Tin–Oxo Clusters Based on Aryl Arsonate Anions

Yun-Peng Xie, Jin Yang, Jian-Fang Ma,* Lai-Ping Zhang, Shu-Yan Song, and Zhong-Min Su[a]

Abstract: Reactions of Ph$_3$SnOH or Ph$_3$SnCl with aryl arsonic acids RAsO$_3$H$_2$, where R = C$_6$H$_5$ (**1**), 2-NH$_2$C$_6$H$_4$ (**2**), 4-NH$_2$C$_6$H$_4$ (**3**), 2-NO$_2$C$_6$H$_4$ (**4**), 3-NO$_2$C$_6$H$_4$ (**5**), 4-NO$_2$C$_6$H$_4$ (**6**), 3-NO$_2$-4-OHC$_6$H$_3$ (**7**), 2-ClC$_6$H$_4$ (**8**) and 2,4-Cl$_2$C$_6$H$_3$ (**9**), gave 18 Sn–O cluster compounds. These compounds can be classified into four types: type **A**: [{(PhSn)$_3$(RAsO$_3$)$_3$(μ_3-O)(OH)(R′O)$_2$}$_2$Sn] (R = C$_6$H$_5$, 2-NH$_2$C$_6$H$_4$, 4-NH$_2$C$_6$H$_4$, 2-NO$_2$C$_6$H$_4$, 3-NO$_2$C$_6$H$_4$, 2-ClC$_6$H$_4$, 2,4-Cl$_2$C$_6$H$_3$, and 3-NO$_2$-4-OHC$_6$H$_3$; R′ = Me or Et); type **B**: [{(PhSn)$_3$(RAsO$_3$)$_2$(RAsO$_3$H)-(μ_3-O)(R′O)$_2$}$_2$] (R = 4-NO$_2$C$_6$H$_4$, R′ = Me); type **C**: [{(PhSn)$_3$(RAsO$_3$)$_3$(μ_3-O)(R′O)$_3$}$_2$Sn] (R = 2,4-Cl$_2$C$_6$H$_3$, R′ = Me); type **D**: [{Sn$_3$Cl$_3$(μ_3-O)(R′O)$_3$}$_2$-(RAsO$_3$)$_4$] (R = 2-NO$_2$C$_6$H$_4$ and 4-NO$_2$-C$_6$H$_4$; R′ = Me or Et). Structures of types **A** and **B** contain [Sn$_3$(μ_3-O)(μ_2-OR′)$_2$] building blocks, while in types **C** and **D** the stannoxane cores are built from two [Sn$_3$(μ_3-O)(μ_2-OR′)$_3$] building blocks. The reactions proceeded with partial or complete dearylation of the triphenyltin precursor. These various structural forms are realized by subtle changes in the nature of the organotin precursors and aryl arsonic acids. The syntheses, structures, and structural interrelationship of these organostannoxanes are discussed.

Introduction

In recent years, there has been considerable interest in organotin compounds due to their applications as catalysts in academia and industry. In addition, organotin compounds are also interesting with regard to their considerable structural diversity. Organotin chemistry is experiencing a renaissance with the discovery of new rings, cages, and clusters containing organo oxo tin motifs in general and monoorgano oxo tin units in particular.[1] So far, several types of organo oxo tin clusters, such as ladder,[2a,b] cube,[2c,d] butterfly,[2d] drum,[2e] cyclic trimer,[2f] football cage,[3] singly and doubly oxygen capped,[2d,4] and doubly and triply bridged ladder,[5] have been prepared, and their structures established by single-crystal X-ray diffraction.

Organo oxo tin clusters with phosphorus-based acids such as [((RSn)$_2$O{O$_2$P(OH)tBu}$_4$)$_2$] (R = Me, nBu, Bz),[6] [(Me$_2$Sn$_2$(OH){O$_2$P(OPh)$_2$}$_3${O$_3$P(OPh)})$_2$],[6a] [{(nBuSn)$_3$(μ_3-O)(OC$_6$H$_4$-4-X)$_3$}$_2$(O$_3$PH)$_4$}] (X = H, Cl, Br, I),[4b,c] [(PhSn)$_6$-(μ-OH)$_2$(μ_3-O)$_2$(μ-OEt)$_4${(ArO)PO$_3$}$_4$] (Ar = 2,6-iPr$_2$C$_6$H$_3$),[11] and [Na$_6$(CH$_3$OH)$_2$(H$_2$O)][{(BzSn)$_3$(PhPO$_3$)$_5$(μ_3-O)-(CH$_3$O)}$_2$Bz$_2$Sn]·CH$_3$OH[7b] display various structural motifs. However, in contrast to the development of organotin compounds of phosphorus-based acids, the chemistry of organo oxo tin clusters with organo arsonates remains unexplored. Up to now, diorgano tin phenyl arsonates and substituted phenyl arsonates have only been studied in the light of IR and Mössbauer spectroscopy and X-ray powder diffraction.[8] Generally, organotin organo arsonate compounds, particularly those containing dianionic organo arsonate ligands, show low solubility due to their oligomeric nature, and this causes difficulty in obtaining single crystals. To the best of our knowledge, there have been no reports on the crystal structures of organotin organo arsonates, and therefore elucidating the structural coordination chemistry of organotin organo arsonates is a challenge in the synthetic chemistry of organo oxo tin clusters. On the other hand, cleavage of Sn−C bonds under the influence of strong acids has long been known and has been used in syntheses involving organotin compounds.[1j,6b,7,9] Among the various organotin compounds, phenyl derivatives of tin are susceptible to

[a] Dr. Y.-P. Xie, Dr. J. Yang, Prof. Dr. J.-F. Ma, Dr. L.-P. Zhang, Dr. S.-Y Song, Prof. Dr. Z.-M. Su
Key Lab of Polyoxometalate Science
Department of Chemistry, Northeast Normal University
Changchun 130024 (China)
Fax: (+86) 431-8509-8620
E-mail: jianfangma@yahoo.com.cn
🖳 Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

Sn–C bond cleavage. To take advantage of this feature, we chose to study the reactions of the phenyltin precursors such as Ph₃SnOH, Ph₃SnCl, with aryl arsonic acids to determine if organotin organo arsonate cages/clusters can be obtained by a solvothermal approach, and also to explore whether products with new structure types are formed.

Conventionally, organotin clusters have been synthesized by controlled hydrolysis of organotin halides[10] or by reaction of an appropriate organotin precursor such as R₃SnOSnR₃, R₃SnOH, (R₂SnO)$_n$, or RSn(O)(OH) with a protic acid such as carboxylic, phosphinic, phosphonic, or sulfonic acid at room temperature or under reflux.[11] Recently, a solventless methodology for the preparation of some of these clusters has also been reported.[12] Previously, we used a solvothermal approach for the preparation of crystalline organotin clusters.[7] We have now used this new synthetic route to prepare four types of tin oxo clusters based on aryl arsonate ligands 1–9, namely, [{(PhSn)₃-
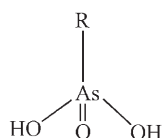
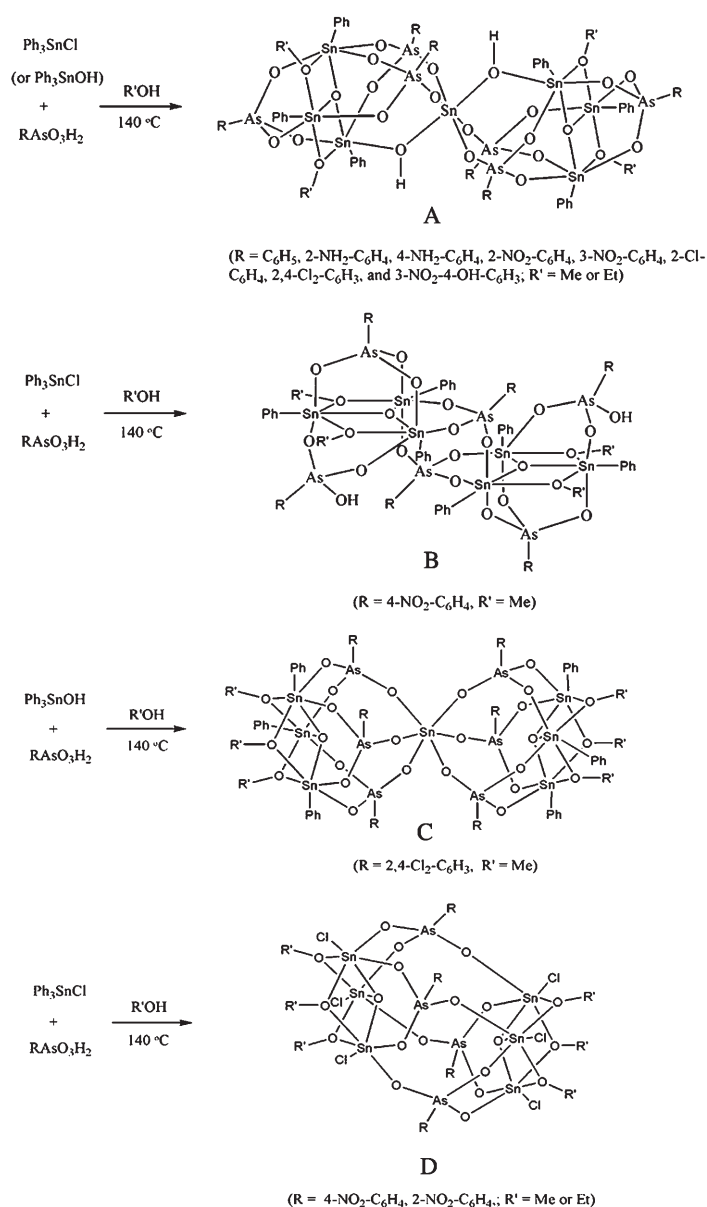[R = C₆H₅(**1**), 2-NH₂-C₆H₄(**2**), 4-NH₂-C₆H₄(**3**), 2-NO₂-C₆H₄(**4**), 3-NO₂-C₆H₄(**5**), 4-NO₂-C₆H₄(**6**), 3-NO₂-4-OH-C₆H₃(**7**), 2-Cl-C₆H₄(**8**), 2,4-Cl₂-C₆H₃(**9**)].

(RAsO₃)₃(μ₃-O)(OH)(R′O)₂}₂Sn] (**A**), [{(PhSn)₃(4-NO₂-C₆H₄AsO₃)₂(RAsO₃H)(μ₃-O)(R′O)₂}₂] (**B**), [{(PhSn)₃(2,4-Cl₂-C₆H₃AsO₃)₃(μ₃-O)(R′O)₃}₂Sn] (**C**) and [{Sn₃Cl₃(μ₃-O)-(R′O)₃}₂(RAsO₃)₄] (**D**). To our knowledge, compounds of types **A**, **B**, and **C** are the first examples of such entities in organotin chemistry. Their crystal structures and a systematic investigation of the effect of the nature of the aryl arsonic acids on the structural types are also presented here.

