal CCl_3F. [d] Relative to external CCl_3F.

Pentamethylcyclopentaarsine, $(MeAs)_5$, has been extensively investigated by ^1H NMR spectroscopy [14, 43, 45, 47, 50]. The predominate feature in the spectrum at ambient temperature is three peaks of relative area of 2/2/1. Five lines of unique chemical shift is predicted if the compound has the solid state structure A [6]. Inasmuch as the ^{13}C spectrum of $(MeP)_5$ [51], ^1H spectra of

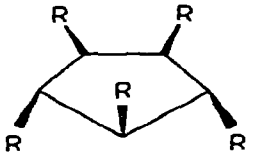


(A)

$(H_3GeAs)_5$ [40] and $(H_2CClAs)_5$ [43], and the ^{19}F spectra of $(CF_3As)_5$ [47] and $(CF_3P)_5$ [52] all show the same 2/2/1 pattern, accidental overlap of five resonances as a cause of this simplification may be ruled out.

Essentially two explanations have been profferred to rationalize the 2/2/1 pattern; the "butterfly wag" of Wells et al. [47], as slightly modified by Rheingold [43], and the time-average plane of West et al. [14]. The former mechanism proposed that a plane of symmetry is generated on the NMR time scale in the liquid phase by a combination of ring puckering, i.e. "butterfly wag", and

inversion at an individual puckering arsenic atom. West assumes that a time-average plane exists without inversion, thus producing a 2/2/1 methyl magnetic environment (Structure B). The spectrum is essentially unchanged down to −55°, making inversion at arsenic unlikely, thus favoring West's proposal.



(B)

High temperature spectra of $(MeAs)_5$ have also been reported by several groups [14, 43, 46, 47, 50]. Early studies on the collapse of the 2/2/1 pattern [46, 47, 50] appear to be in error [14]. Pure, previously unheated $(MeAs)_5$, does not produce a collapse of NMR signals at elevated temperatures [14]. Previously heated or polymer containing $(MeAs)_5$ has impurities such as Me_4As_2 which catalyze ring opening and polymerization [10, 46], and thus greatly alters the NMR spectra. This contention is supported by the fact that $(CF_3As)_5$ maintains the 2/2/1 pattern at high temperature [47].

The temperature dependent spectra of $(EtAs)_5$ and $(n\text{-}PrAs)_5$ have also been recorded [14]. There was some evidence that in $(EtAs)_5$ there are five non-equivalent ethyl groups, although the spectra were too complex for complete analysis.

D. X-ray studies

Electron and X-ray diffraction studies have been the only reliable method of determining the structure of cyclopolyarsines. X-ray studies [3-5] have shown (Fig. 1c) that "arsenobenzene" exists as a six-membered ring in the chair form. There is evidence that $(PhAs)_6$ exists in two crystal forms, monoclinic [3-5, 17] and triclinic [4], however there has been no published data concerning the triclinic form. Electron [53] and X-ray [6] diffraction studies have also been carried out to confirm the pentameric structure of "arsenomethane" (Fig. 1b). "Arsenomethane" crystallizes with a monoclinic unit cell, with the arsenic atoms of one molecule joined in a puckered, five-membered ring. The molecular data for $(MeAs)_5$ and $(PhAs)_6$ have previously been tabulated and compared by

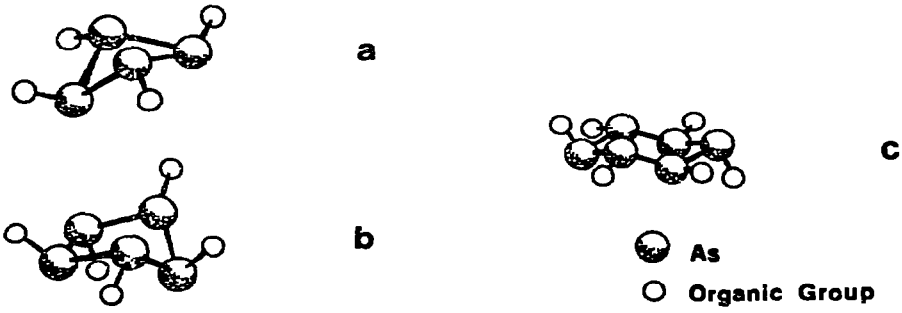


Fig. 1. X-ray crystal structures of a, cyclotetraarsines, b, cyclopentaarsines; and c, cyclohexaarsines.

