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Synthesis and asymmetric catalytic activities of chiral organogallium and indium complexes with ephedrine derivatives as ligands. The crystal structure of [(1*R*, 2*S*)-(Me₂Ga-μ-OCH(C₆H₅)CH(CH₃)-μ-NHCH₃)]₂

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Abstract

Reactions of trimethylgallium or trimethylindium with (1*R*, 2*S*)-(–)-ephedrine derivatives afford compounds [(1*R*, 2*S*)-(Me₂E-μ-OCH(C₆H₅)CH(CH₃)-μ-NRCH₃)]₂ [E = Ga, R = H (**1**), CH₃ (**2**), CH₂Ph (**3**); E = In, R = H (**4**), CH₃ (**5**), CH₂Ph (**6**)] in high yields. The resulting complexes **1–6** have been characterized by ¹H-NMR spectroscopy and elemental analysis. Structure of the compound **1** determined by single-crystal X-ray analysis shows a dimeric feature containing a standard parallelogram Ga₂O₂ core bridging through the oxygen atom of ephedrine group. The catalytic asymmetric isocyanosilylation of meso cyclohexene oxide with trimethylsilyl cyanide has been realized with complexes **1–6** as catalysts.

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Keywords: Organogallium; Organoindium; (–)-Ephedrine derivatives; Crystal structure; Asymmetric catalysis

1. Introduction

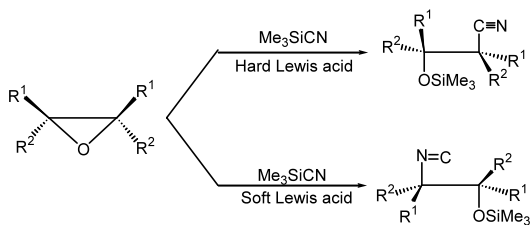
The chemistry of organogallium and indium, which contain either Group 15 or 16 elements, has been mainly aimed at the possible application as organometallic precursors for CVD of semiconductor film [1–4]. Unlike their aluminum analogues, which have been widely used as Lewis acids in catalytic reactions [5–7], organogallium or indium complexes have been lacking in application as catalysts in organic synthesis, especially as chiral catalysts [8]. Because of the difference of Lewis acidity and ion radii amongst the Group 13 elements, we believe that the reaction pattern and reactivity of organogallium and organoindium compounds would be different from those of the organoaluminum ones. It would be valuable to synthesize chiral organogallium and indium com-

plexes and apply them as catalysts in asymmetric reactions.

The desymmetrization of meso epoxides via the enantioselective addition of nucleophiles is an efficient strategy for asymmetric synthesis since it simultaneously establishes two contiguous stereogenic centers. This type of reaction has been successfully accomplished with carbon nucleophiles, thiols, phenols, carboxylic acids, aromatic amines, azides, and halide ions as nucleophiles [9–15]. The reaction of epoxide with trimethylsilyl cyanide (TMSCN) leads to formation of either β-trimethylsilyloxy nitrile (C nucleophilic attack) or β-trimethylsiloxy isocyanide (N nucleophilic attack) depending on the nature of catalyst, due to the ambident nucleophilic character of TMSCN (Scheme 1) [16]. The enantioselective addition of TMSCN to meso epoxides catalyzed by hard Lewis acid (chiral Ti catalyst) has been reported by Hoveyda, which gave β-trimethylsilyloxy nitriles with moderate to high enantiomeric excess [17,18]. We have recently communicated the first example of enantioselective isocyanosilylation of meso

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Scheme 1. Ambident nucleophilic attack of TMSiCN to epoxide catalyzed by different kinds of catalysts.

epoxides with TMSiCN catalyzed by chiral organogallium and indium complexes with binaphthol monoether derivatives as ligand [19].

