Aryl-substituted organomolybdenum (II) complexes for the catalytic epoxidation of olefins

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Supporting Information

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S1. Computational results

Table S1 Summary of computational results.

	Compounds	
	1	**2**
Mulliken charge on Mo	2.583	2.718
HOMO-LUMO-gap [eV]	3.9701	4.1802
Sum of electronic and thermal Enthalpies [eV]	-23743.8	-37246.2
Sum of electronic and thermal Free Energies [eV]	-23745.7	-37248.4

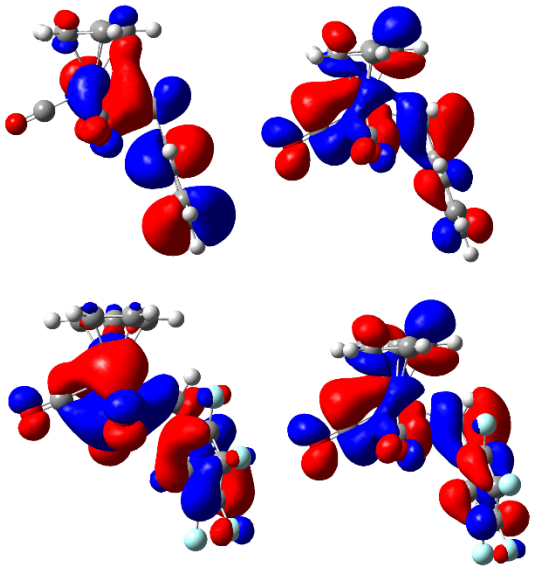

Figure S1 Comparison of the HOMOs (left) and LUMOs (right) of the compounds [CpMo(CO)$_3$R] with R = Bz (**1**) (above), BzF (**2**) (below) in gas phase (B3LYP/6-31+G**(d,p) level of theory).

S1.1 Calculated coordinates for [CpMo(CO)$_3$Bz] (1)

C	-3.32830310	-0.61772787	-0.44940582
H	-3.87316639	-1.32223187	0.16393809
C	-3.29337484	0.80379367	-0.27100760
C	-2.55982414	-0.93452751	-1.60734317
H	-3.80837309	1.36086774	0.49953775
C	-2.50104095	1.35790345	-1.31903640
H	-2.40723350	-1.92221784	-2.02100033
C	-2.05547511	0.28429409	-2.14116870
H	-2.29766726	2.40823795	-1.47809835
H	-1.43037761	0.37806069	-3.01869193
O	0.46531881	2.43368564	1.30281052
O	-1.72857854	-0.43720551	3.14302039
O	0.42756025	-2.72575959	0.57217745
C	-0.08917305	-1.70174290	0.40946113
C	-1.48502235	-0.28240689	2.02095400
C	-0.06418230	1.50241619	0.86201360
Mo	-1.09902111	-0.01263063	0.07874939
C	0.91073071	0.15388922	-1.28061737
H	0.72694515	-0.65487938	-1.98902554
H	0.72298973	1.11062314	-1.76951685
C	2.30016265	0.09273520	-0.74962499
C	2.99760578	-1.12877619	-0.66276828
C	2.99250149	1.26306650	-0.37979893
C	4.31487179	-1.18121094	-0.20594553
H	2.50395117	-2.04848191	-0.96206241
C	4.30996607	1.21314147	0.07671025
H	2.49427211	2.22495048	-0.45610613
C	4.97853656	-0.01062289	0.17235049
H	4.82495296	-2.13904184	-0.15067862
H	4.81617202	2.13378279	0.35396793
H	6.00414196	-0.05029554	0.52755905

Sum of electronic and thermal Enthalpies = -872.6 Hartree (-23743.8 eV)

Sum of electronic and thermal Free Energies = -872.6 Hartree (-23745.7 eV)

S1.2 Calculated coordinates for $[CpMo(CO)_3BzF_5]$ (2)

C	4.19444272	-0.33279115	-0.16316270
H	4.92167152	0.33225991	0.28249353
C	3.61634100	-1.48615009	0.45930773
C	3.68581592	-0.24266085	-1.49078695
H	3.83748258	-1.85049295	1.45302214
C	2.73776664	-2.09714293	-0.48527683
H	3.94401159	0.51025531	-2.22317287
C	2.79181929	-1.32841922	-1.68622699
H	2.16428402	-3.00148399	-0.33379132
H	2.24436085	-1.53457372	-2.59575516
O	-0.28851517	-1.01826234	2.12885260
O	2.60183766	1.67264155	2.70600957
O	1.31872523	3.01131126	-0.87846148
C	1.45412991	1.93015115	-0.49444071
C	2.32455471	1.08569233	1.74817176
C	0.47240603	-0.59884977	1.36453543
Mo	1.86919830	0.05242664	0.09367594
C	-0.07530098	-0.14846801	-1.31742886
H	0.04888421	0.59292370	-2.10517149
H	0.11289116	-1.13937073	-1.72384415
C	-1.46179267	-0.10395708	-0.78699147
C	-2.18675211	1.08721409	-0.64554984
C	-2.15182114	-1.27008109	-0.42590855
C	-3.49436830	1.12785175	-0.17221873
C	-3.45853258	-1.26542914	0.04995933
C	-4.13726114	-0.05656227	0.18131009
F	-1.60626992	2.25625944	-0.98863181
F	-4.14193081	2.29872112	-0.05980183
F	-5.39732113	-0.03289021	0.64025773
F	-4.06825700	-2.41531875	0.38026045
F	-1.53121893	-2.46669899	-0.54443253

