Pergamon

Tetrahedron: *Asymmetry* 12 (2001) 2683–2694

TETRAHEDRON: *ASYMMETRY*

New chiral 2,2′:6′,2″-terpyridine ligands from the chiral pool: synthesis, crystal structure of a rhodium complex and uses in copper- and rhodium-catalyzed enantioselective cyclopropanation of styrene

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Received 11 September 2001; accepted 21 September 2001

Abstract—A number of chiral C_2-symmetric 2,2′:6′,2″ terpyridines $\mathbf{L_1}$–$\mathbf{L_4}$ were synthesized in moderate to good yields from commercially available chiral materials. Copper(II) and rhodium(III) chloride complexes of these ligands were prepared in good yields. The Rh($\mathbf{L_2}$)Cl_3 complex was isolated as a yellow crystalline solid and characterized by X-ray crystallography. Both Cu(**L**)$(OTf)_2$ and Rh(**L**)$(OTf)_3$ were found to be active catalysts in the cyclopropanation of styrene with ethyl diazoacetate. Enantioselectivity up to 82% e.e. was observed.

1. Introduction

In the past 15 years, chiral C_2-symmetric bidentate *N*,*N*-coordinating ligands such as bis-oxazolines,[1–5] sermicorrins[6–9] and 2,2′-bipyridines[10–18] have been reported to be highly efficient catalysts towards a number of asymmetric reactions. However, the utilization of the three-coordinated versions, chiral C_2-symmetric tridentate *N*,*N*,*N*-coordinating ligands, in asymmetric catalysis is scarce. Bis(oxazolinyl)pyridines of the type **1** (pybox), one of the most remarkable examples of this type of ligand, were found to be useful ligands in the Rh-catalyzed hydrosilylation of ketones,[19] the Ru-catalyzed cyclopropanation,[20–22] the epoxidation of alkenes,[23] Cu-catalyzed carbon–carbon bond forming reactions[24–26] and allylic oxidation.[27,28] Another example is bis(pyrazoyl)pyridines **2**, which were used in Cu- and Rh-catalyzed cyclopropanation with good enantioselectivities.[29]

Chiral terpyridines are structurally similar to pybox, but there are very few reports on their syntheses and application in asymmetric catalysis. von Zelewsky et al. recently reported the synthesis of chiral C_2-symmetric terpyridine **3** in good yields by Kröhnke condensation of chiral (1*R*)-(+)-pinocarvone with 2,6-bis(pyridinoacetyl)pyridine.[30] We modified **3** by deprotonation with lithium diisopropylamide (LDA) and alkylation with different alkyl iodides to yield terpyridines **4** and found that they are effective catalytic ligands in the copper-catalyzed asymmetric cyclopropanation of olefins with enantioselectivities of up to 94% (Scheme 1).[31] These satisfactory results led us to further develop new chiral C_2-symmetric terpyridines using a similar synthetic route. We report here the synthesis of chiral terpyridines $\mathbf{L_1}$–$\mathbf{L_4}$ by Kröhnke condensation of chiral α,β-unsaturated ketones **5**–**8** (Scheme 2), which can be prepared easily from readily available chiral ketones or alcohols, with 2,6-bis(pyridinoacetyl)pyridine diiodide. The preparation of their copper(II) and rhodium(III) chloride complexes was carried out and one of the rhodium complexes was characterized by X-ray crystallography. Their uses in the copper- and rhodium-catalyzed asymmetric cyclopropanation of styrene with ethyl diazoacetate were also explored.

2. Results and discussion

2.1. Ligand syntheses

Chiral α,β-unsaturated ketones **5**, **6** and **8** were prepared in good overall yields from the corresponding chiral ketones, (1*R*)-(+)-nopinone, (*R*)-(+)-camphor and (–)-menthone, respectively, according to literature

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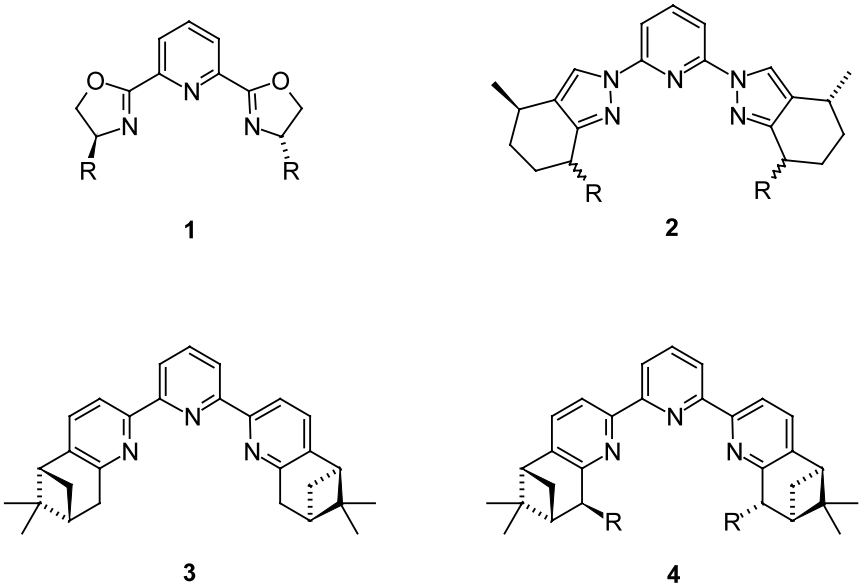
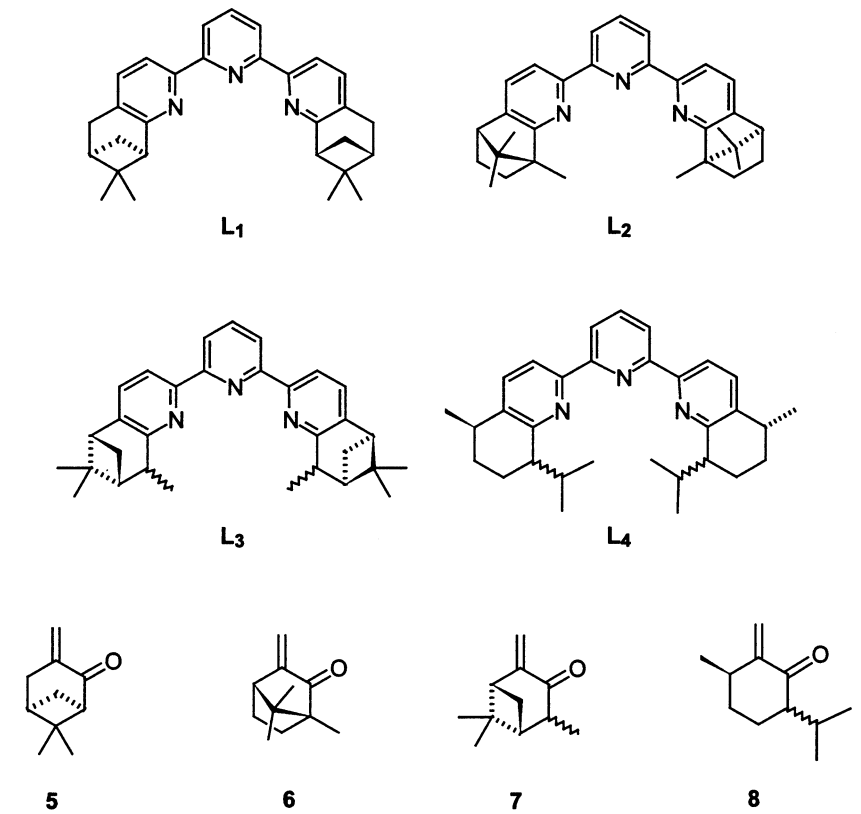
PII: S0957-4166(01)00431-1

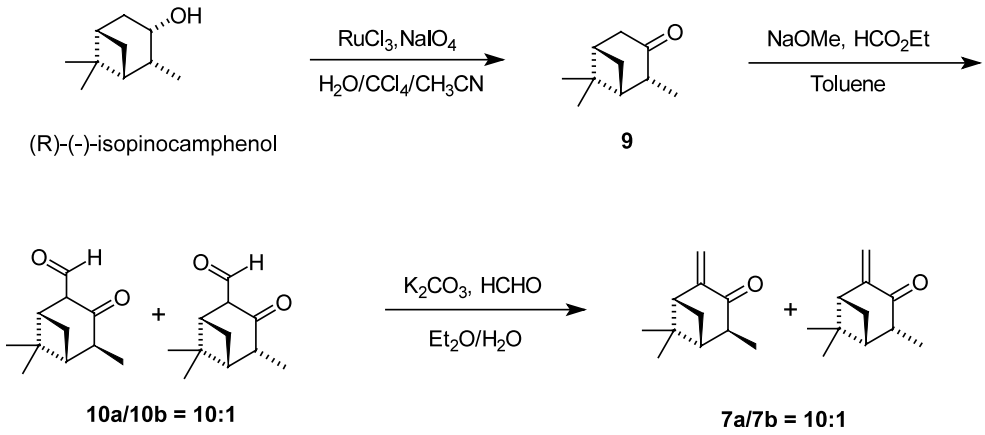


Scheme 1.