Results and Discussion

Synthesis and procedures: All reactions and the four types of products **A**–**D** are summarized in Scheme 1. We studied solvothermal reactions of triphenyltin compounds with aryl arsonic acids. The reactions proceeded with complete or partial dearylation of the triphenyltin compounds, and four types of tin oxo clusters were obtained. Compounds of type **A** were prepared by solvothermal reactions of Ph₃SnOH with RAsO₃H₂ in 1:1 stoichiometry in methanol or ethanol at 140°C. When Ph₃SnOH was treated with 2,4-Cl₂C₆H₃AsO₃H₂ in methanol, block-shaped crystals of **A(9M)** were obtained together with small arrow-shaped crystals of **C(9M)**. The latter can be manually selected from the mixture by means of their shape. Compounds **A(1M, 1E, 2M, 2E, 3M)** can also be obtained by using Ph₃SnCl instead of Ph₃SnOH. Compound **B(6M)** can only be prepared by the reaction of 4-NO₂C₆H₄AsO₃H₂ with Ph₃SnOH in 1:1 molar ratio in methanol. When Ph₃SnCl was treated with 2-

(R = C₆H₅, 2-NH₂-C₆H₄, 4-NH₂-C₆H₄, 2-NO₂-C₆H₄, 3-NO₂-C₆H₄, 2-Cl-C₆H₄, 2,4-Cl₂-C₆H₃, and 3-NO₂-4-OH-C₆H₃; R′ = Me or Et)

(R = 4-NO₂-C₆H₄, R′ = Me)

(R = 2,4-Cl₂-C₆H₃, R′ = Me)

(R = 4-NO₂-C₆H₄, 2-NO₂-C₆H₄; R′ = Me or Et)

Compound	R	R′	Compound	R	R′
A(1M)	C₆H₅(1)	Me	B(6M)	4-NO₂-C₆H₄(6)	Me
A(1E)	C₆H₅(1)	Et	C(9M)	2,4-Cl₂-C₆H₃(9)	Me
A(2M)	2-NH₂-C₆H₅(2)	Me	D(4M)	2-NO₂-C₆H₄(4)	Me
A(2E)	2-NH₂-C₆H₅(2)	Et	D(4E)	2-NO₂-C₆H₄(4)	Et
A(3M)	4-NH₂-C₆H₄(3)	Me	D(6E)	4-NO₂-C₆H₄(6)	Et
A(4E)	2-NO₂C₆H₄(4)	Et			
A(5M)	3-NO₂-C₆H₄(5)	Me			
A(5E)	3-NO₂-C₆H₄(5)	Et			
A(7M)	3-NO₂-4-OH-C₆H₃(7)	Me			
A(7E)	3-NO₂-4-OH-C₆H₃(7)	Et			
A(8E)	2-Cl-C₆H₄(8)	Et			
A(9M)	2,4-Cl₂-C₆H₃(9)	Me			
A(9E)	2,4-Cl₂-C₆H₃(9)	Et			

Scheme 1. Synthetic routes to compounds **A(1M)**–**D(6E)**. **A**–**D** represent structure types, and **1**–**9** aryl arsonate ligands. **M** (CH₃OH) and **E** (CH₃CH₂OH) stand for the solvents used.

$NO_2C_6H_4AsO_3H_2$ in methanol or ethanol (or 4-$NO_2C_6H_4AsO_3H_2$ in ethanol), crystals of **D(4M)**, **D(4E)**, and **D(6E)** were obtained.

On exposure to air, crystals of compounds of type **A**, **B(6M)**, and **C(9M)** became opaque within minutes due to loss of solvent. Since all compounds are insoluble in common solvents (e.g., THF, C_6H_6, CH_3OH, DMSO and CH_2Cl_2), no NMR spectra could be obtained.

Structures of type A: Selected metric parameters for all the structures are listed in Table S1 in the Supporting Information. All compounds of type **A** are isostructural. For example, the X-ray structure of **A(1M)** consists of discrete neutral clusters, and it has a crystallographic inversion center. As illustrated in Figure 1a and Scheme 2, **A(1M)** is composed of two $[Sn_3(\mu_3\text{-O})(\mu_2\text{-OMe})_2]$ units connected via hydroxyl and phenylarsonic ligands to a central tin atom (Sn4). The Sn_3O_3 core of the $[Sn_3(\mu_3\text{-O})(\mu_2\text{-OMe})_2]$ unit is composed of three tin atoms held together by a μ_3-oxo ligand and two μ_2-alkoxo ligands which bind two adjacent tin atoms. The unit contains two four-membered Sn_2O_2 rings. The six atoms of the Sn_3O_3 core are almost coplanar, with a largest deviation from the Sn_3O_3 plane of 0.19 Å for O3. The two Sn_3O_3 planes are almost parallel to one another at a distance of 7.30 Å.

The six phenylarsonate groups in the molecule form bridges between three tin atoms. These bridges fall into three categories. Each of the two phenylarsonate groups (As1 and As1′) is arranged around the outside of one of the symmetry-related $[Sn_3(\mu_3\text{-}O)(\mu_2\text{-OMe})_2]$ units, while As2 and As2′ share two of their oxygen atoms with one $[Sn_3(\mu_3\text{-}O)(\mu_2\text{-OMe})_2]$ unit and their third oxygen atom with Sn4. Each of the remaining two phenylarsonate groups (As3 and As3′) is bound to two tin atoms and contributes to formation of the $\{Sn_3As_1O_4\}$ rings, with its third oxygen atom coordinated to Sn4.

Jurkschat et al. and others have reported a variety of trinuclear organotin oxo clusters $[M(OSntBu_2)_2O\cdot tBu_2Sn(OH)_2]$ (M = Ph_2Si, Me_2Si, CO, MesB, Ph_2P^+) and $[Ph_2Si-(OSntBu_2)_2O\cdot tBu_2SnF_2]$ that adopt a common tricyclic, almost planar $ESn_3O_3X_2$ (E = Si, C, B, P; X = OH, F) structural motif **E**.[13] Each of these tricyclic structures consists of fused six-membered Sn_2EO_3
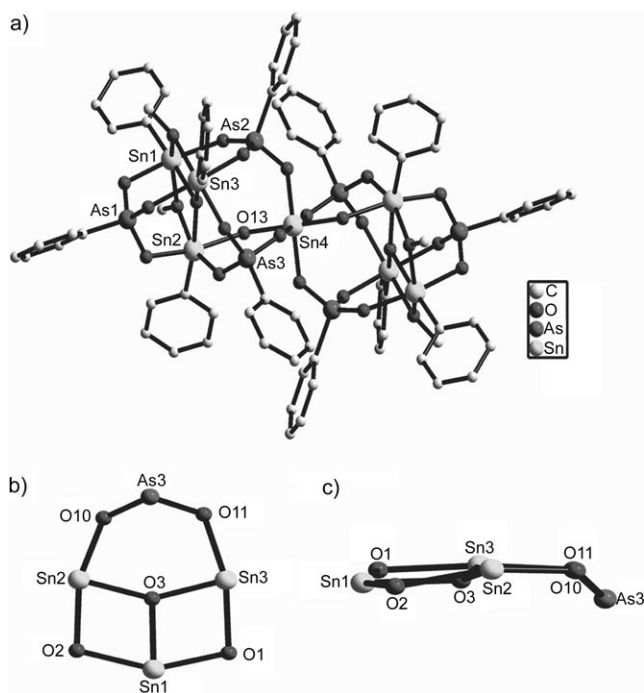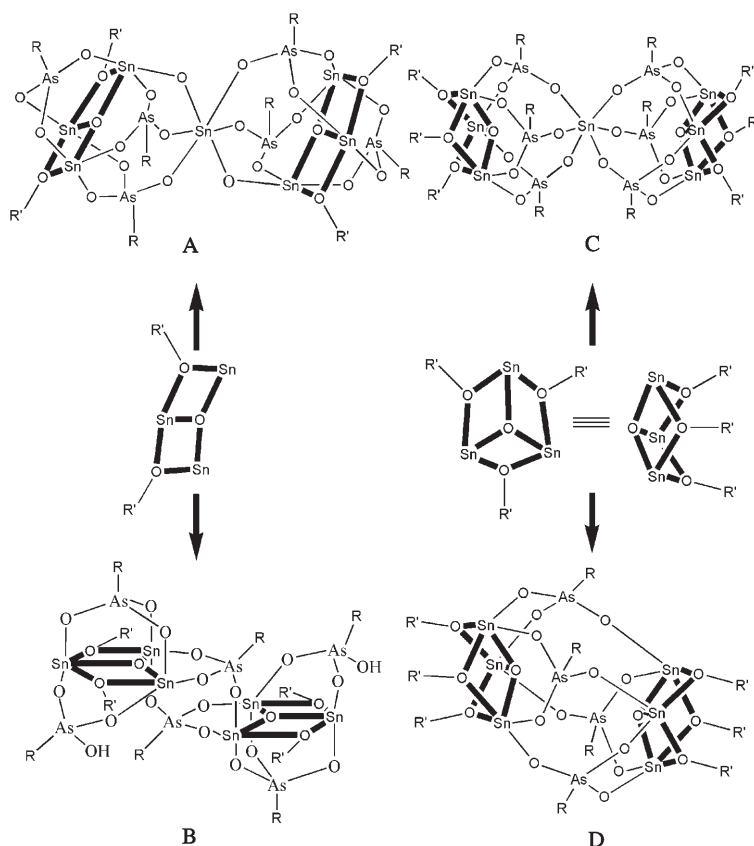

Figure 1. a) View of **A(1M)**. All H atoms have been omitted for clarity. The unlabeled atoms are symmetry-related to the labeled atoms. b and c) Tricyclic structure of **A(1M)**.

Scheme 2. Structures of the various stannoxane cores.

and four-membered Sn_2O_2 rings forming a planar ESn_3O_5 skeleton, with distorted trigonal-bipyramidal coordination at tin. However, a tricyclic structure containing an As atom has not hitherto been isolated.
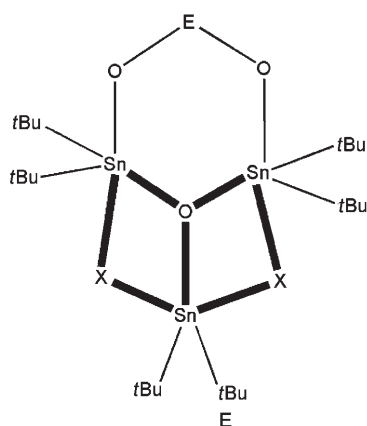
As illustrated in Scheme 2, the structure of **A(1M)** can be described as two tricyclic structures connected by Sn4. The tricyclic structure of compound **A(1M)** consists of fused six-membered Sn_2AsO_3 and four-membered Sn_2O_2 rings giving an $AsSn_3O_4$ skeleton. In contrast to the previously reported tricyclic structures, the $[AsSn_3O_3(MeO)_2]$ structural motif of **A(1M)** is not planar; the As atom deviates from the plane defined by $AsSn_3O_5$ (Figure 1 b and c).

The tin atoms of the two $[Sn_3(\mu_3\text{-}O)(\mu_2\text{-}OMe)_2]$ units are hexacoordinate, are bonded to one carbon atom and five oxygen atoms, and have an octahedral coordination geometry, whereas the Sn4 atom exhibits central MO_6 octahedral coordination by two bridging oxo groups and four oxygen donors from four phenylarsonate units.

Electrical neutrality demands the inclusion of two protons in the molecule of **A(1M)**. Since the positions of the hydrogen atoms could not be obtained from the X-ray data, they were inferred from the geometry of the non-hydrogen atoms. The logical location for these protons is on the bridging oxygen atom O13. Therefore, we conclude that O13 atom corresponds to a bridging hydroxy group.

In accordance with the formation of the previously reported structures, **A(1M)** can be chemically modified at corner positions of the $[Sn_3(\mu_3\text{-}O)(\mu_2\text{-}OMe)_2]$ units, that is, the MeO⁻ groups at the corners can be replaced by R′O⁻

groups (R′=alkyl) by changing the conditions. Based on this idea, ethanol was used instead of methanol, and **A(1E)** was isolated. Compound **A(1E)** has a very similar structure to **A(1M)**, and the structural difference is the replacement of MeO⁻ groups by EtO⁻ groups. The structure of **A(1E)** is shown in Figure S1 in the Supporting Information.