Sum of electronic and thermal Enthalpies = -1368.8 Hartree (-37246.2 eV)

Sum of electronic and thermal Free Energies = -1368.9 Hartree (-37248.4 eV)

S2. X-Ray single crystallography

Data were collected on an X-ray single crystal diffractometer equipped with a CCD detector (APEX II, κ-CCD), a fine-focused sealed tube with MoK$\square$ radiation (λ = 0.71073 Å) and a graphite monochromator, by using the APEX2 software package. [1] The measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on the top of a glass fiber and transferred to the diffractometer. Crystals were frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT. [2] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS. [2] Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps [3], and were refined against all data using the APEX 2 software [1] in conjunction with SHELXL-97 [5] and SHELXLE [6]. Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{iso(H)} = 1.5 \cdot U_{eq(C)}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 and 0.95 Å, respectively, and $U_{iso(H)} = 1.2 \cdot U_{eq(C)}$. If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ with SHELXL-97 [5] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*. [4] Images of the crystal structures were generated by PLATON. [7]

References:

[1] APEX suite of crystallographic software. APEX 2 Version 2008.4. Bruker AXS Inc., Madison, Wisconsin, USA (2008).

[2] SAINT, Version 7.56a and SADABS Version 2008/1. Bruker AXS Inc., Madison, Wisconsin, USA (2008).

[3] Sheldrick, G. M. "**SHELXS-97**", Program for Crystal Structure Solution, Göttingen, (1997).

[4] International Tables for Crystallography, Vol. C, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199), Wilson, A. J. C., Ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992.

[5] Sheldrick, G. M. "**SHELXL-97**", University of Göttingen, Göttingen, Germany, (1997).

[6] Huebschle, C. B., Sheldrick, G. M. & Dittrich, B. "**SHELXLE**", *J. Appl. Cryst.* **2011**, *44*, 1281- 1284.

[7] Spek, A. L. "**PLATON**", A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, (2010).

Table S2. Crystallographic data for compounds **1** and **2.**

	1	**2**
CCDC	1055255	1055256
formula	$C_{15}H_{12}MoO_3$	$C_{15}H_7F_5MoO_3$
fw	336.19	426.15
colour/habit	yellow fragment	yellow fragment
cryst dimensions (mm^3)	0.07x0.13x0.17	0.09x0.14x0.36
cryst syst	orthorhombic	monoclinic
spacegroup	*P b c a*	*P* $2_1/n$ (No. 14);
a, Å	16.6109(4)	8.1106(2)
b, Å	8.7885(2)	14.7261(4)
c, Å	17.8015	12.4891(3)
α, deg	90	90
β, deg	90	100.409(1)
γ, deg	90	90
V, $Å^3$	2598.75(11)	1467.12(6)
Z	8	4
T, K	123	123
D_{calcd}, g cm^{-3}	1.719	1.929
μ, mm^{-1}	1.009	0.963
F(000)	1344.0	832.0
θ range, deg	2.29–25.35	2.77–25.38
Index ranges (*h*, *k*, *l*)	±20, ±10, ±21	±9, ±17, ±15
no. of rflns collected	74161	39156
no. of indep rflns/R_{int}	2382/0.0368	2689/0.0218
no. of obsd rflns ($I>2\sigma(I)$)	2194/2382/0.0368	2466/2689/0.0218
no. of data/restraints/params	2382/0/220	2689/0/217
R1/wR2 ($I>2\sigma(I)$)[a]	0.0213/0.0237	0.0153/0.0179
R1/wR2 (all data)[a]	0.0559/0.0581	0.0358/0.0369
GOF (on F^2)[a]	1.051	1.083
Largest diff peak and hole (e $Å^{-3}$)	1.59/-0.39	0.27/-0.25

[a] $R1 = \sum(||F_o|-|F_c||)/\sum|F_o|$; $wR2 = \{\sum [w(F_o^2-F_c^2)^2]/ \sum[w(F_o^2)^2]\}^{1/2}$; $GOF = \{\sum[w(F_o^2-F_c^2)^2]/(n-p)^{1/2}$