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Mononuclear ruthenium complexes containing chiral aminooxazolines: Syntheses, X-ray studies and catalytic activity ☆

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Dedicated to Prof. Dr. Gerard van Koten on the occasion of his 65th birthday

Abstract

The synthesis and characterisation of three novel mononuclear ruthenium(II) complexes containing one of the following chiral auxiliary ligands: 2-amino-(4*R*)-phenyl-2-oxazoline (amphox), indanyl-2-amino-(4*R*,5*S*)-2-oxazoline (aminox) or indanyl-(2′-anilinyl)-(4*R*,5*S*)-2-oxazoline (aninox) is described using $[Ru_2Cl_4(\eta^6\text{-}p\text{-cym})_2]$ (p-cym = 1-isopropyl-4-methylbenzene) as the Ru starting material. The new complexes have been identified as the neutral derivatives $[RuCl_2(\eta^6\text{-}p\text{-cym})(\text{amphox-}\kappa^1N_{ox})]$ (**1**), $[RuCl_2(\eta^6\text{-}p\text{-cym})(\text{aminox-}\kappa^1N_{ox})]$ (**2**) and the salt $[RuCl(\eta^6\text{-}p\text{-cym})(\text{aninox-}\kappa^2N,N')]Cl$ (**3**). These materials have been fully characterised (elemental analysis, NMR, IR, conductance, MS, etc.) and, in the case of **2** and **3**, structurally elucidated in the solid-state using single crystal X-ray diffraction methods. All three complexes show good catalytic activity (max. conversion >99%, TOF = 424 h^{-1}) but only modest enantio-selectivity (max. ee = 40%) for the transfer hydrogenation reaction of acetophenone with isopropyl alcohol. The complexes were also tested in an asymmetric Diels–Alder reaction involving cyclopentadiene and acrolein (max. conversion >99%, TOF = 42 h^{-1}). In this case, the diastereo-selectivity was good to moderate (max. de = 84%), but the ee values were poor (max. ee = 12%).

Keywords: Oxazoline; Ruthenium; X-ray structure; Arene complex; Catalysis; Transfer hydrogenation; [4+2] Cycloaddition

1. Introduction

The development and understanding of systems that involve the regio- and/or enantio-selective synthesis of organic molecules is a primary goal of organometallic chemistry [1]. Ruthenium complexes, both mono- and multinuclear, are well known for their ability to act as homogeneous catalysts and stoichiometric promoters for a variety of such reactions. These endeavours have led to the successful application of ruthenium-based catalytic processes in a number of fine chemical syntheses (*e.g.*, *Noyori's* asymmetric hydrogenation, *Takasago's* process, *Grubbs*' systems for C–C bond formation, etc.) [1–4].

One of our research interests is focussed on the design and synthesis of organometallic and coordination complexes for fundamental studies and applications in catalysis [5,6]. Our recent investigations into C–C bond-forming reactions (Diels–Alder) promoted by novel triruthenium carbonyl clusters incorporating the aminooxazoline ligands

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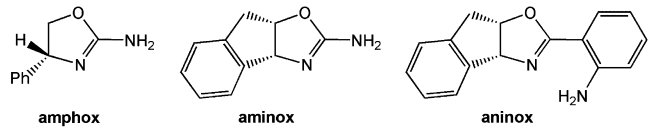


Fig. 1. Aminooxazoline ligands.

amphox, aminox or aninox (Fig. 1) [7], or ligand fragments derived from them, have prompted us to investigate whether mononuclear Ru complexes incorporating these ligands are also active and/or selective catalysts in such reactions. The complimentary development of ruthenium-based transfer hydrogenation systems using a number of N-donor ligands (including hybrid oxazolines) [8–10] gave us clear presidence to also investigate the transfer hydrogenation ability of these new mononuclear systems.