TABLE 3

X-RAY CRYSTAL STRUCTURES OF CYCLOPOLYARSINES

Compound	Molecular data	Reference
$(PhAs)_6$	As—As 2.456 Å As—C 1.966 Å As—As—As 91° As—As—C 100 1°	5
$(CH_3As)_5$	As—As 2.428 Å As—C 1.95 Å As—As—As 97.6-105.6° (avg. 101.8°) As—As—C 97°	6
$(CF_3As)_4$	As—As 2.454 Å As—C 2.012 Å As—As—As 83.6° As—As—C 94.4° As—As—As—As torsion angle 36.8°	55

Donohue [54]. Crystal studies have also been done on the four-membered rings (Fig. 1a): $(CF_3As)_4$ [55], (c-HexAs)$_4$ [13], and (t-BuAs)$_4$ [13]. However, only the cell parameters were given for the two cyclotetraarsines (c-HexAs)$_4$ and (t-BuAs)$_4$. Molecular data for $(PhAs)_6$, $(MeAs)_5$, and $(CF_3As)_4$ are listed in Table 3.

E. Miscellaneous techniques

1. Vibrational spectroscopy

The IR spectra for several cyclopolyarsines have been reported. The solution spectra in benzene have been reported for $(H_3GeAs)_5$ and $(H_3SiAs)_5$ [40]; Nujol mull IR spectra for $(PhAs)_6$ [14, 27, 56], (p-$CH_3C_6H_4As)_6$ [27], and (m-$CH_3C_6H_4)_6$ [27]; neat film IR spectra for $(MeAs)_5$, $(EtAs)_5$ and (n-PrAs)$_5$ [14]; and a vapor phase IR spectrum for $(CF_3As)_4$ [15].

The only Raman spectra in the literature appears to be for $(H_3GeAs)_5$ and $(H_3SiAs)_5$ in solution [40]. They assigned the As—As stretch to peaks at 250-270 cm^{-1}. The Raman spectrum of solid $(PhAs)_6$ has a strong absorbance at 260 cm^{-1} [23], which might correspond to the As—As stretch.

2. Ultraviolet spectroscopy

UV spectra have been reported for $(PhAs)_6$ [27, 56], (p-$CH_3C_6H_4As)_6$ [27], (m-$CH_3C_6H_4As)_6$ [27], and $(CF_3As)_4$ [15]. Considering the small amount of data available, it is not surprising to find that little interpretation of the UV spectra has been made.

3. NQR spectroscopy

^{75}As possesses a nuclear spin with $I = 3/2$, and therefore has a nuclear quadrapole. A nuclear quadrapole resonance spectroscopic study was made of $(PhAs)_6$ and $(C_6F_5As)_4$ [57]. The multiplicity of the resonances was found to be consistent with the number demanded by the previously determined structures [5, 20].

IV. Reactions

Relatively little information exists on the general reactions of cyclopolyarsines, and much of what does exist is pre-1930. Much recent work has been done in the area of the coordination chemistry of cyclopolyarsines towards transition metal carbonyl complexes. The coordination chemistry is discussed in the next section (Section V), while all other reactions are discussed in this section.

A. Oxidation

While no really comprehensive studies on reactions of cyclopolyarsines have been carried out, certainly the most obvious reaction to those working in the area is that with the atmosphere. Cyclopolyarsines are very sensitive to oxidation in solution [27], and yield a variety of products upon oxidation such as organoarsinooxides [3, 41] or As_2O_3 [13]. However, hexaphenylcyclohexarsine, when isolated as a pure solid, is an essentially air-stable compound [21, 58].

B. Polymerization

The conversion of cyclic $(MeAs)_5$ into polymeric chains has been investigated by several groups. Van Wazer and coworkers [46] studied the $(MeAs)_5$ + $Me_2AsAsMe_2$ system (see Section III.C) and found an equilibrium dependence between the polymers and the mole ratio of $(MeAs)_5$ to Me_4As_2. Linear, halogen-terminated polyarsines have been reported to result from the reaction of $(MeAs)_5$ with methyldihaloarsines [43], with the number of —MeAs— units per chain being from two to six. The X-ray crystal structure for one polymeric modification of "arsenomethane" has been reported [9, 10].

