Influence of structural and electronic properties of organomolybdenum(II) compounds of the type $[CpMo(CO)_3R]$ and $[CpMo(O_2)(O)R]$ ($R = Cl, CH_3, CF_3$) on the catalytic oxidation of olefins

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Supporting Information

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S1. 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_α 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 S.1. Crystallographic data for compounds **3** and **6.**

	3	**6**
CCDC	1030682	1030683
formula	$C_9H_5F_3MoO_3$	$C_6H_5F_3MoO_3$
fw	314.07	278.04
colour/habit	clearlight yellow needle	Intense yellow fragment
Cryst dimensions (mm^3)	0.07 × 0.11 × 0.55	0.08× 0.09× 0.34
crystsyst	triclinic	monoclinic
spacegroup	*P 1*	*C 2/c*
a, Å	6.4530(2)	20.5911(3)
b, Å	6.5440(2)	6.9325(1)
c, Å	6.7851(2)	12.3919(2)
α, deg	107.752(1)	90
β, deg	97.132(1)	117.372(1)
γ, deg	107.192(1)	90
V, $Å^3$	253.356(14)	1570.87(4)
Z	1	8
T, K	123(2)	123(2)
D_{calcd}, g cm^{-3}	2.059	2.351
μ, mm^{-1}	1.326	1.693
F(000)	152	1072
θ range, deg	3.24 – 25.37	2.2 – 25.4
Index ranges (*h*, *k*, *l*)	±7, ±7, 0–8	±24, ±8,±14
no. of rflns collected	910	8754
no. of indep rflns/R_{int}	910/0.0224	1447/0.0318
no. of obsd rflns ($I>2\sigma(I)$)	905	1266
no. of data/restraints/params	910/3/145	1447/0/118
R1/wR2 ($I>2\sigma(I)$)[a]	0.0147/0.0381	0.0194/0.0431
R1/wR2 (all data)[a]	0.0147/0.0381	0.0247/0.0448
GOF (on F^2)[a]	1.111	1.043
Largest diff peak and hole (e $Å^{-3}$)	+0.468/-0.289	+0.595/-0.301

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

S2. Computational results - Visualization, coordinates and energies

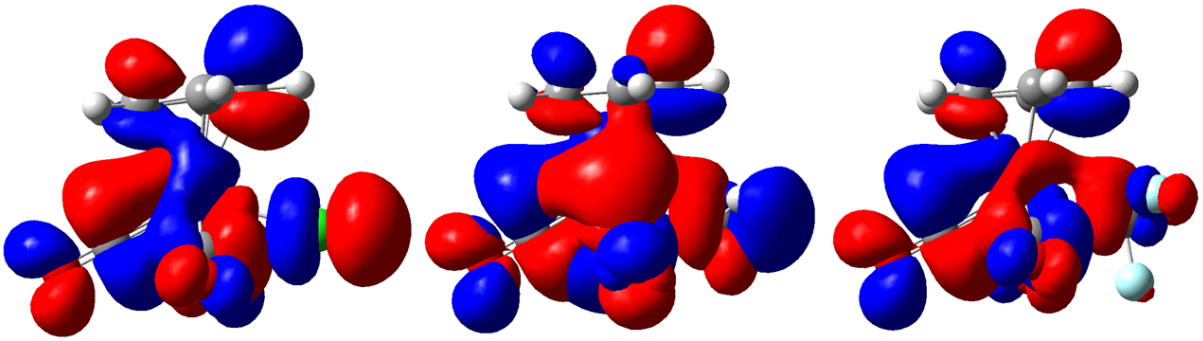

Figure S2.1.LUMOs of the compounds [CpMo(CO)$_3$R] with R = Cl (**1**), CH_3 (**2**) and CF_3 (**3**) (from left to right) in gas phase (B3LYP/6-31+G**(d,p) level of theory.

