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Synthesis, reactivity and structural characterization of some heterometallic complexes containing naked arsenic ligands†

Katherine V. Adams,[a] Nick Choi,[b] Gráinne Conole,[b] John E. Davies,[a] Jason D. King,‡[a] Martin J. Mays,*[a] Mary McPartlin[b] and Paul R. Raithby[a]

[a] *Department of Chemistry, Lensfield Rd., Cambridge, UK CB2 1EW*
[b] *School of Applied Chemistry, University of North London, Holloway Rd., London, UK N7 8DB*

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The reactions of [Co_2(μ-As_2)(CO)$_6$] with [Mo_2Cp_2(CO)$_4$] (Cp = η^5-C_5H_5) and with [(OC)$_4$CoMCp(CO)$_3$] [M = Mo or W] gave, respectively, the known product [Mo_2(μ-As_2)Cp_2(CO)$_4$] **1** and the new heterobimetallic complexes [(OC)$_3$Co(μ-As_2)MCp(CO)$_2$] [M = Mo **2** or W **3**]. The mixed-metal complexes have been treated with PPh_3 to give the substituted complexes [(Ph_3P)(OC)$_2$Co(μ-As_2)MCp(CO)$_2$] [M = Mo **4** or W **5**]. Complex **2** reacted with [Cr(CO)$_5$]·THF to give [(OC)$_3$Co{μ-As_2[Cr(CO)$_5$]$_2$}MoCp(CO)$_2$] **6**. Reaction of [MoWCp$_2$(CO)$_4$] with [Co_2(μ-As_2)(CO)$_6$] does not lead to the complex [MoW(μ-As_2)Cp_2(CO)$_4$] although this can be obtained by co-thermolysis of [Mo_2Cp_2(CO)$_6$] and [W_2Cp_2(CO)$_6$] with grey arsenic which affords three bimetallic products, [MM′(μ-As_2)Cp_2(CO)$_4$] (M = M′ = Mo **1**; M = Mo, M′ = W **7**; M = M′ = W), and four trimetallic products, [M_2M′(μ_3-As)Cp_3(CO)$_6$] (M = M′ = Mo; M = Mo, M′ = W **8**; M = W, M′ = Mo **9**; M = M′ = W). The new heterometallic complexes **2**, **3**, **5**, **6** and **9** have been characterized by X-ray diffraction analyses.

Introduction

Spectroscopic and vapour pressure studies of arsenic in the gaseous state reveal the presence of diatomic As_2, a homologue of N_2.[1] While this is unstable in the condensed phase with respect to tetrahedral As_4 in which three single As–As bonds replace the formal As–As triple bond, stabilization of the As_2 species at transition metal centres has been achieved. Thus complexes containing an As_2 unit attached to two,[2–9] three[2,10] and four[3,8,11,12] transition metal atoms have been synthesized by a variety of methods, as have polymetallic clusters with more than one As_2 ligand.[7,13,14] However, previous studies have not addressed the possibility of synthesizing heterobimetallic complexes containing the diarsenic ligand. In this paper we report new synthetic routes by which such species containing molybdenum or tungsten with cobalt can be prepared. We also report the synthesis of some new heterotrimetallic clusters containing the μ_3-As ligand.

Results and discussion

(a) Reaction of [Co_2(μ-As_2)(CO)$_6$] with [Mo_2Cp_2(CO)$_4$] (Cp = η^5-C_5H_5)

It has been shown recently that the complexes [Mo_2(μ-RCCR′)Cp_2(CO)$_4$] [R = R′ = H or Me; R = H, R′ = Me, Ph or CO_2Me] undergo reaction with [Co_2(CO)$_8$][15] to yield the complexes [Co_2Mo_2(μ_4-RCCR′)(μ-CO)$_4$$Cp_2(CO)_4$] and with [$Ru_3(CO)_{12}$][16] to give [$Mo_2Ru_4$($\mu_3$-CR)$Cp_2(CO)_{12}$]. The former reaction occurs with cleavage of the Mo–Mo bond whereas in the latter case it is cleavage of the C–C bond that yields the bis-alkylidyne product. Given the structural and electronic similarity between alkyne-bridged and As_2-bridged complexes, it was of interest to investigate the reactions of a representative example of the latter class of complex with other metal carbonyls to see whether M–M or As–As bond cleavage would be the preferred mode of reaction of M_2As_2 complexes.

Reaction of [Co_2(μ-As_2)(CO)$_6$] with [Mo_2Cp_2(CO)$_4$] in refluxing toluene for six hours gave orange [Mo_2(μ-As_2)Cp_2(CO)$_4$] **1** in 15% yield. The identity of **1** was established by comparison of the IR spectroscopic data obtained with those previously reported for this complex.[2,3,5,6b] The FAB mass spectrum displayed the expected molecular ion peak. Thus, under these conditions, the reaction between these reagents which would have paralleled that described above involving alkynes, namely the generation of an octahedral tetrametallic complex with cleavage of the Co–Co bond, does not occur. Rather, the As_2 ligand appears to be ‘transferred’ from the dicobalt to the dimolybdenum unit. This unusual reaction has only been noted once before,[17] in the transfer of a P_2 ligand from [Co_2(μ-P_2)(CO)$_6$] to [W_2(O^{i}Pr)$_6$(py)$_2$], generating [W_2P_2(O^{i}Pr)$_6$(py)]. Although alternative mechanisms are possible, the transfer of the P_2 ligand as a discrete unit from one bimetallic fragment to another was suggested as the most likely pathway.[18] In the reaction leading to **1** considered here the lone pairs on the arsenic atoms, which are known to be weak donors,[12] could attack the electronically unsaturated [Mo_2Cp_2(CO)$_4$]. Complete transfer to the new bimetallic fragment could then occur with decomposition of the displaced Co_2(CO)$_6$. In practice a complex mixture of decomposition products is obtained which could not be separated.

Effectively, the [Co_2(μ-As_2)(CO)$_6$] complex simply acts as a carrier of the As_2 unit which is otherwise only available in arsenic vapour at high temperatures. Thus the process may be represented formally as the reaction of As_2 with [Mo_2Cp_2(CO)$_4$]. Viewed in this way it is not dissimilar to the thermolytic reaction of [Mo_2Cp_2(CO)$_6$] with elemental arsenic,[2] during which As_2 may be formed as an intermediate.

(b) Reaction of [Co_2(μ-As_2)(CO)$_6$] with [(OC)$_4$CoMCp(CO)$_3$] [M = Mo or W]

Having established that [Co_2(μ-As_2)(CO)$_6$] acts as a source of ‘free’ As_2, it was of interest to see whether As_2 could be ‘transferred’ to the mixed-metal complexes [(OC)$_4$CoMCp(CO)$_3$]

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3679/

‡ Present address: Department of Chemistry, The University of Montana, Missoula, 59812, Montana, USA.

