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Efficient asymmetric Baeyer–Villiger oxidation of prochiral cyclobutanones using new polymer-supported and unsupported chiral co(salen) complexes

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Abstract. Two heterogeneous catalysts **4** and **5** and three homogenous complexes **1–3** were prepared and used for enantioselective Baeyer–Villiger (B–V) oxidation of prochiral cyclobutanones. Among the prepared catalysts, the supported ones showed better enantioselectivity, good thermal stability and negligible loss of activity over consecutive recycling offset by lower chemical yield.

Keywords. Polymer-supported; enantioselective; Baeyer–Villiger oxidation; cyclobutanones; Co(Salen) Complexes.

1. Introduction

B–V oxidation is a very old and valuable chemical transformation that was first discovered in 1899[1] and subsequently converted into a catalytic process in 1993.[2] Despite its long history, its enantioselective version using transition metal catalysts is relatively recent.[3–12]

B–V oxidation is a two-step reaction: (i) nucleophilic addition of an oxidant giving the Criegee adduct and (ii) rearrangement of the adduct to ester (or lactone). If the starting carbonyl compound is a pro-chiral cyclic one, the products are a pair of enantiomeric lactones (figure 1). The stereochemistry of the B–V reaction is dictated by two factors: face selectivity in oxidant addition and enantiotopos selectivity in migration. However, as Criegee adduct formation is a reversible step and its migration to lactone is an irreversible and rate-determining one, topos-selection in the migration step is considered to strongly influence the stereochemistry of B–V reaction. Interaction of the σ-orbital of the migrating C–C bond and the σ^*-orbital of the O–O bond is crucial for the migration.[13] Therefore, it was expected that high enantioselectivity would be achieved if the σ-bond interacts with the σ^*-bond topos-selectively. It was also considered that the topos-selective interaction would be realized if the Criegee adduct makes a chelate (Criegee adduct B), and the chelate conformation is regulated appropriately. Furthermore, a metallosalen complex with *cis*-structure was considered to be a suitable catalyst for this purpose, because it provides two neighbouring coordinating sites for chelate formation and its metal center is chiral.[4]

As discussed above, each factor shifting the equilibrium between intermediates A and B toward intermediate B, must increase enatioselectivitiy of the reaction. Accordingly, unfavourable steric hindrance next to the center of reaction introduced by ligand, substrate or oxidant proceeds reaction through the less sterically congested transition state A.

[Co(salen)]s show high asymmetric induction[14,15] and high Lewis acidity.[15] In addition, it has been reported that iron, manganese, titanium and some of the cobalt complexes of Schiff base took *cis*-β structure.[4,16,17] On the other hand, it has been reported that electron-withdrawing groups on the salen ligand of the Cu(III) complexes increase enatioselectivitiy of such a reaction.[5]

Keeping these considerations in our mind and in order to investigate electronic and steric effects of ligands on the enantioselectivity and the chemical yield of B–V oxidations, we have synthesized three chairal complexes **1–3**, bearing three different salen ligands.

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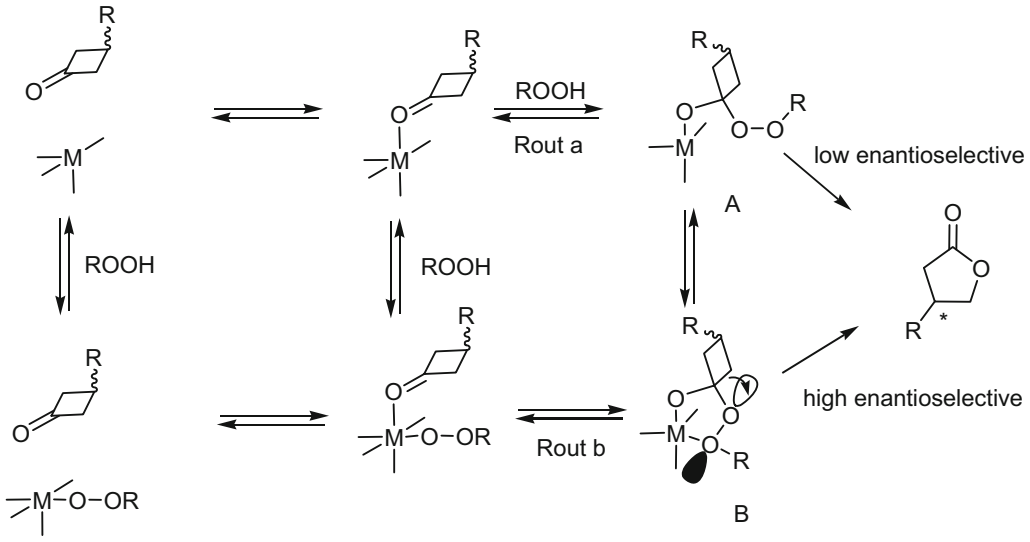


Figure 1. Schematic representation of M-adduct complexes.

