Formal Diels–Alder Reactivity of Co-ordinated Ethyne: Crystal Structure of $[Mo_2(CO)_2(C_{10}H_{10})(\eta\text{-}C_5H_5)_2]$

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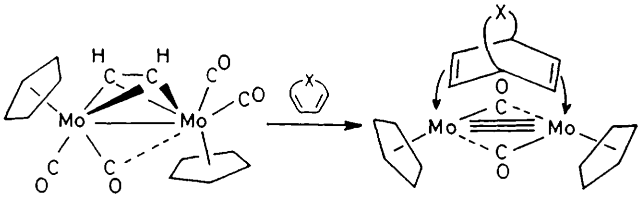
Summary Cyclic 1,3-dienes react with $[Mo_2(CO)_4(\mu\text{-}C_2H_2)(\eta\text{-}C_5H_5)_2]$ to give products arising from formal Diels–Alder addition to the bridging ethyne; the structure of the bicyclo[4.2.2]deca-2,4,7,9-tetraene complex $[Mo_2(CO)_2(C_{10}H_{10})(\eta\text{-}C_5H_5)_2]$, derived from cyclo-octatetraene addition, has been determined by *X*-ray diffraction.

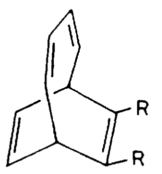
ETHYNE is a poor dienophile and participates in Diels–Alder reactions only under forcing conditions. In electrophilic alkynes, however, the triple bond is more active and cycloaddition with 1,3-dienes proceeds readily. We now describe the activation of ethyne itself towards such cyclisation, through complexation with a di-metal system.



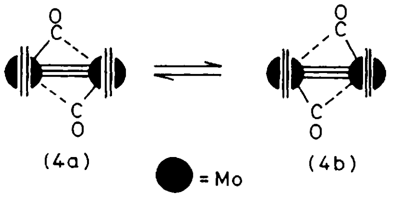
(1)

(2)

a; X = $-[CH_2]_2-$
b; X = $-[CH_2]_2-$
c; X = $-CH{=}CH-CH{=}CH-$
d; X = $-CH{=}CH-CH_2-$

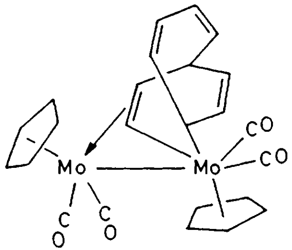


(3)
a; R = H
b; R = Ph



(4a)

(4b)



(5)

The ethyne-bridged di-molybdenum complex $[Mo_2(CO)_4(\mu\text{-}C_2H_2)(\eta\text{-}C_5H_5)_2]$ (**1**),[1,2] whose reactivity towards oligomerisation of alkynes we have described,[3] provides brown-black crystalline complexes of a new structural type (**2**) on heating in octane with cyclohexa-1,3-diene, cyclo-octa-1,3-diene, cyclo-octatetraene or cycloheptatriene, but not with cyclopentadiene. The complex $[Mo_2(CO)_2(C_{10}H_{10})(\eta\text{-}C_5H_5)_2]$ (**2c**), obtained in 25% yield from cyclo-octatetraene, is typical. It displays a band at 1 805 cm^{-1} in the i.r. characteristic of a bridging carbonyl, and n.m.r. spectra {[$^2H_1$]chloroform; ^1H: τ, 3·42 (m, 2H), 3·80, (m, 2H), 4·9—5·2 (m, 2H), 5·08 (s, 10H), and 6·21 (m, 4H); ^{13}C: 49·0 (bridgehead 2 *C*H), 56·3 (co-ordinated olefinic 4 *C*H), 91·4 (2 C_5H_5), 125·9 (unco-ordinated olefinic 2 *C*H), 144·9 (unco-ordinated olefinic 2 *C*H), and 253·5 (2 *C*O) p.p.m.} which identify the presence of bicyclo[4.2.2]deca-2,4,7,9-tetraene (**3a**) as a ligand. The structure of the complex was elucidated through an *X*-ray diffraction study.

Crystal data: $C_{22}H_{20}Mo_2O_2$, *M* 508·2, monoclinic, space group *Cc* (No.9), *a* = 9·230(3), *b* = 16·561(4), *c* = 12·651(3) Å, β = 107·38(2)°, *U* = 1845·4(9) Å^3, *Z* = 4, D_c = 1·83 g cm^{-3}, *F*(000) = 1008, Mo-K_α radiation (λ = 0·71069 Å), μ(Mo-K_α) = 12·3 cm^{-1}. The structure was solved by conventional heavy-atom methods from data collected on a Syntex $P2_1$ four-circle diffractometer to 2θ = 70°. For the 4285 independent reflections *R* = 0·036.†

