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Di-μ-methoxy-bis[(η^5-cyclopentadienyl)(nitrosyl-κN)(trimethylsilylmethyl)molybdenum(II)]

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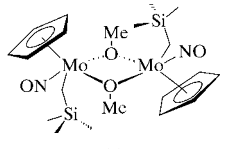
The title complex, $[Mo_2(C_5H_5)_2(CH_3O)_2(C_4H_{11}Si)_2(NO)_2]$, is formed in high yield by treating $[CpMo(NO)(CH_2SiMe_3)_2]$ (Cp is cyclopentadienyl) with methanol. The nitrosyl ligands are nearly linear [O—N—Mo 170.1 (4) and 170.1 (5)°], with short Mo—N bonds [1.769 (4) and 1.776 (4) Å] and long N—O bonds [1.216 (5) and 1.201 (4) Å]. The central four-membered Mo_2O_2 ring exhibits an average Mo—O bond length of 2.15 Å.

Comment

The title compound, $[CpMo(NO)(CH_2SiMe_3)]_2(\mu\text{-}OMe)_2$, (I), is readily formed in high yield by protonation of an alkyl ligand in $[CpMo(NO)(CH_2SiMe_3)_2]$ by MeOH. $SiMe_4$ is generated as a by-product. Only 30 min of reaction time in neat methanol is needed to effect complete conversion. Interestingly, no evidence for the formation of $[CpMo(NO)(OMe)_2]$ is found, even with longer reaction times. Surprisingly, the title complex is isolated as an orange–yellow crystalline solid, even though it is bright red in solution. We have observed similar disparate colour differences before, the usual cause being dimer formation in the solid state. For instance, $[Cp^*Mo(NO)Cl_2]$ (Cp* is pentamethylcyclopentadienyl) exists as a green solution in CH_2Cl_2, presumably as a monomer, but is an orange–red dimer in the solid state, as confirmed by X-ray crystallography (Dryden *et al.*, 1991). Similar to (I), $[Cp^*Mo(NO)Me_2]$ is red in solution and yellow in the solid state (Sharp *et al.*, 2001), where it most likely exists as a nitrosyl-bridged oligomer.

X-ray crystallographic analysis confirms that (I) is dimeric in the solid state. The metal–nitrosyl linkages of (I) are both nearly linear [Mo1—N1—O1 170.1 (4)° and Mo2—N2—O2 170.1 (5)°], thereby indicating that the nitrosyl ligands are acting as 3e donors. Both exhibit short Mo—N distances [Mo1—N1 1.769 (4) Å and Mo2—N2 1.776 (4) Å] and long N—O distances [N1—O1 1.216 (5) Å and N2—O2 1.201 (4) Å] relative to most nitrosyl complexes (Feltham & Enemark, 1981), due to strong π back-donation from the Mo centres. These NO-ligand metrical parameters are almost identical to those observed in $[CpMo(NO)(CH_2SiMe_3)(p\text{-}FC_6H_4O)]$ (Hayton *et al.*, 2002).



(I)

The most interesting structural feature of (I) is the central four-membered Mo_2O_2 ring. The four Mo—O distances are 2.093 (3) (Mo1—O3), 2.144 (3) (Mo2—O3), 2.160 (3) (Mo2—O4) and 2.216 (4) Å (Mo1—O4), with an average of 2.15 Å. These M—O distances are consistent with those reported for other bridging alkoxides, such as $[W_2(OPh)_3(CO)_6]^{3-}$ (mean W—O 2.22 Å; Darensbourg *et al.*, 1988) and $[Mo_2(OPh\text{-}4\text{-}Me)_7(NHMe_2)_2]^-$ (mean bridging Mo—O 2.11 Å; Coffindaffer *et al.*, 1985). The related nitrosyl complex $[CpMo(NO)(CH_2SiMe_3)(p\text{-}FC_6H_4O)]$ exhibits an Mo—O distance of 1.945 (2) Å (Hayton *et al.*, 2002), shorter than the values seen in (I). This is as expected, since the Mo—O bond in $[CpMo(NO)(CH_2SiMe_3)(p\text{-}FC_6H_4O)]$ exhibits some multiple-bond character.

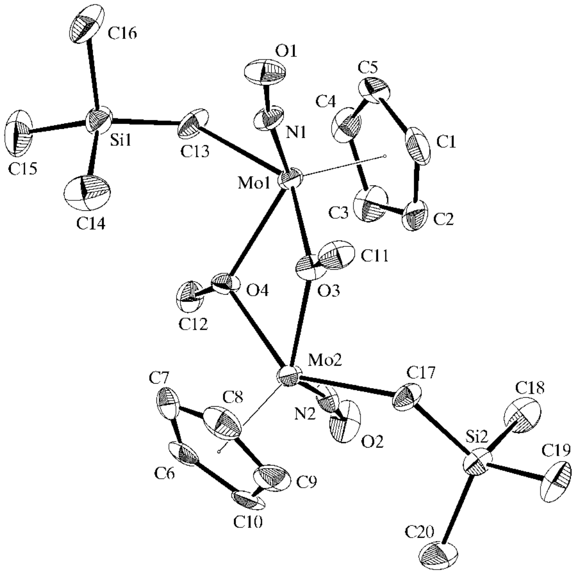


Figure 1
The molecular structure of (I), showing 50% probability ellipsoids. H atoms have been omitted for clarity.

Experimental

In a Schlenk tube, under anaerobic and anhydrous conditions, $[CpMo(NO)(CH_2SiMe_3)_2]$ (356 mg, 0.97 mmol) was dissolved in MeOH (25 ml). After being stirred for 30 min at room temperature, the purple solution had turned bright red. The volume of the solution

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† Deceased October 27, 1998.