Structure of type B: The solvothermal reaction of Ph_3SnOH with $4\text{-}NO_2C_6H_4AsO_3H_2$ in methanol at 140°C for three days gave **B(6M)** as orange crystals in 73% yield. The crystal structure of **B(6M)** has two molecules in the asymmetric unit (Figure 2a). The X-ray crystallographic study on **B(6M)** revealed that the structure consists of discrete neutral clusters. The motif of the molecule contains two $[Sn_3(\mu_3\text{-}O)(\mu_2\text{-}OMe)_2]$ units, connected by two $4\text{-}NO_2C_6H_4AsO_3^{2-}$ units (Figure 2a and Scheme 2). The Sn_3O_3 core comprises three tin atoms held together by a μ_3-O ligand; a further two alkoxide groups act as bridging ligands; the μ_2-oxygen atom of each alkoxide is bound to two adjacent tin atoms. All tin

Figure 2. a) View of the two molecules of **B(6M)** present in its asymmetric unit. The unlabeled atoms are symmetry-related to the labeled atoms. The phenyl groups on tin atoms are omitted except for the carbon atoms bonded to tin atoms. b) Tricyclic structure of **B(6M)**.

atoms are hexacoordinate, bonded to one carbon atom and five oxygen atoms, and have octahedral coordination geometry.

Compound **B(6M)** contains two tricyclic structures, each of which consists of fused six-membered Sn_2AsO_3 and four-membered Sn_2O_2 rings forming a planar $AsSn_3O_4$ skeleton. Like closely related tricyclic structures,[13] the $\{AsSn_3O_5\}$ (As3, Sn1, Sn2, Sn3, O1, O2, O3, O10, O11) structure is almost planar (Figure 2b), and the largest deviation from the plane is 0.18 Å for Sn2. As3 or As3A contributes to formation of the $\{AsSn_3O_5\}$ system by binding to Sn atoms through its two O atoms, and it employs a third oxygen atom to coordinate to the other $\{AsSn_3O_5\}$ system. Therefore, the two $\{AsSn_3O_5\}$ systems are connected with each other by the third oxygen atoms of the two 4-nitrophenylars-

onate groups (As3, As3A). The two {AsSn$_3$O$_5$} systems are almost parallel to each other with a distance between planes of 3.14 Å. Each of the two 4-nitrophenylarsonate (As1, As1A) groups bridges three tin atoms of the {AsSn$_3$O$_5$} system. The remaining two 4-nitrophenylarsonate groups (As2, As2A) form symmetrical bridges between Sn1 and Sn3 (Sn1′ and Sn3′), whereas the third oxygen atom of each is not coordinated. The latter oxygen atoms, O9 and O9A, are protonated. This assignment is based on the fact that the As2−O9 (or As2A−O9A) bond is longer than the value anticipated for a terminal As=O bond.

Comparison of structures A and B: In structures of type **A**, the two [Sn$_3$(μ$_3$-O)(μ$_2$-OR′)$_2$] units are connected to each other by an equator with [Sn(OH)$_2$(RAsO$_3$)$_4$] motif, while the two [Sn$_3$(μ$_3$-O)(μ$_2$-OR′)$_2$] units of **B** are connected to each other by the arsonate motif (4-NO$_2$C$_6$H$_4$AsO$_3$)$_2$. Thus, the distances between two [Sn$_3$(μ$_3$-O)(μ$_2$-OR′)$_2$] units in **A** [for **A(1M)**] and **B** are 7.30 and 3.14 Å respectively. Structures **A** and **B** both contain double tricyclic units, and two O atoms of As3 or As3A are bound to Sn atoms and thus contribute to formation of the {AsSn$_3$O$_5$} system, but the coordination of the third oxygen atom is different. The third oxygen atom of **A** coordinates to tin atom Sn4, whereas that of **B** coordinates to the other {AsSn$_3$O$_5$} system. Clearly, the third coordinating oxygen atom plays an important role in formation of the clusters. For **B**, the {AsSn$_3$O$_5$} structure is almost planar, and the largest deviation from the plane is 0.18 Å for Sn2; whereas for **A**, the {AsSn$_3$O$_5$} structure is not planar; the As atom deviates from the plane defined by AsSn$_3$O$_5$.

Although structures **A** and **B** are clearly related to the previously reported tricyclic structures,[13] there are a number of significant differences. In comparison with reported type **E**, the μ$_2$-OH or -F groups are replaced by μ$_2$-OR′ groups for **A** and **B**. All three Sn atoms of **E** show distorted trigonal-bipyramidal configurations, but all tin atoms of **A** and **B** are hexacoordinate and have octahedral coordination geometry. The Sn−O bond lengths in the tricyclic system also differ (Table 1). Compared with type **E**, shorter Sn−O(μ$_3$) and Sn−O(μ$_2$) bonds are observed in the four-membered rings, and longer Sn−O(As) bonds are found in the six-membered Sn$_2$AsO$_3$ ring.

Structure of type C: Trinuclear tin oxo clusters such as {[*n*-BuSn(OH)O$_2$PPh$_2$]$_3$} have been isolated in the reaction of *n*-butylstannonic acid and diphenylphosphinic acid.[4a] Two units of

the trinuclear tin oxo cluster can be joined to each other in a face-to-face manner with rearrangement in the phosphinate bridges and Sn−O bonds to afford a drum shape.[2e] Double trinuclear tin oxo clusters in which two trinuclear tin oxo clusters are linked in a back-to-back manner by bridging phosphonate ligands have also been reported.[4b,c] We now report a heptanuclear tin oxo arsonate cluster, namely, [{(PhSn)$_3$(2,4-Cl$_2$C$_6$H$_3$AsO$_3$)$_3$(μ$_3$-O)(MeO)$_3$}$_2$Sn] [**C(9M)**]. The crystal structure of **C(9M)** has two molecules in the asymmetric unit. The motif of the molecule consists of two [Sn$_3$O(OMe)$_3$] units and one Sn^{4+} ion (Figure 3 and Scheme 2). In the Sn$_3$O$_4$ core, three tin atoms (Sn1, Sn2, Sn3) are joined together by one O^{2-} ion (O4). A further three alkoxide groups are involved as bridging ligands; the μ$_2$-O atom of each alkoxide is bound to two adjacent tin
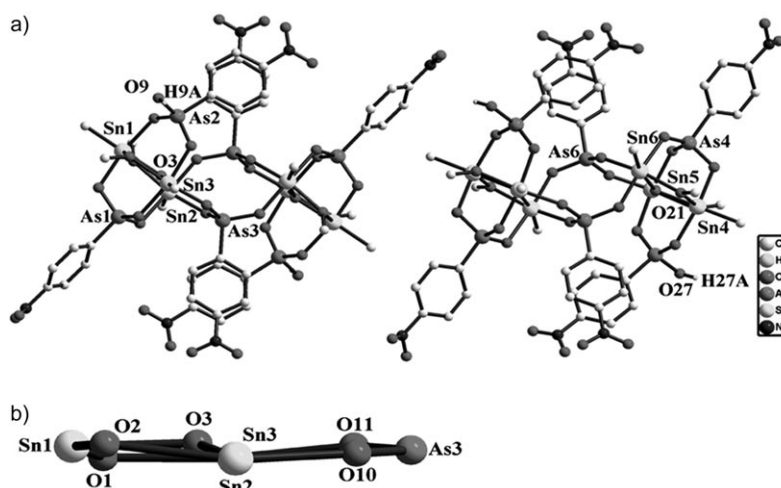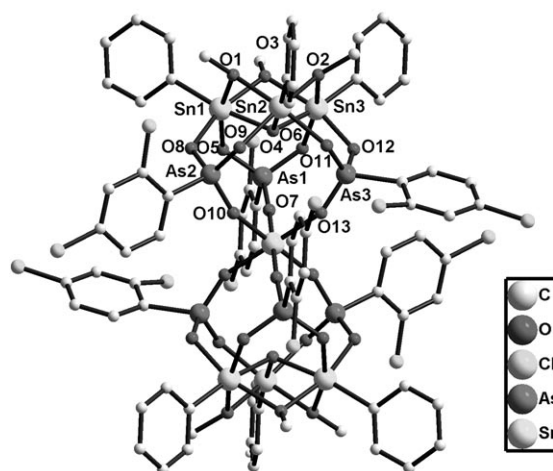

Figure 3. View of the one molecule of **C(9M)** present in its asymmetric unit. The unlabeled atoms are symmetry-related to the labeled atoms. All H atoms have been omitted for clarity.

Table 1. Comparison of bond lengths [Å] in the core structures of selected tricyclic tin oxo clusters.

Compound	Average Sn−O(μ$_3$)	Average Sn−O(μ$_2$)	Average Sn−O(As)	Interpole Sn$_3$O$_3$···Sn$_3$O$_3$
A(1M)	2.067(7)	2.120(2)	2.064(9)	7.3035
A(1E)	2.068(7)	2.126(3)	2.076(4)	7.2899
A(2M)	2.058(3)	2.117(3)	2.069(3)	7.2863
A(2E)	2.055(6)	2.122(7)	2.068(7)	7.2360
A(3M)	2.049(6)	2.119(3)	2.061(7)	7.3284
A(4E)	2.069(3)	2.113(2)	2.075(8)	7.1964
A(5M)	2.066(7)	2.117(2)	2.073(2)	7.2576
A(5E)	2.068(3)	2.116(5)	2.082(6)	7.2577
A(7M)	2.069(3)	2.131(4)	2.070(2)	7.2622
A(7E)	2.067(3)	2.120(8)	2.077(2)	7.2745
A(8E)	2.067(4)	2.120(3)	2.071(7)	7.2867
A(9M)	2.063(7)	2.127(8)	2.072(7)	7.3318
A(9E)	2.061(7)	2.121(5)	2.066(4)	7.2899
B(6M)[a]	2.051(3)	2.130(8)	2.090(1)	3.1391
	2.051(3)	2.126(8)	2.098(5)	3.2132
[Ph$_2$Si(OSn*t*Bu$_2$)$_2$O·*t*Bu$_2$Sn(OH)$_2$][13a]	2.092(2)	2.183(5)	2.019(2)[b]	
[Me$_2$Si(OSn*t*Bu$_2$)$_2$O·*t*Bu$_2$Sn(OH)$_2$][13b]	2.094(7)	2.190(5)	2.003(6)[b]	
[Ph$_2$Si(OSn*t*Bu$_2$)$_2$O·*t*Bu$_2$SnF$_2$][13e]	2.090(3)	2.224(8)[c]	1.990(4)[b]	

[a] Two crystallographically independent molecules are present. [b] Average Sn−O(Si) distance. [c] Average Sn−F average distance.

atoms. For one [Sn$_3$O(OMe)$_3$] unit, each pair of tin atoms is connected to the Sn^{4+} ion through one 2,4-dichlorophenylarsonate group. The two [Sn$_3$O(OMe)$_3$] units are bound to the same Sn^{4+} ion affording a heptanuclear tin oxo arsonate cluster. All tin atoms in **C(9M)** have a coordination number of six, which for atoms Sn1–Sn3 is made up of one phenyl group and five oxygen atoms, while Sn4 is coordinated by six oxygen atoms from six 2,4-dichlorophenylarsonate groups. The average Sn−O(μ_3) bond length is 2.057(3) Å, whereas the Sn−O(μ_2) bond length is 2.121(7) Å. In comparison, Sn−O distances involving the 2,4-dichlorophenylarsonate oxygen atoms are slightly shorter (Table 2).

cupied. Thus, the structure of **F** can be described as a double trinuclear tin oxo cluster connected by Sn^{4+}. In **G**, the heptanuclear tin cluster is composed of two centrosymmetrically related tritin subunits and one Bz$_2$Sn^{2+} group. For **A**, **C**, and **F**, the tin atoms result from complete dearylation and dealkylation reactions, while the Bz$_2$Sn^{2+} group of **G** is generated by partial debenzylation.

