

NEW OBSERVATIONS ON DICYCLOPENTADIENYLMOLYBDENUM COMPLEXES DERIVED FROM DIMETHYL ACETYLENEDICARBOXYLATE. CRYSTAL STRUCTURE OF $[(\eta^5\text{-C}_5\text{H}_5)_2\text{MoOC(O)CH=CCO}_2\text{CH}_3]$

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(Received October 17th, 1985)

Summary

Addition of chloroform to a solution of $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoH}_2$ and dimethyl-acetylenedicarboxylate ($\text{CH}_3\text{CO}_2\text{C}\equiv\text{CCO}_2\text{CH}_3$) in THF at 0°C gives two new complexes: (i) chloro- σ -alkenyl $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoCl}[Z\text{-C}(\text{CO}_2\text{CH}_3)=\text{CH}(\text{CO}_2\text{CH}_3)]$ and (ii) metallacyclic $[(\eta^5\text{-C}_5\text{H}_5)_2\text{MoOC(O)CH=CCO}_2\text{CH}_3]$. An X-ray diffraction study of the latter product revealed the presence of one water molecule per one organometallic molecule in the unit cell: space group $P2_1$, a 12.111(9), b 7.374(2), c 7.830(5) Å, β 93.43(4)°, Z = 2. The Mo–C bond length is 2.180(6) Å. A mechanism involving an intramolecular elimination of CH_4 from the initially formed insertion product $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoH}[Z\text{-C}(\text{CO}_2\text{CH}_3)=\text{CH}(\text{CO}_2\text{CH}_3)]$ is proposed for its formation.

Introduction

Dimethyl acetylenedicarboxylate (abbreviated as dmad) was shown by Nakamura and Otsuka to undergo insertion into one of the two Mo–H bonds in the dicyclopentadienyldihydromolybdenum complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoH}_2$ [1]. A recent X-ray structure analysis showed that the insertion hydrido- σ -alkenyl complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoH}[Z\text{-C}(\text{CO}_2\text{CH}_3)=\text{CH}(\text{CO}_2\text{CH}_3)]$ (I) is the *Z*-isomer resulting from *trans*-insertion of the alkyne [2]. Earlier observations suggested that I undergoes a thermal (110°C) rearrangement to a stable dimethyl fumarate complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}[trans\text{-CH}(\text{CO}_2\text{CH}_3)=\text{CH}(\text{CO}_2\text{CH}_3)]$ (II). σ -Alkenyl complex I reacts with dry HCl to give a chloro- σ -alkyl product $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoCl}[\sigma\text{-CH}(\text{CO}_2\text{CH}_3)\text{-CH}_2(\text{CO}_2\text{CH}_3)]$ (III) [1]. For some related dicyclopentadienylmolybdenum com-

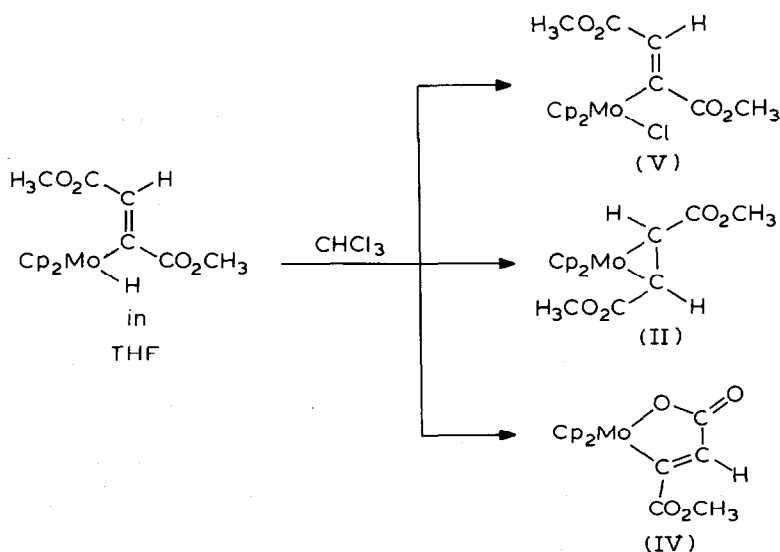
plexes Petersen showed that when the molybdenocene derived from $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{MoCl}_2$ and Na/Hg amalgam is treated with dmad a 16 electron oxo-molybdenum(IV) complex $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mo}(=\text{O})[(\text{CH}_3\text{O}_2\text{C})\text{C}=\text{C}(\text{CO}_2\text{CH}_3)\text{C}_5\text{H}_4\text{CH}_3]$ is formed rather than the expected metallacyclopropene $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Mo}[\text{C}_2(\text{CO}_2\text{CH}_3)_2]$, suggesting that the acetylene chemistry of molybdenocene is more complex than originally thought [3].

