Aqueous "Green" Organometallic Chemistry: Structure of the Molybdocene Monohydride used for Carbonyl Reduction in Water.

by

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SUPPORTING INFORMATION

1. Experimental Methods
   a.) Crystal Structure Analysis
   b.) Synthesis of $Cp_2Mo(H)OTf$
2. Supporting ^1H NMR spectrum
3. Crystallographic data and tables

EXPERIMENTAL METHODS (Supplementary Materials)

Proton (300 MHz) and deuterium (47.7 MHz) NMR spectra were recorded with a Varian Innova-300 spectrometer, and proton chemical shifts were referenced to $(CH_3)_4Si$ (TMS). The parent compound Cp_2MoH_2 was made according to the procedure of Luo and coworkers except NaCp was used instead of LiCp,[1] and all chemical reagents were purchased from Alrich Chemical Co. (Milwaukee, WI) and used as received.

All manipulations used standard Schlenk or dry box techniques under a nitrogen atmosphere, and all aqueous solutions were thoroughly purged with prepurified nitrogen prior to use. The pD measurements were done in D_2O using a Beckman Φ10 pH meter using a glass electrode, and the reported pD values are uncorrected. Stock solutions of $Cp_2Mo(H)OTf$ and acetone derivatives were made in D_2O or methanol-d_4 immediately prior to kinetic measurements.

Crystal Structure Analysis

A crystal of dimension 0.11 x 0.34 x 0.60 mm was sealed in a special glass capillary under argon in the dry box. The orientation parameters and cell dimensions were obtained from the setting angles of an Enraf-Nonius CAD-4 diffractometer for 25 centered reflections in the range $14° \leq \theta \leq 15°$. The supplementary table I summarizes the crystallographic data and final residues. A more extensive table including particulars of data collection and structure refinement is in the supplementary material. The systematic absences indicated the space-group $P2_1/c$. Absorption corrections based on azimuthal scans ("Ψ-scans") were applied. A *SIR92* E-map[2] showed all the non-hydrogen atoms. All hydrogen atoms were located from a difference synthesis and were

[1] Luo, L.; Lanza, G.; Fragala, I.L.; Stern, C.L.; Marks, T.J. *J. Am. Chem. Soc.* **1998**, *120*, 3111-3122.

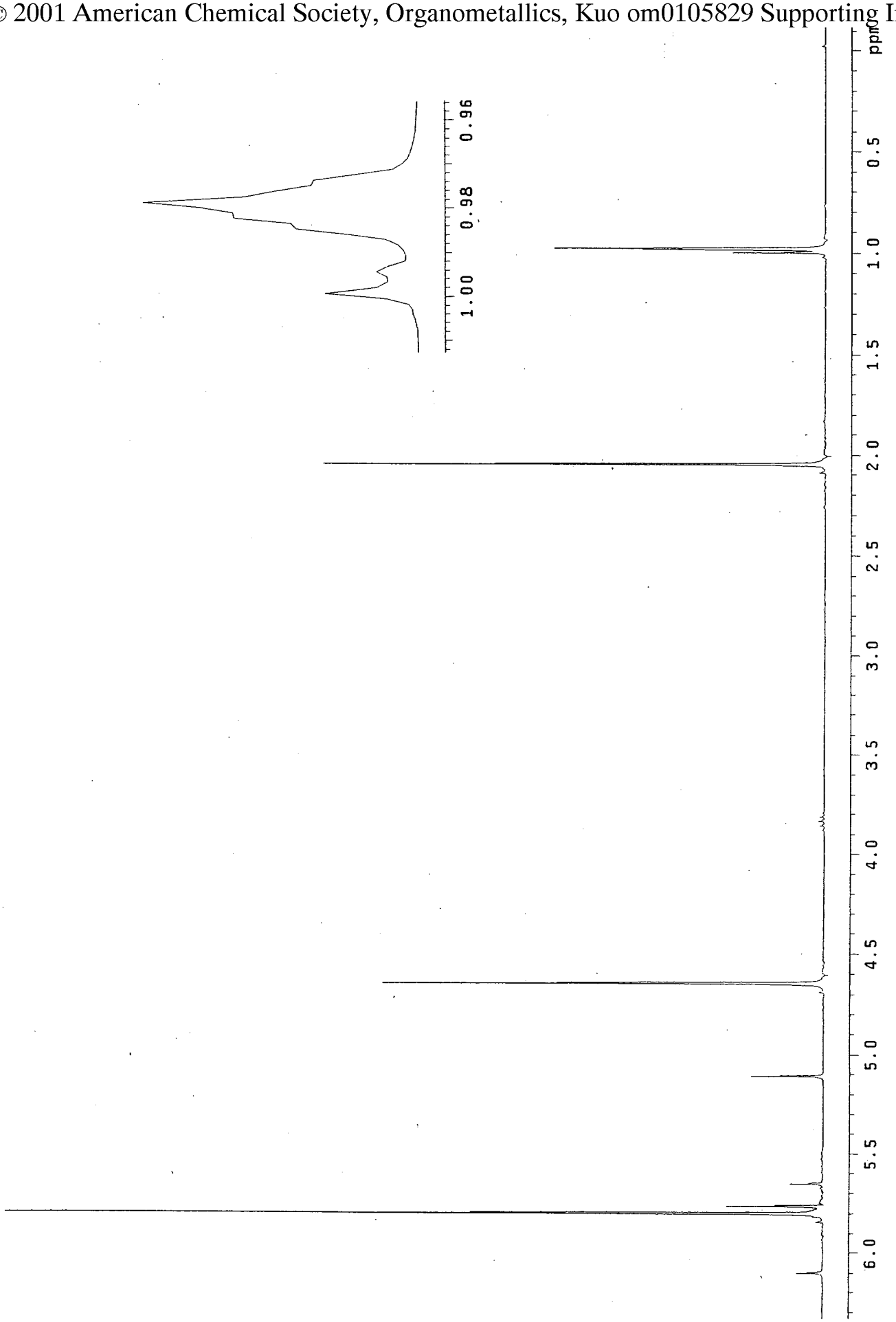
[2] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.C.; Polidori, G.; Gamalli, N. *J. Appl. Crystallography* **1994**, *27*, 435.

