DALTON FULL PAPER

Reactions of diarsines with bi- and tri-metallic carbonyl complexes containing cobalt

Nick Choi,[a] Gráinne Conole,[a] Jason D. King,†[b] Martin J. Mays,*[b] Mary McPartlin[a] and Caroline L. Stone[b]

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

Received 16th August 1999, Accepted 25th November 1999

Reaction of the diarsines As_2R_4 (R = Me or Ph) with alkyne-bridged dicobalt hexacarbonyl complexes leads to products with bridging $(AsR_2)_2O$ ligands and to the production of simple AsR_3 substituted complexes; alkylidyne tricobalt nonacarbonyl complexes exhibit parallel reactivity with As_2R_4. Thermolysis of the complex $[Co_2(\mu\text{-PhCCPh})\{\mu\text{-}(AsMe_2)_2O\}(CO)_4]$ gives the tetra-substituted complex, $[Co_2(\mu\text{-PhCCPh})\{\mu\text{-}(AsMe_2)_2O\}_2(CO)_2]$. Reaction of the heterometallic complex $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}MoCp(CO)_2]$ with As_2Ph_4 affords $[\{(HO)Ph_2As\}(OC)_2Co\{\mu\text{-}C_2(CO_2Me)_2\}MoCp(CO)_2]$, supporting the suggestion of a possible hydrolytic mechanism for the formation of the $(AsR_2)_2O$ bridged complexes.

Introduction

Thermally induced cleavage of the E–E bond of E_2R_4 (E = P, As) in the presence of metal carbonyls has proved a useful route to bis-ER_2-bridged bimetallic complexes.[1] Under milder conditions, complexes have also been synthesised which contain intact E_2R_4 ligands;[1,2] most examples of intact E_2R_4 ligands are for E = P, the number of characterised diarsine complexes being fairly small.[3] The diarsine in such complexes is often generated during the course of the reaction rather than being used as a starting material.

More recently, the reaction of P_2Ph_4 with the alkyne-bridged dicobalt complexes, $[Co_2(\mu\text{-RCCR}')(CO)_6]$ [R = R′ = CO_2Me, Ph or H; R = Ph, Me or CH_2OH, R′ = H], has been investigated under mild conditions.[4] Carbonyl substitution occurs readily to give derivatives in which an intact P_2Ph_4 molecule is coordinated in either a terminal monodentate or bridging bidentate mode. Cleavage of the P–P bond also occurs readily to produce complexes with four- or five-membered phosphametallacycles, *via* a proposed intermediate that possesses two PPh_2 groups, one terminal and one bridging.[4] The related mixed-metal complexes $[(OC)_3Co(\mu\text{-RCCR}')MoCp(CO)_2]$ [R = R′ = CO_2Me; R = Ph, R′ = H] react with P_2Ph_4 to give products that feature four-membered phosphacobaltacycles (Co–C–C–P); mono-substituted derivatives of the alkyne-bridged starting complex have also been isolated, in which the diphosphine is coordinated intact in monodentate mode.[5]

Reaction of the μ_3-alkylidyne tricobalt nonacarbonyl complexes $[Co_3(\mu_3\text{-CR})(CO)_9]$, with P_2Ph_4 initially proceeds to give complexes that contain the intact diphosphine in a terminal or bridging coordination mode.[6] Cleavage of the P–P bond again seems the most likely next step, but in this case metallacycle formation does not ensue. Instead, on chromatographic separation of the reaction mixture, a complex containing a μ-$[(PPh_2)_2O]$ ligand is isolated. For this reaction the intermediacy of a bis-phosphido bridged complex followed by hydrolysis/oxidation (on silica) of the intermediate has been proposed and this proposal is able to account for the generation of the products that feature the μ-$[(PPh_2)_2O]$ ligand.[6]

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

In this paper we report the reactions of the diarsine ligands As_2R_4 (R = Me or Ph) with some bi- and tri-metallic carbonyl complexes containing cobalt and compare them with the reactions of their P_2R_4 analogues.

Results and discussion

(i) Synthesis and spectroscopy

(a) Reaction of $[Co_2(\mu\text{-RCCR}')(CO)_6]$ (R = R′ = Ph; R = Ph, R′ = H; R = Me, R′ = H) with As_2Ph_4. Reaction of $[Co_2(\mu\text{-RCCR}')(CO)_6]$ (R = R′ = Ph; R = Ph, R′ = H; R = Me, R′ = H) with one equivalent of As_2Ph_4 in toluene at 40 °C gave, in addition to unreacted starting materials, green $[Co_2(\mu\text{-RCCR}')(CO)_5(AsPh_3)]$ [R = R′ = Ph (**1a**) (4%) or R = Ph, R′ = H (**1b**) (20%)] and purple $[Co_2(\mu\text{-RCCR}')\{\mu\text{-}(AsPh_2)_2O\}(CO)_4]$ [R = R′ = Ph (**2a**) (60%); R = Ph, R′ = H (**2b**) (10%); R = Me, R′ = H (**2c**) (43%)]. Proposed structures for the products are shown in Fig. 1. All the complexes have been characterised by IR spectroscopy, mass spectrometry and microanalysis. ^1H and ^{13}C NMR data have been collected for complexes **1b**, **2a**, **2b** and **2c**. In addition, X-ray diffraction studies have established the molecular structure shown in Fig. 2(a) for **2b**.

The ^1H NMR spectra of **2a**–**2c** exhibit phenyl resonances. For complex **2a**, no other signals are observed. For **2b** a further singlet at δ 5.75 is ascribed to the acetylenic proton. The ^1H NMR spectrum of **2c** shows two singlets in addition to the phenyl resonances. A signal at δ 5.47 corresponding to one proton is assigned to the acetylenic hydrogen atom, while a further peak at δ 2.68 with three-times the intensity of the first is attributed to the acetylenic methyl group.

The ^{13}C spectrum of **2a** exhibits a broad peak at δ 203.1 due to the carbonyl groups in addition to phenyl resonances. There are two peaks for the *ipso*-carbons of the phenyl groups, indicating that these occur in two distinct environments. One group of phenyl signals can be attributed to the acetylenic phenyl rings, the other to the phenyl groups in the $(AsPh_2)_2O$ ligand. The fact that the four phenyl groups of the bridging ligand are all equivalent must be attributable to a fluxional process, the nature of which is discussed for complex **2c** below.

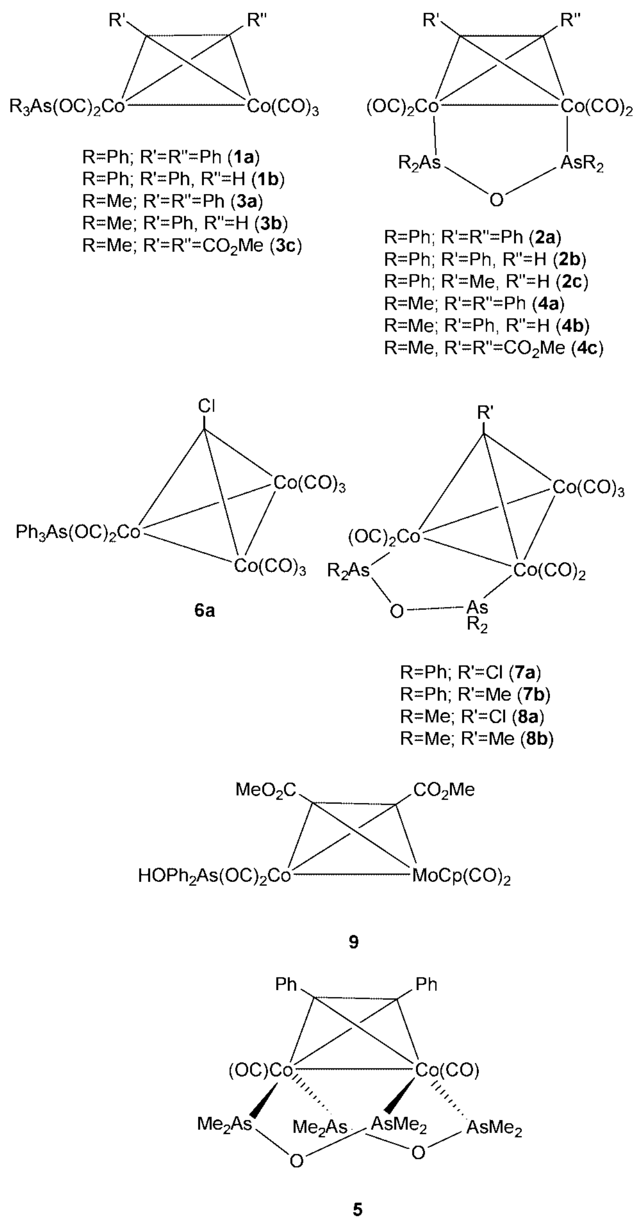


Fig. 1 Proposed structures of the new complexes.

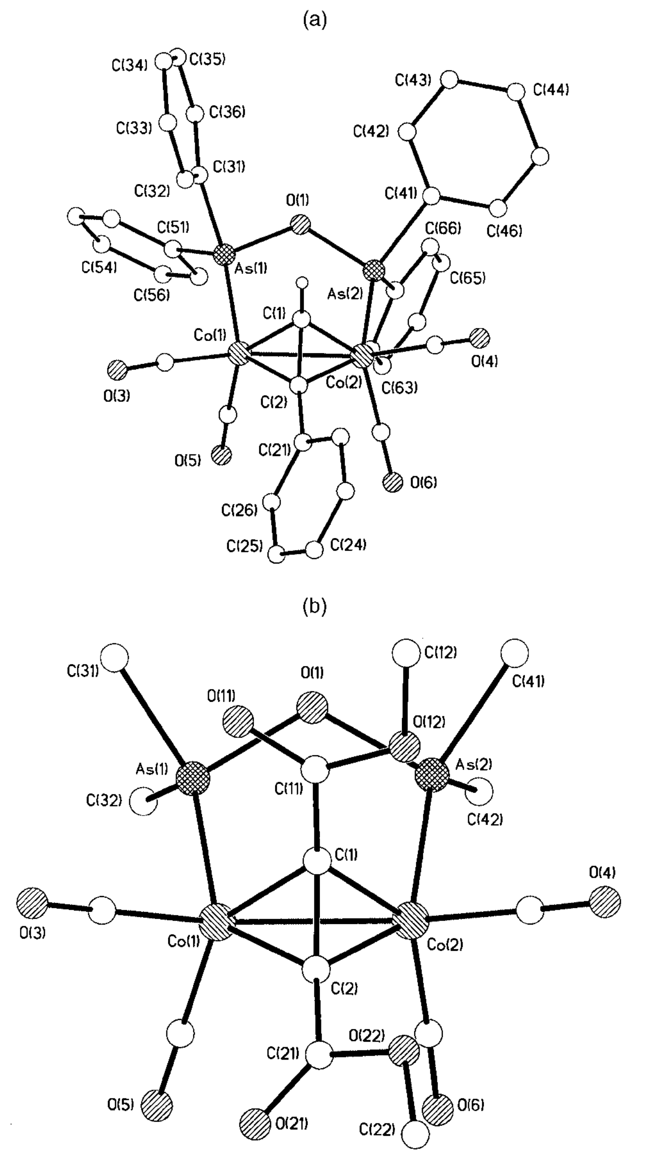


Fig. 2 (a) Molecular structure of $[Co_2(\mu\text{-}PhCCH)\{\mu\text{-}AsPh_2)_2O\}(CO)_4]$ (**2b**) and (b) molecular structure of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(AsMe_2)_2\text{-}O\}(CO)_4]$ (**4c**) including atom numbering scheme.

The ^{13}C NMR spectrum of **2c** includes resonances due to carbonyl and phenyl carbon atoms, singlets at δ 103.4 and δ 73.6 attributable to the acetylenic *C*Me and *C*H carbons respectively and a signal at δ 22.5, which is assigned to the carbon atom of the acetylenic methyl group. There are two *ipso*-carbon signals indicating two environments for the phenyl groups of the $(AsPh_2)_2O$ ligand.

