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Cp*rhodium and iridium complexes with bisoxazolines: synthesis, fluxionality and applications as asymmetric catalysts for Diels–Alder reactions

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Abstract

Reaction of the dimers $[MCl_2Cp^*]_2$ (M = Rh, Ir) with bis-oxazolines [N–N = bis(2-oxazoline) (box), 2,2-bis(2-oxazolinyl)propane (bop), 1,2-bis(2-oxazolinyl)benzene (benbox)] in the presence of $NaSbF_6$ (or KPF_6) gives complexes $[MCl(N–N)Cp^*][EF_6]$ (E = P or Sb) which have been fully characterised. Treatment of some of these with $AgSbF_6$ generates dications $[Rh(OH_2)(N–N)Cp^*]^{2+}$, some of which are fluxional at room temperature. One of these is an enantioselective catalyst for the Diels–Alder reaction of methacrolein and cyclopentadiene. Three complexes, $[RhCl(^i$Pr-box$)Cp^*][SbF_6]$, $[RhCl(^i$Pr-bop$)Cp^*][SbF_6]$ and [RhCl(Et-benbox)$Cp^*][SbF_6$] have been characterised by X-ray crystallography.

Keywords: Cp*rhodium complexes; Cp*iridium complexes; Bisoxazolines

1. Introduction

Chiral half-sandwich complexes have attracted much study both in terms of mechanisms of substitution at a chiral metal centre [1] and as chiral auxiliaries in stoichiometric organic synthesis [2]. More recently, their great potential as chiral catalysts has been demonstrated; the best example so far is the asymmetric transfer hydrogenation of ketones, with enantiomeric excesses (ee) of >99%, using arene ruthenium complexes with a chiral ligand derived from a chiral diamine as catalyst [3]. Half-sandwich complexes containing the Cp*rhodium and iridium moieties have been known for over 30 years [4]. They have been used extensively to study C–H activation [5], and are catalysts or catalyst precursors for a wide range of reactions. For example, Cp*rhodium or iridium complexes catalyse hydrosilylation of alkynes [6], addition of alkenes to aromatic ketones [7], coupling of arenes with silanes [8], oxidation of alcohols [9], and reduce NAD(P) as part of an enzymatic recycling system [10]. In addition, such complexes have been known as hydrogenation catalysts for many years [11]. Recently, examples of asymmetric transfer hydrogenation of ketones using Cp*rhodium or iridium catalysts have also been reported [12]. Wills et al. have shown that isoelectronic arene ruthenium and Cp*rhodium catalysts show different selectivity [13].

In the last decade there has been a surge in interest in chiral nitrogen-donor ligands for use in asymmetric catalysis and bisoxazolines have been particularly successful [14]. However, to date there are relatively few half-sandwich complexes containing oxazoline ligands. A number of arene ruthenium complexes with chiral bidentate ligands containing one oxazoline and one other donor have been reported and used in asymmetric catalysis [15,16]. Chiral bidentate ligands with only one oxazoline can give rise to diastereomers when coordinated in a half-sandwich complex. However, the possibility of formation of diastereomers may be avoided by the use of C_2-symmetrical bisoxazolines. Arene ruthenium complexes with bisoxazolines have been reported [17–20] and have given good results in asymmetric catalysis [19,20]. However, to our knowledge our pre-

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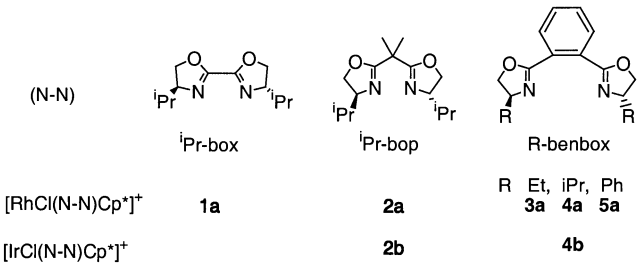
liminary report [21] is the only example of Cp*rhodium or iridium complexes with oxazoline ligands.

In this paper we report the synthesis of several Cp*rhodium and iridium complexes with three different types of C_2-symmetric bisoxazoline (N–N), namely bis(2-oxazoline) (box), 2,2-bis(2-oxazolinyl)propane (bop), 1,2-bis(2-oxazolinyl)benzene (benbox). Some of this material has been communicated previously [21].

2. Results and discussion

2.1. Synthesis and characterisation of [MCl(N–N)Cp*][EF$_6$] (1–5) (M = Rh, Ir; E = P or Sb)

Complexes [MCl(N–N)Cp*][EF$_6$] (**1**–**5**) (M = Rh, Ir; E = P or Sb) were synthesised in high yield by treatment of dimers [MCl$_2$Cp*]$_2$ with two equivalents of the bisoxazoline ligand (N–N) and NaSbF$_6$ (or KPF$_6$) in methanol at reflux. The complexes were characterised by ^{1}H-NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray diffraction for **1a**, **2a** and **3a** (Table 1).