refined. The *TEXSAN* program suite,[3] incorporating complex atomic scattering factors, were used in all calculations to obtain an R_w factor of 0.044.

Synthesis of $Cp_2Mo(H)OTf$ (I)

The parent compound Cp_2MoH_2 (190 mg, 0.83 mmole) was dissolved in 10 mL of C_6H_6. Methyl triflate (180 mg, 1.1 mmole) was added to this stirred solution and the color changed from yellow to dark red. After stirring at room temperature for three hours, the C_6H_6 was removed in vacuo and replaced with H_2O (0.5 mL). The aqueous red solution was filtered and then dried in vacuo to yield 270 mg (0.72 mmole) of the $Cp_2Mo(H)OTf$ monohydride (86% yield). X-ray quality crystals of $Cp_2Mo(H)OTf$ were grown by vapor diffusion of hexane into a benzene solution at room temperature in the dry box.

[3] Molecular Structures Corporation, 3200A Research Forest Drive, The Woodlands, TX 77381, USA. *TeXsan Sofware for Single-Crystal Structure Analysis,* version 1.7, 1997.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1.00

Supplementary material

Crystallographic information

Crystal data

Formula	$C_{11}H_{11}F_3MoO_3S$
Formula weight	376.20
Crystal system	monoclinic
Space-group	$P2_1/c$
a, b, c	12.2250(13), 8.5082(11), 13.1264(7) Å
α, β, γ	90, 104.401(7), 90°
V	1322.4(3) Å^3
Z	4
d_{calc}	1.889 g cm^{-3}
μ	11.8 cm^{-1}
F_{000}	744

Data collection

Crystal appearance	dark red plate
Crystal dimensions	0.11 × 0.34 × 0.60 mm
Diffractometer	Enraf-Nonius CAD-4
Radiation, wavelength	Mo Kα, 0.71073 Å
Monochromator	graphite
Temperature	22 °C
$2\theta_{max}$	60°
Index range *h*, *k*, *l*	0→17, 0→11, -18→17

Scan mode	ω-2θ
Scan speed (on ω)	4.1° min^{-1}
Scan width	(0.90 + 0.35tanθ)°
Reference reflections	3, every 3600 s exposure
No. indep. rflns scanned	4092
R_{int} (on F^2 for $0,k,\pm l$)	0.018