Table 1 Selected bond lengths (Å) and angles (°) for $[(OC)_3Co(\mu\text{-}As_2)MCp(CO)_2]$ [M = Mo **2** or W **3**]

	M = Mo **2**	M = W **3**
M(1)–Co(1)	2.825(1)	2.821(2)
M(1)–As(1)	2.579(1)	2.582(1)
M(1)–As(2)	2.630(1)	2.632(1)
Co(1)–As(1)	2.420(1)	2.429(2)
Co(1)–As(2)	2.394(1)	2.406(2)
As(1)–As(2)	2.305(1)	2.322(2)
M(1)–$C_{carbonyl}$	1.99(1)	1.99(1)
Co(1)–$C_{carbonyl}$	1.783(8)–1.787(9)	1.77(1)–1.80(1)
C–$O_{carbonyl}$	1.134(8)–1.143(9)	1.12(2)–1.16(1)
C–C_{Cp}	1.38(1)–1.43(1)	1.39(2)–1.43(2)
Co(1)–M(1)–As(1)	52.95(3)	53.21(5)
Co(1)–M(1)–As(2)	51.91(3)	52.22(4)
As(1)–M(1)–As(2)	52.51(3)	52.88(4)
M(1)–Co(1)–As(1)	58.30(3)	58.34(5)
M(1)–Co(1)–As(2)	59.83(3)	59.84(5)
As(1)–Co(1)–As(2)	57.21(4)	57.41(6)
M(1)–As(1)–Co(1)	68.75(3)	68.45(5)
M(1)–As(1)–As(2)	64.88(3)	64.67(5)
Co(1)–As(1)–As(2)	60.85(4)	60.80(6)
M(1)–As(2)–Co(1)	68.25(3)	67.93(5)
M(1)–As(2)–As(1)	62.61(3)	62.45(4)
Co(1)–As(2)–As(1)	61.95(4)	61.80(6)

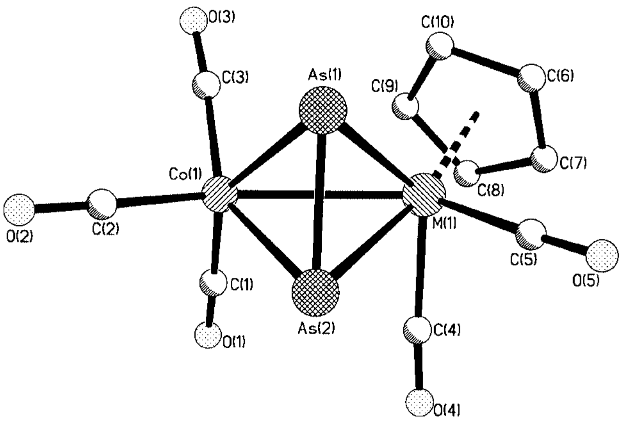


Fig. 1 The molecular structure of $[(OC)_3Co(\mu\text{-}As_2)MCp(CO)_2]$ [M = Mo **2** or W **3**] including the atom numbering scheme. Hydrogen atoms omitted for clarity.

[M = Mo or W], thus leading to heterobinuclear μ-As_2 complexes. The above mixed-metal complexes, like $[Mo_2Cp_2(CO)_4]$, are known to react with alkynes under mild conditions to give alkyne-bridged complexes.

The co-thermolysis of $[Co_2(\mu\text{-}As_2)(CO)_6]$ and $[(OC)_4CoMCp(CO)_3]$ [M = Mo or W] in refluxing THF produced, in addition to unchanged $[Co_2(\mu\text{-}As_2)(CO)_6]$, the orange complexes $[(OC)_3Co(\mu\text{-}As_2)MCp(CO)_2]$ [M = Mo **2** or W **3**] in 36 and 21% yields respectively. Both **2** and **3** have been characterized by IR, ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and microanalysis and by single crystal X-ray diffraction studies.

The molecular structures of the isomorphous complexes **2** and **3**, as determined by X-ray crystallography, are represented in Fig. 1. Selected bond lengths and angles are given in Table 1. Both molecules feature an As_2 ligand bonded 'side-on' to a bimetallic fragment, producing a tetrahedral $CoMAs_2$ unit in each case. The cyclopentadienyl ligand is bonded to metal M such that it is *trans* to the diarsenic 'edge'.

Given the similarity of the covalent radii of molybdenum and tungsten, it is perhaps unsurprising that the Co(1)–Mo(1) bond length [2.825(1) Å] in complex **2** is virtually the same as the Co(1)–W(1) bond length [2.821(2) Å] in **3**. However, both are long compared with corresponding ligand-bridged single bonds found in many other complexes. For example, in the complexes $[(OC)_3Co(\mu\text{-}CF_3CCCF_3)MoCp(CO)_2]$[19] and $[(OC)_3Co(\mu\text{-}PhCCMe)WCp(CO)_2]$,[20] which both adopt a structure analogous to that of **2** and **3**, the metal–metal bond lengths have been determined to be just 2.692(1) and 2.693(1) Å, respectively. The lengths of ligand-bridged Co–Mo and Co–W bonds in other bi- and tri-metallic complexes typically lie in the ranges 2.60–2.75 [19,21] and 2.55–2.76 Å,[20,22] respectively. The long Co–Mo bond found in $[CpCoMo(CO)_3(C_8H_8)]$[23] [2.998(1) Å] is attributed to the steric requirements of the large bridging ligand and it seems likely that the As_2 unit exerts a similar influence in **2** and **3**.

The As(1)–As(2) bond length of 2.305(1) Å in complex **2** lies between that found for the corresponding bond in the homometallic complexes $[Co_2(\mu\text{-}As_2)(CO)_5(PPh_3)]$[4a] [2.273(3) Å, the shortest known] and $[Mo_2(\mu\text{-}As_2)Cp_2(CO)_4]$[5] [2.311(3) Å]. Despite the similarity of the metal–metal (see above) and metal–arsenic (see below) bond lengths in **2** and **3**, the As(1)–As(2) bond length of 2.322(2) Å in **3** is significantly longer than the As–As bond found in **2** or in either of the homometallic examples cited above. In both **2** and **3** the As(1)–As(2) bond is significantly shorter than that found in gaseous As_4 [2.44 Å],[24] $(AsMe)_5$ [2.428(8) Å][25] or $(AsPh)_6$ [2.456(5) Å][26] and shorter also than the mean of those found in the related species $[As_3Co(CO)_3]$ (2.372(5) Å).[4b] This would seem to imply a degree of multiple-bond character in the As–As bonds of **2** and **3**. The trend of decreasing As–As distance on sequential substitution of metal carbonyl fragments into As_4 can be rationalized by considering a delocalized molecular orbital model, first applied to $[As_3Co(CO)_3]$, in which the metal system acts as an 'electron sink' for the arsenic ligand.[4b,27]

In both complexes **2** and **3** the diarsenic unit is twisted to place As(2) closer to cobalt and As(1) closer to molybdenum/tungsten [For **2** Co(1)–As(1) 2.420(1), Co(1)–As(2) 2.394(1), Mo(1)–As(1) 2.579(1), Mo(1)–As(2) 2.630(1) Å; for **3** Co(1)–As(1) 2.429(2), Co(1)–As(2) 2.406(2), W(1)–As(1) 2.582(1), W(1)–As(2) 2.632(1) Å]. The similarity of the Mo–As and W–As bond lengths is noteworthy and consistent with the small difference in the covalent radii of these metal atoms.

The presence of the cyclopentadienyl ligand on the same side of the complex as As(1) and effectively *trans* to As(2) may be a contributing influence to the selective extension of the M–As(2) bond in these complexes. However, twisting of the diarsenic unit is also a feature of the known homometallic analogues of the new complexes.[13] The frequency of this observation in a range of compounds suggests a primarily electronic rather than steric cause.

Twisting of the bridging ligands in the related complex $[Nb_2(\mu\text{-}PhCCPh)_2Cp_2(CO)_2]$ was initially ascribed to non-bonded interactions within the molecule,[28] but examination of molecular orbital diagrams for this complex reveals that the HOMO and LUMO are close in energy and well separated from the other bonding molecular orbitals.[29] Under these circumstances a second-order Jahn–Teller distortion is expected. Twisting of the bridging ligand is one possible modification. The molecular orbital approach has been extended to molecules of the type $[Co_2(\mu\text{-}X_2)(CO)_6]$[30] and it seems likely that this effect contributes to some extent to the As_2 twisting observed in **2** and **3**.

