An Example of Acetaldehyde Bridging Two Metal Atoms. Syntheses and the *X*-Ray Crystal Structure of $Mo_2(CO)_4(\mu,\eta^2\text{-}MeCHO)(\eta\text{-}C_5H_5)_2$

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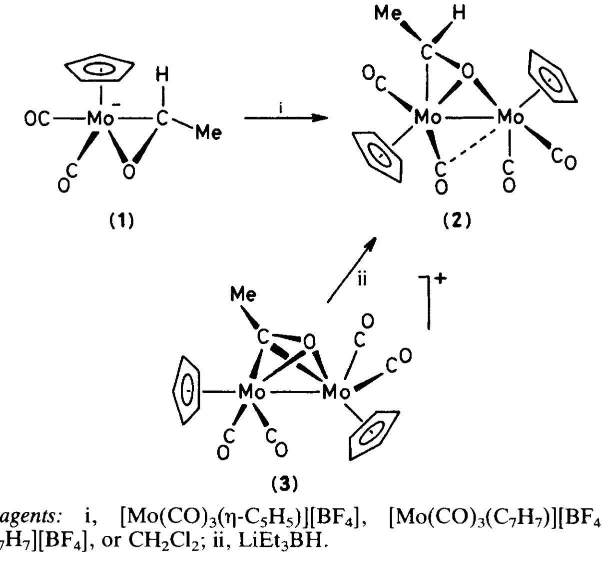
The reactions of $[Mo_2(CO)_4(\mu,\eta^2\text{-}MeCO)(\eta\text{-}C_5H_5)_2][BF_4]$ with $LiEt_3BH$ and of $[Mo(CO)_2(\eta^2\text{-}MeCHO)(\eta\text{-}C_5H_5)]^-$ with $[C_7H_7][BF_4]$ or $[Mo(CO)_3(C_7H_7)][BF_4]$ or $[Mo(CO)_3(\eta\text{-}C_5H_5)][BF_4]$ or CH_2Cl_2 have as common product the bridging acetaldehyde complex $Mo_2(CO)_4(\mu,\eta^2\text{-}MeCHO)(\eta\text{-}C_5H_5)_2$ which is the subject of an *X*-ray crystallographic study.

Acetaldehyde is not a generally recognised ligand for transition metals, but we now report syntheses of an acetaldehyde complex of dimolybdenum which therefore suggests possibilities for molybdenum-influenced aldehyde chemistry. Following our recent synthesis[1] of the anionic molybdenum aldehyde complex $[Mo(CO)_2(\eta^2\text{-}MeCHO)(\eta\text{-}C_5H_5)]^-$ we have commenced a study of its reactivity. Treatment of a solution of (**1**) in tetrahydrofuran with a suspension of $[Mo(CO)_3(\eta\text{-}C_5H_5)][BF_4]$ results in a facile reaction leading to two organomolybdenum products characterised as $[Mo(CO)_3(\eta\text{-}C_5H_5)]_2$ (22%) and $Mo_2(CO)_4(\mu,\eta^2\text{-}MeCHO)(\eta\text{-}C_5H_5)_2$ (**2**)[†] (50%).



Reagents: i, $[Mo(CO)_3(\eta\text{-}C_5H_5)][BF_4]$, $[Mo(CO)_3(C_7H_7)][BF_4]$, $[C_7H_7][BF_4]$, or CH_2Cl_2; ii, $LiEt_3BH$.

A notable feature of the ^{13}C n.m.r. spectrum of (**2**) is a signal at δ 104.4 assigned to the CHO of the aldehyde group and shifted considerably to low frequency compared to free RCHO. Since we were unable to assign a structure unequivocally, (**2**) has been the subject of an *X*-ray crystallographic study.

