# **Ruthenium Complexes with Novel Tridentate N.P.N** Ligands Containing a Phosphonite Bridge between Two **Chiral Oxazolines. Catalytic Activity in Cyclopropanation of Olefins and Transfer** Hydrogenation of Acetophenone<sup>†</sup>

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We compare the coordination behavior of the new chiral ligand (S,S)-bis[1-(4-isopropy]-4,5-dihydrooxazol-2-yl)-1-methylethyl] phenylphosphonite ( $\mathbf{V}$ ), abreviated NOPON<sup>iPr</sup> and referred to as bis(oxazolinyl) phenylphosphonite, toward Ru(II) with that of NOPON<sup>Me2</sup> (IV). Although the similarity between **IV** and **V** led to the expectation that they would coordinate in a similar manner, considerable differences were observed. Whereas reaction of [RuCl<sub>2</sub>- $(\eta^{6}-p$ -cymene)]<sub>2</sub> with **IV** afforded the pentacoordinated complex [RuCl<sub>2</sub>(NOPON<sup>Me</sup><sub>2</sub>)] **1**, the chiral ligand V led instead to the dinuclear, chloride-bridged complex  $[Ru(\mu-Cl)Cl(NOPO N^{iPr}$ ]<sub>2</sub> (3). The crystal structures of 1 and 3 have been determined by X-ray diffraction. The *mer* arrangement of the NOPON<sup>Me2</sup> ligand in **1** results from the presence of the four methyl groups, two of which would point toward each other and lead to a steric clash if a fac geometry were adopted. Preliminary theoretical calculations on 1 at the EHT level indicated that coordination of ethylene parallel to the RuCl<sub>2</sub>P plane would result in a stable situation and it is for steric reasons that ethylene does not coordinate to the metal, either parallel or perpendicular to the RuCl<sub>2</sub>P plane. Coordination of CO to 1 was found to be reversible, whereas bulkier ligands do not coordinate to Ru. Complex 3 is a rare example of a fully characterized complex in which a tridentate chiral bis(oxazoline)-type ligand coordinates in a non-mer fashion. It was evaluated in catalytic reactions such as asymmetric cyclopropanation of styrene with ethyl diazoacetate and transfer hydrogenation of acetophenone in propan-2-ol.

#### Introduction

The design of new ligands leading to high reactivity and enantioselectivity in metal-catalyzed asymmetric synthesis is a field of constant ongoing research activity. In the past decade, oxazoline-based bidentate ligands have proven very valuable in asymmetric catalysis, mainly as heteroditopic ligands, such as the phosphinooxazoline  $\mathbf{I}^{1-6}$  or as bis(oxazoline) ligands with or

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without a coordinating connecting group.<sup>7</sup> However, few groups only have reported on the design of tridentate bis(oxazolinyl)-type ligands where the two oxazolines are linked by a coordinating phosphorus, nitrogen, or

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oxygen atom or by a phenyl group susceptible to subsequent metalation.<sup>8–13</sup> A possible difficulty in using chiral tridentate ligands is that, in comparison to their bidentate analogues, they can offer a larger diversity of binding modes and this requires the coordination geometry of their metal complexes to be characterized with great care. An exact knowledge of the structure of a catalyst precursor is most helpful in order to gain a better insight into the overall reaction and allow subsequent fine-tuning of the catalytic system, although it is intrinsically difficult to identify the active species in a catalytic process. Chiral tridentate ligands have been less extensively used in asymmetric catalysis than their bidentate analogues. Nevertheless, they appear to be effective promoters for asymmetric catalysis 11,14-22 and Nishiyama et al. have developed the chiral tridentate ligand bis(oxazolinyl)pyridine (Pybox; II), which has been successfully used in Cu-catalyzed Diels-Alder reactions, Rh-catalyzed hydrosilylation of ketones, and Ru-catalyzed cyclopropanation of olefins with diazoacetates.<sup>23-25</sup>

We have recently shown that ligand **III** readily binds octahedral Ru centers to form active catalytic precursors for transfer hydrogenation of ketones.<sup>12</sup> In contrast to



**III**, ligand **IV** can form two six-membered chelates in square-planar Pd(II) complexes and could potentially adopt meridional (*mer*) or facial (*fac*) coordination modes

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with metals that have an octahedral coordination geometry.  $^{\rm 26}$ 

Here we report on the coordination behavior of IV toward Ru(II) and compare it to that of the new ligand V, the synthesis of which is also described. Although the similarity between IV and V led to the expectation that they would coordinate in a similar manner, considerable differences were observed. We also performed catalytic reactions such as asymmetric cyclopropanation of styrene with ethyl diazoacetate and transfer hydrogenation of acetophenone.

#### Results

Synthesis, Characterization, and Reactivity of Ligand V and Its Ru Complexes. The synthesis of (S, S)-bis[1-(4-isopropyl-4,5-dihydrooxazol-2-yl)-1-methylethyl] phenylphosphonite, abreviated NOPON<sup>iPr</sup> and referred to as bis(oxazolinyl) phenylphosphonite in the following, is straightforward and was achieved by following the methodology previously developed for  $IV^{26}$  by using enantiomerically pure 4-isopropyl-2-(1-hydroxy-1-methylethyl)-4,5-dihydrooxazole (eq 1). The <sup>1</sup>H



and <sup>13</sup>C NMR spectra are consistent with the lack of any symmetry element in the molecule. The four OC- $(CH_3)_2$  methyl groups appear as four singlet resonances in the <sup>1</sup>H NMR spectrum. The IR spectrum of the pure oil in a capillary tube exhibits a strong band at 1665 cm<sup>-1</sup> assigned to the C=N vibration.