As explained above only one isomer is possible since the complexes are only chiral at the ligand, not at the metal. The free ligands have C_2-symmetry, however, this symmetry is lost on complexation and all the protons become inequivalent, hence the ^{1}H-NMR spectra of **1**–**5** are more complex as a result. The signals for the oxazoline protons shift downfield on coordination, whilst in complexes **1**, **2** and **4**, containing ^{i}Pr substituents, the C*H*Me$_2$ proton shifts downfield compared to free ligand and the Me groups give rise to four doublets, one of which is often shifted upfield. In complexes **2** the loss of C_2-symmetry is also apparent from the observation of two singlets arising from the CMe$_2$ of the backbone of the bisoxazolinyl-propane.

The Cp* signals occur at δ 1.78, 1.68 and 1.61 for **1a**, **2a** and **2b**, respectively, however, for **3a**, **4a** and **4b** they occur at ca. δ 1.28 whilst for **5a** the signal is at δ 0.98. The upfield shift in **3a** and **4a/b** is most likely due to a ring current effect from the benzene backbone of the benbox ligand (see X-ray structure of **3a** below); whilst the greater shift for **5** may be due to an additional ring current effect from one of the phenyl substituents on the oxazolines. Similar effects were noted in related areneruthenium complexes [19]. The major ion in the mass spectrum of each complex corresponds to [MCl(N–N)Cp*]$^+$ with minor ions due to loss of the bisoxazoline to give [MClCp*]$^+$.

Table 1
Crystallographic data for complexes **1a** and **3a**

Empirical formula	$C_{22}H_{35}ClF_6N_2O_2RhSb$ [a]	$C_{26}H_{35}ClF_6N_2O_2PRh$
Formula weight	774.26	690.89
Temperature (K)	150(2)	190(2)
Crystal system	Cubic	Orthorhombic
Space group	$I23$	$P2_12_12_1$
a (Å)	26.8471(6)	13.166(3)
b (Å)	26.8471(6)	14.004(2)
c (Å)	26.8471(6)	16.055(3)
α (°)		
β (°)		
γ (°)		
U (Å^3)	19350.5(7)	2960.2(10)
Z	24	4
D_{calc} (kg cm^{-3})	1.595	1.550
Absorption coefficient (mm)	1.629	0.785
$F(000)$	9172	1408
Crystal size (mm)	0.33 × 0.28 × 0.27	0.53 × 0.46 × 0.38
2θ max	50.0	50.0
% complete	100.0	87.3
Reflections collected	70829	3219
Unique reflections (R_{int})	5700 (0.0383)	3053 (0.0298)
Max/min transmission	0.74, 0.64	0.85, 0.71
Data/restraints/parameters	5700/0/341	3053/0/359
Goodness-of-fit on F^2	1.130	1.086
R_1 indices [$I > 2\sigma(I)$]	0.0399	0.0691
wR_2 (all data)	0.1204	0.1853
Absolute structure parameter	−0.02(3)	−0.06(11)
Largest difference peak and hole (e Å^{-3})	1.943 and −1.273	1.837 and −1.035

[a] H_3OSbF_6 (ca. 12% was also found in the lattice; see Section 3 for details).

Crystals of **1a**, **2a** and **3a** were obtained that were suitable for X-ray crystallography and the structures of the cations are shown in Figs. 1–3, respectively (the structure of **2a** has been reported previously [21] but it is discussed again here for comparison with **1a** and **3a**). In all three complexes the rhodium atom has a pseudooctahedral geometry with the Cp* occupying three adjacent sites of the octahedron. The complexes have a 5-, 6- or 7-membered chelate ring and the bite angles are 75.7(2), 84.0(2) and 83.0(5)°, respectively. In **1a** and **2a** one of the Rh–N bonds is longer than the other (2.158(5) vs. 2.117(4) Å in **1a**, and 2.157(6) vs. 2.117(6) Å in **2a**) and one N–Rh–Cl angle is smaller than the other (82.1(1) vs. 89.1(1)° in **1a** and 82.1(2) vs. 90.2(2)°

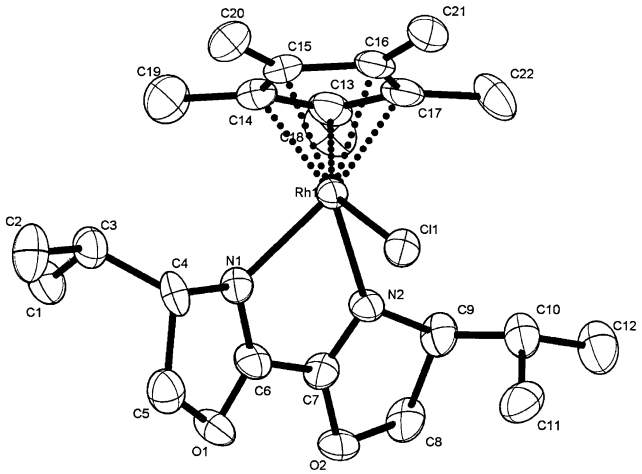


Fig. 1. Structure drawing of the cation of **1a**, showing the atom-labelling scheme. Displacement ellipsoids are shown at the 30% level. H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Rh(1)–N(1) 2.158(5), Rh(1)–N(2) 2.117(4), Rh(1)–Cl(1) 2.394(1), N(2)–Rh(1)–N(1) 75.7 (2). N(2)–Rh(1)–Cl(1) 89.1(1), N(1)–Rh(1)–Cl(1) 82.1(1).

