



Microwave-assisted molybdenum-catalysed epoxidation of olefins

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ABSTRACT

The performance of $\text{CpMo}(\text{CO})_3\text{CH}_3$ as a catalyst precursor in the epoxidation of *cis*-cyclooctene and *R*-(+)-limonene with *tert*-butylhydroperoxide (TBHP), at 55 °C, was investigated for the first time using microwave (MW)-assisted heating, and the results were compared with those obtained using conventional heating with a thermostated oil bath (OB). The reactions were carried out under monophasic (no co-solvent, or with 1,2-dichloroethane, toluene, hexane) or biphasic liquid–liquid (using the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate, $[\text{BMIM}][\text{BF}_4]$) conditions. The heating methods did not affect product selectivity: 100% to cyclooctene oxide, and 93% to limonene oxide (66–72% diastereomeric excess, *trans*-1,2-(+)-limonene oxide) at 80% limonene conversion. However, the initial reaction rates strongly depend on the applied heating method. The favourable MW effect is essentially due to the faster heating up of the reaction mixture increasing the overall epoxidation rate in the early stage of the heating process, which is supported experimentally by a comparison of (i) the measured temperature vs time curves, (ii) the kinetic data for the MW method with that for the OB method where the reagents and reactor walls are pre-heated (OB-preH method), and (iii) the estimated apparent activation energies and pre-exponential factors for the two olefins using the MW, OB, and OB-preH methods. The crystal structure of the molybdenum tricarbonyl catalyst precursor was unveiled from single-crystal X-ray diffraction studies at 150 K. The complex crystallises as a racemic twin in the monoclinic $P2_1$ space group.

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1. Introduction

High oxidation state organometallic oxides have found numerous applications as catalysts for oxidation reactions [1]. The first example of a cyclopentadienyl dioxomolybdenum(VI) complex, CpMoO_2Cl ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), was reported by Cousins and Green in 1963 [2]. After that, several reports about analogous complexes belonging to the families $\text{Cp}'\text{MoO}_2\text{X}$ ($\text{Cp}' = \text{Cp}$, Cp^* ($\eta^5\text{-C}_5(\text{CH}_3)_5$) and $\text{X} = \text{Cl}$, Br) and $\text{Cp}'\text{MoO}_2\text{R}$ ($\text{Cp}' = \text{Cp}$, Cp^* and $\text{R} = \text{CH}_3$, $\text{CH}_2\text{Si}(\text{CH}_3)_3$) emerged [3]. These reports contributed to the unravelling of new synthetic pathways with improved yields. Although it has been known since 1991 that $\text{Cp}^*\text{MoO}_2\text{Cl}$ acts as a liquid-phase catalyst for olefin epoxidation using as oxidant *tert*-butylhydroperoxide (TBHP) [4], the applicability of this type of compounds as oxidation catalysts was for a long time overshadowed by their catalytically active rhenium(VII) congeners Cp^*ReO_3 [5] and CpReO_3 [6], which could be synthesised by easier and more efficient methods when compared to their molybdenum congeners.

An important step in this chemistry was achieved by Romão and co-workers [7] with the discovery that the complexes $\text{Cp}'\text{MoO}_2\text{Cl}$ [$\text{Cp}' = \text{Cp}$, Cp^* , $\eta^5\text{-C}_5(\text{CH}_2\text{Ph})_5$] could be easily prepared from the parent carbonyls, $\text{Cp}'\text{Mo}(\text{CO})_3\text{Cl}$, upon reaction with TBHP. This opened the way to use $\text{Cp}'\text{Mo}(\text{CO})_3\text{Cl}$ complexes as epoxidation catalyst precursors, since these can be in situ oxidised during the catalytic reaction with TBHP, which is used as oxidant. Based on this in situ method, several complexes with a $\text{Cp}'\text{Mo}(\text{CO})_3^+$ core have been studied as olefin epoxidation catalysts under homogeneous conditions [3,8]. With the aim of improving catalyst recyclability, cyclopentadienyl molybdenum tricarbonyl complexes have been supported on mesoporous MCM-41 and MCM-48 materials [9], in ionic liquids [9a,10], and in cyclodextrins [11]. Recently, $\text{CpMo}(\text{CO})_3\text{Cl}$ was also studied as a catalyst in the sulfoxidation of sulfides [12], and the molybdenum acetylide complex $\text{CpMo}(\text{CO})_3(\text{C}\equiv\text{CPh})$ was applied in the dihydroxylation of olefins [13]. In both cases H_2O_2 was used as the oxidant.

The catalytic performances of monomeric cyclopentadiene molybdenum oxides and their carbonyl precursors have always been investigated using conventional thermal heating with an external heat source, typically an oil bath (denoted OB). The OB method involves conduction and convection heat transfer modes with several factors affecting the heating up time (interface area,

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thermal conductivity of the various materials through which heat must be transferred, etc.). The sustainability of chemical reactions has gained relevance, and in this context microwave (MW) heating has been used in an effort to reduce time scales and enhance yields of the target products [14]. On the other hand, MW irradiation leads to in-core volumetric heating, which can result in minimised wall effects of the reaction vessel surface and less energy consumption than the OB method wherein the whole system, including the reaction vessel, must be raised to the desired reaction temperature.

Apart from organic synthesis, MW heating has been applied in fields such as organometallic synthesis [14c,15], homogeneous [16] and heterogeneous catalysis [17], phase transfer catalysis [18], organocatalysis [14e], and biocatalysis [19]. However, there are only a handful of examples in the literature reporting on the MW-assisted transformation of (un)functionalised olefins into epoxides [20]. In the present work, the catalytic performance of $\text{CpMo}(\text{CO})_3\text{CH}_3$ in the liquid-phase epoxidation of olefins with TBHP has been investigated for the first time using MW heating, and the results are compared with those obtained using conventional OB heating. The MW effects have been explained on the basis of experimental evidence. The crystal structure of $\text{CpMo}(\text{CO})_3\text{CH}_3$ is also reported.

2. Experimental

2.1. Materials and methods

Unless otherwise stated all preparations and manipulations were carried out using Schlenk techniques under nitrogen. Solvents were dried by standard procedures (hexane, diethyl ether and THF with Na/benzophenone ketyl; dichloromethane with CaH_2), distilled under nitrogen and used immediately (for THF) or kept over 4 Å molecular sieves. ^1H NMR spectra were obtained using a Bruker CXP 300 spectrometer.

2.2. Synthesis of $\text{CpMo}(\text{CO})_3\text{Me}$ (1)

$\text{CpMo}(\text{CO})_3\text{Me}$ was synthesised by the reaction of $\text{CpMo}(\text{CO})_3\text{Na}$ with CH_3I using the method originally described by Wilkinson in the 1950s [21] and summarised later by King [22]. A more recent and easier procedure developed by Roesky and co-workers was used to synthesise the precursor NaCp [23]. ^1H NMR (300 MHz, CDCl_3 , 298 K, TMS): $\delta = 5.23$ (s, 5H, C_5H_5), 0.30 (s, 3H, CH_3) ppm.

