[CpRu((R)-Binop-F)(H2O)][SbF6], a New Fluxional Chiral Lewis Acid Catalyst: Synthesis, Dynamic NMR, Asymmetric Catalysis, and Theoretical Studies

ALEZRA, Valérie Camille Viviane, et al.

Abstract

The C[2]-symmetric electron-poor ligand (R)-BINOP-F (4) was prepared by reaction of (R)-BINOL with bis(pentafluorophenyl)-phosphorus bromide in the presence of triethylamine. The iodo complex [CpRu((R)-BINOP-F)(I)] ((R)-6) was obtained by substitution of two carbonyl ligands by (R)-4 in the in situ-prepared [CpRu(CO)[2]H] complex followed by reaction with iodoform. Complex 6 was reacted with [Ag(SbF[6])] in acetone to yield [CpRu((R)-BINOP-F)(acetone)][SbF[6]] ((R)-7). X-ray structures were obtained for both (R)-6 and (R)-7. The chiral one-point binding Lewis acid [CpRu((R)-BINOP-F)][SbF[6]] derived from either (R)-7 or the corresponding aquo complex (R)-8 activates methacrolein and catalyzes the Diels–Alder reaction with cyclopentadiene to give the [4 + 2] cycloadduct with an exo/endo ratio of 99:1 and an ee of 92% of the exo product. Addition occurs predominantly to the methacrolein C[α]-Re face. In solution, water in (R)-8 exchanges readily. Moreover, a second exchange process renders the diastereotopic BINOP-F phosphorus atoms equivalent. These processes were studied by the application of variable-temperature [1]H, […]

Reference


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[CpRu((R)-Binop-F)(H2O)][SbF6], a New Fluxional Chiral Lewis Acid Catalyst: Synthesis, Dynamic NMR, Asymmetric Catalysis, and Theoretical Studies

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Abstract: The C2-symmetric electron-poor ligand (R)-BINOP-F (4) was prepared by reaction of (R)-BINOL with bis(pentafluorophenyl)-phosphorus bromide in the presence of triethylamine. The iodo complex [CpRu((R)-BINOP-F)(I)] [(R)-6] was obtained by substitution of two carbonyl ligands by (R)-4 in the in situ-prepared [CpRu(CO)2H] complex followed by reaction with iodoform. Complex 6 was reacted with [Ag(SbF6)] in acetone to yield [CpRu((R)-BINOP-F)(acetone)][SbF6] [(R)-7]. X-ray structures were obtained for both (R)-6 and (R)-7. The chiral one-point binding Lewis acid [CpRu((R)-BINOP-F)][SbF6] derived from either (R)-7 or the corresponding aquo complex (R)-8 activates methacrolein and catalyzes the Diels–Alder reaction with cyclopentadiene to give the [4 + 2] cycloadduct with an exo/endo ratio of 99:1 and an ee of 92% of the exo product. Addition occurs predominantly to the methacrolein C5-Re face. In solution, water in (R)-8 exchanges readily. Moreover, a second exchange process renders the diastereotopic BINOP-F phosphorus atoms equivalent. These processes were studied by the application of variable-temperature 1H, 31P, and 17O NMR spectroscopy, variable-pressure 31P and 17O NMR spectroscopy, and, using a simpler model complex, density functional theory (DFT) calculations. The results point to a dissociative mechanism of the aquo ligand and a pendular motion of the BINOP-F ligand. NMR experiments show an energy barrier of 50.7 kJ mol−1 (12.2 kcal mol−1) for the inversion of the pseudo-chirality at the ruthenium center.

Introduction

Lewis acids play a key role as catalysts in organic synthesis, and applications advance at a rapid pace.1 Our work in this area has focused on the development of stable, chiral, single point coordination transition metal Lewis acids that incorporate C2-symmetric electron-poor bidentate ligands. The readily prepared, mild Fe and Ru Lewis acids 1–3 activate enals and effectively catalyze their asymmetric Diels–Alder reactions with dienes and 1,3-dipolar cycloaddition reactions with nitrones.2,3 The perfluoroaryl phosphinite ligands used in 1−3 create the chiral environment around the coordination site of the enal and offset the donor properties of the cyclopentadienyl- and indenyl-ligands.

Bidentate C2-symmetric chiral ligands have been widely used in asymmetric catalysis.4 Chiral bidentate ligands without C2-
symmetry are more recent but powerful tools for asymmetric catalysis.\(^5\) In CpML\(^1\)L\(^2\) and analogous arene complexes, the pseudotetrahedral metal is a stereogenic center. The use of chiral, disymmetric bidentate L\(^1\)-L\(^2\) ligands then leads to diastereoisomers that differ in the configuration at the metal center.\(^6\)\(^,\)\(^7\) Even when isolated, single diastereoisomers of these optically active complexes are configurationally unstable at the metal center under catalysis conditions and epimerize easily to afford mixtures of diastereomeric complexes.\(^8\) Some of them are nevertheless efficient catalysts for a number of asymmetric transformations because for steric and/or electronic reasons only one of the diastereoisomeric complexes is an efficient catalyst.\(^9\)\(^-\)\(^11\)

