Influence of Cyclodextrins on Catalytic Olefin Epoxidation with Metal–Carbonyl Compounds. Crystal Structure of the TRIMEB Complex with CpFe(CO)$_2$Cl

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The cyclopentadienyl metal–carbonyls CpFe(CO)$_2$Cl and CpMo(CO)$_3$Cl, and their 1:1 inclusion complexes with β-cyclodextrin (β-CD) and permethylated β-CD (TRIMEB), were prepared, and the TRIMEB adduct with CpFe(CO)$_2$Cl was structurally characterized by single-crystal X-ray diffraction. The complex crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 11.189(3)$ Å, $b = 25.149(6)$ Å, $c = 28.964(7)$ Å and $Z = 4$ formula units. One CpFe(CO)$_2$Cl guest molecule, disordered over two sites, is completely enclosed in the TRIMEB cavity. The cyclodextrin molecules pack in columns parallel to the crystallographic a axis and make an angle of 33.6° with the bc plane. The oxidative decarbonylation of the free and encapsulated complexes by aqueous *tert*-butylhydroperoxide (*t*-BuOOH) or aqueous H$_2$O$_2$ was studied at room temperature by quantifying the CO/CO$_2$ liberated in the gas phase. When CpMo(CO)$_3$Cl is encapsulated in CDs, the extent of the decarbonylation by *t*-BuOOH is reduced. The use of H$_2$O$_2$ as oxidant modifies the reactivity in an unexpected fashion. Thus, the β-CD adduct almost totally resists oxidation by H$_2$O$_2$, whereas the TRIMEB adduct decarbonylates faster than the nonincluded complex during the early stages of the reaction. CpMo(CO)$_3$Cl and the two inclusion complexes were examined as catalyst precursors for the epoxidation of cyclooctene at 295 or 328 K, using *t*-BuOOH in decane or water, or aqueous H$_2$O$_2$, as oxidants. Although the free complex is essentially inactive as a catalyst precursor with aqueous H$_2$O$_2$, the introduction of CDs to the system instills significant catalytic activity, with cyclooctene oxide being the only observed reaction product.

Introduction

Recent work has shown that cyclopentadienyl molybdenum tricarbonyl complexes (η^5-C$_5$R$_5$)Mo(CO)$_3$X (X = Cl, alkyl, or *ansa*-alkyl) are effective catalyst precursors in liquid-phase (CHCl$_3$) olefin epoxidation.[1] In situ oxidation by *tert*-butylhydroperoxide (*t*-BuOOH) gives the actual Mo^{VI} catalysts. In several cases it has been shown that the (η^5-C$_5$R$_5$), Cl, and/or alkyl ligands are retained during the in situ oxidation step, leading to the oxide (η^5-C$_5$R$_5$)MoO$_2$X and/or the peroxide (η^5-C$_5$R$_5$)MoO(O$_2$)X.[1a] More complex species may also be formed as in the analogous oxidation of (CpBz)Mo(CO)$_3$Me (CpBz =

C$_5$(CH$_2$Ph)$_5$) that gives [(CpBz)MoO$_2$]$_2$(μ-O).[1d] In any case all of these organometallic oxides are active homogeneous catalysts for cyclooctene epoxidation in CHCl$_3$. Their chemistry in aqueous medium has also been investigated recently,[2] confirming that some of them are active in cyclooctene epoxidation provided that *t*-BuOOH is used as oxidant.[1d] So far, none of them was active with H$_2$O$_2$ as oxidant. Although these homogeneous catalysts can be recovered from the CHCl$_3$ reaction mixtures and reused, the catalytic activities tend to decrease with successive recycling runs, and catalyst losses are inevitable. The classic ways to circumvent these problems are catalyst heterogenization and two-phase homogeneous catalysis. For the complexes (η^5-C$_5$R$_5$)Mo(CO)$_3$X, both alternatives have been

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tested, namely, direct grafting or tethering of the complexes on microporous zeolites and ordered mesoporous materials,[3] and immobilization of the complexes in room temperature ionic liquids.[4]

Another potentially interesting approach for the modification of catalytic systems based on metal complexes involves the use of cyclodextrins (CDs) as protective agents.[5] CDs are cyclic oligosaccharides that form inclusion complexes with a wide range of molecules, including organic and metallo-organic species.[6] The use of cyclodextrins in molybdenum-catalyzed olefin epoxidation may be particularly advantageous in cases where the "free" catalyst is initially highly active but loses activity during the reaction as a result of decomposition. Immobilization in a CD host may help to stabilize the catalyst and also facilitate subsequent recycling. Furthermore, cyclodextrins are excellent organic supports to work in aqueous solutions. We recently described the immobilization of the cyclopentadienyl carbonyl complexes $CpFe(CO)_2Cl$, $CpMo(CO)_3Cl$ and $CpMo(CO)_3CH_2CONH_2$ ($Cp = \eta^5\text{-}C_5H_5$) in native β-CD and permethylated β-CD (TRIMEB) by tailored methods.[5f,7] In general, adducts with a 1:1 (host:guest) stoichiometry were obtained. The inclusion compounds containing $CpMo(CO)_3CH_2CONH_2$ could be used directly as precursors to catalysts for the liquid-phase epoxidation of cyclooctene using *t*-BuOOH.[5f] The results indicated that the β-CD adduct had potential to be used in heterogeneous solid–liquid systems (under nonaqueous conditions with *n*-decane or *n*-decane plus 1,2-dichloroethane), whereas the TRIMEB inclusion compound was more suited to homogeneous (*n*-decane) or liquid–liquid (water/*n*-hexane) biphasic systems.

