σ–η^2 Transformation of an Electron-rich Thioarsenic Heterocyclic Ligand: *X*-Ray Crystal Structure of $[Mo(\eta^2\text{-}\overline{AsSCH_2CH_2S})(CO)_2(\eta\text{-}C_5H_5)]$

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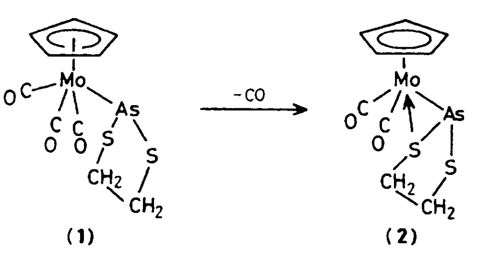
Photolysis of the complex $[Mo(\sigma\text{-}\overline{AsSCH_2CH_2S})(CO)_3(\eta\text{-}C_5H_5)]$ causes elimination of carbon monoxide and formation of $[Mo(\eta^2\text{-}\overline{AsSCH_2CH_2S})(CO)_2(\eta\text{-}C_5H_5)]$ in which the ring behaves as a di-hapto, formally three-electron donor.

Many transition metal complexes of arsenido ($-AsR_2$) ligands have reactivity consequential upon the basicity endowed by the arsenic lone pair of electrons.[1,2] The most common result is the dimerization of many species by displacement of carbon monoxide, though more recently the intramolecular loss of carbon monoxide has produced the species $[Mo(AsBu^t{}_2)(CO)_2(\eta\text{-}C_5H_5)]$ in which the arsenic atom has in effect formed a double bond to the molybdenum.[3] Evidence has been presented for the analogous $[Mo(AsMe_2)(CO)_2(\eta\text{-}C_5H_5)]$ to exist at low temperature.[4]

We are currently investigating a range of acyclic and cyclic electron rich ligands, amongst which we class the $\overline{CH_2\text{–}S\text{–}As\text{–}S\text{–}CH_2}$ cyclic cation, with nominally five available donor lone pairs of electrons. Interaction of the cation with several organometallic anions has resulted in arsenic–metal bonded arsenido type species analogous to the corresponding di-oxo complexes previously reported.[5,6] Exemplary of this class of complex is $[Mo(\sigma\text{-}\overline{AsSCH_2CH_2S})(CO)_3(\eta\text{-}C_5H_5)]$ (**1**), which undergoes loss of carbon monoxide upon photolysis to generate the novel product $[Mo(\eta^2\text{-}\overline{AsSCH_2CH_2S})(CO)_2(\eta\text{-}C_5H_5)]$ (**2**).

Analytical data and mass spectrometry indicated the loss of carbon monoxide; in the i.r. spectra the CO stretching modes changed from 2007, 1945, and 1925 cm^{-1} to 1945 and 1878 cm^{-1}. In (**1**), the non- or very slow-inversion about the arsenic atom renders the hydrogen atoms on opposite faces of the heterocyclic ring non-equivalent, resulting in an A_2B_2 spectrum. Solutions of the bright red crystals of (**2**) show a more complicated ABCD ^1H n.m.r. spectrum. These data strongly suggested the structure shown for (**2**), which has been confirmed by *X*-ray diffraction (Figure 1).†



(**1**) (**2**)

Table 1. A comparison of internal angles in the heterocyclic rings in $[Mo(\eta^2\text{-}\overline{As\text{–}S\text{–}CH_2\text{–}CH_2\text{–}S})(CO)_2(\eta\text{-}C_5H_5)]$ and $Cl\text{–}\overline{Sb\text{–}S\text{–}CH_2\text{–}CH_2\text{–}S}$.

Angle	Free ring	Metal complex
S–Sb(As)–S	92.6(1)	93.3(2)
Sb(As)–S–C	100.3(9)	100.2(3)
S–C–C	111.3(16)	110.3(6)
C–C–S	111.8(17)	112.8(6)
C–S–Sb(As)	96.0(8)	97.4(3)