When a THF solution containing 1 equiv of [RuCl<sub>2</sub>- $(\eta^6$ -p-cymene)]<sub>2</sub> and 2 equiv of **IV** (NOPON<sup>Me<sub>2</sub></sup>) was brought to reflux, quantitative formation of the complex  $[RuCl_2(NOPON^{Me_2})]$  (1) was observed and the complex was isolated in 75% yield (Scheme 1). The <sup>1</sup>H NMR spectrum of 1 is very similar to that of the free ligand, except that the chemical shifts for the complex are downfield with respect to those of IV. It exhibits four singlets for the eight methyl groups and an AB spin system for the methylenic protons. This is indicative of the coordination of both oxazoline arms of the ligand and of the existence in solution of a mirror plane on the NMR time scale, which includes the phenyl ring and the phosphorus and ruthenium atoms. The far-infrared (FIR) spectrum of complex **1** shows an intense  $\nu(Ru-$ Cl) absorption band at 321 cm<sup>-1</sup>, suggestive of a *trans* arrangement of the two chloride ligands, whereas no absorption was observed in the  $290-250 \text{ cm}^{-1}$  region, where the stretching vibrations of a *cis*-RuCl<sub>2</sub> moiety

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Figure 1. ORTEP view of the structure of  $[RuCl_{2}-(NOPON^{Me_2})]$  (1).



would be expected.<sup>27,28</sup> A single-crystal X-ray diffraction study of **1** established that the tridentate ligand adopts a meridional (*mer*) coordination mode with the two chlorides in a *transoid* arrangement (Figure 1). Selected bond distances and angles are given in Table 1.

The Cl–Ru–Cl angle of  $157.30(2)^{\circ}$  is intermediate between the ideal angles in the equatorial plane of a trigonal bipyramid (120°) and of a square-based pyramid (180°). The two P–Ru–Cl angles are nearly identical and equal to  $101.57(2)^{\circ}$  and 101.06(2). The two nitrogen donor atoms are in a *trans* arrangement with a N–Ru–N angle of  $170.92(7)^{\circ}$ . These data lead to a description of the geometry of this pentacoordinated complex as distorted square pyramidal, as expected for a Ru(II) d<sup>6</sup> complex. Interestingly, the solid-state structural features of the two six-membered ring chelates are not identical. The N(1)–Ru–P and N(2)–Ru–P bite angles are of 91.58(5) and 85.72(5)°, respectively. This decrease in the bite angle is accompanied by a pinch of the Ru–

 Table 1. Selected Bond Distances (Å) and Angles (deg) for [RuCl<sub>2</sub>(NOPON<sup>Me2</sup>)] (1)

| ( · · · · · · · · · · · · · · · · · · ·  | - L - S  |   |   |
|--|--|---|---|
| Ru(1)-Cl(1)Ru(1)-Cl(2)Ru(1)-P(1)   | 2.3806(6)<br>2.3849(6)<br>2.0883(6)            | Ru(1)-N(1)<br>Ru(1)-N(2)  | 2.085(2)<br>2.093(2)                            |
| N(1)-C(4) C(4)-C(1) C(1)-O(1) O(1)-P(1)  | 1.272(3)<br>1.511(3)<br>1.455(2)<br>1.602(2)   | N(2)-C(12)<br>C(12)-C(9)<br>C(9)-O(3)<br>O(3)-P(1)  | 1.268(3)<br>1.523(3)<br>1.450(3)<br>1.615(2)    |
| O(1) - C(1) O(2) - C(4)  | 1.359(2)                                       | O(3) - C(12)  | 1.359(3)  |
| Cl(1)-Ru(1)-Cl(2)<br>Cl(1)-Ru(1)-P(1)<br>Cl(2)-Ru(1)-P(1)  | 157.30(2)<br>101.57(2)<br>101.06(2)            | Cl(2)-Ru(1)-N(1)<br>Cl(2)-Ru(1)-N(2)<br>N(1)-Ru(1)-N(2)   | 86.43(5)<br>85.59(5)<br>170.92(7)               |
| Cl(1)-Ru(1)-N(1)<br>N(1)-Ru(1)-P(1)<br>Ru(1)-N(1)-C(4)   | 91.29(5)<br>91.58(5)<br>124.9(2)               | Cl(1)-Ru(1)-N(2)<br>N(2)-Ru(1)-P(1)<br>Ru(1)-N(2)-C(12)   | 97.74(5)<br>85.72(5)<br>125.9(2)                |
| $ \begin{array}{c} N(1) - C(4) - C(1) \\ C(4) - C(1) - O(1) \\ C(1) - O(1) - P(1) \\ O(1) - P(1) \\ D(1) - P(1) \\ D(1) - P(1) \\ D(1) \\ D$ | $131.1(2) \\111.6(2) \\125.36(14) \\116.61(6)$ | $ \begin{array}{c} N(2) - C(12) - C(9) \\ C(12) - C(9) - O(3) \\ C(9) - O(3) - P(1) \\ O(2) - P(1) - P(1) \\ P(1) \\$ | 131.9(2)<br>114.3(2)<br>124.28(14)<br>111.00(c) |
| $\begin{array}{c} C(1) = F(1) = KU(1) \\ C(5) = N(1) = C(4) \\ O(2) = C(4) = N(1) \\ O(2) = C(4) = C(1) \end{array}$   | 107.3(2)<br>116.8(2)<br>112.1(2)               | $\begin{array}{c} C(3) - F(1) - KU(1) \\ C(13) - N(2) - C(12) \\ N(2) - C(12) - O(4) \\ O(4) - C(12) - C(9) \end{array}$  | 107.7(2)<br>116.9(2)<br>111.2(2)                |
|  |  |   |   |

P–O angle of 4° and an opening of the chelate central backbone O–C–C angle of 2°. The geometry around the phosphorus atom (angles and bond distances) remains unchanged when compared to the structure of the free ligand IV.<sup>26</sup>

The IR spectrum of **1** in KBr shows two absorption bands at 1641 and 1626  $\text{cm}^{-1}$ , which is again in agreement with the absence of any symmetry element in the molecule in the solid state.

Complex **1** is thus an unsaturated pentacoordinated 16-electron species. From its X-ray structure, it appears that the accessibility to the sixth, vacant coordination site is fairly hindered due to the close proximity of the chloride atoms and methyl groups. In fact, triphenylphosphine, triphenyl phosphite, nor ethylene react with **1**. However, treating a CDCl<sub>3</sub> solution of **1**, in an NMR tube, with 1 atm of CO at room temperature yielded [RuCl<sub>2</sub>(CO)(NOPON<sup>Me</sup><sub>2</sub>)] (**2**) within 1 min (eq 2).



