Selective *cis*-dihydroxylation of olefins using recyclable homogeneous molybdenum acetylide catalyst

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Abstract

Selective *cis*-dihydroxylation of various olefins has been carried out using molybdenum acetylide complex CpMo(CO)$_3$(C≡CPh) (**1**) as catalyst and hydrogen peroxide as an efficient and environmentally benign oxidant. In case of cyclohexene, very high conversion (95%) and selectivity (86%) for *cis*-dihydroxylated product has been achieved using H$_2$O$_2$ as an oxidant and *t*-butanol as a solvent. *cis*-Dihydroxylation of other substrates like styrene, α-methyl styrene, limonene and cyclopentene has also been carried out with very high selectivity for diol. The catalyst and intermediate species have been characterized using FT-IR, UV–vis spectral analysis and XPS studies as well as cyclic voltametric studies. These studies suggest that molybdenum oxo–peroxo complex is the catalytically active species. The intermediate blue complex when characterized by ESI MS suggested the formation of dimeric molybdenum complex and XPS and cyclic voltametric studies confirm the presence of mixed valence Mo(V) and Mo(VI) in the reaction intermediate. Based on the characterization results possible mechanism for dihydroxylation is proposed. Interestingly, even though the catalyst is homogeneous; it could be recovered quantitatively by extraction in aqueous phase and recycled five times without any appreciable loss in cyclohexene conversion and selectivity for *cis*-1,2-cyclohexanediol.
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1. Introduction

Alkene oxidation is being widely studied because of its importance in the development of synthetic organic chemistry [1]. The osmium tetroxide (OsO$_4$), catalyzed olefin dihydroxylation provides an efficient route for synthesis of vicinal diols, which are valuable synthetic intermediates for pharmaceuticals [2]. Especially, Sharpless asymmetric dihydroxylation (AD) provides highest enantioselectivity, which leads to the chiral process [2a]. Osmium tetroxide is the only efficient catalyst known today for asymmetric dihydroxylation for enantiomerically pure product. High cost, toxicity and possible contamination of the osmium catalyst in the products prohibit its use in industry. To overcome these drawbacks, complexation of osmium with ligands, which are heterogenized on soluble and insoluble polymers [3], silica gel [4], ion exchange [5] or dendrimer [6] support has been attempted by several groups [7]. Another disadvan-

tage of osmium system is the need of various co-oxidants such as *N*-methyl morpholine *N*-oxide (NMO) [8], or K$_3$Fe(CN)$_6$ [9] so as to facilitate the use of OsO$_4$ in catalytic amounts as against stoicheometric amounts in traditional dihydroxylation reactions. Hydrogen peroxide has been used as terminal oxidant [10] for recycle of Os(VI) to Os(VIII) along with NMO and biomimetic flavin [11]. Beller et al. have used molecular oxygen or air as stoicheometric oxidants for osmium catalyzed dihydroxylation with good to excellent chemoselectivity under optimized pH conditions. For α-methyl styrene as model substrate, under slightly elevated oxygen pressure very high yields of diols are obtained even at very low catalyst concentrations [12]. In order to overcome the problem of toxicity, cost and also to have environmentally benign process for dihydroxylation of olefins, there is a need to search for an alternative metal catalyst system for the production of vicinal diols. There are few reports on Os/Re [13], Os/Pd and Os/W [14] catalytic systems for dihydroxylation, however addition of co-oxidant and/or addition of various carboxylic acids for maintaining acidic medium is essential for dihydroxylation. Recently, Feringa et al. [15] have used manganese complexes as catalysts for dihydroxyla-

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tion using hydrogen peroxide as oxidant. However they have shown that the use of various carboxylic acids as co-catalysts is essential in this case, and epoxide was obtained as a major product along with *cis*-diol in many cases. Warwel et al. [16] have reported oxidation of higher olefins with hydrogen peroxide in dioxane solvent forming vicinal diols using Re_2O_7 as catalyst. However selectively *trans*-diol was obtained only in the case of cyclohexene. Bhaumik et al. [17] have used Co(III) containing mesoporous silica as catalyst and H_2O_2, TBHP or oxygen as oxidant for dihydroxylation of cyclohexene, however the selectivity for *trans*-diol is much higher than *cis*-diol. Cyclohexene is used as a model substrate for studying different oxidation catalysts. Noyori et al. [18] have reported oxidation of various olefins including cyclohexenes to dicarboxylic acids with H_2O_2 using sodium tungstate as catalyst and quaternary ammonium hydrogensulphate as phase transfer catalyst. This provides very efficient route for adipic acid synthesis. Recently, Oldenburg and Que [19] have used nonheme iron complexes for *cis*-dihydroxylation of olefins using ten equivalents hydrogen peroxide with respect to catalyst. However turnover numbers reported are extremely low. Beller et al. [20] have shown the efficient use of $FeCl_3$ with 2,6-pyridine dicarboxylic acid and various N containing ligands for epoxidation of olefins using hydrogen peroxide as an oxidant. They have also extended this to asymmetric epoxidation using chiral N containing ligands with excellent yields and *ee* up to 97% [21].

