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Halide-Capped Tellurium-Containing Macrocycles

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The reaction of 1,1,2,3,3-pentamethyltrimethylenephosphinic acid (*cyc*PO_2H) with bis(*p*-methoxyphenyl)tellurium dichloride (**1**) affords a 12-membered macrocycle $[((p\text{-}MeOC_6H_4)_2Te)_2(\mu\text{-}O)(\mu\text{-}cycPO_2)(\mu_4\text{-}Cl)]_2 \cdot C_6H_6$ (**2**) in good yield. The latter reacts with sodium iodide to give $[((p\text{-}MeOC_6H_4)_2Te)_2(\mu\text{-}O)(\mu\text{-}cycPO_2)(\mu_4\text{-}I)]_2 \cdot 4C_6H_6$ (**3**). **2** and **3** are isostructural dicationic macrocycles and contain a $Te_4P_2O_6$ framework. An interesting aspect of both of these structures is that two counter halide atoms are present as capping ligands above and below the macrocyclic plane enabled by Te—X interactions. In contrast to the macrocyclic product obtained with diorganotellurium dihalide the reaction of diphenyltin dichloride with *cyc*PO_2H resulted in the formation of an oxygen-capped cluster $[(PhSn)_3(\mu_3\text{-}O)(\mu\text{-}cycPO_2)_3(\mu\text{-}OH)_3][cycPO_2] \cdot CH_3CN$. The latter is formed by a Sn-Ph cleavage reaction.

Introduction

In recent years there has been a growing interest in the area of organotellurium(IV) chemistry in general and organotelluroxanes in particular because of varied reasons. One, organotelluroxanes are being increasingly studied as oxo-transfer reagents in organometallic/organic synthesis.[1] Two, there has been a fundamental interest in discovering new strategies for the preparation of unusual organotelluroxanes.[2] Some recent developments have also contributed to this impetus.[3] In this regard mention must be made of the new family of organotellurinic acids $[2,6\text{-}Mes_2C_6H_3Te(O)(OH)]_2$ prepared by Beckmann and co-workers[4] which are potential precursors to a large number of organotelluroxanes. Lastly the structural chemistry of organotellurium(IV) compounds has been of interest particularly to study the stereochemical influence of the lone pair of electrons on tellurium.[5] We have been interested in exploring the macrocyclic chemistry of organotelluroxanes because of the paucity of such types of compounds, particularly in relation to other main-group element-containing macrocycles.[6] Available synthetic routes for the preparation of organotellurium(IV) macrocycles can be summarized into three categories: (i) condensation of diorganotelluroxides with protic acids such as carboxylic/phosphinic/sulfonic acids or even active hydroxyl-containing compounds such as silanols;[3a−f] for example, Beckmann and co-workers have reported the formation of a 12-membered tellurasiloxane ring in the condensation reactions of bis(*p*-methoxyphenyl)telluroxide with *t*-$Bu_2Si(OH)_2$;[3d] (ii) treatment of organotellurium halides with protic acids in the presence of a hydrogen halide acceptor such as triethylamine;[3b,c] thus, recently, we have reported the assembly of 16-membered heterobimetallic organotellurium macrocyles from the reaction of bis(*p*-methoxyphenyltellurium) dichlorides with 1,1′-ferrocenedicarboxylic acid;[3c] and (iii) reaction of in situ generated telluronium salt with dicarboxylates;[3f] thus, Kobayashi et al. have synthesized two types of macrocyclic

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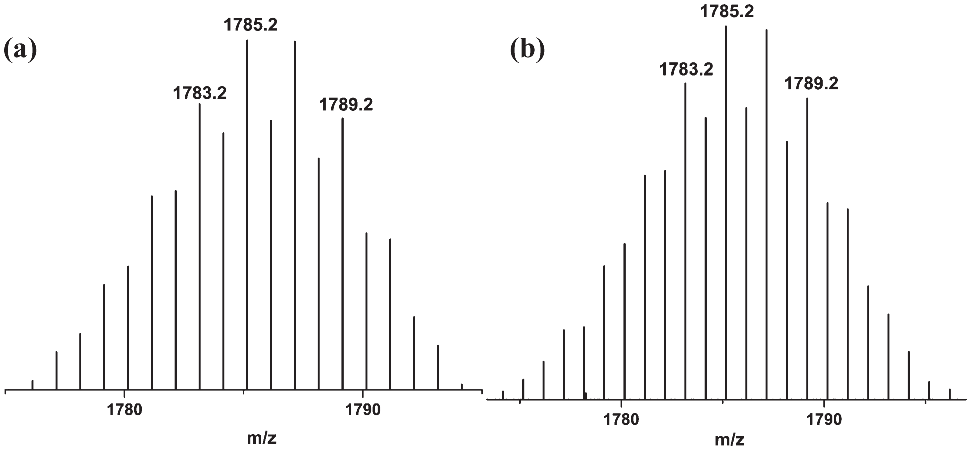


Figure 1. (a) Theoretical and (b) experimental ESI-MS of **2**.

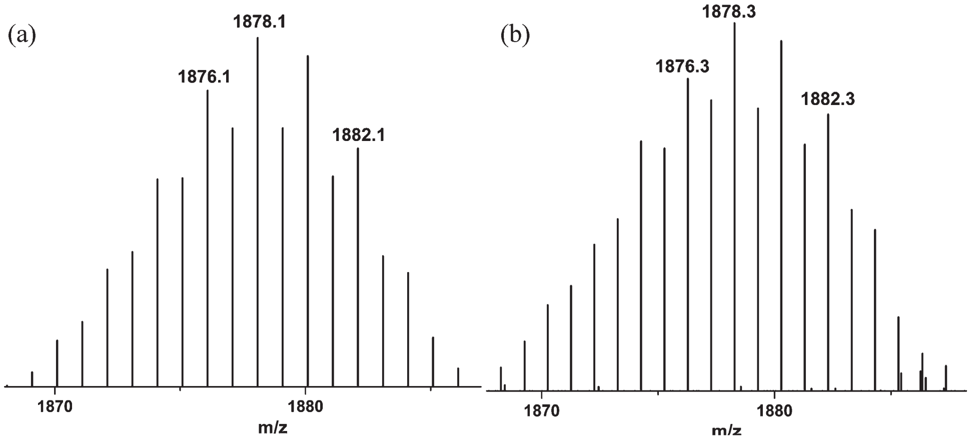
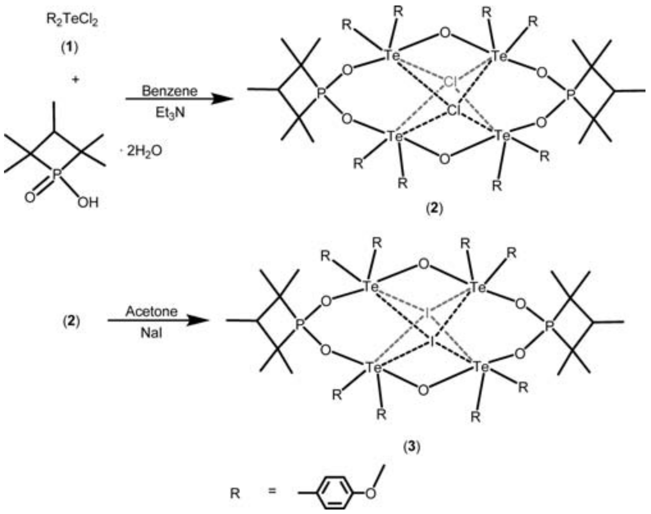
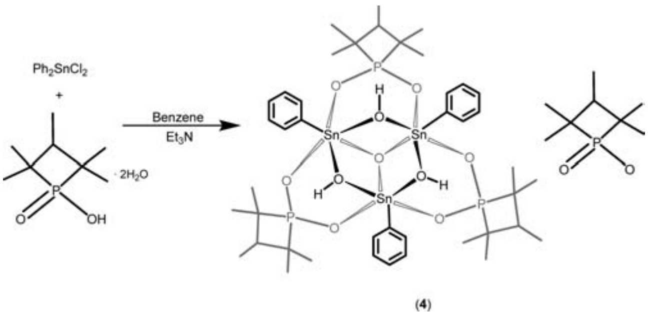