Three-dimensional *X*-ray diffraction data[‡] were collected ($3.5 < 2\theta < 50°$) by the ω-scan method. The 2104 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz

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[†] (**2**): ν(CO) (light petroleum, b.p. 40—60 °C) 1959m, 1932s, 1871s, and 1833m cm^{-1}; ^1H n.m.r. (400 MHz), $\delta(CDCl_3)$ 5.53 (s, 5H, C_5H_5), 5.22 (s, 5H, C_5H_5), 2.16 (q, 1H, *J* 5 Hz, CH), and 1.86 (d, 3H, *J* 5 Hz, Me); ^{13}C n.m.r. (63 MHz), $\delta(C_6D_5CD_3$, −70 °C) 253.2 (CO), 247.9 (CO), 229.2 (CO), 227.8 (CO), 104.4 (Me*C*HO), 98.2 (C_5H_5), 96.0 (C_5H_5), and 30.0 (Me).

[‡] *Crystal Data:* $Mo_2(CO)_4(\mu,\eta^2\text{-}MeCHO)(\eta\text{-}C_5H_5)_2$, $C_{16}H_{14}Mo_2O_5$, $M = 478.08$, crystallises from light petroleum (b.p. 40—60 °C) as thick red plates; crystal dimensions 0.6 × 0.2 × 0.35 mm. Monoclinic, $a = 8.265(4)$, $b = 15.191(13)$, $c = 13.511(9)$ Å, $\beta = 97.89(5)°$, $U = 1680.2(20)$ Å^3, $Z = 4$, $D_c = 1.890$ g cm^{-3}, space group $P2_1/c$ (C^5_{2h}, No. 14), Mo-K_α radiation ($\lambda = 0.710\,69$ Å), $\mu(\text{Mo-}K_\alpha) = 14.77$ cm^{-1}, $F(000) = 936$.

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.

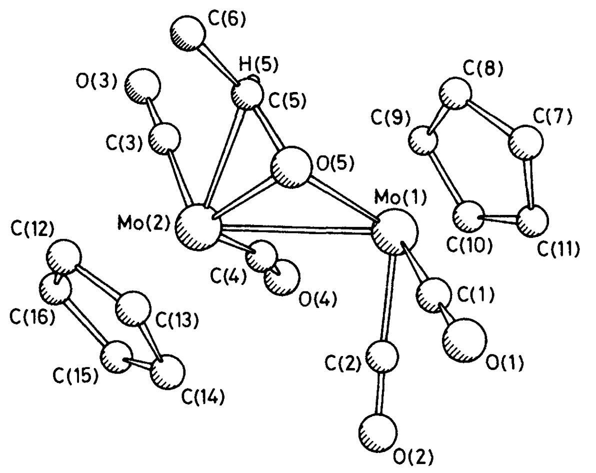

Figure 1. Bond lengths (Å) with estimated standard deviations: Mo(1)–Mo(2) 2.9670(8), Mo(1)–O(5) 2.120(4), Mo(2)–O(5) 2.068(4), Mo(2)–C(5) 2.218(7), C(5)–O(5) 1.354(8), Mo(1)–C(4) 2.721(9); angles (°) O(5)–C(5)–C(6) 116.5(6), Mo(1)–O(5)–Mo(2) 90.22(17), Mo(2)–C(4)–O(4) 166.3(8).

and polarisation effects and for absorption. The structure was solved by standard Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Refinement converged at *R* 0.0362 (anisotropic thermal motion of all non-hydrogen atoms, anomalous scattering for molybdenum).

The molecule (Figure 1) comprises two $Mo(CO)_2(\eta\text{-}C_5H_5)$ units linked through an Mo–Mo bond asymmetrically bridged by acetaldehyde so that the aldehyde is σ bonded (through oxygen) to Mo(1) and η^2 bonded (through both atoms of the C=O group) to Mo(2). The Mo–Mo distance is comparable to those of other single Mo–Mo bonds.[2] The overall configuration of the molecule is *trans* with three of the four carbonyls being linear and the fourth in a semibridging posture and somewhat bent.[2b,3]

It is reasonable to suggest that one route for the formation of (**2**) is by electron transfer from (**1**) to the molybdenum cation. Dimerisation of the resulting 17-electron complex $Mo(CO)_3(\eta\text{-}C_5H_5)$ would lead to the observed $[Mo(CO)_3(\eta\text{-}C_5H_5)]_2$[4] while dimerisation of $Mo(CO)_2(\eta^2\text{-}MeCHO)(\eta\text{-}C_5H_5)$ with loss of MeCHO or combination of both radicals with loss of CO would produce (**2**).

