Pergamon

SCIENCE DIRECT®

Tetrahedron: *Asymmetry* 14 (2003) 845–854

TETRAHEDRON: *ASYMMETRY*

Electronic tuning of the PNNP ligand for the asymmetric cyclopropanation of olefins catalysed by [RuCl(PNNP)]$^+$

Cristina Bonaccorsi, Stephan Bachmann and Antonio Mezzetti*

Department of Chemistry, Swiss Federal Institute of Technology, ETH Hönggerberg, CH-8093 Zürich, Switzerland

Received 14 November 2002; accepted 4 December 2002

Abstract—Cationic ruthenium complexes of the type [RuCl(L)(PNNP)]$^+$ (L = OEt_2, OH_2), where PNNP is the CF_3-subsituted PNNP ligand *N*,*N*′-bis[*o*-(bis(4-trifluoromethylphenyl)phosphino)benzylidene]-(1*S*,2*S*)-diaminocyclohexane **1b**, catalyse the asymmetric cyclopropanation of styrene, α-Me-styrene, and 1-octene with ethyl diazoacetate. These complexes are more active and give higher *cis*- and enantioselectivities than their analogues containing the unsubstituted ligand **1a**. Thus, [RuCl(OEt_2)(**1b**)]PF_6 cyclopropanates α-Me-styrene with 85% *cis* selectivity and 86% ee in 94% isolated yield.

1. Introduction

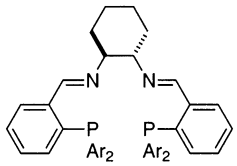
Over the last 15 years, highly enantio- and diastereoselective catalysts for the cyclopropanation of olefins have been developed.[1] Chiral semicorrin, bis(oxazoline) copper catalysts and, more recently, ruthenium complexes[2–7] containing tridentate nitrogen donors (pybox)[8] and salen cobalt(III) complexes[9] have been shown to cyclopropanate styrene derivatives to give mainly the *trans* derivative with enantioselectivities higher than 90% ee. The development of *cis*-selective systems has been slower. Kodadek and Doyle have been pioneers in the field with the introduction of rhodium chiral porphyrins[10] and dirhodium(II) carboxamidates.[11] However, the breakthrough in terms of high enantio- and diastereocontrol has been achieved by Katsuki, whose cobalt salen and ruthenium nitrosyl complexes catalyse the cyclopropanation of styrenes to give the cyclopropane derivatives with excellent *cis*- and enantioselectivity.[12]

We recently reported that the formally 16-electron cations [RuCl(**1a**)]$^+$ (**4a**) (**1a** = *N*,*N*′-bis[*o*-(diphenylphosphino)benzylidene] - (1*S*,2*S*) - diaminocyclohexane) catalyse atom-exchange[13] and atom-transfer[14,15] reactions, including the cyclopropanation of olefins. Precatalyst **4a** cyclopropanates styrene in the presence of diazo esters giving the *cis* isomer with high diastereo- and enantioselectivity.[15] The intermediate carbene complex [RuCl(=C(H)COOEt)(**1a**)] has been detected by ^{1}H and ^{31}P NMR spectroscopy. The investigation of the substrate-based electronic effects has confirmed that an electrophilic mechanism[16] for the carbene transfer to the olefin is operative.[17] The reactions with the electron-rich *p*-substituted styrenes *p*-X-$C_6H_4C(H)=CH_2$ give the highest conversions and diastereo- and enantioselectivities. The trend for all reaction parameters suggested that the transfer of the electronic effect from the substrate to the PNNP ligand should be beneficial both to the activity and the selectivity of the reaction.

It has been shown that the performance of enantioselective catalysts can be boosted by appropriate 'electronic tuning' of the chiral ligand.[18–20] Atom-transfer reactions, such as epoxidation and cyclopropanation, occur without substrate precoordination and are therefore less sensitive to the steric effects of the ligands. Thus, the electronic tuning of the ligands offers a unique chance to improve the selectivity of such reactions, as shown by Jacobsen in the case of the Mn(salen)-catalysed epoxidation of olefins.[19] Additionally, the ruthenium-catalysed asymmetric cyclopropanation of olefins is influenced by ligand-based electronic effects,[21] as well as substrate-based ones.[22] Herein, we present the first results concerning the electronic tuning of PNNP ligands.

* Corresponding author. Tel.: +41 632 61 21; fax: +41 1 632 13 10; e-mail: mezzetti@inorg.chem.ethz.ch

0957-4166/03/$ - see front matter
doi:10.1016/S0957-4166(03)00033-8



Ar = C_6H_5, **1a**
Ar = 4-CF_3-C_6H_4, **1b**

Chart 1.

2. Results and discussion

2.1. PNNP ligands and dichloro complexes

The condensation of the *o*-formyl phosphine P(*p*-CF_3-C_6H_4)$_2$(*o*-C_6H_4CHO) with (*S*,*S*)-(+)-1,2-diaminocyclohexane gave the PNNP ligand *N*,*N*′-bis[*o*-(bis(4-trifluoromethylphenyl)phosphino)benzylidene] - (1*S*,2*S*)-diaminocyclohexane **1b** (Chart 1). Ligand **1b** is neither oxidised nor hydrolysed in the solid state, even on standing in air for months. The ^{31}P NMR chemical shift of **1b** (δ −10.2) is close to that of ligand **1a** (δ −12.9), which confirms that electronic effects through aromatic systems do not markedly affect the ^{31}P chemical shift.[23]

The six-coordinate dichloro complex [$RuCl_2$(**1b**)] (**2b**) was prepared by reaction of **1b** with [$RuCl_2(PPh_3)_3$] in refluxing toluene. Under these conditions, a single isomer is formed, as indicated by the single signal in the ^{31}P NMR spectrum, a singlet at δ 49.5. The single band at 313 cm^{-1} in the Ru–Cl stretching region supports a *trans* arrangement of the chloro ligands. As already observed for ligand **1a**,[14b] the reaction of [$RuCl_2(PPh_3)_3$] with **1b** in dichloromethane at room temperature gave the *trans* isomer described above as the main product (ca. 80%), along with a minor side product (δ 81.4 (d), 45.9 (d), $J_{P,P'}$ = 37.7 Hz, ca. 20%). The latter complex is probably the Δ-*cis*-β isomer (**3b**), which is more stable than the Λ-*cis*-β-isomer by 1.5 kcal/mol.[14b,†]

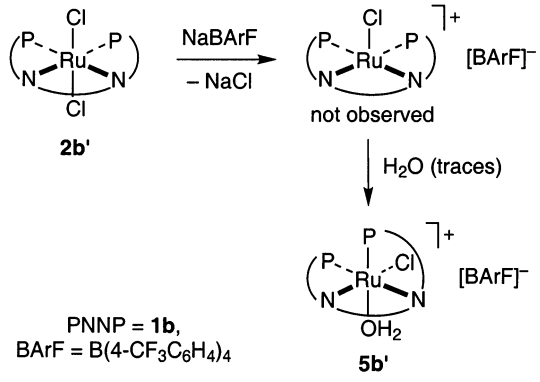
2.2. Reactivity of *trans*-[$RuCl_2$(1b)]

The investigation of the reactivity of the dichloro complex **2b** was targeted to the synthesis of the cationic, formally 16-electron complex [RuCl(PNNP)]PF_6. In fact, our previous studies have shown that such complexes give the best results in catalysis in terms of activity and selectivity.[14] However, owing to the synthetic difficulties we encountered (as described below), we prepared other catalyst precursors containing ligand **1b**, which implied the synthesis and screening in catalysis of their analogues with ligand **1a** for the sake of comparison.

