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Reactions of Co-ordinated Ligands. Part 30.[1] The Transformation of Methylenecyclopropanes into Cationic η^4-Trimethylenemethanemolybdenum Complexes, Reactions with Nucleophilic Reagents, and the Molecular Structure of $[Mo\{\eta^4\text{-}C(CH_2)_3\}(CO)_2(\eta\text{-}C_5Me_5)][BF_4]$ †

Stephen R. Allen, Stephen G. Barnes, Michael Green,* Grainne Moran, and Lynda Trollope
Department of Inorganic Chemistry, The University, Bristol BS8 1TS
Nicholas W. Murrall and Alan J. Welch
Dewar Crystallographic Laboratory, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ
Dima M. Sharaiha
Department of Chemistry, The City University, London EC1V 0HB

Reaction of $[Mo_2(CO)_6(\eta\text{-}C_5Me_5)_2]$ with methylenecyclopropane and $AgBF_4$ in CH_2Cl_2 affords the cationic trimethylenemethane complex $[Mo\{\eta^4\text{-}C(CH_2)_3\}(CO)_2(\eta\text{-}C_5Me_5)][BF_4]$. Methylenecyclopropane and 2,2-dimethylmethylenecyclopropane react with $[Mo(NCMe)_2(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ to give $[Mo\{\eta^4\text{-}C(CH_2)_3\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ and $[Mo\{\eta^4\text{-}C(CH_2)_2CMe_2\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ respectively. A single-crystal *X*-ray diffraction study of $[Mo\{\eta^4\text{-}C(CH_2)_3\}(CO)_2(\eta\text{-}C_5Me_5)][BF_4]$ confirmed that ring opening of methylenecyclopropane had occurred. The complex crystallises in the centrosymmetric orthorhombic space group *Pbca* with $a = 12.822(2)$, $b = 12.311(3)$, $c = 22.660(4)$ Å, and $Z = 8$ ion pairs. The structure has been solved by conventional methods and refined by full-matrix least squares to $R = 0.0674$ for 2 747 observed reflections at 268 ± 1 K. In the cation the trimethylenemethane ligand adopts an orientation that is *syn* with respect to the OC–Mo–CO angle. It is pyramidal with the CH_2 groups bent towards the molybdenum atom by an average of 12.4°. There is intramolecular congestion involving the C_5Me_5 and $C(CH_2)_3$ ligands that may contribute towards the observed asymmetric bonding of the former to the metal atom. Extended Hückel molecular-orbital calculations suggest that the observed *syn* stereochemistry is electronically preferred, and that the barrier to rotation of the $\eta^4\text{-}C(CH_2)_3$ ligand relative to a $Mo(CO)_2(\eta\text{-}C_5H_5)^+$ fragment is high. The stereochemistry of the ring-opening reaction is disrotatory-out as exemplified by the conversion of *cis*- and *trans*-2,3-dimethylmethylenecyclopropane into *syn,syn*-dimethyl and *syn,anti*-dimethyl-trimethylenemethane complexes. The reaction of these cationic η^4-trimethylenemethane complexes with the nucleophiles BH_4^-, OH^-, $CuMe_2^-$, and SPh^- affords η^3-allylic complexes derived from attack on the peripheral carbons.

Methylenecyclopropanes react with compounds of Fe^0, Rh^I, Ir^I, Pt^{II}, and Pt^0 to form simple η^2-bonded alkene complexes in which the three-membered ring remains intact.[2,3] However, these small-ring compounds are also known to undergo transition-metal-mediated reactions where carbon–carbon cleavage occurs. This is illustrated by the reaction of $[Fe_2(CO)_9]$ with methylene-2-phenylcyclopropane forming tricarbonyl(η^4-trimethylenephenylmethane)iron, a detailed study [4] with deuterium-labelled methylene-2-phenylcyclopropane showing that a distotatory-out ring-opening reaction occurs. Furthermore, a recent study [5] of the chloropalladation reactions of methylenecyclopropanes carrying alkyl substituents on the three-membered ring showed that cleavage of the 2,3-σ bond occurred in a disrotatory manner. Ring cleavage also occurs in the palladium(0)-catalysed [6–10] cycloaddition reactions of methylenecyclopropanes, although the question [11] as to whether these reactions involve η^4-trimethylenemethane complexes remains to be answered. We had previously observed [12] that $[Mo(CO)_3(\eta\text{-}C_5Me_5)]^+$ reacts with methylenecyclopropane to form the first cationic η^4-bonded trimethylenemethane complex, and this paper describes a detailed study of this reaction.

Results and Discussion

In exploring the chemistry of cationic molybdenum complexes it was observed that room-temperature addition of $AgBF_4$ to a methylene chloride solution of $[Mo_2(CO)_6(\eta\text{-}C_5Me_5)_2]$ and methylenecyclopropane led to a rapid redox reaction as evidenced by the formation of a silver mirror, and the production of two molybdenum complexes $[Mo(CO)_4(\eta\text{-}C_5Me_5)][BF_4]$ and $[Mo\{\eta^4\text{-}C(CH_2)_3\}(CO)_2(\eta\text{-}C_5Me_5)][BF_4]$ (1). Examination of the ^1H and ^{13}C n.m.r. and i.r. spectra suggested that (1) was a trimethylenemethane complex presumably formed by 2,3-σ-bond cleavage of an intermediate η^2-bonded methylenecyclopropane species. A related reaction occurred when methylenecyclopropane was added to *cis*-bis(acetonitrile)dicarbonyl(η-cyclopentadienyl)molybdenum tetrafluoroborate ‡ dissolved in CH_2Cl_2 affording a good yield of the cation (2), the cyclopentadienyl analogue of (1). The reaction is not limited to unsubstituted methylenecyclopropane since 2,2-dimethylmethylenecyclopropane also reacted smoothly with $[Mo(NCMe)_2(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ to give a good yield of complex (3).

In order to confirm that ring opening had in fact occurred a single-crystal *X*-ray diffraction study was carried out with a suitable crystal of complex (1). Figure 1 represents a perspective view of the cation of (1), and demonstrates the atomic numbering scheme adopted. Table 1 lists the internuclear distances, and Table 2 selected interbond angles. The cation has effective C_s symmetry about the plane defined by atoms

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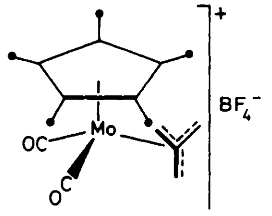
† Dicarbonyl(η-pentamethylcyclopentadienyl)(η^4-trimethylenemethane)molybdenum tetrafluoroborate.

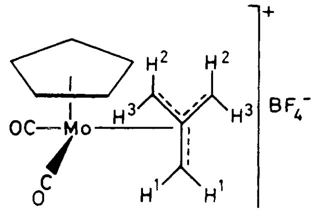
Supplementary data available (No. SUP 23876, 21 pp.): thermal parameters, least-squares planes, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. units employed: cal = 4.184 J; eV ≈ 1.60×10^{-19} J.

‡ Prepared by protonation ($HBF_4\cdot Et_2O$) of $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$ dissolved in CH_2Cl_2 followed by reaction with MeCN.[13]



(1)



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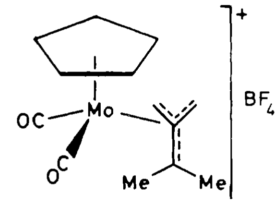

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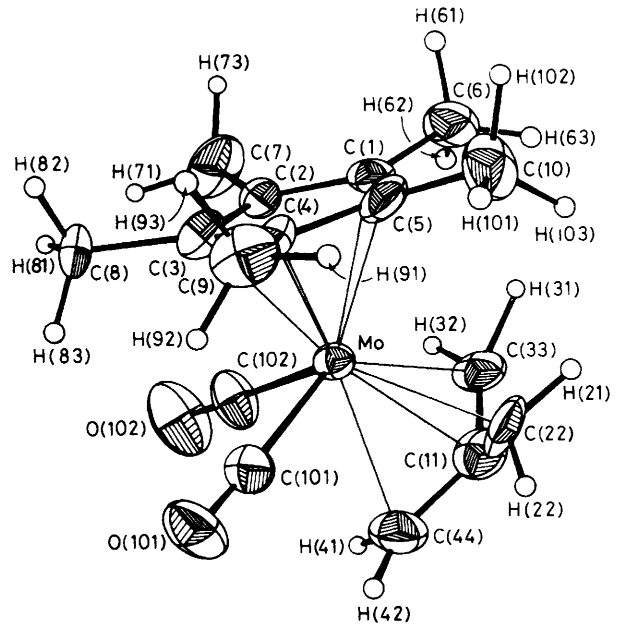
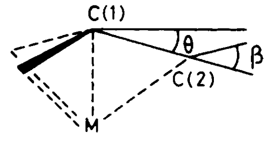


Figure 1. View of the cation $[Mo\{\eta^4\text{-}C(CH_2)_3\}(CO)_2(\eta\text{-}C_5Me_5)]^+$. Thermal ellipsoids are drawn at the 30% probability level, except for H atoms which have an artificial radius of 0.1 Å for clarity. H(72) is obscured by C(7)

Table 1. Internuclear distances (Å) * in complex (1)

Mo–C(1)	2.374(9)	Mo–C(5)	2.349(9)
Mo–C(2)	2.314(8)	Mo–C(4)	2.318(9)
Mo–C(3)	2.296(9)		
Mo–C(11)	2.213(10)		
Mo–C(22)	2.324(9)	Mo–C(33)	2.358(9)
Mo–C(44)	2.392(11)		
Mo–C(101)	2.022(10)	Mo–C(102)	2.032(10)
C(1)–C(2)	1.429(14)	C(5)–C(4)	1.464(14)
C(2)–C(3)	1.433(14)	C(4)–C(3)	1.400(12)
C(5)–C(1)	1.396(14)		
C(1)–C(6)	1.471(13)	C(5)–C(10)	1.518(14)
C(2)–C(7)	1.477(13)	C(4)–C(9)	1.476(13)
C(3)–C(8)	1.504(12)		
C(11)–C(22)	1.460(16)	C(11)–C(33)	1.394(14)
C(11)–C(44)	1.402(17)		
C(101)–O(101)	1.122(11)	C(102)–O(102)	1.114(11)
C(22)–H(21)	1.06(8)	C(33)–H(31)	1.17(8)
C(22)–H(22)	0.91(9)	C(33)–H(32)	1.01(8)
C(44)–H(41)	1.06(8)	C(44)–H(42)	0.90(10)
B–F(1)	1.29(3)	B–F(8)	1.52(7)
B–F(2)	1.40(2)	B–F(9)	1.38(4)
B–F(3)	1.41(5)	B–F(10)	1.43(4)
B–F(4)	1.38(3)	B–F(11)	1.34(2)
B–F(5)	1.44(3)	B–F(12)	1.37(5)
B–F(6)	1.46(3)	B–F(13)	1.39(5)
B–F(7)	1.39(5)	B–F(14)	1.46(7)

* Estimated standard deviations are given in parentheses throughout this paper.



(I)

Mo, C(11), C(44), C(3), and C(8), and Tables 1 and 2 are organised so that parameters related across this approximate mirror are easily compared.

