Chiral Dicationic Bis(aqua) Complexes $[Ru(OH_2)_2(PNNP)]^{2+}$: The Effect of Double Chloride Abstraction on Asymmetric Cyclopropanation

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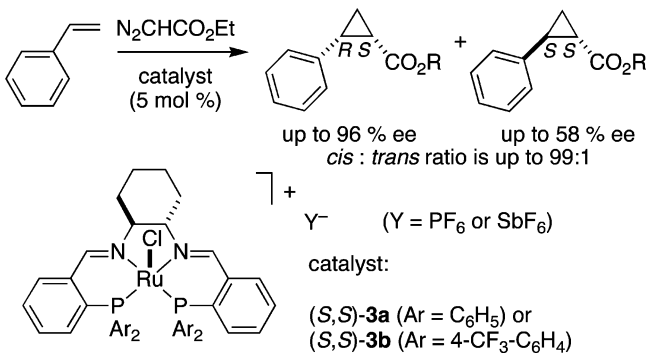
The dichloro complexes $[RuCl_2(PNNP)]$ (**2a**−**c**) undergo double chloride abstraction when treated with $AgSbF_6$ (2 equiv) (PNNP is one of (1*S*,2*S*)-*N*,*N*′-bis[*o*-(diphenylphosphino)benzylidene]cyclohexane-1,2-diamine, **1a**; (1*S*,2*S*)-*N*,*N*′-bis[*o*-(bis(4-trifluoromethylphenyl)phosphino)benzylidene]cyclohexane-1,2-diamine, **1b**; (1*S*,2*S*)-*N*,*N*′-bis[*o*-(bis(3,5-bis(trifluoromethyl)phenyl)phosphino)benzylidene]cyclohexane-1,2-diamine, **1c**). The resulting elusive species form the corresponding bis(aqua) complexes $[Ru(OH_2)_2(PNNP)]^{2+}$ by reaction with water. The bis(aqua) complexes $[Ru(OH_2)_2(PNNP)](SbF_6)_2$ (**6a**−**c**) were fully characterized, including an X-ray structure of **6c**. The X-ray structure of **2c** with the new electron-poor chiral tetradentate PNNP ligand **1c** is also reported. Complexes **6a** and **6c** catalyze the *cis*-selective asymmetric cyclopropanation of styrene, albeit with low yield. The best *cis*:*trans* ratio and enantioselectivity were obtained with **6c** (87:13 and 92% ee for the *cis* isomer, respectively). The products of double chloride abstraction from $[RuCl_2(PNNP)]$ gave moderate to high conversion of styrene (37−70%), but the yield of the cyclopropane product was generally modest (13−64%). The best *cis*- and enantioselectivity were 86:14 and 81% ee, respectively.

Introduction

Chiral tetradentate ligands containing a P_2N_2 donor set (PNNP)[1] have attracted some attention in coordination chemistry and homogeneous catalysis in view of their conformational rigidity, which is expected to produce an effective transfer of chiral information.[2,3] This approach is particularly suitable in combination with five- or six-coordinated complexes. Thus, Gao and Noyori used the bis(amino)bis(phosphino) ligand (1*S*,2*S*)-*N*,*N*′-bis[*o*-(diphenylphosphino)benzyl]cycloexane-1,2-diamine to prepare the octahedral ruthenium(II) complex $[RuCl_2(PNNP)]$, which is an effective catalyst for the asymmetric transfer hydrogenation of ketones.[4] An appealing aspect of chiral tetradentate PNNP ligands is that they have been investigated in less detail than salen ligands[5] and offer, thus, still unexplored potential.

We have used the imino analogue (1*S*,2*S*)-*N*,*N*′-bis[*o*-(diphenylphosphino)benzylidene]cycloexane-1,2-diamine (**1a**) to prepare the five-coordinate cation $[RuCl(\mathbf{1a})]^+$ (**3a**) by reaction of $[RuCl_2(\mathbf{1a})]$ (**2a**) with $TlPF_6$ (1 equiv). The formally 16-electron cation **3a** is highly oxophilic and readily adds water to give $[RuCl(OH_2)(\mathbf{1a})]^+$ (**4a**).[6] Complex **3a** catalyzes the asymmetric epoxidation of olefins with hydrogen peroxide[6,7] and the asymmetric cyclopropanation by decomposition of diazoacetate (Scheme 1).[8] In the latter case, the *cis*- and enantioselectivity were optimized by means of the electronic tuning of the PNNP ligand based on the study of the substrate-based electronic effects.[9] However, electron-poor PNNP ligands strongly disfavor the formation of the Lewis acidic 16-electron complex $[RuCl(PNNP)]^+$, and $[RuCl_2(\mathbf{1b})]$ (**2b**) (**1b** is (1*S*,2*S*)-*N*,*N*′-bis[*o*-(bis(4-trifluoromethylphenyl)phosphino)benzylidene]cyclohexane-1,2-diamine) does not react with $TlPF_6$ to give the corresponding five-coordinate complex.[10]

Scheme 1



Recently, we discovered that the monocationic complex $[RuCl(\mathbf{1b})]Y$ can be prepared by treating $[RuCl_2(\mathbf{1b})]$ (**2b**) with

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† X-ray structures.

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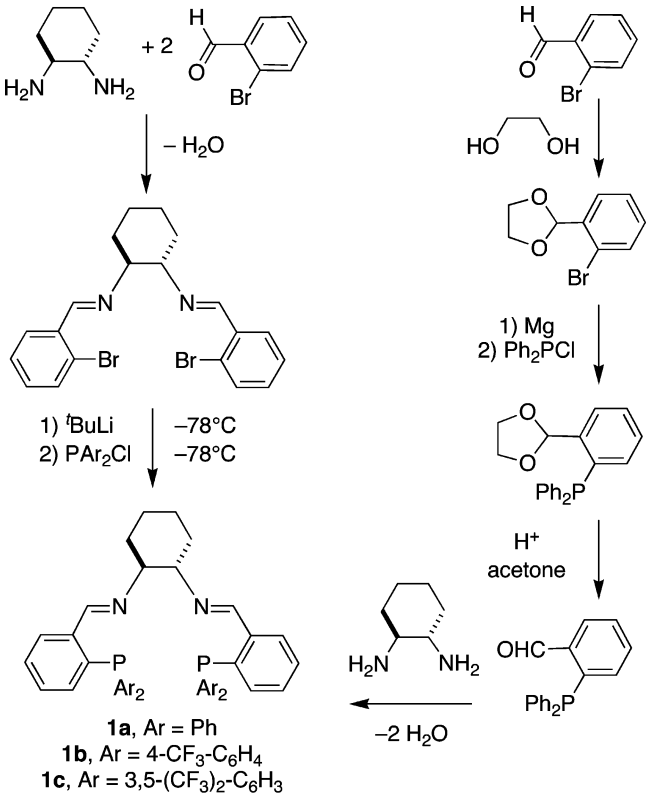
Scheme 2



silver(I) salts (1 equiv) of low-coordinating anions AgY (Y = SbF_6 or BF_4). The resulting 16-electron complex [RuCl(**1b**)]-SbF_6 (**3b**) is the most efficient of the $[RuCl(PNNP)]^+$ series for styrene (Scheme 1) and 1-octene.[11] Additionally, we observed that Ag(I)-based chloride scavengers cause double chloride abstraction from $[RuCl_2(PNNP)]$ when more than 1 equiv of the AgY salt is used.[11] These results prompted us to investigate the double chloride abstraction from $[RuCl_2(PNNP)]$ complexes containing PNNP ligands with different electronic properties. To this goal, we also developed a modular synthesis of substituted PNNP ligands containing a variable number of electron-withdrawing groups, such as in the new ligand (1*S*,2*S*)-*N*,*N*′-bis{2-[bis(3,5-bis(trifluoromethyl)phenyl)phosphino]-benzylidene}cyclohexane-1,2-diamine (**1c**). We report herein the first results concerning double chloride abstraction from $[RuCl_2(PNNP)]$ (PNNP = **1a**, **1b**, or **1c**). These studies, aimed at the preparation of a new family of chiral Lewis acids, eventually led to the dicationic bis(aqua) complexes $[Ru(OH_2)_2(PNNP)]^{2+}$ described below.

Results and Discussion

Synthesis of the PNNP Ligands. The classical synthesis of imine-based PNNP ligands reported by Rauchfuss is based on the condensation of the corresponding phosphinoaldehyde with a diamine in refluxing ethanol.[2,12] Gao[4b] and ourselves[6b] prepared (1*S*,2*S*)-*N*,*N*′-bis[*o*-(diphenylphosphino)benzylidene]-cycloexane-1,2-diamine (**1a**) by minor variations of this method (Scheme 2, right). A disadvantage of this approach is the synthesis of *o*-(diphenylphosphino)benzaldehyde, which is performed according to the published procedure with 55% yield.[12] We developed a simpler synthetic approach that avoids the protection/deprotection step of the formyl group.