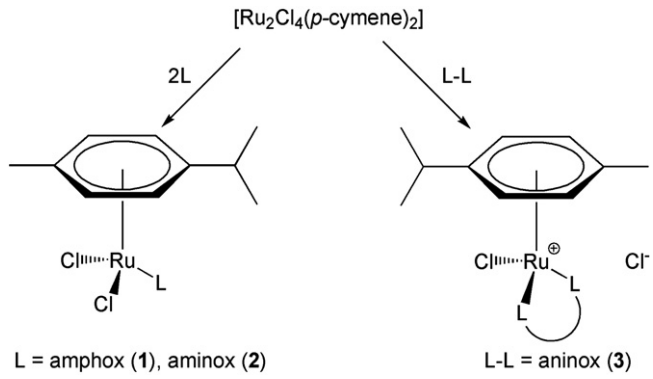
Herein, we detail the synthesis and characterisation of novel aminooxazoline-derived mononuclear ruthenium arene systems and examine their ability to catalytically promote Diels–Alder and transfer hydrogenation chemistry.

2. Results and discussion

2.1. Synthesis and characterisation of compounds 1–3

The treatment of solutions of the known [11] dimer $[Ru_2Cl_4(\eta^6\text{-}p\text{-cym})_2]$ (*p*-cym = *p*-cymene) with a stoichiometric amount (per Ru metal atom) of each of the ligands amphox, aminox or aninox (Fig. 1) gave rise to the isolation of the novel mononuclear complexes **1**–**3**, respectively (Scheme 1).

Confirmation of the mononuclear nature of these materials was obtained *via* a combination of MS and elemental analysis data. The non-conductive nature of complexes **1** and **2** suggested the retention of two metal-bound chloride ligands. Complex **3**, a 1:1 electrolyte, is surmised to contain aninox binding in a bidentate chelating κ^2-*N*,*N*′ bonding motif [12], as observed previously in the cluster complex $[Ru_3(\mu\text{-H})(\mu\text{-}\kappa^2\text{-aninox-H})(CO)_9]$ [7]. Characterisation of all three complexes by NMR spectroscopy, in addition to the known stability of a eighteen electron count, strongly suggests η^6-binding of the *p*-cymene ligand (see Section 4). Therefore, complexes **1** and **2** likely contain a κ^1-bound



Scheme 1.

oxazoline to fill the coordination sphere around the formally d^6 metal atom [13]. These data cannot, however, clearly establish which of the two nitrogen atoms (that of the amino group or that of the oxazoline fragment) is coordinated. In our earlier cluster work, coordination of amphox and aminox to the Ru metal centres occurred in a κ^2-μ^3-fashion through both N atoms [7]. It is interesting to note that the chelating coordination of the chiral aninox ligand in **3**, makes the metal atom stereogenic. Only one of the two possible diastereoisomers is formed; a plausible explanation for this observation is that ligand centred chirality controls the resulting coordination nature at Ru. Single crystals of complexes **2** and **3** were obtained and both were examined by X-ray diffraction methods to unambiguously assign the coordination mode of the aminooxazoline ligands. In addition, the determination of the absolute configuration of the metal atom in complex **3** could be established.

The solid-state structure of **2**, which crystallises in the presence of a (non-coordinating) molecule of dichloromethane, appears in Fig. 2. A representation of the cationic fragment of complex **3** is shown in Fig. 3. The data confirm our hypotheses that both complexes are mononuclear species. Typical Ru–Cl and Ru–cymene bond lengths and angles are observed [10a,13,14]. The amphox ligand is shown to bind through the oxazoline nitrogen atom, as expected [15,16], while aninox binds the metal in a bidentate mode through both of the N atoms (Fig. 3) [7,12]. In compound **3**, the *R* configuration of the free ligand is maintained, while the absolute configuration of the metal is *S* (preference order: arene > Cl > $N_{oxazoline}$ > NH_2) [17]. This represents the first reported complex of aninox as a neutral bidentate ligand.