Despite high efficiency of catalysts **1** and **2** for asymmetric B–V reactions, separation of these from the reaction mixture was a serious problem. Additionally, in order to investigate probable supporting effects, we prepared polymer-supported catalysts **4** and **5**, which were nearly heterogeneous types of catalysts **1** and **2**.

2. Experimental

2.1 *General*

All solvents and commercially available starting materials were supplied by Merk Chemical Co. (Darmstadt, Germany) and Fluka Co. and were used as received. The 3-substituted cyclobutanones were prepared according to the literatures.[18,19] ^{1}HNMR and IR spectrums were recorded on a Bruker BRX-100 AVANCE and Shimadzu-IR 470 spectrometer, respectively. Elemental analysis for CHN was carried out by the CHNO type from the Helaus Co.

2.2 *General procedures*

Complex **2** was synthesized according to Katsuki's procedure.[7c] [Co(salen)] complexes **1** and **3** were also synthesized similarly (figure 2).

2.2a *[Co(salen)] complex **1***: Brown solid. IR (KBr): 3090, 3005, 2912, 2910, 1612, 1554, 1500, 1486, 1436, 1387, 1315, 1210, 1182, 1124, 1076, 1036, 989, 927, 871, 822, 802, 742, 692, 572, 522, 492. Anal. calc. for $C_{34}H_{18}CoIN_6O_{10}$: C, 47.68; H, 2.12; N, 9.81; found: C, 47.11; H, 2.01; N, 9.76.

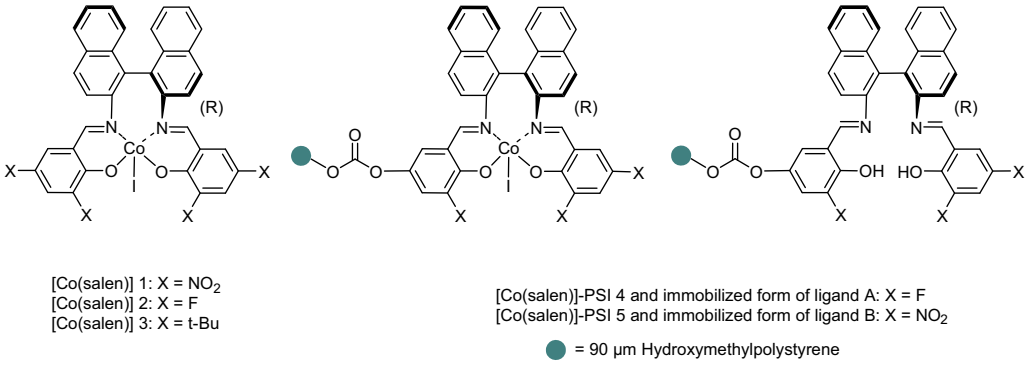


Figure 2. Structures of Co(III)(salen) complexes **1–5** and ligands **A** and **B**.

2.2b *[Co(salen)] complex **3***: Brown solid. IR (KBr): 3059, 2957, 2916, 2870, 1593, 1470, 1419, 1250, 1200, 1173, 1115, 1076, 1028, 984, 922, 809, 798, 739, 681, 561, 509, 484. Anal. calc. for $C_{50}H_{54}CoIN_2O_2$: C, 66.67; H, 6.04; N, 3.11; found: C, 66.59; H, 6.00; N, 3.02.

Polymer-bound ligands **A** and **B** were prepared according to Jacobsen's procedure[15b] (figure 2). To a solution of 2-hydroxy-3,5-dinitrobenzaldehyde (0.7 mmol) and 2,6-dihydroxy-3-nitrobenzaldehyde (0.7 mmol) in EtOH was added (1R)-1,1′-binaphthalene-2,2′-diamine (0.7 mmol) and the mixture was refluxed for 4 h. After cooling to room temperature (rt), the resulting yellow foam was filtered off and dried *in vacuo*. Dissymmetric ligand **B** was separated from the mixture by column chromatography (eluent: diethyl ether/hexanes, 1:20). Dissymmetric ligand **A** was prepared similarly.