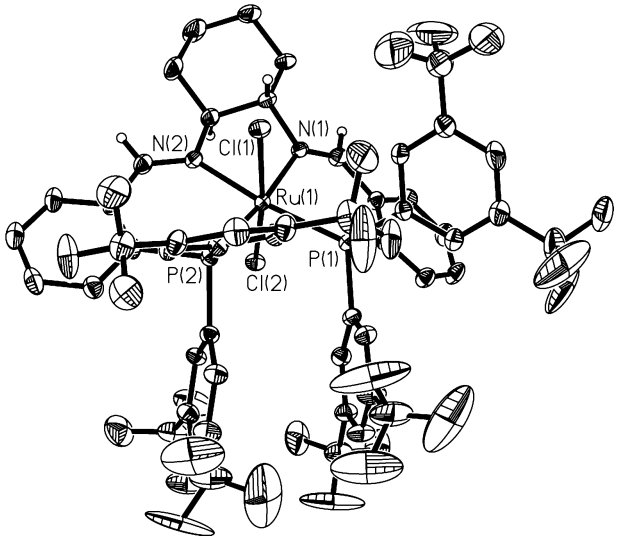


Figure 1. ORTEP view of $[RuCl_2(\mathbf{1c})]$ (**2c**) (30% probability ellipsoids).

In a preliminary experiment, the condensation of (1*S*,2*S*)-diaminocyclohexane with 2-bromobenzaldehyde (2 equiv) gave quantitatively the corresponding diimine, (1*S*,2*S*)-*N*,*N*′-bis(2-bromobenzylidene)cyclohexane-1,2-diamine, which can be isolated and stored (Scheme 2, left). The diimine was selectively lithiated with ^{t}BuLi at −78 °C, and addition of chlorodiphenylphosphine yielded **1a** in 75% yield. This procedure requires less steps than the original one, and the diimine derivative can be exploited as a common framework to prepare PNNP ligands bearing different PAr_2 groups. A further synthetic improvement is that the phosphine, which is the most valuable component, is added in the last step as the easily available chloro derivative PAr_2Cl.

As the introduction of different PAr_2 groups was directed to the synthesis of electron-poor PNNP ligands, we used the new protocol to prepare the previously reported CF_3-substituted ligand **1b**[10] and the new 3,5-bis(CF_3) derivative **1c**. In the case of ligand **1b**, the overall yield based on phosphorus was improved from the previous 50% to 75% with the new protocol. As we have not been able to develop efficient purification methods for **1b** and **1c** so far, the crude products were used to prepare *trans*-$[RuCl_2(PNNP)]$ (PNNP = **1b**, **2b**; PNNP = **1c**, **2c**), which are easily purified by column chromatography.

$[RuCl_2(1c)]$ (2c). The reaction of ligand **1c** with $[RuCl_2(PPh_3)_3]$ in toluene at reflux gave the dichloro complex *trans*-$[RuCl_2(\mathbf{1c})]$ (**2c**). Crystals of **2c** were grown by slow diffusion of hexane into $CDCl_3$. The results of the X-ray study are summarized in Figure 1 and Table 1. The unit cell contains two essentially identical, crystallographically independent molecules of **2c** that are related to each other in a pseudo-centrosymmetric way (see below). The complex has a severely distorted octahedral coordination with *trans* chlorides. Although a stronger Ru−P bond may be expected in connection with the more π-acid ligand **1c**, the Ru−P distances in **2c** (average 2.28 Å) are not significantly different from those of the unsubstituted parent complex **2a** (2.295(2) and 2.288(2) Å).[4a] The Ru−Cl distances in **2c** (average 2.422 Å) and in **2a** (2.439(2) and 2.403-(2) Å) are the same within experimental error, too. The bite angles for the P,N and N,N chelate rings are unexceptional.

Several features indicate that the substituents in the 3,5-positions of the $P(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_2$ groups induce severe steric

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for [$RuCl_2$(1c)] (2c)

molecule 1		molecule 2	
Ru(1)−Cl(1)	2.4135(10)	Ru(2)−Cl(3)	2.4196(11)
Ru(1)−Cl(2)	2.4275(11)	Ru(2)−Cl(4)	2.4260(11)
Ru(1)−P(1)	2.2804(10)	Ru(2)−P(3)	2.2875(10)
Ru(1)−P(2)	2.2778(11)	Ru(2)−P(4)	2.2796(12)
Ru(1)−N(1)	2.077(3)	Ru(2)−N(3)	2.111(3)
Ru(1)−N(2)	2.109(3)	Ru(2)−N(4)	2.110(3)
Cl(1)−Ru(1)−Cl(2)	171.32(4)	Cl(3)−Ru(2)−Cl(4)	172.87(4)
Cl(1)−Ru(1)−P(1)	85.59(4)	Cl(3)−Ru(2)−P(3)	87.37(4)
Cl(1)−Ru(1)−P(2)	94.90(4)	Cl(3)−Ru(2)−P(4)	92.91(4)
Cl(1)−Ru(1)−N(1)	86.17(9)	Cl(3)−Ru(2)−N(3)	81.61(9)
Cl(1)−Ru(1)−N(2)	89.36(10)	Cl(3)−Ru(2)−N(4)	92.04(10)
Cl(2)−Ru(1)−P(1)	102.44(4)	Cl(4)−Ru(2)−P(3)	99.19(4)
Cl(2)−Ru(1)−P(2)	87.15(4)	Cl(4)−Ru(2)−P(4)	88.83(4)
Cl(2)−Ru(1)−N(1)	90.79(9)	Cl(4)−Ru(2)−N(3)	95.59(10)
Cl(2)−Ru(1)−N(2)	82.11(10)	Cl(4)−Ru(2)−N(4)	81.01(10)
P(1)−Ru(1)−P(2)	99.14(4)	P(3)−Ru(2)−P(4)	98.99(4)
P(1)−Ru(1)−N(1)	87.88(9)	P(3)−Ru(2)−N(3)	89.57(9)
P(1)−Ru(1)−N(2)	167.37(10)	P(3)−Ru(2)−N(4)	169.98(10)
P(2)−Ru(1)−N(1)	172.96(9)	P(4)−Ru(2)−N(3)	169.64(10)
P(2)−Ru(1)−N(2)	92.81(11)	P(4)−Ru(2)−N(4)	91.02(10)
N(1)−Ru(1)−N(2)	80.23(14)	N(3)−Ru(2)−N(4)	80.46(13)

crowding in the complex. Thus, the coordination angles about ruthenium widely deviate from 90°, the PAr_2 groups assume a non-C_2-symmetric conformation, and the bis(benzylidene)-cyclohexane unit is distorted away from the usual "stepped" conformation into a saddle-like shape (compare Figure 1 and Figure 1a in ref 4a). The cyclohexyl ring, however, retains its regular chair conformation. Interestingly, the conformation of the two crystallographically independent molecules is such that these are arranged in the asymmetric unit in a fashion that is $P\bar{1}$-symmetric except for the stereogenic (1*S*,2*S*)-cyclohexane-1,2-diamine moiety. This latter observation implies that the steric crowding outweighs the effect of the stereogenic 1,2-cyclohexanediyl bridge in determining the overall conformation of the complex.

Double Chloride Abstraction from [$RuCl_2$(PNNP)] with AgY. We have recently reported that the reaction of [$RuCl_2$(PNNP)] (PNNP = **1a** or **1b**) with $AgSbF_6$ (1 equiv) in CD_2Cl_2 yields the corresponding monocation complexes [RuCl(PNNP)]SbF_6 as the main product, along with variable amounts (up to 24% of total) of a new product featuring broad ^{31}P NMR signals at δ 73 and 43 (1:1 intensity ratio) at room temperature.[11] We now find that, when a second equivalent $AgSbF_6$ is added to this reaction solutions, both chloro ligands are abstracted, as indicated by the precipitation of silver(I) chloride. Similar reactions occur with $AgBF_4$. The double chloride abstraction from [$RuCl_2$(PNNP)] formally produces the fragment [Ru(PNNP)]$^{2+}$, which must coordinate at least a fifth ligand because of its 14-electron count. An investigation of the reaction of **2a**−**c** with $AgSbF_6$ or with $AgBF_4$ (2 equiv) yielded circumstantial evidence of anion coordination, $[SbF_6]^-$ or $[BF_4]^-$, and showed that the resulting products are extremely water-sensitive, which prevented their isolation. A summary of this study is given below (see Supporting Information for further details).

[$RuCl_2$(**1a**)] (**2a**) reacted with $AgSbF_6$ (2 equiv) in CD_2Cl_2 to give a single product (see Experimental Section), but the ^{19}F NMR spectra were not informative because the quadrupole moment of ^{121}Sb (57%) and ^{123}Sb (43%) causes the ^{19}F NMR signal of the $[SbF_6]^-$ anion to broaden.[13] The high-resolution ESI MS trace of the reaction solution showed peaks at *m*/*z* 995 (featuring the isotopic pattern of antimony) and at 380 (with isotopic peaks at the distance of half *m*/*z* units), which were attributed to the monocationic species [Ru(SbF_6)(**1a**)]$^+$ and to the dication [Ru(**1a**)]$^{2+}$ (exact mass 760), respectively. The reaction of **2a** with $AgBF_4$ (2 equiv) gave a mixture of products, whose low-temperature ^{19}F NMR spectra contained signals indicating the desymmetrization of the tetrafluoroborate anion. The *p*-CF_3-substituted derivative **2b** reacted with $AgSbF_6$ to give several products, too, probably including [Ru(SbF_6)(**1b**)]$^+$ (*m*/*z* 1267), whose signal was observed in the high-resolution ESI MS trace of the reaction solution.