Scheme 2.

procedures.[32] Chiral α,β-unsaturated ketones **5** and **6** were obtained in pure isomeric form, while **8** was obtained as an 10:1 epimeric mixture of **8a** and **8b**. The synthetic route for preparation of **7** is outlined in Scheme 3. (*R*)-(−)-Isopinocamphenol was first oxidized to ketone **9** in 90% yield with $NaIO_4$ in the presence of $RuCl_3$ as catalyst and a mixture of CCl_4, H_2O and CH_3CN as solvent.[33] Aldehyde **10** was obtained in 93% yield as a 10:1 epimeric mixture of **10a** and **10b**, by reacting **9** with NaOMe and ethyl formate in toluene at rt. Treatment of **10** with formaldehyde and Na_2CO_3 in Et_2O and H_2O solution gave a 10:1 epimeric mixture of **7a** and **7b** in 80% yield. Terpyridines $\mathbf{L_1}$–$\mathbf{L_4}$ were then synthesized by Kröhnke condensation of α,β-unsaturated ketones **5**–**8**, respectively, with 2,6-bis(pyridinioacetyl)pyridine diiodide (Schemes 4 and 5),[34] which was readily prepared by treating 2,6-diacetylpyridine with iodine in pyridine. Terpyridines $\mathbf{L_1}$ and $\mathbf{L_2}$ were



Scheme 3.

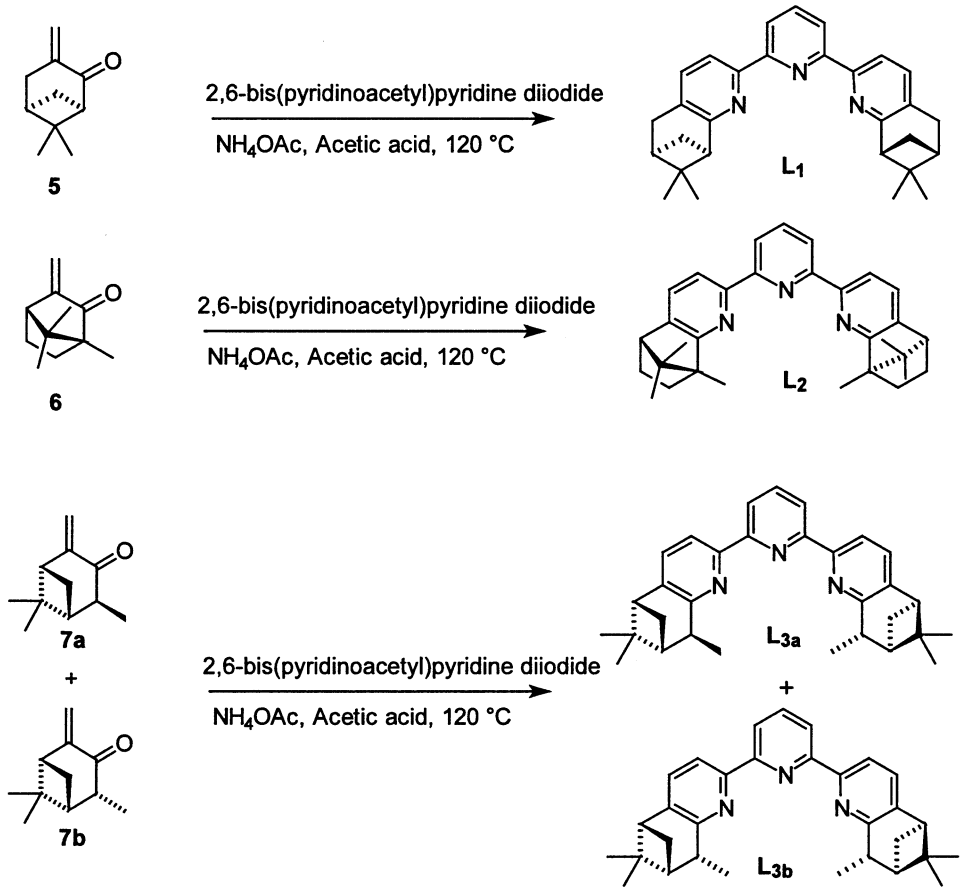
obtained in moderate to good yields in pure form, whereas terpyridines $\mathbf{L_3}$ and $\mathbf{L_4}$ were prepared in yields of 35 and 10%, respectively, as a mixture of diastereomers ($\mathbf{L_{3a}}$, $\mathbf{L_{3b}}$ and $\mathbf{L_{4a}}$, $\mathbf{L_{4b}}$, $\mathbf{L_{4c}}$, respectively), which were separated by column chromatography. We recently reported another procedure for the synthesis of $\mathbf{L_3}$ with similar yield.[31] Interestingly, we found that extensive epimerization occurred if glacial acetic acid was used to prepare $\mathbf{L_4}$ (i.e. $\mathbf{L_{4a}}$:$\mathbf{L_{4b}}$ $\approx$1.1:1). This problem was greatly improved with the use of ethanol as solvent (i.e. $\mathbf{L_{4a}}$:$\mathbf{L_{4b}}$ $\approx$2.4:1).

2.2. Complex syntheses

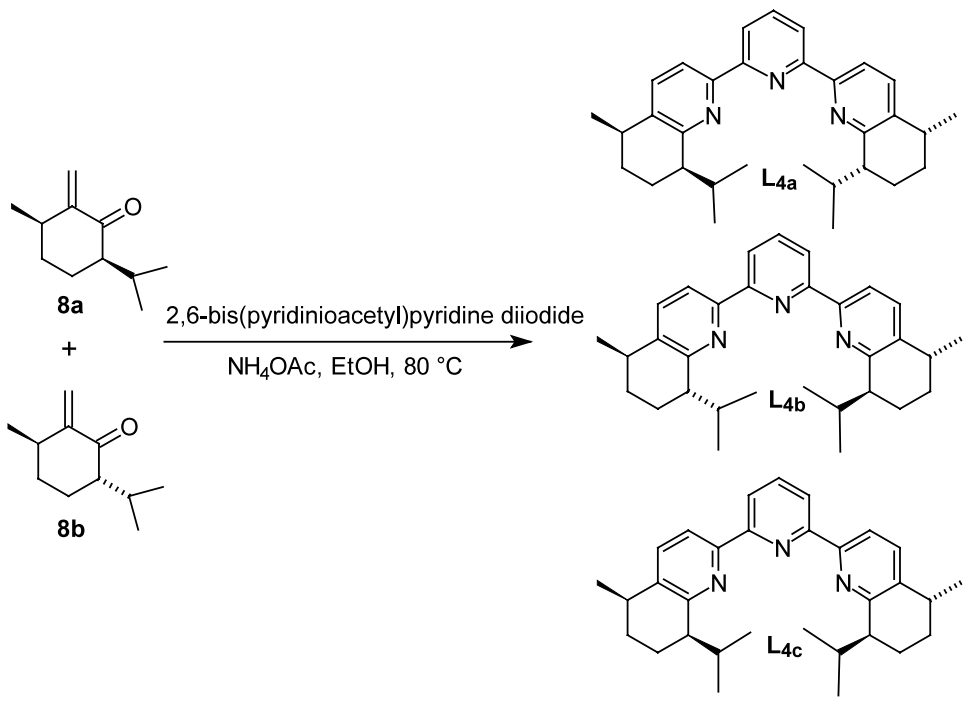
After preparation of these terpyridine ligands, their coordination chemistry with copper(II) and rhodium(III) metal ions was studied. The copper(II)–terpyridine complexes [Cu(**L**)Cl_2] were isolated as green or orange solids in good yields by reaction of a dichloromethane solution of the appropriate terpyridine ligands $\mathbf{L_1}$–$\mathbf{L_2}$ and $\mathbf{L_{3a}}$ with an ethanolic solution of $CuCl_2{\cdot}2H_2O$. Complexes of other terpyrdines were not prepared because of insufficient materials. The rhodium(III)–terpyridine complexes [Rh(**L**)Cl_3] were formed in good yields by treating $\mathbf{L_1}$, $\mathbf{L_2}$, $\mathbf{L_{3a}}$ and $\mathbf{L_{4a}}$, respectively, with rhodium(III) chloride in ethanol. Yellow crystals of Rh($\mathbf{L_2}$)Cl_3 suitable for X-ray crystal analysis were obtained by slow addition of ether into a dichloromethane/ethanolic solution. The crystal structure of Rh($\mathbf{L_2}$)Cl_3 is shown in Fig. 1. The crystal structure of Rh($\mathbf{L_2}$)Cl_3 is a six coordinate molecule and displays a pseudo-octahedral geometry by $\mathbf{L_2}$ and three chloride atoms, both arranged in *mer* configurations. In the asymmetric unit cell there are two distinct molecules. Since they are very similar only one is discussed here. The crystallographic data are summarized in Table 1. Selected bond distances and bond angles are given in Table 2. The bond angles for N(1)–Rh(1)–N(2), N(2)–Rh(1)–N(3), Cl(2)–Rh(1)–N(1) and Cl(1)–Rh(1)–N(3) are 78.8, 81.2, 101.7 and 98.4°, respectively. The angles around the equatorial plane of the rhodium complex total 360.1°, so this is almost planar. The bond lengths of Rh(1)–Cl(1), Rh(1)–Cl(2), Rh(1)–Cl(3), Rh(1)–N(1), Rh(1)–N(2) and Rh(1)–N(3) are 2.346, 2.355, 2.337, 2.134, 1.938 and 2.130 Å, respectively. These bond distances are similar to the other chiral rhodium(III)–terpyridine chloride complexes reported previously.[30]