Figure 2. (a) Theoretical and (b) experimental ESI-MS of **3**.

Scheme 1. Synthesis of **2** and **3**



Scheme 2. Synthesis of **4**



multitelluranes by this methodology.[3f] A survey of the known literature reveals that reactions of organotellurium precursors with phosphorus-based acids have not been studied in much detail.[3e] Our experience of using phosphorus-based protic acids as ligands, particularly in organotin chemistry, has been extremely rewarding, and we have been successful in characterizing many unusual structural forms.[7] In view of this we were interested in exploring the utility of phosphinate ligands in organotellurium chemistry. Accordingly, herein, we report the synthesis and structural characterization of a new family of organotelluroxane-containing macrocycles: $[((p\text{-MeO-}C_6H_4)_2Te)_2(\mu\text{-O})(\mu\text{-}cycPO_2)(\mu_4\text{-Cl})]_2\cdot C_6H_6$ (**2**) and $((p\text{-MeO-}C_6H_4)_2Te)_2(\mu\text{-O})(\mu\text{-}cycPO_2)(\mu_4\text{-I})]_2\cdot 4C_6H_6$ (**3**) [$cycPO_2H$ = 1,1,2,3,3-pentamethyltrimethylenephosphinic acid]. The macrocycles **2** and **3** are structurally very interesting and are quite unprecedented for organotellurium compounds. Both

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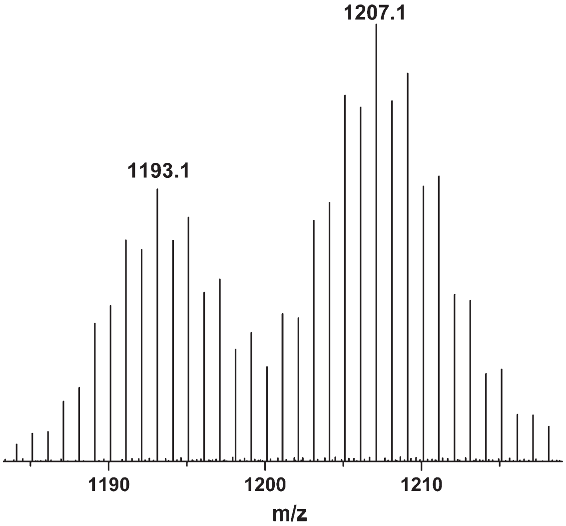

Figure 3. ESI-MS of **4**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**

1			
Te(1)−C(1)	2.108(5)	Te(2)−Cl(3)	2.5142(17)
Te(1)−C(8)	2.120(5)	Te(2)−Cl(4)	2.5160(17)
Te(1)−Cl(1)	2.4868(17)	Te(2)−C(15)	2.106(5)
Te(1)−Cl(2)	2.5540(16)	Te(2)−C(22)	2.120(6)
C(1)−Te(1)−C(8)	95.9(2)	C(15)−Te(2)−C(22)	96.8(2)
C(1)−Te(1)−Cl(1)	90.44(16)	C(15)−Te(2)−Cl(3)	88.52(16)
C(8)−Te(1)−Cl(1)	90.02(16)	C(22)−Te(2)−Cl(3)	89.90(17)
C(1)−Te(1)−Cl(2)	89.58(16)	C(15)−Te(2)−Cl(4)	89.60(16)
C(8)−Te(1)−Cl(2)	88.62(16)	C(22)−Te(2)−Cl(4)	88.98(17)
Cl(1)−Te(1)−Cl(2)	178.63(5)	Cl(3)−Te(2)−Cl(4)	177.68(5)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2** and **3**

2			
Te(1)−C(30)	2.126(4)	Te(2)−C(23)	2.103(4)
Te(1)−C(1)	2.131(4)	Te(2)−C(8)	2.109(4)
Te(1)−O(4)	2.313(3)	Te(2)−O(3)	2.371(3)
Te(1)−O(6)	1.988(3)	Te(2)−O(6)	1.980(3)
P(1)−O(3)	1.510(3)	P(1)−O(4)	1.524(3)
O(6)−Te(1)−C(30)	87.25(14)	O(6)−Te(2)−C(23)	90.24(14)
O(6)−Te(1)−C(1)	88.47(14)	O(6)−Te(2)−C(8)	89.98(14)
C(30)−Te(1)−C(1)	97.38(16)	C(23)−Te(2)−C(8)	98.64(16)
O(6)−Te(1)−O(4)	166.45(11)	O(6)−Te(2)−O(3)	167.17(11)
C(30)−Te(1)−O(4)	82.24(14)	C(8)−Te(2)−O(3)	83.06(14)
C(1)−Te(1)−O(4)	84.44(14)	C(23)−Te(2)−O(3)	80.22(13)
O(3)−P(1)−O(4)	115.60(17)		
3			
Te(1)−C(16)	2.113(5)	Te(2)−O(4)	1.988(3)
Te(1)−C(9)	2.121(5)	Te(2)−C(23)	2.115(5)
Te(1)−O(1)	2.330(3)	Te(2)−C(30)	2.133(5)
Te(1)−O(4)	1.995(3)	Te(2)−O(7)	2.330(3)
P(1)−O(1)	1.513(3)	P(1)−O(7)	1.530(3)
O(4)−Te(1)−C(16)	88.19(16)	O(4)−Te(2)−C(23)	89.11(16)
O(4)−Te(1)−C(9)	90.26(16)	O(4)−Te(2)−C(30)	90.13(16)
C(16)−Te(1)−C(9)	96.55(18)	C(23)−Te(2)−C(30)	94.06(18)
O(4)−Te(1)−O(1)	168.16(12)	O(4)−Te(2)−O(7)	170.51(12)
C(16)−Te(1)−O(1)	81.90(15)	C(23)−Te(2)−O(7)	82.76(15)
C(9)−Te(1)−O(1)	84.50(16)	C(30)−Te(2)−O(7)	85.59(15)
O(1)−P(1)−O(7)	115.98(19)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **4**