2.2. Catalysis

Having established the nature of these three materials, an investigation of the catalytic ability of the complexes

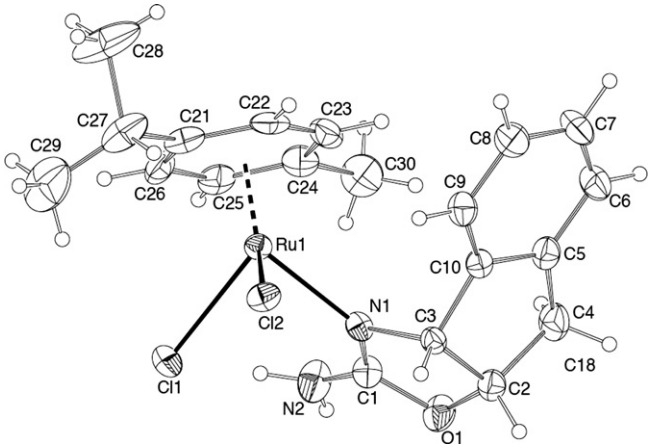


Fig. 2. Molecular view of compound **2**. Selected bond lengths (Å) and angles (°): Ru(1)–N(1) 2.134(4), Ru(1)–Cl(1) 2.422(2), Ru(1)–Cl(2) 2.420(3), Ru(1)–C(arene)$_{av}$ 2.178(6); Cl(1)–Ru(1)–Cl(2) 86.32(8), N(1)–Ru(1)–Cl(1) 88.19(13), N(1)–Ru(1)–Cl(2) 86.61(12).

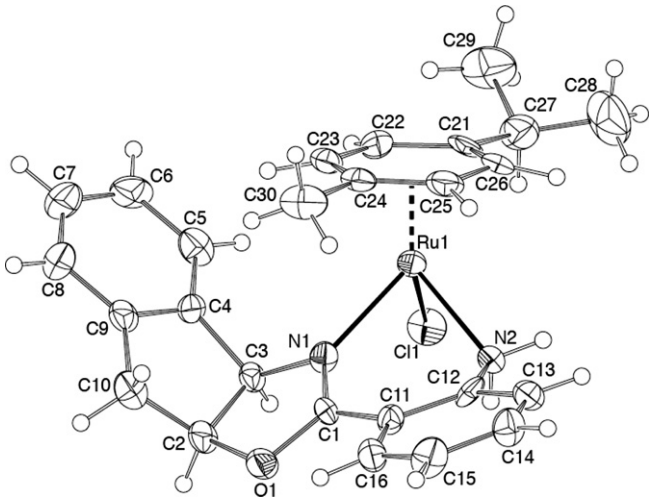
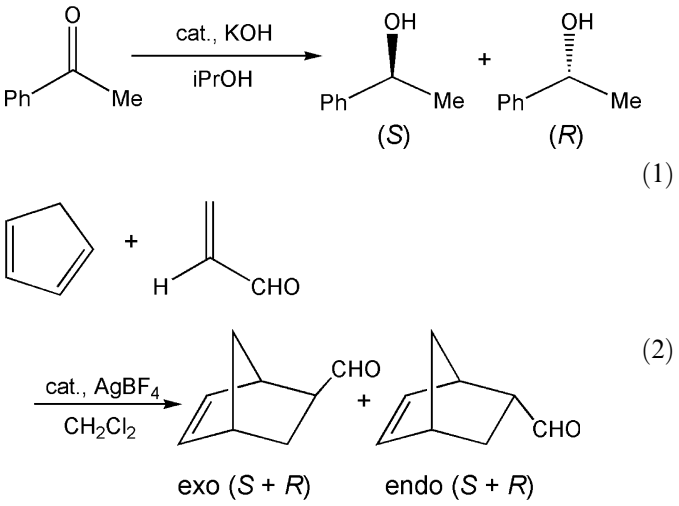


Fig. 3. View of the cationic fragment of complex **3**. Selected bond lengths (Å) and angles (°): Ru(1)–N(1) 2.154(6), Ru(1)–N(2) 2.110(6), Ru(1)–Cl(1), 2.418(2), Ru(1)–C(arene)$_{av}$ 2.201(7); N(1)–Ru(1)–N(2) 80.30(12), N(1)–Ru(1)–Cl(1) 86.19(16), N(2)–Ru(1)–Cl(1) 83.61(17).