The pseudotetrahedral geometry makes this compound class particularly suitable for the study of configurational stability and configurational preference of the metal center and its role in enantioselective catalysis.\(^9\) The ultimate way to investigate racemization of a chiral metal center consists of the use of asymmetric complexes devoid of ligand-based chirality.\(^9\)\(^,\)\(^10\) Over the years, a number of groups have focused on applications in organic transformations of such enantiopurely pincer- and metallo-supramolecular complexes. To the best of our knowledge, complexes with metal-based rather than ligand-based chirality have not been successfully used in asymmetric catalysis. Elegant and pioneering stoichiometric applications stem from the groups of Brunner,\(^11\) Davies,\(^12\) Faller,\(^13\) and Gladysz,\(^14\) among others. For asymmetric catalysis, configurational stability of the catalyst is of essence, as racemization would result in rapid erosion of enantiomeric purity of the product. Investigation of the race-

\[ \text{Scheme 1} \]

mization of optically active complexes devoid of ligand-based chirality is inherently limited to chiroptical measurements.\(^9\)\(^,\)\(^10\)\(^,\)\(^14\)\(^,\)\(^17\) Computational studies have focused on the role of the ligands and the electronic configuration at the metal.\(^15\) Quantitative experimental data on the process of inversion at the metal is still scarce however.\(^8\)\(^,\)\(^10\)\(^,\)\(^14\) In this article we report on a new BINOL-based Ru-Lewis acid catalyst, which catalyzes the asymmetric Diels–Alder reaction of methacrolein and cyclopentadiene.\(^16\) Its NMR characteristics suggested the complex to be suitable to probe the mechanism of the inversion of the pyramidal geometry at the metal center and establish an energy diagram for this process. The mechanistic tools used in this study include variable-temperature \(^1\)H, \(^13\)C, and \(^17\)O NMR spectroscopy, variable-pressure \(^31\)P and \(^17\)O NMR spectroscopy,\(^17\) and, using a simpler model complex, density functional theory (DFT) calculations.

Results and Discussion

Synthesis and Characterization of [CpRu(R)-BINOP-F] Complex. The \(^1\)C-symmetric electron-poor ligand (R)-BINOP-F \(^4\) was prepared by reaction of (R)-BINOL with bis[pentafluoroophenyl])phosphorus bromide in the presence of triethylamine.\(^18\) The hydride complex (R)-5 was obtained by substitution of two carbonyl ligands by (R)-4 in the in situ-prepared [CpRu(CO)\(_2\)] complex (Scheme 1).\(^19\)\(^,\)\(^20\)

\[ \text{Scheme 1} \]


The hydride-labilizing effect was crucial to the success of CO substitution. Attempts to carry out this ligand exchange in the analogous chloro complex were not successful. The robust air-stable hydrido complex (R)-5 was isolated from the crude mixture by column chromatography (aluminum oxide, neutral). Its 1H NMR spectrum in CD2Cl2 showed a doublet of doublets at δ = −11.82 ppm for the Ru-H proton. Subsequent treatment with iodoform in refluxing acetone afforded the air-stable iodo complex (R)-6. Crystals suitable for X-ray diffraction analysis were obtained from a CH2Cl2/MeOH solution (Figure 1).

Synthesis, Characterization, and Catalytic Behavior of [CpRu((R)-BINOP-F)I][SbF6] (L = Acetone, H2O) Complexes. Reaction of a red-orange solution of (R)-6 in acetone/CH2Cl2 with AgSbF6 generated the yellow cationic complex (R)-7, which was isolated by precipitation with Et2O after concentration of the acetone/CH2Cl2 mixture (Scheme 2).

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of Et2O into a solution of (R)-7 in acetone (Figure 2).

The Diels–Alder reaction of methacrolein and cyclopentadiene (1 mol % catalyst, CH2Cl2, −20 °C) was used as a test reaction. Reaction occurred at a similar rate as that of the previously reported complexes [CpRu(BIPHOP-F)I][SbF6] (L = acetone, H2O) 2,3c,d The cycloadduct 9 was isolated in 92% yield, with an exo:endo diastereomeric ratio of 99:1, an enantioselectivity of 92% ee (exo) and 2S absolute configuration (Scheme 3). The aquo complex (R)-8 was formed upon addition of water to a solution of (R)-7 in acetone. The aquo ligand is labile, and this provides another entry to the active catalytic species, the results obtained in the test Diels–Alder reaction being identical in terms of activity and selectivity to those obtained with the acetone complex (R)-7. Ligand 4 forms a nine-membered metallacycle upon coordination to Ru, whereas BIPHOP-F (e.g., in complex 2) forms a seven-membered metallacycle. The effect on the shape of the chiral site of the catalyst is minor though, and it looks very similar to that of 2. The enantioselectivity and the sense of asymmetric induction are identical in both cases. Upon complexation to the metal, the C2-symmetry of the free ligand (R)-4 is lost. Indeed, in the pseudotetrahedral complexes (18) Kündig, E. P.; Dupré, C.; Bourdin, B.; Cunningham, Jr., A. F.; Pons, D. Helv. Chim. Acta 1994, 77, 421.


