A Complex containing Two Side-on (μ_2,η^2-As_2) Ligands. The Synthesis and Structural Characterization of $[(\eta^5\text{-}MeC_5H_4)Mo(CO)]_2(\mu_2,\eta^2\text{-}As_2)_2$

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The thermolytic reaction of cyclo-$(MeAs)_5$ and $[(\eta^5\text{-}MeC_5H_4)Mo(CO)_3]_2$ produces the first structurally characterized example of a $[cpMo(CO)]_2(E_2)_2$ complex (cp = cyclopentadienyl; E = P, As, or ≡CR), $[(\eta^5\text{-}MeC_5H_4)Mo(CO)]_2(\mu_2,\eta^2\text{-}As_2)_2$, which contains extremely short As–As bonds of 2.279(2) and 2.300(2) Å and an Mo–Mo bond of 2.950(1) Å; the two, four-electron donating As_2 ligands are bonded side-on to form a plane perpendicular to the Mo–Mo bond and the two CO and two $(\eta^5\text{-}MeC_5H_4)$ groups are *cis*.

The heavier group-15 elements (P to Bi), 15-electron metal fragments [*e.g.*, $cpMo(CO)_2$(cp = cyclopentadienyl) and $Co(CO)_3$], and methyne (≡CR) readily intermingle in cluster formation by isolobal replacement. The As_2 group, an analogue of N_2 and $(CR)_2$, proved particularly versatile in its ability to form tetrahedrane analogues, *e.g.*, $[cpMo(CO)_2]_2As_2$[1,2] and $[Co(CO)_3]_2As_2$.[3,4] The As_2 ligand can be a four, six, or eight electron donor depending on whether the ligand links two, three, or four metal centres.[2,5,6]

We have shown that, by varying the conditions for thermolysis reactions of $[cpMo(CO)_3]_2$ and the cyclopolyarsines cyclo-$(RAs)_n$ (R = Ph, n = 6; R = Me, n = 5), $[cpMo(CO)_2](\mu_2,\eta^2\text{-}As_2)$[1] and $[cpMo]_2(\mu_2,\eta^4\text{-}As_5)$[7] may be formed. The intermediate composition $[cpMo(CO)]_2(\mu_2,\eta^2\text{-}As_2)_2$ seemed logical but had eluded our isolation; the isoelectronic diacetylene complex $[cpCr(CO)]_2(\mu_2,\eta^2\text{-}C_2H_2)$ has also proved elusive.[8] $[(\eta^5\text{-}C_5Me_5)Mo(CO)]_2(\mu_2,\eta^2\text{-}P_2)_2$

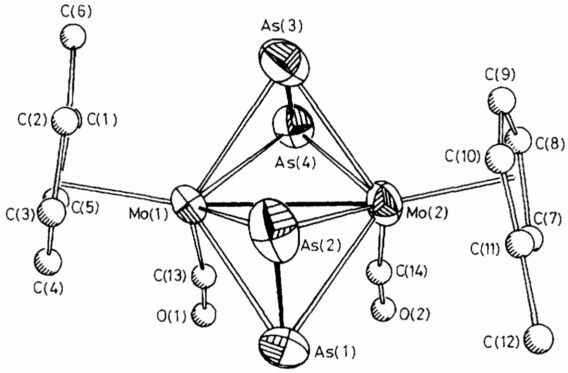

Figure 1. Molecular structure and labelling scheme for (**1**). Mo(1)–Mo(2), 2.950(1); av. Mo–As, 2.626(1); As(1)–As(2), 2.300(2); As(3)–As(4), 2.279(2); As(2) · · · As(3), 3.051(2) Å.

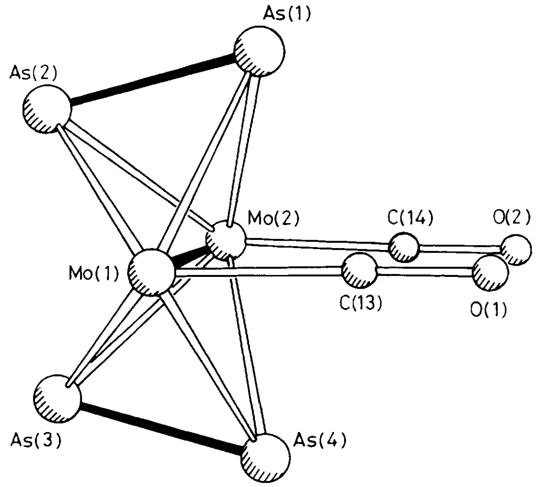

Figure 2. A view of (**1**) along the Mo–Mo vector with (η^5-MeC$_5$H$_4$) rings deleted.

has been spectroscopically identified as a precursor to [(η^5-C$_5$Me$_5$)Mo]$_2$(μ_2,η^6-P$_6$).[9]

We now report the synthesis and crystallographic characterization of [(η^5-MeC$_5$H$_4$)Mo(CO)]$_2$(μ_2,η^2-As$_2$)$_2$ (**1**). Complex (**1**) is isolated in low yield (14%) from [(η^5-MeC$_5$H$_4$)Mo(CO)$_3$]$_2$ (1.93 mmol) and cyclo-(MeAs)$_5$ (2.89 mmol) in 10 ml of toluene (130 °C, 48 h) in a sealed Carius tube (caution: pressures may exceed 30 atm). The filtrate from the cooled reaction mixture was evaporated to dryness, redissolved in CH$_2$Cl$_2$, eluted from an alumina column with 5% CH$_2$Cl$_2$ in hexane, and recrystallized from CH$_2$Cl$_2$–pentane to give deep red, air stable needles.†