In biological systems all molybdenum containing enzymes catalyze redox processes by involving one or two electron transfer per enzyme molecule and this electron transfer depends on the oxidation states of the molybdenum atoms present in the neighboring enzymes [22]. Similar kind of behavior of molybdenum is expected in complexes containing mixed valent molybdenum centres. Various molybdenum complexes and oxides are known to be very good homogeneous as well as heterogeneous catalysts for oxidation/epoxidation reactions. MoO_3 on different solid supports is used for oxidation [23], nitration [24] and transesterification [25] reactions. Bhattacharyya et al. have prepared different Mo(VI) oxo–peroxo or oxo–diperoxo complexes with various ligands and successfully used these complexes for epoxidation of various olefins and oxidation of alcohols to carbonyl compounds [26]. Molybdenum carbonyl complexes with different ligands like halides [27], N-containing [28] and cyclopentadienyl; η^5-C_5R_5; R = H, Me, Ph [29] are mainly used for epoxidation of variety of olefins. Kuehn et al. [30] as well as Goncalves et al. [31] have reported use of $CpMo(CO)_3Cl$ as catalyst for olefin oxidation with very high selectivity for epoxide [32]. Tungsten acetylide complexes are reported to form oxo–peroxo complexes on treatment with H_2O_2 in acidic medium [33]. Hence similar molybdenum complexes are expected to be good oxidation catalysts. To our knowledge there are no reports in the literature on the use of molybdenum catalyst, homogeneous or heterogeneous, for *cis*-dihydroxylation. Here we report for the first time *cis*-dihydroxylation of various olefins catalyzed by homogeneous recyclable molybdenum acetylide complex, $CpMo(CO)_3(C≡CPh)$; $Cp = \eta^5$-C_5H_5 (**1**) using hydrogen perox-

ide or TBHP as oxidant along with detailed cyclic voltammetric investigation of different forms of the Mo catalysts.

2. Experimental

2.1. General

All reagents of commercial grade (Aldrich, SD fine) were used as received unless stated otherwise. Hydrogen peroxide used was 35% w/w in water. THF was dried according to standard method and freshly distilled prior to use. Cyclopentadiene was obtained by freshly cracking dicyclopentadiene (Aldrich make) by distillation prior to use. $CpMo(CO)_3Cl$ was prepared according to literature method [34]. Complex **1** was prepared according to literature method with slight modification [35] as follows.

2.2. Preparation of $CpMo(CO)_3(−C≡CPh)$ (**1**)

A 100 mL 2 necked round bottom flask was charged with $CpMo(CO)_3Cl$ (2.0 g, 0.0071 mol), (H-C≡CPh) (1.05 g, 0.010 mol), catalytic amount of CuI (5 mg) and diethyl amine (50 mL) as solvent. The reaction mixture was stirred at room temperature for 15 min. The progress of the reaction was monitored by TLC using hexane/dichloromethane (80/20) as solvent system. After the reaction was complete, diethyl amine was removed in vacuum. The residue was dissolved in minimum amount (5 mL) of dicholometane and loaded on silica gel column and eluted using hexane/dichloromethane 80/20 (v/v) as solvent system to separate **1** from unreacted $CpMo(CO)_3Cl$.

Yield of $CpMo(CO)_3(−C≡CPh)$ was 1.5 g, 68% based on $CpMo(CO)_3Cl$. The formation of **1** was confirmed by comparing its FT-IR spectrum in KBr; which matched with the reported values $\nu_{(CO)}$, 1940, 2031 cm^{-1}; $\nu_{(C≡C)}$, 2102 cm^{-1} [35].

2.3. Catalytic reactions

In a typical catalytic reaction, 50 mL two neck round bottom flask was charged with olefin (0.02 mol), 35% hydrogen peroxide (0.04 mol), 10 g solvent and catalyst **1** (0.04×10^{-3} mol). The reaction mixture was heated to desired temperature and stirred till completion of the reaction. Reaction was monitored by GC. All samples were analyzed on an Agilent 6890 Gas Chromatograph equipped with a HP-5 dimethyl polysiloxane column (60 m length, 0.25 mm internal diameter, 0.25 μm film thickness) with flame ionization detector and PerkinElmer autosystem XL equipped with a capillary column PE-1 (30 m length, 0.25 mm internal diameter and 1 μm film thickness) with flame ionization detector. The reaction products were confirmed by GC-MS (Model GC Agilent 6890N with HP5 MS 30 m capillary column, MS Agilent 5973 Network MSD and GCIR ((PerkinElmer Spectrum 2001, column DB-1, 25 m length, 0.32 mm internal diameter). The FT-IR was recorded as nujol mull using Shimadzu 8300. The electrospray mass spectra were recorded on a MICROMASS QUATTRO II triple quadrupole mass spectrometer. The sample dissolved in water was introduced into ESI source through syringe pump at the

rate of 5 μL per min. The ESI capillary was set at 3.5 kV. The spectrum was collected in 6 s scans. For each sample the spectra were recorded at a cone voltage of 30 and 80 V.

2.4. Product isolation

In case of cyclohexene, after completion of the reaction, the reaction mixture was cooled to room temperature and solvent was removed in vacuum. To the residue ethyl acetate and water was added and crude diol extracted in organic layer was obtained after removal of the solvent in vacuum. Diol was purified by column chromatography on silica gel using petroleum ether and ethyl acetate (90/10, v/v) solvent system.