Eventually, after failing with $TlPF_6$, NaBArF, or $(EtO_3)PF_6$, chloride abstraction from [$RuCl_2$(**1c**)] (**2c**) occurred with $AgSbF_6$ both in 1:1 and in 1:2 molar ratio, but the resulting products were not identified. In the latter case, the high-resolution ESI MS trace of the reaction solution showed the signal of a dication (on the basis of the isotopic peaks at the distance of half *m*/*z* units) at *m*/*z* 652, whose exact mass corresponds to [Ru(**1c**)]$^{2+}$. A signal at *m*/*z* 1339 featuring the isotopic cluster of antimony can be attributed to the monocationic SbF_6 adduct [Ru(SbF_6)(**1c**)]$^+$. The low reactivity of electron-poor **2c** toward chloride abstraction is in line with our previous observation that electron-withdrawing substituents in the PNNP ligand decrease the stability of the five-coordinate species owing to the reduced electron density at ruthenium and require the use of Ag(I) salts, which are stronger chloride scavengers than Tl(I) salts. On this topic, it should be noted that the previously observed[6] five-coordinate [RuCl(**1a**)]$^+$ (**3a**) is formed even when an excess (2 equiv) of $TlPF_6$ is used. Thus, the abstraction of the second chloro ligand occurs only with $AgSbF_6$ and $AgBF_4$ as the chloride scavenger, but not with $TlPF_6$.

In conclusion, the precipitation of AgCl upon addition of AgY to [RuCl(PNNP)]$^+$ affords circumstantial evidence that double chloride abstraction from [$RuCl_2$(PNNP)] does occur. ESI mass spectrometry, ^{19}F NMR spectroscopy, and the different outcome of the reactions of **2a** with $AgSbF_6$ or $AgBF_4$ are suggestive of counterion coordination, but the formulation of these species remains unclear. Although we cannot exclude completely that, despite all precautions (see Experimental Section), some of these unknown species contain coordinated water, this possibility is restricted to the coordination of a single H_2O molecule, as the corresponding bis(aqua) complexes have been completely characterized (see below). Even though a large number of complexes containing coordinated anions have been reported and are known to react with water to give aqua complexes, their involvement in catalysis is by far less well-documented.[14] As for chloride dissociation from [$RuCl_2$(PNNP)], **2a** is known to give [RuCl(MeCN)(**1a**)]$^+$ by reaction with $AgBF_4$ in acetonitrile,[7] and the chloride-free complex [Ru(O_2CCH_3)$_2$(**1a**H_2)] (where **1a**H_2 is the diamino analogue of **1a**) has been prepared by treating [Ru(O_2CCH_3)$_2$(PPh_3)$_2$] with ligand **1a**H_2.[15] A cyclopropanation catalyst prepared by activation of **2a** with $AgBF_4$ (2 equiv) has been reported, but the nature of the resulting species has not been investigated.[16]

Bis(aqua) Complexes [Ru(OH_2)(PNNP)]$^{2+}$. The products of double chloride abstraction from **2a**−**c** with $AgSbF_6$ react

(13) (a) At room temperature, the ^{19}F NMR spectrum of the reaction solution shows a broad signal ($w_{1/2}$ = 990 Hz) centered at δ −123.5 in the range expected for uncoordinated $[SbF_6]^-$. It should be appreciated that the ^{19}F NMR signal of the $[SbF_6]^-$ anion has, in general, not been observed; see: (b) Honeychuck, R. V.; Hersh, W. H. *Inorg. Chem.* **1989**, *28*, 2869.

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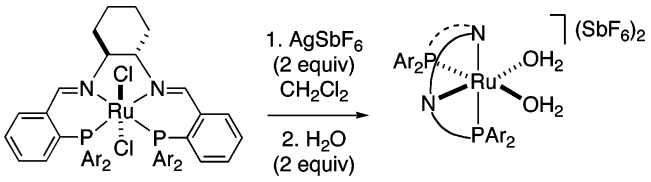
Scheme 3



2a, Ar = Ph
2b, Ar = 4-CF_3-C_6H_4
2c, Ar = 3,5-bis-CF_3-C_6H_3

6a, Ar = Ph
6b, Ar = 4-CF_3-C_6H_4
6c, Ar = 3,5-bis-CF_3-C_6H_3

Table 2. ^{31}P NMR Data (at 20 °C)

	δ (ppm)	$^2J_{P,P}$ (Hz)
$[RuCl_2$(**1c**)] (**2c**)	52.4 (s)	
$[Ru(OH_2)_2$(**1a**)$](BF_4)_2$ (**6a**BF_4)	63.6 (d), 48.3 (d)	29.9
$[Ru(OH_2)_2$(**1a**)$](SbF_6)_2$ (**6a**SbF_6)	63.5 (d), 47.1 (d)	29.7
$[Ru(OH_2)_2$(**1b**)$](SbF_6)_2$ (**6b**)	66.4 (d), 49.3 (d)	29.7
$[Ru(OH_2)_2$(**1c**)$](SbF_6)_2$ (**6c**)	67.5 (d), 51.7 (d)	29.7

with a stoichiometric amount of water to give the corresponding bis(aqua) complexes $[Ru(OH_2)_2(PNNP)]^{2+}$ as a single diastereoisomer (Scheme 3). As the derivative containing the bis(trifluoromethyl)-substituted ligand **1c** has been fully characterized, including an X-ray investigation, it will be discussed first.

The dicationic bis(aqua) complex $[Ru(OH_2)_2$(**1c**)$](SbF_6)_2$ (**6c**) features an AX pattern in the ^{31}P NMR spectrum whose chemical shifts indicate a *cis-β* geometry (Table 2).[10] A ^{31}P−^{1}H HMQC experiment revealed the signal of one aqua ligand at δ 3.4 as a cross-peak to the ^{31}P NMR signal at δ 51.7. A signal at δ 4.5 was attributed to the second aqua ligand on the basis of its ^{1}H NOESY cross-peak to that of noncoordinated water (δ 2.25), which is indicative of rapid exchange ($k \approx 150$ s^{-1}). A complete assignment indicated that the latter signal refers to the aqua ligand *trans* to the deshielded P atom (δ 67.5), which explains its lability, whereas the one resonating at δ 3.4 is *trans* to an imine and, therefore, is more tightly bound to ruthenium and does not exchange with free H_2O on this time scale (mixing time 0.6 s).

The IR spectrum (KBr) shows broad bands at 3626 and 3200 cm^{-1} that are attributed to the stretching modes of coordinated water. For mono(aqua) complexes, the antisymmetric and symmetric stretching vibrations give rise to two broad, sometimes overlapping bands in the region 3200−3550 cm^{-1}, along with the HOH bending near 1600 cm^{-1}.[17] In the neutral palladium complex [Pd(dmba)(Fmes)(H_2O)] (dmba = orthometalated *N,N*-dimethylphenylamine; Fmes = 2,4,6-tris(trifluoromethyl)phenyl), two medium-intensity signals are observed at 3607 and 3529.[18] In a system more similar to ours, the cationic bis(aqua) ruthenium complex $[Ru(Tp^iPr(OH_2)_2(THF)]OTf$ (Tp^iPr = hydrotris(3,5-diisopropylpyrazolyl)borate), the $\nu(OH_2)$ stretching vibrations give weak and broad signals at 3640 and 3359 cm^{-1}.[19]

The analogous reaction of **2b** with $AgSbF_6$ (2 equiv), followed by addition of water (2.2 equiv), yields the bis(aqua) complex $[Ru(OH_2)_2$(**1b**)$]^{2+}$ (**6b**) as a single *cis-β* diastereoisomer, which was characterized in solution (Table 2). One aqua ligand gives a sharp signal at δ 2.91 in the room-temperature ^{1}H NMR spectrum and a strong ^{31}P−^{1}H HMQC cross-peak with the phosphorus atom at δ 49.3, as well as a weak one with the phosphine at δ 66.4. Additionally, the room-temperature ^{1}H NMR spectrum features a very broad signal at δ 2.6 that arises from an aqua ligand in fast exchange with noncoordinated water, as indicated by the broad diagonal peak in the ^{1}H NOESY spectrum. Upon lowering the temperature to −30 °C, this signal decoalesces into two sharp peaks of coordinated and free water at δ 4.45 and 2.59, respectively. In analogy with complex **6c**, and supported by ^{1}H NOESY and ^{31}P−^{1}H HMQC experiments, we attribute the signal at δ 4.45 (−30 °C) to the aqua ligand *trans* to P (at δ 66.4 in the ^{31}P NMR spectrum) and that at δ 2.91 to H_2O *trans* to nitrogen.

