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Communication

Ring-opening of epoxides promoted by organomolybdenum complexes of the type $[(\eta^5\text{-}C_5H_4R)Mo(CO)_2(\eta^3\text{-}C_3H_5)]$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(CH_2R)]$

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ABSTRACT

The cyclopentadienyl molybdenum carbonyl complexes $[(\eta^5\text{-}C_5H_4R)Mo(CO)_2(\eta^3\text{-}C_3H_5)]$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(CH_2R)]$ (R = H, COOH) have been shown to promote acid-catalysed reactions in liquid phase, under moderate conditions. The catalytic alcoholysis of styrene oxide with ethanol at 35 °C gave 2-ethoxy-2-phenylethanol in 100% yield within 30 min for the dicarbonyl complexes and 3–6 h for the tricarbonyl complexes. Steady catalytic performances were observed in consecutive runs with the same catalytic solution, suggesting fairly good catalytic stability. In the second acid-catalysed reaction studied, the isomerization of α-pinene oxide at 55 °C gave campholenic aldehyde and *trans*-carveol in a total yield of up to 86% at 100% conversion. Chemoselectivity is shown to be solvent dependent.

1. Introduction

Epoxides are important organic intermediates, commonly synthesized from olefins, with patented technologies including the use of homogeneous Mo^{VI} catalysts, such as those derived from molybdenum carbonyl catalyst precursors [1–3]. Epoxides can undergo ring-opening reactions in the presence of acid catalysts to give a plethora of useful intermediates and products for the fine chemicals industry [4–6]. Commonly used Lewis acid catalysts such as metal halide salts present numerous drawbacks such as corrosion problems, fast deactivation, the production of large volumes of acidic waste, and the need for high catalyst/substrate ratios. Hence, there is much interest in the development of novel reaction processes catalysed by highly active and highly selective Lewis acids that significantly reduce acidic wastes. The use of organometallic Lewis acids (OLAs) is promising since they are playing an increasingly important role in modern organic synthesis due to the high product selectivities often reachable together with straightforward catalyst optimization through ligand exchange and/or functionalization [7].

Several group 6 (Mo, W) metal carbonyl complexes are OLAs [8] and have been used in a series of acid-catalysed reactions [9–15]. Molybdenum-based catalysts are especially attractive due to the ready availability and low cost of this element. We recently started to explore organomolybdenum complexes for the catalytic isomerization of α-pinene oxide (PinOx) to campholenic aldehyde (CPA). This is an important reaction from two perspectives. Firstly, PinOx is a renewable chemical obtained from α-pinene, which is produced on an industrial scale either by tapping trees (gum turpentine) or as a byproduct of paper pulping. Secondly, CPA is useful as an aroma chemical and as a synthetic intermediate for other aroma chemicals and also for some pharmaceuticals. In particular, it is used for the manufacture of sandalwood-like fragrances [16]. The isomerization of PinOx to CPA tends to be promoted by Lewis acid catalysts, while Brønsted acids give a mixture of compounds in low yields, such as *trans*-carveol (TCV), *trans*-sobrerol, and *p*-cymene. Apart from being expensive ingredients in the flavour industry (e.g., TCV is a constituent of the Valencia orange essence oil), these compounds

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have attracted interest due to their biological activities [17–19]. We obtained encouraging results for the isomerization of PinOx to CPA in the presence of the indenyl allyl dicarbonyl derivative [(η^5-Ind)Mo(CO)$_2$(η^3-C$_3$H$_5$)] [20]: 56% CPA yield at 97% PinOx conversion, 3 h reaction at 35 °C. In a second investigation [21], even better performance was obtained using the dimeric complex [{(η^5-Ind)Mo(CO)$_2$(μ-Cl)}$_2$]: 67% CPA yield at 100% PinOx conversion, 30 min reaction at 35 °C. The latter result is roughly comparable to those reported for the salts ZnCl$_2$ and ZnBr$_2$ [22], used as catalysts in patented technology for the production of CPA [23,24].

Another chemical route for the valorization of epoxides involves ring-opening via alcoholysis to give β-alkoxy alcohol products [25], which are important precursors for a broad range of pharmaceuticals [26]. These reactions can be promoted by Lewis acid catalysts [27,28], for which molybdenum carbonyl complexes are interesting candidates.