Here we wish to report the preparation and characterization of several novel chiral dimethylgallium and indium complexes, [(1*R*, 2*S*)-(Me₂E-μ-OCH(C₆H₅)-CH(CH₃)-μ-NRCH₃)]₂ (E = Ga, In; R = H, CH₃, CH₂Ph), with ephedrine derivatives as chiral ligands, and the X-ray molecular structure of [(1*R*, 2*S*)-(Me₂Ga-μ-OCH(C₆H₅)-CH(CH₃)-μ-NHCH₃)]₂. In addition, the enantioselective isocyanosilylation of meso cyclohexene oxide with TMSiCN was examined using those chiral organogallium and indium complexes as catalysts.

2. Results and discussion

2.1. Synthesis and spectral analysis

Reactions of trimethylgallium or trimethylindium with equivalent ephedrine or *N*-substitute derivatives, [(1*R*, 2*S*)-PhCH(OH)CH(CH₃)NRCH₃, R = H, CH₃, CH₂Ph] [20,21], proceeded smoothly in ether or benzene at ambient temperature with the evolution of methane gas, giving complexes 1–6, as shown in Scheme 2, in nearly quantitative yields. It is worth to notice that when the reaction of (–)-ephedrine and trimethylgallium was carried out at 2:1 ratio, the identical product of 1 was obtained. Thus, the –GaMe₂ unit appears to be remarkably stable in comparison with aluminum analogue [22].

Complexes 1–5 are white solids, whereas the complex 6 is pasty oil. All of these complexes are sensitive to air

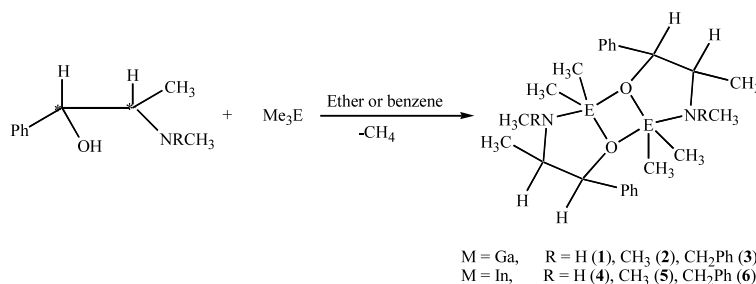
and moisture. Exposure in air, the benzene solution of 1 became cloudy over night and the others would decompose in several minutes. These compounds are very soluble in polar solvent such as diethyl ether and tetrahydrofuran. Complexes 2 and 3 can even be dissolved in hexane, while the complex 1 is soluble in aromatic hydrocarbon solvents. The solubility of the organoindium compounds in hydrocarbon solvents is better than that of the organogallium ones.

Reflecting the electropositive character of the metal center, ¹H-NMR spectra of the compounds consistently exhibited the dimethylgallium hydrogens (δ –0.31 to –0.81 ppm) at significantly upfield of TMS. Exemplified by gallium complexes, there were remarkable differences between ¹H-NMR spectra of the complexes and that of dimethylgallium hydroxide and the free ligands. The ¹H-NMR resonances of the methyl groups in –GaMe₂ of complexes 2 and 3 (δ –0.81 ppm) appeared at upper fields than in the dimethylgallium hydroxide (δ –0.48 ppm), whereas those of complexes 1 (δ –0.31 ppm) appeared at lower field. The reason might be that tertiary amino group has stronger basicity, and thus increases the electron density around the metal. Being compared with those of free ligands, the –NCH₃ signals of complexes 1, 2 and 3 (δ 2.04–2.05 ppm) shifted to upper fields. This demonstrated that intramolecular coordination bonds between the nitrogen atom and the central metal were formed [23,24]. Organoindium complexes 4, 5 and 6 exhibited similar spectra features with those of gallium complexes.

2.2. Crystal structure of 1

Recrystallization of complex 1 in diethyl ether at low temperature provided X-ray diffraction qualified single crystals. The molecular structure of 1, which is shown in Fig. 1, has been determined by X-ray analysis. The crystallographic data is given in Table 1. Selected bond lengths and bond angles are listed in Table 2.

The structure of 1 shows a dimeric feature containing a standard parallelogram Ga₂O₂ core bridging through the oxygen atom of ephedrine group. The bridging oxygen atom bond distances are slightly different to the two Ga centers with a Ga(1)–O(1) distance of 1.922 Å



Scheme 2. Synthesis of chiral organogallium and indium complexes with ephedrine derivatives as ligands.