2.5. Cyclic voltametric studies

The cyclic voltammetric measurements were performed using a three electrode system comprised of platinum wires as counter and working electrodes in dichloromethane containing 0.1 M tetrabutyl ammonium hexaflorophosphate as supporting electrolyte. A Pt quasi reference electrode was used to report all potentials values. Cyclic voltammograms were recorded using a CH instrument model no 400B, after purging the electrolyte with pure Argon. Each time, the working electrode was sonicated in 6% nitric acid and polished manually using 0.3 μm alumina slurry over a fine polishing cloth. Final washings were done by the deionized water followed by acetone. For calibrating the quasi reference electrode, ferrocene was added to the electrolyte to make a 0.1 M solution with respect to supporting electrolyte (tetra butyl ammonium hexaflorophosphate) and cyclic voltammogram was recorded. The $E_{1/2}$ for the ferrocene/ferrocinium redox couple was found to be 0.235 V.

FTIR of complex **1** and complex **1** after addition of H_2O_2 was recorded as KBr pallet using Shimadzu 8300 FTIR spectrometer.

UV–vis spectral analysis was carried out using PerkinElmer Lambda 650 UV–vis spectrometer as t-BuOH solution and t-BuOH as reference in the range 200–800 nm.

XPS experiments were performed in a Vacuum Generators Escalab 220 XL spectrometer using a non-monochromatic Al Kα ($h\upsilon = 1486.6$ eV) operated at 15 kV and 20 mA. The pressure in the sample chamber is maintained at 10^{-9} mbar or lower during the analysis. All the binding energies are with reference to carbon (C1s) at 285 eV. Curve fitting of the Mo3d peaks was done using VG Eclipse Software.

3. Results and discussion

When cyclohexene was treated with H_2O_2 in t-BuOH solvent in presence of catalytic amount of Mo–acetylide complex **1** (**1**/substrate ratio 1/500), cis-1,2-cyclohexane diol was obtained as the major product along with 2-alkoxy cyclohexanol, cyclohexenol and cyclohexenone as minor products (Scheme 1). Monoetherification of diol due to excess of alcohol used as solvent led to the formation of 2-alkoxy cyclohexanol. Cyclohexenol and cyclohexenone are obtained as a result of allylic oxidation. The reaction was monitored by GC and the products were confirmed by GC–MS, GCIR and NMR spec-
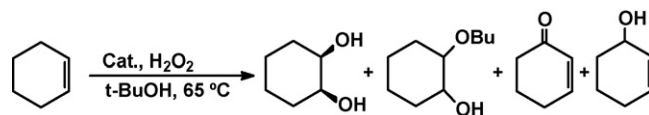
Scheme 1. Dihydroxylation of cyclohexene.

Table 1
Effect of solvent on conversion and selectivity

Entry	Solvent	Conversion, %	Selectivity, %				TON cis-diol
			cis-Diol	Ene-ol	Ene-one	Other	
1	CH_3CN	67	60	17	23	0	201
2	MeOH	91	42	4	6	48[a]	191
3	t-BuOH	95	86	0	5	9[b]	409
4	CH_2Cl_2	69	68	4	19	9	235
5	$CHCl_3$	72	62	23	15	0	223
6	CCl_4	68	60	21	19	0	204

Reaction conditions: Cyclohexene, 0.02 mol; H_2O_2 (35%), 0.04 mol; **1**, 0.04×10^{-3} mol; TOS, 48 h; temperature, 65 °C.
[a] 2-Methoxy cyclohexanol.
[b] 2-Butoxy cyclohexanol.

troscopy. Additionally, cis-1,2-cyclohexanediol was confirmed by its melting point (98 °C). NMR (CDCl$_3$) δ, ppm 2.63 (2H, CHO**H**), 3.35 (2H, C**H**OH), 1.97 (2H, HC**H**$_e$CHOH), 1.71 (2H, HC**H**$_a$CHOH), 1.27 (4H, C**H**$_2$CH$_2$CHOH).

The reaction was carried out in different solvents (Table 1). The results show that alcohols are preferred solvents for this system, as it forms single phase with organic substrate and aqueous hydrogen peroxide. In case of lower alcohols like methanol, etherification was prominent leading to decrease in diol selectivity (entry 2). When bulky alcohol like t-BuOH was used (entry 3), selectivity for ether decreased drastically leading to very high selectivity (86%) for vicinal diol. In case of other solvents (entries 1 and 4–6) conversion as well as selectivity was less compared to alcohol.

In all the cases the turn over number (TON = moles of product formed/moles of **1**) in one cycle for cis-diol was quite high. Especially with t-BuOH as solvent (entry 3) very high TON (409) was obtained showing very high efficiency of the catalyst. Bhaumik et al. [17] have used Co(III) containing mesoporous silica as catalyst for cyclohexene dihydroxylation. The cyclohexene conversions are reported to be in the range of 47–85% with high selectivity for $trans$-diol compared to cis-diol. Using H_2O_2 as oxidant 80.6% cyclohexene conversion is reported with 35.6% selectivity for cis-diol and 64.4% selectivity for $trans$-diol. The maximum TON for cis-diol reported with Co containing silica is 28. Hence the selectivity for cis-diol obtained with **1** is much higher than Co containing silica.