During our recent studies on the electronic properties and reactivity of σ -alkenyl complexes we used an established method for replacement of a hydride by a halide ligand in the hydrido- σ -alkenyl complexes $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoH}(\sigma\text{-CR=CHR'})$ ($\text{R} = \text{CF}_3$, CN , $\text{R}' = \text{H}$; $\text{R} = \text{R}' = \text{CF}_3$, CN) involving dissolution of these complexes in halogenated solvents [4]. The same method applied to the complex I $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoH}[\text{Z-C}(\text{CO}_2\text{CH}_3)=\text{CH}(\text{CO}_2\text{CH}_3)]$ and CHCl_3 gave an unexpected metallacyclic complex $[(\eta^5\text{-C}_5\text{H}_5)_2\text{MoOC}(\text{O})\text{CH}=\text{CCO}_2\text{CH}_3]$ (IV). We report here the structure of IV, together with some other observations on the chemistry of the $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoH}_2$ -dmad system.

Results and discussion

When an equal volume of CHCl_3 was added to a solution of $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoH}[\text{Z-C}(\text{CO}_2\text{CH}_3)=\text{CH}(\text{CO}_2\text{CH}_3)]$ (I) prepared from $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoH}_2$ and dmad in THF at 0°C [1], the colour changed from red to brown-red. Chromatography of the resulting solution gave three products: the expected chloro- σ -alkenyl complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoCl}[\text{Z-C}(\text{CO}_2\text{CH}_3)=\text{CH}(\text{CO}_2\text{CH}_3)]$ (V), the known dimethylfumarate complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}[\text{trans-CH}(\text{CO}_2\text{CH}_3)=\text{CH}(\text{CO}_2\text{CH}_3)]$ (II) [1] and the unexpected metallacyclic complex $[(\eta^5\text{-C}_5\text{H}_5)_2\text{MoOC}(\text{O})\text{CH}=\text{CCO}_2\text{CH}_3]$ (IV) (Scheme 1).

Complexes II and V were identified by their ^1H NMR spectra (Table 1). The ^1H NMR spectrum of IV exhibited four resonances 6.46 ($=\text{CH}$), 5.30 (C_5H_5), 3.80



SCHEME 1

TABLE 1

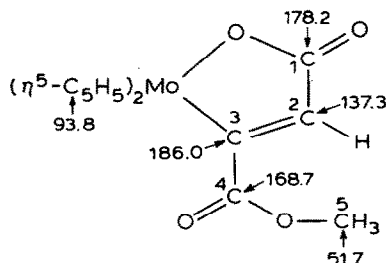
¹H NMR DATA FOR ALL COMPLEXES STUDIED (IN CDCl₃)

