Synthesis, Structure, and Reactivity of a 4-Oxo-η^3-cyclohexenyl Molybdenum Complex; Diastereofacial Selectivity in the Reactions of the Derived Lithium Enolate

Michael Green,† Simon Greenfield, Michael J. Grimshire, Meinolf Kersting, A. Guy Orpen, and Richard A. Rodrigues

Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

Nucleophilic attack on the 1,3-diene cation formed by reaction of 1-methoxycyclohexa-1,3-diene with $[Mo(NCMe)_2(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$ leads to demethylation and formation of the crystallographically identified 4-oxo-η^3-cyclohexenyl complex $[Mo(\eta^3\text{-}C_6H_7O)(CO)_2(\eta^5\text{-}C_9H_7)]$, which is attacked by electrophiles on the oxygen of the oxo-η^3-allyl, and forms an *E*-enolate on deprotonation which reacts selectively with MeI, EtI, and PhCHO on the opposite face of the C_6 ring to which the molybdenum is co-ordinated.

One of the important ways of making carbon–carbon bonds involves the reaction of enolate anions with electrophiles, and recently[1] attention has focused on the reactivity of anions of the general formula $[L_nMC(O)CHR]^-$, which are formed on deprotonation of transition metal acyl complexes. These anions can be readily alkylated, and, when the metal centre is chiral, impressive examples of 1,3-asymmetric induction have been observed. Particularly noteworthy in this respect is the work of Davies[2,3] using the chiral auxiliary $(\eta^5\text{-}C_5H_5)Fe(CO)PPh_3$. In developing the chemistry[4] of the cations $[Mo(\eta^4\text{-}1,3\text{-diene})(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$ we have discovered a new and potentially general way of achieving stereofacial control in the reactions of enolates.

We have previously shown that the labile bisacetonitrile η^5-indenyl cation $[Mo(NCMe)_2(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$ reacts with 1-methoxycyclohexa-1,3-diene to form the brown crystalline 1,3-diene cation (**1**)[4] (Scheme 1). This reacts [tetrahydrofuran (thf), 0 °C] with $K[BHBu^s_3]$ or MeMgI to afford the η^3-allylic complexes (**2**) and (**3**) resulting from selective *exo*-attack on the methoxy-substituted carbon. In extending this study to the reaction of (**1**) with PhMgBr it was observed that two products (**4**) (23% yield) and (**5**) (43% yield) were formed which were easily separated by column chromatography. Analysis and n.m.r. spectroscopy‡ showed that the minor product (**4**) was an η^3-allylic complex analogous to (**2**) and (**3**). However, n.m.r. spectroscopy revealed that (**5**) did not contain either a methyl or a phenyl group, and in addition to the presence of two terminal carbonyl bands at 1960s and 1884s cm^{-1} the i.r. spectrum showed a band at 1635 cm^{-1}. It was then observed that (**5**) was also obtained on chromatographic work-up of the reaction mixture resulting from treatment (CH_2Cl_2, room temp.) of $[Mo(NCMe)_2(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$ with 1-trimethylsilyloxycyclohexa-1,3-diene, implying the occurrence of a facile desilylation reaction promoted by the tetrafluoroborate anion. Finally, it was found that (**5**) could be formed selectively and in high yield (86%) by simply reacting (thf, room temp.) the 1-methoxycyclohexa-1,3-diene cation (**1**) with NaOMe.

