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Half-sandwich molybdenum complexes: molecular structure and catalyst precursors for olefin epoxidation with *tert*-butyl hydroperoxide

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S1. Synthetic procedures

S1.1. General experimental remarks

All of the described manipulations were conducted under an argon atmosphere, using a dry box and standard Schlenk and vacuum line techniques. THF was predried over NaOH and distilled from potassium benzophenone ketyl under argon. Pentane was distilled from Na/K alloy in the presence of 18-crown-6 and benzophenone ketyl under argon. Acetonitrile was distilled over calcium hydride under argon. C_6D_6 was distilled over Na/K alloy. CD_2Cl_2 was carefully distilled over $LiAlH_4$. C_6D_6 and CD_2Cl_2 were stored over 4 Å molecular sieves.

1,2,4-Triphenylcyclopenta-1,3-diene[1] and 2,5-dimethyl-4*H*-cyclopenta[*b*]thiophene were obtained as described.[2] Complexes (**1**) and (**2**) were obtained in good yields according to a slightly modified literature procedure.[3] Complexes Cp'Mo$(CO)_3$Me (Cp'= cyclopentadienyl,[4] indenyl[5]) for catalytic experiments were prepared according to the literature procedures.

Elemental (C/H/N) analyses were performed with a PerkinElmer 2400 Series II elemental CHNS/O analyzer. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AVANCE 400 spectrometer at 25 °C. GC analysis was carried out with a KRISTALL-2000M gas chromatograph equipped with a SolGel-1ms (60 m×0.25 mm×0.25 μm) column and a flame ionization detector. Helium was used as a carrier gas at a rate of 1.364 cc min^{-1} and with a split ratio of 73.3 : 1. The injection temperature was 300 °C, and the column temperature was 100 °C within 5 min and then raised from 100 °C to 300 °C at a rate of 10 °C min^{-1}.

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S1.2. Synthesis of Mo complexes 1 and 2

(η^5-1,2,4-Triphenylcyclopentadienyl)(tricarbonyl)(methyl)molybdenum, **1**

A solution of *n*-BuLi in hexane (2.5 *M*, 1 ml, 2.5 mmol) was added to a cold (–40 °C) solution of 1,2,4-triphenylcyclopentadiene (700 mg, 2.38 mmol) in THF (30 ml). The obtained mixture was stirred for 30 min and allowed to warm slowly to room temperature. Molybdenum hexacarbonyl (600 mg, 2.27 mmol) was added to the mixture which was then refluxed for 20 h. After cooling to room temperature, iodomethane (0.71 g, 0.31 ml, 5.0 mmol) was added; and the mixture was stirred overnight. All volatiles were removed under reduced pressure. The residue was extracted with pentane (40 ml) and filtered. The filtrates were concentrated and cooled to –25 °C to afford orange crystals of **1**. Several single crystals were taken for the X-ray analysis. Yield: 0.620 g (1.27 mmol, 56%). ^{1}H NMR (C_6D_6, 25 °C) δ: 0.51 (s, 3H); 5.54 (s, 2H); 6.96-7.00 (m, 6H); 7.02-7.05 (m, 1H); 7.07-7.12 (m, 4H); 7.23-7.27 (m, 4H). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ: -12.7, 91.8, 110.5, 113.2, 125.8, 128.9, 129.3, 130.2, 132.9, 133.7, 227.8, 240.7. Analysis found (calculated for $C_{27}H_{20}MoO_3$), %: C 66.12 (66.40), H 4.78 (4.13).

(η^5-2,5-Dimethyl-4H-cyclopenta[b]thienyl)(tricarbonyl)(methyl)molybdenum, **2**

Compound **2** was prepared similarly to **1**. 2,5-Dimethyl-4*H*-cyclopenta[*b*]thiophene (0.348 g, 2.31 mmol), *n*-BuLi (1 ml, 2.5 mmol), $Mo(CO)_6$ (0.600 g, 2.27 mmol) and MeI (0.71 g, 0.31 ml, 5.0 mmol) were used to produce orange crystals of **2** (0.450 g, 1.29 mmol, 57%). Single crystals for X-ray diffraction studies were grown by cooling (–25 °C) saturated pentane solution of **2**. ^{1}H NMR (C_6D_6, 25 °C) δ: 0.08 (s, 3H); 1.56 (s, 3H); 1.84 (s, 3H); 4.68 (s, 1H); 4.74 (s, 1H); 5.72 (s, 1H). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ: -5.5, 15.8, 16.5, 78.7, 80.3, 108.2, 115.0, 118.4, 121.8, 147.8. Analysis found (calculated for $C_{13}H_{12}MoO_3S$), %: C 45.05 (45.36), H 3.99 (3.51).

