

Note

Synthesis and X-ray structural determination of pentamethylcyclopentadienyl dichloro oxo molybdenum

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Abstract

Dark red crystals of the paramagnetic complex $\text{Cp}^*\text{MoCl}_2(\text{O})$ ($\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$) were obtained from the reaction of Cp^*MoCl_4 and water. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.654(2)$, $b = 11.150(3)$, $c = 6.545(1)$ Å, $\alpha = 93.76(3)$, $\beta = 91.12(3)$, $\gamma = 85.68(3)^\circ$, $V = 628.3(3)$ Å³, $D_{\text{calc}} = 1.681$ g/cm³ and $Z = 2$. The structure was solved and refined based on 1463 reflections with $F_o \geq 6\sigma(F_o)$ (6104 collected; Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å) and $R = 0.033$. The piano-stool structure, exhibiting a distorted Cp^* ligand, is compared with reported structures for the closely related compounds, $\text{CpMoCl}_2(\text{O})$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), $\text{Cp}^*\text{VCl}_2(\text{O})$ and $\text{Cp}^*\text{ReCl}_2(\text{O})$.

Key words: Crystal structures; Molybdenum complexes; Cyclopentadienyl complexes; Oxo complexes

Introduction

By providing details of molecular structure, X-ray crystallography allows analysis of electronic structure issues such as orbital participation and delocalization. When attempting to prepare a vinylmolybdenum complex for such a study, we instead isolated $\text{Cp}^*\text{MoCl}_2(\text{O})$. This paramagnetic compound, however, is structurally interesting in its own right. The straightforward reaction of Cp^*MoCl_4 ($\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$) [1] with water also afforded the paramagnetic complex $\text{Cp}^*\text{MoCl}_2(\text{O})$ in high yield, following the analogous quantitative conversion reported for CpMoCl_4 to $\text{CpMoCl}_2(\text{O})$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) [2]. Very recently, Rau *et al.* reported the preparation of the title compound by a related route [3]. We report here spectroscopic and X-ray diffraction data for this complex and offer structural compar-

isons with $\text{CpMoCl}_2(\text{O})$ [4], $\text{Cp}^*\text{VCl}_2(\text{O})$ [5] and $\text{Cp}^*\text{ReCl}_2(\text{O})$ [6]. Our data, together with the literature data, allow for independent evaluations of the structural effects of variations in metal and cyclopentadienyl substituents.

Experimental

Preparation of $\text{Cp}^*\text{MoCl}_2(\text{O})$

$\text{Cp}^*\text{MoCl}_2(\text{O})$ was prepared by mixing equimolar amounts of Cp^*MoCl_4 [1] (5.3 mg, 0.018 mmol) and water (0.32 mg, 0.018 mmol) in 2.5 ml tetrahydrofuran under a nitrogen atmosphere at room temperature. The purple color of the starting material turned immediately orange, and EPR spectroscopy indicated an 87% conversion. No diamagnetic products were observed by ¹H NMR. Larger amounts of $\text{Cp}^*\text{MoCl}_2(\text{O})$ were isolated from reactions between Cp^*MoCl_4 and vinylmagnesium chloride in which water was inadvertently admitted via contaminated nitrogen. Vacuum sublimation provided $\text{Cp}^*\text{MoCl}_2(\text{O})$ as a red powder. IR (KBr, cm⁻¹): 2921 (C–H), 1375 (Cp^*), 1023 (Cp^*), 932 (s, Mo=O, lit. 932 [3]); IR (mineral oil): 934 (Mo=O). EPR (toluene): $g = 1.967$, single line overlapped with six-line pattern, $a(^{95}\text{Mo}, ^{97}\text{Mo}) = 36$ G. MS (EI): 319 (M^+), with correct isotope envelope for $\text{C}_{10}\text{H}_{15}\text{Cl}_2\text{MoO}$ from 313 to 325.

