Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Organometallic Chemistry 691 (2006) 2221–2227
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Cp*rhodium complexes with salicyloxazolines: Diastereoselective synthesis, configurational stability and use as asymmetric catalysts for a Diels–Alder reaction

Adam J. Davenport, David L. Davies *, John Fawcett, David R. Russell

Department of Chemistry, University of Leicester, Leicester LE1 7RH, United Kingdom

Received 22 September 2005; received in revised form 28 October 2005; accepted 28 October 2005
Available online 19 December 2005

Abstract

Reaction of $[RhCl_2Cp^*]_2$ ($Cp^* = \eta$-C_5Me_5) with salicyloxazolines in the presence of NaOMe gives complexes [RhCl(R-saloxaz)Cp*] (**1**–**4**) which have been fully characterised. The diastereoselectivity of complexation depends on the substituents and the absolute configuration at the metal centre is unstable in solution. Treatment of **2** with 4-methylpyridine and $NaSbF_6$ in methanol at reflux gave [Rh(4-Mepy){(*S*)-^{i}Pr-saloxaz}Cp*][SbF_6] (**5**) whilst [$Rh(OH_2)$(Me_2-saloxaz)Cp*][SbF_6] (**6**) was prepared by reaction of **1** with $AgSbF_6$. Three complexes, [RhCl(Me_2-saloxaz)Cp*] (**1**), [RhCl{(*S*)-^{i}Pr-saloxaz}Cp*] (**2**), and [$Rh(OH_2)$(Me_2-saloxaz)Cp*][SbF_6] (**6**) have been characterised by X-ray crystallography. Some of the complexes, after treatment with $AgSbF_6$, have been tested as enantioselective catalysts for the Diels–Alder reaction of methacrolein with cyclopentadiene.

Keywords: Rhodium; Chiral; Oxazoline; Asymmetric catalysis

1. Introduction

Chiral half-sandwich complexes have attracted a lot of attention for their potential use in asymmetric catalysis, transfer hydrogenation of ketones with arene ruthenium complexes being a particularly notable example [1]. The isoelectronic Cp*rhodium complexes have also been shown to be active catalysts of asymmetric transfer hydrogenation [2–4], though for certain substrates they show different selectivity to their arene ruthenium analogues [3,4]. It is notable that all of these transfer hydrogenation catalysts contain a chiral ligand and a chiral metal centre. To fully understand the role of chirality at the metal in catalytic processes it is important to know the stability of chirality at the metal and the factors influencing which configuration at the metal is more stable [5]. Examples of Cp*rhodium complexes with chiral bidentate ligands with at least one nitrogen donor atom include complexes of amino acids [3,6] salicylaldimines [7,8], anionic pyrrolylimines [8] and pyridylimines [9]. The chirality at the metal is generally unstable and with anionic bidentate ligands epimerisation can even be fast on the ^{1}H NMR timescale which has led to erroneous conclusions regarding diastereoselectivity of coordination [8].

Over the last decade, oxazoline containing ligands have been extensively studied. They are easily synthesised from readily available chiral aminoalcohols and have proved extremely successful in asymmetric catalysis [10]. Most of these studies involve bis(oxazolines) and phosphino-oxazolines however some work on the coordination chemistry of salicyloxazolines has been reported [11,12]. We and others have recently reported areneruthenium complexes of salicyloxazolines [13,14] we now report the synthesis and properties of some related Cp*rhodium complexes, and assess the diastereoselectivity of coordination, the ease of epimerisation at the metal, and their application as asymmetric

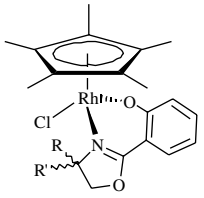
* Corresponding author.
E-mail address: dld3@le.ac.uk (D.L. Davies).

0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.10.053

catalysts for Diels–Alder reactions. Comparisons are made with the corresponding arene ruthenium complexes [13].

2. Results and discussion

The complexes **1**–**4** were prepared by refluxing $[RhCl_2Cp^*]_2$ with two equivalents of ligand and a slight excess of sodium methoxide. All the complexes were isolated as orange powders and are characterised by ^1H NMR spectroscopy, mass spectrometry and by X-ray diffraction for **1** and **2** and the purity was confirmed by microanalysis. The complexes have a chiral metal centre thus, **1** with an achiral ligand exists as a racemate. Complexes **2**–**4** also contain an enantiopure ligand and can, in principle, form two diastereomers A and B (Fig. 1) which have the same configuration at carbon and opposite configuration at the metal.



	R	R^1
1	Me	Me
2	H	^{i}Pr
3	H	CH_2Ph
4	H	Ph

The ^1H NMR spectrum of **1** showed broad (1H) singlets at δ 3.93 and 4.19 due to the ($OCHH^1$) protons, with a broad (3H) singlet at δ 1.45 due to one of the oxazoline methyls the other methyl being under the Cp* resonance at δ 1.34. Cooling this sample to 273 K caused the broad singlets for the OC*H* protons to resolve into sharp doublets, the singlet at δ 1.45 also sharpened. These experiments indicate that chloride exchange and fluxionality of **1** (i.e., racemisation) is occurring at a rate similar to the NMR timescale at room temperature whereas, at 273 K interconversion is slow on the NMR timescale. The corresponding areneruthenium complex [RuCl(Me_2-saloxaz)(mesitylene)] shows well-resolved signals at room temperature [13] hence racemisation of the ruthenium complex is slower than for the comparable rhodium complex. These findings are consistent with the much slower rate of water exchange found for $[Ru(OH_2)(bpy)(mes)]^{2+}$ compared with $[Rh(OH_2)(bpy)Cp^*]^{2+}$ [15]. Similarly, Brunner et al. showed that the rate of epimerisation of Cp*rhodium complexes with salicylaldimines and anionic pyrrolylimines is faster than for the corresponding areneruthenium complexes [8]. The X-ray structure of **1** has been determined and is discussed later. The mass spectrum of **1** shows ions at *m*/*z* 463 and 428 corresponding to $[M]^+$ and $[M - Cl]^+$.