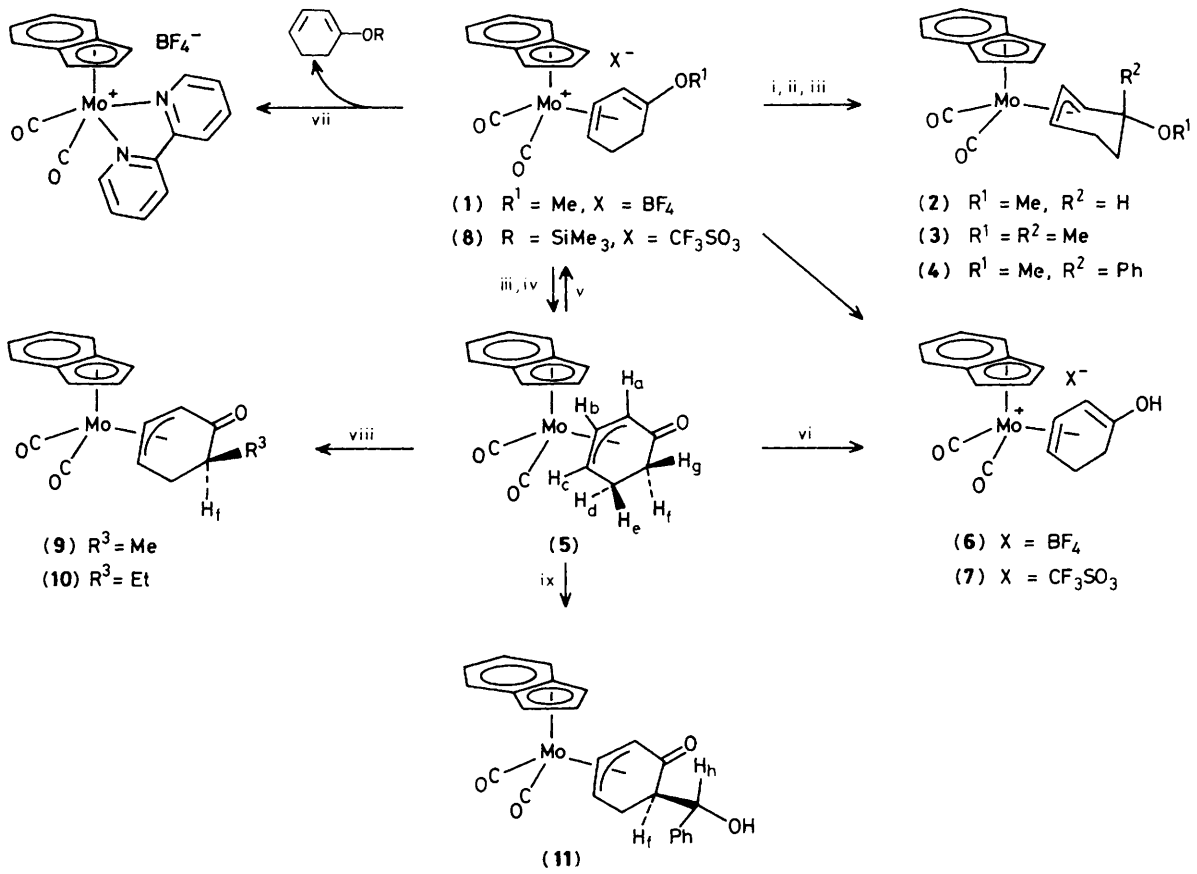
A single crystal *X*-ray diffraction study revealed§ (Figure 1) that (**5**) is a 4-oxo-1—3-η-cyclohexenyl complex, the unit cell containing two crystallographically independent molecules of opposite chirality but otherwise similar geometry. In the *exo*-orientated η^3-cyclohexenyl ligand the Mo(1)–C(6) (inner carbon) distance of 2.183(7) Å is shorter than the two outer Mo–C distances [Mo(1)–C(1) 2.332(7); Mo(1)–C(5) 2.367(7) Å] which is typical for the majority of Mo^{II} *exo*-η^3-allyls; the Mo(1) to C(2) separation of 3.172(8) Å confirms the η^3-bonding mode. The bond distances C(2)–O(1) 1.211(12) and C(1)–C(2) 1.456(11) Å imply some π-interaction between the η^3-allyl and the ketonic carbonyl group. The C_6 ring adopts a very flattened chair conformation where the methylene hydrogens bonded to C(3) and C(4) are nearly eclipsed. As with many other indenyl complexes there is slippage[5] (η^5 to η^3, Δ = 0.117 and 0.156 Å for the two molecules) and some distortion away from a planar C_5 bonded system.

Complexes of this kind have not been previously observed, and it is interesting that addition (CH_2Cl_2, room temp.) of methyl triflate ($MeOSO_2CF_3$) to (**5**) resulted in selective *O*-methylation and the formation of the triflate salt of the cation which is present in (**1**). When (**1**) was treated with 2,2′-bipyridine (bipy), 1-methoxycyclohexa-1,3-diene was smoothly displaced, an observation which has implications for synthetic organic methodology. Protonation ($HBF_4{\cdot}Et_2O$ or CF_3SO_3H, CH_2Cl_2, 0 °C) also occurred on the ketonic oxygen of (**5**) resulting in the formation of the salts (**6**) and (**7**), which can be viewed as species containing the enol of cyclohex-3-en-1-one stabilised by co-ordination onto a $Mo(CO)_2(\eta^5\text{-}C_9H_7)$ cation. The salt (**7**) is also formed on reaction of $[Mo(NCMe)_2(CO)_2(\eta^5\text{-}C_9H_7)][CF_3SO_3]$ with 1-tri-methylsiloxycyclohexa-1,3-diene forming (**8**) which is then disilylated. As would be expected (**6**) and (**7**) are deprotonated by Et_3N to reform (**5**).

† *Present address:* Department of Chemistry, King's College, Strand, London WC2R, 2LS.