Structures of type D: Reaction of Ph$_3$SnCl with RAsO$_3$H$_2$ (R = 2-NO$_2$C$_6$H$_4$, 4-NO$_2$C$_6$H$_4$) in methanol or ethanol afforded hexanuclear tin oxo clusters [{Sn$_3$Cl$_3$(μ_3-O)(R′O)$_3$}$_2$-(RAsO$_3$)$_4$], where R = 2-NO$_2$C$_6$H$_4$, 4-NO$_2$C$_6$H$_4$; R′ = Me, Et. The structures of type **D** are very similar to each other and are clearly related to that of [{(n-BuSn)$_3$(PhO)$_3$O}$_2$-(O$_3$PH)$_4$];[4b,c] compounds of type **D** show spherical cagelike architectures. Because of the similarity of the three structures, only **D(4M)** is described in detail. As shown in Figure 4 and Scheme 2, **D(4M)** consists of two tritin motifs in the form of [Sn$_3$Cl$_3$(μ_3-O)(MeO)$_3$O] connected by four 2-NO$_2$C$_6$H$_4$AsO$_3^{2-}$ ions. In the tritin subunit, three tin atoms (Sn1, Sn2, Sn3) are joined together by one O^{2-} ion (O4). Furthermore, three alkoxide

Table 2. Comparison of bond lengths [Å] in the core structures of tin oxo clusters containing two [Sn$_3$O(OR′)$_3$] units.

Compound	Average Sn−O(μ_3)	Average Sn−O(μ_2)	Average Sn−O(As)	Diametrically opposed As−As	Interpole O(μ_3)···O(μ_3)
C(9M)[a]	2.057(3)	2.121(7)	2.044(2)		7.691(2)
	2.059(6)	2.115(3) 2.029(1)		7.724(3)	
D(4M)	2.060(3)	2.106(3)	2.028(3)	6.568(1) (As1−As1)	3.482(7)
				6.598(1)(As2-As2)	
D(4E)	2.060(3)	2.113(1)	2.027(5)	6.555(1) (As1−As1)	3.474(8)
				6.548(1) (As2−As2)	
D(6E)	2.062(7)	2.099(5)	2.034(3)	6.536(1)	3.481 (5)
13[d],[4b]	2.065(3)	2.172(2)	2.072(2)[b]	6.337(1)[c]	3.778(4)
14[a,d],[4c]	2.058(5)	2.172(6) 2.068(6)[b]	6.283(2)[c]	3.813(2)	
	2.057(5)	2.176(6)	2.064(6)[b]	6.275(3)[c]	3.848(2)
15[a,d],[4c]	2.063(3)	2.177(4)	2.071(4)[b]	6.294(3)[c]	3.805(5)
	2.064(4)	2.181(4)	2.073(4)[b]	6.294(4)[c]	3.827(6)
16[d],[4c]	2.062(7)	2.172(7)	2.080(7)[b]	6.274(5)[c]	3.825(9)

[a] Two crystallographically independent molecules are present. [b] Average Sn−O(P) distance. [c] Average distance between the diametrically opposite phosphorus atoms in the equator.[d] {[(nBuSn)$_3$(μ_3-O)(OC$_6$H$_4$-4-X)$_3$]$_2$(O$_3$PH)$_4$}, where X = H (**13**), Cl(**14**), Br (**15**), and I (**16**).

Comparison of structures A and C: When Ph$_3$SnOH was treated with 2,4-Cl$_2$PhAsO$_3$H$_2$ in methanol, block-shaped crystals of **A(9M)** were obtained together with small arrow-shaped crystals of **C(9M)**. The two types of heptanuclear tin oxo arsonate clusters **A** and **C** have similar compositions, but their structures differ in detail. In **A**, the two [Sn$_3$O-(OR′)$_2$] units are connected to each other by a [Sn(OH)$_2$-(RAsO$_3$)$_4$] motif, while in **C** the two [Sn$_3$O(OR′)$_3$] units are linked to each other by an equator composed with [Sn(2,4-Cl$_2$-PhAsO$_3$)$_6$] motif. In **A**, the central Sn atom (Sn4) has an MO$_6$ octahedral geometry consisting of two bridging oxo groups and four oxygen donors from four organoarsonate units, whereas in **C** Sn4 exhibits an MO$_6$ octahedral geometry consisting of six oxygen donors from six organoarsonate units. In comparison with **A**, the average Sn−O distances [Sn−O(μ_2) and Sn−O(As)] in **C** are slightly shorter.

Heptanuclear tin–sulfur cluster [({n-BuSnS-(O$_2$PPh$_2$)}$_3$O)$_2$Sn][14] (**F**) and heptanuclear tin phosphonate cluster [Na$_6$(CH$_3$OH)$_2$(H$_2$O)][{(BzSn)$_3$(PhPO$_3$)$_5$(μ_3-O)-(CH$_3$O)}$_2$Bz$_2$Sn]·CH$_3$OH[7b] (**G**) have been reported. The core of **F** is a double cube connected at the corners occupied by Sn, and the central Sn atom is bonded to six S atoms. The trinuclear tin oxo cluster can be considered as an incomplete cube, one of the vertexes of which remains unoc-

Figure 4. View of **D(4M)**. All H atoms have been omitted for clarity.

groups are involved as bridging ligands; the μ_2-O atom of each alkoxide group is bound to two adjacent tin atoms. Each tin atom of the tritin subunit is further bound to two oxygen atoms of the 2-nitrophenylarsonate ligands. Each of the 2-nitrophenylarsonate ligands is involved in a tripodal bridging coordination mode. All of the tin atoms are sixfold coordinated by one Cl atom and five O atoms. Interestingly, complete dearylation of Ph$_3$SnCl occurs in the formation of

compound **D(4M)** and plays a crucial role in generating the hexanuclear tin arsonate cluster. In the synthesis of tin oxo cluster $Sn_8O_4L_6$ ($H_2L = 1,1'$-ferrocenedicarboxylic acid), complete dealkylation of nBu_2SnO was observed.[7a] The average $Sn–O(\mu_3)$ bond length is 2.060(3) Å, whereas the $Sn–O(\mu_2)$ bond length is 2.106(3) Å. In comparison, $Sn–O$ distances involving the arsonate oxygen atoms are slightly shorter.

Comparison of structures C and D: Two types of structures (**C** and **D**) have been observed for compounds containing two $[Sn_3O(OR')_3]$ units. In **C**, the two $[Sn_3O(OR')_3]$ units are connected to each other by an equator with $[(2,4\text{-}Cl_2\text{-}PhAsO_3)_6Sn]$ motif, whereas in **D** the two $[Sn_3O(OR')_3]$ units are connected to each other by an $[(2\text{-}NO_2C_6H_4AsO_3)_4]$ arsonate motif. The interpole distance (μ_3-$O\cdots\mu_3$-O) in **C(9M)** is 7.69 Å, and in **D(4M–6E)** it ranges from 3.47 for **D(4E)** to 3.48 Å for **D(4M)**; see Table 2.

Although compounds **D(4M–6E)** are similar to the tin oxo cluster $\{[(nBuSn)_3(\mu_3\text{-}O)(OC_6H_4\text{-}4\text{-}X)_3]_2(O_3PH)_4\}$, where X = H (**13**), Cl (**14**), Br (**15**), and I (**16**), there are some differences.[4b,c] In **13–16**, the chlorine atoms of **D(4M–6E)** are replaced by n-butyl groups and the molecules are organo oxo tin clusters. In the present structures, the chlorine atoms coordinate to the Sn atoms. Consequently, the distances between the diametrically opposite phosphorus atoms in **13–16** range from 6.27 to 6.34 Å, whereas in **D(4M–6E)** the distances between the diametrically opposite arsenic atoms range from 6.54 for **D(6E)** to 6.60 Å for **D(4M)**. The interpole distances ($\mu_3O\cdots\mu_3O$) in **13–16** range from 3.78 to 3.83 Å, but in **D(4M–6E)** they range from 3.47 [**D(4E)**] to 3.48 Å [**D(4M)**] (Table 2). Despite the apparent dissimilarities, the Sn–O cages are structurally quite close.

It is noteworthy that basic $[Sn_3O(OR')_2]$ units (Sn_3O_3) are observed in the molecular structures of type **A–D**. In **A** and **B** the units take the form of $[Sn_3O(OR')_2\{O_2As(O)R\}]$, whereas in **C** and **D** $[Sn_3O(OR')_3]$ units are present. Interestingly, when the OR' groups of $[Sn_3O(OR')_3]$ units in **C** and **D** were substituted by $[O_2As(O)R]$ moieties, new $[Sn_3O(OR')_2\{O_2As(O)R\}]$ units were obtained in **A** and **B**, and a change of structure of the tin oxo cores resulted. Notably, although partial substitution of OR' by $[O_2As(O)R]$ occurred during the preparation of **9M** (a mixture of **A**- and **C**-type structures was obtained in **9M**), the transformation of tin oxo cores from $[Sn_3O(OR')_3]$ to $[Sn_3O(OR')_2\{O_2As(O)R\}]$ was still realized under solvothermal conditions. The Sn_3O_3 core of **A** and **B** comprises three tin atoms held together by a μ_3-O atom; a further two alkoxide groups are involved as bridging ligands; the μ_2-O atom of each alkoxide group is bound to two adjacent tin atoms. Thus, two four-membered Sn_2O_2 rings are formed. The six atoms of the Sn_3O_3 core are almost coplanar. Although in the nonplanar Sn_3O_3 core of **C** and **D** three tin atoms are also joined together by one μ_3-O atom, three alkoxide groups are involved as bridging ligands, and thus the structure of the tin oxo core is different.

In compounds **A(1M)–D(6E)**, the aryl arsonic acids display two kinds of coordination modes: I) three oxygen atoms coordinate to three different metal ions; II) two
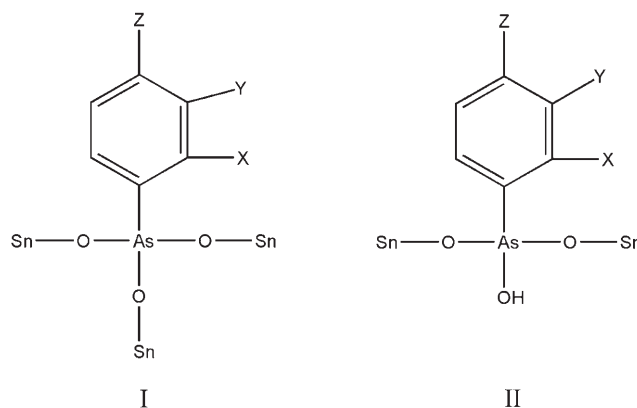
oxygen atoms coordinate to two different metal ions, while the remaining OH group is not coordinated. Generally, similar forms may be expected when the nine different aryl arsonic acids are used. Indeed, compounds **A(1M–9E)** have similar structures, and compounds **D(4M–6E)** also show similar motifs.

