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New chiral 2,2′:6′,2″-terpyridines as ligands for asymmetric catalysis: cyclopropanation and hydrosilylation reactions

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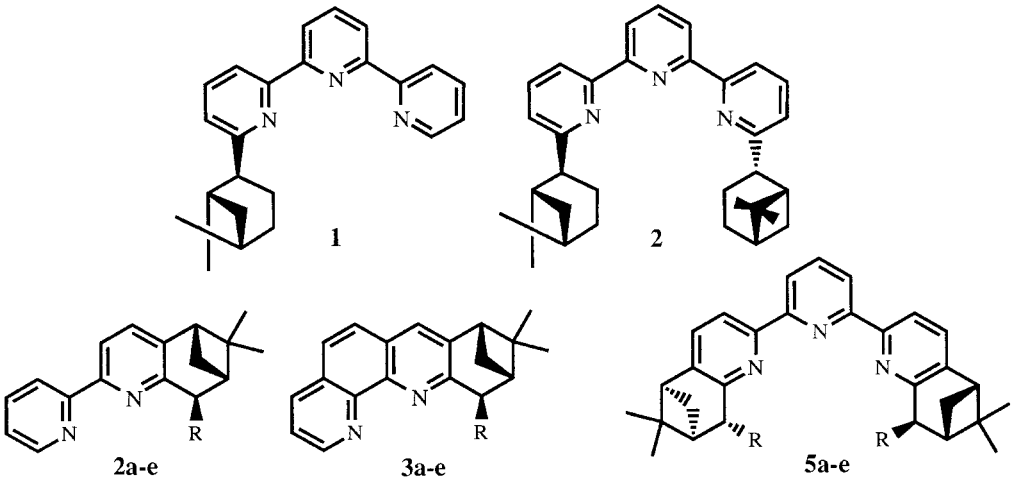
Abstract—A number of new chiral 2,2′:6′,2″-terpyridines were prepared and the corresponding rhodium and ruthenium complexes were assessed as chiral catalysts for the enantioselective hydrosilylation of acetophenone with diphenylsilane and for the cyclopropanation of styrene with ethyl diazoacetate. Enantioselectivities up to 59% in the cyclopropanation and up to 13% in the hydrosilylation were obtained.

1. Introduction

Enantioselective reactions based on chiral nitrogen ligands are currently an actively pursued research area.[1] In this context a number of bidentate-nitrogen ligands have been demonstrated to be useful auxiliaries for metal-promoted asymmetric reactions reaching high levels of stereocontrol. On the other hand the use of *N*,*N*,*N*-terdentate ligands is rather limited[2] with the terdentate C_2-symmetrical bis(oxazolinyl)pyridines (pybox) being the only remarkable exception.[3]

Recently, pursuing our interest in the synthesis and application of chiral pyridine derivatives as ligands in metal complexes for enantioselective catalysis,[4] we have evaluated the utility of the 2,2′:6′,2″-terpyridines (trpy's) **1** and **2** (Scheme 1) as chiral controllers in some enantioselective processes such as the Pd-catalysed allylic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate,[5] the cyclopropanation of styrene with diazoacetates[6] and the hydrosilylation of acetophenone with diphenylsilane.[7]

Our findings showed that the chiral 6,6-dimethylnorpinan-2-yl group was not able to furnish the ligand with a satisfactory enantioselectivity. These disappointing results were ascribed to the conformational mobility of the



Scheme 1. R=**a**: H; **b**: Me; **c**: *n*-Bu; **d**: *i*-Pr; **e**: Bn.