In this work, we set out to explore the catalytic potential of cyclopentadienyl molybdenum carbonyl complexes of the type [(η^5-C$_5$H$_4$R)Mo(CO)$_2$(η^3-C$_3$H$_5$)] and [(η^5-C$_5$H$_5$)Mo(CO)$_3$(CH$_2$R)] (R = H or COOH) for acid-catalysed ring-opening reactions of epoxides, namely the isomerization of PinOx, and alcoholysis of styrene oxide (StyOx) with ethanol, under mild reaction conditions (Fig. 1). To the best of our knowledge, this is the first report on the catalytic performance of metal carbonyl complexes in the alcoholysis of StyOx.

2. Experimental

2.1. Materials and methods

Transmission FT-IR spectra (KBr pellets) were measured on a Mattson 7000 FT-IR spectrometer with 4 cm^{-1} resolution. Styrene oxide (StyOx, > 97%, Fluka), α-pinene oxide (PinOx, > 95%, TCI), 1,2-dichloroethane (DCE, 99%, Aldrich), toluene (≥99.9%, Aldrich) and absolute ethanol (EtOH, 99.8%, Scharlau) were purchased from commercial sources and used as received.

2.2. Synthesis of molybdenum carbonyl complexes **1**–**4**

The π-allyl complex [CpMo(CO)$_2$(η^3-C$_3$H$_5$)] (**1**) (Cp = η^5-C$_5$H$_5$) was synthesized according to the general procedure described previously by Ascenso et al. [29], involving the reaction of [(η^3-C$_3$H$_5$)Mo(CO)$_2$(NCCH$_3$)$_2$Cl] with LiCp. The acid [(η^5-C$_5$H$_4$COOH)Mo(CO)$_2$(η^3-C$_3$H$_5$)] (**2**) was obtained from the reaction of **1** with *n*-BuLi and solid CO$_2$, followed by aqueous work-up [30,31]. The tricarbonyl complex [CpMo(CO)$_3$CH$_3$] (**3**) was synthesized by the reaction of [CpMo(CO)$_3$]Na with CH$_3$I [32]. The reaction of NaCp with Mo(CO)$_6$, followed by addition of 2-chloroacetamide, gave the complex [CpMo(CO)$_3$CH$_2$COONH$_2$], which was subsequently hydrolysed to give [CpMo(CO)$_3$CH$_2$COOH] (**4**) [33].

2.3. Catalytic tests

The catalytic reactions were carried out under air in a magnetically stirred, closed borosilicate reaction vessel (10 mL capacity) which was immersed in an oil bath thermostatted at 35 or 55 °C. Typically, the reactor was loaded with molybdenum complex, substrate (StyOx or PinOx) and a solvent. For the StyOx alcoholysis reaction, the reactor was loaded with molybdenum complex (80 μmol), StyOx (0.82 mmol), and ethanol (2.0 mL). For the PinOx isomerization reaction, the reactor was loaded with molybdenum complex (17 μmol), PinOx (170 μmol), and a solvent (0.5 mL; DCE, toluene or ethanol). The reactor containing the complex and the solvent was pre-heated for 10 min at the reaction temperature, and subsequently the substrate (also pre-heated) was added to the mixture (the reaction time was counted from this instant). The evolutions of the reactions were monitored using a Varian 3800 GC equipped with a BR-5 (Bruker) capillary column (30 m × 0.25 mm; 0.25 μm) and a flame ionization detector, using H$_2$ as the carrier gas. Cyclododecane epoxide was used as an internal standard. The products were identified by GC–MS (Trace GC 2000 Series (Thermo Quest CE Instruments) – DSQ II (Thermo Scientific)), equipped with a capillary DB-5 type column (30 m × 0.25 mm; 0.25 μm), using He as the carrier gas.

3. Results and discussion

3.1. Styrene oxide ring-opening reaction via alcoholysis

Complexes **1**–**4** were explored for the acid-catalysed ring-opening reaction of StyOx with ethanol (also used as solvent) in the temperature range of 35–55 °C. All four complexes are completely

