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Arene–ruthenium complexes with salicyloxazolines: diastereoselective synthesis, configurational stability and applications as asymmetric catalysts for Diels–Alder reactions

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Reaction of the dimers $[RuCl_2(\eta^6\text{-arene})]_2$ (arene = benzene, *p*-cymene, mesitylene) with salicyloxazolines in the presence of NaOMe gives complexes [RuCl(R-saloxaz)(arene)] (**1**–**5**) which have been fully characterised. Complexes [RuL(^{i}Pr-saloxaz)(mes)]Y (L = py, 2-Mepy, 4-Mepy; PPh_3; $Y^- = SbF_6$ or BPh_4) **6**–**9** were prepared by treating the chloride **2a** with ligand L and NaY ($Y^- = SbF_6$ or BPh_4) in methanol at reflux. Halide complexes [RuX(^{i}Pr-saloxaz)-(mes)] (X = Br, **10**; X = I, **11**) were synthesised by treating **2a** with $AgSbF_6$ then with 1.2 equivalents of KBr or NaI, the methyl complex [RuMe(^{i}Pr-saloxaz)(mes)] **12** was synthesised from **2a** by reaction with MeLi. Five complexes, [RuCl(^{i}Pr-saloxaz)(mes)] **2a**, [RuCl(^{t}Bu-saloxaz)(*p*-cymene)] **3b**, [RuCl(Ph-saloxaz)(mes)] **5a**, [Ru(4-Mepy)(^{i}Pr-saloxaz)(mes)][SbF_6] **7**, and [Ru(PPh_3)(^{i}Pr-saloxaz)(mes)][SbF_6] **9**, have been characterised by X-ray crystallography. Treatment of complexes **1**–**5** with $AgSbF_6$ gives cationic species which are enantioselective catalysts for the Diels–Alder reaction of acroleins with cyclopentadiene, the effect of substituents on enantioselectivity has been examined.

In recent years chiral half-sandwich arene–ruthenium complexes have proved to be extremely useful in catalytic asymmetric synthesis; the best example so far being the transfer hydrogenation of ketones with enantiomeric excesses (ee's) of >99% using an arene–ruthenium catalyst containing a chiral diamine based ligand.[1] In addition their pseudo-tetrahedral geometry makes them particularly suitable for the investigation of stereochemistry at the metal centre.[2,3] Arene–ruthenium complexes $[RuCl(L^*)(arene)]^{n+}$ (n = 0, 1; L* = chiral bidentate ligand with hard donor atoms) have attracted much study. Examples include amino acids,[4] salicylaldimines,[5–10] pyridyl imines,[11,12] anionic pyrrolylimines,[13] pyridyloxazolines,[14–16] and we[17] and others[18,19] have reported various bisoxazoline complexes. To use such complexes to study the mechanism of substitution at the metal and to understand their enantioselectivity in catalysis it is essential to know the stability of chirality at the metal.[3,20,21] In general, cationic complexes (n = 1) formed from neutral bidentate ligands tend to give complexes in which the chirality at the metal is stable (at least for several hours or days). However, complexes of anionic chelates often epimerise rapidly at the metal centre even at low temperatures ($t_{½}$ minutes). Such epimerisation is often fast on a chemical timescale but slow on an NMR timescale and this has led to erroneous conclusions regarding stability of the chirality at the metal.[20,22]

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.[23] Most of these studies involve bis(oxazolines) and phosphino-oxazolines however some work on the coordination chemistry of salicyloxazolines has been reported.[24–26] A recent report of an arene–ruthenium complex of a salicyloxazoline[9] prompts us to report the synthesis and properties of some related complexes, in particular an assessment of factors controlling the stereochemistry at the metal, the ease of epimerisation at the metal and some applications as asymmetric catalysts for Diels–Alder reactions.

Results and discussion

The complexes **1**–**5** were prepared by refluxing the relevant dimer, $[RuCl_2(\eta^6\text{-arene})]_2$, with two equivalents of ligand and a slight excess of sodium methoxide. All the complexes were isolated as orange powders and are characterised by ^{1}H NMR spectroscopy, mass spectrometry and microanalysis (except **3a**,**b**) and in some cases X-ray diffraction, **2a**, **3b** and **5a**. Arene–ruthenium complexes $[RuCl(L)(arene)]^{n+}$ (n = 0, 1; L = achiral C_1-symmetry bidentate ligand) have a chiral metal centre. Thus, complex **1** is chiral at the metal and exists as a racemate. Complexes **2**–**5** also contain a chiral 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.

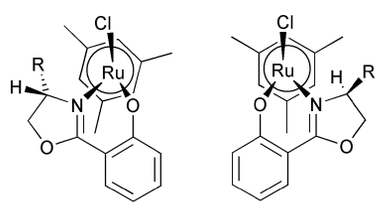
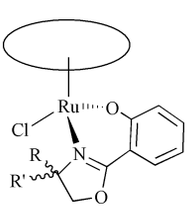


Fig. 1 The two diastereomers of [RuCl(R-saloxaz)(arene)][SbF_6]



	Arene	R	R^1
1a	Mesitylene	Me	Me
2a	Mesitylene	H	^{i}Pr
2b	*p*-Cymene	H	^{i}Pr
2c	Benzene	H	^{i}Pr
3a	Mesitylene	H	^{t}Bu
3b	*p*-Cymene	H	^{t}Bu
3c	Benzene	H	^{t}Bu
4a	Mesitylene	H	CH_2Ph
5a	Mesitylene	H	Ph

The ^{1}H NMR spectrum of the salicyldimethyloxazoline ligand shows two singlets, one for the OCH_2 protons and one for the CMe_2 group, in addition to the aromatic protons. When complexed to ruthenium in **1** the mirror plane is lost and the oxazoline gives rise to two mutually coupled doublets at δ 4.10

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and 4.29 (OCHH[1]) and two singlets at δ 1.41 and 1.62 (CMeMe[1]). These observations are consistent with the chiral nature of the ruthenium atom and indicate that epimerisation at the ruthenium centre is slow on the NMR timescale at room temperature. The mass spectrum of **1** shows ions centred at *m*/*z* 448 and 413 corresponding to $[M]^+$ and $[M - Cl]^+$.

As mentioned above, **2**–**5** can in principle form two diastereomers **A** and **B**. It is noteworthy that in the vast majority of cases, chiral anionic bidentate ligands such as amino acidates[4] and salicylaldimines derived from 1-phenylethylamine[5–9] give rise to two diastereomers when complexed to "(arene)RuCl". These diastereomers interconvert slowly on the NMR timescale, and thus two sets of signals are observed. Complex **2a** shows only one set of well-resolved signals in the ^{1}H NMR spectrum suggesting that only one diastereomer was formed, or that epimerisation at ruthenium *i.e.* interconversion of the diastereomers, is fast on the NMR timescale. The spectrum was recorded at 233 K and gave no evidence for a second isomer. Given that the epimerisation of **1** is slow on the NMR timescale at room temperature it is unlikely that epimerisation of **2a** is fast on the NMR timescale at 233 K. Furthermore, epimerisation of related arene–ruthenium salicylaldimine complexes is also slow on the NMR timescale even at elevated temperature.[5] Thus, we conclude that **2a** is formed with very high diastereoselectivity. In order to confirm which isomer is formed we have carried out an X-ray structure determination of **2a**. The structure (discussed below) shows the isopropyl oxazoline substituent pointing towards the chloride, rather than on the same side as the arene, *i.e.* isomer **B**. This is the same situation as was found for the corresponding pyridyloxazoline complex reported earlier.[16] The isomers **A** and **B** may in principle be distinguished by NOEs between the CH^{i}Pr and the arene; isomer **A** is expected to show an NOE between the ^{i}Pr and the arene whilst isomer **B** is expected to show an NOE between the NCH and the arene. The observation of NOEs (cross peaks in the NOESY spectrum) between the NCH and both signals of the mesitylene and the absence of an NOE between the methyls of the ^{i}Pr and the mesitylene confirmed that isomer **B** is also maintained in solution.

In order to assess the influence of the oxazoline substituent on the diastereoselectivity we have synthesised the related complexes **3a**–**5a**. The ^{1}H NMR spectrum of **3a** showed one set of well-resolved signals consistent with the presence of only one isomer, presumably isomer **B**. However, over a period of time other signals grew in consistent with free ^{t}Bu-saloxazH ligand, thus it appears that this complex is unstable in solution. In contrast, the ^{1}H NMR spectra of **4a** and **5a** each showed the presence of two isomers. Both of these complexes contain an aryl in the oxazoline substituent that may give rise to a β-phenyl effect as has been observed in complexes of salicylaldimines derived from 1-phenylethylamine.[7,27] The β-phenyl effect is characterised by upfield shifts of the signals for the π-bound arene in the ^{1}H NMR spectrum. The benzyl-substituted complex **4a** shows signals for two isomers in the ratio 4:1 with the $C_6H_3Me_3$ protons being observed at δ 4.95 (major) and 4.89 (minor) respectively. These are at very similar chemical shift to those observed for **2a** and **3a** (both at δ 4.89) suggesting there is no β-phenyl interaction in either isomer. (No β-phenyl interaction was found in the related benzyl-substituted pyridyloxazoline complex[16]). To establish which isomer, **A** or **B**, was preferred in solution a NOESY spectrum was run. The NOESY spectrum showed cross peaks between signals of the major isomer at δ 4.71 (NCH) and the peaks at δ 4.95 and 2.24 (mesitylene) as expected for isomer **B**. In addition, chemical exchange correlations were observed between the diastereotopic CH_2Ph protons at δ 2.78 (major) and 2.63 (minor) and between one of the OCH signals at δ 4.35 (major) and 4.16 (minor). These latter correlations indicate that the isomers are interconverting in solution at a rate comparable with the NOESY timescale and that the observed isomer ratio (4 : 1, **B** : **A**) therefore corresponds to the equilibrium ratio. Phenyl-substituted complex **5a** also shows two sets of signals in a 3 : 1 ratio; the mesitylene protons being observed at δ 4.10 and 1.89 (major), and 4.60 and 2.01 (minor), respectively. These are all to higher field than **2a**–**4a** but the comparatively large upfield shifts for the η-arene signals of the major isomer compared to the minor one ($\Delta\delta$ 0.5 ppm $C_6H_3Me_3$ and 0.1 ppm $C_6H_3Me_3$) suggests there may be a β-phenyl interaction in the major isomer which is expected therefore to be isomer **A**. This is in contrast to the related pyridyloxazoline complex $[RuCl(Ph\text{-}pymox)(mes)]^+$ which also exists as two isomers neither of which exhibit a β-phenyl interaction.[16] Crystals of **5a** suitable for X-ray diffraction were obtained and the structure (discussed below) showed the presence of only one diastereomer with the phenyl group pointing towards the mesitylene ring, *i.e.* isomer **A**. Crystals from this batch were dissolved in CD_2Cl_2 at −80 °C and the ^{1}H NMR spectrum recorded at this temperature showed the presence of both isomers in a 3 : 2 (**A** : **B**) ratio. On warming, the ratio of isomers did not change suggesting that the system had already reached equilibrium or that the crystals were a mixture of isomers in this ratio. The latter explanation was ruled out by dissolving crystals from the same batch in $CDCl_3$; the ^{1}H NMR spectrum showed the presence of both isomers in a different ratio, 3 : 1. Thus, epimerisation is clearly taking place in solution, even at −80 °C, as found for related salicylaldimine complexes,[7] and these isomer ratios correspond to equilibrium ratios that are clearly solvent dependent. The ^{1}H NMR spectrum recorded at 323 K (in $CDCl_3$) showed linewidth broadening of the signals providing further confirmation that epimerisation is occurring, though coalescence had not occurred by this temperature. The high field shifts for the mesitylene signals of the major isomer are consistent with isomer **A** as found in the X-ray structure. A NOESY spectrum recorded at 203 K showed an NOE between the NCH proton and the $C_6H_3Me_3$ protons at δ 2.01 in the minor isomer, as expected for isomer **B**. Unfortunately, NOE signals between the phenyl and mesitylene are not helpful because the phenyl signals overlap for the two isomers. In some instances, when recording ^{1}H NMR spectra of **5a** we observed quite broad signals suggesting that the rate of epimerisation had increased. We surmised this might be due to the presence of water (D_2O) in the NMR solvent. When dried CD_2Cl_2 was used sharp signals were observed at room temperature. Addition of two drops of D_2O to this sample gave broad signals. Recording the spectrum of the same sample at 233 K gave well-resolved signals in an unchanged diastereomer ratio. These observations suggest that traces of water increase the rate of epimerisation, though the equilibrium diastereomer ratio is relatively unaffected. It is well established for salicylaldimine complexes that the rate of epimerisation is much faster when water is coordinated in place of chloride.[5,7] Since separate signals due to water coordinated species are not observed for **5a**, the equilibrium between chloride and water coordinated species must lie heavily in favour of chloride coordinated. The significant effect of traces of water on the epimerisation are consistent with epimerisation occurring by loss of chloride rather than opening of the chelate ring.

