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Journal of Organometallic Chemistry 630 (2001) 17–22

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Highly enantioselective Diels–Alder catalysis with a chiral ruthenium bisoxazoline complex

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Received 13 December 2000; received in revised form 27 February 2001; accepted 19 March 2001

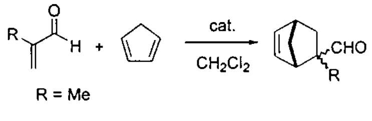
Abstract

When treated with $AgSbF_6$, the cation (−)-[(η^6-cymene)RuCl(L)]SbF_6, where L = (+)-INDABOX = [3a*R*-[2(3′a*R**,8′a*S**),3′aβ,8′aβ]]-(+)-2,2′-methylenebis[3a,8a-dihydro-8*H*-indeno[1,2-d]-oxazol], yields a dication which is an efficient catalyst for the condensation of either methacrolein or ethylacrolein with cyclopentadiene in high ee. For example, the reaction of methacrolein with cyclopentadiene at −24 °C produced (*S*)-(+)-*exo*-2-methylbicyclo[2.2.1]hept-5-ene-2-carboxaldehyde in 95% conversion with de = 96% and ee = 91%. The monocationic catalyst precursor was characterized spectroscopically and by single crystal X-ray diffraction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Diels–Alder reaction; Asymmetric catalysis; Lewis acid catalysis

1. Introduction

Organometallic cations [1] have seen increased use as chiral Lewis-acid catalysts for a variety of carbon–carbon bond forming reactions [2]. With respect to the asymmetric Diels–Alder reaction [3], a common test of the efficacy of a catalyst is the reaction of methacrolein with cyclopentadiene (Scheme 1). Previously, catalysts derived from titanium, boron, and aluminum have been found to be highly effective for these reactions, although many are subject to degradation from moisture. One alternative has been the use of rare earth metal trifluoromethanesulfonates as water-tolerant Lewis-acid catalysts [4]. More recently, some robust late transition metal catalysts (some isolable as aqua complexes, yet still maintaining catalytic activity) have been introduced [5–14].



Scheme 1. Condensation of methacrolein with cyclopentadiene.

Asymmetric Lewis-acid catalysts based on chiral bisphosphine ligands of CpRu, CpRh, and CpFe have been reported [5–8]. Although initial optical yields were modest with these catalysts, Kundig and co-workers [8] have recently developed a more effective CpFe system by increasing the acidity of the metal center with perfluorophenylphosphine ligands. This suggests that more acidic complexes may have a kinetic advantage relative to competitive pathways that might lead to racemic material. We have used the electronic asymmetry inherent in bisphosphine monoxide systems to achieve enantiomeric purities up to 99% with dicationic cymene ruthenium systems [10]. In comparing $CyRu^{2+}$ and $CpRu^{1+}$ systems, we observed that increasing the charge resulted in increased acidity of the metal and consequently, enhanced catalytic activity.

Owing to the increased interest in nitrogen donor ligands in catalysis [15] and the development of chiral oxazoline ligands [16–18], one might anticipate that bisoxazolines or chiral imines might contribute to the development of similar Lewis-acid catalysts for the Diels–Alder reaction [19]. Carmona et al. [13] investigated a Cp*Ir complex with some pyridyl-imines, but generally observed an ee <40%. The best case for enantioselectivity observed by these researchers gave a 46% ee with a 94:6 *exo*/*endo* isomer ratio and required

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PII: S0022-328X(01)00871-3

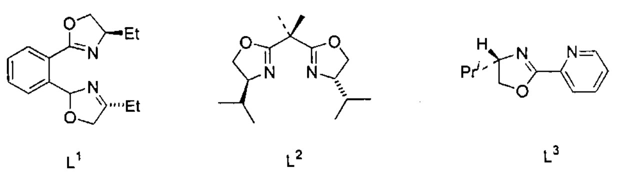


Fig. 1. Some previously investigated bisoxazoline (L^1 and L^2) and pyridyl-oxazoline (L^3) ligands.