2.3. Enantioselective cyclopropanation reactions

Both Cu(**L**)Cl_2 and Rh(**L**)Cl_3 are not active in catalysing the cyclopropanation of styrene with ethyl diazoacetate. However, they become active when the chlorides are replaced with triflate ligands. The copper catalysts, Cu(**L**)$(OTf)_2$, were generated by stirring Cu(**L**)Cl_2 with AgOTf (1:2), followed by reacting with a few equivalents of ethyl diazoacetate for 30 min at 40°C. With $\mathbf{L_2}$ as the ligand, this procedure gave cyclopropane esters in 88% yield with a diastereoselectivity of 24:76 favouring the *trans*-isomer. The e.e. of the *trans*-isomer was 32% and that of the *cis*-isomer was 30%. Alternatively, the copper catalysts could be generated by stirring 2 mol% Cu$(OTf)_2$ and 2.2 mol% **L** in CH_2Cl_2, followed by stirring with a few equivalents of ethyl diazoacetate for 30 min at 40°C. Use of this procedure gave the same diastereoselectivity, enantioselectivity and isolated yield. Because it is more convenient to carry out, results for other ligands were obtained using this procedure and are listed in Table 3. All of the terpyridines examined were found to be active catalysts with yields of the isolated cyclopropane esters ranging from 78 to 88% and enantioselectivities of between 10 and 82%. GC analysis of the reaction mixture indicated the *trans*-/*cis*-ratios were between 63:37 and 76:24 (entries 1–5). Of the terpyridines examined, the best result was achieved with $\mathbf{L_{3a}}$, it gave 72 and 82% e.e. for *trans*- and *cis*-isomers, respectively (entry 3). All of these copper-catalyzed cyclopropanations favoured the *trans*-isomer and the absolute configurations of the cyclopropane esters products formed from styrene were determined to be (1*R*,2*R*) and (1*R*,2*S*) for the *trans*- and *cis*-isomers, respectively.



Scheme 4.



Scheme 5.

In the rhodium-catalyzed cyclopropanation reactions, THF was used as the solvent instead of CH_2Cl_2 due to the poor solubility of some of the Rh-catalysts in CH_2Cl_2. Stirring $RhCl_3$ with **L** for 2 h at rt, then treatment of the mixture with AgOTf did not yield active cyclopropanation catalysts. However, active cat-

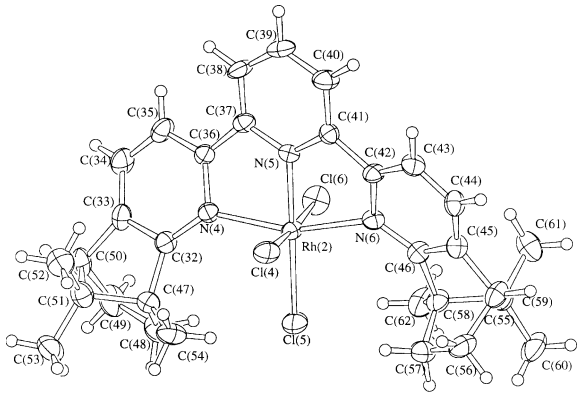


Figure 1. X-Ray crystal structure of Rh(**L**$_2$)Cl$_3$.

Table 1. Crystallographic data for Rh(**L**$_2$)Cl$_3$

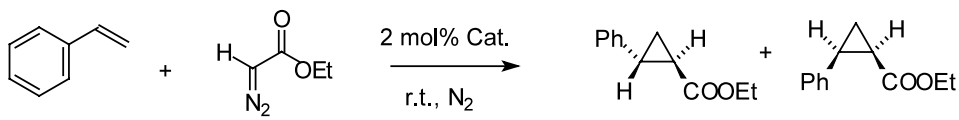
Formula	$RhCl_3N_3C_{31}H_{35}$
Formula weight	658.90
Crystal color	Yellow
Crystal system	Monoclinic
Lattice type	Primitive
Lattice parameters	
a (Å)	15.8410(9)
b (Å)	10.9370(5)
c (Å)	16.994(1)
β (°)	90.13(1)
V (Å^3)	2944.3(2)
Space group	$P2_1$ (#4)
Z value	4
D_{calcd} (g/cm^3)	1.486 (g/cm^3)
Temperature (°C)	0.0
Radiation (Å)	MoKα (λ=0.71069)
μ(MoKα) (cm^{-1})	8.76
$2\theta_{max}$ (°)	55.0
F_{000}	1352.00
No. of reflection measured	Total: 18475
	Unique: 6949 (R_{int}=0.050)
Residuals: R; R_w	0.045; 0.041

Table 2. Structural parameters for Rh(**L**$_2$)Cl$_3$

Atoms	Bond lengths (Å)
Rh(1)–Cl(1)	2.346(2)
Rh(1)–Cl(2)	2.355(2)
Rh(1)–Cl(3)	2.337(2)
Rh(1)–N(1)	2.134(5)
Rh(1)–N(2)	1.938(5)
Rh(1)–N(3)	2.130(6)
	Bond angles (°)
Cl(1)–Rh(1)–Cl(2)	90.92(8)
Cl(1)–Rh(1)–Cl(3)	175.19(7)
Cl(1)–Rh(1)–N(1)	93.9(2)
Cl(1)–Rh(1)–N(2)	88.5(2)
Cl(1)–Rh(1)–N(3)	87.1(2)
Cl(2)–Rh(1)–Cl(3)	93.8(8)
Cl(2)–Rh(1)–N(1)	101.7(1)
Cl(2)–Rh(1)–N(2)	179.3(2)
Cl(2)–Rh(1)–N(3)	98.4(2)
Cl(3)–Rh(1)–N(1)	86.0(1)
Cl(3)–Rh(1)–N(2)	86.8(2)
Cl(3)–Rh(1)–N(3)	91.3(2)
N(1)–Rh(1)–N(2)	78.8(2)
N(1)–Rh(1)–N(3)	159.9(9)
N(2)–Rh(1)–N(3)	81.2(2)

alysts were generated by reacting Rh(**L**)Cl$_3$ with AgOTf in THF for 30 min and used without activation. Based on preliminary optimization of the reaction, we found that changing the ratio of Rh(**L**)Cl$_3$ to AgOTf greatly affected the *cis*/*trans* ratio, % e.e. and the absolute configurations of the products. A ratio of 1:4 for Rh(**L**)Cl$_3$ to AgOTf gave the highest diastereoselectivity and enantioselectivity. All rhodium–terpyridine catalysts were able to catalyze the reaction; enantioselectivities were slightly lower than those obtained with the corresponding copper catalysts (entries 6–9). Terpyridine **L**$_{3a}$ was again the best ligand in terms of both diastereoselectivity (*cis:trans*=7:3) and enantioselectiv-

