A Di-metal Sandwich Complex: *X*-Ray Crystal Structure of $[Mo_2(CO)_4(\mu\text{-}\eta^3,\eta^{3\prime}\text{-}C_8H_8)_2]$

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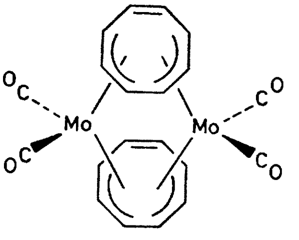
Summary. Red crystalline $[Mo_2(CO)_4(\mu\text{-}\eta^3,\eta^{3\prime}\text{-}C_8H_8)_2]$, a product of the reaction of $[Mo(CO)_6]$ with cyclo-octatetraene in boiling cyclohexane, is shown by *X*-ray diffraction to contain two non-bonded molybdenum atoms sandwiched between two cyclo-octatetraene rings; the rings are bonded to the metal atoms *via* η^3-allyl interactions and rotate freely in solution.

In the preceding communication we described a new mode of dimerisation of cyclo-octatetraene, induced by reaction with $[Mo(CO)_6]$.[1] A minor product of that reaction, when performed in boiling cyclohexane, is red crystalline $[Mo_2(CO)_4(C_8H_8)_2]$ which has been shown by an *X*-ray diffraction study to be only the second crystallographically characterised example of a compound with two metal atoms 'sandwiched' between two monocyclic C_nH_n rings. Communication of this structural identification is prompted by the fact that an *X*-ray diffraction investigation of the first example, $[Ni_2(C_8H_8)_2]$, was hindered by disorder and it was not possible to resolve unequivocally the stereochemistry of the metal–ring interaction.[2]

Crystals of $[Mo_2(CO)_4(\mu\text{-}\eta^3,\eta^{3\prime}\text{-}C_8H_8)_2]$ (**1**) [m.p. 200 °C (decomp.), ν(CO)(cyclohexane) 1 940s and 1 883m cm^{-1}, ^1H n.m.r. ($CDCl_3$) τ 6·0s, ^{13}C n.m.r. (CD_2Cl_2) 74·7 p.p.m. (downfield of $SiMe_4$)] were obtained from dichloromethane solution.



(1)

Crystal data. $C_{20}H_{16}Mo_2O_4$, $M = 502·2$, monoclinic, space group $C2/c$, $a = 17·150(6)$, $b = 7·212(3)$, $c = 15·349(9)$ Å, $\beta = 114·21(2)°$, $U = 1732(10)$ Å^3, $Z = 4$, $D_c = 1·95$ g cm^{-3}, $F(000) = 1008$, Mo-K_α radiation ($\lambda = 0·71069$ Å), μ(Mo-K_α) $= 14·35$ cm^{-1}.

The structure was solved by conventional heavy atom methods from data collected to $2\theta = 55°$ on a Syntex $P3$ diffractometer and refined with isotropic temperature factors for the hydrogen atoms and anisotropic temperature factors for the non-hydrogen atoms. For 2 116 independent reflections $[I > 2·25\sigma(I)]$ $R = 0·036$.†