† As calculated by molecular modelling (see below). In chart 3 of Ref. 14b, the stereodescriptors of the Λ-*cis*-β and Δ-*cis*-β isomers are inverted.

The dichloro complex containing ligand **1b**, *trans*-[$RuCl_2$(**1b**)] (**2b**), does not react with $TlPF_6$ in CH_2Cl_2 at room temperature, whereas the **1a** analogue [$RuCl_2$(**1a**)] (**2a**) reacts smoothly under the same conditions to form the cationic complex [RuCl(**1a**)]$^+$ (**4a**).[14,15] As Tl(I) is a strong chloride scavenger, the failure of **2b** to react with $TlPF_6$ suggests that the five-coordinate fragment [RuCl(**1b**)]$^+$ (**4b**) is a stronger Lewis acid than [RuCl(**1a**)]$^+$ (**4a**). As the molecular modelling studies (see below) show that the steric requirements of ligands **1a** and **1b** are similar, we speculate that the decreased stability of **4b** is an effect of the reduced electron density at ruthenium with ligand **2b** as compared to **2a**. It should be noted that the driving force of chloride dissociation from [RuX_2L_4] to give the 16-electron complexes [MXL_4]$^+$ (M = d^6 ion; X = π-donor ligand) is the removal of the π–π 4-electron repulsion between the filled metal π-orbitals and the filled p_π orbitals of chloride.[24] Clearly, this repulsion is larger in **2a** than in **2b**, which contains the less basic ligand **1b** and is therefore less prone to chloride dissociation. Thus, the introduction of electron-withdrawing CF_3-groups in the PPh_2 ligands stabilises the 18-electron complex **2b** and destabilises the 16-electron species **4b**.

Complex **2b** did react with $AgPF_6$ in $CDCl_3$, but the reaction mixture contained products of hydrolysis of the PF_6^- anion along with several complexes that were not further investigated. Chloride abstraction from **2b** occurred also with Na[B(3,5-di-CF_3-C_6H_3)$_4$] (NaBArF) as the chloride scavenger in CH_2Cl_2 at room temperature. The single product formed features an AX system at δ 65.5 and 47.2 ($J_{P,P'}$ = 30.3 Hz) in the ^{31}P NMR spectrum. On the basis of analytic data and chemical behaviour, we formulate these species as one isomer **5b**′ of the aqua complex [RuCl(OH_2)(**1b**)]$^+$, rather than the five-coordinate [RuCl(**1b**)]$^+$ (Scheme 1). The mass spectrum (ESI) of **5b**BArF displays peaks at *m*/*z* 1107.9 for [**5b**+Na]$^+$ (32%) and at *m*/*z* 1067.2 for [**5b**–H_2O]$^+$ (100%). Additionally, chemical evidence of the identity of **5b** comes from the reactions of [RuCl(OEt_2)(**1b**)]PF_6 and [RuCl(η^1-O_3SCF_3)(**1b**)] with water (see below). We have previously observed the formation of aqua complexes under apparently 'anhydrous' conditions upon



Scheme 1.

Table 1. ^{31}P NMR data of complexes **1a**–**7b**[a]

Complex		δ/ppm	J/Hz	T/K
trans-[$RuCl_2$(**1a**)][b]	(**2b**)	48.0 (s)		300
trans-[$RuCl_2$(**1b**)]	(**2b**)	49.5 (s)		300
cis-[$RuCl_2$(**1b**)]	(**3b**)	81.4 (d), 45.9 (d)	37.7	300
[$RuCl(OH_2)$(**1a**)]$^+$ isomer **I**[b]	(**5a′**)	65.0 (d), 45.5 (d)	31.8	300
[$RuCl(OH_2)$(**1a**)]$^+$ isomer **II**	(**5a″**)	50.9 (d), 42.9 (d)	26.9	300
[$RuCl(OH_2)$(**1b**)]$^+$ isomer **I**	(**5b′**)	65.5 (d), 47.2 (d)	30.3	300
[$RuCl(OH_2)$(**1b**)]$^+$ isomer **II**	(**5b″**)	50.2 (d), 47.9 (d)	27.5	300
[$RuCl(OEt_2)$(**1a**)]$^+$[c]	(**6a**)	72 (br), 45 (br)		300
		68 (br), 46 (br)		273
		66.8 (d), 45.9 (d)[d]	30.6	300
[$RuCl(OEt_2)$(**1b**)]$^+$	(**6b**)	56 (br), 38 (br)	not res.	300
		56.0 (d), 38.4 (d)	29.3	263
[$Ru(OEt_2)_2$(**1b**)]$^{2+}$	(**7b**)	50 (br)		300
		50.0 (s)		263
[$RuCl(\eta^1$-O_3SCF_3)(**1b**)]	(**8b**)	49.6 (d), 48.9 (d)	26.9	300

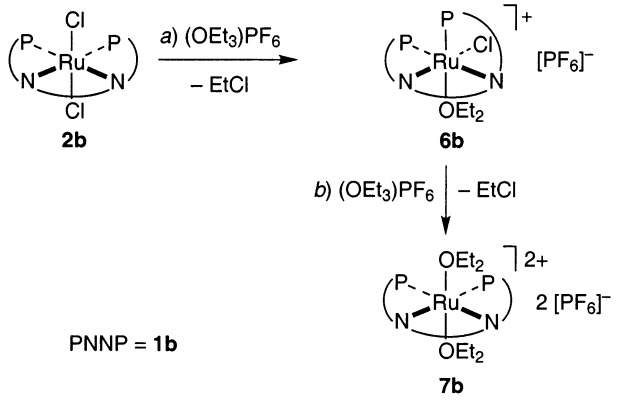
[a] In $CDCl_3$, unless otherwise stated.
[b] From Ref. 29.
[c] In CD_2Cl_2.
[d] In the presence of an excess (32 equiv.) of Et_2O.

chloride abstraction from the related species [$RuCl_2(PPh_3)$(**1c**-κ^3P,N,N)] (**1c** = *N*,*N*′-bis[*o*-(diphenylphosphino)benzyl]-(1*S*,2*S*)-diaminocyclohexane.[14b] The enhanced oxophilicity of the '[RuCl(**1b**)]$^{+}$' fragment as compared to [RuCl(**1a**)]$^+$ is in accordance with ligand **1b** being less electron-rich than **1a**. The presence of adventitious water can be explained by the high hydrophilicity of the $BArF^-$ anion.

An alternative strategy for chloride abstraction from **2a** and **2b** is the removal of one chloro ligand by methylation with $(Et_3O)PF_6$. The **1a** derivative [$RuCl_2$(**1a**)] reacts with $(Et_3O)PF_6$ (1 equiv.) in CD_2Cl_2 over molecular sieves at room temperature. The reaction is quantitative within 15 min and gives [RuCl(OEt_2)(**1a**)]$^+$ (**6a**) instead of the 16-electron complex **4a**. Complex **6a** features a broad AX system at δ 72 and 45, in which the coupling is not resolved. The high frequency signal shifts to δ 68 upon lowering the temperature to 0°C, but remains broad. In contrast, addition of Et_2O (in portions, up to 32 equiv.) at room temperature causes the signals to sharpen progressively into resolved doublets at δ 66.8 and 45.9 with $J_{P,P'}$ = 30.6 Hz (Table 1). Addition of water (10 equiv.) to this solution results in the quantitative formation of aqua complex **5a′** (see below).