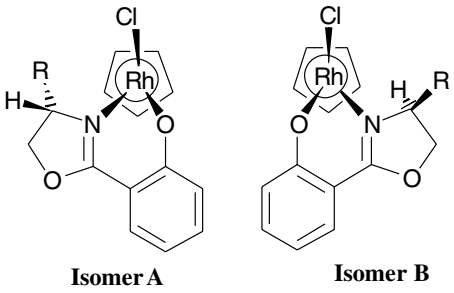


Fig. 1. The two diastereomers of [RhCl(R-saloxaz)Cp*].

As mentioned above, **2**–**4** can in principle form two diastereomers A and B. The ^1H NMR spectrum of complex **2** showed one set of well-resolved signals suggesting that it was formed with very high diastereoselectivity (~100% d.e.) or, that two diastereomers are interconverting quickly on the NMR timescale. Crystallisation from CH_2Cl_2/ether gave X-ray quality crystals and the crystal structure (see below) shows the isopropyl is pointing towards the chloride, rather than the Cp*, thus, minimising unfavourable steric interactions. The corresponding ruthenium complex [RuCl(^{i}Pr-saloxaz)(mesitylene)] gave the same isomer with high diastereoselectivity (>98:2) though both isomers were observed with smaller arenes [13].

The ^1H NMR spectra of complexes **3** and **4** each showed some broad signals at room temperature, suggesting that both isomers, A and B, exist in solution and that epimerisation occurs on the NMR timescale. Complex **3** showed evidence for a minor isomer (25–30%), the spectrum being very similar to the ruthenium analogue [RuCl(Bz-saloxaz)(mesitylene)] which showed a similar 4:1 ratio of isomers [13]. On the basis of the similarity of the spectra the major isomer is assigned as that with the benzyl substituent towards the chloride. Complex **4** only showed the presence of one isomer at room temperature, however, some of the signals were broad. Recording the ^1H NMR spectrum of **4** at 233 K led to the broad signals being resolved into two sets of sharp signals (one for each isomer) in an approximate ratio 3:1. Even at 233 K the signals for the minor isomer were still slightly broad suggesting that the epimerisation had not been 'frozen-out'. To determine the configuration of the major diastereomer a phase-sensitive NOESY experiment was performed at 243 K in $CDCl_3$. The spectrum shows nOes in the major isomer between the NC*H* proton signal at δ 5.75 and the Cp* signal at δ 1.23, and between the phenyl protons signal at δ 7.45 and 7.63 and the Cp* signal at δ 1.23. The latter would not be expected in isomer B. Hence, we assign the major isomer as isomer A with the phenyl substituent more towards the Cp* than the chloride. This is the same orientation as found in the major isomer of the ruthenium analogue [RuCl(Ph-saloxaz)(mesitylene)] [13]. Further evidence for this assignment is the high field shift of the Cp* resonance, at δ 1.23 in the major isomer, consistent with a ring-current effect from the nearby phenyl substituent as found in the

ruthenium analogue. In the minor isomer the Cp* signal is seen at δ 1.40. In addition to nOes, several chemical exchange cross-peaks are observed between the signals of the two isomers as well as some nOes between two non-interchangeable protons consistent with the epimerisation process not having been frozen out.

Thus, salicyloxazoline ligands coordinate diastereoselectively to the Cp*RhCl fragment with the oxazoline substituent oriented towards the chloride except in the case of the phenyl substituted complex. The selectivity is very similar to Ru(mesitylene) analogues [13]. Epimerisation at the metal is occurring at a rate comparable to the NMR timescale and faster than the arene ruthenium analogues as expected [8,15].

The structures of **1** and **2** are shown in Figs. 2 and 3, respectively, with selected bond lengths and angles in Table 1. Complex **2** has isomer B structure with the oxazoline substituent pointing towards the chloride. Since the S_c-configured ligands were used the configuration at rhodium is R_{Rh} (Cp* > Cl > O > N) [16]. The Rh–N, Rh–O and Rh–Cl bond lengths are statistically the same in both complexes, however, there are significant differences in the bond angles. For example, the chelate bite angle N–Rh–O is 83.0(1)° in **1** compared with 87.1(2)° in **2**, and the torsion angle N(1)–C(15)–C(16)–C(21), −16.5° in **1**, is much larger than −3.5°, for the corresponding angle N(1)–C(6)–C(7)–C(12) in **2**. We have previously noted the variation in chelate angle and torsion angle of salicyloxazoline ligands [13].