The complexed η^4-trimethylenemethane present in (1) is pyramidal, not flat. The reasons for pyramidalisation have been well documented [14] and they may be quantified by the two angular parameters θ and β shown in (I), where β is the angle between the line C(1)–C(2) and the plane $C(2)H_2$. For the complex $[Fe\{\eta^4\text{-}C(CH_2)_3\}(CO)_3]$ [15] $\theta = 13.6°$ and $\beta = 14.4°$, and in the case of $[Fe\{\eta^4\text{-}C(CH_2)_2CHPh\}(CO)_3]$ θ values of 13.9, 13.0, and 11.7° are recorded.[16] Tricarbonyl(η^4-7-methylenecyclohepta-1,3,5-triene)iron also contains an iron–trimethylenemethane linkage, with θ = 11.0, 10.1, and 10.1° and β = 14.8, 15.9, and 23.4°.[17]

In complex (1), θ values are 14.6(5), 12.0(6), and 10.6(6)° to C(22), C(33), and C(44) respectively. The bend-back angles at C(22) and C(44) are calculated as 55.1 and 6.1° respectively, whilst the $C(33)H_2$ plane appears to be tipped *towards* the metal atom, with $\beta = -15.7°$. However, the positions of the hydrogen atoms are subject to relatively large errors, and we are less confident about the molecular parameters derived from them.

In all the above species the pyramidalisation of the trimethylenemethane fragment is, although significant, insufficiently severe to cause the distal carbon atoms to approach closer to the metal than does the central one; thus, for the iron complexes [15–17] Fe–C(central) distances lie within the narrow range 1.932—1.946 Å, whilst Fe–C(outer) values span 2.098—2.175 Å. In cation (1) the $Mo–C(CH_2)_3$ distances are longer, but this difference is essentially maintained, Mo–C(11) being 2.213(10) Å whilst Mo–C(22,33,44) lie within 2.324(9)—2.392(11) Å. Some asymmetry in the C–C bonds of the trimethylenemethane ligand of (1) may be evident, the difference between C(11)–C(22) and C(11)–C(33) just lying on the verge of significance. These bond lengths extend in both directions the previous [15–17] range of such distances, 1.405(4)—1.45(2) Å.

Parameters within the $Mo(CO)_2$ moiety are unexceptional, but the η-C_5Me_5 ligand shows some asymmetry that indicates intramolecular steric congestion between it and the trimethylenemethane ligand. Thus, Mo–C(1,5) > Mo–C(2,4) > Mo–C(3), demonstrating that the ligand is slightly tilted away from C(22) and C(33), and H · · · H contacts of 2.03, 2.05, and 2.07 Å exist between H(31) and H(63) and H(62), and H(21) and H(103), respectively. Although, consistent with this,

Table 2. Selected interbond angles (°) *

C(1)–Mo–C(2)	35.5(3)	C(4)–Mo–C(5)	36.6(3)
C(2)–Mo–C(3)	36.2(4)	C(3)–Mo–C(4)	35.3(3)
C(1)–Mo–C(5)	34.4(3)		
C(11)–Mo–C(22)	37.5(4)	C(11)–Mo–C(33)	35.3(4)
C(11)–Mo–C(44)	35.2(4)		
C(22)–Mo–C(44)	60.3(5)	C(33)–Mo–C(44)	61.1(4)
C(22)–Mo–C(33)	62.1(4)		
C(11)–Mo–Z	137.5(6)		
C(101)–Mo–C(102)	88.9(4)		
C(101)–Mo–Z	108.5(7)	C(102)–Mo–Z	107.5(6)
C(101)–Mo–C(11)	102.5(4)	C(102)–Mo–C(11)	101.3(5)
Mo–C(1)–C(2)	70.0(5)	Mo–C(5)–C(4)	70.6(5)
Mo–C(1)–C(5)	71.8(5)	Mo–C(5)–C(1)	73.8(5)
Mo–C(1)–C(6)	128.9(7)	Mo–C(5)–C(10)	131.1(7)
C(5)–C(1)–C(2)	106.7(8)	C(1)–C(5)–C(4)	110.2(8)
C(5)–C(1)–C(6)	125.1(11)	C(1)–C(5)–C(10)	125.5(11)
C(2)–C(1)–C(6)	127.2(9)	C(4)–C(5)–C(10)	123.4(10)
Mo–C(2)–C(3)	71.2(5)	Mo–C(4)–C(3)	71.5(5)
Mo–C(2)–C(1)	74.6(5)	Mo–C(4)–C(5)	72.9(5)
Mo–C(2)–C(7)	130.4(8)	Mo–C(4)–C(9)	131.0(7)
C(1)–C(2)–C(3)	108.4(8)	C(5)–C(4)–C(3)	105.5(8)
C(1)–C(2)–C(7)	123.7(9)	C(5)–C(4)–C(9)	124.8(9)
C(3)–C(2)–C(7)	126.6(6)	C(3)–C(4)–C(9)	128.2(8)
Mo–C(3)–C(2)	72.5(5)	Mo–C(3)–C(4)	73.2(5)
Mo–C(3)–C(8)	127.9(7)		
C(2)–C(3)–C(8)	125.0(9)	C(4)–C(3)–C(8)	125.2(9)
C(2)–C(3)–C(4)	109.2(2)		
Mo–C(101)–O(101)	177.3(9)	Mo–C(102)–O(102)	177.0(10)
Mo–C(11)–C(22)	75.4(5)	Mo–C(11)–C(33)	78.0(6)
Mo–C(11)–C(44)	79.4(6)		
Mo–C(22)–C(11)	67.2(5)	Mo–C(33)–C(11)	66.7(5)
Mo–C(44)–C(11)	65.4(6)		
C(22)–C(11)–C(44)	111.8(11)	C(33)–C(11)–C(44)	119.4(12)
C(22)–C(11)–C(33)	115.4(10)		
Mo–C(22)–H(21)	114(4)	Mo–C(33)–H(31)	99(4)
Mo–C(22)–H(22)	126(5)	Mo–C(33)–H(32)	92(4)
H(21)–C(22)–C(11)	105(4)	H(31)–C(33)–C(11)	126(4)
H(22)–C(22)–C(11)	109(5)	H(32)–C(33)–C(11)	138(5)
H(21)–C(22)–H(22)	118(6)	H(31)–C(33)–H(32)	92(6)
Mo–C(44)–H(41)	105(5)	Mo–C(44)–H(42)	114(6)
H(41)–C(44)–C(11)	125(5)	H(42)–C(44)–C(11)	137(6)
H(41)–C(44)–H(42)	97(7)		

* Z is the centroid of the cyclopentadienyl ring and has fractional co-ordinates −0.015 76(16), 0.198 18(18), 0.161 71(9).

C(1)–C(5) is the shortest pentagonal distance, C–C bonds around the ring are arranged C(1)–C(5), C(3)–C(4) < C(1)–C(2), C(2)–C(3) < C(4)–C(5). The C_5 ring is reasonably planar (root mean square deviation 0.006 Å, see SUP 23876), but shows a small distortion towards an envelope fold across C(2) ··· C(4) of 1.4°, away from the metal atom. It appears that the intramolecular crowding between η-C_5Me_5 and trimethylenemethane ligands does not cause increased out-of-plane bending of the methyl groups pendant to C(1) and C(5) since, referred to the five-atom ring, these are depressed (away from Mo) by 5.9 and 9.2° respectively, *cf.* 9.4, 8.4, and 9.8° for corresponding angles at C(2), C(3), and C(4).

The fluorine atoms of the tetrafluoroborate anion are disordered over 14 positions whose population parameters (p.p.) range from 10 to 55%; B–F distances span 1.29(3)—1.52(7) Å. All F atoms were given the same (fixed) thermal parameter in refinement, but in Figure 2 the anion is drawn such that U_F values are in the ratio of their p.p. Although possible discrete tetrahedra can be picked out [*e.g.* BF-(1,2,4,11), F–B–F angles between 88 and 115°], the disorder is by no means 'clean.'

Figure 3 presents a view of the crystal packing. There are no unusual features.

There are clearly two limiting conformations of the $[Mo\{\eta^4$-

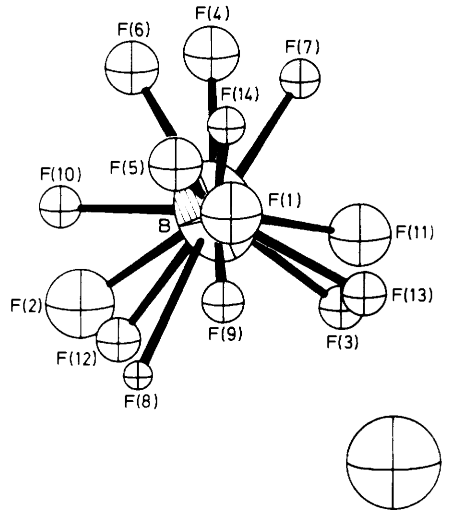


Figure 2. The disordered BF_4^- anion. The thermal parameter of each fluorine sphere represents its fractional occupation. For scaling purposes the lower right-hand sphere corresponds to 100% occupation

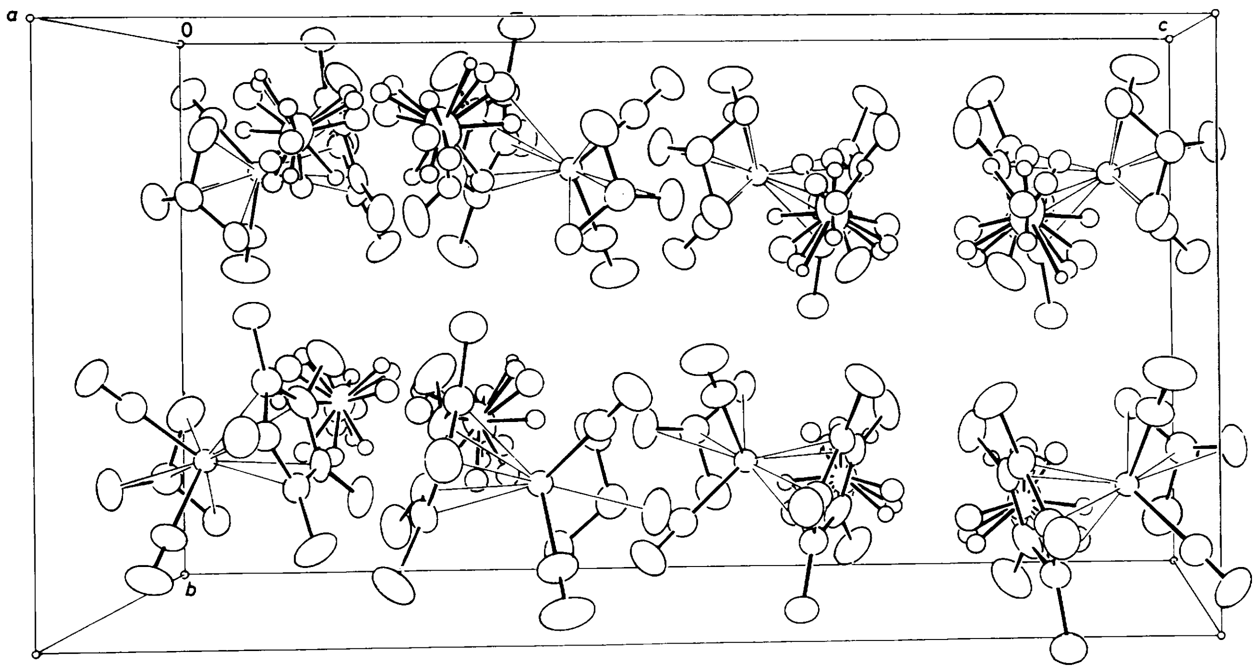
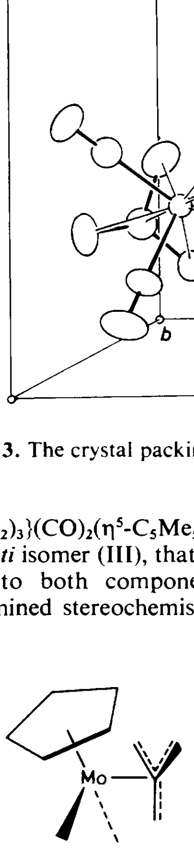
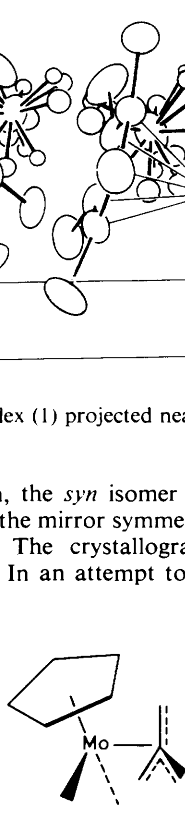