If **2c** adopts in solution the structure found for **2b** in the solid state [Fig. 2(a)], in which the bridging $(AsPh_2)_2O$ ligand occupies equatorial sites on each of the cobalt atoms, then in principle two isomers are possible. In one, the equatorial sites occupied will be closest to the methyl substituent on the alkyne ligand, and in the other they will be closest to the H substituent. Two phenyl resonances are expected for the non-equivalent phenyl groups in each isomer and, accordingly, if both isomers are present in solution, four *ipso*-carbon resonances should be observed. The fact that only two resonances are observed implies either that only one isomer is present in solution or that a fluxional process is operative resulting in isomer interconversion which is fast on the NMR timescale. Such a fluxional process must be operative for **2a** to account for the observations of only one environment for the phenyl groups, and it therefore seems likely to be operative for **2c** as well. Similar fluxionality has been observed previously for the analogous μ-P_2Ph_4 complexes $[Co_2(\mu\text{-}RCCR')(\mu\text{-}P_2Ph_4)(CO)_4]$.[4]

(b) Reaction of $[Co_2(\mu\text{-}RCCR')(CO)_6]$ [R = R′ = Ph; R = Ph, R′ = H; R = R′ = CO_2Me] with As_2Me_4. Reaction of $[Co_2(\mu\text{-}RCCR')(CO)_6]$ [R = R′ = Ph; R = Ph, R′ = H; R = R′ = CO_2Me] with one equivalent of As_2Me_4 in toluene at 40 °C gave, in addition to unreacted starting materials, the monosubstituted trimethyl arsine complexes $[Co_2(\mu\text{-}RCCR')(CO)_5\text{-}(AsMe_3)]$ [R = R′ = Ph (**3a**) (12%); R = Ph, R′ = H (**3b**) (17%), R = R′ = CO_2Me (**3c**) (25%)] and the $(AsMe_2)_2O$ bridged complexes $[Co_2(\mu\text{-}RCCR')\{\mu\text{-}(AsMe_2)_2O\}(CO)_4]$ [R = R′ = Ph (**4a**) (21%); R = Ph, R′ = H (**4b**) (18%); R = R′ = CO_2Me (**4c**) (35%)]. Proposed structures for the products are shown in Fig. 1. All complexes have been characterised by IR, ^1H and ^{13}C NMR spectroscopy and mass spectroscopy. Microanalytical data have been obtained for all complexes with the exception of **3b**. A single crystal X-ray diffraction study of complex **4c** shows it to have the molecular structure shown in Fig. 2(b), which has an overall arrangement of ligands similar to that in **2b** [Fig. 2(a)].

Complexes **4a** and **4c**, bridged by symmetric alkynes, display only one ^1H NMR signal for the methyl groups of the $(AsMe_2)_2O$ ligand whereas **4b** displays two. Similarly, there is a single As*Me* resonance at δ 23.0 in the ^{13}C NMR spectrum of **4a** and at δ 23.2 in the spectrum of **4c** but there are two such signals in the corresponding spectrum of **4b** at δ 23.7 and 23.1. These data indicate that the fluxional process described in detail for **2c** is again operative for **4a**–**c**.

(c) Thermolysis of [Co_2(μ-PhCCPh){μ-($AsMe_2$)$_2$O}$(CO)_4$] (4a). Reflux of [Co_2(μ-PhCCPh){μ-($AsMe_2$)$_2$O}$(CO)_4$] (**4a**) in xylene for 24 h gave deep purple [Co_2(μ-PhCCPh)-{μ-($AsMe_2$)$_2$O}$_2$$(CO)_2$] (**5**) (27%). The complex has been characterised by IR, ^1H and ^{13}C NMR spectroscopy, mass spectroscopy and microanalysis. The molecular structure of **5**, determined by X-ray crystallography, is shown in Fig. 3 and is discussed later.

Although substitution of four carbonyl groups in complexes of the type [Co_2(μ-RCCR′)$(CO)_6$] is not common, examples do exist and the pattern and frequency of the recorded FT-IR spectrum is typical of those reported in the literature for related complexes.[7] The ^1H NMR spectrum of **5** shows resonances due to the phenyl groups, which integrate to ten protons, and it also exhibits two singlets at δ 1.59 and 1.47 which may be attributed to the methyl groups of the bridging ligands. Clearly, in contrast to **4a**, the fluxional process proposed for **2a** can no longer operate and there are now two distinct methyl environments; two environments for the methyl groups on the bridging ligands are also indicated in the ^{13}C NMR by equal-intensity resonances at δ 26.6 and 23.2.

The prolonged heating of [Co_2(μ-PhCCPh){μ-($AsMe_2$)$_2$O}-$(CO)_4$] (**4a**) results in a significant degree of decomposition and it is the free ($AsMe_2$)$_2$O generated by this decomposition which enables **5** to be formed. Under similar conditions Vahrenkamp and Beurich reported that, in an alkylidyne tricobalt complex, two coordinated ($AsMe_2$)$_2$O ligands produce the $AsMe_2$–O–AsMe–O–$AsMe_2$ ligand *via* loss of $AsMe_2$;[8] this tridentate ligand is coordinated at the three axial sites of the tricobalt complex. In the alkyne dicobalt complex **5** the driving force towards coupling of the two ($AsMe_2$)$_2$O ligands provided by this potential mode of coordination is not present.

(d) Reaction of [Co_3(μ_3-CR)$(CO)_9$] (R = Cl or Me) with As_2Ph_4. Reaction of [Co_3(μ_3-CR)$(CO)_9$] (R = Cl or Me) with one equivalent of As_2Ph_4 in toluene at 40 °C gave, in addition to unreacted starting materials, brown [Co_3(μ_3-CR)$(CO)_8$($AsPh_3$)] [R = Cl (**6a**) (18%)] and purple [Co_3(μ_3-CR){μ-($AsPh_2$)$_2$O}-$(CO)_7$] [R = Cl (**7a**) (33%) or Me (**7b**) (22%)]. Proposed structures for the products are shown in Fig. 1. The complexes have been characterised by IR spectroscopy and mass spectrometry. ^1H and ^{13}C NMR spectra and microanalytical data have been obtained for complexes **7a** and **7b** and the molecular structures of **7a** and **7b** have been determined by X-ray crystallography and are shown in Figs. 4 and 5 respectively; the structures will be discussed later.

The IR spectrum of **6a** contains a number of pronounced absorptions in the ν(CO) region. Reference to published IR data[9] suggests that the pattern and frequency of the bands obtained is characteristic of a monosubstituted alkylidyne tricobalt nonacarbonyl cluster. The mass spectrum shows a molecular ion peak at 754 and signals corresponding to 1–8 carbonyl losses. These data are consistent with formulation of the product as [Co_3(μ_3-CCl)$(CO)_8$($AsPh_3$)].

Phenyl resonances are seen in the ^1H spectra of both **7a** and **7b**, with an additional singlet at δ 3.50, integrating to three protons, in the spectrum of **7b**. This is assigned to the apical μ_3-CMe group. A single broad peak due to the carbonyl carbon atoms is observed in the ^{13}C NMR spectra of both complexes. In addition, the spectrum of **7b** shows signals at δ 293.9 and 46.6 for the μ_3-C and μ_3-C*Me* carbon atoms respectively. A signal for this alkylidyne carbon is often missing in ^{13}C spectra of such complexes,[6] as it is in the spectrum of **7a**; proximity of the methyl group in **7b** may be responsible for the enhancement which renders the signal visible. Two peaks for the *ipso*-carbons of the phenyl rings are visible in both spectra, indicating that there are two environments for the phenyl groups.

(e) Reaction of [Co_3(μ_3-CR)$(CO)_9$] (R = Cl or Me) with As_2Me_4. Reaction of [Co_3(μ_3-CR)$(CO)_9$] (R = Cl or Me) with one equivalent of As_2Me_4 in toluene at 35 °C gave, in addition to unreacted starting materials, deep purple [Co_3(μ_3-CR)-{μ-($AsMe_2$)$_2$O}$(CO)_7$] (R = Cl (**8a**) (62%) or Me (**8b**)[8] (59%)]. Both complexes are shown in Fig. 1. They have been characterised by IR, ^1H and ^{13}C NMR spectroscopy, mass spectrometry and microanalysis. The molecular structure of [Co_3(μ_3-CCl)-{μ-($AsMe_2$)$_2$O}$(CO)_7$] (**8a**) has been established by X-ray diffraction and is shown in Fig. 6; this will be discussed later.

In the ^1H spectra of both **8a** and **8b**, a pair of signals can be seen which are attributed to the methyl groups of the bridging ligand. These signals occur at δ 1.79 and 1.73 in the spectrum of **8a** and at δ 1.72 and 1.70 in that of **8b**. Each resonance integrates to six protons, which indicates that two distinct methyl environments are present in each complex. In addition to these signals, there is a further signal at δ 3.75 in the spectrum of **8b**, integrating to three protons, which is assigned to the μ_3-CMe group.

Two environments for the methyl groups of the ligand are also indicated in the ^{13}C NMR spectra. Sharp resonances with approximately equal intensity are located at δ 24.9 and 19.7 in the spectrum of **8a** and corresponding peaks appear in the spectrum of **8b** at δ 25.4 and 21.2. A single carbonyl resonance is detected for each complex and in the case of complex **8b**, the apical μ_3-C is resolved at δ 45.3. The corresponding peak in the spectrum of **8a** is not observed.

(f) Reaction of [(OC)$_3$CO{μ-C_2(CO_2Me)$_2$}MoCp$(CO)_2$] with As_2Ph_4. The reaction of [(OC)$_3$CO{μ-C_2(CO_2Me)$_2$}MoCp-$(CO)_2$] with an excess of As_2Ph_4 in toluene at 35 °C gave [{(HO)Ph_2As}(OC)$_2$Co{μ-C_2(CO_2Me)$_2$}MoCp$(CO)_2$] (**9**) in 43% yield, in addition to unreacted starting material. Complex **9**, shown in Fig. 1, has been characterised by IR, ^1H and ^{13}C NMR spectroscopy, mass spectrometry and microanalysis. The molecular structure of **9** was determined by X-ray crystallography and is shown in Fig. 7.

There exists a number of derivatives of [(OC)$_3$Co{μ-C_2-(CO_2Me)$_2$}MoCp$(CO)_2$] obtained by substitution of the axial carbonyl on cobalt by, for example, a tertiary phosphine[5a,10] and these derivatives have infrared properties similar to those recorded for **9**. The mass spectroscopic and microanalytical data also support the formula given above.

The ^1H NMR spectrum of **9** exhibits, in addition to phenyl resonances, singlets at δ 6.41, 5.45 and 3.48 with integrals of 1H, 5H and 6H, due to the OH, C_5H_5 and CO_2Me groups, respectively. The ^{13}C NMR spectrum indicates carbonyl groups bonded to molybdenum, giving rise to a sharp signal at δ 222.8 and carbonyl groups bonded to cobalt, which produce a broad peak at δ 205. The spectrum also includes phenyl and cyclopentadienyl carbon resonances, the latter occurring at δ 90.7 and singlets at δ 175.4, 72.8 and 52.7 assigned to the *C*O_2Me, *C*CO_2Me and CO_2*Me* carbon atoms, respectively.

(ii) X-Ray crystallographic studies

The X-ray structural studies show that [Co_2(μ-PhCCH)-{μ-($AsPh_2$)$_2$O}$(CO)_4$] (**2b**) and [Co_2{μ-C_2(CO_2Me)$_2$}{μ-($AsMe_2$)$_2$O}$(CO)_4$] (**4c**) have very similar structures which are illustrated in Fig. 2(a) and 2(b), respectively. Each maintains the tetrahedral Co_2C_2 core formed by the alkyne ligand coordinating in 'side-on' mode, with two equatorial carbonyl ligands of the alkyne hexacarbonyldicobalt starting material replaced by the arsenic atoms of a bridging (AsR_2)O ligand. Two carbonyl ligands remain on each cobalt atom of both complexes, one located equatorially, the other occupying the axial position. In the thermolysis product [Co_2(μ-PhCCPh)-{μ-($AsMe_2)_2O$}$_2(CO)_2$] **5** (formed by **4a**, the diphenylacetylene analogue of **4c**) a structure related to those of **2b** and **4c** is observed but with the second μ-[($AsMe_2)_2O$] ligand replacing the remaining equatorial carbonyl ligands, so that **5** has only one carbonyl ligand on each metal, both in axial sites. The crystal of **5** has two molecules per equivalent position and these both have the overall structure illustrated in Fig. 3 for molecule 1. Selected bond lengths and angles for these three related compounds, **2b**, **4c** and **5**, are listed in Table 1 for comparison.

