DALTON
FULL PAPER

Group 6 transition metal carbonyl complexes with chalcogen-bridged diarsenic(III) ligands

Linda H. Doerrer,[a] **Jennifer C. Green,**[a] **Malcolm L. H. Green,***[a] **Ionel Haiduc,**[c]
Christian N. Jardine,[a] **Sofia I. Pascu,**[a] **Luminita Silaghi-Dumitrescu**[c] **and David J. Watkin**[b]

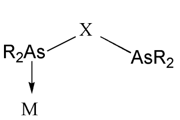
[a] *Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR*
[b] *Chemical Crystallography Laboratory, South Parks Road, Oxford, UK OX1 3PR*
[c] *Department of Chemistry, Babes-Bolyai University Cluj-Napoca, Cluj-Napoca RO-3400, Romania*

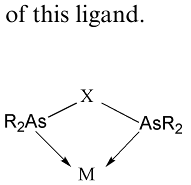
Received 3rd July 2000, Accepted 7th August 2000
First published as an Advance Article on the web 18th September 2000

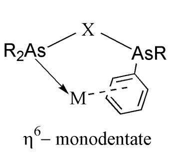
The neutral complexes [$Cr(CO)_4(Ph_2AsOAsPh_2)$] **1**, [$Mo(CO)_4(Ph_2AsOAsPh_2)_2$] **2**, [$Cr(CO)_4(Ph_2AsSAsPh_2)$] **3**, [$Mo(CO)_4(Ph_2AsSAsPh_2)_2$] **4**, [$Cr(CO)_5(Ph_2AsOAsPh_2)$] **5** and [$Cr(CO)_5(Ph_2AsSAsPh_2)$] **6** have been prepared. The crystal structures of compounds **1**–**5** were determined. The diarsenic ligand in **2**, **4**, and **5** is monodentate and in **1** and **3** the ligand is bidentate. The crystal structure of the ligand $Ph_2AsOAsPh_2$ was redetermined and the As–O–As angle found to be 115.98(17)°, significantly less than the value originally reported. Calculations, using density functional theory, assist discussion of the steric and electronic factors influencing the choice of binding mode.

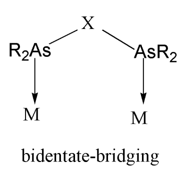
Introduction

Chelating phosphorus(III) ligands of the type R_2PXPR_2 where R = alkyl or aryl and X = CH_2, NH, O or S, are well established in transition metal chemistry[1,2] and the behaviour of this type of ligand towards Group 6 metal carbonyls is well understood.[3–5] The related arsenic(III) ligands $R_2AsXAsR_2$ have also been prepared and characterised,[6–9] however only a few transition metal complexes have been described[10–15] and only isolated examples have crystallographically been characterised, for X = O or S.[12,14,16] Recently, a study on a number of bi- and trimetallic carbonyl complexes containing cobalt of $Ph_2AsOAsPh_2$ and $Me_2AsOAsMe_2$, where these ligands are co-ordinated in a bridging fashion, has been published.[16] We have also reported organoarsenic derivatives with two As^{III} or As^{V} connected by an oxygen or sulfur bridge.[17–19] The various modes of co-ordination that have been found for R_2As^{III}–X–$As^{III}R_2$ ligands (R = alkyl or aryl, X = CH_2, NH, O or S) are shown below. We now report the synthesis and structural investigations of Group 6 metal carbonyl complexes with $Ph_2AsXAsPh_2$ ligands (X = O or S) and density functional theory (DFT) calculations on these systems with the model ligands $H_2AsXAsH_2$. DFT calculations on the $Ph_2AsOAsPh_2$ and $Ph_2AsSAsPh_2$ systems have also been performed. The large difference between the DFT-calculated values of the molecular parameters and those reported in an earlier work on $Ph_2AsOAsPh_2$[20] generated the need to redetermine the crystal structure of this ligand.


monodentate


bidentate chelating


η6– monodentate


bidentate-bridging

Results and discussion

(i) Synthesis

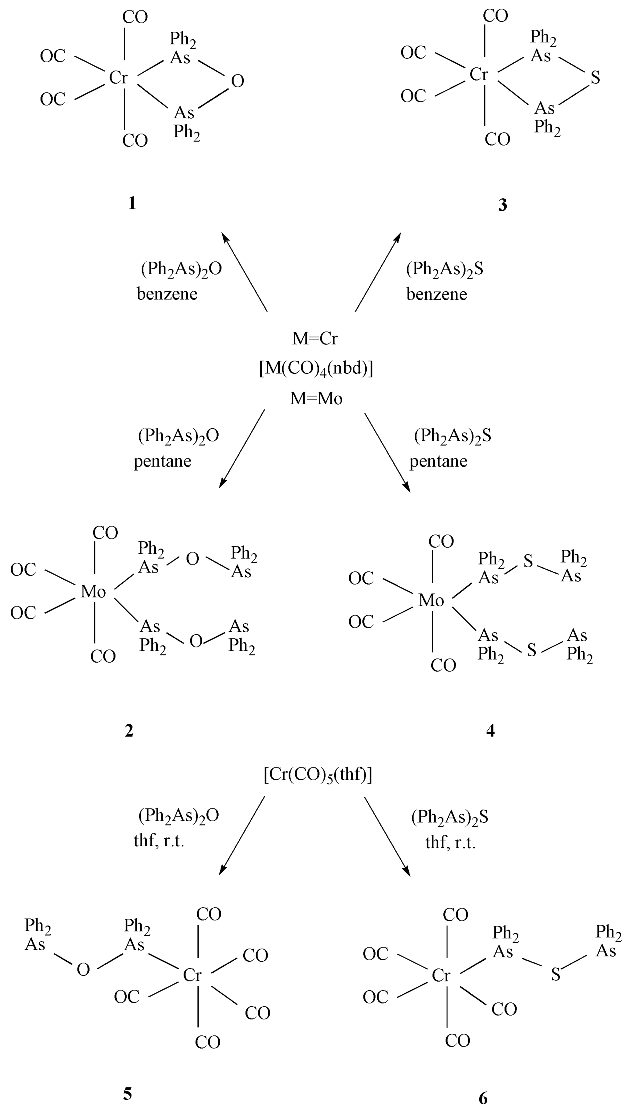
Treatment of [$Cr(CO)_4(nbd)$][21] with one equivalent of $Ph_2AsXAsPh_2$ led to the formation of the complexes [$Cr(CO)_4(Ph_2AsXAsPh_2)$] (**1**, X = O and **3**, X = S).[13] Unexpectedly, the reaction of [$Mo(CO)_4(nbd)$][21] with either one or two equivalents of $Ph_2AsXAsPh_2$ (X = O or S) gave only [$Mo(CO)_4(Ph_2AsXAsPh_2)_2$] (**2**, X = O and **4**, X = S), with the arsenic ligand co-ordinated in a monodentate fashion. The reaction of $Ph_2AsXAsPh_2$ with [$Cr(CO)_6$] in tetrahydrofuran (thf) under photolytic conditions yielded compounds [$Cr(CO)_5(Ph_2AsOAsPh_2)$] **5** and [$Cr(CO)_5(Ph_2AsSAsPh_2)$] **6** (Scheme 1). The progress of reactions was monitored *via* solution IR spectroscopy. Attempts to prepare the molybdenum complexes analogous to **1** and **3** by heating solutions of the ligands in benzene or toluene with [$Mo(CO)_5(thf)$] were unsuccessful and heating **2** and **4** in toluene led to decomposition.

The compounds **1**–**6** are thermally and air stable in the solid state, but solutions exposed to air show slow decomposition. The molybdenum complexes are more air-sensitive than the chromium derivatives, as expected.[22,23] The analytical and spectroscopic data for **1**–**6** are summarised in Table 1.

(ii) Spectroscopy

The ^1H and ^{13}C-{^1H} NMR spectra of complexes **1**–**5** were recorded and details are presented in Table 1. In the ^1H NMR spectra the *ortho*, *meta* and *para* resonances are not always distinguishable. However, the non-chelating co-ordination modes in **2** and **4** generate multiple sets of phenyl resonances due to non-equivalent phenyl groups which are expected on the basis of the structure discussed above. Two sets of phenyl resonances are also observed for **3**, however this may be due to the increase in strain in the ligand due to the S atom, when compared with **1**. In the case of compound **6** three different types of phenyl groups ascribed to restricted rotation about the Cr–As bond were observed in the ^{13}C NMR spectrum, one for the two phenyls connected to the unco-ordinated arsenic and one for each phenyl group bound to the co-ordinated arsenic. The

DOI: 10.1039/b005269h



Scheme 1 Reactions of substituted Group 6 metal carbonyls with the $Ph_2AsXAsPh_2$ ligands, where X = O or S.

carbon atoms of the CO groups exhibit signals in the ^{13}C NMR around δ 200 with CO groups *cis* to the arsenic ligand more deshielded than *trans*-CO groups.