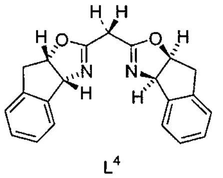


Fig. 2. L^4 = (+)-INDABOX represents a sterically encumbering and rigid bisoxazoline. The (+)- enantiomer is shown. Note that the spatial arrangement of the indenyl moieties can be easily misinterpreted from the diagram. The bold and dashed lines give the stereochemistry relative to indenyl moieties in the plane of the paper. If the oxazolines were in the plane of the paper, the indenyl on the right would be up and that on the left would be down.

a reaction time of 96 h. Evans and co-workers [18] have investigated a variety of Diels–Alder reactions with dicationic Cu complexes bearing bisoxazoline ligands which gave high *exo*/*endo* ratios in addition to high optical yields. Davies et al. [11] investigated two bisoxazolines with Cp*Rh, but products were obtained in 29% ee for L^1 and 2% ee for L^2 (see Fig. 1). A $[Cp^*RhL^3]^+$ complex with L^3 = pyridine–oxazoline ligand, however, gave a 68% ee with a 95:5 *exo*/*endo* isomer ratio in 72 h with a 2% catalyst loading at 0 °C. Based upon these results, it would be anticipated that a more acidic dicationic arene ruthenium complex analogous to the Cp–metal systems would be a more active catalyst. Subsequently, this was confirmed when Davies et al. discovered that the dication formed from $[(\eta^6\text{-mesitylene})RuCl(L^3)]SbF_6$ gave a 75% ee with a 94:6 *exo*/*endo* isomer ratio in a reaction time of 24 h at 0 °C [12].

On the basis of this background information, one might assume that C_2-symmetric bisoxazolines might not be worth pursuing relative to pyridine-imines of CpM or CyM complexes. Regardless, we felt that sufficient steric interaction introduced by a rigid bisoxazoline might offer preferential accessibility of cyclopentadiene to either the *Re* or *Si* face of the bound acrolein. Therefore, we pursued an investigation of the L^4 = (+)-INDABOX = [[3a*R*-[2(3′a*R**,8′a*S**),3′a*β*, 8’a*β*]] - (+) - 2,2’ - methylenebis[3a,8a - dihydro - 8*H*-indeno[1,2-d]-oxazol]] ligand (see Fig. 2) with the CyRu moiety.

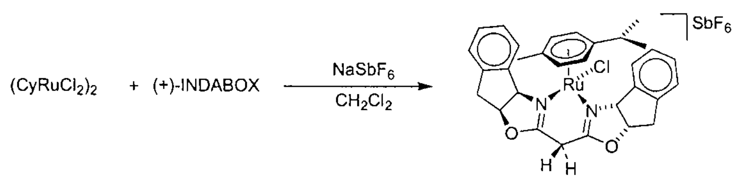
2. Results and discussion

C_2-symmetric ligands are advantageous because they preclude the possibility of multiple isomer formation which is inherent with unsymmetrical ligands such as L^3. Hence, (−)-$[(\eta^6\text{-cymene})RuCl(L^4)]SbF_6$ (**1**), was prepared as a single isomer by cleavage of the $(CyRuCl_2)_2$ dimer with two equivalents of (+)-INDABOX in the presence of $NaSbF_6$ as depicted in Scheme 2. This reaction solution was stirred at ambient temperature for 48 h followed by filtration through Celite. Purification was achieved via crystallization from CH_2Cl_2–Et_2O to yield analytically pure material. It is notable that the sign of the rotation of the complex at the Na_D wavelength is opposite to that of the ligand.

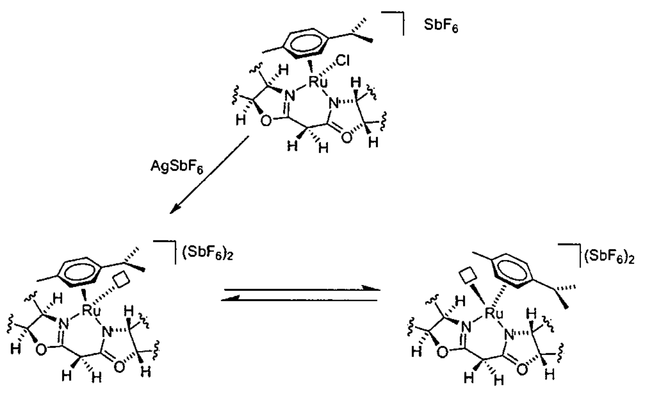
Treatment of $[(\eta^6\text{-cymene})RuCl(L^4)]SbF_6$ with $AgSbF_6$ yielded the dication **2**, presumably as the aqua complex formed from moisture in the solvent. An important feature of this cation is that the 16-electron intermediate formed upon the loss of a weakly bound ligand is prone to rapid inversion. However, with a C_2-symmetric ligand, ‘inversion’ at the metal center (which is a chirotopic center not a stereogenic center) [20] results in a complex with the chiral environment at the metal. Hence, complexation of the dienophile (e.g. methacrolein) involves only one possible configuration at the metal (see Scheme 3). As such, the conformation of the bound dienophile will be controlled by the same interactions with other portions of the complex, regardless of the possibility of inversion. Kurosawa et al. [21] have reported similar inversions with the phenyl-substituted analog of L^2 in $[(\eta^6\text{-benzene})Ru(L)(H_2O)]BF_4$.

