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Enantioselective Diels–Alder reactions catalyzed by samarium iodo binaphthoxides

Nicolas Giuseppone,[a] Isabel Santos [b] and Jacqueline Collin [a,*]

[a]*Laboratoire de Catalyse Moléculaire UPRESA 8075, ICMO, Bâtiment 420 Université Paris-Sud, 91405 Orsay, France*
[b]*Departamento de Quimica, ITN, 2688 Sacavém, Portugal*

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Abstract

Two trivalent samarium iodo binaphthoxide complexes have been investigated as catalysts for enantioselective Diels–Alder reactions. Enantiomeric excesses were improved using 3,3′-bis-orthoanisyl binaphthol as ligand compared to binaphthol, with values up to 81% for the major *endo*-isomer. Performing reactions at different temperatures gave a reversal in the prevailing product configuration. © 2000 Elsevier Science Ltd. All rights reserved.

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Binaphthol and substituted binaphthols are employed as ligands with a wide range of metals to prepare highly enantioselective catalysts.[1] In the case of lanthanides, two types of catalysts with different modes of coordination to these ligands give high enantiomeric excesses in different reactions. Shibasaki has developed heterobimetallic derivatives with the binaphthol ligand coordinated both to the lanthanide and to an alkaline metal which afford high asymmetric inductions for various reactions such as nitroaldolisation or Michael reactions.[2] By adding binaphthol type ligands to ytterbium or scandium triflates in the presence of a base, Kobayashi obtained compounds without naphthoxy bonds between the metal and the oxygen atoms of the binaphthol ligands, which are enantioselective catalysts for cycloaddition reactions.[3–5]

In the course of our investigations we have explored the activity of samarium diiodide, trivalent lanthanide iodides and mixed iodoalkoxides as Lewis acids catalysts.[6,7] With the aim of preparing a new family of enantioselective catalysts we began to study heteroleptic iodo binaphthoxy lanthanides with phenoxy lanthanide oxygen bonds. By reacting the monopotassium salt of (*R*)-binaphthol with trivalent lanthanide iodides we have recently prepared and characterized (*R*)-binaphthoxy diiodo lanthanides **1**[8] which led to racemic products when used as catalysts for various reactions. We now report enantioselective Diels–Alder reactions catalyzed by samarium binaphthoxy iodo complexes.

* Corresponding author. Fax 33 (0) 1 69154680; e-mail: jacollin@icmo.u-psud.fr (J. Collin)

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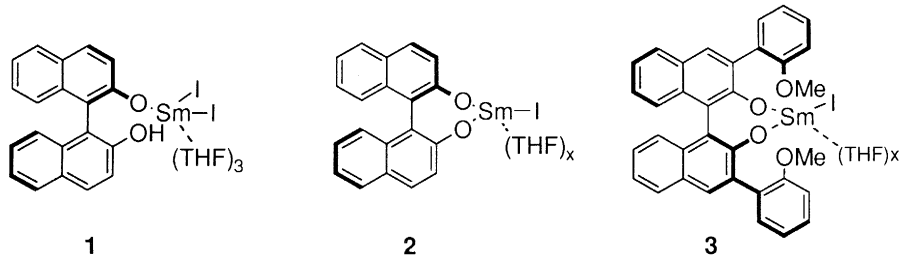
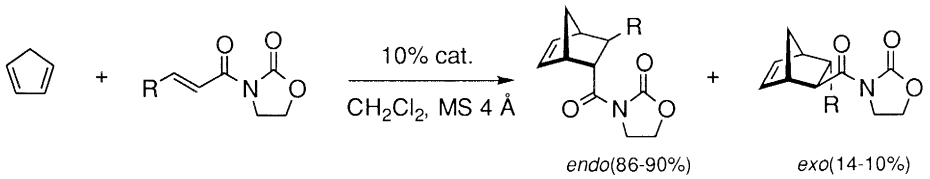
Enantiopure samarium binaphthoxides **2** and **3** have been synthesized by a similar method to the preparation of complex **1**, by reacting the bis-potassium salts of (*R*)-binaphthol and (*S*)-3-3′-bis(2-methoxyphenyl)binaphthol, respectively, with samarium triiodide.[9]



1 **2** **3**

The samarium iodobinaphthoxides **2** and **3** catalyze the Diels–Alder additions of unsaturated acyl oxazolidinones **4** and **5** to cyclopentadiene in methylene chloride in the presence of molecular sieves (which increase the reaction rate), leading to the cycloadducts **6** and **7** with the *endo* products as the major diastereoisomers (Scheme 1).



R = Me **4** **6**

R = H **5** **7**

Scheme 1.

