Pergamon

Tetrahedron Letters, Vol. 35, No. 34, pp. 6325-6328, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)01246-6

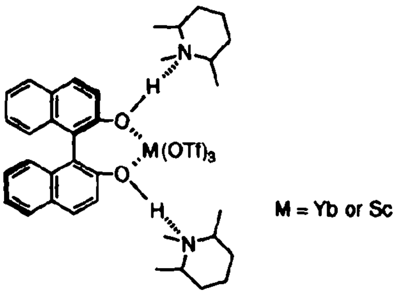
Characterization of Chiral Ytterbium and Scandium Catalysts Based on Their Trifluoromethanesulfonates in Asymmetric Diels-Alder Reactions

Shū KOBAYASHI,* Haruro ISHITANI, Mitsuharu ARAKI, and Iwao HACHIYA

Department of Applied Chemistry, Faculty of Science,
Science University of Tokyo (SUT), Kagurazaka, Shinjuku-ku, Tokyo 162

Abstract: *The unique structure of chiral ytterbium and scandium catalysts (prepared from ytterbium or scandium trifluoromethanesulfonate, (R)-(+)-binaphthol, and a tertiary amine) was determined. The structure was characterized by hydrogen bonds between the phenolic hydrogens of (R)-(+)-binaphthol and the nitrogens of the tertiary amines. Aging and aggregation of the catalysts are also reported.*

Recently, we reported asymmetric Diels-Alder reactions catalyzed by a chiral ytterbium or scandium triflate, which was prepared *in situ* from ytterbium or scandium triflate ($Yb(OTf)_3$ or $Sc(OTf)_3$), (R)-(+)-binaphthol, and a tertiary amine.1) In the presence of the catalyst, 3-acyl-1,3-oxazolidin-2-ones reacted with dienes to afford the endo Diels-Alder adducts in high yields and with good to excellent enantiomeric excesses. Although many striking features were shown in these catalysts, the precise structure and coordination forms have not yet been revealed. In this communication, we report the structure, aging, and aggregation of these catalysts.



Scheme 1. The chiral Yb or Sc catalyst

Table 1. Comparison of the ^{13}C NMR Chemical Shifts (CD_2Cl_2) of the Carbons of the *N*-Methyl Groups of *cis*-1,2,6-Trimethylpiperidine (TMP) and the IR Wave Numbers (CH_2Cl_2) in the Region 930-1000 cm^{-1}

Compound	δ (ppm)	Wave Number (cm^{-1})
TMP	38.2	947
TMP + (R)-(+)-binaphthol	35.1	989, 947
TMP + TfOH	34.1	958
TMP + $Yb(OTf)_3$ + (R)-(+)-binaphthol [a]	37.5	997, 955
TMP + $Yb(OTf)_3$ + (R)-(+)-binaphthol [b]	38.5	982, 935
TMP + $Sc(OTf)_3$ + (R)-(+)-binaphthol	37.5	997, 956

a) 3-Acetyl-1,3-oxazolidin-2-one was added. b) PAA was added.

The new catalysts were prepared by simply mixing $Yb(OTf)_3$ or $Sc(OTf)_3$, (R)-(+)-binaphthol, and a tertiary amine for 0.5 h at 0 °C in dichloromethane. The unique structure shown in Scheme 1 was indicated by ^{13}C NMR and IR spectra. The most characteristic point of the catalysts was the existence of hydrogen bonds between the phenolic hydrogens of (R)-(+)-binaphthol and the nitrogens of the tertiary amines. The ^{13}C NMR spectra indicated these interactions, and the existence of the hydrogen bonds was confirmed by the IR spectra[2] (Table 1). The coordination form of these catalysts may be similar to that of the lanthanide(III)-water or -alcohol complex.[3] It is noted that the structure is quite different from those of conventional chiral Lewis acids based on aluminum,[4] boron,[5] or titanium.[6] In the present chiral catalysts, the axial chirality of (R)-(+)-binaphthol is transferred via the hydrogen bonds to the amine parts, which shield one side of the dienophile effectively. This is consistent with the experimental results showing that amines employed in the preparation of the chiral catalysts strongly influenced the selectivities and that bulky amines gave better selectivities.