Purple-black polymers also form with the reaction of $(MeAs)_5$ with I_2 [10, 43, 59], HCl [53], BCl_3 [51], or BF_3 [51], although the last reaction first produces a yellow precipitate. Polymers also frequently occur as impurities in the preparation of $(EtAs)_5$ [10, 14, 29].

C. Halogenation

Halogens normally react with cyclopolyarsines, except $(MeAs)_5$ (vide supra), to produce arsonous dihalides. Thus, chlorine and $(PhAs)_6$ produces $PhAsCl_2$ [1], and iodine cleaves $(t\text{-}BuAs)_4$ to produce $t\text{-}BuAsI_2$ [13]. However bromine cleaves the C—As bond in $(t\text{-}BuAs)_4$ to produce $AsBr_3$ and t-BuBr [13].

D. Thermolysis

Several investigators have studied thermal decomposition of cyclopolyarsines. Decomposition of $(PhAs)_6$ occurs at 196° to give Ph_3As and elemental arsenic [1, 30]. However, methyl and n-propyl cyclopolyarsines have been reported to undergo thermal decomposition to the diarsine and elemental arsenic [30]. If conditions are strenuous enough (180° for 90 h) [46], $(MeAs)_5$ decomposes to Me_3As and elemental arsenic [29, 30, 46, 60]. It is interesting to note that thermal decomposition of $(n\text{-}Pr)_3As$ has been reported to produce $(n\text{-}PrAs)_5$ [36].

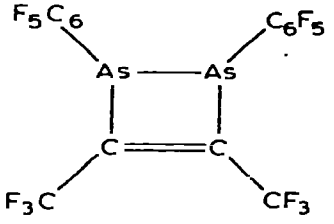
E. Reduction

Relative to cyclopolyphosphines [61 and refs. cited therein], few data

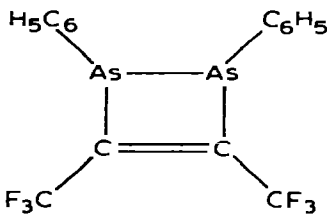
exist on the reduction of cyclopolyarsines. Cyclopolyarsines have been cleaved with the alkali metals Li [62], Na [28], and K [13] to give what has been reported to be $M(RAs)_4M$ [13] or $M(RAs)_2M$ [13, 28, 62]. Electrochemical reduction of $(PhAs)_6$ also cleaves the ring [61]; however, the exact nature of the products is unknown.

F. Miscellaneous

The perfluoromethylarsine rings (n = 4, 5) react with HI and Hg to give perfluoromethylarsine in 90% yield [16]. The reaction of hexafluorobutyne with $(C_6F_5As)_4$ or $(C_6H_5As)_6$ yields the heterocyclic rings C and D, respectively [57].



(C)



(D)

Several miscellaneous reactions reported for cyclopolyarsines are as follows. Diiodophenylarsine cleaves $(PhAs)_6$ to produce Ph(I)As—As(I)Ph [18]. Methyl iodide and cyclopolyarsines reportedly yield $RAsI_2$ and RMe_3AsI [13, 24, 34]. Finally, HCl cleaves the Ge—As bond in $(H_3GeAs)_5$ to give chlorogermane as well as arsine and arsenic subhydrides [40].

V. Coordination compounds

Individual arsenic atoms in cyclopolyarsines are trivalent, and, therefore, in priciple have a lone pair of electrons which may be donated to a Lewis acid such as a transition metal. With the exception of an early study [8] of the reactions of "arsenobenzene" and related derivatives with the metal halides of Cu, Au, Hg, Pt and Pd and with $AgNO_3$, no work had been done in this area until about 1967. Since that time a number of reactions between cyclopolyarsines and transition metal carbonyl compounds have been reported, largely by West and co-workers [45, 63-67], as an adjunct to their studies of cyclopolyphosphines [see ref. 63 and refs. therein].

