Synthesis and Crystal Structures of Ru(II) Complexes Containing Chelating (Phosphinomethyl)oxazoline *P,N*-Type Ligands and Asymmetric Catalytic Transfer Hydrogenation of Acetophenone in Propan-2-ol†

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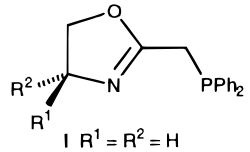
A series of new Ru(II) complexes containing two chelating *P,N* ligands of the type (2-oxazolin-2-ylmethyl)-diphenylphosphine (PCH_2-oxazoline **I**), (2-oxazolin-4,4-dimethyl-2-ylmethyl)diphenylphosphine (PCH_2-oxazoline-Me_2 **II**), and (2-oxazolin-4-(*S*)-isopropyl-ylmethyl)diphenylphosphine (PCH_2-oxazoline-^{i}Pr **III**) have been prepared and characterized by IR, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy and by X-ray diffraction studies in the cases of *cis,cis,cis*-[$RuCl_2(PCH_2$-oxazoline$)_2$] (**1**) and *cis,cis,trans*-[$RuCl_2(PCH_2$-oxazoline-$Me_2)_2$] (**3**). Four different types of octahedral coordination geometries are found for these complexes depending on the ligand. With **I**, *cis,cis,cis* and *trans,trans,trans* geometries were characterized in complexes **1** and **2**, respectively, whereas with ligand **II** only the *cis,cis,trans* isomer **3** was formed. Reaction of the enantiomerically pure ligand **III** with [$RuCl_2$-(COD)]$_n$ afforded a mixture of isomers, and complex *trans,cis,cis*-[$RuCl_2(PCH_2$-oxazoline-^{i}Pr$)_2$] **4** was fully characterized. This complex was used for catalytic transfer hydrogenation of acetophenone in propan-2-ol and led to 96% conversion and 72% ee (3 h, 82 °C, [ketone] = 0.1 M, Ru:ketone:base = 1:200:5). For comparison the crude mixture of complexes gave a higher turnover frequency but a lower enantioselectivity than pure **4**.

Introduction

Heterotopic ligands have been extensively used in coordination and organometallic chemistry owing to their structural features and novel stoeichiometric or catalytic reactivity of their metal complexes. The interest for such ligands stems from the fact that the different (stereo)electronic properties of their donor groups will give rise to selective metal−ligand interactions that may control the reactivity at the metal site.[1−3] In particular, we and others have investigated the properties of complexes containing *P,O*-type ligands, such as phosphinoketones, -esters, -ethers, or -amides.[1,2,4−7] More recently, we have been interested in the coordination behavior of phosphinooxazoline ligands, such as **I** (PCH_2-oxazoline) and **II** (PCH_2-oxazoline-Me_2), which combine the phosphorus donor atom as a soft Lewis base with the harder nitrogen atom of the oxazoline ring.[2] Coordination through the oxygen donor is less likely, particularly with late transition metals, because of the unfavorable energy of its orbitals compared to those of the sp^2-hybridized nitrogen atom. We now extend such studies to the enantiomerically pure ligand **III** (PCH_2-oxazoline-^{i}Pr). Preliminary studies on square planar



I $R^1 = R^2 = H$
II $R^1 = R^2 = Me$
III $R^1 = i$-Pr, $R^2 = H$

Pd(II) complexes of ligands **I** and **II** led to the synthesis of active complexes for alternating ethylene/CO copolymerization.[8] We also found it of interest to study their coordination properties toward metals offering higher coordination numbers. Considering the rich chemistry of Ru complexes with octahedral geometry and their proven successful applications in homogeneous catalysis (e.g., asymmetric hydrogenation),[9−12] we ex-

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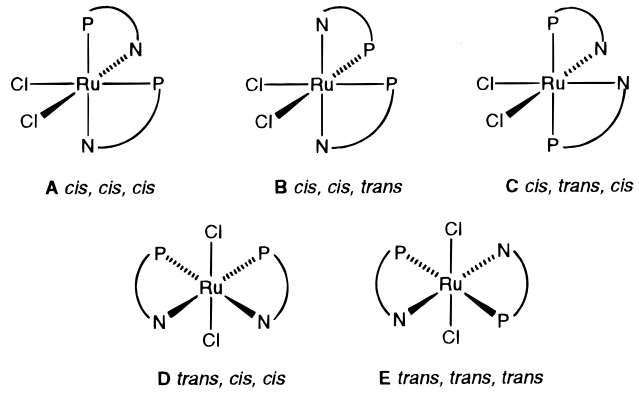
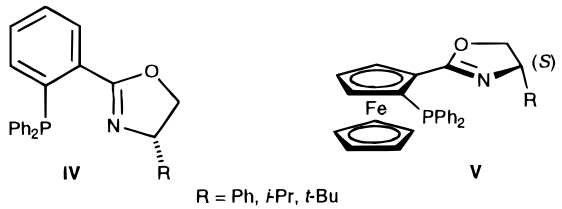
Scheme 1



amined the coordination behavior of these phosphinooxazoline ligands toward Ru. In this paper, we report the synthesis of Ru complexes of general formula [$RuCl_2$(phosphinooxazoline)$_2$], of which the five possible coordination geometries are shown in Scheme 1.