The diastereoselectivity is in large part determined by interactions between the oxazoline substituent and the Cp* or chloride. Thus, replacing the chloride ligand with a more bulky ligand may favour isomer A in which the oxazoline substituent is oriented more towards the Cp*. Knowledge of these effects is important to understand the selectivity of such complexes in catalysis; hence, we have investigated the substitution of chloride in **2** with 4-methylpyridine.

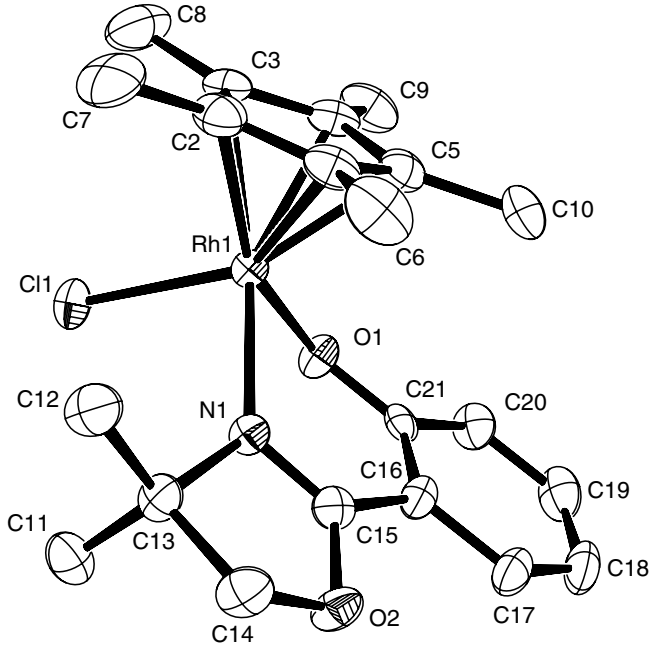


Fig. 2. Ortep diagram showing atom numbering scheme for **1** with 50% displacement ellipsoids. H atoms have been omitted for clarity.

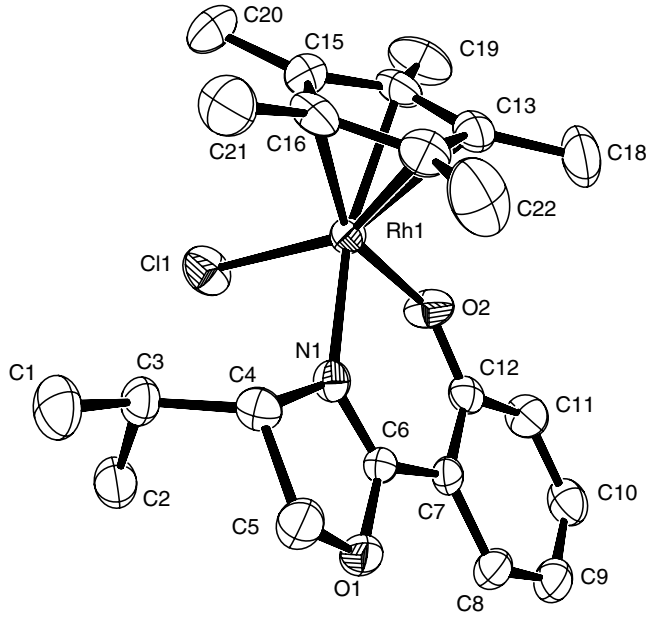


Fig. 3. Ortep diagram showing atom numbering scheme for **2** with 50% displacement ellipsoids. H atoms have been omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

	1	**2**
Rh–N	2.105(4)	2.097(4)
Rh–O	2.092(3)	2.084(4)
Rh–Cl	2.412(1)	2.414(2)
N–Rh–O	83.0(1)	87.1(2)
N–Rh–Cl	91.7(1)	90.6(1)
Cl–Rh–O	87.3(1)	86.4(1)

Reaction of **2** with 4-methylpyridine and $NaSbF_6$ in methanol at reflux gave [Rh(4-Mepy){(*S*)-^{i}Pr-saloxaz}-Cp*][SbF_6] (**5**). The ^{1}H NMR spectrum of **5** contains only one set of signals suggesting only one isomer is formed. The isopropyl group shows two methyl resonances, a doublet at δ 0.93 and a broad signal at 0.05; the high field shift of the latter is consistent with a ring-current effect from the coordinated 4-methylpyridine, suggesting that the isopropyl group is pointing towards the pyridine (isomer B). The broadness of this peak suggests a fluxional process is occurring. At low temperature (213 K) this signal split into two doublets at δ −0.20 and 0.67 in an approximate 20:1 ratio. Other signals due to a minor isomer are also visible at this temperature. Thus at room temperature, sharp, averaged signals are seen except for the signal at δ 0.05, which is still broad because the chemical shift difference for these protons in the two diastereomers is very large (ca. 0.9 ppm).

Thus, even with pyridine coordinated in place of chloride, isomer B is favoured. The corresponding ruthenium complex [Ru(4-Mepy)(^{i}Pr-saloxaz)(mes)][SbF_6] exists as an 85:15 ratio of isomers, the major isomer being B [13]. The ruthenium diastereomers interconvert slowly on the NMR timescale (slight line broadening in some signals and no chemical exchange cross-peaks in the NOESY spectrum) whereas the rhodium diastereomers are in fast exchange, again consistent with faster ligand substitution for Cp*Rh complexes compared with the corresponding arene ruthenium ones [8,15].