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was reduced to 5 ml *in vacuo*, and the Schlenk tube was cooled to 243 K overnight to induce the deposition of orange crystals of (I) (235 mg, 80% yield), which were suitable for X-ray analysis. Compound (I) is moderately air and temperature sensitive, and is best stored at 243 K under a dinitrogen atmosphere. Spectroscopic analysis, IR (Nujol): 1590 cm^{-1} (νNO); ^{1}H NMR (200 MHz, CD_3CN, δ, p.p.m.): 5.95 (*s*, 5H, C_5H_5), 4.74 (*br s*, 3H, OCH_3), 1.79 (*dd*, 2H, CH_2SiMe_3), 0.03 (*s*, 9H, $SiMe_3$); $^{13}C\{^1H\}$ NMR (50 MHz, CD_3CN, δ, p.p.m.): 106.0 (C_5H_5), 79.6 (OCH_3), 37.6 (CH_2Si), 1.74 ($SiCH_3$).

Crystal data

$[Mo_2(C_5H_5)_2(CH_3O)_2$-
$(C_4H_{11}Si)_2(NO)_2]$
M_r = 618.58
Orthorhombic, $Pna2_1$
a = 12.375 (2) Å
b = 15.248 (2) Å
c = 14.119 (2) Å
V = 2664.1 (6) Å^3
Z = 4
D_x = 1.542 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 16 401 reflections
θ = 2.0–30.5°
μ = 1.06 mm^{-1}
T = 180.2 K
Plate, orange
0.30 × 0.20 × 0.03 mm

Data collection

Rigaku ADSC CCD area-detector diffractometer
Area-detector scans
Absorption correction: multi-scan (*d*TREK*; Molecular Structure Corporation, 1997)
$T_{\min}$ = 0.775, $T_{\max}$ = 0.969
24 272 measured reflections
7079 independent reflections
4260 reflections with $I > 3\sigma(I)$
$R_{\rm int}$ = 0.060
$\theta_{\max}$ = 30.6°
$h = -15 \rightarrow 17$
$k = -21 \rightarrow 16$
$l = -16 \rightarrow 18$

Table 1
Selected geometric parameters (Å, °).

Mo1—O3	2.093 (3)	Mo2—O4	2.160 (3)
Mo1—O4	2.216 (4)	Mo2—N2	1.776 (4)
Mo1—N1	1.769 (4)	Mo2—C17	2.237 (5)
Mo1—C13	2.227 (5)	O1—N1	1.216 (5)
Mo2—O3	2.144 (3)	O2—N2	1.201 (4)
O3—Mo1—O4	67.2 (1)	N2—Mo2—C17	86.3 (2)
O3—Mo1—N1	90.1 (2)	Mo1—O3—Mo2	110.2 (2)
O3—Mo1—C13	139.3 (2)	Mo1—O3—C11	122.7 (3)
O4—Mo1—N1	124.4 (2)	Mo2—O3—C11	127.1 (3)
O4—Mo1—C13	81.8 (2)	Mo1—O4—Mo2	105.2 (2)
N1—Mo1—C13	86.2 (2)	Mo1—O4—C12	124.2 (3)
O3—Mo2—O4	67.4 (1)	Mo2—O4—C12	118.3 (3)
O3—Mo2—N2	121.4 (2)	Mo1—N1—O1	170.1 (4)
O3—Mo2—C17	79.9 (1)	Mo2—N2—O2	170.1 (5)
O4—Mo2—N2	89.4 (1)	Mo1—C13—Si1	117.8 (3)
O4—Mo2—C17	138.4 (2)	Mo2—C17—Si2	124.6 (3)

Refinement

Refinement on F^2
$R(F)$ = 0.037
$wR(F^2)$ = 0.063
S = 1.22
7078 reflections
270 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\max}$ = 0.002
$\Delta\rho_{\max}$ = 1.72 e Å^{-3}
$\Delta\rho_{\min}$ = −2.64 e Å^{-3}
Absolute structure: Flack (1983), 2844 Friedel pairs
Flack parameter = 0.032 (4)

The positions of the H atoms on C12 were determined using the *HFIX* 137 function in *SHELXL*97 (Sheldrick, 1997). Subsequent refinements were carried out with the H atoms fixed in these positions, with C—H distances of 0.98 Å. The other H atoms were included in calculated positions and were not refined. The maximum and minimum peaks on the final difference Fourier map are adjacent to atom Mo2.

Data collection: *d*TREK* (Molecular Structure Corporation, 1997); cell refinement: *d*TREK*; data reduction: *d*TREK*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1997) and *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1372). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Coffindaffer, T. W., Niccolai, G. P., Powell, D., Rothwell, I. P. & Huffman, J. C. (1985). *J. Am. Chem. Soc.* **107**, 3572–3583.
Darensbourg, D. J., Sanchez, K. M. & Reibenspies, J. H. (1988). *Inorg. Chem.* **27**, 3269–3270.
Dryden, N. H., Legzdins, P., Batchelor, R. J. & Einstein, F. W. B. (1991). *Organometallics*, **10**, 2077–2081.
Feltham, R. D. & Enemark, J. H. (1981). *Top. Stereochem.* **12**, 155–215.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hayton, T. W., Legzdins, P. & Rettig, S. J. (2002). *Acta Cryst.* C**58**, m68–m69.
Molecular Structure Corporation (1997). *d*TREK* (Version 4.4) and *TEXSAN* (Version 1.8). MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Sharp, W. B., Daff, P. J., McNeil, W. S. & Legzdins, P. (2001). *J. Am. Chem. Soc.* **123**, 6272–6282.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.