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Chiral pyridine imidazolines from C_1-symmetric diamines: Synthesis, arene ruthenium complexes and application as asymmetric catalysis for Diels-Alder reactions

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Abstract

Condensation of mono N-substituted chiral ethylenediamines and pyridine-2-methoxyimidate gives new chiral pyridine imidazolines (**1a**–**c**). These react with $[RuCl_2(mes)]_2$ (mes = 1,3,5-trimethyl benzene) in the presence of $NaSbF_6$ to give complexes $[RuCl(L)(mes)][SbF_6]$ (**5a**–**c**) which after treatment with $AgSbF_6$ are enantioselective catalysts for the Diels-Alder reaction of methacrolein and cyclopentadiene. The imidazoline catalysts are less selective than the corresponding oxazoline ones. Compounds **1a**, **5b** and **5c** have been characterised by X-ray crystallography.

Keywords: Chiral; Half-sandwich; Imidazoline; Asymmetric catalysis

1. Introduction

Over the last 15 or so years certain classes of ligands have become established as being particularly useful in asymmetric catalysis. One such class is oxazolines, particularly bis(oxazolines) and phosphino-oxazolines [1]. More recently the related heterocycles, imidazolines, have attracted some attention for their use in asymmetric catalysis [2–7]. Imidazolines offer the potential advantage of tuning the electronic properties of the ligand by substitution at the $N-1$ position. Indeed such electronic tuning of enantioselectivity has been observed in the addition of diethylzinc to aldehydes with hydroxyalkyl imidazolines [5] and in intramolecular Heck reactions with phosphine imidazolines [6].

We have previously reported the preparation of a chiral pyridine imidazoline derived from 1,2-diphenylethylenediamine [7]. The resultant arene ruthenium complex was not a very good catalyst for the Diels-Alder reaction of methacrolein and cyclopentadiene; however, the corresponding pyridine oxazoline complex with a 4-phenyl substituent is also not a very effective catalyst in this reaction [8]. In order to synthesise more active imidazoline catalysts for this reaction we targeted ligands with an alkyl or benzyl substituent in the 4-position of the imidazoline.

Our previous route to pyridine imidazolines (pymim) involved condensation of the C_2-symmetric 1,2-diphenylethylenediamine with pyridine-2-methoxyimidate and then functionalisation of one nitrogen atom (Scheme 1) [7]. We were concerned that direct reaction of a C_1-symmetric diamine may lead to two isomeric pyridine imidazolines **1** with the chiral centre adjacent to the imine nitrogen (A, desired) or adjacent to the amine nitrogen (B, expected to give less chiral induction). Hence our strategy was to make suitably mono-N-substituted chiral diamines **2** with the stereogenic centre adjacent to the primary nitrogen that should react to give imidazolines **1** (only isomer A).

2. Results and discussion

Our approach to diamines **2** involved the regioselective ring-opening of chiral aziridines with primary amines. This

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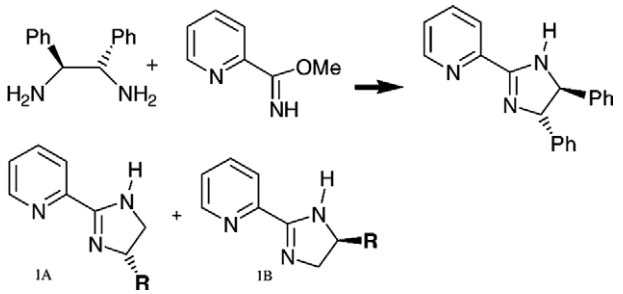
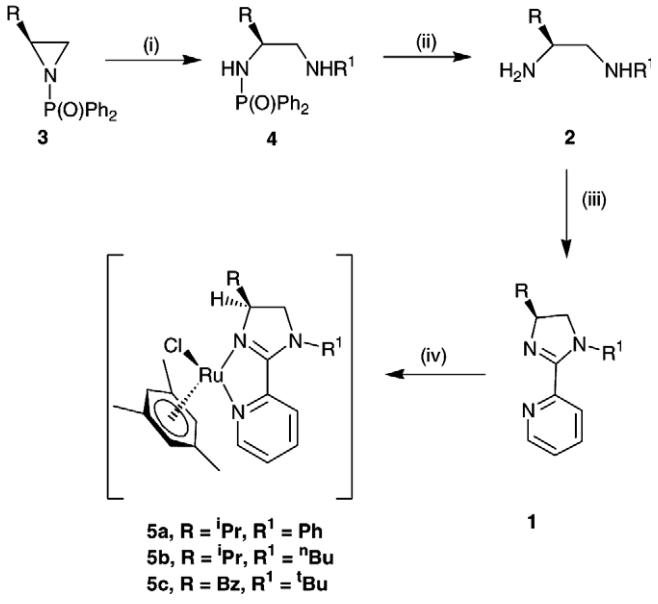


