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X-Ray Structures of $[Cr_2(CO)_6(AsMe)_9]$ and $[Mo_2(CO)_6(AsPr^n)_8]$: the Stabilisation of an As_9 Ring and an As_8 Chain by Co-ordination

By PATRICIA S. ELMES, BRYAN M. GATEHOUSE, DOUGLAS J. LLOYD, and BRUCE O. WEST*
(*Department of Chemistry, Monash University, Wellington Road, Clayton, Victoria, Australia* 3168)

Summary The compound $[Cr_2(CO)_6(AsMe)_9]$ contains a nine-membered As ring co-ordinated to each Cr atom through three As atoms while $[Mo_2(CO)_6(AsPr^n)_8]$ contains a chain of eight As atoms with terminal As atoms bridging both metal atoms and one other arsenic atom in the chain also co-ordinated to each metal, together with an Mo–Mo bond.

CYCLIC phosphines and arsines are known in the free state having rings containing 4, 5, or 6 members.[1] Their reactions with metal carbonyls can lead to complexes in which the cyclic compound has remained intact and co-ordinates through one[1] or more Group V atoms, *e.g.* $[Mo(CO)_4(PEt)_5]$.[2] In other cases the rings fragment and the resulting short chains of AsR or PR groups can bond either to a single metal atom as in $[Fe(CO)_4(AsC_6F_5)_2]$ (As_2 chain)[3] or two as in $[Fe_2(CO)_6(AsMe)_4]$(As_4 chain).[4]

TABLE

Mean intramolecular bond distances (Å)

	$[Cr_2(CO)_6(AsMe)_9]$	$[Mo_2(CO)_6(AsPr^n)_8]$
M–M		3·105(5)
M–As (arsine)	2·44(1)	2·623(6)
(bridging)		2·554(5)
As–As	2·445(8)	2·434(7)
As–C	1·98(4)	2·00(5)
M–C	1·77(4)	1·92(4)
C–O	1·19(7)	1·18(5)

Prior studies have not disclosed the existence of rings greater than $P(As)_6$ although long chains of AsR units have been postulated to exist in certain arseno-compounds.[5,6] Also a polymeric solid form of $(AsMe)_n$ has been shown to have a 'ladder-like' structure.[7]

It has now been established by single-crystal *X*-ray methods that a 9-membered cyclic arsine exists in the complex $[Cr_2(CO)_6(AsMe)_9]$† and a chain of 8 AsMe units in $[Mo_2(CO)_6(AsPr^n)_8]$. These compounds are representative of complexes formed in thermal reactions between Group VI metal carbonyls and cyclic arsines. The arsine compounds have presumably formed by fragmentation and condensation of the original cyclic arsine and are stabilised by co-ordination.

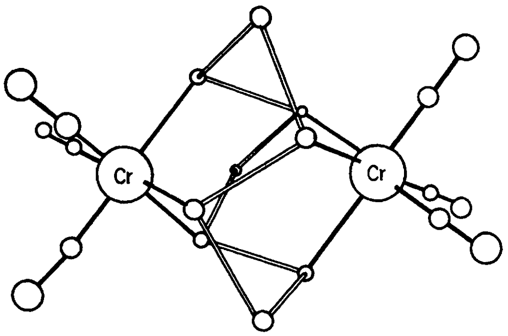

FIGURE 1. Structure of $[Cr_2(CO)_6(AsMe)_9]$; methyl groups are omitted.

Crystal data: $C_{15}H_{27}As_9Cr_2O_6$, monoclinic, $a = 17{\cdot}92$, $b = 10{\cdot}40$, $c = 17{\cdot}00$ Å, $\beta = 90{\cdot}3°$, $Z = 4$, $D_c = 2{\cdot}27$ g cm^{-3}, space group $P2_1/c$. Diffractometer intensity data were collected using Cu-K_α radiation. The data have refined to $R = 0{\cdot}063$ on the basis of 955 reflections with $F_o^2 > 2\sigma(F_o^2)$.