The FT-IR spectra of complexes **2** and **3** each exhibit four strong absorptions in the CO stretching region. The band pattern is very similar to that observed for $[(OC)_3Co(\mu\text{-}RCCR)MoCp(CO)_2]$. The cyclopentadienyl groups give rise to signals in the ^1H and ^{13}C NMR spectra of both **2** and **3**. A weaker sharp singlet at δ 224.1 is due to the two carbonyl carbon atoms bonded to molybdenum, indicating that there is a fluxional process in solution which renders the two carbonyl groups equivalent.

The formation of complexes **2** and **3** shows that a 'transfer' process does occur when $[Co_2(\mu\text{-}As_2)(CO)_6]$ reacts with $[(OC)_4CoMCp(CO)_3]$ [M = Mo or W], yielding the heterobimetallic products, $[(OC)_3Co(\mu\text{-}As_2)MCp(CO)_2]$ (M = Mo or

Table 2 Selected bond lengths (Å) and angles (°) for $[(Ph_3P)(OC)_2Co(\mu\text{-}As_2)WCp(CO)_2]$ **5**

	Molecule 1	Molecule 2
W(1)–Co(1)	2.781(3)	2.832(3)
W(1)–As(11)	2.583(3)	2.576(3)
W(1)–As(12)	2.650(3)	2.637(3)
W(1)–C(13)	1.95(2)	1.95(2)
W(1)–C(14)	1.95(2)	1.95(2)
Co(1)–As(12)	2.383(4)	2.380(4)
Co(1)–As(11)	2.431(4)	2.400(4)
Co(1)–C(12)	1.71(2)	1.70(3)
Co(1)–C(11)	1.71(2)	1.72(2)
Co(1)–P(1)	2.208(7)	2.219(7)
As(11)–As(12)	2.309(5)	2.310(4)
C–O	1.17(2)–1.20(3)	1.17(2)–1.20(3)
P(1)–C_{phenyl}	1.81(3)–1.84(3)	1.81(2)–1.84(2)
Co(1)–W(1)–As(11)	53.73(10)	52.43(9)
Co(1)–W(1)–As(12)	51.97(9)	51.44(9)
As(11)–W(1)–As(12)	52.35(11)	52.58(9)
W(1)–Co(1)–As(11)	58.96(10)	58.29(10)
W(1)–Co(1)–As(12)	61.17(11)	60.05(10)
As(11)–Co(1)–As(12)	57.32(13)	57.79(12)
W(1)–As(11)–Co(1)	67.30(11)	69.28(10)
W(1)–As(11)–As(12)	65.31(11)	65.07(10)
Co(1)–As(11)–As(12)	60.29(13)	60.66(12)
W(1)–As(12)–Co(1)	66.86(11)	68.52(11)
W(1)–As(12)–As(11)	62.34(11)	62.35(10)
Co(1)–As(12)–As(11)	62.39(13)	61.55(12)
W(1)–Co(1)–P(1)	157.7(2)	150.4(2)

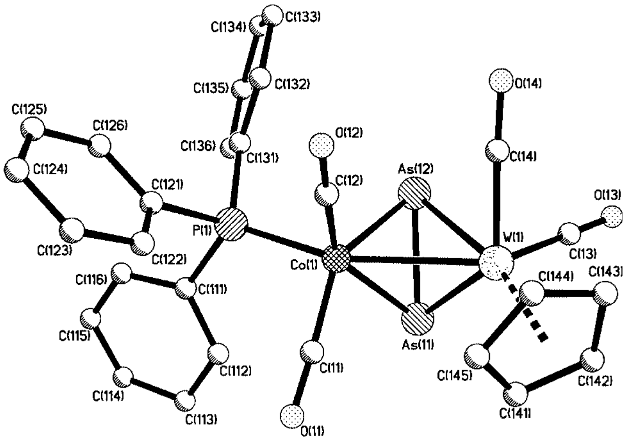


Fig. 2 The molecular structure of $[(Ph_3P)(OC)_2Co(\mu\text{-}As_2)WCp(CO)_2]$ **5**. Details as in Fig. 1.

W). The mechanism for this process is presumed to be similar to that for the reaction of $[Co_2(\mu\text{-}As_2)(CO)_6]$ with $[Mo_2Cp_2(CO)_4]$. The initial step must be loss of CO from $[(OC)_4CoMCp(CO)_3]$ just as CO loss from $[Mo_2Cp_2(CO)_6]$ is required prior to reaction with $[Co_2(\mu\text{-}As_2)(CO)_6]$.

(c) Reaction of $[(OC)_3Co(\mu\text{-}As_2)MCp(CO)_2]$ [M = Mo 2 or W 3] with PPh_3

Reaction of $[(OC)_3Co(\mu\text{-}As_2)MCp(CO)_2]$ (M = Mo or W) with an excess of PPh_3 in refluxing benzene for 20 h gave, in addition to starting material, red-orange $[(Ph_3P)(OC)_2Co(\mu\text{-}As_2)MCp(CO)_2]$ (M = Mo **4** or W **5**) in 58 and 54% yields respectively. Both complexes have been characterized by IR, ^1H and ^{13}C NMR spectroscopy, mass spectrometry and microanalysis. Complex **5** has been the subject of a single crystal X-ray diffraction study.

The molecular structure of complex **5** is presented in Fig. 2. Selected bond lengths and angles are collated in Table 2. The complex crystallizes with two molecules in the asymmetric unit. There are significant differences between some of the bond lengths and angles in these two molecules, thought to be due to correlations between the two molecules in refinement. For purposes of the following discussion the mean values of the bond lengths and angles will be used.

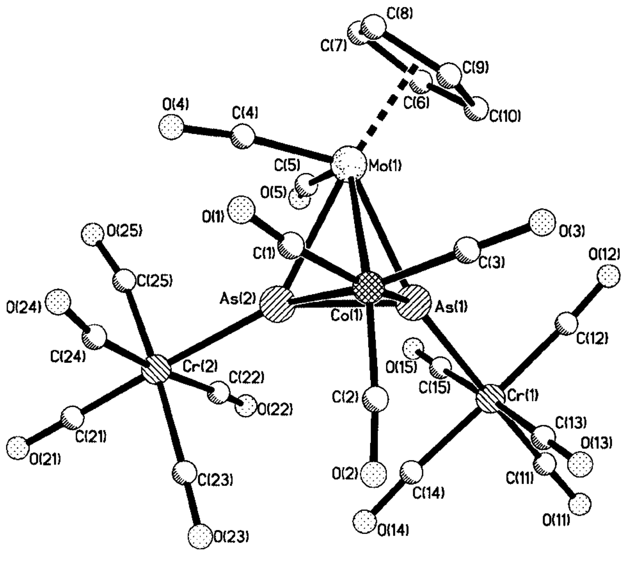


Fig. 3 The molecular structure and atom numbering scheme of $[(OC)_3Co\{\mu\text{-}As_2[Cr(CO)_5]_2\}MoCp(CO)_2]$ **6** formed by reaction of complex **2** with $[Cr(CO)_5]\cdot THF$. There is a slight disorder (60:40) of some of the carbonyl oxygen atoms and the major component is illustrated.

From Fig. 2 it is clear that the phosphine has substituted the axial carbonyl on the cobalt atom and now occupies this site. The regiospecificity of this process has been observed previously in related reactions of Co–Mo and Co–W systems.[21] The phosphorus–cobalt bond is inclined at 25.9° to the projection of the W–Co bond, placing it *trans* to the cyclopentadienyl ligand across the Co–W axis.

Co-ordination of the phosphine brings about a very slight decrease in the length of the Co–W bond from 2.821(2) Å in complex **3** to 2.807(3) Å in **5**. Within the limits of experimental error, the As–As separation of 2.310(5) Å in **5** is virtually the same as the As(1)–As(2) bond length in **3** [2.322(2) Å]. Similarly, the mean W–As and Co–As bond lengths of, respectively, 2.612(3) and 2.399(4) Å for **5** are not significantly different from those of the parent cluster **3** [W–As_{mean} 2.607(1) Å, Co–As_{mean} 2.418(2) Å].