2.2c *Dissymmetric ligand B*: Yellow solid. ^{1}HNMR ($CDCl_3$, 100 MHz): δ 7.1–7.9 (m, 12H), 8.5(s, 1H), 8.8 (s, 1H), 9.3 (s, 1H), 13.0 (bs, 1H). Anal. calc. for $C_{34}H_{21}N_5O_9$: C, 63.45; H, 3.29; N, 10.88; found: C, 63.21; H, 3.21; N, 10.80.

2.2d *Dissymmetric ligand A*: Yellow solid. ^{1}HNMR ($CDCl_3$, 100 MHz): δ 6.9–7.8 (m, 16H), 8.4(s, 1H), 13.2 (bs, 1H). Anal. calc. for $C_{34}H_{21}F_3N_2O_3$: C, 72.59; H, 3.76; N, 4.98; found: C, 72.36; H, 3.71; N, 4.91.

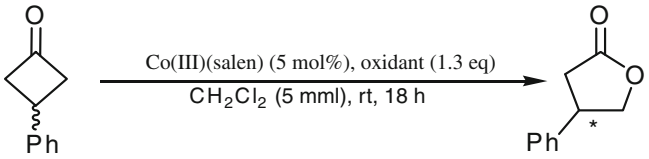
For immobilization of ligads **A** and **B**, hydroxymethyl polystyrene resin (Advanced Chemtech, 2% cross-linked 90 μm beads, 0.8 mmol/g) were firstly activated by 4-nitrophenyl chloroformate according to the Jacobsen's work.[15b] An excess amount of 4-nitrophenyl chloroformate reagent was used to obtain maximum conversion of OH. IR spectra of products showed no absorption at 3460 cm^{-1} (OH). Moreover, the introduction of 4-nitrophenyl carbonate into polymer matrix resulted strong bands at 1770 (C=O) (for the both ligands), 1535, 1345 and 870 cm^{-1} (NO_2) (for ligand **A**).

To a suspension of activated resin (0.4 mmol) in anhydrous DMF (5.0 mL) was added ligand **A** (0.59 mmol), DMAP (0.4 mmol), and DIPEA (0.8 mmol). The resulting orange suspension was shaken at room temperature for 1.5 h, then filtered and rinsed sequentially with DMF, MeOH and CH_2Cl_2 and dried *in vacuo* to yield orange beads as Polymer-bound ligand **A**. Polymer-bound ligand **B** were synthesized in the same manner. Strong bands observed at 1630–1642 cm^{-1} (C=N) (for the both ligands) with disappearance of bands at 1530, 1350 and 860 cm^{-1} (NO_2) (for the ligand **A**) in the IR spectra indicated the high conversion of activated resin to the suitable polymer-bound ligands.

Cobalt insertion into the polystyrene-bound ligands was accomplished by adding solution of $Co(OAc)_2$ (0.4 mmol), which was obtained by heating $Co(OAc)_2.4H_2O$ at 70–80°C under vacuum until its colour turned from pink to purple, in 5 ml of degassed MeOH/Toluen 1:1 to the polymer-bound ligand (0.4 mmol) with gentle stirring. The mixture was heated at 60°C for 24 h and then evaporated and the residue suspended in CH_2Cl_2 (15 ml). To this mixture, I_2 (0.2 mmol) was added. After stirring for 4 h, the mixtures was evaporated and the residue was rinsed with toluene and CH_2Cl_2 several times to obtain complexes **4** and **5**.

Complexing of cobalt ions by polymer-bound ligand resulted in shifting of the imine absorption band location towards lower frequency (about 15 cm^{-1}). Elemental analysis of complexes **4** and **5** indicated 1.81 and 1.86% Co, respectively, corresponding to a final loading of almost 0.30 mmol/g of Co. Procedure of B–V oxidation was followed from Katsuki's procedure.[4]

Table 1. Effects of oxidant, substituent and supporting on enantioselectivity and chemical yield of B–V oxidation.