2.3. Single-crystal X-ray diffraction studies

A portion of $\text{CpMo}(\text{CO})_3\text{CH}_3$ (1), preserved inside a sealed container under inert atmosphere, was immersed in highly viscous FOMBLIN Y perfluoropolyether vacuum oil (LVAC 140/13) purchased from Sigma–Aldrich [24]. A suitable single-crystal was mounted on a Hampton Research CryoLoop with the help of a Stemi 2000 stereomicroscope equipped with Carl Zeiss lenses. Diffraction data were collected at 150(2) K on a Bruker X8 Kappa APEX II CCD area-detector diffractometer (Mo K_α graphite-monochromated radiation, $\lambda = 0.71073$ Å) controlled by the APEX2 software package [25], and equipped with an Oxford Cryosystems Series 700 cryostream monitored remotely using the software interface Cryopad [26].

An initial data collection for indexation purposes failed to provide a reasonable unit cell for the compound. A visual inspection of the collected set of centred reflections using RLATT [27] indicated the presence of a rotational twin (non-merohedral). The collected sub-set, composed of 426 reflections, was deconvoluted using Bruker–Nonius CELL_NOW [28], which unequivocally revealed the existence of a two-component twin with the domains rotated by

Table 1
Crystal and structure refinement data for $\text{CpMo}(\text{CO})_3\text{CH}_3$ (1).

Formula	$\text{C}_9\text{H}_8\text{MoO}_3$
Formula weight	260.09
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	7.5663(4)
b (Å)	7.7019(4)
c (Å)	8.2091(4)
β (°)	96.837(3)
Volume (Å ³)	474.98(4)
Z	2
D_c (g cm ⁻³)	1.819
μ (Mo–K α) (mm ⁻¹)	1.350
Crystal size (mm)	0.18 × 0.16 × 0.03
Crystal type	Yellow plates
θ range	3.64–29.11
Index ranges	$-10 \leq H \leq 10$, $-10 \leq K \leq 10$, $-0 \leq L \leq 11$
Reflections collected	4728
Independent reflections	4728
Completeness to $\theta = 29.11^\circ$	99.8%
Final R indices [$I > 2\sigma(I)$] ^{a,b}	$R1 = 0.0308$, $wR2 = 0.0972$
Final R indices (all data) ^{a,b}	$R1 = 0.0324$, $wR2 = 0.0984$
Weighting scheme ^c	$m = 0.0743$, $n = 0.0$
Largest diff. peak and hole	1.508 and -0.876 eÅ^{-3}

$$^a R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR2 = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}}$$

$$^c w = 1 / [\sigma^2(F_o^2) + (mP)^2 + nP] \text{ where } P = (F_o^2 + 2F_c^2)/3.$$

179.8° about the reciprocal axis $[-1.000 \ 0.001 \ 1.000]$. After the collection of a full data set optimised for one of the domains, the matrix used to relate the two orientations,

$$\begin{pmatrix} 0.091 & 0.002 & -0.909 \\ 0.001 & -1.000 & 0.003 \\ -1.092 & -0.006 & -0.091 \end{pmatrix}$$

was imported into SAINT+ [29] for data integration (the second twin component being identical to the first). Absorption corrections on the full data range were performed using TWINABS [30], revealing that each twin component accounted for ca. 1790 unique discrete reflections, of which 1160 were considered to be overlapped. The structure was solved with the sub-data set taken from one of the domains (including overlapped reflections), and by employing the Patterson synthesis algorithm implemented in SHELXS-97 [31]. All remaining non-hydrogen atoms were located from difference Fourier maps calculated from successive full-matrix least squares refinement cycles on F^2 using SHELXL-97 [31]. All non-hydrogen atoms were successfully refined using anisotropic displacement parameters. The final refinement was performed against the two-component data set using the HKLF 5 format. As a consequence, all reflections were treated as being independent and no value of R_{int} is provided (see Table 1). The Flack parameter [32] refined to 0.53(5), which ensures the statistical presence of a racemic twin.

Hydrogen atoms bound to carbon were located at their idealised positions using appropriate HFIX instructions in SHELXL (43 for the aromatic belonging to the Cp ring and 137 for the coordinated CH_3 group) and included in subsequent refinement cycles in riding-motion approximation with isotropic thermal displacement parameters (U_{iso}) fixed, respectively, at 1.2 or 1.5 times U_{eq} of the carbon atom to which they are attached.

The last difference Fourier map synthesis showed the highest peak (1.508 eÅ^{-3}) and deepest hole (-0.876 eÅ^{-3}) located at 0.83 and 0.42 Å from Mo(1) and H(8), respectively. Information concerning crystallographic data collection and structure refinement details is summarised in Table 1. Selected bond lengths and angles for the molybdenum coordination environment are collected in Table 2. CCDC-722385 contains the supplementary crystallographic

Table 2

Selected bond lengths (in Å) and angles (in degrees) for the molybdenum coordination environment in CpMo(CO)₃CH₃ (**1**)^a.

Mo(1)–C(1)	2.326(3)	Mo(1)–C(5)	2.372(4)
Mo(1)–C(2)	1.984(4)	Mo(1)–C(6)	2.357(3)
Mo(1)–C(3)	1.997(4)	Mo(1)–C(7)	2.319(4)
Mo(1)–C(4)	1.993(4)	Mo(1)–C(8)	2.319(3)
		Mo(1)–C(9)	2.344(3)
		Mo(1)⋯C _g	2.007(1)
C(1)–Mo(1)–C(2)	72.39(13)	C _g ⋯Mo(1)–C(1)	112.10(1)
C(1)–Mo(1)–C(3)	129.60(17)	C _g ⋯Mo(1)–C(2)	127.48(1)
C(1)–Mo(1)–C(4)	72.41(17)	C _g ⋯Mo(1)–C(3)	118.28(1)
C(2)–Mo(1)–C(3)	78.09(17)	C _g ⋯Mo(1)–C(4)	124.21(1)
C(2)–Mo(1)–C(4)	107.36(18)		
C(3)–Mo(1)–C(4)	78.87(15)		

^a C_g—centroid of the coordinated η⁵-Cp aromatic ring [C(5)→C(9)].

data (excluding structure factors) for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.4. Catalytic olefin epoxidation

The liquid-phase catalytic epoxidation reactions were carried out under air and autogeneous pressure, in closed borosilicate (nearly microwave transparent) reaction vessels (5–10 mL capacity) equipped with magnetic stirrers, using two different heating methods: conventional with the aid of a thermostated oil bath (denoted OB) or microwave-assisted heating (denoted MW). Typically, 18 μmol of complex, 1.8 mmol of olefin and 2.75 mmol of oxidant (5.5 M TBHP in decane) were added to the reaction vessel, without additional solvent (other than the decane present in the TBHP solution), or using 2 mL of a volatile organic solvent (hexane, 1,2-dichloroethane (DCE), toluene), or 100 μL of the ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]). For the OB method, the reaction temperature was monitored by inserting a Barnant type K thermocouple into the reaction mixture.

