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The synthesis, structure and reactivity of aldehyde substituted η^3-allylic complexes of molybdenum [1]

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Abstract

Reaction of *cis*-[Mo(NCMe)$_2$(CO)$_2$(η^5-L)][BF$_4$] (L = C_5H_5 or C_5Me_5) with 1-acetoxybuta-1,3-diene gives the cationic complexes [Mo{η^4-*syn*-*s*-*cis*-$CH_2CHCHCH(OAc)$}(CO)$_2$(η^5-L)][BF$_4$], which, on reaction with aqueous $NaHCO_3/CH_2Cl_2$, afford good yields of the *anti*-aldehyde substituted complexes [Mo{η^3-*exo*-*anti*-$CH_2CHCH(CHO)$}(CO)$_2$(η^5-L)] **2** (L = C_5Me_5), **4** (L = C_5H_5)]. The corresponding η^5-indenyl substituted complex **5** was prepared by protonation ($HBF_4 \cdot OEt_2$) of [Mo(η^3-C_3H_5)(CO)$_2$(η^5-C_9H_7)] followed by addition of CH_2=CHCH=CH(OAc) and hydrolysis (aq. $NaHCO_3/CH_2Cl_2$). An X-ray crystallographic study of complex **2** confirmed the structure and showed that there is a contribution from a zwitterionic form involving donation of electron density from the molybdenum to the aldehyde carbonyl group. Treatment of **2** and **4**, in methanol solution, with $NaBH_4$ afforded the alcohols [Mo{η^3-*exo*-*anti*-$CH_2CHCHCH_2(OH)$}(CO)$_2$(η^5-L)] [**6** (L = C_5H_5), **8** (L = C_5Me_5)]; however, prolonged (30 h) reaction with $NaBH_4$/MeOH surprisingly gave good yields of the methoxy-substituted complexes [Mo{η^3-*exo*-*anti*-$CH_2CHCHCH_2(OMe)$}(CO)$_2$(η^5-L)] [**7** (L = C_5H_5), **9** (L = C_5Me_5)], the structure of **7** being confirmed by single crystal X-ray crystallography. This methoxylation reaction can be explained by coordination of the hydroxyl group present in **6** and **8** onto B_2H_6 to form the potential leaving group $HOBH_3^-$, which on ionisation affords [Mo(η^4-*exo*-buta-1-3-diene)(CO)$_2$(η^5-L)]$^+$ which is captured by reaction with OMe^-. Complex **8** is also formed in good yield on reaction of **2** with $HBF_4 \cdot OEt_2$ followed by treatment of the resulting cation [Mo{η^4-*exo*-*s*-*cis*-*syn*-$CH_2CHCHCH(OH)$}(CO)$_2$(η^5-C_5Me_5)][BF$_4$] with Na[BH_3CN]. Reaction of **4** with the Grignard reagents MeMgI, EtMgBr or PhMgCl afforded moderate yields of the alcohols [Mo{η^3-*exo*-*anti*-$CH_2CHCHCH(OH)R$}(CO)$_2$(η^5-C_5H_5)] [**11** (R = Me), **12** (R = Et), **13** (R = Ph)]. Similarly, treatment of **2** with MeLi gave the corresponding alcohol **14**. An attempt to carry out the Oppenauer oxidation [Al(OPr^i)$_3$/Me_2CO] of **11** resulted in an elimination reaction and the formation of the η^3-*s*-pentadienyl complex [Mo{η^3-*exo*-*anti*-$CH_2CHCH(CHCH_2)$}(CO)$_2$(η^5-C_5H_5)], which was structurally identified by X-ray crystallography. Interestingly, oxidation of **6** with [Bu^n_4N][RuO_4]/morpholine-*N*-oxide affords the aldehyde complex, **4** in good yield. Finally, reaction of **11** with [NO][BF$_4$] followed by addition of Na_2CO_3 affords the fur-3-ene complex [Mo{η^2-$\dot{C}H$=$CHCH_2O\dot{C}(H)Me$}(CO)(NO)(η^5-C_5H_5)]. © 1998 Elsevier Science S.A.

Keywords: Molybdenum; η^3-Allyl; X-ray diffraction

1. Introduction

The use of transition metal fragments to control and direct chemical transformations at coordinated organic centres is an important area of study, and while considerable progress has been made with reactions based on the [Mo{η^3-allyl)(CO)$_2$(η^5-C_5H_5)] system [1–3], these studies have been largely concerned with alicyclic molecules, that is with the exception of recent work by Vong et al. [4] and Liu et al. [5], which has focused on the reactivity of *syn*-substituted functional groups, e.g., [Mo{η^3-*syn*-$CH_2CHCH(CHO)$}(CO)$_2$(η^5-C_5H_5)]. We have previously shown [6] that treatment of the labile bis(acetonitrile) complexes [Mo(NCMe)$_2$(CO)$_2$(η^5-L)][BF$_4$] (L = C_5Me_5 or C_9H_7) with the 1-trimethylsilyloxybuta-1,3-dienes Me_3SiOCH=CR^1CH=CHR^2 (R^1=R^2=H; R^1 = Me, R^2 = H; R^1 = H, R^2 = Me) results in initial coordination of the 1,3-diene followed by a rapid fluoride anion initiated desilylation reaction resulting in the formation of *syn* and *anti* 4-oxo-

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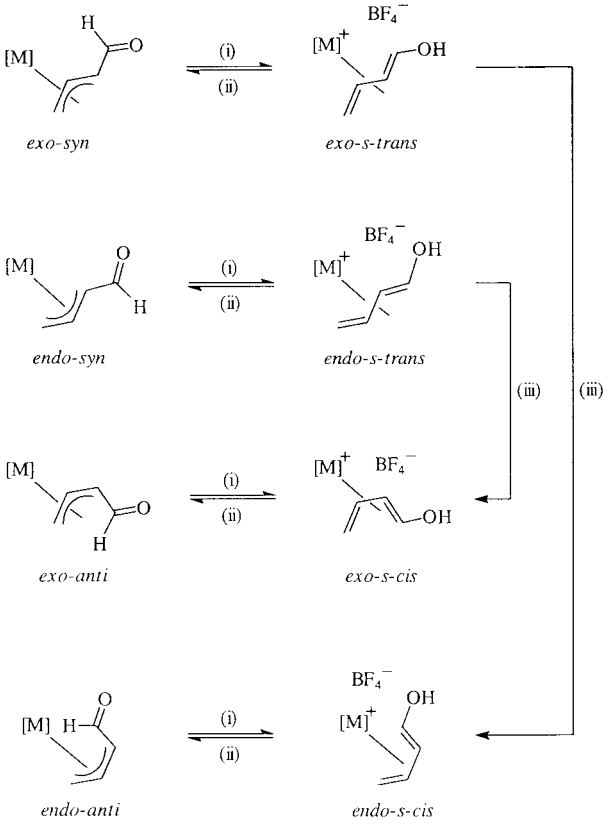
[1] Dedicated to Professor Ken Wade on the occasion of his 65th birthday.

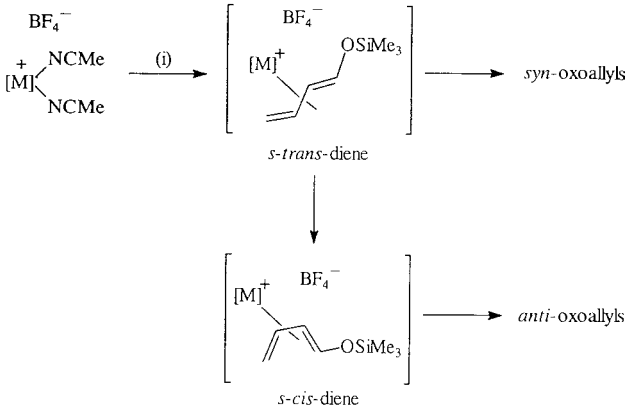
functionalised allyls [Mo{η^3-$CH_2CHCR^1(CHO)$}-$(CO)_2(\eta^5$-L)]. Having previously [6,7] studied the protonation of these complexes and gained insight from our investigations, we believed that it might be possible to devise a selective synthetic pathway to the *anti*-aldehyde substituted systems, the chemistry of which has not been explored. In this paper, we describe the successful development of our ideas and a preliminary study of reactivity.

2. Results and discussion

In studying the protonation of the *syn*- and *anti*-4-oxo-functionalised allyls [Mo{η^3-CH_2CHCH-(CHO)}$(CO)_2(\eta^5$-C_5H_5)] prepared from 1-trimethylsilyloxy-1,3-dienes, it was shown [6], as summarised in Scheme 1, that the *syn*-isomer affords, under kinetic control, a 1-hydroxy-substituted η^4-*s*-*trans*-1,3-diene, which isomerises into the corresponding 1-hydroxy-substituted η^4-*s*-*cis*-1,3-diene complex at room temperature. When the hydroxy-*cis*-1,3-diene cation is deprotonated with triethylamine, the *anti*-aldehyde substituted system is then formed selectively. Initially, it was thought that such a reaction sequence could be adapted to provide a procedure for the selective synthesis of the *anti*-aldehyde systems, but, as the combined yields of

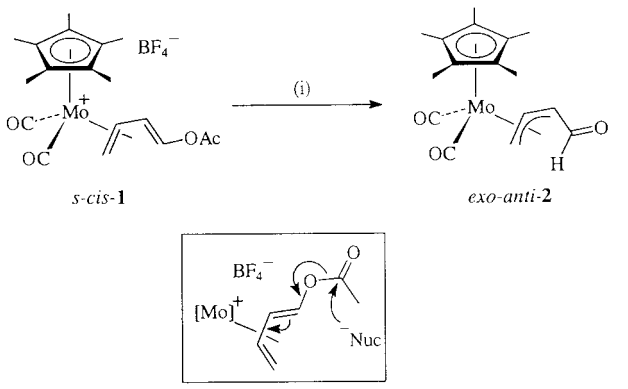


Scheme 1. ((i) = $HBF_4 \cdot OEt_2$; (ii) Et_3N; (iii) R-Temp).



Scheme 2. [M] = $Mo(CO)_2$L,L = η-C_5H_5 or η-C_5Me_5; (i)-Trimethylsilyloxybuta-1,3-diene.

the *syn*- and *anti*-aldehyde complexes are relatively low, it was realised that an alternative synthetic strategy was desirable. Consideration of the detailed steps (Scheme 2) involved in the desilylation reaction sequence surrounding the formation of the *syn*- and *anti*-aldehyde substituted complexes, suggested a possible new approach. Thus, if it is assumed that the kinetic product of the reaction of the 1-trimethylsilyloxybuta-1,3-diene with a cationic bis(acetonitrile) complex is a η^4-*s*-*trans*-1,3-diene complex then the *syn*-aldehyde substituted η^3-allyl must be formed by a rapid desilylation reaction. If the corresponding *anti*-aldehyde substituted system is to be formed then a change in the bonding mode of the 1,3-diene from η^4-*s*-*trans* to η^4-*s*-*cis* must compete effectively with the desilylation of the η^4-*s*-*trans*-trimethylsilyloxy-1,3-diene cation. This suggested that if the *anti*-aldehyde substituted η^3-allyl complex was to be formed selectively, then it would be necessary to use an oxy-substituent on the 1,3-diene, which is less labile than the Me_3SiO system, thus allowing time for complete *trans* to *cis*-isomerisation, which is necessary to establish the correct C_4 geometry for formation of the *anti*-aldehyde. In principle, (see Scheme 3) this could be achieved by first



Scheme 3. (i) $NaHCO_3$(aq.)(pH 8.5), CH_2Cl_2.

coordinating [8] 1-acetoxybuta-1,3-diene onto a $[Mo(CO)_2(\eta^5\text{-}C_5Me_5)]^+$ fragment, it being assumed that the initially formed η^4-*s-trans*-bonded adduct would isomerise at room temperature into the required η^4-*s-cis*-bonded isomer. Nucleophilic attack by hydroxide anion on the resulting acetoxy carbonyl carbon of the coordinated 1-acetoxybuta-1,3-diene would then be expected to lead to the selective formation of the required *anti*-aldehyde complex. It was recognised that this approach, if successful, might, form the basis of a future kinetic enantioselective resolution by utilisation of an esterase such as PLE to hydrolyse the acetoxy group.