Scheme 1.

method has been used previously to produce C_3-symmetric tripodal tetra-amines [9]. Initial attempts used mesyl and nosyl protected aziridines made from L-valinol [9]. Ring opening proceeded as expected with the desired regioselectivity, however deprotection of these proved difficult. Hence, the use of a diphenylphosphonoyl protecting group that is more readily cleaved was investigated (Scheme 2). Chiral aziridines **3**, (R = ^{i}Pr, Bn) were synthesised following the method of Sweeney et al. [10]. Regioselective nucleophilic ring opening was achieved with R^1NH_2 ($R^1 = {}^t$Bu, ^{n}Bu, Ph), by heating to reflux in methanol, to form protected diamines **4**, which were deprotected by bubbling dry HCl gas through CH_2Cl_2/ether solutions to yield hydrochloride salts from which diamines **2** are easily liberated by treatment with base.

The new ligands, **1a**–**c**, were easily synthesised in high yield by reaction of diamines **2** with pyridine-2-methoxyimidate (Scheme 2). Using this procedure the ligands are sufficiently pure for complexation and do not require chromatography which is necessary if pyridine imidazolines are prepared by Lewis acid catalysed condensation of 2-cyanopyridine with the diamine [3,4]. Ligand **1a** was



Scheme 2. (i) R^1NH_2; (ii) HCl(g); (iii) pyridine-2-methoxyimidate; (iv) $[RuCl_2(mes)]_2/NaSbF_6$.

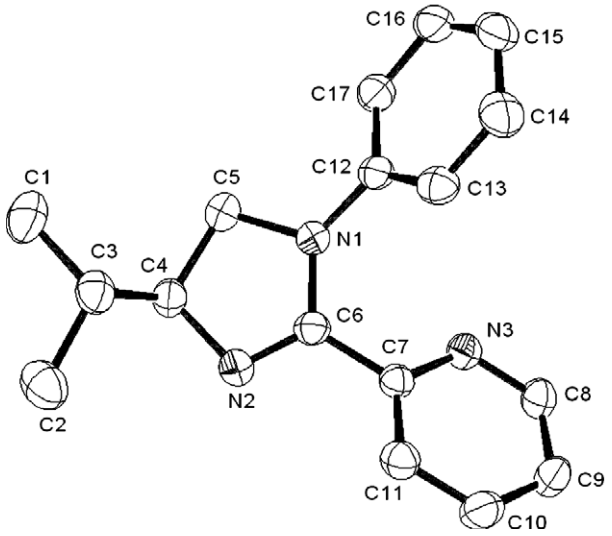


Fig. 1. Ortep drawing of **1a**, showing the atom labelling scheme. Displacement ellipsoids are shown at the 50% level. Selected bond distances (Å) and bond angles (°): N(1)–C(5) 1.467(2), N(1)–C(6) 1.381(2), N(2)–C(6) 1.282(2), N(3)–C(7) 1.344(2), N(3)–C(8) 1.337(3), N(2)–C(4) 1.481(3) and C(6)–N(1)–C(12) 128.2(2), C(6)–N(1)–C(5) 107.4(2), C(5)–N(1)–C(12) 119.9(2).

characterised by X-ray crystallography and the structure with selected bond lengths and bond angles are shown in Fig. 1. The N(1)–C(6) bond [1.381(2) Å] is only slightly longer than the N(3)–C(7) and N(3)–C(8) distances [average 1.341(3) Å] in the pyridine ring, being considerably shorter than the formal single bonds N(2)–C(4) and N(1)–C(5) [average 1.474(3) Å], suggesting some delocalisation in the imidazoline ring. The sum of the bond angles at N(1) is 355.5° also consistent with sp^2 rather than sp^3 hybridisation at N(1).

