

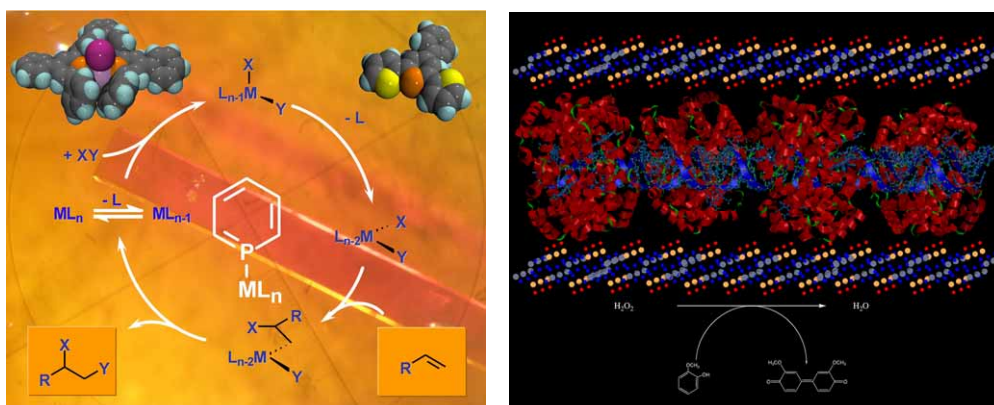
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Emerging Strategies in Catalysis

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Ansa-bridged η^5 -cyclopentadienyl molybdenum and tungsten complexes: synthesis, structure and application in olefin epoxidation†

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Received 17th August 2007, Accepted 18th September 2007

First published as an Advance Article on the web 4th October 2007

DOI: 10.1039/b712673e

Ansa-bridged η^5 -cyclopentadienyl molybdenum and tungsten tricarbonyl complexes of formula $[M(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{-}\eta^1\text{-CH}_2)(\text{CO})_3]$ ($M = \text{Mo}$ or W) were synthesized and the X-ray crystal structure of the tungsten complex is reported. In the epoxidation of cyclooctene the molybdenum compound shows a high catalytic activity, approaching the observed activities for the most reactive unbridged complexes of composition $\text{CpMo}(\text{CO})_3\text{X}$ ($\text{X} = \text{Cl}, \text{CH}_3$). The activity of the tungsten complex is also amongst the highest catalytic activities for the olefinic epoxidation of complexes with the composition $\text{CpW}(\text{CO})_3\text{X}$ and $\text{WO}_2\text{X}_2\text{L}_2$, reported so far. The low ring strain of the *ansa*-bridged system improves the stability of the complexes under oxidative conditions considerably in comparison to derivatives with a shorter bridge and therefore paves the way to introduction of chirality in these systems.

1. Introduction

Epoxidations, in particular chiral ones are of high interest for the synthesis of intermediates in chemical and pharmaceutical processes to generate pure products.¹ Several attempts to achieve chiral epoxidation, *e.g.* with Mo , W and Re based catalysts, have been reported, but the application of these catalysts usually leads only to moderate enantiomeric excesses.² This is largely due to the loss of chirality in the catalysts during the course of the catalytic reaction. The loss of chirality can originate either from catalysts with insufficient stability or due to a weak attachment of the chiral ligands to the metal center resulting in a non-chiral catalyst. Chiral complexes of composition $\text{R}^*\text{-ReO}_3$, *i.e.* derivatives of the highly active but non-chiral oxidation catalyst methyltrioxorhenium(vii) (MTO) can not yet be synthesized.³ Chirality is therefore introduced into the $\text{Re}(\text{VII})$ catalysts by adding a chiral Lewis base ligand to MTO.⁴ The interaction of such Lewis bases with MTO, however, is quite weak so that large excesses of such bases have to be applied to reach reasonable selectivity towards the desired epoxides (catalytic application of MTO alone leads in many cases to Lewis acid induced ring opening to diols).⁵ Nevertheless, only low to moderate enantiomeric excesses can be reached with these $\text{Re}(\text{VII})$ catalysts.^{1c} The cases of catalysts of the type $\text{MoO}_2\text{L}^*\text{R}_2$ are closely related. In these cases the ligand (L^*) metal interaction is seen not to be strong enough to yield good enantiomeric excesses.^{1c,2} Again, the introduction of chirality into these systems through application of covalently attached, chiral