It is observed that higher catalyst loading leads to increase in the reaction rate. When catalyst loading was increased from 0.2 to 1 mol% reaction was complete in 9 h instead of 48 h without change in diol selectivity. In order to check the stability of the catalyst fresh charge of cyclohexene and H_2O_2 was added to the reaction mixture after completion of the reaction with 1 mol% catalyst loading. The reaction was further continued and the turn over frequency (TOF) was determined

Table 2
Batchwise additions of substrate and oxidant without catalyst separation

Cycle[a]	TOS[b], h	Conversion, %	Selectivity				TON	TOF
			Diol	Eneol	Eneone	Ether		
0	9	91	86	00	5.6	8.4	78	8.6
1	18	86	85.5	00	6	7.5	147	8.2
2	27	83	86	00	7	7	214	7.9
3	36	84	84	3	6	7	282	7.8
4	45	92	83.3	5.1	5.6	5.8	343	7.65
5	54	82	84	3.5	6.5	6	413	7.6

Reaction conditions: **1**, 0.2 mmol; temperature, 65 °C; *t*-BuOH, 10 g.

[a] Charge added before each cycle: cyclohexene, 0.020 mol; 35% H_2O_2, 0.04 mmol.

[b] Time up to each cycle.

Table 3
Catalyst recycles study by isolating the catalyst

Recycle[a]	TOS[b], h	Conversion, %	Diol selectivity, %	TOF, h^{-1}
0	9	92	86	8.8
1	9	89.2	85	8.4
2	9	86.9	86	8.3
3	9	85.8	85	8.2
4	9	83.1	84	7.9
5	9	82	83	7.8

Reaction conditions: **1**, 0.2 mmol.

[a] Charge added before each cycle: cyclohexene, 0.020 mol, 35% H_2O_2, 0.04 mmol; *t*-butanol, 10 g.

[b] Time for each cycle separately.

(Table 2). There was no change in TOF even after five additions of reactants.

The stability of the catalyst was further tested by isolating the product in organic phase and recovering the catalyst in aqueous phase for its recycle. The aqueous phase was concentrated to remove maximum water before each recycle. The selectivity for *cis*-diol did not decrease considerably even after five such recycles (Table 3). The decrease in conversion can be attributed to the losses during handling of the small amount of catalyst during recycle. These results clearly show the stability of the molybdenum acetylide catalyst in the reaction media as well its recovery and recycle without any appreciable decrease in catalytic activity and selectivity which is rare case in homogeneous catalysis.

In order to check the wider applicability of this catalyst to other olefins for *cis*-dihydroxylation, various other olefins like styrene, α-methyl styrene, limonene and cyclopentene were tested for its oxidation. The results of these oxidations are given in Table 4. The results for styrene show very high conversion of styrene (>90%) using hydrogen peroxide (entry 1) as well as TBHP (entry 2) with no formation of epoxide. Very high selectivity for diol is obtained with formation of benzaldehyde as minor product. Etherification of styrene diol was observed to very less extent. (H_2O_2 8% and TBHP 10.8%). In case of α-methyl styrene (entry 3 and 4) though the conversion was slightly lower compared to styrene, no formation of epoxide was observed in this case also. Though formation of diol is prominent, it is observed that with longer reaction time, the diol gets converted to 2-phenyl propionaldehyde. The diol selectiv-

ity when H_2O_2 was used as an oxidant decreased from 73% at 5 h to 53% at 9 h with corresponding increase in the 2-phenyl propionaldehyde selectivity. Similarly when TBHP was used as an oxidant the selectivity for diol decreased from 63 (5 h) to 45% (12 h) with corresponding increase in 2-phenyl propionaldehyde selectivity. In case of cyclopentene (entry 8) high conversion (85%) with very high selectivity (82%) for diol was obtained with low selectivity (18%) for allylic oxidation products (cyclopentenone and cyclopentenol). In his case also no epoxide formation was observed. Though in case of limonene also very high conversion was obtained with H_2O_2 (92%) as well as TBHP (86%) the number of products obtained are more. The products obtained are limonene 1,2-diol, limonene 8,9-diol, limonene diepoxide and limonene 1,2-diol 8,9-oxide. Very high selectivity for limonene 1,2-diol (92%) was obtained when TBHP was used compared to H_2O_2 (30%). Though in case of TBHP no epoxide was obtained, in case of H_2O_2, 29% diepoxide was obtained. In both the cases small amount of limonene 1,2-diol 8,9-oxide was obtained. Above results show that in all the cases very high selectivity for diol was obtained though in some cases further etherification of diol was observed. In all the cases either no or very less quantity of epoxide was formed which shows very high efficiency of the catalyst for dihydroxylation. It is also observed that with TBHP the reaction is slow compared to H_2O_2, though no considerable change in the product distribution is observed.

In case of cyclohexene dihydroxylation when less than stoicheometric amount of hydrogen peroxide was added, the reaction did not go to completion with formation of blue colored complex in the reaction mixture. The original color of the reaction mixture was faint yellow. It was observed that when further H_2O_2 was added to the same reaction mixture, the reaction continued with disappearance of the blue color. We have characterised the blue complex in the reaction mixture using various techniques.

The color change of the catalyst from faint yellow to blue and again to faint yellow indicates the redox behavior of molybdenum centre. The blue color is characteristics of mixed valence molybdenum (Mo^{VI} and Mo^V), well known as molybdenum blue. Color of pure Mo(VI) species is faint yellow or brown where as the color of pure Mo(V) species is red [36]. Molybdenum blue species are referred to as compounds coming from redox process resulting in a mixture of Mo(VI) and Mo in lower oxidation state Mo(V) [37]. The presence of mixed valence molybdenum species was confirmed by cyclic voltammetric studies of blue complex, which showed presence of two reversible redox couples, one for Mo(V) to Mo(VI) and back to Mo(V) and other is for Mo(VI) to Mo(V) and back to Mo(VI).

