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Lanthanide iodides, a new family of efficient Lewis acid catalysts

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Contents

Abstract

Samarium diiodide and other lanthanide iodides are very efficient Lewis acid catalysts for numerous reactions such as Mukaiyama aldol and Michael reactions, preparation of enoxysilanes, cycloaddition reactions and ring opening of oxiranes by silylated nucleophiles or amines. Activities and selectivities of catalysts vary with the nature of the metal and the ligands for some reactions. Lanthanide iodides coordinated by a cyclopentadienyl ligand with an asymmetric center and an ether function on a pendant chain have been characterized and tested for catalysis: low enantioselectivities are observed for complexes with intramolecular coordination. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Lanthanide iodides; Catalysis; Cyclopentadienyl complexes; Chirality

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1. Introduction

The interest of organic chemists for lanthanides, centered during a long time on a few applications such as NMR shifts reagents or oxidations by cerium compounds, has dramatically increased during the recent years. Several important routes have been opened in this area. The first one is the description of an easy preparation of samarium diiodide and of its main properties by Kagan and co-workers [1,2], which has been followed by a great number of investigations concerning various reactions induced by this reagent and their applications for synthesis [3–8]. More recently, several lanthanide derivatives have been studied, for their catalytic properties, especially as Lewis acids [9,10] and effective asymmetric catalysts have been discovered [11].

Lanthanide chlorides catalyze Mukaiyama aldol reactions [12], Friedel Crafts [13] and Diels-Alder reactions [14]. The lanthanide β-diketonates such as $Eu(dppm)_3$ or $Yb(fod)_3$, display a wide scope of reactivity, by example for the catalysis of aldolization, ene-reactions [15,16], and various [4+2] cycloadditions such as Diels–Alder or hetero Diels–Alder reactions [17–19]. The interest of lanthanide and scandium triflates for catalysis has been demonstrated by Kobayashi [9,10] and the properties of these compounds have been thoroughly studied by several other groups. Lanthanide triflates are excellent Lewis acid catalysts for Mukaiyama aldol reactions, Michael reactions of β-ketoesters towards enones [20–22], Diels–Alder reactions [23,24], but they are also very active for numerous reactions such as allylation [25–27] or acylation [28]. Reactions involving addition of silyl derivatives onto imines (or on imines prepared in situ), catalyzed by ytterbium triflate, for the synthesis of β-aminoketones or β-amino esters or for the synthesis of quinoline have also been reported [29–33]. Scandium triflate is also especially efficient for the catalysis of Friedel Crafts reactions [34,35]. Other types of reactions are catalyzed by lanthanide alkoxides such as nitroaldolization reactions [36], Meerwein–Ponndorf–Verley Oppenauer reactions [37], ring opening of oxiranes [38].

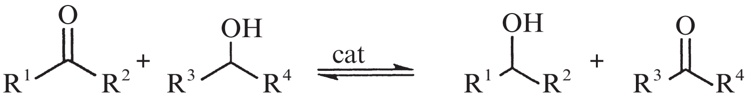
Further families of lanthanide derivatives, bis(cyclopentadienyl) lanthanide complexes, were first described by Marks as very efficient catalysts for hydrogenation or functionalization of olefins [39–42]. These complex also catalyze other reactions such as hydroboration [43] or hydrosilylation [44,45] of alkenes, and the unprecedented intramolecular hydroamination of alkenes and alkynes [46–48]. The compounds used as precatalysts are alkyl, amide or hydride lanthanides complexes with two pentamethylcyclopentadienyl ligands or a permethyl-ansa-cyclopentadienyl ligand. The similar activity of bis(pentamethylcyclopentadienyl) yttrium complex $Cp_2^*YMe(THF)$ for the cyclizations of dienes [49,50], the hydrosilylation of olefins or alkynes [51–53] or sequential cyclization–silylation reactions [54,55] was studied by Molander.

Samarium diiodide for the great majority of its applications is prepared in THF and used for its reductive properties or as a coupling agent in reactions involving radical or organometallic intermediates [3–8]. According to the different reactions, one or several equivalents of samarium diiodide are needed. In the course of our investigations we have found that samarium diiodide could be used as the precursor of catalysts for different types of reactions, such as oxido-reduction, and Lewis acids catalyzed reactions. In this review, in the first part we summarize the reactions using samarium diiodide as a precatalyst and we compare its activity to that of other lanthanide iodides. In a second part we describe our first results in the preparation of chiral lanthanide complexes as potential asymmetric catalysts.

2. Reactions catalyzed by samarium diiodide or lanthanide triiodides

2.1. Meerwein–Ponndorf–Verley/Oppenauer reactions

Meerwein–Ponndorf–Verley reductions of aldehydes and ketones, as well as Oppenauer oxidations have been known for a very long time. In most cases the reactions are promoted by aluminium alkoxides and need stoichiometric amounts or even more of alkoxides. The use of lanthanide iodoalkoxides in catalytic amounts to achieve Meerwein–Ponndorf–Verley reductions of ketones or Oppenauer oxidations of alcohols was disclosed in our laboratory [56,57].



(1)

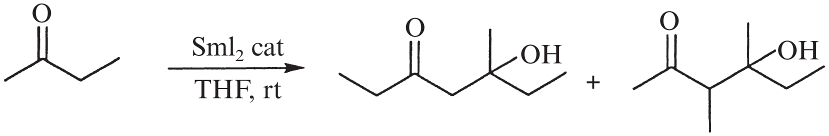
Various methods have been reported for the synthesis of alkoxy-lanthanide compounds. Diiodosamarium or ytterbium *ter*-butoxide are easily prepared from the reactions of SmI_2 or YbI_2 with di-*ter*-butyl peroxide (Eq. (2)).

$$2LnI_2 + t-Bu\text{–}O\text{–}O\text{–}Bu-t \underset{rt}{\overset{THF}{\rightarrow}} 2t-Bu\text{–}O\text{–}LnI_2 \quad Ln = Sm, Yb. \tag{2}$$

t-$BuOSmI_2$ is an efficient catalyst for Meerwein–Ponndorf reductions of aliphatic ketones, aliphatic and aromatic aldehydes and α-ketoesters. These reductions are performed in good yields in refluxing THF with propan-2-ol (4 eq.) as the hydride donor. Samarium diiodoter-butoxide is also a catalyst of Oppenauer oxidations in similar conditions, the choice of the hydride acceptor depending on the substrate (butanone for secondary alcohols, furfuraldehyde for primary alcohols). Therefore we have found later that SmI_2 can be used directly for Oppenauer oxidations of alcohols with butanone at room temperature (0.1 mol eq. SmI_2 with respect to alcohol) [57]. The blue color of SmI_2 disappears rapidly, a long time before the end of the reaction, which indicates that SmI_2 is not the catalytic species. Samarium diiodide allows us to carry out oxidations of a large variety of alcohols (secondary aliphatic, allylic, homoallylic and benzylic alcohols) in milder conditions than with samarium diiodo*ter*-butoxide. In most cases, the oxidations were performed at room temperature instead of refluxing THF, and otherwise reaction times are shorter. Ethers resulting from inter- or intramolecular dehydratation reactions were formed as by-products in the oxidation reactions of allylic alcohols catalyzed by samarium diiodotertbutoxide. The transformation of allylic alcohols in ethers catalyzed by

$SmCl_3$ has been previously studied [58]. These ethers were not observed in Oppenauer reactions catalyzed by samarium diiodide. Therefore, the oxidation of primary alcohols cannot be realized with samarium diiodide as catalyst: aldehydes should be employed as oxidants, and SmI_2 is an excellent catalyst of Tischenko reactions or of aldehyde trimerizations, according to the structures of the aldehydes [57]. Meerwein–Ponndorf reductions by isopropanol (8 eq.) are also catalyzed by SmI_2 (0.1 eq.) at room temperature.

The isolation of β-ketoalcohols resulting from the aldolization of butanone in the presence of samarium diiodide in catalytic amounts (Eq. (3)) suggests that a diiodo-β-ketoalkoxysamarium is the active species for Oppenauer reactions. It was also observed that different diiodo β-ketoalkoxy-samarium showed the same activity as SmI_2 for the catalysis of the oxydation of octan-2-ol by butanone (8 eq).