The coordination of the terminal CO ligand was observed by IR ( $\nu$ (CO) 1988 cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>) and accompanied by an upfield shift of 35 ppm in the <sup>31</sup>P{<sup>1</sup>H} NMR. This large shift is consistent with the coordination of the CO molecule *trans* to the phosphorus atom.<sup>29</sup> The <sup>1</sup>H NMR spectrum of **2** is identical with that of its precursor, except for a slight upfield shift of 0.15 ppm of two methyl groups on the oxazoline backbone. The reversibility of the CO coordination upon standing or under reduced pressure prevented isolation of pure **2** in the solid state, and therefore, no satisfactory elemental analysis could be obtained.

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<sup>*a*</sup> Methyls from <sup>*i*</sup>Pr and OC(CH<sub>3</sub>)<sub>2</sub> omitted for clarity.

We then prepared complexes analogous to **1** and **2** but containing the chiral ligand **V**. Reaction of 2 equiv of **V** with 1 equiv of  $[\operatorname{RuCl}_2(\eta^6-p\text{-}cymene)]_2$  in refluxing THF resulted in the formation of  $[\operatorname{Ru}(\mu\text{-}\operatorname{Cl})\operatorname{Cl}(\operatorname{NOPON}^{\operatorname{iPr}})]_2$ (**3**), which was further purified by crystallization (60% yield) (Scheme 1). The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **3** showed that the proton and carbon nuclei are chemically and magnetically inequivalent. In the <sup>1</sup>H NMR spectrum in C<sub>6</sub>D<sub>6</sub>, the oxazoline protons show a similar pattern for the two arms but their chemical shifts are very different from each other (up to 1.45 ppm), indicating that the oxazoline moieties are placed in very different chemical environments, consistent with a *fac* coordination mode. This feature is in contrast to the NMR data of complex **1**.

All protons of the ligand were assigned using <sup>1</sup>H homonuclear decoupling and 2D COSY NMR experiments. Of particular interest are the oxazoline protons, abbreviated H<sup>a</sup>-H<sup>d</sup> (Chart 1). The resonance of proton H<sup>b</sup> could be easily assigned by virtue of its complexity; this proton couples to H<sup>a</sup> ( ${}^{3}J_{ba} = 9.4$  Hz), to H<sup>c</sup> ( ${}^{3}J_{bc} =$ 3.6 Hz), and to H<sup>d</sup> ( ${}^{3}J_{bd} = 2.4$  Hz). Proton H<sup>b</sup> is strongly deshielded (6.90 ppm), since it lies above the plane defined by the chloride bridges. Proton H<sup>d</sup> is pointing toward the opposite direction, and its chemical shift is very similar to that of the free ligand. The OCH<sub>2</sub> protons H<sup>a</sup> and H<sup>c</sup> could be distinguished by the different magnitudes of their vicinal scalar couplings to H<sup>b</sup>, remembering that in planar five-membered rings, cisvicinal couplings are greater than trans-vicinal couplings.<sup>30</sup> Protons He-Hh were similarly assigned, and the downfield chemical shift of H<sup>h</sup> is consistent with its proximity to a terminal chloride.

The far-IR spectrum of **3** did not show any absorption clearly assignable to a  $\nu$ (Ru–Cl) vibration. A single-crystal X-ray diffraction study of **3** (Figure 2) showed the complex to be a neutral dinuclear Ru(II) species with two bridging chlorides. Selected bond distances and angles are given in Table 2.

Ligand **V** coordinates in a *fac* mode, and the terminal and bridging chlorides are in a mutually *cis* arrangement. Each ruthenium center has an octahedral geometry, and each chloride bridge is symmetric, although the Ru–Cl bonds *trans* to the P atom are much longer than those *trans* to N, consistent with the respective *trans* influences of the P and N donor atoms.<sup>29,31</sup> The



**Figure 2.** ORTEP view of the structure of  $[Ru(\mu-Cl)Cl-(NOPON^{iPr})]_2$  (**3**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for  $[Ru(\mu-Cl)Cl(NOPON^{iPr})]_2$  (3)

| Ru(1)-Cl(1)          | 2.6018(10) | Ru(2)-Cl(4)         | 2.4224(11) |
|----------------------|------------|---------------------|------------|
| Ru(1)-Cl(2)          | 2.3988(11) | Ru(1)-N(1)          | 2.113(3)   |
| Ru(1)-Cl(3)          | 2.4125(11) | Ru(1) - N(2)        | 2.077(3)   |
| Ru(2)-Cl(1)          | 2.6032(11) | Ru(1)-P(1)          | 2.1278(11) |
| Ru(2)-Cl(2)          | 2.4123(10) |                     |            |
| N(1)-C(4)            | 1.273(5)   | O(1)-P(1)           | 1.610(3)   |
| C(4) - C(1)          | 1.516(5)   | O(2)-C(4)           | 1.366(5)   |
| C(1)-O(1)            | 1.432(5)   |                     |            |
| Cl(1)-Ru(1)-Cl(2)    | 82.78(3)   | Ru(1)-Cl(1)-Ru(2)   | 92.22(3)   |
| Cl(1)-Ru(2)-Cl(2)    | 82.50(4)   | Ru(1)-Cl(2)-Ru(2)   | 102.47(4)  |
| Cl(2) - Ru(1) - P(1) | 92.80(4)   | Ru(1)-N(1)-C(4)     | 127.5(3)   |
| P(1)-Ru(1)-N(2)      | 90.42(9)   | N(1)-C(4)-C(1)      | 132.5(4)   |
| N(2)-Ru(1)-Cl(1)     | 94.04(9)   | C(4) - C(1) - O(1)  | 113.3(3)   |
| Cl(3)-Ru(1)-N(1)     | 176.58(10) | C(1) - O(1) - P(1)  | 132.1(3)   |
| Cl(1) - Ru(1) - P(1) | 175.50(4)  | O(1) - P(1) - Ru(1) | 117.14(10) |
| Cl(2) - Ru(1) - N(2) | 174.76(10) | O(2) - C(4) - N(1)  | 116.8(3)   |
| P(1)-Ru(1)-N(1)      | 89.94(9)   | O(2) - C(4) - C(1)  | 110.7(3)   |
| P(1)-Ru(1)-Cl(3)     | 90.19(4)   |                     |            |
|                      |            |                     |            |

Ru–Cl bond lengths of the chloride *trans* to P are much longer (2.6013(10), 2.6032(11) Å) than the mean value of 2.423 Å found for Ru–Cl distances (Cambridge Crystal Data Base search). Note that although the skeleton formed by the donor set exhibits a  $C_2$  axis of symmetry along the two bridging chlorides, the crystal structure has no symmetry element, due to the folding of the PN chelate, as exemplified by the positions of O(3) and O(5).