2.1. The structure of the precursor

In order to gain some insight into the origin of the asymmetric control in catalysis, an investigation of the solid-state structure of (−)-$[(\eta^6\text{-cymene})RuCl(L^4)]SbF_6$



Scheme 2. The preparation of (−)-$[(\eta^6\text{-cymene})RuCl(L^4)]SbF_6$.



Scheme 3. The fluxional rearrangement which results from inversion at the ruthenium center. In spite of the inversion, the incoming dienophile encounters the same chiral environment as it binds to the metal.

Table 1
Crystal data and structure refinement parameters for (−)-[CyRuCl(η^2-INDABOX)]$SbF_6\cdot CHCl_3$ (**1**)

Empirical formula	$SbRuCl_1F_6O_2N_2C_{31}H_{32}\cdot CHCl_3$
Formula weight	956.25
Crystal system	Trigonal
Space group	$P3_221$ (no. 154)
Unit cell dimensions	
a (Å)	12.1349(3)
c (Å)	43.541(1)
V (Å^3)	5552.7(2)
Z	6
D_{calc} (g cm^{-3})	1.716 ($Z = 6$)
Absorption coefficient (cm^{-1})	14.87
Crystal size (mm)	0.22 × 0.15 × 0.07
Diffractometer	Nonius KappaCCD
Monochromator	Graphite
Radiation (λ)	Mo–K$_\alpha$ (0.71073 Å)
Max 2θ (°)	50.2
Unique reflections measured	7479 (including Friedel pairs)
Data used, $F^2 > 3\sigma(F^2)$	4132
Parameters refined	437
p factor	0.01
Final residuals R, R_w	0.051, 0.053
Convergence, largest shift/error	0.00
Goodness-of-fit on F^2	1.59
Largest $\Delta(\rho)$ (e Å^{-3})	0.073

Table 2
Selected bond lengths (Å) and bond angles (°) for (−)-[CyRuCl(η^2-INDABOX)]$SbF_6\cdot CHCl_3$ (**1**)

Bond lengths	
Ru(1)–Cl(1)	2.384(3)
Ru(1)–N(1)	2.122(9)
Ru(1)–N(2)	2.099(7)
Bond angles	
Cl(1)–Ru(1)–N(1)	90.7(2)
Cl(1)–Ru(1)–N(2)	84.4(2)
N(1)–Ru(1)–N(2)	82.8(3)

was undertaken by X-ray diffraction. The results are presented in Tables 1 and 2. An ORTEP view of the complex is depicted in Fig. 3. On viewing the molecule with the cymene up and looking along the Cl–Ru bond, one notes that an indenyl group is oriented upwards on the right and downwards on the left. This view illustrates that there is relatively unrestricted access to a ligand, such as methacrolein, bound to ruthenium from the lower right. The metrical parameters given in Table 2 indicate that the bisoxazoline ligand has a relatively small bite angle of 82.9(3)°. It is also notable that the chloro ligand is not equally displaced from the two nitrogen donors [Cl–Ru–N1 = 90.7(2)° and Cl–Ru–N2 = 84.4(2)°]. The C_2-symmetry of the ligand moiety is not retained when complexed, as shown in Fig. 4. The six-membered chelate ring is distorted towards a boat conformation with the ruthenium atom displaced 0.79 Å and the methylene-bridge carbon being displaced 0.39 Å from the N1–C12–N2–C22 plane. Owing to the unsaturation, there are only minor deviations from planarity at N1–C12 and N2–C22 [Ru–N–C–C11 dihedral angles 20(2)° and 0(2)°] and the six-membered ring is essentially folded at the ruthenium and methylene-bridge (C11).