(3)

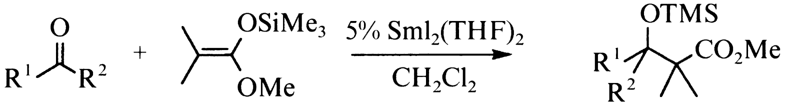
The differences between the β-ketoalkoxy-diiodosamarium and *ter*-butoxy diiodosamarium for the catalysis of Oppenauer reactions show the importance of the structure of the organic part of the catalyst and suggest that samarium alkoxide plays a more complex role than to promote a simple exchange with the alcohol to be oxidized. These iodosamarium alkoxides are more efficient than lanthanide triisopropoxides as catalysts of Meerwein–Ponndorf–Verley reductions, [37,59] and they have found various applications, such as stereoselective Meerwein–Ponndorf–Verley reductions for the synthesis of cytovaricin described by Evans or in sequential reactions described by Molander [60,61]. A samarium iodide compound coordinated with an asymmetric aminodialkoxide ligand has given high enantioselectivies in the asymmetric reduction of aromatic ketones [62]. The use of samarium diiodide to catalyze stereoselective intramolecular Tischenko reactions, resulting in the reduction of β-hydroxyketones has also been reported [63].

2.2. *Mukaiyama aldol and Michael reactions, enoxysilanes formation*

Mukaiyama aldol reactions as well as Michael reactions are fundamental tools for the formation of carbon–carbon bonds in organic chemistry [64–67] and have been widely developed. The use of enoxysilanes or of ketene silyl acetals as nucleophiles, and of $TiCl_4$ in stoichiometric amounts provided a new method to carry out cross aldolizations [68,69]. Many Lewis acids have been alternatively employed, either in stoichiometric or in catalytic amounts. The first Mukaiyama aldol reaction catalyzed by lanthanides was described by Kagan and Vougioukas [12].

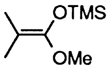
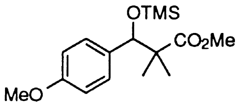
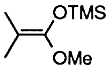
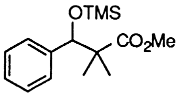
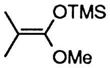
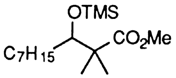
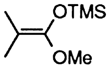
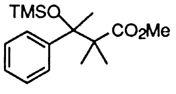
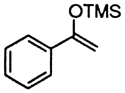
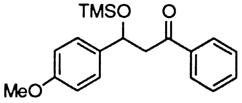
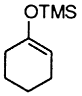
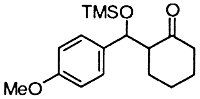
2.2.1. *Aldol reactions. Influence of the catalyst*

In our first investigations we found that samarium diiodide, used as a catalyst in dichloromethane, allows one to perform aldol reactions involving ketene silyl acetals and various aldehydes or acetophenone in high yields (Eq. (4), Table 1) [70,71].



(4)

Table 1
Mukaiyama aldol reactions catalyzed by samarium iodides

Entry	Carbonyl compound	Silylated derivative	Catalyst[a]	Product	Yield[b] (%)
1	*p*-Anisaldehyde		$SmI_2(THF)_2$		95
2			$SmI_3(THF)_3$		95
3			*t*-$BuOSmI_2(THF)_3$		95
4	Benzaldehyde		$SmI_2(THF)_2$		95
5	Octanal		$SmI_2(THF)_2$		90
6			$SmI_3(THF)_3$		73
7			*t*-$BuOSmI_2(THF)_3$		69
8	Acetophenone		$SmI_2(THF)_2$		85
9			$SmI_3(THF)_3$		76
10	*p*-Anisaldehyde		$SmI_2(THF)_2$		89
11			$SmI_3(THF)_3$		100[c]
12			*t*-$BuOSmI_2(THF)_3$		80
13	*p*-Anisaldehyde		$SmI_2(THF)_2$		57[d]
14			$SmI_3(THF)_3$		62[e]
15			*t*-$BuOSmI_2(THF)_3$		66[f]

[a] 5% catalyst in 10 ml CH_2Cl_2.

[b] Isolated yield.

[c] Yield in crude product.

[d] *anti*/*syn*: 33/67.

[e] *anti*/*syn*: 46/54.

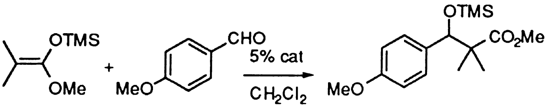
[f] *anti*/*syn*: 50/50.

The catalyst can be easily prepared according to the following procedure: the solvent of the 0.1 M solution of diiodosamarium in tetrahydrofuran [1,2] is evaporated, leaving a blue powder [72]. The diiodosamarium is coordinated by two molecules of THF as indicated by elemental analysis. $SmI_2(THF)_2$ is insoluble in methylene chloride and can be stored under argon without oxidation. After standing for 24 h, the methylene chloride is evaporated, THF is added, and the reductive power of the solution of samarium diiodide is restored, indicating that $SmI_2(THF)_2$ does not react with methylene chloride. Moreover, as shown later, in this solvent the Lewis acidity of $SmI_2(THF)_2$ is enhanced, which allows its use as a precatalyst for various reactions.

Aldol reactions were carried out by adding successively to the blue suspension of $SmI_2(THF)_2$ in CH_2Cl_2 the silyl derivative (ketene silyl acetal or enoxysilane) and the carbonyl compound. Immediately the color of the reaction mixture turned from dark blue to pale yellow, which indicates the formation of a trivalent catalytic species. We therefore tested various lanthanide derivatives, divalent and trivalent, in the reaction involving ketene silyl acetal derived of methyl isobutyrate (KSA) and *p*-anisaldehyde (Table 2). After 5 min at −78 °C, all the iodides afforded 100% conversion, whenever the lanthanide is divalent or trivalent. The other halides, $SmBr_2(THF)_n$, $SmCl_3(THF)_n$ and $YbCl_3(THF)_n$, as well as a samarium triisopropoxide, gave slower reactions than iodides. These results indicate a dramatic influence of iodide for the activity of the catalyst, while the divalent or trivalent state of the precursor appears to be of less importance.

The solvents also have a strong influence on the reaction rate. In dichloromethane

Table 2
Effect of lanthanide compounds on an aldol reaction



Entry	Catalyst	Temp. (°C)	Time[a]
1	$SmI_2(THF)_2$	−78	5 min
2	$t\text{-}BuOSmI_2(THF)_3$	−78	5 min
3	$SmI_3(THF)_3$	−78	5 min
4	$(ArCHOSmI_2)_2$	−78	5 min
5	$EuI_2(THF)_2$	−78	5 min
6	$YbI_2(THF)_2$	−78	5 min
7	$LaI_3(DME)_2$	−78	5 min
8	$YbI_3(DME)_2$	−78	5 min
9	$SmBr_2(THF)_n$	25	1.5 h
10	$SmCl_3(THF)_n$	25	12 h
11	$YbCl_3(THF)_n$	25	4 days
12	$Sm(OiPr)_3$	25	14 days

[a] Reaction time for 100% conversion in the reaction of *p*-anisaldehyde (2 mmol) and KSA (3 mmol) using 5% catalyst (0.1 mmol).

or acetonitrile at −78 °C with 5% mol eq. $SmI_2(THF)_2$, the reactions are fast (100% conversion in less than 5 min). On the other hand, the reactions are considerably slower in THF or in toluene (respectively, 4 or 24 h at room temperature). A sample of commercially available SmI_2 (from Aldrich) exhibited no catalytic activity. Two molecules of THF coordinated on samarium are necessary to carry out the reaction, probably because of the polymeric structure of SmI_2, in the absence of a coordinating solvent. These aldol reactions could be also realized in mixtures of solvents such as THF/CH_2Cl_2, which permits an easier preparation of the catalyst. Catalytic ratio could be lowered to 0.5% mol eq. in the case of the reaction of *p*-anisaldehyde with KSA without decrease of the yield of aldolization product.

The catalytic activities of samarium iodides $SmI_2(THF)_2$, $SmI_3(THF)_3$, and *t*-$BuOSmI_2(THF)_3$ have been compared in various aldol reactions (Table 1). In all cases reactions of aldehydes or acetophenone and KSA afforded condensation products as their silyl ether in good yields whatever the catalyst was (entries 1–9; Table 1). Enoxysilanes derived from acetophenone or cyclohexanone reacted with *p*-anisaldehyde to give the aldolization products in good yields although the reactions are slower than with KSA (entries 10–15; Table 1). No significant difference between the reaction rates of the three catalysts could be noticed, but the diastereoselectivity varies with the samarium compound, the *syn*/*anti* ratio being higher with $SmI_2(THF)_2$.

