An Unusual Molybdenum–Oxygen Interaction in the Product from Reaction of $Mo\{[CH_2]_3Br\}(CO)_3(\eta\text{-}C_5H_4R)$ (R = H, Me) with $LiEt_3BH$; Synthesis and *X*-Ray Structure of $Mo(CO)_2\{\eta^2\text{-}CH{\cdot}O{\cdot}[CH_2]_2CH_2\}(\eta\text{-}C_5H_4Me)$

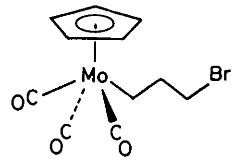
Harry Adams, Neil A. Bailey,* Philip Cahill, Deborah Rogers, and Mark J. Winter*

Department of Chemistry, The University, Sheffield S3 7HF, U.K.

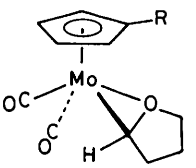
Reaction of $Mo\{[CH_2]_3Br\}(CO)_3(\eta\text{-}C_5H_4R)$ (R = H, Me) with $LiEt_3BH$ in tetrahydrofuran (THF) leads to $Mo(CO)_2\{\eta^2\text{-}CH{\cdot}O{\cdot}[CH_2]_2CH_2\}(\eta\text{-}C_5H_4R)$ (R = H, Me) which contains a new η^2 three-electron ligand bound in part by an unusual molybdenum–oxygen interaction; the structure of the methylcyclopentadienyl derivative has been characterised by *X*-ray diffraction.

Processes resulting in C–H bond formation where the carbon originates from carbon monoxide are regarded as highly significant. We report here such a formation (probably from a hydrido metal carbene intermediate) in which the oxygen originating from carbon monoxide becomes co-ordinated to a mono-molybdenum centre during an unusual cyclisation reaction.

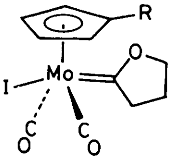
Addition of the hydride donor $LiEt_3BH$ to a solution of $Mo\{[CH_2]_3Br\}(CO)_3(\eta\text{-}C_5H_5)$ (1)[1,2] in tetrahydrofuran (THF) leads to rapid replacement of the carbonyl stretching bands of



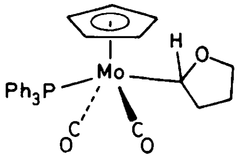
(1)



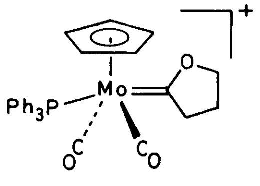
(2), R = H
(3), R = Me



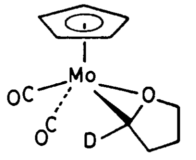
(4), R = H
(5), R = Me



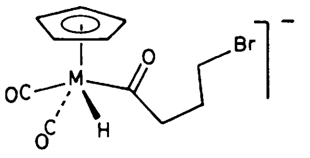
(6)



(7)



(8)



(9)

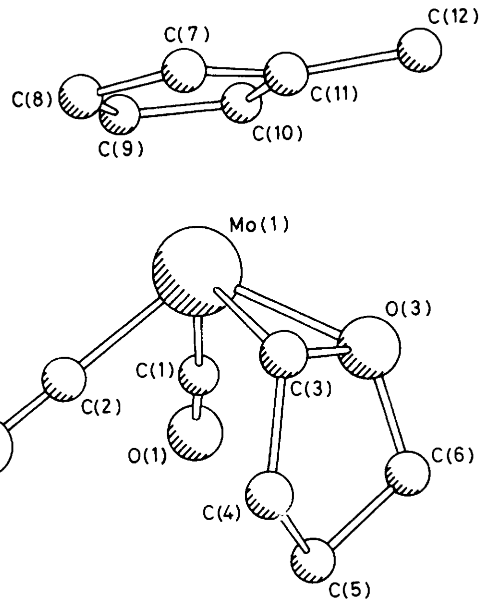


Figure 1. The molecular structure of $\mathrm{Mo(CO)_2\{\eta^2\text{-}\overline{CH\cdot O\cdot[CH_2]_2CH_2}\}(\eta\text{-}C_5H_4Me)}$ (3) with atom labelling. Bond lengths: Mo(1)–O(3) 2.161(4), Mo(1)–C(3) 2.161(5), O(3)–C(3) 1.409(6) Å.

(1) by predominantly two new bands [ν(CO) (THF): 1 925s and 1 829s cm^{-1}] shown after work-up to correspond to the major product (2) which has been fully spectroscopically (mass, i.r., and ^{1}H and ^{13}C n.m.r.) characterised. The same complex is produced in the reaction of compound (4) with $\mathrm{LiEt_3BH}$. We have been unable to obtain single crystals of (2) for a crystallographic study but a suitable sample of the analogous methylcyclopentadienyl complex (3) was obtained from reaction of (5) with $\mathrm{LiEt_3BH}$ under similar conditions.