In recent years, there has been particular interest in using chiral late-transition-metal complexes as catalysts for Diels–Alder reactions since such complexes show less water-sensitivity than the more common titanium, aluminium or boron catalysts [17]. In this regard dicationic Cp*rhodium complexes with chiral diphosphines [18], and pyridylimines [9] catalyse Diels–Alder reactions of acroleins with dienes. We have also reported similar catalysis with Cp*rhodium complexes of bisoxazolines [19] and pyridyloxazolines [20,21].

To test the complexes [RhCl(R-saloxaz)Cp*] as catalysts we chose **2** and **4** since these favour the opposite isomer (B and A, respectively). To use the complexes as catalysts the chloride ligand was abstracted using $AgSbF_6$ and the resulting solutions were filtered through celite to remove AgCl and the solvent was evaporated to give the cations [Rh(solvent)(R-saloxaz)Cp*]$^+$ which were used without further purification. Characterisation of these solvent complexes with chiral ligands is complicated by the possible presence of two rapidly interconverting diastereomers, hence [Rh(OH_2)(Me_2-saloxaz)Cp*][SbF_6] (**6**), made from **1**, which exists as a racemate was isolated and studied in more detail. For arene ruthenium complexes of pyridyloxazolines [22], salicylaldimines [23] and bis-oxazoline-propane [24], aqua complexes are more labile and undergo exchange/epimerisation faster than their respective chloride precursors. The ^{1}H NMR spectrum of **6** shows C_{2v} symmetry, one singlet (6H) is observed for the CMe_2 group and one (2H) for the OCH_2 group. This is consistent with rapid racemisation at the metal and interconversion of the prochiral methyl groups and OCH_2 protons. Lowering the temperature to 223 K leads to no change in the spectrum, hence even at this temperature exchange is fast on the NMR timescale. In addition, no signal is observed for H_2O even at 223 K. This indicates that the rate of interconversion is faster than in the analogous dicationic [Rh(OH_2)(Me_2-pymox)Cp*][SbF_6]$_2$ complex, for which, the signals due to the NCMe_2 and OCH_2 protons resolved into sharp singlets and doublets, respectively [21]. Complex **6** was also characterised by X-ray diffraction and the structure is shown in Fig. 4. The Rh–N and Rh–O(2) bond lengths [2.114(4) and 2.098(3) Å, respectively] are statistically the same as those in the precursor chloride **1**, [2.105(4) and 2.092(3) Å, respectively] whilst the chelate bite angle [82.1(2)°] is slightly smaller than in **1** [83.0(1)°]. The Rh–O(3) bond length to the water [2.189(4) Å] is the same as that in [Rh(OH_2)(prophos)Cp*][SbF_6]$_2$ [18].

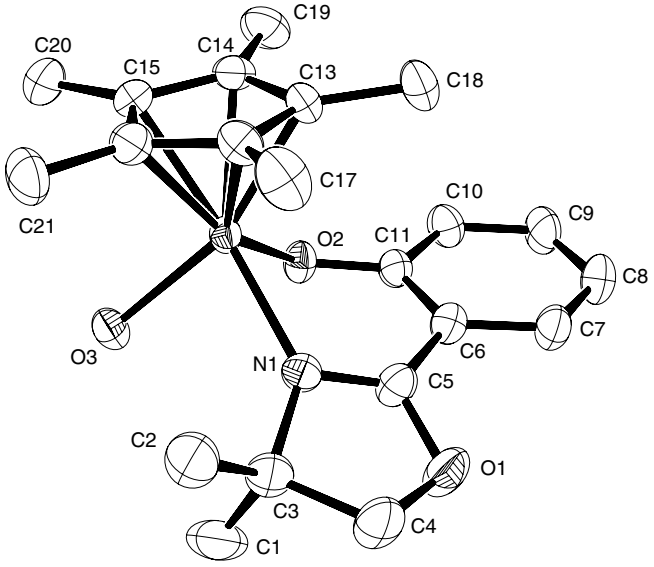


Fig. 4. Ortep diagram showing atom numbering scheme for the cation of **6** with 50% displacement ellipsoids. H atoms have been omitted for clarity. Selected bond distances (Å) and bond angles (°): Rh–N 2.114(4), Rh–O(2) 2.098(3), Rh–O(3) 2.189(4), N–Rh–O(2) 82.1(2).

Table 2
Enantioselective Diels–Alder reaction of methacrolein with cyclopentadiene in dichloromethane catalysed by [MCl(saloxaz)(ring)] (M = Ru, ring = mesitylene; M = Rh, ring = Cp*) after treatment with $AgSbF_6$

exo endo

Entry	Metal	R	Time (h)	Yield (%)	*Exo*:*endo*	ee (%)
1	Ru	^{i}Pr	24	93	95:5	40[a]
2	Rh	^{i}Pr	72	46	94:6	8
3	Ru	Ph	65	91	93:7	13[a]
4	Rh	Ph	72	36	91:9	3

All at 2 mol% catalyst at 0 °C, the (S_C)-configured ligands were used in all cases the major enantiomer of the *exo* product was identified as (1*R*,2*S*,4*R*)-2-methylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde.
[a] Data from [13].

The cations derived from **2** and **4** were used to catalyse the reaction of methacrolein with cyclopentadiene and the results are shown in Table 2 along with results for the corresponding mesitylene ruthenium complexes. As can be seen (entries 2 and 4), the rhodium complexes have only low activity and very low selectivity when compared with the ruthenium catalysts.

