Synthesis and Mechanism of Formation of Dicarbonyl(η^4-trimethylenemethane)(η^5-pentamethylcyclopentadienyl)molybdenum Tetrafluoroborate

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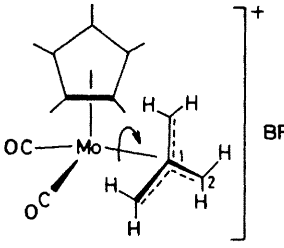
Summary Reaction of $[Mo(CO)_3(\eta^5\text{-}C_5Me_5)]BF_4$ generated from $[Mo(CO)_3(\eta^5\text{-}C_5Me_5)]_2$ and $AgBF_4$ with methylenecyclopropane, *cis*-, and *trans*-2,3-dimethylmethylenecyclopropanes affords dicarbonyl(η^4-trimethylenemethane)(η^5-pentamethylcyclopentadienyl)molybdenum tetrafluoroborate complexes, the stereochemistry of the reactions implicating a disrotatory ring-opening reaction.

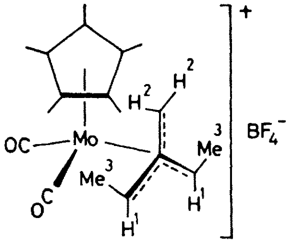
As part of a general interest[1] in transition metal-promoted reactions of small-ring organic molecules, the chemistry of methylenecyclopropane has attracted considerable attention. Catalytic dimerisation and co-dimerisation reactions have been observed,[2] in which the three-membered ring remains intact or undergoes C–C bond fission. In recent studies of reactions which involve cleavage of the 2,3-bond, evidence has been obtained for the intermediacy of η^4-trimethylenemethane-nickel and -palladium complexes.[3,4] These observations complement Noyori's earlier reported conversion by $[Fe_2(CO)_9]$ of a substituted methylenecyclopropane into a tricarbonyl (η^4-trimethylenemethane)iron complex.[5] Despite the obvious interest of such reactions and the potential chemistry of η^4-trimethylenemethane complexes, attempts to understand the mechanism of the ring-opening reaction, and to extend the synthetic reaction to other transition metals, have been unsuccessful.[6,7] In this paper we report the synthesis of the first cationic η^4-trimethylenemethane complex and experiments which provide mechanistic insight into metal-mediated ring-opening reactions.

Addition (room temperature) of silver tetrafluoroborate to a methylene chloride solution of methylenecyclopropane and $[Mo(CO)_3(\eta^5\text{-}C_5Me_5)]_2$ led (4 h) to the formation of silver metal and the methylene chloride soluble air-stable yellow crystalline complex (**1**), dicarbonyl(η^4-trimethylenemethane)(η^5-pentamethylcyclopentadienyl)molybdenum tetrafluoroborate [$\nu_{CO}(CH_2Cl_2)$ 2 055s and 2 012s cm^{-1}; ^1H resonances (CD_3NO_2, 30 °C) τ 7·2 (s, 6H, C - - - - CH_2) and 7·9 (s, 15H, C_5Me_5); ^{13}C resonances (CD_3NO_2, 30 °C) 119·0 (s, C^1), 106·6 (s, C_5Me_5), 69·0 (s, C^2), and 11·6 p.p.m. (s, C_5Me_5)]. The low-field shift of the central carbon C^1 reflects the trend observed[8] for ^{13}C shifts of η^3-allyl complexes, and indicates a higher π-bond order for this central carbon compared to the three terminal (C^2) carbon atoms. The observed magnetic equivalence of the three terminal CH_2 groups implies that at room temperature the trimethylenemethane unit is freely rotating about the metal–central carbon vector.

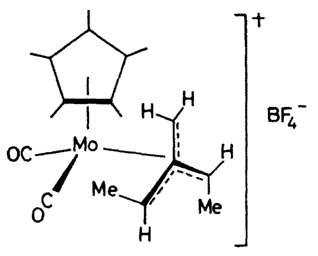
This is the first example of a cationic trimethylenemethane complex and it was important to examine the stereochemistry of the ring-opening reaction. A similar reaction with *cis*-2,3-dimethylmethylenecyclopropane afforded yellow crystals of (**2**) dicarbonyl(η^4-dimethyltrimethylenemethane)(η^5-pentamethylcyclopentadienyl)molybdenum tetrafluoroborate. Examination of the ^{13}C and ^1H n.m.r. spectra† showed that the ring-opening reaction was stereospecific affording only the *syn*-, *syn*-dimethyl substituted isomer (see Scheme). The corresponding reaction with