Keywords: terpyridine ligands; ruthenium and rhodium catalysts; asymmetric cyclopropanation and hydrosilylation reactions.
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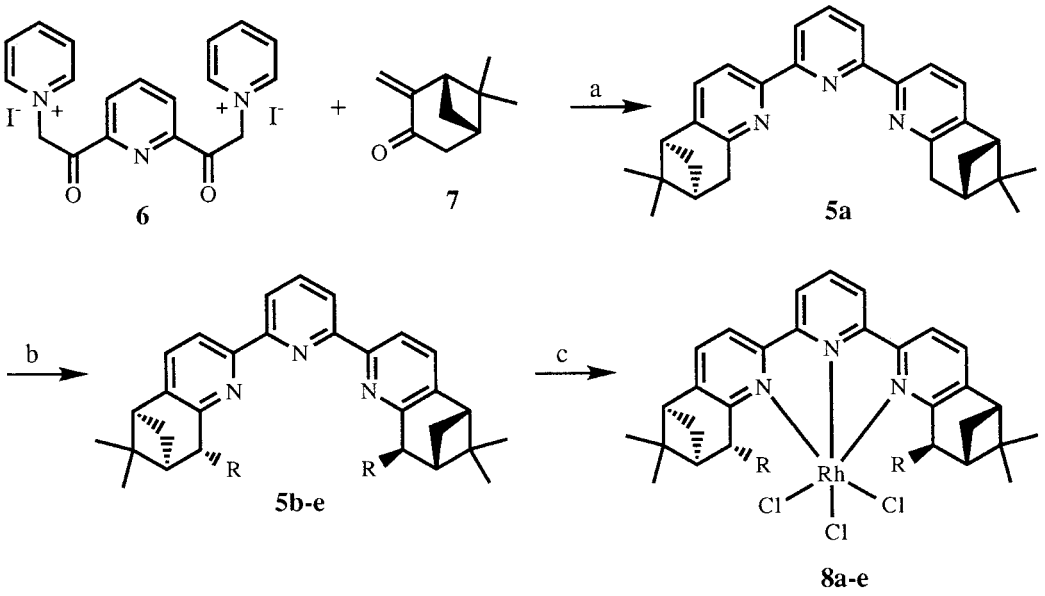


Scheme 2. R: **a**: R=H; **b**: R=Me; **c**: R=*n*-Bu; **d**: R=*i*-Pr; **e**: R=Bn; a: AcOH, $AcONH_4$, reflux, 6 h, 63%; b: LDA, THF, −40°C, 2 h; then MeI or *n*-BuI or *i*-PrI or BnI, 37–55%; c: $RhCl_3{\cdot}3H_2O$, 85–91%.

6,6-dimethylnorpinan-2-yl group which causes a minimization of the steric interaction among the stereogenic centres on the ligand, the substrate and the reagent in the metal complex forming the enantioselective transition state. In fact, it is indicated in the literature that effective chiral controllers are those ligands in which the substituents at the asymmetric centres are forced to be directed toward the metal ion on its complex formation.[8]

Since, 2,2′-bipyridines **3**[9] and 1,10-phenanthrolines **4**,[10] incorporating the 6,6-dimethylnorpinane framework in the form of a cycloalkeno-condensed substituent have found useful application in asymmetric catalysis,[7] we became interested in obtaining an analogue class of trpy's.

In this paper we report the preparation and application of a number of new chiral trpy's of type **5**[11] in the rhodium-catalysed hydrosilylation of acetophenone with diphenylsilane[12] and in the ruthenium- and rhodium-catalysed cyclopropanation of styrene with ethyl diazoacetate.[13]

2. Results and discussion

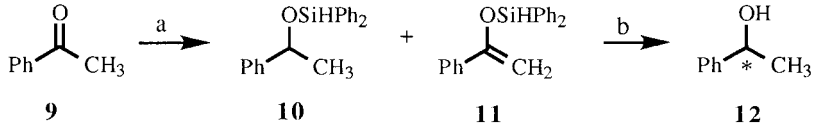
2.1. Synthesis of the ligands

The trpy **5a** was readily accessible by reaction of (−)-pinocarvone **7**[14] with 2,6-bis(pyridinioacetyl)pyridine iodide **6**[15] following the Kröhnke methodology[16] (63% yield) (Scheme 2). Then the red solution of lithiated **5a**, obtained by treatment with lithium diisopropylamine (LDA) at −40°C for 2 h, was quenched with the proper alkyl iodide to give ligands **5b–e** in moderate yields (37–55%). The reactions of alkylation afforded single diastereomers in which the new substituents replace the hydrogen atoms, situated on the two tetrahydroquinoline rings of **5a**, in the *trans*-position to the substituted bridge. Finally, $Rh(trpy)Cl_3$ complexes **8a–e** were prepared in high yield by heating a methanolic solution of **5a–e** with $RhCl_3{\cdot}3H_2O$ (85–91%) under reflux. The enantiomeric excess of **5a** was not determined. (−)-Pinocarvone **7** was prepared from (1*R*)-(+)-α-pinene having an enantiomeric excess (ee) >80%, however, and as no racemization process occurs during this synthesis, an enantiomeric purity >80% can be attributed to this compound and to its derivatives.

