Some Transition-metal Complexes of 1,3,2-Dithiarsolane *

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Reaction of a range of transition-metal carbonyl anions $[M]^-$ with 2-chloro-1,3,2-dithiarsolane results in the formation of the metalloarsines $[M\text{-}AsSCH_2CH_2S]$ $\{M^- = [Mo(CO)_3(\eta\text{-}C_5H_5)]^-$, $[W(CO)_3(\eta\text{-}C_5H_5)]^-$, $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$, $[Mn(CO)_5]^-$, or $[Re(CO)_5]^-\}$. There is no indication on an n.m.r. time-scale of pyramidal inversion about the arsenic atom in these complexes. Photolysis of $[Mo(\sigma\text{-}AsSCH_2CH_2S)(CO)_3(\eta\text{-}C_5H_5)]$ causes elimination of carbon monoxide and formation of $[Mo(\eta^2\text{-}AsSCH_2CH_2S)(CO)_2(\eta\text{-}C_5H_5)]$ in which the dithiarsolane ring behaves as a dihapto, formally, three-electron donor. The reaction of 2-chloro-1,3,2-dithiarsolane with $[Co(CO)_4]^-$ produces the dihapto product $[Co(\eta^2\text{-}AsSCH_2CH_2S)(CO)_3]$ directly.

Two main synthetic routes have been employed in the formation of transition-metal complexes of the arsenido ligand $(\text{-}AsR_2)$. The homolytic fission of a diarsine in the presence of a transition-metal complex[1] has been largely superceded by halide displacement from a halogenoarsine precursor.[2] Recent research has continued to highlight the basicity of the arsenic atom in such metalloarsines. The earlier, well documented[3] dimerisation of mononuclear complexes into species containing bridging arsenido ligands has been supplemented in this respect with the isolation of heterometallic binuclear species,[4] mononuclear borane adducts,[5] quaternisation at the arsenic atom,[6] and the formation of metal–arsenic multiple bonds in mononuclear complexes.[7].

As part of a continuing research programme into electron-rich ligands, we have already reported the formation of a range of transition-metal complexes with open chain arsenic–sulphur substrates, which have resulted in a variety of terminal and bridging modes for these ligands.[8]

In this paper we demonstrate the utilisation of 2-chloro-1,3,2-dithiarsolane[9] as a precursor to M–As bonded complexes of the ligand. This constitutes the first step in the use of such an electron-rich donor as a polyhapto ligand.

Experimental

Materials.—The metal carbonyls $[Mo(CO)_6]$, $[W(CO)_6]$, $[Mn_2(CO)_{10}]$, $[Re_2(CO)_{10}]$, and $[Co_2(CO)_8]$ were obtained commercially and purified by sublimation at 40 °C (0.005 mmHg). The compounds $[Hg\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$,[10] $[\{W(CO)_3(\eta\text{-}C_5H_5)\}_2]$,[11] and $[Fe(CO)_2(\eta\text{-}C_5H_5)I]$[12] were prepared by the literature methods. Reactions with transition-metal carbonyl anions were conducted under an atmosphere of oxygen-free nitrogen using Schlenk techniques. All solvents were rigorously dried and distilled before use.

Infrared spectra of the metal carbonyl region of the complexes were obtained on a Perkin-Elmer 299B spectrometer, and calibrated against the signal of polystyrene at 1 602 cm^{-1}. N.m.r. spectra were recorded on a Bruker AM 250-MHz Fourier-transform spectrometer. Mass spectra were recorded on a V.G. Micromass model MM 16F operating in the electron impact mode. We are grateful to Professor A. H. Jackson of University College, Cardiff for arranging these measurements.

Interaction of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ *and* $ClAsSCH_2CH_2S$.—The compound $[Fe(CO)_2(\eta\text{-}C_5H_5)I]$ (1.2 g, 4 mmol) in tetrahydrofuran (15 cm^3) was treated with sodium amalgam over 90 min to produce a deep red solution of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$. 2-Chloro-1,3,2-dithiarsolane (0.8 g, 4 mmol) in tetrahydrofuran (10 cm^3) was cooled to −78 °C and to this solution was added the solution of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$. The mixture slowly (30 min) turned yellow and was then filtered through a Celite pad. Volatiles were removed under vacuum. The residue was extracted into diethyl ether (10 cm^3) and then filtered through acid-washed Kieselguhr, the filtrate being collected under nitrogen at −78 °C. Diethyl ether was removed under vacuum, and the solid residue dissolved in 20:80 diethyl ether–light petroleum (b.p. 60—80 °C) and chromatographed on alumina. The single yellow band was collected into a vessel at −78 °C and kept at this temperature for 3 h to complete crystallisation. The yellow crystals obtained were separated and dried under vacuum and characterised as $[Fe(AsSCH_2CH_2S)(CO)_2(\eta\text{-}C_5H_5)]$ (Tables 1 and 2).