Table S2.1. Summary of computational results

	compounds		
	1	**2**	**3**
Mulliken charge on Mo	1.025	1.702	1.891
HOMO-LUMO-gap [eV]	3.6635	4.4782	4.3740
Sum of electronic and thermal Enthalpies [eV]	-28897.4	-17458.7	-25561.2
Sum of electronic and thermal Free Energies [eV]	-28898.9	-17460.2	-25562.9
Mo-Ligand-Polarity	0.789	1.616	1.771

S2.2 Calculated coordinates for [CpMo(CO)$_3$Cl] (1)

C	-1.98799900	1.05031000	0.71919000
H	-1.98508600	1.92502200	1.35501300
C	-1.98771000	1.05159400	-0.71694400
C	-2.06754900	-0.30715800	1.15686900
H	-1.98474000	1.92741900	-1.35122900
C	-2.06703400	-0.30513400	-1.15698800
H	-2.10110700	-0.65004000	2.18174600
C	-2.12405500	-1.13024100	-0.00077400
H	-2.09986800	-0.64629600	-2.18246100
H	-2.13743400	-2.21087100	-0.00172400
O	1.77326100	-0.05259700	-2.63421800
O	1.25133800	2.97414800	0.00328700
O	1.77463300	-0.06037000	2.63328300
C	1.16564500	-0.01750400	1.65715000
C	0.79357700	1.91196600	0.00223500
C	1.16480900	-0.01283900	-1.65759400
Mo	0.00132100	0.06871700	0.00014700
Cl	0.85416300	-2.32745600	-0.00266000

S2.3 Calculated coordinates for $[CpMo(CO)_3CH_3]$ (2)

C	-1.82019783	-0.71713523	1.25051445
H	-1.68775007	-1.35336194	2.11480344
C	-1.82030749	0.71630747	1.25077626
C	-2.07475634	-1.15596256	-0.08195241
H	-1.68796713	1.35224152	2.11529403
C	-2.07494141	1.15560462	-0.08152904
H	-2.15552611	-2.18289472	-0.41142726
C	-2.23331364	-0.00003801	-0.89774864
H	-2.15579313	2.18265678	-0.41061061
H	-2.43308789	0.00014462	-1.96024613
O	1.76516347	2.55224243	-0.68997555
O	1.89313294	0.00001597	2.52688384
O	1.76620962	-2.55153250	-0.69039205
C	1.16093503	-1.59677189	-0.43760916
C	1.21573630	-0.00000203	1.58706085
C	1.16031965	1.59716295	-0.43734229
Mo	0.03279605	-0.00003560	-0.03279794
C	0.45995179	0.00019976	-2.33987667
H	-0.00689862	-0.89233949	-2.76219103
H	-0.00705368	0.89273007	-2.76204857
H	1.52003777	0.00032076	-2.59195059

S2.4 Calculated coordinates for $[CpMo(CO)_3CF_3]$ (3)

C	2.10216800	-1.37084900	-0.71527100
H	2.90086600	-1.01419600	-1.35121600
C	2.10117500	-1.36991600	0.72018900
C	0.88852200	-1.97754700	-1.15390000
H	2.89906300	-1.01259500	1.35677400
C	0.88686900	-1.97602300	1.15786000
H	0.58835200	-2.14202300	-2.17967100
C	0.14523900	-2.35034700	0.00168700
H	0.58508000	-2.13921900	2.18336400
H	-0.82615200	-2.82405600	0.00131900
O	-0.47600200	1.58099100	2.64711600
O	2.36994600	2.52566200	-0.00217300
O	-0.47411800	1.57210200	-2.65203800
C	-0.19743600	1.04759300	-1.66325000
C	1.64175200	1.62863600	-0.00125700
C	-0.19889300	1.05292500	1.66036400
Mo	0.37604900	0.05731300	0.00023700
C	-1.89849100	-0.13691100	-0.00011400
F	-2.36409900	-0.84309200	1.08911800
F	-2.36384100	-0.84526800	-1.08793700
F	-2.61931600	1.02275400	-0.00136000

S3. Experimental and calculated fundamental frequencies and force constants

Table S3.1. Experimental and calculated fundamental frequencies for $[CpMo(CO)_3CH_3]$ and $[CpMo(CO)_3CD_3]$.