(24) Aquo complexes of organometallic Lewis acids are frequently observed. Some examples are given in refs 6c,d and 7a–c,e,f and in the following: (a) Takahashi, Y.; Akita, M.; Hikichi, S.; Morooka, Y. Inorg. Chem. 1998, 37, 3186. (b) Takahashi, Y.; Hikichi, S.; Akita, M.; Moro-oka, Y. Chem. Commun. 1999, 1491.
The 17O NMR spectra of a solution of 0.05 mol L\(^{-1}\) -[H\(_2\)O]-BINOP-F ligand split into two

$\frac{\delta}{\text{ ppm}}$ at 0 ppm for the free water (reference) and a

$\frac{\delta}{\text{ ppm}}$ signal at 0.5 mol L\(^{-1}\) -[H\(_2\)O]-BINOP-F in acetone-\(d_6\), as expected,

$\frac{\delta}{\text{ ppm}}$ signal at 0 ppm for the free water (reference) and a

$\frac{\delta}{\text{ ppm}}$ signal at 0.5 mol L\(^{-1}\) -[H\(_2\)O]-BINOP-F in acetone-\(d_6\), as expected,

$\frac{\delta}{\text{ ppm}}$ signal at 0 ppm for the free water (reference) and a

$\frac{\delta}{\text{ ppm}}$ signal at 0.5 mol L\(^{-1}\) -[H\(_2\)O]-BINOP-F in acetone-\(d_6\), as expected,

$\frac{\delta}{\text{ ppm}}$ signal at 0 ppm for the free water (reference) and a

$\frac{\delta}{\text{ ppm}}$ signal at 0.5 mol L\(^{-1}\) -[H\(_2\)O]-BINOP-F in acetone-\(d_6\), as expected,

$\frac{\delta}{\text{ ppm}}$ signal at 0 ppm for the free water (reference) and a

$\frac{\delta}{\text{ ppm}}$ signal at 0.5 mol L\(^{-1}\) -[H\(_2\)O]-BINOP-F in acetone-\(d_6\), as expected,

$\frac{\delta}{\text{ ppm}}$ signal at 0 ppm for the free water (reference) and a

$\frac{\delta}{\text{ ppm}}$ signal at 0.5 mol L\(^{-1}\) -[H\(_2\)O]-BINOP-F in acetone-\(d_6\), as expected,

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$\frac{\delta}{\text{ ppm}}$ signal at 0 ppm for the free water (reference) and a

$\frac{\delta}{\text{ ppm}}$ signal at 0.5 mol L\(^{-1}\) -[H\(_2\)O]-BINOP-F in acetone-\(d_6\), as expected,

$\frac{\delta}{\text{ ppm}}$ signal at 0 ppm for the free water (reference) and a

$\frac{\delta}{\text{ ppm}}$ signal at 0.5 mol L\(^{-1}\) -[H\(_2\)O]-BINOP-F in acetone-\(d_6\), as expected,

$\frac{\delta}{\text{ ppm}}$ signal at 0 ppm for the free water (reference) and a

$\frac{\delta}{\text{ ppm}}$ signal at 0.5 mol L\(^{-1}\) -[H\(_2\)O]-BINOP-F in acetone-\(d_6\), as expected,

$\frac{\delta}{\text{ ppm}}$ signal at 0 ppm for the free water (reference) and a

$\frac{\delta}{\text{ ppm}}$ signal at 0.5 mol L\(^{-1}\) -[H\(_2\)O]-BINOP-F in acetone-\(d_6\), as expected,
showed no water concentration dependence ($[\text{H}_2\text{O}] = 0.56-2.25\text{ mol L}^{-1}$) at 291 K (see Supporting Information). Also, no dependence with added HSbF$_6$ was observed (see Supporting Information). The positive volume of activation, as well as the first-order rate constant, first order in complex concentration and zero order in water concentration, are in accordance with a dissociative mode of activation, and the modest value of $\Delta V^a$ does support an $I_d$ mechanism for the water molecule exchange.

$$\left[\{\text{Ru}(\text{OH}_2)\}\right] + \text{H}_2\text{O} + k_{\text{ex}} \left[\{\text{Ru}(\text{O}^+\text{OH}_2)\}\right] + \text{H}_2\text{O} \quad (R)-8 \rightleftharpoons (R)-8$$

Parameters for water and acetonitrile exchange on a number of ruthenium(II) complexes are given in Table 2. Both H$_2$O and MeCN are greatly labilized by nonleaving $\pi$-bonding ligands. The kinetic trans effect increases the lability by $6 \times 10^{10}$-fold along the sequence [Ru(MeCN)$_6$]$^{2+}$ $<$ [Ru($\eta^2$-C$_6$H$_6$)$_2$]$_2$ $<$ [Ru($\eta^5$-C$_5$H$_5$)]$_3$. This is also accompanied by an increasingly strong d-activation mode as indicated by the growing $\Delta V^a$. A similar trend is also observed for the aquo complexes (Table 2, entries 4–6). We therefore can explain the high rate constant, as well as the strengthened d-activation mode on (R)-8, by the strong labilizing effect of the $\eta^2$-C$_6$H$_6$ ligand (Table 2, entries 3 and 6).

(b) $^{31}$P NMR; Inversion at Ru. The kinetic parameters for the swing motion (eq 2, Figures 5–8) were determined using variable-temperature and variable-pressure $^{31}$P NMR spectroscopy.