Having established that the nature of the oxazoline substituent affects the diastereoselectivity we examined the effect of arene substitution. The ^{1}H NMR spectra of isopropyl-oxazoline complexes **2b** (*p*-cymene), and **2c** (C_6H_6), each showed the presence of two isomers with very similar chemical shifts, indeed many signals overlap, in approximately a 9 : 1 ratio. (Note, complex **2b** was previously reported to be formed as a 77 : 23 mixture of diastereomers[9]). The signals are slightly broad at room temperature, particularly those of the minor isomer, suggesting the isomers are in dynamic equilibrium. NOESY spectra of **2b** (233 K) and **2c** (263 K) were run to try and determine which is the major isomer in solution. For **2c** an NOE was observed between the NCH proton (δ 4.60) and the η-C_6H_6 (δ 5.60) consistent with the major isomer being isomer

B with the isopropyl substituent orientated towards the chloride rather than the η-C_6H_6 ring. The spectrum also showed an exchange cross peak between the isopropyl CH signals at δ 2.67 (major) and 2.41 (minor) confirming that interconversion of the two diastereomers is occurring on the NOESY timescale. For **2b** overlap of signals prevented unambiguous assignment of some of the observed NOEs, however no NOEs were observed between the isopropyl substituent of the oxazoline and the *p*-cymene which would be expected for isomer **A**. Hence we assume that the major isomer of **2b** has isomer **B** structure as found for **2a** and **2c**. Increased diastereoselectivity with mesitylene in place of *p*-cymene or benzene was also found in the corresponding pyridyloxazoline cations $[RuCl(^{i}Pr\text{-pymox})(arene)]^{+}$.[16] Increasing the steric bulk of the oxazoline substituent from ^{i}Pr to ^{t}Bu is expected to further disfavour isomer **A** and therefore increase the diastereoselectivity. In agreement with this, the ^{1}H NMR spectrum of *tert*-butyl-substituted complex **3b** showed the presence of only one diastereomer. The X-ray structure (see below) confirms this has isomer **B** structure, as expected.

The structures of **2a**, **3b** and **5a** are shown in Figs. 2–4, respectively, with selected bond lengths and angles in Table 1. In all cases only one diastereomer is present in the crystal.[28] Complexes **2a** and **3b** both have isomer **B** structure with the oxazoline substituent pointing towards the chloride. Since the S_C-configured ligands were used the configuration at ruthenium is found to be R_{Ru} (arene > Cl > O > N).[29] In contrast, in **5a** the phenyl substituent is oriented more towards the mesitylene ring with the hydrogen towards chloride. In this case the R_c-configured ligand was used, hence the configuration at

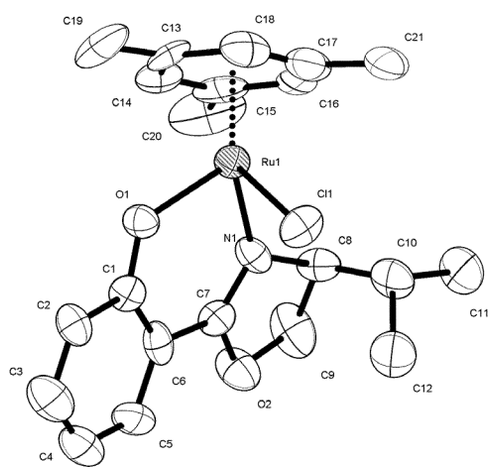


Fig. 2 The molecular structure of **2a** showing the atom label scheme and 50% displacement ellipsoids; H-atoms have been omitted for clarity.

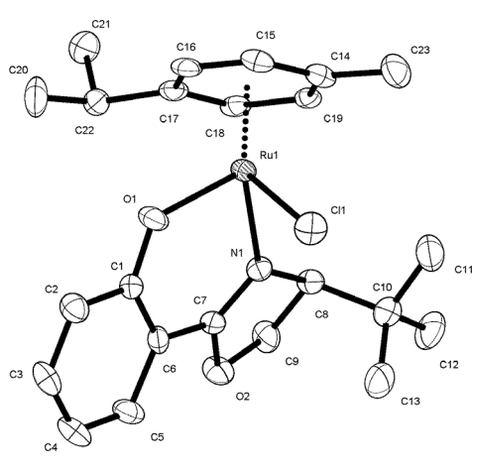


Fig. 3 The molecular structure of **3b** showing the atom label scheme and 50% displacement ellipsoids; H-atoms have been omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for complexes **2a**, **3b** and **5a**

	2a	**3b**	**5a**
Ru–N	2.068(9)	2.124(4)	2.106(5)
Ru–O(1)	2.067(7)	2.058(4)	2.092(4)
Ru–Cl(1)	2.426(3)	2.415(2)	2.412(2)
O(1)–C(1)	1.296(12)	1.303(7)	1.317(7)
C(1)–C(6)	1.407(16)	1.410(8)	1.424(9)
C(6)–C(7)	1.446(15)	1.443(7)	1.443(11)
N–C(7)	1.294(13)	1.298(7)	1.285(9)
N–Ru–O(1)	86.9(3)	88.3(2)	82.9(2)
N–Ru–Cl(1)	87.2(3)	86.9(1)	84.2(1)
Cl–Ru–O(1)	83.5(2)	84.3(1)	86.1(1)
N–C(7)–C(6)–C(1)	13.6	23.5	35.7

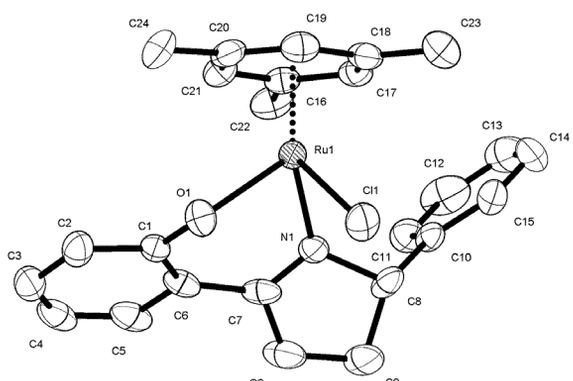


Fig. 4 The molecular structure of **5a** showing the atom label scheme and 50% displacement ellipsoids; H-atoms and solvent have been omitted for clarity.

ruthenium is also R_{Ru}. There are no major differences in bond lengths around the metal in the three compounds. The Ru–N distance, 2.106(5) Å, in **5a** is intermediate between those of **2a** and **3b**, 2.068(9) and 2.124(4) Å, respectively. However the Ru–O(1) distance in **5a**, 2.092(4) Å, is slightly longer than those, 2.067(7) and 2.058(4) Å, in **2a** and **3b**, respectively. The Ru–Cl(1) distances are nearly equal in the three complexes. Perhaps more significantly, the chelate bite angle of **5a** [82.9(2)°] is considerably smaller than those [86.9(3) and 88.3(2)°] of **2a** and **3b**, respectively; the corresponding angle in **2b** is 86.7(3)°.[9] In addition, in **5a** the O–Ru–Cl angle, 86.1(1)°, is slightly larger the N–Ru–Cl angle, 84.2(1)°, whilst in **2a**, **2b**[9] and **3b**, the opposite is true. Thus, in **5a** the twisting of the salicyloxazoline ligand may help relieve steric interactions between the phenyl and the mesitylene whilst in **2a**, **2b** and **3b** the twist in the opposite direction may reduce steric interaction between the oxazoline substituent and the chloride. Another significant difference occurs in the dihedral angles between the phenol and oxazoline rings, in **5a** this angle is 35.7° which is significantly larger than the 13.6 and 23.5° observed for **2a** and **3b**, respectively. This twist within the salicyloxazoline ligand may also allow the phenyl to move away from the mesitylene in **5a** and hence relieve adverse steric interactions. In **5a** the separation between the centroids of the two arenes and the angle between the ring normals are 5.10 Å and 41.7°, respectively. A Schiff-base complex [RuCl(pyrrolealdimine)(C_6H_6)], which exhibits a 'β-phenyl-effect',[13] has corresponding values of 4.74 Å and 51.3°. This evidence combined with the upfield shift of the mesitylene signals of the major isomer in the ^{1}H NMR spectrum suggests that there is a β-Ph-effect in this isomer.