The spectral behaviour suggests that **6a** is in equilibrium with free Et_2O and five-coordinate **4a** even at low temperature or in the presence of a moderate excess of Et_2O. Accordingly, we were unable to detect resolved signals for the OEt_2 ligand under either conditions. The only signals observed in the OCH_2-region were those of free Et_2O (δ 3.48) and of CH_3CH_2Cl (δ 3.6). Attempts of detecting **6a** by MS analysis of concentrated reaction solutions of **2a** with $(Et_3O)PF_6$ were unsuccessful. The FAB mass spectrum showed the peak of [RuCl(**1a**)]$^+$ (m/z = 795, 30%) but not that of [RuCl(OEt_2)(**1a**)]$^+$, suggesting that the ether molecule is loosely bonded. Complex **6a** (and its analogue with ligand **1b**, see below) decompose upon isolation and were therefore prepared in situ for application in catalysis.

With ligand **1b**, the dichloro complex **2b** does not react with a stoichiometric amount of $(Et_3O)PF_6$, which is a further indication of reduced electron density at the metal as compared to **2a**. However, when **2b** is treated with an excess of $(Et_3O)PF_6$ (2 equiv.) in $CDCl_3$ or CD_2Cl_2, a mixture of products is formed after a reaction time of 12 h. The ^{31}P NMR spectrum of the reaction solution shows a broad AX system at δ 56 and 38 (63%) and a broad singlet at δ 50 (37%). Upon cooling to −10°C (in CD_2Cl_2), the broad signals sharpen into an AX system (δ 56.0 and 38.4, $J_{P,P'}$ = 29.3 Hz, ca. 63%) and a singlet at δ 50.0 (ca. 37%). The former signals are attributed to the cationic ether adduct [RuCl(OEt_2)(**1b**)]PF_6 (**6b**) by analogy with the **1a** derivative [RuCl(OEt_2)(**1a**)]$^+$ (**6a**). Together with the presence of a single signal for the iminic and methinic N–C*H* protons of the ligand backbone in the ^{1}H NMR spectra at different temperatures, the singlet at δ 50.0 in the ^{31}P NMR spectrum is indicative of a C_2-symmetric complex, which we tentatively formulate as the



Scheme 2.

bis(ether) adduct $[Ru(OEt_2)(\mathbf{1b})]^{2+}$ (**7b**) (Scheme 2). The above interpretation is supported by the integration of the ^1H NMR signal of CH_3CH_2Cl (relative to the major product **6b**), which corresponds to the observed product distribution (63% **6b** and 37% and **7b**). The low-temperature ^1H and ^{31}P NMR spectra (CD_2Cl_2) show that the **6b**:**7b** ratio is not temperature-dependent. Owing to the fact that an excess of $(Et_3O)PF_6$ is used to prepare **6b**, the OCH_2 spectral region is crowded, and the attribution of the signals of the coordinated Et_2O molecule was not possible.

The mixture of the ether adducts **6b** and **7b** in CD_2Cl_2 reacts with water (ca. 1 equiv. versus **6b**+**7b**) to give a mixture of two species, whose ^{31}P NMR spectrum features two AX systems.[‡] The signals of the major product (60%) correspond to those of the aqua complex $[RuCl(OH_2)(\mathbf{1b})]$ (isomer **I**, **5b′**, Table 1). The signals of the minor product (40%) are identical to those of the isomer **II** of $[RuCl(OH_2)(\mathbf{1b})]^+$ (**5b″**), which is the major product of the reaction of $[RuCl(\eta^1\text{-}O_3SCF_3)(\mathbf{1b})]$ with water (see below).[§]

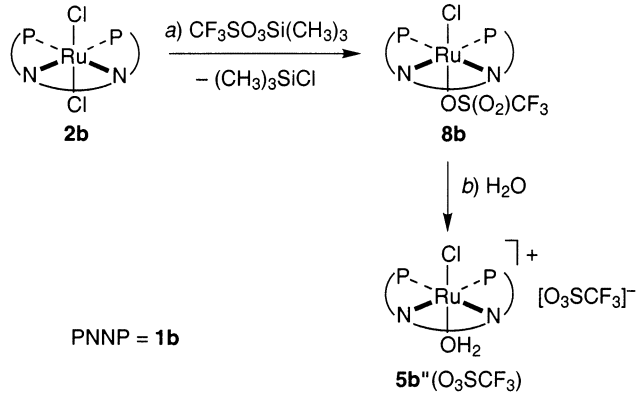
A major drawback of $[RuCl(OH_2)(\mathbf{1b})]PF_6$ is that the PF_6^- anion is hydrolysed upon standing in solution or after isolation in the solid state, which hampers the isolation of a pure product. Attempts aimed at anion metathesis with $NaSbF_6$ were not successful yet. Interestingly, the hydrolysis of the $[PF_6]^-$ anion occurs with **5b**, but not with **5a** as the complex cation. This fact suggests that the acidity of coordinated water is higher in **5b** than in **5a**, a further manifestation of the electronic effect of the PNNP ligand.

In the quest for a strong chloride scavenger that forms a nonhydrolysable anion, we tested trimethylsilyltriflate $(CF_3SO_3Si(CH_3)_3)$. The reaction of **2b** with $CF_3SO_3Si(CH_3)_3$ (1 equiv.) in CH_2Cl_2 at room temperature yielded $[RuCl(\eta^1\text{-}O_3SCF_3)(\mathbf{1b})]$ (**8b**) as a single isomer (Scheme 3). The ^{31}P NMR spectrum displays an AB system ($\delta_A = 49.6$, $\delta_B = 48.9$, $J_{P,P'} = 26.9$ Hz) that, in view of the similar chemical shifts, suggests a *trans* arrangement of the chloro and triflato ligands. The ^{19}F NMR spectrum of **8b** displays a singlet at δ −79.7 for the coordinated triflate.

The triflato complex $[RuCl(\eta^1\text{-}O_3SCF_3)(\mathbf{1b})]$ (**8b**) reacts instantaneously with water (ca. 1 equiv.) in $CDCl_3$ or CH_2Cl_2 to give the corresponding aqua complex $[RuCl(OH_2)(\mathbf{1b})](O_3SCF_3)$ (**5b**O_3SCF_3) (Scheme 3). The ^{31}P NMR spectrum of the reaction solution displays an AX system (δ 50.2 and 47.9, $J_{P,P'} = 27.5$, Table 1), indicating that isomer **II** (**5b″**) is the major product formed (75%). A minor amount of isomer **5b′** (15%) is also detected, along with some unreacted **8b** (10%). The (uncoordinated) triflate counterion shows a signal at δ −78.64 in the ^{19}F NMR spectrum. Whittlesey has recently reported that the ruthenium triflato complexes of the type $[Ru(\eta^1\text{-}O_3SCF_3)(CO)_2(dppe)]$ (dppe = 1,2-bis(diphenylphosphino)ethane)) react with water in an analogous manner.[25] Again, anion metathesis with $NaSbF_6$ was not successful.