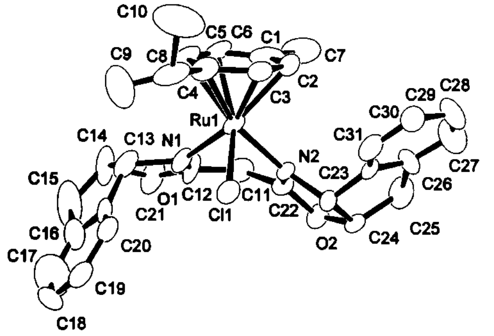


Fig. 3. The ORTEP diagram of (−)-[(η^6-cymene)RuCl(L^4)]SbF_6 showing 30% ellipsoids.

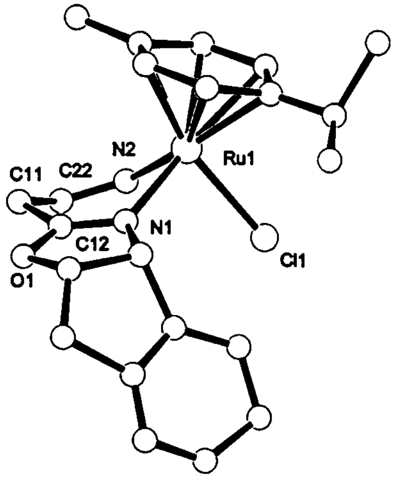


Fig. 4. The conformation of the six-membered ring of **1**. The remote indenyl group is omitted for clarity.

Table 3
Catalytic results for the Diels–Alder reaction between CpH and a substituted acrolein (R = Me, Et) with the catalyst derived from [(η^6-cymene)RuCl(L^4)]SbF_6

Substrate (R)	Loading (%)	Temperature (°C)	Reaction time (h)	Conversion (%)	de	ee (configuration)
Me	10	−78	16	95	96	90 [a,b] (*S*)-(+) [d]
Me	10	−24	16	95	96	91 [a,b] (*S*)-(+) [d]
Me	10	+25	16	100	90	70 [a,b] (*S*)-(+) [d]
Et	10	−78	16	86	84	66 [c]-(+) [e]
Et	10	−24	16	100	95	76 [c]-(+) [e]
Et	10	+25	16	100	85	49 [c]-(+) [e]

[a] The ee was determined by ^{1}H-NMR spectroscopy with Eu(hfc)$_3$ as a chiral shift reagent.

[b] The downfield ^{1}H aldehyde resonance shifted by Eu(hfc)$_3$ had more intensity.

[c] The ee was determined by derivatization of the product with (2*R*,4*R*)-(−)-pentanediol followed by ^{1}H-NMR spectroscopy. In each case, the upfield resonance of the acetal derivatives was more intense.

[d] The absolute configuration was correlated by comparison of the specific rotation to literature values [24].

[e] The absolute configuration was not determined, although polarimetry indicated that the sign of rotation was (+).

2.2. The reactivity of the catalyst

Treatment of (−)-[(η^6-cymene)RuCl(L)]SbF_6 with one equivalent of $AgSbF_6$ resulted in chloride abstraction and thus generation of the dicationic Lewis-acid complex, **2**. Subsequent addition of an aldehyde presumably generated the σ-bound complex. The selective binding via the carbonyl functionality (as opposed to the double bond) has previously been documented in other cymene–ruthenium complexes [10,14,22] and is a function of the hard dicationic metal's preference for a hard donor. The activated aldehyde is thus subject to attack by cyclopentadiene to yield the Diels–Alder adduct.

The catalytic results are summarized in Table 3. The fact that reactions reach completion in less than 24 h attests to the high reactivity of these dicationic catalysts. The high enantioselectivity for the methacrolein reaction is impressive considering the modest selectivity observed with CpRh complexes prepared with other bisoxazolines [11]. The enantioselectivity is even higher for the $[CyRuL^4]^{2+}$ catalyst than for the $[CyRuL^3]^{2+}$ catalyst and demonstrates the superiority of the INDABOX ligand for such applications. Since the indenyl group maintains a rigid conformation for the substituents of the oxazoline, it would appear that this has an advantage compared to conformationally mobile isopropyl or phenyl substituents.

3. Conclusions

The cation (−)-[(η^6-cymene)RuCl(L)]SbF_6 has been found to be a highly effective precatalyst for the enantioselective Diels–Alder reaction between substituted acroleins and cyclopentadiene. The reactivity and high enantioselectivities obtained with the catalyst suggest that it is sufficiently Lewis-acidic to be effective in other asymmetric carbon–carbon bond forming reactions. Further investigations will focus upon testing the generality of the catalysis and extending the applicability of the catalyst to other Lewis-acid catalyzed reactions.

