Supporting Information

Kinetic Studies on the Oxidation of the Methyl Derivative of η⁵-Cyclopentadienyl Carbonyl Molybdenum and the use of its Oxidation Products as Olefin Epoxidation Catalysts

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1. Single Crystal X-Ray Structure Determination of Compound 3

Crystal data and details of the structure determination are presented in Table S1 and Figure S1. Suitable single crystals for the X-ray diffraction study were grown from diethyl ether. A clear yellow fragment was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on a kappa-CCD device (NONIUS MACH3) with an Oxford Cryosystems cooling device at the window of a rotating anode (NONIUS FR591) with graphite monochromated Mo-K $_{\alpha}$ radiation $(\lambda = 0.71073 \text{ Å})$. Data collection was performed at 173 K within the Θ range of $3.45^{\circ} < \Theta <$ 27.81°. A total of 5660 reflections were integrated, corrected for Lorentz polarization, and, arising from the scaling procedure, corrected for latent decay and absorption effects. After merging ($R_{int} = 0.019$), 1711 [1662: $I_0 > 2\sigma$ (I_0)] independent reflections remained and all were used to refine 94 parameters. The structure was solved by a combination of direct methods and difference-Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. Methyl hydrogen atoms were calculated as a part of rigid rotating groups, with $d_{C-H} = 0.98$ Å and $U_{iso(H)} = 1.5U_{eq(C)}$. Aromatic hydrogen atoms were placed in ideal positions and refined using a riding model with $d_{C-H} = of 0.95$ Å and $U_{iso(H)} = 1.2U_{eq(C)}$. Small extinction effects were corrected with the SHELXL-97 procedure [$\varepsilon = 0.013(2)$]. Fullmatrix least-squares refinements were carried out by minimizing $\Sigma w (F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and converged with $R1 = 0.0384 [I_0>2\sigma (I_0)]$, wR2 = 0.0989[all data], GOF = 1.094, and shift/error < 0.001. The final difference-Fourier map shows clearly a disorder, which could not be resolved and modeled without some remaining doubts. This fact is obvious, too, in the unusual high thermal displacement parameters and the positions of the two highest difference-Fourier peaks (Figure S2). As can be seen by Flack's Parameter $\varepsilon = 0.51(15)$ the crystal is twinned and the refinements were completed with the TWIN / BASF option. All calculations were performed with the WINGX system, including the programs DIAMOND, PLATON, SHELXL-97, and SIR92

References: (a) Data Collection Software for Nonius kappa-CCD devices, Delft (The Netherlands), **2001**. (b) Otwinowski, Z.; Minor, W. *Methods in Enzymology* **1997**, 276, 307ff. (c) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. SIR92, *J. Appl. Crystallogr.* **1994**, 27, 435. (d) *International Tables for Crystallography, Vol. C*, Tables 6.1.1.4, 4.2.6.8, and 4.2.4.2 (Ed.: Wilson, A. J. C.), Kluwer Academic Publishers, Dordrecht (The Netherlands), **1992**. (e) Spek, A. L. PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht (The Netherlands), **2007**. (f) Sheldrick, G. M. SHELXL-97, Universität Göttingen, Göttingen (Germany), **1998**. (g) Farrugia, L. J. WinGX (Version 1.70.01 January 2005), *J. Appl. Crystallogr.* **1999**, *32*, 837. (h) Brandenburg K. *DIAMOND, Version 3.1d*, Crystal Impact GbR, Bonn, Germany, 2006.



Figure S1. Ball and stick model of compound **3** in the solid state.

Figure S2 ORTEP style plot of compound **3** in the solid state showing the two highest difference-Fourier peaks Q1 (+1.23 e Å⁻³) and Q2 (+1.17 e Å⁻³)