S1.3. NMR spectra of Mo complexes 1 and 2

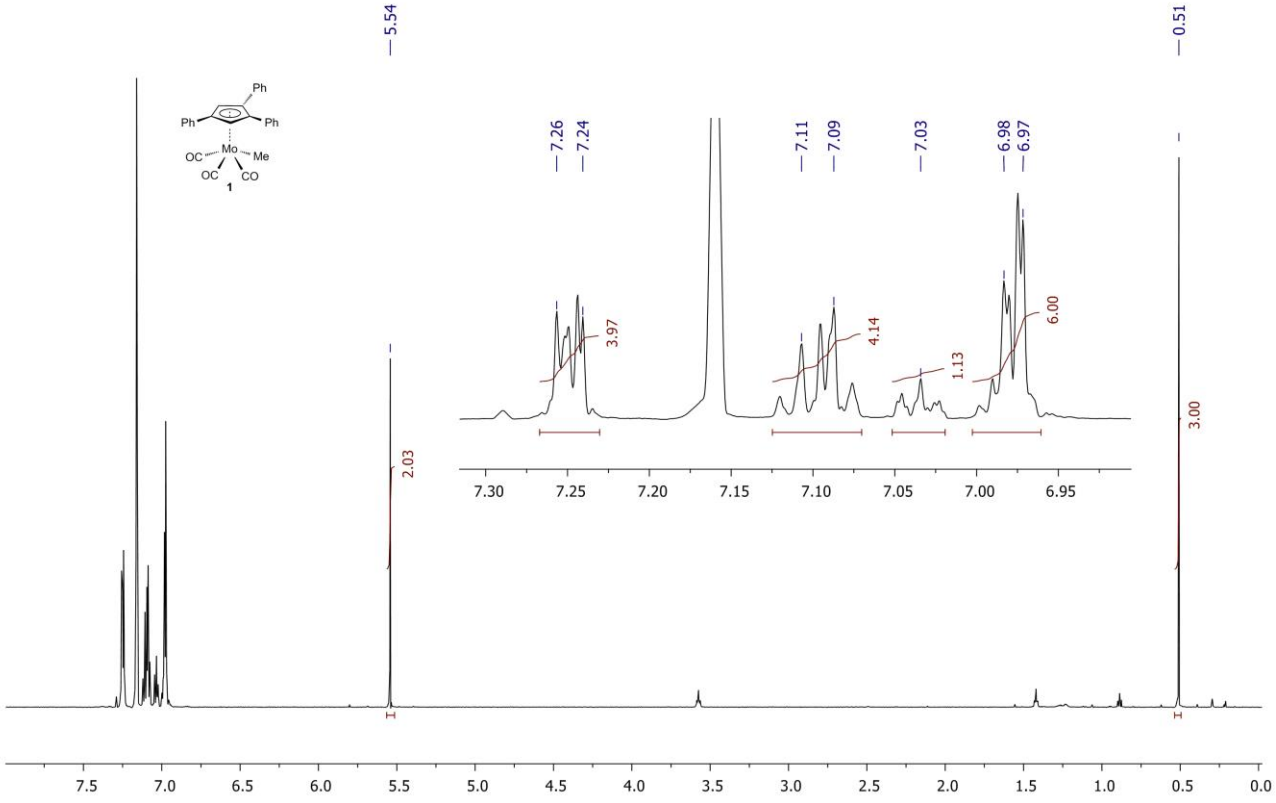

Figure S1. ^{1}H NMR spectrum (C_6D_6, 25 °C, 400 MHz) of the complex **1**

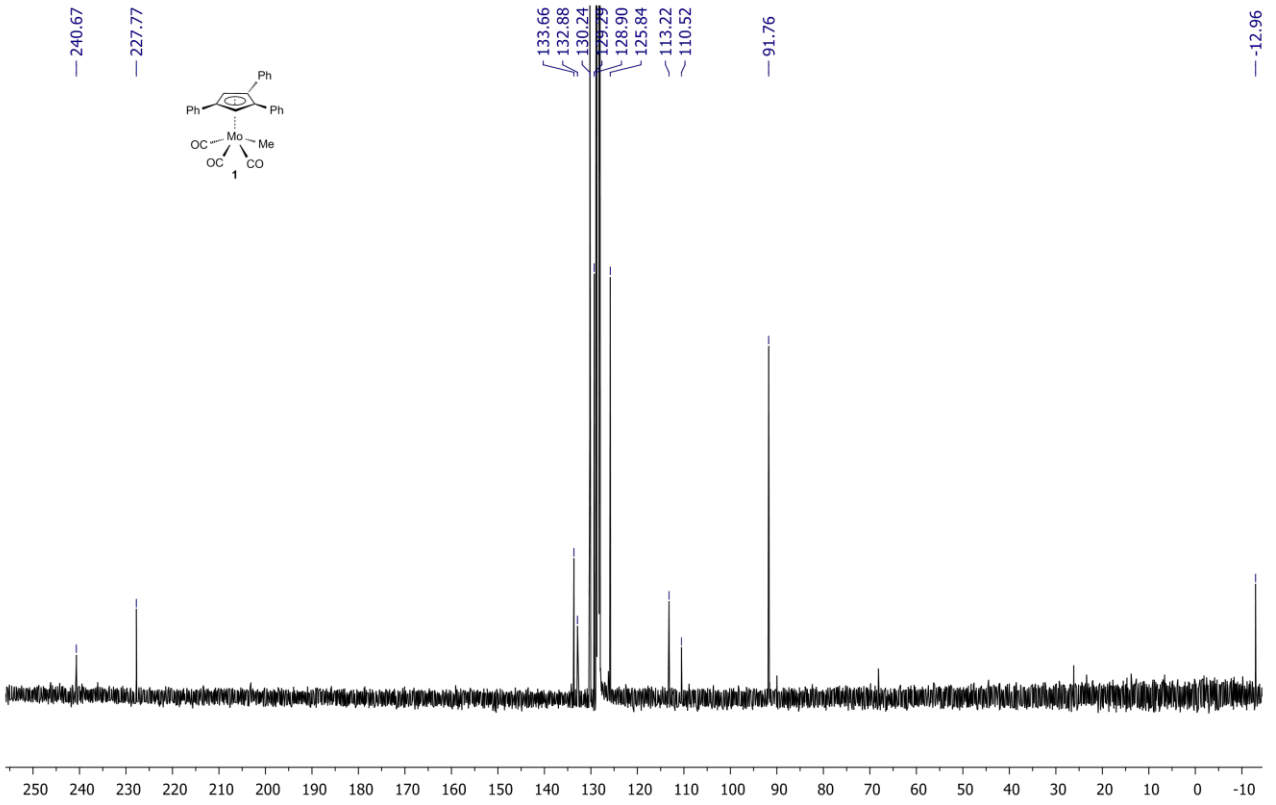

Figure S2. ^{13}C NMR spectrum (C_6D_6, 25 °C, 101 MHz) of the complex **1**

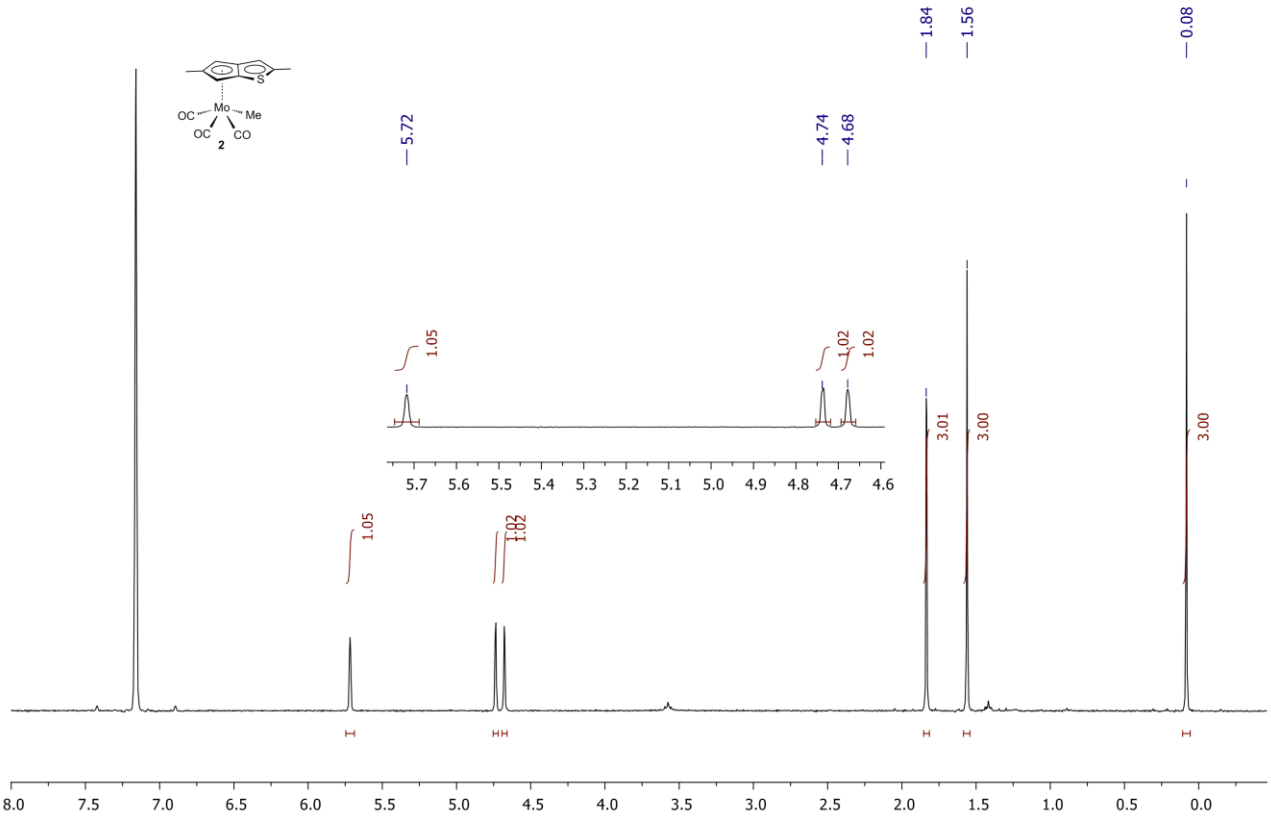

Figure S3. ^{1}H NMR spectrum (C_6D_6, 25 °C, 400 MHz) of the complex **2**

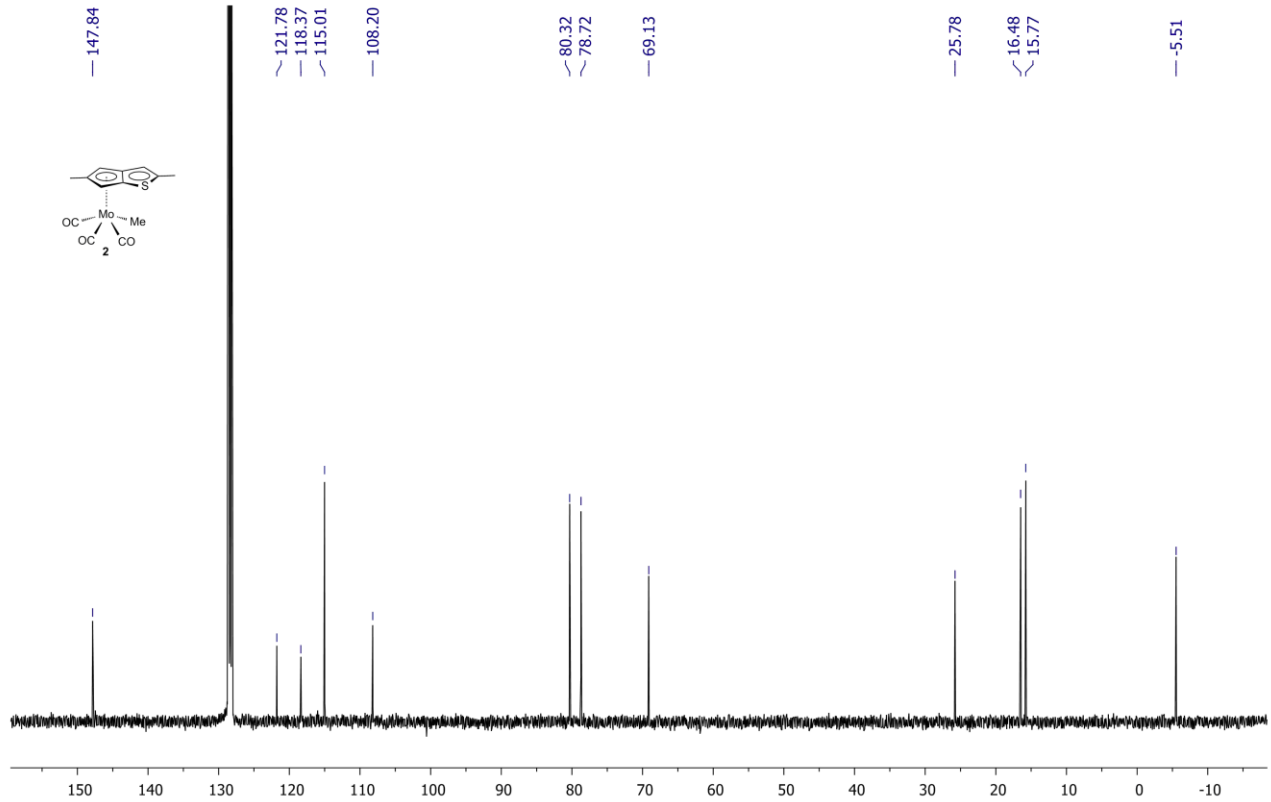

Figure S4. ^{13}C NMR spectrum (C_6D_6, 25 °C, 101 MHz) of the complex **2**

S2. X-ray single crystal diffraction data

S2.1. Crystal data, data collection and structure refinement details

Experimental intensities of single crystal reflections were measured on a *Bruker SMART APEX II* platform, using graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å) and ω-scan mode at 150 K. Data were integrated with the *SAINT* program.[6] Absorption corrections based on measurements of equivalent reflections were carried out by *SADABS* (multi-scan methods).[1] The structures were solved by direct methods with the *SHELXS* program[7] refined by full matrix least-squares on F^2 with *SHELXL2017*/1.[8]