Refinement

Absorption correction	azimuthal (ψ) scans
Rel. corr. factors	0.823-1.000
Sec. extinction parameter (g)	$3.5(8) \times 10^{-7}$
No. rflns in refinement (N)	3211 [$I \geq \sigma(I)$]
No. parameters (V)	216
Function minimized	$\Sigma w(\|F_o\|-\|F_c\|)^2$
Weighting factor w	$1/\sigma^2(F)$
R(F), wR(F)	0.038, 0.044
S	2.19
Max. Δ/σ, last cycle	0.03
Max., min. in final diff. map	1.84 [0.89 Å from Mo], -1.10 e $Å^{-3}$

$$R(F) = \Sigma||F_o|-|F_c||/\Sigma|F_o| \qquad wR(F) = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$$

$$S = [\Sigma w(|F_o|-|F_c|)^2/(N-V)]^{1/2} \qquad I_o(corr) = I_o(1+2gI_c)$$

Table 1

Crystallographic data

Composition	$C_{11}H_{11}F_3MoO_3S$	d_{calc}	1.889 g cm^{-3}
Formula wt	376.20	T	22 °C
Space-group	$P2_1/c$	λ	0.71073 Å
a	12.2250(13) Å	μ	11.8 cm^{-1}
b	8.5082(11) Å	Rel trans coefft	0.823-1.000 (ψ)
c	13.1264(7) Å	No. obs. rflns	3211 [$I \geq \sigma(I)$]
β	104.401(7)°	Total indep. rflns	4092
V	1322.4(3) $Å^3$	R(F), wR(F)	0.038, 0.044
Z	4		

$$R(F) = \Sigma||F_o|-|F_c||/\Sigma|F_o| \qquad wR(F^2) = [\Sigma w(|F_o|^2-|F_c|^2)^2/\Sigma w|F_o|^4]^{1/2}$$

Table 2

Atomic coordinates and equivalent isotropic thermal parameters ($Å^2$)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$$

Atom	x	y	z	B_{eq}
Mo	0.67830(2)	0.52998(3)	0.78658(2)	2.549(6)
S(1)	0.78131(8)	0.17172(10)	0.80375(8)	3.79(2)
F(1)	0.9593(3)	0.1404(6)	0.7327(4)	11.00(15)
F(2)	0.9943(3)	0.1556(5)	0.8963(4)	11.48(13)
F(3)	0.9266(3)	-0.0544(4)	0.8223(4)	10.38(12)
O(1)	0.8030(2)	0.3413(3)	0.8040(2)	3.50(5)
O(2)	0.7187(3)	0.1107(4)	0.7063(3)	6.74(9)
O(3)	0.7494(3)	0.1166(4)	0.8936(3)	7.07(10)
C(1)	0.7241(4)	0.5271(6)	0.6225(3)	4.64(10)
C(2)	0.7386(4)	0.6777(6)	0.6614(3)	4.49(10)
C(3)	0.6323(4)	0.7306(5)	0.6714(3)	4.15(9)
C(4)	0.5527(3)	0.6100(5)	0.6414(3)	4.07(8)
C(5)	0.6116(4)	0.4804(5)	0.6113(3)	4.42(9)
C(6)	0.5779(4)	0.6157(6)	0.8966(3)	4.70(10)
C(7)	0.6611(5)	0.7300(5)	0.8935(3)	5.12(11)
C(8)	0.7679(5)	0.6649(7)	0.9371(3)	5.68(13)
C(9)	0.7510(5)	0.5128(6)	0.9701(3)	5.46(11)
C(10)	0.6349(5)	0.4819(6)	0.9445(3)	4.86(10)
C(11)	0.9237(4)	0.1009(6)	0.8159(6)	6.38(14)
H(1)	0.773(4)	0.467(5)	0.614(4)	5.0(11)
H(2)	0.808(4)	0.720(6)	0.676(4)	5.8(12)

H(3)	0.613(3)	0.827(5)	0.688(3)	4.4(9)
H(4)	0.464(4)	0.616(5)	0.639(3)	5.1(10)
H(5)	0.585(3)	0.381(5)	0.586(3)	4.1(9)
H(6)	0.496(4)	0.612(7)	0.875(4)	7.5(14)
H(7)	0.640(4)	0.842(6)	0.868(4)	6.3(12)
H(8)	0.833(3)	0.693(5)	0.938(3)	3.8(9)
H(9)	0.816(4)	0.450(5)	1.000(4)	5.5(11)
H(10)	0.606(4)	0.370(6)	0.961(4)	6.5(12)
H(11)	0.591(4)	0.381(5)	0.767(3)	5.2(10)

Supporting data

Anisotropic thermal parameters ($Å^2$)