Table 3. Catalytic asymmetric cyclopropanation with chiral copper(II) and rhodium(III) terpyridines



Entry	Catalyst	Solvent	*cis*:*trans*	% E.e. (*trans*)[a]	% E.e. (*cis*)[a]	Yield (%)[b]
1[c]	**L**$_1$+Cu(OTf)$_2$ (1.1:1)	CH_2Cl_2	25:75	26 (1*S*,2*S*)	26 (1*S*,2*R*)	84
2[c]	**L**$_2$+Cu(OTf)$_2$ (1.1:1)	CH_2Cl_2	24:76	32 (1*R*,2*R*)	30 (1*R*,2*S*)	88
3[c]	**L**$_{3a}$+Cu(OTf)$_2$ (1.1:1)	CH_2Cl_2	33:67	72 (1*R*,2*R*)	82 (1*R*,2*S*)	81
4[c]	**L**$_{4a}$+Cu(OTf)$_2$ (1.1:1)	CH_2Cl_2	35:65	23 (1*R*,2*R*)	38 (1*R*,2*S*)	78
5[c]	**L**$_{4b}$+Cu(OTf)$_2$ (1.1:1)	CH_2Cl_2	37:63	18 (1*S*,2*S*)	10 (1*S*,2*S*)	80
6	Rh(**L**$_1$)Cl$_3$+AgOTf (1:4)	THF	42:58	4 (1*R*,2*R*)	1 (1*R*,2*S*)	43
7	Rh(**L**$_2$)Cl$_3$+AgOTf (1:4)	THF	61:39	20 (1*S*,2*S*)	2 (1*S*,2*R*)	45
8	Rh(**L**$_{3a}$)Cl$_3$+AgOTf (1:4)	THF	70:30	65 (1*S*,2*S*)	71 (1*S*,2*R*)	46
9	Rh(**L**$_{4a}$)Cl$_3$+AgOTf (1:4)	THF	39:61	1 (1*S*,2*S*)	5 (1*S*,2*R*)	61

[a] Enantiomeric excesses were determined by HPLC with Daicel Chiralcel OJ column. Absolute configurations were determined by comparing the order of elution of samples with known configuration.[6]

[b] Isolated yield after chromatography.

[c] Diazoacetate (0.2 equiv.) was used for reduction of the Cu(II) catalyst before the start of cyclopropanation.

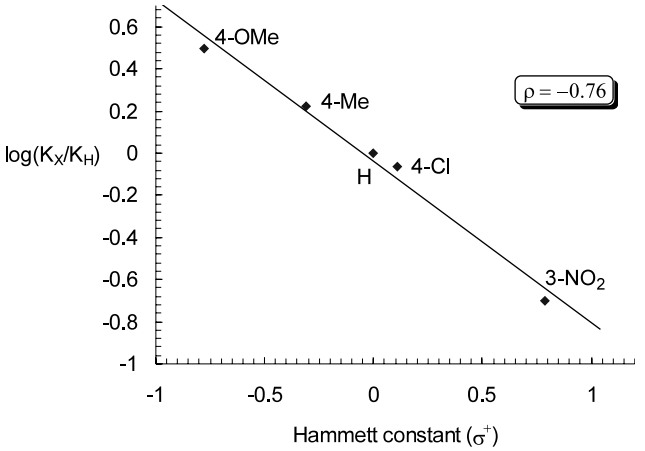


Figure 2. Hammett plot for the cyclopropanation of styrene with EDA using $\mathbf{L_{3a}}$ and $Cu(OTf)_2$ as the catalyst.

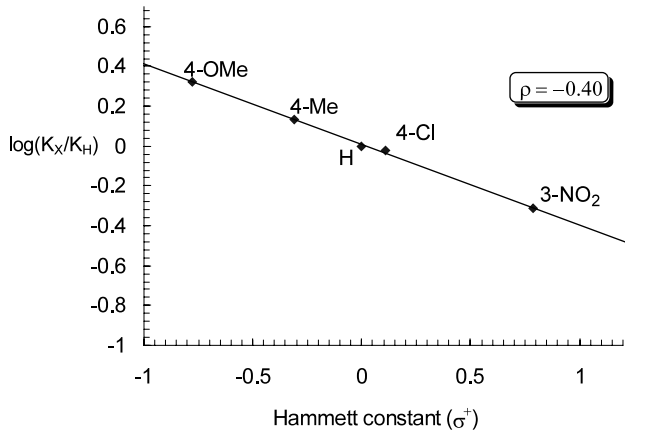
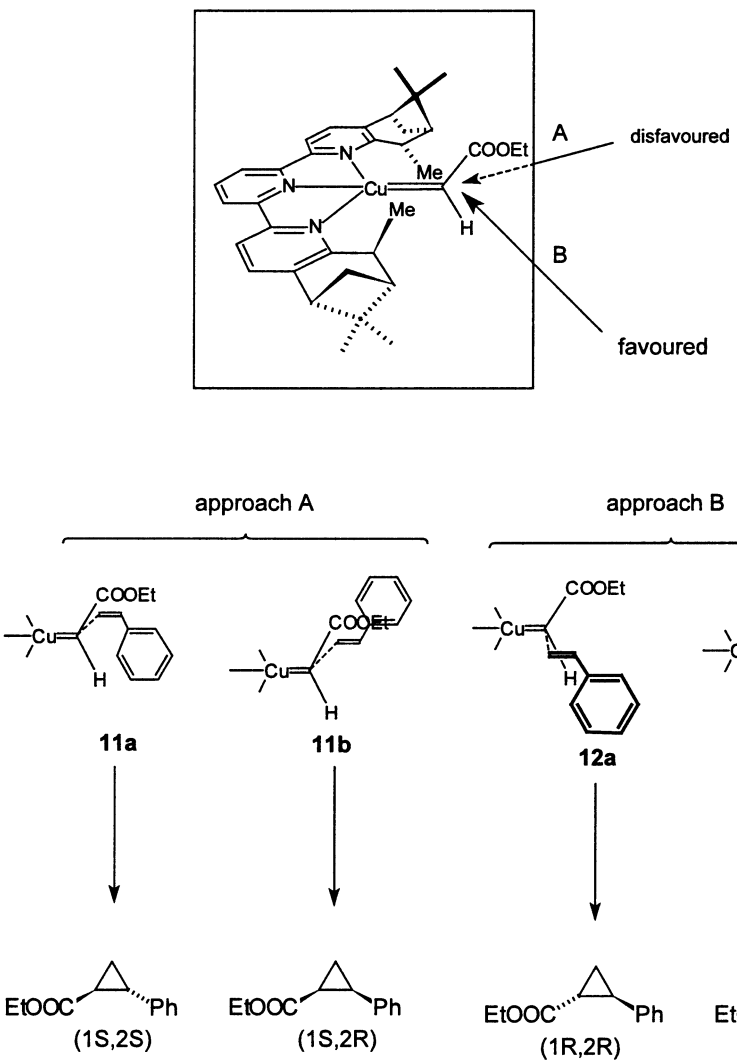
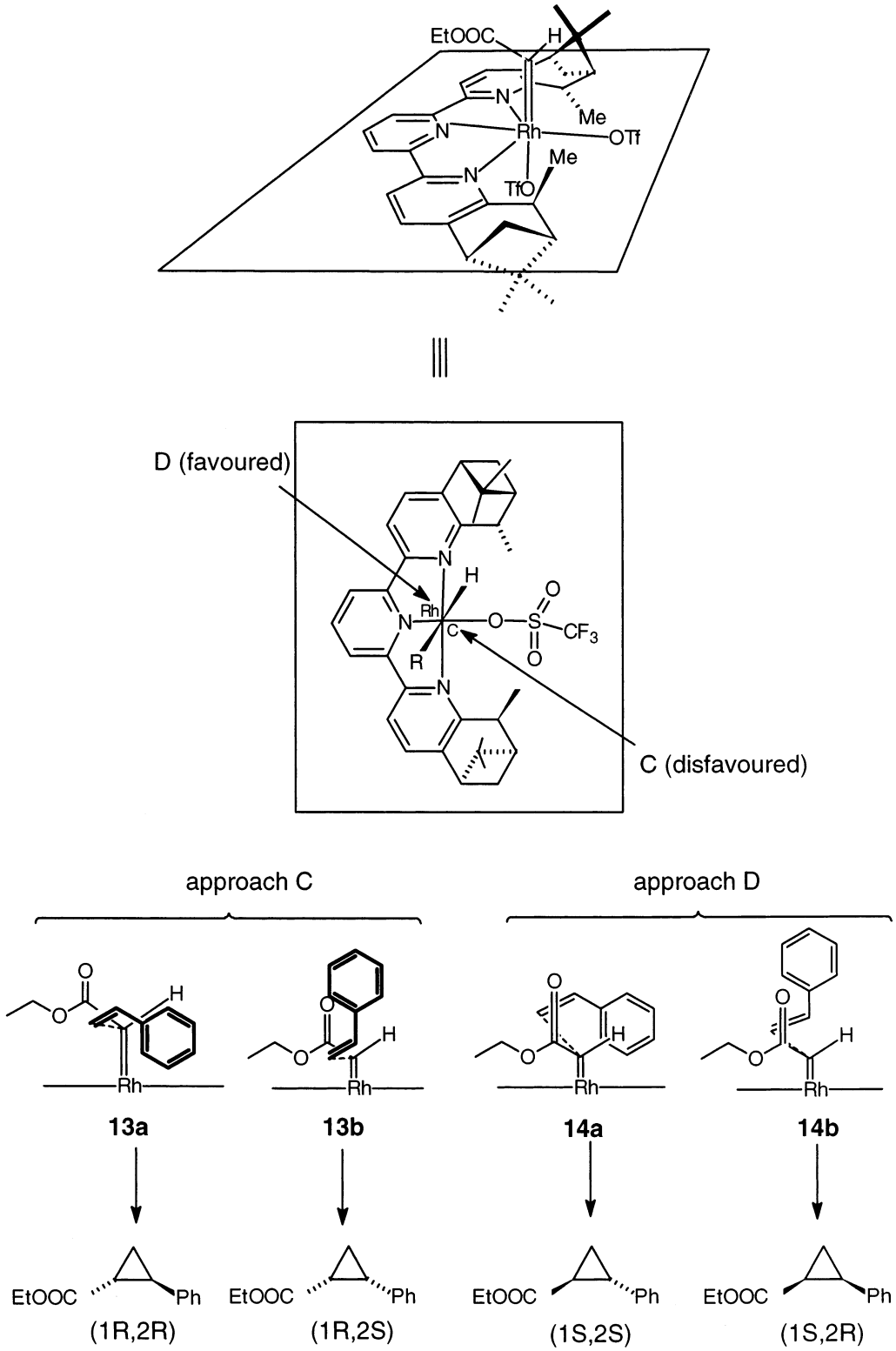