Besides the increase of the reaction rates of the samarium iodides compared to that of the chlorides, the use of samarium diiodide as a catalyst allowed one to obtain the adduct only as its silyl ether, while lanthanide chlorides gave mixtures of hydroxy compounds and silyl ethers. We also tested $Yb(OTf)_3$ and $Sc(OTf)_3$ in the reaction of *p*-anisaldehyde with KSA. These triflates showed the same activity as $SmI_2(THF)_2$, but they afforded the hydroxy compound as the sole product.

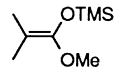
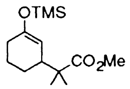
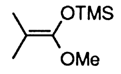
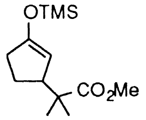
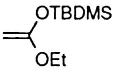
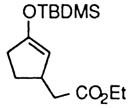
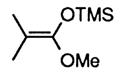
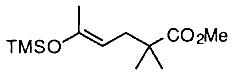
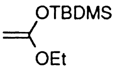
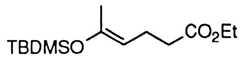
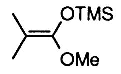
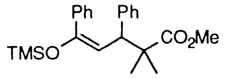
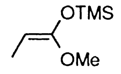
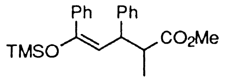
2.2.2. Michael reactions

Samarium diiodide catalyzes the addition of α,β-unsaturated ketones and aldehydes to ketene silyl acetals and enoxysilanes. In the case of α,β-unsaturated ketones, the reactions with ketene silyl acetals were regioselective and led to Michael type adducts in very good yields (see Table 3). The products were obtained as enoxysilanes and readily isolated by filtration of the samarium salts.

In the case of α,β-unsaturated aldehydes, the regioselectivity depends on the substrates (Table 4). The study of various reactions involving cinnamaldehyde shows the dramatic influence of the silyl nucleophile on the regioselectivity. With KSA, 50% of the 1,2-adduct (entry 1; Table 4) were obtained, while silyl ketene acetals derived from methyl propionate or ethyl acetate yielded higher amounts of 1,2-adducts (entry 2 and 3; Table 4). For reactions with octen-2-al, the trend is the same as for reactions with cinnamaldehyde: an increase of the ratio of 1,2-addition with less bulky ketene silyl acetals (entries 6–8; Table 4). A regioselective 1,2-addition was observed with the ketene silyl acetal derived from ethyl acetate. The reactions of α,β-unsaturated aldehydes with silylated nucleophiles give as major products the aldol silyl ethers.

Lanthanides triflates have been reported to catalyze Michael reactions [23,24]. In

Table 3
Michael reactions of α,β-unsaturated ketones with ketene silyl acetals [Catalysed by Sm I_2 $(THF)_2$]

Entry	Carbonyl compound	Silyl derivative	Temp. (°C)	Time (h)	Product	Yield[a,b] (%)
1	Cyclohexen-2-one		−20	5		65
2	Cyclopenten-2-one		−78	1		95
3	Cyclopenten-2-one		−78	0.5		95
4	Buten-3-one		rt	12		86[c]
5	Buten-3-one		rt	24		90[d]
6	Chalcone		−20	5		85[e]
7	Chalcone		−20	4.5		95[f]

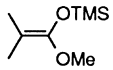
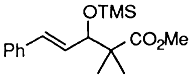
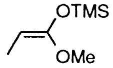
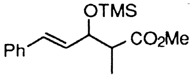
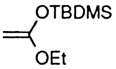
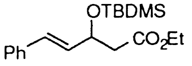
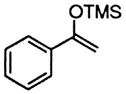
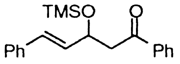
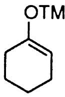
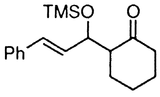
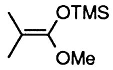
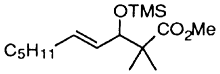
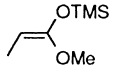
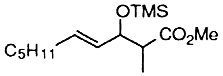
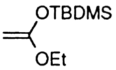
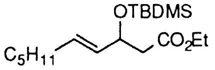
[a] 1.1 eq. of silyl derivative.
[b] isolated yield.
[c] *E*/*Z*, 55/45.
[d] *E*/*Z*, 80/20.
[e] Only one isomer was detected, presumably *E*.
[f] *anti*/*syn* 50/50.

our hands the reactions of cyclopenten-2-one with KSA catalyzed by $Yb(OTf)_3$ or $Sc(OTf)_3$ led to the Michael products as a mixture of the enoxysilane and of the corresponding ketone. Reaction of cinnamaldehyde and KSA with the former catalyst provided a complex mixture.

2.2.3. *Preparation of enoxysilanes*

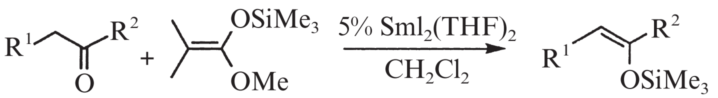
Reactions of aliphatic ketones or bulky aldehydes with the ketene silyl acetal derived from ethyl isobutyrate (KSA) in the presence of a catalytic quantity of $SmI_2(THF)_2$ in CH_2Cl_2, afford the trimethylsilyl enol ether of the carbonyl product [73]. Enoxysilanes were isolated by precipitation and filtration of samarium salts at the end of the reaction providing a simple method to prepare enoxysilanes in good

Table 4
Reactions of α,β-unsaturated aldehydes with silyl derivatives: 1,2- versus 1,4- addition [Catalysed by Sm I_2 $(THF)_2$]

Entry	Carbonyl compound	Silyl derivative	Temp. (°C)	Time	Ratio 1,2-/1,4-[a]	Major product	Yield[b,c] (%)
1	Cinnamaldehyde		−20	45 min	50/50		90
2	Cinnamaldehyde		−20	45 min	66[c]/34		94
3	Cinnamaldehyde		−20	45 min	90/10		83
4	Cinnamaldehyde		rt	4 h	85/15		68
5	Cinnamaldehyde		rt	6.5 h	100[d]/0		52
6	Octen-2-al		−20	4.5 h	80/20		95
7	Octen-2-al		−20	4.5 h	87[e]/13		95
8	Octen-2-al		−20	4.5 h	100/0		80

[a] Determined by ^{1}H NMR and/or GC.
[b] Isolated yield.
[c] *anti/syn* 54/46.
[d] *anti/syn* 50/50.
[e] *anti/syn* 50/50.

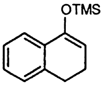
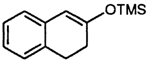
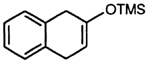
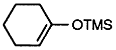
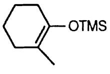
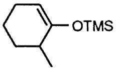
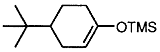
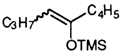
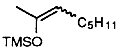
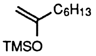
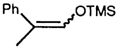
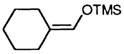
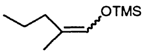
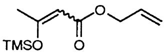
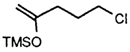
yields using KSA as silylating agent (Eq. (5), Table 5).



(5)

Transformation of cyclic ketones and aldehydes (entries 1–5 and 8–10; Table 5) into enoxysilanes are completed within 30 min by the use of 5% mol eq. of $SmI_2(THF)_2$ and 1.1 eq. of KSA, while reactions with linear ketones (entries 6 and 7; Table 5) are slower and need an higher amount of catalyst. This reaction tolerates various functional groups, such as ether or chloride. As for aldol reactions, the

Table 5
Synthesis of enoxysilanes from ketones and aldehydes

Entry	Carbonyl compound	Enoxysilane		Yield[a]	Z/E
1	α-Tetralone			88[b]	
2	β-Tetralone	 98%	 2%	70[b]	
3	Cyclohexanone			70[b]	
4	2-Methylcyclohexanone	 90%	 10%	74[b]	
5	4-t-Butylcyclohexanone			77[b]	
6	Nonan-5-one[d]			60[c,d]	82/18
7	Octan-2-one			65[c,d]	75/25
8	2-Phenylpropanal			72[b]	90/10
9	Cyclohexylcarboxaldehyde			73[b]	
10	2-Methylpentanal			78[b]	70/30
11	Allyl-3-oxobutanoate			80[c]	82/18
12	5-Chloropentan-2-one[d]	 90%	 10%	75[c]	78/22

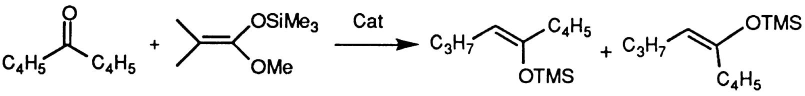
[a] Reactions are performed with 5% $SmI_2(THF)_2$, % isolated yield after distillation.
[b] Reaction time of 30 min.
[c] Reaction time of 24 h.
[d] 10% $SmI_2(THF)_2$ are used.

solvent has a strong influence, the reactions are faster, and the yields higher in CH_2Cl_2 compared with THF.

