

# Metal-Mediated Conversion of Methylcycloarsoxane (CH<sub>3</sub>AsO)<sub>n</sub> to Macrocyclic Octa- and Decanuclear Ligands –Trigonal Bipyramidal Coordination of Trivalent Arsenic

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Reaction of *cyclo*-(CH<sub>3</sub>AsO)<sub>n</sub> with MCl<sub>3</sub> · x H<sub>2</sub>O in acetonitrile at 100 °C affords [MCl<sub>2</sub>{*cyclo*-(CH<sub>3</sub>AsO)<sub>8</sub>}] [M = Ru (**1**), M = Os (**2**)] in which cyclooctamers (CH<sub>3</sub>AsO)<sub>8</sub> are stabilised in a κ<sup>4</sup>As<sup>1,3,5,7</sup> binding mode in the equatorial coordination sphere of the Group 8 metals. In contrast treatment of K<sub>2</sub>PtCl<sub>4</sub> with alternatively AgNO<sub>3</sub> or Ag<sub>2</sub>CO<sub>3</sub> and *cyclo*-(CH<sub>3</sub>AsO)<sub>n</sub> at 100 °C in the same solvent leads to

the formation of respectively octa- or decanuclear cage-like ligands in [Pt<sub>2</sub>{[*cyclo*-(As[CH<sub>3</sub>]OAs[NC(O)CH<sub>3</sub>]O)<sub>2</sub>]<sub>2</sub>}] (**3**) and [Pt<sub>2</sub>{[CH<sub>3</sub>C(O)N]<sub>2</sub>As<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>O<sub>4</sub>]<sub>2</sub>}] (**4**) by metal-assisted reactions between *cyclo*-(CH<sub>3</sub>AsO)<sub>n</sub> and acetonitrile. λ<sup>5</sup>-As<sup>III</sup> atoms in these complexes participate in square-planar Pt<sup>II</sup> coordination and themselves exhibit distorted trigonal bipyramidal coordination geometries.

## Introduction

Although (CH<sub>3</sub>AsO)<sub>n</sub> was synthesised some 140 years ago by A. von Baeyer<sup>[1]</sup> as the first example of an alkylcycloarsoxane, it is only in the past decade that the potential of this class of compounds as ambidentate macrocyclic ligands has been recognised and exploited<sup>[2]</sup>. Both mesityl- and methylcycloarsoxane have been crystallised as cyclic tetramers (RAsO)<sub>4</sub> and characterised by X-ray structural analysis<sup>[3][4]</sup>. In contrast to this apparent preference for the tetrameric form in the solid state, <sup>1</sup>H-NMR investigations have demonstrated that (CH<sub>3</sub>AsO)<sub>n</sub> and (C<sub>2</sub>H<sub>5</sub>AsO)<sub>n</sub> are present as a mixture of cyclic oligomers (*n* = 2–5) in solution<sup>[5][6][7]</sup> for which the nuclearities *n* = 3 and 4 predominate. The dynamic equilibria between such cyclic ionophores can be influenced by the addition of alkali metal cations. Whereas Na<sup>+</sup> cations stabilise the crown shaped cyclic tetramer in [Na{*cyclo*-(C<sub>2</sub>H<sub>5</sub>AsO)<sub>4</sub>-κ<sup>4</sup>O<sub>2</sub>}]SCN, employment of larger cations allows the isolation of pentagonal antiprismatic sandwich units in compounds of the type [M{*cyclo*-(C<sub>2</sub>H<sub>5</sub>AsO)<sub>5</sub>-κ<sup>5</sup>O<sub>2</sub>}]X (M = K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Cs<sup>+</sup>)<sup>[8][9]</sup>.

The presence of an alternative set of *soft* As donor atoms coupled with their apparent low energy barriers to ring contraction or expansion in organic solvents suggests that the alkylcycloarsoxanes should also be capable of exhibiting a rich variety of binding modes in the coordination spheres of transition metals. Indeed, the metal-mediated ring expansion from the predominate cyclic trimers and tetramers to hexameric (RAsO)<sub>6</sub> has been confirmed for the carbonyl transition metal complexes [M(CO)<sub>3</sub>]<sub>2</sub>-{μ-[*cyclo*-(RAsO)<sub>6</sub>]}] (M = Mo; R = CH<sub>3</sub><sup>[10]</sup>, C<sub>2</sub>H<sub>5</sub><sup>[12]</sup>; M = Cr, W; R = C<sub>2</sub>H<sub>5</sub><sup>[7]</sup>) and [ReBr(CO)<sub>2</sub>]<sub>2</sub>{μ-[*cyclo*-(C<sub>2</sub>H<sub>5</sub>AsO)<sub>6</sub>]}]<sup>[11]</sup>, in which the metal atoms are facially co-