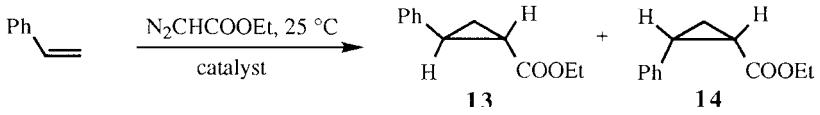
2.2. Rhodium-catalysed asymmetric hydrosilylation

Firstly we compared the results obtained with ligands **1** and **2** for the asymmetric hydrosilylation of acetophenone using rhodium(I)–trpy catalysts prepared in situ from $[Rh(cod)Cl]_2$ (cod=1,5-cyclooctadiene) and the ligand with a molar ratio of rhodium to ligand of 1:1. The degree of hydrosilylation (conversion of acetophenone) and the relative amounts of the silyl enol ether **11** and of the silylalkyl ether **10** were determined by ^1H NMR[17] while the ee was determined by GC on a chiral column on the carbinol **12** obtained after acid hydrolysis (Scheme 3).

To compare the results among all ligands, the reactions were carried out for 24 h at room temperature. After this time moderate levels of conversion with all ligands were obtained (45–59%). Only trpy's **5a,b** gave, although in



Scheme 3. a: $[Rh(cod)Cl]_2$, ligand, H_2SiPh_2; b: p-TsOH, CH_3OH.



Scheme 4.

low yield (29 and 18%, respectively), the desired silylalkyl ethers **10**. The resultant carbinols, however, did not show significant enantioexcesses (7 and 13%, respectively). Surprisingly, the other trpy's **5c–e** afforded the silyl enol ether **11** as the sole product. It is plain that increasing the steric hindrance of the substituent on the tetrahydroquinoline ring favours the formation of **11** to the detriment of **10**.

The particularly disappointing results obtained with Rh(I) catalysts prompted us to examine the ability of the Rh(III) complexes of these ligands. This research was inspired by the works of Nishiyama et al. who showed that trivalent rhodium complexes, derived from terdentate C_2-symmetrical bis(oxazolinyl)pyridines (pybox) and $RhCl_3$ with the aid of $AgBF_4$, are effective chiral catalysts for the hydrosilylation of ketones.[18]

The Rh(trpy)Cl_3 complexes **8a–e** were assessed in the presence of $AgBF_4$, in the hydrosilylation of acetophenone with diphenylsilane. The reaction was carried out at room temperature and stopped after 24 h.

With complexes **8a–e** high levels of conversion (65–95%) and satisfactory yields (55–71%) were obtained but, much to our surprise, the resultant carbinols showed very low enantioexcesses (2–6%).

2.3. Ruthenium(II)- and rhodium(III)-catalysed asymmetric cyclopropanation

It has been shown by Nishiyama et al. that particular ruthenium(II)–pybox complexes are capable of providing high ee's in the enantioselective cyclopropanation of olefins with diazoesters. Interestingly, these authors found that similar results can be also obtained using catalysts prepared in situ from the procatalyst $[RuCl_2(p\text{-cymene})]_2$[19] (*p*-cymene=*p*-isopropyltoluene) and an excess of pybox.

On this basis, the reaction of styrene with ethyl diazoacetate to give the *trans*- and *cis*-cyclopropanes **13** and **14** (Scheme 4) was chosen as the model for the evaluation of the efficiency of trpy's **5a–e** in the ruthenium(II)-catalysed asymmetric cyclopropanation of olefins. The reactions were carried out at room temperature for 24 h by slow addition (2 h) of ethyl diazoacetate to a solution of styrene in methylene chloride containing the ruthenium(II)–ligand adduct. This was prepared in situ by adding two equivalents of ligands **5a–e** to the $[RuCl_2(p\text{-cymene})]_2$

Table 1. Enantioselective cyclopropanation of styrene with ethyldiazoacetate using $[RuCl_2(p\text{-cymene})]_2$[a]

Ligand	Yield[b] (%) **13**+**14**	*trans*:*cis* ratio[c] **13**:**14**	% ee[c]		Configuration[d]	
			13	**14**	**13**	**14**
5a	88	65:35	2	4	1*R*,2*R*	1*S*,2*S*
5b	83	65:35	0	0	–,–	–,–
5c	77	62:38	0	2	–,–	1*R*,2*S*
5d	89	64:36	0	0	–,–	–,–
5e	81	36:64	0	4	–,–	1*S*,2*R*