In these enol reactions, the thermodynamic isomer is formed preferentially and the regioselectivity is not influenced by the temperature: for 2-methyl cyclohexanone the same ratio of isomers was obtained at −78 °C or at room temperature. This discards the hypothesis of the formation of a samarium enolate or of a naked enolate that could lead to kinetic enoxysilane at low temperature.

As for aldol reactions, the influence of the nature of the catalyst on the rate and the stereoselectivity of the enolization reaction was examined. A comparison of

Table 6
Influence of the catalyst on the formation of enoxysilane



Entry	Catalyst	Yield[a]	*Z*/*E*[b]
1	$SmI_2(THF)_2$	90	82/18
2	$SmI_3(THF)_3$	88	78/22
3	$SmI_2OtBu(THF)_3$	78	75/25
4	$LaI_3(DME)_2$	95	90/110
5	$EuI_2(THF)_2$	60	88/12
6	$YbI_3(DME)_2$	84	90/110

[a] Yields measured by GC and NMR after 24 h and using 10% catalyst.
[b] Isomeric ratios *Z*/*E* are measured by GC and NMR.

different catalysts for the transformation of nonan-5-one is shown in Table 6. $SmI_2(THF)_2$ and $SmI_3(THF)_3$ gave similar results (entries 1 and 2; Table 6), indicating that there is little effect of the oxidation state of the catalyst precursor. The best results were recorded with lanthane, europium and ytterbium iodides. $LaI_3(DME)_2$ is the most efficient catalyst considering both activity and selectivity. With the aim to determine whether enoxysilanes could be prepared similarly using lanthanides triflates as catalysts, we tried the reaction of 4-terbutylcyclohexanone with KSA using 5% mol eq. $Yb(OTf)_3$ and obtained the aldol instead of the desired product. The reactivities of lanthanide iodides and triflates are completely different for these reactions. The preparation of enoxysilanes from carbonyl compounds without base is an unprecedented reaction, specific to lanthanide iodides.

Samarium iodides and other lanthanide iodides have a high catalytic activity for Mukaiyama aldol and Michael reactions. The reactions proceed in mild conditions and the condensation products are isolated in very good yields as silyl ethers or enoxysilanes. Two different reactions catalyzed by lanthanide iodides, Michael addition on α,β-unsaturated ketones, or enolization of aldehydes or ketones by ketene silyl acetals, allow an easy isolation of enoxysilanes.

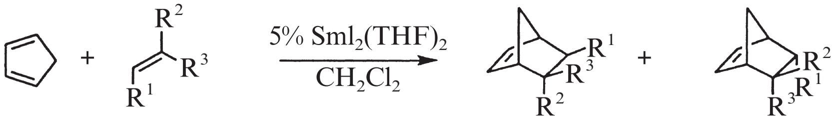
Recently another related application of samarium diiodide as a Lewis acid catalyst, the ene-reactions of unsaturated carbonyl compounds leading to cyclizations reactions has been reported [74].

2.3. *Diels–Alder and hetero Diels–Alder reactions*

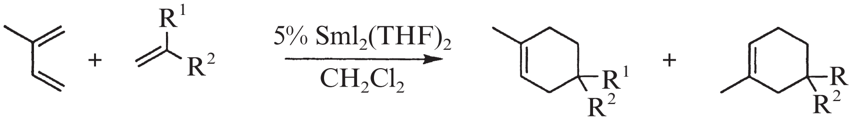
The Diels–Alder and hetero Diels–Alder reactions are useful tools for the six-membered ring formation [75–77]. Numerous Lewis acids are commonly used as promotors or catalysts for these cycloaddition reactions. One of the first examples described was the cycloaddition of dienes with aldehydes, catalyzed by europium compounds, yielding pyrones after acid treatment [78]. Lanthanide β-diketonates

[Eu(hfc)$_3$, Pr(hfc)$_3$, Yb(hfc)$_3$ and Yb(fod)$_3$] are efficient catalysts for inverse electron demand Diels–Alder reactions, as addition of 2-pyrones to electron-rich dienophiles [79–81]. Kobayashi has disclosed the use of ytterbium and scandium triflate in methylene chloride or in a mixture of tetrahydrofuran and water, as reusable catalysts for the Diels–Alder reactions [23,24].

Screening the activity of samarium diiodide in methylene chloride as a Lewis catalyst, we studied Diels–Alder and hetero Diels–Alder cycloadditions [82]. The condensation products between cyclopentadiene or isoprene and various dienophiles were obtained in good yields by the use of 5% mol eq. of SmI$_2$(THF)$_2$ in methylene chloride (Eqs. (6) and (7), Table 7).



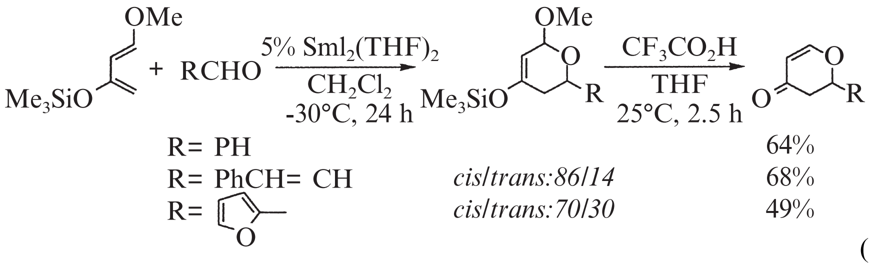
(6)



(7)

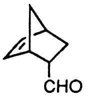
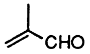
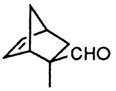
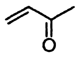
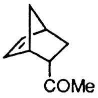
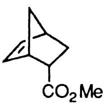
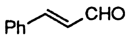
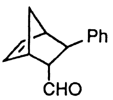
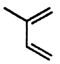
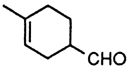
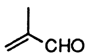
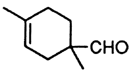
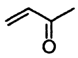
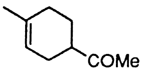
With cyclopentadiene the *endo* product is always the major isomer (entries 1, 3–5; Table 7), except for the reaction with methacrolein (entry 2; Table 7) affording the *exo* isomer as the major product, as usually observed with other Lewis acids [83]. With isoprene the major cycloadducts are the 1,4-substituted cyclohexenes (entries 6–8; Table 7). The cycloaddition reactions are performed in milder conditions than with lanthanide chlorides or triflates and the stereoselectivities compare well with those given by various Lewis acids or other lanthanide compounds.

Cycloaddition reactions between aromatic aldehydes and Danishefsky's diene (1-methoxy-3-trimethylsilyloxy buta-1,3-diene) were conducted in the presence of 5% mol eq. of samarium diiodide in methylene chloride at −30 °C (Eq. (8)). Treatment of the adducts with trifluoroacetic acid afforded pyrones. The yields were similar to those reported for the reactions catalyzed by Eu(fod)$_3$ which require higher temperatures than those using SmI$_2$(THF)$_2$ [78].