groups R^* has not yet been achieved.⁶ Another alternative is utilization of catalysts of the type CpMoO_2R . These compounds are usually stable and easily obtained from $\text{CpMo}(\text{CO})_3\text{R}$ systems *via* oxidation with *tert*-butyl hydroperoxide (TBHP).⁷ Since TBHP is also the oxidizing agent for the olefin epoxidation, it is not necessary to isolate the aforementioned dioxo complexes.⁸ The tricarbonyl systems can be directly applied as catalysts precursors as they are oxidized *in situ* to the catalytic active species. The first attempt to introduce chirality into these systems was carried out using chiral ligands attached to the Cp-ring.⁹ The drawback of that approach, however, is the free rotation of the Cp-ring. With one chiral group attached to the Cp-ring an enantiomeric excess of *ca.* 20% was obtained, being in the expected order of magnitude to be reached with a freely rotating Cp ligand. Accordingly, the next approach chosen was to fix the Cp-ring in place by an *ansa*-bridge between the Cp ligand and the metal ($[M(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{-}\eta^1\text{-CH}_2)(\text{CO})_3]$).¹⁰ A bridge containing two carbon atoms was chosen, the chirality being introduced in the α -position to the Mo-atom. It turned out, however, that two carbon atoms are too short a chain for stable complexation under catalytic conditions. The X-ray structure of the above mentioned compound showed a somewhat elongated Mo–C bond and a significantly bent Cp–C bond, creating a rather strained bridge. Accordingly, in spite of a good initial enantiomeric excess, the chirality faded away quite quickly during the catalytic reaction due to catalyst decomposition caused largely by the breaking of the Mo–C bond.

The lesson learnt from these experiences is to synthesize longer *ansa*-bridges to reduce the strain on the ring and to test the activity of the compound, beginning first with non-chiral systems to find out whether they would be more stable catalysts for olefin epoxidation than their short bridged derivatives. In this work we report on the synthesis of *ansa*-bridged $\text{CpM}(\text{CO})_3\text{R}$ compounds ($M = \text{Mo}, \text{W}$) of composition ($[M(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{-}\eta^1\text{-CH}_2)(\text{CO})_3]$). These compounds turn out to fulfill the requirements described above: they are stable under catalytic conditions and show good catalytic activities.

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† CCDC reference number 658844. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712673e

2. Results and discussion

2.1. Synthesis and spectroscopic examinations

The synthesis of the spiro cyclopentadiene precursor compound—spiro[4,4]nona-6,8-diene—is performed as reported in the literature.¹¹ Complexes **1** and **2** (Chart 1) are prepared *via* some modifications of the literature procedure,¹² by reacting a THF solution of the spiro cyclopentadiene with tricarbonyl complexes of the formula $M(\text{CO})_3(\text{CH}_3\text{CN})_3$ ($M = \text{Mo}, \text{W}$). Complexes **1** and **2** are isolated at -30°C as yellow crystals. Both compounds are stable at room temperature, can be handled in laboratory atmosphere and can be kept under air for some hours without change. The tungsten complex **2** shows even better stability than its molybdenum analogue: it is stable in laboratory atmosphere for days without changes.