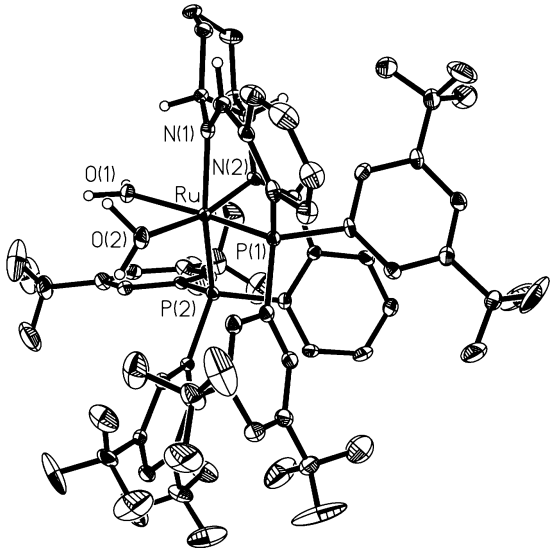


Figure 2. ORTEP view of $[Ru(OH_2)_2$(**1c**)$](SbF_6)_2$ (**6c**) (30% probability ellipsoids).

Also **2a** forms a single *cis-β* diastereoisomer of $[Ru(OH_2)_2$-(**1a**)$](SbF_6)_2$ (**6a**SbF_6) upon treating **2a** with $AgSbF_6$ (2 equiv) and water (2.2 equiv). Neither aqua ligand was detected in the 1D and 2D spectra of $[Ru(OH_2)_2$(**1a**)$](SbF_6)_2$, which is indicative of faster exchange between free and coordinated water in the case of the less Lewis-acidic **6a** derivative. Thus, the overall spectral trend suggests that the exchange rate decreases on going from **6a** to the electron-poor **6c**. The spectral behavior of the dicationic complex $[Ru(OH_2)_2$(**1a**)$]^{2+}$ depends on the counterion, too. The tetrafluoroborate salt $[Ru(OH_2)_2$(**1a**)$](BF_4)_2$ (**6a**BF_4), formed by treating **2a** with $AgBF_4$ (2 equiv) and water, features a sharp ^{1}H NMR singlet at δ 3.18 (with a cross-peak to the ^{31}P NMR doublet at δ 48.3 in the ^{31}P−^{1}H HMQC spectrum) that is attributed to the aqua ligand *trans* to nitrogen by analogy with **6c**. The effect of the counterion on the rate of exchange between free and coordinated water may be mediated by the hydrogen bonds between the aqua ligand and $[SbF_6]^-$ or $[BF_4]^-$. The existence of a network of such hydrogen bonds in the solid state is revealed by the X-ray structure of **6c**$(SbF_6)_2$ (see below). Additional support for this hypothesis comes from the observation that the ^{31}P NMR chemical shifts of **6a**$(SbF_6)_2$ and **6a**$(BF_4)_2$ are slightly different (Table 2).

In sum, based on the spectroscopic data of the aqua complexes, the lability of the water ligand decreases according to **6a** > **6b** > **6c**, that is, parallel to the donor properties of the PNNP ligand. Thus, the Lewis acidity of the 14-electron fragment $[Ru(PNNP)]^{2+}$ increases along the series **1a** < **1b** < **1c**.

X-ray of $[Ru(OH_2)_2$(1c)$](SbF_6)_2$. Crystals of $[Ru(OH_2)_2$(**1c**)$]$-$(SbF_6)_2$ (**6c**) were obtained from a saturated CD_2Cl_2 solution. The asymmetric unit contains one discrete complex dication $[Ru(OH_2)_2$(**1c**)$]^{2+}$, a total of two $[SbF_6]^-$ anions that are

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for [Ru(OH$_2$)$_2$(1c)] (6c), Including Shortest Hydrogen Bonds

Ru−P(1)	2.2524(16)	Ru−P(2)	2.3220(17)
Ru−N(1)	2.106(5)	Ru−N(2)	2.029(5)
Ru−O(1)	2.229(5)	Ru−O(2)	2.180(5)
P(1)−Ru−P(2)	97.35(6)	N(1)−Ru−N(2)	79.0(2)
P(1)−Ru−N(1)	87.94(15)	P(2)−Ru−N(1)	164.25(16)
P(1)−Ru−N(2)	98.08(15)	P(2)−Ru−N(2)	85.59(15)
P(1)−Ru−O(1)	167.39(14)	P(2)−Ru−O(1)	88.53(13)
P(1)−Ru−O(2)	85.87(14)	P(2)−Ru−O(2)	105.19(14)
N(1)−Ru−O(1)	89.34(19)	N(2)−Ru−O(1)	93.5(2)
N(1)−Ru−O(2)	89.9(2)	N(2)−Ru−O(2)	168.0(2)
O(1)−Ru−O(2)	81.82(19)		

	O−H	H···F	O···F	O−H···F
O(1)−H(1A)···F(25)	0.996(11)	1.91(4)	2.839(8)	154(6)
O(1)−H(1B)···F(31)	0.998(11)	1.79(3)	2.756(8)	162(6)
O(2)−H(2B′)···F(34)	1.10(2)	1.79(2)	2.810(7)	152(5)
O(2)−H(2A′)···F(28)	1.01(2)	1.81(2)	2.625(10)	135(3)

disordered over three sites, and a highly disordered dichloromethane molecule. The octahedral coordination of ruthenium is severely distorted because of the Λ-*cis*-*β*-configuration of the PNNP ligand **1c** (Figure 2, Table 3). The same Λ-configuration of (*S*,*S*)-**1c** has been previously attributed to the related complexes [RuCl(OH$_2$)((*S*,*S*)-**1a**)]$^+$ (**4a**) and [RuCl(OEt$_2$)((*S*,*S*)-**1a**)]$^+$ (**5a**) on the basis of molecular modeling.[10] However, [RuCl(py)((*R*,*R*)-**1a**)]$^+$ has the Λ-*cis*-*β* configuration, too,[7] which suggests that a generalized prediction based on the absolute configuration of the diamine is not possible and that the steric requirements of the ancillary ligands are crucial.

The Ru−P, Ru−N, and P−O bond lengths reflect the *trans* influence of the ligand occupying the *trans* position. Thus, the Ru−P(1) distance (2.2524(16) Å, *trans* to O) is much shorter than the Ru−P(2) one (2.3220(17) Å, *trans* to N). This accounts for the largely different ^{31}P NMR chemical shifts of the P atoms[20] and for the diagnostic downfield shift of the phosphine *trans* to the aqua ligand.[10] For the same reason, ruthenium binds more strongly to N(2) (*trans* to O(2), 2.029(5)) than to N(1) (*trans* to P(2), 2.106(5) Å). Also, the aqua ligand O(1) *trans* to P(1) exhibits a longer Ru−O bond (2.229(5) Å) than O(2) (Ru−(O(2) = 2.180(5) Å), which is *trans* to N(2), in agreement with the observation (based on NMR spectroscopy) that O(1) exchanges much more rapidly with free water than O(2). Even though **6c** is a dicationic complex, the Ru−O(1) distance of 2.229(5) Å falls at the upper end of the range observed for aqua ligands *trans* to P-donors in mononuclear ruthenium complexes.[21] The hydrogen atoms on both aqua ligands, which have been located and refined, are involved in a net of hydrogen bonds to the [SbF$_6$]$^-$ anions (Table 3, Figure 3). This is the most striking feature of the crystal packing, with the [SbF$_6$]$^-$ anions pooled together in a "protic pocket" formed by the *cis* aqua ligands of neighboring [Ru(OH$_2$)$_2$(PNNP)]$^{2+}$ cations.

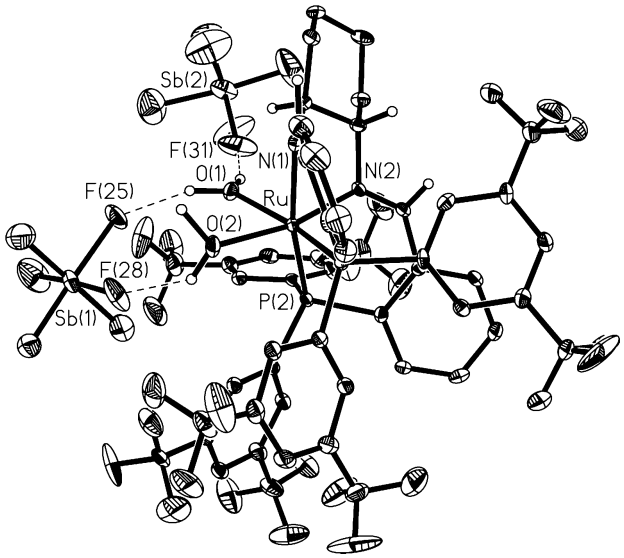

Figure 3. Shortest hydrogen bonds between [Ru(OH$_2$)$_2$(**1c**)](SbF$_6$)$_2$ (**6c**) and the [SbF$_6$]$^-$ anions (30% probability ellipsoids).