(8)

Table 7
Diels–Alder reactions catalyzed by samarium diiodide

Entry	Diene[a]	Dienophile	*T* (°C)	*t* (h)	Major product	*Endo*/*exo*[b]	−1.4/−1.3	Yield (%)[c]
1			−30	2		80/20		80
2			−30	2		10/90		80
3			−30	18		90/10		62
4			rt	24		90/10		92
5			rt	24		80/20		70
6			rt	24			95/5	72
7			rt	24			90/10	65
8			rt	24			85/15	30

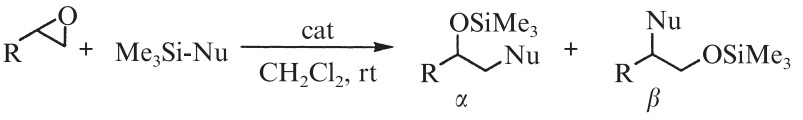
[a] Diene/dienophile: 2/1.
[b] Determined by GC analysis and ^{1}H NMR.
[c] Isolated yield.

2.4. *Ring opening reactions of oxiranes*

The ring opening reactions of epoxides with amines is a very attractive synthetic method to prepare β-aminoalcohols, but due to the low nucleophilicity of amines the reactions are carried out at elevated temperatures and with large excesses of amines. These problems are overcomed by the use of Lewis acids which also allow the opening of epoxides by other nucleophiles such as trimethylsilyl azide, trimethylsilyl cyanide, etc. Several lanthanide derivatives have been described as efficient catalysts for these reactions. The ring opening reactions of oxiranes by thiols or trimethylsilyl cyanide catalyzed by samarium trichloride leading, respectively, to β-hydroxythioethers and β-hydroxynitriles were first reported by Kagan [84,85]. The addition of trimethylsilyl cyanide to epoxides or aziridines was also achieved using a mixture of ytterbium trichloride and butyl lithium as the precursor of the catalyst [86,87]. The active species is probably $Yb(CN)_3$ obtained by the reaction of $YbBu_3$ formed in situ with trimethylsilyl cyanide. The ring opening of epoxides by acetone cyanohydrin catalyzed by lanthanide triisopropoxides gives β-hydroxynitriles [88]. Epoxides are transformed into β-hydroxyazides either by reaction with trimethylsilyl azide catalyzed by ytterbium isopropoxides [38], or by reaction with 1,1,3,3,-tetramethylguanidinium azide catalyzed by ytterbium triflate with octene oxide and Sm I_2 $(THF)_2$ (entry4) the vegioselectivity is reversed [89]. The catalysis by ytterbium triflate of the opening of epoxides by amines yielding β-aminoalcohols was described by two groups [90–93]. However, different reaction conditions were proposed, either the use of methylene chloride by Crotti [90], or the use of tetrahydrofuran or methylene chloride and high pressure by Yamamoto [91]. Recently, the addition of aromatic amines to epoxides catalyzed by samarium trichloride in tetrahydrofuran was also described with similar results [94].

2.4.1. Addition reactions of trimethylsilyl azide or cyanide to oxiranes catalyzed by samarium iodides

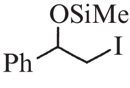
During our studies on the scope of the reactions catalyzed by samarium diiodide, we have examined its activity for the addition of trimethylsilyl azide or trimethylsilyl cyanide to epoxides and compared the activities of other divalent or trivalent samarium derivatives (Eq. (9), Table 8) [95].



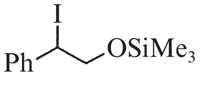
(9)

The ring opening of styrene oxide by trimethylsilyl azide was catalyzed by 5% mol eq. of $SmI_2(THF)_2$ and the silylated azide resulting from the opening on the more hindered side was produced with high selectivity (entry 1; Table 8). Lowering the amount of catalyst to 1% or 2% brought an improvement of the yield as the ratio of by products β-iodotrimethylsilyl ethers 1 and 2 decreased. A trivalent samarium iodide employed as a catalyst [1% mol eq. of t-$BuOSmI_2(THF)_3$] gave the same activity and selectivity than samarium diiodide (entry 2; Table 8).

With octene oxide and Sm I_2 $(THF)_2$ (entry 4) the regioselectivity is reversed.



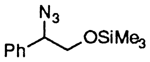
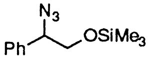
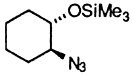
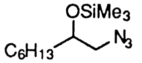
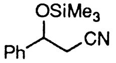
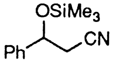
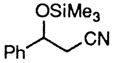
1



2

The addition of trimethylsilyl cyanide to styrene oxide catalyzed by samarium iodides affords the attack preferentially on the less hindered side (entries 5–7; Table 8). The moderate selectivity provided by samarium diiodide was increased by a change of ligand, either by the use of *ter*-butoxydiiodosamarium, either of samarium diiodide coordinated by 2,5-dimethyltetrahydrofuran. In both cases the improvement was due to the presence of a bulky group on the samarium. For the reactions catalyzed by samarium diiodide, we observed a rapid change of color from blue to

Table 8
Ring opening of epoxides by silylated nucleophiles

Entry	Epoxide	Nu	*x*% catalyst	Reaction time	Major product	α/β[a]	Yield[b] (%)
1	Styrene oxide	N_3	5% $SmI_2(THF)_2$	4.5 h		10/90	55[c]
2	Styrene oxide	N_3	1% $SmI_2(OtBu)(THF)_3$	4.5 h		10/90	90
3	Cyclohexene oxide	N_3	1% $SmI_2(THF)_2$	5d			76
4	Octene oxide	N_3	1% SmI_2 $(THF)_2$	5d		84/16	87
5	Styrene oxide	CN	5% $SmI_2(THF)_2$	4.5 h		58/42	70[c]
6	Styrene oxide	CN	5% $SmI_2(DMTHF)_2$[d]	4.5 h		71/29	90[c,e]
7	Styrene oxide	CN	5% $SmI_2(OtBu)(THF)_3$	4.5 h		77/23	90[c,e]

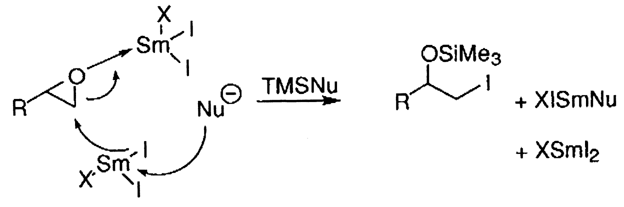
[a] Determined by GC analysis and ^1H NMR.
[b] Isolated yield.
[c] 10% of a mixture of **1**+**2** were isolated.
[d] DMTHF: 2,5-dimethyl tetrahydrofuran.
[e] Based on weight and ^1H NMR of the crude product.

yellow after the addition of the reagents. This indicates that the actual catalyst is probably a trivalent samarium compound. In all the experiments using 5% mol eq. samarium diiodide the trimethylsilyl iodoethers **1** and **2** are formed as about 10% of the crude product. When the amount of catalyst is decreased, only traces of these by-products are detected.

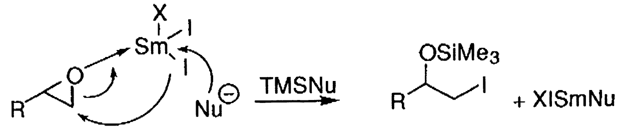
The formation of β-iodoalcohols has been already reported in other reactions involving epoxides and lanthanides such as the rearrangement of terminal epoxides to methyl ketones catalyzed by lanthanide iodides in tetrahydrofuran [96]. Inanaga has suggested that the iodoalcohol could be an intermediate for the deoxygenation of epoxides to olefins by samarium diiodide in tetrahydrofuran [97]. We have also envisaged a similar transfer of the iodine atom from the samarium iodide to the epoxide. Two mechanisms can be proposed as depicted in Scheme 1.

The path 1 corresponds to an "intermolecular" transfer of the iodine atom by addition of the nucleophile to the samarium. The path 2 is an "intramolecular" transfer by a similar process. It has been envisaged that [M]-N_3 (M = Al, Ti, V) are the active species for the addition of trimethylsilyl azide to the epoxide [98] and that $Yb(CN)_3$ is the active species for the addition of the trimethylsilyl cyanide to the epoxide [86,87]. In accordance with these proposals and with the formation of

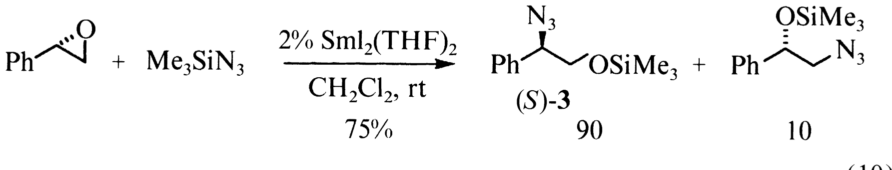
1



2



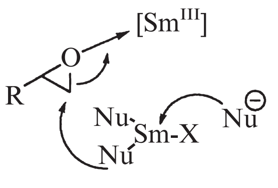
the by-products **1** and **2**, we suggest that in our catalytic system the active species is $XSm(Nu)_2$. To determine whether the addition of the nucleophile to the epoxide is intra or intermolecular, the reaction depicted in Eq. (10) was performed.