Figure 3. Hammett plot for the cyclopropanation of styrene with EDA using $Rh(\mathbf{L_{3a}})Cl_3$ and AgOTf as the catalyst.

ity (65 and 71% e.e. for *trans*- and *cis*-isomer, respectively) (entry 7). Interestingly, the absolute configurations of the products obtained from the rhodium-catalysts were (1*S*,2*S*) and (1*S*,2*R*) for the *trans*- and *cis*-isomers, respectively, which is opposite to the configurations of the products from reactions using the corresponding copper-catalyst (entries 6–9). Similar observations were reported in the literature.[29] In addition, *cis*-cyclopropanes were the more favoured products in some of the rhodium-catalyzed reactions (entries 7 and 8).



Scheme 6.



Scheme 7.

To obtain more information about the nature of the intermediates involved in both the copper- and rhodium-catalyzed cyclopropanations, the rates of cyclopropanation of substituted styrenes relative to that of styrene were measured through competition experiments using $\mathbf{L_{3a}}$ as ligand. The Hammett plots of $\log(k_X/k_H)$ versus σ^+ for copper and rhodium catalysts are shown in Figs. 2 and 3, respectively. In all cases, the reaction rates were higher with the styrenes substituted with electron-donating groups, i.e. 4-methoxy- and 4-methylstyrene, while the styrenes substituted with electron-withdrawing groups such as 4-chloro- and

3-nitrostyrene reacted more slowly. A good σ^+ correlation is obtained with $\rho = -0.76$ and -0.40 for copper– and rhodium–terpyridine catalysts, respectively. The value of ρ for the copper–terpyridine catalyst is similar to other copper catalysts such as copper(I)–tris(pyrazolyl) borate ($\rho = -0.85 \pm 0.07$ correlate to σ) and copper(II)-di-2-pyridyl ketone ($\rho = -0.74$ correlate to σ^+) reported by Pérez et al.[35] and our group,[36] respectively. The value of ρ for the rhodium–terpyridine catalyst is similar to the ruthenium–porphyrin catalyst ($\rho = -0.44 \pm 0.09$ correlate to σ^+) reported by Che et al.[37] The small negative values of ρ obtained support the formation of an electrophilic metal–carbene complex intermediate and only a moderate positive charge build-up at the benzylic position in the transition state in both systems.

Based on the absolute configuration of products obtained from these reactions, the sense of asymmetric induction observed here can be explained by the models shown in Schemes 6 and 7 for copper and rhodium catalysts, respectively. The model for the copper–terpyridine catalyst has been proposed previously by our group[31] and is similar to the one proposed by Pflatz et al. for *N*,*N*-bidentate ligands.[6] In this model, the copper carbene is located in the same plane as the terpyridine ligand. The ester group and the hydrogen of the carbene are positioned directly above and below this plane. A styrene molecule can attack the metal carbene double bond in a parallel fashion, according to pathways A and B. In pathway A, a repulsive steric interaction builds up between the ester group and the adjacent bulky alkyl group of the ligand making the carbene transfer difficult. In pathway B, no such interaction exists during the transfer of the carbene. Thus, it should be favoured over pathway A and leads to *cis*-(1*R*)- or to *trans*-(1*R*)-cyclopropane esters. The formation of *trans*- and *cis*-isomers comes from the two different approaches of styrene, with the phenyl group on the opposite side of the ester in **11a**, **12a** and the phenyl group on the same side of the ester group in **11b**, **12b**, respectively. The *trans*-selectivity in the reaction is attributed to greater steric hindrance between the ester group and the phenyl group in **12b** than **12a**.

Using a model similar to copper–carbene for rhodium–carbene (i.e. carbene locates in the same plane as the terpyridine ligand), it was found that the wrong enantiomers would result (i.e. (1*R*)-isomers) no matter how styrene approached the carbene. The proposed model for rhodium, shown in Scheme 7, is different: the metal–carbene occupies the axial position of the octahedral rhodium (see upper drawing). The carbene plane probably locates at a position bisecting the N–Rh–N bond angle (see lower drawing). The bulky ester group points away from the alkyl group of the ligand and the C–H bond of the carbene is also arranged in such a way as to minimize the steric interaction between the carbene and the alkyl group of the ligand. Similar metal carbene complexes have been observed recently by Che et al. in the case of ruthenium–carbene porphyrin complexes.[37] Styrene approaches the carbene double bond in a more or less perpendicular fashion. Two pathways, C and D, are possible. In pathway C, styrene attacks the carbene from the more hindered face of the rhodium–carbene double bond and is not favoured. In pathway D, styrene approaches from the more open trajectory and the two orientations, **14a** and **14b**, of the styrene led to *cis*-(1*S*) and *trans*-(1*S*) cyclopropane esters, respectively. The two possible orientations of styrene (one with the phenyl group pointing towards the terpyridine ring and the other with the phenyl group pointing away) in this perpendicular approach could also explain the low *trans*:*cis* ratio and the *cis*-selectivity of some catalysts.

In summary, we have successfully synthesized a number of chiral C_2-symmetric 2,2′:6′,2″-terpyridines, $\mathbf{L_1}$–$\mathbf{L_4}$, in moderate to good yields from naturally occurring optically active ketones or alcohol. These ligands are good catalysts for both copper- and rhodium-catalyzed enantioselective cyclopropanation. E.e.s up to 82% were observed. We are continuing our efforts to study the use of these ligands in other catalytic asymmetric reactions.