3. Conclusions

Salicyloxazoline ligands coordinate diastereoselectively to the Cp*RhCl fragment with the oxazoline substituent

oriented towards the chloride except in the case of phenyl substituted complex, as found for the Ru(mesitylene) analogues [13]. Since epimerisation at the metal is occurring at a rate comparable to the NMR timescale the diastereoselectivities are equilibrium values and are therefore due to thermodynamic rather than kinetic preferences. Unlike the corresponding arene ruthenium complexes, monocationic Cp*rhodium salicyloxazoline complexes are very poor catalysts for the Diels–Alder reaction of methacrolein and cyclopentadiene. Thus, so far, only dicationic Cp*rhodium complexes, with neutral bidentate ligands such as diphosphines [18], or pyridyloxazolines [20,21], show good catalytic activity in this reaction.

4. Experimental

The solvents were dried by refluxing over appropriate drying agents under nitrogen as follows, light petroleum (bp 40–60 °C) and diethyl ether over sodium/benzophenone, dichloromethane over calcium hydride and acetone over calcium sulphate. The reactions described were carried out under nitrogen; however, once isolated as pure solids the compounds are air-stable and precautions for their storage are unnecessary. ^{1}H NMR spectra were obtained using Bruker spectrometers, at 300 MHz in $CDCl_3$ unless stated otherwise, chemical shifts were recorded in ppm (referenced to tetramethylsilane or residual protons in the NMR solvent). FAB mass spectra were obtained on a Kratos concept mass spectrometer using an NOBA matrix, electrospray mass spectra were recorded in methanol solution using a Micromass Quattra LC mass spectrometer. Microanalyses were performed by Butterworth laboratories Ltd., Middlesex.

The ligands R,R′-saloxaz (R = ^{i}Pr, Bz or Ph, R′ = H; R = R′ = Me) [11,25] were synthesised by the literature methods, the $ZnCl_2$ catalyst was dried under high vacuum prior to use. The chiral aminoalcohols were prepared by reduction of the relevant amino acid [26] (99% optical purity) (see Table 3).

[RhCl(Me$_2$-saloxaz)Cp] (**1**).* A solution of Me$_2$-saloxaz (102 mg, 0.53 mmol) and NaOMe (33 mg, 0.61 mmol) in MeOH (10 ml) was added to $[RhCl_2Cp^*]_2$ (150 mg, 0.24 mmol) and the solution was heated to reflux for 2 h, giving a dark red/brown solution. The solvent was evaporated, the crude residue was dissolved in CH_2Cl_2 and the solution was filtered through celite, to give a red solution, which was evaporated to afford the crude product which was recrystallised from CH_2Cl_2/ether to give complex **1** in 161 mg yield, 72%. Calc. for $C_{21}H_{27}ClNO_2Rh$: C, 54.38; H, 5.87; N, 3.02. Found: C, 53.43; H, 5.79; N, 3.12%. ^{1}H NMR (CD_2Cl_2, 273 K, 400 MHz) δ 1.34, (br s, 18H, Cp* + NC*Me*), 1.45 (br s, 3H, NC*Me*), 3.93 (d, 1H, $J = 9$ Hz, OC*H*), 4.19 (d, 1H, $J = 9$ Hz, OC*H*′), 6.37 (t, 1H, $J = 8$ Hz, Ar-4-*H*), 6.80 (d, 1H, $J = 8$ Hz,

Table 3
Crystallographic data for complexes **1**, **2** and **6**

	1	**2**	**6**
Empirical formula	$C_{21}H_{27}ClNO_2Rh$	$C_{22}H_{29}ClNO_2Rh$	$C_{21}H_{29}F_6NO_3RhSb \cdot (CH_2Cl_2)$
Formula weight	463.80	477.82	765.02
Temperature (K)	190(2)	190(2)	190(2)
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$
a (Å)	10.238(2)	7.978(1)	9.403(2)
b (Å)	13.548(3)	10.496(1)	11.130(3)
c (Å)	14.959(3)	25.860(3)	14.418(3)
α (°)	90	–	79.92(2)
β (°)	91.11(2)	–	77.22(2)
γ (°)	90	–	87.33(3)
U (Å^3)	2074.5(7)	2165.5(5)	1448.8(6)
Z	4	4	2
D_{calc} (Mg/m^3)	1.485	1.466	1.754
Absorption coefficient (mm^{-1})	0.966	0.928	1.748
F(000)	952	984	752
Crystal size (mm^3)	$0.33 \times 0.16 \times 0.15$	$0.48 \times 0.27 \times 0.18$	$0.32 \times 0.26 \times 0.18$
Theta range (°)	2.72–25.00	2.67–27.00	2.22–27.00
Index ranges	$-1 \leqslant h \leqslant 12$, $-1 \leqslant k \leqslant 16$, $-17 \leqslant l \leqslant 17$	$-1 \leqslant h \leqslant 6$, $-1 \leqslant k \leqslant 13$, $-1 \leqslant l \leqslant 33$	$0 \leqslant h \leqslant 11$, $-13 \leqslant k \leqslant 13$, $-17 \leqslant l \leqslant 18$
Reflections collected	4360	2667	6425
Independent reflections (R_{int})	3631 (0.0246)	2489 (0.0395)	6077 (0.0190)
Data/restraints/parameters	3631/0/235	2489/0/244	6077/6/361
Goodness-of-fit on F^2	1.039	1.070	1.076
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0426$, $wR_2 = 0.0994$	$R_1 = 0.0303$, $wR_2 = 0.0711$	$R_1 = 0.0476$, $wR_2 = 0.1306$
R indices (all data)	$R_1 = 0.0562$, $wR_2 = 0.1082$	$R_1 = 0.0376$, $wR_2 = 0.0781$	$R_1 = 0.0558$, $wR_2 = 0.1390$
Absolute structure parameter		−0.08(6)	0.01(6)
Largest difference in peak and hole (e Å^{-3})	0.863 and −0.837	0.462 and −0.466	1.884 and −0.819