IR spectroscopy studies have been used previously[17] for structural characterisation of these ligands. As no coupling of As–O–As stretching modes with other normal modes is expected,[17,18] a correlation between increasing As–O–As angles and higher stretching frequencies for both symmetric (around 500 cm^{-1}) and antisymmetric modes (around 700 cm^{-1}) was observed for the case of **1**, **2** and **5**. IR spectral assignments in the 2200–1600 cm^{-1} region were made on the basis of the literature data[22,23] for Group 6 complexes with approximate C_{2v} symmetry containing methylene-, ethylene- or phenylene-bridged diarsines(III) of the type $[M(CO)_4(Ph_2AsXAsPh_2)_m]$, $m = 1$ or 2. For compounds **1**–**4** four well spaced bands were observed in the CO region of the spectra. In **5** and **6** the overall symmetry is lower than C_{4v} and the spectra are correspondingly more complicated. Five absorption bands were observed for CO stretching similar to the behaviour of $[M(CO)_5L]$ complexes with M = Cr, Mo or W and ligands such as $Me_2AsSAsMe_2$[10] and $Me_2As(S)SAsMe_2$,[11] $Me_2AsP(CF_3)_2$,[24] Ph_3AsO,[25] and Me_2AsSMe.[26]

In the FAB$^+$ mass spectra for complexes **1**–**6** the molecular ion is observed as a peak of low intensity (with the correct isotope pattern), except for **2** where the highest *m*/*z* value is assigned to the $[M - CO]^+$ ion. A peak corresponding to $[M(Ph_2AsXAsPh_2)]^+$ (M = Cr or Mo, X = O or S) is present in all FAB$^+$ spectra consistent with two phenyl groups π-co-ordinated to the metal, $[M(\eta^6\text{-}C_6H_5)PhAsXAsPh(\eta^6\text{-}C_6H_5)]^+$. This observation is supported by previously reported data.[23,27]

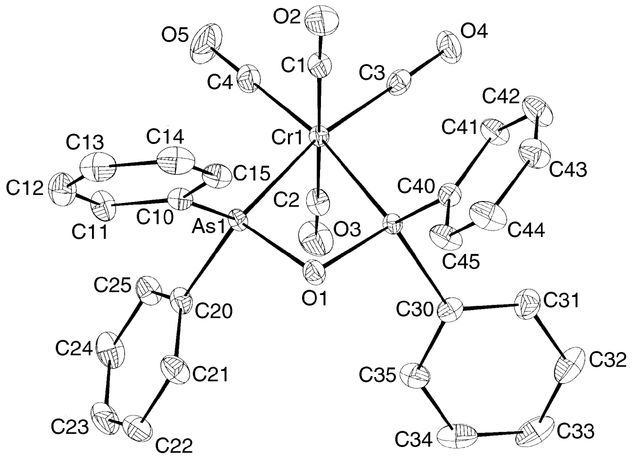


Fig. 1 ORTEP diagram of the molecular structure of $[Cr(CO)_4\{(Ph_2As)_2O\}]$ **1**.

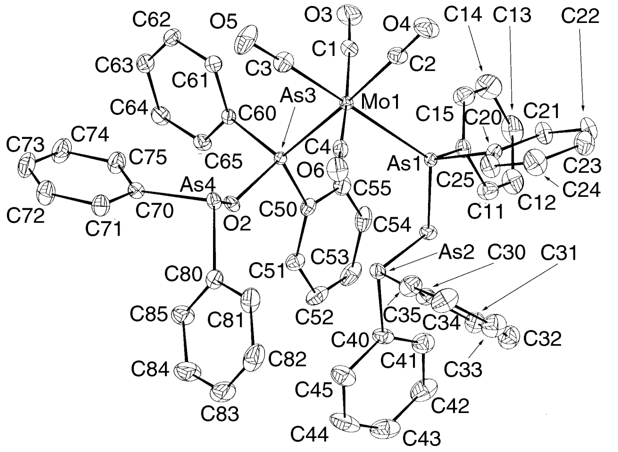


Fig. 2 ORTEP diagram of the molecular structure of $[Mo(CO)_4\{(Ph_2As)_2O\}_2]$ **2**.

(iii) X-Ray crystallographic studies

The molecular structures of compounds **1**–**5** were determined by X-ray crystallography and are shown in Figs. 1–5. Table 2 contains selected structural parameters. The redetermined structure of free $Ph_2AsOAsPh_2$ (ORTEP[28] diagram) is shown in Fig. 6 and the relevant structural parameters are contained in Table 2.

All five complexes display octahedral co-ordination at the metal centre, with two *cis* arsenic-donor atoms in **1**–**4**. The bidentate chelating mode in **1** and **3** results in four-membered inorganic chelate Cr–As–X–As rings. In **1** the oxygen atom is essentially coplanar with the As–Cr–As best plane, whereas in **3** the Cr–S vector deviates from planarity with the As–Cr–As best plane by 6°. In **1**–**5** each co-ordinated arsenic atom has distorted tetrahedral geometry with angles around arsenic ranging from 95 to 127°. Higher M–As–C angle values were found with bidentate chelation in **1** and **3**. The unco-ordinated arsenic atoms in **2**, **4** and **5** display a distorted pyramidal geometry with angles from 95.0(1) to 97.6(1)° in **2**, 92.6(1) to 101.68(11)° in **4**, and 92.38(7) to 98.27(9)° in **5**. The Cr–As bond lengths in Table 2 compare closely with the literature values for $[Cr(CO)_5(Ph_2AsNSO)]$,[29] 2.438(1) Å, and $[Cr(CO)_2\{(\eta^6\text{-}Ph)PhAsCH_2AsPh_2\}]$,[27] 2.406(1) Å, as do the Mo–As bonds with the monodentate co-ordinated Mo–As distance in $[MoBr_2(CO)_2(Ph_2AsCH_2AsPh_2)_2]$,[30] 2.608(5) Å.

Table 1 Analytical and spectroscopic data for compounds **1**–**6**; ^{1}H and ^{13}C NMR data for the ligands