$ \begin{array}{c} (\eta^5\text{-C}_5\text{H}_5)_2\text{Mo} \begin{array}{l} \diagup \text{C}(\text{CO}_2\text{CH}_3)\text{CH}(\text{CO}_2\text{CH}_3) \\ \diagdown \text{H} \end{array} \\ \text{(I)} \end{array} $	6.36(s, 1, =CH), 4.82(s, 10, C ₅ H ₅), 3.67(s, 3, OCH ₃), 3.64(s, 3, OCH ₃), -9.2(broad, MoH). ^a 6.86(s, 1, =CH), 4.76(s, 10, C ₅ H ₅), 3.66(s, 6, OCH ₃), -8.81(s, 1, MoH).
$ \begin{array}{c} \text{H} \quad \text{CO}_2\text{CH}_3 \\ \quad / \\ (\eta^5\text{-C}_5\text{H}_5)_2\text{Mo} \text{---} \text{C} \\ \quad \backslash \\ \text{H}_3\text{CO}_2\text{C} \quad \text{C} \quad \text{H} \\ \text{(II)} \end{array} $	4.63(s, 10, C ₅ H ₅), 3.63(s, 6, OCH ₃), 2.73(s, 2, CH).
$ \begin{array}{c} (\eta^5\text{-C}_5\text{H}_5)_2\text{Mo} \begin{array}{l} \diagup \text{CH}(\text{CO}_2\text{CH}_3)\text{CH}_2(\text{CO}_2\text{CH}_3) \\ \diagdown \text{Cl} \end{array} \\ \text{(III)} \end{array} $	5.32(s, 5, C ₅ H ₅), 5.18(s, 5), 3.60(s, 3, OCH ₃), 3.56(s, 3, OCH ₃), 3.3-2.1(m, 3, =CH-CH ₂).
$ \begin{array}{c} (\eta^5\text{-C}_5\text{H}_5)_2\text{Mo} \begin{array}{l} \diagup \text{O} \quad \text{O} \\ \diagdown \quad \text{C}=\text{C} \\ \quad \quad \backslash \quad / \\ \quad \quad \text{CO}_2\text{CH}_3 \end{array} \cdot \text{H}_2\text{O} \\ \text{(IV)} \end{array} $	6.46(s, 1, =CH), 5.30(s, 10, C ₅ H ₅), 3.80(s, 3, OCH ₃), 1.93(s, 2, H ₂ O).
$ \begin{array}{c} (\eta^5\text{-C}_5\text{H}_5)_2\text{Mo} \begin{array}{l} \diagup \text{C}(\text{CO}_2\text{CH}_3)\text{CH}(\text{CO}_2\text{CH}_3) \\ \diagdown \text{Cl} \end{array} \\ \text{(V)} \end{array} $	6.75(s, 1, =CH), 5.37(s, 10, C ₅ H ₅), 3.66(s, 3, OCH ₃), 3.56(s, 3, OCH ₃).

^a In toluene at 25°C.

(CH₃) and 1.93 ppm (?), integrating in the ratio 1/10/3/2, respectively. Six resonances were present in the ¹³C NMR spectrum of IV, at 186.0, 178.2, 168.7, 137.3, 93.8 and 51.7 ppm; of these only the two last resonances could be assigned unambiguously, to C₅H₅ and CH₃ carbons. X-ray structure analysis of IV revealed a metallacyclic structure with one molecule of water of crystallization per organometallic molecule. This structure will be discussed below, but its availability permitted clear assignment of the fourth ¹H resonance (1.93 ppm, H₂O) and of the remaining four ¹³C resonances (Fig. 1).

A question arises as to which complex is the precursor for the formation of IV: is it the fumarate complex II or the insertion complex I. In order to answer this

Fig. 1. Structure of complex IV showing the assignments for ¹³C resonances in its ¹³C NMR spectrum.

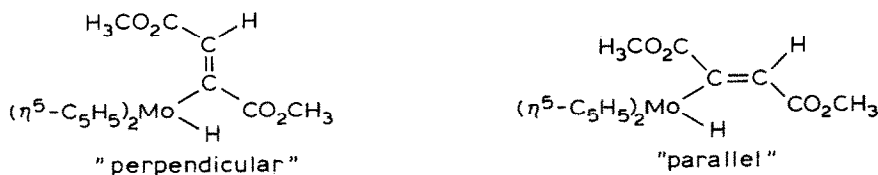


Fig. 2. Conformational orientation of the σ -alkenyl ligand in I.