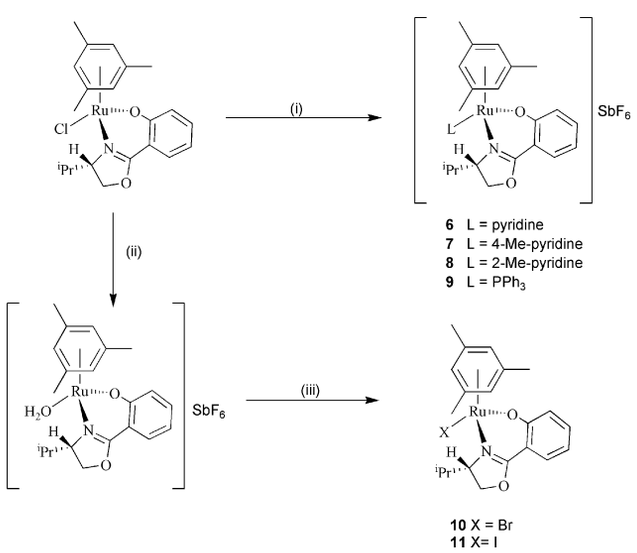
The diastereoselectivities of the alkyl-substituted salicyloxazoline complexes compare favourably with those of many ruthenium half-sandwich complexes. For example, arene–ruthenium complexes with pyridylimines, salicylaldimines and pyrrolecarbaldimines derived from (*S*)-1-phenylethylamine all form mixtures of diastereomers with equilibrium diastereomer

Table 2 Selected bond lengths (Å) and angles (°) for complexes **7** and **9**

	7		**9** (1)	**9** (2)
Ru–N(1)	2.093(4)	Ru–N(1)	2.100(4)	2.093(4)
Ru–O(1)	2.045(4)	Ru–O(1)	2.049(3)	2.057(4)
Ru–N(2)	2.142(5)	Ru–P(1)	2.371(1)	2.377(2)
O(1)–C(1)	1.295(6)	O(1)–C(1)	1.309(6)	1.305(6)
C(1)–C(6)	1.411(8)	C(6)–C(1)	1.412(7)	1.418(7)
C(6)–C(7)	1.455(7)	C(6)–C(7)	1.432(6)	1.443(7)
N(1)–C(7)	1.288(6)	N(1)–C(7)	1.312(6)	1.292(6)
N(1)–Ru–O(1)	84.4(2)	N(1)–Ru–O(1)	83.6(2)	84.5(2)
N(1)–Ru–N(2)	91.5(2)	N(1)–Ru–P(1)	99.0(1)	96.8(1)
N(2)–Ru–O(1)	83.4(2)	P(1)–Ru–O(1)	83.1(1)	80.8(1)
N(1)–C(7)–C(2)–C(1)	10.3	N–C(7)–C(2)–C(1)	5	5.3

ratios ranging from 67 : 33[12] to 86 : 14.[7,8,13] In these cases the diastereoselectivity is affected by the orientation of the CH(Me)Ph group which can rotate about the N–C bond. However, for **2**–**5** the oxazoline-substituents (R) are only able to rotate about the C–C bonds not the C–N bond, hence they are orientated either towards the η-ring (isomer **A**) or towards the chloride ligand (isomer **B**). Thus, when the oxazoline substituent is bulky in three dimensions *e.g.* ^{t}Bu and ^{i}Pr, isomer **A** is particularly unfavourable and a high diastereoselectivity is observed. However, the planar nature of a phenyl or benzyl substituent reduces unfavourable steric interactions with the arene and attractive π–π interactions may even help stabilise isomer **A** leading to reduced diastereoselectivity, and even leading to isomer **A** being preferred for the phenyl substituent. Since epimerisation at the metal occurs on the chemical timescale the observed diastereoselectivities reflect a thermodynamic preference.

As explained above, the diastereoselectivity is in large part due to interactions between the oxazoline substituent and the arene or chloride. In addition, epimerisation is believed to occur *via* loss of chloride. Thus, changing the chloride ligand is expected to alter both the diastereoselectivity and the rate of epimerisation. Knowledge of these effects is important to understand the selectivity of such complexes in catalysis. Hence, we have investigated the substitution of chloride in **2a** with pyridines, PPh_3, OH_2, Br, I or Me (Scheme 1).



Scheme 1 Reagents and conditions: (i) L, $NaSbF_6$ reflux in MeOH; (ii) $AgSbF_6$; (iii) NaX

Complexes [RuL(^{i}Pr-saloxaz)(mes)]SbF_6 (L = py, 2-Mepy, 4-Mepy) **6**–**8** were prepared by treating the chloride **2a** with ligand L and $NaSbF_6$ in methanol at reflux. The ^{1}H NMR spectrum of **6** shows the presence of two diastereomers in an approximate ratio of 5 : 1 though the signals are slightly broad at room temperature and there is evidence for some free pyridine, suggesting that the two isomers are interconverting at a similar rate to the NMR timescale. This ratio did not change with time indicating the equilibrium position had been reached. Hence the spectrum was recorded at low temperature (253 K); sharp signals for two isomers were observed in an 84 : 16 ratio. The isopropyl signals of the major isomer at δ −0.09, 0.87 (CH*MeMe*′) and 1.36 (C*H*MeMe′) are to higher field than those of the minor isomer (δ 0.74, 1.11 and 2.41, respectively). These upfield shifts for the major isomer are thought to be due to the 'ring-current' effect of the pyridine ring, indicating that the isopropyl group is in close proximity to the pyridine in the major isomer (*i.e.* isomer **B**). In an attempt to gain further information the related 4-methylpyridine complex **7** which should give a simpler ^{1}H NMR spectrum was synthesised. The ^{1}H NMR spectrum of **7** is similar to that for **6**, showing two sets of broad signals in a ratio of 85 : 15 with the isopropyl signals of the major isomer shifted to higher field compared with the chloride **2a**. The NOESY spectrum (at 233 K) showed cross-peaks for the major isomer between the isopropyl signals at δ −0.05 (Me), and 1.27 (CH), and the 4-*Me*-py protons at δ 8.55. These NOEs are expected for isomer **B** and are consistent with the highfield shifts of the isopropyl protons caused by the ring-current effect of the 4-methylpyridine. When the NOESY spectrum was recorded at room temperature, additional cross-peaks due to chemical exchange between isomer **A** and **B** were observed, for example, between the signals for the isopropyl methyl groups at δ −0.05 and 0.83 (isomer **B**) and those at δ 0.68 and 1.06 respectively (isomer **A**).

Crystallisation of **7** from CH_2Cl_2–ether gave X-ray quality crystals that had uniform morphology. The X-ray crystal structure is shown in Fig. 5 with selected bond distances and angles in Table 2. The crystals are of a single diastereomer with the isopropyl group directed towards the 4-methylpyridine, which means the configuration of the Ru centre, can be assigned as (R_{Ru}) (mes > O > $N_{(ox)}$ > $N_{(4\text{-Me-py})}$).[29] The Ru–O and Ru–$N(1)_{ox}$ bond lengths [2.045(4) and 2.093(4) Å, respectively] in **7**, are similar to those in the chloride precursor **2a** [2.062(7) and

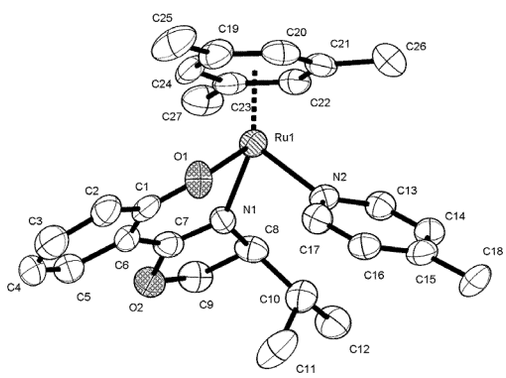


Fig. 5 Structure of the cation of **7** showing the atom label scheme and 50% displacement ellipsoids. H atoms have been omitted for clarity.

2.075(10) Å, respectively]. The effect of replacing chloride with the larger 4-methylpyridine is most noticeable in the bond angles. Thus the chelate angle 84.4(2)° in **7** is slightly less than that, 87.0(3)°, in **2a**, whilst the N(1)–Ru–N(2) angle, 91.5(2)° is larger than the N(1)–Ru–Cl(1), 87.2(3), of **2a** presumably due to increased interactions between the isopropyl substituent and the 4-methylpyridine in **7** rather than with the chloride in **2a**. The length of the Ru–$N(2)_{py}$ bond in **7** [2.142(5) Å], is similar to that, 2.138(5) Å,[7] in [Ru(4-Me-py)(salald)(C_6H_6)]PF_6 (salald = aldimine from salicylaldehyde and 1-phenylethylamine). Dissolution of the X-ray crystal sample at approximately 193 K and then recording the ^{1}H NMR spectrum at 203 K gave a spectrum that contained two sets of well-resolved signals with a diastereomer ratio of 93 : 7. On warming to 213 K, then 233 K, the diastereomer ratio changed to 92 : 8, then 90 : 10 and finally reached equilibrium (85 : 15) at 253 K, after which there was no further change with time. These observations show that epimerisation occurs even at 203 K over a period of 1–2 h. The ^{1}H NMR spectrum of the mother-liquor from the crystallisation also showed two isomers in 85 : 15 ratio, confirming that epimerisation had occurred to restore the equilibrium. These findings are consistent with those for [Ru(4-Me-py)(salald)(C_6H_6)]PF_6,[7] for which dissolution of crystals in d_6-acetone at −80 °C showed the complex to be one diastereomer by ^{1}H NMR, which on warming to −35 °C, epimerised to reach equilibrium after several hours.[7] Thus, the low-temperature dissolution and NOESY ^{1}H NMR experiments confirm that the solid state structure of **7** (isomer **B**) is also the major diastereomer in solution.

The complex [Ru(2-Me-py)(^{i}Pr-saloxaz)(mes)]SbF_6 **8** was synthesised to evaluate the steric effect of 2-methylpyridine compared to 4-methylpyridine. In contrast to **6** and **7**, the ^{1}H NMR spectrum of **8** at room temperature contains only one set of signals some of which are broadened, in particular that for H6 of the 2-methylpyridine. Notably, the isopropyl methyl signals were observed at δ 0.65 and 1.10, *i.e.* neither shifted to much higher field as in the major isomers of **6** and **7**. This suggests that the isopropyl is orientated towards the mesitylene ring such that shielding by the aromatic ring current of 2-methylpyridine is not possible, *i.e.* that the complex adopts isomer **A** structure. The ^{1}H NMR spectrum recorded at 233 K showed the presence of more than two species (including uncoordinated 2-methylpyridine). The NOESY spectrum (CD_2Cl_2 at 233 K) at this temperature showed an NOE in the major species between the C*H*MeMe′ signal (at δ 2.50) and the $C_6H_3Me_3$ singlet (at δ 5.25) confirming that the isopropyl group is orientated towards the mesitylene (isomer **A**), rather than towards the 2-methylpyridine. This is expected, since steric clashes between the isopropyl and the *ortho*-methyl of the 2-methylpyridine are likely to be severe. The minor species included uncoordinated 2-methylpyridine but others could not be identified. The analogous Schiff-base complex [Ru(2-Me-py)(salald)(C_6H_6)]PF_6[7] was reportedly formed with high diastereoselectivity, and additional NMR signals were attributed to rotamers of the complex, due to restricted rotation about the Ru–N_{py} bond.

