# Optimization or Breakthrough? The First Highly *cis*- and Enantioselective Asymmetric Cyclopropanation of 1-Octene by "Electronic and Counterion" Tuning of [RuCl(PNNP)]$^+$ Catalysts

Cristina Bonaccorsi and Antonio Mezzetti*

*Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, ETH Hönggerberg, CH-8093 Zürich, Switzerland*

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The dichloro complexes [$RuCl_2$(**1a**)] (**2a**) and [$RuCl_2$(**1b**)] (**2b**) with the chiral tetradentate PNNP ligands (1*S*,2*S*)-*N*,*N*′-bis[*o*-(diphenylphosphino)benzylidene]cyclohexane-1,2-diamine (**1a**) and (1*S*,2*S*)-*N*,*N*′-bis[*o*-(bis(4-trifluoromethylphenyl)phosphino)benzylidene]cyclohexane-1,2-diamine (**1b**) react with $AgSbF_6$ (1 equiv) to give the highly reactive five-coordinate complexes [RuCl(PNNP)]$SbF_6$ (**3a**$SbF_6$ or **3b**$SbF_6$), which were characterized in solution. The reaction of **2a** or **2b** with $AgBF_4$ gives [RuCl(PNNP)]$BF_4$ along with unidentified products. Complex [RuCl(**1b**)]$SbF_6$ (**3b**$SbF_6$) cyclopropanates 1-octene to ethyl 2-hexylcyclopropane-1-carboxylate (up to 66% overall isolated yield) in the presence of ethyl diazoacetate with unprecedented *cis*-diastereoselectivity (85:15 *cis*:*trans* ratio) and with excellent enantioselectivity (up to 99 and 98% ee for the *cis* and *trans* isomers, respectively). Complex **3b**$SbF_6$ is also an excellent *cis*-selective cyclopropanation catalyst for styrene (96% ee for the *cis* isomer, 99:1 *cis*:*trans* ratio) and α-methylstyrene (96% ee for the *cis* isomer, 92:8 *cis*:*trans* ratio). The catalyst activity depends on the counterion and increases in the order $[BF_4]^- < [SbF_6]^- < [PF_6]^-$, whereas the best stereoselectivity is observed with $[SbF_6]^-$. Molecular modeling calculations are extended to 1-octene and α-methylstyrene and revised to account for the absolute configuration of ethyl *cis*-2-phenylcyclopropane-1-carboxylate (1*S*,2*R*, incorrectly reported as 1*R*,2*S* in a former paper).

## Introduction

Cyclopropanes are of great importance, as the highly strained three-membered ring is present in many natural compounds and bioactive molecules.[1] Also, cyclopropane synthesis from an olefin and a carbene source is a challenge because two stereocenters are formed simultaneously. Thus, much effort has been invested into developing diastereoselective carbene transfer agents, both stoichiometric and catalytic. The major success in this field has been the development of catalysts that give *trans*-cyclopropanes with high diastereo- and enantioselectivity.[2−6] With the notable early exception of haloethyl cyclopropane carboxylic acids,[7] catalysts that selectively produce the thermodynamically less stable *cis* diastereoisomer have been developing at a much slower pace. Apart from stoichiometric carbene transfer from tungsten carbonyl complexes,[8] *cis*-selectivity has been observed only in non-enantioselective cyclopropanation reactions exploiting rhodium(phorphyrin),[9] iron,[10] or copper[11] catalysts. A common feature of these systems is that aliphatic 1-alkenes give lower *cis*-selectivity than styrenes.[11,12] Also, chiral catalysts for the enantioselective cyclopropanation of aliphatic 1-alkenes are invariably *trans*-selective.[2,3,5,6,13−18]

A recent breakthrough in the *cis*-diastereo- and enantioselective cyclopropanation of styrenes has been achieved with M(salen) catalysts (M = Ru[19] or Co)[20] and with five-coordinate ruthenium complexes [RuCl(P-

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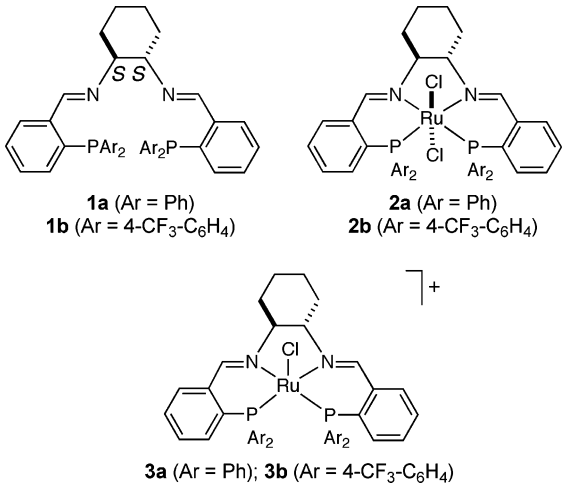
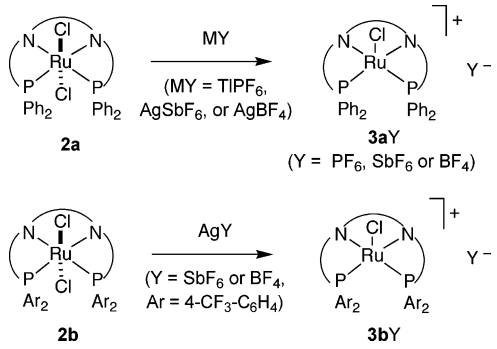
**Chart 1**



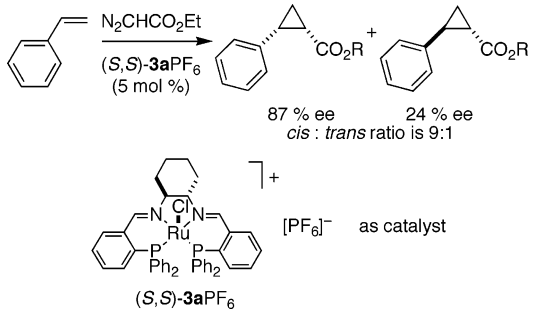

**Scheme 1**




NNP)]$^+$ containing diphosphinodimino[21−23] ligands (PNNP, Chart 1). We have reported that chloride abstraction from [$RuCl_2$(**1a**)] (**2a**; **1a** = (1*S*,2*S*)-*N*,*N*′-bis[*o*-(diphenylphosphino)benzylidene]diaminocyclohexane) with $TlPF_6$ gives [RuCl(**1a**)]$PF_6$ (**3a**$PF_6$, Scheme 1),[24] which cyclopropanates styrene with up to 91:9 *cis*:*trans* ratio and 87% ee for the *cis* isomer (Scheme 2).[21] However, the performance of **3a**$PF_6$ is much lower with 1-octene, the *cis* cyclopropanation product being formed with 60% diastereoselectivity and 64% ee.[22] Also, the yield is only 20%, in agreement with the generalization that 1-alkenes are less reactive than styrenes in the cyclopropanation by decomposition of diazoacetates.[25]

The cyclopropanation of substituted styrenes catalyzed by [RuCl(**1a**)]$^+$ confirmed the electrophilic nature

**Scheme 2**




of the carbene transfer and showed that both the cyclopropane yield and the *cis*- and enantioselectivity increase parallel to the electron density at the C=C double bond.[22] This is an unusual result, as the electronic effects on the stereoselectivity of cyclopropane formation are often small.[25] Reasoning that electron-poor PNNP ligands would boost both activity and stereoselectivity, we prepared the $CF_3$-substituted PNNP ligand (1*S*,2*S*)-*N*,*N*′-bis[*o*-(bis(4-trifluoromethylphenyl)-phosphino)benzylidene]cyclohexane-1,2-diamine (**1b**, Chart 1), but $TlPF_6$ failed to abstract chloride from the dichloro complex [$RuCl_2$(**1b**)] (**2b**).[23] We find now that silver(I) salts such as $AgSbF_6$ and $AgBF_4$ are more powerful halide scavengers than $TlPF_6$ and do react with [$RuCl_2$(PNNP)] even when the PNNP ligand contains electron-withdrawing groups such as $CF_3$. The new five-coordinate [RuCl(**1b**)]$SbF_6$ (**3b**$SbF_6$), prepared by treating [$RuCl_2$(**1b**)] (**2b**) with $AgSbF_6$, catalyzes the cyclopropanation of 1-octene with excellent enantio- and *cis*-diastereoselectivity. To the best of our knowledge, this is the first catalyst that gives high *cis*- and enantioselectivity with a terminal aliphatic olefin.