Both the ^1H and ^{13}C NMR spectroscopic data of complexes **4** and **5** are similar to those obtained for the parent compounds **2** and **3**. The broad singlet at δ −86.3 in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of complex **4** (δ −97.8 in **5**) is typical of a cobalt-bound terminal phosphine.

(d) Reaction of $[(OC)_3Co(\mu\text{-}As_2)MoCp(CO)_2]$ 2 with $[Cr(CO)_5]\cdot THF$

Vigorous stirring of $[(OC)_3Co(\mu\text{-}As_2)MoCp(CO)_2]$ with $[Cr(CO)_5]\cdot THF$ in THF at room temperature gave, in addition to unchanged $[(OC)_3Co(\mu\text{-}As_2)MoCp(CO)_2]$, red-orange $[(OC)_3Co\{\mu\text{-}As_2[Cr(CO)_5]_2\}MoCp(CO)_2]$ **6** in 34% yield. Complex **6** has been characterized by IR and ^1H NMR spectroscopy, mass spectrometry and microanalysis. Additionally, it has been the subject of a single crystal X-ray diffraction experiment.

Fig. 3 shows the molecular structure of complex **6**; selected bond lengths and angles are given in Table 3. The tetrahedral $CoMoAs_2$ core of the parent compound **2** is retained when the two arsenic atoms each co-ordinate to a $Cr(CO)_5$ unit. The As–As bond length of 2.317(3) Å is slightly longer than that of 2.305(1) Å in **2**, consistent with the higher co-ordination numbers at the arsenic centres. There is a significant shortening of all the metal–arsenic bond lengths in **6** compared to those in **2** (see Table 1). This latter trend is explicable in terms of the

Table 3 Selected bond lengths (Å) and angles (°) for $[(OC)_3Co\{\mu\text{-}As_2[Cr(CO)_5]_2\}MoCp(CO)_2]$ **6**

Mo(1)–Co(1)	2.874(4)	Mo(1)–As(1)	2.557(3)
Mo(1)–As(2)	2.608(3)	Co(1)–As(1)	2.408(4)
Co(1)–As(2)	2.357(4)	As(1)–As(2)	2.317(3)
As(1)–Cr(1)	2.469(4)	As(2)–Cr(2)	2.469(4)
$Mo–C_{carbonyl}$	1.91(3)–1.95(3)	$Co–C_{carbonyl}$	1.72(3)–1.76(3)
$Cr–C_{carbonyl}$	1.80(2)–1.93(3)	$C–O_{cobalt}$	1.14(2)–1.25(3)
Co(1)–Mo(1)–As(1)	52.24(9)	Co(1)–Mo(1)–As(2)	50.64(8)
As(1)–Mo(1)–As(2)	53.30(8)	Mo(1)–Co(1)–As(1)	57.08(9)
Mo(1)–Co(1)–As(2)	58.80(9)	As(1)–Co(1)–As(2)	58.2(1)
Mo(1)–Co(1)–C(1)	97.1(9)	Mo(1)–Co(1)–C(2)	148.0(7)
Mo(1)–Co(1)–C(3)	96.6(8)	Mo(1)–As(1)–Co(1)	70.7(1)
Mo(1)–As(1)–As(2)	64.47(9)	Co(1)–As(1)–As(2)	59.8(1)
Cr(1)–As(1)–As(2)	129.6(1)	Mo(1)–As(2)–Co(1)	70.6(1)
Co(1)–As(2)–As(1)	62.0(1)	Mo(1)–As(2)–As(1)	62.23(9)
Cr(2)–As(2)–As(1)	141.2(1)		

enhanced π-acceptor character of the diarsenic unit in **6**, resulting from its co-ordination to the strongly electron-accepting $Cr(CO)_5$ groups, which would produce an increased back donation from the molybdenum and cobalt atoms to the As_2 antibonding orbitals; this is apparently a larger effect than the lengthening of the arsenic covalent radius produced by the increase in co-ordination number. The Co(1)–Mo(1) bond length of 2.874(4) Å in **6** is considerably longer than that of 2.825(1) Å in the parent compound **2**, consistent with the overall loss of electron density from the two metal centres. The twisting of the diarsenic unit observed in both **2** and **3** is also seen in **6** where Mo(1) is closer to As(1) than to As(2) and Co(1) is closer to As(2) than to As(1), both by 0.051 Å. The As(2)–As(1)–Cr(1) angle of 129.6(1)° is much smaller than the As(1)–As(2)–Cr(2) angle of 141.2(1)° a difference that at first sight appears to be related to the different environments of the two extremely bulky $Cr(CO)_5$ groups. This explanation can, however, be ruled out because there are no close contacts between the atoms of these groups and the rest of the molecule. It is interesting that the mean As–As–Cr angle of 135.4° is within the range observed for the C–C–R angle in 'side-on' co-ordinated alkynes [130–150°].[27,31]

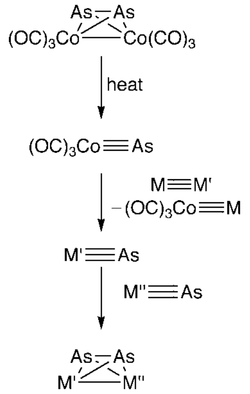
A complicated infrared spectrum is obtained for complex **6** with a large number of terminal *ν*(CO) absorptions Those bands associated with the parent complex remain visible and shifted only slightly, suggesting that some decomposition takes place on dissolution of the adduct. It appears that the Co–Mo bimetallic fragment is sufficiently basic to allow both arsenic atoms to ligate a $Cr(CO)_5$ fragment, forming an adduct which is stable in the solid state.

(e) Reaction of $[MoWCp_2(CO)_4]$ with $[Co_2(\mu\text{-}As_2)(CO)_6]$

The mixed-metal complex $[MoWCp_2(CO)_4]$ reacts with alkynes under the same mild conditions as $[Mo_2Cp_2(CO)_4]$[32] which suggested that this too might yield a new molybdenum–tungsten complex with an As_2 ligand on reaction with $[Co_2(\mu\text{-}As_2)(CO)_6]$. Reaction of $[MoWCp_2(CO)_4]$ with $[Co_2(\mu\text{-}As_2)(CO)_6]$ in refluxing xylene, however, gave only $[(OC)_3Co(\mu\text{-}As_2)MoCp(CO)_2]$ **2** and $[(OC)_3Co(\mu\text{-}As_2)WCp(CO)_2]$ **3** in very low yield. The identities of the products collected were established by comparison of infrared data to those obtained previously.

Although the desired diarsenic-bridged Mo–W complex was not obtained from this reaction the products of the reaction show that a $MCp(CO)_2$ [M = Mo or W] fragment may substitute a $Co(CO)_3$ unit in $[Co_2(\mu\text{-}As_2)(CO)_6]$. This result provides some support for the proposal that the syntheses of $[Mo_2(\mu\text{-}As_2)Cp_2(CO)_4]$ and $[(OC)_3Co(\mu\text{-}As_2)MCp(CO)_2]$ [M = Mo or W] from $[Co_2(\mu\text{-}As_2)(CO)_6]$ occur by stepwise exchange of $Co(CO)_3$ units by $MCp(CO)_2$ fragments rather than by a direct transfer of the As_2 ligand. Reactions of this type for cobalt tetrahedranes are known to occur[33] but mechanisms have not been proposed.