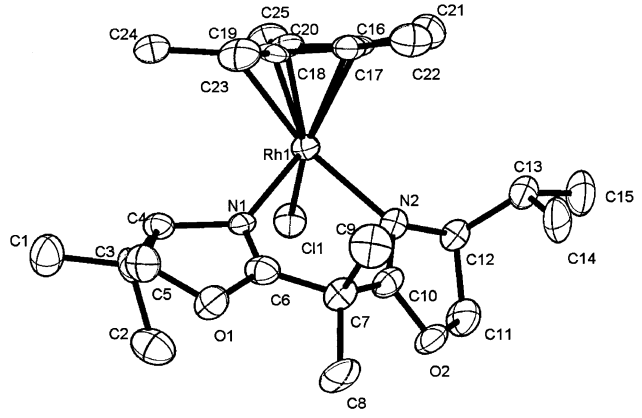


Fig. 2. Structure drawing of the cation of **2a**, showing the atom-labelling scheme. Displacement ellipsoids are shown at the 30% level. H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Rh(1)–N(1) 2.117(6), Rh(1)–N(2) 2.157(6), Rh(1)–Cl(1) 2.406(2), N(2)–Rh(1)–N(1) 84.0(2). N(1)–Rh(1)–Cl(1) 90.2(2), N(2)–Rh(1)–Cl(1) 82.1(2).

in **2a**). In each case the longer Rh–N bond and smaller N–Rh–Cl angle involve the nitrogen of the oxazoline ring with the substituent which is oriented more towards the Cp* rather than towards the chloride. We presume these distortions occur to reduce the steric strain between the oxazoline substituent and the Cp* ring. We noted a similar rotation to relieve steric interactions in pyridyloxazoline complexes [16]. In **2a** the 6-membered ring has an envelope conformation with C(6) and C(7) both pointing away from the chloride, being 0.405 and 0.786 Å, respectively, out of the N(1)–Rh–N(2) plane; C(10) is only 0.055 Å out of this plane. In **3a**, the coordination geometry around rhodium is more symmetrical, the Rh–N(1) and Rh–N(2) distances, 2.116(10) and 2.109(11) Å, respectively, are statistically the same whilst the N(1)–Rh–Cl and N(2)–Rh–Cl bond angles are very similar, 89.5(3) and 91.8(3)°, respectively. In this case, the oxazoline rings are rotated out of the plane of the benzene ring 56.4° (N1–O1) and 38.4° (N2–O2) in opposite directions. This has the effect of relieving steric interactions between the ethyl on C(3) and the Cp* whilst putting the ethyl on C(14) closer to the chloride. The benzene ring lies rather close to the Cp*, with the C(6)–C(26) and C(11)–C(26) distances being 3.36 and 3.39 Å, respectively, consistent with the high field shift for the Cp* (see above).

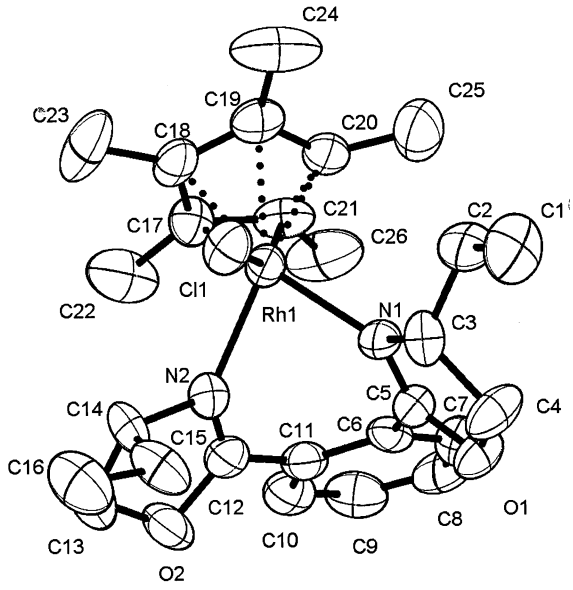


Fig. 3. Structure drawing of the cation of **3a**, showing the atom-labelling scheme. Displacement ellipsoids are shown at the 30% level. H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Rh(1)–N(1) 2.116(10), Rh(1)–N(2) 2.109(11), Rh(1)–Cl(1) 2.409(3), N(2)–Rh(1)–N(1) 82.1(4). N(1)–Rh(1)–Cl(1) 89.5(3), N(2)–Rh(1)–Cl(1) 91.8(3).