4			
Sn(1)−O(5)	2.082(4)	Sn(2)−O(1)	2.062(3)
Sn(1)−O(10)	2.085(3)	Sn(2)−O(7)	2.098(4)
Sn(1)−O(1)	2.091(3)	Sn(2)−O(4)	2.110(4)
Sn(1)−O(4)	2.111(4)	Sn(2)−O(6)	2.122(3)
Sn(1)−O(2)	2.120(3)	Sn(2)−O(3)	2.132(4)
Sn(1)−C(1)	2.121(5)	Sn(2)−C(15)	2.119(5)
Sn(3)−O(1)	2.062(3)	P(1)−O(5)	1.527(4)
Sn(3)−O(8)	2.091(4)	P(1)−O(6)	1.528(4)
Sn(3)−O(9)	2.116(3)	P(2)−O(8)	1.521(4)
Sn(3)−C(29)	2.117(5)	P(2)−O(7)	1.536(4)
Sn(3)−O(2)	2.119(4)	P(3)−O(9)	1.526(4)
Sn(3)−O(3)	2.137(4)	P(3)−O(10)	1.527(4)
O(5)−Sn(1)−O(10)	89.15(14)	O(1)−Sn(2)−O(3)	77.27(14)
O(5)−Sn(1)−O(1)	84.33(14)	O(7)−Sn(2)−O(3)	87.05(14)
O(10)−Sn(1)−O(1)	86.37(13)	O(4)−Sn(2)−O(3)	91.60(14)
O(5)−Sn(1)−O(4)	86.56(14)	O(6)−Sn(2)−O(3)	161.70(14)
O(10)−Sn(1)−O(4)	163.72(14)	O(1)−Sn(3)−O(8)	86.08(13)
O(1)−Sn(1)−O(4)	77.58(13)	O(1)−Sn(3)−O(9)	85.40(13)
O(5)−Sn(1)−O(2)	161.28(14)	O(8)−Sn(3)−O(9)	91.53(13)
O(10)−Sn(1)−O(2)	85.11(14)	O(1)−Sn(3)−O(2)	78.18(13)
O(1)−Sn(1)−O(2)	77.54(13)	O(8)−Sn(3)−O(2)	164.25(13)
O(4)−Sn(1)−O(2)	94.00(14)	O(9)−Sn(3)−O(2)	86.67(14)
O(1)−Sn(2)−O(7)	85.36(13)	O(1)−Sn(3)−O(3)	77.14(14)
O(1)−Sn(2)−O(4)	78.23(13)	O(8)−Sn(3)−O(3)	87.07(14)
O(7)−Sn(2)−O(4)	163.42(14)	O(9)−Sn(3)−O(3)	162.54(14)
O(1)−Sn(2)−O(6)	84.50(14)	O(2)−Sn(3)−O(3)	89.96(14)

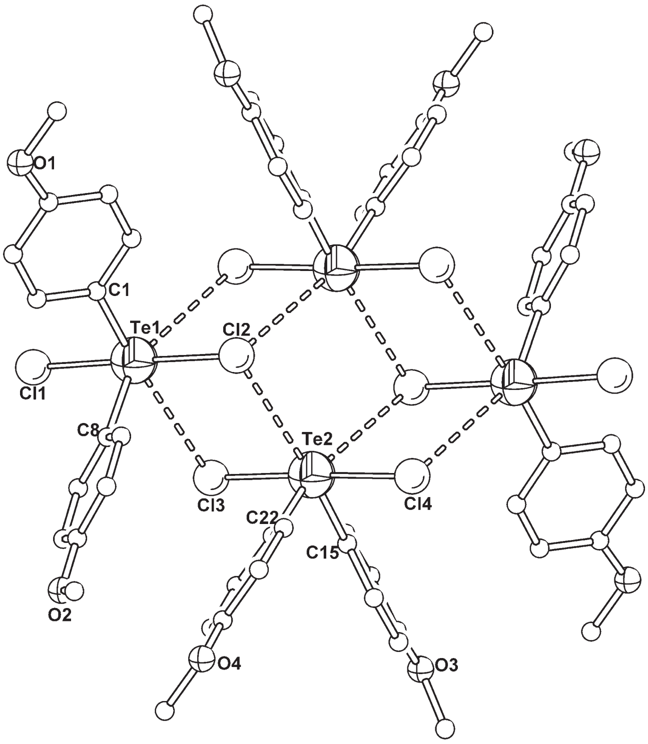

Figure 4. Four molecules of $(p\text{-MeOC}_6\text{H}_4)_2\text{TeCl}_2$ (**1**) associated through secondary Te...Cl interactions leads to the formation of a steplike ladder structure.

these macrocycles are dicationic and contain two halide (Cl^- or I^-) counteranions. However, these anions are noninnocent and function as *capping ligands* being present on the top and bottom of the tellurium-containing macrocycles. The driving force for the observed structures appears to be multiple Te---X interactions that arise as a result of this topology.

In order to compare the reactions of bis(*p*-methoxyphenyl)tellurium dichloride with that of organotin dihalide we performed an analogous reaction of *cyc*P(O)(OH) with

