Transformations of organoarsine-oxides and -sulfides on di- and tri-cobalt carbonyl centres

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Abstract

Conversion of $[Co_3(\mu_3\text{-}CR')\{\mu\text{-}(AsMe_2)_2O\}(CO)_7]$ [R′ = Cl, Me] and $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(AsMe_2)_2O\}(CO)_4]$ to the corresponding bis-dimethylarsinesulfide-bridged complexes $[Co_3(\mu_3\text{-}CR')\{\mu\text{-}(AsMe_2)_2S\}(CO)_7]$ [R′ = Cl (**1a**), Me (**1b**)] and $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(AsMe_2)_2S\}(CO)_4]$ (**2**) can be achieved on their treatment with H_2S (with the elimination of H_2O); this process is reversible. The related bis-diphenylarsinesulfide-bridged complexes, $[Co_3(\mu_3\text{-}CR')\{\mu\text{-}(AsPh_2)_2S\}(CO)_7]$ [R′ = Cl (**3a**), Me (**3b**)] and $[Co_2(R'CCR'')\{\mu\text{-}(AsPh_2)_2S\}(CO)_4]$ [R′ = R′′ = CO_2Me (**4a**), Ph (**4b**)] can be obtained in moderate yield by the direct reaction of $(Ph_2As)_2S$ with $[Co_3(\mu_3\text{-}CR')(CO)_9]$ [R′ = Cl, Me] and $[Co_2(R'CCR'')(CO)_6]$ [R′ = R′′ = CO_2Me, Ph], respectively. The triphenylarsine mono-substituted complex $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5(AsPh_3)]$ (**5**) is also isolated as a product in the reaction leading to **4a**. Thermolysis of **3a** yields $[Co_3(\mu_3\text{-}S)\{\mu\text{-}(AsPh_2)_2O\}\{\mu\text{-}(AsPh_2)S\}(CO)_7]$ (**6**) in low yield while the related thioxo-capped complexes $[Co_3(\mu_3\text{-}S)\{\mu\text{-}(AsMe_2)_2X\}(\mu\text{-}AsMe_2S)(CO)_5]$ [X = S (**7**), O (**8**)] can be obtained in higher yield by thermolysis of $[Co_3(\mu\text{-}CMe)\{\mu\text{-}(AsMe_2)_2O\}(CO)_7]$ in the presence of H_2S. Single crystal X-ray diffraction studies have been performed on **2**, **4a**, **4b** and **8**.
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1. Introduction

While phosphorus(III) ligands of the type $(R_2P)_2X$ (R = hydrocarbyl; X = S, O) are well documented in transition metal chemistry [1,2], the related arsenic(III) ligands $(R_2As)_2O$ and, in particular, $(R_2As)_2S$, have received considerably less attention [3–5]. Indeed, only a handful of complexes have been characterised crystallographically to date that contains bis-diarsinesulfide ligands [4a,5]. Nonetheless, the flexibility of this ligand family has been demonstrated in its ability to adopt monodentate, bidentate-chelating and bidentate-bridging bonding modes.

The free bis-dialkylarsine- and bis-diarylarsine-sulfide ligands themselves are readily accessible and have been prepared by a number of routes [6,7] including a metathesis approach in which the corresponding bis-diarsineoxide can be converted directly with hydrogen sulfide [8]. Interestingly, a related approach using coordinated bis-diarsineoxide ligands has, however, to the knowledge of the authors, not been reported.

In this paper, we describe a study conducted to determine whether the coordinated $(R_2As)_2O$ (R = Me, Ph) ligand in a series of di- and tri-cobalt organometallic complexes would react in the same way as the free ligand, thereby generating a coordinated $(R_2As)_2S$ ligand. In addition, the synthesis of a series of $(R_2As)_2S$-bridged cobalt complexes by direct reaction of $(R_2As)_2S$ with alkyne-dicobalt hexacarbonyl or alkylidyne-tricobalt non-acarbonyl, along with an examination of the arsenic–sulfur bond lability in these complexes, are reported.

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2. Results and discussion

2.1. Metathesis of oxygen for sulfur in $[Co_3(\mu_3\text{-}CR')\{\mu\text{-}(Me_2As)_2O\}(CO)_7]$ and $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(Me_2As)_2O\}(CO)_4]$

Purging a benzene solution of $[Co_3(\mu_3\text{-}CR')\{\mu\text{-}(Me_2As)_2O\}(CO)_7]$ $[R' = Cl$ or Me] with H_2S at ambient temperature gave $[Co_3(\mu_3\text{-}CR')\{\mu\text{-}(Me_2As)_2S\}(CO)_7]$ $[R' = Cl$ (**1a**), Me (**1b**)] in good yield (ca. 48%; Scheme 1). Similarly, $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(Me_2As)_2S\}\text{-}(CO)_4]$ (**2**) can be obtained in good yield (56%) on treatment of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(Me_2As)_2O\}\text{-}(CO)_4]$ with H_2S at room temperature. All the products have been characterised by IR, ^{1}H- and ^{13}C-NMR spectroscopy, mass spectrometry and microanalysis (see Table 1). In addition, complex **2** has been the subject of an X-ray diffraction study (Fig. 1); the structure will be discussed later.

The mass spectra of **1a**, **1b** and **2** show molecular ion peaks consistent with the proposed formulae together with peaks corresponding to the successive loss of up to seven carbonyl groups for **1a** and **1b** and four carbonyl groups for **2**. For all three complexes, the molecular ion peak occurs sixteen mass units higher than for the corresponding dimethylarsineoxide complexes. In the IR spectra for **1a**, **1b** and **2** a similar pattern of peaks is observed to the $(Me_2As)_2O$ analogues, $[Co_3(\mu_3\text{-}CR')\{\mu\text{-}(Ph_2As)_2O\}(CO)_7]$ $(R' = Cl$, Me) and $[Co_2\{C_2(CO_2Me)_2\}\{\mu\text{-}(Me_2As)O\}(CO)_4]$ [3a].

Two equal-intensity resonances, attributable to methyl groups of the bridging $(Me_2As)_2S$ ligand are observed in the ^{1}H-NMR spectra of both **1a** and **1b**, appearing at δ 1.87 ppm and δ 1.80 ppm (**1a**) and at δ 1.82 ppm and δ 1.76 ppm (**1b**). Each resonance integrates to six protons, which indicates that two distinct methyl environments are present in each complex. This is
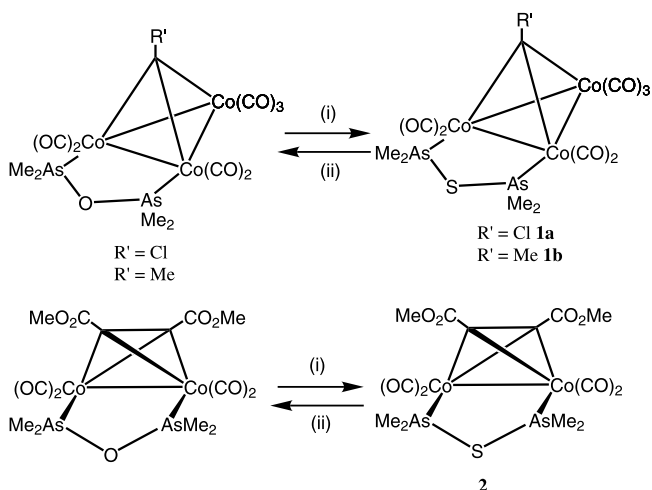
further supported by the ^{13}C-NMR spectra of **1a** and **1b** in which the corresponding methyl resonances are seen at δ 23.4 ppm and δ 18.2 ppm (**1a**) and at δ 21.6 ppm and δ 19.6 ppm (**1b**). In contrast, only one signal for **2** is seen in both the ^{1}H-and ^{13}C-NMR spectra for the methyl groups of the $(Me_2As)_2S$ ligands. This is in agreement with the corresponding data for the complexes $[Co_2\{C_2(CO_2Me)_2\}\{\mu\text{-}(Me_2As)O\}(CO)_4]$ [3a] and $[Co_2\{C_2(CO_2Me)_2\}(\mu\text{-}P_2Ph_4)(CO)_4]$ [9] and has been attributed to a fluxional process operating in solution. It is likely that a similar process is occurring for **2**.