Half-sandwich complexes [RuCl{(*S*)4R-pymimNR^1}-(mes)]SbF_6 (**5a**–**c**) were synthesised from $[RuCl_2(mes)]_2$ by treatment with 2 equiv. of ligand **1a**–**c** and $NaSbF_6$, in refluxing MeOH. The complexes were characterised by ^{1}H NMR spectroscopy, mass spectrometry and microanalysis and by X-ray diffraction for **5b** and **5c**. In **5a**–**c**, both the metal centre and the pyridine imidazoline ligands are chiral so a mixture of diastereomers is possible as found for analogous pyridine oxazoline complexes reported previously [8].

The ^{1}H NMR spectra in CD_2Cl_2 of crude reaction mixtures containing **5a**–**c** each contained a single set of well-resolved signals, with no trace of a second isomer as found previously for the corresponding pyridine oxazoline complexes [8].

Recrystallisation from CH_2Cl_2/ether gave crystals of **5b** and **5c** suitable for X-ray diffraction. The X-ray structures of the cations of **5b** and **5c** are shown in Figs. 2 and 3, respectively, with selected bond distances and angles in Table 1. The ruthenium atoms have a pseudooctahedral geometry with the arene occupying three adjacent sites of the octahedron. The imidazolines are coordinated such

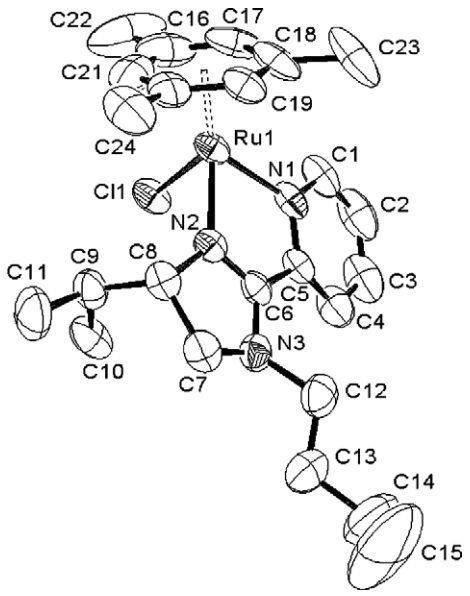


Fig. 2. Ortep drawing of the cation of **5b**, showing the atom labelling scheme. Displacement ellipsoids are shown at the 50% level. H atoms are omitted for clarity.

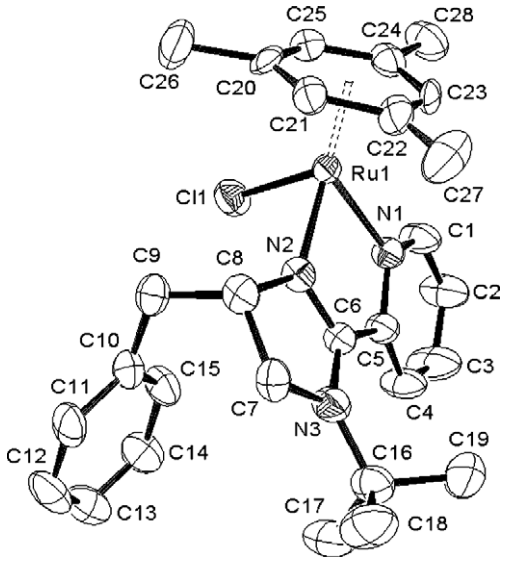


Fig. 3. Ortep drawing of the cation of **5c**, showing the atom labelling scheme. Displacement ellipsoids are shown at the 50% level. H atoms are omitted for clarity.

that the isopropyl or benzyl substituent adjacent to the imine nitrogen is on the same side as the chloride rather than the arene; as found in related pyridine oxazoline complexes [8,11]. After dissolution of crystals of **5b** or **5c** in CD_2Cl_2 at low temperature and recording the ^1H NMR spectra each complex showed only a single diastereomer, which is presumed to be the same as that in the solid-state in each case. A phase-sensitive NOESY spectrum of **5a** recorded at 253 K confirmed that the same isomer is also present in this case.