Treatment of $[Mo(NCMe)_2(CO)_2(\eta^5\text{-}C_5Me_5)][BF_4]$ with 1-acetoxybuta-1,3 diene (CH_2Cl_2,4d) resulted in the formation (71% yield) of the cationic green crystalline complex $[Mo\{\eta^4\text{-}s\text{-}cis\text{-}CH_2{=}CHCH{=}CH(OAc)\}(CO)_2(\eta^5\text{-}C_5Me_5)][BF_4]$ **1**, characterised by elemental analysis, IR and NMR spectroscopy. The IR spectrum showed two terminal carbonyl bands at 2053 and 2006 cm^{-1}, typical of a cationic complex, along with a band at 1759 cm^{-1} due to the $CH_3C(O)O$ group. The ^1H spectrum was broad owing to *exo/endo* isomerisation, but showed resonances characteristic [8] of a η^4-coordinated *cis*-1,3-diene. When **1** was added at room temperature to a vigorously stirred two-phase system of dichloromethane and aqueous sodium bicarbonate (pH 8.5), the green colour was discharged and the organic layer became deep yellow. Workup of the dichloromethane layer by column chromatography on alumina afforded an excellent yield (81%) of the required complex $[Mo\{\eta^3\text{-}exo\text{-}anti\text{-}CH_2CHCH(CHO)\}(CO)_2(\eta^5\text{-}C_5Me_5)]$ **2**, which showed the expected IR and NMR spectra (see Section 3). Thus, this was a major improvement on our earlier work [6] when this complex was obtained in only 8% yield. The same approach was also successful for the synthesis of the corresponding η-cyclopentadienyl complex **4**, which was obtained in 87% yield on hydrolysis in the bi-phasic system of $[Mo\{\eta^4\text{-}s\text{-}cis\text{-}CH_2CHCHCH(OAc)\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ **3** prepared from $[Mo(NCMe)_2(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ and $CH_2{=}CHCH{=}CHOAc$. The η^5-indenyl complex **5** was also obtained in moderate yield (49%) by a variation [9] of this procedure involving low temperature ($-50°C$) addition of $HBF_4 \cdot Et_2O$ to a solution of $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(\eta^5\text{-}C_9H_7)]$ in CH_2Cl_2 followed by addition of 1-acetoxybuta-1,3-diene and then treatment with aqueous $NaHCO_3$.

To establish the nature of the bonding and stereochemistry of the related complexes **2**, **4**, and **5**, a single crystal X-ray diffraction study was conducted with a suitable crystal of **2**. The resulting molecular structure is illustrated in Fig. 1. Fractional atomic coordinates are given in Table 1, while selected bond lengths and interbond angles are listed in Table 2. The *anti*-oxyallyl ligand, which adopts a partially rotated [torsion angle C14–C15–C16–O3–176(1)°] *anti*-η^3-sickle conformation, is bound via C13, C14 and C15 to a $Mo(CO)_2(\eta^5\text{-}C_5Me_5)$ fragment, with O3 of the aldehydic carbonyl

Table 1
Fractional atomic coordinates (1×10^4) for **2**

Atom	*x*	*y*	*z*
Mo(1)	−55(1)	1486(1)	2565(1)
O(1)	−2479(10)	2031(11)	1474(10)
O(1′)	−1910(28)	1168(36)	825(21)
O(2)	−1897(12)	1157(12)	4262(8)
O(2′)	−2491(24)	1901(37)	3655(30)
O(3)	−1768(11)	−683(12)	643(7)
O(3′)	−1787(33)	−677(39)	4343(27)
C(1)	899(6)	3130(7)	3417(5)
C(2)	287(6)	3625(6)	2578(5)
C(3)	872(6)	3139(7)	1734(5)
C(4)	1846(6)	2342(7)	2063(5)
C(5)	1845(6)	2348(7)	3081(5)
C(6)	624(9)	3471(9)	4445(6)
C(7)	−693(8)	4636(8)	2573(8)
C(8)	597(8)	3477(9)	710(6)
C(9)	2769(8)	1719(9)	1420(7)
C(10)	2781(8)	1708(9)	3727(8)
C(11)	−1582(15)	1759(13)	1889(10)
C(11′)	−1238(34)	1240(43)	1406(39)
C(12)	−1251(13)	1273(15)	3648(13)
C(12′)	−1557(56)	1735(51)	3223(24)
C(13)	225(11)	−444(9)	3349(9)
C(14)	768(9)	−401(8)	2420(10)
C(15)	110(9)	−257(10)	1533(8)
C(16)	−1165(14)	−726(14)	1413(12)
C(16′)	−1097(42)	−767(36)	3524(34)

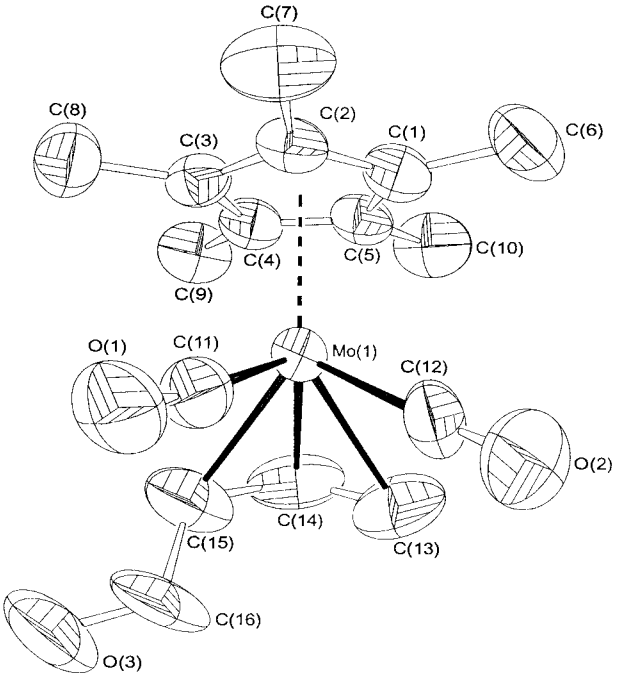


Fig. 1. The molecular structure of **2** showing the numbering scheme used in the text and tables.

Table 2
Selected bond lengths (Å) and angles (°) for **2**

Mo(1)–C(11)	1.93(2)
Mo(1)–C(12)	1.99(2)
Mo(1)–C(13)	2.328(9)
Mo(1)–C(14)	2.198(8)
Mo(1)–C(15)	2.332(9)
Mo(1)–C(3)	2.322(7)
O(3)–C(16)	1.24(2)
C(13)–C(14)	1.41(2)
C(14)–C(15)	1.42(2)
C(15)–C(16)	1.49(2)
C(11)–Mo(1)–C(12)	78.9(6)
C(13)–C(14)–C(15)	124.5(9)
C(14)–C(15)–C(16)	122.0(11)
O(3)–C(16)–C(15)	125.0(14)

group bent away from the metal centre at a non-bonding distance of 3.979 Å. The η^3-allyl backbone adopts an *exo* orientation with respect to the η^5-C_5Me_5 ligand, the C13–C14–C15 bond angle of 124.5(9)° being typical [10] of acyclic η^3-allyl complexes. As with the majority of Mo(II) *exo*-η^3-allyls, the inner carbon atom of the allyl moiety is closer to the metal [Mo–C14, 2.198(8) Å] than both the outer carbons [Mo–C13, 2.328(9) and Mo–C15 2.332(9) Å]. It is interesting to consider the carbon–carbon distances C13–C14 1.41(2) and C14–C15 1.42(2) Å along with the bond distances C16–O3 1.24(2) and C15–C16 1.49(2) Å, which altogether imply a contribution from the canonical form **B** shown in Fig. 2. Such a contribution is also consistent with the observation of a low-frequency [ν(CO) 1644 cm^{-1}] aldehydic carbonyl band in the IR spectrum of **2**. This, of course, suggests that there is a relatively high barrier to rotation about C15–C16.

Having established an efficient procedure for preparing 4-oxo-η^3-butenyl complexes exclusively in the *anti* configuration, attention was next turned to a study of the reactivity of the aldehydic functionality. Addition of $NaBH_4$ to a methanolic solution of the η-cyclopentadienyl substituted complex **4** (present as a mixture of *exo*- and *endo*-isomers) resulted in a fast (0.5 h) reaction, and following chromatographic work-up, a yellow crystalline solid was isolated in 65% yield. Spectroscopic and analytical data supported the formation of the expected hydroxy-substituted η^3-allyl complex [Mo{η^3-*exo-anti*-$CH_2CHCHCH_2(OH)$}$(CO)_2(\eta$-$C_5H_5)$] **6**. An examination of ^{1}H NMR data showed the presence of a single set of well-resolved resonances, readily assignable [11,12] to the *exo–anti* isomer. Comparison of the ^{1}H NMR data with that of similar complexes and consideration of the magnitude of the $J(H^bH^f)$ coupling constant (11.0 Hz) suggested that the hydroxyl group was orientated away from the molybdenum centre, as shown in Scheme 4. Presumably, this *trans* metal hydroxyl relationship arises from initial attack by BH_4^- on the *exo*-face of the rigid η^3-*anti*-$CH_2CHCH(CHO)$ ligand, followed by a rapid rotation about a C–C bond to give the less sterically congested product **6**.

Using MeOH as solvent, the reaction with $NaBH_4$ was rapid (0.5 h), however, prolonged stirring of the reaction mixture gave rise to the serendipitous discovery of an interesting side-reaction. When the reaction of **4** with $NaBH_4$ in MeOH was monitored by TLC, it was evident that within 0.5 h, complete conversion to **6** had occurred; however, on stirring for a further 2 h, continued TLC monitoring showed the gradual formation of an additional product. When the reaction was continued for a total of 30 h, TLC analysis of the resulting mixture revealed the complete consumption of **6**, with the new product being the only detectable species. Following aqueous work-up and column chromatography, this product was isolated as a hexane-soluble, yellow crystalline solid in 69% yield.

From an examination of the NMR spectra, it was evident that an η^1-butenyl complex, adopting an *exo–anti* configuration, had been formed. The ^{1}H spectrum of this compound displayed almost identical resonances to those in the corresponding spectrum of the hydroxyallyl complex **6** (minus the broad signal of the OH group), along with a strong singlet at 3.21 ppm, characteristic of a methoxy-substituent. A resonance at 57.2 ppm in the ^{13}C-{^{1}H} spectrum similarly implied the presence of a methoxy functionality. On the basis of

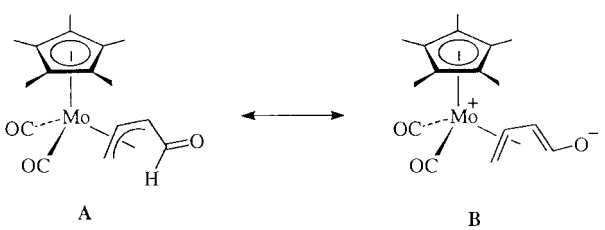
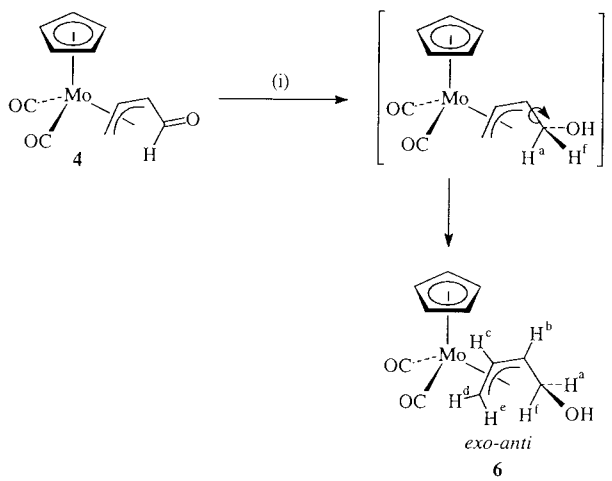
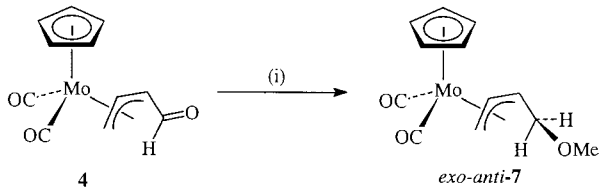


Fig. 2.



Scheme 4. (i) $NaBH_4$, MeOH, 0.5 h.



4 *exo-anti*-**7**

Scheme 5. (i) $NaBH_4$, MeOH, 30 h.

this evidence, the structure of the product was tentatively identified as [Mo{η^3-*exo-anti*-$CH_2CHCHCH_2$-(OMe)}$(CO)_2(\eta^5$-C_5H_5)] **7** (see Scheme 5) and this formulation was supported by elemental analysis and a FAB mass spectrum (FAB MS). The molecular structure was confirmed by a single crystal X-ray diffraction study. The molecular structure is shown in Fig. 3. Fractional atomic coordinates are presented in Table 3, while selected bond lengths and angles are listed in Table 4. The molecule shows bond parameters typical [10] of a [Mo(η^3-allylic)$(CO)_2(\eta^5$-C_5H_5)] complex, themethoxy-substituent being orientated away from the metal, i.e., *trans* to Mo as implied by a $J(H^bH^f)$ coupling of 11.2 Hz.