2.2. Reaction of $[Co_2(\mu\text{-}R'CCR'')(CO)_6]$ and $[Co_3(\mu_3\text{-}CR')(CO)_9]$ with $(Ph_2As)_2S$

The reaction of $[Co_3(\mu_3\text{-}CR')(CO)_9]$ $(R' = Cl$, Me) with $(Ph_2As)_2S$ in toluene at 35 °C afforded greenish-black $[Co_3(\mu_3\text{-}CR')\{\mu\text{-}(Ph_2As)_2S\}(CO)_7]$ $[R' = Cl$ (**3a**), Me (**3b**)] as the sole product in moderate to good yield (54–65%). Conversely, treatment of $[Co_2(\mu\text{-}R'CCR'')(CO)_6]$ $[R' = R'' = CO_2Me$, Ph] with a three-fold excess of $(Ph_2As)_2S$ in toluene at 35–40 °C gave $[Co_2(R'CCR'')\{\mu\text{-}(Ph_2As)_2S\}(CO)_4]$ $[R' = R'' = CO_2Me$ (**4a**), Ph (**4b**)] and $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5(AsPh_3)]$ (**5**) in moderate yield (32%) (Scheme 2). All the complexes have been characterised by IR spectroscopy, mass spectrometry, ^{1}H- and ^{13}C-NMR spectra and microanalysis (see Table 1). In addition, complexes **4a** and **4b** have been the subjects of single crystal X-ray diffraction studies.

Complexes **3a** and **3b** show molecular ions peaks along with peaks corresponding to the fragmentation from the molecular ions of up to seven carbonyl groups. In addition, the IR data for **3a** and **3b** display a similar pattern of bands as compared to the corresponding bis-diphenylarsineoxide-bridged complexes [3a].

The molecular structures of **4a** and **4b** along with the structurally related **2** are shown in Figs. 2, 3 and 1, respectively. They are similar and will be discussed together; selected bond lengths and angles for all the structures are presented in Table 2. Complex **4b** crystallises with two molecules in the asymmetric unit. Slight differences in molecular geometry are apparent but none is of great significance. Averaged values for bond lengths and angles in both molecules are quoted for **4b** throughout the following discussion.

In common with the unsubstituted parent complexes, **2**, **4a** and **4b** have a Co_2C_2 tetrahedral core, derived from a $Co_2(CO)_4$ unit and a bridging alkyne ligand (DMAD in **2** and **4a**, diphenylacetylene in **4b**), which is coordinated in the 'side-on' mode. In each complex, an $(R_2As)_2S$ [R = Me (**2**); R = Ph (**4a** and **4b**)] ligand acts as a bridging bidentate donor. Of the two carbonyl ligands remaining on each cobalt atom, one is located equatorially and the other occupies the axial position. The $(R_2As)_2S$ ligand coordinates to each cobalt atom at

Scheme 1. Reagents and conditions: (i) H_2S, room temperature, $C_6H_5CH_3$; (ii) room temperature, $C_6H_5CH_3$.

Table 1
Spectroscopic and analytical data for the new complexes **1**–**8**

Compound	ν(CO) (cm^{-1}) [a]	^{1}H-NMR, δ (ppm) [b]	^{13}C-NMR, δ (ppm) [c]	FAB mass spectrum	Microanalysis (%) [d]	
					C	H
1a	2072s, 2023vs, 2005w, 1992m, 1982m, 1968w	1.87 (s, 6H, *Me*), 1.80 (s, 6H, *Me*)	202.4 (s, *CO*), 23.4 (s, *Me*), 18.2 (s, *Me*)	662 [M$^+$, M$^+$−n-CO] ($n = 1$−7)	21.61 (21.76)	1.75 (1.83)
1b	2065s, 2056w, 2050w, 2010vs, 1989m, 1981w, 1970w, 1957w, 1865w, 1837w	3.30 (s, 3H, C−*Me*), 1.82 (s, 6H, As−*Me*), 1.76 (s, 6H, As−*Me*)	208.1 (s, *CO*), 44.6 (s, C−*Me*), 21.6 (s, As−*Me*), 19.6 (s, As−*Me*)	642 [M$^+$, M$^+$−n-CO] ($n = 1$−7)	24.01 (24.32)	2.27 (2.36)
2	2049m, 2023vs, 1196s	3.80 (s, 6H, CO$_2$Me), 1.91 (s, 12H, As−*Me*)	200.9 (s, *CO*), 172.3 (s, *CO$_2$*Me), 52.6 (s, CO$_2$*Me*), 21.3 (s, As−*Me*)	614 [M$^+$, M$^+$−n-CO] ($n = 1$−4)	27.47 (27.38)	2.91 (2.95)
3a	2071s, 2021s, 1979w	8.1−6.6 (m, 20H, *Ph*)	203.0 (s, *CO*), 145−129 (*Ph*)	910 [M$^+$, M$^+$−n-CO] ($n = 1$−7)	42.76 (42.21)	2.18 (2.21)
3b	2052s, 2010s, 1978w	–	–	890 [M$^+$, M$^+$−n-CO] ($n = 1$−7)	–	–
4a	2085m, 2052m, 2028s, 2002m, 1707w	7.8−7.2 (m, 20H, *Ph*), 3.61 (s, 6H, *Me*)	200.8 (s, *CO*), 171.7 (s, *CO$_2$*Me), 142−129 (*Ph*), 52.4 (s, CO$_2$*Me*)	862 [M$^+$, M$^+$−n-CO] ($n = 1$−4)	49.18 (49.32)	2.95 (3.00)
4b	2030m, 2003s, 1976m	7.9−6.2 (m, 30H, *Ph*)	203 (s, *CO*), 142−127 (*Ph*)	898 [M$^+$, M$^+$−n-CO] ($n = 1, 2, 4$)	56.16 (56.15)	3.31 (3.37)
5	2089s, 2043sh, 1997w, 1706w	7.7−7.3 (m, 15H, *Ph*), 3.60 (s, 6H, *Me*)	202.2 (s, *CO*), 198.0 (s, *CO*), 173.0 (s, *CO$_2$*Me), 141−129 (*Ph*), 74.0 (s, *C*−CO$_2$Me), 53.2 (s, CO$_2$*Me*)	705 [M$^+$, M$^+$−n-CO] ($n = 1$−5)	47.01 (47.36)	2.97 (3.04)
6	2044s, 2003vs	7.9−6.5 (m, 30H, *Ph*)	146−128 (*Ph*)	1084 [M$^+$, M$^+$−n-CO] ($n = 1$−5)	45.66 (45.41)	3.04 (2.79)
7	2038m, 1994m, 1733s	1.97 (s, 3H, *Me*),1.93 (s, 3H, *Me*), 1.75 (s, 3H, *Me*), 1.70 (s, 6H, *Me*), 1.58 (s, 3H, *Me*)	24.9 (s, *Me*), 24.4 (s, *Me*), 22.2 (s, *Me*), 20.8 (s, *Me*), 20.4 (s, *Me*), 19.5 (s, *Me*)	728 [M$^+$, M$^+$−n-CO] ($n = 1$−5)	18.45 (18.15)	2.46 (2.49)
8	2083m, 1993s, 1732w	1.90 (s, 3H, *Me*), 1.81 (s, 3H, *Me*), 1.70 (s, 6H, *Me*), 1.62 (s, 3H, *Me*), 1.60 (s, 3H, *Me*)	25.7 (s, *Me*), 24.9 (s, *Me*), 24.0 (s, *Me*), 23.0 (s, *Me*), 22.4 (s, *Me*), 20.2 (s, *Me*)	712 [M$^+$, M$^+$−n-CO] ($n = 1$−5)	18.83 (18.56)	2.57 (2.55)