Due to our interest in the reactivity of Ru complexes with multidentate heterotopic ligands that contain oxazoline unit(s) and a phosphorus donor atom,<sup>12</sup> we undertook preliminary studies on asymmetric cyclopropanation of styrene using ethyl diazoacetate and on the asymmetric transfer hydrogenation of acetophenone in propan-2-ol catalyzed by **3** (see Discussion and Table 3 for results and details).

### Discussion

The synthesis of complex [RuCl<sub>2</sub>(NOPON<sup>Me<sub>2</sub></sup>)] (1) from RuCl<sub>2</sub>( $\eta^6$ -*p*-cymene)]<sub>2</sub> according to Scheme 1 was completed after 6 h in refluxing THF (in situ <sup>31</sup>P{<sup>1</sup>H} NMR monitoring), while it took 3 days in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. The behavior of NOPON<sup>Me<sub>2</sub></sup> is therefore analogous to that of Pybox but contrasts with that of **III**, which does not displace *p*-cymene but instead forms mono- and dicationic complexes in which it is bidentate

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**Table 3. Transfer Hydrogenation of Acetophenone** in Propan-2-ol Catalyzed by 3<sup>a</sup>

| run | Ru/ketone/base<br>molar ratio | temp (°C) | time (h) | yield (%) <sup>b</sup> | ee (%) <sup>c</sup> |
|-----|-------------------------------|-----------|----------|------------------------|---------------------|
| 1   | 1/200/24                      | reflux    | 0.5      | 95                     | 27                  |
|     |                               |           | 1        | 98                     | 26                  |
| 2   | 1/200/4                       | reflux    | 0.5      | 84                     | 22                  |
|     |                               |           | 1        | 98                     | 21                  |
| 3   | 1/200/4                       | room temp | 1        | 16                     | 45                  |
|     |                               | 1         | 27       | 32                     | 41                  |
| 4   | $1/200/4^{d}$                 | reflux    | 0.5      | 29                     | 6                   |
|     |                               |           | 8        | 94                     | 4                   |

<sup>a</sup> Reactions were carried out in propan-2-ol using 0.1 M substrate concentration and a 0.1 M solution of <sup>i</sup>PrONa as a base. <sup>b</sup> Chemical yields determined by GC analysis on the crude reaction mixture at the reported time. <sup>c</sup> Determined by GC analysis (Lipodex A, 25 m  $\times$  0.25 mm); absolute configurations (S in all cases) were determined by comparing optical rotations of isolated 1-phenylethanol with literature data.  $\hat{d}$  Experiment run with 1 equiv of added PPh3.

and tridentate, respectively. This was established by comparison with the NMR data for the benzene complexes [RuCl( $\eta^6$ -benzene)(NPN-*N*,*P*)](O<sub>3</sub>SCF<sub>3</sub>) and [Ru- $(\eta^6$ -benzene)(NPN-*N*,*P*,*N*)](O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>.<sup>12</sup> Therefore, the size of the chelate (five- vs six-membered) and/or the nature of the phosphorus atom (phosphonite vs phosphine) appear to play an important role for the substitution of the *p*-cymene ligand. Full characterization of the coordinatively unsaturated complex 1 is interesting, since a similar species with the Pybox ligand II was suggested by Nishiyama to be a key in situ cyclopropanation catalyst but could not be isolated.<sup>32</sup> Attempts to coordinate ethylene to 1 or to introduce it during the synthesis by using a procedure similar to that of Nishiyama et al. for compound 4a (1 equiv of [RuCl<sub>2</sub>- $(\eta^6$ -p-cymene)]<sub>2</sub>, 2 equiv of ligand, CH<sub>2</sub>Cl<sub>2</sub>, room temperature, 1 atm of ethylene, 1 h) either failed or led only to the formation of **1** after 3 days.<sup>25</sup>



This is, however, consistent with Nishiyama's findings that a compound analogous to 4a with an achiral Pyboxdimethyl ligand could not be obtained "due to the small mono-vacant site of the RuCl<sub>2</sub>(Pybox-*dimethyl*) moiety which does not have sufficient space to capture one ethylene molecule on the ruthenium center".<sup>25</sup> Furthermore, preliminary theoretical calculations on [RuCl<sub>2</sub>-(NOPON<sup>Me2</sup>)] at the EHT level of theory have revealed that the two ruthenium metal orbitals  $d_{yz}$  and  $d_{xz}$ , which could interact with the vacant  $\pi^*$  orbital of the ethylene ligand, are almost of the same energy: -10.88 and -11.09 eV, respectively (see Chart 2).<sup>33-35</sup>



This indicates that coordination of the ethylene parallel to the RuCl<sub>2</sub>P plane would represent the most stable situation. Similar calculations were then performed on the hypothetical complex [RuCl<sub>2</sub>(ethylene)(NOPON<sup>Me<sub>2</sub></sup>)], with a fixed orientation of the ethylene parallel to the RuCl<sub>2</sub>P plane, which is electronically and intuitively also sterically the most favorable situation. In comparison to **1**, this complex is stabilized by the coordination of the ethylene, since while the energy level of the HOMO remains in the same energy range, -10.83 eV in **1** and -10.50 eV in [RuCl<sub>2</sub>(ethylene)(NOPON<sup>Me<sub>2</sub></sup>)], the energy gap between the HOMO and the LUMO increases from 1.46 to 2.15 eV. This is the result of the destabilization of the  $d_{z^2}$  orbital (LUMO in 1) through interactions with the filled  $p_z$  ethylene orbitals. However, the energy gain based on electronic criteria is counterbalanced by the fact that in this structure the ethylene protons show contacts with the oxazoline methyls as short as 1.40 Å, which are repulsive in nature. Thus, it is for steric reasons that the ethylene does not bind the Ru center either parallel nor perpendicular to the RuCl<sub>2</sub>P plane.