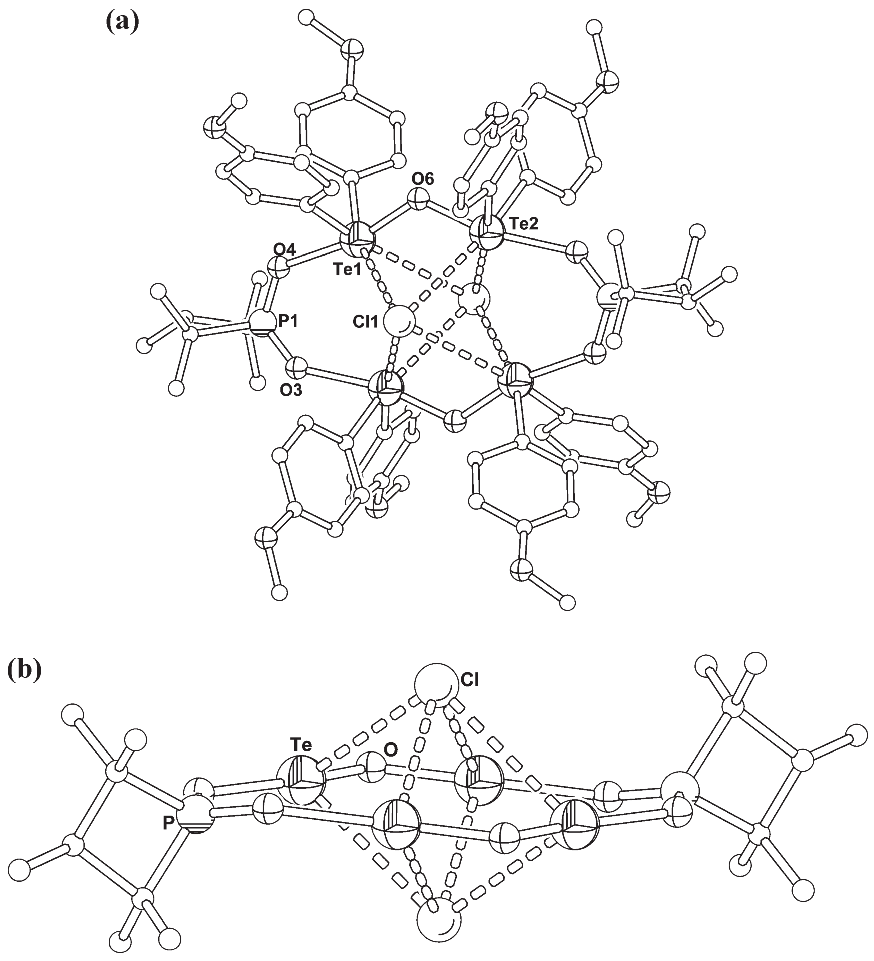

Figure 5. a) Molecular structure of **2**. Hydrogen atoms have been omitted for the sake of clarity. b) Side view of **2**. Aryl groups and hydrogen atoms of phosphinates are omitted for clarity.

Ph_2SnCl_2. We observed the formation of the well-known[8,9] structural type, the O-capped cluster, $[(PhSn)_3(\mu_3\text{-}O)(\mu\text{-}cycPO_2)_3(\mu\text{-}OH)_3][cycPO_2]\cdot CH_3CN$ (**4**). The latter is formed as a result of a Sn-Ph cleavage reaction.[8a] Sn−C cleavage reactions are known and have been used as a deliberate strategy for obtaining organostannoxanes.[8a]

Results and Discussion

Synthesis. Reaction of bis(*p*-methoxyphenyl)tellurium dichloride (**1**) with 1,1,2,3,3-pentamethyltrimethylenephosphinic acid ($cycPO_2H\cdot 2H_2O$) in the presence of triethylamine afforded a 12-membered macrocycle, $[((p\text{-}MeOC_6H_4)_2Te)_2(\mu\text{-}O)(\mu\text{-}cycPO_2)(\mu_4\text{-}Cl)]_2\cdot C_6H_6$ (**2**), in moderate yields (Scheme 1). This compound has a cationic macrocyclic core whose charge is balanced by two chloride anions. It is of interest to note that in contrast to the present situation, the reaction of bis(*p*-methoxyphenyl)telluroxide with diphenylphosphinic acid in a 1:2 ratio is reported to afford a tetraorganoditelluroxane.[3e] Clearly, the course of the reaction is influenced by the precise nature of reactants. Interestingly, halide exchange is very facile, and the reaction of **2** with NaI afforded the iodide containing compound $[((p\text{-}MeOC_6H_4)_2Te)_2(\mu\text{-}O)(\mu\text{-}cycPO_2)(\mu_4\text{-}I)]_2\cdot 4C_6H_6$ (**3**) (Scheme 1). The latter is isostructural with **2** indicating that the exchange of chloride with iodide does not bring about any structural change (vide infra). **2** and **3** are the first examples of macrocycles containing two distinct chemical motifs: an organotellurium phosphinate, $R_2Te{-}O{-}P{-}O{-}TeR_2$ and a ditelluroxane, $R_2Te{-}O{-}TeR_2$. These macrocycles are hypervalent because of Te---X interactions. $^{31}P\{^1H\}$ NMR of **2** and **3** revealed single resonances at δ 48.2 and 49.8 ppm in C_6D_6, respectively. These chemical shifts are upfield shifted in comparison with $cycPO_2H$ (δ 59.83 ppm, $CDCl_3$). An ESI-MS study on **2** and **3** (positive ion mode, CH_3CN) showed peaks at *m*/*z* 1785.2 and 1878.3, respectively (Figures 1 and 2). These correspond to the loss of a halide ion in **2** and **3** and can be assigned due to $[\{((p\text{-}MeOC_6H_4)_2Te)_2(O)(cycPO_2)\}_2\{Cl\}]^+$ and $[\{((p\text{-}MeOC_6H_4)_2Te)_2(O)(cycPO_2)\}_2\{I\}]^+$, respectively. These results suggest that the macrocycles retain their structures in solution.

Reaction of diphenyltin dichloride with $cycPO_2H\cdot 2H_2O$ in the presence of triethylamine yielded $[(PhSn)_3(\mu_3\text{-}O)(\mu\text{-}cycPO_2)_3(\mu\text{-}OH)_3][cycPO_2]\cdot CH_3CN$ (**4**), an organotin O-capped cluster[9] (Scheme 2). **4** contains a cationic

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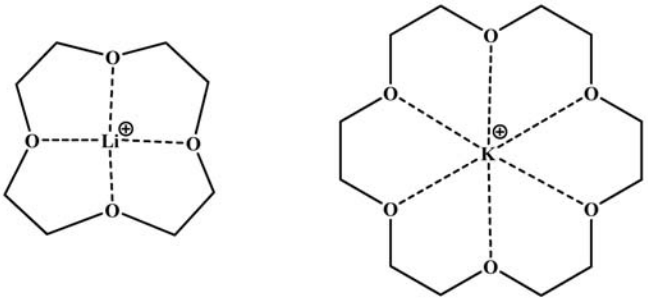
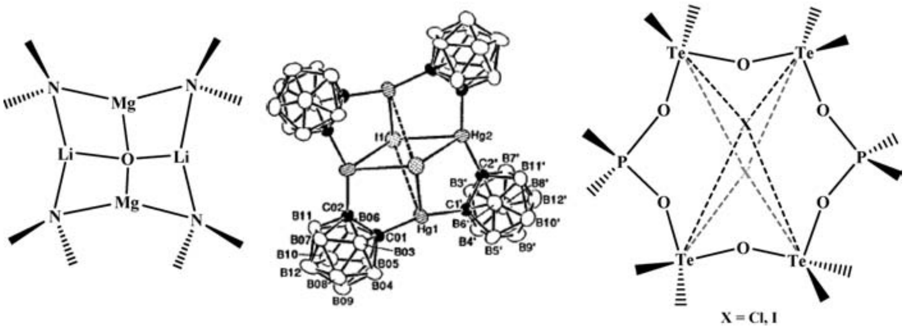
Chart 1. Structural Comparison of Crown Ethers with Inverse Crowns and Their Relationship with **2** and **3**