Ar-6-*H*), 7.12 (t, 1H, $J = 8$ Hz, Ar-5-*H*), 7.37 (d, 1H, $J = 8$ Hz, Ar-3-*H*). MS (FAB^+): *m*/*z* 463, $[M]^+$; and 428, $[M - Cl]^+$.

Complexes (**2**–**4**) were prepared by a similar procedure, the quantities of reagents used and yields obtained are listed below.

[RhCl{(S)-^{i}Pr-saloxaz}Cp] (**2**)*. Complex **2** was prepared from $[RhCl_2Cp^*]_2$ (323 mg, 0.52 mmol), ^{i}Pr-saloxaz (236 mg, 1.15 mmol) and NaOMe (71 mg, 1.31 mmol) in 380 mg yield, 76%. Calc. for $C_{22}H_{29}ClNO_2Rh$: C, 55.30; H, 6.12; N, 2.93. Found: C, 55.05; H, 5.92; N, 2.88%. ^{1}H NMR δ 0.76, 0.93, (2 × d, 3H, $J = 7$ Hz, CH*Me*$_2$), 1.58 (s, 15H, Cp*), 2.80 (m, 1H, C*H*Me$_2$), 4.32 (m, 2H, OC*H*$_2$), 4.46 (m, 1H, NC*H*), 6.39 (ddd, 1H, $J = 8$, 7, 1 Hz, Ar-4-*H*), 6.96 (dd, 1H, $J = 8.5$, 1 Hz, Ar-6-*H*), 7.17 (ddd, 1H, $J = 8.5$, 7, 2 Hz, Ar-5-*H*), 7.48 (dd, 1H, $J = 8$, 2 Hz, Ar-3-*H*). MS (FAB^+): *m*/*z* 477, $[M]^+$; and 442, $[M - Cl]^+$.

[RhCl{(S)-Bz-saloxaz}Cp] (**3**)*. Complex **3** was prepared from $[RhCl_2Cp^*]_2$ (70 mg, 0.11 mmol), Bz-saloxaz (63 mg, 0.25 mmol) and NaOMe (15 mg, 0.28 mmol) in 99 mg yield, 83%. Calc. for $C_{26}H_{29}ClNO_2Rh(H_2O)$: C, 57.42; H, 5.74; N, 2.58. Found: C, 57.13; H, 5.39; N, 2.47%. ^{1}H NMR δ 1.63 (s, 15H, Cp*), 2.92 (m, 1H, C*H*$_2$Ph), 3.88 (m, 1H, C*H*$_2$Ph), 4.33 (m, 2H, OC*H*$_2$), 4.62 (m, 1H, NC*H*), 6.41 (m, 1H, Ar-4-*H*), 7.00 (d, 1H, $J = 8$ Hz, Ar-6-*H*), 7.26 (m, 6H, CH$_2$*Ph* + Ar-5-*H*), 7.46 (m, 1H, Ar-3-*H*). MS (ES^+): *m*/*z* 491, $[M - Cl]^+$.

[RhCl{(S)-Ph-saloxaz}Cp] (**4**)*. Complex **4** was prepared from $[RhCl_2Cp^*]_2$ (70 mg, 0.11 mmol), Ph-saloxaz (60 mg, 0.25 mmol) and NaOMe (15 mg, 0.28 mmol) in 87 mg yield, 75%. Calc. for $C_{25}H_{27}ClNO_2Rh$: C, 58.66; H, 5.32; N, 2.74. Found: C, 58.57; H, 5.65; N, 2.72%. ^{1}H NMR (243 K, 400 MHz). Signals for the minor isomer are shown in parentheses; δ 1.24[1.40] (s, 15H, Cp*), 4.62[4.16] (br , 1H, OC*H*{pro-*S*}), 4.79[4.88] (m, 1H, OC*H*{pro-*R*}), 5.73[5.62] (m, 1H, NC*H*), 6.55[6.44] (m, 1H, Ar-4-*H*), 7.01 (d, 1H, $J = 8$ Hz, Ar-6-*H*), 7.24 (m, 1H, Ar-5-H), 7.45 (m, 4H, *Ph* + Ar-3-*H*), 7.63[7.79] (m, 2H, Ph). MS (ES^+): *m*/*z* 491, $[M - Cl]^+$.

