Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

(η^5-Cyclopentadienyl)(p-fluorophenoxo)(nitrosyl)(trimethylsilylmethyl)molybdenum(II)

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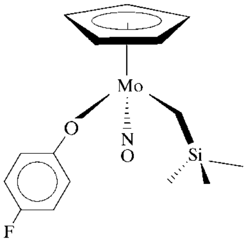
Received 24 August 2001
Accepted 13 November 2001
Online 16 January 2002

The title complex, $[\mathrm{Mo(C_5H_5)(C_6H_4FO)(C_4H_{11}Si)(NO)}]$, is formed by reacting $\mathrm{CpMo(NO)(CH_2SiMe_3)_2}$, where Cp is cyclopentadienyl, with one equivalent of p-$\mathrm{FC_6H_4OH}$. The complex exhibits the expected piano-stool molecular structure, with a linear nitrosyl ligand [Mo—N—O 168.2 (2)°] having Mo—N and N—O distances of 1.764 (2) and 1.207 (3) Å, respectively. The phenoxo Mo—O distance of 1.945 (2) Å is suggestive of some multiple-bond character.

Comment

Many attempts to generate molybdenum– and tungsten–alkoxo complexes in our laboratories have been unsuccessful. The standard metathetical protocol, using a metal–halide precursor with an alkali metal–alkoxide salt, often results in either decomposition or the formation of N—O bond-cleavage products (Legzdins *et al.*, 1996). An alternate procedure, namely protonation of the alkyl ligand in $\mathrm{CpMo(NO)(CH_2SiMe_3)_2}$ by an alcohol to generate the corresponding alkoxo complex and $\mathrm{SiMe_4}$, has now been found to generate a variety of new complexes in good yield. The title compound, $\mathrm{CpMo(NO)(CH_2SiMe_3)}$($p$-$\mathrm{FC_6H_4O}$), (I) (Fig. 1), has been synthesized by this method.



(I)

Compound (I) exhibits a pseudo-tetrahedral geometry around the Mo atom typical of this class of three-legged piano-stool molecules. The Mo—N—O linkage is linear [Mo1—N1—O1 168.2 (2)°], with a short Mo1—N1 distance [1.764 (2) Å] and a long N—O distance [1.207 (3) Å], relative to most other nitrosyls (Feltham & Enemark, 1981). This indicates that the nitrosyl ligand is strongly involved in π-back-bonding with the Mo centre. The phenoxo Mo—O distance is 1.945 (2) Å, significantly longer than the W—O distances in the related complexes $\mathrm{Cp^*W(NO)(OCH_2Ph)_2}$ [1.910 (4) Å] and $\mathrm{Cp^*W(NO)(OCMe_3)_2}$ [Cp* is pentamethylcyclopentadienyl; 1.890 (5) and 1.903 (5) Å; Legzdins *et al.*, 1993], where the metal–oxygen bond has definite multiple-bond character. However, the phenoxo Mo—O distance is shorter than the W—O bonds in $\mathrm{Cp^*W(NO)(OMe)[\eta^2\text{-}O{=}C(Me)CH{=}CPh]}$ [2.001 (7) Å; Legzdins *et al.*, 1998] and $\mathrm{Cp^*W(NO)(OCMe_3)[\eta^2\text{-}N(CMe_3){=}C(CH_2CMe_3)]}$ [1.978 (4) Å; Legzdins *et al.*, 1994]. The W—O bonds in these two compounds, by the nature of the η^2-bound co-ligands, are single bonds, which then suggests that the Mo—O link in (I) is somewhat more than a single bond. Comparison with other W and Mo complexes, namely $\mathrm{Cp^*W(MeCCMe)_2(OPh)}$ [W—O 2.072 (7) Å; O'Regan *et al.*, 1992], $[\mathrm{Cp^*W(Me)_2(OC_6F_5)}]_2(\mu\text{-}\mathrm{N_2})$ [W—O 2.079 (8) Å; O'Regan *et al.*, 1990], and $[\mathrm{Mo_2(OPh\text{-}4\text{-}Me)_7(Me_2NH)_2}]^-$ [Mo—O$_{\mathrm{terminal}}$ 2.03 Å (average); Coffindaffer *et al.*, 1985], further supports this assumption.

