Control over the Dimerisation of Cyclo-octatetraene through Metal Complexation: *X*-Ray Structure of $[Mo(CO)_4(C_{16}H_{16})]$

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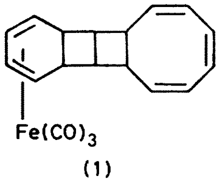
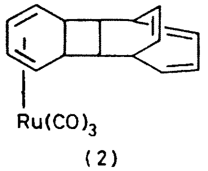
Summary Cyclo-octatetraene reacts with $[Mo(CO)_6]$ in boiling octane to produce $[Mo(CO)_4(C_{16}H_{16})]$, shown by *X*-ray diffraction to contain a new dimer of the hydrocarbon arising formally from a combination of $[2+2]\pi$ and $[2+4]\pi$ cycloaddition, the dimer is released as a stable species upon treatment of the complex with Me_3NO

THE effect of complexation with a metal upon the reactivity of an unsaturated hydrocarbon is an important area of study in organo-metal chemistry Recently a unique illustration of this effect was obtained We observed that the cyclo-octatetraene complex $[Fe(CO)_3(1\text{—}4\text{-}\eta\text{-}C_8H_8)]$ reacts with cyclo-octatetraene to afford $[Fe(CO)_3(C_{16}H_{16})]$ (**1**), containing a dimer arising from formal $[2+2]\pi$ cycloaddition, while with the isostructural $[Ru(CO)_3(1\text{—}4\text{-}\eta\text{-}C_8H_8)]$ formal $[2+4]\pi$ cycloaddition occurs to provide $[Ru(CO)_3(C_{16}H_{16})]$ (**2**), we discussed the mechanism of this metal control over the dimerisation pathway[1,2] In 1961 it was reported that cyclo-octatetraene reacts with $[Mo(CO)_6]$ to form a complex of formulation $[Mo(CO)_4(C_{16}H_{16})]$, no spectroscopic data were provided but it was recorded that the very complicated ^1H n m r spectrum did not allow structural identification[3] The fascinating possibility that molybdenum was inducing yet another pathway for cyclo-octatetraene dimerisation led us to reinvestigate this complex


(1)


(2)

Heating $[Mo(CO)_6]$ with cyclo-octatetraene in octane at reflux for *ca* 1 day gives a 25% yield of pale yellow crystalline $[Mo(CO)_4(C_{16}H_{16})]$ (**3**) [m p 190—192 °C (decomp), ν(CO) (hexane) 2 034m, 1 951sh, 1 948s, and 1 904 s cm^{-1}] In a solvent of lower boiling point such as cyclohexane less of (**3**) is produced and an additional dark red crystalline complex $[Mo_2(CO)_4(C_8H_8)_2]$ (**4**) is formed in low yield, this species is described in the following communication[4] The ^1H n m r spectrum of (**3**) is indeed complicated [τ ($CDCl_3$) 3 52dd (1 H), 3 94m (2 H), 4 14dd (1 H), 4 90m (1 H), 5 54m (3 H), 6 34m (4 H) 7 02m (1 H), 7 30m (2 H), and 7 90m (1 H)], as is the ^{13}C n m r spectrum which contains signals due to four unco-ordinated olefinic carbons (136 6, 136 5, 132 7, and 129 6) four co-ordinated olefinic carbons [103 6, 95 3 (2 C), and 92 8], and eight aliphatic carbons [56 4, 45 2, 44 1, 39 9, 37 2 (2 C), and 34 4 (2 C) p p m (downfield of $SiMe_4$)] There is clearly little symmetry in the molecule, the structure was determined by *X*-ray diffraction

Crystal data $C_{20}H_{16}MoO_4$ $M = 416$ 3, orthorhombic, space group $P2_12_12_1$ (D_2^4, No 19), $a = 9$ 935(7), $b = 13$ 09(1) $c = 12$ 59(1) Å, $U = 1636(2)$ Å^3, $Z = 4$, $D_c = 1$ 66 g cm^{-3}, $D_m = 1$ 56 g cm^{-3}, $F(000) = 840$, Mo-K_α radiation (graphite monochromator), $\bar{\lambda} = 0$ 710 69 Å, μ(Mo-K_α) $= 8$ 0 cm^{-1} The structure was solved by conventional heavy atom methods from data collected on a Syntex $P2_1$ diffractometer to $2\theta = 60°$ at 220 K and refined with isotropic temperature factors for the hydrogen atoms and anisotropic temperature factors for the non-hydrogen atoms For 2 432 independent reflections [$I > 1$ $5\sigma(I)$] $R = 0$ 026 †

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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