In the present article we report on the ability of the CD-$CpM(CO)_nCl$ inclusion compounds to catalyze cyclooctene epoxidation following in situ activation by *t*-BuOOH or H_2O_2. The CO releasing profiles of the compounds are also presented. In the course of this study, single crystals of the $CpFe(CO)_2Cl$ adduct with TRIMEB were obtained, and the structure is described herein. To the best of our knowledge, this is the first report of a crystal structure determination for a TRIMEB−organometallic inclusion complex.

Experimental Section

General Comments. β-CD (Kleptose) was kindly donated by Laboratoires Roquette (France) and heptakis-2,3,6-tri-*O*-methyl-β-CD (TRIMEB) was obtained from Fluka. The oxidants *t*-BuOOH (T-Hydro 70 wt % solution in water or 5.5 M solution in decane) and H_2O_2 (30 wt % solution in water, ACS reagent) were obtained from Sigma-Aldrich. The cyclopentadienyl metal–carbonyl compounds $CpM(CO)_nCl$ [M = Fe, n = 2 (**1**); M = Mo, n = 3 (**2**)] and the corresponding 1:1 cyclodextrin inclusion complexes,

designated as **1**@β-CD, **1**@TRIMEB, **2**@β-CD, and **2**@TRIMEB, were prepared as described previously.[7]

X-ray Crystallography. Orange crystals of **1**@TRIMEB were obtained by cooling of a supersaturated solution of the inclusion complex in a water/ethanol mixture from 313 to 288 K over 30 min. The crystals were mounted on glass fibers using Paratone-N oil and cooled to 100 K in a stream of dry nitrogen. Intensity data were collected on a Bruker-Nonius APEX2 Version 1.8-6 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), and corrected for Lorentz and polarization factors (SAINT and XPREP).[8] The structure was solved by direct methods (SIR97)[9] and refined (on F) by full-matrix least-squares techniques.[10] The cyclopentadienyl iron carbonyl guest molecule was disordered over two sites, the site occupation factors for which were refined and constrained to add up to unity. The atomic positions for molecule **a** were in some cases so close to those for **b** that conventional least-squares refinement was not applicable. A constrained refinement was performed in which the $Fe(CO)_2Cl$ units were assumed to have mirror symmetry, with Fe and Cl in the plane, and to be identical. The cyclopentadienyl groups were made to have 5/m symmetry, but different orientations relative to the $Fe(CO)_2Cl$ fragment were allowed. All C−H distances were constrained at 0.95 Å. Anisotropic temperature factors were refined in the TLS model; a joint TLS for the two part molecules of the complex, and one for the cyclodextrin. Additional librations for pendant side chains of the cyclodextrin were also included.

Crystal Data for 1@TRIMEB. $C_{70}H_{117}ClFeO_{37}$, M_r = 1642.01, orange needle (0.42 × 0.10 × 0.09), orthorhombic, space group $P2_12_12_1$ (No. 19), a = 11.189(3) Å, b = 25.149(6) Å, c = 28.964(7) Å, V = 8150(3) Å^3, Z = 4, ρ_{calc} = 1.338 g cm^{-1}, λ (Mo Kα) = 0.71073 Å, F(000) = 3504, μ = 0.3063 mm^{-1}, T = 100 K, 98473 reflections were collected in the range 2.8° < 2θ < 52.6°, index range $-13 \leq h \leq 13$, $-27 \leq k \leq 31$, $-33 \leq l \leq 36$, of which 16 705 were independent [R(int) = 0.170] and 6527 with $I \geq 3\sigma(I)$ were observed, final R_1 [$I > 3\sigma(I)$] = 0.080, wR_1 [$I > 3\sigma(I)$] = 0.090, $w = \{\{[\sigma_{cs}(F^2) + B + (1 + A)F^2]^{1/2} - |F|\}^2\}^{-1}$ where A = 0.05 and B = 5.0, no data/restraints/parameters 6527/1785/395, goodness of fit on (F) = 1.404. In the final difference map, the highest peak was 1.2(1) e Å^{-3}.

Oxidative Decarbonylation Studies. The oxidative decarbonylation of the two metal–carbonyl compounds and their cyclodextrin adducts was studied by analyzing the gaseous mixture produced during reaction of the compounds with either aqueous *t*-BuOOH or aqueous H_2O_2. The tests were carried out at room temperature under nitrogen in a vessel specially designed for this purpose and equipped with a magnetic stirrer. The concentrations of **1**, **2**, and the inclusion complexes were in the range of 6.8–11.9 mM, and the ratios of concentrations of the oxidants relative to the complexes were 100:1 for **1**, **2**, and the β-CD adducts and 85:1 for the TRIMEB adducts. Samples were taken after 1, 3, 5, and 24 h and analyzed using a Thermofinnigam Trace GC equipped with a CTR1 column from Alltech and a thermal conductivity detector. CO and CO_2 were quantified using a calibration curve recorded prior to the reaction course. No significant amounts of CO and CO_2 were liberated when blank reactions in the absence of the oxidants were performed.