As mentioned previously, both complexes have the imidazoline substituent pointing towards chloride. In the case

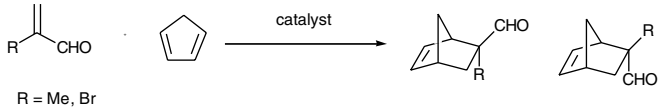
Table 1
Selected bond lengths (Å) and bond angles (°) for complexes **5b** and **5c**

	5b	**5c**
Ru–N(1)	2.112(5)	2.098(8)
Ru–N(2)	2.073(5)	2.057(9)
Ru–Cl	2.406(2)	2.394(3)
N(1)–C(1)	1.339(8)	1.33(2)
N(1)–C(5)	1.356(8)	1.373(14)
N(2)–C(8)	1.473(7)	1.471(13)
N(2)–C(6)	1.282(7)	1.306(13)
N(3)–C(6)	1.359(8)	1.362(14)
N(3)–C(7)	1.465(8)	1.481(14)
C(5)–C(6)	1.468(8)	1.48(2)
N(1)–Ru–N(2)	75.55(18)	74.9(3)

of **5c** the phenyl ring of the benzyl substituent is orientated anti and perpendicular to the mesitylene ring, reducing unfavourable interactions with both the mesitylene and chloride ligand. The $Ru–N(2)_{im}$ distance is shorter than $Ru–N(1)_{py}$, in each complex possibly due to the greater electron donating ability of the imidazoline ring. Similar features are seen for palladium and rhodium pyridine imidazoline complexes [4], whereas in arene ruthenium pyridine oxazoline complexes the $Ru–N_{py}$ and $Ru–N_{ox}$ bond lengths are usually statistically the same [8,11]. In each of **5b** and **5c**, the N(3)–C(6) distance [average 1.361(11) Å] is statistically the same as the N(1)–C(1) and N(1)–C(5) distances in the pyridine ring, being only slightly longer than the formal double bond N(2)–C(6) distance [average 1.294(10) Å] and considerably shorter than the formal single bonds N(2)–C(8) [average 1.472(10) Å] implying a degree of delocalisation across the amidine N(2)–C(6)–N(3) fragment as discussed for the free ligand **1a** above and as found previously for pyridine imidazoline complexes [4,7]. Consistent with this, the sum of the angles around N(3) is 359.5(10)° in **5c**, though it is slightly less, 346.6(6)° in **5b**. Thus **5b** and **5c** are structurally similar to the corresponding pyridine oxazoline complexes confirming that the steric requirements of imidazolines are similar to those of the related oxazolines. This is also consistent with the similar diastereoselectivity observed for formation of these R-pymim complexes and the corresponding R-pymox ones. Hence, the substituent on N(3) can communicate electronically with the metal centre but has minimal steric impact. In the case of **5c** the steric effect of the ^{t}Bu leads to an increased torsion angle [N(1)–C(5)–C(6)–N(2)] of 16.8° between the pyridine and imidazoline rings compared to that of 11.0° in the ^{n}Bu complex **5b**.

In the recent years there has been particular interest in using chiral late-transition-metal complexes as catalysts for Diels-Alder reactions since such complexes show less water-sensitivity than the more common titanium, aluminium or boron catalysts [12]. Cationic arene ruthenium complexes with P,N or P,O bidentate ligands [13], bisoxazolines [14] and pyridine oxazolines [8,11] have all been successfully used as asymmetric catalysts for Diels-Alder reactions.

Table 2
Enantioselective Diels-Alder reaction of methacrolein or bromoacrolein with cyclopentadiene catalysed by [RuCl(L)(mes)] (L = pymim, pymox) after treatment with $AgSbF_6$[a]



Entry	Complex	R	NR^1	Dienophile	Yield	*exo*:*endo*	E.e. (%)
1	**5a**	^{i}Pr	Ph	Methacrolein	45	93:7	26
2	**5b**	^{i}Pr	^{n}Bu	Methacrolein	87	95:5	58
3	**5c**	Bn	^{t}Bu	Methacrolein	48	93:7	19
4	**6**	^{i}Pr		Methacrolein	72	95:5	75
5	**5a**	^{i}Pr	Ph	Bromoacrolein	45	83:17	10
6	**5b**	^{i}Pr	^{n}Bu	Bromoacrolein	92	93:7	50
7	**5c**	Bn	^{t}Bu	Bromoacrolein	50	90:10	3
8	**6**	^{i}Pr		Bromoacrolein	0		

[a] Reactions at 0 °C for 72 h, with 2 mol% catalyst formed in situ except entry 4 only 4 h.

