Ring-opening Reaction of 3,3-Dimethylcyclopropene promoted by a Dimolybdenum Complex

By Geoffrey K. Barker,[a] W. Eamon Carroll,[a] Michael Green,[a] and Alan J. Welch[b]
([a]*Department of Inorganic Chemistry, The University, Bristol* BS8 1TS and
[b]*Department of Chemistry, The City University, London* EC1V 0HB)

Summary The reaction of dicyclopentadienyltetracarbonyldimolybdenum with 3,3-dimethylcyclopropene leads to a ring-opening reaction and the formation of an unusual allyl-bridged dimolybdenum complex, identified by *X*-ray crystallography.

The reaction of cyclopropenes with $Fe_2(CO)_9$[1] or $Ni(cod)_2$[2] (cod = cyclo-octadiene) leads to ring-opening reactions involving C–C bond cleavage. However, only in the case of the iron system has an organometallic product, a vinylketen-iron tricarbonyl complex, been isolated. In the nickel system if an olefin such as dimethyl fumarate is present, a vinyl-substituted cyclopropane is formed, suggesting[2,3] that an intermediate 2,2-dimethylvinylcarbenenickel complex is involved. In the belief that such a species would be more likely to be stabilised in a dinuclear system, the reaction of 3,3-dimethylcyclopropene with dicyclopentadienyltetracarbonyldimolybdenum[4] has been studied.

The reaction (room temperature, 14 days) of an excess of 3,3-dimethylcyclopropene with $[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$ dissolved in toluene led to some polymerization of the olefin and the formation of a red crystalline complex (**1**),† characterised by elemental analysis and mass spectroscopy as a 1:1 adduct. A single crystal *X*-ray diffraction study established the molecular structure shown in the Figure.

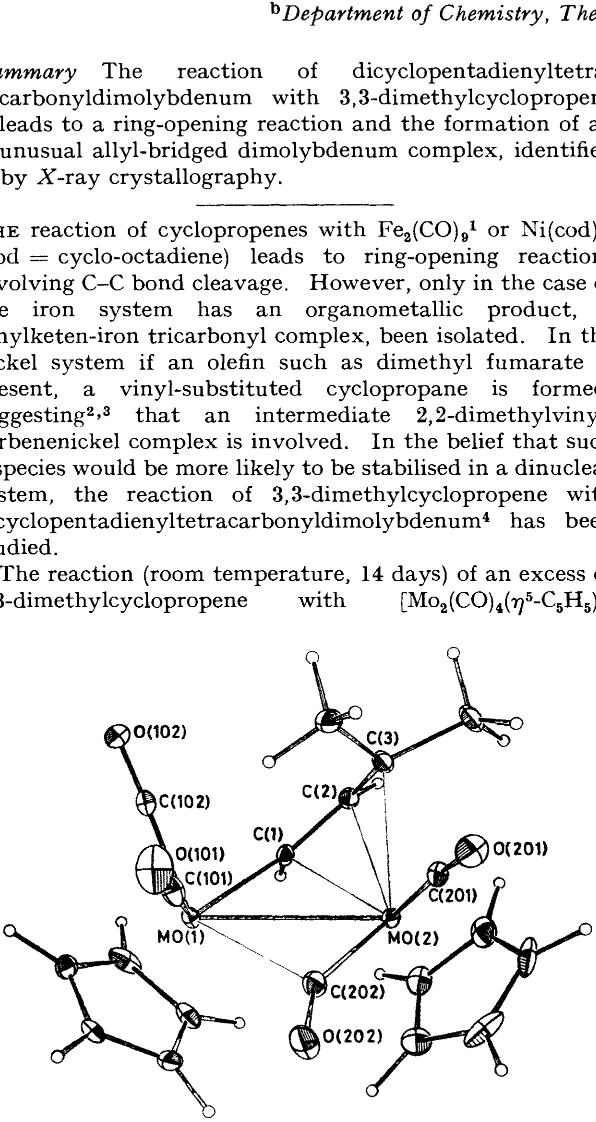
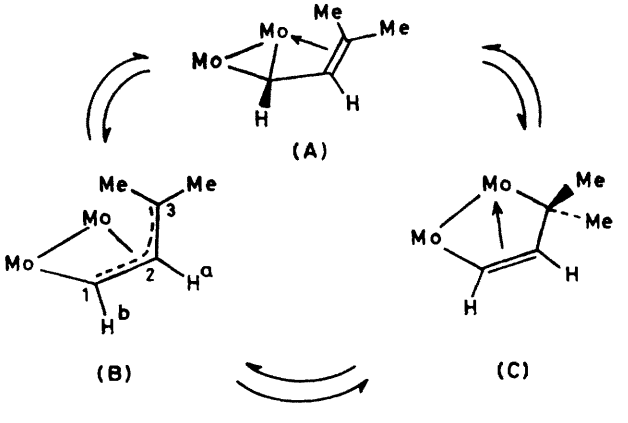