While the novel catalysts have a unique structure, aging was found to take place in both Yb and Sc catalysts. As shown in Table 2, the selectivities decreased in accordance with the stirring time of the catalyst solution and the temperature. It was then found that some additives prevented the catalysts from aging. In the Yb catalyst, additives such as 3-acetyl-1,3-oxazolidin-2-one (**1**) and 3-phenylacetylacetone (PAA) were effective not only in stabilizing the catalyst but also in controlling the enantiofacial selectivities in the Diels-Alder reaction. As for the chiral Sc catalyst, aging was also observed and **1** was a good additive for stabilization of the catalyst, but reverse enantioselectivities due to these additives were not observed. This can be explained by the coordination numbers of ytterbium(III) and scandium(III); while Sc(III) has up to seven ligands, the specific coordination numbers of Yb(III) allow up to twelve ligands.[7]

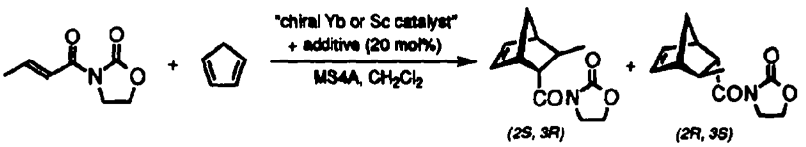
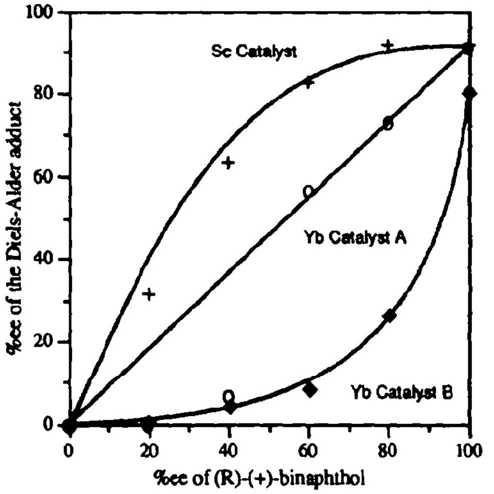


Table 2. Aging of the Catalysts

Metal	Conditions	Additive	Yield (%)	endo/exo	2S,3R/2R,3S (ee (%))[a]	
Yb[b]	0 °C, 0.5 h	—	77	89/11	97.5/ 4.5	(95)
	0 °C, 5.5 h	—	61	87/13	89.0/11.0	(78)
	0 °C, 0.5 h; 23 °C, 5 h	—	77	86/14	82.5/17.5	(65)
	0 °C, 0.5 h	1	77	89/11	96.5/13.5	(93)
	0 °C, 0.5 h	acac[d]	87	85/15	22.5/77.5	(55)
	40 °C, 3 h	PAA	83	93/ 7	9.5/90.5	(81)[e]
Sc[c]	0 °C, 0.5 h	—	97	84/16	92.0/ 8.0	(84)
	0 °C, 0.5 h; 23 °C, 3 h	—	87	80/20	46.5/53.5	(7)
	0 °C, 0.5 h; 23 °C, 3 h	1	92	83/17	89.0/11.0	(78)
	0 °C, 0.5 h; 23 °C, 3 h	acac[d]	90	90/10	47.5/52.5	(5)
	-78 °C, 0.5 h	—	94	89/11	96.0/ 4.0	(92)[f]

a) Enantiomer ratios of endo adducts. b) The reactions were carried out at 0 °C. c) The reactions were carried out at 23 °C, unless otherwise noted. d) Acetylacetone. e) 1,2,2,6,6-Pentamethylpiperidine was used instead of *cis*-1,2,6-trimethylpiperidine. f) The reaction was started at -78 °C and then warmed to 0 °C.