Crown ethers



Inverse crowns



tristannoxane unit with a counter phosphinate anion. Formation of **4** from diphenyltin dichloride occurs through a facile Sn−C cleavage reaction.[8a] Although Sn−C bond cleavage reactions involving Sn-benzyl[3b,7d,8a] or Sn-allyl[8a] groups are particularly facile and are well documented, Sn-Ph cleavage is also quite well-known.[6a,10] The $^{31}P\{^1H\}$ NMR spectrum of **4** shows resonances at δ 47.3 (s) and 61.2−62.3 (m) ppm. The singlet at 47.3 ppm is due to the noncoordinating phosphinate, while the broad multiplet (61.2−62.3 ppm) corresponds to coordinated phosphinate ligands. The $^{119}Sn\{^1H\}$ NMR spectrum of **4** shows a singlet at δ −555.6 (s) ppm. The latter is a signature for such O-capped clusters.[9] The ESI-MS spectrum of **4** (positive ion mode, CH_3OH) shows two most intense peaks due to $[(PhSn)_3(cycPO_2)_3(OH)_2(O)(OCH_3)]$ (*m*/*z* 1193.1) and $[(PhSn)_3(cycPO_2)_3(O)(OCH_3)_2(OH)]$ (*m*/*z* 1207.1) (Figure 3) suggesting that the three bridging hydroxyl groups are labile and are exchanged with solvent methanol. ESI-MS spectrum of **4** in the negative ion mode also was recorded; only one major peak at *m*/*z* 175.1 was observed which can be assigned to $cycPO_2^-$.

X-ray Crystal Structures of 1−4. The solid-state structures of **1-4** were determined by single-crystal X-ray analysis. The metric parameters for **1-4** are given in Tables 1-3. Compound **1**, which is the starting material crystallized in a triclinic system and its asymmetric unit, contains two independent molecules. The structure of **1** shows discrete steplike patterns formed through secondary Te...Cl interactions (Figure 4). Previously another polymorph of **1** has been structurally characterized by Chadha et al.[11] The main difference between **1** and the previously reported structure is the presence of lattice benzene molecules in the former (Supporting Information).

The macrocycles **2** and **3** are isostructural (Figure 5) and contain a 12-membered macrocycle containing two ditelluroxane units and two phosphinate groups. The macrocycle bears a dipositive charge, and to compensate this two chloride ions are present in **2** while in **3** two iodide ions are present. The two phosphinate ligands are involved in a symmetric bridging mode and bind the two ditelluroxane units to form a 12-membered $(Te_4P_2O_6)$ macrocycle (Figure 5). Interestingly in spite of its large size all the atoms of the macrocycle are almost in the same plane. The atoms that deviate most from the mean plane are O3 (0.18 Å) in **2** and P4 (0.47 Å) in **3**. The most interesting feature of the structure is that the two counter-anions are found symmetrically disposed on the top and bottom of the 12-membered inorganic heterocyclic ring in a capping type of interaction (Figure 5).The driving force for this topological disposition of the halide ions is clearly the energetically favorable Te---X interactions. Such a type of halide capping in tellurium−containing macrocycles seems to be totally new. However, among cationic porphyrins anion trapping is known.[12] In the latter the anions are entrapped as a result of hydrogen bonding interactions. Another instance of anion trapping occurs in the inverse-crown systems described by Mulvey and co-workers.[13] For example the inverse-crown $[Li_2Mg_2(TMP)_4(O)]$ (TMPH = 2,2,6,6-tetramethylpiperidine)

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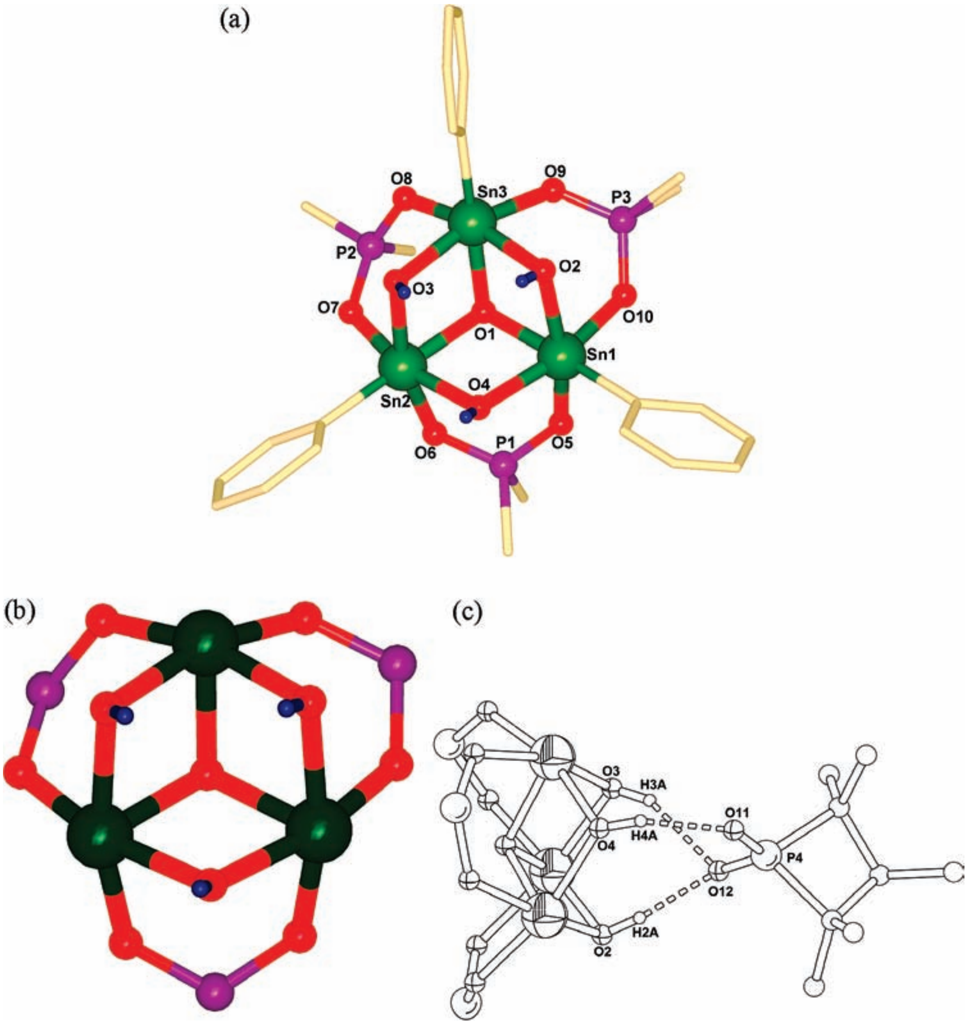

Figure 6. Molecular structure of **4**. Only the phenyl group having carbon and *ipso* carbon of phosphinates are shown. (b) Core structure of **4**. All the aromatic and aliphatic groups have been omitted. (c) Intramolecular hydrogen bonding interaction in **4** between O-capped cluster and free phosphinate anion.

consists of a $Mg_2Li_2N_4$ ring containing a central oxide ion. Halide trapping by mercury atoms in anticrowns has been established earlier.[14] Chart 1 summarizes these situations.