Figure 3. The crystal packing of complex (1) projected nearly onto the (011) plane. Hydrogen atoms are omitted for the sake of clarity

$C(CH_2)_3\}(CO)_2(\eta^5\text{-}C_5Me_5)]^+$ cation, the *syn* isomer (II) and the *anti* isomer (III), that maintain the mirror symmetry common to both component parts. The crystallographically determined stereochemistry is *syn*. In an attempt to explore



syn isomer
(II)



anti isomer
(III)

if this stereochemistry is that which is electronically preferred it is convenient to regard the cation as a combination of $Mo(CO)_2(\eta^5\text{-}C_5Me_5)^+$ and $C(CH_2)_3$ fragments. Frontier orbitals of both fragments (in the case of the metal fragment, the $\eta\text{-}C_5H_5$ analogue) have been reported by Albright.[18] The valence orbitals [19] of $Mo(CO)_2(\eta\text{-}C_5H_5)^+$ (C_s symmetry) are drawn on the left-hand side of Figure 4. The important π orbitals of $C(CH_2)_3$ (refs. 5 and 14) are also shown in Figure 4, in the centre for the *syn* molecular conformation and on the right for the *anti*. Note that the C_4 fragment here is planar, and has D_{3h} symmetry. Our $C(CH_2)_3$ ligand orbitals are labelled in only C_s symmetry (for consistency with those of the metal fragment), with the representations in parentheses denoting their origin.

Inspection of Figure 4 readily leads to an appreciation that the crystallographically observed *syn* stereochemistry is electronically derived, since in this conformation the $1a'$–$2a'(e'')$ and a''–$a''(e'')$ interactions (metal–ligand), both of which are two-electron stabilising interactions, are maximised. In both conformations the $2a'$–$1a'(a_2'')$ interactions are four-electron destabilising, and will have different overlap integrals whose relative magnitude it is difficult to assess by simple inspection. In both cases, however, the destabilisation will be mitigated somewhat by the presence of the higher-lying $3a'$ (metal) orbital, and thus the overall destabilisation could be small in either extreme.

An important difference between the $Mo(CO)_2(\eta\text{-}C_5H_5)^+$ and $Fe(CO)_3$ fragments is that whilst the a'' orbital of the former corresponds to one component of the $2e$ [18,20] set of the latter there is no equivalent of the second $2e$ component, which is noded orthogonally to the first. In the complex $[Fe\{\eta^4\text{-}C(CH_2)_3\}(CO)_3]$ this second $2e$ component interacts in bonding fashion with $a''(e'')$ of $C(CH_2)_3$ in the eclipsed conformation, albeit less effectively than does the first component in the staggered form. The absence of an equivalent stabilising interaction in the *anti* conformer of (1) might reasonably be expected to result in a larger difference in total energy between the two conformers, and indeed it does. For $[Fe\{\eta^4\text{-}C(CH_2)_3\}(CO)_3]$ the staggered-minus-eclipsed energy difference, with flat $C(CH_2)_3$, is calculated [14,18] to be 20.8 kcal mol^{-1}. From extended-Hückel molecular-orbital (EHMO) calculations on idealised models of $[Mo\{\eta^4\text{-}C(CH_2)_3\}(CO)_2(\eta\text{-}C_5H_5)]^+$ using parameters specified in Table 3, we calculate the *syn*-minus-*anti* energy difference in the molybdenum trimethylenemethane complex [flat $C(CH_2)_3$] to be 45.5 kcal mol^{-1}, pyramidalisation ($\theta = 12°$, $\beta = 12°$) affording a slightly greater (46.7 kcal mol^{-1}) difference between the *syn* and *anti* conformers.

This difference is nearly, but not quite, the same as the barrier of rigid rotation of the flat $C(CH_2)_3$ ligand about the metal–ligand axis. In Figure 5 are drawn two nearly parallel curves. They represent the change in the sum of one-electron energies with rotation of the $\eta^4\text{-}C(CH_2)_3$ ligand from the *anti* conformation (angle = 0°) to the *syn* (angle = 60°). The energy scale is in eV, but absolute values are arbitrary, and the upper (less stable) curve is for a flat $C(CH_2)_3$ ligand. Clearly, the *anti* conformer is metastable and resides in a shallow, high-lying potential well. The least stable rotamer occurs when the angle is *ca.* 15.5°, and corresponds to eclipsing (in *z*-axis projection) of a carbonyl ligand by one arm of

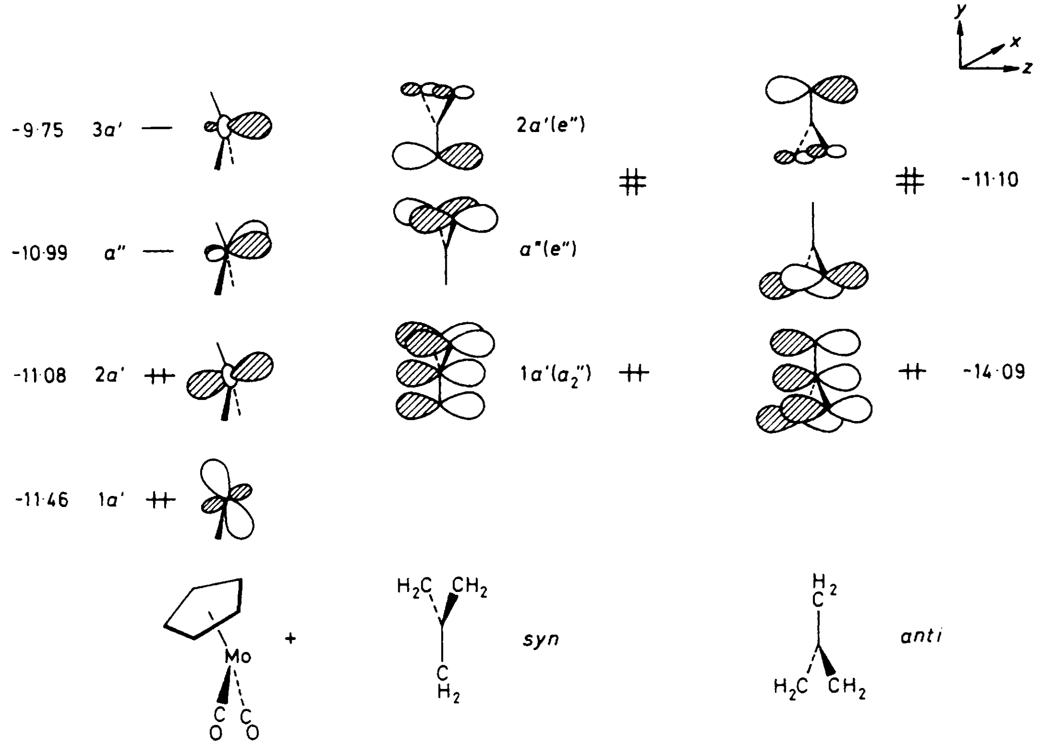


Figure 4. The frontier orbitals of $Mo(CO)_2(\eta-C_5H_5)^+$ and of $C(CH_2)_3$. The Figure is not to scale but the orbital energies (eV) are specified

Table 3. Parameters used in EHMO calculations [a]

Orbital		H_{ii}/eV	ξ_1	Distances (Å) and angles (°) [c]	
Mo	4d [b]	−10.50	4.54	Mo–Z 2.02	OC–Mo–CO 90.0
	5s	−8.34	1.96	Mo–C(O) 1.97	Z–Mo–CO 126.7
	5p	−5.24	1.92	C–H 1.09	OC–Mo–L 90.0
				C–O 1.15	
C	2s	−21.40	1.625	C–Z 1.21	
	2p	−11.40	1.625	C–C(tmm) 1.40	
				$Mo–CH_2$(tmm) 2.36 (flat and bent tmm)	
O	2s	−32.30	2.275	$Mo–C(CH_2)_3$ 1.90 (flat)	
	2p	−14.80	2.275	$Mo–C(CH_2)_3$ 2.2132 (bent)	
				$Mo–C(CH_2{=}CCH_2CH_2)$ 2.36	
H	1s	−13.60	1.30	C=C 1.40	
				$C–C(CH_2CH_2CH_2)$ 1.48	

[a] All calculations were performed using the modified Wolfsberg–Helmholtz formula (J. H. Ammeter, H-B. Burgi, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, 1928, **100**, 3686). [b] ξ_2 = 1.90; c_1 and c_2 (contraction coefficients used in the double ξ expansion) = 0.589 88. [c] Z = Centroid of cyclopentadienyl ring; tmm = trimethylenemethane; L = tmm or methylenecyclopropane.

the η^4-$C(CH_2)_3$ ligand. The barrier to rigid rotation of flat η^4-$C(CH_2)_3$ in $[Mo\{\eta^4-C(CH_2)_3\}(CO)_2(\eta-C_5H_5)]^+$ is 48.4 kcal mol^{-1}, and for bent η^4-trimethylenemethane 48.5 kcal mol^{-1}. Although it is well established that the absolute values of such barriers, as given by the EHMO method, are subject to some uncertainty, since a rigid-rotor model does not allow for any subtlety or complexity in the rotation process, the important point is established that there is a substantial difference in rotational barriers for η^4-trimethylenemethane complexed onto $Fe(CO)_3$ and $Mo(CO)_2(\eta-C_5H_5)^+$ fragments.

In apparent contradiction of this analysis the room-temperature ^1H n.m.r. spectrum of complex (2) shows a singlet at δ 3.36 p.p.m. due to the six methylene protons of the co-ordinated trimethylenemethane. On cooling to −60 °C this resonance collapses, and at −90 °C is replaced by three signals, two doublets at δ 3.23 (H^1) and 3.49 p.p.m. (H^2) [$J(H^1H^2)$ 5 Hz] and a singlet at 3.64 p.p.m. (H^3) for the three inequivalent methylene sites. Estimation [21] of the barrier to apparent rotation by approximation to a simple two-site exchange mechanism afforded a value for $\Delta G_{Tc}^{\ddagger}$ of 9.9 $\pm$ 1 kcal mol^{-1}. The coalescence temperature for the corresponding pentamethylcyclopentadienyl cation (1) was lower (−70 °C) than that observed for (2), and the process was not frozen out at −90 °C.