2.2. Synthesis and characterisation of $[Rh(OH_2)(N–N)Cp^*][SbF_6]_2$ (6–8)

To activate these complexes for use in asymmetric catalysis it is necessary to remove the strongly-bound chloride ligand. Thus, treatment of **1a**, **2a** or **4a** with $AgSbF_6$ in CH_2Cl_2–acetone gave a precipitate of AgCl and the dications $[Rh(OH_2)(N–N)Cp^*]^{2+}$ (**6**–**8**) which were characterised by ^{1}H-NMR spectroscopy and mass spectrometry and in some cases elemental analysis. The water ligand is obtained from the acetone solvent and/or in the work-up which is carried out in air.

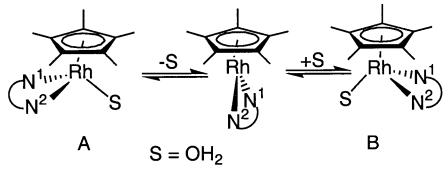
The ^{1}H-NMR spectrum in acetone-d_6 of $[Rh(OH_2)(^i$Pr-box)(mes)$][SbF_6]_2$ (**6**) at room temperature showed apparent C_2-symmetry for the ^{i}Pr-box ligand, thus two 6H doublets (δ 0.90 and 1.13) and a broad 2H multiplet (δ 2.57) are observed for the isopropyl groups and two multiplets (δ 4.95 and 5.15) due to the

oxazoline ring protons. In addition, a very broad signal due to water was observed at ca. δ 3 with no signal for coordinated water. On cooling to 273 K the signal at δ 0.90 had collapsed to a broad hump; by 253 K this had resolved into two signals and the signals at δ 2.57, 4.95 and 5.15 had also split consistently with the loss of C_2-symmetry, and signals due to uncoordinated and coordinated water could be seen at about δ 3.5 and 6.8. Further cooling to 223 K led to further sharpening of the signals and the isopropyl doublet initially at δ 1.13 also split into two as expected. The coordinated water signal was also split into two at δ 7.00 and 7.04, corresponding to coordinated H_2O and HOD, respectively. This high frequency deuterium isotope shift is probably a consequence of hydrogen-bonding of the water to solvent molecules as suggested for related arene ruthenium dications [16,19]. As observed for **6**, the ^{1}H-NMR spectrum of $[Rh(OH_2)(^i$Pr-bop)(mes)$][SbF_6]_2$ (**7**) at room temperature also indicates C_2-symmetry for the bisoxazoline, two 6H doublets (δ 0.90 and 1.17) and a broad 2H multiplet (δ 2.5) are observed for the isopropyl groups, a singlet at δ 1.66 due to the CMe_2 and two multiplets (δ 4.70 and 4.93) due to the oxazoline ring protons. At 213 K the spectrum is consistent with loss of C_2-symmetry though the peaks are still broad, indicating the slow exchange region has not been reached at this temperature. A signal for coordinated water is also visible at this temperature at δ 6.5 with free water at δ 4.9.

The variable temperature NMR spectra above can be explained by an interconversion between species A and B, shown in Scheme 1, via a 16-electron intermediate.

Although A and B are structurally identical, each individual proton of the bis-oxazoline ligand will be in a different environment in each of A and B. Thus, if the interconversion is fast, time-averaging of ^{1}H-NMR signals is expected. We [19] and others [18] have observed similar fluxional behaviour for the analogous dications $[Ru(OH_2)$(R-bop)(arene)$]^{2+}$. However, the low temperature limit could always be reached in the case of the areneruthenium complexes. Hence exchange at rhodium is faster which is consistent with kinetic studies of water exchange [22], and with epimerisation of comparable pyrrolleimine complexes of areneruthenium and Cp*rhodium [23].

It should be noted that the interconversion of A and B (Scheme 1) involves solvent exchange and an inversion



Scheme 1. Proposed fluxionality of solvent complexes $[Rh(OH_2)$(N–N)(arene)$][SbF_6]_2$ (**6**–**8**).

at the metal. If the solvent molecule is water, proton exchange is also feasible, in which case only the water signals should exchange with all other signals being sharp. The ^{1}H-NMR spectrum of $[Rh(OH_2)(^i$Pr-benbox)Cp*$]^{2+}$ (**8**) in acetone-d_6 showed four doublets for the isopropyl groups, i.e. consistent with the loss of C_2-symmetry found in the free ligand. However, at room temperature no signals due to free or coordinated water could be observed. On cooling to 223 K signals were observed for coordinated water at δ 7.5 and a broad peak for free water at δ 3.1. Thus in this case exchange of water is occurring without averaging of the oxazoline signals through inversion at the metal. Inversion at the metal either requires dissociation of one end of the bisoxazoline or involves passing through a transition state in which the two oxazolines are coplanar (Scheme 1). Dissociation of one end of the bis-oxazoline is likely to be similar energy in all three complexes **6**–**8**. Therefore, since the barrier to inversion is clearly much larger in the case of **8**, it is likely that inversion involves making the oxazolines coplanar which would be expected to be much more sterically hindered for the 7-membered ring in **8**. This barrier to planarity of benbox complexes has been noted previously [24,25].

