Metal-Assisted Assembly of Chain and Macrocyclic As−S Ligands from Ethylcycloarsathiane $(C_2H_5AsS)_n$

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Received September 12, 1995

Key Words: Arsenic-sulphur ligands / Macrocyclic ligands / Ethylcycloarsathiane / Ruthenium complexes

Treatment of *cyclo*-$(EtAsS)_n$ with $[RuCl_2(Ph_3P)_3]$ and $[ReBr(CO)_5]$ affords the respective complexes $[RuCl_2\{cyclo\text{-}(EtAsS)_4\}(Ph_3P)]$ (**1**) and $[\{Re(CO)_3\}_2\{\mu\text{-}(Et_4As_4S_5)\}]$ (**2**). Whereas **1** contains a κ^3As coordinated intact cyclotetramer $(EtAsS)_4$, ring cleavage leads to the chain anion $Et_4As_4S_5^{2-}$, stabilised as a bridging hexadentate ligand in **2**. Reaction of MCl_3 with *cyclo*-$(EtAsS)_n$ in toluene in a Carius tube enables the metal-mediated temperature controlled assembly of the novel 16- and 14-membered macrocyclic hexadentate As−S ligands in $[M\{cyclo\text{-}(Et_6As_8S_{10})\}]$ (**3**: M = Os; **4**: M = Ru) and $[Ru\{cyclo\text{-}(Et_4As_6S_{10})\}]$ (**5**). The structures of the products were established by X-ray crystallography.

Our recent studies on the coordination properties of ethylcycloarsoxane $(C_2H_5AsO)_n$, $n = 4-6$[1−3] have demonstrated that such ambidentate macrocycles are capable of acting as ionophores for alkali metal cations in a manner similar to classical crown ethers[2]. Alkylarsoxanes $(RAsO)_n$ (R = Me, Et) exhibit dynamic reorganisation equilibria between different cyclic oligomers in solution (e.g. CCl_4[4]) and the ring size in the sandwich complexes $[M\{cyclo\text{-}(C_2H_5AsO)_n\}_2]SCN$ (M = Na, $n = 4$; M = K, $n = 5$)[2] is ostensibly controlled by the radius of the central cation. A metal-mediated ring expansion from the predominant trimers and tetramers has also been observed for the carbonyl transition metal complexes $[\{M(CO)_3\}_2\{cyclo\text{-}(RAsO)_6\}]$ (M = Mo, R = Me[5], Et[1]; M = Cr, W, R = Et[1]), in which $M(CO)_3$ groups are coordinated facially by the upper and lower three arsenic atoms of a flattened As_6O_6 cuboctahedron.

These findings have prompted us to investigate the complexing ability of the analogous cycloarsathiane $(C_2H_5AsS)_n$, which may be compared with macrocyclic thioethers, a class of ligands of considerable current interest[6]. Although the preparation of alkylarsathianes $(RAsS)_n$ by reaction of $RAsCl_2$ with H_2S was reported in the last century[7] it is only recently that isolated examples have been structurally characterized. An eight-membered As_4S_4 crown with approximately C_{4v} ring symmetry has been established[8−11] for the tetramers $(CH_3AsS)_4$, $(tBuAsS)_4$, $(PhAsS)_4$, and $(C_2H_5AsS)_4$. DiMaio and Rheingold have found that treatment of $(CH_3As)_5$ with S_8 in the presence of $Mo(CO)_6$ in toluene at 125 °C leads to metal-assisted formation of a mixture of $(CH_3AsS)_3$ and $(CH_3AsS)_4$, which could be separated by column chromatography[8]. The complex $[Mo(CO)_3(Me_6As_6S_3)]$, with a nine-membered partially sulphurated arsenic ring, was obtained as a by-product of the above reaction. These authors also reported the reaction of $[\{MoCp(CO)_3\}_2]$ (Cp = C_5H_5) with $(CH_3AsS)_n$ in toluene in a Carius tube at 125 °C, which produces the novel triple-decker sandwich $[(CpMo)_2(\mu\text{-}As_3)(\mu\text{-}AsS)]$ and a number of naked arsenic clusters in low yield. However, no evidence was found for the formation of coordinated cycloarsathianes with either the $Mo(CO)_3$ or the MoCp fragment, suggesting that a metal-mediated ring expansion may well be less facile for cycloarsathianes than for cycloarsoxanes. We now present the transition metal complex $[RuCl_2\{cyclo\text{-}(C_2H_5AsS)_4\}(Ph_3P)]$ (**1**), which contains an intact coordinated cycloarsathiane, and provide examples for the metal-assisted assembly of novel chain and macrocyclic As−S ligands from $(C_2H_5AsS)_n$.