## Results and Discussion

**Chloride Abstraction from [$RuCl_2$(PNNP)].** The electron-poor dichloro complex [$RuCl_2$(**1b**)] (**2b**) reacts with $AgSbF_6$ (1 equiv) to give a single complex, **3b**, which features a broad AX system at $\delta$ 59.2 and 51.7, as indicated by the room-temperature $^{31}$P NMR spectrum of the reaction solution. Upon lowering the temperature to −40 °C, the signals resolve into a sharp AX system at $\delta$ 59.4 and 51.5 ($J_{P,P'}$ = 28.5 Hz). Complex **3b**$SbF_6$ is formulated as the five-coordinate cationic species [RuCl(**1b**)]$SbF_6$ on the basis of the similarity between the $^{31}$P NMR chemical shifts of **3a** and of **3b** (Table 1). Parallel to our previous experience with **3a**$PF_6$,[24b] we were not able to isolate pure **3b**$SbF_6$. This is not surprising, as the electron-poor ligand **1b** destabilizes the 16-electron complex **3b** and enhances its oxophilicity with respect to **3a**. For the sake of comparison, we investigated the reaction of the parent dichloro complex [$RuCl_2$(**1a**)] (**2a**) with $AgSbF_6$. In contrast to **2b**, which gives a single species, **2a** reacts with $AgSbF_6$ (1 equiv) in $CD_2Cl_2$ to give a mixture of products. The main product is the $[SbF_6]^-$ salt of the five-coordinate cation [RuCl(**1a**)]$^+$ (**3a**$SbF_6$) (71% of

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**Table 1. $^{31}$P NMR Data of the Complexes**

| complex | $\delta$ | $^2J_{P,P}$ (Hz) | $T$ (°C) |
|---|---|---|---|
| [RuCl$_2$(**1a**)] (**2a**) | 47.5 (s) | | |
| [RuCl$_2$(**1b**)] (**2b**) | 49.5 (s) | | |
| [RuCl(**1a**)]PF$_6$ (**3a**PF$_6$) | 59.3 (br), 50.0 (br) | | 20 |
| | 59.5 (d), 49.8 (d) | 28.2 | −20 |
| [RuCl(**1a**)]SbF$_6$ (**3a**SbF$_6$) | 59.2 (br), 49.7 (br) | | 20 |
| | 59.5 (d), 49.6 (d) | 28.5 | −20 |
| [RuCl(**1a**)]BF$_4$ (**3a**BF$_4$)[a] | 59.1 (br), 49.5 (br) | | 20 |
| | 59.4 (d), 49.6 (d) | 28.2 | −20 |
| [RuCl(**1b**)]SbF$_6$ (**3b**SbF$_6$) | 59.2 (br), 51.7 (br) | | 20 |
| | 59.4 (d), 51.5 (d) | 28.5 | −40 |
| [RuCl(**1b**)]BF$_4$ (**3b**BF$_4$)[b] | 59.2 (br), 51.9 (br) | | 20 |
| | 59.4 (d), 51.6 (d) | 28.7 | −40 |

[a] Along with **3a**BF$_4$ (77%), an additional product is formed (23%). 20 °C: $\delta$ 42 (br); −60 °C: $\delta$ 54.3 (d, $J_{P,P'}$ = 29.0 Hz, 1 P), 35.7 (d, $J_{P,P'}$ = 29.0 Hz, 1P). [b] Upon lowering the temperature, additional broad signals between $\delta$ 50 and 40 sharpen up and gain in intensity at −40 °C to give a sharp AX system (40% of total) at $\delta$ 55.0 (d), 37.3 (d), $J_{P,P'}$ = 28.7 Hz.

total), whose $^{31}$P NMR signals are identical to those of **3a**PF$_6$ (Table 1).[24b] The nature of the other products formed is under investigation.[26]

Finally, AgBF$_4$ was tested as chloride scavenger for **2a** and **2b**. The electron-poor dichloro complex [RuCl$_2$(**1b**)] (**2b**) reacts with AgBF$_4$ (1 equiv) in CD$_2$Cl$_2$ to give a mixture of (at least two) complexes. The room-temperature $^{31}$P NMR spectrum features a broad AX system at $\delta$ 59.2 and 51.9 that we assign to five-coordinate [RuCl(**1b**)]BF$_4$ (**3b**BF$_4$) based on the similarity with the chemical shifts observed for [RuCl(**1b**)]SbF$_6$. Additional broad signals are present in the range between $\delta$ 50 and 40, which sharpen up and gain in intensity compared to those of **3b**BF$_4$ upon lowering the temperature. At −40 °C, the major species features a sharp AX system at $\delta$ 55.0 and 37.3 ($J$ = 28.7 Hz, ca. 40% of the total integrated intensity). The sharp AX system of the residual five-coordinate **3b** (15% of total) appears at $\delta$ 59.4 and 51.6. Further unidentified complexes show signals between $\delta$ 60 and 36. These spectral changes are fully reversible with temperature and, thus, probably reflect the shift of an equilibrium. Similar observations were made with the reaction of **2a** with AgBF$_4$ (1 equiv) in CD$_2$Cl$_2$, which gives five-coordinate [RuCl(**1a**)]BF$_4$ (**3a**BF$_4$) as the main product (77% based on starting **2a**) (Table 1), along with an additional product that features a broad signal at $\delta$ 42 (23%), which resolves at −60 °C into two doublets at $\delta$ 54.3 and 35.7 ($J_{P,P'}$ = 29.0 Hz). Again, the spectral changes are fully reversible with temperature.

As fluorinated anions are known to interact with 16-electron transition metal fragments,[27] we speculated that [RuCl(PNNP)]$^+$ and [BF$_4$]$^-$ undergo association depending on the nature of the PNNP ligand, a possibility that is consistent with the anion effects observed in catalysis (see below). However, no conclusive evidence of such interactions was found by monitoring the reactions of **2a** and **2b** with TlPF$_6$, AgSbF$_6$, or AgBF$_4$ by low-temperature $^{19}$F NMR spectroscopy (see Supporting Information).

(26) Besides a small amount (up to 5%) of an unidentified complex ($^{31}$P NMR: AX system at $\delta$ 53.4 and 51.0, $J_{P,P'}$ = 30 Hz), the reaction yields a new product, **6a**, in variable amounts (up to 24% of total) in a series of independent experiments. Complex **6a** features broad $^{31}$P NMR signals at $\delta$ 73 and 43 (1:1 intensity ratio) that resolve into an AX system ($\delta$ 69.3 and 40.9, $J$ = 26.9 Hz, CD$_2$Cl$_2$) at −40 °C. As addition of a second equivalent of AgSbF$_6$ converts **2a** quantitatively into **6a** with concomitant precipitation of AgCl, **6a** is assumed to be the product of double chloride abstraction from **2a**. As **3a** is prepared on a milligram scale in a glovebox, the concomitant formation of small amounts of **6a** is possibly caused by small weighing errors owing to electrostatics.

