Chiral pyridylimidazolines: synthesis, arene ruthenium complexes and application in asymmetric catalysis

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Condensation of (1*S*,2*S*)-1,2-diphenylethylenediamine and 2-cyanopyridine gives the chiral pyridylimidazoline (L^1), deprotonation followed by treatment with methyl iodide gives an NMe derivative (L^2). The pyridylimidazolines react with $[RuCl_2(mes)]_2$ (mes = 1,3,5-trimethylbenzene) in the presence of $NaSbF_6$ to give $[RuCl(L)(mes)][SbF_6]$ (**1,2**) which have been characterised by X-ray crystallography. After treatment with $AgSbF_6$ both complexes are enantioselective catalysts for the Diels–Alder reaction of methacrolein and cyclopentadiene.

Over the last decade, chiral oxazoline (dihydrooxazole) containing ligands have been extensively studied and have proved extremely successful in inducing high enantioselectivity in a wide range of reactions.[1] Imidazolines (dihydroimidazoles) are five-membered heterocycles analogous to oxazolines (Fig. 1). Since both heterocycles coordinate through the imine, if the substituent (R^1) is the same they should have similar steric requirements. However, electronically, imidazolines should be somewhat more electron rich due to the decreased electronegativity of nitrogen relative to oxygen. In addition, changing the substituent (R^2) may alter the electronic properties whilst leaving the steric requirements almost unaltered, particularly if there is delocalisation through the amidine (NCN) fragment. Imidazolines, therefore, are ideal ligands to probe electronic effects on enantioselectivity.[2]

Imidazolines have received comparatively little study as ligands, notably an arene ruthenium complex has been reported recently.[3] To date, only two metal complexes have been structurally characterised[4] and no chiral imidazoline complexes have ever been isolated and characterised. The synthesis of chiral imidazolines and their use in controlling diastereoselectivity for organic reactions has been reported.[5] More recently, a bidentate thioimidazoline ligand has been reported to give high enantiomeric excess in the palladium catalysed allylic alkylation though the catalyst was only prepared *in situ*.[6]

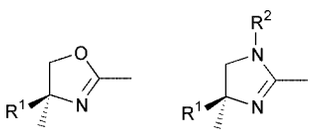
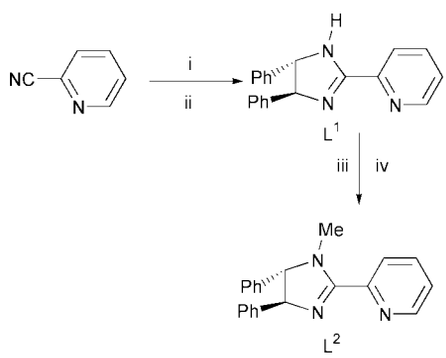


Fig. 1



Scheme 1 (i) Reflux in MeOH with NaOMe (cat); (ii) (1*S*,2*S*)-$H_2NCH(Ph)CH(Ph)NH_2$; (iii) LiN^iPr_2; (iv) MeI.

Results and discussion

Ligand L^1 was prepared from 1,2-diphenylethylenediamine and 2-cyanopyridine according to Scheme 1. The ^{1}H NMR spectrum of L^1 at room temperature shows three broad singlets for the imidazoline ring; cooling to 243 K causes the signals to sharpen into two well resolved doublets at δ 4.86 and 5.13 due to the C*H*Ph groups and a singlet at δ 6.62 due to the NH. Solvent assisted tautomerism has been observed previously for imidazolines.[5] Ligand L^2 was prepared by deprotonation of L^1 followed by treatment with methyl iodide. The ^{1}H NMR spectrum of L^2 contained a singlet at δ 2.99 (3H, N*Me*) and two well resolved doublets at δ 4.36 (CH^aPh) and δ 4.99 (CH^bPh) indicating that tautomerism is not occurring, as expected after substituting hydrogen by methyl. The mass spectra of L^1 and L^2 each show peaks due to the molecular ion $[M + H]^+$ at *m*/*z* 300 and 314 respectively.