Compound[a]	NMR data[b]
1 $[Cr(CO)_4(Ph_2AsOAsPh_2)]$ orange C 52.7 (52.7), H 3.45 (3.1), Cr 7.9 (8.15) IR[c] (CsI): 2024m, 1923s, 1908vs, 1894s, 733m, 496m Mass (FAB$^+$): *m*/*z* 639, $[M + H]^+$; 526, $[M - 4CO]^+$; 229, $[Ph_2As]^+$ (base peak); 227, $[C_{12}H_8As]^+$	^{1}H: 7.37 (m, C_6H_5) ^{13}C: 226.9 (s, *cis*-CO), 220.8 (s, *trans*-CO), 142.8 (s, *ipso*-C of C_6H_5), 131.4 (s, *m*-C of C_6H_5), 130.2 (s, *p*-C of C_6H_5), 129.4 (s, *o*-C of C_6H_5)
2 $[Mo(CO)_4(Ph_2AsOAsPh_2)_2]$ white C 53.95 (54.0), H 3.63 (3.5) IR (CsI): 2022m, 1933s, 1910vs, 1898s, 754m, 739m, 579m, 534m Mass (FAB$^+$): *m*/*z* 1128, $[M - CO]^+$; 1100, $[M - 2CO]^+$; 684, $[M - (Ph_2As)_2O]^+$; 372, $[M - 4CO - (Ph_2As)_2O]^+$; 229, $[Ph_2As]^+$ (base peak); 227, $[C_{12}H_8As]^+$	^{1}H: 7.39 (m, C_6H_5) ^{13}C: 146.7 (s, *ipso*-C of C_6H_5), 144.8 (s, *ipso*-C of C_6H_5), 143.8 (s, *ipso*-C of C_6H_5), 141.3 (s, *ipso*-C of C_6H_5), 131.8–128.6 (12 sets of resonances corresponding to aromatic carbons)
3 $[Cr(CO)_4(Ph_2As)_2S]$ orange C 51.3 (51.4), H 3.4 (3.1), As 23.4 (22.9), S 4.5 (4.9) IR (CsI): 2015m, 1977s, 1929s, 1905vs Mass (FAB$^+$): *m*/*z* 654, $[M]^+$; 542, $[M - 4CO]^+$ (base peak); 229, $[Ph_2As]^+$; 227, $[C_{12}H_8As]^+$	^{1}H: 7.64 (m, 4H, *o*-H of C_6H_5), 7.47 (m, 6H, *m*-H and *p*-H of C_6H_5), 7.52 (m, 4H, *o*-H of C_6H_5), 7.49 (m, 6H, *m*-H and *p*-H of C_6H_5) ^{13}C: 226.7 (s, *cis*-CO), 221.3 (s, *trans*-CO), 141.9 (s, *ipso*-C of C_6H_5), 139.8 (s, *ipso*-C of C_6H_5), 132.8 (s, *m*-C of C_6H_5), 131.1 (s, *m*-C of C_6H_5), 130.8 (s, *p*-C of C_6H_5), 129.9 (s, *p*-C of C_6H_5), 129.4 (s, *o*-C of C_6H_5), 128.9 (s, *o*-C of C_6H_5)
4 $[Mo(CO)_4(Ph_2AsSAsPh_2)_2]$ light yellow C 52.3 (52.55), H 3.6 (3.4), As 26.4 (25.2), S 5.2 (5.4) IR (CsI): 2028m, 1924 (sh), 1916vs, 1883s Mass (FAB$^+$): *m*/*z* 1188, $[M]^+$; 588, $[M - 4CO - (Ph_2As)_2S]^+$; 229, $[Ph_2As]^+$; 227, $[C_{12}H_8As]^+$; 107, [AsS] (base peak)	^{1}H: 7.67 (m, 8H, *o*-H of C_6H_5), 7.49 (m, 12H, *m*-H and *p*-H of C_6H_5), 7.53 (m, 8H, *o*-H of C_6H_5), 7.31 (m, 12H, *m*-H and *p*-H of C_6H_5) ^{13}C: 141.9 (s, *ipso*-C of C_6H_5), 139.5 (s, *ipso*-C of C_6H_5), 132.9 (s, *m*-C of C_6H_5), 131.3 (s, *m*-C of C_6H_5), 130.9 (s, *p*-C of C_6H_5), 129.7 (s, *o*-C of C_6H_5), 129.4 (s, *p*-C of C_6H_5), 128.9 (s, *o*-C of C_6H_5)
5 $[Cr(CO)_5(Ph_2AsOAsPh_2)]$ orange C 52.8 (52.3), H 3.2 (3.0) IR (CsI): 2066w, 2017m, 1947 (sh), 1924s, 1907vs, 739m, 526w Mass (FAB$^+$): *m*/*z* 666, $[M]^+$; 638, $[M - CO]^+$; 582, $[M - 3CO]^+$; 526, $[M - 5CO]^+$ (base peak); 229, $[Ph_2As]^+$; 227, $[C_{12}H_8As]^+$	^{1}H: 7.44 (m, 20H, C_6H_5) ^{13}C: 224.5 (s, *cis*-CO), 199.1 (s, *trans*-CO), 148.0 (s, *ipso*-C of C_6H_5), 143.0 (s, *ipso*-C of C_6H_5), 132.2 (s, *m*-C of C_6H_5), 132.1 (s, *m*-C of C_6H_5), 130.5 (s, *p*-C of C_6H_5), 130.1 (s, *p*-C of C_6H_5), 130.0 (s, *o*-C of C_6H_5), 130.0 (s, *o*-C of C_6H_5)
6 $[Cr(CO)_5(Ph_2AsSAsPh_2)]$ orange C 51.5 (51.05), H 3.3 (2.95) IR (CsI): 2063m, 1990m, 1950s, 1923vs, 1919vs Mass (FAB)$^+$: *m*/*z* 682, $[M]^+$; 654, $[M - CO]^+$; 542, $[M - 4CO]^+$ (base peak); 229, $[Ph_2As]^+$; 227, $[C_{12}H_8As]^+$	^{1}H: 7.59 (m, 4H, *o*-H of C_6H_5), 7.35 (m, 6H, *m*-H and *p*-H of C_6H_5) ^{13}C: 222.5 (s, *cis*-CO), 216.2 (s, *trans*-CO), 141.9 (s, *ipso*-C of C_6H_5), 140.2 (s, *ipso*-C of C_6H_5), 138.9 (s, *ipso*-C of C_6H_5), 133.1 (s, *m*-C of C_6H_5), 132.9 (s, *m*-C of C_6H_5), 131.8 (s, *m*-C of C_6H_5), 130.9 (s, *p*-C of C_6H_5), 129.6 (s, *p*-C of C_6H_5), 129.4 (s, *p*-C of C_6H_5), 129.3 (s, *o*-C of C_6H_5), 129.0 (s, *o*-C of C_6H_5), 128.9 (s, *o*-C of C_6H_5)
$Ph_2AsOAsPh_2$[6,17]	^{1}H: 7.52 (m, 8H, *o*-H of C_6H_5), 7.34 (m, 12H, *m*-H and *p*-H of C_6H_5) ^{13}C: 146.7 (s, *ipso*-C of C_6H_5), 131.1 (s, *m*-C of C_6H_5), 129.6 (s, *p*-C of C_6H_5), 128.7 (s, *o*-C of C_6H_5)
$Ph_2AsSAsPh_2$[17]	^{1}H: 7.56 (m, 8H, *o*-H of C_6H_5), 7.35 (m, 12H, *m*-H and *p*-H of C_6H_5) ^{13}C: 143.3 (s, *ipso*-C of C_6H_5), 134.1 (s, *m*-C of C_6H_5), 130.5 (s, *p*-C of C_6H_5), 130.1 (s, *o*-C of C_6H_5)

[a] Analytical data given as found (calculated) in %. [b] NMR data (CD_2Cl_2, 298 K) given as chemical shift (multiplicity, relative intensity, assignment). [c] IR spectra recorded in CsI in the region of the spectra between 4000 and 400 cm^{-1}; only the most significant signals are reported (cm^{-1}).

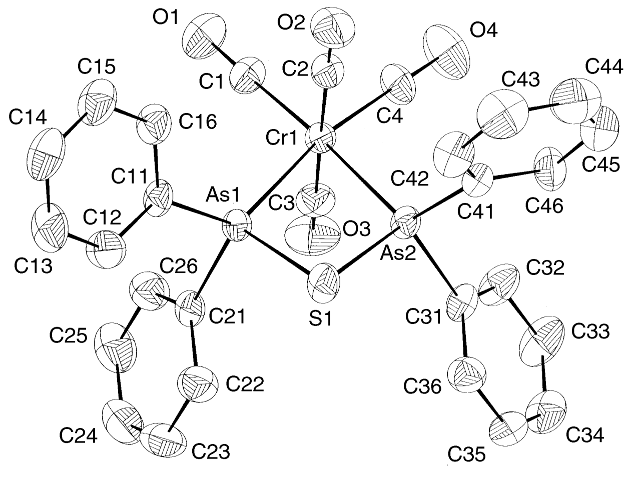


Fig. 3 ORTEP diagram of the molecular structure of $[Cr(CO)_4\{(Ph_2As)_2S\}]$ **3**. Only one molecule from the asymmetric unit is shown.

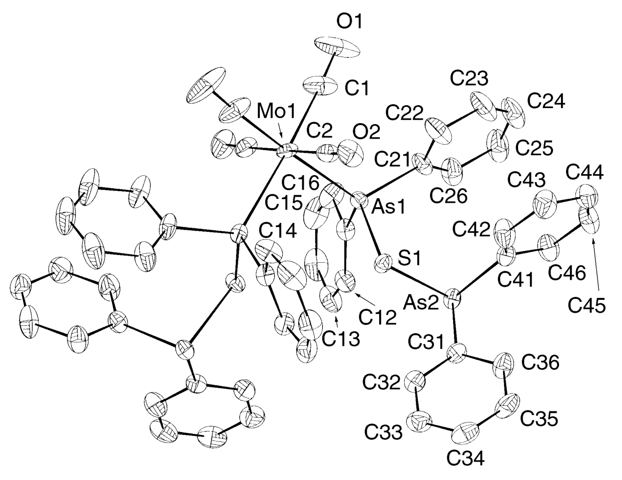


Fig. 4 ORTEP diagram of the molecular structure of $[Mo(CO)_4\{(Ph_2As)_2S\}_2]$ **4**. The asymmetric unit consists of half the molecule shown.