The temperature factor is given by: $T = \exp[-2\pi^2\Sigma_i\Sigma_j U_{ij}h_ih_ja^*_ia^*_j]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.0408(2)	0.0292(2)	0.0270(2)	-0.0021(1)	0.0086(1)	-0.0011(1)
S(1)	0.0464(5)	0.0345(4)	0.0617(6)	-0.0008(4)	0.0110(4)	0.0003(4)
F(1)	0.109(3)	0.136(4)	0.205(5)	0.008(3)	0.099(3)	-0.011(3)
F(2)	0.072(2)	0.106(3)	0.211(5)	0.016(2)	-0.053(3)	-0.024(3)
F(3)	0.096(2)	0.052(2)	0.238(5)	0.025(2)	0.026(3)	-0.001(2)
O(1)	0.044(2)	0.034(1)	0.052(2)	0.002(1)	0.008(1)	0.003(1)
O(2)	0.077(2)	0.064(2)	0.099(3)	-0.003(2)	-0.008(2)	-0.032(2)
O(3)	0.119(3)	0.060(2)	0.105(3)	0.004(2)	0.057(2)	0.027(2)
C(1)	0.073(3)	0.075(3)	0.035(2)	0.017(2)	0.025(2)	0.009(2)
C(2)	0.064(3)	0.066(3)	0.042(2)	-0.013(2)	0.015(2)	0.013(2)
C(3)	0.074(3)	0.039(2)	0.043(2)	0.006(2)	0.012(2)	0.010(2)
C(4)	0.051(2)	0.058(2)	0.042(2)	0.005(2)	0.004(2)	0.010(2)
C(5)	0.085(3)	0.050(2)	0.029(2)	-0.009(2)	0.006(2)	-0.004(2)
C(6)	0.071(3)	0.065(3)	0.049(2)	0.004(2)	0.029(2)	-0.010(2)
C(7)	0.109(4)	0.044(2)	0.047(2)	-0.001(2)	0.029(2)	-0.016(2)
C(8)	0.083(4)	0.091(4)	0.042(2)	-0.034(3)	0.014(2)	-0.025(2)
C(9)	0.090(4)	0.084(4)	0.027(2)	0.017(3)	0.003(2)	-0.004(2)
C(10)	0.097(4)	0.058(3)	0.036(2)	-0.013(2)	0.030(2)	-0.005(2)
C(11)	0.055(3)	0.050(3)	0.135(5)	0.010(2)	0.018(3)	0.001(3)

Supporting data

Intermolecular distances (Å) for non-hydrogen atoms

atom	atom	distance	code	atom	atom	distance	code
F(1)	F(3)	3.116(6)	7562	O(3)	C(1)	3.330(5)	5554
F(2)	C(8)	3.522(6)	7673	O(3)	C(7)	3.462(6)	5451
F(2)	C(2)	3.535(7)	7462	C(1)	C(7)	3.572(6)	5644
F(3)	C(2)	3.538(6)	5451	C(2)	C(8)	3.335(6)	5644
O(2)	C(9)	3.389(6)	5544	C(2)	C(7)	3.497(6)	5644
O(2)	C(3)	3.398(5)	5451	C(4)	C(5)	3.510(5)	6663
O(2)	C(10)	3.426(6)	5544	C(5)	C(5)	3.484(8)	6663
O(2)	C(6)	3.541(6)	6462				

The digits in the code pqrs denote that the second atom is derived from the corresponding atom in the table of atomic coordinates by the action of the symmetry operator numbered s (see below) followed by (p-5), (q-5), and (r-5) unit translations in the +*a*, +*b*, and +*c* directions respectively. For instance, the code 6462 denotes that the second atom has been shifted from x, y, z to 1-x, -½+y, 1½-z.

(1)	+x,	+y,	+z	(2)	-x,	½+y,	½-z
(3)	-x,	-y,	-z	(4)	+x,	½-y,	½+z

Table 3

Bond lengths (Å)

