

Structure of (2,2'-Bipyridyl)dioxobis(trimethylsilyl)molybdenum(VI)

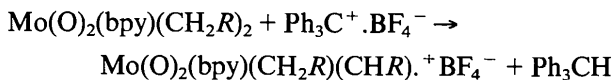
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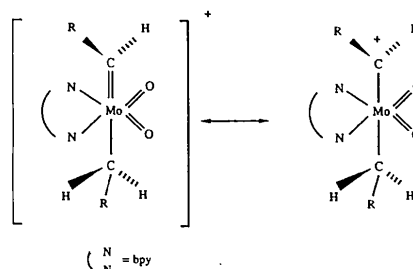
Abstract. $[\text{MoO}_2(\text{C}_{10}\text{H}_8\text{N}_2)(\text{C}_4\text{H}_{11}\text{Si})_2]$, $M_r = 458.6$, monoclinic, $P2_1/n$, $a = 15.816$ (4), $b = 9.924$ (3), $c = 18.561$ (5) Å, $\beta = 114.48$ (5)°, $V = 2651$ (4) Å³, $Z = 4$, $D_m = 1.14$ (2), $D_x = 1.149$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 5.82$ cm⁻¹, $F(000) = 952$, $T = 273$ K, $R = 0.049$ for 864 unique diffractometer data with $I > 3\sigma(I)$. The structure reveals a distorted octahedral coordination geometry around the Mo atom and an intramolecular interaction between one oxo group and the Si atoms.

Introduction. During our research on oxo complexes containing the same metal atom, oxygen and other functionalities (Arzoumanian, Baldy, Lai, Metzger, Nkeng Peh & Pierrot, 1985; Lai, Le Bot & Faure, 1987) we have been studying the reactivity of α -hydrogen in dioxo dialkyl complexes with the general formula $\text{Mo}(\text{O})_2(\text{bpy})(\text{CH}_2R)_2$ (with bpy = 2,2'-bipyridyl and $R = \text{CMe}_3$, Ph, CMe_2Ph , 4-MeO-C₆H₄, SiMe₃) towards hydride acceptors such as the trityl cation Ph_3C^+ . This reagent is commonly used for the preparation of electrophilic alkylidene organometallic species (Sanders, Cohen, Giering, Kenedy & Magatti, 1973; Kiel, Lin, Bodner & Gladysz, 1983; Casey, Crocker, Vosejka, Fagan, Marder & Gohdes, 1988). When CD_2Cl_2 solutions of $\text{Mo}(\text{O})_2(\text{bpy})(\text{CH}_2R)_2$ are reacted at 195 K with one equivalent of $\text{Ph}_3\text{C}^+.\text{BF}_4^-$ an instantaneous reaction occurs which can be described as follows:



Except for $R = 4\text{-MeO-C}_6\text{H}_4$, the ¹H NMR analysis of these solutions showed, besides peaks due to Ph_3CH , 2,2'-bipyridyl and R groups, two apparent high field doublets. These signals might in fact correspond to an AB quartet arising from the non-equivalent methylene protons as in alkylidene complexes such as $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{Ph})(\text{CHPh})$ (Guggenberger & Schrock, 1975). However, in our case, the absence of low field signals in both ¹H and ¹³C NMR spectra is not in agreement with a true alkylidene species. Indeed, EHT calculations permit a description of the Mo—CHR bonding as a hybrid

between a cationic alkylidene and a carbocationic complex (Lai, Djafri, Rajzmann & Pierrot, 1990).



Variable temperature NMR experiments show that the stability of the cationic species is dependent on R and is in the following increasing order: 4-MeO-C₆H₄ \ll $\text{CMe}_3 < \text{Ph} < \text{CMe}_2\text{Ph} \ll \text{SiMe}_3$. In fact, it is only when $R = \text{SiMe}_3$ that the complex is stable for a short period of time at room temperature, otherwise it decomposes below 273 K.