Catalytic Olefin Epoxidation. The liquid-phase oxidation of *cis*-cyclooctene (Cy8) was carried out in a micro reaction vessel equipped with a magnetic stirrer and immersed in a thermostatted oil bath. Two different sets of conditions were employed, referred to as C1 (similar to those used for the oxidative decarbonylation studies, with an oxidant:Mo molar ratio of 100:1) and C2 (similar

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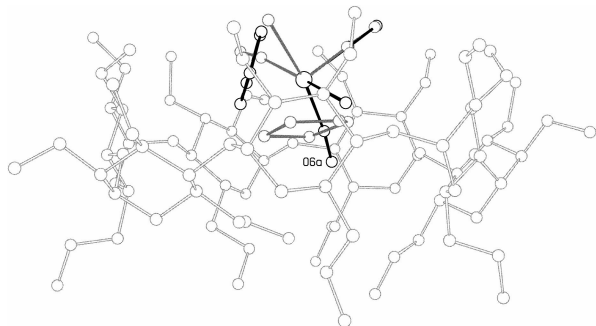
Figure 1. ORTEP drawing of **1**@TRIMEB perpendicular to the best plane through the cyclodextrin. Molecule **a** is drawn in black, **b** in dark grey, and the cyclodextrin is light grey with open bonds.

to those commonly used in the literature for Cy8 epoxidation catalyzed by oxomolybdenum(VI) complexes). Conditions for C1: 295 K, under nitrogen, 1 mL water, 10 μmol Mo, 0.62 mmol Cy8, oxidant = 1 mmol aqueous *t*-BuOOH (denoted as C1-aqBuOOH) or H_2O_2 (denoted as C1-aqH$_2$O$_2$). Conditions for C2: 328 K, under air, without cosolvent, 6.2 μmol Mo, 0.62 mmol Cy8, oxidant = 1 mmol aqueous *t*-BuOOH (denoted as C2-aqBuOOH) or H_2O_2 (denoted as C2-aqH$_2$O$_2$), or 0.62 mmol *t*-BuOOH (5.5 M in decane, denoted as C2-BuOOH). Samples were withdrawn periodically and analyzed using a Varian 3900 GC equipped with a capillary column (SPB-5, 20 m × 0.25 mm × 0.25 μm) and a flame ionization detector. Undecane was used as an internal standard added after the reaction.

Results and Discussion

One of the main aims of the present study is the evaluation of the potential of cyclodextrins to enable and/or improve catalytic epoxidation of olefins with cyclopentadienyl metal–carbonyl compounds in aqueous solution. The whole process requires the preparation of the inclusion complexes of the $CpM(CO)_nCl$ compounds, the understanding of their oxidation by *t*-BuOOH or H_2O_2 in aqueous solution, and the study of the catalytic performance of the resulting species. The varied and still not totally explored chemistry of the $Cp'MoO_2X$ catalysts in aqueous solution suggests the presence of a complex interplay of intermediate active and inactive oxide species. Far from attempting a thorough understanding of the whole system, we briefly surveyed one of the most obvious features of the catalytic system: the oxidative decarbonylation step. Although the catalytic examinations will focus on the $CpMo(CO)_3Cl$ precursor (**2**), the related $CpFe(CO)_2Cl$ (**1**) and its inclusion complexes have been used to get a broader picture of the reactivity of these complexes toward the oxidants *t*-BuOOH and H_2O_2. Since the derivatization of the CD host clearly plays a role in defining solubility and other properties of the inclusion complexes, we decided to study a group of six complexes: **1**, **1**@β-CD, **1**@TRIMEB, **2**, **2**@β-CD, and **2**@TRIMEB.[7]

Fortunately, it was found that upon cooling of a solution of **1**@TRIMEB, crystals of quality suitable for X-ray diffraction characterization were easily obtained, enabling a thorough crystallographic characterization of the adduct.

Crystal Structure of the Inclusion Complex 1@ TRIMEB. The complex **1**@TRIMEB crystallized in a 1:1 stoichiometry (Figure 1). Its structure is isomorphous to the Ub phase described by Cardinael et al.,[11a] a type of packing also found for complexes of TRIMEB with several other organic
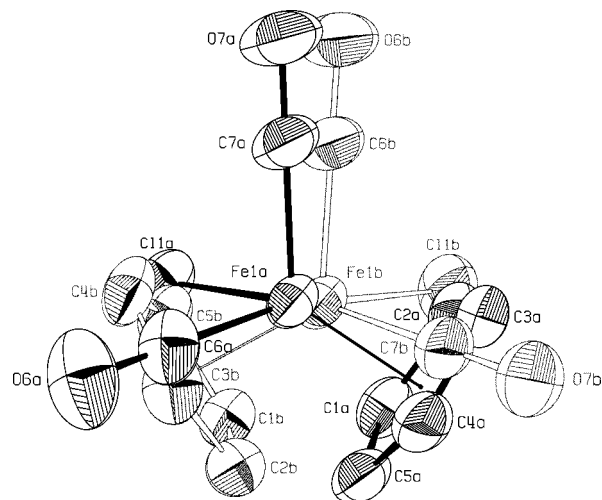