Interaction of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ *and* $ClAsSCH_2CH_2S$.—The compound $[Hg\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (0.7 g, 1 mmol) in tetrahydrofuran (15 cm^3) was treated with sodium amalgam over 60 min to produce $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$. This solution was decanted from excess of amalgam, and, after filtration through a Celite pad, volatiles were removed under vacuum to leave a pale brown amorphous deposit of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$. To this was added 2-chloro-1,3,2-dithiarsolane (0.4 g, 2 mmol) in methylcyclohexane (50 cm^3). The resulting colourless reaction mixture was stored at −20 °C for 24 h. On warming to room temperature, the orange solution was filtered through a Celite pad. Cooling the filtrate to −78 °C gave fine orange crystals, which were removed and dried under vacuum and characterised as $[Mo(AsSCH_2CH_2S)(CO)_3(\eta\text{-}C_5H_5)]$ (Tables 1 and 2).

Similar techniques were used to prepare $[W(AsSCH_2CH_2S)(CO)_3(\eta\text{-}C_5H_5)]$, $[Mn(AsSCH_2CH_2S)(CO)_5]$, and $[Re(AsSCH_2CH_2S)(CO)_5]$ from $Na[W(CO)_3(\eta\text{-}C_5H_5)]$, $Na[Mn(CO)_5]$, and $Na[Re(CO)_5]$ respectively. They were fully characterised by analysis, i.r., n.m.r., and mass spectroscopy (Tables 1 and 2).

Interaction of $Na[Co(CO)_4]$ *and* $ClAsSCH_2CH_2S$.—A red solution of dicobalt octacarbonyl (0.8 g, 2.5 mmol) in tetrahydrofuran (15 cm^3) was reduced over 60 min with sodium amalgam to give a virtually colourless solution which was decanted from excess of amalgam. To this solution was added 2-chloro-1,3,2-dithiarsolane (1.0 g, 5 mmol) and the reaction

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* *Non-S.I. unit employed:* 1 mmHg ≈ 133 Pa.

Table 1. Characterisation of σ-metal dithiarsolane complexes

Complex	M.p. (°C)	Colour	Analysis [a]/% C	Analysis [a]/% H	Metal–carbonyl stretching bands (cm^{-1})	Molecular ion [b]
$[Mo(AsSCH_2CH_2S)(CO)_3(\eta\text{-}C_5H_5)]$	71 (decomp.)	Orange	29.3 (29.1)	2.3 (2.2)	[c] 2 007, 1 945, 1 925	412
$[W(AsSCH_2CH_2S)(CO)_3(\eta\text{-}C_5H_5)]$	65	Orange	23.8 (24.0)	2.0 (1.8)	[d] 2 000, 1 935, 1 915	500
$[Fe(AsSCH_2CH_2S)(CO)_2(\eta\text{-}C_5H_5)]$	211 (decomp.)	Brown	31.2 (31.4)	2.7 (2.6)	[e] 2 003, 1 960	344
$[Mn(AsSCH_2CH_2S)(CO)_5]$	76	Yellow	23.3 (23.2)	1.1 (1.1)	[c] 2 050, 2 030, 2 010, 2 005	362
$[Re(AsSCH_2CH_2S)(CO)_5]$	87	Yellow	16.5 (17.0)	1.9 (0.8)	[c] 2 023, 2 009, 1 983, 1 977	494

[a] Calculated values in parentheses. [b] In each case ions corresponding to sequential loss of all carbon monoxide groups were observed. [c] In methylcyclohexane. [d] In toluene. [e] In tetrahydrofuran.

Table 2. Proton and ^{13}C n.m.r. data for metal σ-dithiarsolane complexes

Complex	^1H (p.p.m.) δ(H_A)[a]	δ(H_B)[a]	δ(C_5H_5)	$^{13}C\text{-}\{^1H\}$ (p.p.m.) δ(CH_2)[b]	δ(C_5H_5)	δ(CO)
$[Mo(AsSCH_2CH_2S)(CO)_3(\eta\text{-}C_5H_5)]$	2.89	3.07	4.51	43.0	93.3	233.7, 225.3 (1:2 intensity)
$[W(AsSCH_2CH_2S)(CO)_3(\eta\text{-}C_5H_5)]$	2.94	3.07	4.60	43.1	92.2	221.8, 215.5 (1:2 intensity)
$[Fe(AsSCH_2CH_2S)(CO)_2(\eta\text{-}C_5H_5)]$	3.03	3.13	4.04	43.6	85.4	214.1
$[Mn(AsSCH_2CH_2S)(CO)_5]$	3.36	3.39		43.1		Not observed
$[Re(AsSCH_2CH_2S)(CO)_5]$	3.48	3.52		42.5		Not observed

[a] Non-equivalent methylene protons of dithiarsolane ring. [b] Carbon atoms of dithiarsolane ring.