Results

The work of DiMaio and Rheingold indicates that cycloarsathianes can be expected to undergo As−S bond cleavage followed by reassembly into new structures in the coordination sphere of transition metal carbonyls at elevated temperature. This prompted us to investigate the reaction of $[RuCl_2(Ph_3P)_3]$ with *cyclo*-$(C_2H_5AsS)_n$ in equimolar ratio ($n = 4$) at room temperature in the expectation that a coordinated cycloarsathiane might be isolable under mild reaction conditions. A ^{31}P-NMR spectrum of the CH_2Cl_2 reaction solution after 12 h contained no less than 11 resonances in the range $\delta = 18.91-64.06$ in addition to the signals of the starting compound and free Ph_3P. Attempts to separate components of the mixture by column chromatography over alumina or silica were unsuccessful. However the monomeric complex $[RuCl_2\{cyclo\text{-}(C_2H_5AsS)_4\}(Ph_3P)]$ (**1**), as the OC-6-43 stereoisomer, could be obtained as a red crystalline product in satisfactory yield by covering the CH_2Cl_2 solution with hexane, **1** crystallizes together with a disordered CH_2Cl_2 molecule (site occupation factor 0.5) in a monoclinic unit cell and contains an intact $(C_2H_5AsS)_4$ ligand. To our knowledge, only one previous example of a coordinated cycloarsathiane has been reported, namely

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[Ag{*cyclo*-($C_2H_5AsS)_4\}_2]CF_3SO_3$, in which the silver atom exhibits a remarkable quadratic-antiprismatic geometry[11]. In contrast to the crown conformation of the tetradentate eight-membered $(AsS)_4$ ring in this Ag(I) complex cation, a boat-chair conformation is observed for the tridentate $(C_2H_5AsS)_4$ ligand in complex **1** (Figure 1). The endocyclic As–E–As angles (E = O, S) are much narrower for the heavier chalcogen in cyclic oligomers of the type $(RAsE)_n$. For instance, an average As–S–As angle of 94(1)° was found for $(CH_3AsS)_n$ (n = 3, 4[8]), a value which is 23° smaller than for the average As–O–As angle in [(mesityl)AsO]$_4$[12]. The narrowness of the As–S–As angles in the $(C_2H_5AsS)_4$ ligand allows the formation of two four-membered chelate rings in **1** with Ru(1)–As(2) as the shared central bond. An analogous coordination of neighbouring As atoms to the same metal atom is prevented in cycloarsoxane complexes by the much larger As–O–As angles. Instead, facial coordination can be achieved for cycloarsoxanes by employment of every second As atom in a twelve-membered $(AsO)_6$ ring, as in [{M(CO)$_3$}$_2${*cyclo*-($C_2H_5AsO)_6$}] (M = Cr, Mo, W[1]). The presence of a pronounced degree of ring strain in the four-membered chelate rings of **1** is apparent from differences in the As–S–As angles of the coordinated cycloarsathiane. Whereas those at S(1) and S(2) [84.0(1) and 83.9(1)°] are markedly narrowed in comparison to $(C_2H_5AsS)_4$ [96.6(9)°] a widening to 98.6(1)° is observed for the angles at S(3) and S(4) in the chair-shaped six-membered chelate ring containing As(1), As(4), and As(3). An analogous trend can be established for the Ru–As–S angles, for which contrasting average values of 99.4(4) and 125(2)° are found for the four- and six-membered chelate rings. Further evidence for considerable strain in the four-membered rings is provided by their very narrow endocyclic As–Ru–As angles of 77.2(1) and 76.8(1)°, which are in striking contrast to the wide angle of 97.8(1)° for As(1)–Ru–As(3). Significant widening is also observed for the S–As–S angle at the bridgehead atom As(2), its value being 107.1(1) as opposed to average values of 102.6(5) for the remaining As atoms in **1** or 103.2(6)° for the cycloarsathiane $(C_2H_5AsS)_4$ itself[11]. The As–S distances in the $(AsS)_4$ ring range from 2.238(3) [As(1)–S(4)] to 2.274(3) Å [As(3)–S(2)] and may be regarded as typical for such bonds in cycloarsathianes for which average values of 2.26(1) in $(CH_3AsS)_4$ and 2.248(4) Å in $(C_2H_5AsS)_4$ have been established. A *trans* influence of the π-acceptor ligand PPh_3 is apparent for Ru(1)–As(2), which is significantly longer [2.446(2) Å] than the Ru–As bonds opposite to the chloride ligands Cl(1) and Cl(2) [2.391(1), 2.407(2) Å].

The remarkably wide Ru–As–C angles of 126.1(3) and 124.4(3) for As(1) and As(2) and particularly 141.3(3)° for As(2) clearly indicate that a facial κ^3As coordination would be impossible for a cyclotrimer $(C_2H_5AsS)_3$. However, both geometrical [e.g. an OC-6-34 arrangement with PPh_3 *trans* to As(1)] and linkage isomers [e.g.s κ^3As^1,S^2,As^4 or κ^3As^1,As^2,S^3 coordination modes] should be possible for **1** and the ^{1}H- and ^{31}P-NMR spectra of the complex indicate that dynamic equilibria are rapidly established in $CDCl_3$ solution at room temperature (Figure 2). Thus, the ^{31}P-NMR spectrum, taken 12 h after the sample was dissolved, contains the seven resonances between δ = 18.91 and 33.55 previously observed for the reaction mixture.