The molecular structure of (**1**) as determined by *X*-ray crystallography‡ is shown in Figures 1 and 2. The two (μ_2,η^2-As$_2$) ligands form a plane (max. dev. 0.007 Å) perpendicular to the Mo–Mo vector. The As$_2$ groups are tilted away from the *cis* carbonyl groups and are not mutually parallel; extensions of the As–As vectors intersect at a 28.5(1)° angle. The (η^5-MeC$_5$H$_4$) rings are also tilted away from the carbonyl groups; each forms a 15(1)° angle to the central As$_4$ plane. The As$_2$ ligands have As–As distances [As(1)–As(2) 2.300(2) and As(3)–As(4) 2.279(2) Å] among the shortest known. These may be compared with As–As distances of 2.273(3) Å in Co$_2$(CO)$_5$[P(C$_6$H$_5$)$_3$]As (the shortest known),[4] 2.279(4) Å in [W(CO)$_5$]$_3$As$_2$,[6] and 2.311(3) Å in [cpMo(CO)$_2$]$_2$As$_2$ (**2**).[1] As seen in (**2**), and in [cp(CO)$_2$Mo]$_2$As$_2$[Cr(CO)$_5$]$_2$,[2] the Mo–As distances at each end of the As$_2$ ligand are significantly inequivalent; in (**1**) the Mo bonds to As(2) and As(3) average 2.590 Å while those to As(1) and As(4) average 2.662 Å. The frequency of this observation and the close similarity in the Mo–As distances among these three structures suggest an electronic rather than steric origin for these differences.

In the related d^4–d^4 complexes [cpNb(CO)]$_2$(C$_2$R$_2$)$_2$ (**3**), R = Ph[10] or CO$_2$Me,[11] which have a proposed Nb=Nb bond, the acetylene molecules are twisted by about 10° from a perpendicular projection on the metal–metal vector. This is attributed to a second-order Jahn–Teller effect.[12] In (**1**), however, this effect is absent, with a projection angle of 90(1)° for either As$_2$ ligand on the Mo–Mo vector.

[(η^5-MeC$_5$H$_4$)Mo(CO)]$_2$(μ_2,η^2-As$_2$)$_2$
(**1**)

[cpMo(CO)$_2$]$_2$As$_2$
(**2**)

[cpNb(CO)]$_2$(C$_2$R$_2$)$_2$
(**3**) R = Ph or CO$_2$Me

If the M.O. diagram for [(CO)$_4$NbNb(CO)$_4$]$^{2+}$, constructed as a model for (**3**),[12] is also applicable to (**1**), the two additional electrons in (**1**) [compared with (**3**)] occupy an Mo–Mo antibonding level in this d^5–d^5 complex. The Mo–Mo distance observed, 2.950(1) Å is, however, shorter than in (**2**) [av. 3.039(2) Å, for two independent molecules].[1] Conventional electron counting methods assign an Mo–Mo bond order of one to (**1**), assuming that the (μ_2,η^2-As$_2$) ligand is a four-electron donor.

Huttner[2] and Scherer[5] (and their coworkers) have shown that co-ordinated P$_2$ and As$_2$ ligands may increase their donor generosity from four to six or eight by co-ordination to 16-electron metal-carbonyl fragments such as Cr(CO)$_5$ and cpMn(CO)$_2$ and we are investigating this reactivity for (**1**).

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† Satisfactory microanalysis data (C, H ± 0.3% of calculated values) were obtained for (**1**). ^{1}H N.m.r. (250 MHz, CDCl$_3$): δ 1.58 (3H, s), 1.95 (3H, s), 4.82, 4.89 (8H, doublet of triplets). I.r. (CH$_2$Cl$_2$) ν_{CO} 1970, 1930, and 1895 cm^{-1}. M.p. 163—165 °C (decomp.).

‡ *Crystal data* (23 °C) for (**1**): triclinic, space group $P\bar{1}$, a = 7.387(2), b = 10.762(3), c = 11.941 Å, α = 103.57(2), β = 92.11(2), γ = 101.83(2)°, U = 899.6(4) Å^3, Z = 2, $D_{calc.}$ = 2.694 g cm^{-3}, μ(Mo-K_α) = 90.8 cm^{-1}. A Nicolet R3m/μ diffractometer was used to collect 4345 data ($4° \leqslant 2\theta \leqslant 55°$) of which 4175 were independent ($R_{int.}$ = 0.77%) and 2940 with $F_o \geqslant 3\sigma(F_o)$ were considered observed. The intensity data were corrected for absorption ($T_{max.} : T_{min.}$ = 0.457 : 0.222). The structure was solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized isotropic contributions; the methyl rotational orientations were obtained from one reliably located H atom in each group. At convergence R = 5.43%, R_w = 6.40%, G.O.F. = 1.546, Δ/σ = 0.010, $\Delta(\rho)$ = 1.80 e Å^{-3} [0.74 Å from C(12) indicating possible unresolved (η^5-MeC$_5$H$_4$) ring disorder; next highest peak 0.74 e Å^{-3}]. N_o/N_v = 15.4. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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