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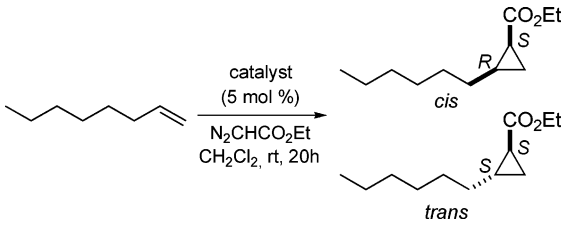
**Table 2. Cyclopropanation of 1-Octene[a]**



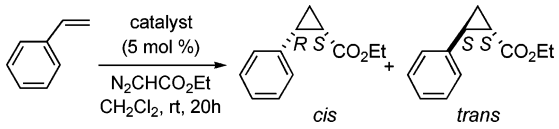

| | | | | | ee (%) | |
|---|---|---|---|---|---|---|
| run | catalyst | eda (equiv) | yield (%) | *cis*:*trans* | *cis* (1*S*,2*R*) | *trans* (1*S*,2*S*) |
| 1 | [RuCl(**1a**)]PF$_6$ (**3a**PF$_6$) | 1 | 15 | 65:35 | 82 | 39 |
| 2[b] | [RuCl(**1a**)]PF$_6$ (**3a**PF$_6$) | 2 | 20 | 60:40 | 64 | 18 |
| 3 | [RuCl(**1a**)]SbF$_6$ (**3a**SbF$_6$) | 1 | 13 | 76:24 | 96 | 75 |
| 4 | [RuCl(**1a**)]BF$_4$ (**3a**BF$_4$) | 1 | 10 | 66:34 | 88 | 55 |
| 5[c] | [RuCl(OH$_2$)(**1a**)]PF$_6$ (**5a**) | 2 | 30 | 60:40 | 47 | 20 |
| 6 | [RuCl(**1b**)]SbF$_6$ (**3b**SbF$_6$) | 1 | 48 | 85:15 | 94 | 96 |
| 7[d] | [RuCl(**1b**)]SbF$_6$ (**3b**SbF$_6$) | 1 | 66 | 85:15 | 99 | 98 |
| 8 | [RuCl(**1b**)]BF$_4$ (**3b**BF$_4$) | 1 | 20 | 84:16 | 93 | 92 |
| 9[c] | [RuCl(OEt$_2$)(**1b**)]PF$_6$ (**4b**) | 2 | 54 | 76:24 | 43 | 13 |

[a] Reaction conditions: ethyl diazoacetate (0.96 mmol, 1 equiv vs olefin) in CH$_2$Cl$_2$ (2 mL) was added over 6 h to a CH$_2$Cl$_2$ solution of 1-octene (0.96 mmol) and the catalyst (0.048 mmol, 5 mol %). The total reaction time was 20 h. Yields of isolated product refer to the sum of *cis* and *trans* isomers. [b] From ref 22. [c] From ref 23. [d] 10 mol % of catalyst was used.

**Catalytic Cyclopropanation of 1-Octene.** The new activation protocol of the dichloro complexes **2a** and **2b** with AgSbF$_6$ or AgBF$_4$ was tested in the cyclopropanation of styrene, α-methylstyrene, and 1-octene by decomposition of ethyl diazoacetate. Both the counterion and the substituents in the PNNP ligand dramatically affected the activity and stereoselectivity of the resulting five-coordinate precatalysts, whereby the most significant results were obtained with 1-octene (Table 2). With [RuCl(**1a**)]$^+$ (**3a**) as catalyst, changing the anion from [PF$_6$]$^-$ to [SbF$_6$]$^-$ increased the enantio- and diastereoselectivity of the formation of ethyl *cis*-2-hexylcyclopropane-1-carboxylate from 82% ee (65:35 *cis*:*trans* ratio) to 96% ee (76:24 *cis*:*trans* ratio) (Table 2, runs 1, 3). The tetrafluoroborate salt **3a**BF$_4$ is slightly less active and less selective than **3a**SbF$_6$ (run 4). The activity of **3a** is low with all counterions. The use of an excess of diazoacetate (2 equiv) improves the cyclopropane yield only marginally and at the cost of lower enantio- and diastereoselectivity (run 2).

Significantly enhanced yield, diastereoselectivity, and enantioselectivity are obtained with the electron-poor [RuCl(**1b**)]SbF$_6$ (**3b**SbF$_6$). Complex **3b**SbF$_6$, prepared in situ from **2b** and AgSbF$_6$ (1 equiv) in CH$_2$Cl$_2$, gives ethyl 2-hexylcyclopropane-1-carboxylate with 94 and 96% ee for the *cis* and *trans* isomers, respectively, and high *cis* selectivity (85:15 *cis*:*trans* ratio) (Table 2, run 6). Interestingly, *both diastereoisomers* are formed with excellent enantioselectivity. The overall isolated yield is improved to 66% by using 10 mol % of the catalyst (run 7). Under these conditions, the enantioselectivity reaches 99 and 98% ee for the *cis* and *trans* isomer, respectively, which is the best result obtained with a [RuCl(PNNP)]$^+$ catalyst.[22,23] Similarly to **3a**, changing

**Table 3. Catalytic Asymmetric Cyclopropanation of Styrene[a]**




| run | complex | eda (equiv) | conv (%) | yield (%) | *cis*:*trans* ratio | ee (%) *cis* (1*S*,2*R*) | ee (%) *trans* (1*S*, 2*S*) |
|---|---|---|---|---|---|---|---|
| 1[b] | [RuCl(**1a**)]$PF_6$ (**3a**$PF_6$) | 1 | 70 | 41 | 91:9 | 87 | 24 |
| 2 | [RuCl(**1a**)]$SbF_6$ (**3a**$SbF_6$) | 1 | 27 | 21 | 91:9 | 95 | 10 |
| 3 | [RuCl(**1a**)]$BF_4$ (**3a**$BF_4$) | 1 | 25 | 22 | 90:10 | 92 | 18 |
| 4[c] | [RuCl($OEt_2$)(**1a**)]$PF_6$ (**4a**) | 2 | 73 | 28 | 84:16 | 80 | 0 |
| 5[c] | [RuCl($OH_2$)(**1a**)]$PF_6$ (**5a**) | 2 | 61 | 28 | 86:14 | 91 | 8 |
| 6 | [RuCl(**1b**)]$SbF_6$ (**3b**$SbF_6$) | 1 | 80 | 69 | 99:1 | 96 | 58 |
| 7 | [RuCl(**1b**)]$SbF_6$ (**3b**$SbF_6$) | 2 | 94 | 74 | 98:2 | 93 | 7 |
| 8 | [RuCl(**1b**)]$BF_4$ (**3b**$BF_4$) | 1 | 58 | 48 | 97:3 | 94 | 16 |
| 9[c] | [RuCl($OEt_2$)(**1b**)]$PF_6$ (**4b**) | 2 | 80 | 54 | 90:10 | 83 | 4 |
| 10[c] | [RuCl($OH_2$)(**1b**)]$PF_6$ (**5b**) | 2 | 34 | 17 | 93:7 | 89 | 15 |

[a] Ethyl diazoacetate (eda) (0.48 mmol, 1 equiv vs olefin) 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 (0.024 mmol, 5 mol %). The total reaction time was 20 h. Conversion and yield (sum of *cis* and *trans* isomers) were determined by GC with decane as the internal standard. [b] From ref 21, under the same conditions. [c] From ref 23.

the counterion from **3b**$SbF_6$ to **3b**$BF_4$ causes the overall yield and enantioselectivity to drop (run 8).

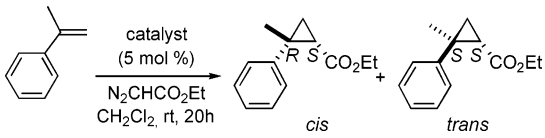
Ethyl 2-hexylcyclopropane-1-carboxylate was isolated after workup, and the *cis* and *trans* diastereoisomers were separated by preparative HPLC on a chiral column, by which the absolute configuration was unambiguously found to be 1*S*,2*R* for the *cis* and 1*S*,2*S* for the *trans* diastereoisomer (see Experimental Section). We correct hereby our previous attribution of the 1*R*,2*S* absolute configuration to the *cis* product.[22] As mentioned before, *cis*-selective cyclopropanation of terminal aliphatic alkenes is rare even with achiral catalysts,[9−11] and to the best of our knowledge, **3b**$SbF_6$ is the first highly enantioselective catalyst.