This suggests that some dynamic process other than rotation is responsible for the room-temperature ^1H equivalence of the η^4-trimethylenemethane hydrogens. In fact what is required is an averaging process which does not interconvert

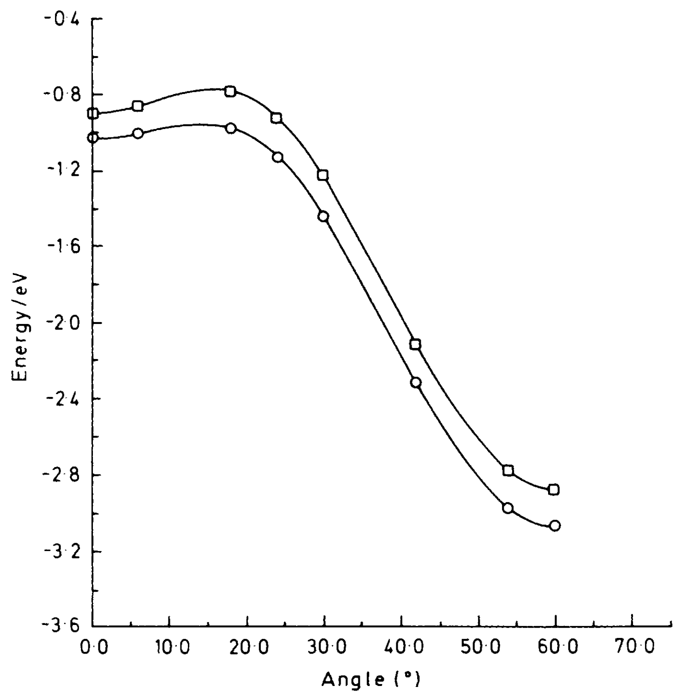
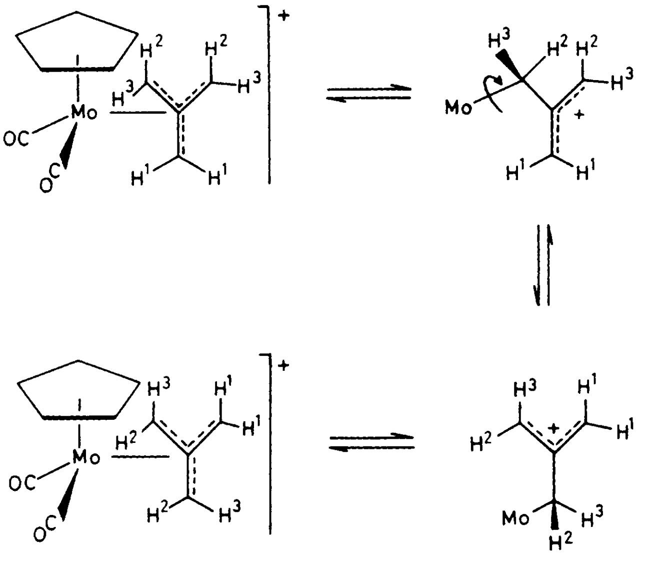
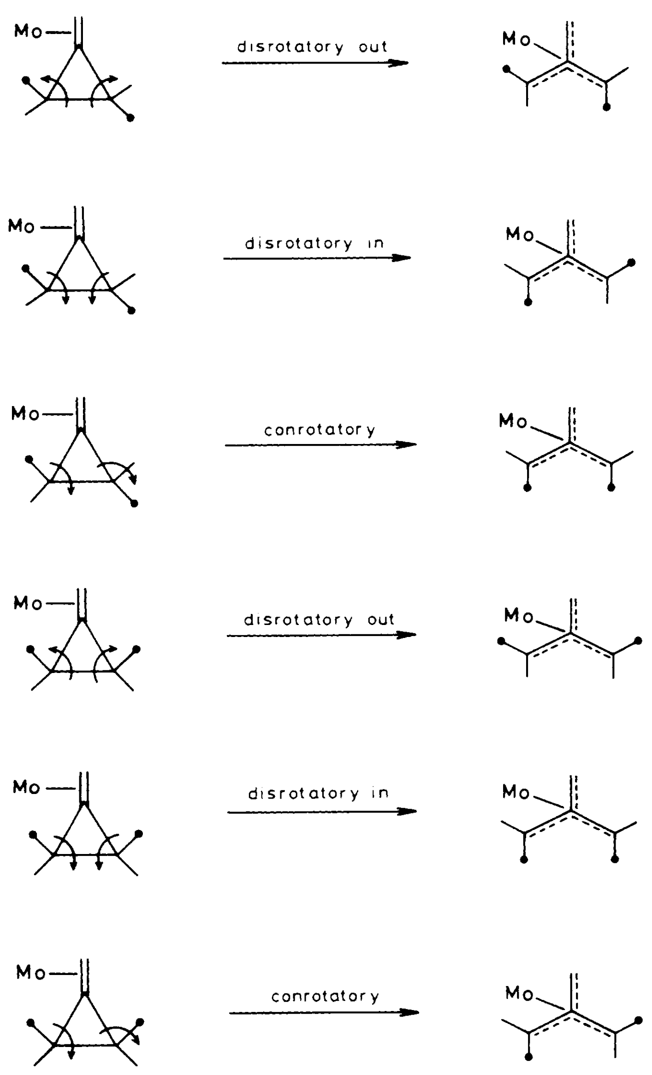


Figure 5. Potentional curves for rotation of the trimethylenemethane ligand about the metal–ligand axis in $Mo(CO)_2(\eta-C_5H_5)^+$. Zero degrees corresponds to a *anti* conformation, 60° corresponds to *syn*. □, Ligand has D_{3h} symmetry; ○, ligand has C_{3v} symmetry ($\theta = \beta = 12°$)



Scheme 1. Ligands omitted for clarity

the *syn* and *anti* conformers. This can be accomplished by the reaction path shown in Scheme 1, where slippage ($\eta^4 \longrightarrow \sigma$) * of the molybdenum fragment occurs so as to form a delocalised allylic carbenium ion, in which rotation about a Mo–C bond is possible. Such a process interconverts H^2 and H^3 with H^1, and because of the presence of a molecular plane of symmetry, H^2 and H^3. This reaction has in a sense a parallel with the σ–π-promoted *syn*–*anti* exchange process observed with η^3-allyl complexes.



Scheme 2. ●— = Me

Thus, the crystallographic study confirmed that 2,3-C–C bond cleavage does in fact occur. If it is assumed that this reaction involves initial η^2-co-ordination of methylenecyclopropane, then from a stereochemical standpoint there are three possible ring-opening pathways. These are disrotating out, disrotating in, and conrotatory, which can in principle be distinguished (see Scheme 2) by examining the corresponding reactions of *cis*- and *trans*-2,3-dimethylmethylenecyclopropane.

Accordingly, $[Mo(NCMe)_2(CO)_2(\eta-C_5H_5)][BF_4]$ was treated with *cis*- and *trans*-2,3-dimethylmethylenecyclopropane in CH_2Cl_2 as solvent affording respectively the *syn,syn*-dimethyl- and the *syn,anti*-dimethyl-trimethylenemethane complexes (4) and (5), characterised by elemental analysis and i.r. and n.m.r.[4] spectroscopy. Similarly, reaction of the *cis*- and *trans*-2,3-dimethylmethylenecyclopropanes with $[Mo_2(CO)_6(\eta-C_5Me_5)_2]$ and $AgBF_4$ in CH_2Cl_2 gave respectively the *syn,syn* (6) and *syn,anti* complex (7). The pentamethylcyclopentadienyl cations (6) and (7) obtained in these reactions were found to be contaminated with variable amounts of $[Mo(CO)_4(\eta-C_5Me_5)][BF_4]$ presumably formed by competitive capture

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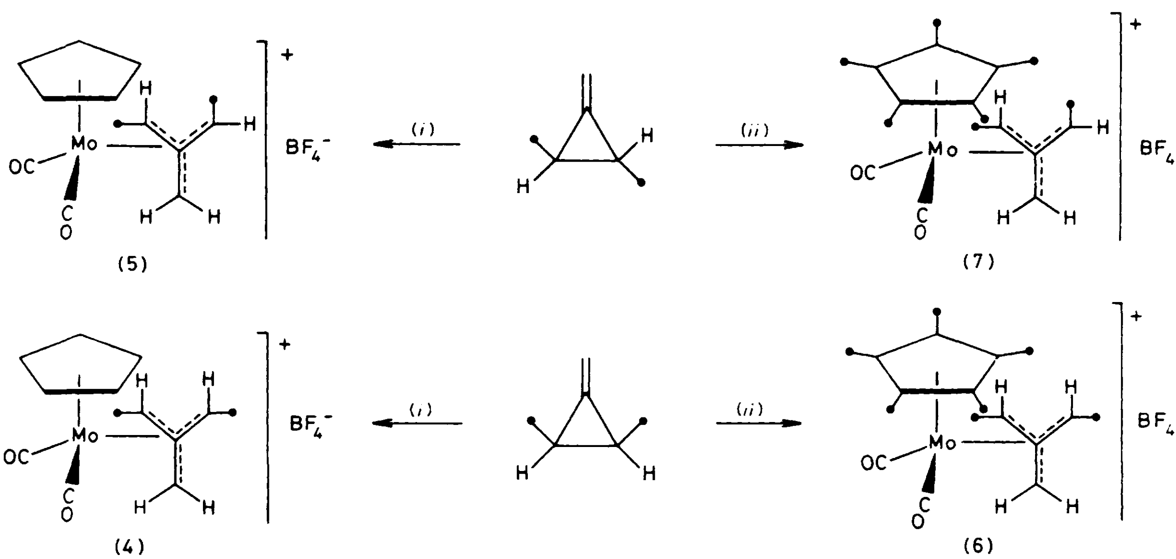
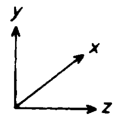
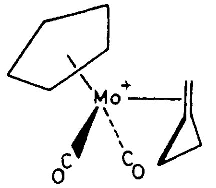
* It is probably not necessary for complete slippage to occur. What is required is that the metal moves towards one of the peripheral carbons reducing the Mo–C bond order sufficiently to allow rotation.



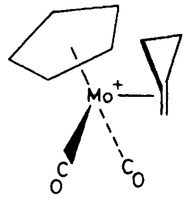
Scheme 3. •— = Me; (*i*) $[\mathrm{Mo(NCMe)_2(CO)_2(\eta\text{-}C_5H_5)}][\mathrm{BF_4}]$; (*ii*) $[\mathrm{Mo_2(CO)_6(\eta\text{-}C_5Me_5)_2}]\text{-}\mathrm{AgBF_4}$

of $[\mathrm{Mo(CO)_3(\eta\text{-}C_5Me_5)}][\mathrm{BF_4}]$ by displaced carbon monoxide. Analytical samples of these cations were obtained by conversion (see later) into the neutral alcohols followed by regeneration of the trimethylenemethane cations with tetrafluoroboric acid–propionic anhydride.