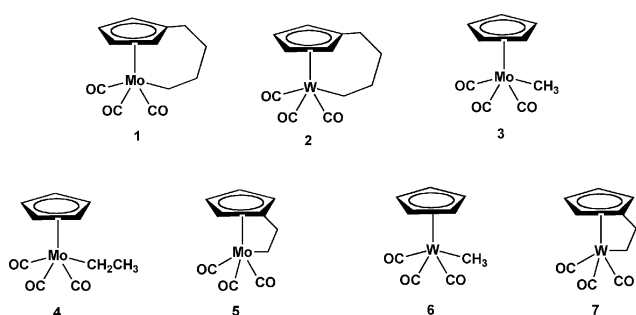


Chart 1

The composition and spectroscopic data of compounds **1** and **2** are determined by elemental analysis, IR-, and NMR-spectroscopy (^1H , ^{13}C , ^{95}Mo (for compound **1**)) as well as fast atom bombardment mass spectroscopy (FAB-MS). The FAB mass spectra show in both cases the molecular peak with an intensity ranging between 20 and 30%, proving the presence of the desired compound. The IR spectra show very strong CO vibrations at *ca.* 2000 and *ca.* 1910 cm^{-1} , weak intensity Cp-CH vibrations at *ca.* 3100 cm^{-1} and medium intensity CH_2 vibrations around 2900 cm^{-1} . Similar vibrations have been observed for related $\text{CpM}(\text{CO})_3\text{R}$ compounds.^{8–10,13} Compounds **1** and **2** also show very similar chemical shifts both in the ^1H and ^{13}C NMR spectra. The protons of the Cp rings of both complexes follow the pattern of an AABB spin system in the ^1H NMR spectra. Other *ansa*-bridged η^5 -cyclopentadienyl carbonyl molybdenum and tungsten complexes show this pattern as well.^{8,10,13} The α - CH_2 protons appear at 1.55 ppm and 1.53 ppm for compounds **1** and **2**, values which lie within the expected range. For $\text{CpMo}(\text{CO})_3(\text{CH}_2)_3\text{Ph}$ the α -protons have been observed at *ca.* 1.7 ppm,¹⁴ for the *ansa*-bridged derivatives with two C atoms in the bridge, the α -protons are shifted toward high field and appear between -0.25 and -0.45 ppm.^{8,10,13} In $\text{CpM}(\text{CO})_3\text{CH}_3$ complexes ($M = \text{Mo}, \text{W}$), the CH_3 protons are observed at 0.39 ppm.¹³ The ^{95}Mo NMR shift for compound **1** is -1697 ppm, being more low field shifted than that of $\text{CpMo}(\text{CO})_3\text{CH}_3$ (-1729 ppm) and more high field shifted than $\text{CpMo}(\text{CO})_3\text{CH}_2\text{CH}_3$ (-1685 ppm).^{8,10} The previously examined *ansa*-bridged systems of type $[\text{M}(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{-}\eta^1\text{-CH}_2)(\text{CO})_3]$ display their ^{95}Mo NMR signals at -1696 , -1708 , and -1728 ppm.^{8,10}

2.2. X-Ray crystal structure of compound **2**

The X-ray crystal structure of the compound **2** has been determined (see Fig. 1). The structure can be described as a distorted four-legged piano stool, similar to that established for analogous tricarbonyl cyclopentadienyl group VI metal complexes.^{8,10,14,15} The angles between contiguous legs range from $72.7(1)^\circ$ to $79.0(1)^\circ$, which are typical values for structures of this type. The cyclopentadienyl ligand is bound in a pentahapto fashion, as inferred from the total value of the angles at the ring (540°) and the metal-ring-carbon distances range from 2.320(4) to 2.366(4) Å. The carbonyl ligands have, as expected, a linear arrangement, with W-C-O angles ranging from $177.5(3)^\circ$ to $179.0(3)^\circ$. The C-O bond lengths are between 1.141(4) and 1.149(4) Å and the averaged W-C_{CO} bond length of 1.986 Å (with bond lengths ranging from 1.975(4) to 2.001(3) Å) are usual for terminal CO groups. The W-C_{sp³} bond distance of 2.337(3) Å is shorter than the W-C_{sp³} distance in the *ansa*-bridged tungsten derivative $[\text{W}(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{-}\eta^1\text{-CH}_2)(\text{CO})_3]$ (2.36(1) Å).^{13c} Considering the somewhat strained W-C bond in the latter compound this is not unexpected, particularly when considering that both bond distances are within the range of W-C_{sp³} bonds described in the literature, *e.g.* $(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{C}_6\text{H}_7)\text{W}(\text{CO})_3\text{Me}$ (2.293(9) Å),^{16a} $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3(\text{C}_5\text{H}_5)$ (2.343(9) Å)^{16b} and $[\{\text{W}(\text{CO})_3\text{Me}\}_2\{\eta^5\text{-C}_9\text{H}_6(\text{CH}_2)_2\}]$ (2.44(1) Å).^{16c} The bond angles in the lateral chain range from $114.1(3)^\circ$ to $116.1(2)^\circ$, showing, as expected, lower ring tension of the four membered *ansa*-bridge in complex **2** compared to the two membered *ansa*-bridges in $[\text{M}(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{-}\eta^1\text{-CRH})(\text{CO})_3]$ ($M = \text{W}, \text{R} = \text{H}$; $M = \text{Mo}, \text{R} = \text{Ph}$) complexes ($97.7(6)^\circ$ and $101.5(8)^\circ$)^{13c} and ($97.1(1)^\circ$ and $100.4(2)^\circ$).¹⁰ The strained lateral chain in the latter compound has been deemed responsible for the easy breaking of the metal-C bond under the