[a] Recorded in dichloromethane solution.
[b] ^{1}H-NMR chemical shifts (δ) in ppm relative to SiMe$_4$ (0.0 ppm), coupling constants in Hz in CDCl$_3$ at 293 K.
[c] Chemical shifts in ppm relative to SiMe$_4$ (0.0), in CDCl$_3$ at 293 K.
[d] Calculated values in parentheses.
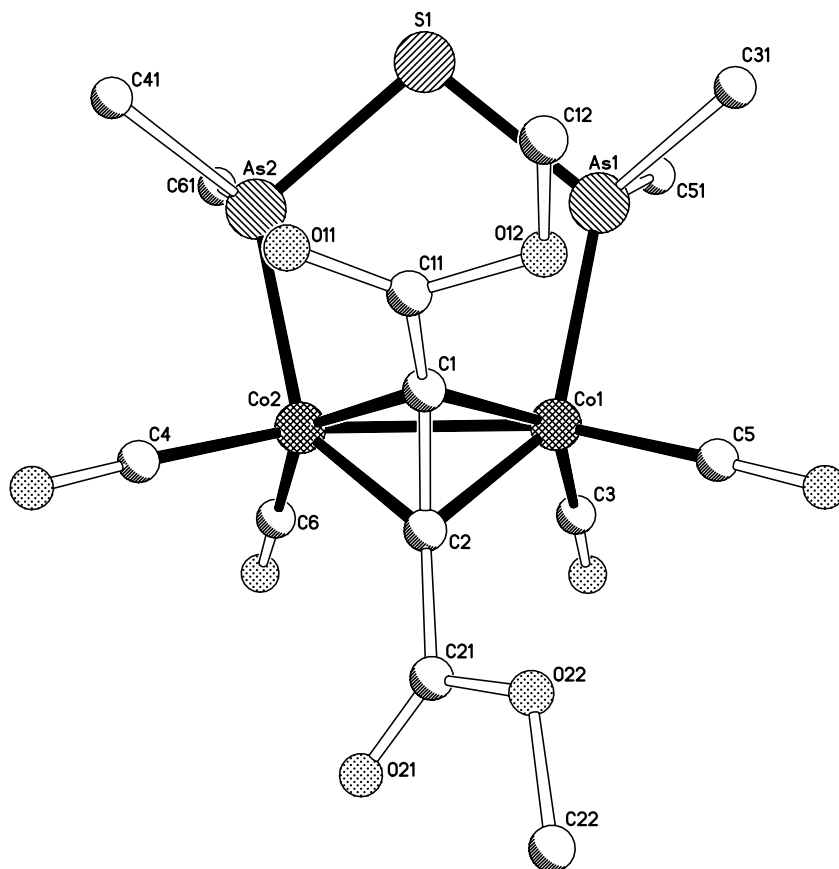
Fig. 1. Molecular structure of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(Me_2As)_2S\}(CO)_4]$ (**2**) including the atom numbering scheme. The hydrogen atoms have been omitted for clarity.
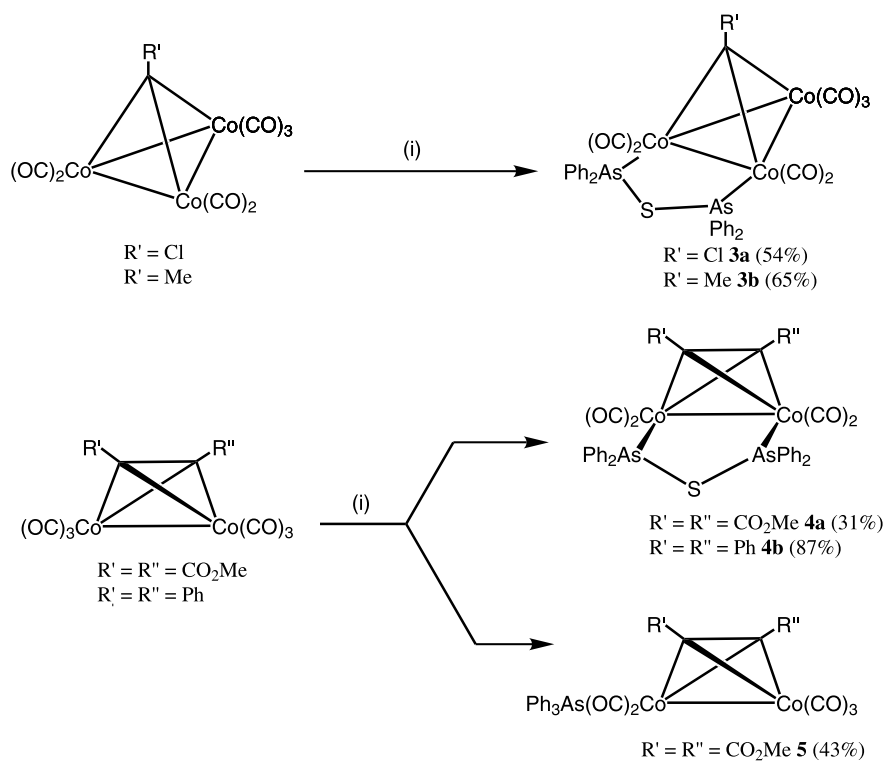
Scheme 2. Reagents and conditions: (i) $(Ph_2As)_2S$, 35 °C, $C_6H_5CH_3$.
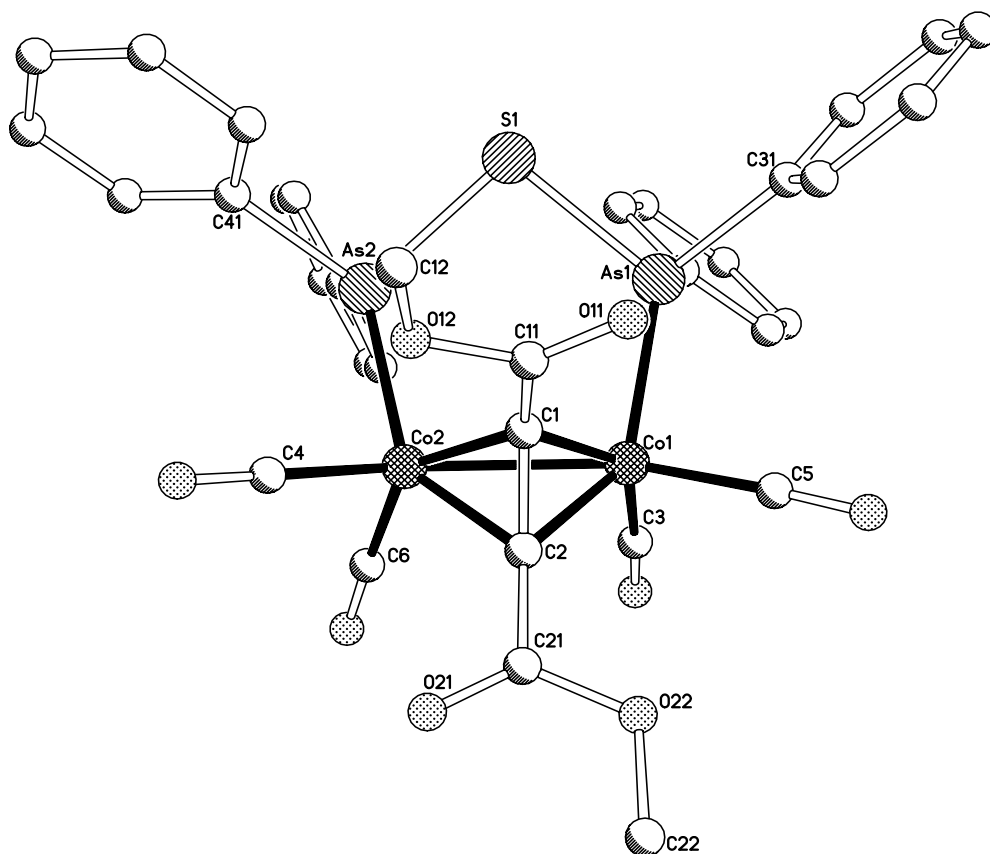
Fig. 2. Molecular structure of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(Ph_2As)_2S\}(CO)_4]$ (**4a**) including the atom numbering scheme. The hydrogen atoms have been omitted for clarity.

the remaining equatorial site. In **2**, the bridging As–S–As ligand and the bridged dicobalt edge form a symmetric pentagonal ring with the Co–As bonds [2.326(1) Å and 2.327(1) Å] and the As–S bonds [2.227(2) Å and 2.231(2) Å] in each case being of equal length. The molecule has an approximate plane of symmetry passing though the midpoint of the metal–metal bond and containing both the acetylenic bond and the sulfur atom. Twisting of the alkyne does, however, mean that it is not perfectly perpendicular to the Co–Co vector. The Co_2As_2S rings of **4a** and **4b** do not exhibit quite such a degree of regularity, probably an effect on the crystal packing of accommodating the more bulky phenyl rings of the arsine ligand.

Comparing the structure of **2** with that of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(Me_2As)_2O\}(CO)_4]$ [3a] and the structures of **4a** and **4b** with that of $[Co_2(\mu\text{-}PhCCH)\{\mu\text{-}(Ph_2As)_2O\}(CO)_4]$ [3a] the major changes involve modifications of the bridging arsine ligand geometry. The narrowing of bond angles subtended at chalcogen atoms as the chalcogen group is descended is a well-documented fact. The H–X–H angle in H_2X is $\sim 105°$ for X = O but only 92.1° for X = S. It is, therefore, unsurprising that the As–S–As angles in complexes **4** [97.02(8)° in **4a**; 100.3(1)° in **4b**] are smaller than the As–O–As angle in

$[Co_2(\mu\text{-}PhCCH)\{\mu\text{-}(Ph_2As)_2O\}(CO)_4]$ [118.4(2)°] and that the As–S–As angle in **2** [100.49(7)°] is smaller than the As–O–As angle in $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(Me_2As)_2O\}(CO)_4]$ [117.7(3)°]. This effect would be expected to bring the arsenic atoms closer together in complexes **2** and **4** if it were not for the fact that the As–S bonds are longer than As–O bonds in complexes such as $[Co_2(\mu\text{-}PhCCH)\{\mu\text{-}(Ph_2As)_2O\}(CO)_4]$ [mean = 1.799(3) Å] or $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(Me_2As)_2O\}(CO)_4]$ [mean = 1.803(5) Å]. This actually results in As...As separations of 3.373 Å and 3.421 Å for **4a** and **4b**, respectively; both values are larger than the distance of 3.089 Å in $[Co_2(\mu\text{-}PhCCH)\{\mu\text{-}(Ph_2As)_2O\}(CO)_4]$ [3a].

