Asymmetric Sulfimidation with *cis*-β Ru(salalen)$(CO)_2$ Complexes as Catalyst

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Ru(salalen)$(CO)_2$ complexes were found to serve as catalysts for asymmetric sulfimidation under irradiation, and high enantioselectivity (up to 90% ee) was obtained. In addition, the structures of two Ru(salalen)$(CO)_2$ complexes that carry the ligands of the same configuration but induce opposite asymmetry to each other, were determined by X-ray diffraction analysis.

Cis-β metal(ONNO) complexes have received much attention due to their unique catalytic performances that have brought about significant advancements in asymmetric synthesis in the last decade (Figure 1).[1] Various highly enantioselective catalytic reactions have been achieved by using cis-β metal-(salen),[2] -(salalen),[3] or –(salan)[4] complex as catalysts. It should be noted that the metal center and the metal-bound amine nitrogen atom in salalen or salan ligand are chiral. In addition, the cis-β metal(salalen) complex is unique in that two ancillary ligands (X and Y) are spatially and electronically non-equivalent. Catalytic potential of optically active salalen complexes as catalyst has already been proved by several studies,[3] but the metal centers of the complexes used for the studies were limited to typical or early transition-metal ions.[1,5] Since late transition-metal complexes are known to show versatile catalysis, we were intrigued by asymmetric catalysis of late transition-metal-(salalen) complexes. Although there have been reported many methods for asymmetric sulfimidation using $ArSO_2N{=}IPh$ as the nitrene precursor,[6] we recently found that *trans*-Ru(salen)(CO) complexes bearing a bulky binaphthyl chiral unit served as excellent catalysts for sulfimidation and aziridination using more atom-efficient azide compounds as the precursor.[7] We expected that a *cis*-β Ru(salalen)(CO) complex would show high asymmetric induction, even if the salalen ligand is structurally simple. Thus, we prepared Ru(salalen)$(CO)_2$ complexes (**1**–**7**) that have a common core salalen structure but differ in C3,3′- and C5,5′-substituents[3d] according to the reported procedure with a slight modification,[7b] and we examined asymmetric sulfimidation using an azide compound. Because two CO ligands have a tendency to coordinate with a metal ion in a cis-position due to its strong trans-effect,[8] the Ru(salalen)$(CO)_2$ complexes were considered to adopt a cis-β configuration. IR spectra of these complexes showed two strong absorptions at 2035–2050 and 1950–1970 cm^{-1}, supporting the presumption that the complexes adopted a cis-β configuration. We also synthesized Ru(salen)$(CO)_2$ complex **8**[8] in the same manner. The IR spectrum of **8** also showed two strong absorptions.

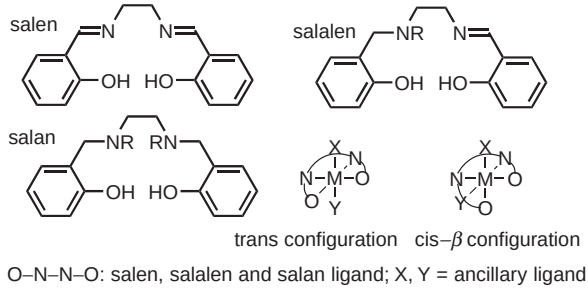
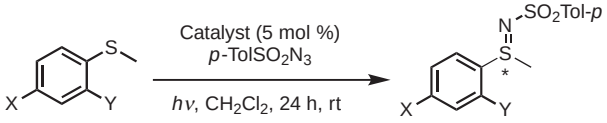


Figure 1. Basic structures of salen, salalen, and salan ligands.

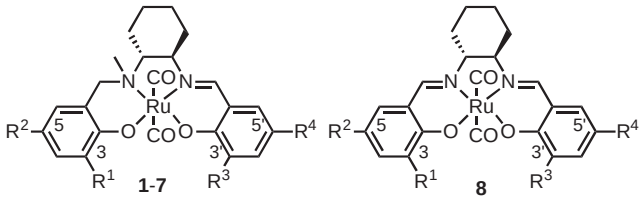
Sulfimidation of methyl phenyl sulfide using *p*-toluenesulfonyl azide was examined with complexes **1**–**8** as catalysts (Table 1). The reaction with **1** showed good enantioselectivity of 87% ee, but the reaction was slow because of slow dissociation of a CO ligand (Entry 1). It has been reported that the dissociation of a CO ligand from $M(CO)_2$-type complexes is promoted by irradiation.[9] Thus, we performed the sulfimidation

Table 1. Asymmetric sulfimidation using various Ru(salen)-$(CO)_2$ complex as catalyst



Entry	Catalyst	X	Y	$h\nu$	Yield/%[a]	ee/%
1	**1**	H	H	−	22	87[b]
2	**1**	H	H	+	82	88[b]
3	**2**	H	H	+	69	76[b]
4	**3**	H	H	+	91	87[b]
5	**4**	H	H	+	97	90[b]
6	**5**	H	H	+	74	76[b]
7	**6**	H	H	+	60	−44[b]
8	**7**	H	H	+	20	−38[b]
9	**8**	H	H	+	7	59[b]
10	**4**	CH_3	H	+	91	87[c]
11	**4**	CH_3O	H	+	93	89[d]
12	**4**	Cl	H	+	61	85[c]
13	**4**	H	Cl	+	0	

[a]Isolated yield. [b]Determined by HPLC analysis using DAICEL CHIRALCEL OJ-H (hexane:*i*-PrOH = 2:1). [c]Determined by HPLC analysis using DAICEL CHIRALCEL OJ-H (hexane: *i*-PrOH = 3:1). [d]Determined by HPLC analysis using DAICEL CHIRALCEL OJ-H (hexane:*i*-PrOH = 1:1).