Figure 2. ORTEP drawing of the disordered iron complex in the inclusion complex **1**@TRIMEB. The molecule with the highest occupation factor, **a**, is drawn in black. Selected bond distances (Å) and angles (deg): Fe1a−C6a = Fe1a−C7a = 1.747(12), Fe1b−C6b = Fe1b−C7b = 1.747(22), Fe1a−Cl1a = 2.252(7), Fe1b−Cl1b = 2.252(22), Fe1a−Cpa = 1.720(10), Fe1b−Cpb = 1.717(23) (Cp is the center of the cyclopentadienyl group), Cpa−Fe1a−C6a = Cpa−Fe1a−C7a = 122.0(6), Cpb−Fe1b−C6b = Cpb−Fe1b−C7b = 125.5(13), Cpa−Fe1a−Cl1a = 121.6(5), Cpb−Fe1b−Cl1b = 122.1(11), C6a−Fe1a−Cl1a = C7a−Fe1a−Cl1a = C6b−Fe1b−Cl1b = C7b−Fe1b−Cl1b = 89.8(4), C6a−Fe1a−C7a = C6b−Fe1b−C7b = 97.5(5).

molecules.[11] The guest molecule in **1**@TRIMEB is disordered over the two sites **a** and **b** with occupation factors of 0.689(5) for **a** and 0.311(5) for **b**. Each iron atom is tetrahedrally coordinated to one cyclopentadienyl group, one chlorine atom, and two carbonyl groups. The iron and one carbonyl of **a** and **b** are almost superimposed, and the two pairs are related by a pseudo mirror plane (Figure 2). The guest molecule is roughly centered above the cyclodextrin with a carbonyl group (C6a-O6a) of **a** directed toward the cavity of the host molecule. Figure 3 shows the packing of the TRIMEB molecules in the crystal. The cyclodextrin molecules pack in columns parallel to the crystallographic *a* axis and make an angle of 33.6° with the *bc* plane.

Oxidative Decarbonylation Studies. Table 1 shows the amounts of CO and CO_2 detected during the reaction of $CpFe(CO)_2Cl$ (**1**), $CpMo(CO)_3Cl$ (**2**), and the cyclodextrin inclusion complexes with a large excess of *t*-BuOOH and H_2O_2 in water. The molybdenum compound **2** reacts faster with *t*-BuOOH than with H_2O_2, giving mainly CO with both oxidants, whereas the iron compound **1** reacts faster with H_2O_2, giving mainly CO_2. With *t*-BuOOH and compound **2**, there is a rapid increase in CO and CO_2 during the first 5 h of reaction, followed by a slow increase up to 24 h. A drop in the CO:CO_2 ratio from about 11:1 at 3 h to 9:1 at 24 h suggests that some species has formed that slowly oxidizes CO to CO_2. The oxidative decarbonylation of **2** with *t*-BuOOH in decane (**2**:*t*-BuOOH = 1:10) proceeds slightly differently.[1c] Thus, this system liberates CO in an essentially quantitative manner after 4 h at room temperature. Traces of CO_2 are found at a CO:CO_2 ratio of ca. 80:1, and this ratio does not vary if the reaction mixture is left

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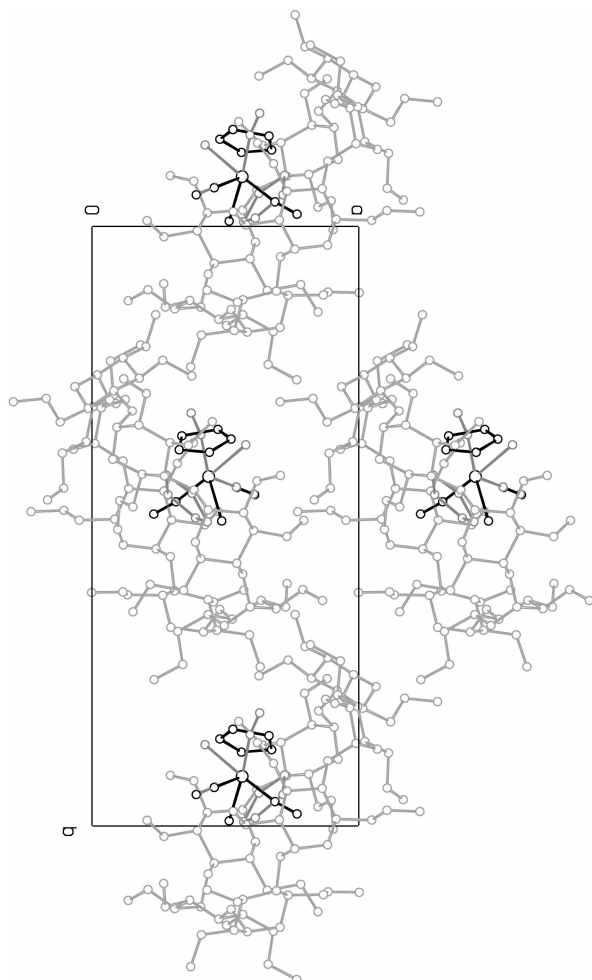
Figure 3. ORTEP drawing of **1**@TRIMEB showing the packing. Molecule **a** is drawn in black, **b** in dark grey, and the cyclodextrin is light grey with open bonds.