It has been argued that ruthenium cyclopropanation catalysts are inefficient with aliphatic alkenes because of the low electrophilic character of the intermediate carbene complex, which restricts their application to activated alkenes such as styrene and vinyl ethers.[25d] We show now that this problem can be overcome by using an electron-poor PNNP ligand such as **1b**, which enhances the electrophilicity of the carbene intermediate and its reactivity with aliphatic olefins. However, this is of advantage only in combination with a five-coordinate catalyst. Indeed, the six-coordinate complexes [RuCl($OH_2$)(**1a**)]$PF_6$ (**5a**) and [RuCl($OEt_2$)(**1b**)]-$PF_6$ (**4b**) give similar selectivities (runs 5, 9) despite the different electronic properties of the PNNP ligand (see also Tables 3 and 4 for different substrates). A possible explanation is that the rate-determining[28] decomposition of the diazoester by the 16-electron species [RuCl-(PNNP)]$^+$ is slowed with the electron-poor ligand **1b** because the corresponding adduct [RuCl($OR_2$)(PNNP)]$^+$ (R = H or Et) is more stable than with **1a**,[23] which disfavors the dissociation of the oxygen donor ligand.

**Styrene.** The results obtained with 1-octene prompted us to study the substrate scope of the new [RuCl(**1b**)]-$SbF_6$ catalyst as well as the anion effects in the homologous series [RuCl(**1a**)]Y (Y = $PF_6$, $SbF_6$, or $BF_4$). As already observed for 1-octene, **3a**$SbF_6$ is less active, but much more selective than **3a**$PF_6$, the enantioselectivity for the *cis* isomer increasing from 87 (**3a**$PF_6$) to 95% ee (**3a**$SbF_6$) (under the same conditions), whereas **3a**$BF_4$ does not perform better than **3a**$SbF_6$ (Table 3, runs 1−3). The electron-poor five-coordinate [RuCl(**1b**)]-$SbF_6$ (**3b**$SbF_6$) gives excellent *cis*-selectivity (99%) and enantioselectivity (96% ee for the *cis* isomer), together with a yield (69%) in the upper region for the [RuCl-(PNNP)]$^+$ catalysts (Table 3, run 6). This is a significant improvement as compared to the former best result with **3a**$PF_6$ (run 1). By using an excess of ethyl diazoacetate (2 equiv), the cyclopropane yield is improved marginally (74%, run 7), but at the cost of a slight decrease in diastereo- and enantioselectivity. We tested also $AgBF_4$ (1 equiv) for the activation of dichloro complex **2b**, although the reaction yields at least a second complex besides [RuCl(**1b**)]$^+$ as described above. The resulting catalytic system is less active and selective than **3b**$SbF_6$ (run 8), in line with the trend observed for **3a**. In accordance with previous experience, the five-coordinate **3b**$SbF_6$ performs better than the previously tested aqua and ether analogues **5b**$PF_6$ and **4b**$PF_6$ (runs 10 and 9).[23] The same trend is observed with the aqua and ether complexes containing **1a** (runs 5 and 4).

Enantiomerically pure ethyl *cis*-2-phenylcyclopropane-1-carboxylate was obtained by preparative HPLC on a chiral column. The optical rotation value ($\alpha_D^{20}$ =

**Table 4. Cyclopropanation of α-Methylstyrene[a]**




| run | cat. | yield (%) | *cis*:*trans* ratio | ee (%) *cis* (1S,2R) | ee (%) *trans* (1*S*,2*S*) |
|---|---|---|---|---|---|
| 1 | **3a**$PF_6$ | 61 | 70:30 | 57 | 18 |
| 2 | **3a**$SbF_6$ | 40 | 84:16 | 80 | 17 |
| 3 | **3a**$BF_4$ | 20 | 80:20 | 85 | 19 |
| 4 | **3b**$SbF_6$ | 33 | 92:8 | 96 | 58 |
| 5[b] | **3a**$PF_6$ | 83 | 86:14 | 49 | 7 |
| 6[c] | 4b | 94 | 85:15 | 86 | 34 |

[a] Reaction conditions: ethyl diazoacetate (0.48 mmol, 1 equiv vs olefin) in $CH_2Cl_2$ (1 mL) was added over 6 h to a $CH_2Cl_2$ solution of α-methylstyrene (0.48 mmol) and the catalyst (0.024 mmol, 5 mol %). The total reaction time was 20 h. Yields of isolated product refer to the sum of *cis* and *trans* isomers. [b] With 2 equiv diazoester, from ref 22. [c] With 2 equiv diazoester, from ref 23.

(28) For a discussion of this assumption, see ref 1b, p 168.

+17, $c = 0.3$, $CHCl_3$) indicated unambiguously that the absolute configuration is 1*S*,2*R*. We have previously attributed the 1*R*,2*S* configuration to the major enantiomer based on a negative sign observed for the optical rotation of the (supposedly) pure *cis* isomer (obtained by chromatographic analysis of the reaction solution on silica gel). We suspect that the negative sign arose from contamination by a small amount of ligand (*S*,*S*)-**1a** ($[\alpha]_D^{20} = -74.9$, $c = 1$, $CHCl_3$) from catalyst decomposition during the workup. As this attribution is pivotal for our previous explanation of the stereochemical course of the reaction, we reexamined our molecular modeling calculations (see below).

**α-Methylstyrene.** The results with α-methylstyrene, a model substrate for 1,1-disubstituted olefins, are reported in Table 4, along with previous results for comparison. Catalyst [RuCl(**1a**)]$^+$ shows anion effects analogous to those observed for 1-octene and styrene: The diastereo- and enantioselectivity for the *cis* isomer markedly increase on going from **3a**$PF_6$ (70% *cis* isomer with 57% ee, run 1) to **3a**$SbF_6$ (84% *cis* isomer with 80% ee, run 2). The largest effect of changing from $[SbF_6]^-$ to $[BF_4]^-$ is the decrease of the yield, which confirms that the catalyst activity increases according to $[BF_4]^- < [SbF_6]^- < [PF_6]^-$. Again, the electron-poor ligand **1b** and the $[SbF_6]^-$ counterion give the best combination: **3b**$SbF_6$ displays excellent enantioselectivity (96% ee) for the *cis* isomer as well as the highest diastereoselectivity (92:8 *cis*:*trans* ratio), but the yield of ethyl 2-methyl-2-phenylcyclopropane-1-carboxylate is low (33%, Table 4, run 4). However, α-methylstyrene is converted nearly quantitatively (92%, as determined by GC using dodecane as the internal standard), which suggests that **3b**$SbF_6$, being the stronger Lewis acid, promotes the polymerization of the electron-rich olefin as competing reaction. In agreement, the dimerization product of α-methylstyrene was observed by GC-MS. Accordingly, the less reactive ether adduct [RuCl($OEt_2$)(**1b**)]$^+$ (**4b**) cyclopropanates α-methylstyrene with 94% yield (but slightly lower selectivity) (run 6).[23]

Finally, catalyst **3b**$SbF_6$ was tested in the cyclopropanation of *cis*-2-hexene, *trans*-2-octene, and 2,5-dimethyl-2,4-hexadiene (as models of internal aliphatic olefins) under the same conditions used for 1-octene, but only traces of cyclopropane products were detected in the reaction mixtures by GC-MS. Complex **3a**$PF_6$ has already been found to be unreactive toward 2,5-dimethyl-2,4-hexadiene, a 1,2-disubstituted olefin.[21] In sum, catalyst **3b**$SbF_6$ gives the best result ever obtained with the Ru/PNNP systems and *terminal* olefins in terms of product yield, *cis*-selectivity, and enantioselectivity and marks the success of the electronic tuning of the PNNP ligand. The improvement on going from [RuCl(**1a**)]$PF_6$ (**3a**$PF_6$) to [RuCl(**1b**)]$SbF_6$ (**3b**$SbF_6$), which is general for all substrates and encompasses cyclopropane yield and diastereo- and enantioselectivity, results from the combination of the (easily understood) electronic properties of the PNNP ligand with the (still) elusive anion effect on the 16-electron complex [RuCl(PNNP)]$^+$.