It is suggested that the formation of **7** involves the steps depicted in Scheme 6. Delivery of hydride anion by BH_4^- to the aldehydic carbonyl group forms the hydroxy-substituted complex **6**, which then reacts with

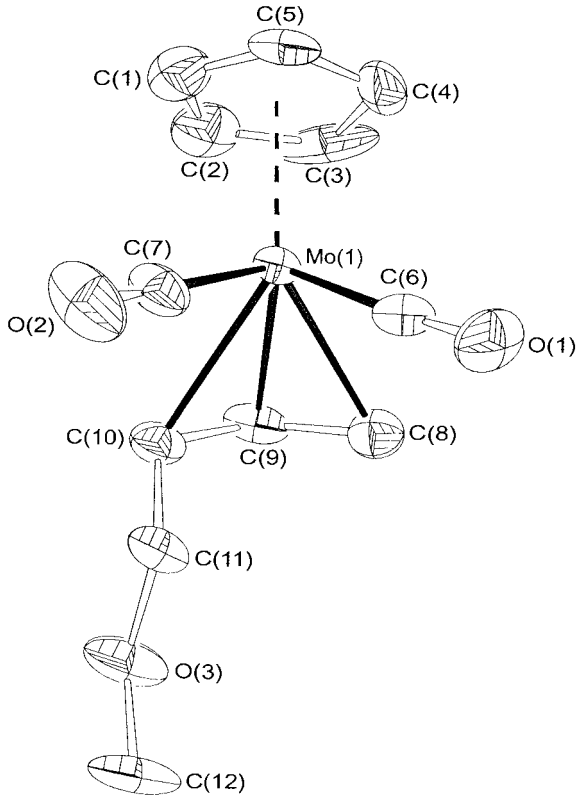


Fig. 3. The molecular structure of **7** showing the numbering scheme used in the text and tables.

Table 3
Atomic coordinates (1×10^4) for **7**

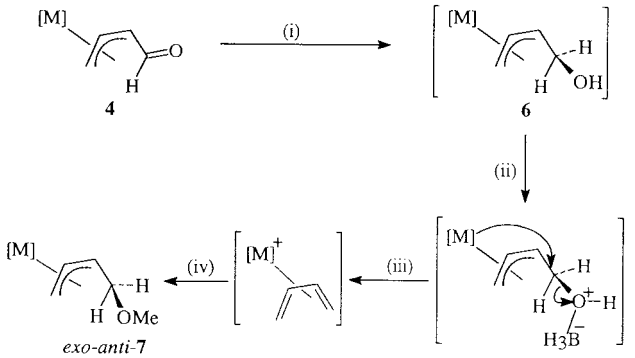
Atom	*x*	*y*	*z*
Mo(1)	2140(1)	176(1)	1296(1)
O(1)	3115(4)	−1063(5)	−97(2)
O(2)	619(5)	3286(5)	368(2)
O(3)	5692(5)	4719(5)	1410(2)
C(1)	−320(8)	−124(7)	1731(4)
C(2)	844(8)	−424(9)	2263(3)
C(3)	1730(6)	−1918(10)	2132(3)
C(4)	962(6)	−2540(6)	1455(3)
C(5)	−259(5)	−1346(7)	1262(3)
C(6)	2779(5)	−553(7)	426(2)
C(7)	1202(5)	2161(6)	715(2)
C(8)	4933(6)	−157(6)	1513(3)
C(9)	4371(5)	1135(7)	1944(2)
C(10)	3658(5)	2715(6)	1653(2)
C(11)	4362(5)	3678(6)	1107(2)
C(12)	6490(7)	5553(9)	906(3)

the by-product B_2H_6 on the oxygen of the hydroxyl group to generate a potentially good leaving group, i.e., $HOBH_3^-$. As illustrated, fragmentation then affords the buta-1,3-diene substituted cation [Mo{η^4-*exo*-1,3-C_4H_6}$(CO)_2(\eta$-C_5H_5)][$HOBH_3$], which is captured by reaction with methanol to form the isolated product **7**.

Support for this mechanism came from a study of the corresponding reaction of **4** with $NaBD_4$ in MeOH over 30 h. Standard chromatographic work-up led to the isolation of a hexane-soluble solid in 60% yield, and examination of the spectroscopic data revealed that the product was a 1:1 mixture of the deuterio-isomers shown in Scheme 7. As required by the mechanism shown in Scheme 6, 'D^-' is delivered to the CHO carbon atom to form an alcohol, which, on coordination of 'BD_3' and dissociative loss of $HOBD_3^-$, forms the cation [Mo{η^4-*exo*-CH(D)=CHCH=CH_2}$(CO)_2(\eta$-C_5H_5)]$^+$. This cation then reacts with OMe supplied by the methanol at either end of the coordinated buta-1,3-diene to form the two isomers shown in Scheme 7.

Table 4
Selected bond lengths (Å) and angles (°) for **7**

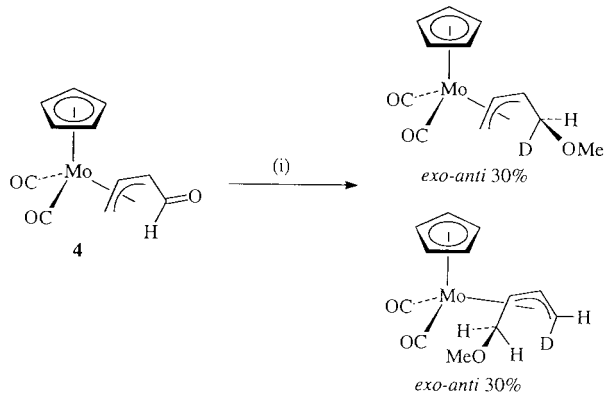
Mo(1)–C(6)	1.942(5)
Mo(1)–C(7)	1.970(5)
Mo(1)–C(9)	2.217(4)
Mo(1)–C(8)	2.320(5)
Mo(1)–C(10)	2.340(4)
O(3)–C(12)	1.417(6)
O(3)–C(11)	1.417(5)
C(8)–C(9)	1.412(7)
C(9)–C(10)	1.411(7)
C(10)–C(11)	1.484(5)
C(6)–Mo(1)–C(7)	80.8(2)
C(12)–O(3)–C(11)	111.6(4)
C(10)–C(9)–C(8)	119.4(4)
C(9)–C(10)–C(11)	121.1(4)
O(3)–C(11)–C(10)	109.4(3)



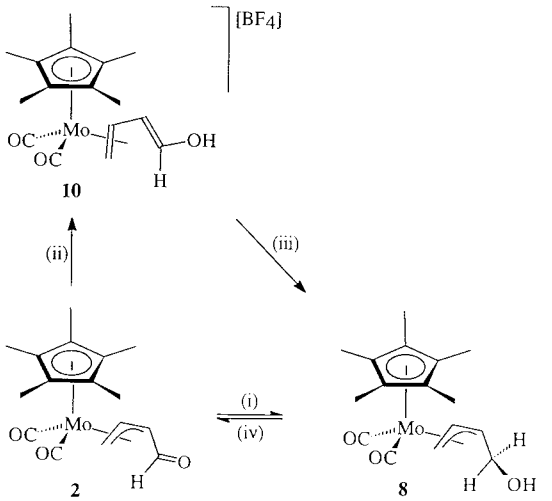
Scheme 6. [M] = $Mo(CO)_2(\eta^5\text{-}C_5H_5)$. (i) $NaBH_4$ / MeOH, 30 h; (ii) $+B_2H_6$; (iii) $-HOBH_3$; (iv) +OMe.

The $\eta^5\text{-}C_5Me_5$ substituted *exo–anti* aldehyde complex **2** showed a similar reactivity towards $NaBH_4$. Treatment of a methanolic solution of **2** with $NaBH_4$ followed by stirring at ambient temperature for 1 h, resulted in the formation of the corresponding *exo–anti* hydroxy complex **8**, isolated as yellow crystals in 62% yield. The NMR spectral data for **8** was similar to the analogous $\eta^5\text{-}C_5H_5$ complex, implying an identical orientation of the η^3-hydroxy allyl ligand. As before, an extended reaction time led to the formation of a methoxy-substituted compound **9** with the analogous spectral features, to **7**.

An alternative synthesis of the alcohol **8** was also explored, which relates to our earlier finding that *O*-protonation (HBF_4) of the *syn*-aldehyde substituted complexes $[Mo\{\eta^4\text{-}exo/endo\text{-}syn\text{-}CH_2CHCH(CHO)\}(CO)_2(\eta^5\text{-}C_5Me_5)]$ affords via an overall rotation about the C^2/C^3 axis of the allyl ligand, the hydroxy-substituted 1.3-diene cation $[Mo\{\eta^4\text{-}exo\text{-}s\text{-}cis\text{-}CH_2CHCHCH(OH)\}(CO)_2(\eta^5\text{-}C_5Me_5)]^+$ **10**. Although, as is summarised in Scheme 1, this cation is deprotonated by triethylamine to form the *anti*-aldehyde substituted complex **2** [6], we reasoned that it might be possible to use a relatively non-basic borohydride to selectively deliver 'H^-' to the hydroxy-substituted carbon of the 1,3-diene. This idea proved to be correct. In



Scheme 7. (i) $NaBD_4 \cdot MeOH$, 30 h.



Scheme 8. (i) $NaBH_4$, thf, 0.5 h; (ii) $HBF_4 \cdot Et_2O \cdot CH_2Cl_2$; (iii) $Na[BH_3CN]$, thf; (iv) $[Bu_4N^n][RuO_4]$, morpholine-*N*-oxide, CH_2Cl_2.

agreement with there being a contribution from the canonical form **B** (Fig. 2), protonation (−78°C) of a solution of **2** in dichloromethane with $HBF_4 \cdot Et_2O$ afforded (90% yield) the orange crystalline complex $[Mo\{\eta^4\text{-}exo\text{-}syn\text{-}s\text{-}cis\text{-}CH_2CHCHCH(OH)\}(CO)_2(\eta^5\text{-}C_5Me_5)][BF_4]$ **10**, (Scheme 8) characterised by elemental analysis, IR and NMR spectroscopy (see Section 3). When $Na[BH_3CN]$ was added (0°C) to a suspension of **10** in thf, a rapid reaction occurred resulting in the formation of the alcohol **8** in excellent yield (85%). Thus, as illustrated in Scheme 8, selective nucleophilic attack by 'H^-' occurs on the hydroxy-substituted carbon atom of the coordinated 1,3-diene, an observation that is in accord with our earlier studies [13] and those of Hansson et al. [14] and Rubio and Liebeskind [15].

Initial attempts to reverse the reduction reaction by oxidation (Swern) were unsuccessful. However, it was found that a catalytic amount of the Ley–Griffiths [16] [2] reagent $[Bu^n_4N][RuO_4]$ in the presence of morpholine-*N*-oxide at room temperature converted the alcohol **6** into **4** in 60% yield, and a similar reaction with **8** afforded **2** in comparable yield (see Scheme 8). This is an interesting result showing that the ruthenium reagent can be used to selectively oxidise an alcohol functionality without destroying a relatively sensitive metal complex.

Returning to the study of nucleophilic attack on the aldehyde carbonyl carbon atom, methylmagnesium iodide was added (−20°C) to a solution of **4** in thf which resulted, on workup, in the formation (70%) of $[Mo\{\eta^3\text{-}exo\text{-}anti\text{-}CH_2CHCHCH(OH)Me\}(CO)_2(\eta^5\text{-}C_5H_5)]$ **11**. Similarly, reactions between **4** and EtMgBr or PhMgCl afforded **12** (53%) and **13** (57%) respectively, and

[2] See also Ref. [17].

reaction of **6** with MeLi gave **14** (75%). All of these diastereomeric complexes, i.e., chiral at the carbon and molybdenum centres, were fully characterised by elemental analysis, IR and NMR spectroscopy.