Treating the ligands with $[RuCl_2(\eta^6\text{-mes})]_2$ in refluxing methanol in the presence of $NaSbF_6$ gives $[RuCl(L)(\eta^6\text{-mes})]SbF_6$ (**1, 2**) in good yield. The complexes contain a chiral metal centre and two diastereomers are possible differing in configuration at the metal. Signals due to the pairs of diastereomers can readily be distinguished by ^{1}H NMR, particularly those due to mesitylene or the pyridine-6-*H*, and hence the diastereomer ratio is easily determined by integration. The ^{1}H NMR spectra of crude reaction mixtures containing **1** or **2** both contain two signals for the $C_6H_3Me_3$ protons, *i.e.* singlets at δ 5.40 and 5.52 for **1** and δ 5.43 and 5.51 for **2**, with diastereomer ratios 53 : 47 and 47 : 53, respectively. The isomer ratios did not change over a month in d_6-acetone, indicating that either the ruthenium configurations are stable under these conditions or that the complexes have already reached the equilibrium diastereomer ratio and the rate of epimerisation is much slower than that of the NMR timescale (see below). Careful recrystallisation from mixtures of acetone–ether gave crystals suitable for X-ray diffraction. The X-ray structures of the cations with selected bond distances and angles are shown in Figs. 2 and 3. In each case only one diastereomer is present in the crystal. The ruthenium atoms have a pseudooctahedral geometry with the arene occupying three adjacent sites of the octahedron. The imidazolines are coordinated such that the phenyl substituent adjacent to the imine nitrogen [C(8) in **1**, C(9) in **2**] is on the same side as the chloride rather than the arene; as found in related pyridyloxazoline complexes.[7,8] The Ru–N(1) and Ru–

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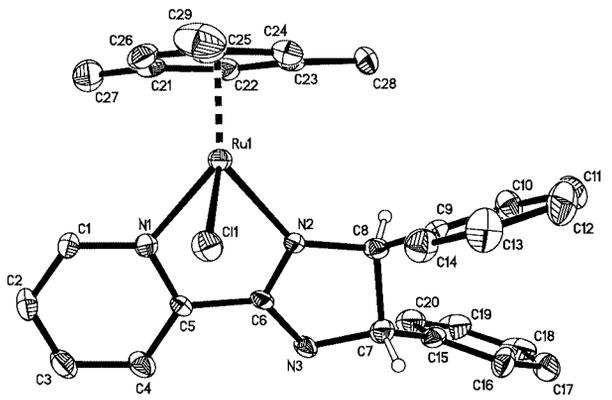


Fig. 2 Molecular structure and atom numbering scheme for the cation of **1**. Selected bond distances (Å) and angles (°): Ru–N(1) 2.115(7), Ru–N(2) 2.097(7), Ru–Cl 2.420(3), N(1)–C(1) 1.348(11), N(1)–C(5) 1.355(11), C(5)–C(6) 1.456(12), N(2)–C(6) 1.301(11), N(2)–C(8) 1.491(11), N(3)–C(6) 1.334(11), N(3)–C(7) 1.464(11), N(2)–Ru–N(1) 76.5(3), N(1)–Ru–Cl 80.5(2), N(2)–Ru–Cl 86.4(2).

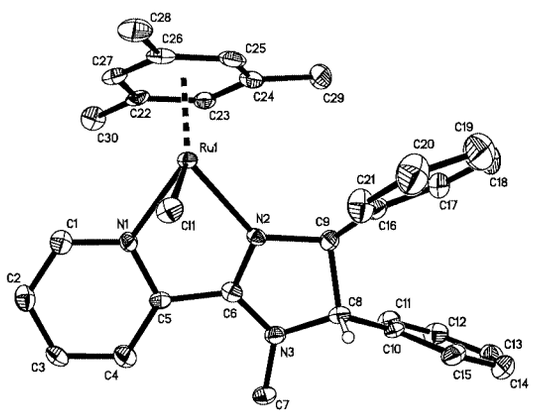
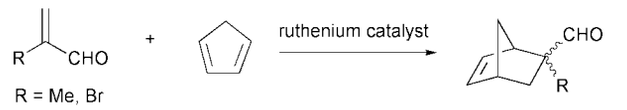