The $(R_2As)_2S$-bridged complexes feature larger Co–Co–As angles [mean = 101.56(4)° (**2**); 100.74(5)° (**4a**); 101.68(7)° (**4b**)] and longer Co–As bonds [mean = 2.327(1) Å (**2**); 2.338(1) Å (**4a**); 2.338(2) Å (**4b**)] than in $[Co_2(\mu\text{-}PhCCH)\{\mu\text{-}(Ph_2As)_2O\}(CO)_4]$ [97.07(4)°, 2.306(1) Å] and $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(Me_2As)_2O\}(CO)_4]$ [97.4(1)°, 2.319(1) Å] which presumably allow the longer As...As separation of the arsine–sulfide ligand to be accommodated by the dicobalt unit without introducing unnecessary strain or producing an unusually long Co–Co bond. The mean metal–
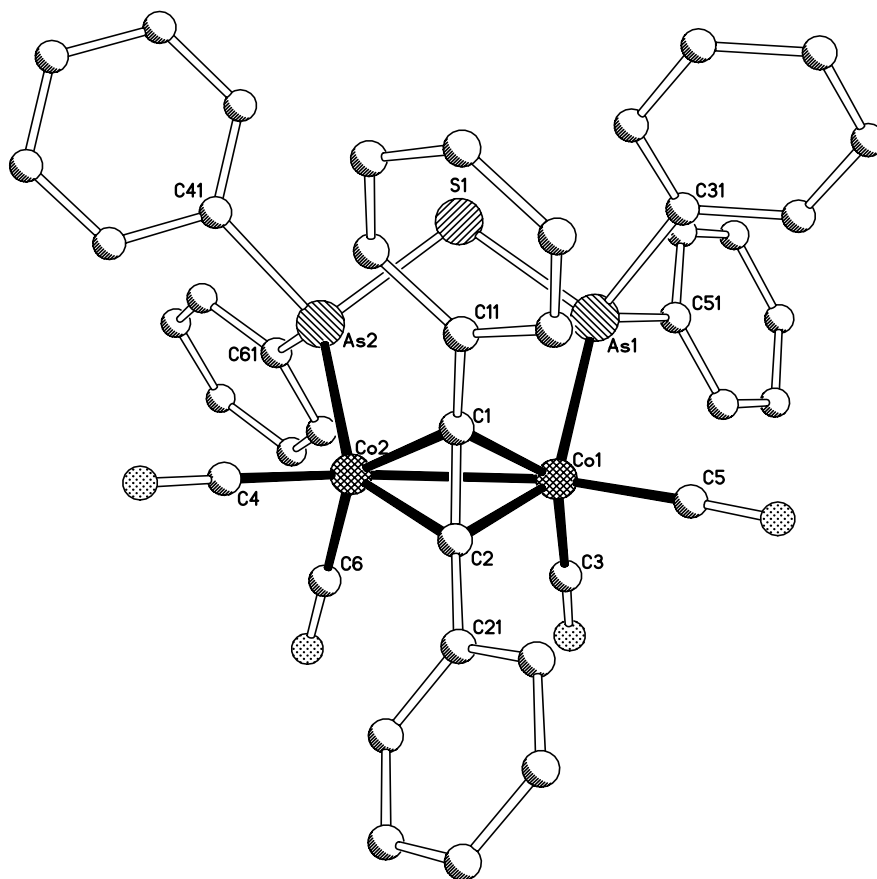
Fig. 3. Molecular structure of [Co$_2$(µ-PhCCPh){µ-(Ph$_2$As)$_2$S}(CO)$_4$] (**4b**) (molecule 1 only) including the atom numbering scheme. The hydrogen atoms have been omitted for clarity.

metal bond lengths for complexes **2**, **4a** and **4b** are fairly unremarkable for Co–Co bonds in this type of complex [3a,10] although as expected from the steric constraints placed on it by the bridging ligand, the metal–metal bond increases in length from 2.477(3) Å in [Co$_2$(µ-C$_2$(CO$_2$Me)$_2$)(CO)$_6$] [10] to 2.495(1) Å in **2** and 2.498(2) Å in **4a**.

The ^{13}C-{^{1}H}-NMR spectra of **4a** and **4b** recorded at room temperature show, as with **2**, only one signal in the terminal carbonyl region. Accordingly, the singlet resonance must signify that the molecules are fluxional, since in a non-fluxional situation two equal-intensity resonances would be expected, one corresponding to the pseudo-axial and the other to the pseudo-equatorial carbonyls. Possible mechanisms for this fluxional process have been discussed elsewhere for [Co$_2$(C$_2$(CO$_2$-Me)$_2$){µ-(Me$_2$As)O}(CO)$_4$] [3a] and [Co$_2$(C$_2$(CO$_2$-Me)$_2$)(µ-P$_2$Ph$_4$)(CO)$_4$] [9].

By comparison with the spectroscopic data of other *mono*-arsine substituted alkyne-bridged dicobalt complexes [3a], **5** may be formulated as [Co$_2$(µ-C$_2$(CO$_2$-Me)$_2$)(CO)$_5$(AsPh$_3$)]. In the ^{1}H-NMR spectrum of **5** phenyl resonances which integrate to 15H and a peak at δ 3.60 ppm are observed. This latter signal corresponds to six protons and is assigned to the CO$_2$*Me* groups.

The ^{13}C-NMR spectrum also shows a number of lines attributable to phenyl carbons of the AsPh$_3$ ligand. There are further sharp signals at δ 173.0 ppm, δ 74.0 ppm and δ 53.2 ppm, assigned to the CO$_2$Me, C–CO$_2$Me and CO$_2$*Me* groups. In the carbonyl region, two resonances are noted at δ 202.2 ppm and δ 198.0 ppm, consistent with substitution of the axial carbonyl at one cobalt atom. Fluxional processes in such systems have been discussed previously [3a].

2.3. Thermolytic reactions

Heating **3a** in toluene at 70 °C for 15 h gave green [Co$_3$(µ$_3$-S){µ-(Ph$_2$As)$_2$O}{µ-(Ph$_2$AsS)}(CO)$_7$] (**6**) in low yield (Scheme 3). Complex **6** has been characterised by IR, ^{1}H- and ^{13}C-NMR spectroscopy, mass spectrometry and microanalysis (see Table 1).

The ^{1}H- and ^{13}C-NMR spectra of **6** exhibit phenyl resonances only. Six resonances attributable to the *ipso*-carbons of the phenyls are clearly visible, indicating that each of the six-phenyl groups in this molecule resides in a chemically distinct environment as expected from the proposed structures.

Reaction of [Co$_3$(µ$_3$-CMe){µ-(Me$_2$As)$_2$O}(CO)$_7$] with H$_2$S in toluene at 70 °C generates [Co$_3$(µ$_3$-S){µ-