In complexes **1**–**5** the Cr–C bonds situated *trans* to arsenic are shorter than those *cis*, as shown in Table 2, and the related C–O bonds are somewhat longer in the *trans* carbonyl groups than the *cis* ones. These data imply that the $Ph_2AsXAsPh_2$ ligands are weaker π acceptors than CO. A similar feature was reported for the phosphorus analogues $[Cr(CO)_4(Ph_2POPPh_2)]$ and $[Mo(CO)_4(Ph_2POPPh_2)]$ in earlier studies.[4] The Cr–C$_{trans}$ bond lengths in compounds **1** and **3** are almost equivalent and show that changing the chalcogen in the As–X–As bridge does not significantly affect back donation.

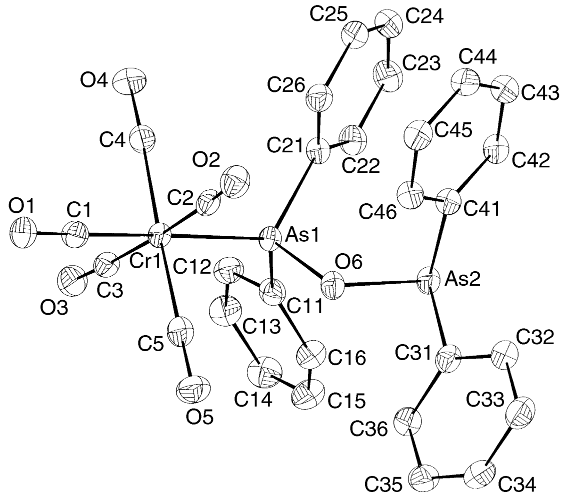


Fig. 5 ORTEP diagram of the molecular structure of $[Cr(CO)_5\{(Ph_2As)_2O\}]$ **5**.

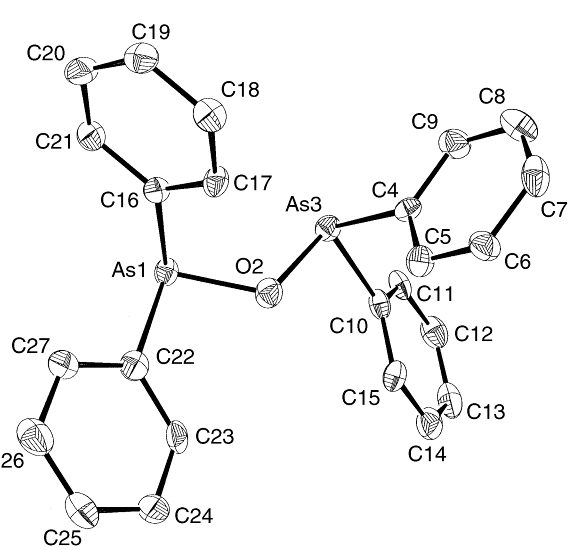


Fig. 6 ORTEP diagram of the molecular structure of $Ph_2AsOAsPh_2$.

The two As–O bond lengths are not equal in the monodentate complexes **2** and **5**, a minimal difference is observed in the bidentate ligand in **1** where the As–O bond lengths are close to those found in $[Co_3(CO)_7(\mu\text{-CCl})\{\mu\text{-Ph}_2AsOAsPh_2\}]$[16] (of 1.921(7) and 1.886(6) Å), $[Co_3(CO)_7(\mu\text{-CMe})\{\mu\text{-Ph}_2AsOAsPh_2\}]$[16] (of 1.808(3) and 1.802(3) Å) and $[Co_2(CO)_4(\mu\text{-PhCCH})\{\mu\text{-Ph}_2AsOAsPh_2\}]$[16] (of 1.806(3) and 1.791(3) Å).

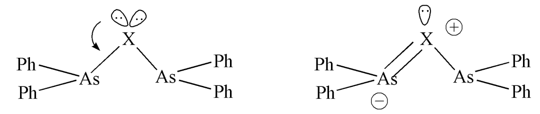
The As–S bond lengths in the chelate complex **3** and the co-ordinated As–S distances in **4** are similar to the corresponding bond lengths in $[(Me_3PtBr)_2(\{\mu\text{-}(Me_2AsSAsMe_2)\})]$[14] (2.223(7) and 2.232(7) Å). The non-co-ordinated As–S distances in **4** more closely match those in free $Ph_2AsSAsPh_2$[31] (of 2.257(3) and 2.43(3) Å), and in bis(phenoxarsin-10-yl)sulfide[32] (of 2.266(3) and 2.282(3) Å).

The As–O–As angle (115.98(17)° in the redetermined structure of the "free" ligand) increases upon monodentate co-ordination to the metal centre in complex **2** (122.2(1)° and 121.73(9)°) or **5** (122.44(7)°). These values are similar to that reported for the free bis(phenoxarsin-10-yl)oxide (of 122.3(1)°[33]) and larger than the ones determined in $[Co_3(CO)_7(\mu\text{-CMe})\{\mu\text{-Ph}_2AsOAsPh_2\}]$[16] (of 114.4(1)°), $[Co_2(CO)_4(\mu\text{-PhCCH})\{\mu\text{-Ph}_2AsOAsPh_2\}]$[16] (of 118.4(2)°), and $[Co_3(CO)_7(\mu\text{-CCl})\{\mu\text{-Ph}_2AsOAsPh_2\}]$[16] (of 108.8(4)°), with bidentate-bridging co-ordination of $Ph_2AsOAsPh_2$ ligand to two Co. The formation of a four-membered ring in **1** leads to an As–O–As angle of only 99.79(8)°.

The As–S–As angles found for the two molecules of the asymmetric unit of complex **3** are 83.44(5) and 84.06(6)°, smaller than in free $Ph_2AsSAsPh_2$[31] (97.21(13)°) and bis(phenoxarsin-10-yl)sulfide[32] (99.87(6)°). The As–S–As angle found for the two ligand units monodentate in **4** are of 106.25(5) and 106.16(5)°, somewhat larger than in **3** or in free $Ph_2AsSAsPh_2$.[31]

The ligand conformation changes noticeably upon co-ordination, in either a mono- or bi-dentate mode. The As–X–As angle increases from that observed in the "free" ligand in the case of monodentate co-ordination and decreases when these ligands are in a bidentate chelate. This contraction is expected for bidentate chelates which form strained four-membered rings, whereas monodentate co-ordination induces no steric strain. Rather the change in angle reflects the new electron distribution within the ligand.

Such changes in unstrained ligands have previously been attributed to a pπ–dπ bonding between a chalcogen lone pair and vacant arsenic 4d orbital.[20] In many compounds of the type $O(MR_n)_2$, where M belongs to the p block and $n = 1–3$, M–O–M angles are larger than predicted by VSEPR theory and compounds containing linear oxygen between two metal centres are common.[34] An alternative explanation was sought from the Second-Order Jahn–Teller (SOJT) effect where a linear AX_2 species containing one or two pairs of non-bonding electrons localised in A will be unstable to bending, resulting in an asymmetric bent conformation.[35–37] The structure of free $Ph_2AsOAsPh_2$ was represented so far by the resonance structures below which show donation of electron density from chalcogen to As with the corresponding increase in As–X bond order and greater approach of the As–X–As unit to linearity.[38]



A **B**

This depiction is not supported by the newly determined structure of $Ph_2AsOAsPh_2$. The As–O separations of 1.809(3) and 1.814(3) Å are comparable with the corresponding bond lengths found in $(C_6F_5)_2AsOAs(C_6F_5)_2$[39] (of 1.792(3) Å), and with the As–O single bond separation found in $Ph_2As(O)OH$[40] (of 1.724(3) Å). These values are larger than the ones determined for the As–O separation in an earlier work[20] (*i.e.* mean As–O of 1.67 Å). This suggests an arsenic–oxygen bond order no greater than one. Also, the As–O–As angle of 115.98(17)° determined by us for the structure of this ligand is comparable with the one determined in $(C_6F_5)_2AsOAs(C_6F_5)_2$ of 116.3(2)° and much smaller than the previously determined value, *i.e.* 137(1)°.[20]

The newly determined molecular parameters of $Ph_2AsOAsPh_2$ are consistent with the ones predicted by calculations at the DFT level and do not favour the possible explanation offered by pπ–dπ or SOJT theory for an unusually large As–O–As.

The variety of As–O–As angles observed in all the studied examples suggests a very flexible nature of this linkage, and domination of packing forces in angle determination.

(iv) DFT calculations

Density functional calculations were carried out in order to investigate possible electronic reasons for the relative stability of monodentate *versus* bidentate co-ordination. Phenyl groups were substituted by hydrogen atoms to reduce computational time. Geometry optimisations were initially carried out for $H_2AsXAsH_2$ (X = O or S), $[M(CO)_4(H_2AsXAsH_2)]$ (M = Cr or Mo; X = O or S) and $[M(CO)_4(H_2AsXAsH_2)_2]$ (M = Cr or Mo; X = O or S).