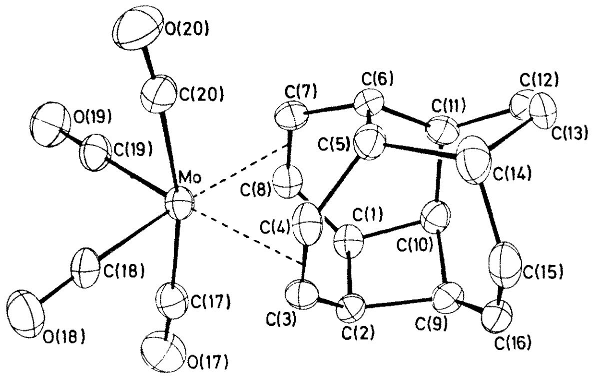


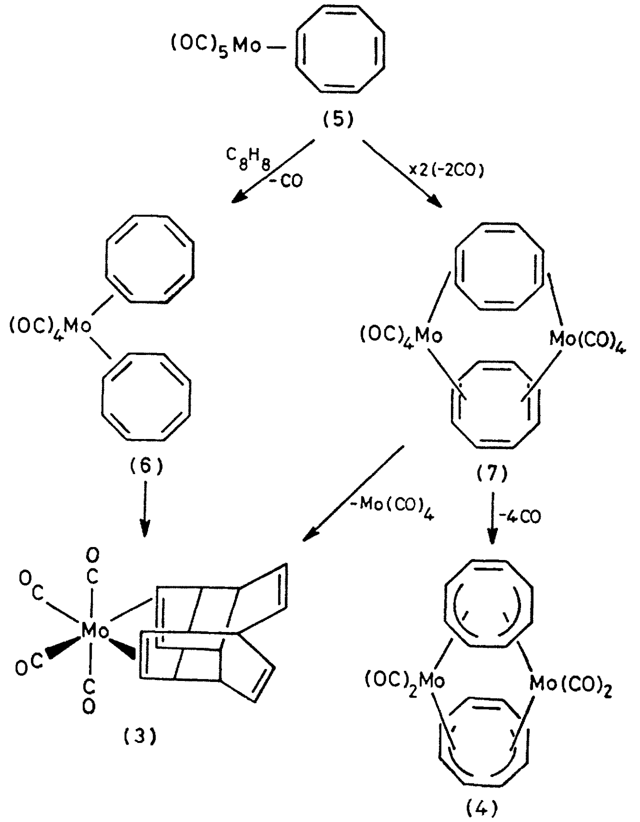
FIGURE. Molecular structure of [Mo(CO)$_4$(C$_{16}$H$_{16}$)] (**3**). Bond lengths: Mo–C(17) 2·041(3), C(17)–O(17) 1·126(4), Mo–C(18) 1·969(3), C(18)–O(18) 1·152(3), Mo–C(19) 1·978(3), C(19)–O(19) 1·143(4), Mo–C(20) 2·050(3), C(20)–O(20) 1·141(4), Mo–C(3) 2·429(2), Mo–C(4) 2·452(2), Mo–C(7) 2·472(3), Mo–C(8) 2·486(3), C(1)–C(2) 1·554(3), C(1)–C(8) 1·486(4), C(1)–C(10) 1·566(4), C(2)–C(3) 1·495(4), C(2)–C(9) 1·564(4), C(3)–C(4) 1·373(4), C(4)–C(5) 1·513(3), C(5)–C(6) 1·552(4), C(5)–C(14) 1·567(4), C(6)–C(7) 1·504(4), C(6)–C(11) 1·541(4), C(7)–C(8) 1·371(4), C(9)–C(10) 1·569(4), C(9)–C(16) 1·499(4), C(10–C(11) 1·531(4), C(11)–C(12) 1·508(4), C(12)–C(13) 1·313(5), C(13)–C(14) 1·508(4), C(14)–C(15) 1·529(4), C(15)–C(16) 1·312(4) Å.

The molecular structure, shown in the Figure and represented by (**3**), is based on a molybdenum atom in octahedral co-ordination with four sites occupied by carbonyl ligands and two *cis* sites by the olefinic double bonds of a new and unsymmetric cage-like dimer of cyclo-octatetraene. The pair of mutually *trans* carbonyl ligands are bent away from the dimer by 5° and have, as expected, Mo–C bond lengths significantly longer (*ca.* 2·05 Å) than those (*ca.* 1·97 Å) of the pair *trans* to the olefinic bonds. The cyclo-octatetraene dimer, each carbon of which bears a hydrogen atom which was located but is omitted from the Figure for clarity, is composed of two C$_8$ ring systems. One of these [C(1—8)] has a tub conformation and is co-ordinated to molybdenum in a 1,5-diene mode through the double bonds C(3)–C(4) and C(7)–C(8). The other C$_8$ ring [C(9—16)] has double bonds between C(12)–C(13) and C(15)–C(16) and is linked to the first by four bridge bonds between C(1)–C(10), C(2)–C(9), C(5)–C(14), and C(6)–C(11).