The FTIR spectrum of catalyst **1** after addition of H_2O_2 (Fig. 1) confirms the formation of molybdenum oxo–peroxo species. The peak at $953 \, cm^{-1}$ confirms the presence of Mo=O terminal bond. The band at $858 \, cm^{-1}$ corresponds to the O–O stretching vibration of peroxo species. The weak bands at 664 and $577 \, cm^{-1}$ can be assigned to the $Mo–O_2$ (peroxo) asymmetric and symmetric stretching vibrations respectively. The IR positions for Mo oxo and peroxo moieties are in good agreement with the literature reports for various Mo oxo–peroxo

Table 4
Oxidation of olefins using catalyst **1**

Entry	Substrate	Oxidant	Temperature, °C	Time, h	Conversion, %	Diol	Selectivity	
							Epoxide	Others
1	Styrene	H_2O_2	65	10	95	82	0	8[a], 10[b]
2	Styrene	TBHP	65	14	92	73.1	0	10.8[a], 16.1[b]
3	α-Methyl styrene	H_2O_2	90	5	65	73	0	27[c]
				9	90	58.3	0	41.7[c]
4	α-Methyl styrene	TBHP	90	5	53	63.4	0	36.6[c]
				12	80	45	0	55[c]
5	Limonene	H_2O_2	65	48	92	30[d], 15[e], 17[f]	29[g]	9[h]
6	Limonene	TBHP	65	48	86	92[d], 6[f]	0	2[h]
7	Cyclopentene	H_2O_2	65	48	65	82	0	18[i]

Reaction conditions: Catalyst **1**, 0.04×10^{-3} mol; substrate, 0.02 mol; oxidant, 0.04 mol; *t*-BuOH, 10 g.

[a] Diolether.
[b] Benzaldehyde.
[c] 2-Phenyl propionaldehyde.
[d] Limonene 1,2-diol.
[e] Limonene 8,9-diol.
[f] Limonene 1,2-diol 8,9 oxide.
[g] Limonene diepoxide.
[h] Unidentified product.
[i] Allylic oxidation products (cyclopentenone 13% + cyclopentenol 5%).

complexes [38]. The acetylide moiety remains intact even after addition of H_2O_2, which is confirmed by broad low intensity band centered at $2100 \, cm^{-1}$ assigned to $\nu(C{\equiv}C)$. The bands due to C–H stretching vibrations of phenyl ring are observed in the range 2854–$2955 \, cm^{-1}$ and the C=C stretching vibrations of the ring are observed at 1464 and $1377 \, cm^{-1}$ even after addition of hydrogen peroxide. The bands due to carbonyl stretching (1940, $2031 \, cm^{-1}$) disappear after addition of H_2O_2. This clearly indicates the removal of all the CO ligands after addition of hydrogen peroxide forming higher oxidation state Mo (VI) complex with retention of acetylide, C≡C–Ph group attached to Mo center. Roskey et al. [39] have reported for first time structural char-

acterization of chloride oxo–peroxo compounds of Mo and W. The structure of the oxo–peroxo has been confirmed by single crystal X-ray diffraction analysis.

UV–vis spectral analysis (Fig. 2) of the blue complex shows absorbance in the UV region at λ_{max} 221 nm and shoulder at 305 and 326 nm. This can be attributed to charge transfer associated with organic group or MoO moiety. Broad absorption in visible region ~747 nm is responsible for the blue color of the complex. It can be due to d–d transitions involving Mo(V) and inter valence charge transfer transition (IVCT) between Mo(V) and Mo(VI) via an oxo bridge. The shoulder peaks at 305 and 326 nm can be attributed to peroxo ligand to metal charge trans-
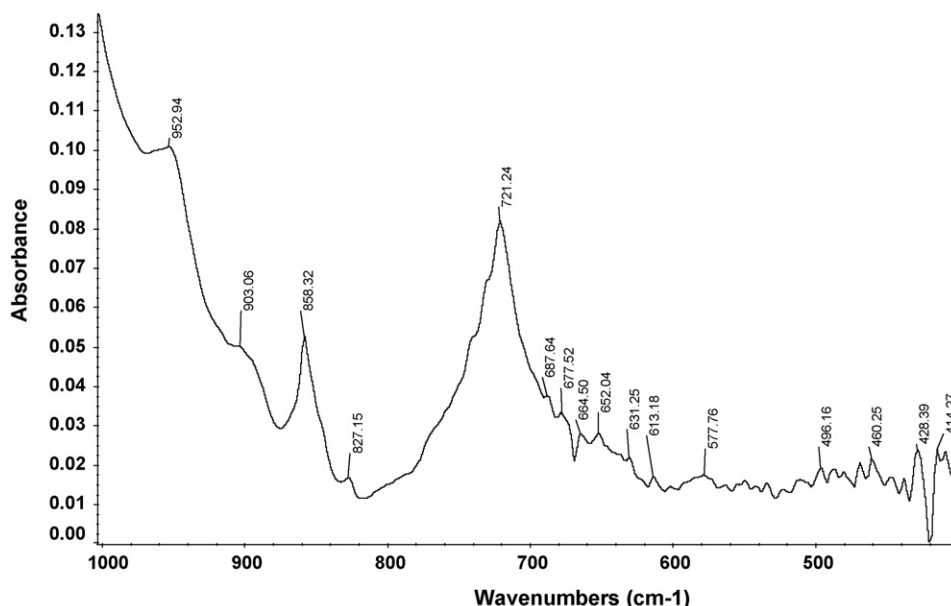