However, a sterically much less demanding "rodlike" molecule such as CO easily coordinates to ruthenium at room temperature. In the IR spectrum of compound **4b** the  $\nu$ (CO) vibration appears at 1965 cm<sup>-1</sup>, while in **2** it is shifted toward higher energy (1988 cm<sup>-1</sup>), thus indicating that the M–CO bond in **4b** is stronger than that in [RuCl<sub>2</sub>(CO)(NOPON<sup>Me<sub>2</sub></sup>)]. This is consistent with the stability of 4b, while 2 easily loses its CO ligand. The phosphorus atom and the CO ligand in 2 both have a high *trans* influence and interact with the same metal orbitals, while in **4b** the nitrogen *trans* to CO has considerably less *trans* influence, thus resulting in an increased strength of the M-CO bond. This difference between the RuCl<sub>2</sub>(NOPON<sup>Me<sub>2</sub></sup>) and RuCl<sub>2</sub>(Pybox) moieties underlines the importance of the electronic effect induced by the multidonor ligand on the reactivity of the complex.

We could not obtain a compound analogous to **1** with the chiral ligand V by following the same procedure as for 1. Instead, we obtained the dinuclear complex [Ru- $(\mu$ -Cl)Cl(NOPON<sup>iPr</sup>)]<sub>2</sub> (**3**). Monitoring of the reaction by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy showed complete consumption of the ligand V. Even though the modes of preparation are the same, 1 and 3 are very different, since the latter contains two bridging chlorides and two tridentate ligands exhibiting a fac coordination mode. This differ-

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Chart 3



mer arrangement not observed

ence should be related to the nature of the substituents on each oxazoline. These are methyl groups in IV, while in **V** there is one <sup>i</sup>Pr group with an S configuration on each oxazoline so that when the two oxazolines are placed in close proximity, as in a *fac* coordination mode, the <sup>i</sup>Pr groups can avoid each other (Chart 3).

If ligand IV were to adopt such a *fac* coordination mode, two of the four methyl groups would have to point toward each other and thus create an unfavorable steric clash. This is not the case in a mer situation. It therefore appears that the coordination mode of our bis(oxazolinyl) phenylphosphonite ligands is controlled by the nature of the oxazoline substituents. Moreover, the fact that no compound of the type [RuCl<sub>2</sub>(mer-NOPON<sup>iPr</sup>)] could be detected indicates that, when given the choice, this new class of ligands prefers to bind in a fac coordination mode.

**Catalytic Studies.** The reactivity of [Ru(*u*-Cl)Cl-(NOPON<sup>iPr</sup>)]<sub>2</sub> (3) was tested toward asymmetric cyclopropanation of styrene using ethyl diazoacetate. The metals of choice for this reaction are usually Pd, Rh, and Cu, and only a limited number of catalysts based on ruthenium have been reported.<sup>25,36-38</sup> Preliminary studies have shown that, under standard reaction conditions, complex 3 mainly catalyzes the dimerization of ethyl diazoacetate to fumarate and maleate and produces low yields of the cyclopropanation products (eq 3).



Running the experiments under more dilute conditions slightly improved the conversion to the cyclopropanation products (15% yield). The *trans/cis* selectivity is low (70:30) and no significant chiral induction was observed. These results are in sharp contrast to the good to excellent trans/cis stereoselectivities observed with Nishiyama's catalysts,<sup>25</sup> but they are comparable to those of other Ru catalysts.<sup>39</sup> It is possible that the fac coordination mode of our ligand prevents the formation of an efficient stereo-demanding chiral pocket around the metal. Nevertheless, enantioselectivity remains always difficult to rationalize.

Complex 3 was also used for preliminary catalytic studies on asymmetric transfer hydrogenation of ketones by propan-2-ol (eq 4). There is considerable



current research activity around this reaction in order both to develop new classes of catalysts and to understand the different steps involved in the overall catalytic process.<sup>40-42</sup>

To allow comparisons with literature data, acetophenone was chosen as a prochiral substrate. Since the conversion rate is dependent on substrate concentration, all experiments were performed using a 0.1 M concentration of substrate.43,44 The best combination of yield and enantiomeric excess was obtained in refluxing propan-2-ol after 1 h (98% conversion, 26% ee) (Table 3, run 1). Reducing the amount of base moderately slows down the turnover frequency of the reaction, but the final conversion remains identical and the enantiomeric excess decreases from 26 to 21%. When the reaction was performed at room temperature, the enantioselectivity increased up to 45% but the conversion was only 16%. Two studies with Ru-based catalysts for asymmetric transfer hydrogenation of ketones have shown that 1 equiv of PPh<sub>3</sub> per ruthenium is needed in the enantioselective step.<sup>9,45</sup> When our catalytic experiment was performed in the presence of 1 equiv of added PPh<sub>3</sub> (Table 3, run 4), we found a slower conversion and a drastically decreased enantiomeric excess (8 h, 94% yield, 4% ee). To gain some insight into the overall catalytic process and to explain the low stereoselectivity, we studied the feasibility of the backward reaction, namely the oxidation of 1-phenylethanol. Exposure of a racemic mixture of 1-phenylethanol in acetone to complex **3** in the presence of *i*-PrONa ([alcohol] = 0.1M, Ru/alcohol/base = 1/200/4, reflux) led to a 3% conversion to acetophenone after 15 h. Thus, it appears that the reverse process is, for kinetic reasons, unlikely to account for the low stereoselectivity obtained with the complex  $[Ru(\mu-Cl)Cl(NOPON^{iPr})]_2$  (3).

Whereas high conversions and enantiomeric excesses have recently been obtained with chiral diamine or phosphino-oxazoline bidentate ligands and with po-

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tentially tridentate chiral ligands,<sup>9,11,19,46</sup> in transfer hydrogenation of ketones in propan-2-ol (up to 95% yield and >99% ee for acetophenone), $^{6,41,43,47}$  there are only very few studies with chiral tridentate ligands where their coordination mode has been firmly established.<sup>21,48,49</sup> Among the latter, our catalyst is of comparable activity but has lower enantioselectivity than the best reported system (99% yield, 71.7% ee),<sup>21</sup> in which the dicationic Ru<sup>2+</sup> complexes were found to be highly superior to their neutral, dichloro precursor complexes. We are currently investigating the synthesis and characterization of dicationic Ru(II) complexes starting from [Ru(*u*-Cl)Cl-(NOPON<sup>iPr</sup>)]<sub>2</sub>.