Crystal data, data collection and structure refinement details are summarized in Table S1. All non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were found from an electron difference-density map difference maps but were positioned geometrically (C-H distance is 0.950 Å for aromatic, 0.980 Å for methyl, and 1.000 Å for Cp hydrogen atoms) and refined as riding atoms with relative isotropic displacement parameters [U_{iso}(H)=1.5U_{eq}(C) for methyl and 1.2U_{eq}(C) for aromatic H atoms]. A rotating group model was applied for methyl groups. The reflections 101 for compound **1** and 001 for **2** were omitted from the refinement as they were affected by the beam stop. The *SHELXTL* program suite[9] was used for molecular graphics.

The S1/C6-H6 and S2/C19-H19 atoms are disordered in the 2,5-dimethyl-4*H*-cyclopenta[*b*]thienyl ligand of both crystallographically independent molecules of **2** (see section S2.3 and Figure S below). The sets of S-C and C-C bond distances were refined to be equal within estimated standard deviations of 0.01Å bond lengths. Similarity restraints on thermal ellipsoids of the disordered atoms were also applied. The further modeling the ligand disorder by using a number of a set of positional and bond-parameter restraints did not improve the crystallographic model of **2** since eight highest residual electron density peaks are located at two Mo atoms but not near the ligands.

The structures have been deposited at the Cambridge Crystallographic Data Center with the reference CCDC numbers 1833971 and 1833970 (Table S1). These data can be obtained free of charge from the CCDC *via* http://www.ccdc.cam.ac.uk/data_request/cif.

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Table S1. Experimental details

Complex	**1**	**2**
Molecular formula	$C_{27}H_{20}MoO_3$	$C_{13}H_{12}MoO_3S$
M_r	488.37	344.23
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	11.7825 (6)	7.9519 (8)
b (Å)	7.1720 (3)	10.8202 (11)
c (Å)	26.9399 (13)	16.6515 (17)
α (°)	90	107.765 (1)
β (°)	101.8255 (7)	92.593 (2)