The complex [Ru(PPh_3)(^{i}Pr-saloxaz)(mes)]Y (Y = SbF_6, BPh_4) **9** was prepared by refluxing **2a** and PPh_3 in methanol in the presence of NaY. The BPh_4 salt crystallised more easily so data are reported for this salt. The ^{1}H NMR spectrum of **9** showed signals due to two diastereomers in a 50 : 50 ratio; in contrast to complexes **6**–**8**, all the signals were sharp at room temperature. The absence of diastereoselectivity suggests that, as a result of the greater steric bulk of PPh_3 compared to pyridine, interactions between the isopropyl and PPh_3 in isomer **B** balance any unfavourable interactions between the isopropyl and mesitylene in isomer **A**. The ^{31}P{^{1}H} NMR spectrum showed two signals at δ 30.13 and 30.90 typical for PPh_3 coordinated to arene–ruthenium.[30] To fully assign the peaks in the ^{1}H NMR spectrum to the particular diastereomer, **A** or **B**, combinations of ^{1}H–^{1}H COSY, ^{1}H-decoupling and ^{1}H–^{1}H NOESY experiments were carried out. A NOESY spectrum at 300 K showed evidence of chemical exchange between the isomers hence the NOESY spectrum was also recorded at 233 K. The NOESY spectrum of **9** at 233 K showed an NOE between the mesitylene signal at δ 5.06 and the isopropyl hydrogen at δ 2.08 and NOEs between the two isopropyl methyls at δ 0.97 and 0.92 with the mesitylene signal at δ 1.68, indicating that all these signals arise from the diastereomer in which the isopropyl group is orientated towards the mesitylene (isomer-**A**). The isopropyl methyl signals of the other isomer (isomer **B**) occur at δ 0.00 and 0.58, *i.e.* to significantly higher field due to the presence a ring current from the adjacent PPh_3. At room temperature the NOESY spectrum on this sample showed chemical exchange cross-peaks, *e.g.* between the isopropyl methyl at δ 0.00 (isomer **B**) and δ 0.97 (isomer **A**) and additional NOEs between signals in one isomer and signals in the other isomer that are non-interchangeable, *e.g.* between δ 2.08 for MeC*H*Me′ isomer **A** and δ 0.58 for Me′CH*Me* isomer **B**. The observation of chemical exchange cross-peaks shows that the rate of epimerisation at room temperature is fast compared to the timescale of the NOESY experiment.

Crystallisation of the BPh_4 salt of **9** gave X-ray quality crystals and the structure of the cation is shown in Fig. 6 with selected bond distances and angles in Table 2. There are two independent molecules in the unit cell both of which are of the same diastereomer, with the isopropyl group directed towards the PPh_3 (isomer **B**), which means the configuration of the Ru centre, can be assigned as (R_{Ru}) (mes > P > O > N).[29] There are no significant differences in bond lengths and angles between the two molecules. The average Ru–O and Ru–N(1) bond lengths [2.053(3) and 2.097(4) Å, respectively] and chelate angle 84.1(2)° in **9**, are statistically the same as those in **7**. However, the N(1)–Ru–P(1) angle, [av. 97.9(1)°] is larger than the N(1)–Ru–N(2) angle, 91.5(2)° in **7** suggesting greater steric interaction between the PPh_3 and the isopropyl than the pyridine and the isopropyl. This is consistent with the lower diastereoselectivity observed with PPh_3. The Ru–P distance of 2.371(1) Å is similar to that, 2.379(3) Å, in [Ru(PPh_3)(salald)(C_6H_6)]PF_6.[7] Dissolution at approximately 193 K (over 1–2 h) of these crystals and recording the ^{1}H NMR spectrum at this temperature gave an isomer ratio (**B** : **A**) of 86 : 14 (at 193 K). The equilibration process was followed by ^{1}H NMR spectroscopy by warming the sample until the final equilibrium diastereomer ratio of 1 : 1 was observed at 300 K. Thus, crystallisation of **9** can occur diastereoselectively, but the sample epimerises to the equilibrium ratio in solution, as found for **7**. The fact that epimerisation of **6**,**7** and **9** is fast on a chemical timescale means that determination of the stereochemistry of their formation (retention or inversion) is impossible.[31]

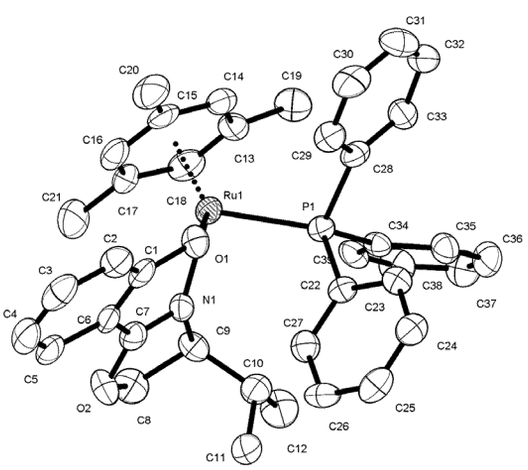


Fig. 6 The molecular structure of one of the unique molecules of **9** showing the atom label scheme and 50% displacement ellipsoids; H-atoms have been omitted for clarity.

The halide complexes [RuX(^{i}Pr-saloxaz)(mes)] (X = Br, **10**; X = I, **11**) were synthesised from the solvent complex [Ru(solvent)(^{i}Pr-saloxaz)(mes)][SbF_6] (solvent = acetone or OH_2). The latter was made by treating **2a** with $AgSbF_6$ in dichloromethane–acetone and filtering the solution through Celite to remove AgCl. The solvent species was not very stable and so was only characterised in solution. The ^{1}H NMR spectrum of the complex showed the presence of only one isomer. A sharp singlet due to free acetone was observed; however no signal for water, coordinated or free, was observed at room temperature. At 253 K a broad singlet was observed at 3.16 which moved to 3.81 at 233 K which we assign to coordinated water. Thus even at 233 K the coordinated water is still dissociating at a rate comparable to the NMR timescale and interconversion of diastereomers could be occurring at a similar rate. However, all the mesitylene and ^{i}Pr-saloxaz signals remained sharp across the temperature range which suggests that the diastereomer ratio is probably high, as expected (see above), since H_2O is a reasonably small ligand.[32]

Treatment of the solvent complex with 1.2 equivalents of KBr or NaI in methanol at room temperature gave an immediate colour change. The ^{1}H NMR spectrum of the crude reaction mixture of **10** showed a single isomer with chemical shifts similar to those of the analogous chloride complex **2a**; thus, we presume that **10** has the same structure as **2a** (*i.e.* isomer **B**). The FAB mass spectrum of **10** showed a minor ion at *m*/*z* 505 (^{79}Br) due to $[M]^+$, with the major ion at *m*/*z* 426 due to $[M - Br]^+$.

The ^{1}H NMR spectrum of the crude reaction mixture of the iodide complex **11**, showed two mesitylene-containing species and two oxazoline-containing species. However, examination of the chemical shifts for the minor species revealed they were due to free ligand (^{i}Pr-saloxazH) and an arene–ruthenium complex showing singlets at δ 2.36 and 5.43. Crystallisation in air from CH_2Cl_2–ether (2–3 days) led to precipitation of a solid and formation of a dark green solution. The solvent was evaporated and the solid residue was washed with chloroform to remove ^{i}Pr-saloxazH and **11**, leaving behind a dark black residue, which was soluble in CD_2Cl_2. The ^{1}H NMR spectrum of the latter only contained resonances at δ 2.36 and 5.43, suggesting a "(mes)Ru" species. The FAB mass spectrum contained a minor peak at *m*/*z* 952 M^+ attributed to $[Ru_2I_4(mes)_2]^+$, the major ion due to $[M - I]^+$ *m*/*z* 824 and minor ions at both *m*/*z* 697 and 577 as a result of further loss of I and then mesitylene. Thus decomposition of **11** occurs with loss of ^{i}Pr-saloxazH and the formation of $[RuI_2(mes)]_2$ possibly aided by the presence of excess iodide.

The reaction was repeated using only one equivalent of NaI. The ^{1}H NMR spectrum recorded straight after dissolution in CD_2Cl_2 only showed signals for **11**. Hence, either it is formed highly diastereoselectively or two diastereomers are epimerising faster than the NMR timescale such that the time averaged spectrum is observed. The latter is unlikely since neither a second set of signals nor line-width broadening was observed in the ^{1}H NMR spectrum at 253 K. In addition, the chloride (**2a**) epimerises slowly on the NMR timescale (see above) and for related complexes the iodide normally epimerises slower than the corresponding chloride.[33] The chemical shifts for the signals of **11** are similar to those of the analogous chloride and bromide complexes **2a** and **10**, respectively. The NOESY spectrum showed NOEs between the NC*H* proton (δ 4.40) and the mesitylene signals (δ 2.28 and 5.00) with no NOEs between the isopropyl methyls and either mesitylene signal, as expected for isomer **B**. Hence the isomer **B** structure with isopropyl next to halide is still favoured even for the more sterically bulky iodide. The same thermodynamic preference for isomer **B** was also found for [RuI(^{i}Pr-pymox)(mes)][SbF_6].[15]

To date, to the best of our knowledge, there are no arene–ruthenium alkyl complexes that have hard donor co-ligands. Thus we attempted preparation of the methyl complex [RuMe(^{i}Pr-saloxaz)(mes)] **12** by treating the chloride **2a** with 1.2 equivalents of MeLi in THF and heating to 40 °C. The reaction was monitored by electrospray mass spectrometry; the observation of an ion at *m*/*z* 440 indicated the presence of the molecular ion, $[RuMe(^i$Pr-saloxaz)(mes)$]^+$, whilst an ion at *m*/*z* 426, $[Ru(^i$Pr-saloxaz)(mes)$]^+$, could arise from **12** or **2a**. The ^{1}H NMR spectrum of the product showed the presence of **12** and a small amount of the free salicyloxazoline ligand. Unfortunately all attempts to separate the latter by crystallisation or even chromatography have failed, thus we have not been able to obtain microanalytical data. The ^{1}H NMR spectrum showed only one isomer at room temperature and at 233 K. A 3H singlet is observed at δ 0.88 due to the Ru–*Me*, the mesitylene signals, δ 2.02 and 4.44 are slightly upfield of the corresponding ones of the halide complexes **2a**, **10** and **11**, (δ 2.21–2.28 and 4.89–5.00) consistent with more electron density on the ruthenium in **12**. The C*H*Me_2 signal occurs at δ 2.02 in **12**, compared to δ 2.70–2.82 in the halide complexes **2a**, **10** and **11**, presumably the downfield shifts in the latter are due to the electronegativity of the halide atom in close proximity. Identification of the preferred diastereomer was achieved by a phase-sensitive NOESY experiment, a cross peak being observed between the singlet at δ 4.44, $C_6H_3Me_3$, and the NC*H* proton at δ 3.98, indicating the presence of isomer **B** with the isopropyl group directed towards the methyl ligand, rather than towards the mesitylene ring.