[Rh(4-Mepy){(S)-^{i}Pr-saloxaz}Cp][SbF$_6$] (**5**)*. Complex **5** was prepared from [RhCl{(*S*)-^{i}Pr-saloxaz}Cp*] (**2**) (57 mg, 0.12 mmol), $NaSbF_6$ (39 mg, 0.15 mmol) and 4-methylpyridine (35 mg, 0.37 mmol) in 80 mg yield, 86%. Satisfactory analysis was not obtained on this compound possibly due to loss of 4-methylpyridine. ^{1}H NMR (400 MHz, CD_2Cl_2, 233 K) δ 0.05 (br, 3 H, CH*Me*$_2$), 0.93 (d, 3H, $J = 7$ Hz, CH*Me*$_2$), 1.43 (s, 15H, Cp*), 1.66 (m, 1H, C*H*Me$_2$), 2.42 (s, 3H, 4-*Me*py), 4.41 (m, 3H, OC*H*$_2$ + NC*H*), 6.54 (m, 1H, Ar-4-*H*), 7.03 (m, 1H, Ar-6-*H*), 7.35 (m, 3H, Ar-4-*H* + py-3,5-*H*), 7.54 (m, 1H, Ar-3-*H*) 8.76 (m, 2H, py-2,6-*H*). MS (FAB^+): *m*/*z* 535, $[M]^+$; and 442, $[M - Mepy]^+$.

[Rh(OH$_2$)(Me$_2$-saloxaz)Cp][SbF$_6$] (**6**)*. $AgSbF_6$ (65 mg, 0.19 mmol) was added to a solution of complex **1** (88 mg, 0.19 mmol) in acetone (10 ml) giving a yellow/orange solution and an immediate precipitate of AgCl. The solution was stirred for 1 h at room temperature (protected from light) and was then filtered through celite (to remove AgCl). The solvent was evaporated, and the solid was washed with chloroform to give an orange hygroscopic solid 127 mg yield, 94%. (The yield is based on OH_2 being coordinated, it is possible some is acetone coordinated which would mean a reduced yield.) Satisfactory analysis was not obtained on this compound possibly due to loss of coordinated solvent. ^{1}H NMR (CD_2Cl_2 273 K, 400 MHz) δ 1.72, (s, 6H, NC*Me*$_2$), 1.78, (s, 15H, Cp*), 4.40 (s, 2H, OC*H*$_2$), 6.88 (t, 1H, $J = 8$ Hz, Ar-4-*H*), 7.20 (d, 1H, $J = 8$ Hz, Ar-6-*H*), 7.49 (t, 1H, $J = 8$ Hz, Ar-5-*H*), 7.70 (d, 1H, $J = 8$ Hz, Ar-3-*H*). MS (FAB^+): *m*/*z* 428, $[M - (OH_2)]^+$.

5. X-ray crystallography

Data for **1**, **2**, and **6** were collected on a Siemens P4 diffractometer using graphite monochromated Mo Kα radiation, $\lambda = 0.7107$ Å. The data were corrected for Lorentz and polarisation effects and semi-empirical absorption corrections based on ψ scans (XEMP; SHELXTL/PC) were applied for **1**, **2** and **6**. The structures were solved by Patterson methods and refined by full-matrix least squares on F^2 using the program SHELXTL-PC [27]. All hydrogen atoms bonded to carbon were included in calculated positions (C–H = 0.96 Å) using a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. In **6** the hydrogens on the coordinated water were not located and the structure includes one molecule of dichloromethane which is disordered. Figures were produced using Ortep-3 for Windows [28]. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 281818–281820.

6. Catalysis

The catalyst was prepared in situ from the chloride complex and one equivalent of $AgSbF_6$ in CH_2Cl_2, the solution was filtered through celite into a Schlenk tube to remove AgCl. Methacrolein (1 mmol) and 2,6-di-*t*-butylpyridine (1 equivalent/mol catalyst) [29] were added to the catalyst solution (0.2 mmol) in CH_2Cl_2 (2 cm^3). The resulting yellow solution was equilibrated at 0 °C before addition of cyclopentadiene (2 mmol). At the end of the reaction the mixture was passed through a plug of silica, the solvent was removed and the product was obtained as a colourless oil. The *exo*:*endo* ratio was determined by ^{1}H NMR spectroscopy and the enantiomeric excess was determined by ^{1}H NMR or GC after conversion to the acetal with (2*R*,4*R*)-pentanediol [30].

Acknowledgements

We thank the EPSRC for a studentship (A.J.D.), Johnson Matthey for the loan of $RhCl_3$ and NSC Technologies for the gift of phenylglycinol.