[a] A solution of the ligand (0.1 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.025 mmol) in CH_2Cl_2 (2 ml) was stirred under argon atmosphere for 30 min. After the addition of styrene (12.5 mmol) the solution of ethyl diazoacetate (2.5 mmol) in CH_2Cl_2 (2.5 ml) was added dropwise over a period of 2 h and then stirred for 24 h.
[b] Isolated yield, based on the diazoacetate, for the mixture of *trans* and *cis* cyclopropanes.
[c] Determined by GC analysis on a chiral column.
[d] Assignment according to Ref. 20.

Table 2. Enantioselective cyclopropanation of styrene with ethyldiazoacetate and Rh(III) complexes[a]

Complex	Yield[b] (%) **13**+**14**	*trans*:*cis* ratio[c] **13**:**14**	% ee[c]		Configuration[d]	
			13	**14**	**13**	**14**
8a	75	46:54	7	0	1*R*,2*R*	–,–
8b	68	34:66	49	59	1*S*,2*S*	1*R*,2*S*
8c	64	46:54	37	45	1*S*,2*S*	1*R*,2*S*
8d	57	71:29	39	33	1*S*,2*S*	1*R*,2*S*
8e	53	57:43	35	25	1*S*,2*S*	1*R*,2*S*

[a] To a solution of Rh(trpy)Cl_3 complex (0.05 mol) in THF (2 ml) was added AgOTf (0.1 mmol) under argon atmosphere. After 30 min stirring, styrene (12.5 mmol) was added and then a solution of ethyl diazoacetate (2.5 mmol) in THF (2.5 ml) was added dropwise over a period of 2 h and then stirred for 24 h.
[b] Isolated yield, based on the diazoacetate, for the mixture of *trans* and *cis* cyclopropanes.
[c] Determined by GC analysis on a chiral column.
[d] Assignment according to Ref. 20.

complex (molar ratio of ruthenium/ligand=112). The results obtained in these runs are summarized in Table 1. Trpy's **5a–e** provided effective Ru(II) catalysts but negligible enantioselectivities.

Subsequently, the behaviour of these derivatives in the Rh(III)-catalysed cyclopropanation reaction of styrene was investigated.

The reactions were carried out at room temperature for 24 h by slow addition of ethyl diazoacetate (2 h) to a solution of styrene in THF containing the active catalyst which was prepared by the addition of two equivalents of silver triflate to the Rh(tryp)Cl_3 complex in THF, a method analogous to that used by Nishiyama et al. to generate pybox–rhodium catalysts used for the asymmetric hydrosilylation of ketones.[18]

The cyclopropanes recovered from the reactions were obtained in moderate yield as a mixture of *trans* and *cis* isomers in a ratio which varies appreciably with the nature of the substituents present on the tetrahydroquinoline rings (Table 2). Enantioselectivities were also moderate with the best result being obtained with the trpy **5b** (59%).

As a general trend, the substitution of two hydrogen atoms onto the basic structure **5a** displayed a positive effect on the enantioselectivity of the reaction leading to an increase of the ee's for both *trans* and *cis* isomers **13** and **14**. However, the increase of the steric bulk of the alkyl substituent from methyl to benzyl led to the reduction of the ee for both cyclopropanes. Notably, the presence of substituents in the backbone of **5b–e** caused a chiral switch of the configuration of *trans* cyclopropanes with respect to that obtained from the unsubstituted ligands **5a**. This fact indicates that the stereochemistry of the reaction is basically dictated by the new stereocentres generated by alkylation and that these stereocentres have a mismatching stereotopic relation with those pre-existing on the bridge.

Taken overall, the obtained results point out that the 2,2′:6′,2″-terpyridine ligands used throughout this work are poorly suitable chiral controllers in the Rh-catalysed hydrosilylation of acetophenone, while they seem to deserve attention for their possible applications in the field of Rh(III)-catalysed cyclopropanation. Further studies on this subject are currently in progress in our laboratory.