It was clearly interesting to also explore the possibility of oxidation of these alcohols into ketone substituted η^3-allyl complexes that would have potential for enolate chemistry. However, an attempt to carry out an Oppenauer oxidation of the alcohol [Mo{η^3-*exo-anti*-$CH_2CHCHCH(OH)Me$}$(CO)_2(\eta^5H_5H_5)$] **11** was unsuccessful. When a solution of **11** and $Al(OPr^i)_3$ in acetone and toluene was heated under reflux, a single product, **15**, was formed. Following chromatographic work-up, a hexane-soluble yellow solid was isolated in 47% yield. From an initial examination of the spectroscopic and analytical data, it was evident that the expected MeCO-substituted η^3-allylic complex had not been formed. The ^{1}H NMR spectrum showed *exo*-η^3-allyl proton resonances at δ4.50 (H^b), 4.19 (H^c), 2.84 (H^d) and 1.47 (H^e), along with three proton resonances attributable to an uncoordinated vinyl group, suggesting that **15** was surprisingly an η^3-pentadienyl complex. In fact, we had previously [6,7] synthesised an analogous η^5-C_5Me_5 substituted complex [Mo{η^3-*exo-anti*-$CH_2CHCH(CH{=}CH_2)$}$(CO)_2(\eta^5$-$C_5Me_5)$] by reaction of **2** with the Wittig reagent $Ph_3P{=}CH_2$, or by deprotonation [18] (NEt_3) of the η^4-penta-1,3-diene cationic complex [Mo{η^3-*exo-syn*-$CH_2{=}CHCH{=}CH(Me)$}$(CO)_2(\eta^5$-$C_5Me_5)$][BF_4], and comparison of the ^{1}H NMR data for **15** with that for the η^5-C_5Me_5 system showed a close correspondence. To confirm the structural identity of **15**, a single crystal X-ray diffraction study was carried out. Fig. 4 shows the geometry of the molecule and the atomic numbering scheme used. Fractional atomic coordinates are given in Table 5, while selected bond lengths and angles are listed in Table 6.

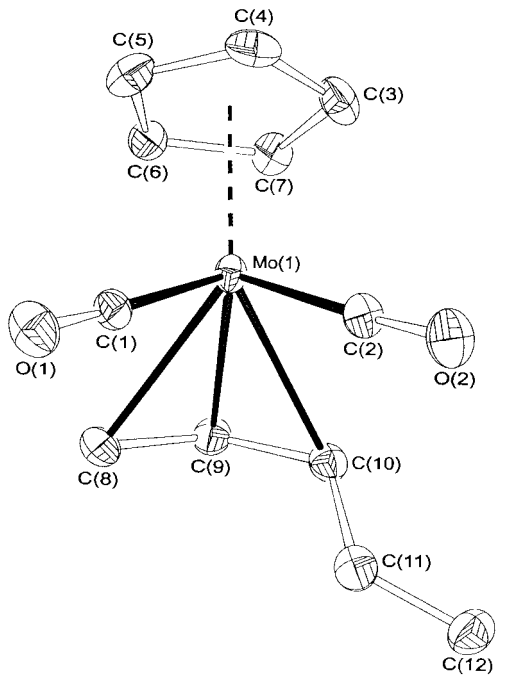


Fig. 4. The molecular structure of **15** showing the numbering scheme used in the text and tables.

Table 5
Atomic coordinates (1×10^4) for **15**

Atom	*x*	*y*	*z*
Mo(1)	2231(1)	2081(1)	2319(1)
O(1)	−121(4)	2284(3)	3616(2)
O(2)	3346(3)	4969(3)	3512(2)
C(1)	778(5)	2192(4)	3142(3)
C(2)	2962(4)	3884(5)	3080(3)
C(3)	2510(5)	3226(5)	911(3)
C(4)	991(5)	3457(5)	1036(3)
C(5)	294(5)	2005(5)	983(3)
C(6)	1345(5)	886(5)	838(3)
C(7)	2723(5)	1643(5)	783(3)
C(8)	2419(4)	−224(4)	3168(3)
C(9)	3732(4)	84(4)	2804(3)
C(10)	4692(4)	1336(4)	3151(3)
C(11)	5041(5)	1783(5)	4131(3)
C(12)	6323(5)	2461(5)	4548(3)

As surmised, the molecule contains a pentadienyl fragment in a *anti*-η^3-sickle conformation in which C8, C9 and C10 are bound to a [$Mo(CO)_2(\eta^5$-$C_5H_5)$] fragment with C11 bent away from the metal. As in the case of the related aldehyde-substituted system **2**, where the plane of the CHO group is rotated relative to the η^3-allyl plane, the vinyl group is partially rotated [torsion angle C9–C10–C11–C12: 151.0(0.4)]. Interestingly, it has recently [19] been reported that the sequential reaction of [W{η^1-$CH_2C{\equiv}CC(Me){=}CH_2$}$(CO)_3(\eta^5$-$C_5H_5)$] with CF_3SO_3H and MeOH affords an η^3-pentadienyl complex [W{η^3-*endo-anti*-η^3-$CH_2C(CO_2Me)CH(CMe{=}CH_2)$}$(CO)_2(\eta^5$-$C_5H_5)$], but in contrast with **15**, an X-ray structure of the tungsten species established that it adopts an *anti*-η^3-U conformation.

Table 6
Bond lengths (Å) and angles (°) for **15**

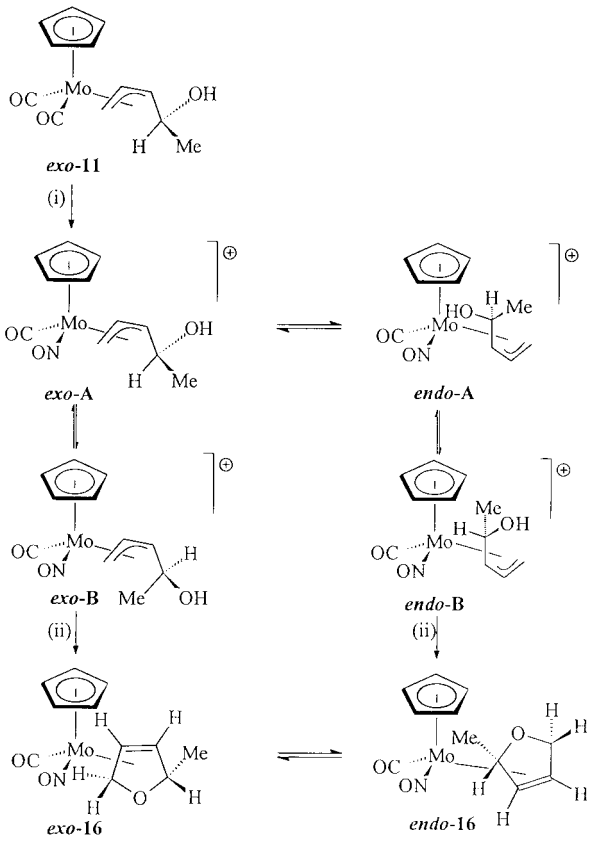
Mo(1)–C(1)	1.938(4)
Mo(1)–C(2)	1.957(4)
Mo(1)_C(5)	2.343(5)
Mo(1)–C(8)	2.343(4)
Mo(1)–C(9)	2.230(4)
Mo(1)–C(10)	2.397(4)
C(8)–C(9)	1.411(6)
C(9)–C(10)	1.421(6)
C(10)–C(11)	1.449(6)
C(11)–C(12)	1.331(7)
C(1)–Mo(1)–C(2)	78.8(2)
C(8)–C(9)–C(10)	120.5(4)
C(9)–C(10)–C(11)	123.7(4)
C(12)–C(11)–C(10)	124.6(4)

The failure to convert **11** into **4** was disappointing; however, preliminary experiments indicate that the Ley–Griffiths ruthenium reagent can also be used to oxidise the alcohols **11**, **12** and **13** to the corresponding *anti*-keto-substituted η^3-allyl complexes, and we are presently exploring this chemistry.

The availability of the hydroxy-substituted η^3-allyls **6**, **8**, **11**, **12** and **13** presented a further opportunity for the stereocontrolled functionalisation of allylic systems. Specifically, it is known [20,21] that the unsubstituted η^3-allyl complexes $[Mo(\eta^3\text{-allyl})(CO)_2(\eta\text{-}C_5H_5)]$ react with $[NO][BF_4]$ in acetonitrile to form the cationic complexes $[Mo(\eta^3\text{-allyl})(CO)(NO)(\eta\text{-}C_5H_5)][BF_4]$, which react selectively with nucleophilic reagents on the end carbons of the η^3-allyl ligand to form alkene complexes. Therefore, in principle, it might be possible to nitrosate the hydroxy-substituted allyl complexes and then promote a cyclisation reaction by removal of a proton from the *pro*-nucleophilic hydroxy centre. Of course, for such a reaction to be successful, there are problems of stereoselectivity, and it is interesting to note that in the study of Liu et al. [5] of the η^3-allylnitroso cation $[Mo\{\eta^3\text{-}exo\text{-}syn\text{-}anti\text{-}EtCHCHCHCH_2CH(OH)Ph\}(CO)(NO)(\eta\text{-}C_5H_5)][BF_4]$, where the hydroxy group is present in an *anti*-allylic side chain, decomplexation occurs and an isoxazole is formed.

Addition (0°C) of $[NO][BF_4]$ to an acetonitrile solution of **11** led to a rapid (0.25 h) reaction and the formation of a nitrosylcarbonyl substituted cation, which was characterised by the presence in the IR spectrum of υ(CO) and υ(NO) bands at 2072 and 1721 cm^{-1}, respectively. Addition of an excess of anhydrous Na_2CO_3 to the acetonitrile solution of this cation resulted in the gradual (4 h) disappearance of these bands and their replacement by bands at 1975 (CO) and 1622 (NO) cm^{-1}. Work-up by column chromatography gave a single yellow band, which on recrystallisation gave a yellow low melting solid characterised by a FAB MS and by ^{1}H NMR as an *exo/endo* mixture of the fur-3-ene substituted complexes $[Mo\{\eta^2\text{-}\dot{C}H{=}CHCH_2O\dot{C}(H)Me\}(CO)(NO)(\eta\text{-}C_5H_5)]$ (60% yield)(Scheme 9).

The diastereoselective formation of **16** is especially interesting because substituted furanyls are building blocks in a wide range of compounds of physiological and pharmacological importance. Particularly interesting is the fact that there is complete control over the stereochemistry at the methyl-substituted carbon atom 2 of the coordinated fur-3-ene, with the implication that if the corresponding chemistry was developed with chiral substituents on the η^5-C_5H_5 ring, then complete enantioselective control could be achieved at this centre. The origins of this selectivity are outlined in Scheme 9. In particular, if it is assumed [4] that NO^+ replaces CO *trans* to the CH(OH)Me group of the *exo*-η^3-allyl **11**, then the *exo*-cationic species **A** is formed. Rotation of the CH(Me)OH *anti*-η^3-allylic group then gives the *exo*-cation **B**, in which the hydroxyl group on deprotonation (Na_2CO_3) is ideally placed for intramolecular nucleophilic attack on the terminal η^3-allylic carbon *cis* to the NO ligand, thus leading to the formation of an *exo/endo* mixture of the neutral fur-3-ene complex **16**. Competing with this sequence of reactions is the reversible formation of the *endo*-cation **A**, which can similarly undergo rotation about a C–C bond to give the *endo*-cation **B**, and since it is known that nucleophilic attack occurs *trans* to the coordinated NO in the *endo*-isomer, this pathway also leads to the same *endo/exo* isomeric mixture of fur-3-ene complexes **16**. We are presently exploring the potential of this synthetic methodology.



Scheme 9. (i) $[NO][BF_4]$, MeCN, 0°C; (ii) Na_2CO_3, MeCN.

3. Experimental

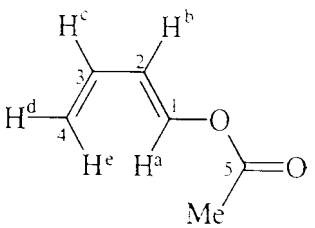
The ^{1}H, ^{13}C-{^{1}H} NMR spectra were recorded on JEOL GX270 and EX400 spectrometers. Data are given for room temperature measurements unless otherwise stated. Chemical shifts are referenced relative to tetramethylsilane. Infrared spectra were recorded on a Nicolet 580P FT-IR spectrometer. Reactions were carried out in

Schlenk tubes under atmospheres of dry oxygen-free nitrogen, using freshly distilled and degassed solvents. Column chromatography was performed using BDH alumina, Brockman activity II.