The compounds tabulated in Table 4 can be divided into two categories, those which apparently still have the cyclopolyarsine ring intact (I through VIII) and those which do not (IX through XXIV). As noted in Table 4, crystal structures have been carried out of only two of the compounds (IX and XIII), and both of these have had the arsenic rings opened (vide infra). The primary criterion used by West [64, 67] to ascertain whether the ring is intact is mass spectral data. If the parent *m/e* peak for the cyclopolyarsine is not present, then it is assumed that the ring has been opened. Until further X-ray studies have been performed, this criterion should be used with care. The number of carbonyl IR stretching frequencies has been used to determine symmetry. This led to

TABLE 4

COORDINATION COMPOUNDS DERIVED FROM CYCLOPOLYARSINES

	Compound	M.p. (°C)	Ring	Reference	Comments
I	$(CO)_5W(PhAs)_6$	163	intact	66	*a*
II	$(CO)_4Mo(PhAs)_6$	200	intact	64, 66, 68	*a*
III	$[(CO)_5Cr]_2(MeAs)_5$	164-165	intact	45, 64	*a, b, c, e*
IV	$[(CO)_5Mo]_2(MeAs)_5$	138-139	intact	45, 64	*a, b, c, e*
V	$[(CO)_5W]_2(MeAs)_5$	165-166	intact	45, 64	*a, b, c, e*
VI	$(CO)_3Mo[(MeAs)_5]_2$	118-119	intact	64	*a, b, c*
VII	$[(CO)_4Mo(MeAs)_5]_3$	260 (decomp.)	intact	45, 64	*a, b, c*
VIII	$[(CO)_4W(MeAs)_5]_x$	220 (decomp.)	intact	45, 64	*a, b, c*
IX	$[(CO)_3Fe]_2(MeAs)_4$	256 (decomp.)	opened	45, 67, 69	*a, b, c, d*
X	$[(CO)_3Fe]_2(EtAs)_4$	135-136	opened	67	*a, b, c*
XI	$[(CO)_3Fe]_2(PhAs)_4$	180-190	opened	67	*a, c, f*
XII	$[(CO)_3Fe]_2(Ph_4As_2)$	180-190	opened	67	*a, c, f*
XIII	$(CO)_4Fe(C_6F_5As)_2$	149-150	opened	65	*a, b, c, d*
XIV	$[(CO)_4Mn]_2(MeAs)_5$	> 300	opened	67	*a, b, c, e*
XV	$[(CO)_3Mn]_2(MeAs)_6$	> 300	opened	67	*a, b, c, e*
XVI	$[(CO)_4Cr(MeAs)_5]_2$	308-309	opened	45, 63, 64	*a, b, c*
XVII	$[(CO)_4Mo(MeAs)_5]_2$	180 darkens	opened	45, 63, 64	*a, b, c*
XVIII	$[(CO)_4W(MeAs)_5]_2$	270 (decomp.)	opened	45, 63, 64	*a, b, c*
XIX	$[(CO)_4Cr(EtAs)_5]_2$	280 (decomp.)	opened	64	*a, b, c*
XX	$[(CO)_4Mo(EtAs)_5]_2$	270 (decomp.)	opened	64	*a, b, c*
XXI	$[(CO)_4W(EtAs)_5]_2$	280 (decomp.)	opened	64	*a, b, c*
XXII	$[(CO)_4Mo(PhAs)_6]_2$	228-229	opened	64	*a, b, c*
XXIII	$[(CO)_3Mo(EtAs)_4]_2$	254-255	opened	64	*a, b, c*
XXIV	$[(CO)_3Mo(n\text{-}PrAs)_4]_2$	198	opened	64	*a, b, c*

[a] IR reported. [b] NMR reported. [c] Mass spectrum reported. [d] Single crystal X-ray structure. [e] Evidence for isomers. [f] Compounds XI and XII were an unseparated mixture.

errors [45] in the original structural assignment of compounds XVI, XVII and XVIII [63, 64].