The MW experiments were carried out in a Discover S-Class (CEM Corporation, USA) microwave oven, at 2.45 GHz, under stirring and simultaneous cooling with compressed air to prevent bulk overheating. Unless otherwise stated (Section 3.2.5), 20 psi air and a fixed power control (FPC) operation mode were used, the last of which allows setting the temperature and MW power input: the power is constant until the temperature set point is reached and then the MW oven switches to a feedback loop to modulate the applied power in order to maintain a constant temperature. The MW power input was optimised for the different solvents and substrates in order to reach 55 °C in 30–40 s, without temperature overshooting. The effects of water present in the solvents and reagents (used as received) are neglected for the sake of simplicity. Zero time was taken as the instant the reaction vessel was immersed in the OB, and in the case of the MW method the instant the FPC operation mode was initiated.

The course of the reactions was monitored using a Varian 3900 GC equipped with a capillary column (SPB-5, 20 m × 0.25 mm) and a flame ionisation detector. For quantification of the products, undecane was used as internal standard added after the reaction. The reaction products were identified by GC-MS (Trace GC 2000 Series (Thermo Quest CE Instruments) - DSQ II (Thermo Scientific)), using He as the carrier gas. Sampling was performed using a single reactor: for the MW method the MW irradiation was interrupted for sampling, which took ca. 45 s from the instant the MW irradiation was interrupted to the instant the reaction temperature set point (55 °C) was reached causing a decrease in temperature of less than 10 °C. The apparent activation energies and pre-exponential factors were estimated applying the method of initial rates and the Arrhenius equation: the volume of the reaction mixture and the

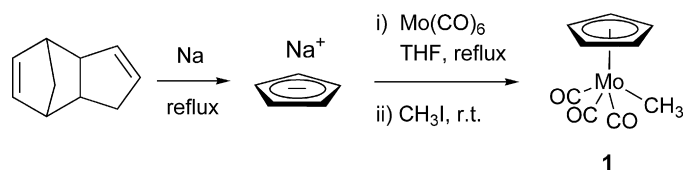
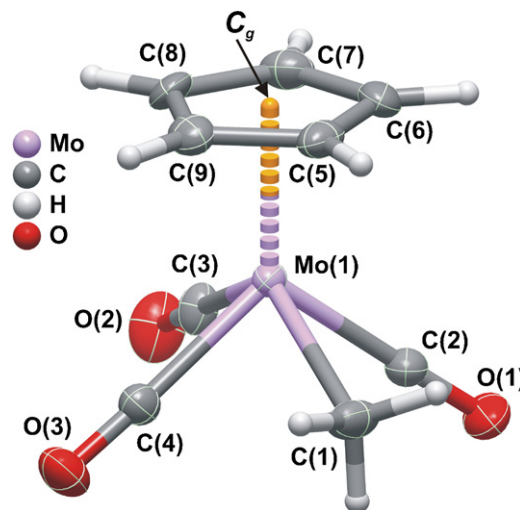
**Scheme 1.**

Fig. 1. Schematic representation of the molecular unit present in the structure of CpMo(CO)₃CH₃ (**1**) showing the labelling scheme for all non-hydrogen atoms. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are represented as small spheres with arbitrary radii. Mo–C bonds to the η⁵-Cp organic ligand have been replaced by a dashed bond to the corresponding centre of gravity (C_g). For selected bond lengths and angles see Table 2.

catalyst:oxidant:olefin ratio of 0.001:1.5:1 were kept constant and initial rates calculated for 1–2 and 5 min reaction for the MW and OB(-preH) methods, respectively.

3. Results and discussion

3.1. Synthesis and characterisation

CpMo(CO)₃Me (**1**) was synthesised by the reaction of CpMo(CO)₃Na (prepared from NaCp and Mo(CO)₆) with CH₃I (Scheme 1). Purification of **1** by sublimation afforded suitable crystals for X-ray diffraction studies, which were carried out at the low temperature of 150 K (Table 1). Even though the first synthesis of CpMo(CO)₃CH₃ dates back to the work by Wilkinson in the fifties [21], its crystal structure has not yet been reported.

In the crystal structure of **1**, the asymmetric unit of the monoclinic unit cell comprises a whole organometallic complex (Fig. 1). Even though a considerable number of organometallic molybdenum tricarbonyl complexes containing a substituted Cp aromatic ring can be found in the literature, as revealed by a search in the Cambridge Structural Database (CSD, version 5.29 with two updates) [33], those with a methyl group directly bound to the metal centre are significantly more scarce, being either dimeric [34] or monomeric [8a,35] complexes. The complex which most resembles that described in the present work is (CpCOCH₃)Mo(CO)₃CH₃, which was reported in 1990 by Rogers et al. [35h]. One likely reason why the crystal structure of **1** has not yet been reported is that, as described in Section 2.3, the compound crystallises as a complex racemic twin in the monoclinic P2₁ space group. Only modern X-ray diffraction techniques were able to properly identify and deconvolute the twinned crystallographic data set.

$\text{CpMo}(\text{CO})_3\text{CH}_3$ has the Mo centre coordinated to three carbonyl ($\text{C}=\text{O}$) groups, one methyl group ($-\text{CH}_3$) and one cyclopentadienyl ring (Cp) (Fig. 1), with the overall coordination geometry resembling a considerably distorted square pyramid having the apical position occupied by the Cp group. The metal centre is raised by ca. 1.04 Å from the average plane composed of the three $\text{C}=\text{O}$ groups and the $-\text{CH}_3$ group. The latter group is further raised by ca. 0.51 Å from the average plane formed by the three carbon atoms of the $\text{C}=\text{O}$ groups, which agrees with the structural properties previously reported by Rogers et al. [35h] (raised value of about 0.44 Å). This structural feature is typical of this type of complexes with known values ranging between 0.09 and 0.81 Å [8a,34,35]. The former value is commonly found in structures with bulky substituents on the Cp ring (e.g., in the structures by Laï et al. [34a,35f]).

The registered Mo–C distances to the Cp group [2.319(3)–2.372(4) Å, Table 2] are typical of an η^5 -coordination fashion, as found in related tricarbonyl complexes (from the CSD: 339 entries, range 2.20–2.50 Å with a median of 2.34 Å). The Mo–C interactions with the $\text{C}=\text{O}$ moieties span from 1.984(4) to 1.997(4) Å, while the bond length with the methyl group is 2.326(3) Å. These values are consistent with those reported for related Cp-molybdenum-containing structures (from the CSD: 1597 entries with bonds to carbonyl, range 1.56–2.37 Å with a median of 1.97 Å; 44 entries with bonds to $-\text{CH}_3$, range 2.03–2.42 Å with a median of 2.24 Å).