Three-dimensional *X*-ray diffraction data for (3) were collected in the range $6.5 < 2\theta < 50°$ on a Stoe Stadi-2 diffractometer by the ω-scan method.† The 1805 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by Patterson and Fourier methods and refined by block-diagonal least-squares. Hydrogen atoms were detected, but placed in calculated positions [C–H 0.96 Å, ∠C–C–H (methyl) 111°]; their contributions were included in structure factor calculations ($B = 7.0$ Å^2) but no refinement of parameters was permitted. The position of atom H(3) was optimised for best agreement with the difference electron density synthesis in a position intermediate between sp^2 and sp^3 hybridisation for atom C(3) but at C–H = 0.96 Å. Refinement converged at R 0.0299 with allowance for anisotropic motion of all non-hydrogen atoms and for the anomalous scattering of molybdenum.‡

The molecular structure of (3) is illustrated in Figure 1. The unambiguous determination of all hydrogen atom positions allows the unequivocal, ordered assignment of O(3) and C(3) as shown. The molybdenum–$\mathrm{C_4H_7O}$ ring system geometry is doubly hinged about O(3)–C(3) (59°) and C(4)–C(6) (31°) while the Mo–O(3) and Mo–C(3) bond lengths are indistinguishable.

One significant feature of this molecule is the η^2-$\mathrm{C_4H_7O}$ group which represents a new three-electron ligand.

The molybdenum–oxygen interaction in (2) is labile; reaction with the ligand $\mathrm{PPh_3}$ results in rapid formation of the spectroscopically characterised (6) which is isolable in high yield. The complex is also isolable from the reaction of cation (7)[3] with $\mathrm{LiEt_3BH}$.

Clearly, possible mechanisms for formation of (2) and (3) are of interest. Reaction of $\mathrm{LiEt_3BD}$ with (1) results in formation of (8) confirming the final location of the hydride-derived hydrogen. We have already postulated mechanisms for reactions of certain other anionic nucleophiles with (1)[2,4] and by analogy feel that (9) represents a plausible intermediate. This structure contains a nucleophilic oxygen acyl atom and a carbenoid carbon atom. Product formation may proceed either by ring closure (eliminating Br$^-$) and subsequent

---

† (3): *Crystal data:* $\mathrm{C_{12}H_{14}MoO_3}$; $M = 302.14$, crystallises from light petroleum (b.p. 40—60 °C) as irregular red crystals, dimensions 0.40 × 0.35 × 0.50 mm. Triclinic, $a = 8.416(9)$, $b = 11.541(12)$, $c = 7.063(3)$ Å, $\alpha = 105.23(3)$, $\beta = 105.71(3)$, $\gamma = 104.938(12)°$, $U = 595.9(9)$ Å^3, $Z = 2$, $D_c = 1.684$ g cm^{-3}, space group $P\bar{1}$ (assumed and confirmed by the analysis), Mo-K_α radiation ($\bar{\lambda} = 0.710\,69$ Å), $\mu(\text{Mo-}K_\alpha) = 10.62$ cm^{-1}, $F(000) = 304$.

‡ Atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication No. SUP 23701 (18 pp) from the British Library. For details of how to obtain this material, see Notice to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, Index issues.

hydride to carbene migration[5] *or* by hydride to carbenoid acyl carbon migration followed by ring closure. In both cases the oxygen atom of the final ligand is situated conveniently to co-ordinate to the metal as the new C–H bond is formed.

With regard to the formation of (**2**) from the reaction of (**4**) with $LiEt_3BH$, there are two possibilities: (i) nucleophilic displacement of I^- from the metal by hydride followed by hydride to carbene migration and ring oxygen co-ordination, and (ii) attack of H^- at the carbene carbon atom followed by elimination of I^- and ring oxygen co-ordination.

We thank the S.E.R.C. for support.

Received, 28th April 1983; Com. 537

References

1 R. B. King and M. B. Bisnette, *J. Organomet. Chem.*, 1967, **7**, 311.
2 N. A. Bailey, P. L. Chell, C. P. Manuel, A. Mukhopadhyay, D. Rogers, H. E. Tabbron, and M. J. Winter, *J. Chem. Soc., Dalton Trans.*, in the press.
3 F. A. Cotton and C. M. Lukehart, *J. Am. Chem. Soc.*, 1971, **93**, 2672.
4 N. A. Bailey, P. L. Chell, A. Mukhopadhyay, H. E. Tabbron, and M. J. Winter, *J. Chem. Soc., Chem. Commun.*, 1982, 215.
5 J. P. Collman and L. S. Hegedus, 'Principles and Applications of Organotransition Metal Chemistry,' University Science Books, Mill Valley, California, 1980.