We have shown that, as with pyridyloxazoline complexes, very diastereoselective coordination of salicyloxazolines to "RuCl(arene)" is possible with ^{i}Pr- or ^{t}Bu-substituents on the oxazoline and with mesitylene as the arene. With other substituents on the oxazoline the salicyloxazoline complexes show reduced diastereoselectivity compared with pyridyloxazoline complexes. In general, the diastereoselectivity is higher for [RuCl(saloxaz)(arene)] complexes than in related salicylaldimine ones. This may be because the chiral centre in the oxazoline is contained within a cyclic system which restricts the orientation of the substituents, whilst in the case of the salicylaldimines the chiral centre is free to rotate about a C–N bond. Similar arguments have been used to explain greater selectivity in allyl–palladium complexes of salicyloxazolines compared to salicylaldimines.[26] However, if the chloride is replaced by a much larger ligand *e.g.* as in [Ru(PPh_3)(^{i}Pr-saloxaz)(mes)]$^+$, there is virtually no diastereoselectivity in the salicyloxazoline complex whilst the corresponding salicylaldimine complexes still provide good diasteroselectivity due to the greater flexibility of the salicylaldimine ligands. The diastereoselectivity in all cases is due to a thermodynamic preference since the chirality at the metal is not stable on the chemical timescale. Epimerisation of the chloride complexes occurs even at low temperatures but is generally slow on the NMR timescale. The rate is affected by the presence of trace amounts of water, consistent with epimerisation by loss of halide rather than by chelate ring opening. Similarly complexes **6**–**9** probably epimerise by loss of the monodentate ligand, as evidenced by exchange with free 2-methylpyridine in the case of **8**.

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 show less water-sensitivity than the more common titanium aluminium or boron catalysts.[34] Following our initial report of asymmetric catalysis of a Diels–Alder reaction with arene–ruthenium pyridyloxazoline[16] complexes, other arene–ruthenium complexes of chiral bisphosphine monoxides,[35] pyridyl imines,[11] bis(oxazolines),[19] and phosphinooxazolines[36] have also been used to catalyse Diels–Alder reactions. All these complexes contain neutral bidentate ligands, hence the actual catalysts are dications [Ru(solvent)(L*)(arene)]$^{2+}$. Earlier

Table 3 Enantioselective Diels–Alder reaction of methacrolein with cyclopentadiene in dichloromethane catalysed by [RuCl(R-saloxaz)(arene)] after treatment with $AgSbF_6$

Entry	Catalyst precursor	R	Temp	Time/h	Yield (%)	*Exo* : *endo*	Ee (%)
1	**2a**	^{i}Pr	RT	15	>95	94 : 6	37
2	**2a**	^{i}Pr	0	24	93	95 : 5	40
3	**2a**	^{i}Pr	−20	72	77	95 : 5	44
4	**3a**	^{t}Bu	0	72	92	97 : 3	38
5	**4a**	Bn	0	72	89	92 : 8	6
6	**5a**	Ph	0	72	91	93 : 7	13
7	**2b**	^{i}Pr	0	72	80	95 : 5	47
8	**2c**	^{i}Pr	0	72	67	95 : 5	48

All at 2 mol% catalyst, ee is for the *exo* isomer.

Table 4 Enantioselective Diels–Alder reaction of bromoacrolein with cyclopentadiene in dichloromethane catalysed by [RuCl(R-saloxaz)(arene)] after treatment with $AgSbF_6$

Entry	Catalyst precursor	R	Yield (%)	*Exo* : endo	Ee (%)
1	**2a**	^{i}Pr	92	95 : 5	44
2	**3a**	^{t}Bu	80	93 : 7	41
3	**4a**	Bn	82	92 : 8	15
4	**5a**	Ph	59	88 : 12	12
5	**2b**	^{i}Pr	>95	95 : 5	53
6	**2c**	^{i}Pr	>95	92 : 8	44

All reactions carried out at 0 °C, for 2 h using 2 mol% catalyst, ee is for the *exo* isomer.

studies showed that monocations $[Ru(C_2H_4)(L^*)Cp]^+$ (L* = chiral diphosphine) catalyse the less Lewis-acid demanding hetero-Diels–Alder but do not catalyse the Diels–Alder reaction.[37] However, Kundig *et al*. have demonstrated that if electron-withdrawing bidentate ligands are used, the monocations $[Ru(solvent)(L^*)(ring)]^+$ (L* = chiral bisphosphonite with fluoroaryl substituents, ring = Cp or indenyl) are sufficiently Lewis acidic to catalyse Diels–Alder reactions of acroleins and dienes.[38,39] In order to further develop chiral half-sandwich Lewis acid catalysts it is important to know the range of Lewis acidity needed to promote specific reactions and the effect of the hard–soft characteristics of the donor atoms. Thus, it was interesting to explore whether arene–ruthenium monocations, $[Ru(solvent)(saloxaz)(arene)]^+$, containing an anionic bidentate ligand with hard donor atoms, are sufficiently Lewis acidic to catalyse Diels–Alder reactions. In addition, complexes with anionic salicyloxazoline ligands have much faster rates of ligand exchange compared with the corresponding pyridyloxazoline complexes,[40] as demonstrated by the ready epimerisation of complexes **6**–**9**. Thus, decreased Lewis acidity may reduce catalytic activity, on the other hand if the substitution at the metal is rate limiting the turnover frequency may be increased with the salicyloxazoline complexes. In addition, the high diastereoselectivity observed, particularly for the mesitylene complexes and alkyl-substituted salicyloxazoline ligands, suggests that in catalytic applications the presence of a second diastereomer is only likely with very large substrates thus, catalysis should proceed through a single chiral catalyst and high enantioselectivity may be possible. To test these hypotheses we have examined a number of these complexes as catalysts for Diels–Alder reactions.

The cations $[Ru(solvent)(R\text{-saloxaz})(arene)]^+$ were prepared from the chlorides by treatment with $AgSbF_6$, as described above for $[Ru(solvent)(^{i}Pr\text{-saloxaz})(mes)]^+$, and were used without further purification to catalyse Diels–Alder reactions. The results of the catalysis of the reaction of cyclopentadiene with methacrolein or bromoacrolein are shown in Tables 3 and 4 respectively. The results will be discussed in terms of the precursor chloride complexes.

At room temperature the reaction of methacrolein with cyclopentadiene, with **2a** as catalyst precursor reached completion in under 15 h, as monitored by ^{1}H NMR spectroscopy, and gave good diastereoselectivity (94 : 6 *exo* : *endo*) and moderate enantioselectivity (37% ee). Lowering the temperature gave slower rates of reaction with small increases in ee (44% at −20 °C). Altering the amount of catalyst (1, 2 or 5 mol%) had little effect on the *exo* : *endo* ratio or enantioselectivity. Hence, further reactions were done with 2 mol% catalyst.

The effect of varying the oxazoline-substituent was investigated (entries 2 and 4–6). Moderate enantioselectivity was found with bulky alkyl groups, ^{i}Pr and ^{t}Bu, while substituents containing aryl groups, Bn and Ph, gave low enantiomeric excess, though in all cases yields and *exo* : *endo* selectivity were good. The poor enantioselectivity achieved with R = Bn, Ph (entries 5 and 6) is consistent with low diastereoselectivity in the complexes (see earlier); hence there may be two competing diastereomeric catalysts in these cases. In isomer **B** the oxazoline substituents will shield one face of the coordinated methacrolein and hence give rise to some enantioselectivity; whereas, in isomer **A** the oxazoline substituent is on the opposite side to the coordinated methacrolein and hence would not be expected to influence the enantioselectivity significantly if at all. Hence, the presence of some of isomer **A** catalyst is expected to give reduced enantiomeric excess.

The effect of arene substitution on the enantioselectivity was probed using complexes **2a**–**c** (R = ^{i}Pr) (entries 2, 7 and 8). The mesitylene-containing catalyst (entry 2), was found to be slightly inferior in terms of enantioselectivity (40% ee) to the *p*-cymene or C_6H_6 catalysts (entries 7 and 8, ~ 48% ee). This is somewhat surprising since the *p*-cymene and C_6H_6-containing catalyst precursors both exist as a mixture of diastereomers whilst the mesitylene complex is only one diastereomer. Using the related $[RuCl(^{i}Pr\text{-pymox})(arene)][SbF_6]$ (arene = C_6H_6, *p*-cymene, mes, C_6Me_6) as catalyst precursors for this reaction, the highest selectivity was found with the mesitylene-containing complex rather than the more bulky hexamethylbenzene complex.[16] Noyori and Hashiguchi found that in asymmetric transfer hydrogenation reactions of ketones catalysed by [RuCl(*p*-TsDPEN)(arene)], the maximum enantioselectivity was observed when the arene is mesitylene.[1] These results suggest that in arene–ruthenium half-sandwich complexes, there is a subtle balance between steric effects of the arene and the bidentate ligand. Further investigations are needed to clarify if this is due mainly to the size of substituents on the arene and/or their relative position. In the case of [RuCl(R-saloxaz)(arene)] optimum enantioselectivity clearly occurs with a less bulky arene

than mesitylene. Using S_C-ligands the major product was identified as (1*R*,2*S*,4*R*)-2-methylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde, by comparison of the sign of the optical rotation and the GC behaviour of the acetal formed from (2*R*,4*R*)-pentanediol with literature values.[41] This is consistent with the isopropyl shielding the *Si* face of the coordinated methacrolein leading to attack of cyclopentadiene at the *Re* face as we described for arene–ruthenium pyridyloxazoline complexes.[16] In conclusion, changing the R-group of the salicyloxazoline ligand, has a significant effect on the enantioselectivity of the reaction between methacrolein and cyclopentadiene. In contrast, lowering the reaction temperature, the catalyst loading, and the substituents on the arene have a much smaller effect.