However, sometimes changes in the substituents on the aryl arsonate ligands can result in different structural types. The influence of substituents on the reactivity of the aryl arsonic acids can be dramatic. For example, the reaction of Ph_3SnOH with $4\text{-}NO_2C_6H_4AsO_3H_2$ affords hexanuclear tin oxo cluster **B**, whereas the reaction of Ph_3SnOH with $2,4\text{-}Cl_2C_6H_3AsO_3H_2$ yields heptanuclear tin oxo cluster **C**. On the other hand, sometimes changes in organotin precursors could result in different structural types. When Ph_3SnOH and $2\text{-}NO_2C_6H_4AsO_3H_2$ are used, the compound **A(4E)** is obtained. However, when Ph_3SnCl and $2\text{-}NO_2C_6H_4AsO_3H_2$ are used under the same reaction conditions, complete Sn–C cleavage results in compounds **D(4M)** and **D(4E)**.

Under solvothermal reaction conditions, the choice of the solvent plays an important role. This is demonstrated by the reactions giving **D(6E)** in ethanol and **B(6M)** in methanol, both of which started with the same mixture of compounds under the same reaction conditions. The reaction of Ph_3SnOH with $2,4\text{-}Cl_2C_6H_3AsO_3H_2$ in methanol affords **C(9M)**, while the reaction of Ph_3SnOH with $2,4\text{-}Cl_2C_6H_3AsO_3H_2$ in ethanol affords **A(9E)**.

Studying the effect of reaction temperature on the formation of **A–D** indicated that they are always obtained in the temperature range of 100–160 °C. Notably, variation of the temperature (100–160 °C) did not result in a change of structure type; higher (>160 °C) and lower (<100 °C) temperatures led to lower yields. The cooling rate also did not influence the structure type, but it has a significant effect on the quality of the crystals. For example, when the reaction mixture was immediately cooled to room temperature during the syntheses of types **A** and **C**, good quality crystals were

obtained. Good-quality crystals of types **B** and **D** were obtained through by cooling to room temperature at a rate of $10°C\,h^{-1}$. Therefore, the cooling method is the key to the formation of good-quality crystals. Since all the compounds were prepared with the same filling volume (10 mL), this may not be a factor that influences formation of the structure type.

Mass spectrometric studies: ESI-MS has been widely used to investigate alkyl derivatives of metals.[15,16] So far, the solution behavior of only few tin oxo clusters has been investigated by ESI-MS.[17] To gain more information on the stability of our compounds in solution, we examined them using ESI-MS. The mass spectra were recorded on a LCQ mass spectrometer (Finnigan MAT) in negative mode. Taking **A(1M)**, **B(6M)**, **C(9M)** and **D(4M)** as examples, their crystals were dissolved in chloroform. The solutions were then analyzed by direct infusion at a flow rate of $5\,\mu L\,min^-$. The ESI-MS of **A(1M)**, **B(6M)**, **C(9M)**, and **D(4M)** are shown in Figures S2–S5 in the Supporting Information. The ESI mass spectrum of **B(6M)** consists of a single peak covering a wide isotopic mass distribution (due to the multiplicity of tin isotopes) centered at m/z 1400.3, which can be assigned to $[M-2H]^{2-}$. Thus, the ESI mass spectrum indicates that the structure of **B(6M)** observed in the solid state is still retained in chloroform solution. However, the ESI mass spectra of **A(1M)**, **C(9M)**, and **D(4M)** show additional peaks (see Figures S2, S4, and S5 in the Supporting Information) which can be attributed to several decomposition products. Therefore, the ESI mass spectra of **A(1M)**, **C(9M)**, and **D(4M)** suggest that their structures are relatively unstable and are easily decomposed in chloroform solution.

Conclusion

Four types of organotin aryl arsonate clusters based on nine aryl arsonate ligands were synthesized under solvothermal conditions. Structure types of **A**–**C** were found and structurally characterized for the first time in organotin compounds. The results reveal that solvothermal synthetic approach is an effective technique for obtaining crystalline organotin aryl arsonates. Moreover, the aryl arsonic acids and organotin precursors played important roles in the formation of different structural forms of the organotin clusters, and access to new structural types can be expected by reactions of other organotin precursors with arsonic acids. Further studies on the structural interrelationship of these diverse organostannoxane compounds are in progress.

Experimental Section

Materials: $2\text{-}NO_2C_6H_4AsO_3H_2$, $3\text{-}NO_2C_6H_4AsO_3H_2$, $2\text{-}ClC_6H_4AsO_3H_2$, and $2,4\text{-}Cl_2\text{-}C_6H_3AsO_3H_2$ were prepared by literature methods.[18] $C_6H_5AsO_3H_2$, $2\text{-}NH_2C_6H_4AsO_3H_2$, $4\text{-}NH_2C_6H_4AsO_3H_2$, 4-

$NO_2C_6H_4AsO_3H_2$, $3\text{-}NO_2\text{-}4\text{-}OHC_6H_3AsO_3H_2$, Ph_3SnOH, Ph_3SnCl and other reagents were purchased from commercial sources.

General characterization and physical measurements: Elemental analysis (C, H, N) was conducted on a Perkin-Elmer 240C elemental analyzer. FTIR spectra were recorded on KBr pellets in the range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. The mass spectra were recorded on a LCQ mass spectrometer (Finnigan MAT) in negative mode.

Synthesis of $[(PhSn)_3(PhAsO_3)_3(\mu_3\text{-}O)(OH)(MeO)_2]_2Sn$ [A(1M)]: Method I: A mixture of Ph_3SnOH (0.183 g, 0.5 mmol) and $PhAsO_3H_2$ (0.101 g, 0.5 mmol) in methanol (10 mL) was heated in a 15 mL Teflon-lined autoclave at 140°C for 3 h. The mixture was cooled to room temperature, and the resulting colorless crystals of **A(1M)** were collected and washed with methanol. Yield: 0.155 g (81% based on Ph$_3$SnOH).

Method II: A mixture of Ph_3SnCl (0.192 g, 0.5 mmol) and $PhAsO_3H_2$ (0.101 g, 0.5 mmol) in methanol (10 mL) was heated in a 15 mL Teflon-lined autoclave at 140°C for 3 days. The mixture was cooled to room temperature, and the resulting colorless crystals of **A(1M)** were collected and washed with methanol. Yield: 0.101 g (53% based on Ph$_3$SnCl). Elemental analysis (%) calcd for $C_{76}H_{74}As_6O_{26}Sn_7$ ($M_r = 2683.70$): C 34.01, H 2.78; found: C 34.08, H 2.69. IR: $\tilde{\nu} = 3731$ (w), 3673 (w), 3624 (w), 3591 (w), 3568 (w), 3052 (w), 2932 (w), 2829 (w), 1515 (w), 1435 (m), 1388 (w), 1096 (m), 1026 (m), 862 (s), 814 (s), 733 (m), 689 (m), 509 (m), 434 (s), 405 (s) cm^{-1}.

Synthesis of $[\{(PhSn)_3(PhAsO_3)_3(\mu_3\text{-}O)(OH)(EtO)_2\}_2Sn]\cdot H_2O\cdot EtOH$ [A(1E)]: Method I: A mixture of Ph_3SnOH (0.183 g, 0.5 mmol) and $PhAsO_3H_2$ (0.101 g, 0.5 mmol) in ethanol (10 mL) was heated in a 15 mL Teflon-lined autoclave at 140°C for 3 days. The mixture was cooled to room temperature, and the resulting colorless crystals of **A(1E)** were collected and washed with ethanol. Yield: 0.158 g (79% based on Ph$_3$SnOH).

Method II: A mixture of Ph_3SnCl (0.192 g, 0.5 mmol) and $PhAsO_3H_2$ (0.101 g, 0.5 mmol) in ethanol (10 mL) was heated in a 15 mL Teflon-lined autoclave at 140°C for 3 days. The mixture was cooled to room temperature, and the resulting colorless crystals of **A(1E)** were collected and washed with ethanol. Yield: 0.146 g (73% based on Ph$_3$SnCl). Elemental analysis (%) calcd for $C_{82}H_{90}As_6O_{28}Sn_7$ ($M_r = 2803.89$): C 35.13, H 3.24; found: C 35.08, H 3.39. IR: $\tilde{\nu} = 3561$ (s), 3479 (s), 3415 (s), 3235 (w), 2361 (s), 1639 (m), 1617 (m), 1480 (w), 1436 (w), 1384 (w), 1096 (m), 1049 (m), 990 (w), 868 (m), 814 (s), 731 (m), 690 (m), 648 (m), 450 (s), 433 (s), 402 (s) cm^{-1}.

Synthesis of $[(PhSn)_3(2\text{-}NH_2C_6H_4AsO_3)_3(\mu_3\text{-}O)(OH)(MeO)_2]_2Sn$ [A(2M)]: **A(2M)** was synthesized by procedures similar to those used for **A(1M)** (Methods I and II) except that $2\text{-}NH_2PhAsO_3H_2$ (0.109 g, 0.5 mmol) was used in place of $PhAsO_3H_2$. Yield: 0.159 g (80% based on Ph$_3$SnOH). Elemental analysis (%) calcd for $C_{76}H_{80}As_6N_6O_{26}Sn_7$ ($M_r = 2773.81$): C 32.91, H 2.91, N 3.03; found: C 32.85, H 2.83, N 2.94. IR: $\tilde{\nu} = 3859$ (w), 3742 (w), 3671 (w), 3362 (m), 3061 (w), 2970 (w), 1619 (m), 1482 (m), 1448 (m), 1383 (w), 1315 (m), 1258 (w), 1161 (w), 1082 (w), 1038 (m), 869 (s), 813 (s), 733 (m), 695 (m), 672 (m), 511 (m), 445 (s), 404 (m) cm^{-1}.

Synthesis of $[\{(PhSn)_3(2\text{-}NH_2C_6H_4AsO_3)_3(\mu_3\text{-}O)(OH)(EtO)_2\}_2Sn]\cdot 2EtOH$ [A(2E)]: **A(2E)** was synthesized by procedures similar to those used for **A(1E)** (Methods I and II) except that $2\text{-}NH_2PhAsO_3H_2$ (0.109 g, 0.5 mmol) was used in place of $PhAsO_3H_2$. Yield: 0.173 g (83% based on Ph$_3$SnOH). Elemental analysis (%) calcd for $C_{84}H_{100}As_6N_6O_{28}Sn_7$ ($M_r = 2922.05$): C 34.53, H 3.45, N, 2.88; found: C 34.85, H 3.63, N 2.94. IR: $\tilde{\nu} = 3924$ (m), 3899 (m), 3860 (m), 3800 (m), 3742 (s), 3673 (m), 3648 (m), 3618 (m), 3590 (s), 3564 (s), 3420 (s), 3061 (w), 2827 (w), 1773 (w), 1741 (w), 1699 (w), 1644 (m), 1620 (m), 1560 (w), 1541 (w), 1515 (w), 1480 (m), 1454 (w), 865 (m), 817 (m), 452 (w), 421 (w), 404 (w) cm^{-1}.

Synthesis of $[\{(PhSn)_3(4\text{-}NH_2C_6H_4AsO_3)_3(\mu_3\text{-}O)(OH)(MeO)_2\}_2Sn]$ [A(3M)]: **A(3M)** was synthesized by procedures similar to those used for **A(1M)** (Methods I and II) except that $4\text{-}NH_2PhAsO_3H_2$ (0.109 g, 0.5 mmol) was used in place of $PhAsO_3H_2$. Yield: 0.160 g (81% based on Ph$_3$SnOH). Elemental analysis (%) calcd for $C_{76}H_{80}As_6N_6O_{26}Sn_7$ ($M_r = 2773.81$): C 32.91, H 2.91, N 3.03; found: C 32.85, H 2.83, N 2.94. IR: $\tilde{\nu} =$

3355 (w), 1625 (m), 1595 (m), 1502 (m), 1308 (m), 1097 (m), 1034 (w), 858 (s), 731 (m), 694 (m), 512 (m), 445 (m), 404 (m) cm^{-1}.