Detailed kinetic parameters of the $^{31}$P NMR study are shown in Table 1. No dependence of the swing motion rate constant ($k_{sw}$) with respect to added HSbF$_6$ was observed. The positive volume and entropy of activation are in accordance with a dissociative mode of activation ($I_d$ or $D$ mechanisms). Considering the high $\Delta V^a$ value along with a positive $\Delta S^a$ value, it is tempting to assign this to a $\eta^1$-$\eta^1$-$\eta^1$ hemidissociation process of the (R)-BINOP-F ligand. However, neither synthetic properties nor NMR measurements substantiate this interpretation. From the observation of different inversion barriers in three Cp*Rh(bisoxazoline) complexes, Davies et al. also concluded that hemidissociation of one oxazoline moiety was an unlikely process. While we cannot completely exclude this possibility, a more likely event is the dissociation of water that triggers the movement of inversion. In addition, failure to observe similar fluxional behaviors in the hydrido and iodo analogues (R)-5 and (R)-6 support this interpretation.26,31

Table 1. Derived Kinetic Parameters for the Variable-Temperature and -Pressure Studies of Water Exchange and Swing Motion on (R)-8 in Acetone

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Water exchange</th>
<th>Swing motion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{298}^\text{ex}$ (s$^{-1}$)</td>
<td>29.200 ± 400</td>
<td>8370 ± 630</td>
</tr>
<tr>
<td>$\Delta H^a$ (kJ mol$^{-1}$)</td>
<td>50.57 ± 1.4</td>
<td>79.14 ± 1.8</td>
</tr>
<tr>
<td>$\Delta S^a$ (J mol$^{-1}$K$^{-1}$)</td>
<td>10.15 ± 4.9</td>
<td>95.60 ± 6.5</td>
</tr>
<tr>
<td>$\Delta V^a$ (cm$^3$ mol$^{-1}$)</td>
<td>4.8 ± 0.6</td>
<td>11.6 ± 0.3</td>
</tr>
<tr>
<td>$\Delta G^a^{298}$ (kJ mol$^{-1}$)</td>
<td>47.54 ± 0.03</td>
<td>50.65 ± 0.40</td>
</tr>
</tbody>
</table>

* $k_{\text{ex}}$ (water exchange); $k_{\text{sw}}$ (swing motion). $\Delta$ At 293.4 K.

---

As shown in Table 1, the rate constant of the water exchange process $k_{ex}$ is about three times higher than the one of the $(R)$-BINOP-F swing motion, $k_{sw}$. This may reflect the two different possibilities of a water molecule to be exchanged in a dissociative mechanism. Indeed, the entering water molecule may exchange either from the same side or from the opposite side of the outgoing ligand, only the second possibility implying a swing motion of the bidentate ligand. To complete experimental observations and provide further information on the exact dissociative process, $D$ and $I_d$ mechanisms were subjected to computational analysis. Note that the associative mechanisms have not been considered in our calculations, since the activation parameters obtained previously do not support such a mechanism. Moreover, it has been shown previously that the approach of an additional ligand to a coordinatively saturated Ru(II) complex is electrostatically disfavored.32

(c) Calculations. Geometry optimization and electronic structure calculations were performed with the Gaussian98 and Gaussian03 programs.33 The DZVP34 basis set were employed for performing explicit solvation simulations.37,38 For the calculation of solvent exchange or racemization processes, the solvent is frequently neglected19–22 or treated implicitly using a continuum model.33,34 In this study, solvent effects were taken into account systematically by means of polarized continuum model (PCM) calculations35 using a self-consistent field technique as implemented in Gaussian03.36,37,44 In this model a quantum mechanically treated solute molecule is placed within the so-called solute cavity. The shape and dimensions of the cavity are determined by the molecular structure. The cavity is surrounded by a continuum dielectric polarized by the solute molecule. In turn, the dielectric polarization generates an electrostatic field at the solute molecule, modifying its electron density. Free energies of solvation were calculated with acetone as a solvent following the experimental conditions ($\epsilon = 20.7$). The geometries were kept optimized as for the gas-phase species (single-point calculations). Due to the rigidity of the structures involved, optimization within PCM changes the relative energies and bond lengths by less than 0.5 kcal mol$^{-1}$ and 0.5 Å, respectively, as it was tested for two geometries (see Table S-11 and S-13 in Supporting Information).

Minimum energy optimizations of the gas-phase structures were based on complete geometry optimizations. Transition state calculations were obtained following the correct normal mode manually or using the transition-state optimization type as implemented in the Gaussian98 program.33 Frequency calcula-

### Table 2. Parameters for Solvent Exchange on Ruthenium(II) Complexes

<table>
<thead>
<tr>
<th>entry</th>
<th>complex</th>
<th>$k_{ex}$ (s$^{-1}$)</th>
<th>$\Delta H^\ddagger$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\ddagger$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$\Delta V^\ddagger$ (cm$^3$ mol$^{-1}$)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Ru(CH$_3$CN)$_6$]$_2$</td>
<td>6.9 x 10$^{-11}$</td>
<td>140.3</td>
<td>33.3</td>
<td>0.4</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>[Ru(μ-C$_5$H$_5$)(CH$_3$CN)$_3$]$^2+$</td>
<td>4.1 x 10$^{-5}$</td>
<td>102.5</td>
<td>15.0</td>
<td>2.4</td>
<td>29</td>
</tr>
<tr>
<td>3</td>
<td>[Ru(μ-C$_5$H$_5$)(CH$_3$CN)$_3$]$^2+$</td>
<td>5.6</td>
<td>86.5</td>
<td>59.6</td>
<td>11.1</td>
<td>29</td>
</tr>
<tr>
<td>4</td>
<td>[Ru(H$_2$O)$_6$]$_2$</td>
<td>1.8 x 10$^{-2}$</td>
<td>87.8</td>
<td>16.1</td>
<td>-0.4</td>
<td>28</td>
</tr>
<tr>
<td>5</td>
<td>[Ru(μ-C$_5$H$_5$)(H$_2$O)$_3$]$^2+$</td>
<td>11.5</td>
<td>75.9</td>
<td>29.9</td>
<td>1.5</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>(R)-8</td>
<td>2.9 x 10$^{-6}$</td>
<td>50.6</td>
<td>10.2</td>
<td>4.8</td>
<td>this study</td>
</tr>
</tbody>
</table>

$^a$ Rate constant for the exchange of a particular coordinated solvent molecule.