X-ray crystallography

Dark red crystals of $\text{Cp}^*\text{MoCl}_2(\text{O})$ were grown by slow evaporation of benzene at room temperature in a nitrogen-filled glove box. A crystal measuring $0.3 \times 0.3 \times 0.3$ mm was coated with grease and mounted on a glass fiber in the glove box and centered at -80°C on a Rigaku AFC5S diffractometer. Unit cell parameters were determined by least-squares refinement of 25 carefully centered, high-angle reflections. The random search also located several weak reflections which were excluded from the least-squares refinement. Axial photographs revealed the presence of a fragment rather than intimate twinning or superlattice effects as the origin of these spurious reflections. The successful solution and unexceptional refinement of the structure confirm this conclusion. After data collection, the structure was solved by direct methods and refined using full matrix least-squares techniques. The structure model incorporated anisotropic thermal parameters for all atoms except for hydrogens. Idealized hydrogen atom positions were introduced assuming a bond distance

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of 1.0 Å for each C–H. Crystal data: triclinic space group $P\bar{1}$, $a=8.654(2)$, $b=11.150(3)$, $c=6.545(1)$ Å, $\alpha=93.76(3)$, $\beta=91.12(3)$, $\gamma=85.68(3)^\circ$, $V=628.3(3)$ Å³, $D_{\text{calc}}=1.681$ g/cm³, $Z=2$. The structure solution and refinement, based on 1463 reflections with $F_o \geq 6\sigma(F_o)$ (6104 collected; Mo $K\alpha$ radiation, $\lambda=0.71073$ Å), converged at $R=0.033$ and $R_w=0.039$.

Results and discussion

X-ray diffraction revealed that $\text{Cp}^*\text{MoCl}_2(\text{O})$ has a typical piano-stool structure, as shown in Fig. 1. Selected bond lengths and angles are listed in Table 1 and atomic positional parameters are listed in Table 2. Bottomley *et al.* [4] have compared the structures of three compounds of the type $\text{Cp}'\text{MCl}_2(\text{O})$ ($\text{Cp}' = \text{Cp}$ or Cp^*): $\text{Cp}^*\text{VCl}_2(\text{O})$ [5], $\text{CpMoCl}_2(\text{O})$ [4] and $\text{Cp}^*\text{ReCl}_2(\text{O})$ [6], and these structures are included in Table 1. With the addition of $\text{Cp}^*\text{MoCl}_2(\text{O})$, the effects of metal variation can be considered in the absence of variations in cyclopentadienyl substituents. Also, the disorder reported for $\text{CpMoCl}_2(\text{O})$ was not observed for $\text{Cp}^*\text{MoCl}_2(\text{O})$. A symmetric Cp ligand was assumed in order to allow refinement of the $\text{CpMoCl}_2(\text{O})$ structure, while the three Cp^* structures show that the cyclopentadienyl ligands are clearly asymmetric (see below).

Bottomley *et al.* noted the existence of profound differences in the Cl–M–Cl angles among the dichloro oxo complexes and found a strong correlation between this angle and the d-orbital configuration [4]. Thus, in $\text{Cp}^*\text{VCl}_2(\text{O})$ (d^0) the angle is 104.6° , in $\text{CpMoCl}_2(\text{O})$ (d^1) the angle is 93.4° and in $\text{Cp}^*\text{ReCl}_2(\text{O})$ (d^2) the angle is 85.4° . The correlation was successfully modeled with extended Hückel calculations. For the d^1 complex $\text{Cp}^*\text{MoCl}_2(\text{O})$, we find the Cl–M–Cl angle to be 93.2° , in close agreement with the Cp analogue.

Bursten and Cayton [7] have reported Fenske–Hall calculations on the closely related $\text{CpRe}(\text{CH}_3)_2(\text{O})$ that

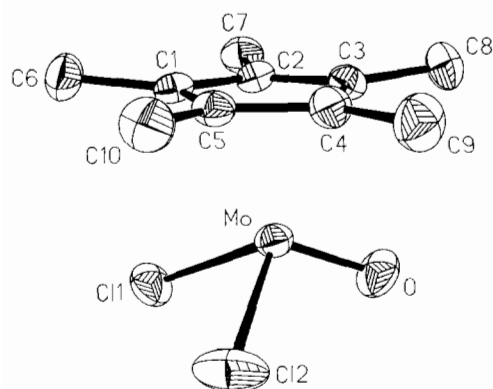


Fig. 1. ORTEP diagram for $\text{Cp}^*\text{MoCl}_2(\text{O})$.