Table 3. Characterisation of η^2-metal dithiarsolane complexes

Complex	Analysis[a]/% C	Analysis[a]/% H	Metal carbonyl stretching bands (cm^{-1})	Molecular ion	^1H N.m.r.[b] (in p.p.m.)	$^{13}C\text{-}\{^1H\}$ N.m.r. (p.p.m.)
$[Mo(\eta^2\text{-}AsSCH_2CH_2S)(CO)_2(\eta\text{-}C_5H_5)]$	27.8 (28.1)	2.4 (2.3)	1 945, 1 878[c]	384	δ(H^1) 2.53 (1) δ(H^2) 2.30 (1) δ(H^3) 1.97 (1) δ(H^4) 1.31 (1)	340.02 (CH_2) 41.15 (CH_2) 90.24 (C_5H_5) 229.69 (CO) 235.55 (CO)
$[Co(\eta^2\text{-}AsSCH_2CH_2S)(CO)_3]$			2 020, 1 980, 1 962[c]	310	δ(H^1) 2.36 (1) δ($H^{2,3}$) 1.90 (2) δ(H^4) 1.12 (1)	

[a] Calculated values in parentheses. [b] Relative intensities in parentheses, $J(H^1H^2)$ = 1.4, $J(H^2H^3)$ = 4.3, $J(H^1H^3)$ = 13.4, $J(H^2H^4)$ = 11.9, $J(H^1H^4)$ = 4.0, and $J(H^3H^4)$ = 12.8 Hz. [c] In tetrahydrofuran solution.

mixture stirred for 30 min. The orange solution was filtered through a Celite pad and volatiles removed under vacuum to leave a brown powder. This residue was dissolved in light petroleum (b.p. 40—60 °C) and chromatographed on an alumina column. Removal of volatiles from the deep orange band gave fine brown crystals (0.31 g, 21%) characterised as $[Co(\eta^2\text{-}AsSCH_2CH_2S)(CO)_3]$ (see Results and Discussion and Table 3).

Photolysis of $[Mo(AsSCH_2CH_2S)(CO)_3(\eta\text{-}C_5H_5)]$.—The compound $[Mo(AsSCH_2CH_2S)(CO)_3(\eta\text{-}C_5H_5)]$ (1.0 g) in light petroleum (80 cm^3), was irradiated by a mercury lamp. The i.r. spectrum in the CO stretching region was monitored during irradiation, and when the bands [ν(CO) 2 007, 1 945, and 1 925 cm^{-1}] of the starting material had been completely replaced by bands at ν(CO) 1 945 and 1 878 cm^{-1} (about 4 h), the volume of liquid was reduced to 20 cm^3 under vacuum and the red solution cooled slowly to −20 °C. Filtration gave red crystals of $[Mo(\eta^2\text{-}AsSCH_2CH_2S)(CO)_2(\eta\text{-}C_5H_5)]$ (Table 3).

Results and Discussion

Equation (1) gives the reaction between 2-chloro-1,3,2-dithiarsolane and a range of metal carbonyl anions, where

$$M^- + ClAsSCH_2CH_2S \longrightarrow M\text{-}AsSCH_2CH_2S + Cl \quad (1)$$

M^- = $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$, $[W(CO)_3(\eta\text{-}C_5H_5)]^-$, $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$, or $[Re(CO)_5]^-$.

The compound $[Mo(\sigma\text{-}AsSCH_2CH_2S)(CO)_3(\eta\text{-}C_5H_5)]$ is a typical product of this reaction, characterised by its elemental analysis, three terminal metal carbonyl signals, and a distinctive computer-simulated parent-ion pattern centred at *m/e* 412 (^{96}Mo). The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum contains two low-field signals (234 and 225 p.p.m.) in a 1:2 intensity ratio which are assigned to the metal carbonyl carbons. This suggests that the complex adopts the piano-stool geometry illustrated in Figure 1. The equivalence of the carbonyl ligands *cis* to the arsenido ligand suggests free rotation about the Mo–As bond.