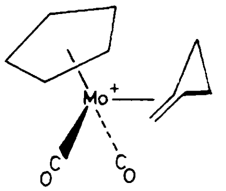




(IV)



(V)



(VI)

These isomeric dimethyl-substituted η^4-trimethylenemethane cations do not inverconvert in refluxing nitromethane, and therefore, the observations summarised in Scheme 3 are consistent with a disrotatory-out ring-opening reaction where the breaking 2,3-σ bond bends away from the metal.* The same stereochemistry, *i.e.* disrotatory out, was also observed experimentally and shown to be electronically favoured in the iron-carbonyl-promoted ring opening of methylene-2-phenylcyclopropane.[4] Disrotatory-out stereospecificity is also observed in the reaction of methylenecyclopropanes with $[\mathrm{PdCl_2(NCPh)_2}]$, where calculations suggest that the activation energy for conrotatory ring opening is substantially higher than that for either disrotatory-in or disrotatory-out opening, and further, whilst all three modes are, strictly speaking, symmetry-allowed transformations, the latter two modes are strongly so.[5]

If similar calculations were to be attempted with the molybdenum system then a necessary first step was to consider the nature of the intermediate just prior to ring opening. A likely candidate is the η^2-bonded alkene complex $[\mathrm{Mo(\eta^2\text{-}CH_2{=}CCH_2CH_2)(CO)_2(\eta\text{-}C_5Me_5}$ or $\mathrm{\eta\text{-}C_5H_5)]^+}$, which on C–C bond cleavage affords a trimethylenemethane cation. Limiting conformations for such species have the alkene function parallel to [two possible conformations, (IV) and (V)] or perpendicular to [(VI)] the mirror plane of the metal fragment. Although it is well established [19,22] that the last conformation is preferred, by *ca.* 20—25 kcal mol^{-1}, in d^6 alkene complexes of the general type $[\mathrm{Mn(\eta^2\text{-}alkene)(CO)_2(\eta\text{-}C_5H_5)}]$, we anticipated that a more facile rotation about the metal–alkene bond would be afforded in the d^4 cation $[\mathrm{Mo(\eta^2\text{-}CH_2{=}CCH_2CH_2)(CO)_2(\eta\text{-}C_5H_5)]^+}$; removal of two electrons from the orbitals of Figure 5 of ref. 19 readily leads to this prediction. We were surprised, therefore, to discover that EHMO calculations on $\eta\text{-}\mathrm{C_5H_5}$ analogues of the three conformations suggested stability decreases of 40.9 kcal mol^{-1} in going from (VI) to (IV) and a further 46.4 kcal mol^{-1} in going from (IV) to (V), *i.e.* a total barrier to rigid rotation of the η^2-methylenecyclopropane ligand about the axis from the molybdenum atom to the midpoint of C=C of >85 kcal mol^{-1}. (Note that here we have not actually explored the barrier to rotation, only the differences between the energies of three obvious points on the rotation cycle, but barrier $\nless$ total difference.)

Detailed examination shows that the origins of these differences largely derive from intramolecular ligand–ligand interactions rather than from substantial changes in the metal–alkene bond strength. In the least stable conformer (V) there are two very short symmetry-related contacts (1.344 Å) between a cyclopentadienyl hydrogen atom and the two nearest methylene hydrogens; the computed overlap population is −0.055. For the other parallel geometry, (IV), the same methylene hydrogens are this time *cis* to the carbonyl groups, C · · · H 1.510 and O · · · H 1.666 Å, and interact in an attrac-

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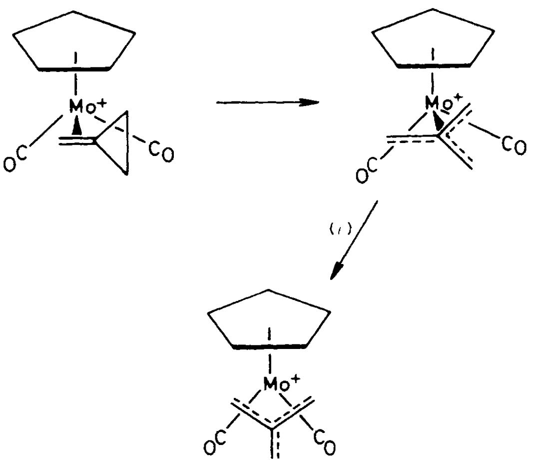
* It should be noted that if the exchange process shown in Scheme 1 also applied to these methyl-substituted η^4-trimethylenemethanes then a substantial substituent effect is implied.

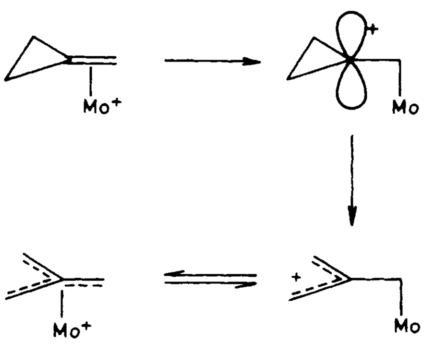
tive sense with the carbonyl carbons (carbon–hydrogen overlap population 0.049) and in a repulsive sense with the carbonyl oxygens (oxygen–hydrogen overlap population −0.043). The most stable conformation, (VI), is characterised by a very weakly repulsive (cyclopentadienyl)-H ··· H-(methylene) contact, 1.933 Å (overlap population −0.001), and by a strong interaction between the methylene hydrogen and the carbonyl π_z system. Although the (single) C ··· H and O ··· H distances here are the same as those in (V) the carbon–hydrogen overlap population is now 0.0835 and the oxygen–hydrogen is −0.049. Further, since a greater proportion of the carbon $2p_z$ atomic orbital is localised in the π_z^*, rather than in the π_z, bond of the CO ligand, the formation of a partial C ··· H bond in the *z* direction perferentially depopulates π^* rather than π, resulting in enhanced C–O bonding; the carbon–oxygen overlap population for the carbonyl ligand adjacent to the cyclopropane ring is 1.165, whereas that for the other CO is proportionally reduced to 1.082. The carbon–oxygen overlap populations in (V) and (IV) are 1.145 and 1.133 respectively.

Thus, the strong conformational preference of the alkene precursor $[\mathrm{Mo}(\eta^2\text{-}\mathrm{CH_2{=}\overline{CCH_2CH_2}})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})]^+$ does not map to that of the η^4-trimethylenemethane complex $[\mathrm{Mo}\{\eta^4\text{-}\mathrm{C(CH_2)_3}\}(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})]^+$ in such a manner that readily allows calculation of the activation energy required for the three ring-opening modes, and therefore, we cannot probe further the reasons why the disrotatory-out mode of ring opening is preferred. Nevertheless, a likely reaction path is that illustrated in Scheme 4, where ring opening of the preferred conformer generates a trimethylenemethane cation, which needs only a 30° rotation in order to descend the potential curve of Figure 5 forming the *syn*-orientated trimethylenemethane complex. A simplified view of the ring-opening step is that the $\mathrm{Mo(CO)_2}(\eta\text{-}\mathrm{C_5H_5})^+$ fragment slips from η^2 to σ thus generating a species not unlike a cyclopropylcarbenium ion (Scheme 5), which opens in the predicted [23] allowed disrotatory manner to form a metalla-substituted allylic carbenium ion, which then reversibly transforms into an η^4-trimethylenemethane cation.



Scheme 4. (*i*) 30° rotation

As mentioned in the introduction these molecules are the first examples of cationic η^4-trimethylenemethane species, and it was therefore important to examine their reactions with nucleophilic reagents. The η^4-trimethylenemethane cations (1)—(7) present five possible sites for nucleophilic attack: the molybdenum centre, co-ordinated carbon monoxide, and the cyclopentadienyl and η^4-trimethylenemethane ligands. In the case of the latter, attack could in principle occur either at one of the three peripheral carbons or on the central carbon atom. In the event, as is shown in Scheme 6, the nucleophiles $\mathrm{OH^-}$, $\mathrm{BH_4^-}$, $\mathrm{CuMe_2^-}$, and $\mathrm{SPh^-}$ all selectively attacked the η^4-trimethylenemethane ligand of (1) to form respectively the η^3-allylic complexes (8), (9), (10), and (11), which were isolated by column chromatography and characterised by elemental analysis and i.r. and mass spectroscopy. The reaction with hydroxide anion to afford complex (8) was first observed on attempting to chromatograph (1) on alumina, and proved useful as a way of obtaining pure (1) uncontaminated with $[\mathrm{Mo(CO)_4}(\eta\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$, since addition of tetrafluoroboric acid–propionic anhydride to (8) regenerated (1) in quantitative yield.



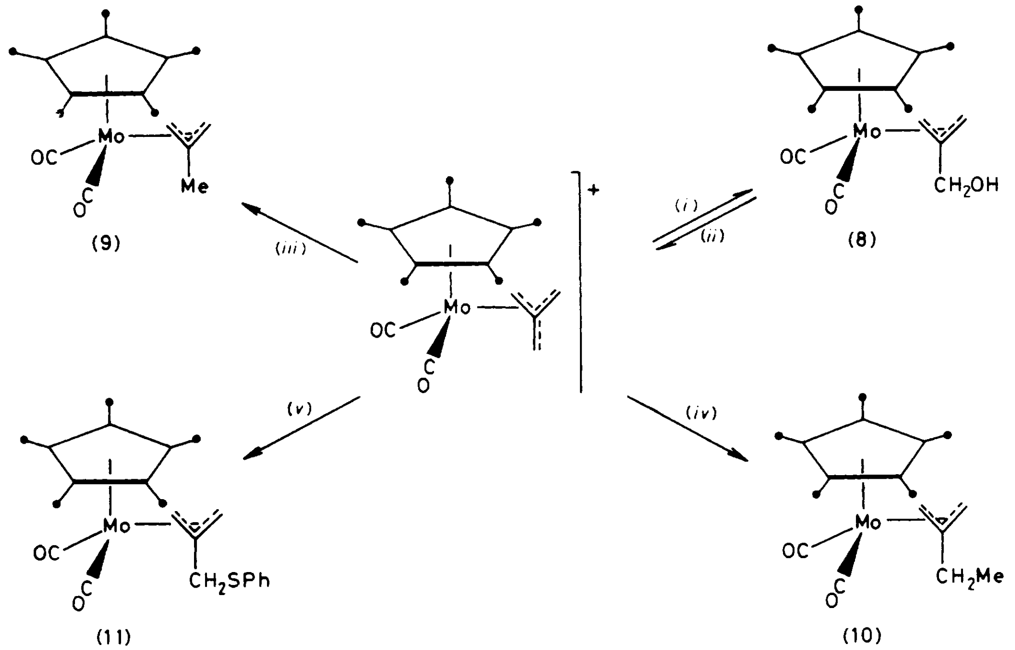
Scheme 5. Ligands omitted for clarity

The corresponding reactions of the methyl-substituted cations (3), (6), and (7) were also examined, the results being summarised in Scheme 7. Reaction of (3) with $\mathrm{BH_4^-}$ in tetrahydrofuran afforded only the 2-isopropyl-substituted η^3-allylic complex (12). In contrast, $\mathrm{BH_4^-}$ with (6) led to attack on both unsubstituted and substituted carbons giving respectively the η^3-allyl species (13) and (14), whereas (7) reacted to give only the one product (14) arising from regioselective attack on a methyl-substituted carbon. This latter result suggests that there is an interplay of electronic and steric effects, which conclusion is reinforced by the reactions with $\mathrm{OH^-}$. The cation (6) reacts regioselectively at the unsubstituted carbon to give the alcohol (15), whereas the reaction of (7) with $\mathrm{OH^-}$ is directed selectively to a substituted carbon atom to form (16).