Pentacoordinated Ru(II) complexes of the type [$RuCl_2(PPh_3)$-(phosphinooxazoline)], which contain a six-membered chelating phosphinooxazoline ligand, either (phosphinoaryl)oxazoline **IV** or (phosphinoferrocenyl)oxazoline **V**, have very recently been used successfully in catalytic asymmetric transfer hydrogenation of ketones in propan-2-ol.[13−15]

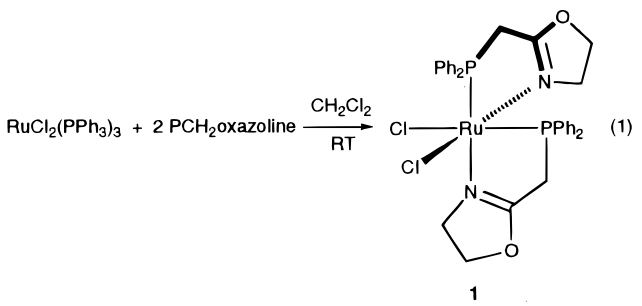


Here we also report our preliminary results on the catalytic asymmetric transfer hydrogenation of acetophenone in propan-2-ol by a Ru complex bearing the enantiomerically pure ligand **III**.

Results

Synthesis and Characterization of the Chiral Ligand III. The synthesis of (2-oxazolin-4-(*S*)-isopropyl-ylmethyl)diphenylphosphine **III**, abreviated PCH_2-oxazoline-^{i}Pr in the following, was performed according to a procedure described by Helmchen et al.[16] The $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ exhibits a singlet at δ −17.2. The ^1H NMR spectrum shows two multiplets at δ 3.80 (2 H) and 4.10 (1 H) characteristic for the three oxazoline protons. The diastereotopic methyl protons of the isopropyl group appear as two doublets at δ 0.80 and 0.85, coupled to the isopropyl proton C*H*$(CH_3)_2$ ($^3J_{HH}$ = 8.1 Hz). The PCH_2 protons appear only as an AB spin system ($^2J_{PH} \sim 0$ Hz) at δ 3.05 and 3.10 with $^2J_{HH}$ = 13.5 Hz.

Synthesis of the Ruthenium Complexes. *cis,cis,cis*-[$RuCl_2$-(P,N)$_2$] (1). Mixing 2 equiv of ligand **I** with 1 equiv of [$RuCl_2$-$(PPh_3)_3$] in CH_2Cl_2 led to a complex of composition [$RuCl_2$-(PCH_2-oxazoline)$_2$], as shown by elemental analysis (eq 1).



The $^{31}P\{^1H\}$ NMR spectrum of this compound exhibits an AB spin system with a $^2J_{PP}$ coupling of 32.5 Hz. Thus it appears that the only possible geometry for **1** is of type **A** since all the other structures have a C_2 axis of symmetry or a mirror plane which should give rise to a singlet in the $^{31}P\{^1H\}$ NMR spectrum. The ^1H NMR spectrum of **1** is in accordance with this lack of any symmetry element in the molecule since all protons are chemically and magnetically different and thus appear as individual resonances integrating for one proton. The IR spectrum (KBr pellet) shows two bands at 1647 and 1636 cm^{-1} assigned to C═N vibrations of two coordinated oxazolines with different *trans* donor atoms (ν(C═N) = 1660 cm^{-1} for the uncoordinated ligand). The *cis,cis,cis* geometry of the molecule was confirmed by a single-crystal X-ray diffraction study. The crystals contain two crystallographically independent, but almost identical, molecules (A and B). A view of the structure of one of them (A) is shown in the Figure 1 together with the atomic numbering system; selected bond distances and angles in them are given in Table 1. The two Ru−N bond distances in the two octahedral complexes differ slightly; the longer, 2.113(6) Å [2.137(6) Å, the values in brackets refer to molecule B], involves the N(2) atom *trans* to phosphorus, the

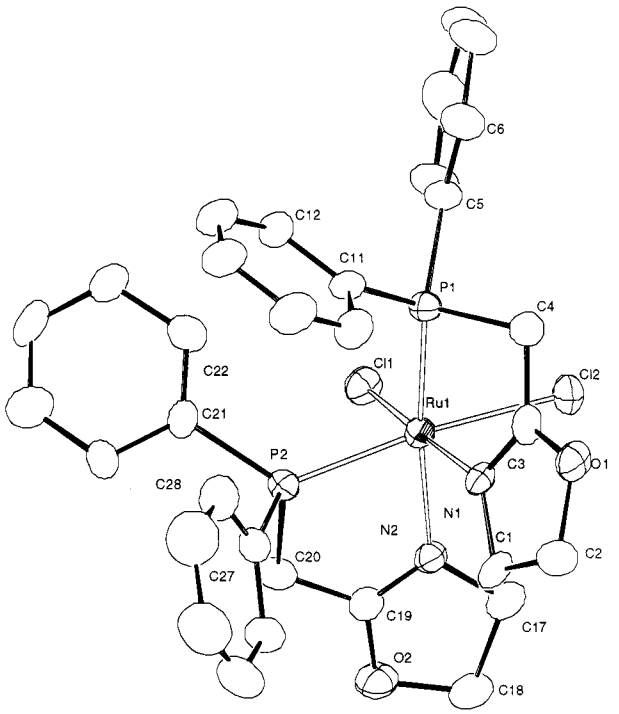


Figure 1. ORTEP view of the structure of the complex **1** together with the atomic numbering scheme. The ellipsoids for the atoms are drawn at the 30% probability level.