3. Experimental

3.1. General

Boiling points are uncorrected. Melting points were determined on a Buchi 510 capillary apparatus and are uncorrected. The ^{1}H NMR (300 MHz) spectra were obtained with a Varian VXR-300 spectrometer. Optical rotations were measured with a Perkin-Elmer 241 polarimeter in a 1 dm tube. Elemental analyses were performed on a Perkin-Elmer 240 B analyser. Gas chromatographic analyses were performed with a HP 5900 chromatograph using He (60 kPa) as the carrier gas.

[Rh(cod)Cl]$_2$, [$RuCl_2$(*p*-cymene)]$_2$, $RhCl_3 \cdot 3H_2O$, ethyl diazoacetate were purchased from Aldrich. 2,6-Bis(pyridinioacetyl)pyridine iodide **6** was obtained from 2,6-diacetylpyridine (Aldrich) following the Ortoleva–King procedure.[15] (−)-Pinocarvone **7** was prepared from (1*R*)-(+)-α-pinene (80+% ee, Acros).[14]

3.1.1. (5*S*,7*S*)-2,6-Bis(6,6-dimethyl-5,6,7,8-tetrahydro-5,7-methanoquinolin-2-yl)pyridine (5a). A solution of 2,6-bis(pyridinioacetyl)pyridine iodide (12 g, 21 mmol), (−)-pinocarvone (6.3 g, 42 mmol), ammonium acetate (32.3 g, 0.42 mol) in glacial acetic acid (120 ml) was heated at 120–125°C for 4 h under nitrogen. Then, most of the acetic acid was removed under reduced pressure and the residue taken up with H_2O (600 ml) and extracted with CH_2Cl_2 (2×150 ml). The organic phase was washed with a 5% NaOH solution and then extracted with a 10% HCl solution. The acid solution was alkalinized with a 10% NaOH solution and extracted with CH_2Cl_2 (2×150 ml). The organic phase was dried on anhydrous Na_2SO_4, the solvent was evaporated and the residue was recrystallized from dichloromethane–diethylether to give pure **5a** as a white solid: 5.57 g (63%); mp 230–232°C; $[\alpha]_D^{25}$ +78 (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.70 (s, 6H), 1.33 (d, 2H, *J*=9.3 Hz), 1.43 (s, 6H), 2.41 (m, 2H), 2.72 (m, 2H), 2.83 (t, 2H, *J*=5.7 Hz), 3.21 (d, 4H, *J*=2.7 Hz), 7.37 (d, 2H, *J*=7.8 Hz), 7.90 (t, 1H, *J*=7.8 Hz), 8.29 (d, 2H, *J*=7.8 Hz), 8.37 (d, 2H, *J*=7.8 Hz). Anal. calcd for $C_{29}H_{31}N_3$: C, 82.62; H, 7.41; N, 9.97. Found: C, 82.67; H, 7.55; N, 9.92.

3.1.2. (5*S*,7*S*,8*R*)-2,6-Bis(6,6,8-trimethyl-5,6,7,8-tetrahydro-5,7-methanoquinolin-2-yl)pyridine (5b). A solution of the trpy **5a** (1.05 g, 2.5 mmol) in anhydrous THF (5 ml) was added at −78°C to a solution of lithium diisopropylamine (5 mmol) in anhydrous THF (25 ml). The resulting solution was stirred at −40°C for 2 h and then a solution of methyl iodide (0.71 g, 5 mmol) in THF (4 ml) was added dropwise at −40°C. After 30 min at −40°C, the solution was allowed to reach room temperature slowly and then treated with H_2O. The organic phase was separated and the aqueous phase extracted with diethylether (3×50 ml). The organic phase was dried on anhydrous Na_2SO_4, the solvent evaporated and the residue purified by chromatography on neutral aluminium oxide (petroleum ether/ethyl acetate=20/1) to give pure **5b** as a white solid: 0.62 g (55%); mp 163–165°C; $[\alpha]_D^{25}$ −15.4 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.69 (s, 6H), 1.35 (d, 2H, *J*=9.6 Hz), 1.44 (s, 6H), 1.49 (d, 6H, *J*=6.9 Hz), 2.19 (m, 2H), 2.59 (m, 2H), 2.82 (t, 2H, *J*=5.4 Hz), 3.27 (m, 2H), 7.34 (d, 2H, *J*=7.8 Hz), 7.90 (t, 1H, *J*=7.8 Hz), 8.30 (d, 2H, *J*=7.5 Hz), 8.45 (d, 2H, *J*=7.5 Hz). Anal. calcd for $C_{31}H_{35}N_3$: C, 82.81; H, 7.85; N, 9.35. Found: C, 82.67; H, 7.97; N, 9.44.