2.3. Catalysis

The Diels–Alder reaction is one of the most important in organic chemistry and great progress has been made in developing enantioselective versions. Recently there has been particular interest in using chiral late-transition-metal catalysts which may show less water-sensitivity than the more common titanium, aluminium or boron catalysts [26]. The first enantioselective half-sandwich rhodium catalysts for the Diels–Alder reaction were reported in 1996, by Carmona et al. who showed that the dicationic complexes $[Rh(H_2O)$(*R*-Prophos)Cp*$]X_2$ (X = BF_4, SbF_6), catalysed the reaction between methacrolein and cyclopentadiene with e.e.s of up to 71% [27]. Carmona also reported that Cp*rhodium and iridium complexes with chiral pyridylimines are catalysts for Diels–Alder reactions though only the iridium complexes showed reasonable enantioselectivity [28].

We have tested the dications $[Rh(OH_2)$(N–N)Cp*$]^{2+}$ as catalysts for the Diels–Alder reaction of methacrolein with cyclopentadiene. Complexes **6** and **8** gave very poor yields, relatively low *exo*:*endo* ratios (85:15), and almost no enantioselectivity consistent with background thermal reaction or catalysis by an achiral impurity. Complex **7** (5 mol%, 24 h) gave a reasonable yield (62%), good *exo*:*endo* selectivity (95:5) but with only modest enantioselectivity (29% e.e.). Thus, these Cp*rhodium complexes are not as active or as enantioselective as bisoxazoline arene ruthenium complexes [19], though surprisingly the only bisoxazoline which

shows activity for rhodium is actually one of the worst ligands for the ruthenium catalysts. The bisoxazoline ligands also give inferior Diels–Alder catalysts to pyridyloxazolines when complexed to Cp*rhodium [21].

In conclusion, we have synthesised a number of complexes $[MCl(N–N)Cp^*][EF_6]$ (M = Rh, Ir; E = P or Sb) containing C_2-symmetrical bisoxazoline ligands. Treatment of some of these with AgCl gave dications $[Rh(OH_2)(N–N)Cp^*]^{2+}$, which in some cases are fluxional at room temperature. These were tested as enantioselective catalysts for the Diels–Alder reaction of methacrolein and cyclopentadiene; only dication **7** showed moderate activity and enantioselectivity.

3. Experimental

Light petroleum (b.p. 40–60 °C) and Et_2O were dried by refluxing over purple sodium/benzophenone under nitrogen, whilst CH_2Cl_2 was purified by refluxing over CaH_2 and acetone from calcium sulphate. The reactions described were carried out under nitrogen; however, once isolated as pure solids compounds **1**–**5** are air-stable and precautions for their storage are unnecessary; cations **6**–**8** decompose over time possibly due to loss of coordinated water. ^{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 Me_4Si or residual protons in the NMR solvent). FAB mass spectra were obtained on a Kratos concept mass spectrometer using an NOBA matrix. Microanalyses were performed by Butterworth laboratories Ltd., Middlesex.

The bis-oxazolines were prepared by literature procedures (box [29], bop [30], benbox [24]) from the relevant aminoalcohol, which in turn was prepared by reduction of the amino acid [31] (99% optical purity). The dimers $[MCl_2Cp^*]_2$ were prepared by a literature method [32].

3.1. Preparations of [MCl(bis-oxazoline)Cp*][SbF6] (1–5)

A mixture of bis-oxazoline (two equivalents), $NaSbF_6$ (two equivalents) and $[MCl_2Cp^*]_2$ (one equivalent) in MeOH (10 cm^3) was heated to reflux for 2 h. A yellow–brown solution was obtained, which was then evaporated and the crude residue dissolved in CH_2Cl_2. Filtration through Celite (to remove NaCl and any black decomposition product), gave a red–orange solution (yellow for iridium complexes), which was evaporated and the crude complex was recrystallised from CH_2Cl_2–ether. The scale and yields for individual complexes are shown below. The PF_6 salts could be prepared similarly using KPF_6; the spectroscopic properties were identical.

3.1.1. [RhCl(iPr-box)Cp*][SbF6] (1a)

Complex **1a** was prepared from $[RhCl_2Cp^*]_2$ (76 mg, 0.113 mmol), ^{i}Pr-box (56 mg, 0.25 mmol) and $NaSbF_6$ (61 mg, 0.24 mmol) in 146 mg yield, 88%. Anal. Calc. for $C_{22}H_{35}ClF_6N_2O_2RhSb$: C, 36.02(34.68); H, 4.81(4.67); N, 3.82(3.68). Figures in parentheses show the effect of 10% impurity of H_3OSbF_6 consistent with the X-ray structure. Found: C, 34.87; H, 4.66; N, 3.75%. ^{1}H-NMR δ 0.83 (d, 3H, $J = 7$, CHMe), 1.02 (m, 9H, 3 × CHMe), 1.78 (s, 15H, Cp*), 2.13 (m, 1H, CHMe$_2$), 2.38 (m, 1H, CHMe$_2$) 4.35 (m, 1H, NCH), 4.65 (t, 1H, $J = 10$, OCH), 4.76 (m, 3H, 2 × OCH + NCH), 5.03 (t, 1H, $J = 9$, OCH). MS (FAB$^+$): m/z 497, $[M]^+$; and 461, $[M-HCl]^+$.