The Co–Co bond lengths in the complexes are 2.484(1) Å (**2b**), 2.493(1) Å (**4c**) and a mean of 2.488(3) Å (**5**) and these are somewhat longer than that of 2.457(1) Å in [Co_2(μ-HCCH)$(CO)_4(PPh_2SBu^n)_2$][11] where the dicobalt unit is bridged only by an alkyne.

The Co–As bond lengths in the complexes have mean values 2.306(1) Å in **2b**, 2.319(1) Å in **4c** and 2.292(2) Å in **5**; the small but significant differences in these lengths may be related to slight variations in π-back bonding from the metal. The methylcarboxylate substituents on the alkyne in **4c** would be expected to enhance its π-acid character relative to the PhCCH ligand in **2b** and consistent with this the C(1)–C(2) alkyne bond in **4c** is 0.057 Å longer than in **2b**. Greater competition for available π-electron density by the alkyne, and the fact that $AsMe_2$ is a weaker π-acceptor than $AsPh_2$, is consistent with the greater mean Co–As bond length in **4c**, 2.319(1) Å compared to 2.306(1) Å in **2b**. In the diphenylacetylene complex, **5**, where two strongly π-acidic carbonyl ligands have been replaced by a second dimethylarsine oxide ligand, the shortest observed mean Co–As distance of 2.292(2) Å is observed. The slight variations in individual Co–As bond lengths within each complex although significant are not easily explained and may be related to a sensitivity of this bond to small changes in conformation. For example in molecule 1 of **5** the Co–As distances are in the range 2.280(2)–2.296(2) (mean 2.288) Å and in molecule 2 are consistently in the slightly higher range 2.285(2)–2.302(2) (mean 2.297) Å; one possible contributing factor to the differences is the mean As–Co–As angle which is 105.3(1)° in molecule 1 compared to 107.2(1)° in molecule 2.

The mean As–O bonds within the diarsine ligands are 1.799(3) (**2b**), 1.803(5) (**4c**) and 1.803(8) Å (**5**) with corresponding As–O–As angles of 118.4(2), 117.7(3) and 116.0(4)° (mean) [*cf.* 1.67(3) Å and 137(2)° in free ($AsPh_2)_2O$[12]]. The changes in these values compared to free ($AsPh_2)_2O$ are consistent with a reduction in p_π–d_π donation from oxygen to arsenic on coordination of the As atom to the π-acidic metal.

Both the complexes [$Co_3(\mu_3$-CR){μ-($AsPh_2)_2O$}$(CO)_7$] [R = Cl (**7a**) and Me (**7b**)] have an approximately tetrahedral core constituted by the capping of a tricobalt face by a μ_3-CR (R = Cl or Me) ligand (Figs. 4 and 5, respectively). Co(1) and Co(2) are bridged equatorially by a bidentate ($AsPh_2)_2O$ ligand and each of these metal atoms is additionally ligated by two carbonyl groups one located axially and the other equatorially. Both equatorial sites and the axial position at Co(3) are occupied by carbonyl groups.

The metallic triangle is not perfectly equilateral in either **7a** or **7b** with metal–metal bonds in the ranges 2.502(2)–2.474(2) Å in **7a** and 2.4836(9)–2.4675(9) Å in **7b** unlike the almost symmetrical range of 2.462(7)–2.475(7) Å in the unsubstituted complex, [$Co_3(\mu_3$-CMe)$(CO)_9$].[13] The bond between Co(3) and the apical carbon is the longest of the three Co–C(1) bonds for both complexes [1.927(9) Å in **7a**; 1.941(4) Å in **7b**].

The most notable difference in the molecular geometries of **7a** and **7b** is in the five-membered Co_2As_2O ring. The pentagonal ring in **7b** is almost symmetric, with Co–As bonds measuring 2.2895(8) Å and 2.2853(8) Å and As–O bond lengths of 1.802(3) Å and 1.808(3) Å. These distances are similar to those determined for [Co_2(μ-PhCCH){μ-($AsPh_2)_2O$}$(CO)_4$] (**2b**) and the As–O–As angle of 114.1(1)° is also comparable with that in **2b** [118.4(2)°]. Both values for this angle contrast sharply

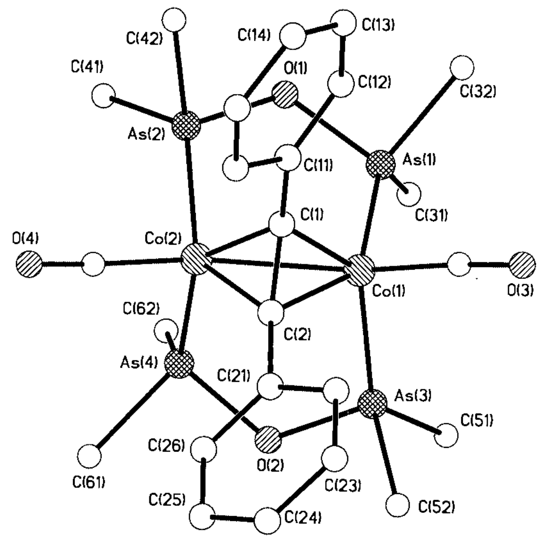


Fig. 3 Molecular structure of [Co_2(μ-PhCCPh){μ-$AsMe_2)_2O$}$_2(CO)_2$] (**5**) including atom numbering scheme.

Table 1 Selected bond lengths (Å) and angles (°) for the dicobalt compounds with bridging ($AsR_2)_2O$ ligands (**2b**, **4c** and **5**)

			5	
	2b	**4c**	Molecule 1	Molecule 2
Co(1)–Co(2)	2.484(1)	2.493(1)	2.485(3)	2.490(3)
Co(1)–As(1)	2.302(1)	2.311(1)	2.296(2)	2.300(2)
Co(1)–As(3)			2.284(2)	2.299(2)
Co(2)–As(2)	2.309(1)	2.327(1)	2.290(2)	2.285(2)
Co(2)–As(4)			2.280(2)	2.302(2)
Co(1)–C(1)	1.950(6)	1.968(7)	1.92(1)	1.93(1)
Co(1)–C(2)	1.923(6)	1.926(6)	1.97(1)	1.93(1)
Co(2)–C(1)	1.954(5)	1.938(6)	1.96(1)	1.97(1)
Co(2)–C(2)	1.967(5)	1.939(7)	1.91(1)	1.93(1)
mean Co–C (CO)	1.773(7)	1.809(8)	1.77(1)	1.76(1)
As(1)–O(1)	1.806(3)	1.822(5)	1.820(8)	1.794(8)
As(2)–O(1)	1.791(3)	1.784(5)	1.804(8)	1.807(8)
As(3)–O(2)			1.805(8)	1.802(8)
As(4)–O(2)			1.791(8)	1.799(8)
mean As–C	1.945(3)	1.949(8)	1.94(1)	1.95(2)
C(1)–C(2)	1.339(7)	1.396(9)	1.36(1)	1.37(1)
C(1)–C(11)		1.503(9)	1.48(1)	1.50(1)
C(2)–C(21)	1.464(7)	1.472(9)	1.51(2)	1.52(1)
As(1)–Co(1)–Co(2)	98.83(5)	96.5(1)	95.45(9)	94.72(9)
As(2)–Co(2)–Co(1)	95.30(4)	98.2(1)	97.32(9)	97.9(1)
As(3)–Co(1)–Co(2)			98.61(9)	98.02(9)
As(4)–Co(2)–Co(1)			93.77(9)	94.57(9)
As(1)–Co(1)–As(3)			105.4(1)	106.97(1)
As(2)–Co(2)–As(4)			105.2(1)	107.5(1)
As(1)–Co(1)–C(1)	96.0(2)	98.1(2)	109.0(4)	106.4(4)
As(1)–Co(1)–C(2)	135.6(2)	137.6(2)	142.0(4)	141.1(4)
As(1)–Co(1)–C(3)	101.9(2)	98.1(3)	100.4(5)	101.7(5)
As(1)–Co(1)–C(5)	103.6(2)	103.8(3)		
As(2)–Co(2)–C(1)	103.2(2)	98.6(2)	97.4(4)	96.6(4)
As(2)–Co(2)–C(2)	138.6(2)	138.3(2)	137.2(4)	136.2(4)
As(2)–Co(2)–C(4)	100.0(2)	97.1(3)	101.2(6)	98.3(6)
As(2)–Co(2)–C(6)	107.7(2)	106.0(2)		
As(3)–Co(1)–Co(2)			98.61(9)	98.02(9)
As(4)–Co(2)–Co(1)			93.77(9)	94.57(9)
As(3)–Co(1)–C(1)			135.1(4)	135.8(4)
As(3)–Co(1)–C(2)			94.9(4)	95.2(4)
As(3)–Co(1)–C(3)			101.1(5)	102.6(5)
As(4)–Co(2)–C(1)			139.4(4)	139.8(4)
As(4)–Co(2)–C(2)			105.1(4)	104.3(4)
As(4)–Co(2)–C(4)			101.2(6)	100.3(6)
Co(1)–As(1)–O(1)	111.4(1)	112.8(2)	114.5(3)	113.3(3)
Co(2)–As(2)–O(1)	114.4(1)	111.7(2)	113.3(3)	112.8(3)
Co(1)–As(3)–O(2)			111.6(3)	112.3(3)
Co(2)–As(4)–O(2)			114.3(3)	112.9(3)
As(1)–O(1)–As(2)	118.4(2)	117.7(3)	115.6(5)	116.0(4)
As(3)–O(2)–As(4)			116.3(4)	115.9(4)

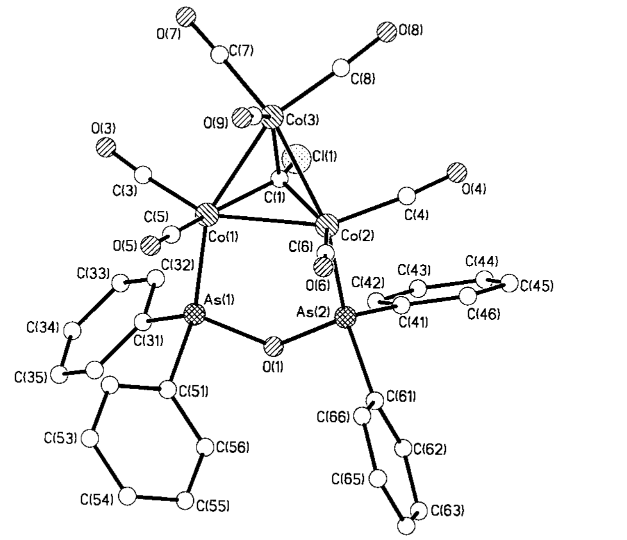


Fig. 4 Molecular structure of $[Co_3(\mu_3\text{-CCl})\{\mu\text{-}(AsPh_2)_2O\}(CO)_7]$ (**7a**) including atom numbering scheme.