Synthesis of [{(PhSn)$_3$(2-NO$_2$C$_6$H$_4$AsO$_3$)$_3$(μ_3-O)(OH)(EtO)$_2$]$_2$Sn]·EtOH [A(4E)]: A(4E) was synthesized by a procedure similar to that used for A(1E) (Method I) except that 2-NO$_2$C$_6$H$_4$AsO$_3$H$_2$ (0.123 g, 0.5 mmol) was used in place of PhAsO$_3$H$_2$. Yield: 0.175 g (80% based on Ph$_3$SnOH). Elemental analysis (%) calcd for C$_{82}$H$_{82}$As$_6$N$_6$O$_{39}$Sn$_7$ ($M_r =$ 3055.89): C 32.22, H 2.70, N 2.75; found: C 32.45, H 2.83, N 2.94. IR: $\tilde{\nu} =$ 3864 (w), 3738 (m), 3680 (w), 3659 (w), 3615 (w), 3417 (m), 1743 (m), 1688 (m), 1643 (m), 1532 (s), 1429 (m), 1384 (s), 1351 (m), 1121 (m), 1042 (m), 873 (m), 444 (w), 430 (w), 420 (w), 403 (m) cm^{-1}.

Synthesis of [{(PhSn)$_3$(3-NO$_2$C$_6$H$_4$AsO$_3$)$_3$(μ_3-O)(OH)(MeO)$_2$]$_2$Sn]·2MeOH [A(5M)]: A(5M) was synthesized by a procedure similar to that used for A(1M) (Method I) except that 3-NO$_2$C$_6$H$_4$AsO$_3$H$_2$ (0.123 g, 0.5 mmol) was used in place of PhAsO$_3$H$_2$. Yield: 0.179 g (83% based on Ph$_3$SnOH). Elemental analysis (%) calcd for C$_{76}$H$_{76}$As$_6$N$_6$O$_{40}$Sn$_7$ ($M_r =$ 3017.80): C 30.25, H 2.54, N 2.78; found: C 30.13, H 2.61, N 2.94. IR: $\tilde{\nu} =$ 3860 (w), 3742 (m), 3673 (w), 3649 (w), 3623 (w), 3591 (w), 3567 (w), 1741 (m), 1699 (m), 1679 (w), 1652 (m), 1537 (s), 1456 (m), 1427 (w), 1393 (w), 1348 (m), 1025 (w), 830 (m), 731 (m), 671 (m), 651 (m), 515 (m), 452 (s), 421 (s), 403 (s) cm^{-1}.

Synthesis of [{(PhSn)$_3$(3-NO$_2$C$_6$H$_4$AsO$_3$)$_3$(μ_3-O)(OH)(EtO)$_2$]$_2$Sn]·EtOH [A(5E)]: A(5E) was synthesized by a procedure similar to that used for A(1E) (Method I) except that 3-NO$_2$C$_6$H$_4$AsO$_3$H$_2$ (0.123 g, 0.5 mmol) was used in place of PhAsO$_3$H$_2$. Yield: 0.183 g (84% based on Ph$_3$SnOH). Elemental analysis (%) calcd for C$_{82}$H$_{82}$As$_6$N$_6$O$_{39}$Sn$_7$ ($M_r =$ 3055.89): C 32.22, H 2.70, N 2.75; found: C 32.45, H 2.83, N 2.94. IR: $\tilde{\nu} =$ 3743 (w), 3673 (w), 3649 (w), 3623 (w), 3591 (w), 3564 (w), 3527 (w), 3417 (m), 3064 (w), 2968 (w), 2886 (w), 1536 (s), 1474 (w), 1427 (w), 1349 (m), 1083 (w), 1038 (m), 877 (s), 822 (s), 730 (m), 694 (m), 669 (m), 548 (m), 502 (m), 453 (m), 424 (s), 405 (s) cm^{-1}.

Synthesis of [{(PhSn)$_3$(3-NO$_2$-4-OHC$_6$H$_3$AsO$_3$)$_3$(μ_3-O)(OH)(MeO)$_2$]$_2$Sn]·2MeOH [A(7M)]: A(7M) was synthesized by a procedure similar to that used for A(1M) (Method I) except that 3-NO$_2$-4-OH-C$_6$H$_3$AsO$_3$H$_2$ (0.131 g, 0.5 mmol) was used in place of PhAsO$_3$H$_2$. Yield: 0.178 g (80% based on Ph$_3$SnOH). Elemental analysis (%) calcd for C$_{78}$H$_{76}$As$_6$N$_6$O$_{46}$Sn$_7$ ($M_r =$ 3113.80): C 30.09, H 2.46, N 2.70; found: C 30.45, H 2.83, N 2.94. IR: $\tilde{\nu} =$ 3648 (w), 3622 (w), 3564 (w), 3417 (w), 3248 (w), 1617 (m), 1575 (m), 1536 (m), 1480 (w), 1422 (w), 1321 (m), 1257 (m), 1190 (w), 1153 (w), 1110 (m), 1076 (m), 1042 (w), 830 (s), 734 (m), 693 (m), 672 (m), 546 (m), 502 (m), 451 (s), 426 (s), 404 (s) cm^{-1}.

Synthesis of [{(PhSn)$_3$(3-NO$_2$-4-OHC$_6$H$_3$AsO$_3$)$_3$(μ_3-O)(OH)(EtO)$_2$]$_2$Sn]·EtOH [A(7E)]: A(7E) was synthesized by a procedure similar to that used for A(1E) (Method I) except that 3-NO$_2$-4-OH-C$_6$H$_3$AsO$_3$H$_2$ (0.131 g, 0.5 mmol) was used in place of PhAsO$_3$H$_2$. Yield: 0.185 g (81% based on Ph$_3$SnOH). Elemental analysis (%) calcd for C$_{84}$H$_{88}$As$_6$N$_6$O$_{46}$Sn$_7$ ($M_r =$ 3197.95): C 31.55, H 2.77, N 2.63; found: C 30.45, H 2.83, N 2.94. IR: $\tilde{\nu} =$ 3246 (w), 1617 (s), 1577 (m), 1538 (m), 1481 (m), 1431 (w), 1322 (m), 1256 (m), 1150 (w), 1102 (w), 1076 (m), 1045 (w), 897 (m), 873 (s), 827 (s), 547 (m), 508 (m), 454 (m), 433 (m), 404 (m) cm^{-1}.

Synthesis of [{(PhSn)$_3$(2-ClC$_6$H$_4$AsO$_3$)$_3$(μ_3-O)(OH)(EtO)$_2$]$_2$Sn]·EtOH [A(8E)]: A(8E) was synthesized by a procedure similar to that used for A(1E) (Method I) except that 2-ClC$_6$H$_4$AsO$_3$H$_2$ (0.119 g, 0.5 mmol) was used in place of PhAsO$_3$H$_2$. Yield: 0.184 g (86% based on Ph$_3$SnOH). Elemental analysis (%) calcd for C$_{82}$H$_{82}$As$_6$Cl$_6$O$_{27}$Sn$_7$ ($M_r =$ 2992.53): C 32.91, H 2.76; found: C 32.78, H 2.83. IR: $\tilde{\nu} =$ 3859 (w), 3742 (m), 3673 (w), 3649 (w), 3623 (w), 3591 (w), 1741 (w), 1699 (w), 1679 (w), 1652 (w), 1560 (w), 1541 (m), 1515 (m), 1456 (m), 1428 (w), 1390 (w), 1120 (w), 1042 (m), 825 (s), 756 (m), 731 (m), 692 (m), 670 (m), 510 (m), 452 (s), 424 (s), 405 (m) cm^{-1}.

Synthesis of [{(PhSn)$_3$(2,4-Cl$_2$C$_6$H$_3$AsO$_3$)$_3$(μ_3-O)(OH)(MeO)$_2$]$_2$Sn] [A(9M)]: A(9M) was synthesized by a procedure similar to that used for A(1M) (Method I) except that 2,4-Cl$_2$C$_6$H$_3$AsO$_3$H$_2$ (0.136 g, 0.5 mmol) was used in place of PhAsO$_3$H$_2$. Block crystals of A(9M) were obtained together with crystals of C(9M). Yield: 0.088 g (40% based on Ph$_3$SnOH). Elemental analysis (%) calcd for C$_{76}$H$_{62}$As$_6$Cl$_{12}$O$_{26}$Sn$_7$ ($M_r =$ 3097.01): C 29.47, H 2.02; found: C 29.58, H 2.13. IR: $\tilde{\nu} =$ 3741 (w), 3673

(w), 3649 (w), 3624 (w), 3591 (w), 3567 (w), 1741 (m), 1651 (w), 1550 (m), 1541 (m), 1515 (w), 1480 (w), 1455 (m), 1429 (m), 1367 (m), 1247 (w), 1143 (m), 1119 (m), 1041 (m), 870 (s), 823 (s), 730 (m), 692 (m), 672 (m), 652 (m), 557 (w), 502 (m), 424 (s), 405 (s) cm^{-1}.

Synthesis of [{(PhSn)$_3$(2,4-Cl$_2$C$_6$H$_3$AsO$_3$)$_3$(μ_3-O)(OH)(EtO)$_2$]$_2$Sn]·EtOH [A(9E)]: A(9E) was synthesized by a procedure similar to that used for A(1E) (Method I) except that 2,4-Cl$_2$C$_6$H$_3$AsO$_3$H$_2$ (0.136 g, 0.5 mmol) was used in place of PhAsO$_3$H$_2$. Yield: 0.183 g (80% based on Ph$_3$SnOH). Elemental analysis (%) calcd for C$_{82}$H$_{76}$As$_6$Cl$_{12}$O$_{27}$Sn$_7$ ($M_r =$ 3199.18): C 30.79, H 2.39; found: C 30.68, H 2.23. IR: $\tilde{\nu} =$ 3742 (w), 3649 (w), 1550 (m), 1516 (w), 1479 (w), 1455 (w), 1429 (w), 1367 (m), 1120 (w), 1097 (w), 1042 (m), 875 (s), 820 (s), 556 (m), 503 (m), 441 (s), 405 (m) cm^{-1}.

Synthesis of [{(PhSn)$_3$(4-NO$_2$C$_6$H$_4$AsO$_3$)$_3$(4-NO$_2$C$_6$H$_4$AsO$_3$H)(μ_3-O)(MeO)$_2$]$_2$] [B(6M)]: A mixture of Ph$_3$SnOH (0.183 g, 0.5 mmol) and 4-NO$_2$C$_6$H$_4$AsO$_3$H$_2$ (0.123 g, 0.5 mmol) in methanol (10 mL) was placed in a 15 mL Teflon reactor. The mixture was heated at 140°C for 3 days and gradually cooled to room temperature at a rate of 10°Ch^{-1}. Colorless crystals of B(6M) were obtained. Yield: 0.171 g (73% based on Ph$_3$SnOH). Elemental analysis (%) calcd for C$_{76}$H$_{68}$As$_6$N$_6$O$_{36}$Sn$_6$ ($M_r =$ 2803.02): C 32.57, H 2.45, N 3.00; found: C 32.45, H 2.83, N 2.94. IR: $\tilde{\nu} =$ 3744 (w), 3649 (w), 3620 (w), 3414 (m), 3101 (w), 3058 (w), 2927 (w), 1648 (w), 1602 (w), 1529 (s), 1480 (w), 1428 (w), 1351 (m), 1088 (m), 1037 (m), 885 (s), 847 (s), 732 (m), 678 (m), 568 (m), 447 (s), 416 (s), 405 (s) cm^{-1}.