complement the extended Hückel calculations mentioned above and allow a qualitative understanding of the structural changes in this series. In both calculations the important frontier orbital (the one that contains either 0, 1 or 2 electrons) is largely $d_{x^2-y^2}$, and in the dimethyl complex this orbital is essentially non-bonding. In the dichloro complexes, this orbital interacts with the π -donating chlorine ligands, favorably in the d^0 complex and unfavorably in the d^2 complex. These arguments are consistent with the observation that the Cl–M–Cl angle shows a large variation among the three complexes.

The M–C and C–C bond distances in Table 1 show that the Cp^* ligands are bound asymmetrically in the three complexes. The distortion is primarily a lengthening of the M–C bonds farthest from the oxo ligand (M–C(1), M–C(5)), indicating that the oxo ligand exerts a strong *trans* influence [8]. The C(1)–C(5) bond is also shortened relative to the other ring bonds, consistent with a weaker donation from this bond to the metal. Contribution from an η^3 resonance structure, as shown below, is consistent with the observed distortion. The rhenium complex shows the most severe asymmetry, with a 0.30 Å variation in M–C distances, while the variation in the vanadium and molybdenum species is 0.15 and 0.11 Å, respectively. These variations correlate very well with the observed O–M–Cp angles, which is consistent with the oxo *trans* influence.



By comparing the two molybdenum complexes, the structural influence of the cyclopentadienyl substituents may be evaluated. The Mo–O bond might be expected to weaken with methyl substitution, due to reduced π donation to the more electron rich metal center. The Mo=O stretching frequencies in the IR spectra are consistent with this expectation: 949 cm^{-1} (Cp, oil mull) [2] versus 934 cm^{-1} (Cp^* , oil mull). However, the diffraction results give a shorter Mo–O bond in the Cp^* complex by $0.060(7)$ Å. This discrepancy is small and might be caused by inaccuracies in the bond lengths of $\text{CpMoCl}_2(\text{O})$, whose crystal structure showed disorder [4]. This disorder may involve Cl–O exchange, an explanation that bears similarity to recent reports of Mo=O bond length inaccuracy arising from disorder involving Mo–Cl contaminants [9].

The other major structural difference between $\text{CpMoCl}_2(\text{O})$ and $\text{Cp}^*\text{MoCl}_2(\text{O})$ is the O–Mo–Cp angle, which is 5.6° smaller in the Cp^* case. The reason for the variation in this angle is unclear, but the extended Hückel calculations of Bottomley *et al.* show that vari-

TABLE 1. Selected bond lengths (Å) and angles (°) in Cp*MCl₂(O) compounds

	Cp*VCl ₂ (O) ^a	Cp*MoCl ₂ (O) ^b	Cp*ReCl ₂ (O) ^c	CpMoCl ₂ (O) ^d
M–O	1.576(8)	1.684(4)	1.700(4)	1.740(6)
M–Cl(1)	2.233(5)	2.341(2)	2.348(2)	2.306(3)
M–Cl(2)	2.215(5)	2.329(2)	2.345(2)	2.297(3)
M–Cp ^e	2.010	2.053	1.972	2.054
M–C(1)	2.437	2.449(5)	2.477(6)	
M–C(2)	2.311	2.339(5)	2.225(5)	
M–C(3)	2.277	2.339(5)	2.180(6)	2.38
M–C(4)	2.280	2.341(6)	2.225(6)	
M–C(5)	2.424	2.445(5)	2.475(6)	
C(1)–C(2)	1.459	1.449(8)	1.462(8)	
C(2)–C(3)	1.432	1.423(8)	1.438(8)	
C(3)–C(4)	1.434	1.410(8)	1.445(8)	1.42
C(4)–C(5)	1.422	1.453(8)	1.454(9)	
C(5)–C(1)	1.384	1.384(8)	1.393(8)	
Cl(1)–M–Cl(2)	104.6(2)	93.2(1)	85.4(1)	93.4(1)
O–M–Cl(1)	102.6(4)	107.1(2)	105.3(2)	103.4(3)
O–M–Cl(2)	104.3(4)	108.5(2)	106.2(2)	102.8(3)
O–M–Cp	118.8	117.1	128.9	122.7
Cl(1)–M–Cp	111.9	113.8	111.3	114.3
Cl(2)–M–Cp	113.3	114.4	111.0	115.6