The close packing of individual $\text{CpMo}(\text{CO})_3\text{CH}_3$ complexes in the crystal structure is essentially mediated by the need to effectively fill the available space, with no structurally significant (i.e., either strong or highly directional) supramolecular interactions being noticeable. This feature was already observed in the structure of $(\text{CpCOCH}_3)\text{Mo}(\text{CO})_3\text{CH}_3$ [35h] even though some weak C–H...O interactions could be considered. $\text{CpMo}(\text{CO})_3\text{CH}_3$ complexes self-organise into layers with a typical herringbone tiling, which alternate in an ABAB... fashion as depicted in Fig. 2. This lack of supramolecular contacts is further evidenced by the geometry of the Mo–C=O bonds: all $\angle(\text{Mo}-\text{C}=\text{O})$ angles are close to linear, varying between ca. 177.0 and 178.9°, which is a clear indication that the terminal oxygen atoms are not deviated due to weak hydrogen bonding with neighbouring donors.

3.2. Catalytic olefin epoxidation

3.2.1. General considerations for the OB and MW methods

The reaction of *cis*-cyclooctene with TBHP in the presence of **1**, without a co-solvent, at 55 °C (using the OB method) gives cyclooctene epoxide as the only product. Initially the reaction is relatively fast giving 66/86% conversion after 20 min/2 h (Fig. 3, Table 3). These results are in agreement with those published in the literature for **1** used in the same reaction, under similar conditions [8a]. The oxidative decarbonylation of **1** with excess TBHP generates a mixture of $\text{CpMoO}_2\text{CH}_3$ and $\text{CpMoO}(\text{O}_2)\text{CH}_3$, which react with TBHP to give different active oxidising species responsible for oxygen atom transfer to the olefin [8a,d]. These initial steps

Table 3

Cyclooctene epoxidation with TBHP in the presence of **1** at 55 °C.

Solvent	Dielectric properties ^a		MW power input (W)	Conversion (%) ^b	
	ϵ'	ϵ''		OB	MW
None	–	–	60	66/86 (65) ^c	77/94 (89) ^c
DCE	10.4	1.321	60	72/98	96/99
Toluene	2.4	0.096	180	47/90	79/96
Hexane	1.9	0.038	210	37/88	78/97

^a Dielectric constant (ϵ') and dielectric loss (ϵ'') at 25 °C.

^b Cyclooctene conversion after 20 min/2 h reaction.

^c Values in parentheses are conversions after 2 h in a second run.

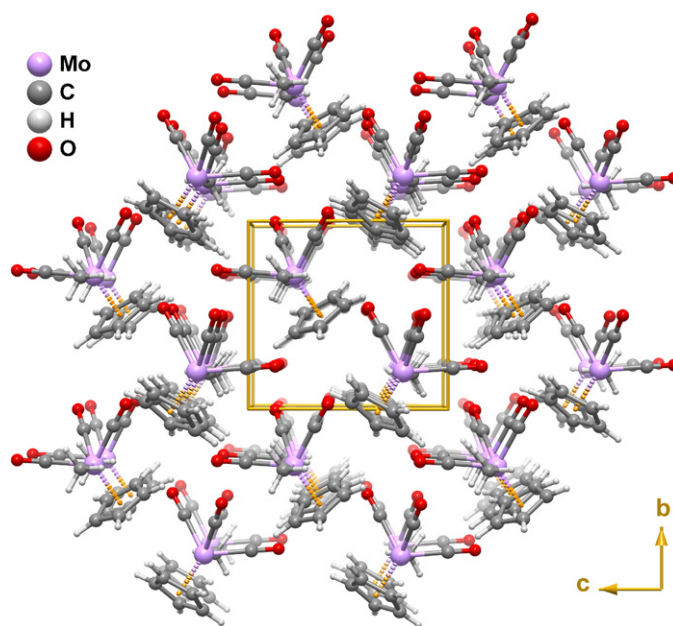


Fig. 2. Crystal packing of $\text{CpMo}(\text{CO})_3\text{CH}_3$ (**1**) viewed in perspective along the [010] crystallographic direction. Mo–C bonds to the η^5 -Cp ring have been omitted and replaced by a dashed bond to the corresponding centre of gravity (C_g).

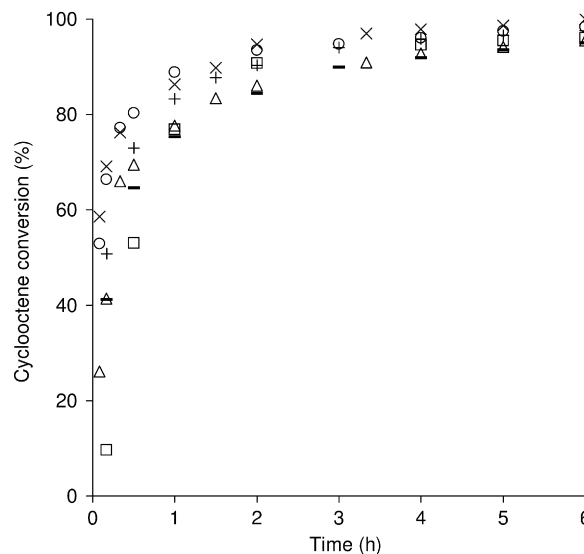


Fig. 3. Cyclooctene epoxidation with TBHP, at 55 °C, using compounds **1** (OB (Δ); OB-preH (\times); MW (\circ)), **1**-stored (OB (+)) without a co-solvent, or using **1** with *tert*-butanol (OB (–)) or diluted with *n*-decane (\square).

may be performed separately, i.e., prior to catalysis, or in situ during catalysis. The latter strategy is more attractive since one step is excluded from the catalyst preparation procedure. The direct use of **1** does not have a detrimental effect on the initial reaction rates [3,8a]. Furthermore, preliminary tests showed that **1** is stable for long periods without strict requirements for package sealing. Thus, when freshly prepared **1** was exposed to ambient light and air for 30 days at room temperature (giving **1**-stored), and then used in a catalytic run, the kinetic curve was nearly coincident with that obtained using **1** (Fig. 3); in fact the conversions with **1**-stored were slightly higher at any given reaction time. This stability is quite attractive when compared with Cp'MoO₂Cl complexes, for example, which need to be stored below room temperature unless the Cp' is fully substituted with benzyl groups (more difficult to synthesise) [7].

The reaction of cyclooctene with TBHP using the MW heating method gives cyclooctene oxide as the only reaction product, similar to that observed for the OB method. However, the initial reaction rate is higher in the case of the MW method, and the conversions after 6 h are similar for both heating methods (96–97%, Fig. 3, Table 3). The rate of the primary decarbonylation process to give active oxidising species may be enhanced by the MW method, leading to faster cyclooctene reaction. For example, several reports in the literature mention that MW heating enhances (when compared with OB heating) the rate of reaction of Mo(CO)₆ with Lewis base ligands (L) to give tetracarbonyl complexes of the type [M(CO)₄L] [15].