The reaction shown in Scheme 3 does not proceed to completion, as the starting complex **8b** (ca. 10%) is detected in the ^{31}P and ^{19}F NMR spectra even in the presence of an excess of water. However, the reaction is not an equilibrium, as addition of molecular sieves to the reaction solution does not convert **5b″** to **8b**. Upon addition of hexane to a solution of **5b**O_3SCF_3 and evaporation of the CH_2Cl_2, the aqua complex **5b″** isomerises to **5b′**. Interestingly, the isomers **I** (**5′**) and **II** (**5″**) of the aqua complex $[RuCl(OH_2)(\mathbf{1b})]^+$ (**5b**) are selectively formed depending on the reaction path. Indeed, the reaction of **2b** with NaBArF gives **5b** as isomer **I** exclusively (**5b′**) (Scheme 1), whereas the triflato complex **8b** reacts with water to give selectively isomer **II** (Scheme 3). As reported previously,[14] $[RuCl(\mathbf{1a})]^+$ reacts with water (1 equiv.) to give isomer **I** of $[RuCl(OH_2)(\mathbf{1a})]^+$ (**5a′**) (Table 1), which isomerises upon isolation to a 7:3 mixture of **5a′** and **5a″**, respectively.

We have tentatively attributed the absolute stereochemistry of the isomeric aqua complexes **5′** and **5″** by using molecular modelling in combination with the analysis of the ^{31}P NMR chemical shifts of a series of $[RuCl(Y)(PNNP)]^{n+}$ complexes (Y = Cl, OH_2, OEt_2), as no crystals of either isomer of **5a** and **5b** have been obtained so far. Considering that the P atom involved in a *trans* P–Ru–N arrangement typically displays ^{31}P NMR chemical shifts in the δ region between 35 and 50, we suggest that isomers **II** (**5a″** and **5b″**) feature a *trans* Cl–Ru–OH_2 arrangements, as shown in Chart 2.



Scheme 3.

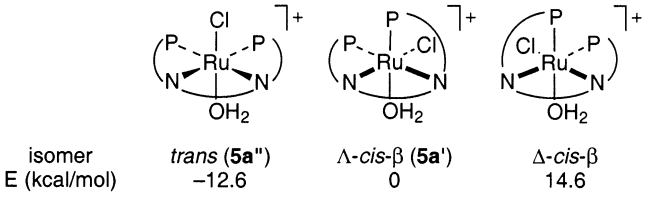


Chart 2.

[‡] If a slight excess of water is used, an additional, broad signal at δ 49 is observed in the ^{31}P NMR spectrum.

[§] We suggest that the dicationic diether complex **7b** abstracts a chloride ion from CD_2Cl_2 by virtue of its high Lewis acidity.

The substantially higher chemical shift of one of the P atoms in isomer **I** must derive from a shorter Ru–P bond, which is compatible with a *trans* P–Ru–O arrangement, as oxygen has a lower *trans* influence than sp^2 nitrogen.[23] Thus, the complexes **5a**′ and **5b**′ probably have a *cis*-β configuration.

UFF-based[26] molecular modelling calculations with the Cerius2 program indicate that the Λ-*cis*-β configuration is more stable than the Δ one. Analysis of the different contributions indicates that the energy difference (ca. 14 kcal/mol) derives from the torsion energy of the Δ isomer being higher than in the Λ one (Chart 2). Molecular modelling indicates that the *trans* isomers (**5a**″ and **5b**″) have the lowest angular strain. In fact, a mixture of the *trans* (**5**″) and Λ-*cis*-β (**5**′) isomers is eventually formed with both ligands. Thus, electronic bonding factors, which are not taken into account in molecular modelling, stabilise the Λ-*cis*-β (**5**′) isomer with respect to the *trans* isomer **5**″. One of these factors is the higher stability of the *trans* P–Ru–OH_2 arrangement as compared to the *trans* Cl–Ru–OH_2 one, which derives from the 4-electron π–π-interactions between the chloro and aqua ligands and the metal π-orbitals in *trans*-Cl–Ru–OH_2 being substituted by push–pull interactions in *trans*-P–Ru–OH_2.[24]

In the same manner, we calculated the probable configuration of the ether adducts $[RuCl(OEt_2)(PNNP)]^+$ (PNNP = **1a**, **6a**; **1b**, **6b**) (Chart 3). As all $[RuCl(OEt_2)(PNNP)]^+$ observed show spectral features analogous to those of isomer **I** of the corresponding aqua complexes, **5a**′ and **5b**′, we propose that they are all *cis*-β isomers. The energy differences between the Λ-*cis*-β and Δ-*cis*-β configurations are significantly smaller than for the aqua complexes **5**. A final observation is that the introduction of the CF_3 groups in the 4-position of the aryl group has no effect on the overall steric crowding of these molecules, as the calculated energies are insensitive to the *trans* substituent in the PPh_2 groups being H or CF_3.

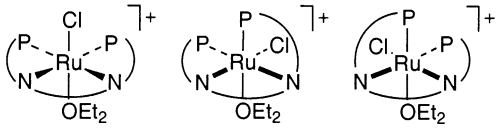
2.3. Cyclopropanation of olefins

The first catalyst precursors screened in the asymmetric cyclopropanation of styrene were the diethyl ether adducts $[RuCl(OEt_2)(PNNP)]PF_6$ (PNNP = **1a**, **6a**; **1b**, **6b**), which were formed in situ. Diazoacetate (2 equiv. versus the olefin) was slowly added to a solution of the catalyst (5 mol%) and the olefin. We chose these reaction conditions because they ensure a fair cyclopropane yield with the less active catalyst and substrates. In general, better enantioselectivity is obtained with an olefin/diazoester ratio of 1:1, but at the cost of a lower cyclopropane yield.

Complex **6a** gave a *cis*:*trans* ratio of 84:16 and 80% ee for the *cis* isomer (Table 2, run 2). For comparison, the previously investigated five-coordinate complex **4a** gave 91:9 *cis*:*trans* ratio and 87% ee with 41% total cyclopropane yield (*cis*+*trans* isomers) (run 1).[15] The ether adduct **6b**, containing the CF_3-substituted ligand **1b**, gives a higher total cyclopropane yield than both **4a** and **6a** (54% yield, run 3) and is as diastereoselective as **4a**. However, its enantioselectivity (83% ee for the *cis* isomer) is only marginally better than that of **6a** (80% ee), and is lower than with **4a** (87%). The latter result, however, was obtained with an olefin/diazo ester ratio of 1:1.

The above results with **6a** and **6b** confirm the previous observation that that *O*-donor ligands significantly decrease the selectivity as compared to the five-coordinate complex **4a**.[14] However, when the *O*-donor is water, the diastereo- and enantioselectivity remain high, but the catalyst activity is reduced. Thus, the isolated aqua complex $[RuCl(OH_2)(\mathbf{1a})]PF_6$ (**5a**PF_6), which is a 7:3 mixture of isomers **I** and **II**, gives a *cis*:*trans* ratio of 86:14 and good enantioselectivity (91% ee) for the *cis* product (run 4), which is close to the best values obtained with the 16-electron complex **4a** (run 1). Thus, we tested the aqua complex $[RuCl(OH_2)(\mathbf{1b})]PF_6$ (**5b**PF_6), which was prepared in situ by reaction of **2b** with $(Et_3O)PF_6$, followed by addition of water (1 equiv.) (run 5). Although the *cis*-selectivity and enantioselectivity for the *cis* product are good, the presence of an excess of *O*-donors (Et_2O and H_2O) has a negative effect on the reactivity of the system (17% total cyclopropane yield).