**The Effect of the Anion: A Discussion.** Although full comparison with all three counterions is available only with **3a** and the $^{31}P$ and $^{19}F$ NMR spectroscopic studies were not conclusive, the anion effects observed in catalysis are indicative of significant cation/anion interactions in solution. We notice that the increase of the catalyst activity along the series $[BF_4]^- < [SbF_6]^- < [PF_6]^-$ parallels the order of decreasing coordinating ability of the anion proposed by Beck, which is $[BF_4]^- > [SbF_6]^- > [PF_6]^-$.[27] There is no general consensus concerning the relative donor strengths of weakly coordinating anions, though. Thus, Beck and Sünkel have suggested that the σ-donor strength decreases according to $[BF_4]^- > [SbF_6]^- \cong [PF_6]^-$, whereas Hersh has proposed that the order of decreasing binding strength is $[SbF_6]^- > [BF_4]^- > [PF_6]^-$ in the adducts [W(Y)$(CO)_3(PR_3)$(NO)] (Y = $PF_6$, $SbF_6$, $BF_4$).[29] Our NMR data suggest that tetrafluoroborate is more coordinating than $[SbF_6]^-$ or $[PF_6]^-$ but give no indication concerning the relative position of the latter anions, which can be inferred, however, from the relative activity of the [RuCl(PNNP)]Y salts in catalysis.

No general trend has been found for the anion effects in catalysis either.[30] Cationic half-sandwich ruthenium(II)[30c] and bis(oxazoline) copper(II)[30a] catalysts for asymmetric Diels–Alder reactions are more active as $[SbF_6]^-$ than as $[PF_6]^-$ or $[BF_4]^-$ salts, whereas [RuCl(PNNP)]$^+$ is most active as $[PF_6]^-$ salt. A puzzling feature of the [RuCl(PNNP)]$^+$ catalysts is that activity and stereoselectivity do not correlate in a simple fashion. In fact, the activity increases according to $[BF_4]^- < [SbF_6]^- < [PF_6]^-$, whereas the enantio- and stereoselectivity decrease along the series $[SbF_6]^- > [BF_4]^- > [PF_6]^-$. In combination with [$RuCl_2$(**1b**)], this makes $AgSbF_6$ the chloride scavenger of choice.

**Empirical Stereochemical Model.** The *cis* selectivity of the [RuCl(PNNP)]$^+$ catalysts has been previously explained by means of an *empirical* model based on molecular modeling calculations that mimic the transition states (TSs) of the carbene transfer from the spectroscopically observed carbene intermediate [RuCl(CHCOOEt)(**1a**)]$^+$ (**7**) to styrene.[21,31] We expand and revise here this model to account for the new substrates and for the correction of the absolute configuration of the major *cis* product of the cyclopropanation of styrene (see above).

In the preliminary calculations with **7** and styrene, the lowest energy was obtained for the 1*S*,2*R* TS, in contrast with the (incorrect) experimental attribution of the 1*R*,2*S* absolute configuration to ethyl *cis*-2-phenylcyclopropane carboxylate (see above). To fit the experimental result, the C=C double bond and the Ru=C vectors were restrained to be parallel in the transition state,[32] which resulted in the 1*R*,2*S* TS being the most

(29) Honeychuck, R. V.; Hersh, W. H. *Inorg. Chem.* **1989**, *28*, 2869.

(30) Selected examples of anion effects in catalysis: (a) Evans, D. A.; Murry, J. A.; von Matt, P.; Norcross, R. D.; Miller, S. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 798. (b) Burckhardt, U.; Baumann, M.; Togni, A. *Tetrahedron: Asymmetry* **1997**, *8*, 155. (c) Kündig, E. P.; Saudan, C. M.; Bernardinelli, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1220. (d) Macchioni, A.; Bellachioma, G.; Cardaci, G.; Travaglia, M.; Zuccaccia, C.; Milani, B.; Corso, G.; Zangrando, E.; Mestroni, G.; Carfagna, C.; Formica, M. *Organometallics* **1999**, *18*, 3061. (e) Pfaltz, A.; Blankenstein, J.; Hilgraf, R.; Hormann, E.; McIntyre, S.; Menges, F.; Schonleber, M.; Smidt, S. P.; Wustenberg, B.; Zimmermann, N. *Adv. Synth. Catal.* **2003**, *345*, 33. (f) Drago, D.; Pregosin, P. S.; Pfaltz, A. *Chem. Commun.* **2002**, 286.

(31) The four diastereomeric TSs between **7** and styrene were modeled with arbitrarily chosen, fixed C···C bond distances. Their energy was minimized by using the Cerius$^2$ program with standard Universal Force Field (UFF) settings: (a) Rappé, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A., III; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024. (b) Rappé, A. K.; Colwell, K. S.; Casewit, C. J. *Inorg. Chem.* **1993**, *32*, 3438.

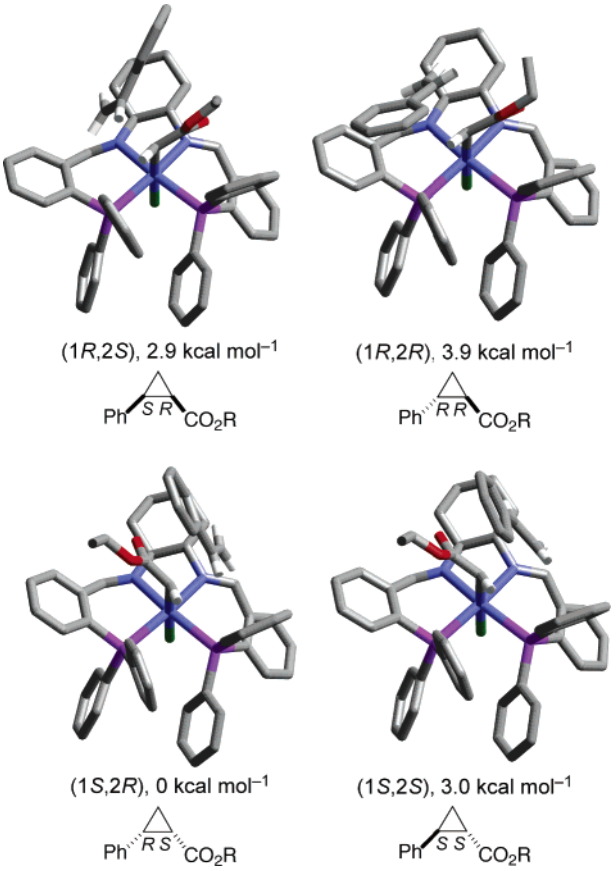



**Figure 1.** Energy-minimized structures of the diastereomeric transition states involving carbene transfer from **7** to styrene (viewed along the Ru−carbene bond).

stable one.[21] We find now that releasing this geometric constraint correctly predicts the 1*S*,2*R* configuration for the major *cis* isomer (Figure 1). The unrestrained TSs are qualitatively similar to the previous ones (see Figure 2 of ref 21) and show the same conformation of the $PPh_2$ groups that blocks the attack of the olefin along the Ru−P vectors as previously discussed.[21] However, upon releasing the constraint, the approaching styrene molecule rotates about the direction of attack, as indicated by the Ru=C···C=C torsion angles (1*S*,2*R*: 21.4°; 1*S*,2*S*: −40.9°; 1*R*,2*S*: 2.4°; 1*R*,2*R*: −14.4°) (Figure 2). The largest rotations—but in a different sense—occur in the 1*S*,2*R* and 1*S*,2*S* TSs and minimize the interaction of the olefin with one phenyl ring of the PNNP ligand and with the axial C(1)-hydrogen of the cyclohexanediyl bridge, respectively.