Table 1. Equivalents of CO and CO₂ Released with Either Aqueous *t*-BuOOH or Aqueous H₂O₂

		t-BuOOH		H₂O₂	
compound	time/h	CO	CO₂	CO	CO₂
CpFe(CO)₂Cl (**1**)	1	0.00	0.00	0.84	1.36
	3	0.04	0.04	0.66	2.62
	5	0.16	0.09	0.45	2.32
	24	0.81	0.97	0.36	2.14
1@β-CD	1	0.00	0.04	0.11	0.21
	3	0.00	0.09	0.10	0.46
	5	0.05	0.15	0.27	1.49
	24	0.62	0.65	0.58	8.24
1@TRIMEB	1	0.00	0.00	0.41	0.43
	3	0.07	0.02	0.66	1.45
	5	0.13	0.07	0.75	2.73
	24	0.50	0.65	0.84	8.94
CpMo(CO)₃Cl (**2**)	1	0.38	0.02	0.09	0.00
	3	1.67	0.15	0.47	0.03
	5	2.63	0.25	1.05	0.09
	24	2.86	0.33	2.87	0.37
2@β-CD	1	0.10	0.00	0.00	0.00
	3	0.20	0.03	0.00	0.00
	5	0.31	0.06	0.00	0.00
	24	0.35	0.20	0.11	0.00
2@TRIMEB	1	0.19	0.00	0.43	0.01
	3	1.02	0.07	1.60	0.11
	5	1.63	0.15	1.94	0.16
	24	1.95	0.25	1.61	2.05

stirring for 24 h. On a preparative scale, the reaction between **2** and *t*-BuOOH forms mainly CpMoO₂Cl, isolated in 55%

yield.[1a] No other products were reported, but it is quite likely that at least CpMoO(O₂)Cl is also formed as described for the similar oxidation of CpMo(CO)₃Me that produces CpMoO₂Me and CpMoO(O₂)Me[1b] and for the Cp*Mo(CO)₃Cl analogue.[12] Other products may include dimers like [CpMoO₂]₂(μ-O) as has been found for the similar oxidation of (CpBz)Mo(CO)₃Me,[1d] as well as their corresponding peroxo species. The formation of such dimers, formally of the composition Cp'MoO₂X where X = [Cp'MoO₃]⁻, suggests that [CpMoO₃]⁻ may also be present.

In the oxidative decarbonylation of **2** with aqueous H₂O₂ as the oxidant, the final outcome (at 24 h) is essentially the same as that observed for aqueous *t*-BuOOH, even though the initial decarbonylation rate is clearly slower. At 5 h only ca. 1.1 equiv of the initially coordinated CO has been liberated (as CO + CO₂) as compared with 2.9 equiv released with *t*-BuOOH.

In the reaction of **1** with *t*-BuOOH, there is a short induction period of about 1 h before evolution of CO and CO₂ begins. During the whole reaction course the amounts of CO and CO₂ are roughly equal, and the decarbonylation is almost complete by 24 h. With H₂O₂ as the oxidant, the highest CO value is at 1 h and then decreases by about 50% to a roughly constant value of 0.4 at 5–24 h. The amount of CO₂ increases sharply during the first 3 h, reaching a maximum of 2.6 equiv. The sharp rise in CO₂ levels between 1 and 3 h cannot be completely explained by the concurrent oxidation of CO, since the total number of equivalents of CO and CO₂ produced after 3 h is 65% higher than the number of carbonyl groups present in **1**. The excess must be due to decomposition of the cyclopentadienyl group. A Fenton-like process may be responsible for this degradation, possibly involving highly reactive hydroxyl free radicals.[13]

When **1** and **2** are encapsulated in cyclodextrins, the extent of the decarbonylation by *t*-BuOOH (after 24 h) is clearly reduced, as might be expected. The amounts of CO and CO₂ detected for **1**@β-CD after a given time period are roughly the same as those detected for **1**@TRIMEB. By contrast, the **2**@TRIMEB adduct liberates 2.2 equiv of initially coordinated CO after 24 h (as CO + CO₂ with CO:CO₂ = 7.8:1), compared with only ca. 0.5 equiv for the **2**@β-CD adduct (CO:CO₂ = 1.8:1). The use of H₂O₂ as oxidant modifies the reactivity in an unexpected fashion. Thus, the **2**@β-CD adduct almost totally resists oxidation by H₂O₂. On the other hand, **2**@TRIMEB decarbonylates faster than unprotected **2** in the initial 5 h and later decarbonylates completely to give more CO₂ than CO. The actual amount of gas liberated (CO + CO₂ = 3.7 equiv) is greater than the expected limit of 3 equiv. This can only mean that a new kind of oxidation catalyst has been formed that is capable of oxidizing either the Cp ring or the cyclodextrin carbons (or both). For the cyclodextrin adducts containing the iron dicarbonyl guest, between 8 and 9 equiv of CO₂ is produced after 24 h, which points to significant decomposition of the organic host molecules.

