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Non-Coordination of the Dimethylamino Group in a Dinuclear Molybdenum Complex with the 1-[2-(Dimethylamino)-ethyl]-2,3,4,5-tetramethylcyclopentadienyl Ligand

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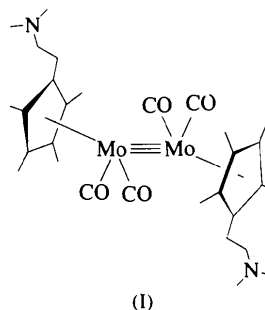
Abstract

The title compound, tetracarbonylbis{ η^5 -1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl}-dimolybdenum(*Mo—Mo*), [Mo₂(C₁₃H₂₂N)₂(CO)₄], is the first molybdenum complex incorporating the hemilabile 1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl ligand. The Mo—Mo distance of 2.510(1) Å is a typical triple-bond distance. The dimethylamino group of the side chain is clearly not coordinated to the metal atom.

Comment

Transition metal complexes incorporating the 1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl ligand (Cp[#]) (Jutzi & Dahlhaus, 1993) are attracting increased interest because the dimethylamino group of the side chain can coordinate to the central metal in an intramolecular manner. Various examples of these complexes have been published (Jutzi, Dahlhaus & Kristen, 1993; Jutzi, Kristen, Dahlhaus, Neumann & Stammler, 1993; Jutzi, Kristen, Neumann & Stammler, 1994). In all these cases, only complexes with an intramolecularly coordinated dimethylamino group have been structurally characterized. The structure of the title compound, (I), represents the first example of a structure having an uncoordinated side chain. The structural

information is therefore valuable as it allows correlation of a set of NMR data with this type of structure. Thus, in future, comments about the coordination mode of the dimethylamino group can be made on the basis of NMR data with higher reliability.



The title molecule consists of two symmetrical halves, each containing a Cp[#]Mo unit and two carbonyl groups. The side chains do not coordinate to the central metal atoms and lie on opposite sides of the Mo—Mo axis. The existence of an Mo≡Mo triple bond is inferred from the bond length of 2.510(1) Å, compared with the Mo—Mo single-bond length in [CpMo(CO)₃]₂ of 3.235(1) Å (Adams, Collins & Cotton, 1974) and the Mo≡Mo triple-bond length in [CpMo(CO)₂]₂ of 2.448(1) Å (Klinger, Butler & Curtis, 1975). All other

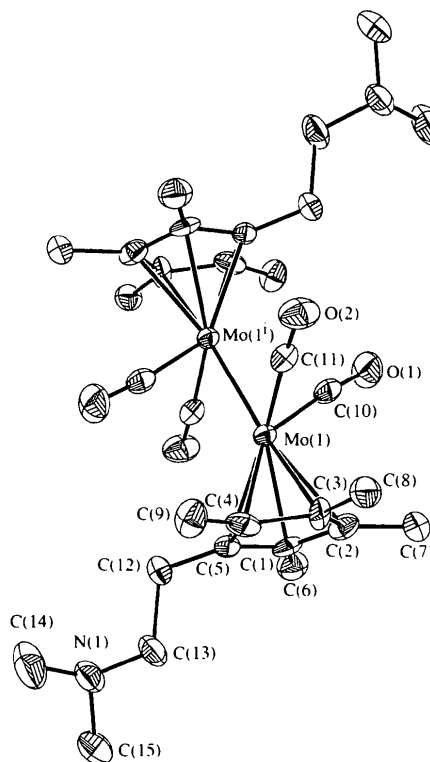


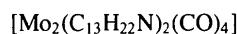
Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

data are within expected ranges. In contrast to the structure of $[\text{CpMo}(\text{CO})_2]_2$, in which the Mo—Mo—Cp angle is nearly 180° (Klinger, Butler & Curtis, 1975), here a smaller Mo—Mo—Cp* angle (161.0°) is observed. A similar value (159°) has been reported for the Cr—Cr—Cp* angle in $[\text{Cp}^*\text{Cr}(\text{CO})_2]_2$ (Potenza, Giordano, Mastropaolo & Efraty, 1974).

Experimental

Synthesis of the title compound was carried out by refluxing an *n*-octane solution of equal amounts of $\text{Mo}(\text{CO})_6$ and free ligand Cp*H for 20 h. Crystals suitable for X-ray diffraction were obtained by recrystallization from a hot *n*-hexane solution (Jutzi, Dahlhaus & Kristen, 1993).