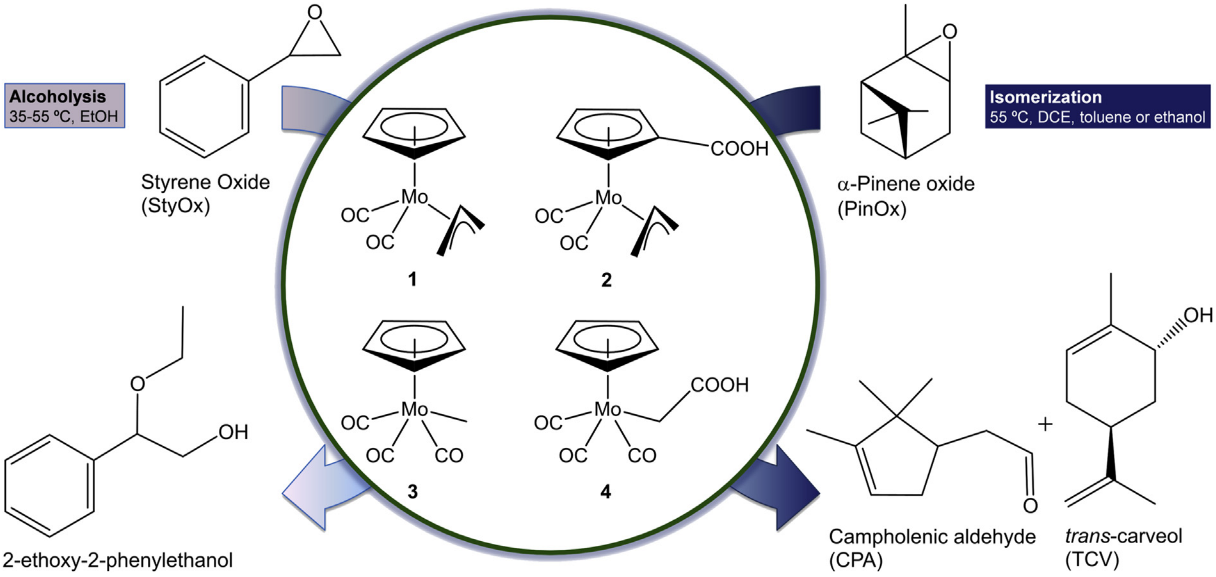

Fig. 1. Acid-catalysed epoxide ring-opening reactions studied in this work.

soluble under the conditions used. In separate tests carried out in the absence of substrate, solutions of complexes **1**–**4** in ethanol were left at 35 or 55 °C for 3 h, and then the solutions were evaporated to dryness under reduced pressure. The FT-IR spectra (not shown) of the resultant solids were unchanged from those of the as-synthesized complexes, suggesting that the complexes are stable under the catalytic reaction conditions used. The only reaction product obtained in the alcoholysis reaction was 2-ethoxy-2-phenylethanol, i.e. selectivity was always 100% (Fig. 1, Table 1).

Complexes **1** and **2** led to a very fast alcoholysis reaction, with 100% conversion reached at 10 min/55 °C or 30 min/35 °C. Complexes **3** and **4** led to a slower alcoholysis reaction, with 100% conversion being reached at 2 h/55 °C or 6 h/35 °C for **3**, and 90 min/55 °C or 3 h/35 °C for **4**. Without catalyst, the reaction was sluggish (3% StyOx conversion at 4 h/55 °C), which emphasizes the catalytic role of the molybdenum complexes. To the best of our knowledge, there are no reports on the catalytic performance of metal carbonyl complexes in the alcoholysis of StyOx. According to the literature, the Lewis acid catalysed alcoholysis of StyOx may involve the coordination of the oxygen atom of the epoxide to the transition metal centre by an acid–base interaction, leading to an increase in the electrophilicity of the carbon atom attached to the phenyl group (polarisation of the C–O bond of the oxirane ring), making it susceptible to nucleophilic attack by the alcohol (ROH) to give the product [34,35].

The catalytic stability was investigated by re-loading the substrate to the same reactor where the catalyst was maintained. These experiments were carried out at 35 °C for complexes **1** and **2**, and at 55 °C for (less active) **3** and **4**. For all complexes, at least 95% StyOx conversion was reached, and 2-ethoxy-2-phenylethanol selectivity was always 100% for four runs (Table 1). In general, an increase in initial reaction rate was observed from run 1 to run 2, and for each complex in runs 2–4 the activity was somewhat steady. Hence, the increasing concentration of 2-ethoxy-2-phenylethanol in the reaction medium did not have a negative effect on the kinetics of consecutive runs. The catalytic results were roughly comparable for each pair of complexes **1** and **2**, or **3** and **4**, and thus the carboxylic acid groups of complexes **2** and **4** do not seem to exert a significant influence on the alcoholysis reaction. The catalytic activity may be associated with the Lewis acidity of the metal centre of the active species involved, which was possibly not considerably affected by the presence of the carboxylic acid group on one of the ligands.