	$[CpMo(CO)_3CH_3]$		$[CpMo(CO)_3CD_3]$		Potential Energy Distribution[d]	Description
	Exper.	Calcd.	Exper.	Calcd.	(%)	of mode
A'$_1$	2012[a]	2010	2010	2004	83 ν_sCO + 10 ν_sMoC	CO sym. stretching
2	1903	1890	1900	1890	81ν_aCO + 11 ν_aMoC	CO asym. stretching
3	598	592	602	592	55 β_sMoCO + 25 β_aMoCO[c] + 8 δ_sCMoC	MoCO bending
4	562	562	562	562	61 β_aMoCO + 21 β_sMoCO + ν_sMoC	MoCO bending
5	502	503	498	503	47 ν_sMoC +14 γ_aMoCO + 13 ν_aMoC	MoC stretching
6	485	484	489	484	48 γ_aMoCO + 15 ν_sMoC + 10 νMoCp	MoCO bending
7	452	450	450	447	53 ν_aMoC + 22 γ_aMoCO + 12 νMoCp	MoC stretching
8	406	408	392	388	70 νMo-Me + 17 ν_aMoC+ 9 ν_sMoC	Mo-Me stretching
9	335	335	333	333	83 νMoCp + 10 ν_sMoC +5 νMo-Me	Mo-Cp stretching
10	131[b]	145	130	139	61 δ_sCpMoMe + 13 δCMoCp + 10 βMoCO	CpMoMe deformation
11	107	110	104	108	43 $\delta_s MoC_3$ + 32 δCMoCp	MoC_3 sym. deformation
12	90	99	90	99	41 δ_aCMoC + 32 δ_aCMoCp + 16 δCpMoMe	CMoC deformation
13	~60	66	~60	66	57 δCMoCp + 26 δCpMoMe	CMoCp deformation
A''$_{14}$	1920	1911	1907	1900	92 ν_aCO + 8 ν_aMoC	CO asym. stretching
15	562	560	562	560	87 β_aMoCO + 6 δ_aCMoCp	MoCO deformation
16	502	508	498	508	72 ν_aMoC + 11 γ_aMoCO + 6 ν_aCO	MoC stretching
17	465	463	470	463	61 γ_aMoCO + 19 δ_aCMoC + 9 δ_sMoCO	MoCO deformation
18	438	432	429	432	85 γ_aMoCO + 5 ν_aCO + 4 δ_aCMoC	MoCO deformation
19	130	144	130	136	δ_aCMoMe + 43 δ_aCMoC	CMoMe deformation
20	-	120	~120	120	91 δCMoCp + 5 β_aMoCO	CMoCp deformation
21	107	104	90	104	76 δ_aCMoC + 21 γ_aMoCO	CMoC deformation

[a]Averaged IR and Raman frequencies were used as fundamentals when the wavenumbers were slightly different or split due to the solid-state effects.
[b]Experimental frequencies below 150 cm^{-1} were assigned on the basis of normal coordinate calculations.
[c] The β(MoCO) are the linear bendings of Mo-C-O groups in the plane of CMoCp, the notation of γ(MoCO) requests the linear bendings perpendicular to the plane of CMoCp.
[d]Potential Energy Distributions (PED) were taken from the result of $[CpMo(CO)_3CH_3]$ calculations.

Table S3.2. Calculated force constants for [$CpMo(CO)_3CH_3$] and [$CpMo(CO)_3CD_3$].

Force constants	Groups involved and descriptions	Numerical values of force constants	Units
K_1(C'O)	C'O opposite to CH_3/CD_3	13.969	a
K_2(CO)	CO close to CH_3/CD_3	14.396	a
F_s(CO,CO)	Interaction between CO, CO groups	0.555	a
F_l(C'O,CO)	Interaction between C'O,CO groups	0.278	a
K(MoC)	Mo-CO	3.108	a
F(MoC,MoC)	Mo-CO	0.011	a
K(Mo-Me)	Mo-CH_3, Mo-CD_3	1.527	a
K(Mo-Cp)	Mo-Cp	3.110	a
H(MoCO)	MoCO linear bending (in plane)	0.865	b
h(MoCO,MoCO)	MoCO , MoCO interaction	0.008	b
H'(MoCO)	MoCO linear bending (out of plane)	0.534	b
h'(MoCO,MoCO)	MoCO, MoCO interaction	0	b
H(CMoMe)	skeletal bending	(0.55)[c]	b
H(CMoC)	skeletal bending	(0.62)	b
H(CMoCp)	skeletal bending	(0.48)	b
H(CpMoMe)	skeletal bending	(0.50)	b
F(MoMe,MoC')	stretch-stretch interaction	(0.10)	a
F(MoMe,MoC)	stretch-stretch interaction	(0.05)	a

Units of force constants are:
a, 10^2 N m^{-1};
b, 10^{-18} N m rad^{-2};
c, The constrained values are listed in brackets.

Table S 3.3 IR and Raman frequencies assigned to the spectroscopic modes of vibration for the complexes **1** – **3** and **2a** [$CpMo(CO)_3CD_3$].