Mo-O(1)	2.186(2)	C(1)-C(5)	1.404(7)
Mo-C(1)	2.356(4)	C(1)-H(1)	0.82(4)
Mo-C(2)	2.329(4)	C(2)-C(3)	1.412(6)
Mo-C(3)	2.257(4)	C(2)-H(2)	0.89(5)
Mo-C(4)	2.235(4)	C(3)-C(4)	1.401(6)
Mo-C(5)	2.281(4)	C(3)-H(3)	0.89(4)
Mo-C(6)	2.237(4)	C(4)-C(5)	1.426(6)
Mo-C(7)	2.248(4)	C(4)-H(4)	1.08(4)
Mo-C(8)	2.311(4)	C(5)-H(5)	0.94(4)
Mo-C(9)	2.356(4)	C(6)-C(7)	1.415(7)
Mo-C(10)	2.300(4)	C(6)-C(10)	1.400(7)
Mo-H(11)	1.63(4)	C(6)-H(6)	0.97(5)
S(1)-O(1)	1.467(2)	C(7)-C(8)	1.403(8)
S(1)-O(2)	1.415(3)	C(7)-H(7)	1.02(5)
S(1)-O(3)	1.411(3)	C(8)-C(9)	1.396(7)
S(1)-C(11)	1.811(5)	C(8)-H(8)	0.82(4)
F(1)-C(11)	1.317(7)	C(9)-C(10)	1.400(7)
F(2)-C(11)	1.274(7)	C(9)-H(9)	0.96(5)
F(3)-C(11)	1.323(6)	C(10)-H(10)	1.05(5)
C(1)-C(2)	1.375(6)		

Table 4

Bond angles (°)

O(1)-Mo-H(11)	82(1)	C(4)-C(5)-H(5)	130(2)
O(1)-S(1)-O(2)	114.8(2)	C(7)-C(6)-C(10)	106.9(4)
O(1)-S(1)-O(3)	114.4(2)	C(7)-C(6)-H(6)	135(3)
O(1)-S(1)-C(11)	99.1(2)	C(10)-C(6)-H(6)	118(3)
O(2)-S(1)-O(3)	115.7(2)	C(6)-C(7)-C(8)	108.6(4)
O(2)-S(1)-C(11)	104.4(3)	C(6)-C(7)-H(7)	122(3)
O(3)-S(1)-C(11)	106.0(3)	C(8)-C(7)-H(7)	129(3)
Mo-O(1)-S(1)	127.0(1)	C(7)-C(8)-C(9)	107.3(5)
C(2)-C(1)-C(5)	109.6(4)	C(7)-C(8)-H(8)	133(3)
C(2)-C(1)-H(1)	127(3)	C(9)-C(8)-H(8)	119(3)
C(5)-C(1)-H(1)	123(3)	C(8)-C(9)-C(10)	108.6(5)
C(1)-C(2)-C(3)	107.1(4)	C(8)-C(9)-H(9)	118(3)
C(1)-C(2)-H(2)	119(3)	C(10)-C(9)-H(9)	133(3)
C(3)-C(2)-H(2)	134(3)	C(6)-C(10)-C(9)	108.5(4)
C(2)-C(3)-C(4)	109.4(4)	C(6)-C(10)-H(10)	132(3)
C(2)-C(3)-H(3)	129(3)	C(9)-C(10)-H(10)	120(3)
C(4)-C(3)-H(3)	122(3)	S(1)-C(11)-F(1)	110.5(4)
C(3)-C(4)-C(5)	106.3(4)	S(1)-C(11)-F(2)	112.9(4)
C(3)-C(4)-H(4)	127(2)	S(1)-C(11)-F(3)	110.3(4)
C(5)-C(4)-H(4)	127(2)	F(1)-C(11)-F(2)	107.3(5)
C(1)-C(5)-C(4)	107.5(4)	F(1)-C(11)-F(3)	107.4(5)
C(1)-C(5)-H(5)	123(2)	F(2)-C(11)-F(3)	108.1(5)
O(1)-Mo-Cp(1)	106.5(5)	O(1)-Mo-Cp(2)	107.0(5)
H(11)-Mo-Cp(1)	99(1)	H(11)-Mo-Cp(2)	104(1)
Cp(1)-Mo-Cp(2)	141.7(4)		

Cp(1), Cp(2) are the centroids of the rings C(1-5) and C(6-10)

Supporting data

Torsion angles (°)

(1)	(2)	(3)	(4)	angle	(1)	(2)	(3)	(4)	angle
Mo	O(1)	S(1)	O(2)	67.0(3)	F(3)	C(11)	S(1)	O(3)	58.4(5)
Mo	O(1)	S(1)	O(3)	-70.1(3)	C(1)	C(2)	C(3)	C(4)	1.8(4)
Mo	O(1)	S(1)	C(11)	177.6(3)	C(1)	C(5)	C(4)	C(3)	-0.8(4)
F(1)	C(11)	S(1)	O(1)	-64.2(4)	C(2)	C(1)	C(5)	C(4)	2.0(4)
F(1)	C(11)	S(1)	O(2)	54.4(4)	C(2)	C(3)	C(4)	C(5)	-0.6(4)
F(1)	C(11)	S(1)	O(3)	177.1(4)	C(3)	C(2)	C(1)	C(5)	-2.3(4)
F(2)	C(11)	S(1)	O(1)	56.0(5)	C(6)	C(7)	C(8)	C(9)	-1.8(5)
F(2)	C(11)	S(1)	O(2)	174.7(4)	C(6)	C(10)	C(9)	C(8)	-0.9(5)
F(2)	C(11)	S(1)	O(3)	-62.7(5)	C(7)	C(6)	C(10)	C(9)	-0.2(4)
F(3)	C(11)	S(1)	O(1)	177.1(4)	C(7)	C(8)	C(9)	C(10)	1.7(5)
F(3)	C(11)	S(1)	O(2)	-64.2(5)	C(8)	C(7)	C(6)	C(10)	1.3(4)