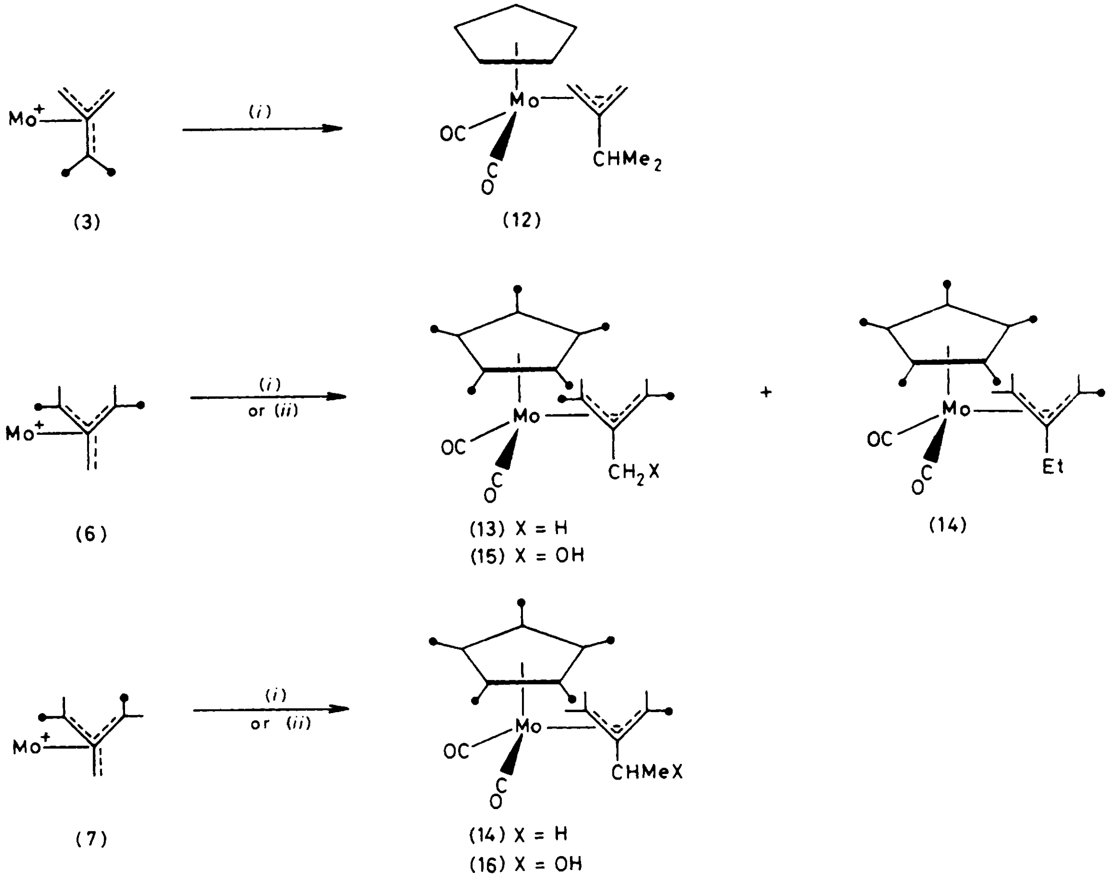
Experimental

The ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra were recorded on JEOL FX 90 Q and FX 200 spectrometers, as appropriate. Data given are for room-temperature measurements and coupling constants are in Hz. Carbon-13 chemical shifts are relative to $\mathrm{SiMe_4}$ with positive values to high frequency of the reference. Tris(acetylacetonato)chromium(III) was added to reduce ^{13}C relaxation times. Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer. All reactions were carried out in Schlenk tubes under an atmosphere of dry oxygen-free nitrogen, using freshly distilled solvents. Methylenecyclopropanes were prepared by the method of Arora and Binger.[24]

Preparation of Dicarbonyl(η-pentamethylcyclopentadienyl)-(η⁴-trimethylenemethane)molybdenum Tetrafluoroborate (1).—An excess of methylenecyclopropane (0.5 g, 10 mmol) was added to a stirred solution of $[\mathrm{Mo_2(CO)_6}(\eta\text{-}\mathrm{C_5Me_5})_2]$ (0.5 g,



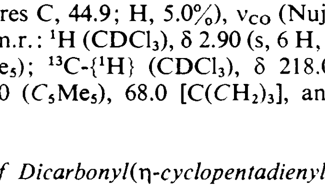
Scheme 6. (*i*) OH^-; (*ii*) tetrafluoroboric acid–propionic anhydride; (*iii*) BH_4^-; (*iv*) $CuMe_2^-$; (*v*) SPh^-



Scheme 7. Ligands omitted for clarity. (*i*) BH_4^-; (*ii*) OH^-

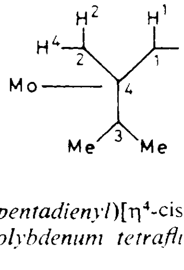
0.8 mmol) in CH_2Cl_2 (30 cm^3) contained in a flask covered in metal foil. Silver tetrafluoroborate (0.31 g, 1.6 mmol) was added, and the reaction mixture stirred at room temperature for 4 h. The resultant reaction mixture was filtered through Kieselguhr, and the volume of the solvent reduced *in vacuo* to 10 cm^3. The resultant solution was chromatographed on an alumina-packed column. Elution with CH_2Cl_2 gave first an orange band containing $[Mo(CO)_4(\eta-C_5Me_5)][BF_4]$. Further elution gave a yellow band containing alcohol (8) (see later). The solution containing (8) was evaporated to dryness *in vacuo*, and the residue dissolved in propionic anhydride (5 cm^3) and cooled to 0 °C. Tetrafluoroboric acid (0.15 cm^3, 30% aqueous solution) in propionic anhydride (5 cm^3) was added. After 1 h diethyl ether was slowly added to give cream *crystals* of (1) (0.42 g, 58%) (Found: C, 45.2; H, 5.0. $C_{16}H_{21}BF_4MoO_2$ requires C, 44.9; H, 5.0%), ν_{CO} (Nujol) 2 056s and 2 004s cm^{-1}. N.m.r.: ^1H ($CDCl_3$), δ 2.90 (s, 6 H, CH_2) and 2.31 (s, 15 H, C_5Me_5); ^{13}C-$\{^1H\}$ ($CDCl_3$), δ 218.0 (CO), 117.0 [$C(CH_2)_3$], 105.0 (C_5Me_5), 68.0 [$C(CH_2)_3$], and 12.0 p.p.m. (C_5Me_5).

Preparation of Dicarbonyl(η-cyclopentadienyl)(η^4-trimethylenemethane)molybdenum Tetrafluoroborate (2).—An excess of methylenecyclopropane (0.5 g, 10 mmol) was added to a stirred suspension of the red complex *cis*-$[Mo(NCMe)_2(CO)_2(\eta-C_5H_5)][BF_4]$[13] (0.4 g, 1 mmol) in CH_2Cl_2 (10 cm^3). After 16 h at room temperature diethyl ether (20 cm^3) was added to the yellow solution. The resultant precipitate was collected and recrystallised (0 °C) from CH_2Cl_2–Et_2O to give cream *crystals* of (2) (0.25 g, 70%) (Found: 36.7; H, 3.1. $C_{11}H_{11}BF_4MoO_2$ requires C, 36.9; H, 3.1%), ν_{CO} (Nujol) 2 065s and 2 020s cm^{-1}. N.m.r.: ^1H (CD_3NO_2), δ 5.88 (s, 5 H, C_5H_5) and 3.36 (s, 6 H, CH_2); ^{13}C-$\{^1H\}$ (CD_3NO_2), δ 215.8 (CO), 115.3 [$C(CH_2)_3$], 91.7 (C_5H_5), and 65.3 p.p.m. [$C(CH_2)_3$]; ^1H (CD_3NO_2, −90 °C), δ 5.88 (s, 5 H, C_5H_5), 3.64 (s, 2 H, H^3), 3.49 [d, 2 H, H^2, $J(H^1H^2)$ 5.0], and 3.23 [d, 2 H, H^1, $J(H^1H^2)$ 5.0].

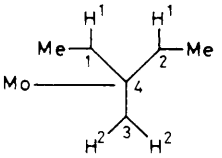


The following cations were synthesised in a similar manner.

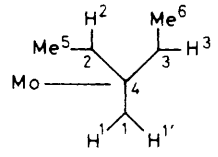
Dicarbonyl(η-cyclopentadienyl)[η^4-dimethylmethylene(dimethylene)methane]molybdenum tetrafluoroborate (3). Yield 70% (Found: C, 39.9; H, 3.9. $C_{13}H_{15}BF_4MoO_2$ requires C, 40.4; H, 3.9%), ν_{CO} (CH_2Cl_2) 2 054s and 2 005s cm^{-1}. N.m.r.: ^1H ([$^2H_6$]acetone), δ 5.94 (s, 5 H, C_5H_5), 3.42 (br s, 2 H, H^1 + H^2), 3.09 (br s, 2 H, H^3 + H^4), and 2.12 (s, 6 H, CMe_2); ^{13}C-$\{^1H\}$ ([$^2H_6$]acetone), δ 218.0 (CO), 125.3 (C^3), 109.1 (C^4), 92.5 (C_5H_5), 54.8 (C^1,C^2), and 24.5 p.p.m.



Dicarbonyl(η-cyclopentadienyl)[η^4-cis-methylenebis(methylmethylene)methane]molybdenum tetrafluoroborate (4). Yield 70% (Found: C, 40.5; H, 3.9. $C_{13}H_{15}BF_4MoO_2$ requires C, 40.4; H, 3.9%), ν_{CO} (CH_2Cl_2) 2 055s and 2 006s cm^{-1}. N.m.r.: ^1H (CD_3NO_2), δ 5.8 (s, 5 H, C_5H_5), 4.0 (m, 2 H, H^1), 3.95 [d, 2 H, H^2, $J(H^1H^2)$ 3.0], and 1.88 [d, 6 H, CH*Me*, *J*(HMe) 3.0]; ^{13}C-$\{^1H\}$ (CD_3NO_2), δ 217.3 (CO), 112.0 (C^4), 92.1 (C_5H_5), 83.5 (C^1,C^2), 61.7 (C^3), and 16.3 p.p.m. (CH*Me*).



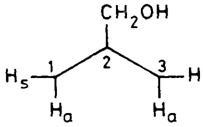
Dicarbonyl(η-cyclopentadienyl)[η^4-trans-methylenebis(methylmethylene)methane]molybdenum tetrafluoroborate (5). Yield 70% (Found: C, 39.6; H, 4.0. $C_{13}H_{15}BF_4MoO_2$ requires C, 40.4; H, 3.9%), ν_{CO} (CH_2Cl_2) 2 049s and 1 997 cm^{-1}. N.m.r.: ^1H ([$^2H_6$]acetone), δ 5.96 (s, 5 H, C_5H_5), 5.13 [dq, 1 H, H^2, $J(H^2Me^5)$ 7.4, $J(H^2H^{1'})$ 3.5], 4.26 [q, 1 H, H^3, $J(H^3Me^6)$ 6.6], 3.58 [d, 1 H, H^1, $J(H^{1'}H^1)$ 1.6], 2.97 [dd, 1 H, $H^{1'}$, $J(H^1H^{1'})$ 1.6], 2.01 [d, 3 H, Me^6, $J(Me^6H^3)$ 6.56], and 1.85 [d, 3 H, Me^5, $J(Me^5H^2)$ 7.44]; ^{13}C-$\{^1H\}$ (CD_3NO_2), δ 218.6 (CO), 112.0 (C^4), 92.5 (C_5H_5), 90.0 (C^3), 82.9 (C^2), 55.5 (C^1), 16.7 (C^6H_3), and 16.0 p.p.m. (C^5H_3).