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† Previously this compound and the related Mo and W derivatives had been assigned the formula $[M_2(CO)_4(AsMe)_5]_2$.[8]

$[Cr_2(CO)_6(AsMe)_9]$ (Figure 1) contains a puckered, nine-membered ring of arsenic atoms, six of which are linked to chromium atoms producing a 'pseudo-cubane' structure containing three edge-bridging arsenic atoms. The crystals are disordered as a result of the existence of two conformers in unequal proportions. The conformers differ only in the position of one of the three arsenic atoms not bonded to chromium and in the orientation of its methyl group. The major conformer has two methyl groups *cis* and one *trans* with respect to one of the chromium atoms. The minor conformer with all three methyl groups *cis* with respect to one chromium atom has almost perfect C_{3v} symmetry, the chromium atoms being sited on the three-fold axis. The ligand configuration around the chromium atoms is octahedral. The metal–arsenic bond lengths are equal [2·44(1) Å] and comparable with previously reported values.[9] The arsenic–arsenic distance [2·445(8) Å] is consistent with those previously found in the cyclic arsines $(AsMe)_5$, 2·428(8) Å[10] and $(AsPh)_6$, 2·456(5) Å.[11] Other alkyl cyclic arsines have also been reported[8] to give similar compounds to those derived from $(AsMe)_5$, *i.e.* $[M_2(CO)_6(AsR)_9]$. Compounds of molecular formula $M_2(CO)_6(AsR)_8$ for R = Et, Pr^n, however, were the major reaction products when $[Mo(CO)_6]$ reacted with $(AsEt)_5$ or $(AsPr^n)_5$.

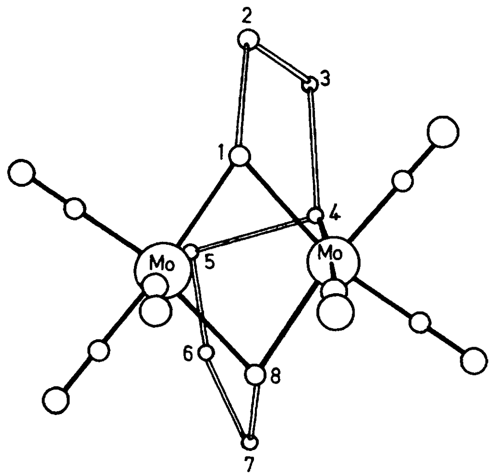

FIGURE 2. Structure of $[Mo_2(CO)_6(AsPr^n)_8]$: n-propyl groups are omitted.

An *X*-ray structural study of $[Mo_2(CO)_6(AsPr^n)_8]$ has confirmed the original molecular formula for the compound and established the existence of an As_8 chain in the molecule.

Crystal data: $C_{30}H_{56}As_8Mo_2O_6$, monoclinic, $a = 21{\cdot}17$, $b = 16{\cdot}97$, $c = 12{\cdot}98$ Å, $\beta = 103{\cdot}2°$, $Z = 4$, $D_c = 1{\cdot}91$ g cm^{-3}, space group $P2_1/n$. Diffractometer data were collected using Mo-K_α radiation. R is 0·063 for 2780 reflections with $F_0^2 > 4\sigma(F_0^2)$.

The structure of the compound (Figure 2) consists of an eight-membered chain of arsenic atoms terminally attached to each molybdenum atom. The EAN rule is satisfied by additional co-ordination from arsenic atoms 4 and 5 to alternate molybdenum atoms and an Mo–Mo interaction [3·105(5) Å] which falls within the established range for Mo–Mo bonds.[12] The molybdenum atoms are thus seven-co-ordinate and lie at the centres of a pair of distorted, edge-shared octahedra. The molybdenum–arsenic bond lengths of 2·554(5) and 2·623(6) Å are similar to those previously reported.[9,13] The molybdenum–carbon bond length is normal;[12] the arsenic–arsenic distance is the same as found in $[Cr_2(CO)_6(AsMe)_9]$. A staggered arrangement of propyl groups occurs along the arsenic chain.

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