‡ Selected spectroscopic data for compound (**5**): ν_{CO} (CH_2Cl_2) 1960s, 1884s, and 1635m cm^{-1}; n.m.r. ^1H (CD_2Cl_2; *J* in Hz), δ 3.63 [dddd, H_c, J_{ac} 1.5, J_{bc} 7.3, $J_{cd} = J_{ce}$ = 2.9], 3.20 [dd, H_a, J_{ab} 6.3, J_{ac} 1.5], 2.16 [dddd, H_c, J_{ce} 2.9, J_{de} 15.6, J_{ef} 7.8, J_{eg} 8.7], 1.94 [dddd, H_d, J_{cd} 2.9, J_{de} 15.6, J_{df} 9.6, J_{dg} 1.9], 1.55 [ddd, H_g, J_{dg} 1.9, J_{eg} 8.7, J_{fg} 18.7], 1.31 [ddd, H_f, J_{df} 9.6, j_{cf} 7.8, J_{fg} 18.9], and 0.21 [dd, H_b, J_{ab} 6.3, J_{bc} 7.3 Hz]. Compound (**9**): n.m.r. ^1H (CD_2Cl_2), δ 3.56 [dddd, H_c, J_{bc} 7.5, J_{cd} 2.8, J_{ce} 2.8, J_{ac} 1.5], 3.22 [dd, H_a, J_{ab} 6.3, J_{ac} 1.5], 2.26 [ddd, H_e J_{ce} 2.8, J_{de} 14.8, J_{ef} 8.6], 1.82 [ddd, H_d, J_{cd} 2.8, J_{de} 14.8, J_{df} 7.9], 1.46 [ddq, H_f, J_{df} 7.9, J_{cf} 8.6, J_{fMe} 6.8], 0.3 [d, Me, J_{fMe} 6.8], and 0.23 [dd, H_b, J_{ab} 6.3, J_{bc} 7.5]. Compound (**11**): n.m.r. ^1H (CD_2Cl_2), δ 5.02 [dd(br.), H_h, C*H*(OH)Ph, J_{fCH} 3.1, J_{hOH} 5.1], 3.52 [dddd, H_c, J_{ac} 1.5, J_{bc} 7.3, J_{cd} 2.3, J_{ce} 2.4], 3.27 [dd, H_a, J_{ab} 5.9, J_{ac} 1.5], 2.93 [d(br.), CH(O*H*)Ph, J_{hOH} 5.1], 2.08 [dddd, H_e, J_{be} 0.8, J_{ce} 2.4, J_{de} 14.2, J_{ef} 7.3], 1.70 [ddd, H_f, J_{df} 8.5, J_{ef} 7.3, J_{fh} 3.1], 1.57 [ddd, H_d, J_{cd} 2.3, J_{de} 14.2, J_{df} 8.5], and 0.16 p.p.m. [ddd, H_b, J_{ab} 5.9, J_{be} 7.3, J_{bc} 0.8].

§ *Crystal Data* for (**5**): $C_{17}H_{14}O_3Mo$, M = 362.2, monoclinic, space group $P2_1$ (No. 4), a = 7.177(2), b = 17.063(8), c = 12.123(5) Å, β = 103.83(3)°, U = 1441.5(9) Å^3, Z = 4, D_c = 1.714, D_m = 1.724 g cm^{-3}, $F(000)$ = 727.76 electrons, graphite-monochromated *X*-radiation, λ = 0.71069 Å, μ(Mo-K_α) = 8.93 cm^{-1}. Intensity data were collected on a Nicolet P3m diffractometer, at ambient temperature, for a unique quadrant of reciprocal space in the range $4 < 2\theta < 50°$. Structure solution was by Patterson and difference Fourier methods. Least squares refinement gave final residuals R (R_w) 0.0382 (0.0338) for 2369 unique, observed [$I > 0.5\sigma(I)$] data. Crystal chirality was not unambiguously determined by the data [η refined to 0.43(17)]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1. i, K[BHBu$^s_3$], thf; ii, MeMgI, thf; iii, PhMgBr, thf; iv, NaOMe, thf; v, $MeOSO_2CF_3$; vi, $HBF_4{\cdot}Et_2O$ or CF_3SO_3H; vii, bipy; viii, $LiN(SiMe_3)_2$, thf, R^3I, −78 °C; ix, $LiN(SiMe_3)_2$, thf, PhCHO, −78 °C.