Our complex $[Fe(AsSCH_2CH_2S)(CO)_2(\eta\text{-}C_5H_5)]$ similarly has only the two strong metal carbonyl absorptions typical of the $Fe(CO)_2(\eta\text{-}C_5H_5)$ fragment. This is in contrast to the four metal carbonyl bands observed in the closely analogous $[Fe(AsOCMe_2CMe_2O)(CO)_2(\eta\text{-}C_5H_5)]$. The latter observation was interpreted[13] as arising from conformational effects about the Fe–As bond.

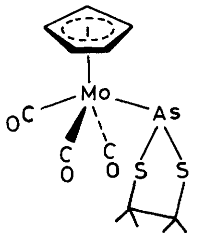


Figure 1. Proposed structure of the monohapto dithiarsolane complex $[Mo(AsSCH_2CH_2S)(CO)_3(\eta\text{-}C_5H_5)]$

In the solid state, closely related species that have been studied by *X*-ray diffraction reveal[14] a puckered ring for the five-membered heterocycle. The ^{13}C n.m.r. spectrum shows the two methylene carbons to be equivalent, suggesting a low-energy ring fluxionality which renders it pseudo-planar on the n.m.r. time-scale. The ring methylene protons are, however, inequivalent, and give rise to the 24-line AA′BB′ spectrum illustrated in Figure 2. This inequivalence arises from the pyramidal geometry about the arsenic(III) imposed by the lone pair. This allows a distinction to be made between the two protons on each carbon; since 'above' and 'below' the plane of the dithiarsolane will remain distinct despite free rotation about the Mo–As bond. Only pyramidal atomic inversion about arsenic would bring about equivalence. No spectroscopic evidence of inversion about arsenic was obtained up to the temperature of decomposition of the complex. The other monohapto dithiarsolane complexes reported in Tables 1 and 2 have remarkably similar AA′BB′ spectra.

The usual consequence of the loss of carbon monoxide from metal carbonyl derivatives of arsenido ligands has been the involvement of the lone pair of electrons on arsenic, either by the

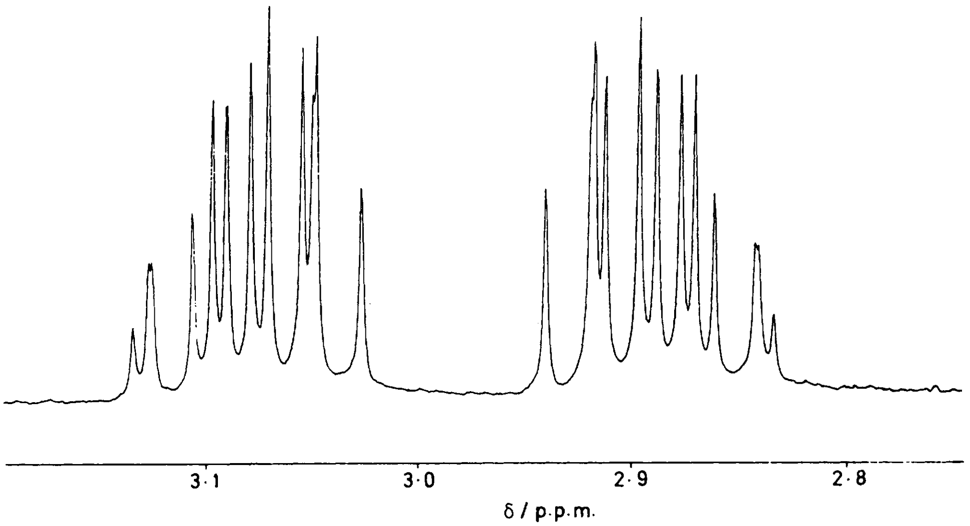


Figure 2. The methylene region of the ^1H n.m.r. spectrum of $[Mo(AsSCH_2CH_2S)(CO)_3(\eta\text{-}C_5H_5)]$