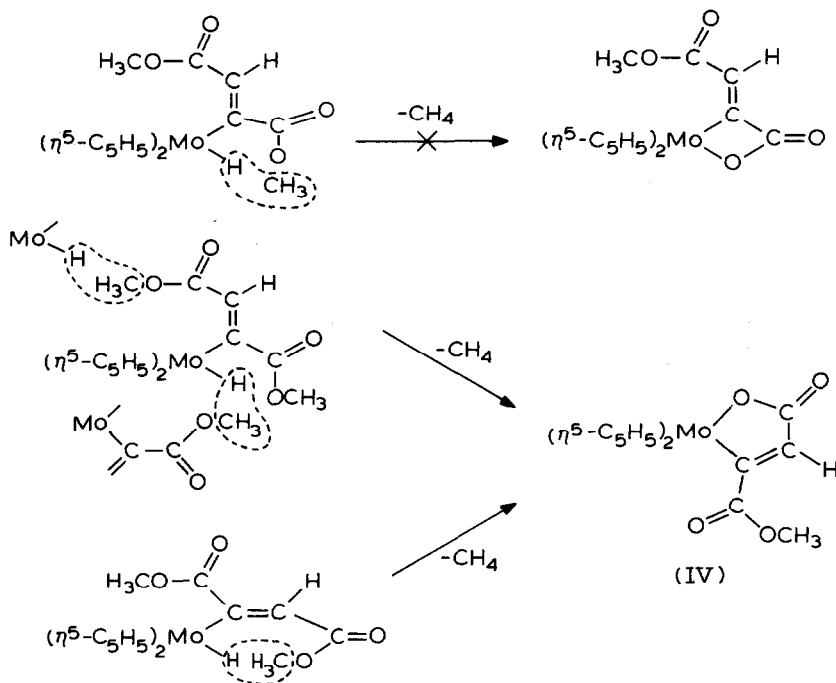
question a solution of II in CHCl_3 was stirred for 3 days at room temperature. The green precipitate formed was identified to be $(\eta^5-\text{C}_5\text{H}_5)_2\text{MoCl}_2$. Three other products were present in solution: methyl fumarate $\text{CH}_3\text{O}_2\text{CCH}=\text{CHCO}_2\text{CH}_3$, chloro- σ -alkenyl complex V and chloro- σ -alkyl complex $(\eta^5-\text{C}_5\text{H}_5)_2\text{MoCl}[\sigma\text{-CH}(\text{CO}_2\text{CH}_3)\text{CH}_2(\text{CO}_2\text{CH}_3)]$ (III). Complex III was prepared earlier by Nakamura and Otsuka by the action of HCl on I [1]. Complex III can also be obtained by chlorination with CHCl_3 of the hydrido- σ -alkyl complex $(\eta^5-\text{C}_5\text{H}_5)_2\text{MoH}[\sigma\text{-CH}(\text{CO}_2\text{CH}_3)\text{CH}_2(\text{CO}_2\text{CH}_3)]$ resulting from the insertion of methylfumarate into one of the two $\text{Mo}-\text{H}$ bonds in $(\eta^5-\text{C}_5\text{H}_5)_2\text{MoH}_2$. The presence of metallacyclic complex IV was not detected in the products of the reaction of II with CHCl_3 .

If IV is formed from I the simplest reaction path would involve elimination of methane and its presence was detected by gas chromatography in a sample of the gases above the reaction mixture. Assuming that there is CH_4 elimination, it is necessary to consider the conformational orientation of the σ -alkenyl ligand in I (Fig. 2) with respect to the line bisecting the $(\eta^5-\text{C}_5\text{H}_5)\text{Mo}(\eta^5-\text{C}_5\text{H}_5)$ and CMoH angles. Such different conformational orientations of σ -alkenyl ligands have been observed in the case of ligands activated by CF_3 groups [4,5].

We deduced from an X-ray structure analysis of I carried out by Herberich, Hesner and Okuda [2] that in the solid state I has a "perpendicular" conformation. If the elimination of CH_4 is an intramolecular process, a four-membered ring should be formed; a five-membered one could arise from an intermolecular elimination (Scheme 2). On the other hand, a "parallel" conformation of σ -alkenyl ligand could lead to the formation of a five-membered ring by an intramolecular elimination.