Table 2 Selected molecular parameters (distances in Å, angles in °) of compounds **1**–**5** and $Ph_2AsOAsPh_2$[a]

1 $[Cr(CO)_4(Ph_2AsOAsPh_2)]$

As1–Cr1	2.4441(4)	Cr1–C1	1.903(2)
As1–O1	1.8211(15)	Cr1–C2	1.900(2)
As2–Cr1	2.4262(4)	Cr1–C3	1.857(2)
As2–O1	1.8081(15)	Cr1–C4	1.863(2)
As1–C10	1.934(2)	O2–C1	1.137(3)
As1–C20	1.927(2)	O3–C2	1.144(3)
As2–C30	1.936(2)	O4–C3	1.157(3)
As2–C40	1.928(2)	O5–C4	1.149(3)

As1–O1–As2	99.79(8)	As1–Cr1–C3	165.58(7)
Cr1–As1–O1	94.88(5)	As2–Cr1–C3	96.38(7)
Cr1–As2–O1	95.83(5)	As1–Cr1–C4	100.70(7)
As1–Cr1–As2	69.495(12)	As2–Cr1–C4	170.08(7)
As1–Cr1–C1	90.94(7)	Cr1–C1–O2	176.7(2)
As2–Cr1–C1	91.25(7)	Cr1–C2–O3	176.2(2)
As1–Cr1–C2	91.38(7)	Cr1–C3–O4	177.3(2)
As2–Cr1–C2	91.56(7)	Cr1–C4–O5	177.4(3)

2 $[Mo(CO)_4(Ph_2AsOAsPh_2)_2]$

As1–Mo1	2.6080(3)	O4–C2	1.143(3)
As1–O1	1.7952(17)	O5–C3	1.149(3)
As2–O1	1.8098(18)	O6–C4	1.142(3)
As3–Mo1	2.6048(3)	As1–C10	1.934(2)
As3–O2	1.7886(17)	As1–C20	1.945(2)
As4–O2	1.8155(17)	As2–C30	1.966(2)
Mo1–C1	2.042(3)	As2–C40	1.951(3)
Mo1–C2	1.996(3)	As3–C50	1.941(2)
Mo1–C3	1.984(3)	As3–C60	1.957(2)
Mo1–C4	2.047(3)	As4–C70	1.955(2)
O3–C1	1.147(3)	As4–C80	1.947(3)

As1–O1–As2	122.2(1)	As1–Mo1–C3	176.07(8)
As3–O2–As4	121.73(9)	As3–Mo1–C3	88.39(8)
Mo1–As1–O1	120.82(6)	As1–Mo1–C4	90.61(7)
Mo1–As3–O2	120.68(5)	As3–Mo1–C4	98.69(7)
As1–Mo1–As3	93.182(9)	Mo1–C1–O3	175.0(2)
As1–Mo1–C1	95.45(7)	Mo1–C2–O4	179.0(2)
As3–Mo1–C1	85.58(8)	Mo1–C3–O5	178.5(3)
As1–Mo1–C2	87.51(8)	Mo1–C4–O6	172.3(2)
As3–Mo1–C2	174.69(8)		

3 $[Cr(CO)_4(Ph_2AsSAsPh_2)]$

Molecule 1

As1–Cr1	2.4629(9)	Cr1–C1	1.862(6)
As1–S1	2.2647(15)	Cr1–C2	1.893(6)
As2–Cr1	2.439(1)	Cr1–C3	1.894(7)
As2–S1	2.2440(14)	Cr1–C4	1.855(5)
As1–C11	1.946(5)	O1–C1	1.133(7)
As1–C21	1.945(5)	O2–C2	1.138(7)
As2–C31	1.934(5)	O3–C3	1.146(7)
As2–C41	1.947(5)	O4–C4	1.143(7)

As1–S1–As2	83.44(5)	As1–Cr1–C3	90.19(17)
Cr1–As1–S1	98.98(4)	As2–Cr1–C3	93.68(18)
Cr1–As2–S1	100.28(4)	As1–Cr1–C4	169.0(2)
As1–Cr1–As2	75.49(3)	As2–Cr1–C4	93.6(2)
As1–Cr1–C1	98.53(19)	Cr1–C1–O1	178.3(6)
As2–Cr1–C1	173.23(19)	Cr1–C2–O2	176.5(5)
As1–Cr1–C2	93.04(17)	Cr1–C3–O3	176.9(5)
As2–Cr1–C2	88.01(18)	Cr1–C4–O4	178.8(6)

Molecule 2

As3–Cr2	2.4648(12)	Cr2–C5	1.847(7)
As3–S2	2.2495(17)	Cr2–C6	1.902(7)
As3–C51	1.938(6)	Cr2–C7	1.868(6)
As3–C61	1.945(7)	Cr2–C8	1.841(7)
As4–Cr2	2.448(1)	O5–C5	1.139(8)
As4–S2	2.2512(19)	O6–C6	1.145(8)
As4–C71	1.943(6)	O7–C7	1.144(8)
As4–C81	1.941(6)	O8–C8	1.157(8)

As3–S2–As4	84.06(6)	C5–Cr2–C6	86.9(3)
Cr2–As3–S2	98.66(5)	As3–Cr2–C7	92.0(2)

Molecule 2 (*continued*)

Cr2–As3–C51	122.79(19)	As4–Cr2–C7	86.60(19)
S2–As3–C51	103.27(19)	As3–Cr2–C8	97.3(2)
Cr2–As3–C61	123.9(2)	As4–Cr2–C8	170.5(3)
S2–As3–C61	102.5(2)	C5–Cr2–C8	94.0(3)
Cr2–As4–S2	99.12(5)	C6–Cr2–C8	88.1(3)
As3–Cr2–As4	75.67(3)	C7–Cr2–C8	87.3(3)
As3–Cr2–C5	168.7(2)	Cr2–C5–O5	178.3(6)
As4–Cr2–C5	93.2(2)	Cr2–C6–O6	174.3(7)
As3–Cr2–C6	92.6(2)	Cr2–C7–O7	176.4(7)
As4–Cr2–C6	98.5(2)	Cr2–C8–O8	177.9(8)

4 $[Mo(CO)_4(Ph_2AsSAsPh_2)_2]$

Mo1–As1	2.6037(7)	As2–C41	1.957(5)
Mo1–As3	2.6030(5)	As3–S2	2.2267(12)
Mo1–C1	2.045(5)	As3–C51	1.941(5)
Mo1–C2	1.980(5)	As3–C61	1.946(5)
Mo1–C3	1.992(7)	As4–S2	2.272(1)
Mo1–C4	2.042(5)	As4–C71	1.965(5)
As1–S1	2.2258(11)	As4–C81	1.977(5)
As1–C11	1.940(5)	O1–C1	1.136(6)
As1–C21	1.955(4)	O2–C2	1.146(6)
As2–S1	2.2703(12)	O3–C3	1.14(1)
As2–C31	1.972(4)	O4–C4	1.144(6)

As1–Mo1–As3	93.059(18)	C11–As1–C21	102.7(2)
As1–Mo1–C1	91.16(16)	S1–As2–C31	92.76(15)
As3–Mo1–C1	88.92(13)	S1–As2–C41	101.69(16)
As1–Mo1–C2	89.1(3)	C31–As2–C41	97.26(19)
As3–Mo1–C2	177.2(2)	Mo1–As3–S2	108.06(3)
C1–Mo1–C2	89.3(2)	Mo1–As3–C51	117.32(16)
As1–Mo1–C3	176.76(19)	S2–As3–C51	101.55(16)
As3–Mo1–C3	89.3(2)	Mo1–As3–C61	118.29(13)
C1–Mo1–C3	91.1(2)	S2–As3–C61	107.47(16)
C2–Mo1–C3	88.6(3)	C51–As3–C61	102.6(2)
As1–Mo1–C4	88.99(15)	S2–As4–C71	102.04(13)
As3–Mo1–C4	91.58(12)	S2–As4–C81	92.20(12)
C1–Mo1–C4	179.47(17)	C71–As4–C81	97.5(2)
C2–Mo1–C4	90.14(19)	As1–S1–As2	106.25(5)
C3–Mo1–C4	88.7(2)	As3–S2–As4	106.16(5)
Mo1–As1–S1	108.06(4)	Mo1–C1–O1	177.1(5)
Mo1–As1–C11	118.37(15)	Mo1–C2–O2	175.9(7)
S1–As1–C11	107.41(14)	Mo1–C3–O3	177.6(7)
Mo1–As1–C21	117.04(17)	Mo1–C4–O4	178.4(5)
S1–As1–C21	101.70(13)		