ordinated by the upper or lower three As atoms of a flattened As<sub>6</sub>O<sub>6</sub> cuboctahedron. An analogous κ<sup>3</sup>As<sup>1,3,5</sup> mode has also recently been established in the mononuclear complexes [RuCl<sub>2</sub>{*cyclo*-(C<sub>2</sub>H<sub>5</sub>AsO)<sub>6</sub>}] and [RhCl<sub>3</sub>{*cyclo*-(C<sub>2</sub>H<sub>5</sub>AsO)<sub>6</sub>}]<sup>[11]</sup>. Analysis of the molecular geometry of the alkylcycloarsoxanes indicates that, whereas (RAsO)<sub>6</sub> cuboctahedra should be capable of facial coordination of a transition metal fragment such as M(CO)<sub>3</sub> with a minimum of conformational change, severe ring strain would clearly be introduced in the case of (RAsO)<sub>3</sub>. Extension of these geometrical arguments leads to the prediction that fourfold equatorial coordination of a transition metal should best be achieved by the κ<sup>4</sup>As<sup>1,3,5,7</sup> mode of a cyclooctamer (RAsO)<sub>8</sub>. Such oligomers are previously unknown as either isolated or coordinated species and have also not been detected in solutions of alkylcycloarsoxanes<sup>[5][6][7]</sup>.

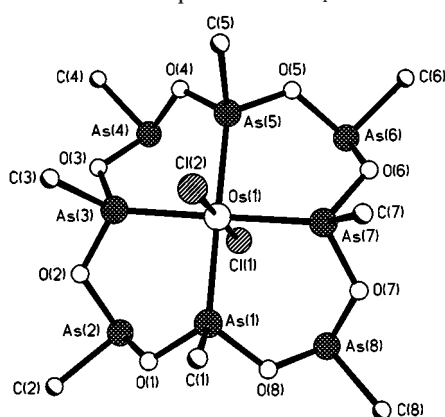
We now report our studies on the reactions of MCl<sub>3</sub> · H<sub>2</sub>O (M = Ru, Os) and K<sub>2</sub>PtCl<sub>4</sub> with (CH<sub>3</sub>AsO)<sub>n</sub> in acetonitrile at 100 °C, which we believed might enable the stabilisation of (CH<sub>3</sub>AsO)<sub>8</sub> in the octahedral coordination spheres of M<sup>II</sup> (obtained by reduction of MCl<sub>3</sub> · H<sub>2</sub>O) or the square-planar coordination sphere of Pt<sup>II</sup>.

## Results

[RuCl<sub>2</sub>{*cyclo*-(CH<sub>3</sub>AsO)<sub>8</sub>}] (**1**) and [OsCl<sub>2</sub>{*cyclo*-(CH<sub>3</sub>AsO)<sub>8</sub>}] (**2**) are isostructural and contain unprecedented cyclooctamers (CH<sub>3</sub>AsO)<sub>8</sub> that are stabilised in the equatorial coordination plane of the Group 8 transition metals. The required reduction of M<sup>III</sup> in the starting compounds MCl<sub>3</sub> · x H<sub>2</sub>O (M = Ru, Os) to M<sup>II</sup> in **1** and **2** is accompanied by ligand cleavage and oxidation to CH<sub>3</sub>AsO(OH)<sub>2</sub>, which can be isolated from the filtrate of

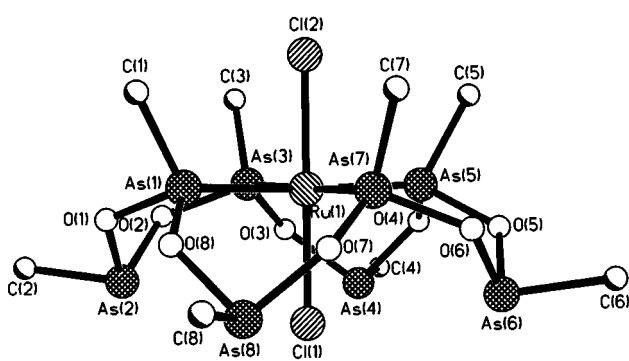
the final reaction mixture. Inspection of the As–Os–As angles [average values 90(1) and 177.4(2)°] and Os–As distances [2.400(3) Å] for the Os<sup>II</sup> octahedral complex **2** depicted in Figure 1 confirm the suitability of the very flexible 16-membered As<sub>8</sub>O<sub>8</sub> macrocycle for its adopted  $\kappa^4\text{As}^{1,3,5,7}$  coordination mode. Similar average As–M–As angles [90(1) and 177.5(2)°] and M–As distances [2.400(4) Å] are found in the isostructural Ru<sup>II</sup> complex **1**. As–O distances to the coordinated arsenic atoms As1, As3, As5, and As7 are on average [**1**, 1.758(7); **2**, 1.75(1) Å] shorter than those to the remaining non-coordinated Group 15 atoms [**1**, 1.799(7); **2**, 1.79(1) Å]. A concomitant widening of the O–As–O angles for the former atoms is apparent [**1**, 99.7(4)° vs. 97.0(2)°; **2**, 99.9(7)° vs. 97.4(8)°].