The geometry around the tellurium atom in **2** and **3** is pseudooctahedral, when taking into account the secondary interaction with chloride or iodide. The mean O−Te−O angles are 166.8(1)° (**2**) and 169.3(1)° (**3**). The average Te−O bond length found in **2** is 1.984(3) Å, while in **3** it is 1.992(5) Å. These distances are considerably shorter than that found in (p-$MeOC_6H_4)_2TeO$ (2.063 Å).[15] Similarly in **2** and **3**, the mean $Te{-}O_{phosphinate}$ bond length is 2.342(3) and 2.330(3) Å which is considerably different than that found in (Ph_2PO_2)(p-$MeOC_6H_4)_2$-TeOTe(p-$MeOC_6H_4)_2(O_2PPh_2)\cdot 2Ph_2PO_2H$ (av Te−O 2.440(2) Å).[3e] The average Te−Cl bond length in **2** is 3.366(1) Å which is longer than that found in (p-$MeOC_6H_4)_2TeCl_2$ (av Te−Cl 2.518(4) Å)[11] but is shorter than the van der Waal radii (3.81 Å).[16] Recently Beckmann et al. have reported [(p-$MeOC_6H_4)_2Te]_2OI_2$,[17] containing μ_4-I coordination where the average Te−I bond length is 3.612(2) Å. In comparison to the latter the Te−I bond length is slightly longer in **3** (3.704(2) Å). Interestingly the Te−I bond distance in (p-$MeOC_6H_4)_2TeI_2$ is 2.9234(8) Å.[18] The mean Te−O−Te angle for **2** is 123.1(1)° which is similar to that found in compounds such as [((p-$MeOC_6H_4)_2Te)_2$(O)(phthalate)]$_2$ (av 120(1)°).[3f]

X-ray analysis of **4** shows that the molecule belongs to the well-known family of O-capped clusters (Figure 6).[8] The basic cationic $Sn_3(\mu\text{-}OH)_3$ framework is present in a chair-shaped conformation. The primary structure comprises of three hydroxides, three phosphinates, and one oxide atom. The latter caps three tin atoms (Figure 6). Each hydroxide and phosphinate function as bridging coordinating ligands that bind two tin centers. Due to μ_3-O capping of the three tin atoms, three distannoxane units are formed. The salient feature of this structure is

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Table 4. X-ray Crystallographic Data for **1** and **2**

parameters	**1**	**2**
empirical formula	$C_{34}H_{34}O_4Cl_4Te_2$	$C_{78}H_{94}Cl_2O_{14}P_2Te_4$
formula weight	903.61	1898.77
temperature [K]	153(2)	153(2)
wavelength [Å]	0.71069	0.71073
crystal system	triclinic	triclinic
space group	$P\overline{1}$	$P\overline{1}$
a [Å]	10.173(5)	11.7246(9)
b [Å]	13.591(5)	13.5217(10)
c [Å]	13.792(5)	14.5973(11)
α [deg]	87.505(5)	67.3540(10)
β [deg]	80.005(5)	66.7430(10)
γ [deg]	68.406(5)	84.0640(10)
V [Å^3]	1745.7(12)	1959.0(3)
Z	2	1
crystal size [mm]	0.3 × 0.2 × 0.1	0.3 × 0.2 × 0.2
D_{calcd} [g cm^{-3}]	1.719	1.609
μ [mm^{-1}]	2.013	1.645
F(000)	884	946
θ range [deg]	2.43−26.37	1.97 to 26.00
limiting indices	$-12 \leq h \leq 12$, $-13 \leq k \leq 16$, $-17 \leq l \leq 16$	$-12 \leq h \leq 14$, $-16 \leq k \leq 16$, $-17 \leq l \leq 17$
reflections collected	10195	11057
independent reflections	6964 (R_{int} = 0.0294)	7507 (R_{int} = 0.0223)
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/ parameters	6964/0/401	7507/0/456
goodness-of-fit on F^2	1.064	1.037
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0445$, $wR_2 = 0.1018$	$R_1 = 0.0370$, $wR_2 = 0.0943$
R indices [all data]	$R_1 = 0.0609$, $wR_2 = 0.1258$	$R_1 = 0.0434$, $wR_2 = 0.1002$

Table 5. X-ray Crystallographic Data for **3** and **4**

parameters	**3**	**4**
empirical formula	$C_{96}H_{112}O_{14}I_2Te_4P_2$	$C_{52}H_{85}NO_{12}P_4Sn_3$
formula weight	2316.00	1396.16
temperature [K]	100(2)	153(2)
wavelength [Å]	0.71073	0.71073
crystal system	triclinic	monoclinic
space group	$P\overline{1}$	$P2(1)/n$
a [Å]	14.3925(6)	13.9771(8)
b [Å]	14.5552(6)	23.5526(14)
c [Å]	14.7395(6)	19.1064(12)
α [deg]	60.8580(10)	90
β [deg]	67.6390(10)	90.7420(10)
γ [deg]	89.2800(10)	90
V [Å^3]	2436.40(17)	6289.2(7)
Z	1	4
crystal size [mm]	0.3 × 0.2 × 0.1	0.2 × 0.2 × 0.1
D_{calcd} [g cm^{-3}]	1.578	1.475
μ [mm^{-1}]	1.911	1.338
F(000)	1144	2840
θ range [deg]	4.17−25.03	2.01 to 26.00
limiting indices	$-14 \leq h \leq 17$, $-16\leq k \leq 17$, $-14 \leq l \leq 17$	$-15 \leq h \leq 17$, $-29 \leq k \leq 27$, $-23 \leq l \leq 14$
reflections collected	12705	35164
independent reflections	8448 (R_{int} = 0.0222)	12349 (R_{int} = 0.0560)
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/ parameters	8448/0/541	12349/3/666
goodness-of-fit on F^2	1.067	1.026
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0390$, $wR_2 = 0.0933$	$R_1 = 0.0504$, $wR_2 = 0.1201$
R indices [all data]	$R_1 = 0.0460$, $wR_2 = 0.0998$	$R_1 = 0.0723$, $wR_2 = 0.1345$