5 $[Cr(CO)_5(Ph_2AsOAsPh_2)]$

As1–Cr1	2.4309(3)	Cr1–C3	1.907(2)
As1–O6	1.7787(13)	Cr1–C4	1.903(2)
As2–O6	1.8380(13)	Cr1–C5	1.912(2)
As1–C11	1.9409(19)	O1–C1	1.147(2)
As1–C21	1.9421(19)	O2–C2	1.145(2)
As2–C31	1.955(2)	O3–C3	1.141(2)
As2–C41	1.949(2)	O4–C4	1.142(3)
Cr1–C1	1.869(2)	O5–C5	1.139(3)
Cr1–C2	1.899(2)		

As1–O6–As2	122.44(7)	As1–Cr1–C5	85.13(6)
Cr1–As1–O6	107.92(4)	Cr1–C1–O1	178.51(17)
As1–Cr1–C1	178.44(6)	Cr1–C2–O2	177.07(16)
As1–Cr1–C2	90.18(5)	Cr1–C3–O3	176.58(16)
As1–Cr1–C3	92.03(6)	Cr1–C4–O4	177.27(17)
As1–Cr1–C4	92.47(6)	Cr1–C5–O5	179.28(18)

$Ph_2AsOAsPh_2$

As1–O2	1.809(3)	As1–C22	1.966(5)
O2–As3	1.814(3)	As3–C4	1.966(4)
As1–C16	1.969(4)	As3–C10	1.958(5)

As1–O2–As3	115.98(17)	O2–As3–C4	96.02(16)
O2–As1–C16	99.83(16)	O2–As3–C10	96.84(16)
O2–As1–C22	94.06(17)	C4–As3–C10	98.27(17)
C16–As1–C22	97.13(18)		

[a] Numbers in parentheses are estimated standard deviations of the last significant figure. Atoms are labelled as indicated in Figs. 1–6.

The results for $H_2AsXAsH_2$ (X = O or S) are given in Table 3. In the case of $H_2AsOAsH_2$ there was a large discrepancy between the calculated As–O–As angle of 112° and that published for $Ph_2AsOAsPh_2$ of 137 ± 1°.[20] The calculation was repeated with a variety of functionals and basis sets but the angle at O was always predicted to be between 111 and 120°. In case the phenyl groups made a substantial difference to this angle a geometry optimisation was carried out for $Ph_2AsOAsPh_2$. The results are given in Table 3. The introduction of the phenyl groups was found to make very little difference to either the As–O distance or the As–O–As bond angle. The crystal structure of $Ph_2AsOAsPh_2$ was therefore redetermined and the experimental results were in accord with the calculations. As determination of the structure of $Ph_2AsSAsPh_2$ had failed to proceed to a full refinement[31] the structure of $Ph_2AsSAsPh_2$ was also calculated in order to seek confirmation of the values obtained by partial refinement of the X-ray data for the "free" ligand. These values are also given in Table 3.

The results of the geometry optimisations on the complexes are given in Table 4 together with experimental values for comparative purposes. Reasonable agreement in the case of the bidentate chromium compounds with both O and S confirms that the model works well for these complexes in spite of the absence of phenyl groups. In these compounds the angle at X (O or S) is doubtless constrained by the four membered ring. In the case of the bidentate molybdenum complexes where comparison with the crystal structures is also possible the biggest deviation between model and experiment is also found in the As–X–As angle, the crystal structures showing a larger angle than the optimised models. In the case of the model monodentate compounds the angles at both O and S lie very close to those calculated for the "free" ligands. This strongly suggests to us that the factors controlling the change in this angle on co-ordination commented on above are steric not electronic.

Table 3 Selected calculated and experimental distances and angles for $R_2AsXAsR_2$

	X–As/Å	As–X–As/°
X = O, R = H calc.	1.82	112
X = O, R = Ph calc.	1.83	111
exp.	1.809(3), 1.814(3)	115.98(17)
X = S, R = H calc.	2.26	95
X = S, R = Ph calc.	2.31	97
exp.	2.257(3), 2.243(3)	97.21(13)

Table 5 gives the energy of formation of the bis-monodentate complexes from the bidentate complex and the "free" ligand for M = Cr or Mo and X = O or S. These energies would of course model best the internal energy change in a gas phase reaction. In all cases the bis-monodentate complexes are found to be more stable. The absolute value of the energy difference is such that entropy effects could favour co-ordination in the chelate mode as is found for Cr. The most striking result is the similarity of the energies for Cr and Mo both with O and S as the bridging ligand. This result suggests that there is no electronic reason for the chelate binding with Cr and the monodentate co-ordination with Mo. The explanation must be sought elsewhere.

Table 6 shows the charges calculated for the chelated compounds using both Mulliken and Voronoi charge partitioning. Though the values of the charges differ between the two methods the trends on chemical substitution are the same. Mo is more positively charged than Cr, and the charge carried is insensitive to whether the ligand contains O or S. O is more negatively charged than S and the charge carried by O or S is insensitive to the nature of the metal. The charge carried by the intervening As atoms depends both on M and X. It is most positive for Cr and O and least positive for Mo and S. The As atoms appear to play the role of a charge buffer in the complex. Changing X has about twice the effect of changing M. The C atoms of the CO groups also show a buffering effect. They are less positively (or more negatively) charged for the molybdenum than the chromium complexes consistent with greater back donation to CO in the former cases. The charge of C is independent of the nature of X.

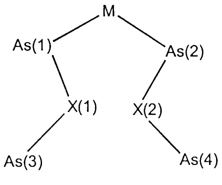
Conclusion

A series of Group 6 carbonyl complexes with $Ph_2AsXAsPh_2$ (X = O or S) ligands in mono- and bi-dentate co-ordination modes have been synthesized. In general, the complexes are

Table 5 Estimated energy difference between monodentate and bidentate binding. $[M(CO)_4(H_2AsXAsH_2)] + H_2AsXAsH_2 \longrightarrow [M(CO)_4(H_2AsXAsH_2)_2]$

M	X	ΔE/kJ mol^{-1}
Cr	O	−45
Cr	S	−25
Mo	O	−45
Mo	S	−24

Table 4 Selected distances (Å) and angles (°) calculated for $[M(CO)_4\{(R_2As)_2X\}_n]$; (R = H). Where available the X-ray values for R = Ph are included in parentheses



$n = 1$	M–As	As–X	As–M–As	As–X–As
M = Cr, X = O	2.36 (2.43)	1.83 (1.82)	71 (69)	97 (100)
M = Cr, X = S	2.38 (2.44)	2.26 (2.26)	77 (75)	82 (83)
M = Mo, X = O	2.53	1.83	67	99
M = Mo, X = S	2.54	2.27	74	85

$n = 2$	M–As(1)	M–As(2)	As(1)–X(1)	As(2)–X(2)	As(3)–X(1)	As(4)–X(2)		As–X(1)–As	As–X(2)–As
M = Cr, X = O	2.33	2.34	1.80	1.80	1.83	1.82	91	113	113
M = Cr, X = S	2.35	2.36	2.27	2.24	2.27	2.26	93	95	97
M = Mo, X = O	2.50 (2.61)	2.52 (2.61)	1.80 (1.80)	1.79 (1.79)	1.83 (1.81)	1.83 (1.82)	90 (93)	113 (122)	113 (122)
M = Mo, X = S	2.52 (2.60)	2.53 (2.60)	2.26 (2.26)	2.24 (2.23)	2.27 (2.27)	2.26 (2.27)	92 (93)	96 (106)	96 (106)

Table 6 Mulliken and Voronoi charges calculated for $[M(CO)_4(H_2AsXAsH_2)]$, where M = Cr or Mo and X = O or S

M, X	Method	M	As	X	C1	O1	C2	O2
Cr, O	Mulliken	−0.62	0.93	−0.72	0.38	−0.37	0.39	−0.37
	Voronoi	0.79	1.78	−0.68	−0.12	−0.14	−0.09	−0.14
Cr, S	Mulliken	−0.62	0.75	−0.37	0.39	−0.37	0.39	−0.38
	Voronoi	0.79	1.54	−0.06	−0.12	−0.14	−0.09	−0.14
Mo, O	Mulliken	−0.04	0.84	−0.71	0.28	−0.36	0.29	−0.37
	Voronoi	1.51	1.69	−0.68	−0.25	−0.13	−0.23	−0.13
Mo, S	Mulliken	−0.05	0.65	−0.35	0.27	−0.35	0.29	−0.37
	Voronoi	1.52	1.44	−0.05	−0.25	−0.13	−0.23	−0.13

quite similar to their phosphorus analogues with regard to their physical properties and spectroscopic characterisation. In contrast to the phosphorus systems, we were unable to synthesize molybdenum tetracarbonyl bidentate chelate complexes. DFT calculations suggested that such compounds may be thermodynamically stable, though no synthetic route has been found. Redetermination of the crystal structure of $Ph_2AsOAsPh_2$ established that there was no unusual change in bond angle at the ligand O atom on monodentate co-ordination, thus no special bonding interactions are indicated.