γ (°)	90	91.198 (2)
V (Å^3)	2228.21 (18)	1362.1 (2)
Z	4	4
d_{calc} (g cm^{-3})	1.456	1.679
μ (mm^{-1})	0.61	1.11
F(000)	992	688
Θ_{min} to Θ_{max} (°)	2.61 to 30.52	1.98 to 29.00
Reflections measured (R_{int})	26784 (0.020)	14771 (0.022)
Independent reflections	6819	7167
Observed [$I > 2\sigma(I)$] reflections	6242	5623
No. of parameters	281	345
No. of restraints	0	24
R1 [$F^2 > 2\sigma(F^2)$]	0.027	0.033
wR2 [F^2]	0.065	0.083
GoF	1.10	1.05
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.86, −0.62	1.40, −0.69
CCDC number	1833971	1833970

S2.2. The structure of (1,2,4-$Ph_3C_5H_2$)Mo(Me)$(CO)_3$

The asymmetric unit contains one molecule of the complex (1,2,4-$Ph_3C_5H_2$)Mo(Me)$(CO)_3$ (Table S1). CN_{Mo}=7. Bond distances and selected angles are presented in Table S2. The C_{Cp}-C_{Cp} averaged bond distance is 1.430Å. Rotation angles between Cp and Ph planes are 35.03(8)° for Ph=C10..C15, 51.55(6)° for C16..C21, and 15.08(8)° for C22..C27. The $C_{ipso(Ph)}$ atom deviations are 0.094(3)Å for C10, 0.146(3)Å for C16, and 0.068(3)Å for C22.