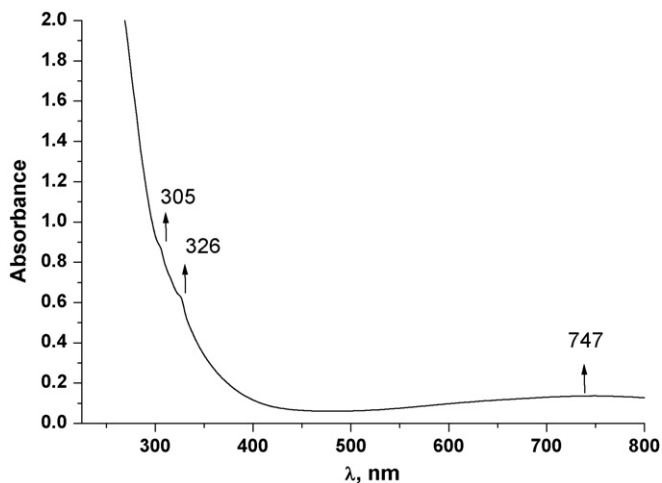Fig. 1. FTIR spectrum of Catalyst **1** after addition of H_2O_2.

Fig. 2. UV–vis spectrum of blue complex.

Fig. 4. XPS spectrum of the Mo(3d) levels of blue complex.

fer (LMCT), which is in good agreement with the literature values reported for peroxo Mo-nicotinic acid complexes (304 and 310 nm) [40]. The UV spectrum of catalyst **1** after addition of hydrogen peroxide (Fig. 3) shows two broad absorptions at 233 and 315 nm, which confirms the formation of molybdenum peroxo species. The UV spectrum of catalyst **1** shows absorption at λ_{max} 270 nm, with a shoulder at 285 nm and a broad band centered at 386. Attempts were made to record the ^{1}H and ^{95}Mo NMR spectrum of blue complex, however no signal was obtained due to presence of paramagnetic Mo(V) center.

XPS studies of the blue complex confirmed the presence of mixed valent molybdenum centers, Mo(VI) and Mo(V). Fig. 4 shows the XPS spectrum of the Mo 3d levels of blue complex. The experimental data represented by solid circles clearly shows the characteristic Mo(3d) doublet composed of the $3d_{5/2}$ and $3d_{3/2}$ levels produced by spin-orbit coupling. Good fitting of the data points is made using two pairs of Gaussian functions, corresponding to two possible 3d doublets of Mo in different oxidation states, viz., Mo(VI) and Mo(V). The contribution from the Gaussian peaks centered at 232.0 and 235.2 eV is major and is assigned to Mo(V). However the minor peaks centered at
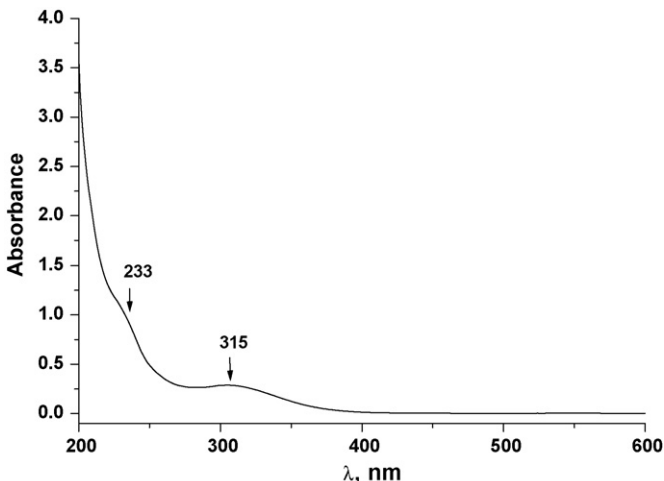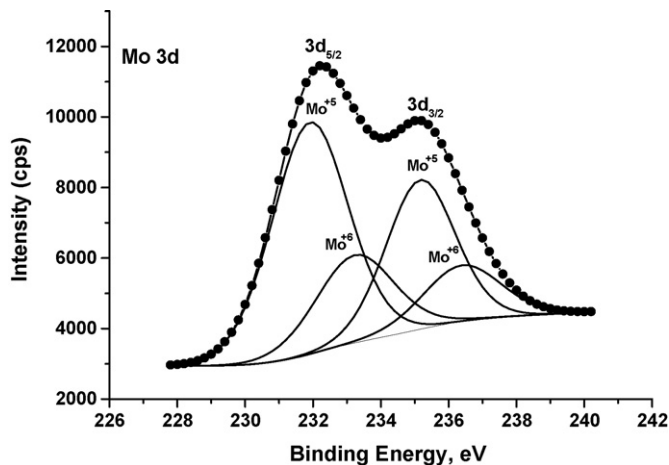
233.4 and 236.4 eV are assigned to Mo(VI). From the ratio of the areas of the two Gaussian pairs, the ratio of Mo(V) to Mo(VI) is 0.72/0.28, which clearly shows that Mo(V) is predominantly present in the blue complex. The binding energies are in agreement with the literature values [41]. Moraes et al. have prepared molybdenum oxide thin films by hot filament metal oxide deposition technique and characterized using XPS which indicates that Mo atoms are in mixed valence state, Mo(VI) (232.7 and 235.8 eV) and Mo(V) (231.6 and 234.6 eV) with high predominance of Mo(VI) and formation of oxygen deficient MoO$_3$ film [42]. Thus XPS results of blue complex support the FTIR as well as UV–vis data for presence of molybdenum centers in mixed oxidation state, Mo(+5) and Mo(+6).