### Notes


(31) For related discussions, see for example: (a) Sluvgovc, C.; Simanko, W.; Moreiter, K.; Schmid, R.; Kirchner, K.; Xiao, L.; Weisenstein, W. Organometallics 1999, 18, 3865. (b) Faller, J. W.; Grimmond, B. J.; Curtis, M. Organometallics 2000, 19, 5174.


Table 3. Geometrical Parameters of (R)-B at the PW91/3-21G* Level and Truncated A–D and H at the PW91/DZVP Level Compared to the X-ray Structure of (R)-7

<table>
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<tr>
<th></th>
<th>truncated PW91/DZVP</th>
<th>entire PW91/3-21G*</th>
<th>(R)-B</th>
<th>(R)-T X-ray</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td>R(Ru–P) Å</td>
<td>2.30</td>
<td>2.33</td>
<td>2.32</td>
<td>2.37</td>
</tr>
<tr>
<td>R(P–O) Å</td>
<td>1.69</td>
<td>1.70</td>
<td>1.68</td>
<td>1.67</td>
</tr>
<tr>
<td>R(C_{Pyramidal}–Ru) Å</td>
<td>1.88</td>
<td>1.85</td>
<td>1.85</td>
<td>1.82</td>
</tr>
<tr>
<td>R(Ru–L) Å</td>
<td>2.28</td>
<td>3.25</td>
<td>3.81/3.85</td>
<td>3.81/3.85</td>
</tr>
<tr>
<td>(\theta)(P–Ru–P)</td>
<td>99.2</td>
<td>99.3</td>
<td>99.9</td>
<td>102.6</td>
</tr>
<tr>
<td>(\theta)(P–Ru–C_{Pyramidal})</td>
<td>122.4</td>
<td>123.5</td>
<td>124.8</td>
<td>128.7</td>
</tr>
<tr>
<td>(\theta)(H–P–H) or (\theta)(C–P–C)</td>
<td>98.4</td>
<td>98.7</td>
<td>99.0</td>
<td>98.8</td>
</tr>
<tr>
<td>(\theta)(H–P–O) or (\theta)(C–P–O)</td>
<td>98.5</td>
<td>98.9</td>
<td>99.8</td>
<td>100.1</td>
</tr>
<tr>
<td>(\phi)(C_{Pyramidal}–Ru–P–P)</td>
<td>-138.5</td>
<td>-141.2</td>
<td>-144.2</td>
<td>-179.0</td>
</tr>
<tr>
<td>or (\phi) (C–P–C–O)</td>
<td>96.7</td>
<td>96.5</td>
<td>98.1</td>
<td>98.5</td>
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Table 4. Energies, Enthalpies, and Free Energies in the Gas Phase for the Racemization of A at the PW91/DZVP Level and PCM Estimates of the Free Energy of Solvation in Acetone$^a$

<table>
<thead>
<tr>
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<tbody>
<tr>
<td></td>
<td>(\Delta A)–B</td>
<td>(\Delta A)–(C + H$_2$D)</td>
<td>(\Delta A)–(D + H$_2$O)</td>
<td>(\Delta \mu)</td>
<td>(\Delta (A + H_2O)–H)</td>
</tr>
<tr>
<td>gas phase</td>
<td>+58.26</td>
<td>+107.79</td>
<td>+110.00</td>
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</tr>
<tr>
<td>(\Delta H^{pe}) (298.15 K)</td>
<td>+57.59</td>
<td>+102.27</td>
<td>+114.05</td>
<td>55.41</td>
<td></td>
</tr>
<tr>
<td>(\Delta G^{pe}) (298.15 K)</td>
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<td>+52.07</td>
<td>+66.80</td>
<td>68.57</td>
<td></td>
</tr>
<tr>
<td>liquid phase (e = 20.7)</td>
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<td>-14.10</td>
<td>-11.09</td>
<td>16.26</td>
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<tr>
<td>(\Delta G_{vdw})</td>
<td>-7.71</td>
<td>-7.71</td>
<td>-7.71</td>
<td>-7.71</td>
<td></td>
</tr>
<tr>
<td>(RT\ln(1/22.4))</td>
<td>+56.99</td>
<td>+30.26</td>
<td>+48.00</td>
<td>+77.12</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ At 298.15 K. All energies are in kJ mol$^{-1}$. \(\Delta H^{pe}\) and \(\Delta G^{pe}\) are values from gas-phase calculations with \(\Delta H^{pe} = \Delta (H_{\text{trans}} + H_{\text{rot}} + H_{\text{ele}} + E_{\text{ele}})\) and \(\Delta G^{pe} = \Delta H^{pe} - T\Delta S^{pe}\) (see ref 46 for more details). \(\Delta G^{pe} = \Delta G^{pe} + \Delta G_{vdw} + RT\ln(1/22.4)\), note that “reduced” solvation energy is used, in which the difference between the molecular motion contributions calculated in vacuo and in solution is neglected. \(\Delta G_{vdw}\) is given by the PCM calculation.