In order to check the existence of both "perpendicular" and "parallel" conformations of I in solution, a variable temperature study in deuterated toluene was carried out in the temperature range -60 to $+58^\circ\text{C}$. This revealed the presence of two sets of ^1H resonances attributed to the presence of both conformers (Fig. 2) at temperatures below 12°C . The isomer ratio was 2/1, and did not vary between -60°C and $+12^\circ\text{C}$. ^1H NMR data given as example at 0°C are: predominant conformer 6.89 ($=\text{CH}$), 4.79 (C_5H_5), 3.70 and 3.62 (OCH_3), -8.87 (MoH); minor conformer 6.99, 4.69, 3.70 and 3.62, and -7.30 , respectively. Thus, it is reasonable to suppose that IV is formed in the presence of CHCl_3 from a "parallel" conformer of I via an intramolecular elimination of methane (Scheme 2). Intermolecular interactions depicted in this Scheme could lead to the polynuclear species.

However, the role of CHCl_3 in this reaction is not understood. When either H_2O or CH_3OH are added (in place of CHCl_3) to the solution of I in THF at 0°C , only the fumarate complex II is formed, but addition of H_2O to the solution of I in 1/1 THF/ CHCl_3 increases the yield of IV up to about 80%. This seems to be a logical consequence of the presence of water molecules in the crystals of I.



SCHEME 2

The dealkylation reactions of CO_2R esters have been previously observed, e.g. by Shaw et al. [6] in the presence of NaI in ethanol and by Braunstein et al. [7] in the presence of BuLi or $\text{C}_3\text{H}_5\text{I}$.

Structure of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{MoOC(O)CH=CCO}_2\text{CH}_3] \cdot \text{H}_2\text{O}$ (IV)

The structure of IV consists of metallacyclic organometallic molecules (Fig. 3) linked via their O(2) atoms to the water molecules (O(5)) by the hydrogen bonds (O(2)–O(5) 2.879(8) Å). Relevant interatomic distances and angles are given in Table 2. The geometry around the molybdenum atom is typical of bent dicyclopentadienyl complexes [8]. The five-membered ring $\text{MoO(1)C(1)C(2)C(3)}$ is almost planar, the largest deviation from the best plane being 0.01 Å (O(1) for C(1) atoms). The angle between this plane and that of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\eta^5\text{-C}_5\text{H}_5)$ (to the centre of gravity of the C_5H_5 rings) is 89.9°.

The $\text{Mo}-\text{C(3)}$ bond length of 2.180(6) Å is shorter than the $\text{Mo}-\sigma\text{-alkyl}$ distances in $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoCl}(\text{CH}_2\text{CH}_3)$ (2.284(10) Å [8]) and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}[\text{S}(\text{C}_6\text{H}_5)]\{\sigma\text{-CH}(\text{CN})\text{CH}_3\}$ (2.306(3) Å [9]) and the $\text{Mo}-\sigma\text{-alkenyl}$ distances in $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoH}[\text{Z-C}(\text{CO}_2\text{CH}_3)=\text{CH}(\text{CO}_2\text{CH}_3)]$ (2.223(6) Å [2]) and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}[\text{S}_2\text{C}(\text{C}_2\text{H}_5)_2]\{\sigma\text{-C}(\text{CN})=\text{CH}_2\}$ (2.232(4) Å [9]) but longer than the $\text{Mo}-\text{C}$ distances in metallacyclopentadiene structure of $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Mo}[\text{C}_2(\text{CF}_3)_2]$ (2.129(7) Å [3]). In this last structure the short $\text{Mo}-\text{C}$ bonds result from the back-donation from the filled metal b_2 orbitals [10] to the empty in-plane π^* orbital of the acetylene. In structure IV, reported here, the O(1) and C(3) atoms interact mainly with the b_2 orbital of the metal and with some combination of $1a_1$ and $2a_1$ orbitals [10]. The metallacyclic