^aRef. 4. Cp* carbon atoms have been renumbered. Values involving Cp differ from those reported in ref. 4. M–C and C–C distances were calculated from the published atomic coordinates. ^bThis work. Standard deviations of the last digit appear in parentheses. ^cRef. 5. Cp* carbon atoms have been renumbered. In ref. 5, a different convention was used to calculate Cp. ^dRef. 3. Since a symmetrical Cp model was used in the refinement, only average values appear for distances involving C(1)–C(5). ^eCp is the center of the C(1)–C(5) ring.

TABLE 2. Atomic positional parameters for Cp*MoCl₂(O)

Atom	x	y	z
Mo	0.2701(1)	0.2897(1)	0.0521(1)
Cl(1)	0.5050(2)	0.2463(1)	0.2250(2)
Cl(2)	0.1432(2)	0.1477(2)	0.2176(3)
O	0.2008(5)	0.4283(4)	0.1404(6)
C(1)	0.3956(7)	0.1882(5)	–0.2510(8)
C(2)	0.3931(7)	0.3182(5)	–0.2542(8)
C(3)	0.2353(7)	0.3621(5)	–0.2742(8)
C(4)	0.1424(7)	0.2641(5)	–0.2646(8)
C(5)	0.2446(7)	0.1550(5)	–0.2548(8)
C(6)	0.5422(7)	0.1060(5)	–0.2505(10)
C(7)	0.5325(7)	0.3885(5)	–0.2588(9)
C(8)	0.1798(8)	0.4909(5)	–0.3016(10)
C(9)	–0.0309(7)	0.2670(6)	–0.2811(10)
C(10)	0.1913(8)	0.0305(5)	–0.2623(10)

ation in the corresponding angle in CpNbCl₂(O) has little effect on the energy of either the complex or the LUMO (which is partially filled in the molybdenum compound) [4]. The differences in the O–Mo–Cp angles and in the Mo=O distances between the two complexes may be strongly coupled. Indeed, a change in the O–Mo–Cp angle would in turn change the nature of the Mo=O d_π–p_π overlap.

Supplementary material

Tables of bond lengths and angles, anisotropic temperature factors, calculated hydrogen positions, and structure factors can be obtained upon request from M.B.S.

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References

- 1 R.C. Murray, L. Blum, A.H. Liu and R.R. Schrock, *Organometallics*, 4 (1985) 953.
- 2 M. Cousins and M.L.H. Green, *J. Chem. Soc.*, (1964) 1567.
- 3 M.S. Rau, C.M. Kretz, G.L. Geoffroy and A.L. Rheingold, *Organometallics*, 12 (1993) 3447.

- 4 F. Bottomley, E.C. Ferris and P.S. White, *Organometallics*, **9** (1990) 1166.
- 5 F. Bottomley, J. Darkwa, L. Sutin and P.S. White, *Organometallics*, **5** (1986) 2165.
- 6 W.A. Herrmann, U. Küsthardt, M. Flöel, J. Kulpe, E. Herdtweck and E. Voss, *J. Organomet. Chem.*, **314** (1986) 151.
- 7 B.E. Bursten and R.H. Cayton, *Organometallics*, **6** (1987) 2004.
- 8 G. Parkin, R.E. Marsh, W.P. Schaefer and J.E. Bercaw, *Inorg. Chem.*, **27** (1988) 3262.
- 9 K. Yoon, G. Parkin and A.L. Rheingold, *J. Am. Chem. Soc.*, **114** (1992) 2210.