$^b$ Vibrational entropy does not include any low-frequency modes corresponding to internal rotation.$^{46,47}$

Structures of (R)-7. The Ru–P and Cp–Ru bond lengths are within \(\pm 0.05\) Å of the experimental value but larger deviations are observed for the P–O and Ru–L bond lengths that are slightly overestimated by the DFT calculations (obviously, the Ru–L bond length cannot be compared with the X-ray structure (\(L = 1\)), but Ru–1 is expected to be larger than Ru–O). Nevertheless the DFT-geometries should give a reasonable picture of the system under investigation here.

The calculated energy barriers for the \(I_0\) and \(D\) mechanisms are displayed in Table 4 and shown in Figures 9 and 10.

Gas-Phase Calculations. D Mechanism. In the D pathway (Figure 6), departure of a water molecule in A first leads to the chiral 16-electron species C. Inversion of the pyramidal geometry of C may then occur via a pendulum movement of the bidentate ligand, through the planar-at-the-metal compound D. Alternatively, this movement can also be described as a rocking motion of the Cp ligand with respect to the Ru–P–P plane.

In the theoretical study of the D mechanism (singlet electronic pathway), two transition states have been located (see Tables 4 and 5 and Figure 9). The first transition state results from the dissociation of the water molecule (B) and is characterized by an imaginary vibrational mode involving almost exclusively the \(\text{Ru}^{\text{II}}–\text{OH}_2\) bond (see Table 5). The second transition state (D) arises from the rocking motion of the Cp ligand as depicted in Table 5 and has a pseudo-C$_2$-symmetry (\(\phi\) (Cp–Ru–P–P) = 179.0°). Furthermore, the lengthening of the Ru–P bonds in D (see Table 3) compared with the pyramidal structures A and C is consistent with the enhanced back-bonding upon pyramidalization.$^{15a}$ In the gas-phase, when neglecting the...
thermal and entropic contributions, the intermediate C is at a higher energy than the transition state B (see Table 4). Stabilization of C is thus strongly linked to the larger translational entropy resulting from the increase in the number of particles (one reactant, two products), as is characteristic for dissociative reactions (see terms $T*S_{\text{trns}}$ for A, C, and H$_2$O in Table S-11, 13, and 16 in Supporting Information).

Comparison to literature data of an analogous interconversion for the complex [[$\eta^6$-C$_6$H$_6$]Ru(C$_6$H$_4$-2-CH$_2$NMe$_2$)(NCMe$_2$)]$^+$.PF$_6^-$ is of interest. The dissociation of the ligand was not investigated in that case, but approximations were similar to ones we have made (truncated species, solvent and counterion neglected). The relative energy between the minima corresponding to (A) and intermediate (C) as well as between their intermediate (C) and transition state (D) are, respectively, within 6.3 and 3.9 kJ mol$^{-1}$ of our gas-phase values.

**$I_d$ Mechanism.** In case of the $I_d$ mechanism, a single transition state (H, Figure 10) has been located. The imaginary
Table 5. Imaginary Mode of the Calculated Transition States

<table>
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<th>B</th>
<th>D</th>
<th>H</th>
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<tbody>
<tr>
<td></td>
<td>$-98.01 \text{cm}^{-1}$</td>
<td>$-113.74 \text{cm}^{-1}$</td>
<td>$-101.38 \text{cm}^{-1}$</td>
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</table>

mode involves a concerted motion of the leaving water molecule with the rocking motion of the Cp ligand (see Table 5). The transition state was found to deviate from the expected pseudo-$C_2$-symmetry (see Table 3, $q' (\text{Cp centroid} - \text{Ru} - \text{P} - \text{P}) = -175.0^\circ$ and $\Delta(\text{Ru} - \text{O}) = 0.04 \text{Å}$). The latter, which has also been located (5 kJ higher in energy), has two coupled imaginary frequencies and hence is a hyper saddle point having no relevance. As shown in Tables 3 and 5, the bond lengths of the incoming and leaving water ligands are 3.81 and 3.85 Å, respectively. The Ru–O bond of the leaving water molecule is elongated by 1.6 Å compared to the equilibrium structure, indicative of the dissociative nature of the interchange. When considering the electronic term only, the energy barrier is lower than that found for the $D$ mechanism (+52.07 kJ mol$^{-1}$). However, for the reasons already mentioned previously, translational entropy disfavors the transition state $H$ and actually lies 11.48 kJ mol$^{-1}$ higher in energy than $B$ and 1.77 kJ mol$^{-1}$ higher than $D$. **Effect of Solvent.** So far, the $\Delta G(298.15 \text{K})$ values have been discussed for the gas-phase ($\Delta G_{\text{gas}}$) and not the “liquid”-phase electronic density. As mentioned before, the effects of the solvent (acetone) have been investigated here using a continuum model, and the calculation of Gibbs free energies of reaction in solution ($\Delta G_{\text{solv}}$) has been estimated according to eq 3$^{50-52}$

$$\Delta G_{\text{solv}} = \Delta G_{\text{gas}} + \Delta G_{\text{solv}} + RT \ln(1/22.4)$$

(3)

where $\Delta G_{\text{solv}}$ is the difference in free energy of solution between the different structures ($\Delta G_{\text{solv}}$) computed using PCM techniques.$^{35}$ Note that a correction term$^{11,53}$ ($RT \ln(1/22.4) = -7.71 \text{kJ mol}^{-1}$) is necessary to account for the change of reference state from gas phase (ideal gas) to solution. Of course, continuum models are by nature unable to account explicitly for specific solute–solvent interactions, but they have been quite successful in describing the general aspects of solvation.$^{44}$ In the calculations reported here, gas-phase geometries were used for the PCM calculations because structure optimization (carried out for some structures; see Tables S-11 and S-13 in Supporting Information) indicated only very small changes ($<2 \text{kJ mol}^{-1}$, $<0.5 \text{Å}$, $<1^\circ$).