| | 3 |
|--|--|
| formula | C ₆ H ₈ MoO ₃ |
| fw | 224.06 |
| color / habit | yellow / fragment |
| cryst dimensions (mm ³) | $0.10 \times 0.18 \times 0.46$ |
| cryst syst | Orthorhombic |
| space group | <i>P</i> 2 ₁ 2 ₁ 2 ₁ (no. 19) |
| <i>a</i> , Å | 6.5225(5) |
| b, Å | 7.9532(5) |
| <i>c</i> , Å | 13.9632(7) |
| $V, Å^3$ | 724.34(8) |
| Ζ | 4 |
| <i>Т</i> , К | 173 |
| $D_{\rm calcd}$, g cm ⁻³ | 2.055 |
| μ , mm ⁻¹ | 1.751 |
| F(000) | 440 |
| θ range, deg | 3.45 - 27.81 |
| Index ranges (h, k, l) | ±8, ±10, -10: 18 |
| no. of rflns collected | 5660 |
| no. of indep rflns / R _{int} | 1711/0.019 |
| no. of obsd rflns $(I > 2\sigma(I))$ | 1662 |
| no. of data/restraints/params | 1711/0/94 |
| $R1 / wR2 (I > 2\sigma(I))^{a}$ | 0.0384 / 0.0984 |
| R1 / wR2 (all data) ^a | 0.0391 / 0.0389 |
| GOF (on F^2) ^a | 1.094 |
| Largest diff peak and hole (e $Å^{-3}$) | +1.23 / -0.72 |

Table S1. Crystallographic Data for $[Mo(\eta^5-C_5H_5)O(O_2)CH_3]$ (3)

^aR1 = $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; wR2 = { $\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]$ }^{1/2}; GOF = { $\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)$ }^{1/2}

Appendix I: Derivation of Eq. 1

The absorbance at 335 nm (A_{335}) can be expressed as fellow:

$$A_{335} = A_p + A_I = [\mathbf{3}].\varepsilon_p + [I].\varepsilon_I \tag{1}$$

where A_p and A_I are the absorbance of **3** and the intermediate (I), and ε_p and ε_I are their extinction coefficients, respectively.

With the total mass balance expression, $[Mo]_T = [3] + [I]$, Eq. 1 can be written as fellow:

$$A_{335} = [\mathbf{3}](\varepsilon_{p} - \varepsilon_{I}) + [Mo]_{T} \cdot \varepsilon_{I}$$
⁽²⁾

Using the equilibrium expression:

$$K_{eq} = [I]/[TBHP][3] = ([Mo]_T - [3])/([TBHP][3])$$
(3)

and therefore,

$$[3] = [Mo]_{T}/(1 + K_{eq}[TBHP])$$
(3a)

Replacing [3] in Eq. 2 by using Eq. 3a

$$A_{335} = (\varepsilon_p - \varepsilon_I)[Mo]_T / (1 + K_{eq}[TBHP]) + [Mo]_T. \varepsilon_I$$
(4)

and

$$A_{335}/[Mo]_{T} = (\varepsilon_{p} - \varepsilon_{I})/(1 + K_{eq}[TBHP]) + \varepsilon_{I}$$
(5)

Appendix II: Derivation of Eq. 4

Based on Scheme 4, the rate of the alkene consumption is:

$$rate = \frac{-d[alkene]}{dt} = k_{ep}[alkene][I]$$
(1)

The change in the intermediate with time can be expressed:

$$\frac{d[I]}{dt} = k_p[\mathbf{3}][TBHP] - k_{-p}[I] - k_{ep}[alkene][I]$$
(2)

Using the total mass balance expression, $[Mo]_T = [3] + [I]$, Eq. 2 becomes:

$$\frac{d[I]}{dt} = k_p[TBHP](Mo]_T - [I]) - k_{-p}[I] - k_{ep}[alkene][I]$$
(3)

Applying steady-state approximation on [I], d[I]/dt = 0, leads to:

$$[I]_{ss} = \frac{k_p[TBHP](Mo]_T}{k_{-p} + k_p[TBHP] + k_{ep}[alkene]}$$
(4)

Replacing the value of [I] in Eq. 1 by [I]_{ss} above, the rate law equation becomes:

$$rate = \frac{-d[alkene]}{dt} = \frac{k_p k_{ep} [alkene] [TBHP] (Mo]_T}{k_{-p} + k_p [TBHP] + k_{ep} [alkene]}$$
(5)



Figure S1. A plot of the observed-first-order rate constant (k_{obs}) against [TBHP] for the reaction of **3** (0.3 mM) with TBHP in CH₂Cl₂ at 20 °C

Appendix III: Estimation of the relative values for the rate constant of the catalysis with

compound 2

In an experiment initially started with **1** (0.2 mM), TBHP (10 mM) and β -methoxystyrene (0.1 mM) the initial rate was 1.3 x 10⁻⁸ M/s. When initially started with **3** under the same conditions, the initial rate was 0.32 x10⁻⁸ M/s (see Figure 6 in the manuscript). From this ratio (1.3/0.32 = 4.1) the relative values of the rate constants for epoxidation with **2** compared with **3** were estimated.