# Use of Trimethylamine *N*-Oxide in the Controlled Air-oxidation of Metal Carbonyl Complexes; Synthesis and Crystal Structure of a Novel Organometallic Oxo Complex of Dimolybdenum

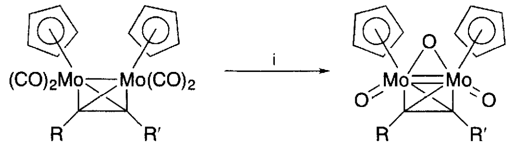
**Joanne C. Stichbury, Martin J. Mays,* Paul R. Raithby, Moira-Ann Rennie and Michael R. Fullalove**

*University of Cambridge Chemical Laboratory, Lensfield Road, Cambridge, UK CB2 1EW*

The air oxidation of $[Mo_2(CO)_4(\mu\text{-}RCCR')(\eta^5\text{-}C_5H_5)_2]$ in the presence of trimethylamine *N*-oxide affords the novel organometallic complexes $[Mo_2O_2(\mu\text{-}O)(\mu\text{-}RCCR')(\eta^5\text{-}C_5H_5)_2]$ (R = R′ = $CO_2Me$ or Ph; R = $CO_2Me$, R′ = H; R = Ph, R′ = H) which are characterised spectroscopically; the structure of $[Mo_2O_2(\mu\text{-}O)(\mu\text{-}MeO_2C\text{–}C_2\text{–}CO_2Me)(\eta^5\text{-}C_5H_5)_2]$ **1** is determined by X-ray crystallography.

Molybdenum–oxo species are important industrially, for example in the heterogeneously catalysed oxidation of propylene to acrolein.[1] Consequently, the synthesis of molybdenum oxo-organometallics has received much attention,[2] but the synthesis of a high-oxidation state transverse-alkyne bridged dimolybdenum oxo-complex has not previously been reported.

We wish to report the synthesis and crystal structure of a novel dimolybdenum organometallic oxo complex which possesses only bridging and terminal oxygen ligands in addition to a bridging alkyne and cyclopentadienyl groups. This complex, $[Mo_2O_2(\mu\text{-}O)(\mu\text{-}MeO_2C\text{–}C_2\text{–}CO_2Me)(\eta^5\text{-}C_5H_5)_2]$ **1**, has been prepared by air oxidation of $[Mo_2(CO)_4(\mu\text{-}MeO_2C\text{–}C_2\text{–}CO_2Me)(\eta^5\text{-}C_5H_5)_2]$ **2**[3] in acetonitrile with an excess of freshly sublimed trimethylamine *N*-oxide (Scheme 1). Trimethylamine *N*-oxide has been widely used in organometallic syntheses, for example in metal carbonyl cluster substitution reactions,[4] and in the isomerisation of *cis*- and *trans*-$[Mo(CO)_2(PPh_3)I(\eta^5\text{-}C_5H_5)]$[5] but has not previously been used as a reagent for the controlled air-oxidation of metal carbonyl complexes. Air oxidation of a solution of **2** in the absence of trimethylamine *N*-oxide resulted only in decomposition products and starting material.