Figure 1. Molecular structure of [OsCl<sub>2</sub>{*cyclo*-(CH<sub>3</sub>AsO)<sub>8</sub>}] (**2**) viewed from above the equatorial OsAs<sub>4</sub> coordination plane



**1** and **2** exhibit approximately  $C_{4v}$  molecular symmetry in which both the coordinating arsenic atoms and their non-coordinating O and As neighbours all effectively belong to common planes. For instance, whereas the former atoms are sited at  $\pm 0.006$  Å from the equatorial Ru<sup>II</sup> coordination plane in **1**, the remaining arsenic atoms As2, As4, As6, and As8 display alternating deviations of  $\pm 0.107$  Å from the second As<sub>4</sub> plane of an As<sub>8</sub>O<sub>8</sub> “double crown” (Figure 2). This conformation of the 16-membered macrocycle is characterised by a torsion angle pattern of the type  $(a, b, -b, -a)_4$ , in which the absolute value of  $a$  varies between 104.5(4) and 124.3(5)° in **1** [105.0(9) and 124.6(9)° in **2**] that of  $b$  between 59.5(5) and 75.0(4)° [58.7(9) and 74.7(9)° in **2**].

Figure 2. Molecular structure of [RuCl<sub>2</sub>{*cyclo*-(CH<sub>3</sub>AsO)<sub>8</sub>}] (**1**) viewed from the side

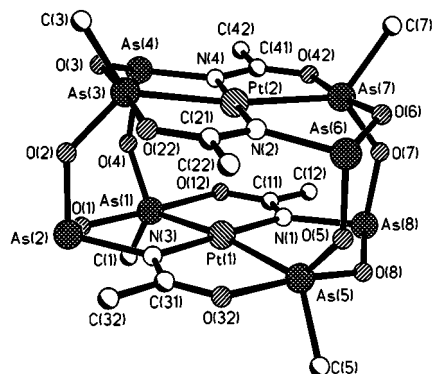
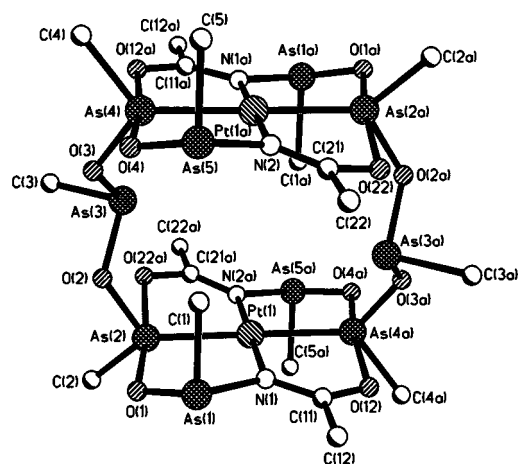


As mentioned in the Introduction previous examples of metal-mediated ring expansion for alkylcycloarsoxanes have been restricted to cyclopentamers and -hexamers. However we have recently investigated the analogous reaction of  $\text{MCl}_3 \cdot \text{H}_2\text{O}$  ( $\text{M} = \text{Ru}, \text{Os}$ ) with *cyclo*-(C<sub>2</sub>H<sub>5</sub>AsS)<sub>*n*</sub> in toluene<sup>[12]</sup>, which leads to the assembly of the novel macrocyclic hexadentate ligand [(C<sub>2</sub>H<sub>5</sub>)<sub>6</sub>As<sub>8</sub>S<sub>10</sub>]<sup>2-</sup> in the octahedral coordination spheres of Ru<sup>II</sup> and Os<sup>II</sup> at temperatures of 105 and 140°C, respectively. In contrast to the cyclooctamers (CH<sub>3</sub>AsO)<sub>8</sub> reported in the present work, two alkyl substituents of the potential macrocyclic ligand (C<sub>2</sub>H<sub>5</sub>AsS)<sub>8</sub> are replaced by terminal thiolate sulphurs in [(C<sub>2</sub>H<sub>5</sub>)<sub>6</sub>As<sub>8</sub>S<sub>10</sub>]<sup>2-</sup>. These *soft* donor atoms then occupy *cis*-sited positions in the resulting transition metal coordination spheres. Contrasting small As–Os–S angles of 80.5(2) and 82.3(3)° in the five-membered chelate rings of [Os-{(C<sub>2</sub>H<sub>5</sub>)<sub>6</sub>As<sub>8</sub>S<sub>10</sub>}] and large As–Os–As angles of 101.2(1) and 100.5(1)° in the six-membered chelate rings of this complex reflect a pronounced deviation from an idealised octahedral geometry.