3.1.2. (5*S*,7*S*,8*R*)-2,6-Bis(6,6-dimethyl-8-butyl-5,6,7,8-tetrahydro-5,7-methanoquinolin-2-yl)pyridine (5c). Compound **5c** was obtained as a white solid following the procedure described for the preparation of **5b** using butyl iodide: 0.64 g (48%); mp 70–75°C; $[\alpha]_D^{25}$ −19.6 (*c* 0.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.60–1.60 (m, 18H), 0.67 (s, 6H), 1.34 (d, 2H, *J*=9.9 Hz), 1.45 (s, 6H), 2.37 (m, 2H), 2.56 (m, 2H), 2.81 (t, 2H, *J*=5.7 Hz), 3.06 (m, 2H), 7.33 (d, 2H, *J*=7.8 Hz), 7.92 (t, 1H, *J*=7.8 Hz), 8.30 (d, 2H, *J*= 7.8 Hz),

8.45 (d, 2H, J=7.8 Hz). Anal. calcd for $C_{37}H_{47}N_3$: C, 83.24; H, 8.88; N, 7.88. Found: C, 83.35; H, 8.78; N, 7.85.

3.1.3. (5*S*,7*S*,8*R*)-2,6-Bis(6,6-dimethyl-8-methylethyl-5,6,7,8-tetrahydro-5,7-methanoquinolin-2-yl)pyridine (5d). Compound **5d** was obtained as a white solid following the procedure described for the preparation of **5b** using isopropyl iodide: 0.47 g (37%); mp 175–180°C; $[\alpha]_D^{25}$ −13.2 (c 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.66 (s, 6H), 0.89 (d, 6H, J=6.9 Hz), 1.20–1.70 (m, 2H), 1.26 (d, 6H, J=6.9 Hz), 1.41 (d, 2H), 1.44 (s, 6H), 2.40 (m, 2H), 2.60 (m, 2H), 2.79 (t, 2H, J=5.7 Hz), 2.93 (m, 2H), 7.35 (d, 2H, J=7.8 Hz), 7.90 (t, 1H, J=7.8 Hz), 8.33 (d, 2H, J=7.8 Hz), 8.44 (d, 2H, J=7.8 Hz). Anal. calcd for $C_{35}H_{43}N_3$: C, 83.11; H, 8.58; N, 8.31. Found: C, 83.08; H, 8.64; N, 8.40.

3.1.4. (5*S*,7*S*,8*R*)-2,6-Bis(6,6-dimethyl-8-methylphenyl-5,6,7,8-tetrahydro-5,7-methanoquinolin-2-yl)pyridine (5e). Compound **5e** was obtained as a white solid following the procedure described for the preparation of **5b** using benzyl iodide: 0.78 g (52%); mp 207–209°C; $[\alpha]_D^{25}$ +158 (c 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.64 (s, 6H), 1.36 (s, 6H), 1.46 (d, 2H, J=9.6 Hz), 2.14 (m, 2H), 2.59 (m, 2H), 2.78 (m, 4H), 3.41 (m, 2H), 3.89 (m, 2H), 7.34 (m, 5H), 7.39 (d, 2H, J=7.8 Hz), 7.93 (t, 1H, J=7.8 Hz), 8.37 (d, 2H, J=7.8 Hz), 8.49 (d, 2H, J=7.8 Hz). Anal. calcd for $C_{43}H_{43}N_3$: C, 85.81; H, 7.21; N, 6.99. Found: C, 85.95; H, 7.14; N, 6.92.

3.1.5. Rh(trpy 5a)Cl_3 (8a). A mixture of appropriate terpyridine (1.19 mmol) and $RhCl_3{\cdot}3H_2O$ (313 g, 1.19 mmol) in methanol (9 ml) was heated under reflux for 4.5 h. After cooling the precipitate was filtered off, and recrystallized from dichloromethane–ethyl ether. Finally the crystals were washed with ethyl ether and dried under vacuo to give pure **8a** as an orange solid: 0.676 g (90%); IR (KBr) $\nu_{C=N}$ 1600 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 0.68 (s, 6H), 1.28 (d, 2H, J=9.9 Hz), 1.38 (s, 6H), 2.47 (m, 2H), 2.61 (dd, 2H, J=9.9, 5.7 Hz), 2.82 (t, 2H, J=5.7 Hz), 4.46 (m, 4H), 7.44 (d, 2H, J=7.8 Hz), 7.83 (d, 2H, J=7.8 Hz), 8.03 (s, 3H). Anal. calcd for $C_{29}H_{31}Cl_3N_3Rh$: C, 55.21; H, 4.95; N, 6.66. Found: C, 55.15; H, 4.89; N, 6.78.