3. Experimental

3.1. General methods

Toluene was distilled under N_2 from sodium. Dichloromethane was distilled over calcium hydride. THF was distilled under N_2 over sodium/benzophenone. Chemicals were of reagent-grade quality obtained commercially. Infrared spectra in the range 500–4000 cm^{-1} as KBr plates were recorded on a Perkin Elmer Model FTIR–1600 spectrometer. Proton and ^{13}C NMR spectra were recorded on a Varian 300 MHz Mercury instrument. Positive ion FAB mass spectra as 3-nitrobenzylalcohol matrices were recorded on a Finnigan MAT 95 spectrometer. Electron ionization mass spectra were recorded on a Hewlett Packard 5890II GC instrument coupled with a 5970 mass selective detector. Elemental analyses were performed on a Vario EL elemental analyzer. Optical rotation was measured by JASCO DIP–370 digital polarimeter. Melting point was measured by Electrothermal digital melting point apparatus.

3.2. 2,6-Bis(pyridinioacetyl)pyridine diiodide[34]

To a solution of 2,6-diacetylpyridine (8 mmol, 1.31 g) in pyridine (10 mL) was added a solution of iodine (16 mmol, 4.06 g) in pyridine (10 mL). The mixture was heated at 110°C for 3 h and after cooling the dull yellow solid was filtered and washed with cold ethanol. This product was characterized by ^1H NMR and IR. Yield = 3.82 g (85%). ^1H NMR ($CDCl_3$): δ 6.98 (s, 4H), 8.26 (dd, 4H), 8.43 (s, 3H), 8.76 (dd, 2H, $J = 7.8$ Hz), 9.14 (d, 4H, $J = 5.7$ Hz); IR (KBr): 3022.9 vs, 2969.5 vs, 2946.6 vs, 1719.6 vs, 1635.7 s, 1491.1 s, 1344.5 s.

3.3. α,β-Unsaturated ketones 5, 6 and 8

Following the literature procedure,[32] **5**, **6** and **8** were obtained in overall yields between 66 and 93%.

3.4. Preparation of ketone 9

(*R*)-(−)-Isopinocamphenol (1.93 g, 12.5 mmol), sodium periodate (10.7 g, 50 mmol) and ruthenium trichloride hydrate (62.5 mg, 2.2 mol%) in carbon tetrachloride (25 mL), acetonitrile (25 mL) and water (38 mL) were stirred vigorously for 4 h at rt. The reaction was quenched with water (50 mL) and the mixture was extracted with CH_2Cl_2 (3×50 mL). The organic layers were dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (Et_2O) to give **9** (90%). IR (KBr): C=O, 1710.9 vs; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (s, 3H), 1.18–1.30 (m, 2H), 1.21 (d, $J=7.1$ Hz, 3H), 1.32 (s, 3H), 1.62–1.84 (m, 1H), 2.04–2.14 (m, 1H), 2.46–2.72 (m, 3H). Mass spectrum m/z: 152 (M^+).

3.5. Preparation of chiral aldehyde 10

A solution of ethyl formate (150 mmol) in toluene (12.5 mL) was added to a suspension of NaOMe (150 mmol) in toluene (75 mL) under N_2. The reaction mixture was stirred for 5 min at rt. A solution of ketone **9** (50 mmol) in dry toluene (12.5 mL) was added and the mixture was stirred for overnight at rt. The reaction was quenched with water (50 mL), the aqueous phase was separated and the organic phase was extracted with 1 M NaOH solution (2×50 mL). The combined aqueous extracts were acidified to pH 1 with concentrated HCl. The aqueous phase was extracted with Et_2O (3×50 mL). The combined organic layers were dried with $MgSO_4$ and the solvent was removed under reduced pressure to give **10** (8.37 g, 93%). The product was characterized by IR, ^{1}H NMR and MS analyses. IR (KBr): C=O, 1656.7 vs; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82 (s, 3H), 1.19 (d, $J=7.4$ Hz, 3H), 1.23–1.31 (m, 1H), 1.35 (s, 3H), 1.92–1.96 (m, 1H), 2.32–2.39 (m, 1H), 2.52–2.62 (m, 2H), 2.64–2.72 (m, 1H), 6.94 (s, 1H). Mass spectrum m/z: 180 (M^+).

3.6. Preparation of α,β-unsaturated ketone 7

Aldehyde **10** (2.7 g, 15 mmol) was mixed with 38–38% w/w formaldehyde (17 mL), water (15 mL), Et_2O (35 mL) and potassium carbonate (5 g). The mixture was stirred under reflux overnight under an N_2 atmosphere. The organic phase was separated and the aqueous phase was extracted with Et_2O (3×50 mL). The combined organic extracts were washed with 1 M NaOH (2×50 mL) and followed with H_2O (50 mL). It was then dried with $MgSO_4$ and the solvent was removed under reduced pressure to give **7** (1.97 g, 80%). IR (KBr): C=O, 1703.9 vs; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83 (s, 3H), 1.16 (d, $J=7.1$ Hz, 3H), 1.38 (s, 3H), 1.98–2.03 (m, 1H), 2.54–2.78 (m, 4H), 4.99 (d, $J=1.6$ Hz, 1H), 5.96 (d, $J=1.6$ Hz, 1H). Mass spectrum m/z: 164 (M^+).

3.7. General procedure for synthesis of terpyridines L_1–L_4

These ligands were synthesized by Kröhnke condensation.[34] 2,6-Bis(pyridinoacetyl)pyridine diiodide (1.5 mmol, 0.84 g), α,β-unsaturated ketone (4.5 mmol) and ammonium acetate were dissolved in glacial acetic acid (2 mL). This mixture was stirred under reflux (120°C) overnight under an N_2 atmosphere. The reaction was quenched by addition of saturated $NaHCO_3$ and the mixture was extracted with Et_2O (3×50 mL). The solvent was removed under reduced pressure and the brown residue obtained was purified by column chromatography or recrystallization. Products were characterized by IR, ^{1}H, ^{13}C NMR, CHN and MS analyses.

Terpyridine L_1: The above procedure was followed using α,β-unsaturated ketone **5**. Workup and recrystallization from acetonitrile gave L_1 (0.38 g, 60%): mp 268–269°C; $[\alpha]_D^{25}=-49.4$ ($c=0.50$, CH_2Cl_2); IR (KBr): 2921.7 s, 1562.3 vs, 1434.0 vs; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.75 (s, 6H), 1.36 (d, $J=9.9$ Hz, 2H), 1.46 (s, 6H), 2.34–2.38 (m, 2H), 2.73–2.80 (m, 2H), 3.01 (d, $J=2.5$, 4H), 3.16 (t, $J=5.5$ Hz, 2H), 7.59 (d, $J=8.0$ Hz, 2H), 7.89 (t, $J=8.0$ Hz, 1H), 8.39 (d, $J=8.0$ Hz, 2H), 8.40 (d, $J=8.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 21.38, 26.09, 30.94, 31.33, 39.23, 40.13, 50.37, 118.80, 120.26, 130.50, 135.90, 137.58, 151.93, 155.38, 165.51; anal. calcd for $C_{29}H_{31}N_3\cdot H_2O$: C, 79.23; H, 7.57; N, 9.56. Found: C, 80.14; H, 7.50; N, 10.07%; positive ion FAB mass spectrum m/z: 422 (MH^+).

Terpyridine L_2: The above procedure was followed using α,β-unsaturated ketone **6**. Workup and purification by column chromatography with petroleum ether–EtOAc (35:1, $R_f=0.3$) gave terpyridine L_2 (0.25 g, 37%): mp 204–206°C; $[\alpha]_D^{25}=-15.9$ ($c=0.53$, CH_2Cl_2); IR (KBr): 2957.1 vs, 1563.9 vs, 1416.0 vs; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.61 (s, 6H), 1.03 (s, 6H), 1.13–1.21 (m, 2H), 1.26–1.33 (m, 2H), 1.41 (s, 6H), 1.87–1.95 (m, 2H), 2.18–2.21 (m, 2H), 2.90 (d, $J=3.6$ Hz, 2H), 7.51 (d, $J=7.7$ Hz, 2H), 7.91 (s, 1H), 8.34 (d, $J=7.7$ Hz, 2H), 8.48 (d, $J=7.7$ Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 10.32, 19.20, 20.03, 26.07, 31.66, 51.38, 54.00, 56.56, 117.46, 119.76, 128.36, 137.47, 141.30, 152.21, 155.63, 169.46; anal. calcd for $C_{31}H_{35}N_3\cdot H_2O$: C, 79.62; H, 7.97; N, 8.99. Found: C, 81.30; H, 8.25; N, 9.19%; positive ion FAB mass spectrum m/z: 450 (MH^+).