(10)

The addition of the trimethylsilyl azide to the (*R*)-styrene oxide in the presence of 2% mol eq. of $SmI_2(THF)_2$ gives the compound **3** as the major product with a (*S*)-configuration.

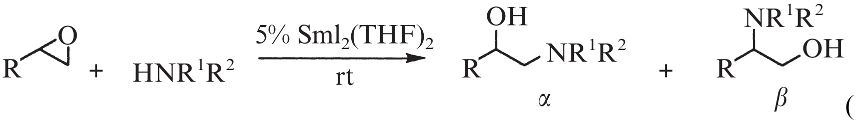
This allows one to propose an "intermolecular" transfer **A** according to Sinou [99] who also observed an inversion in the same reaction catalyzed by $Al(i\text{-}OPr)_3$.



A

2.4.2. *Aminolysis of oxiranes catalyzed by lanthanide iodides*

The catalytic activity of samarium diiodide for the aminolysis of oxiranes was also investigated. The epoxide and the amine are successively added to samarium diiodide in suspension in methylene chloride or in solution in tetrahydrofuran and the color of the reaction mixture turned immediately from blue to yellow. The diiodosamarium efficiently catalyzes this reaction to yield with moderate to excellent selectivities the β-aminoalcohols (Eq. (11), Table 9).



(11)

The regioselectivity depends on the amine used. In most cases, the β-aminoalcohols resulting from the attack of the amine on the less hindered side of the epoxide (isomer α) were obtained (entries 1–4 and 8–12; Table 9). A reverse selectivity was observed for the addition of morpholine and benzylamine to styrene oxide (entries 5–7; Table 9). The addition of *ter*-butylamine to cyclohexene oxide or 1-methylcyclohexene oxide gives only the *trans*-isomer (entries 13 and 14; Table 9). A study of the influence of the solvent, methylene chloride or tetrahydrofuran shows in most cases similar activities and regioselectivities for the aminolysis of epoxides in both solvents (entries 1, 2, 5, 6, 9 and 10; Table 10). The absence of influence of the solvent for the aminolysis of oxiranes differs from the strong effects noticed for Mukaiyama aldol or Michael reactions as indicated above.

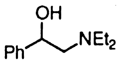
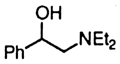
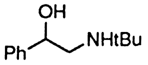
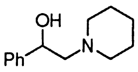
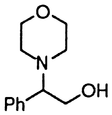
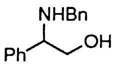
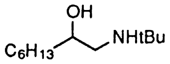
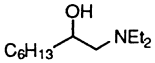
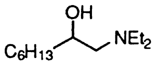
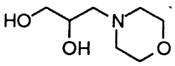
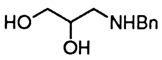
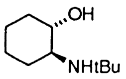
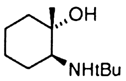
In order to determine the influence of the nature of the lanthanide and of its oxidation state, we tested the catalytic activities of different lanthanide iodides for the addition of diethylamine to octene oxide. The results reported in Table 10 show that the oxidation state and the nature of the metal have an effect on the rate of the reaction. Samarium diiodide appears to be the best catalyst precursor (entry 1; Table 10) and divalent lanthanides are more efficient than the trivalent ones (entries 1 and 2, versus 3–6; Table 10). However, the rapid change of color of samarium diiodide after the addition of reagents is characteristic of the oxidation of a divalent to a trivalent samarium species. To confirm this hypothesis, we have determined by NMR the magnetic susceptibility of samarium in methylene chloride in the presence of octene oxide. The experimental value ($\mu_{\text{exp}} = 1.34$ μb) corresponds to a trivalent samarium compound ($\text{Sm}^{\text{III}} = 1.34$–$2.1$ μb and $\text{Sm}^{\text{II}} = 3.5$–$3.7$ μb) [100–102]. Unfortunatly we were unable to characterize the structure of this samarium species.

2.5. Conclusion

For all the reactions described above, experimental data reveal invariably that samarium diiodide is always the precursor of an active trivalent species and is not the true catalyst. Its special activity seems to be due to its Lewis acidity and its oxophilic character rather than to its reductive power. However, comparison of the catalytic activity of various divalent and trivalent lanthanides iodides leads to conclusions varying with the reactions. For Mukaiyama aldol reactions the presence of the iodide ligand is the main requirement to get good activity, the divalent or trivalent character of the catalyst precursor and the nature of the lanthanide showing no important effect. On the other hand for the opening of epoxides by amines, the divalent character of the lanthanide iodide allows the formation of the trivalent active species more rapidly.

Samarium diiodide is of special interest considering the simple procedure for

Table 9
Aminolysis of epoxides catalyzed by samarium diiodide

Entry	Oxirane	Amine	Solvent	Time	Major product	α/β[c]	Yield (%)[d]
1	Styrene oxide[a]	Et_2NH	CH_2Cl_2	18 h		70/30	68
2	Styrene oxide[a]	Et_2NH	THF	36 h		70/30	63
3	Styrene oxide[a]	$tBuNH_2$	CH_2Cl_2	48 h		77/23	65
4	Styrene oxide[b]	piperidine	CH_2Cl_2	8 h		53/47	56
5	Styrene oxide[b]	morpholine	CH_2Cl_2	6 h		37/63	60
6	Styrene oxide[b]	morpholine	THF	6 h		37/63	84
7	Styrene oxide[b]	$BnNH_2$	CH_2Cl_2	24 h		35/65	70
8	Octene oxide[b]	$tBuNH_2$	CH_2Cl_2	5 d		100/0	77
9	Octene oxide[b]	Et_2NH	CH_2Cl_2	36 h		100/0	64
10	Octene oxide[b]	Et_2NH	THF	36 h		100/0	80
11	Glycidol[b]	morpholine	CH_2Cl_2	4 h		67/33	92[e]
12	Glycidol[b]	$BnNH_2$	CH_2Cl_2	24 h		100/0	67[e]
13	Cyclohexene oxide[b]	$tBuNH_2$	CH_2Cl_2	2 d			95
14	1-Methyl cyclohexene oxide[b]	$tBuNH_2$	CH_2Cl_2	24 h			67

[a] Oxirane/amine: 1/1.5.

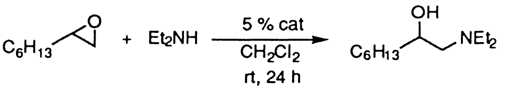
[b] Oxirane/amine: 1/1.

[c] Determined by GC analysis and ^1H NMR.

[d] Isolated yield.

[e] Yield based on weight and NMR of the crude product.

Table 10
Effect of the catalyst on the opening of octene oxide by diethylamine



Entry	Catalyst	Yield (%)[a]
1	$SmI_2(THF)_2$	56
2	$YbI_2(THF)_2$	48
3	$SmI_3(THF)_3$	48
4	$YbI_3(DME)_2$	37
5	$LaI_3(DME)_2$	36
6	$SmI_2(OtBu)(THF)_3$	20

[a] Determined by GC analysis.

reactions requiring anhydrous conditions: lanthanide derivatives are very hygroscopic compounds and the commercially available chlorides or triflates are not completely anhydrous and need to be dried at high temperature under vacuum. The use of the commercially available blue solution of samarium diiodide, otherwise easy to prepare and to keep under argon avoid to dry the catalyst. This is important for reactions involving ketene silyl acetals for instance, for which samarium diiodide gives better results than lanthanide triflates, while the latter are useful for reactions carried out in aqueous solvents.