3.1.2. [RhCl(iPr-bop)Cp*][SbF6] (2a)

Complex **2a** was prepared from $[RhCl_2Cp^*]_2$ (80 mg, 0.129 mmol), ^{i}Pr-bop (90 mg, 0.34 mmol) and $NaSbF_6$ (68 mg, 0.26 mmol) in 159 mg yield, 80%. Anal. Calc. for $C_{25}H_{41}ClF_6N_2O_2PRh \cdot 0.5CH_2Cl_2$: C, 42.11; H, 5.82; N, 3.85. Found: C, 41.74; H, 5.67; N, 3.79% (analysis on PF_6 salt). ^{1}H-NMR δ 0.60, 0.88, 0.93, 1.00 (4 × d, 3H, $J = 7$, CHMe_2), 1.47 (s, 3H, CMe$_2$), 1.66 (s, 3H, CMe$_2$), 1.68 (s, 15H, Cp*), 2.23 (m, 1H, CHMe$_2$), 2.52 (m, 1H, CHMe$_2$), 4.25 (t, 1H, $J = 9$, OCH), 4.52 (m, 5H, 2 × NCH + 3 × OCH). MS (FAB$^+$): m/z 539, $[M]^+$; and 503, $[M-HCl]^+$.

3.1.3. [IrCl(iPr-bop)Cp*][SbF6] (2b)

Complex **2b** was prepared from $[IrCl_2Cp^*]_2$ (80 mg, 0.11 mmol), ^{i}Pr-bop (70 mg, 0.26 mmol) and $NaSbF_6$ (59 mg, 0.23 mmol) in 149 mg yield, 74%. Anal. Calc. for $C_{25}H_{41}ClF_6N_2O_2PIr$: C, 38.78; H, 5.34; N, 3.62. Found: C, 38.74; H, 5.33; N, 3.62% (analysis on PF_6 salt). ^{1}H-NMR (250 MHz) δ 0.61, 0.82, 0.87, 0.94 (4 × d, 3H, $J = 7$, CHMe_2), 1.45 (s, 3H, CMe$_2$), 1.55 (s, 3H, CMe$_2$), 1.61 (s, 15H, Cp*), 2.15 (m, 1H, CHMe$_2$), 2.45 (m, 1H, CHMe$_2$), 4.27 (t, 1H, $J = 9$, OCH), 4.31 (m, 1H, NCH), 4.49 (m, 3H, NCH + 2 × OCH), 4.64 (t, 1H, $J = 9$, OCH). MS (FAB$^+$): m/z 629, $[M]^+$; and 363, $[IrClCp^*]^+$.

3.1.4. [RhCl(Et-benbox)Cp*][SbF6] (3a)

Complex **3a** was prepared from $[RhCl_2Cp^*]_2$ (80 mg, 0.129 mmol), Et-benbox (71 mg, 0.26 mmol) and $NaSbF_6$ (68 mg, 0.26 mmol) in 155 mg yield, 77%. Anal. Calc. for $C_{26}H_{35}ClF_6N_2O_2PRh$: C, 45.20; H, 5.11; N, 4.05. Found: C, 45.28; H, 5.10; N, 3.99% (analysis on PF_6 salt). ^{1}H-NMR (250 MHz) δ 0.77 and 0.96 (2 × t, 3H, $J = 7$, CH$_2Me$), 1.29 (s, 15H, Cp*), 1.62 (m, 2H, CH_2Me), 1.95 (m, 1H, CH_2Me), 2.30 (m, 1H, CH_2Me), 4.12 (tt, 1H, $J = 8$, 2, NCH), 4.6 (m, 5H, 2 × NCH + 3 × OCH), 7.84 (m, 2H, C_6H_4), 8.04 (m, 1H, C_6H_4), 8.16 (m, 1H, C_6H_4). MS (FAB$^+$): m/z 545, $[M]^+$; and 509, $[M-HCl]^+$.

3.1.5. [RhCl(ⁱPr-benbox)Cp][SbF$_6$] (**4a**)*

Complex **4a** was prepared from [RhCl$_2$Cp*]$_2$ (70 mg, 0.11 mmol), ⁱPr-benbox (72 mg, 0.24 mmol) and NaSbF$_6$ (59 mg, 0.23 mmol) in 150 mg yield, 82%. Anal. Calc. for $C_{28}H_{39}ClF_6N_2O_2RhSb\cdot H_2O$: C, 40.51; H, 5.28; N, 3.26. Found: C, 40.12; H, 5.21; N, 3.25%. ^{1}H-NMR δ 0.50, 0.88, 0.98 and 1.00 (4 × d, 3H, $J = 7$, CH*Me*$_2$), 1.28 (s, 15H, Cp*), 2.17 and 2.88 (2 × sept d, 1H, $J = 7$, 2, C*H*Me$_2$), 4.14 (dt, 1H, $J = 7.5$, 3, NCH), 4.28 (dd, 1H, $J = 10.5$, 9.5, OCH), 4.61 (m, 3H, 3 × OCH), 4.92 (ddd, 1H, $J = 10.5$, 6, 2, NCH), 7.78 (m, 1H, C$_6$H$_4$), 7.85 (m, 2H, C$_6$H$_4$), 8.19 (m, 1H, C$_6$H$_4$) [water of solvation observed at δ 1.65]. MS (FAB$^+$): *m/z* 573, [M]$^+$; and 537, [M−HCl]$^+$.