was undertaken. Our earlier work has demonstrated that triruthenium carbonyl clusters incorporating the aminooxazoline ligands amphox, aminox or aninox are capable of promoting catalytic reactions [7]. In order to compare the catalytic activity observed, we have investigated whether the mononuclear Ru complexes incorporating these ligands **1**–**3** are also active and/or selective in two classical reactions: (i) the asymmetric transfer hydrogenation reaction of acetophenone using *i*-PrOH as hydrogen source (Eq. (1)) and (*ii*) the Diels–Alder (*i.e.*, [4+2] cycloaddition) reaction of cyclopentadiene (CpH) and acrolein (Eq. (2))



2.3. Asymmetric transfer hydrogenation

The catalysis was tested using 5 mmol of acetophenone and 0.025 mmol of catalyst (Eq. (1)). *i*-PrOH was used as both the solvent and the hydrogen source. Four equivaent of KOH per mole of catalyst was also employed as a co-catalyst [18]. The "free" ligands (Fig. 1) are known to be ineffective at promoting the hydrogenation reaction [7].

The results are summarised in Table 1. As can be noted from these data, conversion of substrate is quantitative at high temperatures for all three catalysts (Table 1: entries 1–3). Although the TOF's are moderate at best, these values are approximately double those obtained using our previously studied cluster systems [7]. Complex **3** was chosen as the model system to investigate the effects of other factors (temperature, concentration, etc.) on the resulting catalytic product distributions (entries 4–7). At lower temperatures, both activity and selectivity are sacrificed (entries 4 and 5), a fact that has been observed previously [19]. Increasing the concentration of base (entry 6) or reducing the substrate concentration (entry 7) has little effect on selectivity or TOF. The overall enantio-selectivity for all three catalysts is lower when compared with related mononuclear Ru complexes containing N-donor ligands [10a,19], but superior to the previously studied ruthenium cluster systems containing these ligand fragments [7].

2.4. Asymmetric Diels–Alder reaction

The reaction of CpH and acrolein to give bicyclic olefin products (Eq. (2)) was employed to test these systems (Table 2) in enantio-selective [4+2] cycloaddition chemistry. To create a vacant site on complexes **1** and **2**, 1 equiv. of [$AgBF_4$] was used to remove a coordinated chloride. In

Table 1
Results of the catalytic asymmetric transfer hydrogenation of acetophenone using complexes **1**–**3** as pre-catalysts[a]

Entry	Pre-catalyst/ Temperature (°C)	Reaction time (h)	TOF[a] (h^{-1})	%Conversion	%ee
1[b]	**1**/ 82	1	400	99	35 (*S*)
2[b]	**2**/82	1	424	99	34 (*S*)
3[b]	**3**/82	1	384	99	40 (*S*)
4[b]	**3**/45	2	60	20	5 (*S*)
5[b]	**3**/20	2	–	–	–
6[c]	**3**/82	2	390	98	38 (*S*)
7[d]	**3**/82	2	410	99	40 (*S*)

[a] Turnover frequency at 10 min.
[b] Base to catalyst to substrate ratio (B:C:S) = 4:1:200.
[c] B:C:S = 10:1:200.
[d] B:C:S = 4:1:100.

Table 2
Results of the Diels–Alder reaction of CpH and acrolein catalysed by **1**–**3**

Entry	Pre-catalyst/ Temperature (°C)	TOF[a] (h^{-1})	%Conversion	Product ratio (*endo*:*exo*)	ee (isomer)[b]
1	**1**/20	35	99	90:10	8(*S*)
2	**2**/20	39	99	91:9	8(*S*)
3	**3**/20	42	99	92:8	10(*S*)
4	**3**/−20	20	40	90:10	12(*S*)
5	**3**/−50	4	23	90:10	12(*S*)

[a] Turnover frequency at 10 min.
[b] Absolute configuration at C^2.

the case of complex **3**, 2 equiv. were necessary to remove the coordinated chloride, although this complex may also create a vacant site by decoordination of the amino group. All three materials promote the reaction with similar diastereo-selection, TOF and %ee (Table 2: entries 1–3). Admittedly, %ee values are poor overall when compared with related mononuclear systems [20], and mirror our earlier cluster results (%ee = 0 in all cases) [7]. Lower temperatures result in much poorer catalytic performance overall and %ee's are not significantly improved. In contrast, diastereo-selectivity is better than that of the cluster complexes containing these ligands [7].