Figure. The molecular structure of $[Mo_2(CO)_4(CH{\cdot}CH{\cdot}CMe_2)(\eta\text{-}C_5H_5)_2]$. Important internuclear separations include: Mo(1)–Mo(2) 3.1057(9), Mo(1)–C(1) 2·126(6), Mo(1)–C(101) 1·948(7), Mo(1)–C(102) 1·948(7), C(101)–O(101) 1·151(10), C(102)–O(102) 1·152(9), Mo(1) . . . C(202) 2·473(7), Mo(2)–C(1) 2·249(5), Mo(2)–C(2) 2·270(6), Mo(2)–C(3) 2·477(7), Mo(2)–C(201) 1·935(7), Mo(2)–C(202) 1·990(7), C(201)–O(201) 1·153(8), C(202)–O(202) 1·179(9), C(1)–C(2) 1·397(8), and C(2)–C(3) 1·418(9) Å.

Crystal data: $C_{19}H_{18}Mo_2O_4$, M = 502·2, monoclinic, space group $P2_1/a$, a = 17·304(12), b = 7·832(8), c = 14·417(10) Å, β = 113·61(6)°, U = 1790(2) Å^3, Z = 4, D_c = 1·863 g cm^{-3}, $F(000)$ = 992 electrons, μ(Mo-K_α) = 14·0 cm^{-1}. Of a total of 3 510 independent reflection-intensities measured (Enraf Nonius CAD 4 diffractometer, Mo-K_α radiation, λ 0·710 69 Å) to θ_{max} 26·0°, 3 165 [$F \geqslant 2{\cdot}0\,\sigma(F)$] were used to solve (Patterson and difference-Fourier techniques) and refine (full-matrix least squares) the structure to R 0·061, R_w 0·070.‡ The hydrogen atoms bound to C(1) and C(2) (Figure) have been positionally refined, whilst all other hydrogens are set in calculated positions.

As is illustrated by the Figure the reaction has resulted in the 2,3-carbon–carbon bond cleavage of the 3,3-dimethylcyclopropene and the stabilisation of the resulting C_3 fragment by co-ordination (4-electron donor) to the two molybdenum centres. There are three possible bonding modes for the fragment C(1)-C(2)-C(3) to the di-molybdenum centre present in (**1**) and these are illustrated in Scheme 1. The inequivalence of the distance between C(1) and the two molybdenum atoms and the clear semi-bridging nature (Figure) of the C(202)–O(202) group imply that there is little contribution from the bonding mode (A),§ which resembles



Scheme 1.