References

[1] R. Noyori, S. Hashiguchi, Acc. Chem. Res. 30 (1997) 97.
[2] K. Mashima, T. Abe, K. Tani, Chem. Lett. (1998) 1201;
K. Mashima, T. Abe, K. Tani, Chem. Lett. (1998) 1199;
K. Murata, T. Ikariya, R. Noyori, J. Org. Chem. 64 (1999) 2186.
[3] J.W. Faller, A.R. Lavoie, Organometallics 20 (2001) 5245.
[4] D.J. Cross, J.A. Kenny, I. Houson, L. Campbell, T. Walsgrove, M. Wills, Tetrahedron: Asymm. 12 (2001) 1801.
[5] H. Brunner, Angew. Chem., Int. Ed. Engl. 38 (1999) 1194;
H. Brunner, Eur. J. Inorg. Chem. (2001) 905;
C. Ganter, Chem. Soc. Rev. 32 (2003) 130;
J.W. Faller, J. Parr, A.R. Lavoie, New J. Chem. 27 (2003) 899.
[6] R. Kramer, K. Polborn, H. Wanjek, I. Zahn, W. Beck, Chem. Ber. 123 (1990) 767;
D. Carmona, A. Medoza, F.J. Lahoz, L.A. Oro, M.P. Lamata, E. San Jose, J. Organomet. Chem. 396 (1990) C17;
D. Carmona, C. Vega, F.J. Lahoz, R. Atencio, L.A. Oro, P.M. Lamata, F. Viguri, E. San Jose, Organometallics 19 (2000) 2273;
D. Carmona, F.J. Lahoz, R. Atencio, L.A. Oro, M.P. Lamata, F. Viguri, E. San Jose, C. Vega, J. Reyes, F. Joo, A. Katho, Chem. Eur. J. 5 (1999) 1544.
[7] M.L. Loza, J. Parr, A.M.Z. Slawin, Polyhedron 16 (1997) 2321.
[8] H. Brunner, A. Kollnberger, T. Burgemeister, M. Zabel, Polyhedron 19 (2000) 1519.
[9] D. Carmona, C. Vega, F.J. Lahoz, S. Elipe, L.A. Oro, P.M. Lamata, F. Viguri, R. Garcia-Correas, C. Cativiela, M.P. Lopez-Ram deViu, Organometallics 18 (1999) 3364.
[10] A. Pfaltz, Acta Chem. Scand. 50 (1996) 189;
A.K. Ghosh, P. Mathivanan, J. Cappiello, Tetrahedron-Asymm. 9 (1998) 1;
H.A. McManus, P.J. Guiry, Chem. Rev. 104 (2004) 4151.
[11] C. Bolm, K. Weickharott, M. Zender, D. Glasmacher, Helv. Chim. Acta 74 (1991) 717.
[12] M. Gomez, S. Jansat, G. Muller, G. Noguera, H. Teruel, V. Moliner, E. Cerrada, M. Hursthouse, Eur. J. Inorg. Chem. (2001) 1071;
M. GomezSimon, S. Jansat, G. Muller, D. Panyella, M. FontBardia, X. Solans, J. Chem. Soc., Dalton Trans. (1997) 3755;
H. Yang, M.A. Khan, K.M. Nicholas, Organometallics 12 (1993) 3485;
M.M. Abu-Omar, Chem. Commun. (2003) 2102.
J. Arias, C.R. Newlands, M.M. Abu-Omar, Inorg. Chem. 40 (2001) 2185;
E. Shuter, H.R. Hoveyda, V. Karunaratne, S.J. Rettig, C. Orvig, Inorg. Chem. 35 (1996) 368.
[13] A.J. Davenport, D.L. Davies, J. Fawcett, D.R. Russell, Dalton Trans. (2004) 1481.
[14] H. Brunner, B. Nuber, M. Prommesberger, Tetrahedron: Asymm. 9 (1998) 3223.
[15] L. Dadci, H. Elias, U. Frey, A. Hornig, U. Koelle, A.E. Merbach, H. Paulus, J.S. Schneider, Inorg. Chem. 34 (1995) 306.
[16] K. Stanley, M.C. Baird, J. Am. Chem. Soc. 97 (1975) 6598.
[17] D. Carmona, M.P. Lamata, L.A. Oro, Coord. Chem. Rev. 200–202 (2000) 717;
J.S. Johnson, D.A. Evans, Acc. Chem. Res. 33 (2000) 325;
H. Yamamoto, Lewis Acids in Organic Synthesis, Wiley-VCH, Weinheim, Chichester, 2000;
T.K. Hollis, W. Odenkirk, N.P. Robinson, J. Whelan, B. Bosnich, Tetrahedron 49 (1993) 5415.
[18] D. Carmona, C. Cativiela, R. Garcia-Correas, F.J. Lahoz, M.P. Lamata, J.A. Lopez, M.P. Lopez-Ram de Viu, L.A. Oro, E. San Jose, F. Viguri, Chem. Commun. (1996) 1247.
[19] D.L. Davies, J. Fawcett, S.A. Garratt, D.R. Russell, J. Organomet. Chem. 662 (2002) 43.
[20] A.J. Davenport, D.L. Davies, J. Fawcett, S.A. Garratt, L. Lad, D.R. Russell, Chem. Commun. (1997) 2347.
[21] D.L. Davies, J. Fawcett, S.A. Garratt, D.R. Russell, Dalton Trans. (2004) 3629.
[22] A.J. Davenport, D.L. Davies, J. Fawcett, S.A. Garratt, D.R. Russell, J. Chem. Soc., Dalton Trans. (2000) 4432.
[23] S.K. Mandal, A.R. Chakravarty, Inorg. Chem. 32 (1993) 3851.
[24] H. Asano, K. Katayama, H. Kurosawa, Inorg. Chem. 35 (1996) 5760.
[25] C. Bolm, K. Weickhardt, M. Zehnder, T. Ranff, Chem. Ber. 124 (1991) 1173.
[26] M.J. McKennon, A.I. Meyers, K. Drauz, M. Scharm, J. Org. Chem. 58 (1993) 3568.
[27] G.M. Sheldrick, Siemens Analytical X-ray Instruments, Madison, WI, 1990.
[28] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
[29] P.V. Bonnesen, C.L. Puckett, R.V. Honeychuck, W.H. Hersh, J. Am. Chem. Soc. 111 (1989) 6070.
[30] D.A. Evans, J.A. Murry, P.v. Matt, R.D. Norcross, S.J. Miller, Angew. Chem., Int. Ed. Engl. 34 (1995) 798.