The reaction between bromoacrolein and cyclopentadiene has also been examined (Table 4), this reaction is known to proceed with high enantioselectivity, with a number of chiral catalysts.[42] As expected, reactions with bromoacrolein were much faster; the uncatalysed reaction with cyclopentadiene proceeds rapidly at room temperature (>90% yield after 2 h in CD_2Cl_2 solution, with an *exo* : *endo* ratio of 78 : 22). As found with methacrolein, good yields, high diastereoselectivity and moderate enantioselectivity were obtained with alkyl-substituted oxazolines (entries 1 and 2) while benzyl and phenyl substituents (entries 3 and 4) gave low enantiomeric excesses. In the latter cases competition from the thermal reaction may be a problem, particularly for **5a** which also shows lower *exo* : *endo* selectivity. It is notable that the corresponding pyridyloxazoline complexes did not catalyse this reaction at all.[16] Kundig *et al.* have previously reported abstraction of bromide from bromoacrolein as a potential route for catalyst deactivation.[38] This is clearly not a problem with the less Lewis acidic salicyloxazoline complexes.

As for the reaction with methacrolein, the size of the arene has a modest effect on the enantioselectivity (entries 1, 5 and 6). The mesitylene and C_6H_6-containing catalysts (**2a** and **2c**) gave the same enantioselectivity (44% ee) while the *p*-cymene complex (**2b**) gave the highest enantioselectivity (53% ee).

Conclusions

Arene–ruthenium salicyloxazoline complexes can be synthesised easily. Judicious choice of substituents on the arene and the oxazoline allows high diastereoselectivity in complex formation with the oxazoline substituent favouring the position towards chloride (isomer **B**) rather than towards arene (isomer **A**). This is due to a thermodynamic rather than a kinetic preference. Epimerisation of the salicyloxazoline complexes is faster than the corresponding pyridyloxazoline ones as expected, however, this does not lead to higher turnover frequency for Diels–Alder catalysis. We have established that monocationic arene–ruthenium complexes with a chiral bidentate ligand having hard donor atoms are sufficiently Lewis acidic to catalyse Diels–Alder reactions, even without electron-withdrawing substituents. However, the reduced Lewis acidity of a monocationic catalyst, compared to a dicationic one, leads to a reduction in catalytic activity. The enantioselectivity of Diels–Alder reaction of acroleins with cyclopentadiene using arene–ruthenium salicyloxazoline catalysts is relatively modest, possibly due to the more open coordination site in these complexes compared to pyridyloxazoline ones.

Experimental

Light petroleum (bp 40–60 °C) and diethyl ether were dried by refluxing over purple sodium/benzophenone under nitrogen, whilst dichloromethane was purified by refluxing over calcium hydride and acetone from calcium sulfate. 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. Microanalyses were performed by Butterworth laboratories Ltd., Middlesex.

The ligands R,R′-saloxaz (R = ^{t}Bu, ^{i}Pr or Ph, R′ = H; R = R′ = Me)[24,43] were synthesised by 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[44] (99% optical purity). Bromoacrolein was prepared by the literature method.[45]

[RuCl(Me$_2$-saloxaz)(mes)] 1. A solution of Me$_2$-saloxaz (74 mg, 0.30 mmol) and NaOMe (20 mg, 0.30 mmol) in MeOH (10 ml) was added to $[RuCl_2(arene)]_2$ (103 mg, 0.14 mmol) and the resulting suspension 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 69 mg yield, 69%. Calc. for $C_{20}H_{24}ClNO_2Ru$: C, 56.62; H, 5.72; N, 3.09. Found: C, 56.45; H, 5.46; N, 3.02%. ^{1}H NMR δ 1.41, 1.62 (2 × s, 3H, NC*Me*), 2.10 (s, 9H, C_6Me_3), 4.10 (d, 1H, *J* 8, OC*H*), 4.29 (d, 1H, *J* 8, OC*H*′), 4.82 (s, 3H, $C_6H_3Me_3$), 6.48 (ddd, 1H, *J* 8, 7, 1, Ar-4-*H*), 7.02 (dd, 1H, *J* 8.5, 1, Ar-6-*H*), 7.21 (ddd, 1H, *J* 8.5, 7, 2, Ar-5-*H*), 7.48 (dd, 1H, *J* 8, 2, Ar-3-*H*). MS (FAB$^+$): *m*/*z* 448 [M]$^+$ and 413 [M − Cl]$^+$.

Complexes **2**–**5** were prepared by a similar procedure, the quantities of reagents used and yields obtained are listed below.

[RuCl(^{i}Pr-saloxaz)(mes)] 2a. Complex **2a** was prepared from $[RuCl_2(mes)]_2$ (320 mg, 0.55 mmol), ^{i}Pr-saloxaz (247 mg, 1.21 mmol) and NaOMe (74 mg, 1.37 mmol) in 405 mg yield, 80%. Calc. for $C_{21}H_{26}ClNO_2Ru$: C, 54.72; H, 5.69; N, 3.04. Found: C, 54.47; H, 5.55; N, 2.96%. ^{1}H NMR δ 0.74, 0.99, (2 × d, 3H, *J* 7, CH*Me*$_2$), 2.21 (s, 9H, C_6Me_3), 2.82 (m, 1H, C*H*Me$_2$), 4.40 (m, 2H, OCH_2), 4.52 (m, 1H, NC*H*), 4.89 (s, 3H, $C_6H_3Me_3$), 6.39 (t, 1H, *J* 8, Ar-4-*H*), 6.97 (d, 1H, *J* 8, Ar-6-*H*), 7.17 (t, 1H, *J* 8, Ar-5-*H*), 7.45 (d, 1H, *J* 8, Ar-3-*H*). MS (FAB$^+$): *m*/*z* 461 [M]$^+$ and 426, [M − Cl]$^+$.

[RuCl(^{i}Pr-saloxaz)(*p*-cymene)] 2b. Complex **2b** was prepared from $[RuCl_2(p\text{-cymene})]_2$ (64 mg, 0.11 mmol), ^{i}Pr-saloxaz (45 mg, 0.22 mmol) and NaOMe (13 mg, 0.24 mmol), in 74 mg yield, 74%. This compound has been prepared previously.[9] ^{1}H NMR (400 MHz, CD_2Cl_2, 233 K) (isomer ratio **B** : **A** = 9 : 1, data for **A** in square brackets) δ 0.74 [0.86], 1.02 [1.09], 1.13 [1.19], 1.27 [1.30] (4 × d, 3H, *J* 7, CH*Me*$_2$), 2.22 [2.18] (s, 3H, *Me*), 2.56 [2.37], 2.76 [2.87] (2 × m, 1H, C*H*Me$_2$) 4.39 [4.37] (m, 1H, OC*H*), 4.52 (m, 2H, NC*H* + OC*H*), 4.97 [5.23] (d, 1H, *J* 6, cymene) 5.38 (d, 1H, *J* 6, cymene), 5.46 (m, 2H, cymene), 6.38 [6.37] (m, 1H, Ar-5-*H*), 6.78 [6.77] (m, 1H, Ar-3-*H*), 7.14 (m, 1H, Ar-4-*H*), 7.36 [7.32] (m, 1H, Ar-6-*H*). MS (FAB$^+$): *m*/*z* 440, [M − Cl]$^+$.

[RuCl(^{i}Pr-saloxaz)(C_6H_6)] 2c. Complex **2c** was prepared from $[RuCl_2(C_6H_6)]_2$ (136 mg, 0.27 mmol), ^{i}Pr-saloxaz (112 mg, 0.55 mmol) and NaOMe (37 mg, 0.68 mmol), in 207 mg yield, 90%. Calc. for $C_{18}H_{20}ClNO_2Ru{\cdot}0.5CH_2Cl_2$): C, 48.16; H, 4.59; N, 3.04. Found: C, 48.41; H, 5.07; N, 2.43%. ^{1}H NMR (400 MHz, CD_2Cl_2, 263 K) (isomer ratio **B** : **A** = 9 : 1, data for **A** in square brackets) δ 0.85 [0.99], 1.02 [1.08] (2 × d, 3H, *J* 6.5, CH*Me*$_2$), 2.67 [2.41] (m, 1H, C*H*Me$_2$), 4.40 (t, 1H, J 9.5, OC*H*), 4.53 [4.48] (dd, 1H, *J* 9, 3.5, OC*H*′), 4.60 (m, 1H, NC*H*), 5.60 [5.62] (s, 6H, C_6H_6), 6.40 [6.45] (t, 1H, *J* 7.5, Ar-4-*H*), 6.89 [6.93] (d, 1H, *J* 8.5, Ar-6-*H*), 7.14 [7.18] (dt, 1H, *J* 8.5, 1.5, Ar-5-*H*), 7.37

(dd, 1H, *J* 8, 1.5, Ar-3-*H*). MS (FAB$^+$): *m*/*z* 419 [M]$^+$ and 384 [M − Cl]$^+$.

[RuCl(^{t}Bu-saloxaz)(mes)] 3a. Complex **3a** was prepared from [RuCl$_2$(mes)]$_2$ (100 mg, 0.17 mmol), ^{t}Bu-saloxaz (75 mg, 0.34 mmol) and NaOMe (25 mg, 0.47 mmol), in 46 mg yield, 28%. Calc. for $C_{22}H_{28}ClNO_2Ru$: C, 55.63; H, 5.94; N, 2.95. Found: C, 47.94; H, 5.88; N, 1.79%.(the complex appears to have lost ligand). ^{1}H NMR δ 1.18 (s, 9H, C*Me*$_3$), 2.19 (s, 9H, C$_6$*Me*$_3$), 4.33 (m, 2H, OC*H* + OC*H*′), 4.65 (m, 1H, NC*H*), 4.89 (s, 3H, C$_6$*H*$_3$Me$_3$), 6.38 (m, 1H, Ar-4-*H*), 6.98 (dd, 1H, *J* 8.5, 1, Ar-6-*H*), 7.15 (m, 1H, Ar-5-*H*), 7.47 (dd, 1H, *J* 8, 2, Ar-3-*H*). MS (FAB$^+$): *m*/*z* 441 [M − Cl]$^+$.

[RuCl(^{t}Bu-saloxaz)(*p*-cymene)] 3b. Complex **3b** was prepared from [RuCl$_2$(*p*-cymene)]$_2$ (125 mg, 0.21 mmol), ^{t}Bu-saloxaz (94 mg, 0.43 mmol) and NaOMe (28 mg, 0.51 mmol), in 139 mg yield, 70%. ^{1}H NMR δ 1.17 (s, 9H, C*Me*$_3$), 1.17, 1.24 (2 × d, 3H, *J* 7 Hz, CH*Me*$_2$), 2.32 (s, 3H, *Me*), 2.77 (m, 1H, C*H*Me$_2$), 4.35 (m, 2H, OC*H* + OC*H*′), 4.69 (m, 1H, NC*H*) 4.93 (d, 1H, *J* 6, cymene) 5.34 (d, 1H, *J* 6, cymene), 5.40 (d, 1H, *J* 6, cymene), 5.49 (d, 1H, *J* 6, cymene), 6.36 (t, 1H, *J* 7.5, Ar-4-*H*), 6.93 (d, 1H, *J* 8.5, Ar-6-*H*), 7.11 (t, 1H, *J* 8.5, Ar-5-*H*), 7.38 (d, 1H, *J* 8, Ar-3-*H*). MS (FAB$^+$): *m*/*z* 489 [M]$^+$ and 454 [M − Cl]$^+$.