Qualitatively, the calculated energies account for the *cis* selectivity and for the absolute configuration of the *cis* isomer and reproduce the larger enantioselectivity observed for the *cis* isomer than for the *trans* one (the energy differences between the enantiomers of the *cis* and *trans* isomers are 2.9 and 0.9 kcal/mol, respectively) (Table 5). The *cis* selectivity is explained by the repulsion between the phenyl on styrene and the $PPh_2$ groups being larger than the repulsion between the olefin and the carbene substituents (see 1*S*,2*S* and 1*R*,2*R* TSs in Figure 1), whereas the opposite is true for *trans*-selective cyclopropanation catalysts.[1b] The contacts between the C=$CH_2$ group and the PNNP framework

(32) This seemed reasonable, though, as this is the usual assumption for metal-to-olefin carbene transfer: See ref 1b, pp 178−183.

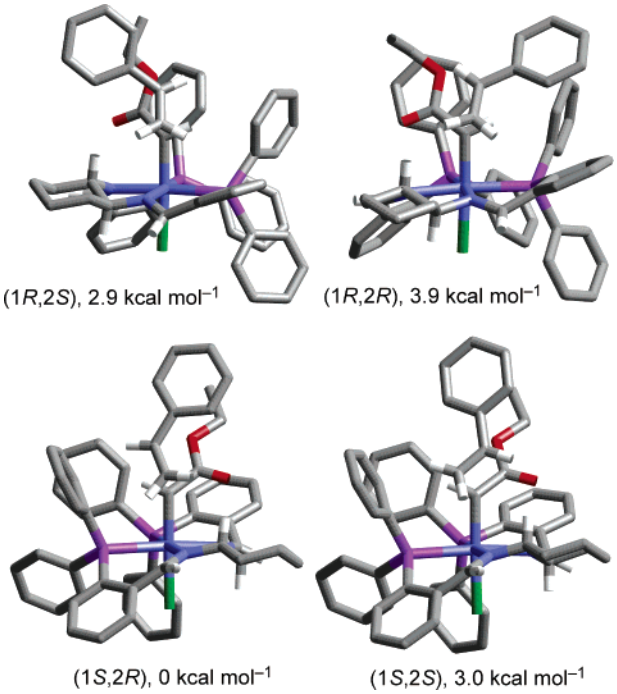



**Figure 2.** Diastereomeric transition states between **7** and styrene (viewed parallel to the PNNP plane).

**Table 5. Relative Energies (in kcal mol$^{-1}$) of "Transition States" Formed by [RuCl(CHCOOEt)(PNNP)]$^+$ (PNNP = 1a or 1b) and Styrene, α-Methylstyrene, and 1-Octene**

| olefin | PNNP | 1*S*,2*R* | 1*R*,2*S* | 1*S*,2S | 1*R*,2*R* |
|---|---|---|---|---|---|
| 1-octene | **1a** | 0 | 1.8 | 3.2 | 1.3 |
| 1-octene | **1b** | 0 | 3.7 | 2.7 | 3.7 |
| styrene | **1a** | 0 | 2.9 | 3.0 | 3.9 |
| styrene | **1b** | 0 | 3.3 | 2.8 | 4.3 |
| α-methylstyrene | **1a** | 0 | 2.4 | 1.9 | 1.1 |
| α-methylstyrene | **1b** | 0 | 2.6 | 1.7 | 3.3 |

account for the enantioselectivity with which the *cis* cyclopropane is formed. The olefin−PNNP contacts are reflected in the angle between the phenylenes, which should be zero in a regular stepped conformation (Figure 2). The most stable 1*S*,2*R* TS, in which styrene approaches from the "open" side, is the least distorted, the dihedral angles being 19.9° (1*S*,2*R*), 32.6° (1*R*,2*S*), 25.0° (1*S*,2*S*), and 24.7° (1*R*,2*R*) (Figure 1). In the least stable 1*R*,2*S* TS, the incoming styrene molecule pushes down the phenylene bridge (Figure 1), as the dihedral angle (32.6°, the largest value in the series) shows. An analogous effect has been suggested for carbene and oxene transfer from chiral salen complexes of manganese(III) and ruthenium(II).[19d]

In sum, the revised MM analysis predicts *cis* selectivity for all substrates and for both ligands (**1a** and **1b**), as well as the correct absolute configuration of all *cis* isomers and most *trans* ones (Table 5). An interesting observation is that the energy gap between the 1*S*,2*R* and 1*R*,2*S* TSs increases for all substrate on going from ligand **1a** to **1b**, suggesting that, besides electronic effects, also subtle steric changes may be responsible for the selectivity improvement. Despite the obvious limitation that the counterion effects are not accounted for in this model, the empirical MM calculations are remarkably reliable and potentially useful for further ligand tailoring.

## Conclusion

The reactivity of the $[RuCl_2(PNNP)]$ complexes critically depends on the electronic properties of the PNNP ligand and on the halide scavenger MY (M = Tl(I) or Ag(I); Y = $PF_6$, $SbF_6$, or $BF_4$). Silver(I) salts seem to be stronger halide scavengers than $TlPF_6$, as they react with electron-poor dichloro complexes, whereas $TlPF_6$ does not. The counterion dramatically affects the performance of the $[RuCl(PNNP)]^+$ catalysts in catalytic cyclopropanation. The best activity and *cis*- and enantioselectivity are achieved with the least coordinating anion that can be introduced in combination with an electron-poor PNNP ligand, confirming that electron deficiency and coordinative unsaturation at ruthenium are pivotal requirements for catalyst performance. Thus, [RuCl(**1b**)]$SbF_6$ gives excellent diastereo- and enantioselectivity, coupled with a good chemical yield, which opens the way to synthetic applications.

## Experimental Section

**General Procedures.** Reactions with air- or moisture-sensitive materials were carried out under an argon atmosphere using Schlenk techniques. $^1H$ and $^{31}P$ NMR spectra were recorded on Bruker DPX spectrometers. $^1H$ positive chemical shifts in ppm are downfield from tetramethylsilane. $^{31}P$ and $^{19}F$ NMR spectra were referenced to external 85% $H_3PO_4$ and external $CFCl_3$, respectively. Optical rotations were measured using a Perkin-Elmer 341 polarimeter with a 1 dm cell. Ligand **1b** [23] and complexes $[RuCl_2(\mathbf{1a})]$[33] (**2a**) and $[RuCl_2(\mathbf{1b})]$[23] (**2b**) were prepared according to literature procedures.

**[RuCl(PNNP)]Y (Y = $SbF_6$ or $BF_4$). General Procedure.** Complex **2** was treated with an equimolar amount of the halide scavenger in freshly distilled $CH_2Cl_2$. Instantaneous precipitation of AgCl was observed. All attempts of isolation failed due to the formation of variable amounts of the corresponding aqua complexes (as checked by addition of water) and of other unidentified species. For its characterization, the reaction solutions were prepared in a glovebox in dry $CD_2Cl_2$ in an NMR tube equipped with a Young valve and then analyzed by $^{31}P$, $^1H$, and $^{19}F$ NMR spectroscopy. Under these conditions, reasonably pure complexes of type **3**Y were observed. Details are given below.

**[RuCl(1a)]$SbF_6$ (3a$SbF_6$).** Complex **2a** (26.0 mg, 0.031 mmol) was reacted with $AgSbF_6$ (10.7 mg, 0.031 mmol). $^1H$ NMR (400 MHz, $CD_2Cl_2$, 253 K): $\delta$ 8.8 (d, 1H, *H*C=N, $J_{P,H}$ = 9.4 Hz), 8.7 (s, 1H, *H*C=N) 7.8−6.0 (m, 26H, arom.), 4.6 (m, 1H, N−C*H*). $^{31}P$ NMR (121 MHz, $CD_2Cl_2$, 293 K): $\delta$ 59.2 (br, 1P), 49.7 (br, 1P); 253 K, $\delta$ 59.5 (d, 1P, $J_{P,P'}$ = 28.5 Hz), 49.6 (d, 1P, $J_{P,P'}$ = 28.5 Hz). $^{19}F$ NMR (376 MHz, $CD_2Cl_2$, 293 K): $\delta$ −124 (br, Sb*F*$_6$).

