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Bis- μ -hydroxo-bis[(benzyl)(nitrosyl-*N*)(η^5 -pentamethylcyclopentadienyl)-molybdenum]

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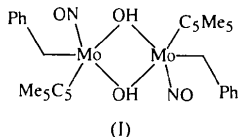
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Abstract

The title complex, $[\text{Mo}_2(\text{OH})_2(\text{NO})_2(\text{C}_7\text{H}_7)_2(\text{C}_{10}\text{H}_{15})_2]$, was obtained in 19% isolated yield from the treatment of $[\text{Mo}(\text{NO})(\text{CH}_2\text{Ph})(\text{OCMe}_3)(\text{C}_{10}\text{H}_{15})]$ in tetrahydrofuran with H_2 (276 kPa). A single-crystal X-ray crystallographic analysis confirmed its bimetallic nature, the near planarity of the central Mo_2O_2 core and the monohaplicity of the CH_2Ph ligands. The complex is diamagnetic ($\chi_M = -517 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$) at room temperature and its ^1H NMR spectrum in C_6D_6 indicates that it exists as a mixture of isomers in this solution.

Comment

In the preparation of the title complex $[\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{Ph})_2(\mu\text{-OH})_2]$, (I), where Cp^* is the η^5 -pentamethylcyclopentadienyl anion, it is interesting that it is the metal–alkoxide linkage that is the preferred site of reactivity when a tetrahydrofuran solution of $[\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{Ph})(\text{OCMe}_3)]$ is exposed to H_2 (276 kPa), the bimetallic product, (I), being isolable from the final reaction mixture in 19% yield. Complex (I) is an amber solid that is soluble in most common organic solvents except paraffin hydrocarbons. As a solid, it may be handled in air for short periods of time, but its solutions are air and moisture sensitive.



The spectral data exhibited by (I) are not particularly helpful in elucidating its molecular structure. In order to provide an unambiguous structural solution, single crystals of (I) were subjected to X-ray crystallographic analysis. An *ORTEP* diagram (Johnson, 1965) of the molecular structure of $[\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{Ph})_2(\mu\text{-OH})_2]$ in the solid state is shown in Fig. 1.

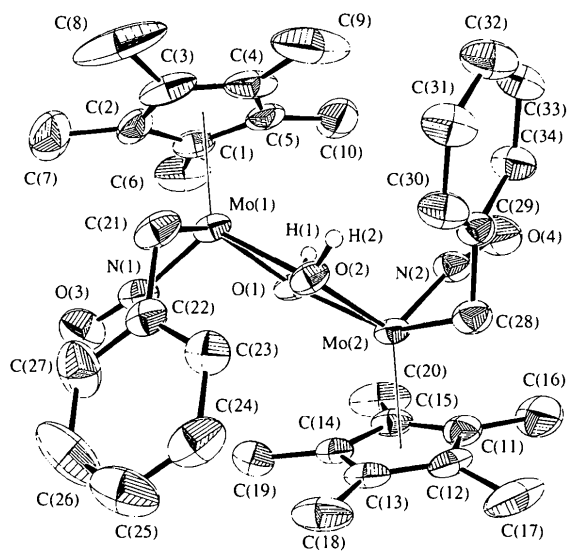


Fig. 1. Perspective view of the title molecule with 33% probability ellipsoids shown for the non-H atoms.

Overall, the geometric parameters of (I) closely resemble those established recently for $[\text{CpMo}(\text{NO})\text{I}_2(\mu\text{-OH})_2]$ (Faller, Chase & Mazzieri, 1995), where Cp is the cyclopentadienyl anion. Complex (I) is a bimetallic species with each Mo atom at the center of a four-legged piano-stool-type polyhedron. The metal atoms are bridged by two hydroxo ligands, forming a slightly asymmetric Mo_2O_2 core. The central four-membered ring is slightly non-planar [the maximum deviation from the weighted mean plane is $0.048(3) \text{ \AA}$ for atom $\text{O}(2)$], with a fold angle of $2.7(1)^\circ$. The Mo—O bond distances are consistent with single Mo—O bonds, the average value for Mo—O single bonds being 1.900 \AA (Orpen, Brammer, Allen, Kennard & Watson, 1989). Furthermore, the $\text{Mo}(1)\cdots\text{Mo}(2)$ and $\text{O}(1)\cdots\text{O}(2)$ separations of $3.5407(9)$ and $2.355(5) \text{ \AA}$, respectively, are not really short enough to be indicative of any bonding interactions between these pairs of atoms. A bond is customarily invoked if the distance between the two atoms is less than 1.25 times the sum of their covalent radii; the covalent radius of Mo is 1.30 \AA , therefore, an Mo—Mo single bond could be invoked if the Mo—Mo distance was less than 3.25 \AA . Since the benzyl groups (1e ligands) and the bridging-hydroxo groups (3e ligands) are involved in simple σ bonds, the valence-electron count at each metal center in (I) is 18. The molar magnetic susceptibility of the complex at room temperature of $\chi_M = -517 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ is consistent with this, thus confirming that it is diamagnetic in the solid state.