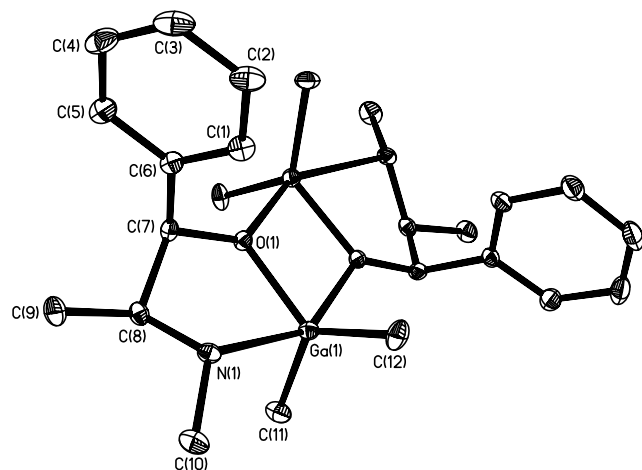


Fig. 1. Molecular structure of bis[dimethyl((-)-ephedrinato)gallium] (1). Hydrogen atoms are omitted for clarity.

Table 1
Crystal data, collection parameters, and refinements

Identification code	1
Empirical formula	C ₂₄ H ₄₀ Ga ₂ N ₂ O ₂
Formula weight	528.02
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	C222(1)
Unit cell dimensions	
<i>a</i> (Å)	11.784(4)
<i>b</i> (Å)	12.933(4)
<i>c</i> (Å)	34.980(11)
α (°)	90
β (°)	90
γ (°)	90
<i>T</i> (K)	293(2)
<i>V</i> (Å ³)	5331(3)
<i>Z</i>	8
<i>F</i> (0 0 0)	2208
<i>D</i> _{calc} (Mg m ⁻³)	1.316
Absorption coefficient (mm ⁻¹)	2.042
Crystal size (mm ³)	0.50 × 0.25 × 0.25
θ Range for data collection	2.33–25.00
Index ranges	13 ≤ <i>h</i> ≤ 14, −15 ≤ <i>k</i> ≤ 14, −41 ≤ <i>l</i> ≤ 27
Reflections collected	13 712
Independent reflections	4693 [<i>R</i> _{int} = 0.0433]
Completeness to θ	25.00 (99.8%)
Absorption correction	SADABS
Max and min transmission	0.670776 and 0.907701
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4693/0/271
Goodness-of-fit on <i>F</i> ²	1.029
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0447, <i>wR</i> ₂ = 0.0904
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0580, <i>wR</i> ₂ = 0.0930
Absolute structure parameter	0.028(16)
Largest difference peak and hole (e Å ⁻³)	0.610 and −0.262

and Ga(1a)–O(1) distance of 2.088 Å. There are three fused-rings in the compound in the form of [3.3.0.0]. The coordination number of the central metal is five, and the geometry around the gallium center can be

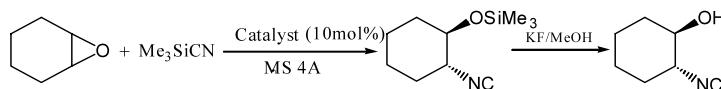
Table 2
Selected bond lengths (Å) and angles (°) for crystal of complex 1