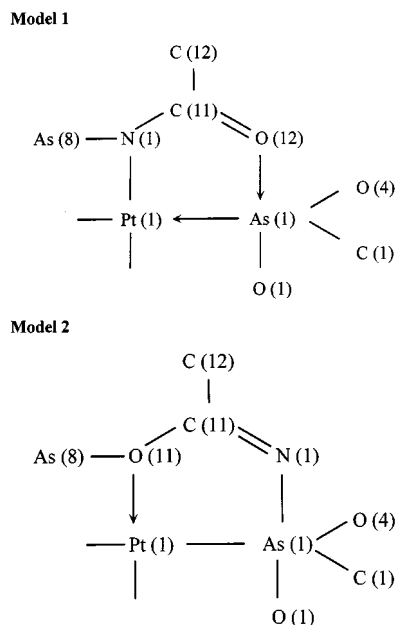
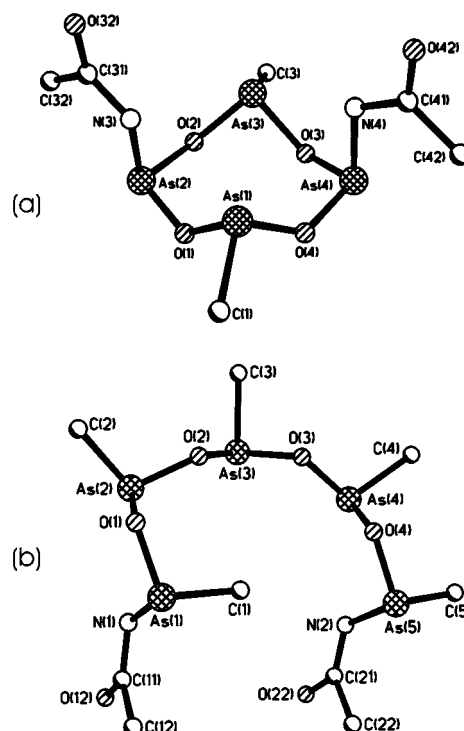
### Macrocyclic Cleavage Products

The apparent suitability of (CH<sub>3</sub>AsO)<sub>8</sub> for  $\kappa^4\text{As}^{1,3,5,7}$  equatorial coordination of transition metals prompted us to investigate whether this cyclooctamer can also be stabilised in the square-planar coordination sphere of Pt<sup>II</sup>. However, we were unable to isolate methylcycloarsoxane complexes by treatment of Pt<sup>II</sup> with (CH<sub>3</sub>AsO)<sub>*n*</sub> following initial precipitation of chloride ions in K<sub>2</sub>PtCl<sub>4</sub> as AgCl. In contrast, the direct reaction of K<sub>2</sub>PtCl<sub>4</sub> with AgNO<sub>3</sub> or alternatively Ag<sub>2</sub>CO<sub>3</sub> and (CH<sub>3</sub>AsO)<sub>*n*</sub> in acetonitrile at 100°C in a Carius tube did lead to the stabilisation of macrocyclic octa- and decanuclear As–O ligands, albeit as metal-mediated cleavage products of the original methylcycloarsoxane. Two dimeric Pt<sup>II</sup> complexes, [Pt<sub>2</sub>{[*cyclo*-(As[CH<sub>3</sub>]OAs[NC(O)CH<sub>3</sub>]O)<sub>2</sub>]}] (**3**) and [Pt<sub>2</sub>{[CH<sub>3</sub>C(O)N]<sub>2</sub>As<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>O<sub>4</sub>]}] (**4**) were isolated in relatively low yields (ca. 25%) under such conditions, depending on the molar ratio of the starting materials. For instance, whereas a 2:3:4 stoichiometric ratio of K<sub>2</sub>PtCl<sub>4</sub>/Ag<sub>2</sub>CO<sub>3</sub>/(CH<sub>3</sub>AsO)<sub>*n*</sub> (for  $n = 1$ ) affords **3**, the arsenic-rich complex **4** can be generated by increasing the (CH<sub>3</sub>AsO)<sub>*n*</sub> content of the starting mixture (molar ratio 2:3:6). An increased Pt/As relationship is required in the presence of AgNO<sub>3</sub> [e.g. a K<sub>2</sub>PtCl<sub>4</sub>/AgNO<sub>3</sub>/(CH<sub>3</sub>AsO)<sub>*n*</sub> molar ratio of 1:3:6 for **3**] to compensate for the partial oxidation of (CH<sub>3</sub>AsO)<sub>*n*</sub> to CH<sub>3</sub>As(O)(OH)<sub>2</sub> by NO<sub>3</sub><sup>-</sup> anions under such conditions. The red crystal sheafs could be separated without difficulty in each case in a manual fashion from precipitated AgCl. To our surprise both compounds contained novel octadentate anionic ligands, that result from metal-assisted reactions between (CH<sub>3</sub>AsO)<sub>*n*</sub> and acetonitrile. The role of Ag<sup>+</sup> cations in directing ligand construction still remains unclear.