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† *Crystal data:* $C_9H_9AsO_2S_2$, $M = 384.15$, triclinic, space group $P\bar{1}$ (No. 2), $a = 12.010(3)$, $b = 12.425(1)$, $c = 9.475(1)$ Å, $\alpha = 111.20(1)$, $\beta = 109.16(1)$, $\gamma = 69.07(1)^\circ$, $U = 1198.5(4)$ Å^3, $Z = 4$, $D_c = 2.129$ g cm^{-3}, $F(000) = 744$, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 41.2$ cm^{-1}, crystal dimension $0.63 \times 0.60 \times 0.33$ mm. The structure was solved by the heavy atom technique and refined by full-matrix least-squares, using absorption corrected data [CAD4 diffractometer, Mo-K_α radiation, graphite monochromator, $3 < 2\theta < 50$, $h(-14 \rightarrow 14)$, $k(-14 \rightarrow 14)$, $l(0 \rightarrow 11)$, 4483 reflections, 3750 independent, $I \geqslant 3\sigma(I)$]. The asymmetric unit contains two crystallographically independent but chemically equivalent molecules. All non-hydrogen atoms were refined anisotropically. Methylene hydrogen atoms were placed into calculated positions (C–H 0.96 Å, $U = 0.10$ Å), but those of the cyclopentadiene rings were not included in the model. A total of 271 parameters were refined. The final residuals R and R_w were 0.038 and 0.046 respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

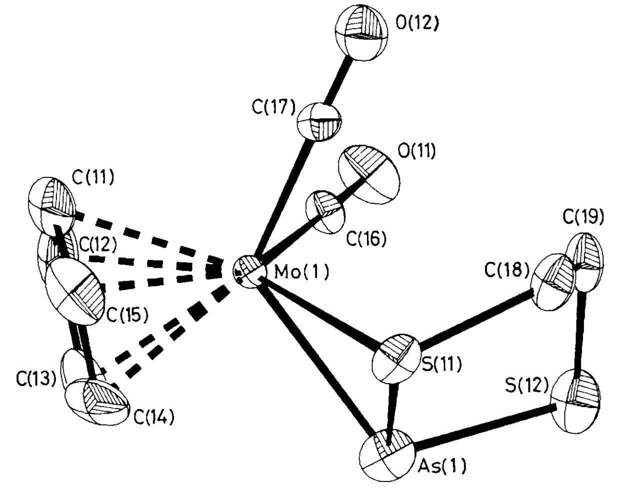

Figure 1. Molecular structure of $[\mathrm{Mo}(\eta^2\text{-}\overline{\mathrm{AsSCH_2CH_2S}})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})]$. Important bond lengths and angles for one of the essentially equivalent molecules in the asymmetric unit are: Mo(1)–As(1) 2.571(4), Mo(1)–S(11) 2.505(5), Mo(1)–C(16) 1.959(8), Mo(1)–C(17) 1.968(8), As(1)–S(11) 2.280(4), As(1)–S(12) 2.252(4), S(11)–C(18) 1.925(9), S(12)–C(19) 1.836(9) Å; As(1)–Mo(1)–S(11) 53.4(1), C(16)–Mo(1)–C(17) 80.6(4)°.

The molecules are composed of the classical $[\mathrm{Mo(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$ fragment to which is bonded the 1,3,2-dithiarsolane ring through the As and one S atom. The geometry about the Mo centre resembles a four-legged piano stool, with the co-ordinated As and S atoms occupying *cis* basal sites. The Mo–As and Mo–S bond lengths are unexceptional, falling in the region previously reported for such contacts.[7,8] Constrained by the As–S bond the As–Mo–S angle is considerably smaller than expected for a typical piano stool complex, whilst the OC–Mo–CO angle is a little larger. Such bonding represents the first step towards the use of such electron-rich rings as polyhapto ligands.

The structure of the unco-ordinated 1,3,2-dithia-arsolane ring has not been determined, but the very closely analogous antimony ring structure is known in 2-chloro-1,3,2-dithiastibolane.[9] A comparison of the geometry about the sulphur atoms in the free and co-ordinated ring systems demonstrates, that the ligand is able to adopt this bidentate bonding mode without strain (Table 1).

An ostensibly similar arsenic–sulphur–metal three-membered ring has been reported[10] in $[\mathrm{W\{As(S)Bu^t_2\}(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$. Here however the arsenic is present as $\mathrm{As^V}$, and geometry about the arsenic is quite different. Bond angles differ by as much as 15° and the multiple nature of the As–S bond is manifest in that it is some 0.11 Å shorter than the corresponding distance in our complex. In the tungsten complex the geometry is pseudo-trigonal bipyramidal with the S in an axial site, whereas in our molybdenum complex the As is clearly tetrahedral.

Received, 2nd February 1987; Com. 121

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