<i>Bond lengths</i>			
Ga(1)–O(1)	1.922(3)	Ga(1)–N(1)	2.346(4)
Ga(1)–C(11)	1.971(6)	Ga(1)–C(12)	1.968(5)
Ga(1)–O(1a)	2.088(3)	Ga(1a)–O(1)	2.088(3)
Ga(1a)–N(1a)	2.346(4)	Ga(1a)–C(11a)	1.971(6)
Ga(1a)–C(12a)	1.968(5)	Ga(1a)–O(1a)	1.922(3)
<i>Bond angles</i>			
O(1)–Ga(1)–C(11)	113.9(2)	O(1)–Ga(1)–C(12)	119.8(2)
C(11)–Ga(1)–C(12)	126.1(3)	O(1)–Ga(1)–O(1a)	73.70(14)
C(11)–Ga(1)–O(1)	99.18(18)	C(12)–Ga(1)–O(1)	99.1(2)
O(1)–Ga(1)–N(1)	75.94(13)	C(11)–Ga(1)–N(1)	98.21(18)
C(12)–Ga(1)–N(1)	91.0(2)	O(1)–Ga(1)–N(1)	149.09(13)
C(7)–O(1)–Ga(1)	124.0(3)	C(7)–O(1)–Ga(1)	129.4(3)
Ga(1)–O(1)–Ga(1a)	106.18(14)	C(10)–N(1)–C(8)	114.3(4)
C(10)–N(1)–Ga(1)	116.4(3)	C(8)–N(1)–Ga(1)	101.6(3)

described as a distorted trigonal bipyramid, in which the axial positions are occupied with coordinate nitrogen N(1) and bridging O(1a), while the apices of the equatorial triangle are O(1) and both gallium methyl carbon atoms. The coordinate bond distance of Ga(1)–N(1) has a value of 2.346 Å, which agrees well with the Ga ← N(sp³) bond lengths in such as Cl₂Ga[N(CH₂CH₂–NEt₂)₂] (2.287 Å) [2], and is obviously longer than those of Ga ← N(sp²) bond lengths in the compounds such as salen(^{*t*}Bu)H(GaEt₂) (2.030 Å) [25], salomphen(^{*t*}Bu)GaMe (2.064 Å) [26], and dimethyl[*N*-salicylidene-2-aminopyridine]gallium (2.095 Å) [27]. Arising upon coordination to the metal, both nitrogen atoms become stereogenic. It is worth to notice that the nitrogen-bonded hydrogen atom remains in the product, although the H atom should be fairly active towards gallium-bonded methyls.

2.3. Enantioselective ring opening of cyclohexene oxide with TMSCN catalyzed by complexes 1–6

The reactions of TMSCN with cyclohexene oxide catalyzed by complex 1–6 were examined. With the addition of MS 4A, these reactions were started at −78 °C and then risen to room temperature and stirred for 10 h, followed by treatment with methanol solution of potassium fluoride to remove −SiMe₃ group, we found that, as envisioned, all the reactions gave the product of β-isocyanocyclohexanol, which was identified by IR and ¹H-NMR analysis, with the absolute configuration 1R, 2R (Scheme 3). As summarized in Table 3, the expected β-isocyanocyclohexanol has been obtained in yields varying from 55 to 78%, with the enantioselectivity varying from 15 to 48% depending on the nature of the catalyst used. It should be noted that the reaction showed much less reactivity and selectivity without MS 4A (Entry 2). The intrinsic role of the MS 4A needs to be further exploited. The isocyanosilylation of cyclohexene oxide catalyzed by catalyst 3 gave the



Scheme 3. The reaction of cyclohexene oxide with TMSCN catalyzed by chiral organogallium and indium complexes.

Table 3

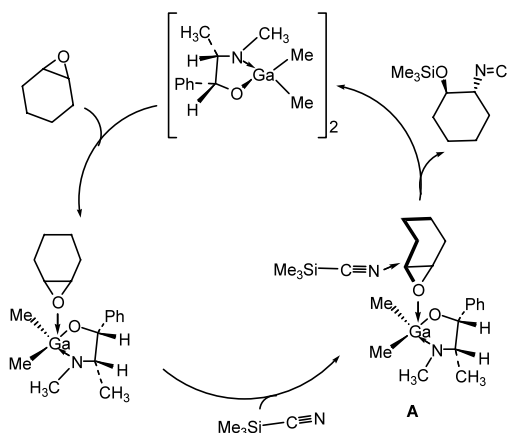
Enantioselective ring opening of cyclohexene epoxide with trimethylsilyl cyanide catalyzed by **1–6**