Figure 1. Molecular structure of **1**. Selected bond lengths [Å] and angles [°]: Ru(1)–As(1) 2.391(1), Ru(1)–As(2) 2.446(2), Ru(1)–As(3) 2.407(2), Ru(1)–Cl(1) 2.433(3), Ru(1)–Cl(2) 2.429(3), Ru(1)–P(1) 2.357(3); As(1)–Ru(1)–As(2) 77.2(1), As(3)–Ru(1)–As(2) 76.8(1), As(1)–Ru(1)–As(3) 97.8(1)

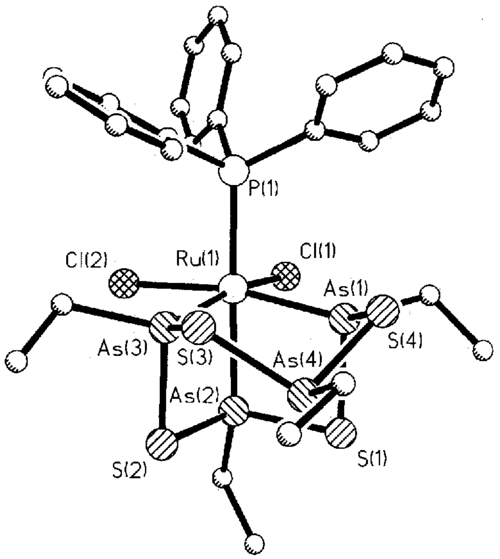
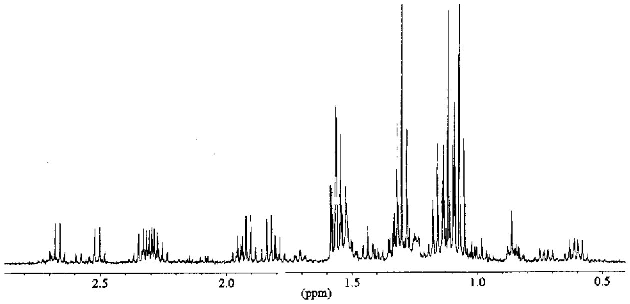
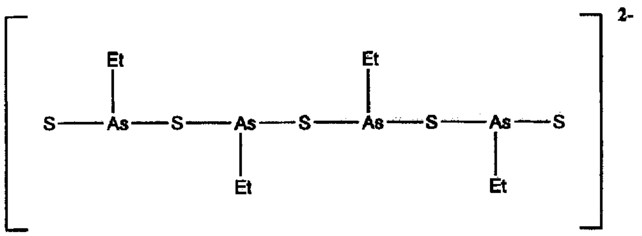


Figure 2. Signals of the ethyl protons in the ^{1}H-NMR spectrum of **1** taken 12 h after the complex was dissolved in $CDCl_3$

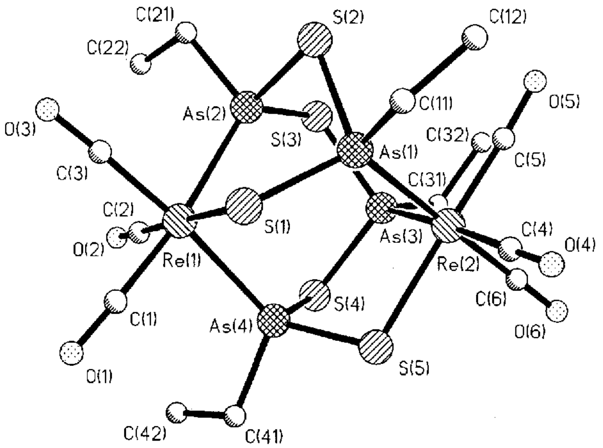


Scheme 1. $Et_4As_4S_5^{2-}$


$$\left[S-\underset{}{\overset{Et}{As}}-S-\underset{Et}{As}-S-\overset{Et}{As}-S-\underset{Et}{As}-S\right]^{2-}$$

In contrast to the retention of an intact cyclotetramer observed in **1**, treatment of [ReBr(CO)$_5$] with $(C_2H_5AsS)_n$ in toluene at reflux leads to As–S bond cleavage and formation of the novel chain $Et_4As_4S_5^{2-}$, which is stabilised as a bridging hexadentate ligand in the dinuclear complex [{Re(CO)$_3$}$_2${μ-($Et_4As_4S_5$)}] (**2**, Figure 3). A possible reaction mechanism would involve an initial bidentate coordination of each of the Re atoms by alternating As atoms of the preferred cyclooligomer $(C_2H_5As)_4$, followed by nucleophilic attack of S^{2-} on As(1) or As(4). The driving force for the formation of **2** is presumably provided by the stability of the resulting Re–S(thiolate) bonds. The As–S(thiolate) distances of 2.167(4) and 2.154(4) Å are, as expected, significantly shorter than the bridging As–S(As) distances in the range 2.217(5)–2.285(5) Å. Interestingly a marked widening is observed for the central As–S–As angle [As(2)–S(3)–As(3), 99.2(2)°] in comparison to the average value of 96.6(9)° established for $(C_2H_5AsS)_4$. The relevant As–S bonds participate in two six-membered chelate rings. In contrast, the As(1)–S(2)–As(2) [91.3(2)°] and As(3)–S(4)–As(4) [92.2(2)°] angles, which are endocyclic to five-membered chelate rings, are somewhat smaller than in the free cycloarsathianes. With the exception of the As–Re–As angles [100.1(1), 99.2(1)°] little deviation [85.3(4)–92.0(5)°] from the idealised octahedral value is observed for the rhenium centres. **2** exhibits effectively C_2 symmetry in the crystal lattice and this symmetry is retained in solution as confirmed by the presence of only two resonances for the CH_2 and CH_3 groups in both the ^{1}H- and ^{13}C-NMR spectra.