Table 2
Selected bond lengths (Å) and angles (°) for **2**, **4a** and **4b**

	2	**4a**	**4b**	
			Molecule 1	Molecule 2
Bond lengths				
Co(1)–Co(2)	2.495(1)	2.498(2)	2.476(2)	2.461(2)
C(1)–C(2)	1.354(7)	1.363(9)	1.34(1)	1.36(1)
Co(1)–C(1)	1.940(5)	1.937(6)	1.98(1)	2.02(1)
Co(1)–C(2)	1.942(5)	1.951(7)	1.96(1)	1.95(1)
Co(2)–C(1)	1.944(5)	1.928(6)	1.96(1)	1.99(1)
Co(2)–C(2)	1.928(5)	1.932(6)	1.96(1)	1.94(1)
Co(1)–As(1)	2.326(1)	2.343(1)	2.327(2)	2.327(2)
Co(2)–As(2)	2.327(1)	2.333(1)	2.350(2)	2.348(2)
As(1)–S(1)	2.227(2)	2.245(2)	2.227(3)	2.240(3)
As(2)–S(1)	2.231(2)	2.258(2)	2.239(3)	2.239(3)
As–C	1.946(5)–1.954(6)	1.946(4)–1.961(3)	1.965(6)–1.981(5)	1.929(6)–1.948(5)
Co–$C_{carbonyl}$	1.775(6)–1.795(7)	1.802(9)–1.813(9)	1.76(1)–1.83(1)	1.76(1)–1.79(1)
C–O	1.135(7)–1.148(6)	1.133(8)–1.150(9)	1.13(1)–1.15(1)	1.14(1)–1.16(1)
Bond angles				
C(1)–C(2)–Co(2)	70.2(3)	69.1(4)	69.9(6)	71.8(6)
C(1)–C(2)–Co(1)	69.5(3)	68.9(4)	70.8(6)	72.8(6)
C(2)–C(1)–Co(1)	69.7(3)	70.0(4)	69.3(6)	67.2(6)
C(2)–C(1)–Co(2)	68.9(3)	69.5(4)	70.0(6)	67.8(6)
Co(1)–C(2)–Co(2)	80.3(2)	80.1(3)	78.4(4)	78.7(4)
Co(1)–C(1)–Co(2)	79.9(2)	80.5(3)	77.9(4)	75.8(4)
C(1)–Co(1)–Co(2)	50.1(1)	49.6(2)	50.7(3)	51.6(3)
C(2)–Co(1)–Co(2)	49.6(2)	49.6(2)	50.8(3)	50.5(3)
C(1)–Co(2)–Co(1)	50.0(2)	49.9(2)	51.4(3)	52.6(3)
C(2)–Co(2)–Co(1)	50.1(2)	50.3(2)	50.8(3)	50.8(3)
C(2)–Co(2)–C(1)	40.9(2)	41.4(3)	40.1(4)	40.4(4)
C(1)–Co(1)–C(2)	40.8(2)	41.1(3)	39.9(4)	40.0(4)
As(1)–Co(1)–Co(2)	101.74(4)	99.69(6)	101.95(7)	103.22(7)
As(2)–Co(2)–Co(1)	101.38(4)	101.79(5)	100.87(7)	100.68(7)
Co(1)–As(1)–S(1)	114.78(6)	113.44(7)	118.3(1)	117.02(9)
Co(2)–As(2)–S(1)	114.61(5)	113.67(6)	117.5(1)	117.90(9)
As(1)–S(1)–As(2)	100.49(7)	97.02(8)	100.0(1)	100.5(1)
C(5)–Co(1)–Co(2)	147.9(2)	147.2(2)	149.2(4)	150.4(4)
C(4)–Co(2)–Co(1)	146.0(2)	147.2(2)	146.7(4)	149.0(4)
Co–As–C_{phenyl}	–	–	116.3(3)–121.3(3)	117.0(2)–122.0(3)
C(2)–C(1)–C(11)	139.3(5)	131.7(6)	139.2(9)	139.0(1)
C(1)–C(2)–C(21)	140.2(5)	134.4(6)	142.0(1)	141.0(1)

$(Me_2As)_2S\}\{\mu\text{-}(Me_2AsS)\}(CO)_5]$ (**7**) and $[Co_3(\mu_3\text{-}S)\{\mu\text{-}(Me_2As)_2O\}\{\mu\text{-}(Me_2AsS)\}(CO)_5]$ (**8**) in moderate yields, respectively (Scheme 3). Both products have been characterised by IR, ^{1}H- and ^{13}C-NMR spectroscopy, mass spectrometry and microanalysis (see Table 1). Additionally, complex **8** has been the subject of a single crystal X-ray diffraction study.

The molecular structure of **8** is shown in Fig. 4; selected bond lengths and angles are presented in Table 3. The complex features a tetrahedral Co_3S core with one edge bridged by an Me_2As–S ligand, which acts as a three-electron donor, and with a second edge bridged by an $(Me_2As)_2O$ unit. Both ligands occupy pseudo-equatorial sites at cobalt. The geometry of the core deviates from that of a regular tetrahedron since, although the tricobalt triangle is approximately isosceles, the three cobalt–apical sulfur distances are all different. The

capping sulfur is displaced toward Co(2) and away from Co(1), giving Co(2)–S(1) and Co(1)–S(1) distances of 2.164(7) Å and 2.191(7) Å, respectively.

In the structurally characterised $(Me_2As)_2O$-bridged alkyne and alkylidyne complexes $[Co_2\{\mu\text{-}C_2(CO_2\text{-}Me)_2\}\{\mu\text{-}(Me_2As)_2O\}(CO)_4]$ and $[Co_3(\mu_3\text{-}CCl)\{\mu\text{-}(Me_2As)_2O\}(CO)_7]$ [3a], the two bridged metal atoms are electronically equivalent. In **8**, this is not the case; Co(3), surrounded by good σ-donors but with only one carbonyl ligand is more electron rich than Co(2). Increased back-donation to As(2) from Co(3) may explain why the Co(3)–As(2) bond [2.264(4) Å] is shorter than the Co(2)–As(1) bond [2.304(4) Å].

Five singlets attributable to methyl groups appear in the ^{1}H-NMR spectra of both **7** and **8**. Four of these signals have an intensity corresponding to three protons but the remaining signal has twice this intensity. In the
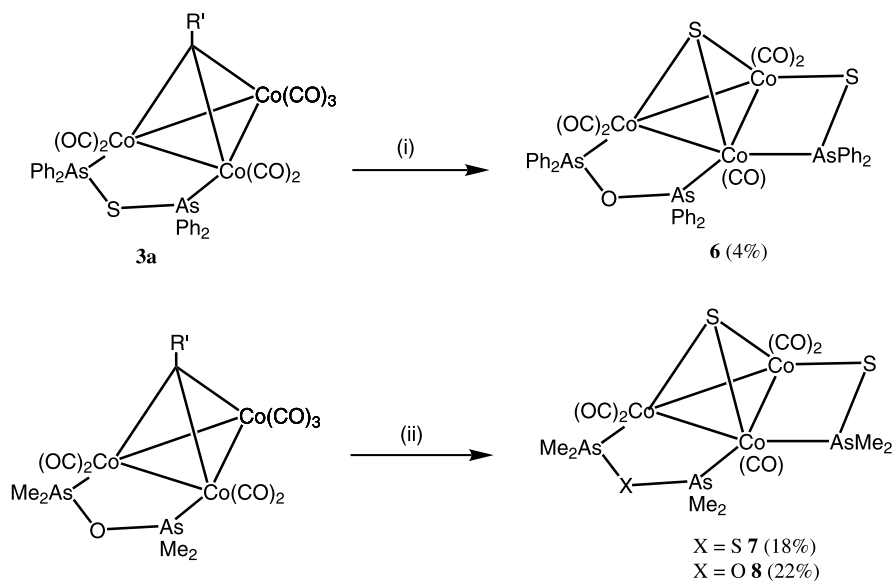
Scheme 3. Reagents and conditions: (i) 70 °C, $C_6H_5CH_3$; (ii) H_2S, 70 °C, $C_6H_5CH_3$.

^{13}C-NMR spectra of the two complexes, six methyl group signals of approximately equal intensity are observed in each case. No further resonances are discernible.

From Fig. 4, which displays the molecular structure of **8**, it can be seen that the six methyl groups occupy six chemically distinct environments. Assuming that the solid-state structure is maintained in solution, six methyl
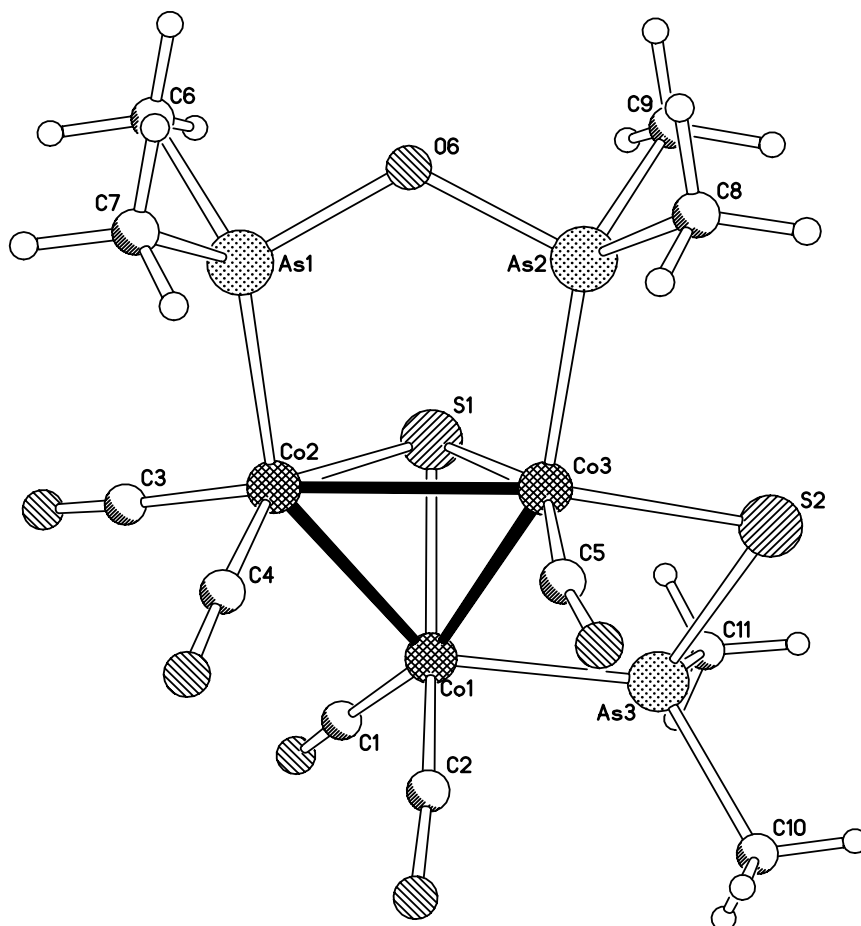

Fig. 4. Molecular structure of [$Co_3(\mu_3$-S){μ-$(Me_2As)_2O$}{μ-(Me_2AsS)}$(CO)_5$] (**8**) including the atom numbering scheme.