As depicted in Figures 3 and 4, the solvent molecules are converted into acetamido [CH<sub>3</sub>C(O)N] building units, whose trigonal planar amide nitrogens (N1–N4 in **3**; N1,

Figure 3. Molecular structure of  $[\text{Pt}_2\{\{\text{cyclo-As}[\text{CH}_3]\text{OAs}[\text{NC}(\text{O})\text{-CH}_3\text{O}_2\}_2\}]$ Figure 4. Molecular structure of  $[\text{Pt}_2\{\{[\text{CH}_3\text{C}(\text{O})\text{N}_2\text{As}_5(\text{CH}_3)_5\text{O}_4\}_2\}]$ 

$\text{N}_2$  and  $\text{C}_i$  symmetry-related atoms in **4** are bonded to both  $\text{Pt}^{\text{II}}$  and  $\text{As}^{\text{III}}$  atoms. Refinements of alternative structural models, in which the positions of the N and O atoms in all four such moieties are exchanged (model 2 in Figure 5), led in both cases to significant deterioration in the  $R$  and  $wR_2$  values. The latter reliability index increases on going from model 1 to model 2 from 0.144 to 0.147 for **3** and from 0.118 to 0.121 for **4** under these circumstances. Structural corroboration of the chosen atom assignments in the macrocyclic As–O ligands of **3** and **4** is provided by the short *trans* sited N–Pt distances [average values: **3**, 2.04(2); **4**, 2.03(1) Å] and the very long coordinative axial O→As distances [average values: **3**, 2.20(2); **4**, 2.27(2) Å], whose values would be most unreasonable for a possible alternative formulation as O→Pt and N–As bonds (model 2). The respectively octa- and decanuclear ligands in these complexes may be regarded as being composed of the monomeric units shown in Figure 6. These are linked into dimers through the weak dative O→As interactions already discussed. Eight-membered  $\text{As}_4\text{O}_4$  rings can be identified for **3**,  $\text{As}_5\text{O}_4$  chains for **4**. The average C–O, C–N and C–C distances of 1.26(2), 1.32(3) and 1.48(3) Å in the  $[\text{CH}_3\text{C}(\text{O})\text{N}]$  units of **3** are similar to the values found for the analogous moieties in **4** [1.30(4), 1.30(4), 1.50(4) Å].

Figure 5. Alternative structural models 1 and 2 for the  $[\text{CH}_3\text{C}(\text{O})\text{N}]$  building units in **3**Figure 6. Monomeric units in the macrocyclic ligands of  $[\text{Pt}_2\{\{\text{cyclo-As}[\text{CH}_3]\text{OAs}[\text{NC}(\text{O})\text{CH}_3\text{O}_2\}_2\}]$  (**3**) and  $[\text{Pt}_2\{\{[\text{CH}_3\text{C}(\text{O})\text{N}_2\text{As}_5(\text{CH}_3)_5\text{O}_4\}_2\}]$  (**4**)

The  $\text{Pt}^{\text{II}}$  atoms in both complexes exhibit square-planar  $\text{As}_2\text{N}_2$  coordination spheres with donor atoms of the same type sited *trans* to one other. Their separation increases from 3.01(1) to 5.49(1) Å on going from **3** to **4**, a state of affairs that is reflected in a concomitant marked decrease in density  $D_{\text{calcd.}}$  from 3.226 to 2.679 g cm<sup>−3</sup>. Four of the arsenic atoms in **3** [As2, As4, As6, As8] and six such atoms

in **4** [As1, As3, As5, and  $C_i$  symmetry related atoms] display typical  $\psi$ -tetrahedral coordination geometries.

### Trigonal Bipyramidal Coordination of As<sup>III</sup>

The remaining arsenic atoms in **3** and **4** participate in Pt<sup>II</sup> coordination and themselves exhibit unique distorted trigonal bipyramidal coordination geometries. Average bond lengths and angles to these  $\lambda^5$ -As atoms are summarised in Table 1. As<sup>III</sup> can be regarded as a weak Lewis acid in its trihalides AsX<sub>3</sub> and its ability to extend its coordination number to 4 ( $\psi$ -trigonal bipyramidal), 5 ( $\psi$ -octahedral), and even 6 (octahedral) is now structurally well documented for such compounds<sup>[13][14][15]</sup>. A similar tendency to participate in secondary bonds has also been reported for As<sup>III</sup>O<sub>3</sub> units, e.g. O...As interactions of length 2.68 Å in Ba<sub>2</sub>As<sub>6</sub>O<sub>11</sub><sup>[16]</sup>. A characteristic property of organoarsenic(III) compounds is, of course, their pronounced Lewis basicity and examples of their dative As→M bonds (M = metal), in which the As<sup>III</sup> atoms display a tetrahedral coordination geometry, are myriad. In contrast, to our knowledge, **3** and **4** provide to first examples of As<sup>III</sup> atoms in a trigonal bipyramidal coordination environment, i.e. of trivalent arsenic behaving simultaneously as a Lewis base and Lewis acid. An analysis of the bond distances in **3** and **4** indicates that the possible alternative assignment of the oxidation state IV to the  $\lambda^5$ -As atoms would be inappropriate. For instance the axial donor O→As interactions involving the acetamido units are much weaker than the opposite As(O)–As bonds (Table 1). This state of affairs manifests itself in the pronounced distortion of the trigonal bipyramidal coordination spheres of the  $\lambda^5$ -As atoms towards the tetrahedra, that are characteristic for organoarsenic(III) complexes. The degree of distortion in **3** may be gauged from the displacements  $\Delta$  of 0.179–0.203 Å for the  $\lambda^5$ -As atoms from the planes of their equatorial substituents towards the axial acetamido O atoms.  $\Delta$  increases on going from **3** to **4** (As2 0.2320 Å, As4 0.2620 Å).