The formation of $[M_2(\mu\text{-}As_2)Cp_2(CO)_4]$ [M = Mo or W] from $[M_2Cp_2(CO)_6]$ and grey arsenic has been proposed to involve condensation of triply bonded $(OC)_2CpMoAs$ fragments[2,34] and a similar process could occur in the reactions (a), (b) and (e). A mechanism based on this proposal is presented in Scheme 1. If such a process operates there is the possibility that it could lead to products other than those isolated, yet there is no $[(OC)_3Co(\mu\text{-}As_2)MoCp(CO)_2]$ recovered from the reaction of $[Mo_2Cp_2(CO)_4]$ and $[Co_2(\mu\text{-}As_2)(CO)_6]$ and no $[Mo_2(\mu\text{-}As_2)Cp_2(CO)_4]$ appears to be produced in reaction (e).



Scheme 1 Possible route to complexes **1**, **2** and **3** *via* triply bonded intermediates (a) M = M′ = M″ = $MoCp(CO)_2$, (b) M = M″ = $Co(CO)_3$, M′ = $MCp(CO)_2$ [M = Mo or W], (e) M″ = $Co(CO)_3$, M = $MoCp(CO)_2$ and M′ = $WCp(CO)_2$ or M′ = $MoCp(CO)_2$ and M = $WCp(CO)_2$.

(f) Reaction of $[Mo_2Cp_2(CO)_6]$ and $[W_2Cp_2(CO)_6]$ with grey arsenic

Most routes to tetrahedral transition metal complexes containing naked arsenic atoms employ arsenic-containing complexes as starting materials but Ziegler *et al.*[2,3,4] successfully synthesized $[M_2(\mu\text{-}As_2)Cp_2(CO)_4]$ and $[M_3(\mu_3\text{-}As)Cp_3(CO)_6]$ by thermolytic reaction of $[M_2Cp_2(CO)_6]$ [M = Mo or W] with grey arsenic. This reaction was presumed to proceed *via* generation of the triply bonded intermediate, $AsMCp(CO)_2$ (M = Mo or W); eqn. (1). If such a triply bonded intermediate

$$[MCp(CO)_3]_2 \xrightarrow[\text{heat}]{As_n} 2\left[(OC)_2CpM{\equiv}As\right] \qquad (1)$$

is indeed involved then by refluxing $[Mo_2Cp_2(CO)_6]$, $[W_2Cp_2(CO)_6]$ and grey arsenic it ought to be possible to synthesize the heterometallic μ-As_2 complex $[MoW(\mu\text{-}As_2)Cp_2(CO)_4]$.

Reaction of $[Mo_2Cp_2(CO)_6]$ and $[W_2Cp_2(CO)_6]$ with grey arsenic in refluxing *p*-xylene for 24 h gives three orange, crystalline, bimetallic products, $[MM'(\mu\text{-}As_2)Cp_2(CO)_4]$ (M = M′ =

Table 4 Selected bond lengths (Å) and angles (°) for $[MoW_2(\mu_3\text{-}As)Cp_3(CO)_6]$ **9**

W(1)–W(2)	3.118(1)	W(1)–Mo(1)	3.124(2)
W(1)–As	2.557(2)	W(2)–Mo(1)	3.097(2)
W(2)–As	2.515(2)	Mo(1)–As	2.547(2)
W(1)–C(1)	2.00(2)	W(1)–C(2)	1.96(2)
W(2)–C(3)	2.00(2)	W(2)–C(4)	2.00(2)
Mo(1)–C(5)	1.96(2)	Mo(1)–C(6)	1.98(2)
C–O	1.13(2)–1.17(2)		
W(2)–W(1)–As	51.45(4)	W(2)–W(1)–Mo(1)	59.50(3)
Mo(1)–W(1)–As	52.12(5)	W(1)–W(2)–Mo(1)	60.34(3)
W(1)–W(2)–As	52.69(5)	Mo(1)–W(2)–As	52.75(5)
W(2)–Mo(1)–W(1)	60.16(3)	W(2)–Mo(1)–As	51.80(5)
W(1)–Mo(1)–As	52.42(5)	W(2)–As–W(1)	75.86(5)
Mo(1)–As–W(1)	75.46(6)	W(2)–As–Mo(1)	75.45(6)

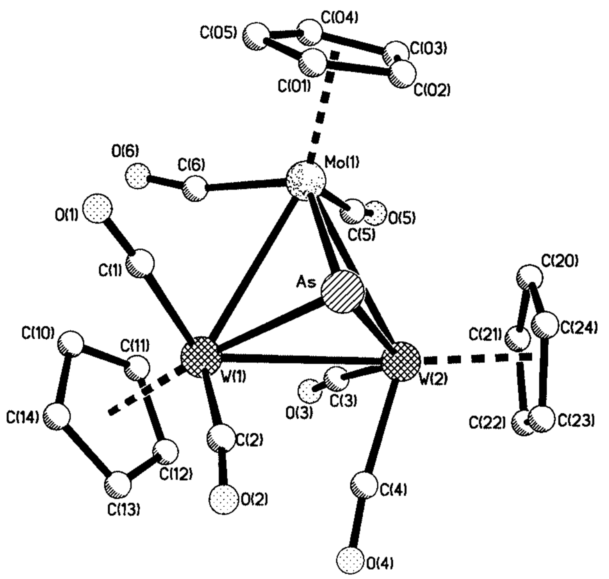


Fig. 4 The molecular structure and atom numbering scheme of $[MoW_2(\mu_3\text{-}As)Cp_3(CO)_6]$ **9** which has some conformational disorder in the solid state; the 70% component of the disorder is shown.

Mo; M = Mo, M′ = W **7**; M = M′ = W), collected in 5, 20 and 6% yield respectively. Four green, crystalline, trimetallic products, $[M_2M'(\mu_3\text{-}As)Cp_3(CO)_6]$ (M = M′ = Mo; M = Mo, M′ = W **8**; M = W, M′ = Mo **9**; M = M′ = W) were also obtained in 1.2, 6, 12 and 4.3% yield respectively. The identities of the complexes $[Mo_2(\mu\text{-}As_2)Cp_2(CO)_4]$, $[W_2(\mu\text{-}As_2)Cp_2(CO)_4]$, $[Mo_3(\mu_3\text{-}As)Cp_3(CO)_6]$ and $[W_3(\mu_3\text{-}As)Cp_3(CO)_6]$ were established by comparison of their infrared spectra with published data for these known compounds.[2,3] The new complexes **7**, **8** and **9** were fully characterized by IR, ^1H and ^{13}C NMR spectroscopy, mass spectrometry and microanalysis.

The structure of complex **9** was confirmed by X-ray analysis. Bond lengths and angles are presented in Table 4 and the overall molecular structure is shown in Fig. 4. Owing to disorder (*ca.* 70 : 30%) of two conformers in the crystal, the positions of $Cp(CO)_2Mo(1)$ and $Cp(CO)_2W(1)$ are randomly interchanged throughout the crystal (see Experimental section) so that in Fig. 4 the atom labelled W(1) is at the site predominantly occupied by W and Mo(1) is at the site predominantly occupied by Mo; the second tungsten atom W(2) is unaffected by the disorder. The parameters involving the two disordered sites should be regarded with some caution, but due to the close similarity in the covalent radii of Mo and W observed in the structures of **2** and **3** some discussion of the bond lengths is possible.