3.2.2. Solvent effects: MW vs OB method

The addition of a co-solvent can affect the overall catalytic reaction, and properties such as solvent polarity can become more significant with MW heating [20b]. Different organic non-coordinating solvents (hexane, toluene, 1,2-dichloroethane (DCE)) were tested in the cyclooctene reaction with TBHP, at 55 °C, using the OB and MW methods. The MW power input was optimised for each solvent to allow the temperature set point to be reached in 30–40 s, without overshooting (fixed power control (FPC) mode, 20 psi air), and followed the order (Table 3): hexane (210 W) > toluene (180 W) ≫ DCE (60 W). Variable amounts of heat may be generated due to MW absorption as a result of differences in the dielectric properties of the solvents (factors associated with the reactor emissivity, geometry and volume are neglected). The dielectric constant (ϵ') and dielectric loss factor (ϵ'') for the solvents (Table 3) follow an opposite order to that observed for the optimised power inputs (ϵ' , ϵ'' , both measured at 25 °C): hexane (1.9, 0.038) < toluene (2.4, 0.096) ≪ DCE (10.4, 1.321) [36]. For both heating methods the type of solvent does not affect the product selectivity, which was always 100% to the epoxide. However, the initial reaction rate (based on conversion after 20 min) for each solvent is higher for the MW method than for the OB one, similar to that observed without a co-solvent (Table 3). Conversion after 20 min follows the same order for both heating methods: hexane ≅ toluene < DCE. Possibly, DCE leads to enhanced stabilisation of polar intermediate states and higher solubility of the active metal species in comparison to the less polar solvents tested (the reaction mixture is initially homogeneous but then becomes opaque suggesting that **1** is more soluble than the related oxo-molybdenum species, under the applied reaction conditions).

3.2.3. Catalyst reuse: MW vs OB method

The effect of the heating method on catalyst recycling was investigated, without a co-solvent, at 55 °C, by adding a new charge of substrate and oxidant to the reaction vessel after the first 6 h (MW) or 24 h (OB) run, and monitoring a second reaction run of the same duration. For both heating methods, the conversion rate decreases from the first to the second run (Fig. 4). The following factors may

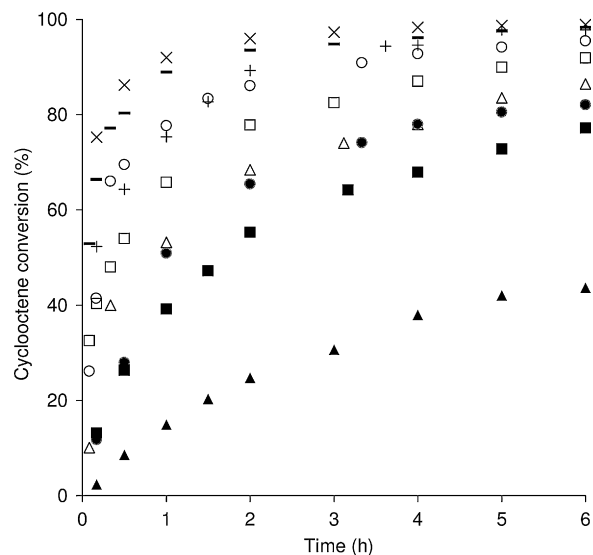


Fig. 4. Cyclooctene epoxidation with TBHP in the presence of complex **1**, at 55 °C, using the OB or MW (FPC mode) heating methods: OB/without co-solvent—1st (○) and 2nd (●) run; OB/[BMIM][BF₄]—1st (△) and 2nd (▲) run; MW/without co-solvent—1st (◻) and 2nd (◻+) run; MW/[BMIM][BF₄]—1st (◻) and 2nd (◻+) run. The same reaction using the DC mode, without co-solvent (×).

cause the reaction to slow down in the second run: (i) lower catalyst and olefin concentrations due to dilution, (ii) changes in the nature of the metal species, (iii) initial existence of *tert*-butanol, a by-product of the TBHP reaction, which may act as a competing base to TBHP in the coordination to the metal complex (Lewis acid) [3a,8b]. Hypothesis (i) is supported by the fact that the dilution of the cyclooctene/TBHP reaction system with *n*-decane (2 mL for 1.8 mmol olefin and 2.75 mmol TBHP) leads to a major reduction in initial reaction rate (conversion at 10 min/30 min is 10%/53%) in comparison to the reaction under more concentrated conditions (41%/70%), Fig. 3. With respect to hypothesis (ii), as mentioned above, the oxidative decarbonylation of **1** using TBHP in excess gives a mixture of the molybdenum(VI) complexes CpMoO₂CH₃ and CpMoO(O₂)CH₃, and it was recently shown that the latter is less active than the former [8a,8d]. Possibly, the concentration of CpMoO(O₂)CH₃ is higher than that of CpMoO₂CH₃ in the second run, causing the reaction to slow down. Hypothesis (iii) may be ruled out because the reaction of cyclooctene in the presence of an equimolar amount of *tert*-butanol (1:TBHP:olefin ratios as indicated in Section 2) gives similar results as those obtained without *tert*-butanol (Fig. 3).

When the kinetic profiles for the first and second runs are compared using the MW and OB methods (Fig. 4), the conversions in the second runs are 79–100% and 28–86% of those recorded for the first run (at any given reaction time between 1 and 6 h) for the MW and OB methods, respectively. The MW method leads to 98% conversion after 5 h in two consecutive runs, whereas in the case of the OB method conversion after 24 h in the second run continues slightly lower (97%) than that observed in the first run (100%). These results may be partly due to: (i) differences in the catalyst use time at 55 °C in each run for the MW and OB methods (the latter requires longer residence times for reaching the same conversion), and (ii) the faster kinetics in the case of the MW method.

3.2.4. Complex **1** in the ionic liquid [BMIM][BF₄]: MW vs OB method

Ionic liquids (ILs) efficiently absorb MW radiation due to their ionic character, which may considerably enhance the rates of chemical reactions [10,37,38]. Furthermore, ILs can be used as alternatives to inorganic solid supports for “immobilising” homo-

geneous catalysts and are “greener” than commonly used volatile organic solvents. The reaction of cyclooctene with TBHP in the presence of **1** was investigated using the IL [BMIM][BF₄], at 55 °C. This IL was chosen since it leads to excellent epoxide selectivity, is relatively stable in comparison to other ILs such as [BMIM][PF₆] [38a], and is relatively cheap. Complex **1** dissolves completely in the IL to give a transparent yellow solution, and the IL is immiscible with cyclooctene. In contrast to that observed for the organic solvents, no solid phase ever appeared in the **1**/IL reaction system. The MW power administered to the **1**/IL system was 20 W, which is lower than that for DCE or without a co-solvent (60 W). This may be due to the lower total volume of the reaction mixture in the case of the IL, and/or to a large amount of heat generated as a result of MW absorption by the IL.