3.1. Preparations

3.1.1. [Mo{η^4-syn-s-cis-$CH_2CHCHCH(OAc)$}$(CO)_2(\eta^5$-C_5Me_5)][BF_4] **1**

An excess of 1-acetoxybuta-1,3-diene (0.460 ml, 0.435 g, 3.88 mmol) was added to a solution of the blood-red complex *cis*-[Mo$(NCMe)_2(CO)_2(\eta^5$-C_5Me_5)][BF_4] (0.177 g, 0.388 mmol) in CH_2Cl_2 (25 ml) and the mixture was stirred at room temperature for 4 days. Monitoring by infrared spectroscopy showed the gradual consumption of the starting material and the formation of a new product. The solvent was removed in vacuo, and the resulting green-brown residue was extracted with CH_2Cl_2 and filtered through Celite. The bottle-green filtrate was concentrated to a small volume under reduced pressure, after which, the addition of Et_2O precipitated a green solid. The supernatant liquid was removed via syringe and the solid washed with several portions of Et_2O, then pentane. A further purification was effected by recrystallisation from CH_2Cl_2/Et_2O to afford green crystals of **1** (0.133 g, 71%) (Found: C, 45.0; H, 5.0. $C_{18}H_{23}BF_4MoO_4$ requires C, 44.5; H. 4.8%). IR (CH_2Cl_2): ν(CO) 2053 vs, 2006 s and 1759 mw cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 6.08 (m, 1H, H^c), 5.97 (m, 1H, H^b), 4.58 [d, 1H, H^a, $J(H^aH^b)$ 6.8], 2.57 [d, 1H, H^d, $J(H^dH^e)$ 7.8], 2.03 (s, 3H, Me), 1.98 (s 15H, C_5Me_5) and 1.05 [d, 1H, H^c, $J(H^cH^d)$ 10.7]; ^{13}C-{^1H} δ 221.6 (CO), 220.3 (CO), 169.3 (C^5), 106.1 (C_5Me_5), 100.1 (C^1), 95.3 (C^2 or C^3), 89.0 (C^2 or C^3), 59.5 (C^4), 20.5 (Me) and 10.8 (C_5Me_5).



3.1.2. [Mo{η^3-exo-anti-$CH_2CHCH(CHO)$}$(CO)_2(\eta^5$-C_5Me_5)] **2**

Sodium hydrogen carbonate (50 ml, of a 0.1 M aqueous solution, pH 8.5, ca. 5.0 mmol) was added to a solution of the green complex **1** (1.94 g, 3.99 mmol) in CH_2Cl_2 (50 ml). The two-phase system was vigorously stirred at room temperature, causing the mixture to turn yellowish in colour. After 2 h, the aqueous layer was removed and extracted several times with CH_2Cl_2. The extracts and organic layer were combined and washed with several portions of water before drying over magnesium sulphate. The mixture was filtered, and the yellow filtrate was concentrated to a small volume under reduced pressure before being chromatographed on alumina. Elution with Et_2O afforded a single yellow fraction which gave, after removal of solvent and recrystallisation from Et_2O, bright yellow crystals of **2** (1.15 g, 81%) (Found: C, 54.0; H, 5.7. $C_{16}H_{20}MoO_3$ requires C, 53.9; H, 5.7%). IR (CH_2Cl_2): ν(CO) 1960 vs, 1883 s and 1644 m cm^{-1}. NMR (CD_2Cl_2): ^1H δ, 7.00 [d, 1H, H^a, $J(H^aH^b)$ 7.8], 3.51 [ddd, 1H, H^c, $J(H^cH^e)$ 11.6, $J(H^cH^d)$ 8.4, $J(H^cH^b)$7.1], 3.42 (m, 1H, H^b), 2.28 [ddd, 1H, H^d, $J(H^dH^c)$ 8.4, $J(H^dH^e)$ 2.8, $J(H^dH^b)$ 1.4], 1.88 (s, 15H, C_5Me_5) and 1.75 [dd, 1H, H^c, $J(H^eH^c)$ 11.6, $J(H^eH^d)$ 2.8]; ^{13}C-{^1H}, δ 237.5 (CO), 237.2 (CO), 184.8 (C^1), 104.9 (C_5Me_5), 80.1 (C^3), 65.0 (C^2), 42.4 (C^4) and 10.4 (C_5Me_5). FAB MS $[MH]^+$ 359, $[M–CO]^+$ 330, $[M–CO]^+$ 302.

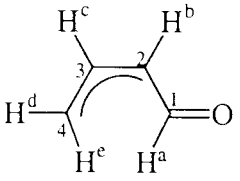
3.1.3. [Mo{η^4-syn-s-cis-$CH_2CHCHCH(OAc)$}$(CO)_2(\eta^5$-C_5H_5)][BF_4] **3**

An excess of 1-acetoxybuta-1,3-diene (9.40 cm^3, 79.0 mmol) was added to a solution of the blood-red complex *cis*-[Mo$(NCMe)_2(CO)_2(\eta^5$-C_5H_5)][BF_4] (3.05 g, 7.90 mmol) in CH_2Cl_2 (55 ml). After stirring at ambient temperature for 2 days, a bright yellow precipitate was observed. Stirring was continued for a further 2 days, resulting in the formation of more precipitate. The mixture was filtered via cannula, and the yellow solid was washed with several portions of CH_2Cl_2, then pentane. Removal of the solvent in vacuo, afforded yellow crystals of **3** (2.80 g, 85%) (Found: C, 37.0; H, 3.2. $C_{13}H_{13}BF_4MoO_4$ requires C, 37.5; H, 3.1%). IR (CH_3NO_2): ν(CO) 2068 vs, 2020 s and 1759 mw cm^{-1}. NMR (d^6-acetone): ^1H, δ 6.48 (br m, 1H, H^b), 6.29 (br m, 1H, H^c), 6.12 (s, 5H, C_5H_5), 6.07 [br d, 1H, H^a, $J(H^aH^b)$ 6.8], 3.01 [ddd, 1H, H^d, $J(H^dH^c)$ 7.8, $J(H^dH^e)$ 2.0, $J(H^dH^b)$ 1.4], 2.38 [br d, 1H, H^c, $J(H^cH^c)$ 10.7] and 2.06 (s, 3 H, Me); ^{13}C-{^1H}, δ 220.2 (CO), 219.2 (CO), 167.9 (C^5), 102.8 (C^1), 93.9 (C^2 or C^3), 91.6 (C_5H_5), 88.3 (C^2 or C^3), 50.0 (C^4), 20.5 (Me).

3.1.4. [Mo{η^3-anti-$CH_2CHCH(CHO)$}$(CO)_2(\eta$-C_5H_5)] **4**

Sodium hydrogen carbonate (75 ml of a 0.1 M aqueous solution, pH 8.5, ca. 7.50 mmol) was added to a solution of the yellow complex **3** (3.00 g. 7.21 mmol) in CH_2Cl_2 (60 ml). The two-phase system was vigorously stirred at room temperature for 0.5 h. The aqueous layer was removed and extracted several times with CH_2Cl_2. The extracts and organic layer were combined

and washed with several portions of water, before drying over magnesium sulphate. The mixture was filtered, and the yellow filtrate was concentrated to a small volume under reduced pressure, before being chromatographed on alumina. Elution with CH_2Cl_2 afforded a bright yellow band which gave, after removal of solvent and recrystallisation from CH_2Cl_2/hexane, bright yellow crystals of **4** (1.80 g, 87%) (Found: C, 46.3; H, 3.5. $C_{11}H_{10}MoO_3$ requires C, 46.2; H, 3.5%). IR (CH_2Cl_2): ν(CO) 1973 vs, 1896 s and 1649 m cm^{-1}. NMR (CD_2Cl_2) *exo–anti*: isomer ^1H, δ 7.14 (br s, 1H, H^a), 5.40 (br s, 5H, C_5H_5), 4.76 (br s, 1H, H^c), 4.05 (br s, 1H, H^b), 3.03 (br s, 1H, H^d) and 1.77 (br s, 1H, H^e); (CD_2Cl_2, −40°C): δ 6.98 [d, 1H, H^a, $J(H^aH^b)$ 7.9], 5.40 (s, 5H, C_5H_5), 4.78 [ddd, 1H, H^c, $J(H^cH^e)$ 11.9, $J(H^cH^d)$ 8.2, $J(H^cH^b)$ 7.0], 4.00 [ddd, 1H, H^b, $J(H^bH^a)$ 7.9, $J(H^bH^c)$ 7.0, $J(H^bH^d)$ 1.4], 3.02 [ddd, 1H, H^d. $J(H^dH^c)$ 8.2, $J(H^dH^e)$ 2.7, $J(H^dH^b)$ 1.4 and 1.68 [dd, 1H, H^e, $J(H^eH^c)$ 11.9, $J(H^cH^d)$ 2.7]. ^{13}C-{^1H}, δ 234.7 (br s, CO), 234.3 (br s, CO), 186.7 (br s, C^1), 92.2 (br s, C_5H_5), 72.2 (br s, C^3), 59.5 (br s, C^2) and 40.2 (br s, C^4); (CD_2Cl_2, −50°C): δ 234.7 (CO), 234.5 (CO), 186.1 (C^1), 92.0 (C_5H_5), 71.8 (C^3) 58.7 (C^2) and 40.0 (C^4).



Endo–anti isomer ^1H, δ 7.84 (br s, 1H, H^a), 5.30 (br s, 5H, C_5H_5), 4.50 (br s, 1H, H^c), 4.19 (br s, 1H, H^b), 2.78 (br s 1H, H^d) and 2.65 (br s, 1H, H^e); (CD_2Cl_2, −40°C): δ 7.71 [d, 1H, H^a, $J(H^aH^b)$ 7.9], 5.30 (s, 5H, C_5H_5), 4.46 [ddd, 1H, H^c, $J(H^cH^e)$ 11.2, $J(H^cH^d)$ 7.3, $J(H^cH^b)$ 6.2], 4.28 [dd, 1H, H^b, $J(H^bH^a)$ 7.9, $J(H^bH^c)$ 6.2], 2.77 [d, 1H, H^d, $J(H^dH^c)$7.3] and 2.65 [d, 1H, H^e, $J(H^eH^c)$ 11.2]; ^{13}C–{^1H}, δ 234.7 (br s, CO), 234.3 (br s, CO), 186.7 (br, s, C^1), 92.2 (br s, C_5H_5), 72.2 (br s, C^3), 59.5 (br s, C^2) and 40.2 (br s, C^4); (CD_2Cl_2 −50°C): δ 235.4 (CO), 235.1 (CO), 186.6 (C^1), 90.9 (C_5H_5), 86.4 (C^3), 61.0 (C^2) and 34.2 (C^4). FAB MS $[M]^+$ 288, $[M–CO]^+$ 260, $[M–2CO]^+$ 232.

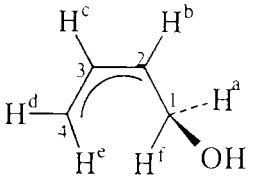
3.1.5. *[Mo{η^3-exo-anti-$CH_2CHCH(CHO)$}$(CO)_2(\eta^5$-C_9H_7)]* ***5***

A solution of the yellow complex [Mo(η^3-C_3H_5)$(CO)_2(\eta^5$-C_9H_7)] (2.83 g, 9.19 mmol) in CH_2Cl_2 (50 ml) was cooled to −50°C. To this was added $HBF_4 \cdot OEt_2$ (1.74 ml, 2.01 g of an 85% Et_2O solution, 10.57 mmol) resulting in an immediate colour change to dark red. After stirring for 0.5 h at −50°C, the mixture was treated with 1-acetoxybuta-1,3-diene (2.73 ml, 22.98 mmol) and allowed to warm to ambient temperature, producing a green-black viscous mixture. This was stirred for a further 1 h and then filtered through Celite to give a dark green solution. The filtrate was concentrated to a dark residue in vacuo, redissolved in CH_2Cl_2 (80 ml) and treated with sodium hydrogen carbonate (135 ml of an aqueous solution, pH 8.5, ca. 13.79 mmol). The two-phase system was vigorously stirred at room temperature for 0.5 h, causing the mixture to turn dark yellow in colour. The aqueous layer was removed and extracted several times with CH_2Cl_2. The extracts and organic layer were combined and washed with several portions of water before drying over magnesium sulphate. The mixture was filtered through a pad of alumina, and the orange-yellow filtrate was concentrated to a small volume under reduced pressure before being chromatographed on alumina. Elution with CH_2Cl_2 afforded a bright yellow fraction which gave, after removal of solvent and recrystallisation from CH_2Cl_2/hexane, bright yellow crystals of **5** (1.51 g, 49%) (Found: C, 53.5; H, 3.6. $C_{15}H_{12}MoO_3$ requires C, 53.6; H, 3.6%). IR (CH_2CL_2): υ(CO) 1973 vs, 1896 s and 1649 m cm^{-1}. NMR (CD_2Cl_2): ^1H (−20°C), δ 7.25–7.08 (m, 4H, indenyl), 6.86 [d, 1H, H^a, $J(H^aH^b)$ 8.2], 6.18 (m, 1H, indenyl), 6.06 (m, 1H, indenyl), 5.60 (m, 1H, indenyl), 3.35 [ddd, 1H, H^b, $J(H^bH^a)$ 8.2, $J(H^bH^c)$ 7.4, $J(H^bH^d)$ 1.3]. 2.52 [ddd, 1H, H^d, $J(H^dH^c)$ 8.7, $J(H^dH^c)$ 2.2, $J(H^dH^b)$ 1.3], 1.83 [dd, 1H, H^c, $J(H^cH^e$ 12.2 $J(H^cH^d)$ 2.2] and 0.40 [ddd, 1H, H^c, $J(H^cH^e)$ 12.2, $J(H^cH^d)$ 8.7, $J(H^cH^b)$ 7.4]; ^{13}C-{^1H}, δ 235.2 (CO), 234.1 (CO), 185.6 (C^1), 126.5, 126.4 (indenyl), 124.4, 124.0 (indenyl), 112.6, 112.3 (indenyl), 89.5 (indenyl), 87.9 (C^3). 81.0, 80.2 (indenyl), 69.2 (C^2) and 48.2 (C^4). FAB MS, $[MH]^+$ 339, $[M–CO]^+$ 310, $[M–2CO]^+$ 282.