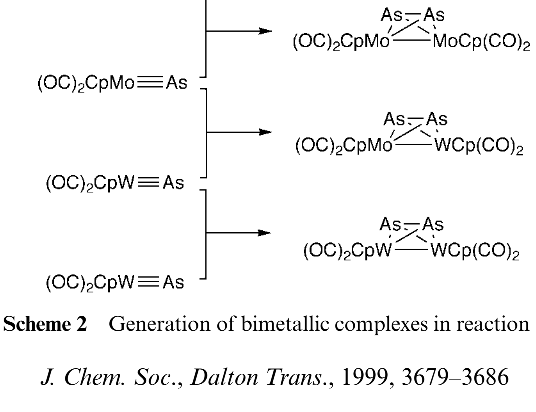
The core of the cluster consists of a MoW_2 triangle capped by a naked μ_3-As ligand. The three M–M bond lengths are in the narrow range 3.097(2)–3.124(2) Å and are equal within experimental error. This is consistent with the results for the two separate molecules **2** and **3**, where equivalent Co–Mo and Co–W bonds lengths were virtually identical (see above). The μ_3-As atom is not exactly above the centroid of the triangle of metal atoms but is displaced towards the ordered tungsten atom W(2); the W(1)–As and Mo(1)–As bond lengths are not significantly different from their mean value of 2.552(2) Å but the W(2)–As bond length of 2.515(2) Å is markedly shorter. The difference in metal–arsenic bond lengths may be related to differences in the orientation of the $M(CO)_2Cp$ groups.

The ^1H NMR spectrum of complex **8** has two sharp singlets at δ 5.05 and 5.06, integrating to 10 and 5 protons, respectively. These are attributable to the protons of the three cyclopentadienyl rings, one of which coordinates to each metal. Thus the first resonance corresponds to the two Mo-bound cyclopentadienyls and the second to the single W-bound ligand. A similar spectrum is obtained for complex **9**, with two singlets at δ 5.07 and 5.09, the first resonance corresponding to W-bound Cp and having twice the integral of the second. All three cyclopentadienyl ligands are in distinct environments in the solid state structure of **9** so that a fluxional process which renders equivalent the two Mo-bound Cp groups in **8** and the two W-bound Cp groups in **9** must be operating in solution.

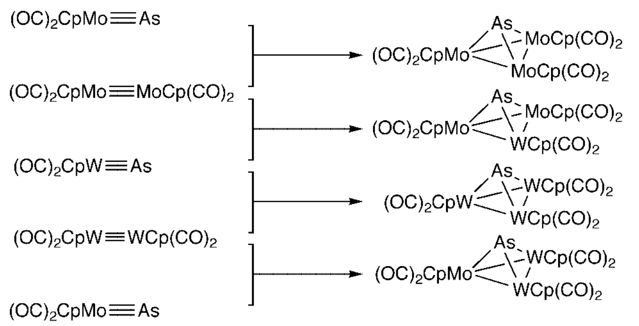
Two singlets are observed in the ^{13}C NMR spectrum of complex **8** at δ 89.5 and 87.3. Again these are due to the Cp ligands and since the first signal appears twice as intense as the second this is assigned to the Mo-bound ligands. In the analogous spectrum for complex **9** the two Cp resonances occur at δ 88.6 and 87.8 with the second signal, which is twice as intense as the first, being attributed to the W-bound ligands.

Clear, sharp singlets are also seen for the carbonyl carbon resonances for both complexes. For a complex of the type $[M_2M'(\mu_3\text{-}As)Cp_3(CO)_6]$, if the $MCp(CO)_2$ and $M'Cp(CO)_2$ groups are assumed to 'spin round' in solution then there will be only one environment for the pair of carbonyls bound to M′ but the carbonyls bound to M are diastereotopic and remain inequivalent. In the ^{13}C NMR spectrum of complex **8** there are two Mo–CO resonances (δ 229.7, 223.2) and one W–CO resonance (δ 214.0) but in the spectrum of **9** there are two W–CO resonances (δ 210.8, 216.1) and one Mo–CO resonance (δ 233.2). A weak pair of satellite peaks are resolved either side of the W–CO signal for complex **8**, caused by coupling of carbonyl carbon atoms to ^{183}W ($I = \frac{1}{2}$, 15% abundance).

The reaction is presumed initially to generate the triply bonded intermediates $(OC)_2CpMAs$ (M = Mo or W) as proposed by Ziegler. Reaction of two such intermediates gives rise to a bimetallic product, whereas the trimetallic complexes are produced by reaction of $(OC)_2CpMAs$ with $[MCp(CO)_2]_2$ (M = Mo or W). Thus all the possible bimetallic and trimetallic species depicted respectively in Schemes 2 and 3 are obtained as reaction products. The higher yield of **9** as compared to **8** may reflect a thermodynamic preference based on the greater



Scheme 2 Generation of bimetallic complexes in reaction (h).



Scheme 3 Generation of trimetallic complexes in reaction (h).

strength of metal–metal bonds involving tungsten as compared to molybdenum.

Experimental

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen, using solvents that were freshly distilled from the appropriate drying agent. Ultraviolet irradiation experiments were performed using a 125 W Hanovia medium pressure mercury vapour lamp. Infrared spectra were recorded in *n*-hexane or dichloromethane solution in 0.5 mm NaCl cells, using a Perkin-Elmer Paragon 1000 Fourier-Transform spectrometer or a Perkin-Elmer 1600 series spectrometer. Fast atom bombardment mass spectra were obtained on a Kratos MS890 instrument, fast ion bombardment mass spectra on a Kratos MS50 instrument. 3-Nitrobenzyl alcohol was used as a matrix. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM400 or WM250 spectrometers using the solvent resonance as an internal standard, ^{31}P NMR spectra on a Bruker WM250 spectrometer with $P(OMe)_3$ used as a standard. Microanalyses were performed by the Microanalytical Department, University of Cambridge.

Preparative thin layer chromatography was carried out on 1 mm plates prepared at the University Chemical Laboratory, Cambridge. Column chromatography was performed on Kieselgel 60 (70–230 mesh). Products are given in order of decreasing R_f values.

Unless otherwise stated, all reagents were obtained from commercial suppliers and used without further purification. The complex $[Co_2(\mu\text{-}As_2)(CO)_6]$ was prepared as described.[4]

(a) Reaction of $[Co_2(\mu\text{-}As_2)(CO)_6]$ and $[Mo_2Cp_2(CO)_4]$

The complex $[Mo_2Cp_2(CO)_6]$ (281 mg, 0.57 mmol) was refluxed in toluene (70 ml) for 18 h, while purging the solution with nitrogen; $[Co_2(\mu\text{-}As_2)(CO)_6]$ (500 mg, 1.15 mmol) was then added and the mixture refluxed with stirring for 6 h. After removal of reaction solvents under vacuum, the residue was dissolved in the minimum quantity of dichloromethane and adsorbed onto silica. The silica was pumped dry and transferred to the top of a silica chromatography column. Elution with hexane–dichloromethane (1:1) gave orange $[Mo_2(\mu\text{-}As_2)Cp_2(CO)_4]$ **1** (50 mg, 15%) as the only product.

(b) Reaction of $[Co_2(\mu\text{-}As_2)(CO)_6]$ with $[(OC)_4CoMoCp(CO)_3]$

The complexes $[Co_2(CO)_8]$ (490 mg, 1.4 mmol) and $[Mo_2Cp_2(CO)_6]$ (700 mg, 1.4 mmol) were photolysed together in THF (200 ml) for 24 h after which time the resulting solution was poured into a nitrogen-filled flask, $[Co_2(\mu\text{-}As_2)(CO)_6]$ (1.25 g, 2.9 mmol) added and the mixture refluxed with stirring for 20 min. After removal of the reaction solvent under vacuum the residue was treated as in reaction (a). Elution with hexane–dichloromethane (9:1) gave unchanged $[Co_2(\mu\text{-}As_2)(CO)_6]$ (305 mg) and red-orange crystalline $[(OC)_3Co(\mu\text{-}As_2)MoCp(CO)_2]$ **2** (514 mg, 36%). Crystals of **2** suitable for diffraction were grown by slow evaporation at 0 °C of an *n*-hexane–dichloromethane solution of this complex (Found: C, 23.66; H, 1.30. $C_{10}H_5As_2CoMoO_5$ requires C, 23.56; H, 0.99%). Mass spectrum: *m*/*z* 512 (M^+) and $M^+ - n$CO ($n = 1$–5). $\tilde{\nu}_{max}$/cm^{-1} (hexane) 2055s, 2027w, 2011s, 1990vs and 1943s. NMR ($CDCl_3$): ^{1}H, δ 5.37 [s, 5 H, Cp]; ^{13}C (^{1}H composite pulse decoupled), δ 224.1 [s, Mo–CO] and 86.6 [s, Cp].