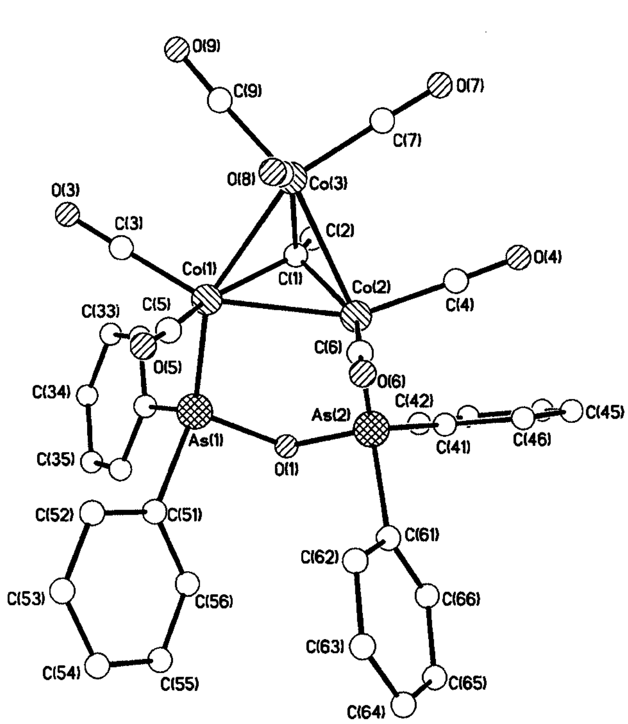


Fig. 5 Molecular structure of $[Co_3(\mu_3\text{-CMe})\{\mu\text{-}(AsPh_2)_2O\}(CO)_7]$ (**7b**) including atom numbering scheme.

with that found in free $(AsPh_2)_2O$ [137(2)°],[12] the reasons for the compression of the angle on coordination having been covered in the discussion of the structure of **2b**.

The As–O–As angle in **7a** is, however, significantly smaller [108.8(4)°] than that in **2b** or in **7b** and the As–O bonds are longer in **7a** [1.886(6) and 1.921(7) Å] than in **7b**. It is surprising that complexes **2b** and **7b**, with obvious differences in their molecular cores, have Co_2As_2O rings with similar geometries, whilst larger differences in geometry are seen in the Co_2As_2O rings of complexes **7a** and **7b**, whose cores are almost identical. There appears to be no electronic or geometric explanation of this observation.

Despite the difference described above, the mean Co–Co–As angles remain constant within the given error limits (96.14° in **7a**; 96.91° in **7b** *cf.* 97.07° in **2b**) and the Co–As bond lengths for **7a** and **7b** are also practically identical.

The molecular structure of $[Co_3(\mu_3\text{-CCl})\{\mu\text{-}(AsMe_2)_2O\}(CO)_7]$ (**8a**) is presented in Fig. 6. Selected bond lengths and angles for the three related complexes **8a**, **7a** and **7b** are listed in

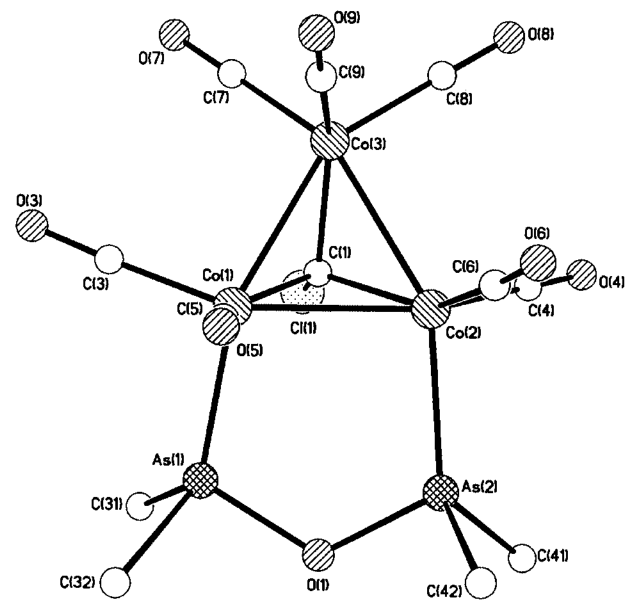


Fig. 6 Molecular structure of $[Co_3(\mu_3\text{-CCl})\{\mu\text{-}(AsMe_2)_2O\}(CO)_7]$ (**8a**) including atom numbering scheme.

Table 2 Bond lengths (Å) and angles (°) for the tricobalt compounds with bridging $(AsR_2)_2O$ ligands (**7a**, **7b** and **8a**)

	7a	7b	8a
Co(1)–Co(2)	2.502(2)	2.4836(9)	2.478(2)
Co(1)–Co(3)	2.474(2)	2.4784(8)	2.462(2)
Co(2)–Co(3)	2.488(2)	2.4675(9)	2.459(2)
Co(1)–As(1)	2.293(2)	2.2895(8)	2.266(2)
Co(2)–As(2)	2.287(2)	2.2853(8)	2.264(2)
As(1)–O(1)	1.921(7)	1.808(3)	1.774(7)
As(2)–O(1)	1.886(6)	1.802(3)	1.788(7)
mean As–C	1.926(6)	1.946(2)	1.93(1)
Co(1)–C(1)	1.86(1)	1.895(4)	1.841(9)
Co(2)–C(1)	1.86(1)	1.908(4)	1.86(1)
Co(3)–C(1)	1.927(9)	1.941(4)	1.90(1)
C(1)–Cl(1)/C(2)	1.76(1)	1.502(5)	1.75(1)
mean Co–C $(CO)_{ax}$	1.81(1)	1.816(5)	1.81(1)
mean Co–C $(CO)_{eq}$	1.77(1)	1.784(5)	1.78(1)
Co(1)–Co(2)–Co(3)	59.44(6)	60.07(2)	59.8(1)
Co(1)–Co(3)–Co(3)	60.57(6)	60.28(2)	60.5(1)
Co(2)–Co(1)–Co(3)	59.99(6)	59.64(3)	59.7(1)
As(1)–Co(1)–Co(2)	96.51(6)	95.87(3)	98.6(1)
As(2)–Co(2)–Co(1)	95.77(7)	97.95(3)	93.5(1)
Co(2)–Co(1)–C(1)	47.8(3)	49.4(1)	48.3(3)
Co(3)–Co(1)–C(1)	50.4(3)	50.6(1)	49.9(3)
Co(1)–Co(2)–C(1)	47.6(3)	49.0(1)	47.6(3)
Co(3)–Co(2)–C(1)	50.2(3)	50.7(1)	49.9(3)
Co(1)–Co(3)–C(1)	47.9(3)	48.9(1)	47.8(3)
Co(2)–Co(3)–C(1)	47.7(3)	49.5(1)	48.5(3)
Co(1)–As(1)–O(1)	113.4(2)	112.76(9)	112.2(2)
Co(2)–As(2)–O(1)	115.4(2)	111.76(8)	114.2(2)
As(1)–O(1)–As(2)	108.8(4)	114.4(1)	115.9(4)

Table 2 for comparison. The structure features a tetrahedral Co_3C core, formed by the capping of a tricobalt face by a chloromethylidyne ligand, μ_3-CCl. This core is the same as that of **7a**; indeed the overall structure is closely comparable to that of **7a** and it will not be discussed in detail for that reason. It is worth noting that the bridged Co–Co bond is the longest of the three M–M bonds in the complex, which was also found to be the case for complexes **7a** and **7b**. At 2.478(2) Å, it is, however, significantly shorter than the corresponding bond in **7a** [2.502(2) Å]. The geometry of the arsine oxide ligand is comparable to that for the same ligand in complex **4c**. The As–O bond lengths are 1.788(7) Å and 1.774(7) Å [*cf.* 1.822(5) and 1.784(5) Å in **4c**] and the angle at oxygen is 115.9(4)° [117.7(3)°

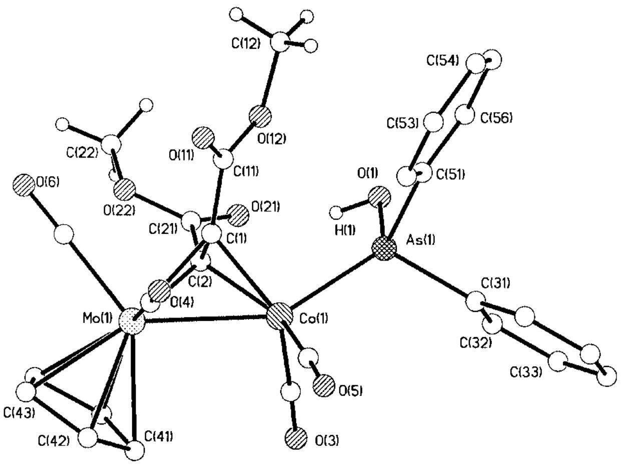


Fig. 7 Molecular structure of [{(HO)Ph_2As}$(OC)_2$Co{μ-$C_2(CO_2Me)_2$}MoCp$(CO)_2$] (**9**) including atom numbering scheme.

Table 3 Selected bond lengths (Å) and angles (°) for [{(OH)Ph_2As}$(OC)_2$Co{μ-$C_2(CO_2Me)_2$}MoCp$(CO)_2$] (**9**)

Co(1)–Mo(1)	2.704(1)	Co(1)–C(1)	1.960(5)
Co(1)–C(2)	1.956(5)	Mo(1)–C(1)	2.138(5)
Mo(1)–C(2)	2.140(5)	As(1)–Co(1)	2.312(1)
As(1)–O(1)	1.770(4)	As(1)–C(31)	1.943(3)
As(1)–C(51)	1.951(3)	C(1)–C(2)	1.383(7)
Co(1)–$C_{carbonyl}$	1.785(7), 1.796(7)		
Mo(1)–$C_{carbonyl}$	1.997(7), 2.024(7)		
C–O	1.135(7)–1.147(7)		
C(1)–Mo(1)–Co(1)	45.9(1)	C(2)–Mo(1)–Co(1)	45.8(1)
C(2)–Mo(1)–C(1)	37.7(2)	As(1)–Co(1)–Mo(1)	149.8(4)
C(1)–Co(1)–Mo(1)	51.6(2)	C(2)–Co(1)–Mo(1)	51.7(2)
C(1)–Co(1)–C(2)	41.4(2)	Co(1)–As(1)–O(1)	115.2(1)
Co(1)–As(1)–C(31)	118.82(7)	Co(1)–As(1)–C(31)	121.4(1)
Co(1)–C(1)–Mo(1)	82.5(2)	C(2)–C(1)–Mo(1)	71.2(3)
C(2)–C(1)–Co(1)	69.2(3)	Co(1)–C(2)–Mo(1)	82.5(2)
C(1)–C(2)–Mo(1)	71.1(3)	C(1)–C(2)–Co(1)	69.5(3)
C(2)–C(1)–C(11)	134.2(5)	C(1)–C(2)–C(21)	129.7(5)

in **4c**]. The Co–As bond lengths in **8a** are equal [2.264(2) and 2.266(2) Å] within the limits of experimental error but the reason why they should be so much shorter than the corresponding bonds in **4c** [2.327(1) and 2.311(1) Å] is unclear.

The structure of [{(HO)Ph_2As}$(OC)_2$Co{μ-$C_2(CO_2Me)_2$}MoCp$(CO)_2$] (**9**) is shown in Fig. 7. Selected bond lengths and angles are presented in Table 3. A dimethylacetylene dicarboxylate ligand coordinates to the cobalt–molybdenum fragment in the 'side-on' mode such that the acetylenic and Co–Mo bonds are almost perpendicular. The core of this molecule is thus a $CoMoC_2$ tetrahedron. The cyclopentadienyl ligand is bonded to molybdenum on the opposite side of the molecule to the acetylenic 'edge'. Two carbonyl groups also ligate this metal atom. The cobalt atom carries two carbonyl ligands, which occupy equatorial sites. The axial carbonyl has been replaced by a molecule of diphenylarsinous acid, $AsPh_2OH$, which bonds to cobalt *via* the arsenic atom.

The $CoMoC_2$ core is distorted from a regular tetrahedron. Firstly, the Co–Mo and acetylenic bonds are obviously of different lengths. The Co–Mo distance of 2.704(1) Å is within the range expected for Co–Mo bond in complexes such as this (2.60–2.75 Å).[5a] The acetylenic bond [1.383(7) Å] is also of a length typical for DMAD (dimethyl acetylenedicarboxylate) coordinating a bimetallic unit in this fashion.[4] The alkyne does not lie equidistant from both metal centres. Rather, it is displaced away from molybdenum and towards cobalt, leading to Co–C_{DMAD} bond lengths of 1.960(5) Å and 1.956(5) Å and Mo–C_{DMAD} bond lengths of 2.140(5) Å and 2.138(5) Å. This observation is in accord with the larger radius of molybdenum as compared with cobalt. These values also show that in this complex, the alkyne lies approximately perpendicular to the Co–Mo bond without any significant degree of twisting.