Table 3
Selected bond lengths (Å) and angles (°) for **8**

Bond lengths	
Co(1)–Co(2)	2.535(4)
Co(2)–Co(3)	2.527(4)
Co(3)–As(2)	2.264(4)
Co(1)–S(1)	2.191(7)
Co(3)–S(1)	2.157(7)
As(3)–S(2)	2.203(7)
As(2)–O(6)	1.79(2)
As–C$_{methyl}$	1.91(2)–1.98(2)
Co(1)–Co(3)	2.482(4)
Co(2)–As(1)	2.304(4)
Co(1)–As(3)	2.295(4)
Co(2)–S(1)	2.164(7)
Co(3)–S(2)	2.334(7)
As(1)–O(6)	1.77(2)
Co–C$_{carbonyl}$	1.71(3)–1.80(3)
C–O	1.13(3)–1.19(4)

Bond angles	
Co(3)–Co(1)–Co(2)	60.5(1)
As(3)–Co(1)–Co(3)	78.5(1)
S(1)–Co(1)–As(3)	94.4(2)
S(1)–Co(2)–Co(1)	54.9(2)
S(1)–Co(2)–Co(3)	54.1(2)
S(2)–Co(3)–Co(1)	94.2(2)
As(2)–Co(3)–Co(2)	100.1(2)
S(1)–Co(3)–S(2)	100.7(3)
O(6)–As(2)–Co(3)	110.5(6)
Co(2)–S(1)–Co(1)	71.2(2)
Co(3)–S(1)–Co(2)	71.6(2)
As(1)–O(6)–As(2)	120.0(1)
S(1)–Co(1)–Co(2)	53.9(2)
S(1)–Co(1)–Co(3)	54.5(2)
Co(3)–Co(2)–Co(1)	58.7(1)
As(1)–Co(2)–Co(3)	93.7(1)
S(1)–Co(3)–Co(1)	55.8(2)
Co(1)–Co(3)–Co(2)	60.8(1)
S(1)–Co(3)–Co(2)	54.3(2)
O(6)–As(1)–Co(2)	114.4(6)
S(2)–As(3)–Co(1)	103.4(2)
Co(3)–S(1)–Co(1)	69.6(2)
As(3)–S(2)–Co(3)	83.6(2)

Scheme 4. Proposed reversible bridge opening/closing on addition/elimination of H$_2$X [X = O, S].

In effect, addition of H$_2$S reverses the condensation process to generate one R$_2$AsOH ligand and a neighbouring R$_2$AsSH ligand. Condensation can then reoccur to eliminate H$_2$S, regenerating the starting material, or to eliminate H$_2$O, yielding the (R$_2$As)$_2$S derivative. Whilst the H$_2$S purge continues, solutions of the (R$_2$As)$_2$O complexes can be converted quantitatively to the sulfide derivative but, once purging ceases the process begins to reverse either partially or, in some cases, completely.

While it is clear that the bis-diarsine sulfide complexes do form, they fairly readily reconvert to the bis-diarsine oxide derivatives at room temperature. On carrying out the reaction with H$_2$S at higher temperature, however, the initially generated (R$_2$As)$_2$S complex undergoes cleavage of one As–S bond giving new sulfur-containing species. Formation of these species is not reversible even when the H$_2$S purge ceases.

Thermolysis of the complex, [Co$_3$(μ_3-CMe){μ-(Me$_2$As)$_2$O}(CO)$_7$] in the presence of H$_2$S presumably produces initially the arsine–sulfide analogue **1b** via the mechanism which has already been discussed for the dinuclear complexes **1a** and **1b** (Scheme 4). The pathway by which this complex is subsequently converted into [Co$_3$(μ_3-S){μ-(Me$_2$As)$_2$O}{μ-Me$_2$AsS}(CO)$_5$] must involve arsenic–sulfur bond rupture and the excision of an AsMe$_2$ group but the precise mechanism is unclear.

As described in Section 2.2, the direct reaction of (Ph$_2$As)$_2$S with the alkylidyne-tricobalt and alkyne-dicobalt complexes yields the expected complexes **3** and **4** with bridging (Ph$_2$As)$_2$S ligands. More noteworthy is the simultaneous formation of the *mono*-Ph$_3$As-substituted complex **5**. We have also observed this type of side-product in the reaction of other alkyne-

signals would be expected in both the carbon and proton NMR spectra. These are observed in the ^{13}C-NMR spectrum but in the ^{1}H spectrum, two of the signals are presumably coincident. Since it is proposed that **6** shares the same structure as complex **8**, similar arguments apply to an analysis of its NMR spectra.

2.4. Reaction pathway

The proposed pathway for the reaction of the bound (R$_2$As)$_2$O ligand with H$_2$S to generate a coordinated (R$_2$As)$_2$S molecule is based on the hydrolytic mechanism previously proposed for the formation of bridged (R$_2$As)$_2$O complexes from As$_2$R$_4$ bridged complexes (Scheme 4) [3a].

bridged dicobalt complexes with $(Ph_2As)_2S$ although not with $[Co_2(\mu\text{-}PhCCPh)(CO)_6]$ [11]. Thermal modification of the free $(Ph_2As)_2S$ ligand to give free $AsPh_3$ is not known and it is possible that this is a metal-mediated process, requiring coordination of $(Ph_2As)_2S$ in a monodentate mode followed by As–S bond cleavage and simultaneous As–C bond formation for the dicobalt complexes (Scheme 5). The R–As=S species liberated belongs to the known group of thioarsenoso compounds, which usually exist as oligomers $(R\text{-}As\text{-}S)_n$ in solution [12].

Thermolysis of the $(Ph_2As)_2S$-bridged alkylidyne tricobalt complex **3a** yields $[Co_3(\mu_3\text{-}S)(CO)_5\{\mu\text{-}(Ph_2As)_2O\}\{\mu\text{-}(Ph_2AsS)\}]$ (**6**). This is not unexpected on the basis of the reaction that generates **7** and **8** and the synthetic pathway is, presumably, essentially the same. It is notable, however, that in the present case, where thermolysis does not take place in the presence of H_2S, only the product with an $(Ph_2As)_2O$ bridge is formed; there is no trace of the corresponding $(Ph_2As)_2S$-bridged complex. It may be that this does not form during the reaction or that it does form but is desulfurised under the conditions employed. The implication is that the $(Me_2As)_2S$-bridged product, **7**, is obtained only because
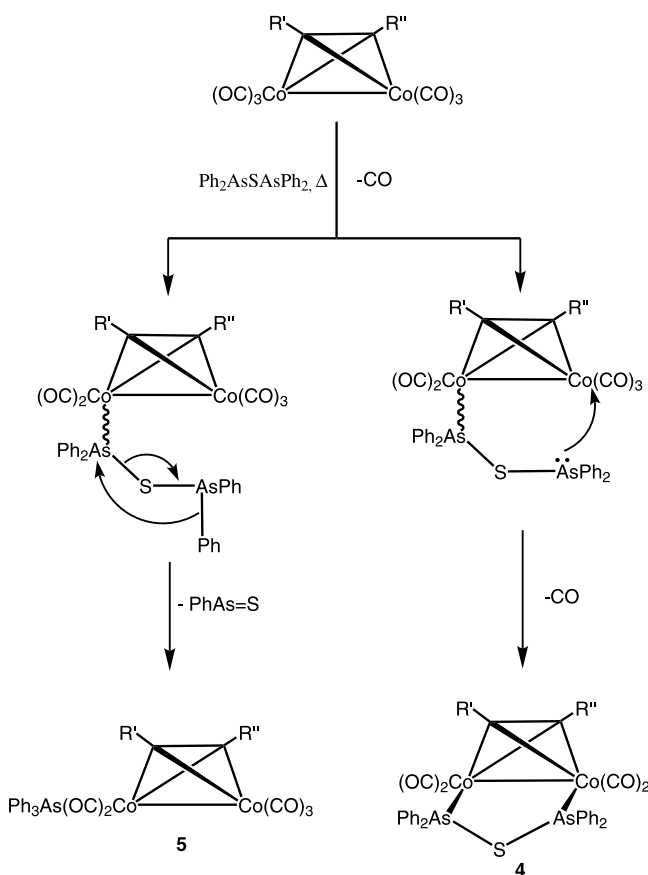
the $(Me_2As)_2O$-bridged product **8** goes on to react with H_2S.

