metal-organic compounds

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$(\eta^{5}$ -Cyclopentadienyl)(*p*-fluorophenoxo)(nitrosyl)(trimethylsilylmethyl)molybdenum(II)

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The title complex, $[Mo(C_5H_5)(C_6H_4FO)(C_4H_{11}Si)(NO)]$, is formed by reacting CpMo(NO)(CH₂SiMe₃)₂, where Cp is cyclopentadienyl, with one equivalent of *p*-FC₆H₄OH. The complex exhibits the expected piano-stool molecular structure, with a linear nitrosyl ligand $[Mo-N-O \ 168.2 \ (2)^{\circ}]$ 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 CpMo(NO)-(CH₂SiMe₃)₂ by an alcohol to generate the corresponding alkoxo complex and SiMe₄, has now been found to generate a variety of new complexes in good yield. The title compound, CpMo(NO)(CH₂SiMe₃)(*p*-FC₆H₄O), (I) (Fig. 1), has been synthesized by this method.



Compound (I) exhibits a pseudo-tetrahedral geometry around the Mo atom typical of this class of three-legged pianostool molecules. The Mo-N-O linkage is linear [Mo1-N1-OO1 168.2 (2)°], with a short Mo1-N1 distance [1.764 (2) Å]

† Deceased October 27, 1998.





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

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 $Cp*W(NO)(OCH_2Ph)_2$ [1.910 (4) Å] and 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 Cp*W(NO)(OMe)[η^2 -O=C (Me)CH=CPh] [2.001 (7) Å; Legzdins et al., 1998] and Cp* $W(NO)(OCMe_3)[\eta^2-N(CMe_3)=C(CH_2CMe_3)]$ [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 Cp*W(MeCCMe)₂(OPh) [W-O 2.072 (7) Å; O'Regan et al., 1992], [Cp*W(Me)₂(OC₆F₅)]₂(μ-N₂) [W-O 2.079 (8) Å; O'Regan et al., 1990], and [Mo₂- $(OPh-4-Me)_7(Me_2NH)_2$ [Mo $-O_{terminal}$ 2.03 Å (average); Coffindaffer et al., 1985], further supports this assumption.

Experimental

In a Schlenk tube, under anaerobic and anhydrous conditions, (η^{5} -C₅H₅)Mo(NO)(CH₂SiMe₃)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}). ¹H NMR (200 MHz, C₆D₆): δ 6.81 (*t*, 2H, C–H_m), 7.02 (*dd*, 2H, C–H_o), 5.19 (*s*, 5H, C₅H₅), 2.48 (*d*, 1H, CH₂SiMe₃), 1.97 (*d*, 1H, CH₂SiMe₃), 0.17

 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, SiCH₃). ¹³C NMR (200 MHz, C₆D₆): δ 118.6 (C–F), 116.1 (C–H_o), 115.6 (C–H_m), 104.7 (C₅H₅), 49.3 (CH₂Si), 1.93 (SiCH₃).

Crystal data

 $[Mo(C_5H_5)(C_6H_4FO)-$ Z = 2 $(C_4H_{11}Si)(NO)]$ $D_{\rm r} = 1.517 {\rm Mg m}^{-3}$ $M_r = 389.35$ Mo $K\alpha$ radiation Triclinic, P1 Cell parameters from 4985 reflections a = 7.0052 (7) Åb = 9.0510 (9) Å $\theta = 3.1 - 27.9^{\circ}$ References c = 14.021 (2) Å $\mu = 0.85 \text{ mm}^{-1}$ $\alpha = 103.510(5)^{\circ}$ T = 180.2 K $\beta = 98.776(5)^{\circ}$ Irregular, red $\gamma = 91.830 (4)^{\circ}$ $0.25 \times 0.20 \times 0.06 \text{ mm}$ $V = 852.2 (1) \text{ Å}^3$

Data collection

Rigaku/ADSC CCD diffractometer
 φ and ω scans3422 independent reflections
2674 reflections with $I > 3\sigma(I)$ Absorption correction: multi-scan
 $(d*TREK; Molecular Structure
Corporation, 1996–1998)<math>R_{int} = 0.043$
 $m_{max} = 27.9^{\circ}$
 $h = -7 \rightarrow 8$
 $K = -11 \rightarrow 10$ 7376 measured reflections $l = -18 \rightarrow 15$

Refinement

Refinement on F^2 R(F) = 0.029 $wR(F^2) = 0.072$ S = 0.863422 reflections 190 parameters H-atom parameters not refined
$$\begin{split} &w = 1/[\sigma^2(F_o^2)]\\ &(\Delta/\sigma)_{\rm max} = 0.001\\ &\Delta\rho_{\rm max} = 0.60 \mbox{ e } \mbox{ Å}^{-3}\\ &\Delta\rho_{\rm min} = -0.92 \mbox{ e } \mbox{ Å}^{-3} \end{split}$$
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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*.

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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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