#### **Experimental Section**

All reactions were performed under purified nitrogen. Solvents were purified and dried under nitrogen by conventional methods. The <sup>1</sup>H NMR spectra were recorded at 300.13 MHz,  $^{31}P\{^1H\}$  NMR spectra at 81.0 or 121.5 MHz, and  $^{13}C\text{--}$ <sup>1</sup>H} NMR spectra at 75.4 MHz on a FT Bruker AC200 or AC300 instrument; IR spectra were recorded in the 4000-400 cm<sup>-1</sup> range on a Bruker IFS66 FT spectrometer and far-IR spectra in the region 500-90 cm<sup>-1</sup> on a Bruker ATS 83 spectrometer. All the complexes are air-stable for a short period of time but are best kept under an inert atmosphere. The compound  $[Ru(\mu-Cl)Cl(\eta^6-p-cymene)]_2$  was prepared according to the literature procedure.<sup>50,51</sup>

Synthesis of the Ligand NOPON<sup>iPr</sup> (V). 4-Isopropyl-2-(1-hydroxy-1-methylethyl)-4,5-dihydrooxazole<sup>52,53</sup> (0.845 g, 4.94 mmol) and triethylamine (2.1 mL, 15 mmol) were mixed in a 100 mL Schlenk flask. The solution was cooled to -78 °C, and dichlorophenylphosphine (0.335 mL, 2.47 mmol) was quickly injected, affording an immediate white precipitate. The reaction mixture was slowly warmed to room temperature over 4 h and was stirred further for 8 h. The THF was removed under reduced pressure, and the pale yellow oil obtained was dissolved in 70 mL of toluene. The white suspension was filtered off over Celite, and the solution was evaporated to dryness, affording a pale yellow oil. Purification by column chromatography (silica, eluent 1/6 ethyl acetate/pentane,  $R_f$ 0.6) gave the ligand in its pure form: yield 0.830 g, 75%. IR (capillary):  $\nu$  (cm<sup>-1</sup>) 1665 (C=N). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.13 MHz):  $\delta$  0.80 (d, 6 H,  ${}^{3}J_{\text{HH}} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.85 (d, 6 H,  ${}^{3}J_{\rm HH} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.54 (s, 3 H, OC(CH<sub>3</sub>)<sub>2</sub>), 1.57 (s, 3 H, OC(CH<sub>3</sub>)<sub>2</sub>), 1.66 (s, 3 H, OC(CH<sub>3</sub>)<sub>2</sub>), 1.69 (s, 3 H, OC(CH<sub>3</sub>)<sub>2</sub>), 1.70 (sept, 2 H,  ${}^{3}J_{HH} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.80 (m, 2 H, NCH), 3.85 (m, 2 H, OCHH), 4.15 (m, 2 H, OCHH), 7.25-7.35 (m, 3 H, aryl H), 7.60-7.70 (m, 2 H, aryl). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75.4 MHz):  $\delta$  17.4 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 17.5 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 18.4 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 18.5 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 26.7–28.1 (m, OC(CH<sub>3</sub>)<sub>2</sub>), 32.0 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 32.1 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 69.6 (s, OCH<sub>2</sub>), 69.7 (s, OCH2), 71.6 (s, NCH(CH3)2), 71.7 (s, NCH), 75.3 (m, OC(CH3)2), 127.2 - 130.0 (m, aryl), 143.7 (d,  $J_{PC} = 11.5$  Hz, *ipso*-C of aryl), 168.4 (s, C=N).  ${}^{31}P{}^{1}H$  NMR (CDCl<sub>3</sub>, 81.0 MHz):  $\delta$  150.6. Anal. Calcd for C<sub>24</sub>H<sub>37</sub>N<sub>2</sub>O<sub>4</sub>P: C, 64.27; H, 8.31; N, 6.25. Found: C, 64.21; H, 8.26; N, 6.19.

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[RuCl<sub>2</sub>(NOPON<sup>Me</sup><sub>2</sub>)] (1). In a Schlenk tube were placed together the ligand  $\mathbf{I}^{26}$  (0.108 g, 0.257 mmol) and [RuCl<sub>2</sub>( $\eta^{6}$ p-cymene)]2 (0.078 g, 0.126 mmol) in THF (15 mL), and the reddish solution was refluxed for 6 h. The mixture was cooled to room temperature, and the solvent was removed under vacuum. The reddish solid was washed with a 1/3 Et<sub>2</sub>O/ pentane mixture ( $2 \times 15$  mL) and dried in vacuo (0.115 g, 75%). IR (KBr):  $\nu$  (cm<sup>-1</sup>) 1641 s (C=N), 1626 s (C=N). Far-IR (polyethylene): v (cm<sup>-1</sup>) 321 vs (trans-RuCl<sub>2</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.13 MHz): 8 1.55 (s, 6 H, NC(CH<sub>3</sub>)(CH<sub>3</sub>)), 1.60 (s, 6 H, NC-(CH<sub>3</sub>)(CH<sub>3</sub>)), 1.80 (s, 6 H, OC(CH<sub>3</sub>)(CH<sub>3</sub>)), 2.05 (s, 6 H, OC-(CH<sub>3</sub>)(CH<sub>3</sub>)), AB spin system  $\delta_A$  4.10 (d, <sup>2</sup>J<sub>HH</sub> = 8.1 Hz, OCHH),  $\delta_{\rm B}$  4.25 (d, <sup>2</sup>J<sub>HH</sub> = 8.1 Hz, OCH*H*), 7.35 (m, 3 H, aryl), 7.70 (m, 2 H, aryl). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75.4 MHz):  $\delta$  25.2 (s, NC( $CH_3$ )<sub>2</sub>) 27.4 (s, NC( $CH_3$ )<sub>2</sub>), 27.9 (d,  ${}^{3}J_{PC} = 5.2$  Hz, OC- $(CH_3)_2$ ), 29.3 (s, OC $(CH_3)_2$ ), 70.9 (s, NC $(CH_3)_2$ ), 79.4 (d,  ${}^2J_{PC} =$ 5.6 Hz, OC(CH<sub>3</sub>)<sub>2</sub>), 81.2 (s, OCH<sub>2</sub>), 125.2–132.0 (m, aryl), 171.0 (s, C=N).  ${}^{31}P{}^{1}H$  NMR (CDCl<sub>3</sub>, 121.5 MHz):  $\delta$  196.9. Anal. Calcd for  $C_{22}H_{33}ClN_2O_4PRu$ : C, 44.60; H, 5.61; N, 4.73. Found: C, 44.57; H, 5.40; N, 4.53.