In general, phosphine ligands are soft donors and do not impart an oxophilic character to their ruthenium(II) complexes, whereas aqua complexes are quite frequent with hard ligands (such as nitrogen donors)[22] according to the principle of symbiosis.[23] However, the hardness of the metal ion can be increased by a number of factors that include the effect of charge and that of hard co-ligands.[24] Thus, the affinity of ruthenium(II) for water is increased by strong *π*-accepting co-ligands (in particular CO)[21b−d,k,l] or by hard donors (such as nitrogen and oxygen)[21a−e,g] or in dicationic complexes.[21d−f,h] These factors often act in combination with each other.[24]

In the case of [Ru(OH$_2$)$_2$(PNNP)]$^{2+}$, the *cis* arrangement of the two aqua ligands is electronically favored because of the *trans* influence arguments discussed above. Additionally, this configuration allows a push−pull interaction[25] between the *π*-accepting phosphine and the *π*-donating oxygen and avoids the extensive four-electron filled−filled interactions[26] between

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(21) Ru(II) complexes (Ru−O distances are in the range 2.166−2.229 Å): (a) Albers, M. O.; Liles, D. C.; Singleton, E. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *43*, 860. (b) Harding, P. A.; Preece, M.; Robinson, S. D.; Henrick, K. *J. Chem. Soc., Dalton Trans.* **1988**, 415. (c) Sun, Y.; Taylor, N. J.; Carty, A. J. *Inorg. Chem.* **1993**, *32*, 4457. (d) Mahon, M. F.; Whittlesey, M. K.; Wood, P. T. *Organometallics* **1999**, *18*, 4068. (e) Nenegas-Yazigi, D.; Lever, A. B. P.; Lough, A. J.; Vega, A.; Paredes-Garcia, V.; Costamagna, J.; Latorre, R. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2000**, *56*, e323. (f) Bickley, J. F.; Higgins, S. J.; Stuart, C. A.; Steiner, A. *Inorg. Chem. Commun.* **2000**, *3*, 211. (g) Kuznetsov, V. P.; Yap, G. P. A.; Alper, H. *Organometallics* **2001**, *20*, 1300. (h) Albertin, G.; Antoniutti, S.; Bacchi, A.; Boato, M.; Pelizzi, G. *J. Chem. Soc., Dalton Trans.* **2002**, 3313. (i) Smolenski, P.; Pruchnik, F. P.; Ciunik, Z. *Inorg. Chem.* **2003**, *42*, 3318. Ru(III) (2.216(5) Å): (j) Dinelli, L. R.; Batista, A. A.; Wohnrath, K.; De Araujo, M. P.; Queiroz, S. L.; Bonfadini, M. R.; Oliva, G.; Nascimento, O. R.; Cyr, P. W.; MacFarlane, K. S.; James, B. R. *Inorg. Chem.* **1999**, *38*, 5341. Ru(0) (2.201(3), 2.241(5) Å): (k) Sustmann, R.; Patzke, B.; Boese, R. *J. Organomet. Chem.* **1994**, *470*, 191. (l) Shiotsuki, M.; Miyai, H.; Ura, Y.; Suzuki, T.; Kondo, T.; Mitsudo, T. *Organometallics* **2002**, *21*, 4960.

(22) See, for instance: Stultz, L. K.; Binstead, R. A.; Reynolds, M. S.; Meyer, J. T. *J. Am. Chem. Soc.* **1995**, *117*, 2520, and references therein.

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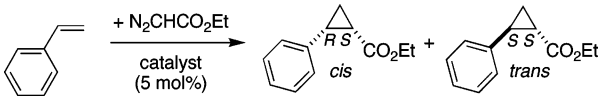
Table 4. Catalytic Asymmetric Cyclopropanation of Styrene[a]



run	complex	eda (equiv)	conv (%)	yield (%)	*cis*:*trans* ratio	ee *cis* (1*S*,2*R*)	ee *trans* (1*S*, 2*S*)
1	$[RuCl(\mathbf{1a})]SbF_6$ (**3a**)[b]	1	27	21	91:9	95	10
2	$[RuCl(\mathbf{1b})]SbF_6$ (**3b**)[b]	1	80	69	99:1	96	58
3	$[RuCl_2(\mathbf{1c})]$ (**2c**) + $AgSbF_6$	1	47	33	71:29	94	78
4	$[RuCl_2(\mathbf{1a})]$ (**2a**) + $2AgBF_4$	2	37	21	57:43	36	59 (1*R*,2*R*)
5	$[RuCl_2(\mathbf{1a})]$ (**2a**) + $2AgSbF_6$	2	65	64	55:45	61	64 (1*R*,2*R*)
6	$[RuCl_2(\mathbf{1b})]$ (**2b**) + $2AgSbF_6$	2	83	28	86:14	81	35
7	$[RuCl_2(\mathbf{1c})]$ (**2c**) + $2AgSbF_6$	2	70	13	53:47	21 (1*R*,2*S*)	10
8	$[Ru(OH_2)_2(\mathbf{1a})](SbF_6)_2$ (**6a**)	2	57	6	62:38	48	9 (1*R*,2*R*)
9	$[Ru(OH_2)_2(\mathbf{1c})](SbF_6)_2$ (**6c**)	2	25	10	87:13	92	65
10	$[RuCl(OH_2)(\mathbf{1a})]PF_6$ (**4a**)[c]	2	61	28	86:14	91	8
11	$[RuCl(OEt_2)(\mathbf{1a})]PF_6$ (**5a**)[c]	2	73	28	86:14	80	rac

[a] See Experimental Section for analytical details. [b] From ref 11. [c] From ref 10.

the d^6 metal center and the oxygen atoms that would occur with mutually *trans* aqua ligands. Obviously, the electronic factors outweigh the angular strain of the *cis*-β arrangement of the PNNP ligand. However, in the case of **6c**, the bulky$(CF_3)_2C_6H_3$ groups may contribute to stabilize the *cis*-β-configuration. In fact, the structure of **2c** shows that the *trans* configuration of ligand **1c** is highly crowded.

Catalytic Cyclopropanation. Both the products of double chloride abstraction and the bis(aqua) complexes **6a** and **6c** were tested as catalysts in the asymmetric cyclopropanation of styrene by decomposition of ethyl diazo acetate. For the sake of comparison with $[RuCl(\mathbf{1a})]SbF_6$ (**3a**SbF_6) and $[RuCl(\mathbf{1b})]SbF_6$ (**3b**SbF_6),[11] we first tested the system formed by activation of dichloro complex **2c** with $AgSbF_6$ (1 equiv), which results in a mixture of unidentified complexes as discussed above. The resulting catalytic system gives a *cis*:*trans* ratio of 71:29, which is in the lower range for five-coordinate complexes of the type $[RuCl(PNNP)]^+$, but the enantioselectivity for both the *cis* and *trans* isomers is rather high, 94% and 78% ee respectively (Table 4, run 3). However, this system is less active than **3b**SbF_6, the cyclopropane yields being 33% and 69%, respectively (runs 3 vs 2).

Overall, the catalysts produced by double chloride abstraction from **2a**−**c** are not *cis*-selective and give modest enantiomeric excesses, with the **2b**/$2AgSbF_6$ catalytic system as an exception (run 6, 86:14 *cis*:*trans* ratio, 81% ee for the *cis* isomer). A surprising trend in this series is that the cyclopropane yield decreases parallel to the donor properties of the PAr_2 groups (runs 5−7).

The main feature of the bis(aqua) complexes **6a** and **6c** is that they are the least effective in each homologous series with the same PNNP ligand. Thus, $[Ru(OH_2)_2(\mathbf{1a})]^{2+}$ (**6a**, run 8) gives lower cyclopropane yield as compared to **3a** (run 1), **2a**/2AgY (Y = BF_4, SbF_6; runs 4, 5), or the monocationic chloroaqua and chloro(diethyl ether) species $[RuCl(L)(\mathbf{1a})]^+$ (runs 10, 11).[10] An analogous observation holds for ligand **1c** (runs 3, 7, 9). In view of the low cyclopropane yield, the *cis*- and enantioselectivity obtained with **6c** is not really useful (run 9), and, therefore, **6b** was not tested.

In general, all the new catalysts give lower performances in terms of cyclopropane yield and/or *cis*- and enantioselectivity than the corresponding $[RuCl(PNNP)]^+$. Some trends concerning their activity and chemoselectivity can be recognized. A first surprising result is that electron-poor PNNP ligands do not necessarily increase the cyclopropane yield. In fact, **2c**/$AgSbF_6$ (1 or 2 equiv, runs 3, 7) and the bis(aqua) complex **6c** (run 9) give yields not exceeding 33%. This is not consistent with the expectation that ligand **1c** would impart the highest electrophilicity, and thus the highest reactivity, to the carbene intermediate as compared to **1a** and **1b**. A closer inspection shows that the low yield results from different causes, depending on the catalytic system. The bis(aqua) complex **6c** is intrinsically low reactive, as conversion and yield are comparable. In contrast, the doubly abstracted species with **1b** and **1c** give high olefin conversion but low cyclopropane yield (runs 6, 7), which is attributed to styrene polymerization (or oligomerization) competing with cyclopropanation.[11] Olefin polymerization becomes increasingly important with the increasing Lewis acidity of the catalyst, as observed in the homogeneous series $[RuCl_2(PNNP)]$/$2AgSbF_6$ with ligands **1a**, **1b**, and **1c** (runs 5−7). However, as the reactivity of the Ru/PNNP fragment is modulated by the ancillary ligand(s), the most Lewis acidic Ru/PNNP fragments do not give necessarily active polymerization catalysts, as discussed below.