Entry	Catalyst	Yield ^a (%)	ee ^b (%) (config.) ^c
1	no	0	0
2 ^d	1	40	14 (1 <i>R</i> , 2 <i>R</i>)
3	1	55	26 (1 <i>R</i> , 2 <i>R</i>)
4	2	61	41 (1 <i>R</i> , 2 <i>R</i>)
5	3	67	48 (1 <i>R</i> , 2 <i>R</i>)
6	4	65	15 (1 <i>R</i> , 2 <i>R</i>)
7	5	69	23 (1 <i>R</i> , 2 <i>R</i>)
8	6	78	35 (1 <i>R</i> , 2 <i>R</i>)

^a Isolated yield based on cyclohexene oxide.^b Enantioselectivity excess values were determined by HPLC analysis using a DAICEL CHIRAL OD-H column.^c The absolute configuration was determined by converting β -isocyanocyclohexanol to β -aminocyclohexanol [28] and then comparing the optical rotations with literature values [29].^d Without MS 4A.

best selectivity up to 48% ee with the yield of 67% (Entry 5). We found that gallium complexes (**1–3**) showed better result in enantioselectivity but lower yields than indium complexes (**4–6**). It is particular worthy to note that the substituents in the amino group of catalysts had a significant effect on the enantioselectivity of the asymmetry ring opening reaction. This is exemplified by a comparison of catalysts **1**, **2** and **3**. Better enantioselectivities and yields were achieved by using steric $-NMe$ and $-NBn$ ephedrine derivatives as ligands.

A proposal mechanism for the catalytic asymmetric epoxide opening is shown in Scheme 4. A gallium (or indium) metal appears to function as a soft Lewis acid,

Scheme 4. Working model for the ring opening of cyclohexene oxide with Me_3SiCN catalyzed by chiral Ga-complexes.

activating epoxide and also controlling the orientation of epoxide due to coordination of an axial lone pair, allowing for the cleavage of C–O bond by backside attack. Based on the structure of complex **1** and the absolute configuration of the product (1*R*, 2*R*) obtained by this catalyst, enantiomeric induction in the present system can be understood by assuming the transition state A. ^{13}C -NMR measurement of a mixture of complex **1** and Me_3SiCN exhibited no resonance of Ga–CN species. This strongly supported Ga–CN species, which most probably led to formation of cyanosilylation product, was not involved in this reaction [16].

3. Experimental

3.1. General procedures

All reactions were performed in a glove box under nitrogen. The solvents were refluxed with sodium benzophenone and distilled under nitrogen prior to use. (1*R*, 2*S*)-(–)-Ephedrine was obtained by neutralization of commercial available (1*R*, 2*S*)-(–)-Ephedrine hydrochloride. Derivatives of (1*R*, 2*S*)-(–)-ephedrine were prepared according to the literatures [20,21]. Trimethylgallium and trimethylindium were provided by the National 863 Program Advanced Material MO Precursors R&D Center of China.

1H -NMR data were collected on a Bruker ARX-300 spectrometer, with chemical shifts referenced to $SiMe_4$ as internal standard. Infrared spectra were obtained as KBr pellets with a 5DX-FT-2 spectrometer. Elemental analyses were performed on a Perkin–Elmer 240 C elemental analyzer.

3.2. Determination of enantiomeric purity

Enantiomeric excesses (ee's) were determined by HPLC analysis performed on JASCO HPLC systems consisting of the following: pump, Shimadzu LC-10AD; detector, Shimadzu SPD-6A UV Spectrophotometric Detector, measured at 220 nm; column DAICEL CHIRALPAK OD-H; mobile phase, hexane/2-propanol; flow rate, 0.5 ml min^{-1} .