Entry	Catalyst	Oxidant	Yield%	ee%[c]
1[a]	1	H_2O_2[d]	54	58
2	2	H_2O_2[d]	39	55
3	3	H_2O_2[d]	25	18
4	4	H_2O_2[d]	21	59
5[a]	5	H_2O_2[d]	51	61
6[a]	1	UHP	53	62
7	2	UHP	40	61
8	3	UHP	22	24
9	4	UHP	27	65
10[a]	5	UHP	46	67
11[b]	1	mCPBA	65	0
12[b]	2	mCPBA	69	0
13[b]	3	mCPBA	78	0
16[a]	1	TBHP	53	0
17	2	TBHP	48	0
18	3	TBHP	64	0

[a]Reaction was stirred for 30 minutes. [b]Reaction was carried out at −78°C in the presence of 1 equiv. of *N*-methylmorpholine *N*-oxide. [c]Determined by GC column LipodexB. [d]Aqueous hydrogen peroxide (30%)

3. Results and discussions

Complexes **1–5** were examined for asymmetric B–V oxidation of 3-phenylcyclobutanone by different oxidants (table 1). Just for comparison, we used catalyst **2** reported already by Katsuki *et al.*[7c]

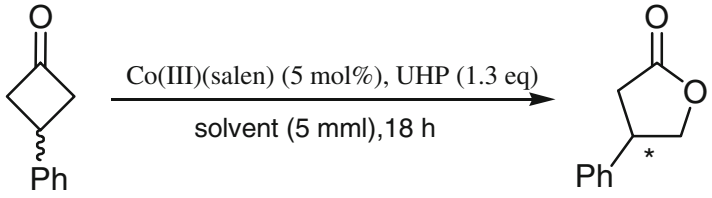
The order of enentioselectivity and chemical yield of reactions using catalyst **1–3** was revealed as **1**>**2**>**3** (table 1, entries 1–3). Among the examined reactions, the one was performed with a combination of H_2O_2 and catalyst **1**, bearing a ligand with four strong withdrawing substituents of NO_2, showed the moderate chemical yield of 54% and good enentioselectivity of 58% at a short time of 30 minutes (table 1, entry 1). Catalyst **2** catalysed such a reaction with comparable enentioselectivity, but with lower yield and longer time of reaction (table 1, entry 2). On the other hand, four steric substituents of *t*-butyl, on the catalyst **3** were considered to decrease enentioselectivity to the extent of 18% (table 1, entry 3). The unfavourable steric effect introduced by four *t*-Butyl groups lead reaction to proceed mainly through the non-chelated Criegee adduct A, resulting in low enentioselectivity.

Reactions performed by H_2O_2 in the presence of supported catalysts **4** and **5** showed slightly better enentioselectivities (59% and 61%, respectively) offset by lower chemical yields (table 1, entries 1, 2, 4, 5).

Furthermore, the use of UHP (urea.H_2O_2 adduct) instead of aqueous H_2O_2, for all the reactions, slightly improved enentioselectivities (table 1, entries 6–10). Additionally, the reactions performed with a combination of catalyst **1–3** and mCPBA (meta-chloroperbenzoic acid) or TBHP (*t*-butyl hydroperoxide) as oxidants showed no enentioselectivities (table 1, entries 11–18). This probably suggested that the oxidants such as TBHP and *m*-CPBA attacked the carbonyl group in an intermolecular fashion giving non-chelated Criegee adduct A, while hydrogen peroxide was coordinated to the metal ion and attacked the carbonyl group to give chelated Criegee adduct B (figure 1).

The effects of solvent and temperature on enantioselectivities and chemical yields of the above reactions by UHP in the presence of catalysts **1–5** were also examined (table 2). Al reactions performed in polar solvents such as AcOEt, CH_3CN, THF and alcohols showed slightly better enantioselectivities and chemical yields

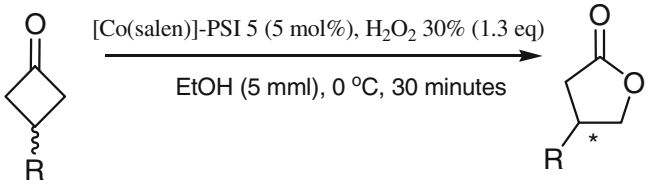
Table 2. Effects of solvent and temperature on enantioselectivity and chemical yield of B–V oxidation.