Complex (**2**) is also formed (20%) during reaction of $[C_7H_7][BF_4]$ with (**1**) together with the known $Mo(CO)_2(\eta^3\text{-}C_7H_7)(\eta\text{-}C_5H_5)$[5] (13%) and $[Mo(CO)_3(\eta\text{-}C_5H_5)]_2$ (18%) as other organomolybdenum products. Acetaldehyde has been detected (g.c.–mass spectrometry) in this reaction but we have not analysed for MeCHO in the other reactions. The η^3-tropyl complex presumably arises from loss of MeCHO from an undetected $Mo(\sigma\text{-}C_7H_7)(CO)_2(MeCHO)(\eta\text{-}C_5H_5)$ intermediate. We also find that (**2**) is formed in low yield (5%) from the reaction of (**1**) with $[Mo(CO)_3(\eta\text{-}C_7H_7)][BF_4]$ together with $Mo(CO)_2(\eta^3\text{-}C_7H_7)(\eta\text{-}C_5H_5)$[5] (50%) and a ditropyl complex $(OC)_3MoC_7H_7\text{-}C_7H_7Mo(CO)_3$ (21%).[6]

We also note that removal of tetrahydrofuran from a preparation of (**1**) and addition of dichloromethane to the subsequent dark oily material results after work-up in reasonable yields of (**2**) (31%). Again this is probably the consequence of an electron-transfer process.

Elucidation of the structure of (**2**) led to the idea that the known μ-acyl complex (**3**)[7] might react with a hydride donor to produce (**2**); this is indeed the case. Treatment of a suspension of (**3**) in tetrahydrofuran with $LiEt_3BH$ leads after work-up to good yields of (**2**) (59%). An i.r. spectrum of the reaction mixture clearly indicates the formation of some $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ but no attempt was made to isolate this.

Complex (**2**) is formally the addition of MeCHO across the $Mo\equiv Mo$ bond in $[Mo(CO)_2(\eta\text{-}C_5H_5)]_2$.[8] We are intrigued by our failure as yet to obtain (**2**) by this route in separate experiments under both thermal and photochemical conditions.

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References

1 J. T. Gauntlett, B. F. Taylor, and M. J. Winter, *J. Chem. Soc., Chem. Commun.*, 1984, 420.

2 (a) R. D. Adams, D. M. Collins, and F. A. Cotton, *Inorg. Chem.*, 1974, **13**, 1086; (b) W. I. Bailey, Jr., D. M. Collins, and F. A. Cotton, *J. Organomet. Chem.*, 1977, **135**, C53.

3 R. J. Klingler, W. M. Butler, and M. D. Curtis, *J. Am. Chem. Soc.*, 1978, **100**, 5034.

4 D. S. Ginley, C. R. Bock, and M. S. Wrighton, *Inorg. Chim. Acta*, 1977, **23**, 85.

5 R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1964, **3**, 785.

6 (a) E. W. Abel, M. A. Bennett, R. Burton, and G. Wilkinson, *J. Chem. Soc.*, 1958, 4559; (b) N. A. Bailey, D. G. Willett, and M. J. Winter, unpublished results.

7 K. Sünkel, K. Schloter, W. Beck, K. Ackermann, and U. Schubert, *J. Organomet. Chem.*, 1983, **241**, 333.

8 M. D. Curtis and R. J. Klingler, *J. Organomet. Chem.*, 1978, **161**, 23.