Treatment of **5a–c** with $AgSbF_6$ generates dications $[Ru(solvent)(R\text{-}pymim)(mes)]^{2+}$ which can catalyse the Diels-Alder reaction between methacrolein or bromoacrolein and cyclopentadiene. Results for these and the related cation $[Ru(solvent)(^i Pr\text{-}pymox)(mes)]^{2+}$ (**6**) [8] are shown in Table 2. The effect of differing electronic properties of the NR^1 group can be seen by comparing entries 1 and 5 (NPh) with entries 2 and 6 (N^nBu) for the R = ^{i}Pr catalysts. With the ^{n}Bu group the catalyst gives good enantioselection (58% and 50% e.e.) and *exo*:*endo* selectivity (95:5 and 93:7) with either methacrolein or bromoacrolein as dienophile. In comparison, the selectivities are dramatically reduced (26% and 10% e.e.) and (93:7 and 83:17 *exo*:*endo*), for the comparable reactions with R^1 = Ph, suggesting an element of electronic control is possible, by selecting an electron donating (^{n}Bu) or withdrawing (Ph) group. It should be noted that the *exo*:*endo* ratio 83:17 (entry 5) is similar to that of the thermal reaction, indicating complex **5a** is a poor catalyst for the reaction of bromoacrolein and CpH. Substituting R = ^{i}Pr with Bn, lowers the enantioselectivity of both reactions from 58% to 19% e.e. for methacrolein and from 50% to 3% e.e. for bromoacrolein. Reduced selectivity with a benzyl-substituent in place of an isopropyl is consistent with the results from pyridine oxazoline [8] and salicyloxazoline-containing [15] catalysts. The imidazoline complexes are less active and selective than the analogous oxazoline complexes [11] for the methacrolein/CpH reaction (compare entries 1 and 2 versus entry 4), but they are more active for the bromoacrolein/CpH reaction (compare entries 5 and 6 versus entry 8), indeed the oxazoline complexes do not catalyse this reaction. Kundig has previously noted that strong Lewis acids may fail as catalysts for bromoacrolein reactions due to abstraction of the bromide by the catalyst [16]. In the reaction with methacrolein 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 the literature values [17]. The absolute configuration of the major *exo* product is consistent with the imidazoline substituent shielding the *Si* face of the coordinated methacrolein leading to attack of cyclopentadiene at the *Re* face as we have discussed previously for the ruthenium pyridyloxazoline complexes [8].

In conclusion, imidazolines are structurally similar to oxazolines but are more basic therefore giving less Lewis acidic complexes than corresponding oxazolines. Hence, imidazolines are stronger donors than oxazolines and this difference can be fine tuned by substitution on the amine nitrogen of the imidazoline. The ability to tune the Lewis acidity of half-sandwich complexes whilst maintaining their gross geometrical features may prove beneficial for their use in asymmetric catalysis [5–7].

3. Experimental

Petroleum ether 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 sulphate. The reactions described were carried out under nitrogen; however, once isolated as pure solids the compounds are air-stable and precautions for their storage are unnecessary. ^{1}H NMR spectra were obtained using Bruker 250, 300 and 400 MHz spectrometers in CD_2Cl_2 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. Bromoacrolein [18], and $[RuCl_2(mes)]_2$ [19] were prepared using the literature procedures.

3.1. Preparation of pyridine imidazolines *1*

A mixture of pyridine-carboxyimidate (303 mg, 2.22 mmol), the appropriate diamine (2.22 mmol) and

$CHCl_3$ (1 cm^3) was stirred overnight at 60 °C. The solvent was evaporated and the residue dissolved in CH_2Cl_2 and then washed with three 15 cm^3 portions of water. The aqueous layers were extracted with dichloromethane (40 cm^3) and the combined organic layers were dried over $MgSO_4$ and evaporated to give an off-white solid. The purity of the solids was checked by NMR spectroscopy and the ligands were used without further characterisation.