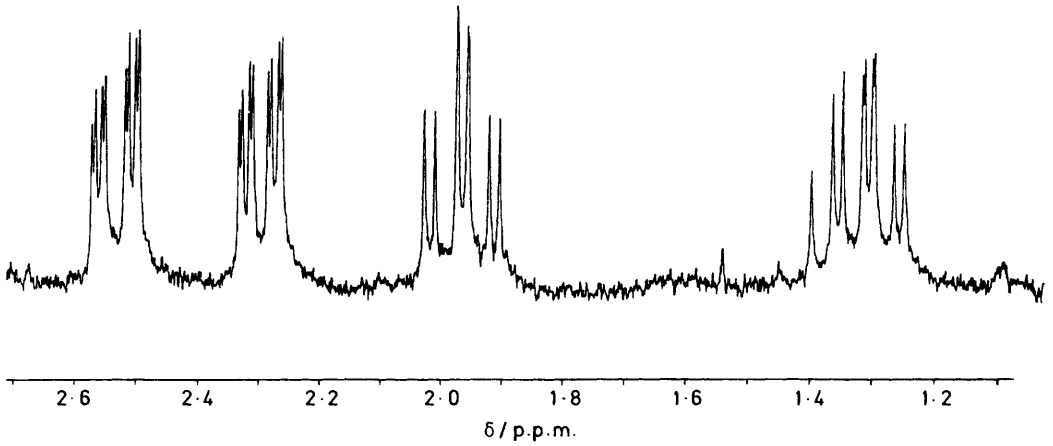
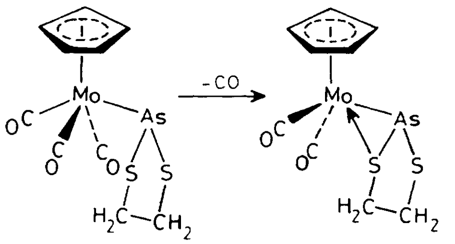


Figure 3. The methylene region of the ^1H n.m.r. spectrum of $[Mo(\eta^2\text{-}AsSCH_2CH_2S)(CO)_2(\eta\text{-}C_5H_5)]$

formation of dimeric species[3] or by the formation of a metal–arsenic multiple bond.[7]

Photolysis of $[\mathrm{Mo}(\sigma\text{-}\overline{\mathrm{AsSCH_2CH_2S}})(\mathrm{CO})_3(\eta\text{-}\mathrm{C_5H_5})]$ in solution caused a darkening of the colour and an accompanying change in the CO stretching frequencies in the i.r. spectrum. Loss of carbon monoxide had brought about the formation of the mononuclear $[\mathrm{Mo}(\eta^2\text{-}\overline{\mathrm{AsSCH_2CH_2S}})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})]$. The $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectrum (Table 3) shows distinctive resonances for the two metal carbonyl groups and also two separate resonances for the carbon atoms in the dithiarsolane ring. The low symmetry of the complex is further illustrated by the $^1\mathrm{H}$ n.m.r. spectrum of the dithiarsolane ring which reveals the four distinct resonances of an ABCD spin system as illustrated in Figure 3. These observations strongly suggested that the displaced carbon monoxide group had been replaced by one of the sulphur atoms of the dithiarsolane ring as illustrated in equation (2). This dihapto structure of $[\mathrm{Mo}(\eta^2\text{-}\overline{\mathrm{AsSCH_2CH_2S}})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})]$ has been confirmed[15] by an *X*-ray crystal study. The geometry about the molybdenum atom retains the four-legged piano-stool configuration, with the co-ordinated As and S atoms occupying *cis* basal sites. We believe this represents the first formation of an arsenic(III)–sulphur–metal ring, though a similar ring containing $\mathrm{As^V}$ has been noted.[2b]



(2)

This use of the sulphur atom to replace the lost carbon monoxide ligand is of particular interest. It contrasts with the loss of carbon monoxide in the corresponding dioxarsolane complexes,[7] where the lone pair of electrons on the arsenic is utilised to form an arsenic–metal multiple bond. This difference in behaviour presumably reflects the greater basicity and size of the sulphur atom for such utilisation.

We have failed to isolate the monohapto species $[\mathrm{Co}(\overline{\mathrm{AsSCH_2CH_2S}})(\mathrm{CO})_4]$ from reaction of the 2-chloro-1,3,2-dithiarsolane with the tetracarbonylcobaltate anion. Whilst the monohapto complex may have been formed as an intermediate step, the complex $[\mathrm{Co}(\overline{\mathrm{AsSCH_2CH_2S}})(\mathrm{CO})_3]$ was isolated. Although this complex proved too unstable for us to obtain high quality elemental analytical data, we were able to characterise it, to our satisfaction, as a dihapto complex analogous to the previously reported molybdenum species. In the ABCD $^1\mathrm{H}$ n.m.r. spectrum (Table 3) two of the component multiplets overlapped to give three resultant multiplets of intensity ratio 1:2:1. There were three sharp metal carbonyl stretching modes and a molecular ion at *m/e* 310 corresponding exactly to the computer simulation for the stoicheiometry of the $[\mathrm{Co}(\eta^2\text{-}\overline{\mathrm{AsSCH_2CH_2S}})(\mathrm{CO})_3]$ molecule.

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