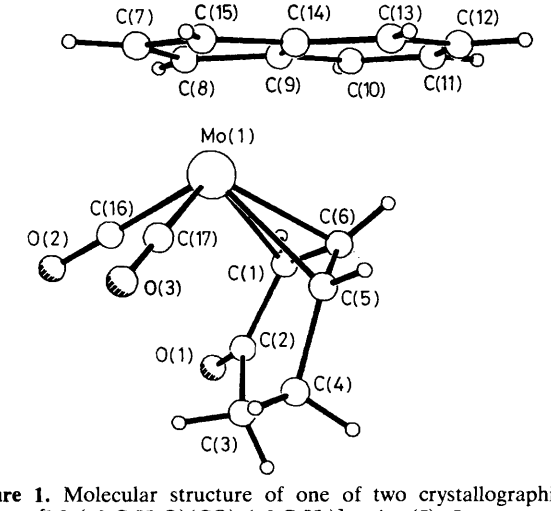


Figure 1. Molecular structure of one of two crystallographically distinct $[Mo(\eta^3\text{-}C_6H_7O)(CO)_2(\eta^5\text{-}C_9H_7)]$ units (**5**). Important geometric parameters for molecule 1 [molecule 2] include: bond lengths (Å): Mo(1)–C(1) 2.332(7) [2.338(9)], Mo(1)–C(6) 2.183(7) [2.179(8)], Mo(1)–C(5) 2.367(7) [2.384(7)], C(1)–C(2) 1.456(11) [1.446(12)], C(2)–O(1) 1.211(12) [1.236(10)], C(4)–C(5) 1.524(12) [1.537(12)], Mo(1) · · · C(2) 3.172(8) [3.149(8)]. Torsion angles (°): C(5)–C(6)–C(1)–C(2) −30.7(10) [28.4(12)], C(6)–C(1)–C(2)–C(3) 12.9(11) [−15.9(13)], C(1)–C(2)–C(3)–C(4) −5.8(12) [13.8(13)], C(2)–C(3)–C(4)–C(5) 14.7(12) [−22.0(13)], C(3)–C(4)–C(5)–C(6) −31.9(11) [34.1(11)].

When anhydrous Na_2CO_3 was added to a stirred solution of the oxo-η^3-allyl complex (**5**) in CD_3OD, monodeuteriation occurred on the carbon atom α to the oxo group implying the intermediacy of an *E*-enolate anion. With this encouragement we treated (**5**) (−78 °C, thf) with $LiNPr^i_2$ or $LiN(SiMe_3)_2$ followed by addition (−78 °C) of MeI or EtI, which resulted in the formation in 87% yield of the yellow crystalline *exo*-alkyl substituted oxo-η^3-allyls (**9**) and (**10**) (Scheme 1). Examination of the reaction mixture by n.m.r. spectroscopy‡ and h.p.l.c. showed that alkylation of the enolate had occurred with complete diastereofacial selectivity. When the *E*-enolate obtained from (**5**) and $LiN(SiMe_3)_2$ was treated (−78 °C, thf) with 1 equiv. of benzaldehyde the aldol condensation product (**11**) was obtained as a yellow crystalline material in good yield. Again n.m.r. spectroscopy† and h.p.l.c. showed that the reaction was facially selective resulting in the formation of only one isomer, which on the basis of the ^1H n.m.r. spectrum[6] is assigned the illustrated *threo*-structure.

The diastereofacial selectivity which is observed in these reactions presumably arises because the sterically large $Mo(CO)_2(\eta^5\text{-}C_9H_7)$ fragment effectively shields one face of the six-membered ring resulting in selective attack by the electrophiles on the *exo*-face of the *E*-enolate. In the reactions leading to (**9**) and (**10**) a chiral carbon centre is generated, whereas in the case of the aldol product (**11**) two chiral carbon centres are formed. Because molecules of (**1**) and (**5**) are asymmetric it should be possible to obtain these species as optically pure enantiomers. Reaction of the derived enan-

tiomeric enolates with electrophiles should then lead to the formation of (**9**), (**10**), and (**11**) with high enantiomeric selectivity. Importantly, it should also be possible to extend these procedures to the synthesis of acyclic and other alicyclic oxo-η^3-allyls.

We thank the S.E.R.C. for support and for a studentship (R. A. R.), the Deutsche Akademischen Austauschdienst for financial support, and N. J. W. Warhurst for help with the h.p.l.c. experiments.

Received, 18th August 1986; Com. 1180

References

1 P. C. Heah, A. T. Patton, and J. A. Gladysz, *J. Am. Chem. Soc.*, 1986, **108**, 1185, and references therein.
2 S. G. Davies and J. C. Walker, *J. Chem. Soc., Chem. Commun.*, 1986, 495.
3 S. G. Davies, I. M. Dordor-Hedgecock, K. H. Sutton, J. C. Walker, C. Bourne, R. H. Jones, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1986, 607, and references therein.
4 M. Green, S. Greenfield, and M. Kersting, *J. Chem. Soc., Chem. Commun.*, 1985, 18.
5 Y. N. Al-Obaidi, M. Green, N. D. White, J-M. Bassett, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1981, 494.
6 K. K. Heng, J. Simpson, and R. A. J. Smith, *J. Org. Chem.*, 1981, **46**, 2932.