Fig. 3 Molecular structure and atom numbering scheme for the cation of **2**. Selected bond distances (Å) and angles (°): Ru–N(1) 2.091(6), Ru–N(2) 2.094(6), Ru–Cl 2.412(2), N(1)–C(1) 1.341(9), N(1)–C(5) 1.373(10), C(5)–C(6) 1.468(10), N(2)–C(6) 1.311(9), N(2)–C(9) 1.500(9), N(3)–C(6) 1.344(9), N(3)–C(8) 1.469(10), N(2)–Ru–N(1) 76.4(2), N(1)–Ru–Cl 81.3(2), N(2)–Ru–Cl 85.5(2).

N(2) distances, to pyridine and imine respectively, are the same within each complex, and are also statistically the same as the corresponding distances [2.104(5) and 2.105(5) Å] in the related cation $[RuCl(Ph\text{-}pymox)(mes)]^+$ (**3**) [Ph-pymox = 2-(4-phenyl-oxazolin-2-yl)pyridine].[8] The Ru–Cl distances are 2.420(3) and 2.412(2) Å, and the chelate bite angles 76.5(3) and 76.4(2)°, for **1** and **2** respectively, compared with 2.403(2) Å and 76.4(2)° in **3**.[8] Thus, as described above, the steric requirements of the imidazoline ligands are very similar to the related oxazolines and the substituent on C(7) (or C(8) in **2**) doesn't seem to have much effect on the geometry at the metal. In each of **1** and **2**, the N(3)–C(6) distance 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 and considerably shorter than the formal single bonds N(2)–C(8) in (**1**) and N(2)–C(9) in (**2**); implying a degree of delocalisation across the amidine N(2)–C(6)–N(3) fragment. In **2**, the sum of the angles around N(3) is 358.3° which is also consistent with delocalisation across the amidine.

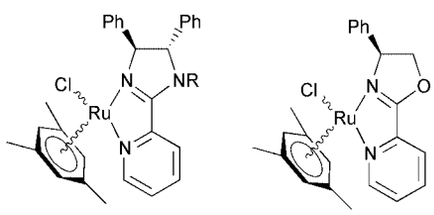
In each case, dissolution of crystals of **1** or **2** in CD_2Cl_2 at low temperature and recording the ^1H NMR spectrum showed a single diastereomer which is assumed to be the same as that found in the solid state. In acetone solution the single diastereomers undergo epimerisation at the metal reaching equilibrium (*ca*. 45 : 55 mixture of diastereomers) over a period of 1–2 days at room temperature compared with about 40 days at 40 °C for cation **3**.[8] The increased rate of epimerisation

Table 1 Enantioselective Diels–Alder reaction of methacrolein or 2-bromoacrolein with cyclopentadiene in dichloromethane using catalysts prepared from $[RuCl(L)(mes)]^+$



Catalyst	Dienophile	*t*/h	Yield (%)[a]	(*exo* : *endo*)	Ee[b]
1	Methacrolein	72	90	94 : 6	45
2	Methacrolein	72	35	93 : 7	31
3	Methacrolein	72	71	94 : 6	58
1	2-Bromoacrolein	48	66	84 : 16	17
2	2-Bromoacrolein	48	68	91 : 9	26

[a] Isolated yield. [b] Enantiomeric excess of the major *exo* product.



1, R = H
2, R = Me

3

is consistent with the increased electron donor properties of the imidazoline providing greater stabilisation of the presumed 16-electron intermediate than with the oxazoline.