Terpyridine L_3: The above procedure was followed using α,β-unsaturated ketone **7**. Workup and purification by column chromatography with petroleum ether–EtOAc (60:1) gave terpyridine L_3 (0.24 g, 36%). Two diastereomers (major isomer L_{3a}: $R_f=0.3$; minor isomer L_{3b}: $R_f=0.25$) were obtained in a ratio of 16:1. Major product L_{3a}: mp 224–226°C; $[\alpha]_D^{25}=+2.8$ ($c=0.50$, CH_2Cl_2); IR (KBr): 2916.0 vs, 1562.5 vs, 1429.4 vs; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.69 (s, 6H), 1.34 (d, $J=9.6$ Hz, 2H), 1.43 (s, 6H), 1.49 (d, $J=7.1$ Hz, 6H), 2.17–2.21 (m, 2H), 2.54–2.61 (m, 2H), 2.80–2.83 (t, $J=5.8$ Hz, 2H), 3.25–3.31 (m, 2H), 7.34 (d, $J=8.0$ Hz, 2H), 7.89–7.94 (t, $J=7.7$ Hz, 1H), 8.31 (d, $J=8.0$ Hz, 2H), 8.46 (d, $J=7.7$ Hz, 2H); ^{13}C NMR ($CDCl_3$): δ

18.41, 21.04, 26.40, 28.70, 38.93, 41.48, 46.78, 47.17, 117.78, 119.95, 133.37, 137.49, 141.93, 153.27, 155.55, 159.88; anal. calcd for $C_{31}H_{35}N_3 \cdot H_2O$: C, 79.62; H, 7.97; N, 8.99. Found: C, 77.95; H, 7.93; N, 8.80%. Positive ion FAB mass spectrum m/z: 450 (MH^+).

Terpyridine L_4: The above procedure was modified using α,β-unsaturated ketone **8** and ethanol as solvent. Workup and purification by column chromatography with petroleum ether–acetone–Et_2O (90:1:1) gave 0.066 g (10%) of terpyridines $\mathbf{L_{4a-c}}$. $\mathbf{L_{4a}}$ (0.024 g); $\mathbf{L_{4b}}$ (0.010 g); $\mathbf{L_{4c}}$ (0.026 g); mixture of $\mathbf{L_{4a}}$, $\mathbf{L_{4b}}$ and $\mathbf{L_{4c}}$ (0.006 g).

Terpyridine L_{4a}: Mp 155–158°C $[\alpha]_D^{25} = -58.8$ ($c = 0.50$, CH_2Cl_2); IR (KBr) 2959.4 vs, 2929.9 vs, 2870.8 m, 1557.6 vs, 1428.6 vs; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.77 (d, $J = 6.9$ Hz, 6H), 1.12 (d, $J = 6.9$ Hz, 6H), 1.30 (d, $J = 7.2$ Hz, 6H), 1.73–1.96 (m, 8H), 2.90–3.15 (m, 6H), 7.57 (d, $J = 8.0$ Hz, 2H), 7.87–7.92 (t, $J = 8.0$ Hz, 1H), 8.36 (d, $J = 8.0$ Hz, 2H), 8.45 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 17.35, 18.41, 20.90, 22.96, 28.57, 29.92, 32.48, 46.29, 118.00, 120.44, 137.06, 137.48, 138.31, 153.01, 155.63, 158.43; anal. calcd for $C_{31}H_{39}N_3 \cdot H_2O$: C, 78.94; H, 8.76; N, 8.91. Found: C, 79.09; H, 8.56; N, 8.70%; positive ion FAB mass spectrum m/z: 454 (MH^+).

Terpyridine L_{4c}: Mp 124–125°C; $[\alpha]_D^{25} = -49.0$ ($c = 0.53$, CH_2Cl_2); IR (KBr) 2950.0 vs, 2870.8 m, 1561.3 m, 1432.3 vs; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.71 (d, $J = 6.6$ Hz, 3H), 0.77 (d, $J = 6.6$ Hz, 3H), 1.10 (d, $J = 8.8$ Hz, 3H), 1.12 (d, $J = 8.8$ Hz, 3H), 1.30 (d, $J = 6.9$ Hz, 3H), 1.33 (d, $J = 6.9$ Hz, 3H), 1.65–2.20 (m, 8H), 2.89–3.19 (m, 6H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.88–7.93 (t, $J = 8.0$ Hz, 1H), 8.35 (d, $J = 8.0$ Hz, 2H), 8.45 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 17.17, 17.38, 18.45, 20.81, 20.92, 21.48, 21.59, 22.97, 28.54, 29.71, 29.99, 30.51, 31.18, 32.50, 32.89; anal. calcd for $C_{31}H_{39}N_3 \cdot H_2O$: C, 78.94; H, 8.76; N, 8.91. Found: C, 80.96; H, 8.76; N, 9.27%; positive ion FAB mass spectrum m/z: 454 (MH^+).

3.8. General procedure for preparation of copper(II)–terpyridine complexes [Cu(L)Cl$_2$]

A solution of terpyridine **L** (0.4 mmol) in dichloromethane (5 mL) was added dropwise to a solution of $CuCl_2 \cdot 2H_2O$ (0.068 g, 0.4 mmol) in ethanol (5 mL). The solution was stirred under reflux overnight to ensure complete complexation. The solution was then cooled and diethyl ether was added until a precipitate was formed. The product was filtered and washed with diethyl ether. The complex was characterized by IR, UV, CHN and MS analyses.

Cu(L_1)Cl$_2$: The above procedure was followed using $\mathbf{L_1}$ to give Cu($\mathbf{L_1}$)Cl_2 (0.18 g, 83%). IR (KBr): 2964.3 s, 2914.7 m, 1593.4 m, 1454.2 s; visible spectrum (CH_2Cl_2), λ_{max} (ε): 339 nm (21000), 353 nm (20000), 901 nm (210); anal. calcd for $C_{29}H_{31}N_3CuCl_2 \cdot CH_2Cl_2$: C, 56.20; H, 5.19; N, 6.55. Found: C, 56.53; H, 5.06; N, 6.74%; positive ion FAB mass spectrum m/z: 519 (M^+–Cl).

Cu(L_2)Cl$_2$: The above procedure was followed using $\mathbf{L_2}$ to give Cu($\mathbf{L_2}$)Cl_2 (0.20 g, 85%). IR (KBr): 2960.6 vs, 2873.7 m, 1582.3 s, 1479.9 s; visible spectrum (CH_2Cl_2), λ_{max} (ε): 302 nm (31000), 333 nm (25000), 860 nm (150); anal. calcd for $C_{31}H_{35}N_3CuCl_2 \cdot H_2O$: C, 61.84; H, 6.19; N, 6.98. Found: C, 61.80; H, 6.16; N, 7.24%; positive ion FAB mass spectrum m/z: 547 (M^+–Cl).

Cu(L_{3a})Cl$_2$: The above procedure was followed using $\mathbf{L_{3a}}$ to give Cu($\mathbf{L_{3a}}$)Cl_2 (0.19 g, 80%); IR (KBr): 2926.2 vs, 1573.8 m, 1427.1 m; visible spectrum (CH_2Cl_2), λ_{max} (ε): 347 nm (17000), 474 nm (880), 887 nm (110); anal. calcd for $C_{31}H_{35}N_3CuCl_2 \cdot H_2O$: C, 57.44; H, 5.57; N, 6.28. Found: C, 55.60; H, 5.72; N, 6.23%; positive ion FAB mass spectrum m/z: 547 (M^+–Cl).

3.9. General procedure for preparation of rhodium(III)–terpyridine complexes Rh(L)Cl$_3$

A mixture of terpyridine **L** (0.2 mmol) and rhodium(III) chloride (0.2 mmol) in ethanol (10 mL) was stirred under reflux overnight to ensure complete complexation. The solution was cooled and the solvent was removed. The product was recrystallized from dichloromethane/Et_2O to yield a yellow solid, which was filtered and washed with diethyl ether. The complex was characterized by IR, ^{1}H NMR, UV spectroscopy, CHN analysis and MS analysis.