The cyclooctene reaction in the presence of **1**/IL is slightly faster (especially in the initial stage) using the MW method instead of the OB one, and the epoxide is always the only reaction product, which is formed in 86% and 92% yield after 6 h for the OB and MW methods, respectively (Fig. 4). Such a small difference may be due to the mass transfer resistances involved in the liquid-liquid biphasic system, which levels off the temperature effect on the reaction kinetics.

When the catalyst/IL system is recovered and reused (following the procedure described in Ref. [37]), the cyclooctene reaction is slower than in the first batch, using the OB or MW method (Fig. 4). Active metal species may be partially extracted with the reagents/products during the work up procedures applied for IL/catalyst recycling, decreasing the catalyst concentration in the second batch and consequently affecting the overall reaction rate for both heating methods.

3.2.5. Factors responsible for the MW effect

Several explanations of the MW effects have been put forward, and it is somewhat controversial whether thermal (e.g., heating up time, temperature gradients) and/or specific (e.g., changes in thermodynamic properties and reaction profile) factors are mainly responsible [14b,d]. In order to get insight into the thermal effects, the temperature of the reaction mixture was measured as a function of time for the OB and MW methods (with and without co-solvent). For the OB method, the reaction temperature vs time curves for the three co-solvents are roughly coincident with that measured without a co-solvent (Fig. 5). While ca. 7 min were required to reach 55 ± 1 °C using the OB method, the same temperature was reached in less than 45 s using the MW one: for the OB method the temperature at ca. 45 s was always less than 38 °C. Hence, the observed MW effect (i.e., rate enhancement) may be simply due to the faster heating up of the reaction mixture increasing the overall epoxidation rates early on in the heating process. This hypothesis is further supported by a comparative study of the kinetic data obtained for the MW method (without co-solvent) with that obtained for an experiment performed in a similar fashion to the OB method, except that the oxidant and olefin were pre-heated separately (10 min at 55 °C) prior to their addition to the pre-heated reactor containing **1** (denoted OB-preH method). The kinetic profile for the OB-preH

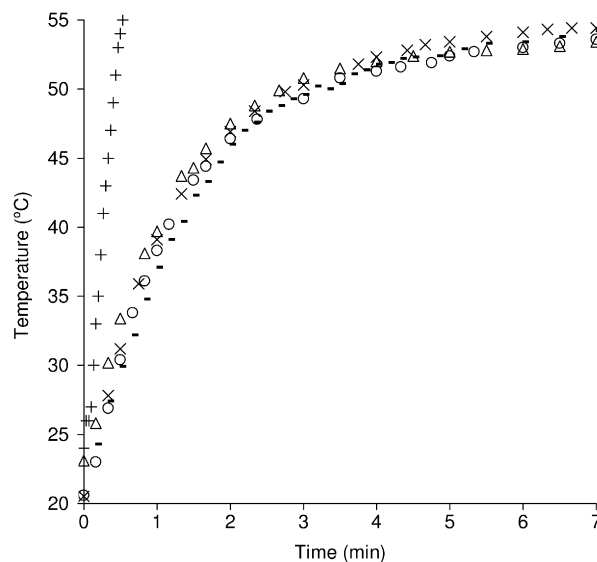


Fig. 5. Dependence of the temperature of the cyclooctene reaction mixture on time, using OB heating without co-solvent (—), with toluene (Δ), with 1,2-dichloroethane (×), or with hexane (○), or using MW heating without co-solvent (+).

method is nearly coincident with that observed for the MW method (Fig. 3).

The effect of the heating method was further investigated for the reaction of *R*-(+)-limonene with TBHP in the presence of **1**, without a co-solvent, during 2 h at 55 °C (Table 4). The main reaction product is 1,2-epoxy-*p*-menth-8-ene (limonene oxide), which is an intermediate used in the synthesis of perfumes, drugs, and food additives [39]. The optimised power input (OPI) using the FPC mode for limonene (15 W) was less than that for cyclooctene (60 W), possibly due to differences in the dielectric properties of the olefins, as discussed above for the different solvents. Similar to that observed for cyclooctene, the MW method enhances the initial reaction rate without affecting product selectivity: selectivity to limonene oxide at 80% conversion is 93% for both heating methods and the diastereoisomeric excess of *trans*-1,2-(+)-limonene oxide over *cis*-(1,2)-(+)–limonene oxide is 66% and 72% for the OB and MW methods, respectively.

The apparent activation energy (*E_a*) and pre-exponential factors were estimated for limonene and cyclooctene in the temperature range of 45–65 °C, using the OB, OB-preH and MW methods (Table 4). The values of *E_a* and pre-exponential factors are similar for the OB-preH and MW methods, but different for the OB method. The contrasting results observed for the OB method are due to the fact that the initial reaction rates are not calculated at the desired temperature as a result of the relatively slow heating process, and are thus erroneous. The similar results for the MW and OB-preH methods suggest that MW radiation does not induce relevant “selective heating” effects (e.g., thermodynamic properties, specific interactions, favourable reaction coordinate), under the applied reaction conditions.

Table 4
Olefin epoxidation with TBHP in the presence of **1** at 55 °C (without co-solvent).

Olefin	Conversion (%) ^a			<i>E_a</i> (kJ mol ⁻¹) and pre-exponential factor (mmol h ⁻¹)		
	MW	OB-preH	OB	MW	OB-preH	OB
<i>cis</i> -Cyclooctene	77/94	76/95	66/86	184 2.4 × 10 ³⁰	187 7.4 × 10 ³⁰	93 1.6 × 10 ¹⁵
<i>R</i> -(+)-Limonene	80/91	85/88	59/80	113 3.3 × 10 ¹⁹	107 3.5 × 10 ¹⁹	68 9.5 × 10 ¹⁰

^a Olefin conversion after 20 min/2 h reaction. The OPI for cyclooctene and limonene was 60 and 15 W, respectively.

Despite the similar results obtained using the MW and OB-preH methods, the former seems more attractive since pre-heating reagents implies additional process and energy costs. The reaction of *cis*-cyclooctene using the MW method can be further optimised to improve the catalytic results and/or minimise the energy consumption. For the fixed power control (FPC) mode (solventless conditions, 60 W, 55 °C), decreasing the pressure of air in the cooling system from 20 to 6 psi leads to temperature overshooting to 62 °C and consequently higher conversions are reached (66/89% and 81/93% after 10/60 min, for 20 and 6 psi air). For the lower air pressure, the optimised MW power input (OPI) is 40 W. As an alternative to the FPC operation mode, the dynamic control (DC) mode allows 15 s pre-mixing of the reaction mixture at room temperature prior to MW irradiation and the power varies (always smaller than or equal to the chosen MW power set point) until the temperature set point is reached: the OPI for 55 °C and 20 psi air is 60 W, similar to the FPC mode. However, the DC mode further enhances the initial reaction rate in comparison to the FPC mode: cyclooctene conversion after 10 min is 75% for the DC mode and 66% for the FPC mode, and after ca. 30 min the kinetic curves are roughly coincident (Fig. 4).