In recent years there has been much interest in using chiral transition-metal-based Lewis acids as catalysts for Diels–Alder reactions.[9,10] Treatment of **1** or **2** with $AgSbF_6$ generates dications $[Ru(solvent)(L)(mes)]^{2+}$ which can catalyse the Diels–Alder reaction between methacrolein (methacrylaldehyde) or 2-bromoacrolein (2-bromoacrylaldehyde) and cyclopentadiene. Results for these and the related cation **3**[8] are shown in Table 1. 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*)-pentane-2,4-diol with literature values.[11] The absolute configuration of the major *exo* product is consistent with the phenyl 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] Complex **2** has the most electron-donating chelate ligand and is therefore the least Lewis acidic, consistent with this, it has the lowest activity and selectivity for the reaction between methacrolein and cyclopentadiene. Complex **1** also gives slightly reduced enantioselectivity compared to the oxazoline complex **3**. In the reaction between 2-bromoacrolein and cyclopentadiene, complex **2** is more selective than **1**, giving a higher *exo* : *endo* ratio and increased enantioselectivity. (Pyridyl-oxazoline complexes (*e.g*. **3**) are not catalysts for this reaction).[8] A weaker Lewis acid may be advantageous with the more reactive dienophile 2-bromoacrolein, indeed bromine abstraction has been reported in a strongly Lewis acidic cyclopentadienyl ruthenium complex.[10a] In addition, the greater reactivity means that for complex **1** some of the product may arise from the thermal reaction which gives an *exo* : *endo* ratio of 80 : 20.

In summary, we have synthesised new chiral pyridylimidazolines and have shown that, as expected, their steric requirements are very similar to the corresponding pyridyloxazolines. Whilst the enantioselectivities reported here for **1** and **2** are only modest, they demonstrate that imidazolines can be used in place of oxazolines as chiral directing groups and that electronic tuning of Lewis acidity and enantioselectivity is feasible with such ligands.

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 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 300 or 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) and *J* values are given in Hz. FAB mass spectra were obtained on a Kratos concept mass spectrometer using a 3-nitrobenzyl alcohol (NOBA) matrix, electrospray mass spectra were obtained on a Micromass Quattro LC in MeOH or MeCN. Microanalyses were performed by Butterworth laboratories Ltd., Middlesex. Polarimetric measurements were made on a Perkin Elmer 341 instrument at ambient temperature at 589 nm, concentration in g per 100 cm^3 solution and are given in units of 10^{-1} deg cm^2 g^{-1}. 2-Bromoacrolein,[12] $[RuCl_2(mes)]_2$, [13] pyridine-2-carboximidate[14] and (1*S*,2*S*)-1,2-diphenylethylenediamine[15] were prepared using literature procedures; on the basis of the optical rotation the diamine was at least 97% optically pure.

Preparation of L^1

A mixture of pyridine-2-carboximidate (303 mg, 2.22 mmol), (1*S*,2*S*)-1,2-diphenylethylenediamine (471 mg, 2.22 mmol) and $CHCl_3$ (1 cm^3) was stirred overnight at 60 °C. The resulting pale yellow paste was evaporated, 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. Recrystallisation from CH_2Cl_2–hexane afforded a white crystalline solid. Yield = 627 mg (85%). Calc. for $C_{20}H_{17}N_3$: C, 80.24; H, 5.72; N, 14.04. Found: C, 80.06; H, 5.84; N, 14.54%. ^{1}H NMR (400 MHz, $CDCl_3$, 243 K) δ 4.86 (dd, 1H, *J* 1, 9, C*H*^{a}Ph), 5.13 (d, 1H, *J* 9, C*H*^{b}Ph), 6.62 (br s, 1H, NH), 7.36 (m, 10H, 2 × Ph), 7.48 (ddd, 1H, *J* 1, 5, 7.5, py 5-*H*), 7.88 (dt, 1H, *J* 2, 7.5, py 4-*H*), 8.34 (td, 1H, *J* 1, 8, py 3-*H*), 8.66 (ddd, 1H, *J* 1, 2, 5, py 6-*H*). FAB-MS *m*/*z* 300 $[M + H]^+$. [*a*] −66 (*c* = 0.100, CH_2Cl_2).