3.3. Bis[*dimethyl*((–)-ephedrinato)gallium] (**1**)

Me_3Ga (4.2 mmol) in 14 ml of Et_2O was added dropwise to a stirred solution of (–)-ephedrine (0.5 g,

3.0 mmol) in Et₂O (4 ml) at room temperature (r.t.) (ca. 30 min). During the addition of Me₃Ga, a vigorous evolution of gas was observed. The resulting solution continued to stir over night and a white precipitate formed. The solution was decanted leaving a white solid that was washed with Et₂O and dried in vacuo. Yield: 0.78 g (98%). Found: C, 54.88; H, 7.57; N, 5.33. Anal. Calc. for C₂₄H₄₀Ga₂N₂O₂: C, 54.57; H, 7.64; N, 5.30%. ¹H-NMR (CDCl₃, ppm): δ 7.31 (m, 5H), 5.04 (s, 1H), 3.05 (s, 1H), 2.05 (s, 3H), 2.42 (s, 1H), 0.88 (d, *J* = 6.54 Hz, 3H), -0.31 (s, 6H).

3.4. Bis[*dimethyl*((-)-*N*-methylephedrinato)gallium] (2)

To a solution of (-)-*N*-methylephedrine (0.18 g, 1 mmol) in C₆H₆ (2 ml), Me₃Ga (2 mmol) in 2 ml of C₆H₆ was added with stirring at r.t. A vigorous evolution of gas was observed. The resulting solution continued to stir over night followed by refluxing for 0.5 h. Volatiles were removed in vacuo to give a white solid. Yield: 0.26 g (96%). Found: C, 56.38; H, 7.57; N, 5.27. Anal. Calc. for C₂₆H₄₄Ga₂N₂O₂: C, 56.12; H, 7.91; N, 5.04%. ¹H-NMR (CDCl₃, ppm): δ 7.21 (m, 5H), 5.0 (d, *J* = 5.1 Hz, 1H), 3.15 (s, 1H), 2.50 (s, 3H), 2.05 (s, 3H), 1.04 (d, *J* = 6.96 Hz, 3H), -0.81 (s, 6H).

3.5. Bis[*dimethyl*((-)-*N*-benzylephedrinato)gallium] (3)

To a solution of (-)-*N*-benzylephedrine (1 mmol) in C₆H₆ (6 ml), Me₃Ga (2 mmol) in 2 ml of C₆H₆ was added with stirring at r.t. A vigorous evolution of gas was observed. The resulting solution continued to stir over night followed by refluxing for 0.5 h. Volatiles were removed in vacuo and the residue was crystallized from CH₂Cl₂-hexane (1:1) to give a white solid. Yield: 0.34 g (96%). Found: C, 64.17; H, 7.45; N, 3.66. Anal. Calc. for C₃₈H₅₂Ga₂N₂O₂: C, 64.41; H, 7.34; N, 3.95%. ¹H-NMR (CDCl₃, ppm): δ 7.23 (m, 10H), 5.19 (s, 1H), 3.85 (s, 2H), 3.3 (b, 1H), 2.14 (s, 3H), 1.05 (d, *J* = 6.09 Hz, 3H), -0.81 (s, 6H).

3.6. Bis[*dimethyl*((-)-ephedrinato)indium] (4)

Me₃In (1.08 mmol) in C₆H₆ (16 ml) was added dropwise to the solution of (-)-ephedrine (0.15 g, 0.9 mmol) in C₆H₆ (2 ml) at r.t. (ca. 30 min). During the addition of Me₃In, a vigorous evolution of gas was observed. The resulting solution continued to stir over night followed by refluxing for 1.5 h. Volatiles were removed in vacuo and the residue was crystallized from hot petroleum ether (b.p.: 60–90 °C) to give a white crystal. Yield: 0.26 g (95%). Found: C, 46.69; H, 6.53; N, 4.38. Anal. Calc. for C₂₄H₄₀In₂N₂O₂: C, 46.60; H, 6.47; N, 4.53%. ¹H-NMR (CDCl₃, ppm): δ 7.30 (m, 5H), 4.82

(d, *J* = 3.6 Hz, 1H), 2.71 (m, 1H), 2.51 (s, 1H), 2.30 (d, *J* = 6.45 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 3H), -0.48 (s, 6H).