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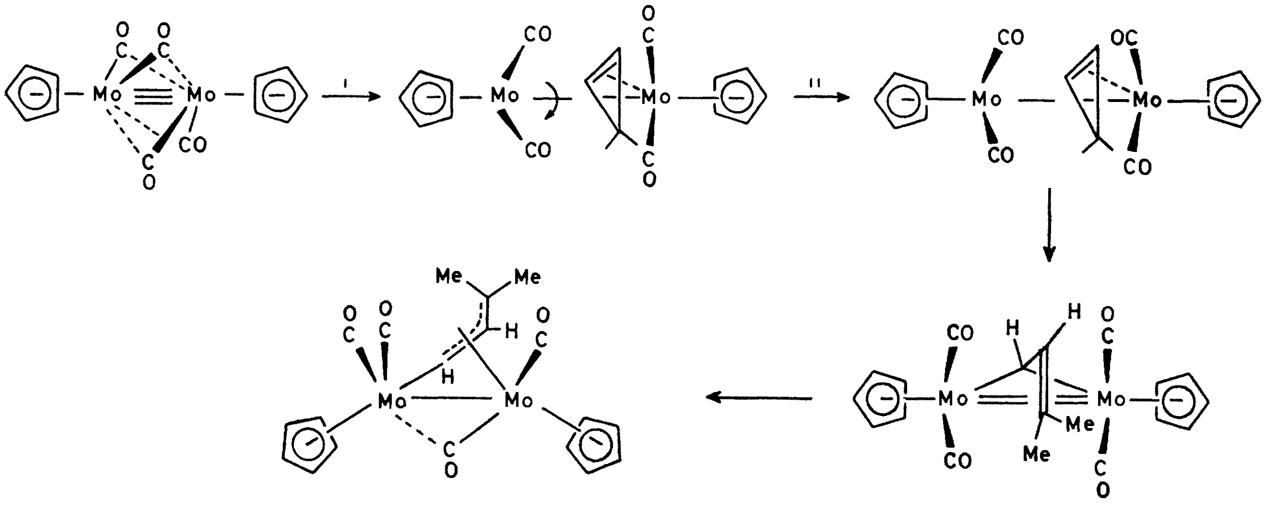
† I.r. $\nu_{CO}(CH_2Cl_2)$ 1 944s, 1 901m, 1 849m, and 1 769m cm^{-1}; ^{1}H n.m.r. (CD_2Cl_2, room temperature), τ −0·73 (d, 1 H, H^b, J\{HH\} 10 Hz), 4·12 (d, 1 H, H^a, J\{HH\} 10 Hz), 4·62 (s, 5 H, C_5H_5), 4·87 (s, 5 H, C_5H_5), 9·3 (s, 3 H, Me), and 9·9 (s, 3 H, Me).

‡ 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.

§ In contrast, the bonding mode (A) is preferred in the solid state structure of the complex $[Fe_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1,\eta^3\text{-}C(CO_2Me)C(CO_2Me)CHMe\}(\eta\text{-}C_5H_5)_2]$: A. F. Dyke, S. A. R. Knox, P. J. Naish, and G. E. Taylor, *J. Chem. Soc., Chem. Commun.*, 1980, 803.

a μ-vinylcarbene system, and suggest instead a σ [to Mo(1)], η-allyl [to Mo(2)] description, i e structure (B) Apart from the observed differences in metal–C(1) lengths, the overall arrangements of the organo-dimetal fragment resembles that observed[5] in the molecule $[W_2(CO)_9(\mu\text{-CH CH CMe}_2)]$, especially in terms of a long metal–C(3) interaction, 2 477(7) Å in complex (**1**), in spite of a significant twist (*ca* 32°) about C(2)–C(3) to give a maximum overlap with the second molybdenum centre, this interaction leading to the formation of a bridged vinylcarbene-complex This bridged species then changes its bonding mode in concert with the formation of a semi-bridged carbonyl to form the dinuclear complex (**1**) Thus, this reaction provides an interesting example of the involvement of two metal centres in an unusual ring-opening reaction where the formal bond order between the two metal centres changes to accomodate the various interactions A metal-metal bond order 'switch' has recently been postulated[9] in the linking of acetylenes at a dimetal centre



(1)

SCHEME 2 i, 3,3-Dimethylcyclopropene, ii, rotation

The formation of complex (**1**) is especially interesting in view of the report[6,7] that the $Mo\equiv Mo$ bond present in $[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$ does not react with olefins We suggest that the 3,3-dimethylcyclopropene co-ordinates on to one of the good acceptor orbitals[8] present on opposite sides of the Mo–Mo vector (Scheme 2) This is followed by rotation of one of the $C_5H_5Mo(CO)_2$ groups, thus allowing interaction with the second molybdenum centre.

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