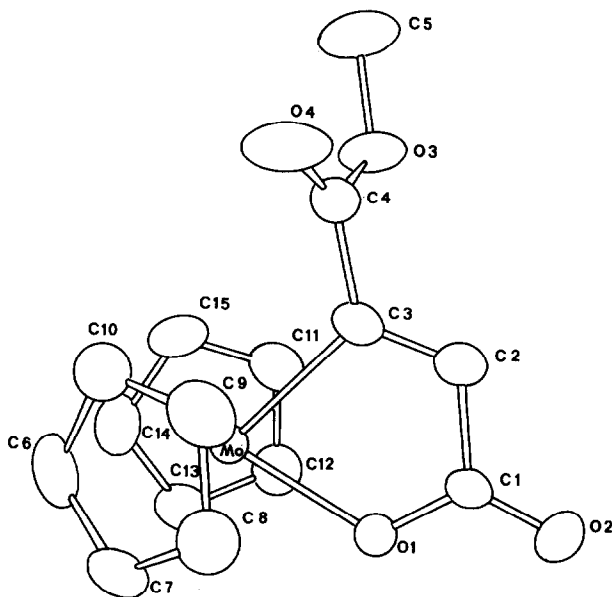


Fig. 3. ORTEP drawing of the organometallic molecule $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoOC(O)CH=CHCO}_2\text{CH}_3$ in IV showing the atom labelling scheme.

structure, involving the presence of the unsaturated C(2)–C(3) bond and electron-withdrawing atoms, may favour delocalization of electron density over the ring and thus strengthen the Mo–C(3) bond compared with respect to the relevant bonds in terminal σ -alkenyl complexes. Other distances and angles in the structure of IV are normal. An analogous metallacyclic structure of a platinum compound $[(\text{PPh}_3)_2\text{PtOC(O)CH=CH}]$ was recently described by Scherer et al. [11]. Taking into account the standard deviations observed for IV and for the platinum complex, the structural parameters inside the metallacyclic entity in both molecules are nearly the same.

TABLE 2

INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Mo–O(1)	2.113(5)	O(1)–Mo–C(3)	74.1(2)
Mo–C(3)	2.180(6)	Mo–O(1)–C(1)	120.0(3)
Mo–CY(1)	1.962	O(1)–C(1)–O(2)	123.4(6)
Mo–CY(2)	1.972	O(1)–C(1)–C(2)	114.5(7)
C(1)–O(1)	1.289(8)	O(2)–C(1)–C(2)	122.1(7)
C(1)–O(2)	1.229(9)	C(1)–C(2)–C(3)	115.1(7)
C(2)–C(1)	1.496(9)	C(2)–C(3)–C(4)	121.2(6)
C(2)–C(3)	1.315(10)	C(3)–C(4)–O(3)	111.6(5)
C(3)–C(4)	1.483(9)	C(3)–C(4)–O(4)	125.0(6)
C(4)–O(3)	1.324(8)	O(3)–C(4)–O(4)	123.3(6)
C(4)–O(4)	1.192(8)	C(4)–O(3)–C(5)	117.4(6)
O(3)–C(5)	1.451(8)	CY(1)–Mo–CY(2)	139.4

CY(1) is the gravity center of C(6)–C(10) atoms.

CY(2) is the gravity center of C(11)–C(15) atoms.

Experimental

The reactions were performed under nitrogen using standard Schlenk tube techniques. Solvents were purified by standard methods and purged with nitrogen before use. $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoH}_2$ was prepared by an established method [12]. Commercial dmad (Aldrich) was used. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-FX 100 spectrometer. Chemical shifts (δ values) are relative to internal of TMS.

Preparation of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{MoOC(O)CH=CCO}_2\text{CH}_3] \cdot \text{H}_2\text{O}$ (IV).