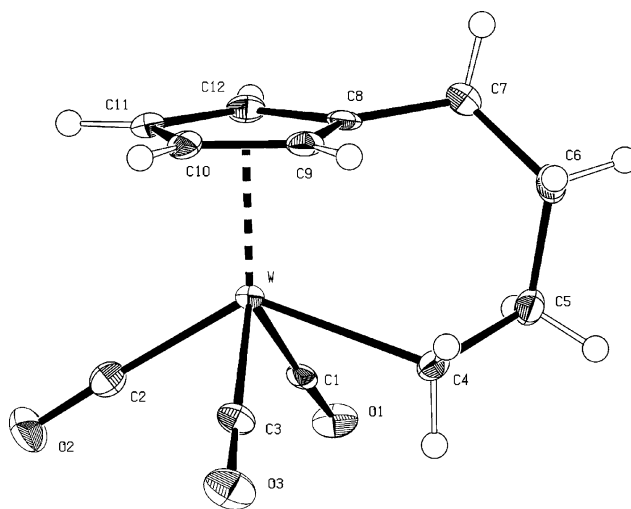


Fig. 1 ORTEP style plot^{17e} of compound **2** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and bond angles ($^\circ$): W-C1 1.983(4), W-C2 2.001(3), W-C3 1.975(4), W-C4 2.337(3), W-C8 2.356(3), W-C9 2.320(4), W-C10 2.341(4), W-C11 2.348(4), W-C12 2.366(4), W-Cg 2.011; C1-W-C2 $79.0(1)$, C1-W-C3 $104.3(2)$, C1-W-C4 $72.8(1)$, C1-W-Cg 127.9 , C2-W-C3 $76.2(1)$, C2-W-C4 $130.6(1)$, C2-W-Cg 120.1 , C3-W-C4 $72.7(1)$, C3-W-Cg 126.5 , C4-W-Cg 109.2 , W-C4-C5 $116.1(2)$, C4-C5-C6 $114.5(3)$, C5-C6-C7 $114.1(3)$, C6-C7-C8 $114.6(3)$. Cg denotes the center of gravity of the cyclopentadienyl ligand.

epoxidation conditions. Accordingly, concluding from these afore described X-ray data, a higher stability under catalytic conditions should be expected for compounds **1** and **2**.

2.3. Application in epoxidation catalysis

Compounds **1** and **2** were tested as catalysts for the epoxidation of cyclooctene with TBHP. The details concerning the catalytic reaction are given in the Experimental. Blank reactions show that no significant amount of epoxide was formed in the absence of a catalyst. A catalyst : substrate: oxidant ratio of 1 : 100 : 200 was used in all experiments unless stated otherwise. For cyclooctene no significant formation of by-products (*e.g.* diol) was observed. Both catalytic reactions show similar time-dependent curves, in which the yield increases steadily in the first one or two hours of the reaction and then slows down (first order kinetics, see Fig. 2). The reason for this slowing down has been ascribed largely to the formation of the by-product *tert*-butanol, which competes with TBHP for coordination to the catalyst complex.^{7,8}