**[RuCl(1a)]$BF_4$ (3a$BF_4$).** Complex **2a** (26.6 mg, 0.032 mmol) was treated with $AgBF_4$ (6.2 mg, 0.032 mmol). $^1H$ NMR (500 MHz, $CD_2Cl_2$, 213 K): **3a**$BF_4$, $\delta$ 8.8 (d, 1H, *H*C=N, $J_{P,H}$ = 10 Hz), 8.6 (br, 1H, *H*C=N), 7.7−6.3 (m, 28H, arom.), 4.5 (m, 1H, N−C*H*). $^{31}P$ NMR (202 MHz, $CD_2Cl_2$): **3a**$BF_4$ (77%, 293 K), $\delta$ 59.1 (br, 1P), 49.5 (br, 1P); 253 K, $\delta$ 59.4 (d, 1P, $J_{P,P'}$ = 28.2 Hz), 49.6 (d, 1P, $J_{P,P'}$ = 28.2 Hz). Unidentified product (23%, 293 K): $\delta$ 42 (br); 213 K: $\delta$ 54.3 (d, 1P, $J_{P,P'}$ = 29.0 Hz), 35.7 (d, 1P, $J_{P,P'}$ = 29.0 Hz). $^{19}F$ NMR (376 MHz, $CD_2Cl_2$ 293 K): $\delta$ −151.6 (br, $w_{1/2}$ = 60 Hz, 4F, B*F*$_4$); 213 K, $\delta$ −150.8 (br, $w_{1/2}$ = 98 Hz, 4F, B*F*$_4$).

**[RuCl(1b)]$SbF_6$ (3b$SbF_6$).** Complex **2b** (18.5 mg, 0.017 mmol) was treated with $AgSbF_6$ (5.8 mg, 0.017 mmol) in $CD_2Cl_2$. $^1H$ NMR (200 MHz, $CD_2Cl_2$, 293 K): $\delta$ 8.9 (br, 1H, *H*C=N), 8.8 (br, 1H, *H*C=N), 6.9−7.9 (m, 24H, arom.), 4.7 (m, 1H, N−C*H*). $^{31}P$ NMR (202 MHz, $CD_2Cl_2$, 293 K): $\delta$ 59.2 (br, 1P), 51.7 (br, 1P); 233 K, $\delta$ 59.4 (d, 1P, $J_{P,P'}$ = 28.5 Hz), 51.5 (d, 1P, $J_{P,P'}$ = 28.5 Hz). $^{19}F$ NMR (188 MHz, $CD_2Cl_2$, 293 K): $\delta$ −63.4 (m, 12F, C*F*$_3$), the signal of $[SbF_6]^-$ was too broad to be observed.

**[RuCl(1b)]$BF_4$ (3b$BF_4$).** The reaction of **2b** (33 mg, 0.029 mmol) with $AgBF_4$ (5.8 mg, 0.029 mmol) in $CD_2Cl_2$ was monitored by $^{31}P$ and $^{19}F$ spectroscopy. Along with the signals of **3b**$BF_4$, the room-temperature $^{31}P$ NMR spectrum shows broad signals of an unidentified complex. $^{31}P$ NMR (161 MHz, $CD_2Cl_2$, 293): $\delta$ 59.2 (br, 1P, **3b**), 51.9 (br, 1P, **3b**), 50−40 (br, unknown). Upon lowering the temperature, the unidentified signals gain in intensity with respect to **3b**$BF_4$. $^1H$ NMR (500 MHz, $CD_2Cl_2$, 233 K): $\delta$ 9.5 (d, 1H, *H*C=N, $J_{P,H}$ = 10.5 Hz), 8.5 (s, 1H, *H*C=N), 8.3−6.3 (m, 22H, arom.). $^{31}P$ NMR (161 MHz, $CD_2Cl_2$, 233 K): $\delta$ 55.0 (d, 1P, $J_{P,P'}$ = 28.7 Hz, unknown, 40%), 37.3 (d, 1P, $J_{P,P'}$ = 28.7 Hz, unknown, 40%), 59.4 (d, 1P, $J_{P,P'}$ = 28.7 Hz, **3b**, 15%), 51.6 (d, 1P, $J_{P,P'}$ = 28.7 Hz, **3b**, 15%). The variable-temperature $^{19}F$ NMR spectra show the desymmetrization of $[BF_4]^-$ upon lowering the temperature. $^{19}F$ NMR (376 MHz, $CD_2Cl_2$, 293 K): $\delta$ −63.4 (m,12F, C−*F*), −153.1 (br, $w_{1/2}$ = 400 Hz, 4F, B−*F*); 233 K, $\delta$ −63.2 (m, 12F, C−*F*), −150.4 (br, $w_{1/2}$ = 130 Hz, 3.2F, B−*F*), −144 to −148 (br, 0.8F, B−*F*).

**Standard Catalytic Run: 1-Octene.** Complex **2a** or **2b** (0.048 mmol) was treated with an equimolar amount of $AgSbF_6$ (16.4 mg, 0.048 mmol) or $AgBF_4$ (9.4 mg, 0.048 mmol) in $CH_2Cl_2$. After 2 h, silver chloride was filtered off (glass microfiber filter). The olefin (150 $\mu$L, 0.96 mmol) was added to the filtered solution of the catalyst in $CH_2Cl_2$. A solution of distilled ethyl diazoacetate (0.96 mmol, 100 $\mu$l) in $CH_2Cl_2$ (2 mL) was added over 6 h by syringe pump. The solution was stirred for an additional 14 h. After evaporation of the solvent, the product was isolated by column chromatography (alumina) with hexane/acetyl acetate (9:1) as the eluent. The isolated yields refer to the sum of the *cis* and *trans* isomers. Achiral GC analysis: Optima 5, 25 m, He carrier (100 kPa); temperature program 50 °C isotherm for 5 min, then to 200 °C at 5 °C/min. $t_R$ (min): 1-octene, 4.8; ethyl *cis*-2-hexylcyclopropane-1-carboxylate, 24.6; ethyl *trans*-2-hexylcyclopropane-1-carboxylate, 25.1. The enantiomeric excesses of the *cis* and *trans* isomers were determined by chiral GC analysis: Supelco Beta Dex 120, 1.4 mL He $min^{-1}$; temperature program 90 °C isotherm for 150 min. $t_R$ (min): *cis*, (1*S*,2*R*), 93.6; *cis*, (1*R*,2*S*), 97.6; *trans*, (1*R*,2*R*), 111.4; *trans*, (1*S*,2*S*), 112.4.

**Determination of the Absolute Configuration.** The *cis* and *trans* diastereoisomers were separated by preparative chiral HPLC (Chiralcel OJ, 25 × 2 cm, 10 $\mu$m, hexane), but the resolution of the enantiomers failed. The absolute configurations of the major enantiomers of the *cis* and *trans* products were assigned by comparison of the $[\alpha]_D^{20}$ values with those previously reported for 2-methylcyclopropanecarboxylic acid[34] and methyl 2-pentylcyclopropane-1-carboxylate.[35] The *cis* isomer is mainly ethyl (1*S*,2*R*)-2-hexylcyclopropane-1-carboxylate (94% ee, by chiral GC analysis, see above, $[\alpha]_D^{20}$ = +41, *c* = 0.75, $CHCl_3$). Chiral GC analysis (to check peak attribution, see above for conditions): $t_R$ (min): 93.6 (1*S*,2*R*, major), 97.6 (1*R*,2*S*, minor). $^1H$ NMR (250 MHz, $CDCl_3$,): $\delta$ 4.15 (q, 2H, O$CH_2$$CH_3$, *J* = 7.16 Hz), 1.68 (ddd, 1H, *J* = 5.5, 7.9, 8.9 Hz), 1.5 (m, 1H), 1.38−1.17 (m, 10H, hexyl-$CH_2$), 1.29 (t, 3H, O$CH_2$$CH_3$, *J* = 7.16 Hz), 1.05−0.88 (m, 2H), 0.90 (*t*, 3H, hexyl-$CH_3$, *J* = 6.0 Hz). The *trans* isomer is mainly ethyl (1*S*,2*S*)-2-hexylcyclopropane-1-carboxylate (at 96% ee, by chiral GC, $[\alpha]_D^{20}$ = +63, *c* = 0.05, $CHCl_3$).