Intrinsically low-reactive species give both lower cyclopropane yield and lower styrene conversion. Such is the case of bis(aqua) complex **6c** (25% conversion, 10% yield), as compared to **6a**, which gives 57% styrene conversion, but only 6% cyclopropane yield (runs 9, 8). This is perfectly in line with the slow water exchange observed in solution for the bis(aqua) complex of the electron-poor ligand **1c**. Obviously, these 18-electron complexes must undergo dissociation of one H_2O ligand to react either to form the carbene intermediate of cyclopropanation or to induce polymerization. The same considerations apply to **2c**/$AgSbF_6$ (1 equiv), as it can be argued that the highly acidic cationic fragment $[RuCl(\mathbf{1c})]^+$ binds the anion more strongly than $[RuCl(\mathbf{1b})]^+$ to give an inert 18-electron complex. On the same lines, **2a** + $2AgBF_4$ is less active than **2a** + $2AgSbF_6$ (runs 4, 5) because the tetrafluoroborate anion interacts more strongly with ruthenium cationic species that $[SbF_6]^-$, as we have previously observed.[11]

In sum, the interplay of the donor properties of the PNNP and of the ancillary ligand(s) determines the efficiency of these catalysts in terms of cyclopropane yield. The above results stress the pivotal role played by the bulky, π-donating chloro ligand in stabilizing the five-coordinate, 16-electron complex $[RuCl(PNNP)]^+$,[24,25] which is reactive, yet stable enough to be the main species formed by chloride abstraction with a number of

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PNNP ligands. Furthermore, $[RuCl(PNNP)]^+$ reacts with ethyl diazoacetate to form a *trans* carbene complex, as previously observed with $[RuCl(\mathbf{1a})]PF_6$,[8] both for electronic reasons (the push−pull effect between the carbene and chloro ligands) and because of the stereochemistry of ligand addition to 16-electron complexes.[10,27] In fact, we have preliminary evidence that ligand exchange on six-coordinate complexes of the type *cis*-*β*-$[RuX(L)(PNNP)]^{n+}$ occurs with retention of the *cis*-*β* configuration.

As the previously developed stereochemical model for carbene transfer to styrene suggests that $[RuCl(PNNP)]^+$ is pivotal for high *cis*- and enantioselectivity,[8,11] we speculate that at least two reasons may account for low stereoselectivity observed with the $[Ru(OH_2)_2(PNNP)]^{2+}$ and $[RuCl_2(PNNP)]$/2AgY catalysts. As for steric effects, the X-ray structure of **2c** shows that the 3,5-disubstitution pattern of ligand **1c** causes severe crowding with respect to the unsubstituted analogue $[RuCl_2(\mathbf{1a})]$,[4a] which can be thought to destabilize the *trans* carbene intermediate with respect to one of its *cis* isomers. Additionally, the formation of a *cis* carbene is favored in the bis(aqua) complexes by the mechanism of ligand substitution and, in the chloride-free species, by the lack of the *π*-donor chloride. In both cases, these effects may influence the enantio- and diastereoselectivity to the extent of reversing the sense of asymmetric induction in the *cis* cyclopropane isomer, as observed with catalyst **2c** + $AgSbF_6$ (2 equiv) (run 7).

Conclusion

Double chloride abstraction from $[RuCl_2(PNNP)]$ by silver(I) salts of low-coordinating anions yields highly hygroscopic products that react with water to produce the corresponding dicationic bis(aqua) complexes $[Ru(OH_2)_2(PNNP)]^{2+}$. The latter are, to the best of our knowledge, the first chiral bis(aqua) complexes of ruthenium. Preliminary tests in the asymmetric cyclopropanation of styrene show that both $[Ru(OH_2)_2(PNNP)]^{2+}$ and the chloride-free catalysts formed from $[RuCl_2(PNNP)]$ and $AgSbF_6$ (2 equiv) are less efficient in terms of cyclopropane yield and enantio- and diastereoselectivity than their monochloro analogues $[RuCl(PNNP)]^+$. The low yield obtained with the chloride-free complexes containing electron-poor PNNP ligands is attributed to the high Lewis acidity of the Ru/PNNP fragments, which either promote olefin polymerization as competing reaction to cyclopropanation or strongly bind ancillary ligands, such as water or the fluorinated anions, to give inert 18-electron complexes.

Experimental Section

General Comments. Reactions with air- or moisture-sensitive materials were carried out under an argon atmosphere using Schlenk techniques. ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on Bruker DPX spectrometers. The CD_2Cl_2 solvent was distilled over CaH_2 and immediately stored in a glovebox under purified nitrogen. ^1H and ^{13}C 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. ESI MS measurements were performed using a Finnigan TSQ Quantum instrument. IR spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Complexes $[RuCl_2(\mathbf{1a})]$[4a] (**2a**) and $[RuCl_2(\mathbf{1b})]$[10] (**2b**) were prepared according to literature procedures.

(1*S*,2*S*)-*N*,*N*′-Bis(2-bromobenzylidene)cyclohexane-1,2-diamine. (1*S*,2*S*)-(+)-1,2-Diaminocyclohexane (1.142 g, 0.01 mol) and 2-bromobenzylaldehyde (3.701 g, 0.02 mol, 2 equiv) were dissolved in freshly distilled toluene (50 mL), and the solution was refluxed in a Dean-Stark apparatus for 12 h. The solvent was evaporated under high vacuum, and the pure product was obtained as a dense yellow oil in quantitative yield (4.5 g, >99%). $[\alpha]_D^{20} = -2.6 \pm 0.1$ (*c* 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ 8.56 (s, 2H, *H*C═N), 7.93−7.89 (m, 2H, arom.), 7.48−7.45 (m, 2H, arom.), 7.28−7.17 (m, 4H, arom.), 3.51 (m, 2H, N−C*H*), 1.87 (m, 6H, CH_2), 1.52 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$): δ 160.1 (s, 2 C, H*C*═N), 134.8 (s, 2 C, arom.), 132.7 (s, 2 C, arom), 131.4 (s, 2 C, arom), 128.9 (s, 2 C, arom), 127.4 (s, 2 C, arom), 124.6 (s, 2 C, arom); 73.6 (s, 2 C, N-*C*H); 32.8 (s, 2 C, *C*H_2), 24.3 (s, 2 C, *C*H_2). IR (KBr, cm^{-1}): 1633 (s, $\nu_{C=N}$), 753 (s, ν_{C-Br}). Anal. Calcd for $C_{20}H_{20}N_2Br_2$: C, 53.60; H, 4.50; N, 6.25. Found: C, 53.76; H, 4.64; N, 6.01.

(1*S*,2*S*)-*N*,*N*′-Bis[*o*-(diphenylphosphino)benzylidene]cyclohexane-1,2-diamine (1a). (1*S*,2*S*)-*N*,*N*′-Bis(2-bromobenzylidene)-cyclohexane-1,2-diamine (0.100 g, 0.223 mmol) was dissolved in THF, and the solution was cooled to −80 °C. A 2.3 M solution of ^{t}BuLi (0.19 mL, 0.45 mmol, 2 equiv) in pentane was added dropwise. The solution turned dark red-violet. The reaction solution was stirred at −80 °C for 40 min, then chlorodiphenylphosphine (0.099 g, 82 *μ*L, 0.45 mmol, 2 equiv) was added dropwise. Upon warming to room temperature during 3 h, the reaction solution became pale yellow. The solvent was evaporated, and CH_2Cl_2 was added. Filtration of the salts and evaporation of the solvent in a vacuum gave **1a** as a yellow solid. Yield: 75% (110 mg). ^{31}P NMR (101 MHz, $CDCl_3$): δ −13.9 (s, 2P). Same properties as previously reported.[6b]

(1*S*,2*S*)-*N*,*N*′-Bis{2-[bis(4-trifluoromethylphenyl)phosphino]-benzylidene}cyclohexane-1,2-diamine (1b). (1*S*,2*S*)-*N*,*N*′-Bis(2-bromobenzylidene)cyclohexane-1,2-diamine (0.2 g, 0.45 mmol) was dissolved in THF (15 mL). To the cooled solution (−80 °C), a 1.7 M pentane solution of ^{t}BuLi (0.53 mL, 0.90 mmol, 2 equiv) was added dropwise. The solution turned dark red-violet. The reaction solution was stirred at −80 °C for 1 h, and then bis(4-trifluoromethylphenyl)chlorophosphine (0.318 g, 0.89 mmol, 2 equiv) was added dropwise. The solution was allowed to reach room temperature during 3 h, during which its color turned pale yellow. The solvent was evaporated in high vacuum, the solid residue was dissolved in CH_2Cl_2, and the salts were filtered off. Evaporation of the solvent gave **1b** was a yellow solid. Yield: 75%. ^{31}P NMR (101 MHz, $CDCl_3$): δ −10.2 (s, 2P). Same properties as previously reported.[10]

(1*S*,2*S*)-*N*,*N*′-Bis{2-[bis(3,5-bis(trifluoromethyl)phenyl)-phosphino]benzylidene}cyclohexane-1,2-diamine (1c). (1*S*,2*S*)-*N*,*N*′-Bis(2-bromobenzylidene)cyclohexane-1,2-diamine (0.755 g, 1.69 mmol) was dissolved in THF (15 mL), and the solution was cooled to −78 °C. Upon dropwise addition of a 1.7 M pentane solution of ^{t}BuLi (1.98 mL, 3.37 mmol, 2 equiv), the solution color turned dark red-violet. After stirring at −78 °C for 45 min, neat bis(3,5-bis(trifluoromethyl)phenyl)chlorophosphine (1.66 g, 3.37 mmol, 2 equiv) was added dropwise. The reaction solution, which had become pale yellow, was allowed to reach room temperature under stirring during 3 h, and then MeOH (1 mL) was added. The solvents were evaporated under high vacuum, the residue was dissolved in benzene, and the salts were filtered off. The product **1c** was obtained together with undentified impurities, and all attempts of purification failed. The reaction crude was used to prepare **2c** (see below). ^{31}P NMR ($CDCl_3$): δ −12.7 (s, 2 P).