[RuCl(Bz-saloxaz)(mes)] 4a. Complex **4a** was prepared from [RuCl$_2$(mes)]$_2$ (115 mg, 0.20 mmol), Bz-saloxaz (109 mg, 0.43 mmol) and NaOMe (27 mg, 0.49 mmol) in 141 mg yield, 71%. Calc. for $C_{25}H_{26}ClNO_2Ru{\cdot}0.5CH_2Cl_2$: C, 55.54; H, 4.93; N, 2.54. Found: C, 55.90; H, 4.91; N, 2.47%. ^{1}H NMR (400 MHz) (isomer ratio **B** : **A** = 4 : 1, data for **A** in square brackets) δ 2.24 [2.16] (s, 9H, C$_6$*Me*$_3$), 2.78 [2.63] (dd, 1H, *J* 11, 14, C*H*Ph), 3.96 [3.93] (dd, 1H, *J* 3.5, 14, C*H*′Ph), 4.35 [4.16 + 4.35] (m, 2H, OC*H* + OC*H*′), 4.71 [4.58] (m, 1H, NC*H*) 4.95 [4.89] (s, 3H, C$_6$*H*$_3$Me$_3$), 6.41 [6.50] (t, 1H, *J* 8, Ar-4-*H*), 7.02 (d, 1H, *J* 8.5, Ar-6-*H*), 7.27 (m, 6H, Ar-5-*H* + CH$_2$*Ph*), 7.46 (dd, 1H, *J* 8, 2, Ar-3-*H*). MS (FAB$^+$): *m*/*z* 509 [M]$^+$ and 474 [M − Cl]$^+$.

[RuCl(Ph-saloxaz)(mes)] 5a. Complex **5a** was prepared from [RuCl$_2$(mes)]$_2$ (147 mg, 0.25 mmol), Ph-saloxaz (133 mg, 0.56 mmol) and NaOMe (34 mg, 0.63 mmol) in 185 mg yield, 76%. Calc. for $C_{24}H_{24}ClNO_2Ru$: C, 58.24; H, 4.89; N, 2.83. Found: C, 58.27; H, 4.76; N, 2.92%. ^{1}H NMR (400 MHz, 233 K) (isomer ratio **A** : **B** = 3 : 2, data for **B** in square brackets) δ 1.89 [2.01] (s, 9H, C$_6$*Me*$_3$), 4.10 [4.60] (s, 3H, C$_6$*H*$_3$Me$_3$), 4.82 (m, 2H, OC*H* + OC*H*′), [4.20 + 4.92] [2 × t, *J* 8.5, OC*H* + OC*H*′], 5.51 [5.75] (t, 1H, *J* 10, NC*H*), 6.60 [6.43] (t, 1H, *J* 7.5, Ar-4-*H*), 6.99 [6.80] (d, 1H, *J* 8, Ar-6-*H*), 7.17 [7.18] (t, 1H, *J* 7.5, Ar-5-*H*), 7.6 (br, overlapping m, 6H, *Ph* + Ar-3-*H*). MS (FAB$^+$): *m*/*z* 495 [M]$^+$ and 460 [M − Cl]$^+$.

[Ru(py)(^{i}Pr-saloxaz)(mes)][SbF$_6$] 6. To a solution of [RuCl(^{i}Pr-saloxaz)(mes)] (**2a**) (60 mg, 0.13 mmol) in MeOH (10 ml) was added NaSbF$_6$ (38 mg, 0.15 mmol) and pyridine (43 mg, 0.54 mmol). The mixture was heated to reflux temperature for 2 h with continuous stirring. On cooling a white precipitate was observed. The solvent was evaporated and the residue re-dissolved in CH_2Cl_2 prior to filtering through Celite. The resulting red solution was evaporated to afford the crude complex. Recrystallisation from CH_2Cl_2–ether (or $CHCl_3$–ether) gave **6** as a crystalline red–orange solid in 66 mg yield, 70%. Calc. for $C_{26}H_{31}F_6N_2O_2RuSb$: C, 42.18; H, 4.22; N, 3.78. Found: C, 41.79; H, 4.12; N, 3.35%. ^{1}H NMR (CD_2Cl_2, 253 K) (isomer ratio **B** : **A** = 84 : 16, data for **A** in square brackets) δ −0.09 [0.74] (d, 3H, *J* 7 Hz, CH*Me*$_2$), 0.87 [1.11] (d, 3H, *J* 7 Hz, CH*Me*$_2$), 1.36 [2.41] (m, 1H, C*H*Me$_2$), 2.07 (s, 9H, C$_6$*Me*$_3$), 4.47 (m, 2H, OC*H* + OC*H*′), 4.56 [4.72] (m, 1H, NC*H*), 5.10 (s, 3H, C$_6$*H*$_3$Me$_3$), 6.58 [6.22] (t, 1H, *J* 7.5, Ar-4-*H*), 7.06 [6.85] (d, 1H, *J* 8, Ar-6-*H*), 7.30 [6.98] (m, 1H, Ar-5-*H*), 7.52 (m, 3H, Ar-3-*H* + py-3,5-*H*), 7.91 (m, 1H, py-4-*H*) 8.91 [8.60] (br, 2H, py-1,6-*H*). MS (FAB$^+$): *m*/*z* 426, [M − py]$^+$.

Complexes **7**–**9** were prepared by a similar procedure, the quantities of reagents used and yields obtained are listed below.

[Ru(4-Mepy)(^{i}Pr-saloxaz)(mes)][SbF$_6$] 7. Complex **7** was prepared from [RuCl(^{i}Pr-saloxaz)(mes)] (**2a**) (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%. Calc. for $C_{27}H_{33}F_6N_2O_2RuSb$: C, 42.99; H, 4.41; N, 3.71. Found: C, 42.94; H, 4.43; N, 3.81%. ^{1}H NMR (400 MHz, CD_2Cl_2, 233 K) (isomer ratio **B** : **A** = 85 : 15, data for **A** in square brackets) δ −0.05 [0.68] (d, 3H, *J* 7 Hz, CH*Me*$_2$), 0.83 [1.06] (d, 3H, *J* 7 Hz, CH*Me*$_2$), 1.27 (m, 1H, C*H*Me$_2$), 2.02 (s, 9H, C$_6$*Me*$_3$), 2.40 [2.32] (s, 3H, 4-*Me*py), 4.40 (m, 3H, OC*H*$_2$ + NC*H*), 4.97 [5.02] (s, 3H, C$_6$*H*$_3$Me$_3$), 6.52 [6.16] (m, 1H, Ar-4-*H*), 6.99 [6.75] (m, 1H, Ar-6-*H*), 7.23 [7.07] (m, 1H, Ar-4-*H*), 7.23 [7.10] (m, 2H, py-3,5-*H*), 7.43 [6.91] (m, 1H, Ar-3-*H*) 8.55 [8.22] (m, 2H, py-2,6-*H*). MS (FAB$^+$): *m*/*z* 519 [M]$^+$ and 426, [M-Mepy]$^+$.

[Ru(2-Mepy)(^{i}Pr-saloxaz)(mes)][SbF$_6$] 8. Complex **8** was prepared from [RuCl(^{i}Pr-saloxaz)(mes)] (**2a**) (61 mg, 0.13 mmol), NaSbF$_6$ (41 mg, 0.16 mmol) and 2-methylpyridine (37 mg, 0.40 mmol) in 72 mg yield, 72%. Calc. for $C_{27}H_{33}F_6N_2O_2RuSb$: C, 42.99; H, 4.41; N, 3.71. Found: C, 42.60; H, 4.18; N, 3.46%. ^{1}H NMR (250 MHz, CD_2Cl_2) δ 0.65 (d, 3H, *J* 6.5, CH*Me*$_2$), 1.10 (d, 3H, *J* 7, CH*Me*$_2$), 2.13 (s, 9H, C$_6$*Me*$_3$), 2.50 (m, 1H, C*H*Me$_2$), 2.84 (s, 3H, 2-*Me*py), 4.51 (t, 1H, *J* 8.5 OC*H*), 4.61 (m, 1H, OC*H*′), 4.72 (m, 1H, NC*H*), 5.25 (s, 3H, C$_6$*H*$_3$Me$_3$), 6.50 (t, 1H, *J* 7.5, Ar-4-*H*), 7.05 (d, 1H, *J* 7.5 Ar-6-*H*), 7.30 (m, 3H, Ar-3+5-H, py-*H*), 7.49 (d, 1H, *J* 7.5, py-H), 7.99 (t, 1H, *J* 7, py-*H*), 8.59 (d, 1H, *J* 5.5, py-6-*H*). MS (FAB$^+$): *m*/*z* 426, [M − (Me-py)]$^+$.

[Ru(PPh$_3$)(^{i}Pr-saloxaz)(mes)][BPh$_4$] 9. Complex **9** was prepared from [RuCl(^{i}Pr-saloxaz)(mes)] (**2a**) (51 mg, 0.11 mmol), NaBPh$_4$ (45 mg, 0.13 mmol) and PPh$_3$ (35 mg, 0.13 mmol) in 104 mg yield, 94%. Calc. for $C_{63}H_{61}BNO_2PRu$: C, 75.14; H, 6.11; N, 1.39. Found: C, 74.38; H, 6.01; N, 1.35%. ^{1}H NMR (CD_2Cl_2) (isomer ratio **B** : **A** = 1 : 1, data for **A** in square brackets) δ 0.00 [0.92] (d, 3H, *J* 7, CH*Me*$_2$), 0.58 [0.97] (d, 3H, *J* 7, CH*Me*$_2$), 1.21 [2.08] (m, 1H, C*H*Me$_2$), 1.71 [1.68] (s, 9H, C$_6$*Me*$_3$), 3.74 [3.20] (m, 1H, NC*H*), 4.37 [2.87] (m, 1H, OC*H*), 4.48 [5.06] (s, 3H, C$_6$*H*$_3$Me$_3$), 4.53 [4.14] (m, 1H, OC*H*′), 6.51 [6.61] (m, 1H, Ar-4-*H*), 6.80–7.90 (m, 38H, Ar-3,4,6-*H* + PPh$_3$ + BPh$_4^-$). ^{31}P-{^{1}H} NMR δ 30.13 [30.90] MS (FAB$^+$): *m*/*z* 688, [M]$^+$ and 426, [M − PPh$_3$]$^+$.