3.1. Cyclic voltammetric studies

In the following section, we report the electrochemical investigation of Mo catalysts in various steps. Our results summarize the redox behavior of a blue complex containing molybdenum in two different oxidation states viz. Mo (V) and Mo (VI). Voltammetric response of 0.1 M catalyst **1** in dichloromethane shows no peak corresponding to the redox behavior of catalyst (Fig. 5A). The cyclic voltammetric response of the same catalyst after addition of hydrogen peroxide (Fig. 5B) shows the time dependent increment in the irreversible oxidation peak at potential −0.080 V (whereas a slightly time dependent shift towards negative potential −0.370 V), which indicates the direct conversion of electro inactive species Mo (0) to stable higher oxidation state species Mo (VI) [43]. The slight oxidation peak could be observed in the voltammograms after the addition of the H$_2$O$_2$ to the catalytic solution, due to the oxygen adsorption on the platinum wire in a potential window between −0.5 and −0.2 V v/s Fc/Fc$^+$ redox couple. Due to this reason the shift of nearly 290 mV in potential towards negative potential is seen.

The voltammograms for blue molybdenum intermediate complex is shown in Fig. 6, which illustrates at a point of cathodic potential cycle (−0.65 and −0.96 V v/s Fc/Fc$^+$) indicates a one electron per molybdenum reduction and the same occurs in the case of anodic potential cycle giving the second

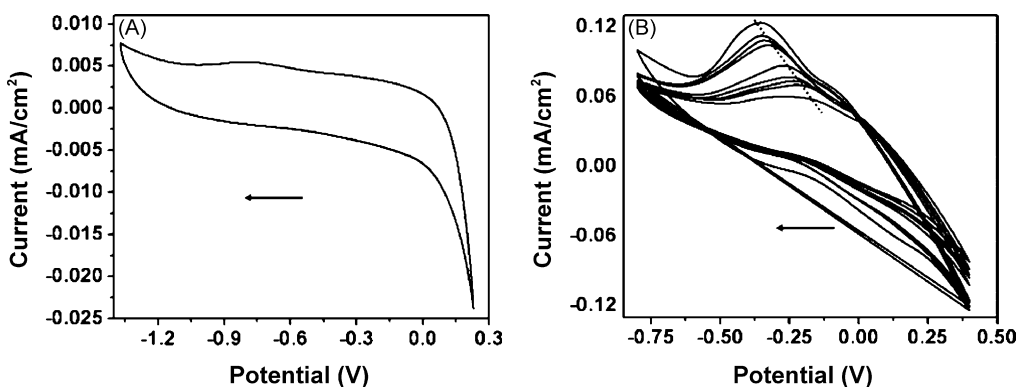Fig. 3. UV–vis spectrum of catalyst **1** after addition of hydrogen peroxide.

Fig. 5. (A) Cyclic voltammogram of catalyst **1** in CH_2Cl_2 at 50 mV/s scan rate (B) Time dependent (after each 5 min) cyclic voltammograms of catalyst **1** after addition of H_2O_2 at 50 mV/s scan rate.
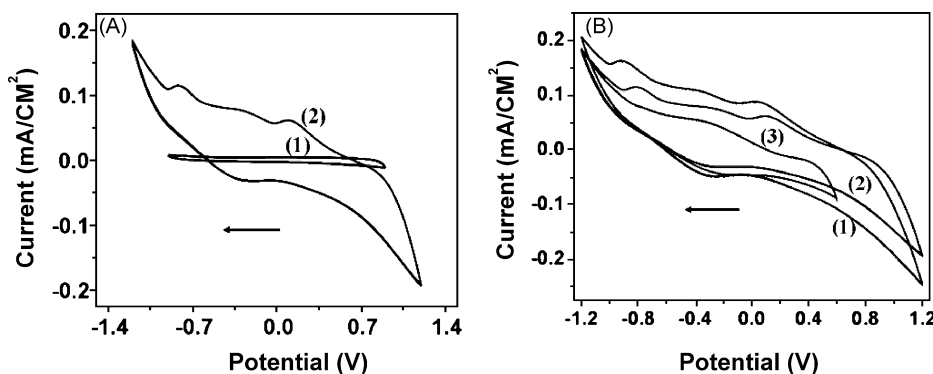

Fig. 6. (A) Superimposed cyclic voltammograms of blank (1) and of blue complex (2) in CH_2Cl_2 using 0.1 M tetrabutyl ammoniumhexaflorophosphate as a supporting electrolyte. (B) Cycle dependence redox peaks of blue complex.

pair of peaks at −0.3 and −0.89 V v/s Fc/Fc⁺ respectively. A cyclic voltammogram of the freshly prepared complex recorded immediately interestingly indicates that the peaks at −0.96 and −0.89 V dominates initially and with time the −0.65 and −0.3 V peaks increase in height, these voltammetric results confirms that the −0.96 V species is coupled with −0.89 V species and the −0.3 V peak is coupled with the −0.89 V peak. The first two peaks are for two forms of Mo (VI) and the second two peaks are for Mo (V).