The reactivity problem cannot be circumvented by using the $[B(4\text{-}CF_3C_6H_4)_4]^-$ salts of the aqua complexes, **5a**BArF and **5b**BArF, owing to the effect of the anion on the selectivity. Indeed, when $[RuCl(OH_2)(\mathbf{1a})]$BArF, formed in situ by reaction of **2a** with NaBArF,¶ is used instead of **5a**PF_6, the *cis* selectivity drops from 86% (run 4) to 72% (run 6), and the enantioselectivity for the *cis* products falls from 91% to 34%. Dramatic effects of the anion on the selectivity of ruthenium-catalysed Diels–Alder reaction have been reported recently.[27] Interestingly, however, the CF_3-derivative **5b**′BArF performs much better than **5a**BArF and yields the *cis* cyclopropane with an excellent diastereoselectivity (98:2 *cis*:*trans* ratio) and 80% ee (run 7).

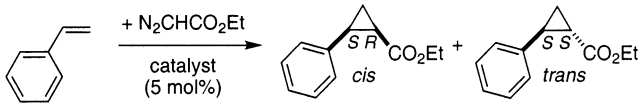


isomer	*trans*	Λ-*cis*-β (**6a**)	Δ-*cis*-β
E (kcal/mol)	−12.4	0	3.1
isomer	*trans*	Λ-*cis*-β (**6b**)	Δ-*cis*-β
E (kcal/mol)	−7.4	0	3.0

Chart 3.

¶ The reaction product is a 1:1 mixture of **4a**BArF and **5a**′BArF.

Table 2. Asymmetric cyclopropanation of styrene[a]



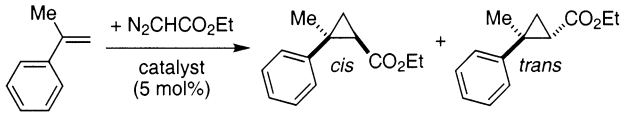
Run	Complex	Conv. (%)	Yield (%)	*cis*:*trans*	Ee (%)[b]	
					cis (1*R*,2*S*)	*trans* (1*S*,2*S*)
1[c,d]	[RuCl(**1a**)]PF_6 (**4a**)	70	41	91:9	87	24
2	[RuCl(OEt_2)(**1a**)]PF_6 (**6a**)	73	28	84:16	80	0
3	[RuCl(OEt_2)(**1b**)]PF_6 (**6b**)	80	54	90:10	83	4
4	[RuCl(OH_2)(**1a**)]PF_6 (**5a**PF_6)	61	28	86:14	91	8
5	[RuCl(OH_2)(**1b**)]PF_6 (**5b**PF_6)	34	17	93:7	89	15
6[d,e]	[RuCl(OH_2)(**1a**)]BArF (**5a**BArF)	56	12	72:28	34	39
7[d]	[RuCl(OH_2)(**1b**)]BArF (**5b**BArF)	84	35	98:2	80	13
8	[RuCl(η^1-O_3SCF_3)(**1a**)] (**8a**)	53	20	75:25	64	3
9	[RuCl(η^1-O_3SCF_3)(**1b**)] (**8b**)	0	0	–	–	–
10	[RuCl(OH_2)(**1b**)](O_3SCF_3) (**5b**O_3SCF_3)	68	9	92:8	90	1

[a] Reaction conditions: ethyl diazoacetate (0.96 mmol, 2 equiv. versus olefin, unless otherwise stated) in CH_2Cl_2 (1 mL) was added over 6 h to a CH_2Cl_2 solution of styrene (0.48 mmol) and the catalyst (24 μmol, 5 mol%). The total reaction time was 20 h.
[b] The absolute configurations (1*R*,2*S*) were obtained by the sign of the specific rotation of the isolated products.[12b,d]
[c] From Ref. 15.
[d] 1 equiv. of ethyl diazoacetate (0.48 mmol) was used.
[e] The catalysts is a 1:1 mixture of **5a**′BArF and **4a**.

Finally, the triflato complexes [RuCl(η^1-O_3SCF_3)(**1a**)] (**8a**) and [RuCl(η^1-O_3SCF_3)(**1b**)] (**8b**) were prepared in situ and tested in the cyclopropanation of styrene. Catalyst **8a** is moderately active and gives relatively low selectivity (run 8). Complex **8b** is completely inactive (run 9), but can be activated by adding H_2O (1 equiv.). The resulting aqua complex *trans*-[RuCl(OH_2)-(**1b**)](O_3SCF_3) (**5b**′′O_3SCF_3) displays good selectivity but a low yield of the cyclopropane was obtained (run 10). Again, the combination of different oxygen donors (water and the triflate counterion) is detrimental to the reactivity of the system.

To assess the advantages of using the electron-poor ligand **1b** with a broader range of olefins, we investigated α-methylstyrene (Table 3) and 1-octene (Table 4) in the catalytic cyclopropanation with [RuCl(L)-(PNNP)]$^+$ (PNNP = **1a** or **1b**). In the case of α-methylstyrene, the aqua (**5a**PF_6) and ether (**6a**) complexes of ligand **1a** do not show a better performance

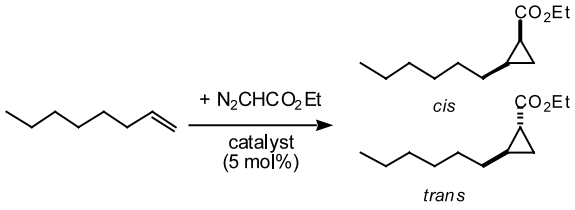
Table 3. Asymmetric cyclopropanation of α-methylstyrene[a]



Run	Complex	Yield (%)	*cis*:*trans*	Ee (%)[b]	
				cis	*trans*
1[c]	[RuCl(**1a**)]PF_6 (**4a**)	83	86:14	49	7
2	[RuCl(OH_2)(**1a**)]PF_6 (**5a**PF_6)	72	66:34	61	11
3[c]	[RuCl(OEt_2)(**1a**)]PF_6 (**6a**)	90	76:24	23	18
4	[RuCl(OEt_2)(**1b**)]PF_6 (**6b**)	94	85:15	86	34

[a] Reaction conditions: ethyl diazoacetate (1.92 mmol, 2 equiv. versus olefin,) in CH_2Cl_2 (2 mL) was added over 6 h to a CH_2Cl_2 solution of α-methylstyrene (0.96 mmol) and the catalyst (48 μmol, 5 mol%). The total reaction time was 20 h. The yields refer to the isolated product as the sum of (*cis*)- and (*trans*)-isomers.
[b] The absolute configuration was not determined.
[c] From Ref. 17.