Preparation of L^2

To a dry degassed colourless solution of L^1 (319 mg, 1.06 mmol) in THF (24 ml) at 243 K was added a cyclohexane solution of LDA (1.5 M, 2.13 cm^3, 2.44 mmol), the solution immediately turned dark purple. After stirring for four hours dry MeI (73 µl, 1.17 mmol) was added and the reaction mixture allowed to slowly warm to room temperature over two hours, which was accompanied by a colour change to pale yellow–brown. Evaporation gave a brown crude residue which was dissolved in CH_2Cl_2 and then washed with three 20 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 a pale brown oily residue. The oil was chromatographed on silica, with $CHCl_3$–MeOH–NEt_3 (80 : 15 : 5) as eluent. Evaporation of the fore-run gave an oil; recrystallisation from various laboratory solvents failed to give a solid product, however the resultant pale brown oil, L^2 (247 mg, 74%) was pure by ^{1}H spectroscopy. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.99 (s, 3H, N*Me*), 4.36 (d, 1H, *J* 10.5, C*H*^{a}Ph), 4.99 (d, 1H, *J* 10.5, C*H*^{b}Ph), 7.32 (m, 11H, 2 × *Ph* + py 5-*H*), 7.81 (dt, 1H, *J* 2, 8, py 4-*H*), 8.10 (td, 1H, *J* 1, 7.5, py 3-*H*), 8.71 (ddd, 1H, *J* 1, 2, 5, py 6-*H*). FAB-MS *m*/*z* 314 $[M + H]^+$; the high resolution spectrum of this ion was consistent with the proposed formulation.

[RuCl(L^1)(mes)][SbF$_6$] 1

A solution of L^1 (38 mg, 0.126 mmol) and $NaSbF_6$ (33 mg, 0.126 mmol) in MeOH (10 cm^3) was added to $[RuCl_2(mes)]_2$ (37 mg, 0.0631 mmol) and the resulting suspension was heated to reflux for two hours. 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 **1** (99 mg, 99%). Calc. for $C_{29}H_{29}ClF_6N_3RuSb\cdot H_2O$: C, 43.01; H, 3.86; N, 5.19. Found: C, 42.78; H, 3.34; N, 4.91%. (Note, although no H_2O is found in the X-ray structure, NMR samples often showed the presence of water.) ^{1}H NMR (300 MHz, d_6-acetone) δ 2.08[2.09] (s, 9H, C_6Me_3), 5.16[5.10] (d, 1H, *J* 11.5[6.5], CH^{a}Ph), 5.40[5.52] (s, 3H, C_6Me_3), 5.77[5.19] (d, 1H, *J* 11.5[6.5], CH^{b}Ph), 7.35–7.47* (m, 10H, Ph), 7.95* (t, 1H, *J* 6, py-H), 8.37* (m, 2H, py-H), 9.02[9.22] (br s, 1H, NH), 9.44[9.64] (d, 1H, *J* 5.5, py 6-H). Signals for the solid state isomer are shown first with the other isomer in square brackets, * indicates that the signal for the second isomer is coincident with the first. MS (ES$^+$) *m*/*z* 556 $[M]^+$.