3.1.6. Rh(trpy 5b)Cl_3 (8b). Compound **8b** was obtained as an orange solid following the procedure described for the preparation of **8a**: 0.666 g (85%); IR (KBr) $\nu_{C=N}$ 1610 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 6H), 1.43 (s, 6H), 1.61 (d, 6H, J=6.6 Hz), 1.62–1.68 (m, 2H), 2.21–2.27 (m, 2H), 2.56–2.44 (m, 2H), 2.84 (t, 2H, J=6.0 Hz), 5.61–5.71 (m, 2H), 7.44 (d, 2H, J=6.9 Hz), 7.5 (d, 2H, J=7.8 Hz), 8.00–8.15 (m, 3H). Anal. calcd for $C_{31}H_{35}Cl_3N_3Rh$: C, 56.51; H, 5.35; N, 6.38. Found: C, 56.55; H, 5.30; N, 6.42.

3.1.7. Rh(trpy 5c)Cl_3 (8c). Compound **8c** was obtained as an orange solid following the procedure described for the preparation of **8a**: 0.789 g (89%); IR (KBr) $\nu_{C=N}$ 1610 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 6H), 0.87 (t, 6H, J=6.9 Hz), 1.10–1.28 (m, 8H), 1.46 (s, 6H), 1.61–1.79 (m, 4H), 2.42–2.51 (m, 4H), 2.81 (t, 2H, J=4.7 Hz), 2.94–3.06 (m, 2H), 5.57–5.63 (m, 2H), 7.39 (d, 2H, J=7.8 Hz), 7.75 (d, 2H, J=7.8 Hz), 7.96 (d, 2H, J=7.8 Hz), 7.97–8.03 (m, 1H). Anal. calcd for $C_{37}H_{47}Cl_3N_3Rh$: C, 59.81; H, 6.38; N, 5.65. Found: C, 59.72; H, 6.43; N, 5.72.

3.1.8. Rh(trpy 5d)Cl_3 (8d). Compound **8b** was obtained as an orange solid following the procedure described for the preparation of **8a**: 0.850 g (91%); IR (KBr) $\nu_{C=N}$ 1610 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 0.48 (d, 6H, J=6.9 Hz), 0.86 (s, 6H), 1.07 (d, 6H, J=6.9 Hz), 1.42 (s, 6H), 1.64 (d, 2H, J=8.7 Hz), 2.42–2.53 (m, 4H), 2.78 (t, 2H, J=5.4 Hz), 3.76–3.88 (m, 2H), 5.25–5.41 (m, 2H), 7.45 (d, 2H, J=7.8 Hz), 7.83 (d, 2H, J=6.8 Hz), 8.04 (d, 2H, J=6.9 Hz), 8.10–8.16 (m, 1H). Anal. calcd $C_{35}H_{43}Cl_3N_3Rh$: C, 58.79; H, 6.06; N, 5.88. Found: C, 58.74; H, 6.11; N, 5.91.

3.1.9. Rh(trpy 5e)Cl_3 (8e). Compound **8e** was obtained as an orange solid following the procedure described for the preparation of **8a**: 0.869 g (90%); IR (KBr) $\nu_{C=N}$ 1610 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 6H), 1.58 (d, 2H, J=13.2 Hz), 1.98–2.07 (m, 2H), 2.38 (t, 4H, J=12.3 Hz), 2.79–2.83 (m, 2H), 4.64 (dd, 2H, J=13.2, 4.1 Hz), 6.14–6.20 (m, 2H), 7.17 (d, 2H, J=7.5 Hz), 7.26–7.35 (m, 4H), 7.47 (d, 2H, J=7.5 Hz), 7.60 (d, 4H, J=7.2 Hz), 7.85 (d, 2H, J=6.9 Hz), 7.94–8.06 (m, 2H), 8.09–8.12 (m, 1H). Anal. calcd for $C_{43}H_{43}C1_3N_3Rh$: C, 63.68; H, 5.34; N, 5.18. Found: C, 63.79; H, 5.29; N, 5.22.