R = R′ = $CO_2Me$ or Ph; R = $CO_2Me$, R′ = H; R = Ph, R′ = H

**Scheme 1** *Reagents and conditions*: i, Excess $Me_3NO$, air, MeCN, 298 K

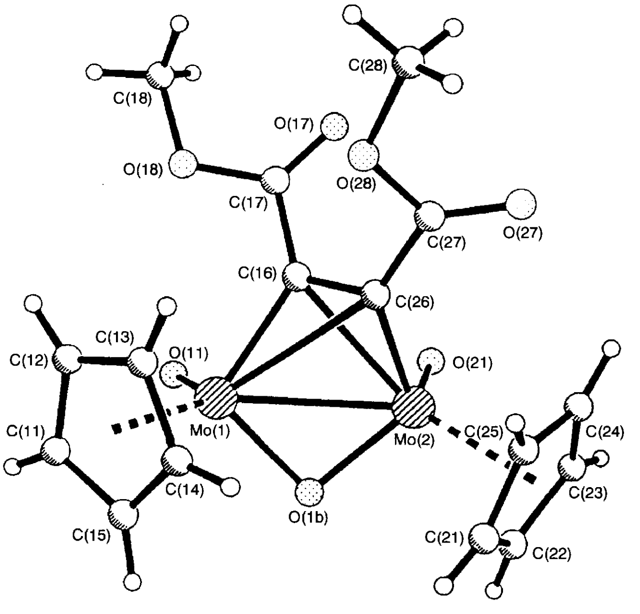


**Fig. 1** ORTEP representation of $[Mo_2O_2(\mu\text{-}O)(\mu\text{-}MeO_2C\text{–}C_2\text{–}CO_2Me)(\eta^5\text{-}C_5H_5)_2]$ in the crystal (thermal ellipsoids are drawn at the 50% probability level). Selected bond lengths (Å) and angles (°): Mo(1)–Mo(2) 2.7875(6), Mo(1)–O(11) 1.688(2), Mo(1)–O(1b) 1.921(2), Mo(2)–O(1b) 1.930(2), Mo(2)–O(21) 1.706(2), Mo(1)–O(1b)–Mo(2) 92.73(9).

Complex **1** is the first example of a transverse alkyne bridged complex derived from $[Mo_2(CO)_4(\mu\text{-}RCCR')(\eta\text{-}C_5H_5)_2]$ in which all four CO ligands have been displaced. Its formation under such mild conditions is of particular interest. Displacement of all four CO ligands of $[Mo_2(CO)_4(\mu\text{-}RCCR')(\eta\text{-}C_5H_5)_2]$ has previously always been associated with a transformation of the alkyne bridge, for example in the high-temperature reaction of $[Mo_2(CO)_4(\mu\text{-}RCCR')(\eta^5\text{-}C_5H_5)_2]$ with an excess of alkyne to form 'flyover' complexes[6] or in the reaction with $PPh_2Cl$ to form an α-phosphino vinyl ligand.[7]

Complex **1** has been fully characterised by spectroscopy† and X-ray crystallography‡ (Fig. 1). The Mo–Mo bond length [2.7875(6) Å] is shortened with respect to the length of the Mo–Mo single bond [2.977(1) Å] reported for the related carbonyl complex $[Mo_2(CO)_4(\mu\text{-}EtCCEt)(\eta^5\text{-}C_5H_5)_2]$[8] and is consistent with the presence of the Mo=Mo double bond[6] required for the complex to obey the 18-electron rule. The average molybdenum–oxygen distances of 1.697 Å for the terminal oxo ligand and 1.926 Å for the oxo bridge are comparable with corresponding bond lengths reported for similar structures such as $[\{(MoO(\mu\text{-}O)(\eta^5\text{-}C_5H_5)\}_2]$[9] and $[\{(MoO(I)(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}O)]$.[10]

The related complexes $[Mo_2O_2(\mu\text{-}O)(\mu\text{-}RC_2R')(\eta^5\text{-}C_5H_5)_2]$ for R = R′ = Ph; R = $CO_2Me$, R′ = H and R = Ph, R′ = H have also been prepared in varying yields and characterised spectroscopically. The reactivity of these high oxidation state molybdenum(IV) species in comparison with their parent carbonyl complexes [11] is under investigation.

We wish to thank the EPSRC for financial support (J. C. S.).