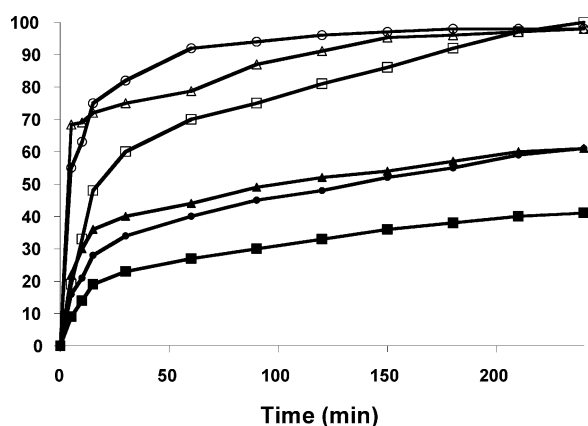


Fig. 2 Time dependent yield of cyclooctene epoxide in the presence of compounds **1** (○), **2** (●), the literature known Mo compounds CpMo(CO)₃CH₃ (**3**, △), [Mo(η⁵-C₅H₄(CH₂)₃-η¹-CH₂)(CO)₃] (**5**, □) and the literature known W compounds CpW(CO)₃CH₃ (**6**, ▲), and [W(η⁵-C₅H₄(CH₂)₃-η¹-CH₂)(CO)₃] (**7**, ■). The measurements were executed with 1 mol% catalyst charge at 55 °C in the case of the molybdenum complexes **1**, **3** and **5** and at 90 °C in the case of the tungsten complexes **2**, **6** and **7**. The values for compounds **3** and **5** have been taken from ref. 8.

The catalytic activities of complexes **1** and **2** have been compared to the literature known Mo complexes (see Chart 1) CpMo(CO)₃CH₃ (**3**), CpMo(CO)₃C₂H₅ (**4**), and CpMo(CO)₃(CH₂CH₂) (**5**) and the literature known W compounds CpW(CO)₃CH₃ (**6**), and CpW(CO)₃(CH₂CH₂) (**7**). The turnover frequencies (TOFs) at 55 °C with a catalyst : substrate : oxidant ratio of 1 : 100 : 200 after a reaction time of 5 min are 820 h⁻¹ for **3**, 230 h⁻¹ for **4** and 250 h⁻¹ for **5**. For compound **1** the TOF is 660. For the W compounds at 90 °C the TOFs are 270 (**6**), 110 (**7**) and 200 (**2**) h⁻¹. While the examined Mo complexes reach complete conversions within 4 h at 55 °C, the W compounds, despite their lower activity reach a complete epoxide yield (between 90 and 100%) within 24 h at 90 °C reaction temperature. The time dependent curves for three selected Mo and three selected W catalysts are given in Fig. 2. Applying a catalyst : substrate : oxidant ratio of 1 : 1000 : 2000 leads to TOFs of 6000 (**3**) and 4900 (**1**) h⁻¹.⁸ The latter value also surpasses the TOF obtained

with the Cl derivative (*ca.* 4000 h⁻¹, obtained under equivalent conditions).⁷

Examinations of the long term stability of **1** under catalytic conditions (repeated additions of new substrate) also show that the catalytic active species is much more stable than obtained from compound **5**. This seems to be due to the more stable ring in the case of **1**.

3. Experimental

3.1. Synthesis and characterization

All preparations and manipulations were performed using standard Schlenk techniques under an Argon atmosphere. Solvents were dried by standard procedures (THF, *n*-hexane and Et₂O over Na/benzophenone; CH₂Cl₂ over CaH₂), distilled under an argon atmosphere and used immediately (THF) or kept over 4 Å molecular sieves. TBHP was purchased from Aldrich as 5.0–6.0 mol% solution in *n*-decane and used after drying over molecular sieves to remove the water (<4% when received). Microanalyses were performed in the Mikroanalytisches Labor of the TU München in Garching. Mid-IR spectra of isolated compounds were measured on a Bio-Rad FTS 525 spectrometer using KBr pellets. ¹H-, ¹³C- and ⁹⁵Mo-NMR spectra were obtained using a Bruker Avance DPX-400 spectrometer. Mass spectra were obtained with a Finnigan MAT 311 A and a MAT 90 spectrometer; Catalytic runs were monitored by GC methods on a Hewlett-Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphasex 120 and a Hewlett-Packard integration unit HP 3396 Series II. Spiro[4,4]nona-6,8-diene was synthesised and purified according to literature procedures.¹¹