Figure 3. Molecular structure of **2**. Selected bond lengths [Å] and angles [°]: Re(1)–As(2) 2.552(2), Re(1)–As(4) 2.571(2), Re(1)–S(1) 2.485(5), Re(2)–As(1) 2.561(2), Re(2)–As(3) 2.555(2), Re(2)–S(5) 2.493(4), As(1)–S(1) 2.167(4), As(1)–S(2) 2.285(5), As(4)–S(5) 2.154(4), As(4)–S(4) 2.284(4), As(2)–S(2) 2.218(6), As(2)–S(3) 2.235(4), As(3)–S(3) 2.242(4), As(3)–S(4) 2.217(5); As(1)–S(2)–As(2) 91.3(2), As(2)–S(3)–As(3) 99.2(2), As(1)–S(4)–As(4) 92.2(2)



The increased degree of π back bonding to the carbonyl ligands in **2** in comparison to the starting compound $[ReBr(CO)_5]$ is reflected in the observed shifts of the ν(CO) frequencies. For **2** values of 2038, 1980, 1958, and 1819 cm^{-1} were recorded, which are on average significantly narrower than in $[ReBr(CO)_5]$[13] with values of 2150, 2044, and 1985 cm^{-1}. The ^{13}C-NMR chemical shifts for **2** appear also at lower field compared to the *trans* sited carbonyl groups in $[ReBr(CO)_5]$ (**2**: δ = 186.34, 187.19, 188.80; $[ReBr(CO)_5]$[14] δ = 177.0). A similar phenomenon was previously observed in the compounds $[\{M(CO)_3\}_2\{$*cyclo*-$(EtAsO)_6\}]$[1] (M = Cr, Mo, W).

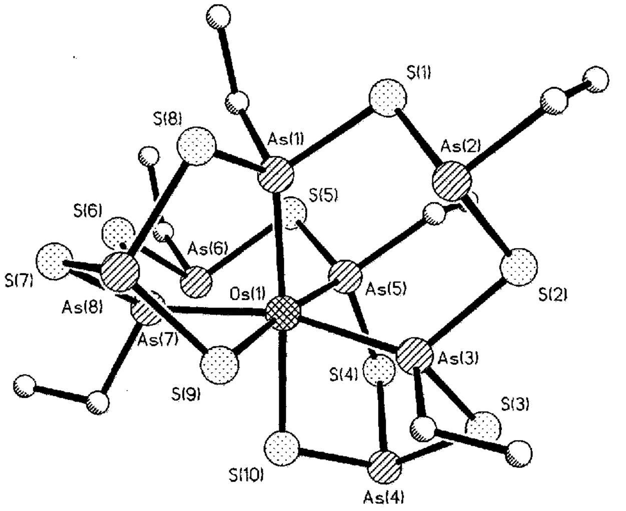
Small As–S ligands such as As_2S, As_2S_2, and As_2S_3 have been prepared by reaction of As_4S_4 and As_4S_3 with reactive transition metal complexes[15,16]. Treatment of As_4S_4 with MoS_4^{2-} allows the isolation of the complex anion $[Mo_2O_2S_2(\mu\text{-}As_4S_{12})]^{2-}$, in which the familiar $Mo_2O_2S_2^{2+}$ fragment is strapped by a tetradentate $As_4S_{12}^{4-}$ ligand containing a central As_2S_6 eight-membered ring[17]. Our preparation of **2** with its bridging $Et_4As_4S_5^{2-}$ unit suggests that cycloarsathianes could offer a copious source of novel As–S ligands in carbonyl transition metal complexes.