3.1.6. *[Mo{η^3-exo-anti-$CH_2CHCHCH_2(OH)$}$(CO)_2(\eta^5$-C_5H_5)]* ***6***

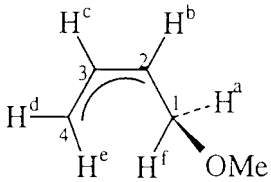
Sodium borohydride (0.02 g, 0.529 mmol) was added to a solution of **4** (0.10 g, 0.349 mmol) in methanol (10 ml), and the mixture was stirred at ambient temperature for 0.5 h. Monitoring by infrared spectroscopy indicated the complete consumption of starting material and the formation of a new product. Water (0.5 ml) was added, and the mixture was stirred for 0.5 h before the solvents were removed in vacuo. The yellow residue was extracted with several portions of Et_2O, which were concentrated to a small volume under reduced pressure and chromatographed on alumina. Elution with Et_2O/hexane (1:1) afforded a yellow fraction which gave, after removal of solvents and recrystallisation from CH_2Cl_2/pentane, yellow crystals of **6** (0.065 g, 65%)(Found:C, 46.0; H, 4.2, $C_{11}H_{12}MoO_3$ requires C, 45.9; H, 4.2%). IR(CH_2Cl_2): υ(CO) 1948 s and 1865 s

cm^{-1}. NMR ($CDCl_3$): ^1H, δ 5.28 (s, 5H, C_5H_5), 4.12 [ddd, 1H, H^c, $J(H^cH^e)$ 11.4, $J(H^cH^b)$ 7.7, $J(H^cH^d)$ 7.5], 3.93(m, 1H, H^b), 3.78 (m, 1H, H^a), 2.94 [ddd, 1H, H^d, $J(H^dH^c)$ 7.5, $J(H^dH^e)$ 2.4, $J(H^dH^b)$ 1.6], 2.14 [dd, 1H, H^f, $J(H^fH^b)$ 11.0], 1.50 (br s, 1H, OH) and 1.41 [dd, 1H, H^e, $J(H^eH^c)$ 11.4, $J(H^eH^d)$ 2.4]; ^{13}C-{^1H}, δ 236.8 (CO), 236.3 (CO), 91.6 (C_5H_5), 69.1 (C^1). 66.6 (C^3), 53.9(C^2) and 38.1 (C^4). FAB MS, $[M-OH]^+$ 273, $[M-OH-CO]^-$ 245, $[M-OH-2CO]^+$ 217.



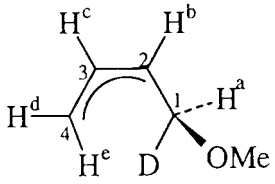
3.1.7. [Mo{η^3-exo-anti-$CH_2CHCHCH_2(OMe)$}$(CO)_2$-(η^5-C_5H_5)] 7

An excess of sodium borohydride (0.02 g, 0.529 mmol) was added to a solution of **4** (0.10 g, 0.349 mmol) in methanol (10 ml), and the mixture was stirred at ambient temperature for 30 h. Monitoring by TLC showed the formation of a new product ($R_f = 0.9$, alumina/CH_2Cl_2). Water (0.5 ml) was added and the mixture was stirred for 0.5 h, after which the solvents were removed in vacuo. The yellow residue was extracted with several portions of Et_2O, which were concentrated to an oil under reduced pressure and redissolved in a small volume of hexane, before being chromatographed on alumina. Elution with hexane afforded a yellow band which gave, after removal of solvent and recrystallisation from hexane (−30°C), yellow crystals of **7** (0.073 g, 69%) (Found: C, 47.6; H, 4.7 $C_{12}H_{14}MoO_3$ requires C, 47.7; H, 4.7%). IR (CH_2Cl_2): ν(CO) 1948 vs and 1863 cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 5.30 (s, 5H, C_5H_5), 4.21 [ddd, 1H, H^c, $J(H^cH^e)$ 11.4, $J(H^cH^b)$ 7.7, $J(H^cH^d)$ 7.6], 3.77 [dddd, 1H, H^b, $J(H^bH^f)$ 11.2, $J(H^bH^c)$ 7.7, $J(H^bH^a)$ 3.7, $J(H^bH^d)$ 1.6], 3.62[dd, 1H, H^a, $J(H^aH^f)$ 11.0, $J(H^aH^b)$ 3.7], 3.21 (s, 3H, OMe), 2.96 [ddd, 1H, H^f, $J(H^fH^b)$ 11.2, $J(H^fH^a)$ 11.0] and 1.35 [dd, 1H, H^c, $J(H^eH^c)$ 11.4, $J(H^eH^d)$ 2.4]; ^{13}C-{^1H}, δ 237.5, (CO), 237.0 (CO), 92.0 (C_5H_5), 71.7 (C^1), 67.1 (C^3), 57.2 (OMe), 53.9 (C^2) and 38.0 (C^4). FAB MS, $[M]^+$ 304, $[M-OMe]^+$ 245, $[M-OMe-CO]^+$ 245, $[M-OMe-2CO]^+$ 217.

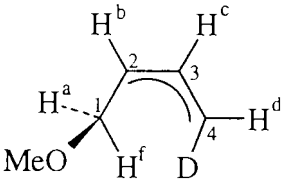


3.2. Reaction of [Mo{η^3-anti-$CH_2CHCH(CHO)$}-$(CO)_2$(η^5-C_5H_5)] 4 with $NaBD_4$

An excess of sodium borodeuteride (0.012 g, 0.287 mmol) was added to a solution of the yellow complex **4** (0.06 g, 0.210 mmol) in methanol (7 ml) and the mixture was stirred for 30 h. Water (0.5 ml) was added and the mixture was stirred for 0.5 h, after which the solvents were removed in vacuo. The yellow residue was extracted with several portions of Et_2O, which were concentrated to an oil under reduced pressure and redissolved in a small volume of hexane, before being chromatographed on alumina. Elution with hexane afforded a single yellow fraction which gave, after removal of solvent and recrystallisation from hexane (−30°C), a 1:1 isomeric mixture of [Mo(η^3-*exo-anti*-$CH_2CHCHCH(OMe)D$}$(CO)_2$(η^5-C_5H_5)] **7a** and [Mo(η^3-*exo-anti*-$CHDCHCHCH_2(OMe)$}$(CO)_2$(η^5-C_5H_5)] **7b** obtained as a yellow solid (0.038 g, 60%). (Found: C, 46.9; H, 4.6, $C_{12}H_{13}DMoO_3$ requires C, 47.5; H, 4.3%). IR (CH_2Cl_2); ν(CO) 1948 vs and 1865 s cm^{-1}. NMR ($CDCl_3$): ^1H, **7a**, δ 5.28 (s, 5H, C_5H_5), 4.18 [ddd, 1H, H^c, $J(H^cH^e)$ 11.4, $J(H^cH^b)$ 7.7, $J(H^cH^d)$ 7.6], 3.78 (m, 1H, H^b), 3.62 (m, 1H, H^a), 3.25 (s, 3H, OMe), 2.95 [dd, 1H, H^d, $J(H^dH^c)$ 7.6, $J(H^dH^e)$ 2.4] and 1.38 [dd, 1H, H^e, $J(H^eH^d)$ 2.4].



^1H, **7b**, δ 5.28 (s, 5H, C_5H_5), 4.18 (m, 1H, H^c), 3.78 (m, 1H, H^b), 3.64 [dd, 1H, H^a, $J(H^aH^f)$ 10.9, $J(H^aH^b)$ 3.7], 3.25 (s, 3H, OMe), 2.95 [dt, 1H, H^d, $J(H^dH^c)$ 7.6, $J(H^dD)$ 2.4] and 1.85 [dd, 1H, H^f, $J(H^fH^b)$ 11.1, $J(H^fH^a)$ 10.9].



^{13}C-{^1H} for **7a** and **7b**, δ 237.6 (CO), 237.1 (CO), 91.7 (C_5H_5), 71.8 (br s. C^1), 66.6 (C^3), 57.6 (OMe), 53.4 (C^2) and 38.1 (br s, C^4).

3.2.1. [Mo{η^3-exo-anti-$CH_2CHCHCH_2(OH)(CO)_2$(η^5-C_5Me_5)] 8

Sodium borohydride (0.013 g, 0.321 mmol) was added to a solution of the yellow complex **2** (0.104 g, 0.292 mmol) in methanol (10 ml), and the mixture was

stirred at ambient temperature for 1 h. Monitoring by infrared spectroscopy indicated the complete consumption of starting material and the formation of a new product. Water (0.5 ml) was added, and the mixture was stirred for 0.5 h before the solvents were removed in vacuo. The yellow residue was extracted with several portions of Et_2O, which were concentrated to a small volume under reduced pressure and chromatographed on alumina. Elution with Et_2O afforded a yellow band which gave, after removal of solvent and recrystallisation from CH_2Cl_2/hexane, afforded yellow crystals of **8** (0.065 g, 62%) (Found: C. 53.3; H, 6.0. $C_{16}H_{22}MoO_3$ requires C, 53.6; H, 6.2%). IR (CH_2Cl_2): ν(CO) 1935 vs and 1852 s cm^{-1}. NMR (CD_2Cl_2: ^1H, δ 3.64 [dd, 1H, H^a. $J(H^aH^t)$ 11.4, $J(H^aH^b)$ 3.6], 3.22[ddddd,1H, H^b, $J(H^bH^f)$ 11.2, $J(H^bH^c)$ 7.6, $J(H^bH^a)$ 3.6, $J(H^bH^d)$ 1.5, $J(H^bH^e)$ 0.6], 2.85 [ddd, 1H, H^c, $J(H^cH^c)$ 11.9, $J(H^cH^d)$ $J(H^cH^b)$ 7.6], 2.25 [ddd, 1H, H^d, $J(H^dH^c)$ 7.6, $J(H^dH^e)$ 2.4, $J(H^dH^b)$ 1.5], 2.07 [dd, 1H, H^f, $J(H^fH^a)$ 11.4, $J(H^fH^b)$ 11.2], 1.86 (s, 15H, C_5Me_5), 1.51 (br s, 1H, OH) and 1.46 [ddd, 1H, H^e, $J(H^cH^c)$ 11.9, $J(H^eH^d)$ 2.4, $J(H^eH^b)$ 0.6]; ^{13}C-{^1H}, δ 240.3 (CO), 239.8 (CO), 103.9 (C_5Me_5), 74.0 (C^3), 62.4 (C^1), 61.8 (C^2), 41.9 (C^4) and 10.3 ($C_5\mathit{Me}_5$). FAB MS, $[MH]^+$ 359, $[M-2H-2CO]^+$ 330, $[M-2H-2CO]^+$ 302.

3.2.2. [Mo{η^3-exo-anti-$CH_2CHCHCH_2(OMe)$}$(CO)_2$-(η^5-C_5Me_5)] **9**

An excess of sodium borohydride (0.021 g, 0.544 mmol) was added to a solution of **2** (0.097 g, 0.272 mmol) in methanol (10 cm^3), and the mixture was stirred at ambient temperature for 2 d. Monitoring by TLC showed the formation of a new product ($R_f = 0.92$, alumina/CH_2Cl_2). Water (0.5 cm^3) was added, and the mixture was stirred for 0.5 h, after which the solvents were removed in vacuo. The yellow residue was extracted with several portions of Et_2O, which were concentrated to an oil under reduced pressure and redissolved in a small volume of hexane, before being chromatographed on alumina. Elution with hexane afforded a yellow band which gave, after removal of solvent and recrystallisation from hexane (−30°C), afforded yellow crystals of **9** (0.066 g, 65%) (Found: C, 54.4; H, 6.7. $C_{17}H_{24}MoO_3$ requires C, 54.8; H, 6.5%). IR (CH_2Cl_2): ν(CO) 1935 vs and 1850 s cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 3.56 [dd, 1H, H^a, $J(H^aH^f)$ 10.9, $J(H^aH^b)$ 3.6], 3.20 (s, 3H, OMe), 3.05 [dddd, 1H, H^b, $J(H^bH^f)$ 11.1, $J(H^bH^c)$ 7.8, $J(H^bH^a)$ 3.6, $J(H^bH^d)$ 1.6], 2.92 [ddd, 1H, H^c, $J(H^cH^e)$ 11.2, $J(H^cH^b)$ 7.8, $J(H^cH^d)$ 7.5], 2.25 [ddd, 1H, H^d, $J(H^dH^c)$ 7.5, $J(H^dH^e)$ 2.4, $J(H^dH^b)$ 1.6], 1.86 (s, 15H, C_5Me_5), 1.80 [dd, 1H, H^f, $J(H^fH^b)$ 11.1, $J(H^fH^a)$ 10.9] and 1.43 [dd, 1H, H^e, $J(H^eH^c)$ 11.2, $J(H^eH^d)$ 2.4]; ^{13}C-{^1H}, δ 240.6 (CO), 240.0 (CO), 103.9 (C_5Me_5), 75.2 (C^3), 72.0 (C^1), 57.9 (C^2), 57.0 (OMe), 41.8 (C^4) and 10.3 ($C_5\mathit{Me}_5$). FAB MS, $[M-OMe]^+$ 343, $[M-OMe-CO]^+$ 315, $[M-OMe-2CO]^+$ 287.