**Styrene.** Complex **2a** or **2b** (0.024 mmol) was treated with an equimolar amount of $AgSbF_6$ (8.2 mg, 0.024 mmol) or $AgBF_4$ (4.7 mg, 0.024 mmol) in freshly distilled $CH_2Cl_2$. After 2 h, silver chloride was filtered off (glass microfiber filter). Styrene

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(0.48 mmol, 55 $\mu$l) and decane (internal standard for GC analysis, 80 $\mu$L) were added to the solution of the catalyst in $CH_2Cl_2$. A solution of distilled ethyl diazoacetate (0.48 or 0.96 mmol, 50 or 100 $\mu$L) in $CH_2Cl_2$ (1 mL) was added to the solution over 6 h by syringe pump. The solution was stirred for an additional 14 h. Styrene conversion and yield of the *cis* and *trans* products were determined by GC analysis after filtration over alumina to remove the catalyst. Achiral GC analysis: Optima 5, 25 m, He carrier (100 kPa); temperature program 50 °C isotherm for 5 min, then to 200 °C at 5 °C/min. $t_R$ (min): styrene, 8.5; decane, 12.8; ethyl *cis*-2-phenylcyclopropane carboxylate, 26.6; ethyl *trans*-2-phenylcyclopropane carboxylate, 27.8. The enantiomeric excesses of the *cis* and *trans* isomers were determined by chiral GC analysis: Supelco Beta Dex 120, 1.4 mL He $min^{-1}$; temperature program 120 °C isotherm for 70 min. $t_R$ (min): *cis*, (1*S*,2*R*), 52.8; *cis*, (1*R*,2*S*), 55.8; *trans*, (1*R*,2*R*), 63.1; *trans*, (1*S*,2*S*), 65.1.

**Determination of the Absolute Configuration.** Pure ethyl (1*S*,2*R*)-2-phenylcyclopropane carboxylate (*cis*) and ethyl (1*S*,2*S*)-2-phenylcyclopropane carboxylate (*trans*) were obtained by separation of the reaction products (after column chromatography on alumina with hexane/acetyl acetate (9:1) as eluents) on a preparative chiral HPLC (Chiralcel OJ, 25 × 2 cm, 10 $\mu$m, hexane). The absolute configuration of the isolated diastereo- and enantiomerically pure products was assigned by comparison of the sign of the optical rotation with literature values.[4,36] Ethyl (1*S*,2*R*)-2-phenylcyclopropane-1-carboxylate (*cis*): $[\alpha]_D^{20} = +17$ ($c = 0.3$, $CHCl_3$). Chiral GC analysis (to check peak attribution, see above for conditions), $t_R$ (min): 52.8. $^1$H NMR (300 MHz, $CDCl_3$,): $\delta$ 7.3−7.2 (m, 5H, aryl-*H*), 3.89 (q, 2H, $OCH_2CH_3$, $J = 7.1$ Hz), 2.60 (ddd, 1H, $J = 7.5$, 8.6, 9.3 Hz), 2.10 (ddd, 1H, $J = 5.6$, 7.8, 9.3 Hz), 1.73 (ddd, 1H, $J = 5.1$, 5.6, 7.5 Hz), 1.34 (ddd, 1H, $J = 5.1$, 7.8, 8.6 Hz), 0.99 (t, 3H, $OCH_2CH_3$, $J = 7.1$ Hz). Ethyl (1*S*,2*S*)-2-phenylcyclopropane-1-carboxylate (*trans*): $[\alpha]_D^{20} = +290$ ($c = 0.09$, $CHCl_3$).

**α-Methylstyrene.** Complex **2a** or **2b** (0.024 mmol) was treated with an equimolar amount of $AgSbF_6$ (8.2 mg, 0.024 mmol) or $AgBF_4$ (4.7 mg, 0.024 mmol) in $CH_2Cl_2$. After 2 h, silver chloride was filtered off (glass microfiber filter). The olefin (62 $\mu$L, 0.48 mmol) was added to the filtered solution of the catalyst in $CH_2Cl_2$. A solution of distilled ethyl diazoacetate (0.48 mmol, 50 $\mu$l) in $CH_2Cl_2$ (1 mL) was added over 6 h by syringe pump. The solution was stirred for an additional 14 h. After evaporation of the solvent, the product was isolated by column chromatography (alumina) with hexane/acetyl acetate (9:1) as the eluent. The isolated yields refer to the sum of the *cis* and *trans* isomer. In a selected example, olefin conversion was checked by quantitative GC with dodecane as internal standard. Achiral GC analysis: Optima 5, 25 m, He carrier (100 kPa); temperature program 50 °C isotherm for 5 min, then to 200 °C at 5 °C/min. $t_R$ (min): α-methylstyrene, 12.0; ethyl *cis*-2-methylphenylcyclopropane-1-carboxylate, 26.3; ethyl *trans*-2-methylphenylcyclopropane-1-carboxylate, 27.6. The enantiomeric excesses of the *cis* and *trans* isomers were determined by chiral GC analysis: Supelco Beta Dex 120, 1.4 mL He $min^{-1}$; temperature program 120 °C isotherm for 70 min. $t_R$ (min): *cis*, (1*R*,2*S*), 40.5; *cis*, (1*S*,2*R*), 42.8; *trans*, (1*S*,2*S*), 51.5; *trans*, (1*R*,2*R*), 52.7.

**Determination of the Absolute Configuration.** Pure ethyl (1*S*,2*R*)-2-methylphenylcyclopropane-1-carboxylate (*cis*) and ethyl (1*S*,2*S*)-2-methylphenylcyclopropane-1-carboxylate (*trans*) were obtained by separation on a preparative chiral HPLC column (Chiralcel ODH, 25 × 2 cm, 5 $\mu$m, hexane). The absolute configuration of the isolated diastereo- and enantiomerically pure products was assigned by comparison of the sign of the optical rotation with literature values.[37] Ethyl (1*S*,2*R*)-2-methylphenylcyclopropane-1-carboxylate (*cis*): $[\alpha]_D^{20} = +55$ ($c = 0.51$, $CHCl_3$). Chiral GC analysis (to check peak attribution, see above for conditions), $t_R$ (min): 42.8. $^1$H NMR (250 MHz, $CDCl_3$,): $\delta$ 7.3−7.2 (m, 5H, aryl-*H*), 3.85 (m, 2H, $OCH_2CH_3$), 1.93 (dd, 1H, $J = 5.4$, 7.5 Hz), 1.80 (dd, 1H, $J = 4.5$, 7.5), 1.49 (s, 3H, $CCH_3$), 1.17 (dd, 1H, $J = 4.5$, 5.4 Hz), 0.97 (t, 3H, $OCH_2CH_3$, $J = 7.1$ Hz). Ethyl (1*S*,2*S*)-2-methylphenylcyclopropane-1-carboxylate (*trans*): $[\alpha]_D^{20} = +268$ ($c = 0.28$, $CHCl_3$).

**Molecular Modeling.** Molecular modeling calculations were performed on a Silicon Graphics $O_2$ platform with the Cerius$^2$ program (MSI) using standard UFF settings.[31a] The C···C distances between the olefin and carbene C atoms are fixed empirically at 2.50 (C2) and 2.65 Å (C1) to fit the qualitative diastereo- and enantioselectivity trends for the three different substrates.

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**Supporting Information Available:** Description of the variable-temperature $^{19}$F NMR spectroscopic experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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