[RuCl(L^2)(mes)][SbF$_6$] 2

A solution of L^2 (99 mg, 0.316 mmol) and $NaSbF_6$ (82 mg, 0.316 mmol) in MeOH (10 cm^3) was added to $[RuCl_2(mes)]_2$ (92 mg, 0158 mmol) and the resulting suspension was heated to reflux for two hours. 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 **2** (247 mg, 97%). Calc. for $C_{30}H_{31}ClF_6N_3RuSb\cdot H_2O$: C, 43.74; H, 4.03; N, 5.10. Found: C, 43.73; H, 3.80; N, 4.59%. (Note, although no H_2O is found in the X-ray structure, NMR samples often showed the presence of water.) ^{1}H NMR (400 MHz, d_6-acetone) δ 2.07[2.10] (s, 9H, C_6Me_3), 3.38[3.35] (s, 3H, NMe), 5.00[4.97] (d, 1H, *J* 12[7.5], CH^{a}Ph), 5.43[5.51] (s, 3H, C_6Me_3), 5.69[5.10] (d, 1H, *J* 12[8], CH^{b}Ph), 7.40–7.67* (m, 10H, Ph), 7.96* (ddd, 1H, *J* 1, 5.5, 7, py-H), 8.35[8.37] (dt, 1H, *J* 1.5, 8, py-H), 8.60[8.58] (dt, 1H, *J* 1.5, 8, py-H), 9.49[9.70] (ddd, 1H, *J* 0.5, 1.5, 5.5, py 6-H). Signals for the solid state isomer are shown first with the other isomer in square brackets, * indicates that the signal for the second isomer is coincident with the first. MS (ES$^+$) *m*/*z* 570 $[M]^+$.

Crystal structure determinations

Crystal data for 1. $C_{29}H_{29}ClF_6N_3RuSb$, $M = 791.82$, orthorhombic, space group $P2_12_12_1$, $a = 8.159(3)$, $b = 17.370(5)$, $c = 21.182(7)$ Å, $U = 3002.0(17)$ Å^3, $Z = 4$, $D_c = 1.752$ g cm^{-3}, $\mu = 1.553$ mm^{-1}, $F(000) = 1560$, graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data collected on a Siemens P4 diffractometer at 200 K. 4137 reflections collected with $1.9 < \theta < 27.0°$, 4051 unique ($R_{int} = 0.0192$). Final $R_1[F^2 > 2\sigma(F^2)] = 0.047$, $wR_2 = 0.106$ for all data. Flack parameter −0.07(5).

Crystal data for 2. $C_{30}H_{31}ClF_6N_3RuSb$, $M = 805.85$, orthorhombic, space group $P2_12_12_1$, $a = 8.566(3)$, $b = 17.569(8)$, $c = 20.345(5)$ Å, $U = 3062(2)$ Å^3, $Z = 4$, $D_c = 1.748$ g cm^{-3}, $\mu = 1.525$ mm^{-1}, $F(000) = 1592$, graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data collected on a Siemens P4 diffractometer at 200 K. 4130 reflections collected with $2.0 < \theta < 27.0°$, 4049 unique ($R_{int} = 0.0361$). Final R_1 $[F^2 > 2\sigma(F^2)] = 0.046$, $wR_2 = 0.113$ for all data. Flack parameter −0.03(4). In both cases an absorption correction based on psi-scan data was applied and the structures were solved by Patterson methods and refined using full matrix least squares on F^2 (SHELXL96).[16] Anisotropic displacement parameters used for all atoms, hydrogens included in calculated positions (C–H 0.96 Å), with isotropic displacement parameters set to 1.2 U_{eq}(C).

CCDC reference numbers 164495 (**1**) and 164496 (**2**). See http://www.rsc.org/suppdata/p1/b1/b103175a/ for crystallographic files in .cif or other electronic format.

Catalysis

The relevant complex (**1**, **2**, or **3**) (0.02 mmol) and one equivalent of $AgSbF_6$ were stirred in CH_2Cl_2 : acetone (7 : 1) (8 cm^3) protected from the light for 1 h. After this time the mixture was filtered through Celite to remove AgCl, the solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (2 cm^3) to provide a yellow–orange solution of the catalyst. Methacrolein or 2-bromoacrolein (1 mmol) and 2,6-di-*tert*-butylpyridine[17] (0.02 mmol) were added to this solution which was cooled to 0 °C before addition of cyclopentadiene (2 mmol). At the end of the reaction, the mixture was passed through a silica plug (to remove catalyst), the solvent was removed and the product was obtained as a colourless oil. The *exo* : *endo* ratio was determined by NMR spectroscopy. The enantiomeric excess was determined by NMR or GC after conversion to the acetal with (2*R*,4*R*)-pentane-2,4-diol, according to the method of Evans *et al.*[11]

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