3.1.10. Asymmetric hydrosilylation of acetophenone using [Rh(cod)Cl]$_2$: typical procedure. The catalyst was prepared by dissolving under argon the precursor $[Rh(cod)Cl]_2$ (10 mg, 0.02 mol), the ligand (0.2 mmol) and acetophenone (1 ml, 8.5 mmol) in CCl_4 (2 ml). After 30 min stirring, the mixture was cooled at 0°C and diphenylsilane (1.6 ml, 8.6 mmol) was added. The solution was slowly warmed up to room temperature and then stirred for 24 h. A sample was then taken (0.2 ml), diluted with $CDCl_3$ (0.4 ml) and a ^{1}H NMR was recorded to determine the amount of silylenol ether (**11**/**10**+**11**), the degree of hydrosilylation (conversion of acetophenone, **10**+**11**/**9**+**10**+**11**) and the chemical yield of silylalkyl ether (**10**/**9**+**10**+**11**).[14] The following integrals were used for the analysis: δ=5.70 ppm (s, Si—H, silylenol ether, **11**), δ=5.40 ppm (s, Si—H, silylalkyl ether, **10**) and δ=2.50 ppm (s, CH_3, acetophenone, **9**).

The mixture was diluted with methanol (10 ml) and treated with a few crystals of p-TsOH. After 30 min stirring at room temperature the solvent was evaporated and the residue was distilled in a kugelrohr apparatus at 130°C/2 Torr. The enantiomeric excess (ee) was determined by GC analysis on a diethyl-t-butylsilyl β-cyclodextrin column operated at 60°C for 5 min, then programmed at 3°C min^{-1} to 150°C. Retention times: 23.75 min [(*R*)-1-phenylethanol] and 24.20 min [(*S*)-1-phenylethanol].

3.1.11. Asymmetric hydrosilylation of acetophenone using Rh(trpy)Cl_3 complexes: typical procedure. A mixture of Rh(trpy)Cl_3 complex (0.08 mol), ligand (0.32 mmol), $AgBF_4$ (31 mg, 0.16 mmol) and acetophenone (0.93 ml, 8.0 mmol) was stirred at 25°C for 1 h. Diphenylsilane (2.37 ml, 12.8 mmol) was added at 0°C and then the mixture was slowly warmed to 25°C and stirred for 24 h. After this time the mixture was worked up as described above.

3.1.12. Asymmetric cyclopropanation of styrene using Rh(trpy)Cl_3 complexes: typical procedure. To a solution

of Rh(trpy)Cl_3 complex (0.05 mol), in THF (2 ml) was added AgOTf (25.7 mg, 0.1 mmol) under argon atmosphere. After 30 min stirring, styrene (1.43 ml, 12.5 mmol) was added and then a solution of ethyl diazoacetate (0.263 ml, 2.5 mmol) in THF (2.5 ml) was added dropwise over a period of 2 h. The mixture was stirred for 24 h and then the solvent and excess olefin were removed under vacuum. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate=15/l) to afford a mixture of ethyl *trans*- and *cis*-2-phenylcyclopropane-1-carboxylates as a colourless oil. The *trans*/*cis* ratio and the ee were determined by GC analysis on a diethyl-*t*-butylsilyl β-cyclodextrin capillary column 25 m×0.25 mm operated at 60°C for 5 min, then programmed at 3°C min^{-1} to 160°C. Retention times: 33.2 (1*S*,2*S*) and 33.5 (1*R*,2*R*) min for *trans*-**13**; retention times: 31.4 (1*S*,2*R*) and 31.8 (1*R*,2*S*) min for *cis*-**14**. The results are reported in Table 2.

3.1.13. Asymmetric cyclopropanation of styrene using [$RuCl_2$(*p*-cymene)]$_2$: typical procedure. A solution of the ligand (0.1 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (15.3 mg, 0.025 mmol) in CH_2Cl_2 (2 ml) was stirred under argon atmosphere for 30 min. After the addition of styrene (1.43 ml, 12.5 mmol), a solution of ethyl diazoacetate (0.263 ml, 2.5 mmol) in CH_2Cl_2 (2.5 ml) was added dropwise over a 2 h period. After 2 h stirring at room temperature, the mixture was worked up as described above. The results are reported in Table 1.

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