Cyclooctene Epoxidation. The influence of cyclodextrins on the catalytic activity of CpMo(CO)₃Cl (**2**) was tested by comparing the performance of **2**, **2**@β-CD, and **2**@TRIMEB as catalyst precursors in the epoxidation of cyclooctene using *t*-BuOOH in decane or water, or aqueous H₂O₂, as oxidants and

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(13) (a) Goldstein, S.; Meyerstein, D. *Acc. Chem. Res.* **1999**, *32*, 547–550, and references therein. (b) Rodriguez, M. L.; Timokhin, V. I.; Contreras, S.; Chamarro, E.; Esplugas, S. *Adv. Environ. Res.* **2003**, *7*, 583–595. (c) Anastasi, A. E.; Lienke, A.; Comba, P.; Rohwer, H.; McGrady, J. E. *Eur. J. Inorg. Chem.* **2007**, 65–73.

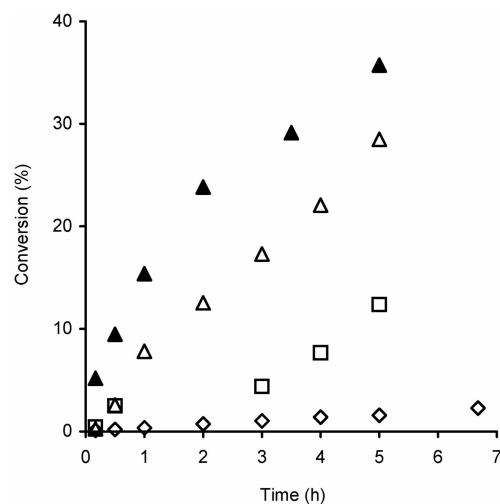**Table 2. Cyclooctene Epoxidation with CpMo(CO)₃Cl (2) and the Two Cyclodextrin Inclusion Complexes at 328 K**

sample	oxygen donor	initial activity (mol mol$_{Mo}^{-1}$ h^{-1})[a]	run 1/run 2 conversions (%)[b]
2	*t*-BuOOH in decane	403	95/84[c]
2@β-CD	*t*-BuOOH in decane	283	98/92[d]
2@TRIMEB	*t*-BuOOH in decane	364	95/82[c]
2	*t*-BuOOH aqueous	108	80
2@β-CD	*t*-BuOOH aqueous	102	80
2@TRIMEB	*t*-BuOOH aqueous	106	79
2	H₂O₂	<1[e]	5
2@β-CD	H₂O₂	6[e]	45/62[c]
2@TRIMEB	H₂O₂	2[e]	16

[a] Calculated for 10 min reaction time. [b] Cyclooctene conversion at 24 h reaction time for the first and second runs. [c] The second run was carried out by recharging the reactor at 24 h with equimolar amounts of oxidant and cyclooctene. [d] The second run was carried out using the solid recovered from the first run. [e] Calculated for 3 h reaction time.

no additional solvent. In general, the reaction was entirely selective for epoxidation with no byproduct (e.g., the 1,2-diol) observed. When the aqueous solutions of the oxidants were used, the reaction mixtures consisted of two immiscible liquid phases, i.e., an organic phase containing cyclooctene and cyclooctene oxide and an aqueous phase containing the oxidant, cyclodextrin, and molybdenum species. With the exception of **2@β-CD**, no solid precipitated upon addition of cyclooctene. Control experiments carried out without the precursors or in the presence of β-CD hydrate or TRIMEB showed that the noncatalytic contributions were negligible.

Under the reaction conditions referred to as C1-aqH₂O₂, which comprise a reaction temperature (295 K) and oxidant: precursor molar ratio (100:1) equal to those used in the oxidative decarbonylation studies, the cyclooctene conversions at 24 h were less than 2% for all three molybdenum-containing compounds used as catalyst precursors. Referring to the CO/CO₂ measurements described above, this very low activity cannot be attributed to a very slow oxidative decarbonylation step (at least for **2** and **2@TRIMEB**). With *t*-BuOOH as the oxidant instead of H₂O₂ (C1-aqBuOOH), cyclooctene conversion reached 41% after 24 h when the bulk compound **2** was used as the catalyst precursor. A conversion of 32% was obtained for **2@β-CD**, which is quite respectable given that the oxidative decarbonylation studies indicate that the extent of decarbonylation under these conditions is probably greatly reduced as compared with that of nonincluded **2**. Surprisingly, even though the oxidative decarbonylation is faster with the more soluble **2@TRIMEB** adduct, no catalytic activity was observed under these conditions. The difference in catalytic activity for the three molybdenum-containing compounds are therefore not easily correlated with the CO/CO₂ evolution results and are presumably related with differences in the kinetics of formation of the oxomolybdenum species, as well as differences in the nature and stability of these species.

The results described above are in line with previous findings that established that Cp*MoO₂Cl and [Cp*MoO₂]₂(μ-O) are unable to activate aqueous H₂O₂ for cyclooctene epoxidation.[1d] Indeed, we were able to confirm that the low activity of **2** continues even after increasing the reaction temperature to 328 K and increasing the oxidant:precursor molar ratio to 160:1 (C2-aqH₂O₂; Table 2, Figure 4). Interestingly, the results depicted in Table 2 and Figure 4 reveal that, to a certain extent, the introduction of cyclodextrins to the system instills some catalytic epoxidation activity under these particular reaction conditions with aqueous H₂O₂ as the oxidant. Albeit very small in absolute terms, the relative differences in reaction rate between the three