Crystal data



$M_r = 688.55$

Monoclinic

$P2_1/n$

$a = 9.561(2) \text{ \AA}$

$b = 16.723(4) \text{ \AA}$

$c = 10.536(3) \text{ \AA}$

$\beta = 115.87(2)^\circ$

$V = 1515.8(6) \text{ \AA}^3$

$Z = 2$

$D_x = 1.509 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 27 reflections

$\theta = 2.4\text{--}12.5^\circ$

$\mu = 0.863 \text{ mm}^{-1}$

$T = 178(2) \text{ K}$

Irregular

$0.40 \times 0.30 \times 0.05 \text{ mm}$

Red

$R_{\text{int}} = 0.0666$

$\theta_{\text{max}} = 27.57^\circ$

$h = 0 \rightarrow 12$

$k = 0 \rightarrow 21$

$l = -13 \rightarrow 12$

5 standard reflections

monitored every 100

reflections

intensity decay: 2%

Data collection

Siemens $P2_1$ diffractometer

ω scans

Absorption correction:

ψ scans (SHELXTL-Plus; Sheldrick, 1990)

$T_{\text{min}} = 0.388$, $T_{\text{max}} = 0.559$

3695 measured reflections

3495 independent reflections

1630 observed reflections

$[I > 2\sigma(I)]$

Refinement

Refinement on F^2

$R(F) = 0.0628$

$wR(F^2) = 0.2220$

$S = 1.009$

3483 reflections

178 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0992P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 1.503 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -1.359 \text{ e \AA}^{-3}$

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992),

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^*$$

	x	y	z	U_{eq}
Mo1	0.11331 (7)	0.00177 (4)	0.11984 (6)	0.0214 (2)
O1	0.0261 (8)	0.1802 (4)	0.0366 (7)	0.053 (2)
O2	-0.1613 (7)	-0.0007 (4)	0.1983 (7)	0.047 (2)

N1	0.5966 (9)	-0.2173 (5)	0.1242 (8)	0.042 (2)
C1	0.3803 (9)	0.0135 (5)	0.2152 (9)	0.029 (2)
C2	0.3375 (10)	0.0495 (5)	0.3146 (9)	0.032 (2)
C3	0.2752 (11)	-0.0096 (5)	0.3642 (7)	0.038 (2)
C4	0.2721 (10)	-0.0857 (6)	0.2949 (9)	0.035 (2)
C5	0.3416 (9)	-0.0688 (5)	0.2027 (8)	0.027 (2)
C6	0.4580 (11)	0.0571 (6)	0.1380 (10)	0.042 (2)
C7	0.3707 (11)	0.1342 (5)	0.3684 (10)	0.040 (2)
C8	0.2195 (10)	-0.0020 (6)	0.4803 (9)	0.036 (2)
C9	0.2186 (12)	-0.1655 (5)	0.3211 (10)	0.041 (2)
C10	0.0524 (10)	0.1121 (6)	0.0606 (9)	0.034 (2)
C11	-0.0658 (9)	0.0006 (5)	0.1614 (8)	0.028 (2)
C12	0.3803 (10)	-0.1295 (5)	0.1190 (9)	0.035 (2)
C13	0.5491 (11)	-0.1591 (6)	0.2004 (10)	0.044 (2)
C14	0.5250 (15)	-0.2944 (7)	0.1182 (15)	0.069 (4)
C15	0.7634 (12)	-0.2246 (7)	0.1891 (13)	0.065 (3)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Mo1—Mo1'	2.5101 (14)	Mo1—C4	2.324 (8)
Mo1—C1	2.307 (7)	Mo1—C5	2.292 (8)
Mo1—C2	2.368 (8)	Mo1—C10	1.954 (9)
Mo1—C3	2.363 (7)	Mo1—C11	1.944 (8)
C10—Mo1—C11	85.0 (4)		

Symmetry code: (i) $-x, -y, -z$.

All non-H atoms were refined anisotropically. H atoms were included in calculated positions using a riding model [$U(\text{H}) = 1.2U_{\text{eq}}$ for CH_2 groups and $U(\text{H}) = 1.5U_{\text{eq}}$ for CH_3 groups]. Methyl groups were constrained to idealized symmetry with fixed C—H distances and were allowed to rotate about the C—C axes.