4. Experimental

4.1. General procedures

All synthetic manipulations were carried out using standard Schlenk techniques under an inert atmosphere. Reagent-grade CH_2Cl_2 and Et_2O were used as solvents without further purification. The ligand (+)-INDABOX = [3a*R* - [2(3′a*R**,8′a*S**),3′aβ,8′aβ]] - (+)-2,2′ - methylenebis[3a,8a - dihydro - 8*H* - indeno[1,2 - d]-oxazol], methacrolein (95%), 2-ethylacrolein (85%), and $AgSbF_6$ were all purchased from Aldrich and were used without further purification. A synthesis of INDABOX has been published [23]. The enantiomeric excess in each product was determined by addition of the chiral shift reagent europium tris[3-(heptafluoropropylhydoxymethylene)-(+)-camphorate] (98%) to an aliquot of the Diels–Alder product in $CDCl_3$. Integration and peak fitting was performed using the NUTS (NMR Utility Transform Software for Windows 95/NT) and the Jandel PeakFit program Version 4. ^{1}H-NMR spectra were recorded on a Bruker 500 MHz or Bruker 400 MHz spectrometer, and chemical shifts are reported in ppm relative to the residual solvent peaks (^{1}H). Circular dichroism spectra were recorded on an AVIV Model 202 spectrometer equipped with a 450 W xenon arc lamp. Spectra were recorded from 800 to 230 nm in 1.0 nm intervals with a 0.2 s averaging time. CD spectra were taken in CH_2Cl_2 with a 1 mm path length quartz cell and thermostated to 25.0 °C. UV–vis spectra were acquired on a Cary 3E spectrophotometer using a 1 cm quartz cell. Optical rotations were measured on a Perkin–Elmer model 341 polarimeter at 589 nm and 25.0 °C, using a 1 dm path length. Correlations with absolute configuration used published specific rotations [24]. IR spectra were measured on a Nicolet FT-IR spectrometer. X-ray crystallographic structure determination utilized a Nonius KappaCCD diffractometer. Elemental analyses were carried out by Atlantic Microlab, Inc., Norcross, GA.

4.2. Preparation of $[(\eta^6\text{-cymene})\mathrm{RuCl}(L^4)]\mathrm{SbF_6}$ (**1**)

A Schlenk tube was charged with $(\mathrm{CyRuCl_2})_2$ (67 mg, 0.11 mmol), (+)-INDABOX (72 mg, 0.22 mmol), $\mathrm{NaSbF_6}$ (57 mg, 0.22 mmol), and a stir bar. The tube was evacuated and was backfilled with nitrogen before immersion in liquid nitrogen. An aliquot of $\mathrm{CH_2Cl_2}$ (20 ml) was introduced by a syringe and the resultant solution was degassed with two freeze–pump–thaw cycles. The reaction mixture was allowed to warm to ambient temperature and was stirred for 48 h, after which it was filtered through a plug of Celite and was reduced in volume on a rotary evaporator to 3 ml. Then, $\mathrm{Et_2O}$ (5 ml) was added and crystals began to form as orange plates. The crystals were collected after 2 h, washed with a solution of 50:50 $\mathrm{Et_2O–CH_2Cl_2}$ (2 ml) and dried under reduced pressure to yield analytically pure material (yield: 136 mg, 74%). ^{1}H-NMR ($\mathrm{CDCl_3}$, 293 K, δ ppm): 8.18 (d, 1H, $J = 7.6$ Hz, N=C*H*); 7.89 (d, 1H, $J = 7.5$ Hz, N=C*H*); 7.53 (t of d, 1H, $J = 7.5$ Hz, $J = 1.3$ Hz, Ar–*H*); 7.44 (m, 2H, Ar–*H*); 7.30–7.24 (m, 4H, Ar–*H*); 6.10 (app t of d, 1H, $J = 7.0$ Hz, $J = 1.8$ Hz, OC–*H*); 5.81 (d, 1H, $J = 7.7$ Hz, OCHCH–*H*); 5.77 (d of d, 1H, $J = 8.5$ Hz, $J = 1.6$ Hz, Ar–*H*); 5.67 (d, 1H, $J = 6.0$ Hz, Cy–*H*); 5.64 (d, 1H, $J = 6.0$ Hz, Cy–*H*); 5.58 (app t of d, 1H, $J = 8.4$ Hz, $J = 5.2$ Hz, O–C*H*); 5.46 (d, 1H, $J = 6.0$ Hz, Cy–*H*); 4.57 (d, 1H, $J = 6.0$ Hz, Cy–*H*); 4.10 (t of d, 1H, $J = 20.5$ Hz, $J = 1.5$ Hz, N=CC*H*); 3.62 (d of d, 1H, $J = 17.9$ Hz, $J = 8.4$ Hz, OCHCH–*H*); 3.57 (d, 1H, $J = 20.5$ Hz, N=CC*H*); 3.45 (distorted m, 1H, OCHCH–*H*); 3.27 (d of d, 1H, $J = 17.9$ Hz, $J = 5.2$ Hz, OCHCH–*H*); 2.99 (spt, 1H, $J = 6.9$ Hz, $(\mathrm{CH_3})_2$–C*H*); 1.85 (s, 3H, Cy–$\mathrm{C}H_3$); 1.34 (d, 3H, $J = 6.9$ Hz, $\mathrm{Cy(CH_3)}$–$\mathrm{C}H_3$), 1.25 (d, 3H, $J = 6.9$ Hz, $\mathrm{Cy(CH_3)}$–$\mathrm{C}H_3$). IR (KBr, $\mathrm{cm^{-1}}$): ν(C=N) 1659. UV–vis: $\lambda_{\max}$ (nm) ($\varepsilon \times 10^3$, $\mathrm{M^{-1}\,cm^{-1}}$) ($\mathrm{CH_2Cl_2}$, 293 K): 264 (0.32), 272 (0.25), 316 (1.00), 426 (0.78). CD: ($\mathrm{CH_2Cl_2}$, 293 K, $\lambda_{\max/\min}$ (nm), $\Delta\varepsilon$ ($\mathrm{M^{-1}\,cm^{-1}}$): 394 (−2.67), 323 (+0.92), 272 (−2.83), 266 (−3.00), 241 (−5.08), 218 (+14.66). $[\alpha]_{\mathrm{D}}^{20}$ −15.8° ($\mathrm{CH_2Cl_2}$). Anal. Found: C, 44.38; H, 3.88; N, 3.32. Calc. for $\mathrm{C_{31}H_{32}N_2O_2ClF_6SbRu}$: C, 44.49; H, 3.85; N, 3.35%.