Table 1. Average bond lengths [Å] and angles [°] to the trigonal bipyramidal  $\lambda^5$ -As atoms in **3** and **4** (ax = axial, eq = equatorial)

	<b>3</b>	<b>4</b>
As–Pt	2.387(6)	2.382(1)
As–C	1.90(2)	1.93(3)
As–O <sub>eq</sub>	1.741(6)	1.772(9)
As–O <sub>ax</sub> (As)	1.834(6)	1.82(2)
As–O <sub>ax</sub> (C)	2.20(2)	2.27(2)
Pt–As–C	128(2)	128.4(9)
Pt–As–O <sub>eq</sub>	127.3(8)	122(2)
C–As–O <sub>eq</sub>	102(1)	104.9(8)
Pt–As–O <sub>ax</sub> (As)	99.5(6)	101.8(6)
Pt–As–O <sub>ax</sub> (C)	87.0(2)	85.7(1)
(As)O <sub>ax</sub> –As–O <sub>ax</sub> (C)	173.3(6)	172.4(4)

Our present work demonstrates that the previously unknown cyclooctamers (CH<sub>3</sub>AsO)<sub>8</sub> can be stabilised in the equatorial coordination plane of transition metals. At elevated temperatures, cleavage and metal-mediated reaction

with solvent acetonitrile can afford novel cage-like multidentate ligands. The presence of silver cations (as provided by AgNO<sub>3</sub> or Ag<sub>2</sub>CO<sub>3</sub>) to remove chloride ions as AgCl is a necessary prerequisite for the construction of the respectively octa- and decanuclear ligands in **3** and **4**.

### Experimental Section

All manipulations were performed in an Ar atmosphere in carefully dried solvents. – FAB MS: Fisons VG Autospec with 3-nitrobenzyl alcohol as matrix. – FTIR: Perkin-Elmer 1760X. – Elementary analyses: Carbo Erba 1106 (for **3** and **4**) and Mikroanalytisches Labor Beller, Göttingen (for **1** and **2**). – *cyclo*-(CH<sub>3</sub>AsO)<sub>n</sub> was prepared by alkaline hydrolysis<sup>[7]</sup> of CH<sub>3</sub>AsCl<sub>2</sub>.

[RuCl<sub>2</sub>{*cyclo*-(CH<sub>3</sub>AsO)<sub>8</sub>}] (**1**): RuCl<sub>3</sub>·*x* H<sub>2</sub>O (21 mg, 0.1 mmol) was combined in a Carius tube (Duran glass, medium-walled 4 mm, diameter 16 mm, length 12 cm, volume approximately 10 cm<sup>3</sup>) with *cyclo*-(CH<sub>3</sub>AsO)<sub>n</sub> (106 mg, 1.0 mmol for *n* = 1) dissolved in 1.5 ml of acetonitrile. The tube was flame sealed, heated to 100°C over 40 h and allow to cool slowly to room temperature over a further 80 h. After opening, the solid state product was filtered off and washed with acetonitrile to afford yellow **1**. Yield 72.4 mg (71%). – C<sub>8</sub>H<sub>24</sub>As<sub>8</sub>Cl<sub>2</sub>O<sub>8</sub>Ru (1019.6): calcd. C 9.4, H 2.4, As 58.8; found C 9.4, H 2.3, As 58.8. – FAB-MS [*m/z* (%): 482(1) [As<sub>5</sub>Me<sub>4</sub>O<sub>3</sub>]<sup>+</sup>, 395(4) [As<sub>4</sub>Me<sub>2</sub>O<sub>4</sub>]<sup>+</sup>, 329(10) [As<sub>4</sub>Me<sub>2</sub>]<sup>+</sup>, 289(13) [As<sub>3</sub>MeO<sub>3</sub>]<sup>+</sup>, 259(16) [As<sub>2</sub>Me<sub>3</sub>O<sub>4</sub>]<sup>+</sup>. – IR (KBr):  $\tilde{\nu}$  = 2999 cm<sup>−1</sup> (w), 2907 (w), 830 (s), 803 (s), 773 (s), 684 (s), 623 (m), 584 (s), 526 (s, br).

[OsCl<sub>2</sub>{*cyclo*-(CH<sub>3</sub>AsO)<sub>8</sub>}] (**2**): OsCl<sub>3</sub>·*x* H<sub>2</sub>O (31 mg, 0.1 mmol) and *cyclo*-(CH<sub>3</sub>AsO)<sub>n</sub> (106 mg, 1.0 mmol for *n* = 1) were heated in 1.5 ml of acetonitrile in a Carius tube with the similar temperature programme as for **1**. Yield 74.3 mg of yellow **2** (67%). – C<sub>8</sub>H<sub>24</sub>As<sub>8</sub>Cl<sub>2</sub>O<sub>8</sub>Os (1108.7): calcd. C 8.7, H 2.2, As 54.0; found C 8.6, H 2.1, As 53.9. – FAB-MS [*m/z* (%): 482(2) [As<sub>5</sub>Me<sub>4</sub>O<sub>3</sub>]<sup>+</sup>, 395(5) [As<sub>4</sub>Me<sub>2</sub>O<sub>4</sub>]<sup>+</sup>, 329(12) [As<sub>4</sub>Me<sub>2</sub>]<sup>+</sup>, 289(13) [As<sub>3</sub>MeO<sub>3</sub>]<sup>+</sup>, 259(22) [As<sub>2</sub>Me<sub>3</sub>O<sub>4</sub>]<sup>+</sup>. – IR (KBr):  $\tilde{\nu}$  = 3001 cm<sup>−1</sup> (m), 2907 (m), 829 (s), 773 (s), 683 (s), 628 (s), 584 (s), 528 (s, br).