Data collection: *P3 Data Collection Program* (Siemens, 1989). Cell refinement: *SHELXTL-Plus* (Sheldrick, 1990). Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1159). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(η^5 -Cyclopentadienyl)oxo(peroxo-*O,O'*)-(trimethylsilylmethyl)tungsten and the Related (η^5 -Pentamethylcyclopentadienyl)-oxo(peroxo-*O,O'*)(trimethylsilylmethyl)-tungsten-Tetracyanoethylene (2/1) Complex

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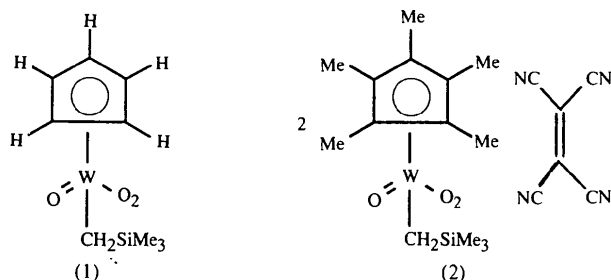
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Abstract

The two organometallic molecules, [WO(C₅H₅)(C₄H₁₁-Si)(O₂)] and [WO(C₁₀H₁₅)(C₄H₁₁Si)(O₂)] [2:1 complex with C₆N₄ (TCNE, ethenetetracarbonitrile)], have similar piano-stool structures and separate oxo and peroxo ligands [W—O(oxo) = 1.69 (3) and 1.727 (7), W—O(peroxo) = 1.91 (mean), O—O = 1.43 (3) and 1.426 (11) Å]. The 2:1 complex contains a TCNE molecule disordered over two sites, sandwiched between two organometallic molecules, with O(peroxo)···C(TCNE) distances of 2.94(2)–3.33(2) Å (the asymmetric unit is one Cp*W molecule and half of a TCNE molecule disordered over two sites).

Comment

The organometallic complex molecules [CpW(O)-(O₂)(CH₂SiMe₃)], (1), where Cp is C₅H₅, and [Cp*W(O)(O₂)(CH₂SiMe₃)], where Cp* is Me₅C₅ and which forms the 2:1 complex, (2), with TCNE, have very similar structures (see Fig. 1) and dimensions



(Table 2); the dimensions are also similar in the uncomplexed Cp* compound, except for possible oxo/peroxo disorder (Faller & Ma, 1988). Both have piano-stool structures, with separate oxo and peroxo ligands. The W—O(oxo) bond distances [1.69 (3) and 1.727 (7) Å for (1) and (2), respectively] correspond to double bonds, while the W—O(peroxo) lengths [1.87 (3) and 1.92 (3) Å for (1) and 1.896 (8) and 1.931 (7) Å for (2)] are characteristic for single bonds (Allen *et al.*, 1989). The O—O(peroxo) bond distances [1.43 (3) for (1) and 1.426 (11) Å for (2)] are close to normal single-bond lengths, and the peroxo ligands are symmetrically bonded to W. The dimensions of the alkyl ligands are normal (Allen *et al.*, 1987, 1989): W—CH₂ = 2.14 (4) and 2.156 (11), CH₂—Si = 1.85 (4) and 1.849 (11), Si—Me = 1.81 (4)—1.88 (4) and 1.83 (2)—1.87 (2) Å for (1) and (2), respectively; the W—CH₂—Si angles are somewhat enlarged [119 (2) and 117.6 (6)°], probably as a result of steric interactions between the methyl groups and oxo ligands. The Cp ligand dimensions are rather inaccurately determined as a result of the high thermal motion (or possible disorder). The rings are approximately planar. In (1), deviations from the mean ring plane range from 0.02 (6) for C2 to 0.11 (5) Å for C4. In (2), deviations of the ring atoms from their mean plane range from 0.002 (9) for C4 to 0.017 (9) Å for C2; the

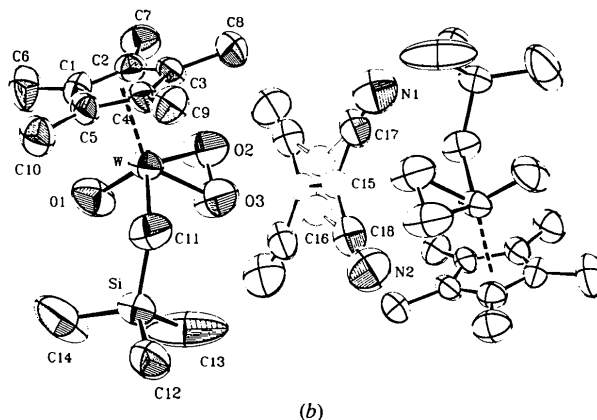
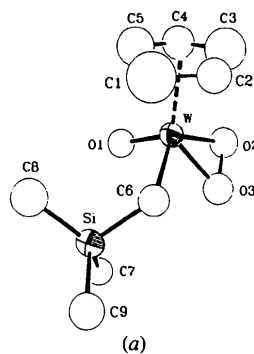


Fig. 1. Views of the molecular structures of (a) (1) and (b) (2), with 50% probability ellipsoids.