3. Conclusions

This work has disclosed the synthesis of the first mononuclear ruthenium complexes of the ligands amphox, aminox and aninox. All three materials have been fully characterised, including solid-state structural elucidation in the case of complexes **2** and **3**. The complexes are active catalysts for both transfer hydrogenation and [4+2] cycloaddition chemistry. Enantio-selectivity with these systems is moderate at best although conversion levels are acceptable. These results suggest that this class of ligands is worthy of further investigations in the areas of coordination chemistry and catalysis.

4. Experimental

4.1. General

All reactions were carried out using standard Schlenk inert atmosphere (dry N_2) techniques using freshly distilled solvents (THF, hexane, toluene and diethyl ether from Na; halocarbons and acetonitrile from CaH_2; acetone from anhydrous $CaSO_4$) [21]. ''Hexane'' refers to petroleum ether of the 50–65 °C boiling point range and ''ether'' refers to diethyl ether. IR spectra were recorded on a Perkin Elmer FT Paragon-1000 Spectrometer using CaF_2 solution cells and the reported data are accurate to within ± 2 cm^{-1}. NMR spectra were recorded on various Bruker FT NMR spectrometers (AC-200, AV-300, Advance 300, DPX-300 and an AMX-400). Elemental analyses were carried out using a Perkin–Elmer 2400 Elemental Analyser. Mass spectra (MS) were measured at the Mass Spectroscopy Service of the University of Santiago de Compostela using the Fast Atom Bombardment (FAB) technique from *m*-nitrobenzylic alcohol matrices; [M$^+$] data refers to the most abundant molecular ion isotopomer. Conductivity measurements were carried out on a Jenway PCM3 conductance apparatus at 20 °C from an acetone solution of approximately 5×10^{-4} M. The compounds $[Ru_2Cl_4(\eta^6\text{-cym})_2]$ [11], 2-amino-(4*R*)-phenyl-2-oxazoline (amphox), indanyl-2-amino-(4*R*,5*S*)-2-oxazoline (aminox) and indanyl-(2′-anilinyl)-(4*R*,5*S*)-2-oxazoline (aninox) were prepared by the literature methods [7,22]. All other chemicals were obtained commercially.

4.2. Synthetic procedures

4.2.1. [$RuCl_2(\eta^6$-*p*-cym)(amphox-κ^1N_{ox})] (**1**)