[RuCl$_2$(1c)] (2c). $[RuCl_2(PPh_3)_3]$ (1.62 g, 1.69 mmol) and crude **1c** (ca. 2.2 g, 1.8 mmol, 1 equiv) were dissolved in toluene, and the resulting solution was refluxed for 10 h. After evaporation of toluene, the orange solid was filtered over alumina with hexane and then with toluene as eluents. Overall yield based on the phosphine: 41%. ^1H NMR (300 MHz, $CDCl_3$): δ 8.98 (m, 2H, *H*C═N), 7.9−7.3 (m, 20H, arom.), 6.4 (m, 2H, arom.), 4.1 (m, 2H, N−C*H*), 2.8 (*d*, 2H, NCH−C*H*H′, $J_{H,H'}$ = 12 Hz), 2.1−2.0 (m, 4H, CH_2), 1.5 (m, 2H, CH_2). ^{31}P NMR (121 MHz, $CDCl_3$): δ

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52.4 (s, 2P). ^{19}F NMR (188 MHz, $CDCl_3$): δ −63.4 (m, 24F). MS (MALDI): *m/z* 1374 (M^+, 14), 1339 (M^+ − Cl, 20), 1303 (M^+ − 2Cl − 1, 100). Anal. Calcd for $C_{52}H_{32}Cl_2F_{24}N_2P_2Ru$: C, 45.43; H, 2.35; N, 2.04. Found: C, 45.56; H, 2.41; N, 1.92.

Reaction of 2c with AgSbF$_6$ (1 equiv). Complex **2c** (29.7 mg, 21 μmol) and $AgSbF_6$ (7.4 mg, 21 μmol) were dissolved in dry CD_2Cl_2 in a NMR tube fitted with a Young valve under an atmosphere of purified nitrogen in a glovebox. A white salt precipitated from the solution. ^{31}P NMR (121 MHz, CD_2Cl_2): δ 76 (br, 24% of the total intensity), 61.4 (d, $^2J_{P,P'}$ = 29.1 Hz, 8%), 54.1 (d, $^2J_{P,P'}$ = 29.1 Hz, 8%), 50 (br, 32%), 47 (br, 28%). ^{31}P NMR (121 MHz, CD_2Cl_2, −40 °C): δ 78 (br, 9% of the total intensity), 76 (br, 13%), 70 (br, 6%), 61.5 (d, $^2J_{P,P'}$ = 29.0 Hz, 8%), 53.5 (d, $^2J_{P,P'}$ = 29.0 Hz, 8%), 52 (br, 10%), 50 (br, 13%), 48 (br, 9%), 45 (br, 24%).

[Ru(OH$_2$)$_2$(1a)](SbF$_6$)$_2$ (6a). Complex **2a** (100 mg, 0.12 mmol) was dissolved in freshly distilled CH_2Cl_2 (5 mL), and $AgSbF_6$ (82 mg, 0.24 mmol, 2 equiv) was added. The solution was stirred for 10 h, and then the salts were filtered off. Upon addition of water (2.2 equiv), the brown solution turned yellow. Crystallization from CH_2Cl_2/hexane gave a yellow solid (136 mg, 90% yield). To remove any residual water, the solid was heated at 60 °C under high vacuum for 12 h. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.01 (d, 1H, *H*C═N, $J_{P,H}$ = 9.3 Hz), 8.73 (s, 1H, *H*C═N), 8.7−6.5 (m, 28H, arom.), 3.98 (m, 1H, N−C*H*), 2.68 (m, 2H, CH_2), 2.27 (m, 2H, CH_2), 1.7−1.9 (m, 3H, CH_2), 1.20 (m, 1H, CH_2), 0.86 (m, 1H, CH_2). The signals of water (either free or coordinated) were not detected at room temperature. ^{31}P NMR (121 MHz, CD_2Cl_2): δ 63.5 (d, 1P, $^2J_{P,P'}$ = 29.7 Hz), 47.1 (d, 1P, $^2J_{P,P'}$ = 29.7 Hz). ^{19}F NMR (188 MHz, CD_2Cl_2): δ −116 (br, $w_{1/2}$ = 5200 Hz, 12F). MS (MALDI): *m/z* 995 (M^+ + SbF_6, 8), 779 (M^+ − H_2O, 100), 573 (M^+ − 2PPh$_2$, 14). IR (KBr, cm^{-1}): 3625 (w, ν_{OH}), 3200 (w br, ν_{OH}), 3060 (m), 2940 (m), 2842 (m), 1986 (m) 1622 (m, $\nu_{C=N}$), 1483 (m), 1436 (s), 1311 (m), 1132 (m), 1096 (s), 999 (m). Anal. Calcd for $C_{44}H_{44}N_2O_2F_{12}P_2RuSb_2$: C, 41.70; H, 3.50; N, 2.21. Found: C, 40.14; H, 3.91; N, 1.92.

[Ru(OH$_2$)$_2$(1a)](BF$_4$)$_2$ (6a(BF$_4$)$_2$). Complex **2a** (27 mg, 0.032 mmol) and $AgBF_4$ (12.6 mg, 0.064 mmol, 2 equiv) were dissolved in dry CD_2Cl_2 in an NMR tube fitted with a Young valve under an atmosphere of purified nitrogen in a glovebox. The solution was stirred for 10 h, and water (2.2 equiv) was added to the brown solution, which turned yellow. The complex was characterized in solution. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.00 (d, 1H, *H*C═N, $J_{P,H}$ = 9.6 Hz), 8.73 (s, 1H, *H*C═N), 8.01−6.50 (m, 28H, arom.), 5.10 (br, 2H, H_2O), 4.12 (m, 1H, N−C*H*), 3.18 (s, 2H, H_2O), 2.5 (br, free H_2O), 2.8−2.5 (m, 2H, CH_2), 2.1−1.8 (m, 4H, CH_2), 1.43 (m, 1H, CH_2), 1.20 (m, 1H, CH_2), 0.80 (m, 1H, CH_2). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 63.6 (d, 1P, $^2J_{P,P'}$ = 29.9 Hz), 48.3 (d, 1P, $^2J_{P,P'}$ = 29.9 Hz). ^{19}F NMR (188 MHz, CD_2Cl_2): δ −149.4 (br, B*F*$_4$, $w_{1/2}$ = 27 Hz, 8F).

[Ru(OH$_2$)$_2$(1b)](SbF$_6$)$_2$ (6b). Complex **2b** (35 mg, 0.032 mmol) and $AgSbF_6$ (21.8 mg, 0.063 mmol, 2 equiv) were dissolved in dry CD_2Cl_2 in an NMR tube fitted with a Young valve under an atmosphere of purified nitrogen in a glovebox. The solution was stirred for 3 h, and water (2.2 equiv) was added to the brown solution, which turned yellow. The complex was characterized in solution. ^{1}H NMR (500 MHz, CD_2Cl_2, 293 K): δ 9.03 (d, 1H, *H*C═N, $J_{P,H}$ = 9.5 Hz), 8.84 (s, 1H, *H*C═N), 8.08−7.05 (m, 23H, arom.), 6.49 (m, 1H, arom.), 4.06 (m, 1H, N−C*H*), 2.91 (s, 2H, *H*$_2$O), 2.72 (m, 1H, CH_2), 2.56 (br, *H*$_2$O, free and coordinated in rapid exchange), 2.38 (m, 1H, CH_2), 1.92 (m, 4H, CH_2), 1.41 (m, 1H, CH_2), 1.27 (m, 1H, CH_2), 0.85 (m, 1H, CH_2); (400 MHz, CD_2Cl_2, 243 K): δ 8.96 (d, 1H, *H*C═N, $J_{P,H}$ = 9.2 Hz), 8.79 (s, 1H, *H*C═N), 8.08−6.76 (m, 23H, arom.), 6.44 (m, 1H, arom.), 4.45 (s, 2H, *H*$_2$O), 4.00 (m, 1H, N−C*H*), 3.25 (s, 2H, *H*$_2$O), 2.65 (m, 1H, CH_2), 2.59 (br, *H*$_2$O, free) 2.33 (m, 1H, CH_2), 1.84 (m, 4H, CH_2), 1.32 (m, 2H, CH_2), 0.85 (m, 1H, CH_2). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 172.9 (d, 1C, H*C*═N, $J_{P,C}$ = 5.6 Hz), 166.5 (s, 1C, H*C*═N, $J_{P,H}$ = 5.6 Hz), 140.3−121.7 (36C, arom.), 79.5 (s, 1C, N−*C*H$_2$), 69.5 (s, 1C, N−*C*H$_2$), 31.7 (s, 1C, *C*H$_2$), 31.5 (s, 1C, *C*H$_2$), 24.9 (s, 1C, *C*H$_2$), 23.4 (s, 1C, *C*H$_2$). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 66.4 (d, 1P, $J_{P,P'}$ = 29.7 Hz), 49.3 (d, 1P, $J_{P,P'}$ = 29.7 Hz). ^{19}F NMR (376 MHz, CD_2Cl_2, 293 K): δ −64.0 (m, 12F, C*F*$_3$), −122 (br, 12F, Sb*F*$_6$, $w_{1/2}$ = 1.4 kHz, 233 K): δ −63.7 (m, 12F, C*F*$_3$), −121 (br, 12F, Sb*F*$_6$, $w_{1/2}$ = 790 Hz).