Dicarbonyl[η^4-cis-methylenebis(methylmethylene)methane](η-pentamethylcyclopentadienyl)molybdenum tetrafluoroborate (6). Yield 60% (Found: C, 47.6; H, 5.7. $C_{18}H_{25}BF_4MoO_2$ requires C, 47.4; H, 5.5%), ν_{CO} (CH_2Cl_2) 2 045s and 2 000s cm^{-1}. N.m.r.: ^1H (CD_3NO_2), δ 3.75 [d, 2 H, H^1, $J(H^1H^2)$ 3.0], 2.80—2.55 (m, 2 H, H^2), 2.1 (s, 15 H, C_5Me_5), and 1.8 [d, 6 H, Me, $J(MeH^1)$ 9.0]; ^{13}C-$\{^1H\}$ (CD_2Cl_2), δ 219.4 (CO), 114.4 (C^4), 104.6 (C_5Me_5), 87.8 (C^1,C^2), 61.3 (C^3), 14.9 (Me), and 11.0 p.p.m. (C_5Me_5).

Dicarbonyl[η^4-trans-methylenebis(methylmethylene)methane](η-pentamethylcyclopentadienyl)molybdenum tetrafluoroborate (7). Yield 58% (Found: C, 46.9; H, 5.6. $C_{18}H_{25}BF_4MoO_2$ requires C, 47.4; H, 5.5%), ν_{CO} (CH_2Cl_2) 2 040s and 1 996s cm^{-1}. N.m.r.: ^1H (CD_2Cl_2), δ 4.53 [dq, 1 H, H^2, $J(H^2Me^5)$ 7.0, $J(H^2H^1)$ 7.0], 3.6 [d, 1 H, H^1, $J(H^1H^{1'})$ 1.1], 2.72 [q, 1 H, H^3, $J(Me^6H^3)$ 7.0], 2.0 (s, 15 H, C_5Me_5), 1.91 [d, 3 H, Me^6, $J(Me^6H^3)$ 7.0], 1.61 [dd, 1 H, $H^{1'}$, $J(H^1H^{1'})$ 1.1]; ^{13}C-$\{^1H\}$ (CD_2Cl_2), δ 221.7 (CO), 115.8 (C^4), 106 (C_5Me_5), 89.0 (C^3), 87.3 (C^2), 62.1 (C^1), 16.7 (Me^6), 15.1 (Me^5), and 12.5 p.p.m. (C_5Me_5).

Reactions of Complex (1).—(*a*) *With hydroxide anion.* A solution of complex (1) (0.5 g 1.17 mmol) in CH_2Cl_2 (15 cm^3) was placed on an alumina (Brockman, activity II) packed column. Elution with CH_2Cl_2 afforded a yellow band which was collected. Removal of the solvent and recrystallisation (−78 °C) from CH_2Cl_2 afforded yellow *crystals* of (8) (0.27 g, 75%) (Found: C, 53.5; H, 5.9%; *M* 358. $C_{16}H_{22}MoO_3$ requires C, 53.6; H, 6.2%; *M* 358), ν_{CO} (CH_2Cl_2) 1 939s and 1 863s cm^{-1}. N.m.r.: ^1H (C_6D_6), δ 3.75 (s, 2 H, CH_2OH), 3.20 (s, 2 H, H_s), 1.51 (s, 15 H, C_5Me_5), and 0.67 (s, 2 H, H_a) (*exo* isomer); 3.67 (s, 2 H, CH_2OH), 3.06 (s, 2 H, H_s), 1.51 (s, 15 H, C_5Me_5), and 0.54 (s, 2 H, H_a) (*endo* isomer) (*exo*/*endo* = ½); ^{13}C-{^{1}H}, δ 240.0 (CO), 102.0 (C^2), 101.0 (C_5Me_5), 75.0 (CH_2OH), 47.0 (C^1,C^3), and 10.0 p.p.m. (C_5Me_5).



(*b*) *With sodium tetrahydroborate.* An excess of $NaBH_4$ (0.1 g, 2.6 mmol) was added to a stirred suspension of complex (1) (0.5 g, 1.17 mmol) in tetrahydrofuran (20 cm^3). After 3 h at room temperature, the solvent was removed *in vacuo* and the residue extracted with hexane. Chromatography on alumina and elution with hexane gave a pale yellow band. Recrystallisation (−78 °C) from hexane gave yellow *crystals* of (9) (0.3 g, 75%) (Found: C, 55.6; H, 6.7%; *M* 342. $C_{16}H_{22}MoO_2$ requires C, 56.1; H, 6.4%; *M* 342), ν_{CO} (hexane) 2 047s and 1 877s cm^{-1}. N.m.r.: ^{1}H (C_6D_6), δ 3.0 (s, 2 H, H_s), 1.8 (s, 3 H, Me), 1.6 (s, 15 H, C_5Me_5), and 0.6 (s, 2 H, H_a) (*endo* isomer); ^{13}C-{^{1}H} (C_6D_6), δ 106.5 (C^2), 102.1 (C_5Me_5), 47.7 (C^1,C^3), and 10.9 p.p.m. (C_5Me_5).

(*c*) *With lithium dimethylcuprate.* Addition of lithium dimethylcuprate [CuI (0.15 g, 7.8 mmol), LiMe·LiBr (0.8 cm^3, 1.4 mmol)] in diethyl ether (4 cm^3) to a stirred suspension (−78 °C) of complex (1) (0.3 g, 0.7 mmol) resulted in the rapid development of a bright yellow colour. After 1 h at room temperature the solvent was removed *in vacuo* and the residue extracted with pentane. Chromatography on alumina and elution with pentane gave a yellow band which was collected. Recrystallisation (−78 °C) from pentane gave yellow *crystals* of (10) (0.22 g, 88%) (Found: C, 57.2; H, 7.0%; *M* 356. $C_{17}H_{24}MoO_2$ requires C, 57.3; H, 6.8%; *M* 356), ν_{CO} (pentane) 1 950s and 1 880s cm^{-1}. N.m.r.: ^{1}H (C_6D_6), δ 3.0 (s, 2 H, H_s), 1.83 [q, 2 H, CH_2CH_3, *J*(HH) 5.0], 1.61 (s, 15 H, C_5Me_5), 1.10 [t, 3 H, CH_2CH_3, *J*(HH) 5.0], and 0.58 (s, 2 H, H_a) (*endo* isomer).

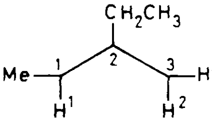
(*d*) *With sodium thiophenoxide.* A solution of NaSPh (0.13 g, 0.98 mmol) in tetrahydrofuran (10 cm^3) was added dropwise to a stirred (−30 °C) suspension of complex (1) (0.4 g, 0.94 mmol) in tetrahydrofuran (10 cm^3). The reaction mixture was allowed to warm to room temperature and the solvent removed *in vacuo*. Extraction with diethyl ether followed by chromatography on alumina and recrystallisation (−78 °C) from hexane gave yellow *crystals* of (11) (0.33 g, 78%) (Found: C, 58.4; H, 5.8%; *M* 450. $C_{22}H_{26}MoO_2S$ requires C, 58.7; H, 5.8%; *M* 450); ν_{CO} (hexane) 1 950s and 1 880s cm^{-1}. N.m.r.: ^{1}H ($CDCl_3$), δ 7.2—7.5 (m, 5 H, Ph), 3.08 (s, 2 H, H_s), 2.87 (s, 2 H, CH_2SPh), 1.82 (s, 15 H, C_5Me_5), and 0.64 (s, 2 H, H_a) (*endo* isomer); ^{13}C-{^{1}H} (C_6D_6), δ 242.0 (CO), 137—127 (Ph), 105.6 (C^2), 102.3 (C_5Me_5), 47.4 (C^1,C^3), 45.4 (CH_2SPh), and 10.6 p.p.m. (C_5Me_5).

The following η^3-allyl complexes were synthesised in a similar manner.

Dicarbonyl(η-*cyclopentadienyl*)(η^3-2-*isopropylallyl*)*molybdenum* (12). Yield 65% (Found: C, 57.2; H, 5.3%; *M* 300. $C_{13}H_{16}MoO_2$ requires C, 57.2; H, 5.3%; *M* 300), ν_{CO} (hexane) 1 959s and 1 887s cm^{-1}. N.m.r.: ^{1}H (C_6D_6), δ 4.61 (s, 5 H, C_5H_5), 2.75 (br s, 2 H, H_s), 2.05 [septet, 1 H, $CHMe_2$, *J*(MeH) 6.8], 1.56 [br s, 2 H, H_a], and 1.05 [d, 6 H, $CHMe_2$, *J*(MeH) 6.8]; ^{13}C-{^{1}H} (C_6D_6), δ 241.8 (CO), 92.6 (C^2), 90.6 (C_5H_5), 35.7 ($CHMe_2$), 34.3 (C^1,C^3), and 24.1 p.p.m. ($CHMe_2$).

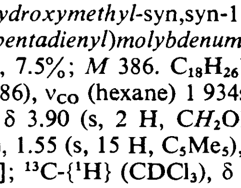
Dicarbonyl(η-*pentamethylcyclopentadienyl*)(η^3-syn,syn-1,3-2-*trimethylallyl*)*molybdenum* (13). Yield 65% (Found: C, 58.4; H, 7.4%; *M* 370. $C_{18}H_{26}MoO_2$ requires C, 58.4; H, 7.0%; *M* 370), ν_{CO} (hexane) 1 939s and 1 865s cm^{-1}. N.m.r.: ^{1}H (C_6D_6), δ 1.88 [d, 6 H, CHMe, *J*(MeH) 6.3], 1.74 (s, 3 H, 2-Me), 1.60 (s, 15 H, C_5Me_5), 0.88 [q, 2 H, CHMe, *J*(MeH) 6.3] (*endo* isomer); ^{13}C-{^{1}H} (C_6D_6), δ 244.6 (CO), 119.4 (C^2), 101.9 (C_5Me_5), 60.6 (CHMe), 28.3 (Me), 16.0 (CHMe), and 10.5 p.p.m. (C_5Me_5).

Dicarbonyl(η^3-2-*ethyl*-syn-1-*methylallyl*)(η-*pentamethylcyclopentadienyl*)*molybdenum* (14). Yield 35% (Found: C, 57.5; H, 7.3%; *M* 370. $C_{18}H_{26}MoO_2$ requires C, 58.4; H, 7.0%; *M* 370), ν_{CO} (hexane) 1 940s and 1 850s cm^{-1}. N.m.r.: ^{1}H (C_6D_6), δ 2.88 (s, 1 H, H^3), 2.23 (m, 1 H, CH_2CH_3), 1.82 [d, 3 H, Me, *J*(MeH) 6.1], 1.69 (m, 1 H, CH_2CH_3), 1.60 (s, 15 H, C_5Me_5), 1.21 [q, 1 H, H^1, *J*(H^1Me) 6.1], 1.04 [t, 3 H, CH_2CH_3, *J*(HMe) 6.0], and 0.22 (s, 1 H, H^2); ^{13}C-{^{1}H} (C_6D_6), δ 244.3 (CO), 244.0 (CO), 118.0 (C^2), 102.0 (C_5Me_5), 62.3 (C^1), 44.1 (C^3), 28.3 (CH_2CH_3), 16.6 (Me), 15.3 (CH_2CH_3), and 10.66 p.p.m. (C_5Me_5).