Synthesis of [{(PhSn)$_3$(2,4-Cl$_2$C$_6$H$_3$AsO$_3$)$_3$(μ_3-O)(MeO)$_3$]$_2$Sn]·H$_2$O [C(9M)]: See synthesis of A(9M). Yield: 0.045 g (20% based on Ph$_3$SnOH). Elemental analysis (%) calcd for C$_{76}$H$_{68}$As$_6$Cl$_{12}$O$_{27}$Sn$_7$ ($M_r =$ 3143.07): C 29.04, H 2.18; found: C 29.58, H 2.13. IR: $\tilde{\nu} =$ 3731 (w), 3671 (w), 3648 (w), 3624 (w), 3591 (w), 3051 (w), 2930 (w), 2827 (w), 1740 (w), 1651 (w), 1550 (m), 1541 (m), 1515 (w), 1480 (w), 1455 (w), 1429 (m), 1367 (m), 1247 (w), 1143 (m), 1119 (m), 1041 (m), 870 (s), 823 (s), 730 (m), 692 (m), 672 (m), 652 (m), 557 (w), 502 (m), 424 (s), 404 (s) cm^{-1}.

Synthesis of [{Sn$_3$Cl$_3$(μ_3-O)(MeO)$_3$]$_2$(2-NO$_2$C$_6$H$_4$AsO$_3$)$_4$] [D(4M)]: A mixture of Ph$_3$SnCl (0.192 g, 0.5 mmol) and 2-NO$_2$C$_6$H$_4$AsO$_3$H$_2$ (0.123 g, 0.5 mmol) in methanol (10 mL) was placed in a 15 mL Teflon reactor. The mixture was heated at 140°C for 3 days and then gradually cooled to room temperature at a rate of 10°Ch^{-1}. Colorless crystals of D(4M) were obtained. Yield: 0.159 g (90% based on Ph$_3$SnCl). Elemental analysis (%) calcd for C$_{30}$H$_{34}$As$_4$Cl$_6$N$_4$O$_{28}$Sn$_6$ ($M_r =$ 2123.13): C 16.97, H 1.61, N 2.64; found: C 17.02, H 1.72, N 2.68. IR: $\tilde{\nu} =$ 3924 (m), 3899 (m), 3861 (m), 3799 (m), 3780 (m), 3731 (s), 3673 (m), 3649 (m), 3624 (m), 3592 (m), 3569 (w), 2942 (m), 2840 (w), 1741 (w), 1699 (w), 1541 (w), 1516 (m), 1456 (m), 1345 (m), 822 (m), 674 (m), 452 (m), 420 (m), 404 (m) cm^{-1}.

Synthesis of [{Sn$_3$Cl$_3$(μ_3-O)(EtO)$_3$]$_2$(2-NO$_2$C$_6$H$_4$AsO$_3$)$_4$] [D(4E)]: A mixture of Ph$_3$SnCl (0.192 g, 0.5 mmol) and 2-NO$_2$C$_6$H$_4$AsO$_3$H$_2$ (0.123 g, 0.5 mmol) in ethanol (10 mL) was placed in a 15 mL Teflon reactor. The mixture was heated at 140°C for 3 days and then gradually cooled to room temperature at a rate of 10°Ch^{-1}. Colorless crystals of D(4E) were obtained. Yield: 0.167 g (91% based on Ph$_3$SnCl). Elemental analysis (%) calcd for C$_{36}$H$_{46}$As$_4$Cl$_6$N$_4$O$_{28}$Sn$_6$ ($M_r =$ 2207.29): C 19.59, H 2.10, N 2.54; found: C 19.52, H 2.20, N 2.62. IR: $\tilde{\nu} =$ 3741 (w), 3591 (w), 3416 (m), 3097 (w), 2975 (w), 1627 (w), 1540 (s), 1465 (w), 1351 (m), 1314 (w), 1119 (m), 1025 (w), 849 (s), 733 (m), 675 (m), 462 (s), 420 (s), 405 (m) cm^{-1}.

Synthesis of [{Sn$_3$Cl$_3$(μ_3-O)(EtO)$_3$]$_2$(4-NO$_2$C$_6$H$_4$AsO$_3$)$_4$] [D(6E)]: D(6E) was synthesized by a procedure similar to that used for D(4E) except that 4-NO$_2$C$_6$H$_4$AsO$_3$H$_2$ (0.123 g, 0.5 mmol) was used in place of 2-NO$_2$C$_6$H$_4$AsO$_3$H$_2$. Yield: 0.156 g (85% based on Ph$_3$SnCl). Elemental analysis (%) calcd for C$_{36}$H$_{46}$As$_4$Cl$_6$N$_4$O$_{28}$Sn$_6$ ($M_r =$ 2207.29): C 19.59, H 2.10, N 2.54; found: C 19.72, H 2.22, N 2.65. IR: $\tilde{\nu} =$ 3838 (w), 3735 (w), 3417 (m), 3104 (m), 2974 (w), 1647 (w), 1602 (w), 1529 (s), 1354 (m), 1095 (m), 1030 (m), 843 (s), 737 (w), 576 (w), 509 (w), 450 (m), 420 (m), 405 (m) cm^{-1}.

X-ray crystallography: Single-crystal X-ray diffraction data for compounds A(1M), A(1E), and A(7E) were recorded on a Bruker Apex CCD diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda =$ 0.71073 Å) at 293 K. Diffraction data for other compounds were collect-

ed on a Rigaku RAXIS-RAPID single-crystal diffractometer with Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 293 K. Absorption corrections were applied using multiscan technique.[19] All structures were solved by direct methods with SHELXS-97[20] and refined by full-matrix least-squares tech-

niques using the SHELXL-97 program[21] within WINGX.[22] The detailed crystallographic data and structure refinement parameters for the compounds are summarized in Table 3. CCDC-660733, 660734, 660735, 660736, 660737, 660738, 660739, 660740, 660741, 660742, 660743, 660744,

Table 3. Crystal data and structure refinements for **A(1M)–D(6E)**.

	A(1M)	**A(1E)**	**A(2M)**	**A(2E)**	**A(3M)**	**A(4E)**
formula	$C_{76}H_{74}As_6O_{26}Sn_7$	$C_{82}H_{90}As_6O_{28}Sn_7$	$C_{76}H_{80}As_6N_6O_{26}Sn_7$	$C_{84}H_{100}As_6N_6O_{28}Sn_7$	$C_{76}H_{80}As_6N_6O_{26}Sn_7$	$C_{82}H_{82}As_6N_6O_{39}Sn_7$
formula weight	2683.70	2803.89	2773.81	2922.05	2773.81	3055.89
crystal system	monoclinic	triclinic	triclinic	triclinic	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a [Å]	17.038(3)	14.011(4)	11.185(3)	14.016(4)	17.018(3)	13.124(4)
b [Å]	20.073(3)	14.611(4)	13.181(5)	14.387(7)	19.448(4)	13.541(4)
c [Å]	13.089(3)	15.026(4)	16.417(7)	15.178(5)	14.004(4)	17.080(8)
α [°]	90	91.124(5)	89.310(17)	90.883(15)	90	100.223(13)
β [°]	100.091(4)	109.568(4)	87.809(15)	108.974(12)	102.13(10)	104.020(13)
γ [°]	90	112.029(5)	72.107(13)	112.549(14)	90	113.924(9)
V [Å³]	4407.2(16)	2649.4(13)	2301.7(15)	2638.4(17)	4531(2)	2558.4(15)
Z	2	1	1	1	2	1
ρ_{calcd} [g cm⁻³]	2.022	1.757	2.001	1.839	2.033	1.983
F(000)	2572.0	1354	1334	1418.0	2668	1476
reflns collected/unique	10252/2784	10105/8082	10066/8401	11704/7998	10314/3566	11499/8172
GOF on F²	0.919	1.040	1.052	1.098	0.942	1.047
R_1 [$I > 2\sigma(I)$][a]	0.0691	0.0390	0.0421	0.0531	0.0685	0.0555
wR_2 [$I > 2\sigma(I)$][b]	0.1354	0.1102	0.1081	0.1362	0.1019	0.1358

	A(5M)	**A(5E)**	**A(7M)**	**A(7E)**	**A(8E)**	**A(9M)**
formula	$C_{78}H_{76}As_6N_6O_{40}Sn_7$	$C_{82}H_{82}As_6N_6O_{39}Sn_7$	$C_{78}H_{76}As_6N_6O_{46}Sn_7$	$C_{84}H_{88}As_6N_6O_{46}Sn_7$	$C_{82}H_{82}As_6Cl_6O_{27}Sn_7$	$C_{76}H_{62}As_6Cl_{12}O_{26}Sn_7$
formula weight	3017.80	3055.89	3113.80	3197.95	2992.53	3097.01
crystal system	triclinic	monoclinic	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a [Å]	12.728(6)	17.834(5)	13.132(6)	11.943(2)	13.315(4)	13.781(4)
b [Å]	14.420(6)	16.010(3)	14.483(8)	14.933(2)	13.450(5)	22.323(6)
c [Å]	15.318(6)	18.305(4)	15.078(8)	16.419(3)	16.967(6)	16.705(4)
α [°]	106.335(16)	90	104.967(19)	98.047(2)	98.406(14)	90
β [°]	93.324(18)	91.355(10)	104.778(18)	104.070(2)	106.683(12)	94.540(12)
γ [°]	97.639(17)	90	100.715(18)	103.524(2)	113.164(13)	90
V [Å³]	2661(2)	5225(2)	2579(2)	2700.9(7)	2557.6(15)	5123(2)
Z	1	2	1	1	1	2
ρ_{calcd} [g cm⁻³]	1.884	1.942	2.005	1.966	1.943	2.008
F(000)	1454.0	2952.0	1502.0	1550.0	1440.0	2956.0
reflns collected/unique	12096/7978	11896/9157	11483/7738	10366/8634	11539/8617	11599/6438
GOF on F²	1.062	1.080	1.072	0.964	1.071	1.038
R_1 [$I > 2\sigma(I)$][a]	0.0595	0.0396	0.0658	0.0295	0.0463	0.0656
wR_2 [$I > 2\sigma(I)$][b]	0.1511	0.1094	0.1643	0.0722	0.1161	0.1528

	A(9E)	**B(6M)**	**C(9M)**	**D(4M)**	**D(4E)**	**D(6E)**
formula	$C_{82}H_{76}As_6Cl_{12}O_{27}Sn_7$	$C_{76}H_{68}As_6N_6O_{36}Sn_6$	$C_{76}H_{68}As_6Cl_{12}O_{27}Sn_7$	$C_{30}H_{34}As_4Cl_6N_4O_{28}Sn_6$	$C_{36}H_{46}As_4Cl_6N_4O_{28}Sn_6$	$C_{36}H_{46}As_4Cl_6N_4O_{28}Sn_6$
formula weight	3199.18	2803.02	3143.07	2123.13	2207.29	2207.29
crystal system	monoclinic	triclinic	triclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$Pbca$	$C2/c$
a [Å]	14.780(5)	14.722(4)	13.095(5)	11.560(3)	14.207(4)	30.852(5)
b [Å]	21.717(6)	16.789(5)	17.119(5)	20.827(7)	20.711(5)	10.404(5)
c [Å]	16.860(5)	21.093(5)	24.170(5)	13.173(4)	21.540(4)	25.099(5)
α [°]	90	94.300(11)	75.041(5)	90	90	90
β [°]	91.431(13)	97.976(11)	79.054(5)	110.342(11)	90	126.751(5)
γ [°]	90	111.080(11)	75.885(5)	90	90	90
V [Å³]	5410(3)	4773(2)	5030(3)	2973.7(15)	6338(3)	6455(4)
Z	2	2	2	2	4	4
ρ_{calcd} [g cm⁻³]	1.964	1.950	2.075	2.371	2.313	2.271
F(000)	3072.0	2704	3008.0	2000.0	4192	4192
reflns collected/unique	12309/6256	21208/11703	21949/8025	6755/5068	7230/4756	7364/4801
GOF on F²	1.021	1.018	1.026	1.061	1.057	1.054
R_1 [$I > 2\sigma(I)$][a]	0.0649	0.0599	0.1038	0.0366	0.0471	0.0419
wR_2 [$I > 2\sigma(I)$][b]	0.1319	0.1346	0.2239	0.0853	0.1025	0.1027

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/}$.