Treatment of (**3**) with Me$_3$NO in boiling benzene provides the new dimer quantitatively as a pale yellow, slightly air- and light-sensitive, waxy hydrocarbon. Both ^{1}H [τ (CDCl$_3$) 3·46dd (1 H), 3·68m (1 H), 3·84m (3 H), 4·24m (1 H), 4·50m (1 H), 4·84dd (1 H), 6·50m (1 H), 6·74m (2 H), 7·02m (3 H), 7·46m (1 H), and 7·66m (1 H)] and ^{13}C (δ 140·6, 137·7, 134·8, 133·1, 132·2, 129·2, 128·0, 125·6, 49·2, 41·3, 37·9, 37·8, 37·4, 36·8, 35·3, and 34·8 p.p.m.) n.m.r. spectra indicate the presence of eight olefinic and eight aliphatic CH groups, suggesting that the dimer has not rearranged upon removal from complexation. This conclusion is supported by its reaction with [Mo(CO)$_6$] in boiling heptane, which yields (**3**) rapidly.

Whereas (**1**) and (**2**) are *formally* products of [2+2]π and [2+4]π dimerisations of cyclo-octatetraene, respectively, the new dimer may be viewed as arising from combined formal [2+2]π [carbons C(1,2) with C(10,9)] and [2+4]π [carbons C(6,5) with C(11—14)] cycloadditions. However, neither of the dimers within (**1**) and (**2**), which also are liberated by Me$_3$NO, was transformed to give (**3**) when heated with [Mo(CO)$_6$].

Heating cyclo-octatetraene alone is known to provide dimers other than the one described here, which must therefore arise as a result of molybdenum complexation. We have, however, established that neither (**4**), which contains the necessary two cyclo-octatetraene rings, nor the known cyclo-octatetraene complex [Mo(CO)$_4$(1,2,5,6-η-C$_8$H$_8$)],[5] which contains a tub-bonded ring like that in (**3**), is involved. When solid (**4**) is heated to decomposition only cyclo-octatetraene is released, while in octane at reflux with [Mo(CO)$_6$] no trace of (**3**) is formed. Heating [Mo(CO)$_4$(1,2,5,6-η-C$_8$H$_8$)] with cyclo-octatetraene effects rapid decomposition into [{Mo(CO)$_4$}$_2$(η^8-C$_8$H$_8$)].[5] This latter observation shows that the reaction of [Mo(CO)$_6$] with cyclo-octatetraene must proceed from what is surely the first intermediate [Mo(CO)$_5$(η^2-C$_8$H$_8$)] (**5**) to the eventual product (**3**) without passing through the η^4-complex [Mo(CO)$_4$(1,2,5,6-η-C$_8$H$_8$)]. Significantly, reflux in heptane of [Mo(CO)$_5$(thf)] (thf = tetrahydrofuran) with an equimolar quantity of cyclo-octatetraene, designed to produce initially (**5**) in the same way that [Mn(CO)$_2$(η^2-C$_8$H$_8$)-(η-C$_5$H$_5$)][6] is generated from [Mn(CO)$_2$(thf)(η-C$_5$H$_5$)], gave (**3**) rapidly in 35% yield together with a small amount of (**4**).



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Plausible routes from (**5**) to (**3**) involve [Mo(CO)$_4$(η^2-C$_8$H$_8$)$_2$] (**6**) or [{Mo(CO)$_4$(C$_8$H$_8$)}$_2$] (**7**), as shown in the Scheme. The latter could lose CO to give (**4**) or eject [Mo(CO)$_4$] while, like (**6**), undergoing a succession of carbon–carbon bond formation steps to produce (**3**). The sequence of carbon–carbon bond formation is obscure, but various viable pathways can be constructed based on the established step-wise character of cycloaddition reactions at a transition metal centre[7] and on the known chemistry of metallocycles[8] A rationalisation for the formation of (**1**) and (**2**) with iron and ruthenium carbonyls has been presented,[1] we believe the new mode of dimerisation represented by (**3**) may be traced to the affinity of Mo^0 for the 1,5- rather than the 1,3-diene co-ordination preferred by Fe^0 or Ru^0

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[1] A P Humphries and S A R Knox, *J Chem Soc , Dalton Trans* , 1978, 1514

[2] R Goddard and P Woodward, *J Chem Soc , Dalton Trans* , 1979, 661

[3] M A Bennett, L Pratt, and G Wilkinson, *J Chem Soc* , 1961, 2037

[4] A H Connop, F G Kennedy, S A R Knox, and G H Riding, *J Chem Soc , Chem Commun* , following communication

[5] H D Kaesz, S Winstein, and C G Kreiter, *J Am Chem Soc* , 1966, **88**, 1319

[6] I B Benson, S A R Knox, R F D Stansfield, and P Woodward, *J Chem Soc , Chem Commun* , 1977, 404

[7] M Bottrill, R Davies, R Goddard, M Green, R P Hughes, B Lewis, and P Woodward, *J Chem Soc , Dalton Trans* , 1977, 1252

[8] G Wilke, *Pure Appl Chem* , 1978, **50**, 677