2.5. Conclusions

The observation that reversible substitution of S for O takes place in complexes with bridging As–O–As ligands supports the mechanism previously published for formation of As–O–As complexes from diarsines via complexes with AsR_2OH ligands [3a]. As expected, direct reaction of bis-diphenylarsine sulfides with di- and tri-cobalt complexes gives As–S–As bridged complexes in good yields without formation of complexes with pendant ligands. Metal-mediated As–S bond rupture in such complexes may explain the formation of R_3As-substituted derivatives. Thermally induced As–S bond rupture in As–S–As bridged tricobalt complexes can lead to complexes that contain an AsR_2–S unit.

3. Experimental

3.1. General techniques

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen, using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use [13]. Preparative thin-layer chromatography was carried out on 1 mm plates prepared at the Department of Chemistry, Cambridge. Column chromatography was performed on Kieselgel 60 (70–230 mesh). Products are given in order of decreasing R_f values. 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 spectrometer using the solvent resonance as an internal standard. Microanalyses were performed by the Microanalytical Department, University of Cambridge.

Unless otherwise stated, all reagents were obtained from commercial suppliers and used without further purification. The compounds $[Co_2(\mu\text{-}R'CCR'')(CO)_6]$ $(R' = R'' = CO_2Me,\ Ph)$ [14], $[Co_3(\mu_3\text{-}CR')(CO)_9]$ $(R' = Me\ or\ Cl)$ [15], were prepared by literature methods. Complexes $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(Me_2As)_2O\}(CO)_4]$ and $[Co_3(\mu_3\text{-}CR')\{\mu\text{-}(Me_2As)_2O\}(CO)_7]$ $[R' = Cl,\ Me]$ were synthesised by the procedures described previously [3a]. The oxide, $(Ph_2As)_2O$ [16], was synthesised by reaction of PhMgBr and As_2O_3.

Scheme 5. Possible pathway for the direct reaction of $[Co_2(\mu\text{-}R'CCR'')(CO)_6]$ with $(Ph_2As)_2S$.

Treatment of this oxide with H_2S generated $(Ph_2As)_2S$ [8].

3.2. Reaction of $[Co_3(\mu\text{-}CR')\{\mu\text{-}(Me_2As)_2O\}(CO)_7]$ and H_2S

i) R' = Cl. $[Co_3(\mu\text{-}CCl)\{\mu\text{-}(Me_2As)_2O\}(CO)_7]$ (386 mg, 0.60 mmol) was dissolved in benzene (70 ml) and purged with H_2S at room temperature for 10 min. After removal of all volatiles under reduced pressure, 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 bluish-black $[Co_3(\mu\text{-}CCl)\{\mu\text{-}(Me_2As)_2S\}(CO)_7]$ (**1a**) (179 mg, 45%) and deep purple, crystalline $[Co_3(\mu\text{-}CCl)\{\mu\text{-}(Me_2As)_2O\}(CO)_7]$ (185 mg, 48%).

ii) R' = Me. $[Co_3(\mu\text{-}CMe)\{\mu\text{-}(Me_2As)_2O\}(CO)_7]$ (307 mg, 0.49 mmol) was dissolved in benzene (70 ml) and purged with H_2S at room temperature for 10 min. By employing a similar work-up as in (i), bluish-black $[Co_3(\mu\text{-}CMe)\{\mu\text{-}(Me_2As)_2S\}(CO)_7]$ (**1b**) (148 mg, 47%) and deep purple, crystalline $[Co_3(\mu\text{-}CMe)\{\mu\text{-}(Me_2As)_2O\}(CO)_7]$ (150 mg, 49%) were isolated.

3.3. Reaction of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(Me_2As)_2O\}(CO)_4]$ and H_2S

$[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(Me_2As)_2O\}(CO)_4]$ (368 mg, 0.60 mmol) was dissolved in toluene (70 ml) and purged with H_2S at room temperature for 10 min. After removal of the volatiles under reduced pressure, 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 (4:1) gave red $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(Me_2As)_2S\}(CO)_4]$ (**2**) (212 mg, 56%) and red, crystalline $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(Me_2As)_2O\}(CO)_4]$ (140 mg, 38%). Crystals of **2** suitable for X-ray diffraction were grown by slow evaporation at 0 °C of a hexane/CH_2Cl_2 solution of the complex.

3.4. Reaction of $[Co_3(\mu_3\text{-}CR')(CO)_9]$ and $(Ph_2As)_2S$

i) R' = Cl. $[Co_3(\mu_3\text{-}CCl)(CO)_9]$ (571 mg, 1.20 mmol) and $(Ph_2As)_2S$ (1.76 g, 3.6 mmol) were dissolved in toluene (60 ml) and heated at 35 °C with stirring for 20 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 purple $[Co_3(\mu_3\text{-}CCl)\{\mu\text{-}(Ph_2As)_2S\}(CO)_7]$ (**3a**) (590 mg, 54%). Two other brown products followed in very minor yield; these were not collected.

ii) R' = Me. $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ (488 mg, 1.07 mmol) and $(Ph_2As)_2S$ (1.57 g, 3.2 mmol) were dissolved in toluene (60 ml) and heated at 35 °C with stirring for 24 h. By employing a similar work-up to (i), but using hexane/CH_2Cl_2 (9:1) as eluent, gave $[Co_3(\mu_3\text{-}CMe)\{\mu\text{-}(Ph_2As)_2S\}(CO)_7]$ (**3b**) (619 mg, 65%).

3.5. Reaction of $[Co_2(\mu\text{-}R'CCR'')(CO)_6]$ and $(Ph_2As)_2S$

i) R' = R'' = CO_2Me. $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ (238 mg, 0.56 mmol) and $(Ph_2As)_2S$ (0.97 g, 1.98 mmol) were dissolved in toluene (60 ml) 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 adsorbed onto silica. The silica was pumped dry and transferred to the top of a silica chromatography column. Elution with hexane/ethyl acetate (4:1) gave unreacted $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$, $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5(AsPh_3)]$ (**5**) (170 mg, 43%) and $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\{\mu\text{-}(Ph_2As)_2S\}(CO)_4]$ (**4a**) (148 mg, 31%). Crystals of **4a** suitable for X-ray diffraction were grown by slow evaporation at 0 °C of a hexane/CH_2Cl_2 solution of the complex.

ii) R' = R'' = Ph. $[Co_2(\mu\text{-}PhCCPh)(CO)_6]$ (264 mg, 0.57 mmol) and $(Ph_2As)_2S$ (840 mg, 1.7 mmol) were dissolved in toluene (60 ml) and heated at 35 °C with stirring for 24 h. By employing a similar work-up to (i), but using hexane/CH_2Cl_2 (4:1) as eluent, gave $[Co_2(\mu\text{-}PhCCPh)\{\mu\text{-}(Ph_2As)_2S\}(CO)_4]$ (**4b**) (444 mg, 87%). Crystals of **4b** suitable for X-ray diffraction were grown by slow evaporation at 0 °C of a hexane/CH_2Cl_2 solution of the complex.

3.6. Thermolysis of $[Co_3(\mu_3\text{-}CCl)\{\mu\text{-}(Ph_2As)_2S\}(CO)_7]$ (**3a**)

Complex **3a** (2.00 g, 2.20 mmol) was dissolved in toluene (50 ml) and heated with stirring at 70 °C for 15 h. After removal of all volatiles under reduced pressure, 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 unreacted $[Co_3(\mu_3\text{-}CCl)\{\mu\text{-}(Ph_2As)_2S\}(CO)_7]$ and green $[Co_3(\mu_3\text{-}S)\{\mu\text{-}(Ph_2As)_2O\}\{\mu\text{-}(Ph_2AsS)\}(CO)_5]$ (**6**) (100 mg, 4%).