In solution, (I) most likely exists as a mixture of isomers. The solid-state molecular structure has the Cp^* ligands *trans* with respect to each other; however, there are no steric reasons why this complex could not

also exist in the *cis* configuration, as is found in the solid-state structure of [CpMo(NO)I]₂(μ-OH)₂ (Faller, Chase & Mazzieri, 1995). It is also possible to envision diastereomers for each of these geometric isomers.

$S = 2.010$
4156 reflections
379 parameters
 $w = 1/\sigma^2(F)$
 $(\Delta/\sigma)_{\max} = 0.001$

Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

Experimental

The complex [Cp*Mo(NO)(CH₂Ph)(OCMe₃)] (Legzdins, Lundmark & Rettig, 1993) (0.57 g, 1.3 mmol) was dissolved in tetrahydrofuran (40 ml). An IR spectrum of this red-orange solution exhibited two absorption bands at 1595 and 1585 cm⁻¹ attributable to the NO and CH₂Ph ligands, respectively (Legzdins, Lundmark & Rettig, 1993). This solution was pressurized to 276 kPa with H₂ in a Fisher-Porter pressure vessel and the reaction mixture stirred for 4 d with no color change being evident. After this time, an IR spectrum of the reaction solution exhibited a single broad band at 1618 cm⁻¹. The solution was taken to dryness *in vacuo* and the remaining residue extracted with Et₂O (2 × 10 ml). The extracts were filtered through Celite (2 × 5 cm) supported on a sintered glass frit and the filtrate concentrated under reduced pressure. Amber crystals of analytically pure (I) (0.092 g, 19% yield) formed when the saturated solution was maintained at 243 K for 2 d.

Crystal data

[Mo₂(OH)₂(NO)₂(C₇H₇)₂-(C₁₀H₁₅)₂]
 $M_r = 738.63$
Monoclinic
 $P2_1/c$
 $a = 15.822(4) \text{ \AA}$
 $b = 12.660(4) \text{ \AA}$
 $c = 16.657(2) \text{ \AA}$
 $\beta = 91.70(2)^\circ$
 $V = 3335(1) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.471 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.7107 \text{ \AA}$
Cell parameters from 25 reflections
 $\theta = 12.8\text{--}15.2^\circ$
 $\mu = 0.789 \text{ mm}^{-1}$
 $T = 294.2 \text{ K}$
Prism
 $0.30 \times 0.25 \times 0.25 \text{ mm}$
Amber

Data collection

Rigaku AFC-6S diffractometer
 ω - 2θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
 $T_{\min} = 0.932$, $T_{\max} = 1.000$
8318 measured reflections
8036 independent reflections

4156 observed reflections
 $[I > 3\sigma(I)]$
 $R_{\text{int}} = 0.044$
 $\theta_{\max} = 27.5^\circ$
 $h = 0 \rightarrow 20$
 $k = 0 \rightarrow 16$
 $l = -21 \rightarrow 21$
3 standard reflections monitored every 200 reflections
intensity decay: 1.2%

Refinement

Refinement on F
 $R = 0.0400$
 $wR = 0.0399$
 $\Delta\rho_{\max} = 0.52 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.43 \text{ e \AA}^{-3}$
Extinction correction: none