the presence of four six-membered and three four-membered inorganic rings. The mean Sn−O−Sn angle at the capping oxygen is 103.6° which is similar to that observed in $[\{n\text{-BuSn(OH)}(O_2PPh_2)\}_3O][O_2PPh_2]$ (av 103.6(2)°).[9b] It should be mentioned that an analogous structure is known among titanium and zirconium carboxylates also.[19] The three tin atoms in **4** are equivalent and have an octahedral environment (C, 5O). The framework Sn−O bond lengths range from 2.062(3) to 2.137(4) Å. Interestingly, the oxygen of the free phosphinate ligand is hydrogen-bonded with hydroxyl groups present in the $Sn_3(\mu\text{-OH})_3$ core (O4−H4A...O11 1.844(62), O3−H3A... O12 1.977(42), O2−H2A...O12 1.827(38) Å) (Figure 6).

Conclusions

An unusual chloride-capped tellurium-containing macrocycle, $[((p\text{-MeOC}_6H_4)_2Te)_2(\mu\text{-O})(\mu\text{-}cyc\text{PO}_2)(\mu_4\text{-Cl})]_2\cdot C_6H_6$ (**2**), has been isolated in the reaction of $(p\text{-MeOC}_6H_4)_2TeCl_2$ with $cyc\text{PO}_2H$. The chloride ions present in **2** can be readily exchanged by iodides to afford $[((p\text{-MeOC}_6H_4)_2Te)_2(\mu\text{-O})(\mu\text{-}cyc\text{PO}_2)(\mu_4\text{-I})]_2\cdot 4C_6H_6$ (**3**). **2** and **3** are isostructural and contain dicationic macrocycles made up of a $Te_4P_2O_6$ framework. In both of these compounds halide counterions are present as capping ligands on the top and bottom of the macrocycle. This structural feature arises mainly as a result of Te---X interactions. Although anion trapping has been noted earlier with porphyrin-based macrocycles, the current report is the first using a Te-containing macrocycle. In contrast to the reaction of $(p\text{-MeOC}_6H_4)_2TeCl_2$ the analogous reaction with Ph_2SnCl_2 affords $[(PhSn)_3(\mu_3\text{-O})(\mu\text{-}cyc\text{PO}_2)_3(\mu\text{-OH})_3]$-$[cyc\text{PO}_2]\cdot CH_3CN$ (**4**). The latter is formed as a result of a Sn-Ph bond cleavage reaction. **4** belongs to the well-known O-capped cluster family of organostannoxanes.

Experimental Section

Reagents and General Procedures. Solvents and other general reagents used in this work were purified according to standard procedures. 2,4,4-Trimethyl-2-pentene, tellurium tetrachloride, and diphenyltin dichloride were purchased from Sigma Aldrich Ltd. Aluminum chloride, phosphorus trichloride, and anisole were purchased from s.d.Fine Chemicals, Mumbai. Bis(*p*-methoxyphenyl)tellurium dichloride and 1,1,2,3,3-pentamethyltrimethylenephosphinic acid were synthesized according to literature procedures.[20]

Instrumentation. Melting points were measured using a JSGW melting point apparatus in glass capillaries and are uncorrected. Elemental analyses were carried out using a Thermoquest CE instruments model EA/110 CHNS-O elemental analyzer. ^{1}H and ^{31}P NMR spectra were recorded on a JEOL-JNM LAMBDA model 400 spectrometer using C_6D_6 or $CDCl_3$ operating at 400 MHz. ESI-MS analyses were performed on a Waters Micromass Quattro Micro triple quadrupole mass spectrometer. Electrospray ionization (positive ion, full scan mode) was used keeping acetonitrile as solvent and nitrogen gas for desolvation. Capillary voltage was maintained at 2 kV, and cone voltage was kept at 31 kV. The temperature maintained for the ion source was 100 °C and for desolvation 350 °C. The yields obtained are calculated based on the oragnotellurium or organotin reagent.

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Synthesis. $[((p\text{-MeOC}_6\text{H}_4)_2\text{Te})_2(\mu\text{-O})(\mu\text{-}cyc\text{PO}_2)(\mu_4\text{-Cl})]_2\cdot\text{C}_6\text{H}_6$ (**2**): In 10 mL of benzene, dihydrated 1,1,2,3,3-pentamethyltrimethylenephosphinic acid (0.152 g, 0.72 mmol) and triethylamine (0.08 g, 0.79 mmol) were added and then stirred for 5 min to get a clear solution. To this bis(*p*-methoxyphenyl)tellurium dichloride (0.31 g, 0.75 mmol) (**1**) was added, and the reaction mixture was then stirred for a further 24 h and filtered. The filtrate was kept for slow evaporation at room temperature. Colorless crystals were isolated. These were washed with benzene and then dried in air. Yield: 0.18 g, 51%. Mp: 199−201 °C. Anal. Calcd for $\text{C}_{78}\text{H}_{94}\text{Cl}_2\text{O}_{14}\text{P}_2\text{Te}_4$ (**2**): C, 49.34; H, 4.99. Found: C, 49.19; H, 4.89. ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 8.05 (d, 16H, J = 7 Hz, Ar), 6.49 (d, 16H, J = 8 Hz, Ar), 2.91(s, 24H, -OCH_3), 0.95 (m, 2H, HCCH_3), 0.66 (d, 12H, J = 18 Hz, PCCH_3), 0.56 (d, 12H, J = 17 Hz, PCCH_3), 0.25 (m, 6H, H_3CCH). ^{31}P NMR (202 MHz, C_6D_6, ppm): δ 48.2 (s). ESI-MS: m/z (%) 403.0 $[(p\text{-MeOC}_6\text{H}_4)_2\text{Te}(\text{CH}_3\text{COO})]^+$ (100), 519.1 $[(p\text{-MeOC}_6\text{H}_4)_2\text{Te}(cyc\text{PO}_2)]^+$ (81), 717.1 $[((p\text{-MeOC}_6\text{H}_4)_2\text{Te})_2(\text{O})(\text{OH})]^+$ (18), 759.0 $[((p\text{-MeOC}_6\text{H}_4)_2\text{Te})_2(\text{O})(\text{CH}_3\text{COO})]^+$ (24), 875.1 $[((p\text{-MeOC}_6\text{H}_4)_2\text{Te})_2(\text{O})(cyc\text{PO}_2)]^+$ (84), 1785.2 $[\{((p\text{-MeOC}_6\text{H}_4)_2\text{Te})_2(\text{O})(cyc\text{PO}_2)\}_2\{\text{Cl}\}]^+$ (11), 1926.7 $[\{((p\text{-MeOC}_6\text{H}_4)_2\text{Te})_2(\text{O})(cyc\text{PO}_2)\}_2\{cyc\text{PO}_2\}]^+$ (5).