3. Asymmetric lanthanide iodides

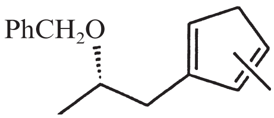
The potential for lanthanide compounds to be used for asymmetric catalysis has emerged only recently and the most important discoveries were reported from the three groups of Kobayashi [9,10,103–106], Shibasaki [11,107–112] and Marks [113–117]. The two former prepared catalysts coordinated by binaptol or other ligands of the same family. Kobayashi added binol to lanthanide triflates in the presence of various additives and obtained good enantioselectivities for several reactions. Shibasaki in most of his work used bimetallic compounds prepared by reactions of alkaline salts of binaphthol with lanthanide isopropoxides. These derivatives contain a Lewis acid center and a Bronsted base and their structures have been elucidated only recently. On the other hand Marks prepared asymmetric bis (cyclopentadienyl) complexes and developed them as catalysts or precatalysts for enantio selective reactions, hydrogenation [113], hydroamination [114,116] or hydrosilylation [117].

Different methods can be followed for the preparation of an asymmetric catalyst. Either an asymmetric ligand or a salt of this ligand is added to a known catalyst and the species thus formed is studied as an enantioselective catalyst. Alternatively a well-defined complex coordinated by an asymmetric ligand is isolated and characterized before its use as a catalyst. We have envisaged these two routes, and first tried to catalyze different reactions by samarium diiodide in the presence of asymmetric Lewis bases. The use of various types of ligands, chiral alcohols, amines, or phoshorated derivatives did not give significant asymmetric inductions for aldolization or Diels–Alder reactions. We then attempted the preparation of complexes with a chiral ligand more strongly ligated to the lanthanide.

3.1. Preparation of lanthanide iodide cyclopentadienyl complexes

Our project was the synthesis of asymmetric complexes and the study of their catalytic activities for the reactions that we had previously studied with samarium diiodide or other lanthanide iodides. To keep the catalytic activity which is supposed to be related with the presence of iodine, we planned to prepare well-defined lanthanide iodides. We focused on cyclopentadienyl ligands known to allow the stabilization and the isolation of a large number of lanthanides complexes [118–121]. A cyclopentadienyl ligand with a pendant chain bearing an ether function, the 2-methoxyethylcyclopentadienyl ($C_5H_4CH_2CH_2OMe = Cp^O$) has been used by Qian to synthesize bis or tri (cyclopentadienyl) lanthanides compounds [122–128]. For most of these complexes one or two oxygen atoms of the ligands are intramolecularly coordinated to the lanthanide center. Several properties of the 2-methoxyethylcyclopentadienyl ligand make it especially suitable for the preparation of lanthanide complexes: a bidentate ligand is well adapted to metals with high coordination numbers such as lanthanides, ether group is a very good ligand for these metals, and the chain substituting the cyclopentadienyl seems to have the good length for intramolecular coordination. We thus thought that it would be interesting to prepare lanthanide complexes coordinated by a similar ligand with the chiral center on the side-chain. The intramolecular chelation, if occuring, should prevent solvent coordination to the metal, and moreover improve the asymmetric induction during the catalysis by bringing the stereogenic center into close proximity to the lanthanide atom.

This project required us to prepare a cyclopentadienyl ligand with both a chiral center and an ether function on the side-chain. The synthesis of such a ligand with a methoxy group in the β-position of the cycle has already been described [129] albeit with very low yields. So we devised a simple method to prepare an anologous asymmetric cyclopentadiene with a benzyl ether in β-position. The (*S*)-(2-benzyloxypropyl) cyclopentadiene represented below, was prepared in four steps from (*S*)-ethyl lactate [130].



The next step was to obtain a cyclopentadienyl salt that could be employed to coordinate this ligand on the lanthanide atom. We attempted the reaction of (*S*)-(2-benzyloxypropyl) cyclopentadiene with different bases. The best result was obtained by the use of potassium hydride which permits the isolation in good yield of the potassium salt ((S)-Cp′K, as a powder which can be kept under argon (Eq. (12)).

$$(S)\text{–Cp'H}+\text{KH} \underset{-20\ ^{\circ}\text{C}}{\overset{\text{THF}}{\rightarrow}} (S)-\text{Cp'K}+1/2\text{H}_2$$

$$(S)\text{–Cp'H}=(S)\text{–C}_5\text{H}_5\text{CH}_2\text{CH(CH}_3\text{)OCH}_2\text{Ph}. \qquad (12)$$

The bis(cyclopentadienyl) samarium and lanthanum complexes were prepared by reacting two equivalents of (S)-Cp′K with the corresponding lanthanide iodides [131]. An easy isolation of these compounds was allowed by the precipitation of potassium iodide. $[(S)\text{-Cp}']_2\text{LnI}$ (Ln = Sm, La) were fully characterized by NMR and elemental analysis and by FTICR/MS for the samarium compound (Eq. (13)).

$$2(S)\text{–Cp'K}+\text{SmI}_3\text{(THF)}_3 \underset{\text{rt, 18 h}}{\overset{\text{THF}}{\rightarrow}} [(S)\text{–Cp'}]_2\text{SmI}+2\text{KI}$$

$$2(S)\text{–Cp'K}+\text{LaI}_3\text{(DME)}_2 \underset{\text{rt, 18 h}}{\overset{\text{THF}}{\rightarrow}} [(S)\text{–Cp'}]_2\text{LaI}+2\text{KI}. \qquad (13)$$

The X-ray diffraction study of the chiral compound $[(S)\text{-Cp}']_2\text{SmI}$ that we have previously described [131] confirms the (S) configuration and reveals the expected bent metallocene structure similar to those reported for the achiral Cp_2^OLnI (Ln = La, Sm, Yb, Y) [122]. $[(S)\text{-Cp}']_2\text{SmI}$ has a monomeric structure and the samarium ion is penta-coordinated by the two cyclopentadienyl rings, one iodide and the two oxygen atoms of the (S)-Cp′ ligands, in an approximately trigonal bipyramidal geometry, with the two oxygen atoms in apical positions. The formal coordination number of the samarium is nine. As expected the two oxygen atoms of the cyclopentadienyl ligands are intramolecularly coordinated to the samarium atom, forming two chelated five membered rings.

The ^{1}H NMR and ^{13}C NMR spectra of complexes $[(S)\text{-Cp}']_2\text{LnI}$ (Ln = Sm, La) reveal the presence of only one diastereomer. Either the minor isomer $[(S)\text{-Cp}'][(R)\text{-Cp}']\text{LnI}$ is formed in a very low amount, or it has been separated during the recrystallization of the complexes, or both isomers have the same spectra. The variable temperature studies of complexes $[(S)\text{-Cp}']_2\text{LnI}$ in d_8-toluene as well as in d_2-methylene chloride, indicate a fluxional behavior for both compounds. At low temperature (223 K) the non-equivalence of the two cyclopentadienyl rings is observed in ^{1}H NMR spectra of the samarium and the lanthanum complexes. An exchange process is responsible for the magnetic equivalence observed at room temperature while decreasing the temperature slows down this exchange which becomes NMR-detectable. The activation energies for the fluxional process at the coalescence temperature $\Delta G\ddagger_{\text{Tc}}$ were calculated and found to be similar for both complexes $\{[(S)\text{Cp}']_2\text{SmI}$: Tc = 263 K, $\Delta G\ddagger_{\text{Tc}} = 50 \pm 2$ kJ mol^{-1}; $[(S)\text{-Cp}']_2\text{LaI}$: Tc = 253 K, $\Delta G\ddagger_{\text{Tc}} = 52 \pm 2$ kJ mol$^{-1}\}$.

This exchange process can be explained either by a Berry pseudorotation or by decoordination-reassociation of the ether group of the side-chain. Similar temperature dependent intermolecular exchange processes have been recently recognized for several lanthanide complexes possessing ligands with versatile coordination modes [132–135].