The dimer $[Ru_2Cl_4(\eta^6\text{-}p\text{-cym})_2]$ (100 mg, 0.163 mmol) and amphox (58.3 mg, 0.359 mmol) were dissolved together in CH_2Cl_2 (35 mL) and the mixture was then stirred at ambient temperature for a period of 30 min. The colour of the solution changed from red to orange. The solvent was removed under reduced pressure and the resulting solid was then dissolved in acetone (5 mL). The yellow–orange coloured solid product was precipitated by the addition of an excess of hexane. The solid was washed with further hexane (2×10 mL) and then dried *in vacuo*. Yield 102 mg (67%). Found: C, 48.57; H, 5.11; N, 6.02. $C_{19}H_{24}Cl_2N_2ORu$ requires: C, 48.72; H, 5.16; N, 5.98%. FAB-MS (*m*/*z*): 468; calcd. 468 [M]$^+$. NMR (ppm: CD_2Cl_2) $\delta_H = 7.62$–7.34 (m, 5H, 5CH_{Ph}), 5.52 (d, $J = 5.8$ Hz, 1H, C$H_{p\text{-cym}}$), 5.47 (t, $J = 4.6$ Hz, 1H, CH_{amox}), 5.25 (d, $J = 5.8$ Hz, 1H, C$H_{p\text{-cym}}$), 5.03 (d, $J = 5.8$ Hz, 1H, C$H_{p\text{-cym}}$), 4.86 (d, $J = 5.8$ Hz, 1H, C$H_{p\text{-cym}}$), 4.67 (t, $J = 4.6$ Hz, 1H, CH_{amox}), 4.47 (t, $J = 4.6$ Hz, 1H, CH_{amox}), 4.13 (s, br, 2H, NH_2), 2.98 (sept, $J = 6.7$ Hz, 1H C$H_{p\text{-cym}}$), 2.04 (s, 3H, C$H_{3(p\text{-cym})}$), 1.35 (d, $J = 6.7$ Hz, 3H, C$H_{3(p\text{-cym})}$), 1.20 (d, $J = 6.7$ Hz, 3H, C$H_{3(p\text{-cym})}$); δ_C (DEPT + ^{13}C{^{1}H}) = *C*: 170.4, 132.6, 103.9, 95.7; *C*H: 130.7, 129.4 (2C), 126.4 (2C), 81.3, 80.9, 79,2, 78.4, 70.6, 32.5; *C*H$_2$: 75.6; *C*H$_3$: 22.0, 21.5, 20.9.

4.2.2. [$RuCl_2(\eta^6$-*p*-cym)(aminox-κ^1N_{ox})] (**2**)

$[Ru_2Cl_4(\eta^6\text{-}p\text{-cym})_2]$ (100 mg, 0.163 mmol) and aminox (59.6 mg, 0.359 mmol) were dissolved together in THF (30 mL) and the mixture was then stirred at ambient temperature for 1 h. The colour of the solution remained red during the course of the reaction. The volume of the solution was reduced to about 5 mL and the orange coloured solid product was precipitated with excess hexane and then washed with further hexane (2×10 mL) and then dried *in vacuo*. Yield 112 mg (77%). Found: C, 50.11; H, 5.11; N, 5.87. $C_{20}H_{24}Cl_2N_2ORu$ requires: C, 50.00; H, 5.03; N, 5.83%. FAB-MS (*m*/*z*): 480; calcd. 480 [M]$^+$. NMR (ppm: CD_2Cl_2) $\delta_H = 7.55$ (d, $J = 10.0$ Hz, 1H, N*H*), 7.42–7.23 (m, 4H, 4 C*H*), 5.67 (d, $J = 6.0$ Hz, 1H, C$H_{p\text{-cym}}$), 5.55 (d, $J = 6.0$ Hz, 1H, C$H_{p\text{-cym}}$), 5.32 (d, $J = 6.0$ Hz, 1H, C$H_{p\text{-cym}}$), 5.20 (d, $J = 6.0$ Hz, 1H, C$H_{p\text{-cym}}$), 5.20 (ddd, $J = 7.9$ Hz, 7.3 Hz, 4.7 Hz, 1H, C*H*), 4.90 (d, $J = 7.9$ Hz, 1H, C*H*), 4.35 (d, J = 10.0 Hz, 1H, N*H*), 3.50 (dd, $J = 17.6$ Hz, 7.3 Hz, 1H, C*H*), 3.01 (sept, $J = 6.3$ Hz, 1H, C$H_{p\text{-cym}}$), 2.8 (dd, $J = 17.6$ Hz, 4.3 Hz, 1H, C*H*), 2.16 (s, 3H, C$H_{3(p-\text{cym})}$), 1.30 (d, $J = 6.3$ Hz, 3H, C$H_{3(p\text{-cym})}$), 1.26 (d, $J = 6.3$ Hz, 3H, C$H_{3(p\text{-cym})}$); δ_C (DEPT + ^{13}C{^{1}H}) = *C*: 161.9, 142.7, 137.3, 133.7, 103.6; *C*H: 135.7, 134.3, 133.8, 132.9, 85.1, 84.4, 82.7, 81.3, 75.2, 73.8, 31.9; *C*H$_2$: 49.3; *C*H$_3$: 24.1, 21.9, 19.4.