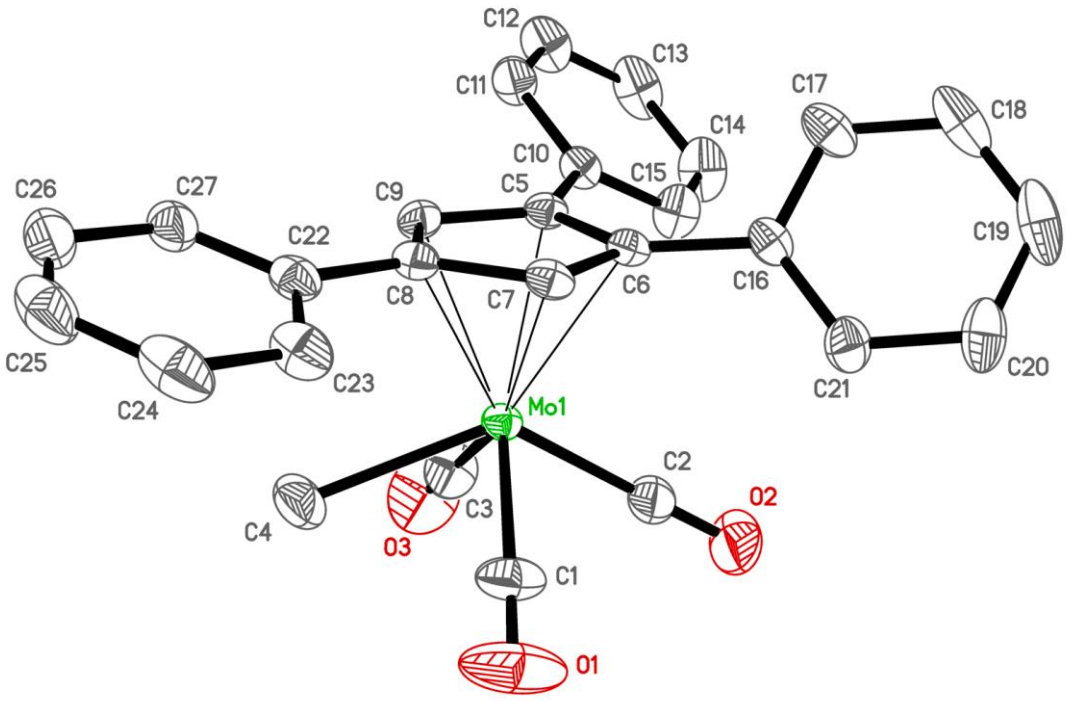

Figure S5. Molecular structure of (1,2,4-$Ph_3C_5H_2$)Mo(Me)$(CO)_3$, (**1**). Thermal ellipsoids are set to 50% probability level. H atoms are omitted.

Table S2. Selected geometric parameters (Å, º) for (1,2,4-$Ph_3C_5H_2$)Mo(Me)$(CO)_3$, (**1**)

Mo1—C1	1.9785 (18)	C8—C22	1.474 (2)
Mo1—C3	1.9811 (18)	C10—C11	1.394 (2)
Mo1—C2	1.9842 (18)	C10—C15	1.392 (2)
Mo1—C4	2.3119 (18)	C11—C12	1.394 (2)
Mo1—C5	2.3518 (14)	C12—C13	1.373 (3)
Mo1—C6	2.3660 (14)	C13—C14	1.387 (3)
Mo1—C7	2.3658 (14)	C14—C15	1.389 (2)
Mo1—C8	2.3696 (15)	C16—C21	1.391 (2)
Mo1—C9	2.3267 (15)	C16—C17	1.393 (2)
O1—C1	1.133 (2)	C17—C18	1.393 (3)
O2—C2	1.147 (2)	C18—C19	1.376 (3)
O3—C3	1.142 (2)	C19—C20	1.381 (3)
C5—C6	1.4380 (19)	C20—C21	1.390 (2)
C5—C9	1.429 (2)	C22—C27	1.390 (2)
C5—C10	1.4827 (19)	C22—C23	1.398 (2)
C6—C7	1.423 (2)	C23—C24	1.392 (3)
C6—C16	1.485 (2)	C24—C25	1.377 (3)
C7—C8	1.422 (2)	C25—C26	1.380 (3)
C8—C9	1.438 (2)	C26—C27	1.399 (2)
C1—Mo1—C2	80.19(9)	C1—Mo1—C4	73.07(9)
C2—Mo1—C3	77.59(8)	O1—C1—Mo1	173.61 (18)
C3—Mo1—C4	71.75(8)	O2—C2—Mo1	179.40 (18)
C1—Mo1—C3	108.80(8)	O3—C3—Mo1	178.9 (2)