Table 1
Alcoholysis of styrene oxide with ethanol in the presence of complexes **1**–**4**.[a]

Complex	Run	Time (min)	Temp. (°C)	Conv. (%)[b]
1	1	1/10	55	67/100
	1	1/30	35	65/99
	2	1/30	35	77/99
	3	1/30	35	72/98
	4	1/30	35	71/98
2	1	1/10	55	71/99
	1	1/30	35	60/98
	2	1/30	35	83/99
	3	1/30	35	76/98
	4	1/30	35	75/95
3	1	1/30/60/120	55	7/21/58/100
	2	1/30	55	78/99
	3	1/30	55	77/99
	4	1/30	55	83/97
	1	1/60/360	35	1/15/99
4	1	1/30/60/90	55	12/46/93/100
	2	1/30	55	74/100
	3	1/30	55	79/99
	4	1/30	55	77/98
	1	1/60/180	35	3/64/100

[a] Reaction conditions: 80 μmol of Mo, 0.82 mmol StyOx, 2.0 mL ethanol, [Mo] = 0.038 M.

[b] StyOx conversion. The only product was 2-ethoxy-2-phenylethanol (100% selectivity).

3.2. *α-Pinene oxide ring-opening reaction via isomerization*

The reaction of PinOx in the presence of complexes **1**–**4**, at 55 °C with DCE as solvent, gave mainly CPA, together with TCV, *trans*-pinocarveol (PCV), and iso-pinocamphone (IPC) (Fig. 1, Table 2). As found for ethanol, separate solubility tests performed for DCE in the absence of substrate confirmed that the complexes are stable in this solvent at 55 °C (exemplified in Fig. 2 for complexes **3** and **4**). The best catalytic results in terms of CPA and TCV total yield at 24 h were obtained for complex **4** (51% CPA yield and 21% TCV yield at 100% conversion). These results are superior to the total yields of CPA and TCV reported previously by some of us for indenyl complexes of the type $[(\eta^5\text{-IndR})Mo(CO)_2(\eta^3\text{-}C_3H_5)]$ (R = H, CH_3, $Si(CH_3)_3$) [20], and somewhat inferior to those obtained with $[\{(\eta^5\text{-Ind})Mo(CO)_2(\mu\text{-Cl})\}_2]$ [21] (Table 2). The observed differences in catalytic results may be partly due to differences in catalyst solubility, stability and acidity of active species.

As mentioned in the introduction, the isomerization of PinOx to CPA tends to be promoted by Lewis acid catalysts, while Brønsted acidity can favour TCV [36,37]. Hence, the catalytic results for **1**–**4** suggest that the active species are of Lewis acid type. Complex **2** led to slower reaction than **1** and, on the other hand, complex **4** led to faster reaction than **3**. Thus, for each pair of complexes no direct relationship between the Brønsted acidity associated with the carboxylic acid groups and catalytic activity can be established.

The reaction of PinOx in the presence of complex **2** was further examined using toluene or ethanol as solvent instead of DCE (Table 2). The reaction rate decreased in the order ethanol > toluene > DCE. On the other hand, the total yield of CPA and TCV at 100% conversion was higher for toluene than for ethanol. Unidentified reaction products were formed in ethanol, which were not detected for the other solvents. Possibly, ethanol acts as a non-innocent solvent (as is the case for the alcoholysis of StyOx), broadening the product spectrum. A comparison of the catalytic results for DCE and toluene as solvents shows that the molar ratio TCV/CPA at 55–62% conversion is higher for the latter (ca. 2.8 compared with 0.3 for DCE). The DCE solvent molecules (dielectric constant = 10.36; dipole moment = 1.75 D [38]) may unfavourably interact with the carboxylic acid function of the catalyst (e.g. via H-bonding), affecting TCV formation. These effects may be less important for the much less polar solvent toluene (dielectric constant = 2.38; dipole moment = 0.36 D [38]).