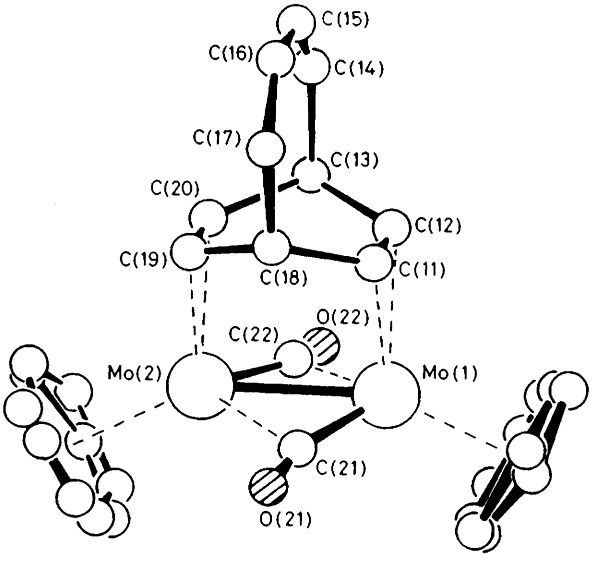


FIGURE. Molecular structure of $[Mo_2(CO)_2(C_{10}H_{10})(\eta\text{-}C_5H_5)_2]$ (**2c**). Bond lengths: Mo(1)–Mo(2) 2·504(1), Mo(1)–C(21) 1·994(6), Mo(1)–C(22) 2·290(7), Mo(2)–C(21) 2·367(7), Mo(2)–C(22) 1·994(8), Mo(1)–C(11) 2·315(4), Mo(1)–C(12) 2·286(4), Mo(2)–C(19) 2·277(4), Mo(2)–C(20) 2·303(4), Mo(1)–C(C_5H_5) (mean) 2·33(2), Mo(2)–C(C_5H_5) (mean) 2·36(1), C(11)–C(12) 1·405(6), C(12)–C(13) 1·510(6), C(13)–C(14) 1·529(7), C(14)–C(15) 1·339(12), C(15)–C(16) 1·439(12), C(16)–C(17) 1·325(11), C(17)–C(18) 1·514(6), C(18)–C(11) 1·503(6), C(18)–C(19) 1·519(6), C(19)–C(20) 1·390(8), C(20)–C(13) 1·517(7) Å.

The molecular structure (Figure) shows that the cyclo-octatetraene ring has undergone 1,4-addition to co-ordinated ethyne to produce bicyclo[4.2.2]deca-2,4,7,9-tetraene of *mm* symmetry. The molecule as a whole has only two-fold symmetry, however, because the carbonyl bridges between the two molybdenum atoms are not symmetrical. The cyclopentadienyl rings are also inequivalently disordered relative to their staggered co-planar counterparts, on Mo(1) in the ratio 0·30:0·70 and on Mo(2) 0·53:0·47. Around each molybdenum atom the co-ordination can be regarded as capped octahedral with three sites for C_5H_5, one for the olefinic link, two for the bridging carbonyls, and a capping Mo≡Mo triple bond interaction [2·504(1) Å] as required by the eighteen-electron rule. The atom sequences C(13—18), C(13,12,11,18), and C(13,20,19,18) are each co-planar, with a dihedral angle between the last two of 142°.

This structure for (**2c**) requires there to be two environments for the co-ordinated olefinic carbon (and hydrogen)

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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.

atoms and yet only one is observed in the n.m.r. spectrum at ambient temperature (see above). This apparent incompatibility is a consequence of dynamic behaviour in solution. For example, at ambient temperature (**2b**) displays a single ^{13}C n.m.r. signal at 60·9 p.p.m. for the carbons under discussion. On cooling, this signal broadens, collapses, and is replaced at -60 °C by the two signals expected, at 63·1 and 58·4 p.p.m. We attribute this behaviour to a carbonyl exchange process (**4a**) $\rightleftharpoons$ (**4b**), which when rapid will produce a single time-averaged environment for the four co-ordinated olefinic carbons. From the coalescence temperature (240 K) the free energy of activation of the process is calculated as 47·2 kJ mol^{-1}, close to the 43·5 kJ mol^{-1} observed[4] for bridge-terminal carbonyl exchange in $[\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$.

A complex of formulation $[\{Fe(CO)_3\}_2(C_{10}H_{10})]$, obtained from heating bullvalene with $[Fe_2(CO)_9]$, has also been identified[5] as containing (**3a**). Of more significance to this work, however, is the reaction of cyclo-octatetraene(tricarbonyl)iron with diphenylacetylene, which has been shown to produce unco-ordinated 7,8-diphenylbicyclo[4.2.2]deca-2,4,7,9-tetraene (**3b**).[6,7] Although this has been described[7] as an example of a thermally 'forbidden' $[2+6]\pi$ cycloaddition made 'allowed' through metal participation, more recent work[8] has suggested that such reactions of electrophilic alkynes with co-ordinated hydrocarbons proceed by a step-wise rather than concerted mechanism. The same is probably true of the formal Diels-Alder cyclisations described here, with an intermediate like (**5**) involved in conversion of (**1**) into (**2c**); *cf.* the formation of ferroles through addition of alkynes to di-iron alkyne-bridged complexes.[9]

With acyclic 1,3-dienes, (**1**) does not yield complexes similar to (**2**). A surprising reaction occurs with hexa-2,4-diene; ethyne is displaced and the diene isomerises to yield the hex-3-yne complex $[Mo_2(CO)_4(\mu\text{-}EtC_2Et)(\eta\text{-}C_5H_5)_2]$ analogous to (**1**).

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