Rh(L_1)Cl$_3$: The above procedure was followed using $\mathbf{L_1}$ to give Rh($\mathbf{L_1}$)Cl_3 (0.09 g, 71%). IR (KBr): 3058.0 s, 2920.8 vs, 2866.9 vs, 1595.6 m, 1580.1 m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96 (s, 6H), 1.11 (d, $J = 10.2$ Hz, 2H), 1.60 (s, 6H), 2.28–2.35 (m, 2H), 2.75–2.83 (m, 2H), 3.04–3.11 (m, 4H), 5.53–5.56 (m, 2H), 7.66 (d, $J = 7.5$ Hz, 2H), 7.85 (d, $J = 7.5$ Hz, 2H), 7.97 (d, $J = 7.5$ Hz, 2H), 8.10 (t, $J = 7.5$ Hz, 1H); visible spectrum (CH_2Cl_2), λ_{max} (ε): 354 nm (21000), 312 nm (20500), 428 nm (540); anal. calcd for $C_{29}H_{31}N_3RhCl_3$: C, 55.20; H, 4.95; N, 6.66. Found: C, 54.67; H, 4.74; N, 6.12%; positive ion FAB mass spectrum m/z: 594 (M^+–Cl).

Rh(L_2)Cl$_3$: The above procedure was followed using $\mathbf{L_2}$ to give Rh($\mathbf{L_2}$)Cl_3 (0.10 g, 76%). IR (KBr): 3058.9 s, 2961.8 vs, 2873.2 s, 1601.6 m, 1578.6 m; ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.39 (s, 6H), 0.97 (s, 6H), 1.32–1.41 (m, 2H), 1.78 (s, 6H), 1.97–2.06 (m, 2H), 2.17–2.28 (m, 2H), 2.55–2.64 (m, 2H), 2.89 (d, $J = 3.9$ Hz, 2H), 7.66 (d, $J = 7.5$ Hz, 2H), 7.81 (d, $J = 7.5$ Hz, 2H), 7.95 (d, $J = 7.8$ Hz, 2H), 8.19 (t, $J = 7.8$ Hz, 2H); visible spectrum (CH_2Cl_2), λ_{max} (ε): 300 nm (22500), 335 nm (20500), 348 nm (22000), 433 nm (490); anal. calcd for $C_{31}H_{35}N_3RhCl_3 \cdot H_2O$: C, 54.99; H, 5.51; N, 6.21. Found: C, 55.30; H, 5.17; N, 5.83%; positive ion FAB mass spectrum m/z: 622 (M^+–Cl).

Rh(L_{3a})Cl$_3$: The above procedure was followed using $\mathbf{L_{3a}}$ to give Rh($\mathbf{L_{3a}}$)Cl_3 (0.12 g, 91%); IR (KBr): 3071.7 s, 2924.5 vs, 2866.9 vs, 1602.4 m, 1581.8 m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (s, 6H), 1.42 (d, 2H), 1.44 (s, 6H), 1.61 (d, $J = 6.6$ Hz, 6H), 2.23–2.28 (m, 2H), 2.48–2.55 (m, 2H), 2.84–2.88 (m, 2H), 5.62–5.70 (m, 2H), 7.46 (d, $J = 7.8$ Hz, 2H), 7.83 (d, $J = 7.8$ Hz, 2H), 8.02

(d, $J=7.8$ Hz, 2H), 8.13 (t, $J=7.8$ Hz, 1H); visible spectrum (CH_2Cl_2), λ_{max} (ε): 306 nm (9500), 354 nm (8000), 432 nm (590); anal. calcd for $C_{31}H_{35}N_3RhCl_3\cdot H_2O$: C, 55.00; H, 5.51; N, 6.21. Found: C, 54.00; H, 5.60; N, 5.95; positive ion FAB mass spectrum m/z: 622 (M^+-Cl).

Rh(L_{4a})Cl_3: The above procedure was followed using L_{4a} to give Rh(L_{4a})Cl_3 (0.087 g, 66%); IR (KBr): 3070.1 m, 2953.6 vs, 2870.8 s, 1457.9 m, 1435.9 m; anal. calcd for $C_{31}H_{39}N_3RhCl_3$: C, 56.15; H, 5.93; N, 6.34. Found: C, 56.67; H, 6.25; N, 6.05%. This complex is not soluble in common organic solvent, ^1H NMR and UV spectral analysis were not carried out. Positive ion FAB mass spectrum m/z: 626 (M^+-Cl).

3.10. X-Ray crystallographic analysis and data collection

Single crystals of Rh(L_2)Cl_3 suitable for X-ray structure analysis were grown by slow diffusion of ether into a dichloromethane/ethanolic solution. These yellow crystals were air stable. Diffraction data were obtained on a Rigaku AFC7R diffractometer at 0°C. Intensity data were corrected for Lorentz and polarization effects. Absorption corrections based on χ-scan technique were also applied. The structure was solved by the direct method (SIR 92) and refined on F by least-squares analysis. The absolute structure of the molecule was determined by analysis of both configurations including the anomalous scattering effect. The Flack parameter was refined to give a value of 0.008(1). Hydrogen atoms were placed in their ideal positions (C-H, 0.95 Å) and included in the structure factor calculations but were not refined. All calculations were performed on Silicon Graphic workstation using package TeXsan. Crystal data and details of measurements are summarised in Table 1. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 169906.

3.11. Procedure for copper-catalyzed cyclopropanation

To a two-neck round bottom flask were added $Cu(OTf)_2$ (0.0072 g, 0.02 mmol), CH_2Cl_2 (2 mL) and **L** (0.022 mmol) under nitrogen. The solution was stirred at rt for 2 h. Styrene (0.417 g, 4 mmol) and ethyl diazoacetate (0.2 mmol) were added and the mixture was stirred at rt for 0.5 h. A solution of ethyl diazoacetate (1 mmol) in CH_2Cl_2 (0.5 mL) was added to the reaction mixture over a period of 4 h using a syringe pump. After the addition of ethyl diazoacetate, the mixture was allowed to stir for 16 h at rt. The mixture was then worked-up by removing the solvent and the crude product obtained was purified by column chromatography (hexane/EtOAc). All the cyclopropanes obtained are known compounds and were characterized by ^1H, ^{13}C NMR, IR and GC–MS. Enantiomeric excesses of the cyclopropanes were determined by HPLC with Daicel Chiralcel OJ column. Absolute configurations were determined by comparing the order of elution of samples with a known configuration.[6] Diastereoselectivities (*cis*-/*trans*-ratio) were measured by GC with Ultra 2-crosslinked 5% PhMesilcone (25 m×0.2 mm×0.33 μm) column.

3.12. General procedure for rhodium-catalyzed cyclopropanation

To a two-neck round bottom flask were added Rh(**L**)Cl_3 (0.02 mmol) and AgOTf (0.02 g, 0.08 mmol) under an N_2 atmosphere. THF (1.5 mL) was added and the solution was stirred at rt for 0.5 h. Styrene (0.52 g, 5 mmol) was added to the mixture. A solution of ethyl diazoacetate (0.114 g, 1 mmol) in THF (0.5 mL) was slowly added to the reaction mixture over a period of 4 h using a syringe pump. After the addition of ethyl diazoacetate, the mixture was allowed to stir for 16 h at rt. The mixture was worked-up as described above.

3.13. General procedure for competition reactions of copper catalysts

To a two-neck round bottom flask were added $Cu(OTf)_2$ (0.0036 g, 0.01 mmol), CH_2Cl_2 (1 mL) and L_{3a} (0.011 mmol) under nitrogen. The solution was stirred at rt for 2 h. Styrene (1 mmol) and substituted styrene (1 mmol) were added to the stirred solution. Ethyl diazoacetate (0.5 mmol) in CH_2Cl_2 (0.5 mL) was added to the reaction mixture in one portion. The mixture was allowed to stir for 16 h at rt. The ratios of the resulting cyclopropanes were determined by GC.

3.14. General procedure for competition reactions of rhodium-catalysts

To a two-neck round bottom flask were added Rh(L_{3a})Cl_3 (0.02 mmol), THF (1.5 mL) and AgOTf (0.02 g, 0.08 mmol) under nitrogen. The solution was stirred at rt for 0.5 h. Styrene (2.5 mmol) and substituted styrene (2.5 mmol) were added to the stirred solution. Ethyl diazoacetate (1.0 mmol) in THF (0.5 mL) was added slowly to the reaction mixture over 2 h using a syringe pump. The mixture was allowed to stir for 16 h at rt. The ratios of the resulting cyclopropanes were determined by GC.

Acknowledgements

Financial support for this research from the Hong Kong Research Grants Council (grant no. 9040543) and City University of Hong Kong (grant no. 7001062) is gratefully acknowledged.

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