The angle of 149.8(4)° between the Mo–Co and Co–As bonds is fairly typical given that the arsine occupies the axial site. The Co–As bond measures 2.312(1) Å and the As–O bond is 1.770(5) Å in length which indicates that this is an As–O single bond and not an As=O bond. These data are comparable with those determined for [$(dmgH)_2$ClCo($AsPh_2OH$)][14] [Co–As 2.322(1) Å; As–O 1.781(7) Å]. Given that this complex contains the $AsPh_2OH$ ligand coordinated to Co(III), it is unsurprising that the Co–As bond in which the cobalt has a formal oxidation state of zero is somewhat shorter.

The geometry about arsenic is that of a distorted tetrahedron. The angles between the Co–As bond and the three remaining bonds to arsenic are in the range 115.2(1) to 121.4(1)°, whereas angles between these latter three bonds are compressed to 98.5(3)–100.3(3)°.

(iii) Reaction pathways

The major product in the above reactions with homometallic clusters is typically a complex featuring a single bis-diarsine oxide ligand bridging a Co–Co bond. Formation of such products is immediately reminiscent of the work of Vahrenkamp and Beurich[8] in which the aminoarsine, $AsMe_2NMe_2$, was used to produce mono- and bis-substituted derivatives of alkylidyne tricobalt nonacarbonyl complexes. These derivatives were found to be extremely sensitive to hydrolysis, giving complexes which featured a bridging $(AsMe_2)_2O$ ligand. The same research group found that the mononuclear complex, $(OC)_5W$–$AsMe_2Cl$, reacted with H_2O to give the binuclear complex $(OC)_5W$–$AsMe_2$–O–$AsMe_2$–$W(CO)_5$.[15] Chromatography on silica was found to be sufficient to convert the complex, $(OC)_4Fe$–$AsMe_2Cl$ to $(OC)_4Fe$–$AsMe_2$–O–$AsMe_2$–$Fe(CO)_4$.[16] More recently, it has been shown that both P_2Ph_4 and PPh_2H can react with alkylidyne tricobalt nonacarbonyl clusters to yield products with bridging $(PPh_2)_2O$ ligands.[6]

The proposed pathway for the formation of complexes containing the $(AsR_2)_2O$ ligand from As_2R_4 is shown in Fig. 8 for the reactions with [Co(μ-RCCR′)$(CO)_6$]. It seems likely that mono-substitution by As_2R_4 will initially give intermediate **A**. Stable complexes of this type have been isolated from reactions of the alkyne-bridged dicobalt complex with P_2Ph_4.[17] The As_2R_4 ligand in the substituted complex could then attack the second cobalt centre to give a μ-As_2R_4 intermediate **B**. Again stable complexes of this type have been isolated in the corresponding reactions with P_2Ph_4 although an alternative intermediate **C**, which involves substitution by a second As_2R_4 ligand cannot be excluded. The next step, which has no parallel in the corresponding reactions with P_2Ph_4 could involve the hydrolytic/oxidative reaction of either **B** or **C** to give a bis-AsR_2(OH)-substituted intermediate **D**. Condensation of the two AsR_2OH ligands with elimination of H_2O would then give the observed μ-$(AsR_2)_2O$ products. Although the reactions were carried out under anhydrous and anaerobic conditions, work up in air on silica, which can contain small quantities of water, most likely effects the hydrolysis/oxidation, as has been observed in a number of other cases.[6,16] An analogous pathway is proposed for the tricobalt systems and in this case the hydrolytic/oxidative process does have precedents in the conversion of $AsMe_2NMe_2$, PPh_2H or P_2Ph_4 to $(AsMe_2)_2O$ or $(PPh_2)_2O$ on reaction with these trimetallic clusters.[6,8]

This hydrolytic/oxidative mechanism is further supported by the reaction of As_2Ph_4 with the DMAD-bridged cobalt–molybdenum complex, which yields as the sole isolable product a mono-$AsPh_2OH$-substituted complex (**9**) in which the arsine ligand occupies the axial site at cobalt. At the temperature employed in this reaction, substitution at molybdenum does not occur but substitution of As_2Ph_4 at cobalt presumably occurs as

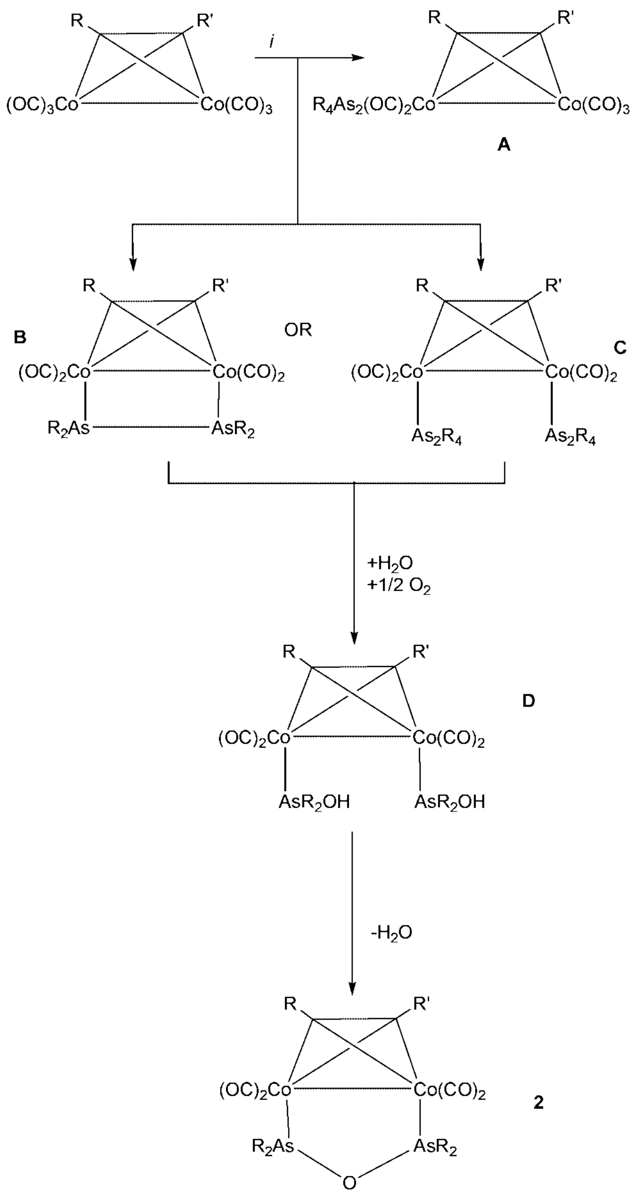


Fig. 8 Possible mechanism for formation of bis-arsine oxide-bridged complexes. (*i*) As_2R_4 [R = Me or Ph], heat.

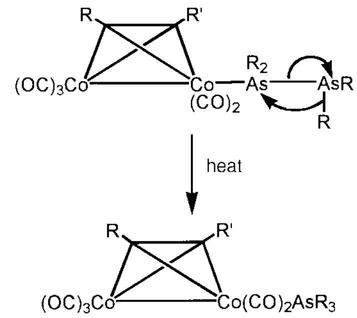
it did for the homometallic complexes and is then followed by cleavage of the As–As bond in a hydrolytic/oxidative process that generates two molecules of the arsenous acid, $AsPh_2(OH)$, one coordinated to cobalt and one free. Since in this instance there is no equivalent ligand bound to the adjacent metal centre, condensation to form the $(AsPh_2)_2O$ ligand is not possible and the $AsPh_2(OH)$-substituted species can therefore be isolated as the stable complex **9**. While esters of the arsenous acids have been isolated, the free acids themselves are not fully characterised[18] and only one other complex containing an $AsPh_2OH$ ligand has had its structure determined.[14]

An alternative route to the $(AsPh_2)_2O$ complexes would involve air-oxidation of the free diarsines prior to their coordination; the oxidised ligand could then simply coordinate to afford the isolated products. Although the controlled oxidation of diarsines[19,20] is known to generate $(AsR_2)_2O$, if $(AsR_2)_2O$ existed in solution prior to interaction with the cluster, a product with a 'pendant' $(AsR_2)_2O$ ligand would be expected. Although the absence of such species in the case of the homometallic clusters could be explained by their facile conversion to the bridged products isolated, in the Co–Mo system formation of bridged products does not appear to be possible and the absence of 'pendant' $(AsR_2)_2O$ products here suggests that oxidation of the diarsine does not occur before interaction with the cluster. Given the rigorous exclusion of oxygen during the reaction, it is unlikely that the oxidation of the ligand occurs prior to work up and the proposed conversion of the coordinated arsine to a μ-$(AsR_2)_2O$ ligand has a precedent in the work of Vahrenkamp.

Disproportionation of diarsines is a known reaction, yielding tertiary arsines and elemental arsenic at high temperatures. Tetraphenyldiarsine, for example, has been reported to disproportionate in this way at 300 °C *in vacuo*.[20]

$$3As_2Ph_4 \xrightarrow[\text{in vacuo}]{300\,^{\circ}\text{C}} 2As + 4AsPh_3$$

The isolation of mono-AsR_3-substituted complexes in some of the reactions studied suggests that the disproportionation reaction can occur at ambient temperatures when As_2R_4 is coordinated to a transition metal. This may occur as shown below:



The fate of the AsR groups, excised in reactions of this type has been discussed by Rheingold and Di Maio.[21] Disproportionation into elemental arsenic and AsR_2 groups with dimerisation of the latter to generate diarsines is the preferred process.

$$2AsR \longrightarrow As + AsR_2$$

$$2AsR_2 \longrightarrow As_2R_4$$

Conclusions

The above reactions show that the diarsines As_2R_4 (R = Me or Ph) react differently from the diphosphine P_2Ph_4 with alkyne-bridged dicobalt systems. While E–E bond cleavage is apparent for E = P or As, in the case of E = As arsenido-bridged products are not isolated as they are for E = P nor are cobaltacyclic complexes isolated in which AsR_2 has combined with the bridging organic ligand in the way that PR_2 fragments are known to do.[17] Rather, As–O bond formation is the preferred process and it has been possible to isolate in good yield and structurally characterise a number of complexes that possess μ-$(AsR_2)_2O$ ligands. This is also observed where diarsines react with alkylidyne tricobalt clusters and in this case the outcome parallels that obtained when these clusters are reacted with diphosphines.[6]

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 CH_2Cl_2 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 were obtained on a Kratos MS50 instrument. Nitrobenzyl alcohol was used as a matrix. ^1H and ^{13}C

NMR spectra were recorded on Bruker AM400 or WM250 spectrometers using the solvent resonance as an internal 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 Kieslgel 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 compounds $[Co_2(\mu\text{-}RCCR')(CO)_6]$[22] (R = R′ = CO_2Me, Ph; R = H, R′ = Ph, Me), $[Co_3(\mu_3\text{-}CR)(CO)_9]$[23] (R = Me or Cl) and $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}MoCp(CO)_2]$[24] were prepared by literature methods.