3.3. Formation of **8** by protonation of **2** followed by nucleophilic attack

(a) A solution of **2** (0.104 g, 0.292 mmol) in CH_2Cl_2 (15 ml) was cooled to −78°C and treated with $HBF_4 \cdot Et_2O$ (0.10 g, 0.09 ml of an 85% Et_2O solution, 1.05 mmol) causing a slight darkening in colour. The mixture was allowed to warm to room temperature and stirred for 1 h. The resulting orange solution was filtered through Celite and then concentrated to a small volume (3 ml) under vacuo. Addition of Et_2O precipitated an orange solid, which was washed with Et_2O and recrystallised from CH_2Cl_2/Et_2O to afford orange crystals of [Mo{(η^4-*exo-syn-s-cis*-$CH_2CHCHCH$-(OH)}$(CO)_2$(η^5-C_5Me_5)][BF_4] **10** (0.111 g, 86%) (Found: C, 43.5; H,4.5. $C_{16}H_{21}BF_4MoO_3$ requires C, 43.2; H,4.7%). IR(CH_2Cl_2): ν(CO) 1993 vs and 1927 vs cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 5.67 [d, 1H, H^a, $J(H^aH^b)$ 9.3], 4.30 [dd, 1H, H^b, $J(H^aH^b)$ 9.3, $J(H^bH^c)$ 6.3], 4.11 [ddd, 1H, H^c, $J(H^bH^c)$ 6.3, $J(H^cH^d)$ 8.6, $J(H^cH^e)$ 11.6], 2.20 [d, 1H, H^d, $J(H^cH^d)$ 8.6], 1.41[d, 1H, H^e, $J(H^cH^e)$ 11.6].

(b) Sodium cyanoborohydride (0.249 ml of a 1 M solution in thf, 0.249 mmol) was added to a cooled (0°C) suspension of the cation **10** (0.110 g, 0.249 mmol) in thf (20 ml). The reaction mixture was stirred for 1 h at 0°C before being allowed to warm to ambient temperature. After stirring, the yellow solution for 1 h at room temperature, the solvent was removed in vacuo, and the residue was chromatographed on alumina. Elution with Et_2O afforded a yellow fraction which gave, after removal of solvent and recrystallisation from CH_2Cl_2/hexane, yellow crystals of **8** (0.090 g, 85%), identified by comparison of the IR and NMR spectra of an authentic sample.

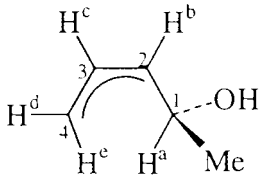
3.4. Oxidation of **6** to form the aldehyde complex **4**

Morpholine-*N*-oxide (0.274 g, 2.34 mmol) was added to a solution of **6** (0.450 g, 1.56 mmol) in CH_2Cl_2 (5 ml) which contained 4 Å molecular sieves. After stirring at room temperature for 10 min, [Bu^n_4N][RuO_4] (0.027 g, 0.078 mmol) was added. The reaction was monitored by IR spectroscopy and was complete after 10 h. The reaction mixture was diluted with CH_2Cl_2 (50 ml) and washed with sodium sulphite solution (0.5 M, 10 ml), and NaCl (0.5 M, 10 ml). The organic layer was dried (Na_2SO_4) and the volatile material removed in vacuo. The residue was extracted with CH_2Cl_2 (10 ml) and filtered through a small pad of alumina, the volume reduced in vacuo to 3 ml and chromatographed on alumina. Elution with CH_2Cl_2 gave a single yellow band, which, on recrystallisation from CH_2Cl_2/hexane, afforded bright yellow crystals of **4** (0.268 g, 60%) identified by IR and NMR spectroscopy.

An identical procedure was followed for the conversion of **8** into **2**.

3.4.1. [Mo{η^3-exo-anti-$CH_2CHCHCH(OH)Me$}$(CO)_2$-(η^5-C_5H_5)] **11**

Methylmagnesium iodide (2.10 ml of a 3.0 M solution in thf, 6.29 mmol) was added to a cooled (−20°C) solution of the yellow complex **4** (1.44 g, 5.03 mmol) in thf (50 ml). The mixture was allowed to warm to ambient temperature and stirred for 2 h. Monitoring by infrared spectroscopy indicated that the reaction had gone to completion. The mixture was quenched with water (1 ml) and stirred for a further 0.5 h, causing the mixture to turn red-brown in colour. The solvents were removed in vacuo and the residue extracted with CH_2Cl_2 and filtered through a small pad of alumina. The red filtrate was concentrated to a small volume under reduced pressure before being chromatographed on alumina. Elution with CH_2Cl_2 afforded a major yellow fraction which gave, after removal of solvent and recrystallisation from CH_2Cl_2/hexane, yellow crystals of **11** (1.07 g, 70%) (Found: C, 47.2; H, 4.6. $C_{12}H_{14}MoO_3$ requires C, 47.7; H, 4.7%). IR (CH_2Cl_2): ν(CO) 1943 vs and 1850 cm^{-1}. NMR (CD_2Cl_2): ^{1}H, δ 5.30 (s, 5H, C_5H_5), 4.01 [ddd, 1H, H^c, $J(H^cH^e)$ 11.7, $J(H^cH^b)$ $J(H^cH^d)$ 7.9], 3.82 [ddd, 1H, H^b, $J(H^bH^a)$ 8.3, $J(H^bH^c)$ 7.9, $J(H^bH^d)$ 1.8], 3.04 [ddd, 1H, H^d, $J(H^dH^c)$ 7.9, $J(H^dH^e)$ 2.0, $J(H^dH^b)$ 1.8], 2.89 [dqd, 1H, H^a, $J(H^aH^b)$ 8.3, $J(H^aMe)$ 6.2, $J(H^aOH)$ 3.3], 2.35 [d, 1H, OH, $J(H^aOH)$ 3.3], 1.44 [dd, 1H, H^e, $J(H^eH^c)$ 11.7, $J(H^cH^d)$ 2.0] and 1.18 [d, 1H, Me, $J(MeH^a)$ 6.2]; ^{13}C-{^{1}H}. δ 242.5 (CO), 237.6 (CO), 92.2 (C_5H_5), 70.5 (C^1), 68.5 (C^3), 65.2 (C^2), 40.8 (C^4) and 29.3 (Me). FAB MS $[M]^+$ 304, $[M–OH]^+$ 287, $[M–OH–CO]^+$ 259, and $[M–OH–2CO]^+$ 231.

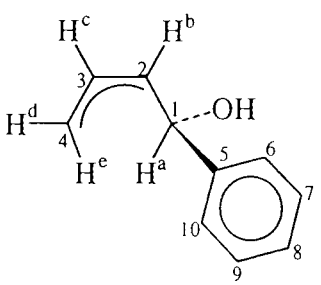


3.4.2. [Mo{η^3-exo-anti-$CH_2CHCHCH(OH)Et$}$(CO)_2$-(η^5-C_5H_5)] **12**

Ethylmagnesium bromide (0.46 ml of a 3.0 M solution in Et_2O, 1.38 mmol) was added to a cooled (0°C) solution of **4** (0.20 g, 0.66 mmol) in thf (20 ml). The mixture was allowed to warm to ambient temperature and stirred for 2 h. Monitoring by infrared spectroscopy indicated that the reaction had gone to completion. The mixture was quenched with water (1 ml) and stirred for a further 0.5 h at room temperature. Solvents were removed in vacuo and the residue extracted with Et_2O and filtered through Celite. The filtrate was concentrated to an oily residue under reduced pressure before being chromatographed on alumina. Elution with hexane afforded a major yellow fraction which gave, after removal of solvent and recrystallisation from hexane, yellow crystals of **12** (0.110 g, 53%) (Found: C, 49.4; H, 5.1. $C_{13}H_{16}MoO_3$ requires C, 49.4; H, 5.1%). IR (CH_2Cl_2): ν(CO) 1941 vs and 1850 s cm^{-1}. NMR ($CDCl_3$): ^{1}H δ 5.28 (s, 5H, C_5H_5), 4.00 [ddd, 1H, H^c, $J(H^cH^e)$ 11.6, $J(H^cH^b)$ 8.1, $J(H^cH^d)$ 7.9], 3.79 [ddd, 1H, H^b, $J(H^bH^a)$ 8.5, $J(H^bH^d)$ 1.9], 3.05 [ddd, 1H, H^d, $J(H^dH^c)$ 7.9, $J(H^dH^e)$ 2.1, $J(H^dH^b)$ 1.9], 2.63 (m, 1H, H^a), 2.47 [d, 1H, OH, J(OH, H^a) 3.1], 1.66–1.46 (m, 2H, CH_2), 1.41 [dd, 1H, H^e, $J(H^eH^c)$ 11.6, $J(H^eH^d)$ 2.1] and 0.90 [t, 3H, CH_3, $J(CH_3CH_2)$ 7.4]; ^{13}C-{^{1}H}, δ 241.4 (CO), 236.4 (CO), 91.9 (C_5H_5), 75.2 (C^1), 66.9 (C^3), 65.2 (C^2), 40.9 (C^4), 36.2 (CH_2) and 10.2 (Me). FAB MS, $[M]^+$ 318, $[M–OH]^+$ 301, $[M–OH–CO]^+$ 273 and $[M–OH–2CO]^+$ 245.

3.4.3. [Mo{η^3-exo-anti-$CH_2CHCHCH(OH)Ph$}$(CO)_2$-(η^5-C_5H_5)] **13**

Phenylmagnesium chloride (0.70 ml of a 2.0 M solution in thf, 1.40 mmol) was added to a cooled (0°C) solution of **4** (0.20 g, 0.66 mmol) in thf (20 ml). The mixture was allowed to warm to ambient temperature and stirred for 2 h. Monitoring by infrared spectroscopy indicated that the reaction had gone to completion. The mixture was quenched with water (0.5 ml) and stirred for a further 0.5 h at room temperature. Solvents were removed in vacuo and the residue extracted with Et_2O and filtered through Celite. The filtrate was concentrated to an oily residue under reduced pressure and chromatographed on alumina. Elution with hexane gave, after removal of solvent and recrystallisation from hexane, yellow crystals of **13** (0.014 g, 57%) (Found: C, 56.7; H, 4.1, $C_{17}H_{16}MoO_3$ requires C, 56.1; H, 4.4%). IR (CH_2Cl_2): ν(CO) 1946 vs and 1858 s cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 7.31–7.18 (m, 5H, C_6H_5), 5.24 (s, 5H, C_5H_5), 4.01 [ddd, 1H, H^b. $J(H^bH^a)$ 8.9. $J(H^bH^c)$ 8.4, $J(H^bH^d)$ 1.8], 3.85 [ddd, 1H, H^c, $J(H^cH^e)$ 11.7, $J(H^cH^b)$ 8.4, $J(H^cH^d)$ 7.9], 3.67 [dd, 1H, H^a, $J(H^aH^b)$ 8.9, $J(H^aOH)$ 2.9], 3.04 [ddd, 1H, H^d, $J(H^dH^c)$ 7.9, $J(H^dH^c)$ 2.2, $J(H^dH^b)$ 1.8], 2.61 [d, 1H, OH, J(OH,H^a) 2.9] and 1.58 [dd, 1H, H^e, $J(H^eH^c)$ 11.7, $J(H^eH^d)$ 2.2]; ^{13}C-{^{1}H}, δ 147.5 (C^5), 128.4 (C^6 and C^{10}), 127.3 (C^7 and C^9), 125.5 (C^8), 91.9 (C_5H_5), 75.7 (C^1), 66.8 (C^3), 65.1 (C^2) and 42.3 (C^4). FAB MS, $[M]^+$ 366, $[M–OH]^+$ 349.