Entry	Solvent	Temperature	Yield%					ee%[a]				
			Catalyst NO.					Catalyst NO.				
			1[b]	2	3	4	5[b]	1[b]	2	3	4	5[b]
1	EtOH	−10°C	75	56	36	53	67	80	75	35	77	83
2	EtOH	0°C	72	54	33	46	64	77	71	32	75	81
3[c]	EtOH	0°C	73	51	35	48	63	76	72	34	76	80
4	EtOH	RT	62	48	31	43	53	73	70	30	74	79
5	Hexan	RT	55	39	19	25	45	61	59	19	65	68
6	Toluene	RT	39	21	15	19	40	68	65	23	67	70
7	Benzene	RT	41	19	16	17	37	60	58	21	64	67
8	CH_2Cl_2	RT	53	40	22	27	46	62	61	24	65	67
9	AcOEt	RT	64	47	27	34	51	71	68	28	72	75
10	CH_3CN	RT	59	44	26	32	48	70	69	27	71	76
11	THF	RT	59	48	25	36	51	71	67	28	70	73
12	EtOH	30°C	54	39	27	41	52	64	60	21	73	79
13	EtOH	40°C	46	28	18	41	53	51	46	11	71	77

[a]Determined by GC column Lipodex B, absolute configuration not assigned. [b]Reaction was stirred for 30 minutes. [c]Aqueous hydrogen peroxide (30%) was used as terminal oxidant

Table 3. Asymmetric B–V oxidation of 3-arylphenylcyclobutanone in the presence of fresh and recycled [Co(salen)]-PSI 5.



Entry	R	Yield%	ee%[a]
1	4-$MeOC_6H_4$	66	79
2[b]	4-$MeOC_6H_4$	65	79
3[c]	4-$MeOC_6H_4$	63	78
4[d]	4-$MeOC_6H_4$	64	80
5[e]	4-$MeOC_6H_4$	65	78
6	4-MeC_6H_4	59	77
7	Ph	50	75
8	4-BrC_6H_4	47	66
9	4-ClC_6H_4	39	61
10	4-FC_6H_4	32	54

[a]Determined by GC column Lipodex B. [b–e]Reusability of the recovered catalyst in new runs

than those in non-polar solvents such as hexane, toluene and CH_2Cl_2 (table 2, entries 4–11).

Lowering the reaction temperature particularly to −10°C improved enantioselectivities and chemical yields of all the reactions (table 2, entries 1 and 2). At −10°C, the reaction performed by UHB in the presence of catalyst **5** revealed good enantioselectivity of 83% (table 2, entry 1).

It is noteworthy that aqueous H_2O_2 (30%) can be used as terminal oxidant nearly as efficiently as UHP when ethanol was used as solvent (table 2, entries 2 and 3). On the other hand, raising temperature up to 40°C adversely affected the enantioselectivities and chemical yields obtained by homogeneous catalysts **1–3** while those were obtained by heterogeneous catalysts **4** and **5** nearly remained constant (table 2, entries 12, 13).

Additionally, various 3-substituted cyclobutanones by UHP in the presence of [Co(salen)]-PSI **5** were oxidized (table 3). The enantioselectivities and chemical yields of reactions were influenced by the electronic properties of the substrates. Derivatives bearing more electron-donating groups of methoxy and methyl were converted into the corresponding lactones with higher enantioselectivities and chemical yields (table 3, entries 1, 6–10).

Finally, our study revealed that [Co(salen)]-PSI **5** could be reused without significant loss of its enantioselectivity by at least 4 times (table 3, entries 2–5).

4. Conclusion

This study demonstrates the synthetic applicability of homogeneous [Co(salen)] and heterogeneous [Co(salen)]-PSI complexes in B–V oxidation of 3-arylcyclobutanones. Our studies revealed that electron deficiency of catalyst increases enantioselectivity and chemical yield of B–V reactions as long as these catalysts possess enough space for formation of the chelated Criegee adduct B. The attachment of [Co(salen)] complexes on the functionalized polystyrene provides catalysts **4** and **5** which can be reused several times without significant loss of their activities. We have also demonstrated that supported catalysts **4** and **5** are featured by: (i) no significant loss of enantioselectivity in the catalytic systems with increasing of temperature up to 40°C; (ii) higher enantioselectivity in comparison with their homogeneous analogues.

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