3.7. Bis[*dimethyl*((-)-*N*-methylephedrinato)indium] (5)

Me₃In (1.326 mmol) in C₆H₆ (6 ml) was added dropwise to the solution of (-)-*N*-methylephedrine (0.2 g, 1.12 mmol) in 2 ml of C₆H₆ at r.t. (ca. 30 min). During the addition of Me₃In, a vigorous evolution of gas was observed. The resulting solution continued to stir over night followed by refluxing for 0.5 h. Volatiles were removed in vacuo and the residue was crystallized from hexane to give a white crystal. Yield: 0.35 g (97%). Found: C, 48.28; H, 6.69; N, 4.46. Anal. Calc. for C₂₆H₄₄In₂N₂O₂: C, 48.30; H, 6.81; N, 4.33%. ¹H-NMR (CDCl₃, ppm): δ 7.21 (m, 5H), 4.96 (d, ³*J* = 3.09 Hz, 1H), 2.28 (s, 1H), 2.17 (s, 6H), 0.76 (d, ³*J* = 6.84 Hz, 3H), -0.52 (s, 6H).

3.8. Bis[*dimethyl*((-)-*N*-benzylephedrinato)indium] (6)

Me₃In (1.326 mmol) in C₆H₆ (6 ml) was added dropwise to (-)-*N*-benzylephedrine (1 mmol) in C₆H₆ (6 ml) at r.t. (ca. 30 min). During the addition of Me₃In, a vigorous evolution of gas was observed. The resulting solution continued to stir over night followed by refluxing for 0.5 h. Volatiles were removed and the residue was dried in vacuo to give an oil. Yield: 0.36 g (92%). Found: C, 57.23; H, 6.69; N, 3.69. Anal. Calc. for C₃₈H₅₂In₂N₂O₂: C, 57.14; H, 6.51; N, 3.51%. ¹H-NMR (CDCl₃, ppm): δ 7.28 (m, 10H), 5.16 (s, 1H), 3.57 (s, 2H), 2.37 (b, 1H), 2.01 (s, 3H), 0.82 (d, *J* = 6.39 Hz, 3H), -0.521 (s, 6H).

3.9. General procedure for asymmetric ring opening of epoxy cyclohexane with TMSCN

A mixture of catalyst (0.2 mmol) and 0.4 g molecular sieve (4A) in dichloromethane (15 cm³) was stirred at -78 °C. After 15 min, cyclohexene oxide (2 mmol) and TMSCN (2.4 mmol) were added and the resulting mixture was risen to r.t. gradually and stirred for another 10 h, followed by treatment with methanol solution of potassium fluoride (0.8 g in 10 cm³ methanol) for 5 h. The reaction mixture was filtered, concentrated and separated by flash chromatography (petroleum ether and ethyl acetate as the eluent) to give the β-isocyanocyclohexanol as a white solid. ¹H-NMR (CDCl₃, 300 MHz): δ 3.84–3.31 (m, 2H), 2.66 (s, 1H), 2.18–1.18 (m, 8H). IR (KBr): ν = 3347, 2147 cm⁻¹. HPLC (DAICEL CHIRALPAK OD-H, *n*-hexane/*i*-PrOH = 100:0.5): Rt = 10.25 min, 12.25 min.

3.10. X-ray structure determination of crystal **1**

The crystal of **1** was grown from diethyl ether. In the glove box, a crystal suitable for X-ray diffraction studies was pasted on the top of glass fiber with Araldite® glue, removed from the glove box, mounted on a goniometer head for data collection. Intensities of the complex were collected on a Siemens SMART-CCD diffractometer with graphite-monochromatic Mo-K α radiation ($\lambda = 0.71073$ and Aring) and reduced using SMART and SAINT program [30]. A SADABS program was applied for absorption correction. The structure was solved by direct methods and refined on F^2 using full-matrix least-squares methods using SHELXTL version 5.1 [31]. Anisotropic thermal parameters were refined for non-hydrogen atoms. Selected bonds and angles of complex **1** are listed in Table 1. Crystallographic data are summarized in Table 2. The overall molecular geometry of complex **1** with the atomic labeling scheme is shown in Fig. 1.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC 182132. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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