*[RuCl(**1a**)(mes)][SbF_6] (**5a**)*. A solution of **1a** (20 mg, 0.08 mmol) and $NaSbF_6$ (20 mg, 0.08 mmol) in MeOH (10 cm^3) was added to $[RuCl_2(mes)]_2$ (22 mg, 0.04 mmol) and the resulting suspension was heated to reflux for 2 h. An orange/brown coloured solution was obtained, which was evaporated and the crude residue was dissolved in CH_2Cl_2. Filtration through celite gave a red solution, which was evaporated to afford **5a** (54 mg, 95%). Calc. for $C_{26}H_{31}ClF_6N_3RuSb(0.5CH_2Cl_2)$: C, 39.77; H, 4.03; N, 5.25. Found: C, 40.04; H, 4.00; N, 5.24%. ^{1}H NMR δ 0.87 (d, 3H, *J* 7, *Me*CHMe′), 0.97 (d, 3H, *J* 6.5, MeCH *Me′*), 2.25 (s, 9H, C_6Me_3), 2.25 (m, 1H, MeC*H*Me′), 3.93 (dd, 1H, *J* 10, 5, NCH*H′*), 4.54 (t, 1H, *J* 10, NC*H*H), 4.76 (m, 1H, NC*H*), 5.36 (s, 3H, C_6Me_3), 6.87 (d, 1H, J 7.5, Py-3-*H*), 7.02 (d, 1H, *J* 7, N–*Ph*), 7.39 (m, 2H, N–*Ph*), 7.51 (m, 1H, Py-5-*H*), 7.56 (m, 2H, N–*Ph*), 7.65 (dt, 1H, *J* 1.5, 8, Py-4-*H*), 9.15 (d, 1H, *J* 5, Py-6-*H*). MS (FAB^+): *m*/*z* 522 $[M]^+$, 487 [M−Cl].

*[RuCl(**1b**)(mes)][SbF_6] (**5b**)*. A solution of **1b** (66 mg, 0.27 mmol) and $NaSbF_6$ (70 mg, 0.27 mmol) in MeOH (10 cm^3) was added to $[RuCl_2(mes)]_2$ (78 mg, 0.13 mmol) and the resulting suspension was heated to reflux for 2 h. An orange/brown coloured solution was obtained, which was evaporated and the crude residue was dissolved in CH_2Cl_2. Filtration through celite gave a red solution, which was evaporated to afford **5b** (181 mg, 91%). Calc. for $C_{24}H_{35}ClF_6N_3RuSb$: C, 39.07; H, 4.78; N, 5.70. Found: C, 38.18; H, 4.46; N, 5.23%. ^{1}H NMR δ 0.73 (d, 3H, *J* 6.5, *Me*CHMe′), 0.97 (d, 3H, *J* 7.5, MeCH*Me′*), 0.98 (t, 3H, *J* 7.5, ^{n}Bu–CH_3), 1.42 (m, 2H, CH_2–^{n}Bu), 1.64 (m, 2H, CH_2–^{n}Bu), 2.24 (m, 1H, MeC*H*Me′) 2.25 (s, 9H, C_6Me_3), 3.35 (m, 1H, NC*H′*), 3.81 (dd, 1H, *J* 10, 5.5, NC*H*), 3.94 (m, 2H, NCH_2–^{n}Bu), 4.62 (m, 1H, NC*H*), 5.30 (s, 3H, C_6Me_3), 7.63 (t, 1H, *J* 6.5, Py-5-*H*), 7.78 (d, 1H, *J* 8, Py-3-*H*), 8.00 (t, 1H, *J* 8, Py-4-*H*), 9.17 (d, 1H, *J* 5.5, Py-6-*H*). MS (FAB^+): *m*/*z* 502 $[M]^+$, 467 [M−Cl].

*[RuCl(**1c**)(mes)][SbF_6] (**5c**)*. A solution of **1c** (50 mg, 0.17 mmol) and $NaSbF_6$ (46 mg, 0.17 mmol) in MeOH (10 cm^3) was added to $[RuCl_2(mes)]_2$ (50 mg, 0.09 mmol) and the resulting suspension was heated to reflux for 2 h. An orange/brown coloured solution was obtained, which was evaporated and the crude residue was dissolved in CH_2Cl_2. Filtration through celite gave a red solution, which was evaporated to afford **5c** (127 mg, 94%). Calc. for $C_{28}H_{35}ClF_6N_3RuSb$: C, 42.79; H, 4.49; N, 5.35. Found: C, 42.60; H, 4.39; N, 5.21%. ^{1}H NMR δ 1.48 (s, 9H, N–*Bu^t*), 2.32 (s, 9H, C_6Me_3), 2.67 (dd, 1H, *J* 14.5, 10.5, C*H*H′Ph), 3.44 (dd, 1H, *J* 14.5, 4, CH*H′*Ph), 3.68 (dd, 1H, *J* 11, 7.5, NC*H′*), 4.01 (dd, 1H, *J* 11, 10, NC*H*), 4.79 (ddd, 1H, {*J* = 10.5, 10, 7.5 Hz}, NC*H*), 5.37 (s, 3H, C_6Me_3), 7.32 (m, 5H, Ph), 7.68 (dt, 1H, *J* 1.5, 5.5, Py-5-H), 8.01 (dt, 1H, *J* 7.0, 1.5, Py-4-H), 8.15 (d, 1H, *J* 8.0,