Table 4. Asymmetric cyclopropanation of 1-octene[a]



Run	Complex	Yield (%)	*cis*:*trans*	ee (%)[b]	
				cis (1*R*,2*S*)	*trans* (1*S*,2*S*)
1[c]	[RuCl(**1a**)]PF_6 (**4a**)	20	60:40	64	18
2	[RuCl(OH_2)(**1a**)]PF_6 (**5a**PF_6)	30	60:40	47	20
3	[RuCl(OEt_2)(**1b**)]PF_6 (**6b**)	54	76:24	43	13

[a] Reaction conditions: ethyl diazoacetate (1.92 mmol, 2 equiv. versus olefin,) in CH_2Cl_2 (2 mL) was added over 6 h to a CH_2Cl_2 solution of α-methylstyrene (0.96 mmol) and the catalyst (48 μmol, 5 mol%). The total reaction time was 20 h. The yields refer to the isolated product as the sum of (*cis*)- and (*trans*)-isomers.
[b] The absolute configuration was determined by the sign of the specific rotation.[29]
[c] From Ref. 17.

(runs 2, 3) as compared with five-coordinate **4a** (run 1, Table 3). However, when the ether adduct [RuCl(OEt_2)(**1b**)]PF_6 (**6b**) is used, the *cis* cyclopropane derivative is obtained in nearly quantitative yield with high selectivity (85%) and good ee (86%) (run 4). These values are better than those obtained with a related $[RuCl(PNNP)]^+$ system[17] and are not far from the best ones ever obtained with this substrate by Katsuki with [RuCl(salen)(NO)] (83:17 *cis*:*trans* ratio, 97% ee for *cis* isomer)[12a] and [Co(salen)] (83:17 *cis*:*trans* ratio, 99% ee).[12c]

Catalyst **6b** is also promising in connection with an aliphatic olefin such as 1-octene (Table 4). Thus, **6b** (54% isolated yield) is more active than **4a** and **5a**PF_6, and gives the highest *cis*-selectivity (76%, run 3). Although the enantioselectivity is still low (43% ee), these results suggest that electronic tuning of the PNNP ligands can open the way to the highly *cis*- and enantioselective cyclopropanation of alkyl-substituted olefins, which are particularly unreactive with most catalytic systems. In fact, no *cis*-selective cyclopropanation catalyst is known for these substrates, whereas some highly *trans*- and enantioselective systems have been reported.[2a,8b,22c,28]

3. Final remarks

The introduction of electron-withdrawing functionalities into the PPh_2 groups improves the activity of the $[RuCl(L)(PNNP)]^+$ catalysts. A drawback is the formation of adducts with oxygen donors, which partially cancels the electronic effect from the ligand. It is still unclear whether the decreased selectivity of the cyclopropanation reaction in the presence of oxygen donors is a consequence of reduced activity of the catalyst (that is, reduced rate of formation of the carbene complex). An alternative explanation is that the oxygen-donor adducts $[RuCl(L)(PNNP)]^{n+}$ (L = OEt_2, OH_2, triflato) and the five-coordinate complex $[RuCl(PNNP)]^+$ react with ethyl diazoacetate forming different isomers of the carbene complex $[RuCl(=CHCOOEt)(PNNP)]^+$, which might influence the diastereoselectivity of the carbene transfer to the olefin. We have previously reported that the five-coordinate complex **4a** reacts with ethyl diazoacetate to form the thermodynamically preferred isomer *trans*-$[RuCl(CHCOOEt)(\mathbf{1a})]^+$ at room temperature.[15] The corresponding reaction of the adducts $[RuCl(L)(\mathbf{1a})]^+$ will be the object of future studies.

4. Experimental

4.1. General

Reactions with air- or moisture-sensitive materials were carried out under an argon atmosphere using Schlenk techniques or in a glove box under purified nitrogen. Solvents were purified by standard procedures. The ^1H, ^{31}P, and ^{19}F NMR spectra were measured on Bruker AVANCE 200, 250, or 300 instruments with $SiMe_4$ (^1H), 85% H_3PO_4 (^{31}P), and $CFCl_3$ (^{19}F) as external standards. MS measurements, HPLC, GC, specific rotations, and elemental analyses, as well as UFF calculations, were described before.[15] Complexes $[RuCl_2(\mathbf{1a})]$[29] and $[RuCl(OH_2)(\mathbf{1a})]PF_6$[14b] (**5a**) were prepared as described in the literature.

4.2. *N*,*N*′-Bis[*o*-(bis(4-trifluoromethylphenyl)phosphino)-benzylidene]-(1*S*,2*S*)-diaminocyclohexane, 1b

(1*S*,2*S*)-(+)-1,2-Diaminocyclohexane (67.8 mg, 0.59 mmol) and 2-(bis(4-trifluoromethylphenyl)phosphino)-benzaldehyde (503 mg, 1.18 mmol, 2 equiv.) were dissolved in toluene (30 mL) and the solution was heated

under reflux for 10 h. Toluene was evaporated and the resulting yellow oil was recrystallised from CH_2Cl_2/toluene. Yield: 0.43 g (78%). $[\alpha]_D^{20}$ +51.6±0.1 (*c* 1.04, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ 8.30 (*d*, 2H, *H*C=N, $J_{P,H}=3.4$ Hz), 7.6–7.2 (*m*, 24H, arom.), 2.95 (*m*, 2H, N-C*H*), 1.21–1.67 (*m*, 8H, CH_2). ^{31}P NMR (101 MHz, $CDCl_3$): δ −10.2 (*s*, 2P). MS (EI): *m*/*z* 930 (M^+, 3), 785 (M^+−Ph, 46), 424 (M^+−2PPh, 100). IR (KBr, cm^{-1}): 1605 (*s*, $\nu_{C=N}$), 1329 (*s*, CF_3), 1166 (*s*, CF_3), 1132 (*s*, CF_3), 599 (*s*, CF_3).

4.3. *trans*-[$RuCl_2$((*S*,*S*)-1b)], 2b

[$RuCl_2(PPh_3)_3$] (382 mg, 0.401 mmol, 1 equiv.) was added to a solution of **1b** (374 mg, 0.401 mmol) in toluene and the resulting solution was heated under reflux for 10 h. After evaporation of toluene, the resulting red solid was recrystallised from CH_2Cl_2/hexane. Yield: 0.38 g (86%). $[\alpha]_D^{20}$ −189±1 (*c* 0.25, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 8.91 (*d*, 2H, *H*C=N, $J_{P,H}=8.37$ Hz), 7.71–6.70 (*m*, 24H, arom.), 4.15 (*d*, 2H, N-C*H*, $J_{H,H'}=8.1$ Hz), 2.75 (*d*, 2H, NCH-C*H*H′, $J_{H,H'}=10.7$ Hz), 2.12 (*m*, 2H, CH_2), 1.99 (*m*, 2H, CH_2), 1.48 (*m*, 2H, CH_2). ^{31}P NMR (121 MHz, $CDCl_3$): δ 49.54 (*s*, 2P). ^{19}F NMR (282 MHz, $CDCl_3$): δ −63.45 (*s*, 6F), −63.61 (*s*, 6F). MS (MALDI): *m*/*z* 1102 (M^+, 30), 1067 (M^+−Cl, 2), 1031 (M^+−2Cl, 100), 885 (M^+−2Cl−Ph, 2). IR (CsI, cm^{-1}): 1606 (*m*, $\nu_{C=N}$), 1330 (*s*, CF_3), 1172 (*s*, CF_3), 1128 (*s*, CF_3), 602 (*s*, CF_3), 313 (*w*, Ru–Cl). Anal. calcd for $C_{48}H_{36}Cl_2F_{12}N_2P_2Ru$: C, 52.28; H, 3.29; N, 2.54. Found: C, 52.40; H, 3.48; N, 2.35%. In an alternative route, [$RuCl_2(PPh_3)_3$] was added to a dichloromethane solution of **1b** and the resulting solution was stirred at room temperature for 10 h. In addition to **2b** (80%), *cis*-[$RuCl_2$((*S*,*S*)-**1b**)] (**3b**) (20%) was also obtained. ^{31}P NMR ($CDCl_3$): δ 81.4 (*d*, 1P, $J_{P,P'}=37.7$ Hz), 45.9 (*d*, 1P, $J_{P,P'}=37.7$ Hz).