Figure 4. Kinetic profiles of cyclooctene epoxidation using aqueous H₂O₂ as oxidant, at 328 K (conditions C2-aqH₂O₂), in the presence of CpMo(CO)₃Cl (**2**) (◇), **2@β-CD** (△ run 1, ▲ run 2), and **2@TRIMEB** (□).

compounds becomes more pronounced (Table 2). Whereas the species derived from **2** are essentially inactive, cyclooctene epoxidation with the precursors **2@β-CD** and **2@TRIMEB** attains epoxide yields at 24 h of 45% and 16%. The reaction mixtures containing the cyclodextrins turned yellow (especially in the organic phase), whereas that initially containing complex **2** turned blue (in the aqueous phase), signaling decomposition. A color change to yellow is expected when molybdenum(VI) organometallic oxides such as CpMoO₂X are formed from tricarbonyl precursors.[1a,d] The cyclodextrin hosts therefore seem to have a beneficial effect on the performance of **2** as a catalyst precursor under these conditions. We may speculate that the CD hosts allow a more selective transformation of the precursor complex into the active metal species and/or enhance the stability of the resultant active species (by promoting a hydrophobic medium in the vicinity of the metal complexes).

To further assess the stability of the catalyst system derived from the inclusion complex **2@β-CD**, a second reaction run was carried out by recharging the reactor with the olefin and H₂O₂ after 24 h. As shown in Figure 4, the reaction rate for the second run was even higher than that for the first run, possibly due to the higher initial molar ratio of oxidant:olefin in the second run as a result of the incomplete consumption of the oxidant in the first run. The catalytic performance in the first run may also be held back by a sluggish oxidative decarbonylation step (cf. the CO/CO₂ release study carried out at 295 K). We cannot exclude the additional possibility that the catalyst initially formed may decompose to an even more active catalyst as the catalysis proceeds.[1g] The catalyst system would be very attractive if the workup procedure could involve the straightforward separation of the epoxide by decantation of the organic phase after all of the olefin had been used up. Unfortunately, this is not possible because the catalyst does not remain entirely encapsulated and is distributed in all phases as shown by the following experiment. The reaction mixture was cooled to ambient temperature after 24 h and centrifuged, and the organic phase was removed. The reactor containing the aqueous phase and the solid was then recharged with H₂O₂ and cyclooctene in amounts identical to those used in the first run. Conversion after 24 h was only 4% compared with 45% in the first run, indicating that the organic phase contained dissolved active species, which play a major role in the epoxidation reaction. Further workup
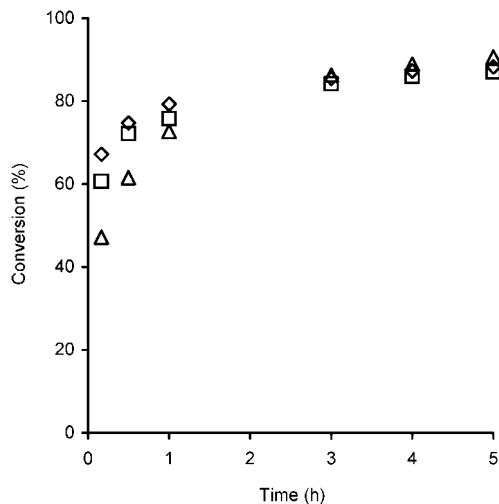
Figure 5. Kinetic profiles of cyclooctene epoxidation using *t*-BuOOH (in decane) as oxidant, at 328 K (conditions C2-BuOOH), in the presence of CpMo(CO)$_3$Cl (**2**) (◇), **2**@β-CD (△), and **2**@TRIMEB (☐).

procedures would therefore be required for catalyst−product separation. These results may also explain, in part, why no clear parallel can be drawn between the different catalytic performances and the corresponding CO/CO$_2$ release profiles.

When the cyclooctene epoxidation reaction was performed under the conditions referred to as C2-aqBuOOH (328 K, oxidant:precursor = 160:1), the catalytic results for compounds **2**, **2**@β-CD, and **2**@TRIMEB improved significantly compared with those obtained under the C1-aqBuOOH and C2-aqH$_2$O$_2$ conditions. Interestingly enough, the behavior of the three compounds was "leveled" since the kinetic profiles for all three systems were nearly coincident (not shown), and the initial activities (102–108 mol mol$_{Mo}^{-1}$ h^{-1}) and conversions after 24 h were very similar (ca. 80%, Table 2). The reasonably high conversions obtained after 24 h indicate that the catalysts tolerate water to a considerable extent under the conditions used and confirm previous exploratory results with Cp*MoO$_2$Cl and [Cp*MoO$_2$]$_2$(μ-O) as catalysts in aqueous *t*-BuOOH.[1d]