As shown in Table 4, the largest values of $\Delta \Delta G_{\text{solv}}$ are observed between $A$ and $C$ (14.10 kJ mol$^{-1}$) and $A$ and $D$ (11.09 kJ mol$^{-1}$). Its origin lies in the solvation energy of the separated molecules and the complex. The separation of one charged molecule ($A$) into another charged molecule ($C$) and a water molecule is strongly favored in polar solvent because of the latter’s dipole moment. As a consequence, when solvent effects are included, the free energy of both $C$ and $D$ is lowered, while the energy of $B$ remains fairly unchanged. For similar reasons, the energy of transition state $H$ increases (+16.26 kJ mol$^{-1}$). The effect of an acetone environment thus distinctly favors the $D$ mechanism over the $I_d$ mechanism.

It is clear that because of the approximations made,$^{55}$ the computed values cannot be directly correlated with the experimental value $\Delta G^{298\text{K}}$ displayed in Table 1 ($+50.65 \pm 0.40 \text{kJ mol}^{-1}$), but it is likely, nevertheless, that a $D$ mechanism is energetically favored at 298 K.

**Concluding Remarks**

The combined NMR and theoretical studies support a dissociative mechanism for the inversion of the ruthenium center geometry of [Cp((R)-BINOP-F)(H$_2$O)][SbF$_6$] (R)-8 in acetone. Previous theoretical studies$^{54}$ on half-sandwich complexes [CpML$_4$($\text{L}^2$-$\text{L}^2$)] gave inversion barriers lower than 15 kcal mol$^{-1}$. The data on complex (R)-8 do not challenge this finding, but it must be emphasized that the theoretical estimate of free energy values should be taken with caution. Provided that the mechanism that leads to this “inversion” at the chirotopic metal center does not involve partial dissociation of the chiral ligand, it is not expected to lead to an erosion of product enantioselectivity in catalysis. An identical stereochemical environment exists in the catalyst–substrate complex at all times. Conversely, in analogous enantiomerically pure complexes devoid of ligand-based chirality, this inversion leads to racemization at the metal. While the prospect of using “chiral at the metal” complexes as catalysts is a very attractive proposition, this may only be
realizable with complexes that link the auxiliary arene or Cp ligand with the other ligands and hence suppress racemization. 6f

Experimental Section

General Methods. All synthetic manipulations were carried out using standard Schlenk techniques under an inert atmosphere. All solvents were dried and distilled before use according to standard laboratory procedures. 1H, 13C, and 31P NMR spectra were recorded on Bruker AMX400 and Bruker Avance 500 spectrometers. Iodoform and AgSBF6 were purchased from Fluka. Ru(CO)3Cl2 was prepared according to the literature. 29 The Diels–Alder reaction of methacrolein with cyclopentadiene catalyzed by (R)-7 and (R)-8 was realized following previously described procedures.2 All 1P and 1O NMR spectra for the determination of the kinetic parameters were recorded on a Bruker ARX400 spectrometer operating at 162 and 54 MHz, respectively. The temperature was determined by substituting the sample with a Pt-100 resistor. 56 The variable-pressure dropwise to a solution of (CH2Cl2, 1H), 7.79 (d, J = 7.9 Hz, 1H), 7.67 (d, J = 8.2 Hz, 1H), 7.45 (d, J = 9.1 Hz, 1H), 7.37 (ddd, J = 7.9, 6.6, 1.3 Hz, 1H), 7.34 (ddd, J = 8.2, 7.0, 1.3 Hz, 1H), CuHaCl2), 7.15 (ddd, J = 8.2, 6.6, 1.3 Hz, 1H), 7.08 (ddd, J = 8.2, 7.0, 1.3 Hz, 1H), 6.63 (d, J = 8.5 Hz, 1H), 6.45 (d, J = 8.5 Hz, 1H), 4.72 (s, 5H). 13C NMR (CDCl3, 125 MHz, rt): δ 150.9 (d, J(CP) = 4.0 Hz), 149.3 (d, J(CP) = 4.0 Hz), 133.7, 133.4, 133.1, 131.2, 130.7, 130.4, 128.0, 127.9, 127.7, 127.2, 126.5, 126.1, 125.4, 125.2, 125.0, 122.6 (d, J(CP) = 3.4 Hz), 122.5 (d, J(CP) = 2.3 Hz), 122.1, 88.1. 31P NMR (CDCl3, 202 MHz, rt): δ 113.8 (q, 5JAB, 6JAB = 1258 Hz, JAB = 66 Hz).