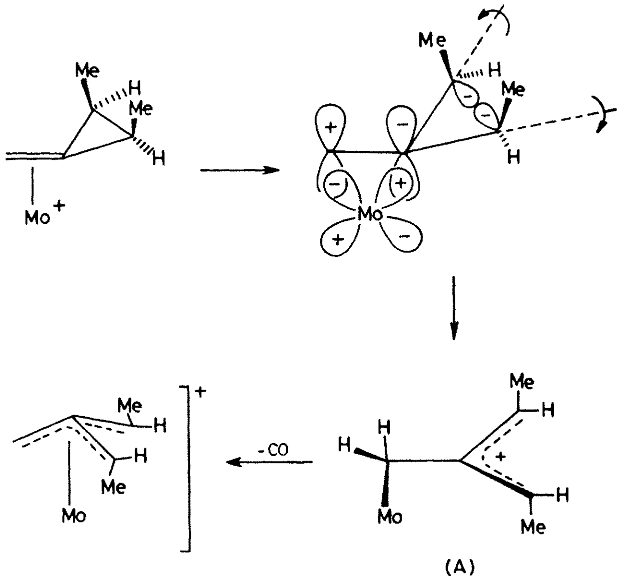
(1)



(2)



(3)



Scheme. Ligands omitted for clarity.

† $\nu_{CO}(CH_2Cl_2)$ 2 045 s and 2 000 s cm^{-1}; ^1H resonances (CD_3NO_2, 30 °C) τ 6·25 (d, 2H, H^2, $^4J_{21}$ 2 Hz.); 7·2—7·45 (m, 2H, H^1), 7·9 (s, 15H, C_5Me_5), and 8·2 (d, 6H, Me^3, $^3J_{31}$ 9 Hz.); ^{13}C resonances (CD_3NO_2, 30 °C) 115·6 (s, C^1), 105·8 (s, C_5Me_5), 87·9 (s, C^3), 61·9 (s, C^2), 14·9 (s, Me^3), and 11·0 p.p.m. (s, C_5Me_5).

trans-2,3-dimethylmethylenecyclopropane selectively produced yellow crystals of the isomeric *syn*-, *anti*-dimethyltrimethylenemethane complex (**3**).

If we make the reasonable assumption that the reaction involves capture of a 16-electron species $[Mo(CO_3)(\eta^5$-$C_5Me_5)]BF_4$ (generated by redox cleavage of the Mo–Mo bond) by the methylenecyclopropane then co-ordination would be expected in the case of *cis*-2,3-dimethylmethylenecyclopropane to occur preferentially on the face of the olefin opposite to the methyl groups. Previous studies[7] suggest that co-ordination would result in bending of the 3-membered ring away from the metal. Thus, the observed stereochemistry of the product (**2**) requires that a *disrotatory*[9] ring-opening reaction occurs (see Scheme) in such a way as to increase the electron density on the side of the three-membered ring opposite to the co-ordinated molybdenum. As illustrated, the resulting overlap results in the metal changing its bonding mode from π to σ, and the formation of a delocalised allylic carbonium ion. Loss of carbon monoxide and interaction of the electrophilic centre with the metal, which slides over to become bonded to all four carbon atoms, completes the reaction sequence.‡ It is interesting that a zwitterionic species related to the intermediate (A) has been implicated[10] in the 1,3-chloropalladation of 2,3-dimethylenecyclopropanes to form η^3-allylic species.

We are exploring the reactions of (**1**), (**2**), and (**3**) with nucleophilic reagents where attack can, in principle, occur either at the central or outer carbon atoms, and also the synthetic implications of this ready metal-promoted ring-opening reaction.

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‡ *Added in proof*: Recently (A. R. Pinhas and B. K. Carpenter, *J.C.S. Chem. Comm.*, 1980, 17) a disrotatory outward ring-opening process has also been established for the iron carbonyl promoted conversion of 2-phenylmethylene[3-$^2H_1$]cyclopropane to a η^4-trimethylene methane complex. However, in contrast with the molybdenum system loss of carbon monoxide appears to occur before ring-opening.

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