Dropwise addition of 0.41 g (2.9 mmol) of dmad in 10 ml of THF to a solution of 0.66 g (2.9 mmol) of $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoH}_2$ in 40 ml of THF at 0°C resulted in an immediate colour change from yellow to red. After 1 h stirring at 0°C , 40 ml of CHCl_3 was added and stirring was continued for 2 h at 0°C and 15 h at room temperature. The color changed to brown-red. Solvents were removed in vacuo, and the residue was dissolved in a minimum of methylene chloride and chromatographed on a "Florisil" column. Elution with CH_2Cl_2 gave the fumarate complex II in 10% yield. The second band, eluted with $\text{CH}_2\text{Cl}_2/2\%$ THF, gave chloro- σ -alkenyl complex V in 33% yield and the third, eluted with methanol, gave IV in 40% yield. Recrystallization of this last complex in CH_2Cl_2 /heptane gave complex IV $[(\eta^5\text{-C}_5\text{H}_5)_2\text{MoOC(O)CH=CCO}_2\text{CH}_3] \cdot \text{H}_2\text{O}$ as red well-shaped crystals which were used for X-ray analysis.

X-ray structure analysis of IV

A dark red crystal of IV was mounted on a Enraf-Nonius CAD-4 four-circle diffractometer. The unit cell was determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic routines.

TABLE 3
ATOMIC COORDINATES FOR IV

Atom	x	y	z	Atom	x	y	z
Mo	0.28081(3)	0.000	0.04787(5)	C(13)	0.3799(5)	0.270(1)	0.0617(9)
O(1)	0.4047(3)	-0.1614(6)	0.1742(5)	C(14)	0.2674(6)	0.3011(9)	0.0014(9)
O(2)	0.4491(4)	-0.3549(7)	0.3837(6)	C(15)	0.1989(5)	0.256(1)	0.1349(9)
O(3)	0.0598(3)	-0.0492(7)	0.4097(6)	H(6)	0.230(6)	0.12(1)	-0.284(9)
O(4)	0.0059(4)	-0.194(1)	0.1711(6)	H(7)	0.395(6)	-0.04(1)	-0.263(9)
O(5)	0.3588(4)	0.4011(8)	0.6263(6)	H(8)	0.348(6)	-0.35(1)	-0.120(9)
C(1)	0.3803(5)	-0.2645(9)	0.2993(7)	H(9)	0.160(6)	-0.35(1)	-0.073(9)
C(2)	0.2606(4)	-0.264(1)	0.3367(8)	H(10)	0.065(6)	-0.02(1)	-0.151(8)
C(3)	0.1980(5)	-0.1533(8)	0.2410(7)	H(11)	0.251(6)	0.18(1)	0.39(1)
C(4)	0.0780(5)	-0.1351(9)	0.2656(8)	H(12)	0.441(6)	0.16(1)	0.310(9)
C(5)	-0.0544(5)	-0.024(2)	0.4509(9)	H(13)	0.430(6)	0.30(1)	0.01(1)
C(6)	0.2316(6)	0.0263(9)	-0.2314(7)	H(14)	0.245(6)	0.35(1)	-0.100(9)
C(7)	0.3297(5)	-0.080(1)	-0.2245(8)	H(15)	0.131(6)	0.28(1)	0.120(9)
C(8)	0.3052(6)	-0.2429(9)	-0.1441(8)	H(51)	-0.055(5)	0.02(1)	0.57(8)
C(9)	0.1928(6)	-0.240(1)	-0.0995(8)	H(52)	-0.092(6)	0.04(1)	0.372(9)
C(10)	0.1460(6)	-0.072(1)	-0.1535(8)	H(53)	-0.092(6)	-0.12(1)	0.436(9)
C(11)	0.2687(6)	0.200(1)	0.2758(8)	H(1(05))	0.382(5)	0.45(1)	0.537(8)
C(12)	0.3783(5)	0.211(1)	0.2293(8)	H(2(05))	0.374(5)	0.43(1)	0.716(9)