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Mo(1)	0.31558 (3)	0.46156 (3)	0.31836 (3)	0.0470 (1)
Mo(2)	0.19914 (3)	0.50994 (3)	0.13731 (3)	0.0455 (1)
O(1)	0.3010 (2)	0.4239 (2)	0.1929 (2)	0.052 (1)
O(2)	0.2192 (2)	0.5500 (3)	0.2596 (2)	0.053 (1)
O(3)	0.4947 (3)	0.5256 (4)	0.3047 (3)	0.094 (2)
O(4)	0.1010 (3)	0.3197 (3)	0.0913 (3)	0.098 (2)
N(1)	0.4180 (3)	0.5081 (4)	0.3056 (3)	0.061 (2)
N(2)	0.1399 (3)	0.3959 (3)	0.1189 (3)	0.059 (2)
C(1)	0.3492 (4)	0.2881 (4)	0.3406 (3)	0.057 (2)
C(2)	0.3687 (5)	0.3407 (4)	0.4119 (4)	0.067 (2)
C(3)	0.2920 (6)	0.3733 (5)	0.4445 (4)	0.084 (3)
C(4)	0.2249 (5)	0.3399 (6)	0.3931 (5)	0.086 (3)
C(5)	0.2591 (5)	0.2836 (4)	0.3295 (4)	0.067 (2)
C(6)	0.4126 (5)	0.2315 (5)	0.2908 (4)	0.099 (3)
C(7)	0.4531 (6)	0.3530 (6)	0.4522 (5)	0.129 (4)
C(8)	0.2820 (8)	0.4167 (6)	0.5281 (4)	0.180 (5)
C(9)	0.1339 (6)	0.3568 (8)	0.4080 (7)	0.185 (5)
C(10)	0.2109 (6)	0.2279 (6)	0.2651 (5)	0.122 (3)
C(11)	0.1941 (4)	0.5391 (5)	-0.0001 (3)	0.069 (2)
C(12)	0.1835 (4)	0.6421 (5)	0.0334 (4)	0.066 (2)
C(13)	0.2603 (4)	0.6676 (4)	0.0753 (3)	0.057 (2)
C(14)	0.3154 (4)	0.5848 (4)	0.0676 (3)	0.054 (2)
C(15)	0.2751 (4)	0.5032 (4)	0.0229 (3)	0.058 (2)
C(16)	0.1303 (6)	0.4849 (7)	-0.0555 (4)	0.126 (3)
C(17)	0.1140 (5)	0.7176 (6)	0.0141 (5)	0.121 (3)
C(18)	0.2785 (5)	0.7707 (5)	0.1183 (4)	0.096 (3)
C(19)	0.4056 (5)	0.5822 (6)	0.0978 (4)	0.092 (3)
C(20)	0.3170 (5)	0.4023 (5)	-0.0038 (4)	0.108 (3)
C(21)	0.2999 (4)	0.5958 (4)	0.4047 (3)	0.067 (2)
C(22)	0.3207 (4)	0.7022 (4)	0.3729 (3)	0.055 (2)
C(23)	0.2568 (4)	0.7696 (5)	0.3444 (4)	0.067 (2)
C(24)	0.2762 (6)	0.8716 (5)	0.3156 (4)	0.089 (3)
C(25)	0.3577 (8)	0.9035 (6)	0.3155 (5)	0.111 (4)
C(26)	0.4184 (6)	0.8397 (7)	0.3414 (6)	0.127 (4)
C(27)	0.4014 (5)	0.7396 (6)	0.3705 (5)	0.095 (3)
C(28)	0.0785 (4)	0.5931 (4)	0.1625 (3)	0.058 (2)
C(29)	0.0309 (4)	0.5551 (4)	0.2352 (3)	0.055 (2)
C(30)	0.0241 (4)	0.6175 (4)	0.3014 (4)	0.065 (2)
C(31)	-0.0220 (4)	0.5871 (5)	0.3661 (4)	0.076 (2)
C(32)	-0.0617 (4)	0.4905 (5)	0.3654 (4)	0.084 (3)
C(33)	-0.0558 (4)	0.4271 (5)	0.3002 (4)	0.075 (2)
C(34)	-0.0100 (4)	0.4576 (5)	0.2353 (4)	0.068 (2)

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

Mo(1)—O(1)	2.149 (3)	Mo(2)—O(2)	2.114 (3)
Mo(1)—O(2)	2.109 (4)	Mo(2)—N(2)	1.744 (4)
Mo(1)—N(1)	1.743 (5)	Mo(2)—C(11)	2.318 (5)
Mo(1)—C(1)	2.287 (5)	Mo(2)—C(12)	2.415 (5)
Mo(1)—C(2)	2.323 (5)	Mo(2)—C(13)	2.460 (5)
Mo(1)—C(3)	2.419 (6)	Mo(2)—C(14)	2.400 (5)
Mo(1)—C(4)	2.467 (6)	Mo(2)—C(15)	2.284 (5)
Mo(1)—C(5)	2.432 (6)	Mo(2)—C(28)	2.231 (6)
Mo(1)—C(21)	2.244 (5)	Mo(2)—CP(2)	2.05
Mo(1)—CP(1)†	2.06	O(3)—N(1)	1.234 (6)
Mo(2)—O(1)	2.134 (3)	O(4)—N(2)	1.227 (5)
O(1)—Mo(1)—O(2)	67.1 (1)	O(1)—Mo(2)—C(28)	143.0 (2)
O(1)—Mo(1)—N(1)	91.7 (2)	O(2)—Mo(2)—N(2)	115.6 (2)
O(1)—Mo(1)—C(21)	141.3 (2)	O(2)—Mo(2)—C(28)	79.1 (2)