3.1.6. [IrCl(ⁱPr-benbox)Cp][SbF$_6$] (**4b**)*

Complex **4b** was prepared from [IrCl$_2$Cp*]$_2$ (80 mg, 0.10 mmol), ⁱPr-benbox (66 mg, 0.22 mmol) and NaSbF$_6$ (57 mg, 0.26 mmol) in 138 mg yield, 77%. Anal. Calc. for $C_{28}H_{39}ClF_6IrN_2O_2Sb$: C, 37.41; H, 4.37; N, 3.12. Found: C, 37.04; H, 4.54; N, 2.74%. ^{1}H-NMR (250 MHz) δ 0.61, 0.90, 0.98 and 0.99 (4 × d, 3H, $J = 7$, CH*Me*$_2$), 1.26 (s, 15H, Cp*), 2.12 and 3.01 (2 × sept d, 1H, $J = 7$, 2.5, C*H*Me$_2$), 4.13 (dt, 1H, $J = 6$, 3, NCH), 4.40 (dd, 1H, $J = 10$, 9, OCH), 4.66 (m, 3H, 3 × OCH), 5.09 (ddd, 1H, $J = 10$, 5.5, 2, NCH), 7.77 (m, 1H, C$_6$H$_4$), 7.86 (m, 2H, C$_6$H$_4$), 8.18 (m, 1H, C$_6$H$_4$). MS (FAB$^+$): *m/z* 663, [M]$^+$; and 363, [IrClCp*]$^+$.

3.1.7. [RhCl(Ph-benbox)Cp][SbF$_6$] (**5a**)*

Complex **5a** was prepared from [RhCl$_2$Cp*]$_2$ (60 mg, 0.10 mmol), Ph-benbox (79 mg, 0.21 mmol) and NaSbF$_6$ (55 mg, 0.21 mmol) in 147 mg yield, 84%. Anal. Calc. for $C_{34}H_{35}ClF_6N_2O_2RhP$: C, 51.89; H, 4.48; N, 3.56. Found: C, 51.47; H, 4.37; N, 3.42% (analysis on PF$_6$ salt). ^{1}H-NMR δ 0.98 (s, 15H, Cp*), 4.54 (dd, 1H, $J = 9$, 2, OCH), 4.69 (t, 1H, $J = 10$, OCH), 4.86 (dd, 1H, $J = 9$, 5.5, OCH), 5.07 (t, 1H, $J = 9$, OCH), 5.38 (dd, 1H, $J = 8$, 2, NCH), 5.55 (dd, 1H, $J = 10.5$, 5.5, NCH), 6.94 (m, 2H, Ph), 7.29 (m, 3H, Ph), 7.39 (m, 3H, Ph), 7.52 (d, 2H, $J = 8$, Ph), 7.92 (t, 1H, $J = 7$, C$_6$H$_4$), 7.99 (dt, 1H, $J = 1$, 8, C$_6$H$_4$), 8.17 (d, 1H, $J = 8$, C$_6$H$_4$), 8.30 (d, 1H, $J = 8$, C$_6$H$_4$). MS (FAB$^+$): *m/z* 641, [M]$^+$; and 605, [M−HCl]$^+$.

*3.2. Preparations of [Rh(OH$_2$)(bis-oxazoline)(arene)][SbF$_6$]$_2$ (**6–8**)*

A solution of AgSbF$_6$ (one equivalent) in acetone (0.5 cm^3) was added to a solution of [RhCl(bis-oxazoline)Cp*][SbF$_6$] (one equivalent) in CH$_2$Cl$_2$ (4 cm^3), giving an immediate precipitate of AgCl and a yellow–orange coloured solution. The solution was stirred for 30 min at room temperature (protected from light), and was filtered through Celite in air to remove AgCl. Evaporation, followed by recrystallisation from acetone–ether, afforded orange powders. The scale and yields for individual complexes are shown below.