At room temperature (*R*)-binaphthoxy iodo samarium **2** catalyzes the cycloaddition of oxazolidinones **4** and **5** in 100% conversion but with only low enantiomeric excesses (Table 1, entries 1 and 4). When the Diels–Alder reaction of the oxazolidinone **5** is performed at a lower temperature (−25°C, entry 5), the enantioselectivity of the reaction is increased while the reaction is completed within a short time. Heteroleptic iodo binaphtoxide **2** is an efficient catalyst for this type of cycloaddition, with higher activity than that obtained when samarium diiodide is used as a precatalyst.[10,11] This led us to assume that samarium binaphthoxy iodo complexes coordinated with bulkier ligands could still present catalytic activity. We prepared complex **3** from the binaphthol bis substituted in 3,3′ positions by the *o*-anisyl groups. This ligand described by Yamamoto[12] introduces both higher steric hindrance than binaphthol and the possibility of tri- or tetra-coordination to the samarium. We were pleased to find that the iodosamarium complex **3** at room temperature catalyzes the addition of cyclopentadiene on substrates **4** within a short reaction time (entry 6) and on substrate **5** providing the major diastereoisomer with 66% *ee* (entry 2). For the reaction of substrate **5** at −25/−28°C, going from catalyst **2** to **3** resulted in an improvement of the enantiomeric excess of the major *endo* product, 28 to 81%, respectively (entries 5 and 8).

The influence of temperature on the reactions of **4** and **5** with cyclopentadiene using iodobinaphtoxy samarium complex **3** as catalyst was then examined. The bulkier oxazolidinone **4** gave slower reactions, 2 days were required for total conversion at 0°C (entry 3). Surprisingly, products of opposite configurations were obtained in reactions performed at room temperature (66% *ee*) and at 0°C (15% *ee*) (entries 2 and 3). The study of Diels–Alder reaction with substrate **5** could be achieved within a wider range of temperatures. A decrease of temperature from 20 to −28°C gives an improvement in the enantiomeric excess of the major *endo* isomer (18% to 81%) with an inversion of the absolute configuration (entries

Table 1
Diels–Alder reactions catalyzed by samarium binaphthoxy iodo complexes **2** and **3**

Entry	R	Catalyst	Temp. (°C)	t (h)[a]	*ee* (*endo*) (%)[b]	Absolute configurations
1	Me	**2**	20	6	15	*1R, 2R, 3S, 4S*
2	"	**3**	20	12	66	*1S, 2S, 3R, 4R*
3	"	"	0	48	15	*1R, 2R, 3S, 4S*
4	H	**2**	20	0.5	18	*1S, 4S, 5S*
5	"	"	-25	0.8	28	"
6	"	**3**	20	0.5	18	*1R, 4R, 5R*
7	"	"	0	4	64	*1S, 4S, 5S*
8	"	"	-28	2	81	"
9	"	"	-50	12	26	"
10	"	"	-60	48	30	*1R, 4R, 5R*
11	"	"	-78	"	34	"

[a]Reaction time for 100% conversion. [b] *ee* are measured by HPLC with (*S,S*)Whelk-O1 for adduct **6** and Chiracel OD-H for **7**.

6–8). At lower temperatures the enantiomeric excess decreases before a reversal of the prevailing configuration of product **7** (entries 10–11). This type of variation of diastereo- or enantioselectivity with temperature has already been reported for different reactions, and occurs when entropy and enthalpy play in favour of opposite isomers.[13,14] However, examples of catalytic asymmetric reactions providing good enantioselectivities in both directions at different temperature are scarce[15] and the variation of enantioselectivity is explained by competing reaction pathways via diastereoisomeric intermediates. According to Scharf,[14] effects of temperature on selectivity are indicative of reactions proceeding via competing pathways of different energies. We do not have enough data concerning the behaviour of complex **3** in solution to explain the variations of enantioselectivities. However, due to the different possibilities of coordination of the bis *o*-anisyl binaphthol on samarium bi, tri and/or tetradentate complexes can be formed. The presence of two catalytic species is one amongst the different hypotheses that can be assumed to rationalize the reversal in the sense of enantioselection.

Studies are currently underway to investigate the structure of complex **3**, as well as the influence of various parameters on the enantioselectivity of these Diels–Alder reactions. We are also studying the potentialities of iodobinaphtoxy lanthanides as a new family of enantioselective Lewis acid catalysts for various types of reactions.

General procedure for Diels–Alder reactions. All manipulations were carried out under an argon atmosphere using Schlenk or glovebox techniques. Catalysts **2** or **3** (0.1 mmol) and cyclopentadiene (3 mmol) were successively added to the mixture of oxazolidones **4** or **5** (1 mmol) and molecular sieves (50 mg) in 10 mL of dichloromethane. After usual work-up [10] products **6** or **7** were purified by preparative thin layer chromatography on silica gel (toluene:AcOEt, 60:40). Enantiomeric excesses were measured by HPLC with (*S,S*) Whelk-01 for adduct **6** (Hexane:*i*PrOH, 98:2; flow: 1 mL/min; retention times 37 and 39.5 min for *exo* enantiomers and 41.5 and 47 min for *endo* enantiomers) and with Chiracel OD-H for adduct **7** (Hexane:*i*PrOH, 98:2; flow: 1 mL/min; retention times 34 and 35 min for *exo* enantiomers, and 40 and 44 min for *endo* enantiomers).

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