 $[RuCl_2(CO)(NOPON^{Me_2})]$  (2). CO was bubbled through a  $CDCl_3$  solution of  $[RuCl_2(NOPON^{Me_2})]$  (0.015 g in 0.5 mL) for 1 min in an NMR tube. The solution went from reddish to light orange within 30 s. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  (cm<sup>-1</sup>) 1988 (CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.13 MHz):  $\delta$  1.35 (s, 6 H, NC(CH<sub>3</sub>)(CH<sub>3</sub>)), 1.55 (s, 6 H, NC(CH<sub>3</sub>)(CH<sub>3</sub>)), 1.70 (s, 6 H, OC(CH<sub>3</sub>)(CH<sub>3</sub>)), 1.90 (s, 6 H, OC(CH<sub>3</sub>)(CH<sub>3</sub>)), AB spin system  $\delta_A$  3.85 (d,  ${}^2J_{HH}$  = 8.1 Hz, OCH*H*),  $\delta_B$  4.15 (d,  ${}^2J_{HH} = 8.1$  Hz, OC*H*H), 7.40 (m, 3 H, aryl), 8.05 (m, 2 H, aryl). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 121.5 MHz): δ 161.2.

 $[Ru(\mu-Cl)Cl(NOPON^{iPr})]_2$  (3). In a Schlenk tube were placed together the ligand V (0.213 g, 0.475 mmol) and [RuCl<sub>2</sub>- $(\eta^{6}$ -p-cymene)]<sub>2</sub> (0.145 g, 0.237 mmol) in THF (15 mL), and the reddish solution was refluxed for 3 h. The mixture was cooled to room temperature, and the solvent was removed in vacuo to afford a brown-yellow powder which was washed with  $2 \times 10$  mL of pentane. Recrystallization from a 1/3 THF/ hexane mixture gave pure **3** (0.177 g, 60%). IR (KBr):  $\nu$  (cm<sup>-1</sup>) 1639 (C=N). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300.13 MHz):  $\delta$  0.55 (d, 3 H, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.90 (d, 3 H,  ${}^{3}J_{HH}$  = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.00 (d, 3 H,  ${}^{3}J_{HH}$  = 7.1 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.15 (d, 3 H,  ${}^{3}J_{HH}$  = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.40 (s, 3 H, OC(CH<sub>3</sub>)(CH<sub>3</sub>)), 1.60 (s, 3 H, OC(CH<sub>3</sub>)(CH<sub>3</sub>)), 1.65 (s, 3 H, OC(CH<sub>3</sub>)(CH<sub>3</sub>)), 1.67 (s, 3 H, OC- $(CH_3)(CH_3)$ , 2.15 (sept of d, 1 H,  ${}^{3}J_{HH} = 7.1$  Hz,  ${}^{3}J_{HH^{b}} = 2.4$ Hz,  $CH^{d}(CH_{3})_{2}$ ), 3.75 (dd with appearance of t, 1 H,  ${}^{2}J_{H^{e}H^{g}} =$ 8.7 Hz,  ${}^{3}J_{\text{H}^{e}\text{H}^{f}}(\text{cis}) = 8.9$  Hz, OCHH<sup>e</sup>), 3.95 (dd, 1 H,  ${}^{2}J_{\text{H}^{c}\text{H}^{a}} =$ 8.2 Hz,  ${}^{3}J_{\mathrm{H}^{c}\mathrm{H}^{b}}(\mathrm{trans}) = 3.6$  Hz, OCH<sup>e</sup>H), 4.10 (dd, 1 H,  ${}^{2}J_{\mathrm{H}^{g}\mathrm{H}^{e}}$ = 8.7 Hz,  ${}^{3}J_{H^{g}H^{f}}(\text{trans}) = 2.0$  Hz, OCH<sup>g</sup>H), 4.20 (sept of d, 1 H,  ${}^{3}J_{\text{HH}} = 6.8 \text{ Hz}, {}^{3}J_{\text{HH}} = 1.8 \text{ Hz}, CH(CH_{3})_{2}), 5.40 \text{ (dd, 1 H, } {}^{2}J_{\text{H}^{a}\text{H}^{c}}$ = 8.2 Hz,  ${}^{3}J_{\text{H}^{a}\text{H}^{b}}(\text{cis})$  = 9.4 Hz, OCH*H*<sup>a</sup>), 5.45 (m with appearance of dt,  ${}^{3}J_{H^{f}H^{e}}(cis) = 8.9 \text{ Hz}$ ,  ${}^{3}J_{H^{f}H^{g}}(trans) = 2.0 \text{ Hz}$ ,  ${}^{3}J_{H^{g}H^{h}} =$ 1.8 Hz, NCH<sup>g</sup>), 6.90 (m with appearance of dt,  ${}^{3}J_{H^{b}H^{a}}$ (cis) = 9.4 Hz,  ${}^{3}J_{\text{H}^{b}\text{H}^{c}}(\text{trans}) = 3.6$  Hz,  ${}^{3}J_{\text{H}^{b}\text{H}^{d}} = 2.4$  Hz, NCH<sup>b</sup>), 7.05– 7.25 (m, 3 H, aryl), 8.65-8.75 (m, 2 H, aryl). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 75.4 MHz):  $\delta$  15.0 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 15.5 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 19.2 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 19.8 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 28.3 (d,  ${}^{3}J_{PC} = 5.8$  Hz,  $OC(CH_3)_2$ ), 29.6 (d,  ${}^{3}J_{PC} = 5.4$  Hz,  $OC(CH_3)_2$ ), 29.9 (s, OC- $(CH_3)_2$ , 30.3 (d,  ${}^{3}J_{PC} = 7.4$  Hz, OC $(CH_3)_2$ ), 68.4 (s, OCH<sub>2</sub>), 69.7 (s, OCH<sub>2</sub>), 72.5 (s, NCH(CH<sub>3</sub>)<sub>2</sub>), 73.9 (s, NCH(CH<sub>3</sub>)<sub>2</sub>), 77.0 (s,  $OC(CH_3)_2)$ , 77.1 (d,  ${}^2J_{PC} = 5.4$  Hz,  $OC(CH_3)_2)$ , 126.5–134.0 (m, aryl), 140.5 (d, J<sub>PC</sub> = 80.0 Hz, *i*-C of aryl), 168.2 (s, C=N), 171.7 (s, C=N). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121.5 MHz):  $\delta$  191.1. Anal. Calcd for C<sub>24</sub>H<sub>37</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub>PRu: C, 46.46; H, 6.01; N, 4.51. Found: C, 46.40; H, 5.99; N, 4.16.