O(1)—Mo(1)—CP(1)	108.5	O(2)—Mo(2)—CP(2)	126.9
O(2)—Mo(1)—N(1)	115.2 (2)	N(2)—Mo(2)—C(28)	88.0 (2)
O(2)—Mo(1)—C(21)	78.6 (2)	N(2)—Mo(2)—CP(2)	117.4
O(2)—Mo(1)—CP(1)	125.9	C(28)—Mo(2)—CP(2)	104.6
N(1)—Mo(1)—C(21)	86.7 (2)	Mo(1)—O(1)—Mo(2)	111.5 (1)
N(1)—Mo(1)—CP(1)	118.8	Mo(1)—O(2)—Mo(2)	113.9 (1)
C(21)—Mo(1)—CP(1)	106.0	Mo(1)—N(1)—O(3)	168.6 (4)
O(1)—Mo(2)—O(2)	67.3 (1)	Mo(2)—N(2)—O(4)	168.1 (4)
O(1)—Mo(2)—N(2)	92.8 (2)	Mo(1)—C(21)—C(22)	115.3 (4)
O(1)—Mo(2)—CP(2)	107.6	Mo(2)—C(28)—C(29)	116.5 (3)

† CP(1) and CP(2) are the unweighted centroids of the C(1)–C(5) and C(11)–C(15) rings, respectively.

The H atoms were fixed in calculated positions (O—H 0.87 and C—H 0.98 Å, with displacement parameters 1.2 times greater than those of the parent atoms). The orientations of the hydroxy and methyl H atoms were based on difference map positions. Some of the Cp* methyl C atoms exhibit markedly anisotropic displacement parameters. This is consistent with a combination of moderate molecular libration and some oscillation of the Cp* ligands about the metal-ring centroid vectors and is a feature often noted for Cp* complexes.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985, 1992). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including intermolecular contacts and torsion angles, together with analytical, IR, ¹H NMR, mass spectral and magnetic susceptibility data, and a discussion of the spectral data have been deposited with the IUCr (Reference: FG1147). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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mer-{Bis[dimethyl(diphenylphosphino-methyl)silyl]amine-*N,P,P'*}dihydrido(iodo)iridium(III)

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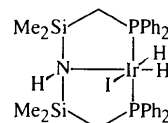
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Abstract

The [Ir(H)₂I(C₃₀H₃₇NP₂Si₂)] molecule has irregular octahedral coordination geometry, with the tridentate amine NH(SiMe₂CH₂PPh₂)₂ ligand meridionally coordinated. The amine N—H bond is *syn* to the Ir—I linkage as a consequence of intramolecular N—H···I hydrogen bonding. Important bond lengths include Ir—I 2.7862 (4), Ir—P 2.285 (1) (× 2), Ir—N 2.339 (4), and Ir—H 1.43 (4) and 1.46 (5) Å.

Comment

The geometrical parameters of [Ir(H)₂I{NH(SiMe₂CH₂-PPh₂)₂}] (I), are very similar to those reported (Fryzuk, MacNeil & Rettig, 1987) for the closely related compounds [Ir(Me)(H)I{NH[SiMe₂CH₂P(Pr)₂]₂}], [Rh(H)₂I{NH[SiMe₂CH₂P(Pr)₂]₂}], [Ir(H)₂Cl{NH(SiMe₂-CH₂PPh₂)₂}.toluene and [Ir(Me)I₂{NH(SiMe₂CH₂-PPh₂)₂}.benzene (Fryzuk *et al.*, 1992). Each of these



(I)

structures has slightly irregular octahedral coordination geometry with the tridentate NH(SiMe₂CH₂PR₂)₂ ligand meridionally coordinated to the metal atom with the halide ligand positioned *syn* to the amine N—H bond. This arrangement, as well as the stereoselectivity of the reactions leading to the hydride complexes, results from the formation of a weak intramolecular N—H···halide hydrogen bond. In the title compound, this weak N—H···I interaction has the geometry H···I 2.95 (5), N···I 3.536 (4) Å and N—H···I 135 (4)°. The H···I distance is significantly shorter than the sum of the van der Waals radii (3.35 Å; Bondi, 1964).