4.2.3. [$RuCl(\eta^6$-*p*-cym)(aninox-κ^2N,N')]Cl (**3**)

The dimer $[Ru_2Cl_4(\eta^6\text{-}p\text{-cym})_2]$ (100 mg, 0.163 mmol) and aninox (85.6 mg, 0.359 mmol) were dissolved together

in THF (35 mL) and the mixture was then stirred at ambient temperature for 6 h. The colour of the solution changed from red to yellow during the course of the reaction and a yellow precipitate formed. This solid was removed by decantation and the greenish-yellow coloured solid product was then washed with ether (2 × 15 mL) and then dried *in vacuo*. Yield 144 mg (77%). Found: C, 55.90; H, 5.17; N, 5.14. $C_{26}H_{28}Cl_2N_2ORu$ requires: C, 56.11; H, 5.07; N, 5.03%. FAB-MS (*m*/*z*): 521; calcd. 521 $[M-Cl]^+$. Conductance (acetone): 122 $mol^{-1}\ \Omega^{-1}\ cm^2$. NMR (ppm: CD_2Cl_2) $\delta_H = 10.22$ (d, $J = 10.1$ Hz, 1H, N*H*), 8.91 (d, $J = 7.8$ Hz, 1H, C*H*), 7.83 (d, $J = 6.6$ Hz, 1H, C*H*), 7.70 (d, $J = 7.8$ Hz, 1H, C*H*), 7.63 (t, $J = 7.8$ Hz, 1H, C*H*), 7.54 (d, $J = 6.6$ Hz, 1H, C*H*), 7.45 (d, $J = 6.6$ Hz, 1H, C*H*), 7.39 (d, $J = 6.6$ Hz, 1H, C*H*), 7.31 (t, $J = 7.8$ Hz, 1H, C*H*), 5.80 (ddd, $J = 7.9$ Hz, 6.8 Hz, 4.7 Hz, 1H, C*H*), 5.74 (d, $J = 7.9$ Hz, 1H, C*H*), 5.42 (d, $J = 5.9$ Hz, 1H, C$H_{p\text{-cym}}$), 5.25 (d, $J = 5.9$ Hz, 1H, C$H_{p\text{-cym}}$), 5.16 (d, $J = 5.9$ Hz, 1H, C$H_{p\text{-cym}}$), 5.08 (d, $J = 5.9$ Hz, 1H, C$H_{p\text{-cym}}$), 4.52 (d, $J = 10.1$ Hz, 1H, N*H*), 3.74 (dd, $J = 17.6$ Hz, 7.8 Hz, 1H, C*H*), 3.31 (dd, $J = 17.6$ Hz, 4.7 Hz, 1H, C*H*), 2.81 (sept, $J = 6.6$ Hz, 1H, C$H_{p\text{-cym}}$), 1.57 (s, 3H, C$H_{3(p\text{-cym})}$), 0.96 (d, $J = 6.6$ Hz, 3H, C$H_{3(p\text{-cym})}$), 0.89 (d, $J = 6.6$ Hz, 3H, C$H_{3(p\text{-cym})}$); δ_C (DEPT + $^{13}C\{^1H\}$) = *C*: 162.4, 145.1, 141.1, 137.4, 119.4, 105.9, 96.0; *C*H: 135.2, 130.7, 129.7, 128.6, 127.2, 126.4, 125.6, 122.9, 84.7, 84.0, 83.1, 82.0, 79.5, 75.7, 30.5; *C*H_2: 39.9; *C*H_3: 22.8, 20.4, 17.6.

5. Catalytic studies

5.1. Transfer hydrogenation reactions

All reactions were carried out in Schlenk tubes under nitrogen, using magnetic stirrers and thermostated oil baths. *i*-Propanol was used as solvent. Acetophenone was distilled under nitrogen prior to use [21]. In a typical experiment, the metal complex (0.025 mmol), KOH (0.1 mmol; solution 0.34 M in *i*-propanol) and 20 mL of *i*-propanol were introduced into a Schlenk flask and submerged in an oil bath regulated at 90 °C. After 10 min, acetophenone (5 mmol) was added and the mixture was heated for the time period noted in Table 1. Conversions and enantiomeric excesses were determined by GC, using a chiral GAMMA-DEX fused-silica capillary column (0.25 mm i.d.) and *p*-xylene as the internal standard.