Table 3
Crystallographic data for complexes **1a**, **5b** and **5c**

	1a	**5b**	**5c**
Empirical formula	$C_{17}H_{19}N_3$	$C_{24}H_{35}ClF_6N_3RuSb$	$C_{28}H_{35}ClF_6N_3RuSb$
Formula weight	265.35	737.82	785.86
Temperature (K)	200(2)	200(2)	200(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	7.744(2)	9.083(1)	8.0067(13)
b (Å)	11.060(2)	15.031(4)	17.323(2)
c (Å)	16.926(3)	20.902(3)	22.141(3)
U (Å^3)	1449.8(5)	2853.8(8)	3071.0(7)
Z	4	4	4
Density (calculated) (Mg m^{-3})	1.216	1.717	1.700
Absorption coefficient (mm^{-1})	0.073	1.966	1.517
F(000)	568	1464	1560
Crystal size (mm)	0.56 × 0.31 × 0.27	0.51 × 0.42 × 0.37	0.74 × 0.30 × 0.17
Θ range (°)	2.20–25.01	1.95–48.03	2.18–27.00
Index ranges	$0 \leqslant h \leqslant 9$, $-13 \leqslant k \leqslant 1$, $-1 \leqslant l \leqslant 20$	$-19 \leqslant h \leqslant 1$, $-21 \leqslant k \leqslant 0$, $-29 \leqslant l \leqslant 11$	$0 \leqslant h \leqslant 9$, $-1 \leqslant k \leqslant 22$, $-1 \leqslant l \leqslant 28$
Reflections collected	1761	5453	3920
Independent reflections [R_{int}]	1692 [0.0140]	5249 [0.0185]	3854 [0.0485]
Data/restraints/parameters	1692/0/182	5249/0/361	3854/0/362
Goodness-of-fit, F^2	1.089	1.033	1.008
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0317$, $wR_2 = 0.0687$	$R_1 = 0.0421$, $wR_2 = 0.0847$	$R_1 = 0.0542$, $wR_2 = 0.1340$
R indices (all data)	$R_1 = 0.0407$, $wR_2 = 0.0729$	$R_1 = 0.0652$, $wR_2 = 0.0943$	$R_1 = 0.0724$, $wR_2 = 0.1621$
Absolute structure parameter	−8(3)	−0.07(4)	−0.01(7)
Largest difference in peak and hole (e Å^{-3})	0.129 and −0.111	1.051 and −0.960	1.051 and −1.616

Py-3-H), 9.18 (d, 1H, *J* 5.5, Py-6-H). MS (ES^+): *m*/*z* 550 $[M]^+$.

4. X-ray crystallography

Details of the structure determinations of crystals of **1a**, **5b** and **5c** are given in Table 3. Data were collected on a Siemens P4 diffractometer using graphite monochromated Mo Kα radiation, $\lambda = 0.7107$ Å. The data were corrected for Lorentz and polarisation effects and semi-empirical absorption corrections based on ψ scans (XEMP; SHELXTL/PC) were applied for **5b**–**c**. The structures were solved by Patterson methods and refined by full-matrix least-squares on F^2 using the program SHELXTL-PC [20]. 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. Figures were produced using Ortep-3 for Windows [21]. Atomic coordinates, bond lengths and bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 294572–294574.

5. Catalysis

The catalyst was prepared in situ from the chloride complex **5a**–**c** and 1 equiv. of $AgSbF_6$ in CH_2Cl_2, the solution was filtered through celite into a Schlenk tube to remove AgCl. The acrolein (1 mmol) and 2,6-di-*t*-butylpyridine (1 equiv./mol catalyst) were added to the catalyst solution (0.2, or 0.5 mmol) in CH_2Cl_2 (2 cm^3). 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 ^1H NMR spectroscopy and the enantiomeric excess was determined by ^1H NMR or GC after conversion to the acetal with (2*R*,4*R*)-pentanediol [17].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.04.028.

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