Experimental

Fourier-transform ^{1}H NMR spectra were recorded on a Bruker AM 300 spectrometer at 300 MHz and ^{13}C-{H} NMR spectra on a Varian Unity plus 500 spectrometer at 125 MHz. ^{1}H and ^{13}C shifts are reported with respect to δ 0.0 for $SiMe_4$. Infrared spectra were recorded in CsI between 4000 and 400 cm^{-1} on a Perkin-Elmer FT-IR spectrometer. Microanalyses were performed by the microanalytical laboratory of the Inorganic Chemistry Laboratory, University of Oxford and FAB$^+$ mass spectra by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea, UK. All reactions were carried out under N_2 using standard Schlenk techniques. Solvents were dried over suitable reagents and freshly distilled under N_2 before use.

The compounds $[Mo(CO)_4(nbd)]$,[21] $[Cr(CO)_4(nbd)]$,[21] $Ph_2AsOAsPh_2$,[6] and $Ph_2AsSAsPh_2$[7,8] were prepared as previously described. Preparation of $[Cr(CO)_4(Ph_2AsOAsPh_2)]$ and $[Cr(CO)_4(Ph_2AsSAsPh_2)]$ has previously been reported[13] and here we present a modified synthetic route for isolating these compounds.

Preparations

$[Cr(CO)_4(Ph_2AsOAsPh_2)]$ 1. A portion of $[Cr(CO)_4(nbd)]$ (500 mg, 1.95 mmol) in 100 mL of benzene was treated with $Ph_2AsOAsPh_2$ (920 mg, 1.95 mmol). After stirring for 12 h the volatiles were removed *in vacuo*. The orange solid (920 mg, crude yield 74%) was washed with pentane and crystals with mp 125 °C appeared from a 1 : 4 mixture of diethyl ether and pentane after storing at −20 °C.

$[Mo(CO)_4(Ph_2AsOAsPh_2)_2]$ 2. The compound $[Mo(CO)_4(nbd)]$ (250 mg, 0.84 mmol) and $Ph_2AsOAsPh_2$ (400 mg, 0.84 mmol) were stirred together in 50 mL pentane for 3 h at room temperature. The white precipitate formed was filtered off, washed with pentane and recrystallised from a 1 : 4 mixture of CH_2Cl_2 and pentane to give white crystals of **2** with mp 114 °C (150 mg, yield 43%) after storing at −20 °C. Repeating this experiment with a 1 : 2 ratio of reagents resulted in the same product $[Mo(CO)_4(Ph_2AsOAsPh_2)_2]$ (771 mg, yield 80%).

$[Cr(CO)_4(Ph_2AsSAsPh_2)]$ 3. A mixture of $[Cr(CO)_4(nbd)]$ (200 mg, 0.78 mmol) and $Ph_2AsSAsPh_2$ (383 mg, 0.78 mmol) in 100 mL benzene was stirred for 12 h. The volatiles were removed *in vacuo* and the residual solid was purified by washing with pentane and recrystallised from a mixture of CH_2Cl_2 and pentane. Cooling to −20 °C gave orange block-shaped crystals of complex **3** with mp 112 °C (300 mg, 60% yield).

$[Mo(CO)_4(Ph_2AsSAsPh_2)_2]$ 4. A solution of $[Mo(CO)_4(nbd)]$ (100 mg, 0.33 mmol) in 50 mL pentane was treated with $Ph_2AsSAsPh_2$ (164 mg, 0.33 mmol) dissolved in 50 mL pentane. A light yellow precipitate occurred after stirring for 1 h at room temperature. After removal of solvent the resultant solid was dried *in vacuo* and washed with pentane. Recrystallisation from a 1 : 4 mixture of CH_2Cl_2 and pentane at −20 °C gave pale yellow crystals of complex **4**, mp 115 °C (89.5 mg, yield 45%).

$[Cr(CO)_5(Ph_2AsOAsPh_2)]$ 5. A suspension of $[Cr(CO)_6]$ (100 mg, 0.45 mmol) in THF (50 mL) was irradiated with a broad band UV lamp for 5 h at room temperature under N_2. $Ph_2AsOAsPh_2$ (215.5 mg, 0.45 mmol) was added and the mixture stirred for 24 h at room temperature. Volatiles were removed *in vacuo* and traces of $[Cr(CO)_6]$ were removed by sublimation. The residual solid was washed with pentane. Recrystallisation from a 1 : 4 mixture of CH_2Cl_2 and pentane at −20 °C gave bright yellow crystals of complex **5**, mp 80 °C (151 mg, yield 49%).

$[Cr(CO)_5(Ph_2AsSAsPh_2)]$ 6. A suspension of $[Cr(CO)_6]$ (160 mg, 0.72 mmol) in THF (50 mL) was irradiated with a broad band UV lamp for 5 h at room temperature under N_2. $Ph_2AsSAsPh_2$ (356.4 mg, 0.72 mmol) was added and the mixture stirred for 24 h at room temperature. After filtration the solution was stored at −20 °C overnight and orange crystals of complex **6** mp 122 °C, precipitated in an almost quantitative yield.

Crystal structure determination

Crystals of compound **1** were grown from a mixture of Et_2O and pentane (1 : 4) at −20 °C, those of **2**, **3**, **4** and **5** from (1 : 4) CH_2Cl_2 and pentane at 0 °C and isolated by filtration. Crystals of ligand $Ph_2AsOAsPh_2$ were grown from slow diffusion of pentane into a concentated solution of ligand in benzene at room temperature, under N_2. Attempts to crystallise this ligand under air lead to the isolation of two different forms of arsinic acid $Ph_2As(O)OH$[40] and $[Ph_2As(O)OH]_2$,[41] with known crystal structures. In all cases, a specimen crystal was selected under an inert atmosphere, covered with paratone-N oil, and mounted on the end of a glass fibre. Crystal data are summarised in Table 7.

Data collection and processing. Data were collected on an Enraf-Nonius DIP2000 image plate diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). The images were processed with the DENZO and SCALEPACK programs.[42] Corrections for Lorentz and polarisation effects were performed.

Structure solution and refinement. All solution, refinement, and graphical calculations were performed using the CRYSTALS[43] and CAMERON[44] software packages. The crystal

Table 7 Crystallographic data for compounds **1**–**5** and $Ph_2AsOAsPh_2$

	$[Cr(CO)_4(Ph_2AsOAsPh_2)]$ **1**	$[Mo(CO)_4(Ph_2AsOAsPh_2)_2]$ **2**	$[Cr(CO)_4(Ph_2AsSAsPh_2)]$ **3**	$[Mo(CO)_4(Ph_2AsSAsPh_2)_2]$ **4**	$[Cr(CO)_5(Ph_2AsOAsPh_2)]$ **5**	$Ph_2AsOAsPh_2$
Formula	$C_{28}H_{20}As_2CrO_5$	$C_{52}H_{40}As_4MoO_6$	$C_{28}H_{20}As_2CrO_4S$	$C_{26}H_{20}As_2Mo_{0.5}O_2S_6$	$C_{29}H_{20}As_2CrO_6$	$C_{24}H_{20}As_2O$
M	638.30	1156.52	1308.73		666.31	474.27
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1/c$	$P2_1/n$
a/Å	9.939(2)	10.831(4)	10.790(6)	10.456(2)	10.6640(3)	11.4240(9)
b/Å	11.591(5)	13.264(4)	13.288(7)	26.817(5)	9.160(3)	29.9061(3)
c/Å	13.010(5)	17.913(6)	19.381(6)	17.543(4)	26.2380(5)	5.8810(4)
α/°	106.770(2)	86.080(2)	79.572(3)			
β/°	95.13(2)	87.157(2)	85.858(3)	96.14(3)	92.816(2)	92.863(3)
γ/°	112.79(2)	65.773(2)	82.035(3)			
V/Å^3	1288.2	2340.6	2766.1	4890.7	2687.3	2006.7
T/K	150	125	298	150	125	150
Z	2	2	2	8	4	4
Total no. data	7268	13000	13010	12945	18543	10812
No. unique data	4872	9009	10569	4703	5582	4079
R_{int}	0.034	0.043	0.053	0.038	0.036	0.0007
μ(Mo-Kα)/mm^{-1}	3.01	3.12	2.88	3.07	2.89	3.34
R	0.0282	0.0265	0.0444	0.0379	0.0272	0.0563
wR	0.0327	0.0307	0.0489	0.0373	0.0325	0.0394

structures were solved by direct methods using the SIR 92[45] program and refined by full-matrix least squares procedure on F. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon-bound hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters. An empirical absorption correction[46] was applied.