3.2.1. [Rh(OH$_2$)(ⁱPr-box)Cp][SbF$_6$]$_2$ (**6**)*

Complex **6** was prepared from **1a** (70 mg, 0.095 mmol) and AgSbF$_6$ (33 mg, 0.096 mmol) in 85 mg yield, 94%. Anal. Calc. for $C_{22}H_{37}F_{12}N_2O_3RhSb_2$: C, 27.76; H, 3.92; N, 2.94. Found: C, 28.11; H, 4.31; N, 2.51%. ^{1}H-NMR (acetone-d_6, 223 K) δ 0.65, 0.99, 1.07 and 1.08 (4 × d, 3H, $J = 6$, CH*Me*$_2$), 1.94 (s, 15H, Cp*), 2.30 (m, 1H, C*H*Me$_2$), 2.67 (m, 1H, C*H*Me$_2$), 3.88 (br, uncoordinated H$_2$O), 4.70 (m, 1H, NCH), 4.85 (t, 1H, $J = 11$, OCH), 4.94 (t, 1H, $J = 11$, OCH), 5.10 (m, 1H, NCH), 5.24 (m, 2H, 2 × OCH), 7.00 (br, coordinated H$_2$O). MS (ES$^+$): *m/z* 698, [M−H$_2$O+SbF$_6$]$^+$.

3.2.2. [Rh(OH$_2$)(ⁱPr-bop)Cp][SbF$_6$]$_2$ (**7**)*

Complex **7** was prepared from **2a** (100 mg, 0.13 mmol) and AgSbF$_6$ (45 mg, 0.13 mmol) in 120 mg yield, 93%. Only characterised in solution. ^{1}H-NMR (400 MHz, 213 K, acetone-d_6) δ 0.54, 0.96 (2 × br s, 3H, CH*Me*$_2$), 1.04 (br, 6H, CH*Me*$_2$), 1.55 and 1.77 (2 × br s, 3H, CMe$_2$), 1.90 (s, 15H, Cp*), 2.30, 2. 16 (2 × br m, 1H, C*H*Me$_2$), 3.9 (br s, uncoordinated H$_2$O) 4.36 (t, 1H, $J = 10$, OCH), 4.52 (m, 1H, NCH), 4.88 (t, 1H, $J = 10$, OCH), 4.25, 4.53, 4.79, 4.89, 5.00, 5.08 (6 × br m, 1H, oxazoline), 6.55 (br s, 2H, coordinated H$_2$O). MS (FAB$^+$): *m/z* 740, [M−H$_2$O+SbF$_6$]$^+$.

3.2.3. [Rh(OH$_2$)(ⁱPr-benbox)Cp][SbF$_6$]$_2$ (**8**)*

Complex **8** was prepared from **4a** (60 mg, 0.074 mol) and AgSbF$_6$ (27 mg, 0.078 mmol) in 73 mg yield, 96%. Anal. Calc. for $C_{28}H_{41}F_{12}N_2O_3RhSb_2$: C, 32.71; H, 4.02; N, 2.72. Found: C, 32.59; H, 3.99; N, 2.64%. ^{1}H-NMR (acetone-d_6) δ 0.58, 0.85, 0.98, 1.19 (4 × d, 3H, $J = 7$, CH*Me*$_2$), 1.46 (s, 15H, Cp*), 2.10 (m, 1H, C*H*Me$_2$), 2.41 (m, 1H, C*H*Me$_2$), 4.46 (m, 1H, NCH), 4.60 (t, 1H, $J = 10$, OCH), 4.71 (m, 1H, NCH), 5.07 (m, 3H, 3 × OCH), 7.47 (s, 2H, coordinated H$_2$O), 8.13 (m, 3H, C$_6$H$_4$), 8.38 (m, 1H, C$_6$H$_4$). MS (FAB$^+$): *m/z* 774, [M−H$_2$O+SbF$_6$]$^+$.

3.3. Catalysis reactions

The catalyst was prepared in situ from the chloride complex and one equivalent of AgSbF$_6$ in CH$_2$Cl$_2$ under a nitrogen atmosphere; the solution was filtered through Celite into a Schlenk tube to remove AgCl. Methacrolein (1 mmol) and 2,6-di-*t*-butylpyridine [33] (one equivalent/mol catalyst) were added to the catalyst solution (0.05 mmol) in CH$_2$Cl$_2$ (2 cm^3). The resulting yellow solution was stirred for 5 min before addition of cyclopentadiene (2 mmol). At the end of the reactions, 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 after conversion to the acetal with (2*R*,4*R*)-pentanediol [34].

3.4. X-ray structure determinations

Data for **1a** were collected on a Bruker Apex 2000 CCD diffractometer. The structure of **2a** has been reported previously [21]. Data for **3a** were collected on a Siemens P4 diffractometer using graphite monochromated Mo–K_α radiation, $\lambda = 0.7107$ Å. The data were corrected for Lorentz and polarisation effects and semi-empirical absorption corrections based on ψ scans were applied. The structures were solved by Patterson methods and refined by full-matrix least-squares on F^2 using the program SHELXTL-PC [35]. 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. For **1a**, the cation was refined without difficulty whilst the three (SbF_6) anions were refined as disordered on special sites with 1/3, 1/3 and 1/2 occupancy to give a total 1.17:1.00 ratio of SbF_6:Rh. Excess electron density on a 1/12 special position was refined as O (of H_3O^+), however the remaining H_3O (1/12) was not located. The F atoms treated as disordered were refined with isotropic displacement parameters.

4. Supplementary material

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 189784 for **1a**, 182/648 for **2a**, and 189785 for **3a**. 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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