TABLE 4
THERMAL PARAMETERS FOR IV

Atom	$B_{1,1}$	$B_{2,2}$	$B_{3,3}$	$B_{1,2}$	$B_{1,3}$	$B_{2,3}$
Mo	0.00341(2)	0.00795(5)	0.00802(4)	-0.0005(2)	0.00138(5)	-0.0000(2)
O(1)	0.0038(2)	0.0125(8)	0.0129(6)	0.0014(8)	0.0035(6)	0.007(1)
O(2)	0.0045(3)	0.018(1)	0.0183(8)	0.005(1)	0.0005(8)	0.012(2)
O(3)	0.0035(2)	0.025(2)	0.0168(7)	0.0001(9)	0.0039(7)	-0.0.011(1)
O(4)	0.0039(3)	0.040(2)	0.0192(9)	-0.009(1)	0.0032(8)	-0.021(2)
O(5)	0.0073(4)	0.022(1)	0.0134(7)	0.003(1)	0.0038(9)	0.006(2)
C(1)	0.0038(3)	0.011(1)	0.0127(9)	-0.001(1)	0.0042(5)	0.004(2)
C(2)	0.0032(3)	0.017(1)	0.0137(9)	-0.003(1)	0.0021(9)	0.004(2)
C(3)	0.0037(3)	0.012(1)	0.0104(8)	-0.004(1)	0.0038(9)	-0.002(2)
C(4)	0.0040(4)	0.015(1)	0.0120(9)	-0.000(1)	0.002(1)	0.003(2)
C(5)	0.0042(4)	0.043(3)	0.019(1)	0.001(2)	0.004(1)	-0.018(4)
C(6)	0.0110(6)	0.012(1)	0.0088(7)	-0.001(2)	-0.001(1)	0.003(2)
C(7)	0.0065(4)	0.015(1)	0.011(9)	-0.002(1)	0.006(1)	-0.005(2)
C(8)	0.0082(5)	0.011(1)	0.0121(9)	0.002(1)	0.001(1)	-0.009(2)
C(9)	0.0076(5)	0.014(1)	0.0131(9)	-0.007(1)	0.002(1)	-0.010(2)
C(10)	0.0060(4)	0.019(1)	0.0110(9)	-0.003(1)	-0.001(1)	-0.007(2)
C(11)	0.0068(5)	0.016(1)	0.014(1)	-0.003(1)	0.005(1)	-0.004(2)
C(12)	0.0061(4)	0.012(1)	0.0130(9)	-0.002(1)	-0.000(1)	-0.008(2)
C(13)	0.0054(4)	0.013(1)	0.019(1)	-0.006(1)	0.005(1)	-0.001(2)
C(14)	0.0083(6)	0.010(1)	0.016(1)	-0.000(1)	-0.003(1)	0.002(2)
C(15)	0.0046(4)	0.014(1)	0.021(1)	0.004(1)	0.005(1)	-0.008(2)

Crystal data: $C_{15}H_{16}MoO_5$, $M = 368.24$, monoclinic, $a = 12.111(9)$, $b = 7.374(2)$, $c = 7.830(5)$ Å, $\beta = 93.43(4)^\circ$, $U = 698.1$ Å³, $Z = 2$, $\mu(Mo-K_\alpha) 9.0$ cm⁻¹. Space group $P2_1$ (C_2^2 , No 4). The intensities of 1475 independent planes, measured using ω - 2θ scan (θ_{min} 2°, θ_{max} 28°), with $I > 3\sigma(I)$ were used in the solution and refinement of the structure. All calculations were carried out using the Enraf-Nonius SDP program library [13]. Neutral atom scattering factors and anomalous dispersion corrections applied to all non-hydrogen atoms were those given by Cromer and Waber [14]. The structure was solved and refined by conventional three-dimensional Patterson, difference Fourier and full-matrix least-squares methods. All non-hydrogen atoms were refined with anisotropic thermal parameters and the difference Fourier map at this stage gave the positions of hydrogen atoms. Final refinement of all parameters (B_{iso} for H atoms fixed at 4.0 Å²) led to the following residuals: $R = 0.0303$, $R_w = 0.0371$. These factors calculated for the enantiomorphic form in a polar $P2_1$ space group were slightly higher (0.0307 and 0.0377, respectively) so the original set of parameters was retained. The weighting scheme employed was $w^{-1} = \sigma^2(F) = 1/4\{\sigma(I)/(I) + 0.06^2(I)\}$. The final atomic coordinates and thermal parameters are given in Tables 3 and 4.

Tables of observed and calculated structure factors (9 pages) may be obtained from the Authors.

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