(c) Reaction of $[(OC)_4CoWCp(CO)_3]$ with $[Co_2(\mu\text{-}As_2)(CO)_6]$

The complexes $[Co_2(CO)_8]$ (400 mg, 1.2 mmol) and $[W_2Cp_2(CO)_6]$ (780 mg, 1.2 mmol) were photolysed together in THF (200 ml) for 24 h after which time the resulting solution was poured into a nitrogen-filled flask; $[Co_2(\mu\text{-}As_2)(CO)_6]$ (1.05 g, 2.4 mmol) was added and the mixture refluxed with stirring for 30 min. After removal of the reaction solvent under vacuum the residue was treated as in reaction (a). Elution with hexane–dichloromethane (9:1) gave a trace of unchanged $[Co_2(\mu\text{-}As_2)(CO)_6]$ and orange crystalline $[(OC)_3Co(\mu\text{-}As_2)WCp(CO)_2]$ **3** (305 mg, 21%). Crystals of **3** suitable for diffraction were produced by recrystallization from dichloromethane solution (Found: C, 20.19; H, 0.85. $C_{10}H_5As_2CoO_5W$ requires C, 20.09; H, 0.84%). Mass spectrum: *m*/*z* 598 (M^+) and $M^+ - n$CO ($n = 1$–5). $\tilde{\nu}_{max}$/cm^{-1} (CH_2Cl_2) 2051s, 2001s, 1985vs and 1924m. NMR ($CDCl_3$): ^{1}H, δ 5.41 [s, 5 H, Cp]; ^{13}C (^{1}H composite pulse decoupled), δ 210.6 [s, W–CO] and 84.4 [s, Cp].

(d) Reaction of $[(OC)_3Co(\mu\text{-}As_2)MoCp(CO)_2]$ 2 and PPh_3

The complex $[(OC)_3Co(\mu\text{-}As_2)MoCp(CO)_2]$ **2** (100 mg, 0.20 mmol) and PPh_3 (0.52 g, 2.0 mmol) were refluxed in benzene (60 ml) with stirring for 20 h. After removal of the solvent under reduced pressure, the residue was treated as in reaction (a). Elution with hexane–dichloromethane (4:1) gave unchanged starting material (25 mg) and orange-red crystalline $[(Ph_3P)(OC)_2Co(\mu\text{-}As_2)MoCp(CO)_2]$ **4** (83 mg, 58%) as the only product (Found: C, 43.55; H, 2.69. $C_{27}H_{20}As_2CoMoO_4P$ requires C, 43.58; H, 2.71%). Mass spectrum: *m*/*z* 746 (M^+) and $M^+ - n$CO ($n = 1$–4). $\tilde{\nu}_{max}$/cm^{-1} (CH_2Cl_2) 1997m, 1965vs, 1946m and 1913w. NMR ($CDCl_3$): δ 7.5–7.3 [m, 15 H, Ph] and 5.32 [s, 5 H, Cp]; ^{13}C (^{1}H composite pulse decoupled), δ 226.3 [s, Mo–CO], 208.4 [s, Co–CO], 137.5–128.1 [Ph] and 85.9 [s, Cp].

(e) Reaction of $[(OC)_3Co(\mu\text{-}As_2)WCp(CO)_2]$ 3 and PPh_3

The complex $[(OC)_3Co(\mu\text{-}As_2)WCp(CO)_2]$ **3** (272 mg, 0.46 mmol) and PPh_3 (1.20 g, 4.6 mmol) were refluxed in benzene (60 ml) with stirring for 20 h. After removal of the solvent under reduced pressure, the residue was treated as in reaction (a). Elution with hexane–dichloromethane (4:1) gave unchanged starting material (75 mg) and red crystalline $[(Ph_3P)(OC)_2Co(\mu\text{-}As_2)WCp(CO)_2]$ **5** (206 mg, 54%) as the only product. Crystals of **5** suitable for diffraction were grown by slow evaporation at room temperature of a benzene solution of the complex (Found: C, 38.72; H, 2.32. $C_{27}H_{20}As_2CoO_4PW$ requires C, 38.98; H, 2.42%). Mass spectrum: *m*/*z* 832 (M^+) and $M^+ - n$CO ($n = 1$–4). $\tilde{\nu}_{max}$/cm^{-1} (CH_2Cl_2) 1994m, 1962vs, 1943m and 1905w. NMR ($CDCl_3$): δ 7.5–7.3 [m, 15 H, Ph] and 5.36 [s, 5 H, Cp]; ^{13}C (^{1}H composite pulse decoupled), δ 212.1 [s, W–CO], 137.6–128.1 [Ph] and 83.8 [s, Cp].

(f) Reaction of $[(OC)_3Co(\mu\text{-}As_2)MoCp(CO)_2]$ 2 with $[Cr(CO)_5]\cdot$THF

The complex $[Cr(CO)_6]$ (150 mg, 0.68 mmol) in THF (250 ml) was irradiated for 12 h, $[(OC)_3Co(\mu\text{-}As_2)MoCp(CO)_2]$ **2** (174 mg, 0.34 mmol) was then added and stirred vigorously for 20 h. After removal of the reaction solvent under vacuum, the residue was dissolved in the minimum quantity of dichloromethane and applied to the base of silica TLC plates. Elution with hexane–dichloromethane (3:2) gave unchanged $[(OC)_3Co(\mu\text{-}As_2)MoCp(CO)_2]$ **2** (45 mg), followed by red-orange

Table 5 X-Ray crystallographic and data processing parameters for complexes **2**, **3**, **5**, **6** and **9**

	2	**3**	**5**	**6**	**9**
Empirical formula	$C_{10}H_5As_2CoMoO_5$	$C_{10}H_5As_2CoO_5W$	$C_{27}H_{20}As_2CoO_4PW$	$C_{20}H_5As_2CoCr_2MoO_{15}$	$C_{21}H_{15}AsMoO_6W_2$
Formula weight	509.85	597.76	832.02	893.95	901.89
T/K	293(2)	293(2)	293(2)	293(2)	295(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$ (no. 2)	$P2_1/n$	$P2_1/c$
a/Å	8.899(2)	8.899(2)	12.7720(10)	8.913(4)	14.042(2)
b/Å	14.465(2)	14.471(3)	20.831(2)	19.628(6)	7.5130(15)
c/Å	11.046(2)	11.046(2)	10.493(2)	16.694(4)	20.877(4)
α/°	—	—	90.430(10)	—	—
β/°	91.440(10)	91.42(3)	103.480(10)	99.77(3)	91.762(9)
γ/°	—	—	90.820(10)	—	—
U/Å^3	1421.4(5)	1422.0(5)	2714.3(6)	2878.4(16)	2201.5(7)
Z	4	4	4	4	4
μ(Mo-Kα)/mm^{-1}	6.678	13.876	7.355	4.076	12.512
Reflections collected	3466	3443	5576	4100	5104
Independent reflections	3263 [*R*(int) = 0.0365]	3243 [*R*(int) = 0.0478]	5032 [*R*(int) = 0.0726]	3071 [*R*(int) = 0.1017]	3875 [*R*(int) = 0.0363]
Final *R*1, *wR*2					
$I > 2\sigma(I)$	0.0409, 0.0959	0.0428, 0.1122	0.0539, 0.1457	0.0746, 0.1284	0.0625, 0.1595
all data	0.1101, 0.1831	0.0810, 0.1347	0.1131, 0.1715	0.1815, 0.1560	0.0949, 0.1803

$[(OC)_3Co\{\mu\text{-}As_2[Cr(CO)_5]_2\}MoCp(CO)_2]$ **6** (86 mg, 34%). Crystals of **6** suitable for diffraction were grown from a dichloromethane–hexane solution of the complex by slow evaporation at 0 °C (Found: C, 25.83; H, 0.68. $C_{20}H_5As_2CoCr_2MoO_{15}$ requires C, 26.87; H, 0.56%). Mass spectrum: *m*/*z* 894 (M^+) and $M^+ - n$CO (n = 5 or 7). $\tilde{\nu}_{max}$/cm^{-1} (CH_2Cl_2) 2075m, 2054s, 2024m, 2003s, 1991m, 1967m, 1953vs and 1941m. ^{1}H NMR ($CDCl_3$): δ 5.39 [s, 5 H, Cp].