[Ru(OH$_2$)$_2$(1c)](SbF$_6$)$_2$ (6c). Complex **2c** (63 mg, 0.046 mmol) was dissolved in freshly distilled CH_2Cl_2 (5 mL), and $AgSbF_6$ (31 mg, 0.092 mmol, 2 equiv) was added. The solution was stirred for 10 h, and the salts were filtered off. Water (2.2 equiv) was added, and the brown solution turned to yellow. Crystallization from CH_2Cl_2/hexane gave a yellow solid (77 mg, 94% yield). The solid was heated at 60 °C under high vacuum for 12 h to remove any residual water. ^{1}H NMR (700 MHz, CD_2Cl_2): δ 9.10 (d, 1H, *H*C═N, $J_{P,H}$ = 9.8 Hz), 8.91 (s, 1H, *H*C═N), 8.26−7.14 (m, 19H, arom.), 6.29 (m, 1H, arom.), 4.51 (br, 2H, H_2O), 4.17 (m, 1H, N−C*H*), 3.43 (s, 2H, H_2O), 2.77 (m, 1H, CH_2), 2.32 (m, 1H, CH_2), 2.04 (m, 1H, CH_2), 1.98 (m, 1H, CH_2), 1.95 (m, 1H, CH_2), 1.73 (m, 1H, N−C*H*), 1.44 (m, 1H, CH_2), 1.30 (m, 1H, CH_2), 0.91 (m, 1H, CH_2). ^{13}C NMR (176 MHz, CD_2Cl_2): δ 173.0 (s, 1C, H*C*═N), 166.6 (s, 1C, H*C*═N), 140.7−119.2 (36C, arom.), 79.7 (s, 1C, N−*C*H), 69.2 (s, 1C, N−*C*H), 31.2 (s, 1C, *C*H$_2$), 30.8 (s, 1C, *C*H$_2$), 24.7 (s, 1C, *C*H$_2$), 22.6 (s, 1C, *C*H$_2$). ^{31}P NMR (283 MHz, CD_2Cl_2): δ 67.5 (d, 1P, $J_{P,P'}$ = 29.7 Hz), 51.7 (d, 1P, $J_{P,P'}$ = 29.7 Hz). ^{19}F NMR (188 MHz, CD_2Cl_2): δ −63 (m, 24F), the signal of $[SbF_6]^-$ was too broad to be observed. MS (MALDI): *m/z* 1323 (M^+ − H_2O, 94), 1303 (M^+ − 2H_2O, 100), 1109 (M^+ − H_2O − Ar, 56), 1089 (M^+ − 2H_2O − Ar, 4), 895 (M^+ − H_2O − 2Ar, 18). IR (KBr, cm^{-1}): 3626 (w, ν_{OH}), 3200 (w br, ν_{OH}), 3088 (m), 2946 (m), 2850 (m), 1620 (m, $\nu_{C=N}$), 1440 (m), 1357 (s, CF_3), 1280 (s, CF_3), 1182 (s, CF_3), 1137 (s, CF_3), 1096 (s, CF_3). Anal. Calcd for $C_{52}H_{36}F_{36}N_2O_2P_2RuSb_2$: C, 34.48; H, 2.00; N, 1.55. Found: C, 34.70; H, 2.10; N, 1.61.

X-ray of [RuCl$_2$(1c)] (2c). Red crystals of **2c** were grown by slow diffusion of hexane into $CDCl_3$. Crystal data for $C_{52}H_{32}Cl_2F_{24}N_2P_2Ru$: triangular prism (0.68 × 0.45 × 0.23 mm), triclinic, *P*1, cell dimensions (293 K) a = 12.5439(18) Å, b = 12.7227(19) Å, c = 17.051(3) Å, α = 94.138(3)°, β = 91.495(3)°, γ = 101.742(3)°, and V = 2655.0(7) Å^3 with Z = 1 and D_c = 1.720 Mg/m^3, μ = 0.581 mm^{-1} (Mo Kα, graphite monochromated), λ = 0.71073 Å, F(000) = 1 364. The data were collected at 293 K on a Bruker AXS SMART APEX platform in the θ range 1.66−28.28°. The structure was solved with SHELXTL using direct methods. The unit cell contains two essentially identical, crystallographically independent molecules of the complex that are related to each other—except for the stereogenic cyclohexyl ring—by a pseudoinversion center. Of the 27 500 measured reflections with index ranges $-16 \le h \le 16$, $-16 \le k \le 16$, $-22 \le l \le 22$, 23 982 independent reflections were used in the refinement (full-matrix least squares on F^2 with anisotropic displacement parameters for Ru, P, Cl, and nondisordered F atoms). Hydrogen atoms were introduced at calculated positions and refined with the riding model and individual isotropic thermal parameters for each group. Final residuals were R_1 = 0.0308 (for 22 085 reflections with $I > 2\sigma(I)$), R_1 = 0.0339 (all data), wR_2 = 0.0799 (all data), GOF = 1.049. The absolute structure parameter refined to 0.014(14). Max. and min. difference peaks were +0.722 and −0.375 e Å^{-3}, the largest and mean Δ/σ = 0.036 and 0.002.

X-ray of [Ru(OH$_2$)$_2$(1c)]SbF$_6$ (6c). Red crystals of **6c** were grown from CD_2Cl_2. Crystal data for $C_{52.5}H_{37}ClF_{36}N_2O_2P_2RuSb_2$: yellow cube (0.23 × 0.17 × 0.12 mm), orthorhombic, $C222_1$, cell dimensions (200 K) a = 12.3100(15) Å, b = 22.511(2) Å, c = 47.384(6) Å, and V = 13 131(3) Å^3 with Z = 8 and D_c = 1.875 Mg/m^3, μ = 1.277 mm^{-1} (Mo Kα, graphite monochromated), λ = 0.71073 Å, F(000) = 7 192. The data were collected at 200 K on

a Bruker AXS SMART APEX platform in the θ range 0.86−26.37°. The structure was solved with SHELXTL using direct methods. The unit cell contains, besides $[Ru(OH_2)_2(\mathbf{1c})]^{2+}$, the $[SbF_6]^-$ anions and a disordered CH_2Cl_2 molecule. The $[SbF_6]^-$ are distributed over three sites, Sb(1)/Sb(1′), Sb(2), and Sb(3) (the latter in a special position), with occupancies 0.599 + 0.343, 0.928, and 0.5, respectively. Of the 39 875 measured reflections with index ranges $-15 \le h \le 11$, $-22 \le k \le 28$, $-59 \le l \le 57$, 13 418 independent reflections were used in the refinement (full-matrix least squares on F^2 with anisotropic displacement parameters for Ru, P, Cl, and nondisordered F atoms). Hydrogen atoms were introduced at calculated positions and refined with the riding model and individual isotropic thermal parameters for each group, whereas the H atoms on O(1) were located and refined. Final residuals were $R_1 = 0.0543$ (for 11 736 reflections with $F > 4\sigma(F)$), $R_1 = 0.0640$ (all data), $wR_2 = 0.1312$ (all data), GOF = 1.090. The absolute structure parameter refined to −0.036(22). Max. and min. difference peaks were +1.76 and −0.63 e Å^{-3}, the largest and mean $\Delta/\sigma = 0.004$ and 0.000. Selected interatomic distances and angles are reported in Tables 1 (**2c**) and 3 (**6c**).

Catalytic Cyclopropanation of Styrene. Solutions of **6a**−**c** were prepared with freshly distilled CH_2Cl_2 (2 mL). The catalysts formed by chloride abstraction were prepared in situ by reacting **2a**−**c** (0.024 mmol) with the appropriate amount of AgY (0.024 or 0.048 mmol) or $AgBF_4$ (9.4 mg, 0.048 mmol) in freshly distilled CH_2Cl_2 (2 mL). After 2 h, silver chloride was filtered off (glass microfiber filter). Styrene (0.48 mmol, 55 μL) and decane (internal standard for GC analysis, 80 μL) were added to the catalyst solution. A solution of distilled ethyl diazoacetate (0.48 or 0.96 mmol, 50 or 100 μL) in CH_2Cl_2 (1 mL) was added over 6 h by syringe pump. After stirring for an additional 14 h the solution was filtered over alumina to remove the catalyst. Styrene conversion and yield of the *cis* and *trans* products were determined by GC analysis with decane as the 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): styrene, 8.5; decane, 12.8; ethyl *cis*-2-phenylcyclopropane carboxylate, 26.6; ethyl *trans*-2-phenylcyclopropane carboxylate, 27.8. The enantiomeric excess 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. For the determination of the absolute configuration, see ref 11.

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Supporting Information Available: Details of double chloride abstraction reactions and X-ray crystallographic data (cif files) for complexes **2c** and **6c** are available free of charge via the Internet at http://pubs.acs.org.

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