In order to try to obtain a better understanding of the peculiar behaviour of $\text{Mo}(\text{O})_2(\text{bpy})(\text{CH}_2\text{SiMe}_3)_2$ we decided to study the crystal structure of this new dioxo complex.

Experimental. The title compound as well as the other dioxo complexes mentioned were prepared by interaction of $\text{Mo}(\text{O})_2(\text{bpy})\text{Br}_2$ with two equivalents of the appropriate Grignard reagent (Schrauzer, Hughes, Ross, Strampach, Ross & Schlemper, 1983). An improvement of the method involved chromatography under nitrogen of the crude products on a silica gel column before crystallization. Data for title compounds: IR (KBr mull): ν MoO 895 and 927 cm⁻¹; ¹NMR (CDCl_3): δ 9.55–7.40 (m , 8H), 0.10 (s , 4H), 0.05 (s , 18H).

Crystal (0.3 \times 0.2 \times 0.2 mm) grown from alcohol/ether solution, sealed in a capillary under inert atmosphere, mounted on a CAD-4 diffractometer (graphite monochromator for Mo $K\alpha$). Unit-cell parameters refined by least squares on $\sin\theta/\lambda$ values for 25 reflections ($14 < \theta < 16^\circ$). Density obtained by flotation: $D_m = 1.14$ (2) g cm⁻³. Intensity measured using $\omega/2\theta$ scan of 0.91 to 10.06 min⁻¹, over a range of $(0.8 + 0.35 \tan\theta)^\circ$, $\theta_{\text{max}} = 20^\circ$. Intensities of three

Table 1. *Positional and thermal parameters with their e.s.d.'s in parentheses*

	x	y	z	B(Å ²)
Mo	0.40785 (8)	0.0551 (1)	0.65896 (7)	3.47 (4)
O1	0.3326 (6)	0.0233 (9)	0.7015 (5)	4.7 (3)*
O2	0.4481 (6)	-0.0936 (9)	0.6345 (5)	4.5 (2)*
N1	0.3849 (6)	0.286 (1)	0.6735 (5)	3.1 (3)*
N2	0.4955 (6)	0.188 (1)	0.6117 (5)	2.8 (3)*
C1	0.3267 (8)	0.328 (1)	0.7076 (7)	3.8 (4)*
C2	0.3141 (9)	0.462 (1)	0.7152 (8)	4.6 (4)*
C3	0.3598 (9)	0.557 (1)	0.6906 (8)	5.2 (4)*
C4	0.4223 (9)	0.519 (1)	0.6575 (8)	5.0 (4)*
C5	0.4327 (8)	0.377 (1)	0.6508 (7)	4.0 (4)*
C6	0.4938 (8)	0.323 (1)	0.6168 (7)	3.1 (3)*
C7	0.5463 (9)	0.406 (1)	0.5903 (8)	4.6 (4)*
C8	0.6012 (9)	0.346 (2)	0.5565 (8)	5.7 (4)*
C9	0.6026 (9)	0.206 (1)	0.5510 (8)	4.8 (4)*
C10	0.5484 (8)	0.127 (1)	0.5803 (7)	3.6 (4)*
C11	0.3090 (8)	0.108 (1)	0.5384 (7)	3.1 (3)*
C12	0.1249 (9)	0.117 (2)	0.5586 (8)	6.0 (4)*
C13	0.2004 (9)	-0.157 (1)	0.5368 (8)	4.8 (4)*
C14	0.124 (1)	0.037 (2)	0.3989 (3)	5.9 (4)*
C15	0.5345 (8)	0.102 (1)	0.7653 (7)	3.8 (4)*
C16	0.501 (1)	-0.155 (2)	0.8447 (8)	6.5 (5)*
C17	0.4587 (9)	0.115 (2)	0.8918 (8)	5.8 (4)*
C18	0.6595 (9)	0.036 (2)	0.9372 (8)	5.5 (4)*
Si1	0.1908 (3)	0.0216 (4)	0.5095 (3)	4.3 (1)*
Si2	0.5367 (3)	0.0231 (5)	0.8581 (3)	4.3 (1)*