[Pt<sub>2</sub>{[*cyclo*-(As[CH<sub>3</sub>]OAs[NC(O)CH<sub>3</sub>]O)<sub>2</sub>]}] (**3**): K<sub>2</sub>PtCl<sub>4</sub> (105 mg, 0.25 mmol), AgNO<sub>3</sub> (127 mg, 0.75 mmol), and *cyclo*-(CH<sub>3</sub>AsO)<sub>n</sub> (159 mg, 1.50 mmol for *n* = 1) were heated to 100°C in 1.5 ml of acetonitrile over a period of 16 h in a sealed Carius tube. After cooling to room temperature over 80 h the tube was opened and the sheafs of red crystals of **3** separated manually from precipitated AgCl. Yield after washing 34.2 mg (26%). – C<sub>12</sub>H<sub>24</sub>As<sub>8</sub>N<sub>4</sub>O<sub>12</sub>Pt<sub>2</sub> (1405.9): calcd. C 10.2, H 1.7, N 4.0; found C 9.3, H 1.4, N 3.6. – FAB-MS [*m/z* (%): 329(13) [As<sub>4</sub>Me<sub>2</sub>]<sup>+</sup>, 289(14) [As<sub>3</sub>MeO<sub>3</sub>]<sup>+</sup>. – IR (KBr):  $\tilde{\nu}$  = 3011 (w), 2920 (w), 1516 (s), 1385 (s), 1029 (m), 820 (s), 781 (s), 679 (m), 628 (m), 597 (m), 477 (s).

[Pt<sub>2</sub>{[*cyclo*-(CH<sub>3</sub>C(O)N)<sub>2</sub>As<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>O<sub>4</sub>]}] (**4**): K<sub>2</sub>PtCl<sub>4</sub> (206 mg, 0.50 mmol), Ag<sub>2</sub>CO<sub>3</sub> (208 mg, 0.75 mmol), and *cyclo*-(CH<sub>3</sub>AsO)<sub>n</sub> (159 mg, 1.50 mmol for *n* = 1) were heated to 100°C in 1.5 ml of acetonitrile with the similar temperature programme as for **3**. After cooling to room temperature the tube was opened and the sheafs of red crystals of **4** separated manually from precipitated AgCl. Yield after washing 33.0 mg (25%). – C<sub>18</sub>H<sub>42</sub>As<sub>10</sub>N<sub>4</sub>O<sub>12</sub>Pt<sub>2</sub> (1645.9): calcd. C 13.1, H 2.6, N 3.4; found C 12.8, H 2.4, N 3.1. – FAB-MS [*m/z* (%): 603(1) [As<sub>2</sub>Me<sub>4</sub>O<sub>3</sub>Pt]<sup>+</sup>, 498(2) [As<sub>5</sub>Me<sub>4</sub>O<sub>4</sub>]<sup>+</sup>, 482(2) [As<sub>5</sub>Me<sub>4</sub>O<sub>3</sub>]<sup>+</sup>, 345(10) [As<sub>2</sub>Pt]<sup>+</sup>, 329(11) [As<sub>4</sub>Me<sub>2</sub>]<sup>+</sup>, 289(13) [As<sub>3</sub>MeO<sub>3</sub>]<sup>+</sup>. – IR (KBr):  $\tilde{\nu}$  = 3001 (w), 2965 (w), 1499 (s), 1402 (s), 1231 (w), 1022 (w), 792 (m), 763 (m), 731 (s), 698 (s), 567 (m), 511 (m).



*X-ray Structural Analyses:* Siemens P4 diffractometer, graphite monochromator, Mo- $K_\alpha$  radiation ( $\lambda = 0.71073$  Å), SHELXS-86<sup>[17]</sup> for structure solution by direct methods and SHELXL-93<sup>[18]</sup> for refinement by full-matrix least squares. Semi-empirical absorption corrections were applied to the intensity data by use of  $\psi$  scans. Hydrogen atoms were included at calculated positions<sup>[19]</sup>.