(g) Reaction of $[MoWCp_2(CO)_4]$ and $[Co_2(\mu\text{-}As_2)(CO)_6]$

The complexes $[Mo_2Cp_2(CO)_6]$ (400 mg, 0.82 mmol) and $[\{WCp(CO)_3\}_2]$ (544 mg, 0.82 mmol) were refluxed in xylene (100 ml) with stirring for 3 d; $[Co_2(\mu\text{-}As_2)(CO)_6]$ (790 mg, 1.81 mmol) was added and further refluxed. After removal of the solvents under reduced pressure, the residue was treated as in reaction (a). Elution with hexane–dichloromethane (4:1) gave $[(OC)_3Co(\mu\text{-}As_2)MoCp(CO)_2]$ **2** (90 mg, 10%) and $[(OC)_3Co(\mu\text{-}As_2)WCp(CO)_2]$ **3** (82 mg, 8%).

(h) Reaction of $[Mo_2Cp_2(CO)_6]$ and $[W_2Cp_2(CO)_6]$ with grey arsenic

The complex $[Mo_2Cp_2(CO)_6]$ (500 mg, 1.02 mmol), $[WCp(CO)_3]_2$ (677 mg, 1.02 mmol) and grey arsenic (765 mg, 10.2 mmol) were refluxed in xylene (70 ml) with stirring for 24 h. After removal of the reaction solvent under vacuum, the residue was treated as in reaction (a). Elution with hexane–dichloromethane (9:1) gave orange $[Mo_2(\mu\text{-}As_2)Cp_2(CO)_4]$ (60 mg, 5%), red-orange $[MoW(\mu\text{-}As_2)Cp_2(CO)_4]$ **7** (274 mg, 20%), orange $[W_2(\mu\text{-}As_2)Cp_2(CO)_4]$ (85 mg, 6%), green $[Mo_3(\mu_3\text{-}As)Cp_3(CO)_6]$ (12 mg, 1.2%), green $[Mo_2W(\mu_3\text{-}As)Cp_3(CO)_6]$ **8** (61 mg, 6%), green $[MoW_2(\mu_3\text{-}As)Cp_3(CO)_6]$ **9** (142 mg, 12%) and green $[W_3(\mu_3\text{-}As)Cp_3(CO)_6]$ (58 mg, 4.3%). Crystals of **9** suitable for diffraction were grown from a solution of *n*-hexane–dichloromethane at −20 °C.

Complex **7** (Found: C, 25.20; H, 1.59. $C_{14}H_{10}As_2MoO_4W$ requires C, 25.03; H, 1.50%): mass spectrum *m*/*z* 672 (M^+) and $M^+ - n$CO (n = 1–4); $\tilde{\nu}_{max}$/cm^{-1} (CH_2Cl_2) 1972w, 1950s and 1898m; NMR ($CDCl_3$) ^{1}H, δ 5.17 [s, 5 H, Mo–Cp], 5.13 [s, 5 H, W–Cp]; ^{13}C (^{1}H composite pulse decoupled) δ 225.5 [s, Mo–CO], 211.3 [s, W–CO], 84.29 [s, Mo–Cp] and 82.28 [s, W–Cp]. Complex **8** (Found: C, 30.88; H, 1.79. $C_{14}H_{10}As_2MoO_4W$ requires C, 30.99; H, 1.86%): *m*/*z* 814 (M^+) and $M^+ - n$CO (n = 1–6); $\tilde{\nu}_{max}$/cm^{-1} (CH_2Cl_2) 1970w, 1936s, 1900m and 1871w; NMR ($CDCl_3$) ^{1}H, δ 5.06 [s, 5 H, W–Cp], 5.05 [s, 10 H, Mo-Cp]; ^{13}C (^{1}H composite pulse decoupled), δ 229.7 [s, Mo–CO], 223.2 [s, Mo–CO], 214.0 [d, $^1J_{CW}$ = 184 Hz, W–CO], 89.5 [s, Mo–Cp] and 87.3 [s, W–Cp]. Complex **9** (Found: C, 28.13; H, 1.79. $C_{21}H_{15}AsMoO_6W_2$ requires C, 27.97; H, 1.68%): *m*/*z* 902 (M^+) and $M^+ - n$CO (n = 1–6); $\tilde{\nu}_{max}$/cm^{-1} (CH_2Cl_2) 1970w, 1935s, 1897m and 1868w; NMR ($CDCl_3$) ^{1}H, δ 5.09 [s, 5 H, Mo–Cp] and 5.07 [s, 10 H, W–Cp]: ^{13}C (^{1}H composite pulse decoupled), δ 233.2 [s, Mo–CO], 216.1 [s, W–CO], 210.8 [W–CO], 88.6 [s, Mo–Cp] and 87.8 [s, W–Cp].

Crystal structure determinations

X-Ray intensity data were collected on a Rigaku AFC5R four-circle diffractometer for complexes **2**, **3** and **5** and on a Siemens P4 four-circle diffractometer for **6** and **9**. Details of data collection, refinement and crystal data are listed in Table 5. Lorentz-polarization corrections were applied to the data of all compounds. Absorption corrections based on ψ-scans were applied to the data of **2**, **3** and **5**. After refinement with isotropic displacement parameters for all atoms, empirical corrections were also applied to the data of **6** and **9**.[35]

The positions of the metal atoms and most of the non-hydrogen atoms were located from direct methods,[36] and the remaining non-hydrogen atoms were revealed from subsequent Fourier-difference syntheses. Refinement was based on F^2. In the crystal of complex **5** there are two independent molecules and chemically equivalent bond lengths in the two molecules were "tied" in the refinement. The only crystals that could be obtained of **6** diffracted relatively poorly at high angle. Relatively high displacement parameters for some carbonyl atoms and the Cp ring indicated some rotational disorder of the $Cr(CO)_5$ groups and at Mo(1), but this was only resolved for three of the terminal oxygen atoms O(5), O(24) and O(25). Weak restraints were applied to the anisotropic displacement parameters of C(7), C(9) and C(10) to prevent their becoming non-positive definite. The structure of **9** consisted of a random distribution of two conformers in a 70:30 ratio throughout the crystal, so that in the observed molecular image all the atoms superimposed within experimental error, but W and Mo shared the same two sites [with relative occupancies 0.70/0.30 at the site labelled W(1) and 0.30/0.70 at the site labelled Mo(1)].

The hydrogen atoms of the cyclopentadienyl rings of complexes **6** and **9** were not included in structure factor calculations. All other hydrogen atoms were placed in calculated positions with displacement parameters equal $1.2U_{eq}$ of the parent carbon atoms. In the final cycles of full-matrix least-squares refinement anisotropic displacement parameters were assigned to the metal and arsenic atoms in **9** and in the other structures to all non-hydrogen atoms.

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See http://www.rsc.org/suppdata/dt/1999/3679/ for crystallographic files in .cif format.

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