[Ru(solvent)(^{i}Pr-saloxaz)(mes)]SbF$_6$. To a solution of AgSbF$_6$ (1.05 equivalents) in acetone (0.5 ml) was added a solution of [MCl(^{i}Pr-saloxaz)(mes)] (**2a**) (1.0 equivalents) in CH_2Cl_2 (4 ml), giving a yellow–orange solution and an immediate AgCl precipitate. 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. This was then used for further reactions. ^{1}H NMR (400 MHz CD_2Cl_2) δ 0.557, 1.20, (2 × d, 3H, *J* 7, CH*Me*$_2$), 2.25 (s, 9H, C$_6$*Me*$_3$), 2.66 (m, 1H, C*H*Me$_2$), 4.69 (m, 2H, OC*H*$_2$), 5.00 (m, 1H, NC*H*), 5.51 (s, 3H, C$_6$*H*$_3$Me$_3$), 6.83 (t, 1H, *J* 8, Ar-4-*H*), 7.28 (d, 1H, *J* 8, Ar-6-*H*), 7.44 (t, 1H, *J* 8, Ar-5-*H*), 7.59 (d, 1H, *J* 8, Ar-3-*H*). MS (FAB$^+$): 426, [M − solvent]$^+$.

Synthesis of [RuBr(^{i}Pr-saloxaz)(mes)] 10. A solution of AgSbF$_6$ (50 mg, 0.15 mmol) in acetone (0.5 ml) was added to a solution of [RuCl(^{i}Pr-saloxaz)(mes)] (**2a**) (64 mg, 0.14 mmol) in CH_2Cl_2 (4 ml), giving a yellow–orange solution and an immediate precipitate of AgCl. The solution was stirred for one hour at room temperature (protected from light) and was then filtered through Celite (to remove AgCl). The solvent was evaporated,

Table 5 Crystallographic data for complexes **2a**, **3b 5a**, **7** and **9**

	2a	**3b**	**5a**	**7**	**9**
Empirical formula	$C_{21}H_{26}ClNO_2Ru$	$C_{23}H_{30}ClNO_2Ru$	$C_{24}H_{24}ClNO_2Ru{\cdot}CHCl_3$	$C_{27}H_{33}F_6N_2O_2RuSb$	$C_{63}H_{61}BNO_2PRu$
Formula weight	460.95	489.00	614.33	754.37	1006.98
Temperature/K	190(2)	190(2)	190(2)	200(2)	180(2)
Crystal system	Tetragonal	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P4_12_12$	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$P2_1$
a/Å	12.272(3)	6.666(1)	7.737(1)	10.542(1)	14.8561(6)
b/Å	12.272(3)	17.697(5)	16.171(1)	16.152(2)	16.7720(7)
c/Å	27.260(12)	18.595(8)	9.984(1)	16.811(2)	20.3864(9)
β/°			93.38(1)		99.774(1)
U/Å^3	4105.2(25)	2193.6(12)	1247.0(2)	2862.3(5)	5005.9(4)
Z	8	4	2	4	4
D_c/Mg m^{-3}	1.492	1.481	1.636	1.751	1.336
μ/mm^{-1}	0.908	0.854	1.081	1.538	0.392
F(000)	1888	1008	620	1496	2104
Crystal size/mm	0.11 × 0.42 × 0.55	0.76 × 0.20 × 0.12	0.61 × 0.16 × 0.16	0.37 × 0.05 × 0.04	0.04 × 0.15 × 0.18
θ Range/°	2.78–25.00°.	2.19–26.97°.	2.04–27.00°	1.75–25.00°.	1.01–27.00°.
Index ranges	0/14, −1/14, −1/32	−7/0, −21/1, −22/1	−1/9, −19/1, −11/11	−12/12, −19/19, −19/19	−18/18, – 21/21, −25/26
Reflections collected	4322	2500	2759	20825	42686
Independent reflections (R_{int})	3511 (0.0391)	2439 (0.0372)	2450 (0.0157)	5033 (0.0525)	20957 (0.0555)
Data/restraints/parameters	3511/0/240	2439/0/259	2450/1/289	5033/0/358	20957/1/1253
Goodness-of-fit on F^2	1.105	1.037	1.091	0.925	0.760
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0637$, $wR2 = 0.1422$	$R1 = 0.0343$, $wR2 = 0.0843$	$R1 = 0.0361$, $wR2 = 0.0954$	$R1 = 0.0374$, $wR2 = 0.0616$	$R1 = 0.0457$, $wR2 = 0.0720$
R indices (all data)	$R1 = 0.0950$, $wR2 = 0.1690$	$R1 = 0.0383$, $wR2 = 0.0875$	$R1 = 0.0364$, $wR2 = 0.0957$	$R1 = 0.0454$, $wR2 = 0.0640$	$R1 = 0.0750$, $wR2 = 0.0927$
Absolute structure parameter	−0.06(13)	−0.08(5)	0.01(6)	−0.01(2)	−0.022(19)
Largest diff. peak and hole/e Å^{-3}	0.947 and −1.396	0.668 and −0.834	1.381 and −1.225	0.76 and −0.411	0.891 and −0.517

and the orange solid was washed with chloroform. The solid was redissolved in MeOH (3 ml), KBr (18 mg, 0.15 mmol) in a minimum of H_2O was added, and the mixture was stirred at room temperature for 1 h, during which time the solution changed colour from orange to red. The methanol was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 and filtered through Celite. Evaporation of the solvent afforded the crude product which was recrystallised from $CHCl_3$–ether to give **10** in 59 mg yield, 75%. Calc. for $C_{21}H_{26}BrNO_2Ru{\cdot}0.5CHCl_3$: C, 45.70; H, 4.73; N, 2.48. Found: C, 45.91; H, 5.12; N, 2.40%. ^{1}H NMR δ 0.74, 1.02, (2 × d, 3H, *J* 6.5 Hz, CHMe_2), 2.12 (s, 9H, C_6Me_3), 2.70 (m, 1H, C*H*Me$_2$), 4.36–4.58 (m, 3H, OCH_2 + NC*H*), 4.98 (s, 3H, $C_6H_3Me_3$), 6.45 (t, 1H, *J* 7.5, Ar-4-*H*), 6.99 (d, 1H, *J* 8, Ar-6-*H*), 7.21 (td, 1H, *J* 8, 2, Ar-5-*H*), 7.49 (dd, 1H, *J* 8,2, Ar-3-*H*). MS (FAB$^+$): *m*/*z* 505 [M]$^+$ (^{79}Br), 426, [M − Br]$^+$.

Synthesis of [RuI(^{i}Pr-saloxaz)(mes)] 11. This was prepared in a similar way to **10** from [RuCl(^{i}Pr-saloxaz)(mes)] (**2a**) (32 mg, 0.07 mmol) $AgSbF_6$ (24 mg, 0.07 mmol) and NaI (11 mg, 0.07 mmol) to give **11** in 29 mg yield, 62%. Calc. for $C_{21}H_{26}INO_2Ru{\cdot}CHCl_3$: C, 39.33; H, 4.05; N, 2.08. Found: C, 39.37; H, 4.23; N, 2.29%. ^{1}H NMR δ 0.82, 1.10, (2 × d, 3H, *J* 6.5 Hz, CHMe_2), 2.28 (s, 9H, C_6Me_3), 2.81 (m, 1H, C*H*Me$_2$), 4.33 (m, 1H, OC*H*), 4.40 (m, 1H, NC*H*), 4.51 (m, 1H, OC*H*′), 5.00 (s, 3H, $C_6H_3Me_3$), 6.37 (t, 1H, *J* 7.5, Ar-4-*H*), 6.89 (d, 1H, *J* 8, Ar-6-*H*), 7.24 (t, 1H, *J* 8, Ar-5-*H*), 7.41 (d, 1H, *J* 8, Ar-3-*H*). MS (FAB$^+$): *m*/*z* 554 [M]$^+$ and 426 [M − I]$^+$.

Preparation of [RuMe(^{i}Pr-saloxaz)(mes)] 12. To a degassed solution of [RuCl(^{i}Pr-saloxaz)(mes)] (**2a**) (200 mg, 0.43 mmol) in THF (15 ml) was added MeLi (0.27 ml, 0.43 mmol, solution in hexane). The mixture was heated to 40 °C for 4 h with continuous stirring. On cooling a white precipitate was observed. The solvent was evaporated and the residue re-dissolved in CH_2Cl_2 prior to filtering through Celite. The crude product was chromatographed on silica, with hexane–ethyl acetate (3 : 1) as eluent. Evaporation of the fore-run gave **12** as a dark red solid (82 mg, 43%), which was pure by ^{1}H NMR spectroscopy. However, attempts at recrystallisation failed hence elemental analysis has not been obtained. ^{1}H NMR: (400 MHz) δ 0.69 (d, 3H, *J* 7, *Me*CHMe′), 0.88 (s, 3H, Ru–*Me*), 0.90 (d, 3H, *J* 7, MeCH*Me*′), 2.02 (s, 9H, $C_6H_3Me_3$ + m, 1H, MeC*H*Me′), 3.98 (m, 1H, NC*H*), 4.24 (t, 1H, *J* 9, OC*H*), 4.36 (dd, 1H, *J* 8.5, 4, OC*H*′), 4.44 (s, 3H, $C_6H_3Me_3$), 6.34 (t, 1H, *J* 7, Ar-4-*H*), 6.76 (d, 1H, *J* 8.5, Ar-6-*H*), 7.11 (t, 1H, *J* 8, Ar-5-*H*), 7.49 (dd, 1H, *J* 8, 2, Ar-3-*H*). *m*/*z* 441 (15%) [M]$^+$ and *m*/*z* 426 (70%) [M − Cl]$^+$.

X-Ray crystallography

Data for **2a**, **3b**, **5a** and **7** were collected on a Siemens P4 diffractometer using graphite-monochromated Mo-Kα radiation, λ = 0.7107 Å. Data for **9** were collected on a Bruker Apex 2000 CCD diffractometer. The data were corrected for Lorentz and polarisation effects and semi-empirical absorption corrections based on ψ scans (XEMP; SHELXTL/PC) were applied for **3b**, **5a** and **7**. The structures were solved by Patterson methods and refined by full-matrix least squares on F^2 using the program SHELXTL-PC[46]. 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. Crystallographic data are given in Table 5.

CCDC reference numbers 228962–228966.

See http://www.rsc.org/suppdata/dt/b4/b400747f/ for crystallographic data in CIF or other electronic format.

Catalysis

The catalyst was prepared *in situ* from the chloride complex and one equivalent of $AgSbF_6$ in CH_2Cl_2–acetone and the solution was filtered through Celite into a Schlenk tube to remove AgCl. The solvent was evaporated and CH_2Cl_2 (2 ml), acrolein (1 mmol) and 2,6-di-*tert*-butylpyridine (1 equivalent/mol catalyst) were added. The resulting yellow solution was equilibrated at the appropriate temperature before addition of diene (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 or GC after conversion to the acetal with (2*R*,4*R*)-pentanediol.[41]

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