S2.3. The structure of (2,5-$Me_3C_7H_3S$)Mo(Me)$(CO)_3$

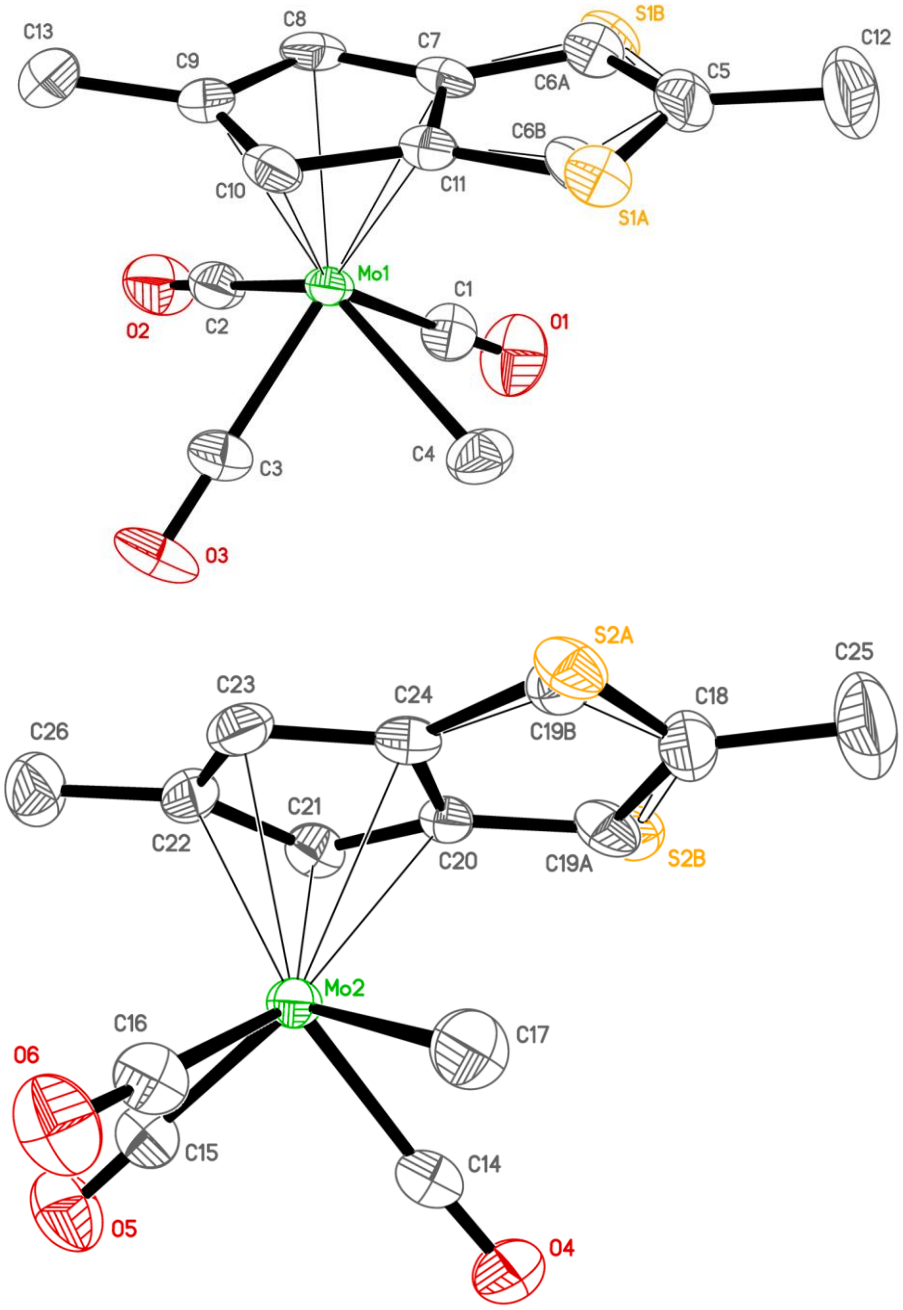

Figure S6. Two crystallographically independent molecules (top and bottom) in the crystal structure of (2,5-$Me_3C_7H_3S$)Mo(CH_3)$(CO)_3$, (**2**). The 2,5-$Me_3C_7H_3S$ ligand in each molecule is disordered over two positions (atoms S1, C6, left and S2, C19, right). The second components of the disorder are shown with open solid lines. Thermal ellipsoids are set to 50% probability level. H atoms are omitted.