Acknowledgements

[1] a) V. Chandrasekhar, K. Gopal, P. Thilagar, *Acc. Chem. Res.* **2007**, *40*, 420; b) V. Chandrasekhar, S. Nagendran, V. Baskar, *Coord. Chem. Rev.* **2002**, *235*, 1; c) R. R. Holmes, *Acc. Chem. Res.* **1989**, *22*, 190; d) E. R. T. Tiekink, *Appl. Organomet. Chem.* **1991**, *5*, 1; e) E. R. T. Tiekink, *Trends Organomet. Chem.* **1994**, *1*, 71; f) V. K. Jain, *Coord. Chem. Rev.* **1994**, *135–136*, 809; g) Y. Yamamoto, N. Asao, *Chem. Rev.* **1993**, *93*, 2207; h) G. Prabusankar, B. Jousseaume, T. Toupance, H. Allouchi, *Angew. Chem.* **2006**, *118*, 1277; *Angew. Chem. Int. Ed.* **2006**, *45*, 1255; i) J. Beckmann, D. Dakternieks, A. Duthie, F. S. Kuan, K. Jurkschat, M. Schürmann, E. R. T. Tiekink, *New J. Chem.* **2004**, *28*, 1268; j) V. Chandrasekhar, K. Gopal, P. Sasikumar, R. Thirumoorthi, *Coord. Chem. Rev.* **2005**, *249*, 1745; k) V. Chandrasekhar, P. Sasikumar, P. Thilagar, *Organometallics* **2007**, *26*, 4386.

[2] a) R. R. Holmes, C. G. Schmid, V. Chandrasekhar, R. O. Day, J. M. Holmes, *J. Am. Chem. Soc.* **1987**, *109*, 1408; b) G.-H. Xu, J.-F. Ma, H.-X. Yu, S.-L. Li, Y.-Y Liu, J. Yang, Z.-M. Su, C.-F. Shi, *Organometallics* **2006**, *25*, 5996; c) K. C. Kumara Swamy, R. O. Day, R. R. Holmes, J. Am. Chem. Soc. **1987**, *109*, 5546; d) R. R. Holmes, K. C. Kumara Swamy, C. G. Schmid, R. O. Day, *J. Am. Chem. Soc.* **1988**, *110*, 7060; e) V. Chandrasekhar, R. O. Day, R. R. Holmes, *Inorg. Chem.* **1985**, *24*, 1970; f) J. Janssen, J. Magull, H. W. Roesky, *Angew. Chem.* **2002**, *114*, 1425; *Angew. Chem. Int. Ed.* **2002**, *41*, 1365.

[3] a) C. Eychenne-Baron, F. Ribot, N. Steunou, C. Sanchez, F. Fayon, M. Biesemans, J. C. Martins, R. Willem, *Organometallics* **2000**, *19*, 1940; b) C. Eychenne-Baron, F. Ribot, N. Steunou, C. Sanchez, F. Fayon, F. Banse, F. Ribot, P. Tolédano, J. Maquet, C. Sanchez, *Inorg. Chem.* **1995**, *34*, 6371; c) F. Ribot, C. Sanchez, R. Willem, J. C. Martins, M. Biesemans, *Inorg. Chem.* **1998**, *37*, 911; d) C. Eychenne-Baron, F. Ribot, C. Sanchez, *J. Organomet. Chem.* **1998**, *567*, 137; e) D. Dakternieks, H. Zhu, E. R. T. Tiekink, R. Colton, *J. Organomet. Chem.* **1994**, *476*, 33.

[4] a) R. O. Day, J. M. Holmes, V. Chandrasekhar, R. R. Holmes, *J. Am. Chem. Soc.* **1987**, *109*, 940; b) V. Chandrasekhar, V. Baskar, J. J. Vittal, *J. Am. Chem. Soc.* **2003**, *125*, 2392; c) V. Chandrasekhar, V. Baskar, K. Gopal, J. J. Vittal, *Organometallics* **2005**, *24*, 4926.

[5] a) D. Dakternieks, A. Duthie, B. Zobel, K. Jurkschat, M. Schürmann, E. R. T. Tiekink, *Organometallics* **2002**, *21*, 647; b) M. Mehring, G. Gabriele, S. Hadjikakou, M. Schürmann, D. Dakternieks, K. Jurkschat, *Chem. Commun.* **2002**, 834; c) M. Mehring, M. Schürmann, H. Reuter, D. Dakternieks, K. Jurkschat, *Angew. Chem.* **1997**, *109*, 1150; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1112.

[6] a) K. C. Kumara Swamy, C. G. Schmid, R. O. Day, R. R. Holmes, *J. Am. Chem. Soc.* **1990**, *112*, 223; b) V. Chandrasekhar, V. Baskar, A. Steiner, S. Zacchini, *Organometallics* **2002**, *21*, 4528.

[7] a) G.-L. Zheng, J.-F. Ma, Z.-M. Su, L.-K. Yan, J. Yang, Y.-Y. Li, J.-F. Liu, *Angew. Chem.* **2004**, *116*, 2463; *Angew. Chem. Int. Ed.* **2004**, *43*, 2409; b) S.-Y. Song, J.-F. Ma, J. Yang, L.-L. Gao, Z.-M. Su, *Organometallics* **2007**, *26*, 2125.

[8] a) A. W. Walde, H. E. Van Essen, T. W. Zhornik, US 4762811; [*Chem. Abstr.* **1957**, *51*, 4474]; b) B. L. Chamberland, A. G. McDiarmid, *J. Chem. Soc.* **1961**, 445; c) G. K. Sandhu, *Indian J. Chem. Sect: A.* **1978**, *16*, 1105; d) S. S. Sandhu, G. K. Sandhu, *Synth. Commun. Synth. React. Inorg. Metal-Org. Chem.* **1977**, *7*, 45; e) S. S. Sandhu, J. Kaur, G. K. Sandhu, *Synth. Commun. Synth. React. Inorg. Metal-Org. Chem.* **1974**, *4*, 437; f) S. S. Sandhu, G. K. Sandhu, S. K. Pushkarna, *Synth. Commun. Synth. React. Inorg. Metal-Org. Chem.* **1981**, *11*, 197; g) S. S. Sandhu, S. S. Sandhu Jr, G. K. Sandhu, R. V. Parish, O. Parry, *Inorg. Chim. Acta* **1982**, *58*, 251; h) D. Cunningham, P. Firtear, K. C. Molloy, J. J. Zuckerman, *J. Chem. Soc. Dalton Trans.* **1983**, 1523.

[9] R. K. Ingham, S. D. Rosenberg, H. Gilman, *Chem. Rev.* **1960**, *60*, 459.

[10] a) V. Chandrasekhar, C. G. Schmid, S. D. Burton, J. M. Holmes, R. O. Day, R. R. Holmes, *Inorg. Chem.* **1987**, *26*, 1050; b) G.-L. Zheng, J.-F. Ma, J. Yang, Y.-Y. Li, X.-R. Hao, *Chem. Eur. J.* **2004**, *10*, 3761.

[11] a) S. J. Blunden, R. Hill, D. G. Gillies, *J. Organomet. Chem.* **1984**, *270*, 39; b) T. Chivers, J. H. G. van Roode, J. N. R. Ruddick, J. R. Sams, *Can. J. Chem.* **1973**, *51*, 3702; c) R. E. Ridenour, E. E. Flagg, *J. Organomet. Chem.* **1969**, *16*, 393; d) M. Mehring, C. Löw, M. Schürmann, K. Jurkschat, *Eur. J. Inorg. Chem.* **1999**, 887; e) M. Mehring, I. Vrasidas, D. Horn, M. Schürmann, K. Jurkschat, *Organometallics* **2001**, *20*, 4647; f) F. Ribot, C. Eychenne-Baron, C. Sanchez, *Phosphorus Sulfur Silicon Relat. Elem.* **1999**, *150–151*, 41, and references therein; g) V. Chandrasekhar, R. Boomishankar, A. Steiner, J. F. Bickley, *Organometallics* **2003**, *22*, 3342.

[12] V. Chandrasekhar, V. Baskar, R. Boomishankar, K. Gopal, S. Zacchini, J. F. Bickley, A. Steiner, *Organometallics* **2003**, *22*, 3710.

[13] a) J. Beckmann, K. Jurkschat, B. Mahieu, M. Schürmann, *Main Group Met. Chem.* **1998**, *21*, 113; b) F. Cervantes-Lee, H. K. Sharma, I. Haiduc, K. H. Pannell, *J. Chem. Soc. Dalton Trans.* **1998**, 1; c) H. Reuter, Ph.D. Thesis, University of Bonn, Germany, 1986; d) P. Brown, M. F. Mahon, K. C. Molloy, *J. Chem. Soc. Dalton Trans.* **1992**, 3503; e) J. Beckmann, K. Jurkschat, M. Schürmann, D. Suter, R. Willem, *Organometallics* **2002**, *21*, 3819; f) J. Beckmann, D. Dakternieks, A. Duthie, K. Jurkschat, M. Mehring, C. Mitchell, M. Schürmann, *Eur. J. Inorg. Chem.* **2003**, 4356.

[14] K. C. Kumara Swamy, R. O. Day, R. R. Holmes, *J. Am. Chem. Soc.* **1988**, *110*, 7543.

[15] A. J. Canty, P. R. Traill, R. Colton, I. M. Thomas, *Inorg. Chim. Acta* **1993**, *210*, 91.

[16] A. J. Canty, R. Colton, I. M. Thomas, *J. Organomet. Chem.* **1993**, *455*, 283.

[17] D. Dakternieks, H. Zhu, E. R. T. Tiekink, R. Colton, *J. Organomet. Chem.* **1994**, *476*, 33.

[18] a) W. A. Jacobs, M. Heidelberger, J. P. Rolf, *J. Am. Chem. Soc.* **1918**, *40*, 1583; b) C. S. Palmer, R. Adams, *J. Am. Chem. Soc.* **1922**, *44*, 1369; c) F. F. Blicke, G. L. Welster, *J. Am. Chem. Soc.* **1937**, *59*, 534.

[19] a) T. Higashi, Program for Absorption Correction, Rigaku Corporation, Tokyo, Japan, **1995**; b) G. M. Sheldrick, SADABS, University of Göttingen, Germany, **1997**.

[20] G. M. Sheldrick, SHELXS-97, A Program for Automatic Solution of Crystal Structure, University of Geottingen, Germany, **1997**.

[21] G. M. Sheldrick, SHELXL-97, A Program for Crystal Structure Refinement, University of Göttingen, Germany, **1997**.

[22] L. J. Farrugia, WINGX, A Windows Program for Crystal Structure Analysis, University of Glasgow, UK, **1988**.