The best catalytic results are obtained when a decane solution of *t*-BuOOH is used instead of aqueous *t*-BuOOH. Under these conditions, referred to as C2-BuOOH, the reaction mixtures consist of only one liquid phase, avoiding mass transfer limitations, and cyclooctene oxide is obtained as the only product in nearly quantitative yields after 24 h (Table 2). The kinetic profiles show no induction periods, and a rapid increase of epoxide yield takes place during the first 30 min, followed by a slowing down of the reaction (Figure 5). Similar behavior has been reported for several mononuclear, distorted tetrahedral[1a,c,3b,5f] or octahedral[14] molybdenum(VI) complexes bearing the fragment [MoO$_2$Cl]$^+$ used as catalysts in the same reaction, under similar conditions. Differences in catalytic activity for the three compounds are only evident for the first hour of reaction. The initial activities (in mol mol$_{Mo}^{-1}$ h^{-1}) decrease in the order **2** (403) > **2**@TRIMEB (364) > **2**@β-CD (283). Under the reaction conditions used, compounds **2** and **2**@TRIMEB are

completely soluble in the reaction medium, whereas a solid–liquid system is obtained for **2**@β-CD, which may partly explain the lower initial activity observed for the β-CD adduct. The lower initial activity of the CD adducts compared with nonincluded **2** may also be because the second-sphere oligosaccharide ligands have a negative effect on the rate of oxidative decarbonylation of compound **2** and/or the activity of the resultant molybdenum(VI) oxidizing species.

For the C2-BuOOH systems containing **2**, **2**@β-CD and **2**@TRIMEB, the reaction mixtures turned from red to yellow after addition of the oxidant *t*-BuOOH, which is consistent with the oxidative decarbonylation of the tricarbonyl complex to give the complex CpMoO$_2$Cl.[1a] The stabilities of the catalysts were investigated by carrying out two 24 h reaction runs at 328 K. For the homogeneous systems involving **2** and **2**@TRIMEB, the reactors were recharged at 24 h with equimolar amounts of cyclooctene and *t*-BuOOH. For the heterogeneous system with **2**@β-CD, the solid phase was easily separated from the reaction mixture by filtration or centrifugation and used in a second reaction run after thorough washing with *n*-hexane and drying at room temperature. Although the kinetic profiles were always similar for the two consecutive runs, the reactions were slower in the second runs. Conversions at 24 h decreased from 95% to ca. 83% for **2** and **2**@TRIMEB and from 98% to 92% for **2**@β-CD (Table 2). Nevertheless, quite high yields of at least 80% were achieved in the second reaction run. The IR spectrum of the solid recovered from the reaction system with **2**@β-CD still contained ν(CO) bands in the region of 1900–2000 cm^{-1}, albeit of very weak relative intensity compared to the original compound, indicating that extensive oxidative decarbonylation had taken place during the first run. ICP-AES analysis indicated that the Mo content of the residue in the **2**@β-CD system decreased ca. 54%, which practically coincides with the 52% decrease in initial activity from run 1 to run 2, suggesting that all Mo species retained in the CD host are active in the second run. A leaching test was performed in order to investigate the homo/heterogeneous nature of the catalytic reaction. After 10 min the reaction mixture was hot-filtered, and the solution was left to react for a further 5 h. In this period of time the epoxide yield increased 27% compared to 44% obtained without filtration. Hence, the oxidative decarbonylation leads to active metal species, which are both encapsulated in the CD host and dissolved in the reaction medium.

The lower activities observed in the second runs with the homogeneous systems derived from **2** or **2**@TRIMEB could be due to the gradual formation of inactive species, such as the η^2-peroxo complex CpMo(O$_2$)OCl in the presence of excess *t*-BuOOH.[1e] However, in the case of the nonincluded complex **2**, duplicating the initial amount of *t*-BuOOH resulted in an increase in the initial reaction rate from 403 to 462 mol mol$_{Mo}^{-1}$ h^{-1}. A second possibility concerns the well established detrimental effects of *t*-BuOH,[1d] which is formed during the reaction through the decomposition of *t*-BuOOH. In this regard, the use of solid catalysts such as the β-CD adduct is potentially advantageous since it helps avoid the accumulation of high amounts of *t*-BuOH in the same phase as the catalyst after several catalytic runs.

Conclusions

The ability of cyclodextrins to modulate cyclooctene epoxidation catalyzed by organometallic oxides generated in situ through the reaction of CpMo(CO)$_3$Cl with the oxidants *t*-BuOOH or H$_2$O$_2$ has been thoroughly examined. The results indicate that dissociation of the inclusion complexes occurs to

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varying degrees, depending on the type of host and the reaction conditions used. We have found that the in situ oxidation of free $CpMo(CO)_3Cl$ by aqueous t-BuOOH gives rise to an active catalyst, whereas oxidation by aqueous H_2O_2 does not. This is consistent with the current literature, which indicates that H_2O_2 is unable to be activated to olefin epoxidation by octahedral or pseudo-octahedral $MoO_2X_2L_2$ or $Cp'MoO_2X$ complexes. Hence, the most important finding reported here is that the introduction of CDs to the H_2O_2 system is able to instill significant catalytic activity, with cyclooctene oxide being the only observed reaction product. Although additional characterization work, such as in situ spectroscopic studies, will be required to fully understand these results, it seems likely that the protective effects of cyclodextrins play an important role. Future studies will be dedicated to the optimization of these catalytic systems. One obvious approach will be to examine differently substituted $(\eta^5\text{-}C_5R_5)Mo(CO)_3X$ precursors, since the catalyst performance of complexes such as $(\eta^5\text{-}C_5R_5)MoO_2X$ has been shown to depend on the cyclopentadienyl ligand.

Supporting Information Available: Crystallographic data in CIF format for the inclusion complex **1**@TRIMEB. This material is available free of charge via the Internet at http:/pubs.acs.org.

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