X-ray Structural Analyses.54 Crystals of [RuCl2- $(NOPON^{Me_2})](1)$  suitable for X-ray diffraction were obtained from a 1/3 CH<sub>2</sub>Cl<sub>2</sub>/pentane mixture and those of [Ru( $\mu$ -Cl)Cl-(NOPON<sup>iPr</sup>)]<sub>2</sub> (3) from a 1/3 THF/hexane mixture. The structures were solved by heavy-atom Patterson methods and

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Table 4. Crystallographic Data for the Structural<br/>Analysis of Complexes 1 and 3

|   | 1                              | 3                               |
|---|--------------------------------|---------------------------------|
| empirical formula                                 | $C_{22}H_{33}Cl_2N_2O_4PR_u$   | $C_{48}H_{74}Cl_4N_4O_8P_2Ru_2$ |
| fw  | 592.46                         | 1241.03                         |
| cryst syst  | monoclinic                     | monoclinic                      |
| space group                                       | P2 <sub>1</sub> /a (No. 14)    | P21 (No. 4)                     |
| a (Å)   | 15.425(2)                      | 11.5291(13)                     |
| b (Å)   | 9.4508(13)                     | 17.329(2)                       |
| <i>c</i> (Å)                                      | 12.6782(14)                    | 14.4236(4)                      |
| $\beta$ (deg)                                     | 103.3545(5)                    | 104.6653(5)                     |
| $V(Å^3)$  | 2606.6(4)                      | 2787.7(4)                       |
| Ζ   | 4                              | 2                               |
| $D_{\text{calcd}}$ (g cm <sup>-3</sup> )          | 1.51                           | 1.478                           |
| radiation; $\lambda$ (Å)                          | Μο Κα; 0.710 69                | Μο Κα; 0.710 69                 |
| <i>F</i> (000)                                    | 1216                           | 1280                            |
| $\mu  ({\rm cm}^{-1})$                            | 8.97                           | 8.43                            |
| cryst size (mm)                                   | $0.10 \times 0.20 \times 0.30$ | $0.40\times0.35\times0.20$      |
| $\theta$ range (deg)                              | $2.0 < \theta < 30$            | $2.0 < \theta < 30$             |
| temp (K)  | 180                            | 180                             |
| scan mode   | ω                              | ω                               |
| no. of rflns $(I > 3\sigma(I))$                   | 4472                           | 7443                            |
| no. of variables                                  | 289                            | 612                             |
| residuals ( $R$ ; $R_w$ ) <sup>a</sup>            | 0.027; 0.023                   | 0.028; 0.0604                   |
| goodness of fit (GOF) <sup>a</sup>                | 1.27                           | 1.436                           |
| max peak in final<br>diff map (e/Å <sup>3</sup> ) | 0.86                           | 1.01                            |

<sup>a</sup>  $R = \sum_{hkl} (||F_0| - |F_c||) / \sum_{hkl} |F_0|; R_w = [\sum_{hkl} W(|F_0| - |F_c|)^2 / \sum_{hkl} WF_0^2]^{1/2}, W = 1/\sigma^2(F_0); \text{ GOF} = [\sum_{hkl} W(|F_0| - |F_c|)^2 / (n_{\text{data}} - n_{\text{variables}})]^{1/2}.$ 

expanded Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in calculated positions with C-H = 0.98 Å. The numbers of reflections and parameters and the values of the residuals are given in Table 4.

**Catalytic Experiments. Cyclopropanation.** A typical procedure for cyclopropanation of styrene and ethyl diazoacetate is as follows: to a solution of **3** (0.0093 g, 0.015 mmol) and styrene (0.85 mL, 7.5 mmol) in 10 mL of  $CH_2Cl_2$  was added

a CH<sub>2</sub>Cl<sub>2</sub> solution of ethyl diazoacetate (1.5 mmol, ca. 1 M) through a microsyringe controlled by a mechanical feeder for 8 h under argon. After it was stirred for an additional 8 h, the mixture was passed through a 1 cm silica gel column to remove metal impurities. Conversion and enantioselectivity were determined by gas chromatography using a  $\beta$ -CD No. 8 column (0.5 bar of H<sub>2</sub>, 90 °C, 0.3 °C/min).

**Transfer Hydrogenation.** A typical procedure for catalytic transfer hydrogenation of acetophenone is as follows: in a 50 mL two-neck round-bottom flask fitted with a reflux condenser was dissolved **3** (0.0062 g, 0.01 mmol) in 19.5 mL of *i*-PrOH. Acetophenone (0.234 mL, 2.0 mmol) was added, and the yellow solution was brought to the desired temperature. The solution was stirred for 10 min, and a solution of *i*-PrONa in *i*-PrOH (0.1 M) was added. Note that the volume of *i*-PrOH was adjusted so that all catalytic runs are performed with an initial concentration in acetophenone of 0.1 M.

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**Supporting Information Available:** Tables giving details of the structure determination, atomic coordinates, including those of the hydrogen atoms, anisotropic thermal parameters, and all bond distances and angles for complexes **1** and **3**, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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