1		**2**		**2a**		**3**		
IR	**Raman**	**IR**	**Raman**	**IR**	**Raman**	**IR**	**Raman**	**Assignment**
3123m	3127m	3113m	3123m	3113m	3123m	3126m	1303m	ν_s(CH), Cp
3118m								ν_a(CH), Cp
3103m	3111w		3100w		3102w		3108w	ν_a(CH), Cp
		2981m	2982m	2233m	2236m			$\nu_a(CH_3/CD_3)$
		2902m	2905m	2116m	2114m			$\nu_s(CH_3/CD_3)$
		2020w,sh	2019m	2018w,sh	2018m			ν_s(C≡O)
						2060w,sh	2056m	ν_s(C≡O)
2040vs	2041vs	2006s	2003s	2004s	2002s	2048s	2042s	ν_s(C≡O)
	1974w			1948w,sh	1945w,sh	1980w,sh	1977s	ν_a(C≡O)
1969vs	1960s	1920m,sh	1921s,sh	1920m,sh	1920s,sh	1963s	1962vs	ν_a(C≡O)
	1949vs							ν_a(C≡O)
1932vs	1930m	1903vs	1900vs	1901vs	1889vs	1934vs	1932s	ν_a(C≡O)
1924s,sh						1916m,sh		ν_a(C≡O)
1421m	1422vw	1423m	1425m	1423m	1421m,b	1430m	1427m	ν_a(CC), Cp
		1423m	1420m	1062m	1061m			$\delta_a(CH_3/CD_3)$
1354w	1355vw	1354w	1352w	1353w	1352w		1356w	ν_a(CC), Cp
		1161m	883m	881s				$\delta_s(CH_3/CD_3)$
1110vw	1109s	1109vw	1107s	1109vw	1107s	1113vw	1109s	ν_s(CC), Cp
1064m	1061m	1060m	1061m	1062m	1061m		1069m	β(CH), Cp
						1050s	1057m	$\nu_a(CF_3)$
						1043s		$\nu_a(CF_3)$
1014m		1011m	1011vw	1012m	1009vw	1012s		β(CH), Cp
1005m	1007vw				1003vw	1004s	1005vw	β(CH), Cp
						982s	978vw	$\nu_s(CF_3)$
822s	816vw	825s	822vw	822s	821vw	831m	827m	γ(CH), Cp
						695m	692m	$\rho_s(CF_3)$
		613w	608vw	488vs				$\rho(CH_3/CD_3)$
				475s	475s			$\rho(CH_3/CD_3)$
601w	~600vw	613w	608vw	614w,sh		613w		δ_s(MoCO)
561s	560vw	587s	584vw	597s	596w	573s	571w	δ_s(MoCO)
524s	~520vw	562vs	562m	561vs	563vw	546vs	544w	β_a(MoCO)
		755w	758vw	548s,sh	549vw			$\rho(CH_3/CD_3)$
						525w	521w	$\delta_a(CF_3)$
						512w		$\delta_a(CF_3)$
471s	464w	502w,sh		498m,sh	498w,sh	479s	477w	ν_s(MoC)
471s	464w	489vs	482m	488vs	490w,sh	479s	477w	γ_a(MoCO)
		465w,sh		463w,sh	476ms	455ms	458ms	β_a(MoCO)
432w	428vw							β_a(MoCO)
432w	428vw	451s	453m	448s	451s	430vs	432m	ν_a(MoC)
415m	420vw	437m	438vs	429ms	429s	404m	402m	γ(MoCO)
		405w	408ms	392m	391m			ν(MoC), CH_3/CD_3
	383w,sh							ν_a(MoCp), tilt
	371m	355w	355s	353m	352vs	366w	361w,sh	ν_a(MoCp), tilt
361s[a]	350w,sh	335w	334vs	334w	333vs			ν_s(MoCp)
337vw[a]	338ms					352vw	350vs	ν_s(MoCp)
281vs[a]	278w							ν(MoCl)
						251s	249s	ν(MoC), CF_3
						234m	233m	$\rho(CF_3)$
			173s	125vw,sh	160s			$\tau(CH_3/CD_3)$
			160m		148m			$\tau(CH_3/CD_3)$
		130w,sh	133w		130w,sh	137w	137w,m	δ(CpMoR)
		107w		104w		119w	119w	δ_s(CMoC)
						106vw		δ_s(CMoC)
			90w,sh		90w,sh			δ_a(CMoC)
		60vw				60vw		δ(CMoCp)

a Far infrared data taken from ref. 25

b Notation of fundamental modes: ν – stretching; δ – bending or deformation; ρ – rocking; β – in plane, γ – out of plane deformation; τ – torsion; subscript 's' symmetric, subscript 'a' anti-symmetric.