Fig. 6B shows an increment in peak currents of Mo (VI) and Mo (V) accompanied by a shift to more positive values in the first two cycles indicating increased difficulty in oxidation. This could be attributed to some structural changes accompanying oxidation of the Mo centers, decreasing the thermodynamic feasibility (known from the formal potentials) of the anodic processes [44]. Interestingly, both the anodic peaks are found to merge in the third cycle giving rise to one broad peak at an intermediate potential, which could be due to the formation of mixed valence [Mo (VI) and Mo (V)] species.

3.2. Mechanistic studies

Traditional OsO_4 catalyzed dihydroxylation takes place by the mechanism where C=C double bond undergoes either 3 + 2 addition to O=Os=O to form 5 membered metallacycle or it undergoes 2 + 2 addition to Os=O to give 4 membered metallacycle followed by rearrangement [45]. During the five membered

ring formation Os(VIII) gets reduced to Os(VI), which is reoxidised using co-oxidant. Recently, Che et al. [46] have reported stoichiometric *cis*-dihydroxylation of alkenes using $[(Me_3tanc)(CF_3CO_2)Ru^{VI}O_2]^+$ complex where dioxo ligands are in *cis*-configuration. In this reaction the 3 + 2 cyclo addition of alkene to *cis*-dioxo moiety has been proved by isolating
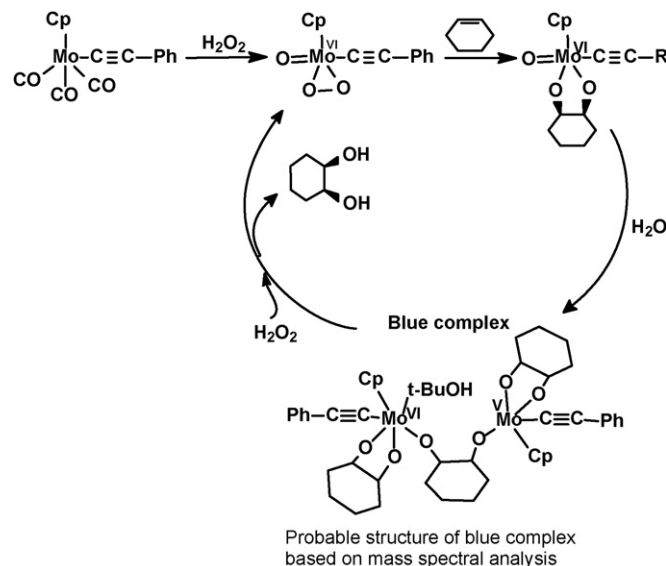
Scheme 2. Proposed mechanism for cyclohexene dihydroxylation.

and characterizing the adduct by single crystal X-ray diffraction analysis. This gives an evidence for five membered metallacycle as intermediate for *cis*-dihydroxylation using MO_2 systems. Geoffroy [47] has reported $2+2$ cyclo addition of ketene to $Cp*WO_3^-$ anion where C=C bond of ketene adds to W=O to give four membered ring. Many organic and inorganic moieties add across one of the W=O bond of $Cp*WO_3^-$ to give cyclic or acyclic addition products.

The speculated mechanism for molybdenum acetylide **1** catalyzed dihydroxylation is given in Scheme 2, where in the first step Mo oxo–peroxo complex is formed in presence of H_2O_2, which has been confirmed by FTIR and UV–vis spectral analysis. In the second step $3+2$ addition of C=C of cyclohexene to Mo-peroxo moiety takes place to give five membered metallacycle intermediate. In this case $2+2$ addition followed by rearrangement to give 5 membered ring does not look probable as initial presence of 2 rings (3 membered M-peroxo and 4 membered ring) on one metal centre would be sterically hindered, hence $3+2$ addition seems more probable. Dimerisation of the intermediate after probable reaction with water to give blue complex before the diol is liberated followed by reaction of Mo(IV) species thus formed with H_2O_2 to give again Mo-oxo–peroxo complex completes the catalytic cycle. The probable structure of blue complex is suggested based on the ESI-MS studies of the mixture.

In the case of cyclohexene initial epoxide formation followed by hydrolysis of epoxide ring to yield diol does not look probable, as no trace of epoxide was observed in GC analysis. Kholdeeva et al. [48] have reported epoxide ring opening to give selective *trans*-diol formation using polyoxometalate. However in case of cyclohexene only *cis*-isomer is obtained without formation of even trace amount of *trans*-isomer.

4. Conclusion

In summary molybdenum acetylide complex has proven to be an efficient catalyst for dihydroxylation of olefins with high conversion and selectivity for vicinal diols. This molybdenum acetylide complex is highly stable and can be recycled efficiently. This system overcomes the drawbacks of osmium systems as well as no co-catalyst or co-oxidant is needed. Hydrogen peroxide acts as efficient and environmentally benign oxidizing agent. Very high TON is obtained when *t*-butanol is used as solvent. This catalyst has potential to be used for asymmetric dihydroxylation (AD) with use of chiral cyclopentadiene as ligand instead of simple cyclopentadiene.

Acknowledgments

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