[CpRu((R)-BINOL-F)(Aceton)] [SBF6] (7). A solution of AgSBF6 (952 mg, 2.71 mmol) in dried CH2Cl2 (27 mL) was added at room temperature to (R)-6 (784 mg, 0.60 mmol) in a mixture of dried acetone (10 mL) and CH2Cl2 (13 mL). The mixture was stirred at room temperature for 30 min. After evaporation of the solvent under vacuum, the residue was dissolved in a 1:1 mixture of acetone and CH2Cl2 and filtered through Celite. After evaporation of volatiles under vacuum, the product was purified by dissolving in acetone and precipitation by addition of EtOAc to give compound (R)-7 as an orange solid (847 mg, 95%). 1H NMR (acetone-d6, 400 MHz, 40 °C): δ 8.13 (d, J = 9.1 Hz, 2H), 7.87 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 9.1 Hz, 2H), 7.47 (dd, J = 8.1 Hz, J = 7.3 Hz, 2H), 7.26 (dd, J = 8.1 Hz, J = 7.3 Hz, 2H), 6.58 (d, J = 8.1 Hz, 2H), 5.07 (s, 5H). 1H NMR (acetone-d6, 400 MHz, 40 °C): δ 8.18 (d, J = 9.6 Hz, 2H), 8.00–7.94 (m, 2H), 7.77–7.70 (m, 2H), 7.54–7.46 (m, 2H), 7.35–7.23 (m, 2H), 6.57 (d, J = 8.6 Hz, 1H), 6.42 (d, J = 8.3 Hz, 1H), 5.14 (s, 5H). 13C NMR (acetone-d6, 100 MHz, 40 °C): δ 150.8, 133.8, 133.0, 131.9, 128.8, 128.7, 127.4, 125.5, 123.0, 122.2, 87.2. 31P NMR (acetone-d6, 162 MHz, 40 °C): δ 123.8. 31P NMR (acetone-d6, 162 MHz, 40 °C): δ 124.3 (q, 5JAB, 6JAB = 2931 Hz, JAB = 64 Hz).

[CpRu((R)-BINOL-F)(H2O)][SBF6] (8). H2O (9 μL, 0.5 mmol) was added to an orange solution of (R)-7 (125 mg, 0.085 mmol) in CH2Cl2 (1 mL) at room temperature. The solution was stirred for 5 min, and the volatiles were removed in vacuo. The solid residue was dissolved in CH2Cl2 (1 mL); water (9 μL, 0.5 mmol) was added, and the solution was stirred for 5 min before the volatiles were evaporated under vacuum. Another cycle of dissolution–addition of water–stirring–evaporation gave the aquo complex (R)-8 as a yellow solid (120 mg, 98%). 1H NMR (acetone-d6, 400 MHz, 25 °C): δ 8.10 (d, J = 9.1 Hz, 2H), 7.86 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 9.1 Hz, 2H), 7.47 (dd, J = 8.1 Hz, J = 7.2 Hz, 2H), 7.26 (dd, J = 8.1 Hz, J = 7.2 Hz, 2H), 6.60 (d, J = 8.1 Hz, 2H), 5.04 (s, 5H). 1H NMR (acetone-d6, 400 MHz, 40 °C): δ 8.16 (d, J = 9.1 Hz, 2H), 7.94–7.90 (m, 2H), 7.73–7.69 (m, 2H), 7.51–7.45 (m, 2H), 7.30–7.22 (m, 2H), 6.61 (d, J = 8.6 Hz, 1H), 6.45 (d, J = 8.6 Hz, 1H), 5.71 (bs, 2H), 5.06 (s, 5H). 13C NMR (acetone-d6, 100 MHz, 40 °C): δ 149.8, 123.9, 131.8, 130.8, 127.7, 126.4, 124.5, 121.8, 121.6, 86.0. 31P NMR (acetone-d6, 40 °C): δ 149.8, 148.1, 132.0, 131.4, 131.0, 130.8, 130.2, 129.6, 127.3, 127.0, 126.9, 125.7, 125.5, 123.7, 123.4, 121.6, 121.3, 119.7, 86.5. 31P NMR (acetone-d6, 162 MHz, 25 °C): δ 123.3. 31P NMR (acetone-d6, 162 MHz, 40 °C): δ 122.9 (q, 5JAB, 6JAB = 2439 Hz, JAB = 61 Hz).
X-ray Crystallographic Analysis. Cell dimensions and intensities were measured at 200 K on a Stoe STAD4 diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.5418 Å) for [CpRu-((R)-BINOP-F)I] (R)-6 and on a Stoe IPDS diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) for [CpRu((R)-BINOP-F)(acetone)][SbF6] (R)-7. Data were corrected for Lorentz and polarization effects and for absorption. The structures were solved by direct methods (SIR97), and all other calculations were performed with XTAL system and ORTEP programs. [CpRu((R)-BINOP-F)I] (R)-6: C60H30Cl2F22O1P2Ru, M = 1392.5, d = 1.901 g cm⁻³, orthorhombic, P2₁2₁2₁, Z = 4, a = 13.038(1), b = 16.812(1), c = 22.199(2) Å, U = 4865.9(2) Å³; 6880 measured reflections, 5979 unique reflections of which 5272 were observables (|Fo| > 4σ(Fo)). Full-matrix least-squares refinement based on F gave final values R = 0.043, wR = 0.042, and Flack parameter x = -0.01(3). Hydrogen atoms of the complex were placed in calculated positions. Both Et₂O solvent molecules are disordered and refined with population parameters of 0.5 and restraints on bond lengths and bond angles.

Acknowledgment. Financial support for this work by the Swiss National Science Foundation is gratefully acknowledged. We thank the Ministère des Affaires Etrangères of France for a Lavoisier grant to V.A.

Supporting Information Available: Listing of experimental data obtained from variable-temperature, -pressure, and -concentration ¹⁷O and ³¹P NMR experiments and X-ray crystallographic files (CIF) for (R)-6 and (R)-7. This material is available free of charge via the Internet at http://pubs.acs.org.