Only one compound, namely $(CO)_5W(PhAs)_6$, has been reported [66] where the intact ring behaves as a monodentate ligand (compound I). The structure is apparently as in Fig. 2a, although no mass spectral datum has been reported confirming the existence of the intact ring. $(CO)_4Mo(PhAs)_6$, compound II, apparently is the only known example [64, 66] of a cyclopolyarsine ring behaving as a bidentate ligand. As indicated in Fig. 2b, it is assumed that alternate positions of the ring coordinate. Earlier reports of $(CO)_4Mo(PhAs)_4$ [68] and of $(CO)_3Mo(PhAs)_6$ [56] are probably either compound II or XXII. The analytical data for compound III, $[(CO)_5Cr]_2(MeAs)_5$; IV, $[(CO)_5Mo]_2(MeAs)_5$; and V, $[(CO)_5W]_2(MeAs)_5$ are consistent with a bridging $(MeAs)_5$ ring. Compound VI, $(CO)_3Mo[(MeAs)_5]_2$ (Fig. 2c), has one bidentate $(MeAs)_5$ ring and one monodentate $(MeAs)_5$ ring attached to the single, transition metal atom. $[(CO)_4Mo(MeAs)_5]_3$, compound VII, and $[(CO)_4W(AsMe)_5]_x$, compound VIII, are presumed to be $(CO)_4M$ polymers (M = Mo or W) linked by bridging $(MeAs)_5$ rings.

A complete crystal structure has been determined for compound IX, $[(CO)_3Fe]_2(MeAs)_5$ [69], and all analytical data indicate that compounds X and XI [67] have the same basic structure. As indicated in Fig. 2d, what was the five-membered ring $(MeAs)_5$ has been opened and shortened to become a bridging $(MeAs)_4$ chain. Compounds X and XI are simply ethyl- and phenyl-cyclopolyarsine ring derivatives, respectively.

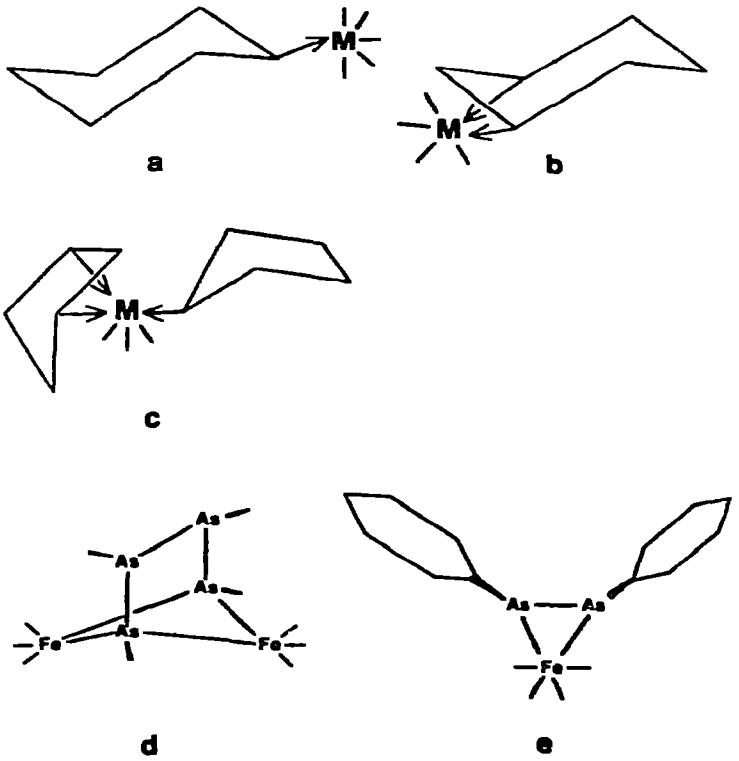


Fig. 2. Some modes of coordination for cyclopolyarsine-derived carbonyl complexes.

Compound XIII, $(CO)_4Fe(C_6F_5As)_2$, contains a bidentate arsenic chain. The X-ray structure [65] (Fig. 2e) indicates that in this case the $(C_6F_5As)_4$ ring has been cleaved to become a diarsine bidentate ligand. This compound represents the only known sample of a phosphorus or arsenic compound which is analogous to azo derivatives. The compound might be considered to be a $C_6F_5As{=}AsC_6F_5$ derivative, although the As—As bond length (2.39 Å) is considerably longer than an As—As "double" bond of 2.27 Å [70].

The remaining compounds (XIV through XXIV), though synthesized from cyclopolyarsines, all have been reported to contain arsenic chains rather than rings. Proposed structures are very speculative, based primarily on IR spectroscopy.

Acknowledgment

The support of the Robert A. Welch Foundation is gratefully acknowledged.

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