$[((p\text{-MeOC}_6\text{H}_4)_2\text{Te})_2(\mu\text{-O})(\mu\text{-}cyc\text{PO}_2)(\mu_4\text{-I})]_2\cdot 4\text{C}_6\text{H}_6$ (**3**): Sodium iodide (0.008 g, 0.053 mmol) was added to a solution of **2** (0.05 g, 0.026 mmol) in acetone (5 mL) and then stirred for 24 h. The mixture was filtered, and the solvent was evaporated in *vacuo* affording a yellow solid. This was recrystallized from hot benzene. Yield: 0.046 g, 75%. Mp: 201−202 °C. Anal. Calcd for $\text{C}_{96}\text{H}_{112}\text{O}_{14}\text{I}_2\text{Te}_4\text{P}_2$ (**3**): C, 49.78; H, 4.87. Found: C, 49.65; H, 4.80. ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 8.08 (d, 16H, J = 8 Hz, Ar), 6.45 (d, 16H, J = 8 Hz, Ar), 2.67 (s, 24H, -OCH_3), 0.95 (m, 2H, HCCH_3), 0.72 (d, 12H, J = 18 Hz, PCCH_3), 0.59 (d, 12H, J = 18 Hz, PCCH_3), 0.21 (m, 6H, H_3CCH). ^{31}P NMR (202 MHz, C_6D_6): δ 49.8 (s) ppm. ESI-MS: m/z (%) 519.1 $[(p\text{-MeOC}_6\text{H}_4)_2\text{Te}(cyc\text{PO}_2)]^+$ (100), 717.2 $[((p\text{-MeOC}_6\text{H}_4)_2\text{Te})_2(\text{O})(\text{OH})]^+$ (18), 875.1 $[((p\text{-MeOC}_6\text{H}_4)_2\text{Te})_2(\text{O})(cyc\text{PO}_2)]^+$ (86), 1878.3 $[\{((p\text{-MeOC}_6\text{H}_4)_2\text{Te})_2(\text{O})(cyc\text{PO}_2)\}_2\{\text{I}\}]^+$ (9), 1926.7 $[\{((p\text{-MeOC}_6\text{H}_4)_2\text{Te})_2(\text{O})(cyc\text{PO}_2)\}_2\{cyc\text{PO}_2\}]^+$ (5), 1986.9 $[\{((p\text{-MeOC}_6\text{H}_4)_2\text{Te})_2(\text{O})(cyc\text{PO}_2)\}_2\{cyc\text{PO}_2\}\{\text{CH}_3\text{COOH}\}]^+$ (2), 2238.2 $[\{((p\text{-MeOC}_6\text{H}_4)_2\text{Te})_2(\text{O})(cyc\text{PO}_2)(\text{I})\}_2\{\text{CH}_3\text{COOH}\}\{cyc\text{PO}_2\text{H}\}]$ (5).

$[(\text{PhSn})_3(\mu_3\text{-O})(\mu\text{-}cyc\text{PO}_2)_3(\mu\text{-OH})_3][cyc\text{PO}_2]\cdot\text{CH}_3\text{CN}$ (**4**): To a clear solution of dihydrated 1,1,2,3,3-pentamethyltrimethylenephosphinic acid (0.08 g, 0.38 mmol) and triethylamine (0.08 g, 0.79 mmol) in 40 mL of benzene was added diphenyltin dichloride (0.13 g, 0.38 mmol) all at once. After stirring for 24 h the reaction mixture was filtered and evaporated to obtain an oil. This was once again redissolved in a hot acetonitrile/methanol mixture. Block-shaped (**4**) and needle-shaped crystals were separated from the mixture. Needle-shaped crystals were of poor quality for X-ray diffraction. Block-shaped crystals from the mixture were easily separated by extraction with diethyl ether and once again recrystallized from acetonitrile. Yield: 0.08 g, 46%. Mp: 186−187 °C. Anal. Calcd for $\text{C}_{52}\text{H}_{85}\text{NO}_{12}\text{P}_4\text{Sn}_3$ (**4**): C, 44.73; H, 6.14; N, 1.00. Found: C, 44.65; H, 6.11; N, 0.93. ^{1}H NMR (500 MHz, CDCl_3, ppm): δ 0.67−1.33 (m, 60H, $-\text{CH}_3$), 1.40−1.60 (m, 4H, −CH), 7.28 (m, 9H, Ph), 7.39 (m, 6H, Ph). ^{31}P NMR (202.5 MHz, CDCl_3, ppm): δ 47.3 (s), 61.2−62.3 (m). ^{119}Sn NMR (186.5 MHz, CDCl_3, ppm): δ −555.6 (s). ESI-MS: m/z (%) 1175.1 $[(\text{PhSn})_3(cyc\text{PO}_2)_3(\text{OCH}_3)(\text{O})_2]^+$ (16), 1193.1 $[(\text{PhSn})_3(cyc\text{PO}_2)_3(\text{OH})_2(\text{O})(\text{OCH}_3)]^+$ (62), 1207.1 $[(\text{PhSn})_3(cyc\text{PO}_2)_3(\text{O})(\text{OCH}_3)_2(\text{OH})]^+$ (100). ESI-MS: m/z (%) 175.1 $[cyc\text{PO}_2]^-$ (100).

X-ray Crystallography. Crystal data of **1-4** are given in Tables 4 and 5. Single crystals suitable for X-ray crystallographic analyses were isolated by a slow evaporation of benzene (**1-3**) and acetonitrile (**4**), respectively. The crystal data for compounds **1-4** have been collected on a Bruker SMART CCD diffractometer using a Mo Kα sealed tube. The program SMART[21a] was used for collecting frames of data, indexing reflection, and determining lattice parameters, SAINT[21a] for integration of the intensity of reflections and scaling, SADABS[21b] for absorption correction, and SHELXTL[21c,d] for space group and structure determination and least-squares refinements on F^2. All structures were solved by direct methods using the programs SHELXS-97[21e] and refined by full-matrix least-squares methods against F^2 with SHELXL-97.[21e] Hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model. Hydrogen atoms for hydroxyl group (**4**) were identified by Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement parameters. In compound **2**, phosphinate carbon C17 and C18 are disordered over two positions (60:40) and are fixed satisfactorily. Similarly, in compound **4** having phosphinate carbon C7, C10, C14, C24, C35, C37, and C38 are also disordered over two positions and are fixed. The figures have been generated using *Diamond 3.1f* software.[21f]

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Supporting Information Available: Cif files and Figures S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org

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