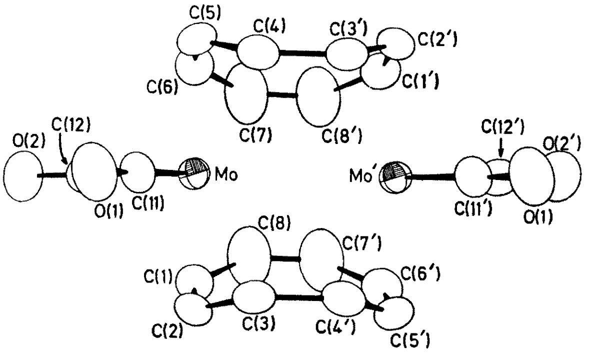


Figure 1. Molecular structure of $[Mo_2(CO)_4(\mu\text{-}\eta^3,\eta^{3\prime}\text{-}C_8H_8)_2]$ (**1**). Bond lengths: Mo–C(1) 2·421(3), Mo–C(2) 2·309(3), Mo–C(3) 2·425(3), Mo–C(4) 2·423(3), Mo–C(5) 2·311(3), Mo–C(6) 2·412(4), Mo–C(11) 1·936(3), Mo–C(12) 1·944(4), C(11)–O(1) 1·159(4), C(12)–O(2) 1·144(4), C(1)–C(2) 1·403(5), C(2)–C(3) 1·415(5), C(3)–C(4) 1·434(5), C(4)–C(5) 1·417(5), C(5)–C(6) 1·387(5), C(6)–C(7) 1·403(7), C(7)–C(8) 1·368(8), C(8)–C(1) 1·395(7), Mo···Mo' 3·416(1), Mo···C(7) 2·899(7), Mo···C(8) 2·925(7) Å. Bond angles: MoC(11)O(1) 177·1(3), MoC(12)O(2) 177·7(4), C(11)MoC(12) 78·7(2), C(11)MoMo' 116·4(1), C(12)MoMo' 164·8(1), C(1)C(2)C(3) 128·3(3), C(4)C(5)C(6) 128·6(4), C(2)MoMo' 89·1(1), C(5)MoMo' 90·2(1)°.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The molecule in the crystal lies astride a 2-fold axis which in Figure 1 lies perpendicular to the diagram, bisecting the Mo $\cdots$ Mo vector. There is thus an imposed crystallographic C_2 symmetry, though the molecule as a whole has idealised C_{2v} symmetry. Two molybdenum atoms, each bearing two terminal carbonyl ligands, are sandwiched between two cyclo-octatetraene rings. The metal atoms are bonded to the rings *via* adjacent η^3-allyl interactions, leaving an unco-ordinated olefinic bond C(7)–C(8) [1·368(8) Å] within each. A view (Figure 2) of the molecule perpendicular to that in Figure 1 shows that the molybdenum atoms lie precisely between the central allylic carbons. The rings adopt a very flattened tub conformation with the carbon atoms deviating by less than ±0·25 Å from the mean plane, and with angles at carbon in the range 128—137° (regular octagon = 135°). Co-ordination with two carbonyls and two η^3-allyls will produce, in the absence of any additional bonding interactions, an unusual sixteen valence electron configuration for low oxidation state molybdenum. However, the Mo $\cdots$ Mo distance of 3·416(1) Å is certainly not compatible with the double bonding which would provide an eighteen electron configuration {*e.g.* in $[Mo_2(CO)_2(\mu\text{-}SBu^t)_2(\eta\text{-}C_5H_5)_2]$ Mo=Mo is 2·616(2) Å}[3] and is longer than the single Mo–Mo bond of 3·235(1) Å in $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$.[4] It therefore appears that there is no substantial interaction between the metal atoms. In this light it is surprising that cyclo-octatetraene does not function as an eight electron bridging ligand in (**1**), as it does in $[Fe_2(CO)_5C_8H_8)]$[5] and $[Mn_2(CO)_6(C_8H_8)]$.[6]

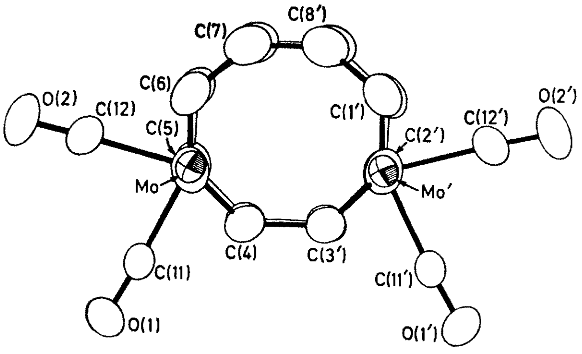

FIGURE 2. View of $[Mo_2(CO_4(\mu\text{-}\eta^3, \eta^{3'}\text{-}C_8H_8)_2]$ (**1**) perpendicular to that shown in Figure 1.

On the basis of the structure described here it seems likely that of the two possible geometries discussed[2] for $[Ni_2(C_8H_8)_2]$, that which corresponds to (**1**) is adopted. Wilke has suggested that a di-nickel complex may be involved in the nickel-catalysed cyclotetramerisation of ethyne to cyclo-octatetraene, and has reported that $[Ni_2(C_8H_8)_2]$ does produce the olefin when treated with ethyne.[7] We have observed that (**1**) also reacts with ethyne, either thermally or photochemically, but to produce a purple-black insoluble powder which has not yet been identified. G.l.c. analysis of the reaction solution reveals no indication of free cyclo-octatetraene. Although containing formally sixteen electron molybdenum, (**1**) resists CO incorporation at moderate pressures but yields $[Mo(CO)_6]$ at 100 atm. It is unchanged by hydrogen at 100 atm pressure and 100 °C.

The fluxional rotation of the cyclo-octatetraene rings in (**1**), for which evidence is provided by the single ^1H and ^{13}C n.m.r. shifts for the ligands, is remarkably free. The ^1H resonance remains a sharp singlet at −100 °C.

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