Macrocyclic As–S Ligands

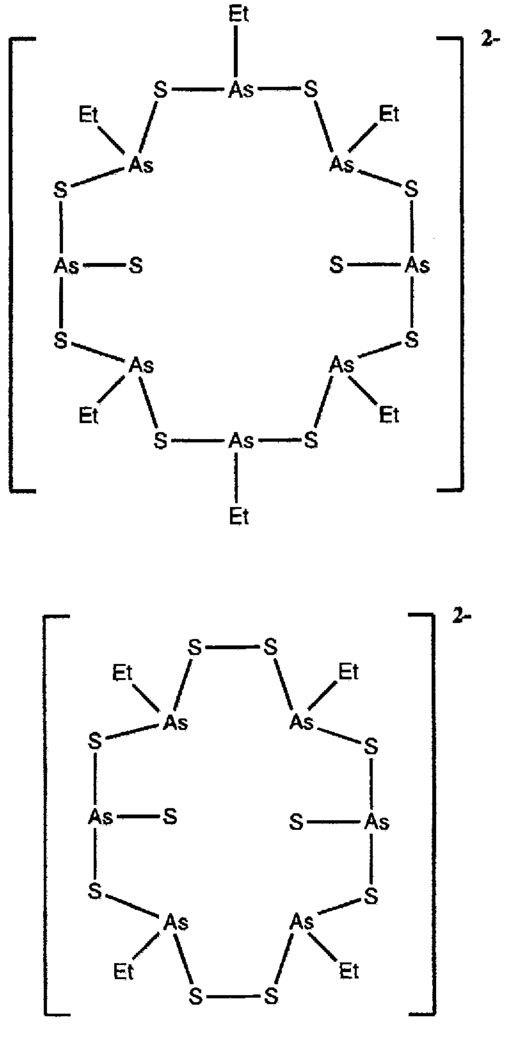
In view of the well-known stability of M–S(thiolate) bonds for transition metals M in lower oxidation states, it was of interest to establish whether treatment of $(C_2H_5AsS)_n$ with transition metal halides such as $OsCl_3$ or $RuCl_3$ can also lead to a metal-mediated assembly of As–S ligands. We found that the reaction of MCl_3 (M = Os, Ru) with $(C_2H_5AsS)_n$ in toluene in a Carius tube at respectively 140 °C (70 h) or 105 °C (24 h) leads to the formation of the coloured crystalline products **3** and **4**, which are insoluble in all common organic solvents. Attempts to separate further soluble products from the reaction mixture by column chromatography were unsuccessful. Compounds **3** and **4** are isostructural and crystallize in the monoclinic space group *C2/c*. As the crystal quality of **4** was poor, structural details will only be discussed for the Os(II) complex **3** (Figure 4), which contains the novel hexadentate macrocyclic ligand $Et_6As_8S_{10}^{2-}$. Bond angles in the range 80.5(2)–101.2(1)° are observed for the distorted octahedral coordination sphere at the central metal atom. Limiting values are provided by the As(3)–Os(1)–S(10) and As(7)–Os(1)–S(9) angles [80.5(2), 82.3(3)°], which belong to five-membered chelate rings, and the As(1)–Os(1)–As(3) and As(5)–Os(1)–As(7) angles [101.2(1), 100.5(1)°], which are endocyclic to six-membered chelate rings. As–S–As angles in the 16-membered $(AsS)_8$ ring may be compared with the average value of 96.6(9)° in $(C_2H_5AsS)_4$, with those in the five-membered chelate rings in the range 95.3(4)–97.9(4)° being similar, those in six-membered chelate rings in the range 99.6(4)–101.7(4)° wider. In contrast, the S–As–S angles [94.3(2)–100.7(4)°] are narrowed in comparison to the average value of 103.2(6) for $(C_2H_5AsS)_4$. As is to be expected, the As–S(thiolate) distances to the *cis*-coordinated sulphur atoms S(9) and S(10) [2.194(11), 2.212(10) Å] are shorter than the bridging As–S(As) distances in the range 2.234(9)–2.286(9) Å, which are typical for As–S rings and cages. *Trans* influences are apparent for the bond distances in the Os coordination sphere, with the *cis*-sited Os(1)–As(1) and Os(1)–As(5) bonds [2.414(4), 2.412(4) Å] being significantly shorter than the *trans*-sited Os(1)–As(3) and Os(1)–As(7) bonds [2.450(4), 2.449(3) Å].

The reduction of M(III) to M(II) (M = Os, Ru) required for the preparation of complexes **3** and **4** poses the question as to the nature of the accompanying oxidation. It seems reasonable to assume that S–S bond formation will be involved and this hypothesis is, at least, partially substantiated by the isolation of a second Ru(II) complex $[Ru\{$*cyclo*-$(Et_4As_6S_{10})\}]$ (**5**), obtained by employment of a longer reaction time (70 h) at higher temperature (140 °C).

Figure 4. Molecular structure of **3**. Selected bond lengths [Å] and angles [°]: Os(1)–As(1) 2.414(4), Os(1)–As(3) 2.450(4), Os(1)–As(5) 2.412(4), Os(1)–As(7) 2.449(3), Os(1)–S(9) 2.400(11), Os(1)–S(10) 2.414(9), As(4)–S(10) 2.212(10), As(8)–S(9) 2.194(11)

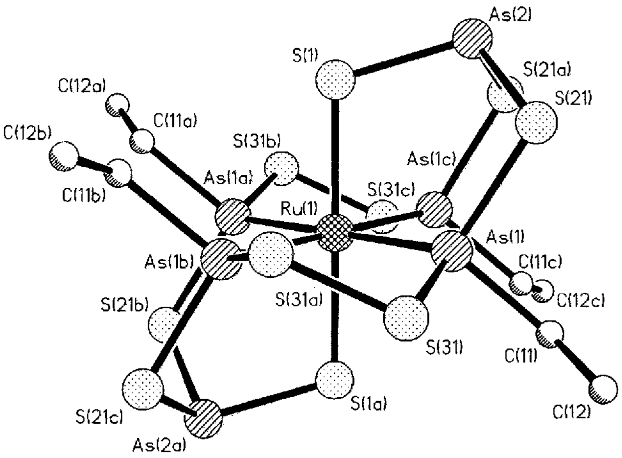


Scheme 2. $Et_6As_8S_{10}^{2-}$ and $Et_4As_6S_{10}^{2-}$



An analogous Os(II) complex could not be prepared, even at considerably higher temperature (200 °C). The novel 14-membered ring of the hexadentate macrocyclic ligand $Et_4As_6S_{10}^{2-}$, which exhibits crystallographic C_{2h} symmetry with As(2) and S(1) in a mirror plane, is smaller than in **3**/**4** and contains two S–S bonds. Disorder is observed for the sulphur atoms and the ethyl group attached to As(1); site occupation factors of 0.5 were assigned to the atoms S(21)/S(22), S(31)/S(32), C(11)/C(12), and C(21)/C(22), which were refined under bond length constraints. The molecular dimensions of the macrocyclic ligand will therefore not be discussed in detail. In contrast to **3**/**4**, the thiolate sulphur atoms S(1)/S(1a), are sited *trans* to one another in complex **5**, which contains only five-membered chelate-rings. The 14-membered ring is effectively perfectly dimensioned for octahedral coordination of Ru(II), as evidenced by the similar Ru–As and Ru–S distances [2.391(2), 2.378(6) Å] and the very minor deviations [88.7(1)–91.3(1)°] from the idealised octahedral angle. This finding is in accordance with the assumed relative thermodynamic stability of **5** in comparison to **4**, which can be presumed to be an intermediate product on the route to the former complex.