4.4. [$RuCl(OH_2)$(1b)]BArF, 5bBArF

$NaB(4\text{-}CF_3\text{-}C_6H_4)_4$ (NaBArF) (100 mg, 0.11 mmol, 1 equiv.) was added to a solution (5 mL) of **2b** (122 mg, 0.11 mmol) in dichloromethane. The red solution was stirred for 10 h at room temperature. After filtration over Celite, the solvent was evaporated, and the brown solid was recrystallised from CH_2Cl_2/hexane. Yield: 0.164 g (77%). ^1H NMR (250 MHz, $CDCl_3$): δ 8.77 (*d*, 1H, *H*C=N, $J_{P,H}=9.9$ Hz), 8.64 (*s*, 1H, *H*C=N), 7.60–6.60 (*m*, 36H, arom.), 4.39 (*m*, 2H, N-C*H*), 2.45–2.30 (*m*, 2H, N-C*H*), 1.7 (*m*, 2H, CH_2), 1.2 (*m*, 4H, CH_2). ^{31}P NMR (101 MHz, $CDCl_3$): δ 65.5 (*d*, 1P, $J_{P,P'}=30.3$ Hz), 47.2 (*d*, 1P, $J_{P,P'}=30.3$ Hz). MS (MALDI): *m*/*z* 1067 (M^+−H_2O, 2), 1031 (M^+−H_2O−Cl, 100), 885 (M^+−H_2O−Cl−Ph, 2). MS (ESI): *m*/*z* 1107.9 ([*M*+Na]$^+$, 32), 1067.2 (M^+−H_2O, 100). IR (KBr, cm^{-1}): 1610 (*m*, $\nu_{C=N}$), (*s*, CF_3), 1208.4 (*s*, CF_3), 1139 (*s*, CF_3), 685 (*s*, CF_3). Anal. calcd for $C_{80}H_{50}BClF_{36}N_2OP_2Ru$: C, 49.31; H, 2.59; N, 1.44. Found: C, 49.34; H, 2.70; N, 1.61%.

4.5. [$RuCl(OEt_2)$(1a)]PF_6, 6a

Complex **2a** (30 mg, 36 μmol) and $(Et_3O)PF_6$ (9 mg, 36 μmol) were solved in dry CD_2Cl_2 over molecular sieves and stirred for 15 min. As the complex decomposed during crystallisation from CH_2Cl_2/hexane, it was characterised in solution (see Section 2). ^1H NMR (250 MHz, CD_2Cl_2): δ 8.82 (*d*, 1H, $J_{P,H}=9.5$ Hz, N=C*H*), 8.60 (*s*, 1H, N=C*H*), 8.0–6.0 (*m*, 28H, arom.). ^{31}P NMR (101 MHz, CD_2Cl_2, 273 K): δ 68 (*br*, 1P), 46 (*br*, 1P), −144.4 (septet, 1P, $J_{P,F}=714$ Hz, PF_6) (see also Table 1).

4.6. [$RuCl(OEt_2)$(1b)]PF_6, 6b

Complex **2b** (18 mg, 0.015 mmol) was dissolved in CD_2Cl_2 (1 mL) in an NMR tube fitted with a Young valve under an atmosphere of purified nitrogen in a glove box. After addition of $(Et_3O)PF_6$ (8 mg, 0.032 mmol, 2 equiv.), the reaction was monitored by ^{31}P NMR spectroscopy. After 12 h complete conversion was observed. As the complex decomposed during crystallisation from CH_2Cl_2/hexane, it was characterised in solution. ^1H NMR (250 MHz, CD_2Cl_2, 300 K): δ 9.37 (*d*, 1H, *H*C=N, $J_{P,H}=10.0$ Hz, **6b**, 63%), 8.92 (*br*, 1H, *H*C=N, **6b**, 63%), 8.24 (*s*, 2H, *H*C=N, **7b**, 37%). ^{31}P NMR (101 MHz, CD_2Cl_2, 300 K): δ 56 (br, 1P, **6b**, 63%), 50 (br, 2P, **7b**, 37%), 38 (br, 1P, **6b**, 63%), −143.2 (septet, 1P, $J_{P,F}=714$ Hz, PF_6). ^{31}P NMR (CD_2Cl_2, 263 K): δ 56.0 (d, 1P, $J_{P,P'}=29.3$ Hz, **6b**, 63%), 50.0 (s, 2P, **7b**, 37%), 38.4 (d, 1P, $J_{P,P'}=29.3$, **6b**, 63%), −143.2 (septet, 1P, $J_{P,F}=714$ Hz, PF_6).

4.7. [$RuCl(\eta^1\text{-}O_3SCF_3)$(1b)], 8b

Complex **2b** (85 mg, 0.077 mmol) was dissolved in CH_2Cl_2 and $CF_3SO_3Si(CH_3)_3$ (0.014 mL, 0.077 mmol) was added dropwise at 0°C. The red solution was stirred for 3 h at room temperature and then the solvent was evaporated to give a red solid. Yield: 70 mg (85%). ^1H NMR (200 MHz, $CDCl_3$): δ 9.23 (*d*, 1H, *H*C=N, $J_{P,H}=9.2$ Hz), 8.92 (*d*, 1H, *H*C=N, $J_{P,H}=9.2$ Hz), 7.80–6.20 (*m*, 24H, arom.), 4.62 (*m*, 1H, N-C*H*), 4.20 (*m*, 1H, N-C*H*), 3.06 (*d*, 1H, NCH-*CH*H′, $J_{H,H'}=9.0$ Hz), 2.67 (*d*, 1H, NCH-*CH*H′, $J_{H,H'}=9.0$ Hz), 2.14 (*m*, 2H, CH_2), 1.90 (*m*, H, C*H*H′), 1.65 (*m*, H, C*H*H′), 1.43 (*m*, 2H, CH_2). ^{31}P NMR (81 MHz, $CDCl_3$): δ 49.6 (*d*, 1P, $J_{P,P'}=26.9$ Hz), 48.9 (*d*, 1P, $J_{P,P'}=26.9$ Hz). ^{19}F NMR (188 MHz, $CDCl_3$): δ −63.3 (*s*, 3F, **1b**-CF_3), −63.74 (*s*, 6F, **1b**-CF_3), −63.75 (*s*, 3F, **1b**-CF_3), −79.7 (*s*, 3F, Ru–OSO_2CF_3). MS (MALDI): *m*/*z* 1067 (M^+−CF_3SO_3, 2), 1031 (M^+−CF_3SO_3−Cl, 100), 885 (M^+−CF_3SO_3−Cl−Ph, 3). The crystals contain 1 molecule CH_2Cl_2 per **9b**, as determined by ^1H NMR spectroscopy. Anal. calcd for $C_{48}H_{36}Cl_2F_{12}N_2P_2Ru{\cdot}CH_2Cl_2$: C, 46.15; H, 2.94; N, 2.15. Found: C, 46.62; H, 3.37; N, 2.16%.