4. Conclusions

The comparison of microwave-assisted heating with conventional oil bath heating for olefin epoxidation using $\text{CpMo}(\text{CO})_3\text{CH}_3$ (1) as the catalyst precursor and TBHP as the oxidant has demonstrated that the heating method does not affect product selectivity (giving the epoxide as the only product from cyclooctene, and limonene oxide as the main product in >90% selectivity from *R*-(+)-limonene), but may significantly affect the reaction rate. In comparison with the OB method, the MW method benefits the initial reaction rate and shorter residence times are required for reaching the same conversion, which is favourable for process intensification. The MW method is also advantageous when volatile organics or the ionic liquid [BMIM][BF₄] are used as solvents, although low microwave absorbing solvents such as toluene and hexane require higher OPIs. The use of 1,2-dichloroethane as the co-solvent increases the rate of olefin epoxidation over that observed in the absence of a co-solvent, with the OPIs being the same (60 W) for both systems.

The observed MW effect (rate enhancement) under the applied reaction conditions is due to a faster heating up of the reaction mixture (resulting in a higher initial reaction rate) rather than to “selective heating” effects (e.g., thermodynamic properties, specific interactions, favourable reaction coordinate, reported in the literature for numerous other reaction systems). This hypothesis has been supported by (i) measuring the temperature as a function of time for the OB and MW methods, (ii) pre-heating the reagents and the reactor walls using the oil bath prior to reaction, which gives comparable catalytic results to those observed for the MW method, and (iii) the fact that for different olefins the MW and OB-preH methods give comparable *E_a* and pre-exponential factors (which are different from those using the OB method). In contrast to the MW method, the OB-preH method involves pre-heating the reagents, representing additional process and energy costs. For the MW method, the operating conditions may be further optimised, e.g., lower OPIs (energy consumption) are possible by decreasing the pressure of air in the cooling system.

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References

- [1] H.W. Roesky, I. Haiduc, N.S. Hosmane, *Chem. Rev.* 103 (2003) 2579.
- [2] M. Cousins, M.L.H. Green, *J. Chem. Soc.* (1963) 889.
- [3] (a) C. Freund, M. Abrantes, F.E. Kühn, *J. Organomet. Chem.* 691 (2006) 3718 (and references cited therein); (b) F.E. Kühn, A.M. Santos, M. Abrantes, *Chem. Rev.* 106 (2006) 2455 (and references cited therein).
- [4] M.K. Trost, R.G. Bergman, *Organometallics* 10 (1991) 1172.
- [5] W.R. Thiel, R.W. Fischer, W.A. Herrmann, *J. Organomet. Chem.* 459 (1993) C9.
- [6] F.E. Kühn, W.A. Herrmann, R. Hahn, M. Elison, J. Blumel, E. Herdtweck, *Organometallics* 13 (1994) 1601.
- [7] M. Abrantes, A.M. Santos, J. Mink, F.E. Kühn, C.C. Romão, *Organometallics* 22 (2003) 2112.
- [8] (a) J. Zhao, A.M. Santos, E. Herdtweck, F.E. Kühn, *J. Mol. Catal. A: Chem.* 222 (2004) 265; (b) A.A. Valente, J.D. Seixas, I.S. Gonçalves, M. Abrantes, M. Pillinger, C.C. Romão, *Catal. Lett.* 101 (2005) 127; (c) A. Capapé, A. Raith, F.E. Kühn, *Adv. Synth. Catal.* 351 (2009) 66; (d) A.M. Al-Ajlouni, D. Veljanovski, A. Capapé, J. Zhao, E. Herdtweck, M.J. Calhorda, F.E. Kühn, *Organometallics* 28 (2009) 639; (e) M. Abrantes, F.A.A. Paz, A.A. Valente, C.C.L. Pereira, S. Gago, A.E. Rodrigues, J. Klinowski, M. Pillinger, I.S. Gonçalves, *J. Organomet. Chem.* 694 (2009) 1826.
- [9] (a) K.R. Jain, F.E. Kühn, *Dalton Trans.* (2008) 2221 (and references cited therein); (b) M. Abrantes, S. Gago, A.A. Valente, M. Pillinger, I.S. Gonçalves, T.M. Santos, J. Rocha, C.C. Romão, *Eur. J. Inorg. Chem.* (2004) 4914; (c) A.M. Sakhivel, A.S.T. Abrantes, F.E. Chiang, F.E. Kühn, *J. Organomet. Chem.* 691 (2006) 1007; (d) M.A. Abrantes, C.C. Sakhivel, F.E. Romão, F.E. Kühn, *J. Organomet. Chem.* 691 (2006) 3137.
- [10] F.E. Kühn, J. Zhao, M. Abrantes, W. Sun, C.A.M. Afonso, L.C. Branco, I.S. Gonçalves, M. Pillinger, C.C. Romão, *Tetrahedron Lett.* 46 (2005) 47.
- [11] (a) S.S. Braga, S. Gago, J.D. Seixas, A.A. Valente, M. Pillinger, T.M. Santos, I.S. Gonçalves, C.C. Romão, *Inorg. Chim. Acta* 359 (2006) 4757; (b) S.S. Balula, A.C. Coelho, S.S. Braga, A. Hazell, A.A. Valente, M. Pillinger, J.D. Seixas, C.C. Romão, I.S. Gonçalves, *Organometallics* 26 (2007) 6857.
- [12] C.A. Gamelas, T. Lourenço, A.P. da Costa, A.L. Simplicio, B. Royo, C.C. Romão, *Tetrahedron Lett.* 49 (2008) 4708.
- [13] A.V. Biradar, B.R. Sathe, S.B. Umbarkar, M.K. Dongare, *J. Mol. Catal. A: Chem.* 285 (2008) 111.
- [14] (a) P. Lidström, J. Tierney, B. Wathey, J. Westman, *Tetrahedron* 57 (2001) 9225; (b) A. de la Hoz, Á. Díaz-Ortiz, A. Moreno, *Chem. Soc. Rev.* 34 (2005) 164; (c) M. Ardon, G. Hogarth, D.T.W. Oscroft, *J. Organomet. Chem.* 689 (2004) 2429; (d) W.C. Conner, G.A. Tompsett, *J. Phys. Chem. B* 112 (2008) 2110; (e) A. Bruckmann, A. Krebs, C. Bolm, *Green Chem.* 10 (2008) 1131.
- [15] (a) S.L. VanAtta, B.A. Duclos, D.B. Green, *Organometallics* 19 (2000) 2397; (b) A.C. Coelho, F.A. Almeida Paz, J. Klinowski, M. Pillinger, I.S. Gonçalves, *Molecules* 11 (2006) 940.
- [16] M. Larhed, C. Moberg, A. Hallberg, *Acc. Chem. Res.* 35 (2002) 717.
- [17] S.K. Badamali, J.H. Clark, S.W. Breden, *Catal. Commun.* 9 (2008) 2168.
- [18] D. Bogdal, A. Loupy, *Org. Process Res. Dev.* 12 (2008) 710.
- [19] D.D. Young, J. Nichols, R.M. Kelly, A. Deiters, *J. Am. Chem. Soc.* 130 (2008) 10048.
- [20] (a) S. Berardi, M. Bonchio, M. Carraro, V. Conte, A. Sartorel, G. Scorrano, *J. Org. Chem.* 72 (2007) 8954; (b) R. Luque, S.K. Badamali, J.H. Clark, M. Fleming, D.J. Macquarrie, *Appl. Catal. A: Gen.* 341 (2008) 154; (c) J.M. Hidalgo, M.J. Jurado, J.M. Campelo, R. Luque, A.A. Romero, *Catal. Lett.* 126 (2008) 179; (d) U.R. Pillai, E. Sahle-Demessie, R.S. Varma, *Tetrahedron Lett.* 43 (2002) 2909; (e) G. Wang, Z. Liu, Y. Liu, G. Liu, M. Xu, L. Wang, *Chin. J. Catal.* 29 (2008) 1159; (f) A.A. dos Santos, E.P. Wendler, F. De, A. Marques, F. Simonelli, *Lett. Org. Chem.* 1 (2004) 47; (g) G.D. Yadav, I.V. Borkar, *AIChE J.* 52 (2006) 1235.
- [21] (a) T.S. Piper, G. Wilkinson, *J. Inorg. Nucl. Chem.* 3 (1956) 104; (b) T.S. Piper, G. Wilkinson, *Naturwissenschaften* 42 (1955) 625.
- [22] R. King, *Organometallic Synthesis*, vol. 1, Academic Press, New York, 1965.
- [23] T.K. Panda, M.T. Gamer, P.W. Roesky, *Organometallics* 22 (2003) 877.
- [24] T. Kottke, D. Stalke, *J. Appl. Crystallogr.* 26 (1993) 615.
- [25] APEX2, Data Collection Software (version 2.1-RC13), Bruker AXS, Delft, The Netherlands, 2006.
- [26] Cryopad, Remote monitoring and control (version 1.451), Oxford Cryosystems, Oxford, UK, 2006.
- [27] RLATT: Reciprocal Lattice Viewer (version 3.0), Bruker AXS, Madison, WI, USA, 2000.
- [28] G.M. Sheldrick, Bruker-Nonius CELL.NOW, Bruker AXS, Delft, The Netherlands, 2004.
- [29] SAINT+, Data Integration Engine (version 7.23a), Bruker AXS, Madison, WI, USA, 2005.
- [30] G.M. Sheldrick, TWINABS: An Empirical Absorption Correction Program (version 1.05), Bruker AXS, Madison, WI, USA, 2002.