The diarsine As_2Me_4[25] was prepared by reduction of cacodylic acid $[Me_2As(O)(OH)]$. The oxide, $(AsPh_2)_2O$,[26,27] was synthesised by reaction of PhMgBr and As_2O_3. Treatment of this oxide with HCl generated $AsPh_2Cl$.[27,28] Coupling of $AsPh_2Cl$ and $LiAsPh_2$[29] afforded As_2Ph_4.[30]

(i) Reaction of $[Co_2(\mu\text{-}PhCCPh)(CO)_6]$ and As_2Ph_4

$[Co_2(\mu\text{-}PhCCPh)(CO)_6]$ (250 mg, 0.54 mmol) and As_2Ph_4 (4 ml, 0.15 M in toluene, 0.6 mmol) were dissolved in toluene (60 ml) and heated at 40 °C with stirring for 9 h. After removal of the reaction solvent under vacuum, the residue was dissolved in the minimum quantity of CH_2Cl_2 and applied to the base of silica TLC plates. Elution with hexane/CH_2Cl_2 (4 : 1) gave unreacted $[Co_2(\mu\text{-}PhCCPh)(CO)_6]$ (51 mg), green $[Co_2(\mu\text{-}PhCCPh)(CO)_5(AsPh_3)]$ (**1a**) (16 mg, 4%), purple $[Co_2(\mu\text{-}PhCCPh)\{\mu\text{-}(AsPh_2)_2O\}(CO)_4]$ (**2a**) (287 mg, 60%). Complex **1a** (Found: C, 59.86; H, 3.48. $C_{37}H_{25}AsCo_2O_5$ requires C, 59.86; H, 3.39%). Mass spectrum, *m*/*z* 742 (M^+) and $M^+ - n$CO (*n* = 1–5). ν_{max}/cm^{-1} (CH_2Cl_2), 2061s, 2012s, 2001 (sh), 1961w. NMR ($CDCl_3$), ^1H, δ 7.4–6.7 [m, 25H, *Ph*]; ^{13}C, δ 140.1–126.5 [*Ph*], 86.3 [s, *C*Ph]. Complex **2a** (Found: C, 56.85; H, 3.33. $C_{42}H_{30}As_2Co_2O_5$ requires C, 57.17; H, 3.43%). Mass spectrum, *m*/*z* 882 (M^+) and $M^+ - n$CO (*n* = 1–4). ν_{max}/cm^{-1} (CH_2Cl_2), 2030m, 2003s, 1977m. NMR ($CDCl_3$), ^1H, δ 7.5–7.0 [m, 30H, *Ph*]; ^{13}C, δ 203.1 [s, CO], 142.9–126.3 [*Ph*].

(ii) Reaction of $[Co_2(\mu\text{-}PhCCH)(CO)_6]$ and As_2Ph_4

$[Co_2(\mu\text{-}PhCCH)(CO)_6]$ (1.093 g, 2.82 mmol) and As_2Ph_4 (18.8 ml, 0.15 M in toluene, 2.82 mmol) were dissolved in toluene (60 ml) and heated at 40 °C with stirring for 15 h. After removal of the reaction solvent under vacuum, the residue was dissolved in the minimum quantity of CH_2Cl_2 and adsorbed onto silica. The silica was pumped dry and transferred to the top of a silica chromatography column. Elution with hexane/CH_2Cl_2 (4 : 1) gave unreacted $[Co_2(\mu\text{-}PhCCH)(CO)_6]$ (116 mg), brown-green $[Co_2(\mu\text{-}PhCCH)(CO)_5(AsPh_3)]$ (**1b**) (368 mg, 20%) and purple $[Co_2(\mu\text{-}PhCCH)\{\mu\text{-}(AsPh_2)_2O\}(CO)_4]$ (**2b**) (227 mg, 10%). Crystals of **2b** suitable for diffraction were grown by slow evaporation at 0 °C of an *n*-hexane/CH_2Cl_2 solution of the complex. Complex **1b** (Found: C, 55.77; H, 3.11. $C_{31}H_{21}AsCo_2O_5$ requires C, 55.88; H, 3.18%). Mass spectrum, *m*/*z* 666 (M^+) and $M^+ - n$CO (*n* = 1–5). ν_{max}/cm^{-1} (hexane), 2063m, 2012s, 2002 (sh), 1961w. NMR ($CDCl_3$), ^1H, δ 8.0–6.5 [m, 20H, *Ph*], 5.69 [s, 1H, CH]; ^{13}C, δ 139.6–128.5 [*Ph*]. Complex **2b** (Found: C, 53.76; H, 3.18. $C_{36}H_{26}As_2Co_2O_5$ requires C, 53.63; H, 3.25%). Mass spectrum, *m*/*z* 806 (M^+) and $M^+ - n$CO (*n* = 1–4). ν_{max}/cm^{-1} (CH_2Cl_2), 2031m, 2004s, 1977m. NMR ($CDCl_3$), ^1H, δ 7.7–7.1 [m, 25H, *Ph*], 5.75 [s, 1H, CH]; ^{13}C, δ 143.2–126.9 [*Ph*], 70.5 [s, CH].

(iii) Reaction of $[Co_2(\mu\text{-}MeCCH)(CO)_6]$ and As_2Ph_4

$[Co_2(\mu\text{-}MeCCH)(CO)_6]$ (726 mg, 2.23 mmol) and As_2Ph_4 (14.9 ml, 0.15 M in toluene, 2.24 mmol) were dissolved in toluene (60 ml) and heated at 40 °C with stirring for 9 hours. After removal of the reaction solvent under vacuum, the residue was dissolved in the minimum quantity of CH_2Cl_2 and adsorbed onto silica. The silica was pumped dry and transferred to the top of a silica chromatography column. Elution with hexane/CH_2Cl_2 (4 : 1) gave unreacted $[Co_2(\mu\text{-}MeCCH)(CO)_6]$ (20 mg), $[Co_2(\mu\text{-}MeCCH)\{\mu\text{-}(AsPh_2)_2O\}(CO)_4]$ (**2c**) (476 mg, 43%). Complex **2c** (Found: C, 49.43; H, 3.11. $C_{31}H_{24}As_2Co_2O_5$ requires C, 50.03; H, 3.25%). Mass spectrum, *m*/*z* 744 (M^+) and $M^+ - n$CO (*n* = 1–4). ν_{max}/cm^{-1} (CH_2Cl_2), 2028m, 1998s, 1971m. NMR ($CDCl_3$), ^1H, δ 7.5–7.4 [m, 20H, *Ph*], 5.47 [s, 1H, CH], 2.68 [s, 3H, C*Me*]; ^{13}C, δ 205.8 [s, 2CO], 202.7 [s, 2CO], 143.4–128.6 [*Ph*], 103.4 [s, *C*Me], 73.6 [s, CH], 22.5 [s, C*Me*].

(iv) Reaction of $[Co_2(\mu\text{-}PhCCPh)(CO)_6]$ and As_2Me_4

$[Co_2(\mu\text{-}PhCCPh)(CO)_6]$ (500 mg, 108 mmol) and As_2Me_4 (250 mg, 1.19 mmol) were dissolved in toluene (60 ml) and heated at 40 °C for 15 h. After removal of the reaction solvent under vacuum, the residue was dissolved in a minimum quantity of CH_2Cl_2 and adsorbed onto silica. The silica was pumped dry and transferred to the top of a silica chromatography column. Elution with hexane/CH_2Cl_2 (3 : 2) gave red-brown $[Co_2(\mu\text{-}PhCCPh)(CO)_5(AsMe_3)]$ (**3a**) (75 mg, 12%), two products in very minor yield which were not collected and deep purple, crystalline $[Co_2(\mu\text{-}PhCCPh)\{\mu\text{-}(AsMe_2)_2O\}(CO)_4]$ (**4a**) (147 mg, 21%). Crystals of **3a** suitable for diffraction were grown by slow evaporation at 0 °C of an *n*-hexane/CH_2Cl_2 solution of the complex. Complex **3a** (Found: C, 47.31; H, 3.36. $C_{22}H_{19}AsCo_2O_5$ requires C, 47.51; H, 3.44%). Mass spectrum, *m*/*z* 556 (M^+) $M^+ - n$CO (*n* = 1–5). ν_{max}/cm^{-1} (CH_2Cl_2), 2058s, 2006vs, 1998 (sh), 1958w, 1606w. NMR ($CDCl_3$), ^1H, δ 7.7–7.2 [m, 10H, Ph], 1.47 [s, 9H, Me]; ^{13}C, δ 204.7 [s, 2CO], 200.9 [s, 3CO], 140.7–126.7 [*Ph*], 86.1 [s, *C*Ph], 29.7 [s, Me]. Complex **4a** (Found: C, 40.20; H, 3.45. $C_{22}H_{22}AsCo_2O_5$ requires C, 41.67; H, 3.50%). Mass spectrum, *m*/*z* 634 (M^+) and $M^+ - n$CO (*n* = 1–4). ν_{max}/cm^{-1} (CH_2Cl_2), 2026s, 1997vs, 1970s, 1604w. NMR ($CDCl_3$), ^1H, δ 7.5–7.3 [m, 10H, *Ph*], 1.58 [s, 12H, Me]; ^{13}C, δ 203.5 [s, CO], 142.0–126.0 [*Ph*], 95.3 [s, CPh], 23.0 [s, Me].

(v) Reaction of $[Co_2(\mu\text{-}PhCCH)(CO)_6]$ and As_2Me_4

$[Co_2(\mu\text{-}PhCCH)(CO)_6]$ (740 mg, 1.91 mmol) and As_2Me_4 (410 mg, 1.95 mmol) were dissolved in toluene (60 ml) and heated at 40 °C for 24 h. After removal of the reaction solvent under vacuum, the residue was dissolved in the minimum quantity of CH_2Cl_2 and applied to the base of silica TLC plates. Elution with hexane/CH_2Cl_2 (4 : 1) gave purple $[Co_2(\mu\text{-}PhCCH)(CO)_5(AsMe_3)]$ (**3b**) (156 mg, 17%), a trace of a yellow-brown product which was not collected and deep purple, crystalline, $[Co_2(\mu\text{-}PhCCH)\{\mu\text{-}(AsMe_2)_2O\}(CO)_4]$ (**4b**) (200 mg, 18%). Complex **3b**. Mass spectrum, *m*/*z* 480 (M^+) and $M^+ - n$CO (*n* = 1–5). ν_{max}/cm^{-1} (CH_2Cl_2), 2062s, 2007vs, 1996 (sh), 1959m, 1606w. NMR ($CDCl_3$), ^1H, δ 7.7–7.3 [m, 5H, Ph], 5.85 [s, 1H, CH], 1.44 [s, 9H, Me]; ^{13}C, δ 205.4 [s, 1CO], 204.7 [s, 1CO], 201.2 [s, 3CO], 139.9–126.6 [*Ph*], 84.8 [s, *C*Ph], 68.2 [s, CH], 32.6 [s, Me]. Complex **4b** (Found: C, 34.10; H, 3.17. $C_{16}H_{18}As_2Co_2O_5$ requires C, 34.44; H, 3.25%). Mass spectrum, *m*/*z* 558 (M^+) and $M^+ - n$CO (*n* = 1–4). ν_{max}/cm^{-1} (CH_2Cl_2), 2027m, 1997vs, 1969s. NMR ($CDCl_3$), ^1H, δ 7.5–7.2 [m, 5H, *Ph*], 5.84 [s, 1H, CH], 1.67 [s, 3H, Me], 1.62 [s, 3H, Me]; ^{13}C, δ 205 [s, 2CO], 202 [s, 2CO], 141.9–126.4 [*Ph*], 98.5 [s, *C*Ph], 72.2 [s, CH], 23.7 [s, Me], 23.1 [s, Me].

(vi) Reaction of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ and As_2Me_4

$[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ (520 mg, 1.21 mmol) and As_2Me_4 (260 mg, 1.23 mmol) were dissolved in toluene (60 ml) and heated at 35 °C for 15 h. After removal of the reaction solvent under vacuum, the residue was dissolved in the minimum quantity of CH_2Cl_2 and applied to the base of silica TLC plates. Elution with hexane/ethyl acetate (7 : 3) gave orange $[Co_2\{\mu\text{-}$

$C_2(CO_2Me)_2\}(CO)_5(AsMe_3)]$ (**3c**) (160 mg, 25%) and deep red, crystalline $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(AsMe_2)_2O\}(CO)_4]$ (**4c**) (252 mg, 35%). Crystals of **4c** suitable for diffraction were grown by slow evaporation at 0 °C of an *n*-hexane/CH_2Cl_2 solution of the complex. Complex **3c** (Found: C, 32.24; H, 2.87. $C_{14}H_{15}AsCo_2O_9$ requires C, 32.33; H, 2.91%). Mass spectrum, *m/z* 520 (M^+) and $M^+ - n$CO (n = 1–5). ν_{max}/cm^{-1} (CH_2Cl_2), 2082s, 2033vs, 2021s, 1985m, 1704m. NMR ($CDCl_3$), ^1H, δ 3.79 [s, 6H, CO_2Me], 1.34 [s, 9H, AsMe]; ^{13}C, δ 203 [s, 2CO], 199 [s, 3CO], 172.0 [s, *C*O_2Me], 73.4 [s, *C*CO_2Me], 52.7 [s, CO_2*Me*], 13.7 [s, AsMe]. Complex **4c** (Found: C, 27.90; H, 2.92. $C_{14}H_{18}As_2Co_2O_9$ requires C, 28.12; H, 3.03%). Mass spectrum, *m/z* 598 (M^+) and $M^+ - n$CO (n = 1–4). ν_{max}/cm^{-1} (CH_2Cl_2), 2059s, 2023vs, 1997s, 1698m. NMR ($CDCl_3$), ^1H, δ 3.80 [s, 6H, CO_2Me], 1.69 [s, 12H, Me]; ^{13}C, δ 200.8 [s, CO], 172.6 [s, *C*O_2Me], 79.2 [s, *C*CO_2Me], 52.6 [s, CCO_2*Me*], 23.2 [s, AsMe].