Figure 5. Molecular structure of **5**. Selected bond lengths [Å] and angles [°]: Ru(1)–As(1) 2.391(2), Ru(1)–S(1) 2.378(6), As(2)–S(1) 2.181(6)



Our present work indicates that intact cycloarsathianes may be stabilised in the coordination sphere of transition metals under mild conditions. At elevated temperature ring cleavage and metal-assisted assembly can afford novel macrocyclic ligands, particularly well-adapted for the coordination of the directing metal atom.

Experimental

All manipulations were carried out in an Ar atmosphere in carefully dried solvents. – FAB MS: Fisons VG Autospec with 3-nitrobenzyl alcohol as matrix. – ^1H, ^{13}P NMR: Bruker AM 400. – FT-IR[18]: Perkin-Elmer 1700 and 1760. – Elementary analyses: Carlo Erba 1106. – *cyclo*-$(C_2H_5AsS)_n$ was prepared by the reaction of $(C_2H_5AsO)_n$ with H_2S as described previously[11].

[RuCl$_2${cyclo-(C$_2$H$_5$AsS)$_4$}(Ph$_3$P)] (**1**): A solution of *cyclo*-$(C_2H_5AsS)_n$ (0.120 g, 0.22 mmol for n = 4) and $[RuCl_2(Ph_3P)_3]$[19]

(0.211 g, 0.22 mmol) in 5 ml of CH_2Cl_2 was stirred at room temperature for 2 h. After a few minutes the colour changed from brown to deep-red. The volume was reduced to 1.5 ml and the solution covered with hexane to afford **1** as a red crystalline product. Yield 0.049 g (21%). – $C_{26}H_{35}As_4Cl_2PRuS_4$ (978.5): calcd. C 31.9, H 3.6; found C 32.8, H 4.4. – FAB MS; *m/z* (%): 980 (2) [M^+], 943 (7) [$M^+ - Cl$], 839 (3) [$M^+ - Cl - C_2H_5As$]. – IR (KBr): $\tilde{\nu}$ = 1483 cm^{-1} (s), 1450 (s), 1434 (vs), 1212 (s), 1090 (s), 1030 (s), 753 (vs), 729 (vs), 699 (vs), 527 (vs), 512 (vs), 496 (s), 409 (vs), 383 (vs), 351 (vs).

[{Re(CO)$_3$}$_2${μ-(Et$_4$As$_4$S$_5$)}] (**2**): A solution of *cyclo*-$(C_2H_5AsS)_n$ (0.262 g, 0.48 mmol for $n = 4$) and [$ReBr(CO)_5$] (0.087 g, 0.21 mmol) was heated with stirring in 10 ml of toluene at reflux for 5 min. The volume was reduced to 2 ml and the yellow solution covered with hexane to afford **2** as a yellow crystalline product. Yield 0.051 g (43%). – $C_{14}H_{20}As_4O_6Re_2S_5$ (1116.7): calcd. C 15.1, H 1.8; found C 14.9, H 1.5. – FAB MS; *m/z* (%): 1117 (1) [M^+], 1089 (1) [$\{Re(CO)_3\}_2(Et_3As_4S_5)]^+$, 818 (1) [$\{Re(CO)_3\}(Et_4As_4S_5)]^+$, 547 (7) [$(Et_4As_4S_5)]^+$, 515 (10) [$(Et_4As_4S_4)]^+$. – ^1H NMR ($CDCl_3$): δ = 1.32 (t, 6H, CH_2CH_3), 1.35 (t, 6H, CH_2CH_3), 2.21 (q, 4H, CH_2CH_3), 2.37 (q, 4H, CH_2CH_3). – ^{13}C NMR ($CDCl_3$): δ = 10.74, 12.35 (2 s, CH_2CH_3), 35.13, 36.01 (2 s, CH_2CH_3), 186.34, 187.19, 188.80 (3 s, C=O). – IR (KBr): $\tilde{\nu}$ = 2038 cm^{-1} (vs), 1980 (s), 1958 (vs), 1919 (vs) (C≡O), 1449 (m), 1029 (m), 718 (w), 610 (m), 590 (m), 511 (w), 467 (w), 452 (w), 427 (m), 379 (m), 348 (m).

[Os{cyclo-(Et$_6$As$_8$S$_{10}$)}] (**3**): $OsCl_3$ (0.135 g, 0.45 mmol) was combined in a Carius tube (Duran glass, medium-walled 4 mm, diameter 16 mm, length 12 cm, volume approximately 10 cm^3) with *cyclo*-$(C_2H_5AsS)_n$ (0.497 g, 0.91 mmol for $n = 4$) dissolved in 1.5 ml of toluene. The tube was flame sealed, heated at 140°C for 70 h and allowed to cool slowly to room temperature. After opening, the solid product was filtered off and washed with methanol to afford red-brown **3**. Yield 0.098 g (17%). – $C_{12}H_{30}As_8O_5S_{10}$ (1284.5): calcd. C 11.2, H 2.3; found C 10.0, H 1.4. – IR (KBr): $\tilde{\nu}$ = 1445 cm^{-1} (s), 1373 (s), 1220 (s), 1029 (s), 722 (s), 710 (s), 403 (s), 389 (s), 347 (s).