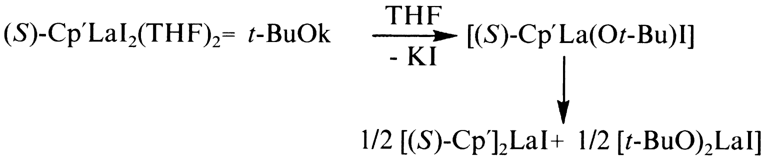
Mono (cyclopentadienyl) diiodide samarium and lanthanum complexes were prepared by the reaction of one equivalent of the potassium salt (*S*)-Cp′K with the triiodide lanthanides in tetrahydrofuran at room temperature (Eq. (14)). The NMR spectra and elemental analysis indicate different formulas for the two compounds. For $[(S)\text{Cp}']\text{SmI}_2(\text{THF})_3$ the NMR spectrum as well as an X-Ray diffraction study show the presence of three molecules of THF and the absence of intramolecular coordination of the oxygen of the cyclopentadienyl ligand on the samarium atom. On the other hand for the lanthanum complex only two THF are coordinated and the side arm of the chain of the cyclopentadienyl ligand is chelated.

$$(S)\text{–Cp}'\text{K}+\text{SmI}_3(\text{THF})_3 \xrightarrow[\text{rt, 18 h}]{\text{THF}} (S)\text{–Cp}'\text{SmI}_2(\text{THF})_3+\text{KI}$$

$$(S)\text{–Cp}'\text{K}+\text{LaI}_3(\text{DME})_2 \xrightarrow[\text{rt, 18 h}]{\text{THF}} (S)\text{–Cp}'\text{LaI}_2(\text{THF})_2+\text{KI}. \qquad (14)$$

In order to prepare solvent free lanthanide compounds which are supposed to display high catalytic activities due to an unsaturated coordination sphere, we tried to react the complex $[(S)\text{–Cp}']\text{LaI}_2(\text{THF})_2$ with Me_3SiI according to a described procedure [136]. Instead of the expected $[(S)\text{–Cp}']\text{LaI}_2$ the reaction resulted in the cleavage of the ether bond and in the loss of the benzylic group. However, the treatment of $[(S)\text{–Cp}']\text{LaI}_2(\text{THF})_2$ with hot toluene removes all the THF molecules from the coordination sphere of the lanthanum atom and leads to the formation of a product which probably has an oligomeric structure $[(S)\text{Cp}'\text{LaI}_2]_x$ and is soluble only in donor solvents.

Lanthanide compounds coordinated by three different ligands, such as cyclopentadienyl, alkoxide and iodide are as yet unknown. The reaction of $[(S)\text{Cp}']\text{LaI}_2(\text{THF})_2$ with *t*-BuOK was carried out to attempt the preparation of such a complex which could have interesting properties for catalysis. The expected product $[(S)\text{–Cp}']\text{LaI}(\text{O}t\text{-Bu})$ could not be isolated but a disproportionation reaction yielded to a mixture of $[(S)\text{–Cp}']_2\text{LaI}(\text{THF})_2$ and the mixed lanthanum alkoxy-iodide $\text{LaI}(\text{O}t\text{-Bu})_2$ (Eq. (15)).



$$(S)\text{-Cp}'\text{LaI}_2(\text{THF})_2\!=\, t\text{-BuOk} \xrightarrow[\text{- KI}]{\text{THF}} [(S)\text{-Cp}'\text{La}(\text{O}t\text{-Bu})\text{I}]$$

$$\downarrow$$

$$1/2\,[(S)\text{-Cp}']_2\text{LaI}+\ 1/2\,[t\text{-BuO})_2\text{LaI}] \qquad (15)$$

3.2. *Catalysis with lanthanides iodides*

The mono and bis (cyclopentadienyl) samarium and lanthanum iodides, thus synthesized are all stable in methylene chloride. The study of their catalytic properties was realized in this solvent which give the highest catalytic activities for the other lanthanides iodides. We first examined these asymmetric lanthanide iodides for the Diels–Alder reaction. The cycloaddition of methacrolein and cyclopentadiene was selected as a test reaction (Eq. (16); Table 11).

(16)

All the complexes are efficient catalysts yielding total conversion within 24 h with a high selectivity in the *exo* isomer, similar to that obtained with $SmI_2(THF)_2$, and not varying noticeably with the different catalysts. With all catalysts the enantiomeric excesses were modest and the asymmetric induction was not improved by lowering the reaction temperature (entries 1 and 2; Table 11). Nevertheless, with the bis (cyclopentadienyl) complexes $[(S)\text{–Cp}')]_2LnI$ (Ln = Sm, La) and with the mono (cyclopentadienyl) complex $[(S)\text{–Cp}')]LaI_2(THF)_2$, which exhibit intramolecular coordination of the cyclopentadienyl ligand, a significant asymmetric induction in the Diels–Alder reaction, was measured. On the other hand the reaction catalyzed by the complex $[(S)\text{–Cp}')]SmI_2(THF)_3$ (entry 4; Table 11) in which the asymmetric center is far away from samarium is not enantioselective. Interesting to note is the preferential formation of the two enantiomers *R* and *S* by catalysis with two different complexes coordinated by the same ligand (entries 1 and 5; Table 11).

Investigating the catalytic activity of the complex $[(S)\text{–Cp}']_2SmI$ for various reactions, we found low enantiomeric excesses for the aldol reaction of *p*-anisaldehyde with KSA and for the aminolysis of cyclohexene by *t*-$BuNH_2$. These first experiments have not given asymmetric inductions useful for catalysis, yet these results could perhaps be improved by changes of experimental conditions, especially by increasing the ratios of catalyst which were very low compared to those employed in other systems (5% with the asymmetric cyclopentadienyl lanthanides iodides instead of 10% or 20% with most asymmetric Lewis acid catalyzed reactions). However, the occurence of small inductions in relation with the intramolecular coordination of

Table 11
Catalysis of a Diels–Alder reaction

Entry	Catalyst[a]	Time	*Exo*/*endo*[b]	e.e.(%)[c]
1	$[(S)\text{–Cp}']_2SmI$	24 h	92/8	11(*R*)
2	$[(S)\text{–Cp}']_2SmI$	4 d[c]	93/7[d]	5(*R*)
3	$[(S)\text{–Cp}']_2LaI$	3 h	90/10	3(*R*)
4	$[(S)\text{–Cp}']SmI_2(THF)_3$	18 h	88/12	0
5	$[(S)\text{–Cp}']LaI_2(THF)_2$	23 h	90/10	13(*S*)
6	$[(S)\text{–Cp}'LaI_2]_x$	18 h	92/8	0

[a] All reactions are performed in CH_2Cl_2 at room temperature except[d].
[b] Determined by ^1H NMR and GC for 100% conversion.
[c] Determined by optical rotation $[\alpha]_D$ and ^1H NMR with $Eu(hfc)_3$.
[d] Reaction temperature −30 °C.

the side-chain is of importance. It indicates that chelated asymmetric ligands with the chiral center maintained close to the metal by coordination with a donor atom are interesting for asymmetric catalysis.

3.3. Conclusion

We have synthesized the first examples of organolanthanide complexes coordinated by an asymmetric cyclopentadienyl ligand with an ether group on the chiral center, which have been followed by the preparation of compounds with other similar ligands [137]. The lanthanide iodide complexes catalyze Diels–Alder or aldol reactions, the presence of one or two bulky ligands does not suppress the catalytic activity observed with lanthanide di or triiodides. The intramolecular coordination of the oxygen is observed for most of the complexes, the bis (cyclopentadienyl) iodo samarium and lanthanum and the mono (cyclopentadienyl) lanthanum diiodide, but not for the corresponding mono (cyclopentadienyl) samarium. These results, as well as the comparison with the complexes coordinated with the parent achiral cyclopentadienyl ligand Cp^O, [122–128] show that small steric effects can have a dramatic influence on the structure of the complex. Intramolecular coordination is highly dependent upon the size of the ether groups of the side-chain.

4. Outlook

Lanthanide iodides exhibit a large scope of reactivity as Lewis acid catalysts. Their catalytic activities are higher than those of chlorides and in some cases they show different reactivity patterns than lanthanide triflates. By comparison of the behavior of several samarium iodides it was noticed that a change of ligand brings an increase of activity for Meerwein–Ponndorf–Verley/Oppenauer reactions, and of the selectivity for the opening of oxiranes by trimethyl silyl cyanide, or for aldol reactions. By the easy exchange of iodide with other ligands the improvement of selectivities should be possible, and enantioselective aldol reactions should be realized in the future. Our first results concerning catalysis with asymmetric cyclopentadienyl iodides indicate that enantioselectivity is connected with intramolecular coordination. The low enantioselectivities induced by these complexes could be the consequence of the coordination–reassociation process observed in solution. The coordination site liberated by the ether could be occupied by the substrate and then the asymmetric center should move away from the lanthanide. A bidentate cyclopentadienyl asymmetric ligand bound to the metal with a covalent bond should be more efficient to hold the asymmetric center close to the lanthanide than the cyclopentadienyl described above. We are currently studying the synthesis of such complexes and their catalytic properties.

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