* Atoms were refined isotropically. The anisotropically refined atom is given in the form of the isotropic equivalent displacement defined as: $B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

 Table 2. *Selected bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses*

Mo—O1	1.71 (2)	C5—C6	1.46 (3)
Mo—O2	1.74 (2)	C6—C7	1.39 (3)
Mo—N1	2.36 (2)	C7—C8	1.40 (3)
Mo—N2	2.34 (2)	C8—C9	1.41 (2)
Mo—C11	2.20 (2)	C9—C10	1.43 (2)
Mo—C15	2.20 (2)	C11—Si1	1.90 (1)
N1—C1	1.38 (2)	C12—Si1	1.88 (2)
N1—C5	1.35 (2)	C13—Si1	1.88 (2)
N2—C6	1.35 (2)	C14—Si1	1.88 (1)
N2—C10	1.35 (2)	C15—Si2	1.88 (2)
C1—C2	1.36 (2)	C16—Si2	1.84 (2)
C2—C3	1.38 (2)	C17—Si2	1.84 (2)
C3—C4	1.42 (2)	C18—Si2	1.89 (1)
C4—C5	1.43 (3)		
O1—Mo—O2	111.4 (5)	O1—Mo—N1	87.5 (4)
O1—Mo—N2	156.3 (4)	O1—Mo—C15	100.0 (5)
O1—Mo—C11	100.2 (5)	O2—Mo—C11	97.0 (4)
O2—Mo—N1	161.1 (4)	O2—Mo—C15	96.8 (4)
O2—Mo—N2	92.4 (4)	N1—Mo—N2	68.8 (4)
N1—Mo—C11	78.7 (4)	N1—Mo—C15	79.5 (5)
N2—Mo—C11	76.4 (5)	N2—Mo—C15	75.9 (4)
C11—Mo—C15	149.5 (6)		

standard reflections measured every 10 000 s show a loss of intensity of 10.6% and a linear correction was applied on the 3287 measured reflections; 2700 symmetry-related reflections averaged (agreement factor on $I = 0.028$), and 1587 unique reflections. Owing to the poor quality of the diffraction pattern only 864 reflections with $I > 3\sigma(I)$ were kept for structure determination; $0 \leq h \leq 12$, $0 \leq k \leq 8$, $-12 \leq l \leq 11$.

The structure was solved and refined using the *SDP* software package (Frenz, 1978) via the standard heavy-atom procedure and completed by Fourier methods. H atoms introduced (with $B_{eq} = 6 \text{ Å}^2$) at idealized positions in the calculation before last refinement cycles but not refined. Full-matrix least-squares refinement included anisotropic thermal parameters for the Mo atom, only 106 parameters, and minimized the function $w(F_o - F_c)^2$, $w = 1/\sigma^2$. Final refinement with $R = 0.049$ ($wR = 0.065$), $S = 2.43$, $(\Delta/\sigma)_{max} = 0.23$; a final difference synthesis did not reveal any peak of density $> 0.35 \text{ e Å}^{-3}$.

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). No correction for absorption or secondary extinction.

Discussion. Final positional and thermal parameters are presented in Table 1.* A view of the molecule and the numbering scheme are given in Fig. 1. Relevant bond distances and bond angles are given in Table 2. This structure reveals a distorted octahedral coordination geometry around the Mo atom. The oxo groups are essentially coplanar with the bpy ligand: the dihedral angle between the bpy plane and the plane defined by O1—O2—Mo—N1—N2 is $1(1)$ or $179(1)^\circ$; the C11—Mo—C15 angle is $149.5(6)^\circ$. Bond angles and distances found in the (bpy)Mo(O)₂

* Lists of anisotropic thermal parameters, bond angles, bond distances, hydrogen coordinates and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53865 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