CCDC reference number 186/2138.

See http://www.rsc.org/suppdata/dt/b0/b005269h/ for crystallographic files in .cif format.

Computational details

All calculations were carried out using the Amsterdam density functional (ADF) program system.[47] The electronic configurations of the molecular systems were described by an uncontracted triple-ζ basis set of Slater-type orbitals (STOs). Hydrogen, carbon, oxygen, sulfur and arsenic were given an extra polarisation function. The cores of the atoms were frozen, C and O up to 1s, S up to 2p, As up to 3p, Cr up to 2p and Mo up to 3d. First-order relativistic corrections were made to the cores of all atoms using the Pauli formalism. Energies were calculated using Vosko, Wilk and Nusair's local exchange correlation potential[48] with non-local-exchange corrections by Becke[49] and non-local correlation corrections by Perdew.[50,51] The non-local correction terms were not utilised in calculating gradients during geometry optimisations.

Acknowledgements

We thank the University of Oxford for a Georgescu Scholarship (to S. I. P.), St. John's College Oxford for a Junior Research Fellowship (L. H. D.) and the EPSRC for support of this work.

References

1 D. E. Corbridge (Editor), *Phosphorus, An Outline of its Chemistry, Biochemistry and Technology*, Elsevier, Amsterdam, 1980.
2 G. M. Kosolapoff and L. Maier (Editors), *Organic Phosphorus Compounds*, Wiley Interscience, New York, 1973.
3 K. Merzweiler and H. J. Kersten, *Z. Naturforsch., Teil B*, 1991, **46**, 1025.
4 E. H. Wong, L. Prasad, E. J. Gabe and F. C. Bradley, *J. Organomet. Chem.*, 1982, **236**, 321.
5 F. A. Cotton, L. R. Falvello, M. Tomas, G. M. Gray and C. S. Kraihanzel, *Inorg. Chim. Acta*, 1984, **82**, 129.
6 F. F. Blicke and F. D. Smith, *J. Am. Chem. Soc.*, 1929, **51**, 1558.
7 K. Sommer, *Z. Anorg. Allg. Chem.*, 1970, **377**, 120.
8 K. Sommer, *Z. Anorg. Allg. Chem.*, 1971, **383**, 136.
9 B. Ross, W. Marzi and W. Axmacher, *Chem. Ber.*, 1980, **113**, 2928.
10 H. Vahrenkamp, *Chem. Ber.*, 1972, **105**, 3574.
11 E. W. Ainscough, A. M. Brodie and G. Leng-Ward, *J. Chem. Soc., Dalton Trans.*, 1974, 2437.
12 H. Beurich and H. Vahrenkamp, *Chem. Ber.*, 1981, **114**, 2542.
13 L. Weber and D. Wewers, *Organometallics*, 1985, **4**, 841.
14 E. W. Abel, M. A. Beckett, P. A. Bates and M. B. Hursthouse, *J. Organomet. Chem.*, 1987, **325**, 261.
15 E. W. Abel and M. A. Beckett, *Polyhedron*, 1987, **6**, 1255.
16 N. Choi, C. Conole, J. D. King, M. J. Mays, M. McPartlin and C. L. Stone, *J. Chem. Soc., Dalton Trans.*, 2000, 395.
17 L. Silaghi-Dumitrescu, M. N. Gibbons, I. Silaghi-Dumitrescu, J. Zukermann-Schpector, I. Haiduc and D. B. Sowerby, *J. Organomet. Chem.*, 1996, **517**, 101.
18 L. Silaghi-Dumitrescu, S. Pascu, I. Silaghi-Dumitrescu, I. Haiduc, M. N. Gibbons and D. B. Sowerby, *J. Organomet. Chem.*, 1997, **549**, 187.
19 L. Silaghi-Dumitrescu, S. I. Pascu, I. Silaghi-Dumitrescu and I. Haiduc, *Rev. Roum. Chim.*, 1997, **42**, 747.
20 W. R. Cullen and J. Trotter, *Can. J. Chem.*, 1963, **41**, 2983.
21 M. A. Bennett, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 1961, 2037.
22 R. Colton and C. J. Rix, *Aust. J. Chem.*, 1970, **23**, 441.
23 R. Colton and C. J. Rix, *Aust. J. Chem.*, 1971, **24**, 2461.
24 J. Grobe and D. Le Van, *J. Flourine Chem.*, 1984, **24**, 25.
25 E. W. Ainscough, A. M. Brodie and A. R. Furness, *J. Chem. Soc., Dalton Trans.*, 1973, 2360.
26 H. C. Boehm, R. Gleiter, J. Grobe and D. Le Van, *J. Organomet. Chem.*, 1983, **247**, 203.
27 G. B. Robertson and P. O. Whimp, *Inorg. Chem.*, 1974, **13**, 1047.
28 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
29 T. Chivers, K. S. Dhathathreyan, C. Lensink and J. F. Richardson, *Inorg. Chem.*, 1988, **27**, 1570.
30 M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1972, 627.
31 S. I. Pascu and L. H. Doerrer, unpublished results. Partially refined crystal structure of $C_{24}H_{20}As_2S$, $M = 490.33$, monoclinic, space group $P2_1/c$, $a = 5.9470(3)$, $b = 17.0500(12)$, $c = 20.5860(16)$ Å, $\beta = 90.741(5)$°, $V = 2087.2$ Å^3, $Z = 4$, $T = 125$ K, μ(Mo-Kα) 3.30 mm^{-1}, $R = 0.1633$, $wR = 0.1412$. Selected molecular parameters: As1–S1–As2 97.21(13)°; As1–S1 2.257(3), As2–S1 2.243(3), As1–C1 1.950, As1–C11 2.001(12), As2–C21 1.946(12) and As2–C31 1.940(15) Å.
32 W. K. Grindstaff, A. W. Cordes, C. K. Fair, R. W. Perry and L. B. Handy, *Inorg. Chem.*, 1972, **11**, 1852.
33 E. A. Meyers, C. A. Applegate and R. A. Zingaro, *Phosphorus, Sulfur Relat. Elem.*, 1987, **29**, 317.
34 N. Burford, *Coord. Chem. Rev.*, 1992, **112**, 1.
35 C. Glidewell, *Inorg. Chim. Acta*, 1973, **7**, 69.
36 C. Glidewell, *Inorg. Chim. Acta*, 1975, **12**, 219.
37 C. Glidewell, *Inorg. Chim. Acta*, 1978, **29**, L283.
38 Ch. Elschenbroich and A. Salzer, *Organometallics, A Concise Introduction*, VCH, Weinheim, 1st edn., 1989, ch. 9, p. 157.
39 A. L. Rheingold, D. L. Staley and M. E. Fountain, *J. Organomet. Chem.*, 1989, **365**, 123.

40 V. K. Belskii, *Sov. Phys. Crystallogr.*, 1982, **27**, 31.
41 L. Silaghi-Dumitrescu, I. Haiduc, M. N. Gibbons and D. B. Sowerby, *Studia Univ. Babes-Bolyai*, *Ser. Chem.*, 1996, **41**, 43.
42 Z. Otowinowski and W. Minor, *Methods Enzymol.*, 1996, 276.
43 D. J. Watkin, C. K. Prout, J. R. Carruthers and P. W. Betteridge, CRYSTALS, Issue 10, Chemical Crystallography Laboratory, Oxford, 1996.
44 D. J. Watkin, C. K. Prout and L. J. Pearce, CAMERON, Chemical Crystallography Laboratory, Oxford, 1996.
45 A. Altomare, G. Cascarano, G. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.
46 N. Walker and D. Stuart, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 158.
47 G. Velde and E. J. Baerends, ADF(version 2.3), Department of Theoretical Chemistry, Vrije Universiteit Amsterdam, 1996.
48 S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200.
49 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 2398.
50 J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.
51 J. P. Perdew, *Phys. Rev. B*, 1986, **34**, 7046.