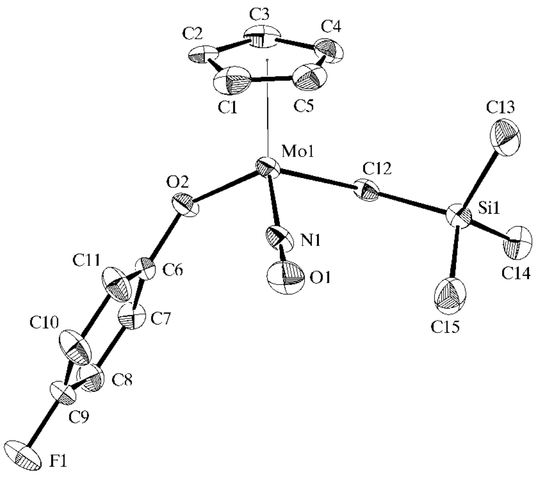


Figure 1
The molecular structure of (I) showing 50% probability ellipsoids. H atoms have been omitted for clarity.

Experimental

In a Schlenk tube, under anaerobic and anhydrous conditions, $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Mo(NO)(CH_2SiMe_3)_2}$ (100 mg, 0.27 mmol) was combined with p-fluorophenol (31 mg, 0.27 mmol), and the mixture was dissolved in tetrahydrofuran (THF, 20 ml). The resulting purple solution was stirred for 3 d at room temperature, whereupon it became deep red. The THF was removed *in vacuo*, and the resulting red oil was dissolved in hexanes (30 ml) and filtered through a column of celite (2 × 2 cm). The volume of this filtrate was reduced to 4 ml, and it was then cooled to 243 K overnight to induce the deposition of (I) as a dark-red powder (64 mg, 60% yield). X-ray quality crystals were grown from a concentrated hexanes solution at 243 K over a period of several weeks. IR (Nujol): 1635 cm^{-1} (ν_{NO}). ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$): δ 6.81 (*t*, 2H, C—H$_m$), 7.02 (*dd*, 2H, C—H$_o$), 5.19 (*s*, 5H, $\mathrm{C_5H_5}$), 2.48 (*d*, 1H, $\mathrm{CH_2SiMe_3}$), 1.97 (*d*, 1H, $\mathrm{CH_2SiMe_3}$), 0.17

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† Deceased October 27, 1998.

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Table 1
Selected geometric parameters (Å, °).

Mo1—O2	1.945 (2)	Mo1—C4	2.405 (3)
Mo1—N1	1.764 (2)	Mo1—C5	2.333 (3)
Mo1—C1	2.288 (3)	Mo1—C12	2.133 (3)
Mo1—C2	2.386 (3)	N1—O1	1.207 (3)
Mo1—C3	2.443 (3)		
O2—Mo1—N1	100.84 (9)	Mo1—O2—C6	128.5 (2)
O2—Mo1—C12	107.86 (9)	Mo1—N1—O1	168.2 (2)
N1—Mo1—C12	96.0 (1)	Mo1—C12—Si1	129.2 (1)

(*s*, 9H, $SiCH_3$). ^{13}C NMR (200 MHz, C_6D_6): δ 118.6 (C—F), 116.1 (C—H_o), 115.6 (C—H_m), 104.7 (C_5H_5), 49.3 (CH_2Si), 1.93 ($SiCH_3$).

Crystal data

$[Mo(C_5H_5)(C_6H_4FO)(C_4H_{11}Si)(NO)]$
$M_r = 389.35$
Triclinic, $P\overline{1}$
$a = 7.0052$ (7) Å
$b = 9.0510$ (9) Å
$c = 14.021$ (2) Å
$\alpha = 103.510$ (5)°
$\beta = 98.776$ (5)°
$\gamma = 91.830$ (4)°
$V = 852.2$ (1) Å^3
$Z = 2$
$D_x = 1.517$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4985 reflections
$\theta = 3.1$–27.9°
$\mu = 0.85$ mm^{-1}
$T = 180.2$ K
Irregular, red
0.25 × 0.20 × 0.06 mm

Data collection

Rigaku/ADSC CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*d*TREK*; Molecular Structure Corporation, 1996–1998)
$T_{min} = 0.71$, $T_{max} = 0.95$
7376 measured reflections
3422 independent reflections
2674 reflections with $I > 3\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 27.9°$
$h = -7 \rightarrow 8$
$k = -11 \rightarrow 10$
$l = -18 \rightarrow 15$

Refinement

Refinement on F^2
$R(F) = 0.029$
$wR(F^2) = 0.072$
$S = 0.86$
3422 reflections
190 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.92$ e Å^{-3}

The absorption correction was based on a three-dimensional analysis of symmetry-equivalent data and was performed along with batch scaling in a single step. The resulting transmission factors, therefore, include contributions from absorption, crystal decay, and detectable variations in beam intensity. The C—H distances are 0.98 Å.

Data collection: *d*TREK* (Molecular Structure Corporation, 1996–1998); 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, 1992–1997); software used to prepare material for publication: *TEXSAN*.

The authors thank NSERC and UBC for funding. They also thank Drs W. B. Sharp and B. O. Patrick for helpful discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1210). Services for accessing these data are described at the back of the journal.

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