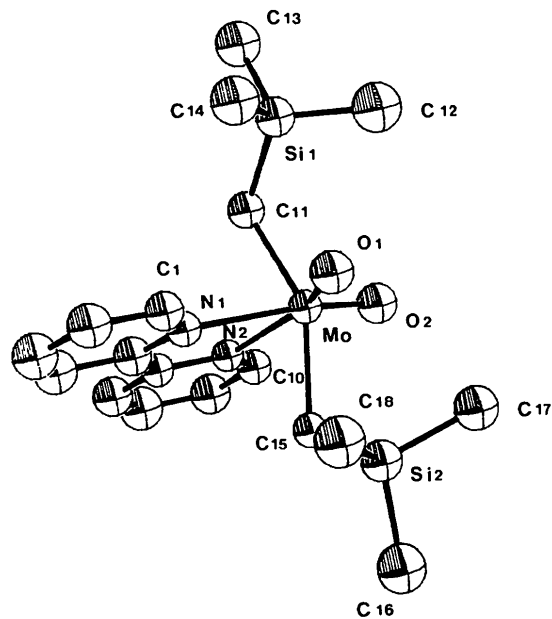


Fig. 1. View of the molecule and numbering of the atoms.

moiety show no significant differences with those found in comparable complexes (Schrauzer *et al.*, 1983, and references therein). The most noticeable feature of this structure is an unsymmetrical mode of interaction between the oxo groups and the Si atoms. O1 is in close contact with Si1 and Si2 with shorter distances than the corresponding van der Waals interaction (3.6 Å): O1 is 3.32 (1) Å distant from Si1 and Si2 whereas O2 is at 3.95 (1) Å from Si1 and Si2. More pronounced are the differences in the torsional angles. Thus O1—Mo—C11—Si1 and O1—Mo—C15—Si2 angles are -27 and $+25^\circ$ and O2—Mo—C11—Si1 and O2—Mo—Si2—C15 angles are $+86$ and -88° respectively. Crystal packing cannot account for these intramolecular interactions, the molecules of the title compound being packed without any remarkable close contact.

Although it is premature to draw definite conclusions, it is likely that both structural features and electronic effects due to silicon (Ibrahim & Jorgensen, 1989) could account for the stability of the cationic species obtained by a hydrogen abstraction from Mo(O)₂(bpy)(CH₂SiMe₃)₂.

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(4,4'-Dimethyl-2,2'-bipyridyl-*N,N'*)bis(isocyanato)platinum(II)

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Abstract. [Pt(NCO)₂(C₁₂H₁₂N₂)], $M_r = 463.37$, orthorhombic, $Cmc2_1$, $a = 18.722$ (6), $b = 11.889$ (5), $c = 6.688$ (5) Å, $V = 1488.7$ (9) Å³, $Z = 4$, $D_x = 2.067$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 90.59$ cm⁻¹, $F(000) = 864$, $T = 291$ (1) K, $R = 0.052$ for 735 reflections with $F \geq 6\sigma_F$. The structure consists of square-planar coordinated Pt atoms, surrounded by four N atoms; of these, two belong to the bidentate bipyridyl ligand and two belong to the two pseudohalide groups which occupy *cis* positions. The bite angle of the bipyridyl ligand is 82.3 (9)°, significantly larger than the value reported earlier for the unsubstituted bipyridyl ligand, 76 (2)°. The metal atom is displaced 0.10 (5) Å below the plane of the four N atoms. The non-bonding Pt—Pt distance is 0.258 (5) Å longer in the title compound than in the

unsubstituted ligand complex, leading to significant differences in the chemical and spectroscopic properties of the two homologues.

Introduction. Complexes of Pt^{II} generally exhibit square-planar coordination around the metal atom with sp^2d hybridization of the metal orbitals. In a number of such complexes, an interesting color change can be observed on heating the neat compounds (Rosenblatt & Schleede, 1933; Schilt, 1962, 1963; Textor & Oswald, 1974; Che, He, Poon & Mak 1989). These changes have been associated with a change in the bonding mode of a polydentate ligand, with hydration changes (Bielli, Gidney, Gillard & Heaton, 1974) and/or with stacking of the monomer units to optimize orbital overlap of the d_z2p_z orbitals and concomitant interaction between adjacent Pt atoms. In an effort to understand the detailed

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