3.7. Reaction of $[Co_3(\mu\text{-}CMe)\{\mu\text{-}(AsMe_2)_2O\}(CO)_7]$ and H_2S at 70 °C

Complex $[Co_3(\mu\text{-}CMe)\{\mu\text{-}(Me_2As)_2O\}(CO)_7]$ (326 mg, 0.52 mmol) was dissolved in toluene (70 ml). The solution was heated to 70 °C and purged with H_2S for 45 min. After removal of all volatiles under reduced

Table 4
X-ray crystallographic and data processing parameters for complexes **2**, **4a**, **4b** and **8**

Complex	**2**	**4a**	**4b**	**8**
Empirical formula	$C_{14}H_{18}As_2Co_2O_8S$	$C_{11}H_{18}As_3Co_3O_6S_2$	$C_{42}H_{30}As_2Co_2O_4S$	$C_{34}H_{26}As_2Co_2O_8S$
Formula weight	614.04	711.92	898.42	862.31
Temperature (K)	293(2)	293(2)	293(2)	295(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions				
a (Å)	9.445(2)	12.757(2)	12.178(4)	11.442(3)
b (Å)	14.476(3)	10.024(3)	18.256(4)	12.726(3)
c (Å)	16.947(4)	18.918(4)	20.038(4)	13.234(3)
α (°)	–	–	115.261(11)	78.16(2)
β (°)	98.84(2)	100.06(2)	103.961(17)	72.22(2)
γ (°)	–	–	93.46(2)	73.76(2)
V (Å^3)	2289.5(9)	2382(1)	3842(2)	1746.6(7)
Z	4	4	4	2
μ (Mo–K$_\alpha$) (mm^{-1})	4.442	6.396	2.668	2.938
Crystal size (mm^3)	$0.48 \times 0.34 \times 0.27$	$0.30 \times 0.15 \times 0.10$	$0.48 \times 0.48 \times 0.44$	$0.40 \times 0.32 \times 0.12$
Reflections collected	8580	3499	12438	7153
Independent reflections	4038 [$R_{int} = 0.0517$]	3328 [$R_{int} = 0.06$]	10658 [$R_{int} = 0.0559$]	6141 [$R_{int} = 0.0405$]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0435$, $wR_2 = 0.0695$	$R_1 = 0.0795$, $wR_2 = 0.1833$	$R_1 = 0.0641$, $wR_2 = 0.1120$	$R_1 = 0.0570$, $wR_2 = 0.1123$
R indices (all data)	$R_1 = 0.0950$, $wR_2 = 0.0810$	$R_1 = 0.2040$, $wR_2 = 0.3112$	$R_1 = 0.1711$, $wR_2 = 0.1406$	$R_1 = 0.1183$, $wR_2 = 0.1352$

pressure, 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 brown [Co$_3$(μ_3-S){μ-(Me$_2$As)$_2$S}{μ-(Me$_2$AsS)}(CO)$_5$] (**7**) (68 mg, 18%) and purple [Co$_3$(μ_3-S){μ-(Me$_2$As)$_2$O}{μ-(Me$_2$AsS)}(CO)$_5$] (**8**) (81 mg, 22%). Crystals of **8** were grown by evaporation at 0 °C of a hexane/CH_2Cl_2 solution of the complex.

3.8. Crystal structure determinations of complexes 2, 4a, 4b and 8

For **2**, **4a** and **4b** X-ray intensity data were collected on a Siemens P4 four-circle diffractometer and for **8** on a Rigaku AFC5R four-circle diffractometer. Table 4 lists details of data collection, refinement and crystal data. The crystals of **8** diffracted very weakly, possibly due to solvent loss. Data were corrected for Lorentz and polarisation factors.

For all structures, the positions of the metal atoms and most of the non-hydrogen atoms were located by direct methods [17] and subsequent difference-Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Refinement [17] was based on F^2. Phenyl rings were refined with idealised geometries. The phenyl and methyl hydrogen atoms were placed in calculated positions with displacement parameters equal to, respectively, 1.2 and 1.5 times U_{eq} of the parent carbon atoms. There were two independent molecules per equivalent position in the crystal structure of **4b**. Absorption corrections were applied to the data of **8**, **4a** and **4b** using ψ-scans [18] and after initial refinement

with isotropic displacement parameters, empirical absorption corrections were applied to the data of **2** [19]. Anisotropic displacement parameters were assigned in structures **2**, **4a** and **4b** to all non-hydrogen atoms and in **8** to the cobalt, arsenic and sulfur atoms only.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 157608–157611 for compounds **2**, **4a**, **4b** and **8**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac. uk or www: http://www.ccdc.cam.ac.uk).

References

[1] (a) F.A. Cotton, C.R. Falvello, M. Tomas, G.M. Gray, C.S. Kraihanzel, Inorg. Chim. Acta 82 (1984) 129;
(b) H. Einspahr, J. Donohue, Inorg. Chem. 13 (1974) 1839;

(c) S. Hoehne, E. Lindner, J.-P. Gumz, Chem. Ber. 111 (1978) 3818.

[2] (a) E.H. Wong, L. Prasad, E.J. Gabe, F.C. Bradley, J. Organomet. Chem. 236 (1982) 321;
(b) E.H. Wong, F.C. Bradley, L. Prasad, E.J. Gabe, J. Organomet. Chem. 263 (1984) 167;
(c) C. Zeiher, J. Mohyla, I.-P. Lorenz, W. Hiller, J. Organomet. Chem. 286 (1985) 159;
(d) R.E. Marsh, Acta Crystallogr. Sect. B 53 (1997) 317;
(e) F.C. Bradley, E.H. Wong, E.J. Gabe, F.L. Lee, Y. Lepage, Polyhedron 6 (1987) 1103;
(f) D.J. Irvine, D.J. Cole-Hamilton, J. Barnes, P.K.G. Hodgson, Polyhedron 8 (1989) 1575;
(g) D.J. Irvine, C. Glidewell, D.J. Cole-Hamilton, J.C. Barnes, A. Howie, J. Chem. Soc. Dalton Trans. (1991) 1765;
(h) G.A. Acum, M.J. Mays, P.R. Raithby, H.R. Powell, G.A. Solan, J. Chem. Soc. Dalton Trans. (1997) 3427;
(i) E. Lindner, S. Hoehne, J.-P. Gumz, Z. Naturforsch. B 35 (1980) 937;
(j) U. Florke, H.-J. Haupt, Z. Kristallogr. 192 (1990) 293;
(k) A.D. Burrows, M.F. Mahon, M.T. Palmer, M. Varrone, Inorg. Chem. 41 (2002) 1695.

[3] (a) N. Choi, G. Conole, J.D. King, M.J. Mays, M. McPartlin, C.L. Stone, J. Chem. Soc. Dalton Trans. (2000) 395;
(b) E.W. Abel, M.A. Beckett, Polyhedron 6 (1987) 1255;
(c) H. Beurich, H. Vahrenkamp, Chem. Ber. 114 (1981) 2542;
(d) H. Vahrenkamp, Chem. Ber. 105 (1972) 3574.

[4] (a) L.H. Doerrer, J.C. Green, M.L.H. Green, I. Haiduc, C.N. Jardine, S.I. Pascu, L. Silaghi-Dumitrescu, D.J. Watkin, J. Chem. Soc. Dalton Trans. (2000) 3347;
(b) H. Vahrenkamp, Chem. Ber. 105 (1972) 3574;
(c) E.W. Ainscough, A.M. Brodie, G. Leng-Ward, J. Chem. Soc. Dalton Trans. (1974) 2437;
(d) L. Weber, D. Wewers, Organometallics 4 (1985) 841.

[5] E.W. Abel, M.A. Beckett, P.A. Bates, M.B. Hursthouse, J. Organomet. Chem. 325 (1987) 261.

[6] R.A. Zingaro, K.J. Irgolic, D.H. O'Brien, L.J. Edmunson, Jr., J. Am. Chem. Soc. 93 (1971) 5677.

[7] (a) K. Sommer, Z. Anorg. Allg. Chem. 377 (1970) 120;
(b) K. Sommer, Z. Anorg. Allg. Chem. 383 (1971) 136.

[8] A. Michaelis, Liebigs Ann. Chem. 321 (1902) 141.

[9] A.J.M. Caffyn, M.J. Mays, G.A. Solan, D. Braga, P. Sabatino, G. Conole, M. McPartlin, H.R. Powell, J. Chem. Soc. Dalton Trans. (1991) 3103.

[10] D. Gregson, J.A.K. Howard, Acta Crystallogr. Sect. C 39 (1983) 1024.

[11] J.D. King, M.J. Mays, G.A. Solan, unpublished results.

[12] (a) R.A. Zingaro, R.E. McGlothin, R.M. Hedges, Trans. Faraday Soc. 59 (1963) 798;
(b) L. Anschütz, H. Wirth, Chem. Ber. 89 (1956) 1530;
(c) A.-J. Di Maio, A.L. Rheingold, Inorg. Chem. 29 (1990) 798.

[13] W.L.F. Armarego, D.D. Perrin, Purification of Laboratory Chemicals, 4th ed., Butterworth–Heinemann, London, 1996.

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

[15] (a) D. Seyferth, J.E. Hallgren, P.L.K. Hung, J. Organomet. Chem. 50 (1973) 265;
(b) J.J. Eisch, R.B. King (Eds.), Organometallic Syntheses, Vol. 1, Academic Press, London, 1965.

[16] (a) F. Sachs, H. Kantoriwicz, Chem. Ber. 41 (1908) 2767;
(b) F.F. Blicke, F.D. Smith, J. Am. Chem. Soc. 51 (1929) 1558.

[17] SHELXTL, PC version 5.03, Siemens Analytical Instruments, Inc., Madison, WI, 1994.

[18] A.C.T. North, D.C. Philips, F.S. Matthews, Acta Crystallogr. Sect. A 24 (1968) 351.

[19] N. Walker, D. Stuart, Acta Crystallogr. Sect. A 39 (1983) 158.