[Ru{cyclo-(Et$_6$As$_8$S$_{10}$)}] (**4**): $RuCl_3 \cdot 3\ H_2O$ (0.104 g, 0.40 mmol) was combined in a Carius tube (see **3** above) with *cyclo*-$(C_2H_5AsS)_n$ (0.455 g, 0.84 mmol for $n = 4$) dissolved in 1.5 ml of toluene. The tube was flame sealed, heated at 105°C for 24 h and allowed to cool slowly to room temperature. After opening, the yellow-brown solid was filtered off and washed with methanol to afford **4**. Yield 0.321 g (64%). – $C_{12}H_{30}As_8RuS_{10}$ (1195.5): calcd. C 12.1, H 2.5; found C 12.3, H 2.1. – IR (KBr): $\tilde{\nu}$ = 1445 cm^{-1} (s), 1374 (s), 1220 (s), 1029 (s), 722 (s), 711 (s), 404 (s), 387 (s), 347 (s).

[Ru{cyclo-(Et$_4$As$_6$S$_{10}$)}] (**5**): $RuCl_3 \cdot 3\ H_2O$ (0.067 g, 0.26 mmol) was added to a 1.5 ml toluene solution of *cyclo*-$(C_2H_5AsS)_n$ (0.290 g, 0.53 mmol for $n = 4$) in a Carius tube (see **3** above). The tube was flame sealed, heated to 140°C for 70 h and allowed to cool slowly to room temperature. After opening, the solid product was filtered off and washed with methanol to afford red-coloured crystals of **5**. Yield 0.067 g (25%). – $C_8H_{20}S_{10}As_6Ru$ (987.4): calcd. C 9.7, H 2.0; found C 9.8, H 1.6. – IR (KBr): $\tilde{\nu}$ = 1436 cm^{-1} (s), 1372 (m), 1218 (s), 1027 (s), 721 (s), 696 (s), 638 (s), 543 8s), 521 (s), 403 (s), 387 (m), 347 (m).

X-Ray Structural Analyses: Siemens P4 diffractometer, graphite monochromator, Mo-K_α radiation (λ = 0.71073 Å), SHELXTL PLUS programs[17] for structure solution by direct methods and refinement by full-matrix least-squares. Semi-empirical absorption corrections were applied to the intensity data by use of ψ-scans. Hydrogen atoms were included at calculated positions with group isotropic temperature factors for **1** (phenyl rings), **2**, and **3** (ethyl groups)[18].

1 · 1/2 CH_2Cl_2: $C_{26}H_{35}As_4Cl_2PRuS_4 \cdot 0.5\ CH_2Cl_2$, M = 1020.9, monoclinic, space group $P2_1/n$, a = 12.293(4), b = 20.744(5), c = 15.090(5) Å, β = 92.58(3)°, V = 3844(3) Å^3, Z = 4, $D_{calcd.}$ = 1.764 g · cm^{-3}, μ = 4.31 mm^{-1}. Crystal size 0.44 × 0.52 × 0.62 mm; ω-scan, scan range: 2Θ ≤ 55° ($0 \leq h \leq 15, 0 \leq k \leq 26, -19 \leq l \leq 19$), 9338 reflections collected, 8710 symmetry-independent reflections (R_{int} = 0.032), max./min. transmission: 0.108/0.072; 369 parameters refined; $w^{-1} = \sigma^2(F_o) + 0.0001\ F_o^2$, R = 0.057, R_w = 0.054 for 4772 reflections with $F_o^2 > 2\sigma(F_o^2)$; largest difference peak: 1.25 eÅ^{-3}. Anisotropic temperature factors for the Ru, As, Cl, S, and P atoms.

2: $C_{14}H_{20}As_4O_6Re_2S_5$, M = 1116.7, triclinic, space group $P\bar{1}$, a = 9.528(2), b = 10.796(2), c = 14.507(3) Å, α = 77.46(2), β = 82.94(2), γ = 73.10(1)°, V = 1390.9(5) Å^3, Z = 2, $D_{calcd.}$ = 2.666 g · cm^{-3}, μ = 13.82 mm^{-1}. Crystal size: 0.20 × 0.30 × 0.32 mm; ω-scan, scan range: 2Θ ≤ 50° ($0 \leq h \leq 11, -11 \leq k \leq 12, -16 \leq l \leq 17$), 4874 symmetry-independent reflections collected; max./min. transmission: 0.072/0.037; 194 parameters refined; $w^{-1} = \sigma^2(F_o) + 0.0001\ F_o^2$, R = 0.054, R_w = 0.050 for 3788 reflections with $F_o^2 > 2\sigma(F_o^2)$; largest difference peak: 1.87 eÅ^{-3}. Anisotropic temperature factors for the Re, As, and S atoms.