**1:**  $\text{C}_8\text{H}_{24}\text{As}_8\text{Cl}_2\text{O}_8\text{Ru}$ ,  $M = 1019.6$ , monoclinic, space group  $P2_1/c$ ,  $a = 11.777(2)$ ,  $b = 15.600(3)$ ,  $c = 14.404(3)$  Å,  $\beta = 97.71(3)^\circ$ ,  $V = 2622.4(9)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calcd.}} = 2.583$  g cm<sup>-3</sup>,  $\mu = 10.85$  mm<sup>-1</sup>. Crystal size  $0.34 \times 0.50 \times 0.70$  mm;  $\omega$ -scan, scan range:  $20 \leq 50^\circ$  ( $0 \leq h \leq 14$ ,  $0 \leq k \leq 18$ ,  $-17 \leq l \leq 16$ ), 4573 symmetry independent reflections from 4806 collected ( $R_{\text{int}} = 0.030$ ), max./min. transmission: 0.023/0.006; 252 parameters refined;  $R = 0.041$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.096$  [all reflections],  $S = 1.05$ ;  $\Delta\rho_{\text{max}} = 0.85$  eÅ<sup>-3</sup>,  $\Delta\rho_{\text{min}} = -0.87$  eÅ<sup>-3</sup>.

**2:**  $\text{C}_8\text{H}_{24}\text{As}_8\text{Cl}_2\text{O}_8\text{Os}$ ,  $M = 1108.7$ , monoclinic, space group  $P2_1/c$ ,  $a = 11.778(2)$ ,  $b = 15.559(3)$ ,  $c = 14.439(3)$  Å,  $\beta = 97.59(3)^\circ$ ,  $V = 2622.8(9)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calcd.}} = 2.808$  g cm<sup>-3</sup>,  $\mu = 15.11$  mm<sup>-1</sup>. Crystal size  $0.38 \times 0.50 \times 0.50$  mm;  $\omega$ -scan, scan range:  $20 \leq 47.5^\circ$  ( $0 \leq h \leq 13$ ,  $0 \leq k \leq 17$ ,  $-16 \leq l \leq 16$ ), 3966 symmetry independent reflections from 4162 collected ( $R_{\text{int}} = 0.048$ ), max./min. transmission: 0.023/0.006; 252 parameters refined;  $R = 0.048$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.124$  [all reflections],  $S = 1.03$ ;  $\Delta\rho_{\text{max}} = 1.04$  eÅ<sup>-3</sup>,  $\Delta\rho_{\text{min}} = -1.26$  eÅ<sup>-3</sup>.

**3:**  $[\text{Pt}_2\{\{\text{cyclo}-(\text{As}[\text{CH}_3]\text{OAs}[\text{NC}(\text{O})\text{CH}_3]\text{O}\}_2\}]$ ,  $M = 1405.9$ , monoclinic, space group  $P2_1/n$ ,  $a = 11.638(2)$ ,  $b = 13.110(3)$ ,  $c = 19.781(4)$  Å,  $\beta = 106.46(4)^\circ$ ,  $V = 2894.4(10)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calcd.}} = 3.226$  g cm<sup>-3</sup>,  $\mu = 18.79$  mm<sup>-1</sup>. Crystal size  $0.40 \times 0.40 \times 0.44$  mm;  $\omega$ -scan, scan range:  $20 \leq 50^\circ$  ( $0 \leq h \leq 13$ ,  $0 \leq k \leq 15$ ,  $-23 \leq l \leq 22$ ), 5064 symmetry independent reflections from 5315 collected ( $R_{\text{int}} = 0.073$ ), max./min. transmission: 0.256/0.156; 331 parameters refined;  $R = 0.055$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.144$  [all reflections],  $S = 1.05$ ;  $\Delta\rho_{\text{max}} = 2.53$  eÅ<sup>-3</sup>,  $\Delta\rho_{\text{min}} = -2.14$  eÅ<sup>-3</sup>.

**4:**  $[\text{Pt}_2\{\{\text{CH}_3\text{C}(\text{O})\text{N}\}_2\text{As}_5(\text{CH}_3)_5\text{O}_4\}_2]$ ,  $M = 1645.9$ , monoclinic, space group  $P2_1/n$ ,  $a = 10.356(2)$ ,  $b = 12.801(3)$ ,  $c =$

$15.410(3)$  Å,  $\beta = 92.93(3)^\circ$ ,  $V = 2040.2(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calcd.}} = 2.679$  g cm<sup>-3</sup>,  $\mu = 14.95$  mm<sup>-1</sup>. Crystal size  $0.30 \times 0.32 \times 0.46$  mm;  $\omega$ -scan, scan range:  $20 \leq 45^\circ$  ( $0 \leq h \leq 11$ ,  $0 \leq k \leq 13$ ,  $-16 \leq l \leq 16$ ), 2616 symmetry independent reflections from 2791 collected ( $R_{\text{int}} = 0.032$ ), max./min. transmission: 0.016/0.006; 215 parameters refined;  $R = 0.046$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.119$  [all reflections],  $S = 1.02$ ;  $\Delta\rho_{\text{max}} = 0.93$  eÅ<sup>-3</sup>,  $\Delta\rho_{\text{min}} = -1.01$  eÅ<sup>-3</sup>.

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 [19] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data (deposition numbers 102190 – 102193) may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. Code + 44 (0)1223/ 336-033, e-mail: deposit@chemcrs.cam.ac.uk).

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