4.3. Diels–Alder catalysis with $[(\eta^6\text{-cymene})\mathrm{RuCl}(L^4)]\mathrm{SbF_6}$

A centrifuge tube was charged with $[(\eta^6\text{-cymene})\mathrm{RuCl(L)}]\mathrm{SbF_6}$ (19 mg, 0.02 mmol) and $\mathrm{AgSbF_6}$ (7 mg, 0.02 mmol). To this was added $\mathrm{CH_2Cl_2}$ (2 ml) and the tube was agitated in order to rinse the walls of the tube. Within 10 min, a precipitate developed (presumably AgCl) and the tube was centrifuged in order to pellet the solid. The clear solution was removed by a syringe and was added to a vial which had been previously charged with the respective acrolein (0.21 mmol). The resultant orange solution was cooled to the desired temperature for 30 min, after which it was added to a precooled solution of CpH (0.17 g, 2.1 mmol) in $\mathrm{CH_2Cl_2}$ (2 ml) and was stored at the desired temperature for 16 h. After this time, an aliquot of the reaction mixture (~1 ml) was added to a flask with pentane (5 ml) which resulted in the precipitation and recovery of the catalyst. This solution was filtered through Celite and the filtrate was evaporated on a rotary evaporator to yield the product as a clear oil.

4.4. X-ray crystallography

Single crystals suitable for X-ray analysis were formed by slow evaporation from a $\mathrm{CHCl_3}$ solution of **1**. Crystallographic data are summarized in Table 1. The structure was determined from data collected with a Nonius KappaCCD at 0 °C. A phase change was observed on cooling to −90 °C and the crystals cracked; hence a higher temperature was used. Lorentz and polarization corrections were applied to all data. The structure was solved by direct methods (SIR92) using the TEXSAN crystal structure analysis package and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ in all cases. Hydrogen atoms were placed at calculated positions before each refinement and were included in the refinement, but were not refined. The solvent was found to be disordered and the $\mathrm{CHCl_3}$ was modeled with the chlorine atoms distributed over four positions with 75% occupancy. The correct polarity and space group for **1** was determined by reference to the known configuration of (+)-INDABOX and by refinement of the opposite hand, which gave $R_w = 0.0540$ compared to $R_w = 0.0528$ for the correct configuration.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 153984 for compound **1**. 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).

Acknowledgements

These studies were supported by the National Science Foundation.

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