Yb Catalyst A : Yb(OTf)$_3$ + (R)-(+)-binaphthol + TMP + 1
Yb Catalyst B : Yb(OTf)$_3$ + (R)-(+)-binaphthol + TMP + PAA
Sc Catalyst : Sc(OTf)$_3$ + (R)-(+)-binaphthol + TMP

Fig. 1. Correlation between the ee of the Diels-Alder adduct and the ee of (R)-(+)-binaphthol

It was also suggested that aggregation of the catalysts influenced the selectivities in the Diels-Alder reactions, and we next examined the reaction of 3-(2-butenoyl)-1,3-oxazolidin-2-one with cyclopentadiene using (R)-(+)-binaphthol in lower enantiomeric excesses.8) The results are shown in Fig. 1. Very interestingly, a positive nonlinear effect was observed in the chiral Sc catalyst.9) In the chiral Yb catalysts, on the other hand, the effect was dependent on the additives. The extent of asymmetric induction in catalyst A did not deviate from the enantiomeric excesses of (R)-(+)-binaphthol in the range 60-100% ee,9) while a negative nonlinear effect was observed in catalyst B. These results can be ascribed to a difference in aggregation between the Sc catalyst, Yb catalyst A, and Yb catalyst B.8b)

In summary, unique and unprecedented properties of chiral ytterbium and scandium catalysts compared with other conventional chiral Lewis acid catalysts have been revealed. We are now pursuing the development of new asymmetric reactions using these catalysts as well as the clarification of the precise reaction mechanism and transition states.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan. I. H. thanks the JSPS fellowship for Japanese Junior Scientists.

References and Notes

1) (a) Kobayashi, S.; Hachiya, I.; Ishitani, H.; Araki, M. *Tetrahedron Lett.* **1993**, *34*, 4535. (b) Kobayashi, S; Ishitani, H. *J. Am. Chem. Soc.* **1994**, *116*, 4083. (c) Kobayashi, S.; Araki, M.; Hachiya, I. *J. Org. Chem. in press.*
2) Fritsch, J.; Zundel, G. *J. Phys. Chem.* **1981**, *85*, 556.
3) For example, Harrowfield, J. M.; Kepert, D. L.; Patrick, J. M.; White, A. H. *Aust. J. Chem.* **1983**, *36*, 483. *Review:* Hart, F. A. In *Comprehensive Coordination Chemistry, Vol. 3;* Wilkinson, G., Ed.; Pergamon Press: New York, 1987; p. 1059.
4) (a) Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1989**, *111*, 789. (b) Bao, J.; Wulff, W. D.; Rheingold, A. L. *ibid.* **1993**, *115*, 3814.
5) (a) Kaufmann, D.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 545. (b) Hattori, K.; Yamamoto, H. *J. Org. Chem.* **1992**, *57*, 3264.
6) (a) Reetz, M. T.; Kyung, S.-H.; Bolm, C.; Zierke, T. *Chem. Ind.* **1986**, *824*. (b) Mikami, K.; Terada, M.; Nakai, T. *J. Am. Chem. Soc.* **1990**, *112*, 3949.
7) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry; Fifth Edition,* John Wiley & Sons: New York, 1988, p.955.
8) (a) Oguni, N.; Matsuda, Y.; Kaneko, T. *J. Am. Chem. Soc.* **1988**, *110*, 7877. (b) Kitamura, M.; Okada, S.; Suga, S.; Noyori, R. *ibid.* **1989**, *111*, 4028. (c) Puchot, C.; Samuel, O.; Dunach, E.; Zhao, S.; Agami, C.; Kagan, H. *ibid.* **1986**, *108*, 2353.
9) Lower enantiomeric excesses of the product were observed when (R)-(+)-binaphthol in less than 60% ee was used. This may be ascribed to turnover of the catalyst.

(*Received in Japan* 13 *April* 1994; *accepted* 24 *May* 1994)