3: $C_{12}H_{30}As_8OsS_{10}$, M = 1284.5, monoclinic, space group $C2/c$, a = 35.664(7), b = 10.738(2), c = 17.688(4) Å, β = 107.18(2)°, V = 6472(2) Å^3, Z = 8, $D_{calcd.}$ = 2.637 g · cm^{-3}, μ = 12.71 mm^{-1}. Crystal size: 0.28 × 0.40 × 0.52 mm; ω-scan, scan range: 2Θ ≤ 47.5 ($0 \leq h \leq 40, 0 \leq k \leq 12, -20 \leq l \leq 18$), 5233 reflections collected, 4859 symmetry-independent reflections (R_{int} = 0.054); max./min. transmission: 0.024/0.005; 241 parameters refined; $w^{-1} = \sigma^2(F_o) + 0.0001\ F_o^2$, R = 0.086, R_w = 0.084 for 2926 reflections with $F_o^2 > 2\sigma(F_o^2)$; largest difference peak: 3.13 eÅ^{-3}. Anisotropic temperature factors for the Os, As, and S atoms.

4: $C_{12}H_{30}As_8RuS_{10}$, M = 1195.5, monoclinic, space group $C2/c$, a = 35.778(7), b = 10.725(2), c = 17.685(6) Å, β = 107.24(3)°, V = 6481(4) Å^3, Z = 8, $D_{calcd.}$ = 2.392 g · cm^{-3}, μ = 9.25 mm^{-1}. **4** is isostructural with **3**.

5: $C_8H_{20}As_6RuS_{10}$, M = 987.4, orthorhombic, space group $Cmca$, a = 18.401(6), b = 13.690(5), c = 10.609(4) Å, V = 2672(1) Å^3, Z = 4, $D_{calcd.}$ = 2.454 g · cm^{-3}, μ = 8.74 mm^{-1}. Crystal size: 0.14 × 0.40 × 0.46 mm; ω-scan, scan range: 2Θ ≤ 50° ($-21 \leq h \leq 0, 0 \leq k \leq 16, -12 \leq l \leq 0$), 1335 symmetry-independent reflections collected; max./min. transmission: 0.112/0.052; 80 parameters refined; $w^{-1} = \sigma^2(F_o) + 0.0004\ F_o^2$, R = 0.063, R_w = 0.069 for 751 reflextions with $F_o^2 > 2\sigma(F_o^2)$; largest difference peak: 1.32 eÅ^{-3}. The coordination sphere of As(1) is disordered; site occupation factors of 0.5 were employed for the atoms C(11)/C(12), C(21)/C(22) (ethyl group), S(21)/S(22) and S(31)/S(32). Anisotropic temperature factors for the Ru, As, and S atoms.

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[1] W. S. Sheldrick, T. Häusler, *Z. Naturforsch. Teil B* **1993**, *48*, 1069.
[2] W. S. Sheldrick, T. Häusler, *Z. Anorg. Allg. Chem.* **1993**, *619*, 1984.
[3] W. S. Sheldrick, T. Häusler, *Z. Anorg. Allg. Chem.* **1994**, *620*, 334.
[4] M. Durand, J.-P. Laurent, *J. Organomet. Chem.* **1974**, *77*, 225.
[5] A. L. Rheingold, A.-J. DiMaio, *Organometallics* **1986**, *5*, 393.
[6] S. R. Cooper, S. C. Rawle, *Struct. Bonding (Berlin)* **1990**, *72*, 1; A. J. Blake, M. Schröder, *Adv. Inorg. Chem.* **1990**, *35*, 1.
[7] A. von Baeyer, *Liebigs Ann.* **1858**, *107*, 279.
[8] A. J. DiMaio, A. L. Rheingold, *Inorg. Chem.* **1990**, *29*, 798.
[9] J. T. Share, W. T. Pennington, A. W. Cordes, *Acta Crystallogr. Sect. C* **1988**, *41*, 1831.

[10] G. Bergerhoff, H. Namgung, *Z. Kristallogr.* **1979**, *150*, 209.

[11] T. Häusler, W. S. Sheldrick, *Z. Naturforsch. Teil B* **1994**, *49*, 1215.

[12] A. M. Arif, A. H. Cowley, M. Pakulski, *J. Chem. Soc., Chem. Commun.* **1987**, 165.

[13] E. W. Abel, I. S. Butler, *Trans. Farad. Soc.* **1967**, *63*, 45.

[14] M. J. Webb, W. A. G. Graham, *J. Organomet. Chem.* **1975**, *65*, 119.

[15] M. DiVaira, P. Stoppioni, *Coord. Chem. Rev.* **1992**, *120*, 259; M. DiVaira, P. Stoppioni, M. Perazzini, *Inorg. Chim. Acta* **1987**, *132*, 37.

[16] I. Bernal, H. Brunner, W. Meier, H. Pfisterer, J. Wachter, M. L. Ziegler, *Angew. Chem.* **1984**, *96*, 428; H. Brunner, H. Kavermann, B. Nuber, J. Wachter, M. L. Ziegler, *Angew. Chem.* **1986**, *98*, 551; H. Brunner, L. Poll, J. Wachter, B. Nuber, *J. Organomet. Chem.* **1994**, *471*, 117.

[17] G. A. Zank, T. B. Rauchfuss, S. R. Wilson, *J. Am. Chem. Soc.* **1984**, *106*, 7621.

[18] T. Häusler, *Dissertation*, Ruhr-Universität Bochum, **1995**.

[19] R. K. Poddar, U. Agarwala, *Indian J. Chem.* **1971**, *9*, 477.

[20] *SHELXTL PLUS*, Siemens Analytical X-ray Instruments, Madison, Wi; **1991**.

[21] Further details of the crystal structure investigations are available on request from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, with specification of the deposition numbers CSD-380078–380081, the names of the authors, and the journal reference.

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