Dicarbonyl(η^3-2-*hydroxymethyl*-syn,syn-1,3-*dimethylallyl*)(η-*pentamethylcyclopentadienyl*)*molybdenum* (15). Yield 72% (Found: C, 56.7; H, 7.5%; *M* 386. $C_{18}H_{26}MoO_3$ requires C, 56.0; H, 6.8%; *M* 386), ν_{CO} (hexane) 1 934s and 1 850s cm^{-1}. N.m.r.: ^{1}H (C_6D_6), δ 3.90 (s, 2 H, CH_2OH), 1.90 [d, 6 H, CHMe, *J*(HMe) 6.2], 1.55 (s, 15 H, C_5Me_5), and 0.86 [q, 2 H, CHMe, *J*(HMe) 6.2]; ^{13}C-{^{1}H} ($CDCl_3$), δ 243.0 (CO), 128.9 (C^2), 101.9 (C_5Me_5), 66.4 (CH_2OH), 61.7 (C^1,C^3), 15.4 (CHMe), and 10.5 p.p.m. (C_5Me_5).

Dicarbonyl[η^3-2-(1′-*hydroxyethyl*)-syn-1-*methylallyl*](η-*pentamethylcyclopentadienyl*)*molybdenum* (16). Yield 70% (Found: C, 55.4; H, 7.1%; *M* 386. $C_{18}H_{26}MoO_3$ requires C, 56.0; H, 6.8%; *M* 386), ν_{CO} (hexane) 1 944s and 1 872s cm^{-1}. N.m.r.: ^{1}H (C_6D_6), δ 4.16 [q, 1 H, H^4, *J*(MeH) 6.6], 2.88 (s, 1 H, H^3), 2.0 [d, 3 H, CHMe, *J*(MeH^1) 6.2], 1.55 (s, 15 H, C_5Me_5), 1.35 [d, 3 H, CH(OH)CH_3, *J*(MeH^4) 6.6], and 1.15 [q, 1 H, H^1, *J*(H^1Me) 6.2]; ^{13}C-{^{1}H} (C_6D_6), δ 243.9 (CO), 243.3 (CO), 112.5 (C^2), 101.9 (C_5Me_5), 69.5 (CHOH), 62.3 (C^1), 40.3 (C^3), 21.1 (CHMe), 15.4 (CHOHMe), and 10.4 p.p.m. (C_5Me_5).



Molecular Structure Determination of Complex (1).—A single crystal of uniform dimensions (*ca.* 0.2 mm) was sealed (epoxy-resin) inside a Lindemann capillary under an atmosphere of dry nitrogen. Unit-cell dimensions and the space group were established by oscillation and zero- and first-level (equi-inclination) Weissenberg photography (Cu-K_α *X*-radiation).

Data collection was carried out, using the same crystal, on an Enraf-Nonius CAD4 diffractometer at Queen Mary College, London. The crystal was slowly cooled to 268 ± 1 K in a cold air stream. When steady state had been achieved 25 relatively low-angle reflections were centred (program

Table 4. Fractional co-ordinates of atoms, with standard deviations

Atom	x	y	z	p.p.
Mo	0.01524(6)	0.24354(6)	0.07924(3)	1.0000
C(1)	0.0534(8)	0.2567(8)	0.1815(4)	1.0000
C(2)	−0.0527(7)	0.2863(9)	0.1709(4)	1.0000
C(3)	−0.1066(7)	0.1932(7)	0.1483(4)	1.0000
C(4)	−0.0364(6)	0.1066(7)	0.1431(4)	1.0000
C(5)	0.0635(7)	0.1481(9)	0.1647(4)	1.0000
C(6)	0.1339(9)	0.3221(11)	0.2112(5)	1.0000
C(7)	−0.1004(10)	0.3879(10)	0.1926(7)	1.0000
C(8)	−0.2228(6)	0.1850(10)	0.1407(5)	1.0000
C(9)	−0.0598(10)	−0.0091(8)	0.1322(5)	1.0000
C(10)	0.1569(9)	0.0761(11)	0.1775(6)	1.0000
C(101)	−0.0644(7)	0.1455(8)	0.0236(4)	1.0000
O(101)	−0.1120(6)	0.0916(7)	−0.0059(4)	1.0000
C(102)	−0.0844(8)	0.3660(8)	0.0584(5)	1.0000
O(102)	−0.1425(7)	0.4303(7)	0.0475(5)	1.0000
C(11)	0.1540(8)	0.2879(9)	0.0264(5)	1.0000
C(22)	0.1715(8)	0.1748(10)	0.0432(5)	1.0000
C(33)	0.1587(8)	0.3628(9)	0.0725(4)	1.0000
C(44)	0.0755(10)	0.2976(13)	−0.0163(5)	1.0000
B	0.0572(7)	−0.3231(13)	0.1621(6)	1.0000
F(1)	−0.0416(20)	−0.3063(22)	0.1675(11)	0.4314
F(2)	0.0827(15)	−0.3899(15)	0.1142(9)	0.5538
F(3)	0.092(4)	−0.394(4)	0.2067(22)	0.2238
F(4)	0.115(3)	−0.2284(23)	0.1609(12)	0.3358
F(5)	−0.041(3)	−0.273(3)	0.1481(15)	0.3320
F(6)	0.1160(24)	−0.2378(21)	0.1325(12)	0.3323
F(7)	0.114(4)	−0.245(3)	0.1923(24)	0.1779
F(8)	0.010(5)	−0.425(6)	0.134(4)	0.1009
F(9)	−0.042(3)	−0.366(4)	0.1646(18)	0.2077
F(10)	0.111(3)	−0.331(3)	0.1070(18)	0.2075
F(11)	0.1042(17)	−0.3482(16)	0.2133(9)	0.4542
F(12)	0.074(4)	−0.413(3)	0.1274(21)	0.2326
F(13)	0.065(3)	−0.380(4)	0.2146(22)	0.2313
F(14)	−0.032(5)	−0.249(5)	0.166(3)	0.1644
H(21)	0.233(6)	0.177(6)	0.074(4)	1.0000
H(22)	0.179(6)	0.134(6)	0.010(4)	1.0000
H(31)	0.195(6)	0.348(6)	0.119(4)	1.0000
H(32)	0.116(6)	0.427(6)	0.087(4)	1.0000
H(41)	0.034(6)	0.370(6)	−0.026(6)	1.0000
H(42)	0.050(7)	0.257(6)	−0.046(5)	1.0000
H(61)	0.1200	0.3203	0.2582	1.0000
H(62)	0.1317	0.4051	0.1958	1.0000
H(63)	0.2096	0.2875	0.2018	1.0000
H(71)	−0.1810	0.3909	0.1789	1.0000
H(72)	−0.0590	0.4566	0.1744	1.0000
H(73)	−0.0963	0.3906	0.2402	1.0000
H(81)	−0.2582	0.2639	0.1463	1.0000
H(82)	−0.2536	0.1298	0.1734	1.0000
H(83)	−0.2401	0.1545	0.0971	1.0000
H(91)	0.0122	−0.0543	0.1295	1.0000
H(92)	−0.1024	−0.0173	0.0913	1.0000
H(93)	−0.1065	−0.0403	0.1681	1.0000
H(101)	0.1444	−0.0041	0.1595	1.0000
H(102)	0.1675	0.0705	0.2247	1.0000
H(103)	0.2257	0.1114	0.1578	1.0000

SEARCH) and their angles used to generate the first cell and orientation matrix. After rapid collection of data within the range $\theta = 14-15°$ (Mo-K_α X-radiation; $\lambda_{\alpha1} = 0.709\,26$, $\lambda_{\alpha2} = 0.713\,54$ Å) 25 reflections selected from this shell were carefully centred (SETANG) to furnish, by least-squares refinement, accurate cell parameters and the orientation matrix used in data collection.

Crystal data. $C_{16}H_{21}BF_4MoO_2$, $M = 427.75$, orthorhombic, $a = 12.822(2)$, $b = 12.311(3)$, $c = 22.660(4)$ Å, $U = 3\,576.9$ Å^3, $D_m = 1.5$ g cm^{-3} (flotation), $Z = 8$ ion pairs, $D_c = 1.58$ g cm^{-3}, $F(000) = 1\,728$ electrons, μ(Mo-K_α) = 6.9 cm^{-1}, space group $Pbca$ (D_{2h}^{15}, no. 61) from systematic absences.

Intensity data were collected ($+h$ $+k$ $+l$) between $1.5 < \theta < 27.0°$ by θ—2θ scans in which scan widths (s.w.) were calculated from the equation s.w. = 0.85 + 0.35 tan θ. The intensities of two standard reflections ($\bar{4}\ \bar{6}\ 6$ and $\bar{2}\ \bar{2}\ 14$) were remeasured once every hour, but subsequent analysis of their net counts as individual functions of time revealed no significant crystal decomposition or movement, or source variation, over the *ca.* 45 h of data collection. 3 893 Reflections were corrected for Lorentz and polarisation effects (but not for X-ray absorption). Of these, 2 747 had $F_o > 2.0\sigma(F_o)$ and were used for structure solution and refinement.

The metal atom was sought by analysis of the Patterson function. Two feasible solutions (0.00, 0.25, 0.17 and 0.00, 0.25, 0.08 and their respective symmetry equivalents) allowed all prominent peaks to be assigned, but only adoption of the second ultimately gave a molecular model that refined well. With unit weights assigned to all reflections, remaining non-hydrogen atoms were located from a difference Fourier, and refined by full-matrix least squares, first isotropically and then (except for F atoms) anisotropically. After convergence of this model (R *ca.* 0.08) F_o moduli were weighted according to $w^{-1} = \sigma^2(F_o) + 0.035\ F_o^2$. The BF_4^- anion showed spherical partial disorder that has been modelled by the use of 14 fractional fluorine atoms with population parameters (p.p.) of 0.101—0.554 (Σp.p. = 3.99), these being optimised by least squares after assignment of $U_F{}^* = 0.10$ Å^2.

Methyl functions were treated as rigid groups with C–H 1.08 Å, but hydrogen atoms of the trimethylenemethane ligand were located (from a difference Fourier to which the contributions from low-angle reflections were artificially enhanced) and subsequently allowed positionally to refine. For all H atoms U was fixed at 0.08 Å^2.

Refinement (2 747 data, 256 variables) converged at $R = 0.0674$, $R' = 0.0983$. A final difference Fourier showed no peak > 0.7 e Å^{-3}, nor trough < -0.7 e Å^{-3}, and there was no unusual systematic variation of the root-mean-square deviation of a reflection of unit weight *versus* parity group, $(\sin\theta)/\lambda$, F_o, h, k, or l. Table 4 lists the derived atomic coordinates. Structure solution and refinement employed the SHELX 76 programs [25] implemented on the University of London Computer Centre CDC 7600 and University of Edinburgh ICL 2972 computers. Least-squares planes (SUP 23876) were analysed using XANADU [26] and Figures constructed using Johnson's ORTEP-II.[27]

Acknowledgements

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* The isotropic thermal factor is defined as exp $[-8\pi^2U(\sin^2\theta)/\lambda^2]$.

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