The asymmetric unit consists of two independent molecules (2,5-$Me_3C_7H_3S$)Mo(Me)$(CO)_3$ (Figure S). The CH fragment and the S atom are nearly equally disordered over two positions in 2,5-$Me_3C_7H_3S$ ligand of each molecule with the S1A,C6A,H6A/S1B,C6B,H6B and S2A,C19A,H19A/S2B,C19B,H19B disorder ratios being of 0.528(3)/0.472(3) and 0.517(3)/0.483(3), correspondingly. Bond distances and selected angles are presented in Table S3. The averaged C_{Cp}-C_{Cp} bond lengths are 1.423Å for C7..C11 and 1.423Å for C20..C24. Folding angles between 5-membered rings are 5.7(4)° (C7-C8-C9-C10-C11 and C7-C6A-C5-S1A-C11

planes) [5.4(4)° for C7-C8-C9-C10-C11 and C7-S1B-C5-C6B-C11], 4.6(3)° (C20-C21-C22-C23-C24 and C20-C24-S2A-C18-C19A) [4.8(4)° for C20-C21-C22-C23-C24 and C20-C24-19B-C18-S2B]. Values of $C_{(Me)}$ atom deviations from the 5-membered rings are 0.189(6)Å for C13 and the C7-C8-C9-C10-C11 plane, 0.014(9)Å for C12 and C7-C6A-C5-S1A-C11 [0.03(1)Å for C12 and C7-S1B-C5-C6B-C11], 0.189(5)Å for C26 and C20-C21-C22-C23-C24, 0.010(9)Å for C25 and C20-C24-S2A-C18-C19A [0.055(9)Å for C25 and C20-C24-19B-C18-S2B].

Table S3. Selected geometric parameters (Å, º) for $(2,5\text{-}Me_3C_7H_3S)Mo(Me)(CO)_3$.

Mo1—C1	1.986 (3)	Mo2—C14	1.989 (3)
Mo1—C2	1.981 (3)	Mo2—C15	1.980 (3)
Mo1—C3	1.977 (3)	Mo2—C16	1.981 (3)
Mo1—C4	2.328 (3)	Mo2—C17	2.302 (3)
Mo1—C7	2.391 (3)	Mo2—C20	2.377 (3)
Mo1—C8	2.311 (3)	Mo2—C21	2.306 (3)
Mo1—C9	2.310 (3)	Mo2—C22	2.314 (3)
Mo1—C10	2.342 (3)	Mo2—C23	2.365 (3)
Mo1—C11	2.430 (3)	Mo2—C24	2.434 (3)
O1—C1	1.136 (4)	O4—C14	1.138 (4)
O2—C2	1.141 (4)	O5—C15	1.148 (4)
O3—C3	1.136 (4)	O6—C16	1.143 (4)
S1A—C5	1.603 (4)	S2A—C18	1.628 (4)
S1A—C11	1.734 (3)	S2A—C24	1.705 (3)
C6A—C5	1.477 (10)	C19A—C20	1.456 (8)
C6A—C7	1.480 (8)	C19A—C18	1.474 (9)
S1B—C5	1.600 (4)	S2B—C18	1.599 (4)
S1B—C7	1.702 (3)	S2B—C20	1.746 (3)
C6B—C11	1.456 (8)	C19B—C24	1.475 (8)
C6B—C5	1.482 (10)	C19B—C18	1.482 (10)
C5—C12	1.508 (5)	C18—C25	1.503 (5)
C7—C8	1.424 (4)	C20—C21	1.423 (4)
C7—C11	1.423 (4)	C20—C24	1.425 (4)
C8—C9	1.428 (4)	C21—C22	1.435 (4)
C9—C10	1.424 (4)	C22—C23	1.415 (4)
C9—C13	1.504 (5)	C22—C26	1.502 (4)
C10—C11	1.424 (4)	C23—C24	1.418 (4)
C1—Mo1—C2	77.94(14)	C14—Mo2—C15	79.75(13)
C2—Mo1—C3	79.21(13)	C15—Mo2—C16	78.29(12)
C1—Mo1—C3	104.53(14)	C14—Mo2—C16	106.34(13)
C3—Mo1—C4	72.02(13)	C16—Mo2—C17	72.00(13)
C1—Mo1—C4	72.99(13)	C14—Mo2—C17	72.98(14)
O1—C1—Mo1	178.3 (3)	O4—C14—Mo2	176.9(3)
O2—C2—Mo1	179.7 (3)	O5—C15—Mo2	179.1(3)
O3—C3—Mo1	179.1 (3)	O6—C16—Mo2	178.7(3)

S3. Catalytic experiments

The epoxidation tests were conducted using 1-octene (40 g) and Bu^tOH/nonane/Bu^tOOH (18:2.9:0.9:1 molar ratio) reaction mixture master batch charged into a glass flask equipped with a reflux condenser and an internal thermocouple. The reaction temperature was brought to 80 °C and maintained at that temperature using a water bath. The reaction was started by addition of 0.01 mmol of the complex sample.

The progress of epoxidation reaction was monitored by analyzing samples of the reaction mixture by iodometric titration for active peroxide content and gas chromatography for composition.