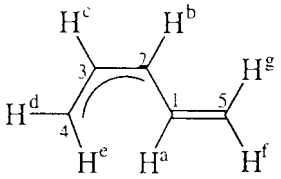


*3.4.4. [Mo{η^3-exo-anti-$CH_2CHCHCH(OH)Me$}$(CO)_2$-(η^5-C_5Me_5)] **14***

Methyllithium (0.305 ml of a 1.4 M solution in Et_2O, 0.427 mmol) was added to a cooled (−78°C) solution of **2** (0.117 g, 0.328 mmol) in thf (10 ml). The mixture was stirred at −78°C for 1 h and at ambient temperature for 15 h, during which time the colour of the solution turned red. An excess of water (0.060 ml, 3.28 mmol) was added and the mixture stirred for a further 2 h at room temperature. The solvents were removed in vacuo and the orange-red residue was extracted with CH_2Cl_2 and filtered through Celite. The orange filtrate was reduced to a small volume under reduced pressure before being chromatographed on alumina. Elution with hexane and then CH_2Cl_2/hexane (1:3) afforded a yellow fraction which gave, after removal of solvent and recrystallisation from pentane (−35°C), yellow crystals of **14** (0.092 g, 75%)(Found: C, 54.6; H, 6.4. $C_{171}H_{24}MoO_3$ requires C, 54.8; H, 6.5%). IR (CH_2Cl_2): υ(CO) 1929 vs and 1836 s cm^{-1}. NMR (CD_2Cl_2):^{1}H, δ 3.12 [dddd, 1H, H^b, $J(H^bH^a)$ 8.2, $J(H^bH^c)$ 7.8, $J(H^bH^d)$ 1.7, $J(H^bH^e)$ 0.7], 2.87 [dqd, 1H, H^a, $J(H^aH^b)$ 8.2, $J(H^aMe)$ 6.1, $J(H^aOH)$ 3.2], 2.71 [ddd, 1H, H^c. $J(H^cH^e)$ 11.7, $J(H^cH^d)$ 8.4, $J(H^cH^b)$ 7.8], 2.32 [ddd, 1H, H^d, $J(H^dH^c)$ 8.4, $J(H^dH^e)$ 2.2, $J(H^dH^b)$ 1.7], 1.86 (s, 15H, C_5Me_5), 1.53 [ddd, 1H, H^e, $J(H^cH^e)$ 11.7, $J(H^cH^d)$ 2.2, $J(H^eH^b)$ 0.7] and 1.41 [d, 3H, Me, $J(MeH^a)$ 6.1]; ^{13}C-{^{1}H}, δ 245.6 (CO), 239.8 (CO), 104.0 (C_5Me_5), 73.5, 73.4 (C^1 and C^3), 71.0 (C^2), 43.7 (C^4), 28.9 (Me) and 10.3 (C_5Me_5).

*3.5. Attempted Oppenauer oxidation of [Mo{η^3-exo-anti-$CH_2CHCHCH(OH)Me$} $(CO)_2(\eta^5$-$C_5H_5)$] **11***

An excess of dry acetone (15 ml, 204 mmol) was added to a solution of the yellow complex **11** (0.70 g, 2.32 mmol) in toluene (37 ml). To this was added aluminium tri-isopropoxide (1.42 g, 6.95 mmol) and the mixture was heated to reflux for 5.5 h. Monitoring by infrared spectroscopy and TLC indicated the formation of a new compound. After cooling to ambient temperature, the solvent was removed in vacuo and the yellow residue was extracted with CH_2Cl_2. The organic extracts were combined and concentrated to an oil before being chromatographed on alumina. Elution with hexane–CH_2Cl_2 (5:1) afforded a major yellow fraction which gave, after removal of solvent and recrystallisation from hexane (−30°C), yellow crystals of [Mo{η^3-*exo-anti*-$CH_2CHCH(CHCH_2)$}$(CO)_2(\eta^5$-$C_5H_5)$] **15** (0.31 g, 47%) (Found: C, 50.4; H, 4.2. $C_{12}H_{12}MoO_2$ requires C, 50.7; H, 4.3%). IR (CH_2Cl_2): υ(CO) 1950 s and 1867 s, υ(C=C) 1617 m cm^{-1}, NMR (CH_2Cl_2): ^{1}H, δ 5.29 (s, 5H, C_5H_5), 4.99 [dd, 1H, H^g, $J(H^gH^a)$ 16.2, $J(H^gH^f)$ 1.6], 4.72 [dd, 1H, H^f, $J(H^fH^a)$ 10.3, $J(H^fH^g)$ 1.6], 4.50 [ddd, 1H, H^b, $J(H^bH^a)$ 10.1, $J(H^bH^c)$ 7.7, $J(H^bH^d)$ 1.4], 4.33 [ddd, 1H, H^a, $J(H^aH^g)$ 16.2, $J(H^aH^f)$ 10.3, $J(H^aH^b)$ 10.1], 4.19 [ddd, 1H, H^c, $J(H^cH^e)$ 11.5, $J(H^cH^b)$ 7.7, $J(H^cH^d)$ 7.5], 2.84 [ddd, 1H, H^d, $J(H^dH^c)$ 7.5, $J(H^dH^e)$ 2.5, $J(H^dH^b)$ 1.4] and 1.47 [dd, 1H, H^e, $J(H^eH^c)$ 11.5, $J(H^eH^d)$ 2.5]; ^{13}C-{^{1}H}, δ 237.6 (CO), 236.6 (CO), 134.8 (C^1), 110.8 (C^5), 91.7 (C_5H_5), 66.5 (C^3), 64.6 (C^2) and 34.7, (C^4). FAB MS, $[MH]^+$ 287, $[M-CO]^+$ 258 and $[M-2CO]^+$ 230.



*3.6. Reaction of **4** with [NO][BF_4]*

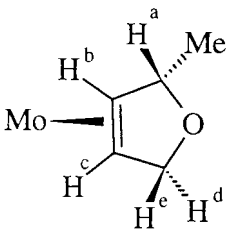
Complex **4** (0.05 g, 0.16 mmol) was dissolved in acetonitrile (15 ml) and cooled to 0°C. Solid [NO][BF_4] (0.02 g, 0.19 mmol) was added, and after stirring for 0.25 h, the solvent was removed in vacuo from a sample, and the IR spectrum recorded in CH_2Cl_2. The spectrum showed υ(NO) bands at 2072 and 1721 cm^{-1}, respectively. An excess of Na_2CO_3 (1.0 g) was then added to the remainder of the acetonitrile solution and stirring continued for 4 h at room temperature. The solvent was removed in vacuo, and the residue extracted into dichloromethane. Chromatography on alumina and elution with CH_2Cl_2/hexane (1:2) afforded a single yellow band that was collected. Removal of the solvent in vacuo gave a yellow low melting solid [Mo{η^2-$\dot{C}H$=$CHCH_2O\dot{C}$(H)Me}(CO)(NO)(η^5-C_5H_5] **16** (0.030 g, 62%). IR (CH_2Cl_2): υ(CO) 1975, υ(NO) 1622 cm^{-1}. NMR (CD_2Cl_2): ^{1}H (major product *exo*) δ 5.72 [dq, 1H, H^a, $J(H^aH^b)$ 15.1, $J(H^aMe)$ 6.7], 5.55 (s, 5H, C_5H_5), 5.09 [ddq, 1H, H^b, $J(H^bH^a)$ 15.1, $J(H^bH^c)$ 11.6, $J(H^bMe)$ 1.5], 3.97[ddd, 1H, H^c, $J(H^cH^d)$ 10.8, $J(H^cH^e)$ 10.8], 2.46 [dd, 1H, H^d, $J(H^dH^c)$ 10.8, $J(H^dH^e)$ 1.9], 2.30 [dd, 1H, H^e, $J(H^eH^c)$ 10.8, $J(H^eH^d)$ 1.9], 1.70 [d, 3H, Me, $J(MeH^a)$6.7, $J(MeH^b)$ 1.5]; (minor product *endo*) δ 5.78 [dq, 1H, H^a, $J(H^aH^b)$ 15.1, $J(H^aMe)$ 6.7], 5.53 (s, 5H, C_5H_5), 5.00 [ddq, 1H, H^b, $J(H^bH^a)$ 12.0, $J(H^bMe)$ 1.5], 3.61 [ddd, 1H, H^c, $J(H^cH^b)$ 12.0 $J(H^cH^d)$ 9.8, $J(H^cH^e)$ 9.8], 2.34 [dd, 1H, H^d, $J(H^dH^c)$ 9.8, $J(H^dH^e)$ 1.6], 1.93 [dd, 1H, H^e,

Table 7
Crystallographic details for compounds **2**[a], **7** and **15**

Complex	**2**	**7**	**15**
Empirical formula	$C_{16}H_{20}MoO_3$	$C_{12}H_{14}MoO_3$	$C_{12}H_{12}MoO_2$
Formula weight	356.26	302.17	284.16
Crystal size	0.2×0.2×0.2 mm	0.4×0.4×0.3 mm	0.2×0.2×0.2 mm
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	10.919(2)	8.338(2)	9.001(1)
b (Å)	10.578(2)	7.511(2)	8.699(1)
c (Å)	13.724(2)	19.661(6)	14.522(2)
β (°)	90.18(2)	98.34(2)	101.25(1)
U (Å^3)	1585.1(5) Å^3	1218.3(6) Å^3	1115.2(2) Å^3
D_c (g cm^{-3})	1.493 Mg/m^3	1.647 Mg/m^3	1.692 Mg/m^3
μ(Mo−K$_\alpha$) (mm^{-1})	0.831	1.065	1.152
F(000)	728	608	568
Crystal dimensions (mm)	0.2×0.2×0.2	0.4×0.4×0.3	0.2×0.2×0.2
θ range (°)	2–22	2–24	2–24
Index ranges	$0 \le h \le 11$; $-11 \le k \le 0$; $-14 \le l \le 14$	$0 \le h \le 9$; $0 \le k \le 8$; $-22 \le l \le 22$	$-10 \le h \le 0$; $0 \le k \le 9$; $-16 \le l \le 16$
No. data collected	2054	2060	1868
No. reflections with $I > 2\sigma(I)$	1583	1715	1489
Independent reflections	1932 [R(int) = 0.0197]	1914 [R(int) = 0.0253]	1748 [R(int) = 0.0192]
Absorption correction	−	DIFABS	−
Maximum, minimum absorption corrections	−	1.187, 0.714	−
Data/restraints/parameters	1928/0/241	1914/4/160	1748/11/174
Goodness-of-fit on F^2	0.991	1.191	0.859
R1, *wR2* [$I > 2\sigma(I)$]	0.0393, 0.1218	0.0343, 0.1266	0.0317, 0.0921
R1, *wR2* (all data)	0.0514, 0.1295	0.0385, 0.1298	0.0407, 0.0972
Maximum, minimum residual electron density (e Å^{-3})	0.458, −0.462	0.838, −0.825	0.891, −0.886
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0752P)^2 + 5.1908P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Extinction coefficient	0.0052(9)	0.0015(12)	0.0029(10)

[a]Details in common: λ(Mo−K$_\alpha$) 0.70930 Å; $T = 293$ K; $Z = 4$; Ext. expression $F_c = kF_c[1 + 0.001\ F_c^2\lambda^3/\sin 2\Theta]^{-1/4}$

$J(H^eH^c)$ 9.8, $J(H^eH^d)$ 1.6], 1.80 [dd, 3H, Me, $J(MeH^a)$ 6.7, $J(MeH^b)$ 1.5], FAB MS, $[M]^+$ 303, $[M-CO]^+$ 275.



3.7. Crystallography

3.7.1. Crystal structure determinations

Many of the details of the structure analyses carried out on compounds **2**, **7** and **15** are listed in Table 7. Data collections were carried out on a CAD4 diffractometer, and corrections for Lorentz and polarisation effects were applied in all cases. The structures were solved by Patterson methods and refined using the SHELX suite of programs [22–24]. Structural diagrams were generated using ORTEX [25]. Non-hydrogen atoms were refined anisotropically for all 3 compounds.

It became evident that there was some disorder at an early stage in the refinement of **2**, both of the allyl methoxy fragment and of the carbonyls. Typically, O1, O2, O3, C11, C12 and C16 were seen to be disordered with their primed equivalents in the ratio 70:30. Only the major structure is illustrated in the molecular plot.

All hydrogen atoms were located in **15** and refined at a fixed distance of 0.98 Å from the relevant parent atoms as were H8A, H8B, H91 and H101 (attached to C8, C9 and C10) in **7**. The remaining hydrogens in the latter complex, and those associated with the η^5-C_5Me_5 ring in **2** were included at calculated positions. Location of the hydrogens on the oxyallyl ligand in **2** was precluded by the disorder.

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