*Received, 10th April 1995; Com. 5/02280K*

---

## Footnotes

† *Spectroscopic data* for $[Mo_2O_2(\mu\text{-}O)(\mu\text{-}MeO_2C\text{–}C_2\text{–}CO_2Me)(\eta^5\text{-}C_5H_5)_2]$: Yield 31%. IR (in $CH_2Cl_2$, KBr solution cells) 1690 [ν(CO)], 894, 799 and 645 $cm^{-1}$ [ν(Mo=O) and ν(Mo–O)]. $^1H$ NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 6 H, $CO_2Me$) and 6.14 (s, 10 H, $C_5H_5$); $^{13}C$ NMR (400 MHz, $CDCl_3$) δ 212.6 (s, 2 C, $CO_2Me$), 89.7 (s, 10 C, $C_5H_5$) and 52.5 (s, 2 C, $CO_2CH_3$). FAB-MS *m/z* 513 [($M^+$ + 1) for $C_{16}H_{16}{}^{96}Mo_2O_7$]. Satisfactory microanalysis ($C_1H$).

‡ *Crystal data* for $[Mo_2O_2(\mu\text{-}O)(\mu\text{-}MeO_2C\text{–}C_2\text{–}CO_2Me)(\eta^5\text{-}C_5H_5)_2]$: $C_{16}H_{16}Mo_2O_7$, $M_r = 512.17$, monoclinic, space group $P2_1/n$, $a = 9.758(2)$, $b = 14.253(3)$, $c = 12.630(3)$ Å, $\beta = 99.42(3)°$, $U = 1732.9(7)$ Å$^3$, $T = 153(2)$ K, $Z = 4$, $D_c = 1.963$ g $cm^{-3}$, $F(000) = 1008$, λ(Mo-Kα) = (0.71073 Å, μ(Mo-Kα) = 14.82 $cm^{-1}$. Orange prisms, 0.19 × 0.21 × 0.25 mm. 5695 Reflections measured, $7.0 < 2\theta < 50°$. Absorption correction: minimum and maximum transmission 0.853 and 0.941. Refinement on $F_o{}^2$ for 3043 data and 228 parameters (all non-H anisotropic), $wR2 = 0.0607$ (all data), conventional $R = 0.0245$ (2635 data with $F_o > 4\sigma F_o$). The computer programs SHELXTL-PLUS[12] and SHELXL93[13] were used for structure solution and refinement.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

## References

1 G. W. Keulks, L. D. Krenzke and T. M. Notermann, *Adv. Catal.*, 1978, **27**, 183.

2 F. Bottomley and L. Sutin, *Adv. Organomet. Chem.*, 1988, **28**, 339.

3 W. I. Bailey, Jr., M. H. Chisholm, F. A. Cotton and L. A. Rankel, *J. Am. Chem. Soc.*, 1978, **100**, 5764.

4 R. J. Lawson and J. R. Shaply, *J. Am. Chem. Soc.*, 1976, **98**, 7433; B. F. G. Johnson, J. Lewis and D. Pippard, *J. Chem. Soc., Dalton Trans.*, 1981, 407; U. Koelle, *J. Organomet. Chem.*, 1978, **155**, 53.

5 D. J. Blumer, K. W. Barnett and T. L. Brown, *J. Organomet. Chem.*, 1979, **173**, 71.

6 S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1978, 221.

7 G. Conole, K. A. Hill, M. McPartlin, M. J. Mays and M. J. Morris, *J. Chem. Soc., Chem. Commun.*, 1989, 688.

8 W. I. Bailey, Jr., F. A. Cotton, J. D. Jamerson and J. R. Kolb, *J. Organomet. Chem.*, 1976, **121**, C23; W. I. Bailey, Jr., D. M. Collins and F. A. Cotton, *J. Organomet. Chem.*, 1977, **135**, C53.

9 C. Couldwell and C. K. Prout, *Acta Crystallogr., Sect. B*, 1978, **34**, 933.

10 C. Couldwell and C. K. Prout, *Acta Crystallogr., Sect. B*, 1980, 1481.

11 G. A. Acum, M. J. Mays, P. R. Raithby and G. A. Solan, *J. Organomet. Chem.*, 1995, **492**, 65.

12 SHELXTL-PLUS, program version 4.0, Siemens analytical X-Ray Instruments, Madison, WI, 1990.

13 G. M. Sheldrick, SHELXL93, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1993.