Attempts were made to identify metal species formed during the catalytic reaction. This was accomplished for complex **4** by adding pentane to the reaction solution after 3 h and 24 h (in separate experiments), giving the solids denoted **4**-DCE(cat-3h) and **4**-DCE(cat-24h), respectively. The FT-IR spectra of **4**-DCE(cat-3h) and **4**-DCE(cat-24h) were similar to that of **4**, suggesting that the predominant metal species were of the type **4** (Fig. 2). Nevertheless, it is worth mentioning that the colour of the catalytic reaction solution changed slightly from yellow (initially) to greenish-yellow after 24 h. Thus, one cannot rule out the possibility that different active species may be formed from **4**. It has been previously reported that molybdenum(II) carbonyl complexes can undergo decarbonylation in the presence of air/water giving different species [21]. Very small amounts of air and/or water may be dissolved in the reagents/solvent, and influence the stability of the molybdenum carbonyl complexes.

4. Concluding remarks

In this work we have shown that complexes of the type [(η^5-

Table 2
Acid-catalysed conversion of α-pinene oxide, in the presence of complexes **1**–**4**, and comparison with literature data for molybdenum carbonyl complexes.[a]

Catalyst	Solvent	Time (h)	Conv.[b] (%)	Product yield (%)				Ref.
				CPA	TCV	PCV	IPC	
1	DCE	24	99	37	14	11	4	This work
2	DCE	24	62	27	8	11	2	This work
	Ethanol	0.017	100	21	37	4	3	This work
	Toluene	6/24	55/100	9/27	25/59	1/7	1/3	This work
3	DCE	24	50	18	4	5	6	This work
4	DCE	24	100	51	21	10	1	This work
$[\{(\eta^5\text{-Ind})Mo(CO)_2(\mu\text{-Cl})\}_2]$	DCE	0.017	100	68	9	3	8	[21]
$[(\eta^5\text{-Ind})Mo(CO)_2(\eta^3\text{-}C_3H_5)]$	DCE	2.5	92	40	17	5	7	[20]
$[(\eta^5\text{-IndCH}_3)Mo(CO)_2(\eta^3\text{-}C_3H_5)]$	DCE	1	66	38	13	4	7	[20]
$[(\eta^5\text{-IndSi(CH}_3)_3)Mo(CO)_2(\eta^3\text{-}C_3H_5)]$	DCE	1	61	33	12	2	4	[20]

[a] Reaction conditions: 17 μmol Mo, 170 μmol PinOx, 55 °C, 0.5 mL solvent, [Mo] = 0.032 M.
[b] Conversion of PinOx.

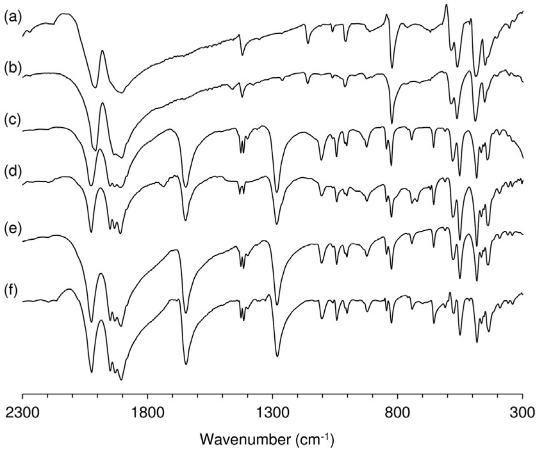

Fig. 2. FT-IR spectra of complexes (a) **3** and (c) **4**, and the recovered solids (b) **3**-DCE, (d) **4**-DCE, (e) **4**-DCE(cat-3h) and (f) **4**-DCE(cat-24h).

$C_5H_4R)Mo(CO)_2(\eta^3\text{-}C_3H_5)]$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(CH_2R)]$ are interesting for catalytic epoxide ring-opening reactions, namely the isomerization of α-pinene oxide and the ethanolysis of styrene oxide. The chemoselectivity of the isomerization reaction is solvent dependent. With DCE as solvent, complex **4** led to the highest combined yield of CPA and TCV (72% at 100% conversion), the former being the predominant isomer. A higher combined yield of 86% at 100% conversion was possible with complex **2** in toluene, with TCV being the predominant isomer. In the ethanolysis reaction performed at 35 °C, 2-ethoxy-2-phenylethanol was formed in up to 100% yield. To the best of our knowledge, this is the first report that describes the use of metal carbonyl complexes to promote the alcoholysis of styrene oxide. Steady performances were observed in consecutive catalytic runs. Supported catalysts prepared using similar types of complexes may therefore be interesting to study as heterogeneous acid catalysts for epoxide ring-opening reactions.

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