(vii) Thermolysis of $[Co_2(\mu\text{-}PhCCPh)\{\mu\text{-}(AsMe_2)_2O\}(CO)_4]$ (4a)

$[Co_2(\mu\text{-}PhCCPh)\{\mu\text{-}(AsMe_2)_2O\}(CO)_4]$ (**4a**) (405 mg, 0.64 mmol) was dissolved in xylene (60 ml) and refluxed for 24 h. After removal of reaction solvent under vacuum, the residue was dissolved in a minimum quantity of CH_2Cl_2. TLC of this showed it to contain one product only. By recrystallisation from CH_2Cl_2, deep purple, $[Co_2(\mu\text{-}PhCCPh)\{\mu\text{-}(AsMe_2)_2O\}_2(CO)_2]$ (**5**) (140 mg, 27%) was recovered. Crystals suitable for diffraction were grown by slow evaporation at 0 °C of a CH_2Cl_2 solution of the complex. Complex **5** (Found: C, 35.74; H, 4.14. $C_{24}H_{34}As_4Co_2O_4$ requires C, 35.85; H, 4.26%). Mass spectrum, *m/z* 804 (M^+) and $M^+ - n$CO (n = 1–2). ν_{max}/cm^{-1} (CH_2Cl_2), 1940 (sh), 1925s. NMR ($CDCl_3$), ^1H, δ 7.4–7.1 [m, 10H, *Ph*], 1.59 [s, 12H, Me], 1.47 [s, 12H, Me]; ^{13}C, δ 145.5–127.8 [*Ph*], 97.0 [s, *C*Ph], 26.6 [s, Me], 23.2 [s, Me].

(viii) Reaction of $[Co_3(\mu_3\text{-}CCl)(CO)_9]$ and As_2Ph_4

$[Co_3(\mu_3\text{-}CCl)(CO)_9]$ (920 mg, 1.93 mmol) and As_2Ph_4 (13 ml, 0.15 M in toluene, 1.95 mmol) were dissolved in toluene (60 ml) and heated at 40 °C with stirring for 4 h. After removal of the reaction solvent under vacuum, the residue was dissolved in the minimum quantity of CH_2Cl_2 and adsorbed onto silica. The silica was pumped dry and transferred to the top of a silica chromatography column. Elution with hexane/CH_2Cl_2 (4:1) gave unreacted $[Co_3(\mu_3\text{-}CCl)(CO)_9]$ (300 mg, 33%), brown $[Co_3(\mu_3\text{-}CCl)(CO)_8(AsPh_3)]$ (**6a**) (264 mg, 18%) and purple $[Co_3(\mu_3\text{-}CCl)\{\mu\text{-}(AsPh_2)_2O\}(CO)_7]$ (**7a**) (563 mg, 33%). Crystals of **7a** suitable for diffraction were grown by slow evaporation at 0 °C of an *n*-hexane/CH_2Cl_2 solution of the complex. Complex **6a**. Mass spectrum, *m/z* 754 (M^+) and $M^+ - n$CO (n = 1–8). ν_{max}/cm^{-1} (hexane), 2085s, 2062m, 2043s, 2032s, 2023s, 2004m, 1979w. Complex **7a** (Found: C, 42.72; H, 2.23. $C_{32}H_{20}As_2ClCo_3O_8$ requires C, 42.96; H, 2.25%). Mass spectrum, *m/z* 894 (M^+) and $M^+ - n$CO (n = 1–7). ν_{max}/cm^{-1} (CH_2Cl_2), 2071m, 2021s, 1980w. NMR ($CDCl_3$), ^1H, δ 7.6–7.3 [m, 20H, *Ph*]; ^{13}C, δ 278 [s, μ_3-CCl], 202.4 [s, CO], 142.1–128.8 [*Ph*].

(ix) Reaction of $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ and As_2Ph_4

$[Co_3(\mu_3\text{-}CMe)(CO)_9]$ (500 mg, 1.10 mmol) and As_2Ph_4 (7.3 ml, 0.15 M in toluene, 1.10 mmol) were dissolved in toluene (60 ml) and heated at 40 °C with stirring for 15 h. After removal of the reaction solvent under vacuum, the residue was dissolved in the minimum quantity of CH_2Cl_2 and adsorbed onto silica. The silica was pumped dry and transferred to the top of a silica chromatography column. Elution with hexane/CH_2Cl_2 (9:1) gave unreacted $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ (200 mg, 40%), and purple $[Co_3(\mu_3\text{-}CMe)\{\mu\text{-}(AsPh_2)_2O\}(CO)_7]$ (**7b**) (210 mg, 22%). Crystals of **7b** suitable for diffraction were grown by slow evaporation at 0 °C of an *n*-hexane/CH_2Cl_2 solution of the complex. Complex **7b** (Found: C, 45.04; H, 2.55. $C_{33}H_{23}As_2Co_3O_8$ requires C, 45.34; H, 2.65%). Mass spectrum, *m/z* 874 (M^+) and $M^+ - n$CO (n = 1–7). ν_{max}/cm^{-1} (CH_2Cl_2), 2062m, 2009s. NMR ($CDCl_3$), ^1H, δ 7.7–7.2 [m, 20H, *Ph*], 3.50 [s, 3H, Me]; ^{13}C, δ 293.9 [s, μ_3-*C*Me], 203.7 [s, CO], 142.8–128.8 [Ph], 46.6 [s, C*Me*].

(x) Reaction of $[Co_3(\mu_3\text{-}CCl)(CO)_9]$ and As_2Me_4

$[Co_3(\mu_3\text{-}CCl)(CO)_9]$ (345 mg, 0.72 mmol) and As_2Me_4 (160 mg, 0.76 mmol) were dissolved in 60 ml toluene and heated at 35 °C for 3 h. After removal of reaction solvent under vacuum, the residue was dissolved in a minimum quantity of CH_2Cl_2 and adsorbed onto silica. The silica was pumped dry and transferred to the top of a silica chromatography column. Elution with hexane/CH_2Cl_2 (4:1) gave unreacted $[Co_3(\mu_3\text{-}CCl)(CO)_9]$ and deep purple, crystalline $[Co_3(\mu_3\text{-}CCl)\{\mu\text{-}(AsMe_2)_2O\}(CO)_7]$ (**8a**) (289 mg, 62%). Crystals of **8a** suitable for diffraction were grown by slow evaporation at 0 °C of an *n*-hexane/CH_2Cl_2 solution of the complex. Complex **8a** (Found: C, 22.42; H, 2.04. $C_{12}H_{12}As_2ClCo_3O_8$ requires C, 22.30; H, 1.87%). Mass spectrum, *m/z* 646 (M^+) and $M^+ - n$CO (n = 1–7). ν_{max}/cm^{-1} (CH_2Cl_2), 2072m, 2022vs, 2005w, 1994w, 1982w. NMR ($CDCl_3$), ^1H, δ 1.79 [s, 6H, Me], 1.73 [s, 6H, Me]; ^{13}C, 202.5 [s, CO], 24.9 [s, Me], 19.7 [s, Me].

(xi) Reaction of $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ and As_2Me_4

$[Co_3(\mu_3\text{-}CMe)(CO)_9]$ (330 mg, 0.72 mmol) and As_2Me_4 (160 mg, 0.76 mmol) were dissolved in 60 ml toluene and heated at 40 °C for 5 h. After removal of reaction solvent under vacuum, the residue was dissolved in a minimum quantity of CH_2Cl_2 and adsorbed onto silica. The silica was pumped dry and transferred to the top of a silica chromatography column. Elution with hexane/CH_2Cl_2 (1:1) gave deep purple, crystalline $[Co_3(\mu_3\text{-}CMe)\{\mu\text{-}(AsMe_2)_2O\}(CO)_7]$ (**8b**) (266 mg, 59%). Complex **8b** (Found: C, 24.76; H, 2.31. $C_{13}H_{15}As_2Co_3O_8$ requires C, 24.95; H, 2.42%). Mass spectrum, *m/z* 626 (M^+) and $M^+ - n$CO (n = 1–7). ν_{max}/cm^{-1} (CH_2Cl_2), 2064m, 2010s, 1990w. NMR ($CDCl_3$), ^1H, δ 3.75 [s, 3H, CMe], 1.72 [s, 6H, Me], 1.70 [s, 6H, Me]; ^{13}C, δ 203.9 [s, CO], 45.3 [s, *C*Me], 25.4 [s, AsMe], 21.2 [s, AsMe].

(xii) Reaction of $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}MoCp(CO)_2]$ and As_2Ph_4

$[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}MoCp(CO)_2]$ (785 mg, 1.56 mmol) and As_2Ph_4 (31 ml, 0.15 M in toluene, 4.65 mmol) were dissolved in 60 ml toluene and heated at 35 °C with stirring for 24 h. After removal of the reaction solvent under vacuum the residue was dissolved in the minimum quantity of CH_2Cl_2 and applied to the base of silica TLC places. Elution with hexane/acetone (3:1) gave, in addition to unreacted starting material, red-orange $[\{(HO)Ph_2As\}(OC)_2Co\{\mu\text{-}C_2(CO_2Me)_2\}MoCp(CO)_2]$ (**9**) (514 mg, 43%). Crystals suitable for diffraction were grown by slow evaporation at room temperature of an *n*-hexane/CH_2Cl_2 solution of the complex. Complex **9** (Found: C, 45.10; H, 3.07. $C_{27}H_{22}AsCoMoO_9$ requires C, 45.02; H, 3.08%). Mass spectrum, *m/z* 720 (M^+) and $M^+ - n$CO (n = 1–4). ν_{max}/cm^{-1} (CH_2Cl_2), 2033m, 2000s, 1971m, 1955 (sh). NMR ($CDCl_3$), ^1H, δ 7.7–7.2 [m, 10H, *Ph*], 6.41 [s, 1H, AsOH], 5.45 [s, 5H, Cp], 3.48 [s, 6H, Me]; ^{13}C, δ 222.8 [s, MoCo], 205 [s, CoCO], 175.4 [s, *C*O_2Me], 142.8–128.7 [*Ph*], 90.7 [s, Cp], 72.8 [s, *C*CO_2Me], 52.7 [s, CO_2*Me*].

(xiii) Crystal structure determinations: data collection, structure solution and refinement

X-Ray intensity data were collected on a Siemens P4 four-circle diffractometer for **2b**, **5**, **7a**, **7b** and **9** and for **4c** and **8a** on a Philips PW1100 four-circle diffractometer. Details of data collection, refinement and crystal data are listed in Table 4. Lorentz-polarisation and absorption corrections were applied to the data of all the compounds.