4.8. [$RuCl(OH_2)$(1b)](O_3SCF_3), 5bO_3SCF_3

Water (3.2 μL, 18 μmol, 1 equiv.) was added to a $CDCl_3$ solution of **8b** (20 mg, 18 μmol). The ^1H, ^{31}P, and ^{19}F NMR spectra of the reaction solution, recorded immediately after the addition of water, indicated the presence of **5b**″ (75%) and **5b**″ (15%) along with unreacted **8b** (10%). The species distribution did not change with time even in the presence of an excess of water

after 1 day. As the formation of **5b**O_3SCF_3 is not quantitative, the characterisation of the complex in the solid state was not attempted. Data for **5b**′′: ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.2 (*d*, 1H, *H*C=N, $J_{P,H}=9.5$ Hz), 8.9 (*d*, 1H, *H*C=N, $J_{P,H}=9.5$ Hz), 7.8–6.1 (*m*, 24H, arom.), 3.9–3.7 (*m*, 2H, N–C*H*). ^{31}P NMR (81 MHz, $CDCl_3$): δ 50.2 (*d*, 1P, $J_{P,P'}=27.5$ Hz), 47.9 (*d*, 1P, $J_{P,P'}=27.5$ Hz). ^{19}F NMR (188 MHz, $CDCl_3$): δ −78.64 (*s*, 3F, uncoordinated $[O_3SCF_3]^-$).

4.9. Catalytic cyclopropanation

4.9.1. Catalyst preparation. [RuCl(OEt_2)(PNNP)]PF_6 (PNNP = **1a**, **6a**: PNNP = **1b**, **6b**): (Et_3O)PF_6 (**1a**, 1 equiv.; **1b**, 2 equiv.) was added to a CH_2Cl_2 (1 mL) solution of **2** (24 μmol), and the solution was stirred for 5 h. The formation of the ether adduct was indicated by a colour change during this time. [RuCl(OH_2)(**1b**)]PF_6 (**5b**): H_2O (1 equiv.) was added to **6b** prepared as described above. [RuCl(OH_2)(PNNP)]BArF (PNNP = **1a** or **1b**): NaBArF (1 equiv.) was added to a CH_2Cl_2 solution (1 mL) of **2a** or **2b** (24 μmol), and the solution was stirred overnight. The resulting brown solution was filtered over Celite and added to the olefin. [RuCl(O_3SCF_3)(PNNP)] (PNNP = **1a**, **8a**; PNNP = **1b**, **8b**): $CF_3SO_3Si(CH_3)$ (4.3 μL, 1 equiv.) was added a CH_2Cl_2 solution (1 mL) of **2a** or **2b** (24 μmol) at 0°C, and the solution was stirred at room temperature for 3 h. [RuCl(H_2O)(PNNP)](O_3SCF_3): H_2O (1 equiv.) was added to **8b** prepared as described above.

4.9.2. Standard catalytic run. The reactions with styrene and all catalyst precursors were carried out according to the following procedure: A solution of the catalyst (24 μmol, 5 mol% versus styrene) in CH_2Cl_2 (1 mL) was added to styrene (0.48 mmol) under argon. A CH_2Cl_2 solution (1 mL) of distilled ethyl diazoacetate (0.96 mmol, 2.0 equiv.) was added to the reaction mixture over 6 h by syringe pump. The solution was stirred for additional 14 h, and then analysed as described below. For the other substrates, see Tables 3 and 4. Analytical details are given below.

4.9.3. Styrene. Olefin conversion and yields of *cis* and *trans* product were determined by GC analysis with decane as internal standard. Samples for chiral GC analysis were prepared by filtration over a plug of alumina to remove the catalyst. Achiral GC analysis: Macherey–Nagel SE 54, 30 m, He carrier (92 kPa). Temperature program: 50°C isotherm for 5 min, then to 200°C at 5°C/min. R_t (min): styrene, 10.2; decane, 14.25; ethyl *cis*-2-phenyl-cyclopropane carboxylate, 28.2; ethyl *trans*-2-phenyl-cyclopropane carboxylate, 29.7. The enantiomeric excesses of the *cis* and *trans* products were determined by chiral GC analysis: Supelco Beta Dex 120, 1.4 mL He min^{-1}; temperature program: 110°C for 10 min, 5°C/min to 150°C, isotherm for 20 min. R_t (min): *cis*-(1*R*,2*S*), 26.0; *cis*-(1*S*,2*R*), 26.38; *trans*-(1*R*,2*R*), 28.09; *trans*-(1*S*,2*S*), 28.34. The GC peaks were attributed by comparison with an authentic sample with a known *trans*/*cis* ratio (99:1, Lancaster). The absolute configurations were determined by the sign of the optical rotation of the isolated products.[12b]

4.9.4. α-Methylstyrene. After evaporation of the solvent, the product was isolated by column chromatography (alumina) with hexane/AcOEt (9:1) as eluent. The yields refer to the isolated product as the sum of *cis*- and *trans*-isomers. The absolute configuration was not determined. For spectroscopic data, see Ref. 17. Achiral GC analysis: Macherey–Nagel SE 54, 30 m, carrier 92 kPa He. Temperature program: 50°C isotherm for 5 min, then to 200°C at 5°C/min. R_t (min): ethyl *cis*-2-methyl-phenylcyclopropane-1-carboxylate, 28.2; ethyl *trans*-2-methyl-phenylcyclopropane-1-carboxylate, 29.5. Chiral GC analysis: Supelco Beta Dex 120, 1.4 mL He min^{-1}; temperature program: 140°C isotherm, R_t (min) *cis*-**I**, 16.0; *cis*-**II**, 16.5; *trans*-**I**, 19.6, *trans*-**II**, 19.8.

4.9.5. 1-Octene. After evaporation of the solvent, the product was isolated by column chromatography (alumina) with hexane/AcOEt (9:1) as eluent. The yields refer to the isolated product as the sum of *cis*- and *trans*-isomers. The absolute configuration was determined by the sign of the optical rotation.[30] For spectroscopic data, see Ref. 17. Anal. calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18; O, 16.14. Found: C, 72.69; H, 11.16; O, 16.32%. Achiral GC analysis: Macherey–Nagel SE 54, 30 m, carrier 92 kPa He. Temperature program: 50°C isotherm for 5 min, then to 200°C at 5°C/min. R_t (min): ethyl *cis*-2-hexylcyclopropane-1-carboxylate, 26.1; ethyl *trans*-2-hexylcyclopropane-1-carboxylate, 26.6. Chiral GC analysis: Supelco Beta Dex 120, 1.4 mL He min^{-1}; temperature program: 90°C isotherm, R_t (min) *cis*-(1*R*,2*S*), 96.9; *cis*-(1*S*,2R), 100.9; *trans*-(1*R*,2*R*), 113.7, *trans*-(1*S*,2*S*), 114.9.

Acknowledgements

We thank the Swiss National Science Foundation for support (grant 20-55685.98).

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