The sign is positive if a clockwise motion of atom 1 would superimpose it on atom 4 when the direction of view is from atom 2 to atom 3.

Supporting data

Least-squares mean planes (deviation in Å)

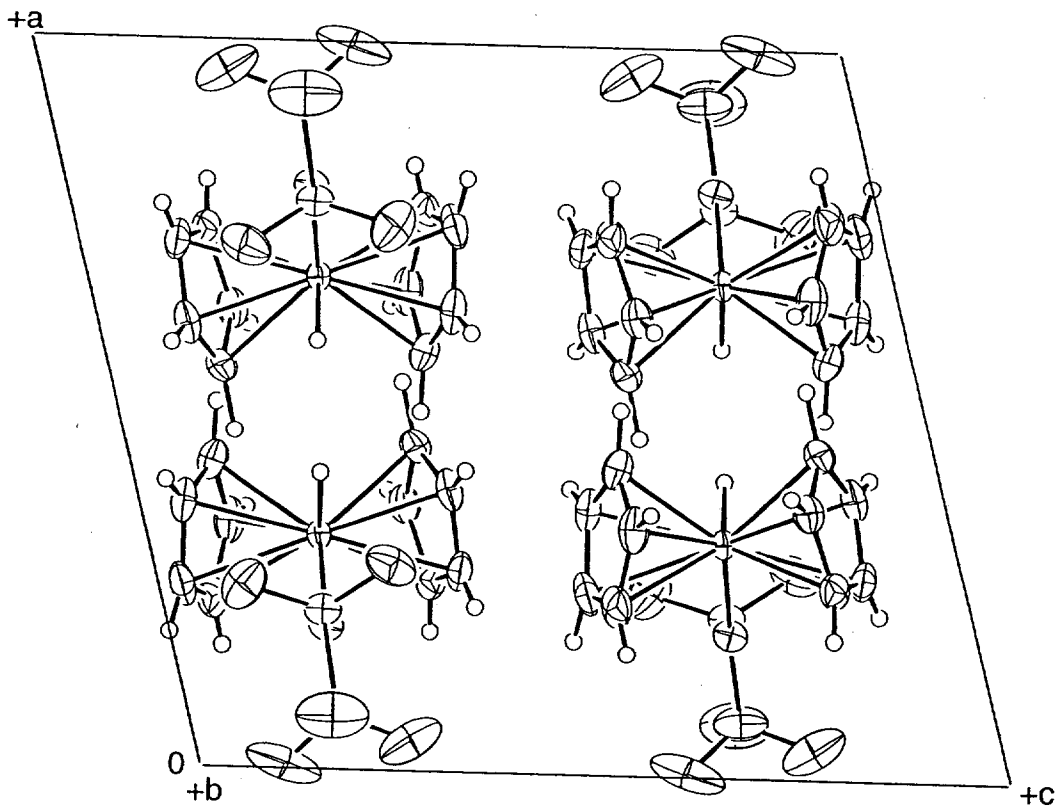
Plane 1	Defining atoms	Distance	Other atoms	Distance
	C(1)	-0.013(4)	Mo	1.952
	C(2)	0.012(4)		
	C(3)	-0.007(4)		
	C(4)	-0.001(4)		
	C(5)	0.008(4)		

Mean deviation from plane: 0.008 Å; χ^2, 28.6

Plane 2	Defining atoms	Distance	Other atoms	Distance
	C(6)	0.004(4)	Mo	1.952
	C(7)	-0.008(4)		
	C(8)	0.011(4)		
	C(9)	-0.008(4)		
	C(10)	0.001(4)		

Mean deviation from plane: 0.006 Å; χ^2, 16.1

Dihedral angle between planes: 136.7°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0
+b
+c