Table 4 Crystallographic and data processing parameters for complexes **2b**, **4c**, **5**, **7a**, **7b**, **8a** and **9**

	2b	**4c**	**5**	**7a**	**7b**	**8a**	**9**
Formula	$C_{36}H_{26}As_2Co_2O_5$	$C_{14}H_{18}As_2Co_2O_9$	$C_{24}H_{34}As_4Co_2O_4$	$C_{32}H_{20}As_2ClCo_3O_8$	$C_{33}H_{23}As_2Co_3O_8$	$C_{12}H_{12}As_2ClCo_3O_8$	$C_{27}H_{22}AsCoMoO_9$
M	806.27	573.96	804.05	894.56	874.14	646.30	720.24
Temperature/K	293(2)	293(2)	297(2)	295(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	17.766(7)	9.628(2)	17.387(3)	16.843(4)	12.081(2)	9.198(2)	11.938(4)
b/Å	9.446(2)	14.327(3)	18.918(4)	11.199(3)	12.489(2)	17.117(3)	14.533(3)
c/Å	21.693(6)	16.624(3)	19.785(3)	19.844(5)	13.650(3)	14.104(2)	16.455(3)
α/°	—	—	—	—	68.55(2)	—	—
β/°	110.02(4)	97.11(2)	111.142(7)	110.87(2)	70.46(1)	105.28(2)	99.94(2)
γ/°	—	—	—	—	64.55(2)	—	—
U/Å^3	3420(2)	2275.4(3)	6070(2)	3500(2)	1689.9(5)	2142.1(3)	2812(1)
Z	4	4	8	4	2	4	4
μ(Mo-Kα)/mm^{-1}	2.930	4.38	5.447	3.407	3.447	5.52	2.254
Reflections collected	12436	3219	8960	12717	11808	3123	17092
Independent reflections	6022	2759 [$I/\sigma(I) > 3$]	7420	6162	5904	2700 [$I/\sigma(I) > 3$]	8202
Final R indices $I > 2\sigma(I)$	$R_1 = 0.0493$, $wR_2 = 0.0761$	$R = 0.0399$, $R' = 0.0399^a$	$R_1 = 0.0699$, $wR_2 = 0.1413$	$R_1 = 0.0697$, $wR_2 = 0.1412$	$R_1 = 0.0342$, $wR_2 = 0.0728$	$R = 0.0451$, $R' = 0.0451^a$	$R_1 = 0.0545$, $wR_2 = 0.1010$
All data	$R_1 = 0.1198$, $wR_2 = 0.0928$	—	$R_1 = 0.1452$, $wR_2 = 0.1601$	$R_1 = 0.1613$, $wR_2 = 0.1792$	$R_1 = 0.0582$, $wR_2 = 0.0807$	—	$R_1 = 0.1330$, $wR_2 = 0.1247$

[a] $I > 3\sigma(I)$.

For two of the compounds, **4c** and **8a**, the positions of the metal atoms were deduced from Patterson syntheses and for **2b**, **5**, **7a**, **7b** and **9** the positions of the metals and most of the non-hydrogen atoms were located from direct methods. For **4c** and **8a** refinement was based on F,[31] and for the remaining structures **2b**, **5**, **7a**, **7b** and **9** refinement was based on F^2.[32] The remaining non-hydrogen atoms, in all cases, and the hydroxyl proton in **9**, were revealed from subsequent difference-Fourier syntheses. In the crystal of **5** there are two independent molecules, which are virtually identical and equivalent parameters in the two molecules were "tied" in the refinement. All the phenyl rings were constrained to refine as rigid hexagons. With the exception of the hydroxyl proton in **9**, all hydrogen atoms were placed in calculated positions with displacement parameters equal to 1.2 and 1.5 U_{eq} of the parent carbon atoms for phenyl and methyl hydrogen atoms, respectively. Semi-empirical absorption correction using ψ-scans[33] were applied to the data of **2b**, **5**, **7b** and **9**, and after initial refinement with isotropic displacement parameters empirical absorption corrections[34] were applied to the data of **7a**, **4c** and **8**. All non-hydrogen atoms were assigned anisotropic displacement parameters in the final cycles of full-matrix least-squares refinement.

CCDC reference number 186/1755.

See http://www.rsc.org/suppdata/dt/a9/a906611j/ for crystallographic files in .cif format.

Acknowledgements

We thank the Defence Evaluation and Research Agency (Fort Halstead) for financial support to J. D. K.

References

1 (*a*) R. G. Hayter, *J. Am. Chem. Soc.*, 1963, **85**, 3120; (*b*) R. G. Hayter, *Inorg. Chem.*, 1963, **2**, 1031; (*c*) R. G. Hayter, *J. Am. Chem. Soc.*, 1964, **86**, 823; (*d*) R. G. Hayter, *Inorg. Chem.*, 1964, **3**, 711; (*e*) R. G. Hayter and L. F. Williams, *Inorg. Chem.*, 1964, **3**, 717; (*f*) R. G. Hayter and L. F. Williams, *J. Inorg. Nucl. Chem.*, 1964, **26**, 1977; (*g*) J. Chatt and D. A. Thornton, *J. Chem. Soc.*, 1964, 1005; (*h*) J. Chatt and D. T. Thompson, *J. Chem. Soc.*, 1964, 2713; (*i*) J. Grobe, *Z. Anorg. Allg. Chem.*, 1964, **331**, 63; (*j*) R. G. Hayter, *Preparative Inorganic Reactions*, ed. W. L. Jolly, Wiley, New York, 1965, vol. 2, p. 211; (*k*) W. Hieber and R. Kummer, *Z. Naturforsch.*, *Teil B*, 1965, **20**, 271; (*l*) B. E. Job, R. A. N. McLean and D. T. Thompson, *Chem. Commun.*, 1966, 895; (*m*) J. P. Candlin, K. K. Joshi and D. T. Thompson, *Chem. Ind.* (*London*), 1966, 1960; (*n*) W. Hieber and R. Kummer, *Chem. Ber.*, 1967, **100**, 148; (*o*) W. Hieber and W. Opavsky, *Chem. Ber.*, 1968, **101**, 2996; (*p*) M. Cooke, M. Green and D. Kirkpatrick, *J. Chem. Soc. A*, 1968, 1507.

2 (*a*) R. C. Dobbie, M. J. Hopkinson and D. Whittaker, *J. Chem. Soc.*, *Dalton Trans.*, 1972, 1030; (*b*) H. Vahrenkamp, *Chem. Ber.*, 1978, **111**, 3472; (*c*) A. B. Burg and W. Mahler, *J. Am. Chem. Soc.*, 1958, **80**, 2334; (*d*) M. Brockhais, F. Staudacher and H. Vahrenkamp, *Chem. Ber.*, 1072, **105**, 3176; (*e*) A. Trenkle and H. Vahrenkamp, *Chem. Ber.*, 1981, **114**, 1343; (*f*) J. Grobe, M. Köhne-Wächter and D. Le Van, *J. Organomet. Chem.*, 1985, **280**, 331.

3 (*a*) F. A. Cotton and T. R. Webb, *Inorg. Chim. Acta*, 1974, **10**, 127; R. Borowski, D. Rehder and K. J. von Deuten, *J. Organomet. Chem.*, 1981, **220**, 45; (*b*) H. Vahrenkamp and W. Ehrl, *Angew. Chem.*, *Int. Ed. Engl.*, 1971, **10**, 513; (*c*) G. Huttner, H.-G. Schmid and H. Lorenz, *Chem. Ber.*, 1976, **109**, 3741; (*d*) E. Röttinger, A. Trenkle, R. Müller and H. Vahrenkamp, *Chem. Ber.*, 1980, **113**, 1280.

4 A. J. M. Caffyn, M. J. Mays, G. A. Solan, D. Braga, P. Sabatino, G. Conole, M. McPartlin and H. R. Powell, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 3103.

5 (*a*) A. Martín, M. J. Mays, P. R. Raithby and G. A. Solan, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 1431; (*b*) S. L. Ingham, M. J. Mays, P. R. Raithby, G. A. Solan, B. V. Sundavadra, G. Conole and M. Kessler, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 3607.

6 G. A. Acum, M. J. Mays, P. R. Raithby, H. R. Powell and G. A. Solan, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 3427.

7 P. H. Bird, A. R. Fraser and D. N. Hall, *Inorg. Chem.*, 1977, **16**, 1923.

8 H. Beurich and H. Vahrenkamp, *Chem. Ber.*, 1981, **114**, 2542.

9 (*a*) P. A. Dawson, B. H. Robinson and J. Simpson, *J. Chem. Soc.*, *Dalton Trans.*, 1979, 1762; (*b*) K. Hinkelmann, J. Heinze, H. T. Schacht, J. S. Field and H. Vahrenkamp, *J. Am. Chem. Soc.*, 1989, **111**, 5078; (*c*) B. H. Robinson and W. S. Tham, *J. Organomet. Chem.*, 1969, **16**, 45; (*d*) T. W. Mathewson, B. H. Robinson and W. S. Tham, *J. Chem. Soc. A*, 1971, 1457.

10 G. Sànchez, F. Momblona, G. Carcía, G. López, E. Pinilla and A. Monge, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 2271.

11 G. Conole, M. Kessler, M. J. Mays, G. E. Pateman and G. A. Solan, *Polyhedron*, 1998, **17**, 2993.

12 W. R. Cullen and J. Trotter, *Can. J. Chem.*, 1963, **41**, 2983.

13 P. W. Sutton and L. F. Dahl, *J. Am. Chem. Soc.*, 1967, **89**, 261.

14 M. Pizzey, L. Mihichuck, R. J. Barton and B. E. Robertson, *Can. J. Chem.*, 1984, **62**, 285.

15 H. Vahrenkamp, *Chem. Ber.*, 1972, **105**, 3574.

16 W. Ehrl and H. Vahrenkamp, *Chem. Ber.*, 1973, **106**, 2556.

17 A. J. M. Caffyn, M. J. Mays, G. Conole, M. McPartlin and H. R. Powell, *J. Organomet. Chem.*, 1992, **436**, 83.

18 B. J. Aylett, *Organometallic Compounds*, *School of Polymer Technology.2*, Wiley, New York, 4th edn., 1979, vol. 1, pp. 413 and 424.

19 C. W. Porter and P. Borgstrom, *J. Am. Chem. Soc.*, 1919, **41**, 2048.

20 W. Steinkopf and G. Schwen, *Chem. Ber.*, 1921, **54**, 1437.

21 A.-J. Di Maio and A. L. Rheingold, *Chem. Rev.*, 1990, **90**, 169.

22 (*a*) H. W. Sternberg, R. A. Greenfield, J. H. Wotiz, R. A. Friedel, R. Markby and I. Wender, *J. Am. Chem. Soc.*, 1954, **76**, 1457; (*b*) R. A. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiz, R. Markby and I. Wender, *J. Am. Chem. Soc.*, 1956, **78**, 120; (*c*) U. Kruerke and W. Hübel, *Chem. Ber.*, 1961, **94**, 2829.

23 (*a*) D. Seyferth, J. E. Hallgren and P. L. K. Hung, *J. Organomet. Chem.*, 1973, **50**, 265; (*b*) *Organometallic Syntheses*, ed. J. J. Eisch and R. B. King, Academic Press Inc., London, 1965, vol. 1.

24 R. Yanez, N. Lugan and R. Mathieu, *Organometallics*, 1990, **9**, 2998.

25 V. Auger, *C.R. Hebd. Seances Acad. Sci.*, 1906, **142**, 1151.

26 F. Sachs and H. Kantoriwicz, *Chem. Ber.*, 1908, **41**, 2767.

27 F. F. Blicke and F. D. Smith, *J. Am. Chem. Soc.*, 1929, **51**, 1558.

28 A. E. Goddard, *Textbook of Inorganic Chemistry*, ed. J. Newton Friend, Charles Griffin and Co. Ltd., London, 1930, vol. XI, pt. II, p. 113.

29 D. Wittenberg and H. Gilman, *J. Org. Chem.*, 1958, **23**, 1063.

30 J. Chatt and D. A. Thornton, *J. Chem. Soc.*, 1964, 1005.

31 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.

32 SHELTXL (PC version 5.03), Siemens Analytical Instruments Inc., Madison, WI, 1994.

33 A. C. T. North, D. C. Philips and F. S. Matthews, *Acta Crystallogr.*, *Sect. A*, 1968, **24**, 351.

34 N. Walker and D. Stuart, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 158.

Paper a906611j