- [31] (a) G.M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 64 (2008) 112; (b) G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
- [32] H.D. Flack, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 39 (1983) 876.
- [33] (a) F.H. Allen, *Acta Crystallogr. Sect. B* 58 (2002) 380; (b) F.H. Allen, W.D.S. Motherwell, *Acta Crystallogr. Sect. B* 58 (2002) 407.
- [34] (a) R. Lai, J.-F. Berthome, I. Lyothier, C. Scheidecker, S. Martin, *Inorg. Chim. Acta* 350 (2003) 568; (b) M. Tamm, K. Baum, R. Fröhlich, P. Saarenketo, *Organometallics* 20 (2001) 1376; (c) R. Fierro, T.E. Bitterwolf, A.L. Rheingold, G.P.A. Yap, L.M. Liable-Sands, *J. Organomet. Chem.* 524 (1996) 19; (d) P. Jutzi, J. Schnittger, B. Neumann, H.-G. Stammler, *J. Organomet. Chem.* 410 (1991) C13; (e) W.L. Bell, C.J. Curtis, A. Miedaner, C.W. Eigenbrot, R.C. Haltiwanger, C.G. Pierpont, J.C. Smart, *Organometallics* 7 (1988) 691; (f) P.H. Bird, M.R. Churchill, *Inorg. Chem.* 7 (1968) 349.
- [35] (a) A.M. Martins, R. Branquinho, J.L. Cui, A.R. Dias, M.T. Duarte, J. Fernandes, S.S. Rodrigues, *J. Organomet. Chem.* 689 (2004) 2368; (b) H. Sitzmann, M.D. Walter, G. Wolmershauser, *Acta Crystallogr. Sect. E* 58 (2002) M777; (c) R. Lai, A. Archavlis, R. Faure, M. Sanz, *J. Chem. Soc., Dalton Trans.* (1997) 3259; (d) R. Lai, S. Martin, *Tetrahedron: Asymmetr.* 7 (1996) 2783; (e) B.E. Mouatassim, H. Elamouri, J. Vaissermann, G. Jaouen, *Organometallics* 14 (1995) 3296; (f) R. Lai, L. Bousquet, A. Heumann, *J. Organomet. Chem.* 444 (1993) 115; (g) H.G. Alt, J.S. Han, R.D. Rogers, *J. Organomet. Chem.* 445 (1993) 115; (h) R.D. Rogers, J.L. Atwood, M.D. Rausch, D.W. Macomber, *J. Crystallogr. Spectrosc. Res.* 20 (1990) 555.
- [36] B. Hayes, *Microwave Synthesis: Chemistry at the Speed of Light*, CEM Publishing, 2002.
- [37] (a) D.V. Kuznetsov, V.A. Raev, G.L. Kuranov, O.V. Arapov, R.R. Kostikov, *Russ. J. Org. Chem.* 41 (2005) 1719; (b) N.E. Leadbeater, H.M. Torenius, *J. Org. Chem.* 67 (2002) 3145.
- [38] (a) A.A. Valente, Ž. Petrovski, L.C. Branco, C.A.M. Afonso, M. Pillinger, A.D. Lopes, C.C. Romão, C.D. Nunes, I.S. Gonçalves, *J. Mol. Catal. A: Chem.* 218 (2004) 5; (b) S. Gago, S.S. Balula, S. Figueiredo, A.D. Lopes, A.A. Valente, M. Pillinger, I.S. Gonçalves, *Appl. Catal. A: General* 372 (2010) 67.
- [39] (a) A. Bordoloi, F. Lefebvre, S.B. Halligudi, *J. Mol. Catal. A: Chem.* 270 (2007) 177; (b) P. Oliveira, M.L. Rojas-Cervantes, A.M. Ramos, I.M. Fonseca, A.M.B. do Rego, *J. Vital, Catal. Today* 118 (2006) 307.