1: $R^1{=}R^2{=}R^3{=}R^4{=}$ *t*-Bu
2: $R^1{=}R^2{=}R^3{=}$ *t*-Bu, $R^4{=}$ MeO
3: $R^1{=}R^2{=}R^3{=}$ *t*-Bu, $R^4{=}$ Br
4: $R^1{=}R^2{=}R^3{=}$ *t*-Bu, $R^4{=}$ H
5: $R^1{=}R^2{=}$ Cl, $R^3{=}R^4{=}$ *t*-Bu
6: $R^1{=}R^2{=}$ *t*-Bu, $R^3{=}R^4{=}$ Br
7: $R^1{=}R^2{=}$ *t*-Bu, $R^3{=}R^4{=}$ Cl
8: $R^1{=}R^2{=}R^3{=}R^4{=}$ *t*-Bu

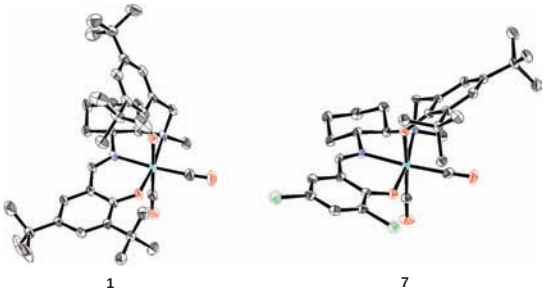


Figure 2. The ORTEP drawings of complexes **1** and **7**. All the hydrogen atoms are omitted for clarity.

under irradiation using a halogen lamp as the light source and found that the reaction was remarkably accelerated without impairing enantioselectivity (Entry 2). We also examined the sulfimidation using other complexes (**2**–**7**) as catalysts under irradiation. The substituents at C3, C5, and C5′ affected stereoselectivity to a small extent, and complexes (**1**–**5**) showed the same sense and similar level of enantioselectivity (Entries 2–6). The optimal enantioselectivity of 90% ee was obtained with complex **4** (Entry 5). In contrast, the substituent at C3′ significantly influenced stereoselectivity: replacement of the C3′-*t*-butyl group with a chloro or bromo substituent not only reduced enantioselectivity but also reversed its sense (c.f. Entries 2, 7, and 8). On the other hand, the catalytic activity of complex **8** that carries the same substituents as **1** was poor under identical conditions, and its asymmetric induction was moderate (Entry 9).

Under the optimized conditions, we examined sulfimidation of several other aryl methyl sulfides. The reaction of p-substituted sulfides proceeded with good enantioselectivity (85–89% ee) and acceptable yields (Entries 10–12), but the reaction of o-Cl-substituted sulfide did not proceed under the conditions (Entry 13).[10]

We also examined sulfimidation of sulfides other than aryl methyl sulfides, but the reaction rates were slow and enantioselectivity was moderate.[11]

During this study, we obtained single crystals of complexes **1** and **7** that induced asymmetry in an opposite sense to each other from a mixture of hexane and CH_2Cl_2, respectively. X-ray analyses of these crystals demonstrated that both complexes adopt cis-β configuration; however, complex **1** possesses a folded structure, while complex **7** possesses a stepped structure (Figure 2). In both **1** and **7**, one CO ligand occupies the equatorial position and the other occupies the axial position, as expected from IR measurements.

In summary, we were able to demonstrate that Ru(salalen)-$(CO)_2$ complexes bearing a *t*-butyl group at C3 and C3′ serve as good catalysts for asymmetric sulfimidation, though their structures are simple. In addition, we could determine the structures of complexes **1** and **7** unambiguously by X-ray analysis.[12] The present study will open an avenue for a practical asymmetric sulfimidation methodology. Further study on the mechanism of asymmetric induction is now proceeding in our laboratory.

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References and Notes

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10 The sulfimidation of $CH_3SC_6H_4$(*o*-OMe) was also sluggish. These results indicate that the electronic effect of the o-substituent is not responsible for low reactivity of o-substituted aryl methyl sulfides.

11 For examples, the reactions of ethyl phenyl sulfide and *n*-decyl methyl sulfide for 24 h gave the corresponding sulfimides of 50 and 48% ees in 12 and 24% yields, respectively.

12 CCDC 651311 and 651312 (for complexes **1** and **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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