5.2. Diels–Alder reactions

The asymmetric [4 + 2] cycloaddition reactions were carried out using dichloromethane as solvent. Cyclopentadiene was freshly obtained from its dimer by distillation [21]. Acrolein was distilled under nitrogen prior to use. In a typical experimental run, the metal complex (0.025 mmol), cyclopentadiene (3 mmol; dissolved in 2 mL of dichloromethane), acrolein (0.5 mmol; dissolved in 2 mL of dichloromethane), $[AgBF_4]$ (0.025 mmol when **1** or **2** were tested or 0.05 mmol in the case of **3**) and 10 mL of dichloromethane were placed into a Schlenk tube and the mixture was stirred in a thermostated bath. Conversion data, the *endo*:*exo* ratio and the enantiomeric excesses were determined by GC using a chiral GAMMA-DEX fused-silica capillary column (0.25 mm i.d.) and *p*-xylene as the internal standard. The configuration of the products was determined by comparison of their $[\alpha]_D$ values with those found in the literature [23].

6. X-ray crystallography

Crystals of complexes **2** · CH_2Cl_2 and **3** were obtained by the slow evaporation technique from dichloromethane solutions. Selected measurement, crystal and refinement data can be found in Table 3. Diffraction data were measured on a Bruker AXS SMART 1000 diffractometer, using graphite-monochromated Mo Kα radiation. Semi-empirical absorption corrections were applied with SADABS [24]. Structures were solved by direct methods and refined by full matrix least-squares against F^2 with SHELXTL [25]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were set in calculated positions and refined

Table 3
X-ray diffraction data for complexes **2** · CH_2Cl_2 and **3**

	2 · CH_2Cl_2	**3**
Formula	$C_{20}H_{24}Cl_2N_2ORu \cdot CH_2Cl_2$	$C_{26}H_{28}Cl_2N_2ORu$
Formula weight (g/mol)	565.31	556.47
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
a (Å)	11.131(8)	12.638 (8)
b (Å)	8.092 (5)	8.231 (5)
c (Å)	13.783 (9)	12.893 (8)
V (Å^3)	1199.07	1182.35 (13)
β	105.032 (11)	118.167 (9)
Z	2	2
F (000)	572	568
D_{calc} (g cm^{-3})	1.566	1.563
Radiation (*λ* in Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
μ (mm^{-1})	1.114	0.911
Crystal size (mm)	0.20 × 0.12 × 0.09	0.21 × 0.07 × 0.03
Temperature (K)	293 (2)	299 (2)
θ Limits (°)	1.53–23.29	1.79–23.35
Min./max. *h*, *k*, *l*	−12/12, −9/8, −15/15	−14/14, −9/9, −14/14
Collected reflections	7698	7635
Unique reflections	3440	3390
Reflections with $I > 2\sigma(I)$	2981	2605
Absorption correction	SADABS	SADABS
Max./min. transmission	0.900/0.850	0.975/0.925
Parameters/restraints	268/1	292/1
Goodness-of-fit on F^2	1.015	1.000
Final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.0340$, $wR_2 = 0.0696$	$R_1 = 0.0446$, $wR_2 = 0.0764$
R indices (all data)	$R_1 = 0.0425$, $wR_2 = 0.0719$	$R_1 = 0.0671$, $wR_2 = 0.0821$
Max./min. ($\Delta\rho$/e Å^{-3})	0.453/−0.346	0.616/−0.370
Absolute structure parameter	−0.03 (5)	+0.02 (5)

as riding atoms. The molecular plots were made with the PLATON program package [26]. The WINGX program system [27] was used throughout the structure determinations.

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Appendix A. Supplementary material

CCDC 644035 and 644036 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.06.058.

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