[Mo(η⁵-C₅H₄(CH₂)₃-η¹-CH₂)(CO)₃] (1**).** The addition of a THF (*ca.* 20 ml) solution of the ligand spiro[4,4]nona-6,8-diene (0.40 g, 3.3 mmol) to Mo(CO)₃(CH₃CN)₃ (0.85 g, 2.8 mmol) drop wise at 0 °C produces a yellow suspension, which is stirred overnight at 25 °C. Volatiles are removed under vacuum, the sticky residue is extracted with 15 ml of *n*-hexane (three times), filtered, and the obtained yellow filtrates are concentrated. After cooling to –30 °C yellow crystals are obtained. Yield (0.34 g, 40%). C₁₂H₁₂O₃Mo (300). Calcd: C 48.02, H 4.03; found: C 47.68, H 3.83. IR (KBr, ν/cm⁻¹): 3112 (w, ν CH of Cp-ring), 2898 and 2867 (m, ν CH₂), 2002, 1908 (vs, ν CO); ¹H-NMR (CDCl₃, 400 MHz, 25 °C): δ (ppm) = 1.55 (m, 2H, Mo-CH₂), 1.75, 1.78 (m, 4H, -CH₂-CH₂-), 2.32 (t, 2H, Cp-CH₂), 5.10, 5.12 (m, 4H, ABBB system of the Cp ring); ¹³C-NMR (CDCl₃, 100.28 MHz, 25 °C): δ (ppm) = 239.9, 227.9 (CO), 110.9, 91.3, 88.0 (Cp ring), 28.0 (Cp-CH₂), 26.7 (CH₂), 25.1 (CH₂), 5.0 (Mo-CH₂). ⁹⁵Mo-NMR (CDCl₃, 26.07 MHz, 25 °C): δ (ppm) = –1697 ppm. FAB-MS (NBA as FAB-matrix) *m/z* (%); M⁺ = 302 (26).

[W(η⁵-C₅H₄(CH₂)₃-η¹-CH₂)(CO)₃] (2**).** The addition of a THF (*ca.* 20 ml) solution of the ligand spiro[4,4]nona-6,8-diene (0.35 g, 2.9 mmol) to W(CO)₃(CH₃CN)₃ (1.03 g, 2.65 mmol) at 0 °C produces a bright yellow suspension, which is stirred overnight at 25 °C and then refluxed for 4 h. After cooling at room temperature, all volatiles are removed under vacuum and the sticky residue is extracted with 15 ml of *n*-hexane (three times) and filtered. The obtained bright yellow filtrates are concentrated and after cooling to –30 °C yellow crystals are obtained. Yield (0.9 g, 60%).

$C_{12}H_{12}O_3W$ (388.06). Calcd: C 37.12, H 3.14; found: C 37.09, H 3.11. IR (KBr, ν/cm^{-1}): 3109 (w, ν CH of Cp-ring), 2908 and 2854 (m, ν CH_2), 1999, 1912 (vs, ν CO); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, 25°C): δ (ppm) = 1.53 (m, 2H, W- CH_2), 1.70, 1.78 (m, 4H, - CH_2 - CH_2 -), 2.38 (t, 2H, Cp- CH_2), 5.16, 5.24 (m, 4H, AABB system of the Cp ring); $^{13}\text{C-NMR}$ (CDCl_3 , 100.28 MHz, 25°C): δ (ppm) = 229.2, 217.5 (CO), 110.1, 90.0, 86.9 (Cp ring), 28.1 (Cp- CH_2), 26.4 (CH_2), 25.1 (CH_2), -7.3 (W- CH_2). FAB-MS (NBA as FAB-matrix) m/z (%): M^+ = 388 (23).

3.2. Single crystal X-ray structure determination of compound 2

Crystal data and details of the structure determination are presented in Fig. 1 and Table 1. Suitable single crystals for the X-ray diffraction study were grown from *n*-hexane. A clear yellow fragment was stored under perfluorinated ether, transferred in to 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 ($\lambda = 0.71073 \text{ \AA}$). Data collection was performed at 123 K within the θ range of $1.89^\circ < \theta < 25.38^\circ$. A total of 23 404 reflections were integrated, corrected for Lorentz, polarization, and absorption effects (DELABS^{17e}). After merging ($R_{\text{int}} = 0.050$), 2081 [$1994: I_o > 2\sigma(I_o)$] independent reflections remained and all were used to refine 146 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. All hydrogen atoms were placed in ideal positions and refined using a riding model, with methylene and aromatic $d_{\text{C-H}}$ distances of 0.99 and

0.95 \AA , respectively, and $U_{\text{iso(H)}} = 1.2U_{\text{eq(C)}}$. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ and converged with $R1 = 0.0164$ [$I_o > 2\sigma(I_o)$], $wR2 = 0.0382$ [all data], GOF = 1.162 and shift/error < 0.001 . The final difference-Fourier map shows no striking features.¹⁷

CCDC reference number 658844.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712673e

3.3. Catalytic reactions

The catalytic reactions were performed in air, within a reaction vessel (equipped with a magnetic stirrer) which was immersed in a thermostated bath at 55°C for Mo-complexes and additionally at 90°C in the case of W-complexes as catalysts. The catalytic procedure is described below.

Cis-Cyclooctene (800 mg, 7.3 mmol), mesitylene (1 g, internal standard) and 1 mol% (73 μmol) of the catalysts (**1** or **2**) were added to the reaction vessel. The reaction begins with the addition of TBHP (2.65 mL, 5.5 M in *n*-decane). The course of the reaction was monitored by quantitative GC analysis. Samples taken were diluted with CH_2Cl_2 , and treated with a catalytic amount of MgSO_4 and MnO_2 to remove water and destroy the excess of peroxide. The resulting slurry was filtered and the filtrate obtained was injected into a chiral GC column. The conversion of cyclooctene, and the formation of cyclooctene oxide were calculated from calibration curves ($r^2 = 0.999$) recorded prior to the reaction course.

4. Conclusions

Ansa-bridged Mo and W compounds of composition $[\text{M}(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{-}\eta^1\text{-CH}_2)(\text{CO})_3]$ can be successfully applied as catalysts in olefin epoxidation reactions without noticeable catalyst decomposition or cleavage of the M-C bridge during the reaction. The catalytic activity lies in the same order of magnitude as that of complexes of composition $\text{CpMo}(\text{CO})_3\text{R}$, where R is CH_3 and Cl, which are the most active catalysts of this type described to date. The reaction proceeds smoothly towards epoxide, no diols are formed as by-products. The far greater stability and higher activity of the new *ansa*-bridged Mo and W compounds when compared to derivatives with shorter *ansa*-bridges is striking. It seems therefore reasonable to synthesise chiral derivatives of the complexes presented in this work, with the chirality either on the *ansa*-bridge or on the Cp ring. The hindering of Cp-ring rotation and the stable *ansa*-bridge should both manifest in stable enantiomeric excesses in the products. Another useful application would be the heterogenisation of such molecules (both chiral and non-chiral) to allow better and easier catalyst recovery. Research in these directions is currently ongoing in our laboratories.

Acknowledgements

J. Z. thanks the Hochschul- und Wissenschaftsprogramm (HWP-II): Fachprogramm Chancengleichheit für Frauen in Forschung und Lehre for a postdoctoral grant. K. R. J. is grateful to the Bayerische Forschungsförderung für eine Ph.D. grant. K. R. J. and F. E. K. further thank the International Graduate School for Science and Engineering (IGSSE) and the research network

Table 1 Crystallographic data for $[\text{W}(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{-}\eta^1\text{-CH}_2)(\text{CO})_3]$ (**2**)

2	
Formula	$\text{C}_{12}\text{H}_{12}\text{WO}_3$
Formula weight	388.06
Color/habit	Yellow/fragment
Crystal dimensions/mm ³	$0.18 \times 0.20 \times 0.24$
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
$a/\text{\AA}$	11.2909(1)
$b/\text{\AA}$	8.1047(1)
$c/\text{\AA}$	12.9838(2)
$\beta/^\circ$	107.4344(5)
$V/\text{\AA}^3$	1133.56(2)
Z	4
T/K	123
$D_{\text{calc}}/\text{g cm}^{-3}$	2.274
μ/mm^{-1}	10.178
$F(000)$	728
θ -range/ $^\circ$	1.89–25.38
Index ranges (h, k, l)	$\pm 13, \pm 9, \pm 15$
No. of rflns collected	23 404
No. of indep. rflns/ R_{int}	2081/0.050
No. of obsd rflns ($I > 2\sigma(I)$)	1994
No. of data/restraints/params	2081/0/146
$R1/wR2$ ($I > 2\sigma(I)$) ^a	0.0164/0.0378
$R1/wR2$ (all data) ^a	0.0175/0.0382
GOF (on F^2) ^a	1.162
Largest diff peak and hole/e \AA^{-3}	+1.12/−0.86

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

NanoCat for financial support. F. E. K. additionally acknowledges the Fonds der Chemischen Industrie for continuous financial support.

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