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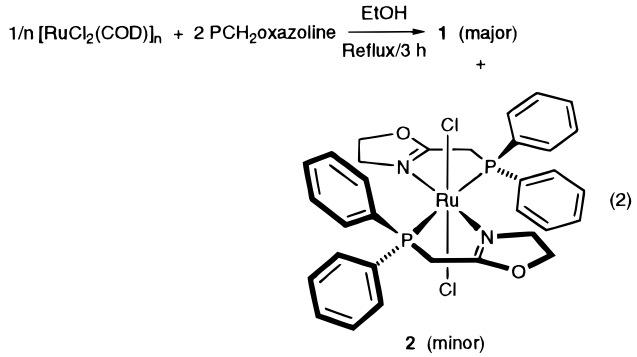
Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**

molecule A		molecule B	
	Bond Distances		
Ru(1)−N(1)	2.080(6)	Ru(1)−N(1)	2.067(5)
Ru(1)−N(2)	2.113(6)	Ru(1)−N(2)	2.137(6)
Ru(1)−P(2)	2.249(2)	Ru(1)−P(2)	2.260(2)
Ru(1)−P(1)	2.292(2)	Ru(1)−P(1)	2.283(2)
Ru(1)−Cl(1)	2.452(2)	Ru(1)−Cl(1)	2.451(2)
Ru(1)−Cl(2)	2.478(2)	Ru(1)−Cl(2)	2.472(2)
P(1)−C(4)	1.873(7)	P(1)−C(4)	1.844(7)
P(2)−C(20)	1.899(8)	P(2)−C(20)	1.871(7)
O(1)−C(3)	1.347(9)	O(2)−C(19)	1.341(8)
O(1)−C(2)	1.485(9)	O(2)−C(18)	1.492(10)
O(2)−C(19)	1.340(9)	O(1)−C(3)	1.359(8)
O(2)−C(18)	1.455(10)	O(1)−C(2)	1.501(10)
N(1)−C(3)	1.300(9)	N(1)−C(3)	1.302(8)
N(1)−C(1)	1.471(9)	N(1)−C(1)	1.469(9)
N(2)−C(19)	1.239(9)	N(2)−C(19)	1.288(9)
N(2)−C(17)	1.456(9)	N(2)−C(17)	1.469(9)
C(1)−C(2)	1.532(10)	C(1)−C(2)	1.505(10)
C(3)−C(4)	1.462(11)	C(3)−C(4)	1.490(10)
	Bond Angles		
N(1)−Ru(1)−N(2)	92.3(2)	N(1)−Ru(1)−Cl(1)	173.07(16)
N(1)−Ru(1)−P(2)	98.36(18)	N(2)−Ru(1)−Cl(1)	83.42(17)
N(2)−Ru(1)−P(2)	81.11(18)	P(2)−Ru(1)−Cl(1)	86.35(9)
N(1)−Ru(1)−P(1)	78.75(17)	P(1)−Ru(1)−Cl(1)	105.23(8)
N(2)−Ru(1)−P(1)	170.46(17)	N(1)−Ru(1)−Cl(2)	86.50(18)
P(2)−Ru(1)−P(1)	103.16(9)	N(2)−Ru(1)−Cl(2)	89.19(18)
P(2)−Ru(1)−Cl(2)	169.27(8)	N(1)−Ru(1)−Cl(1)	171.90(16)
P(1)−Ru(1)−Cl(2)	87.13(9)	N(2)−Ru(1)−Cl(1)	84.23(16)
Cl(1)−Ru(1)−Cl(2)	88.02(9)	P(2)−Ru(1)−Cl(1)	90.34(9)
C(4)−P(1)−Ru(1)	99.7(2)	P(1)−Ru(1)−Cl(1)	104.95(7)
C(3)−N(1)−Ru(1)	119.6(5)	N(1)−Ru(1)−Cl(2)	86.16(18)
C(19)−N(2)−Ru(1)	122.1(5)	N(2)−Ru(1)−Cl(2)	89.39(17)
N(1)−C(3)−C(4)	123.2(7)	P(2)−Ru(1)−Cl(2)	170.23(7)
O(1)−C(3)−C(4)	120.4(7)	P(1)−Ru(1)−Cl(2)	86.07(8)
C(3)−C(4)−P(1)	104.6(5)	Cl(1)−Ru(1)−Cl(2)	87.75(9)
N(2)−C(19)−C(20)	121.8(7)	C(4)−P(1)−Ru(1)	100.6(2)
O(2)−C(19)−C(20)	118.4(7)	C(3)−N(1)−Ru(1)	120.4(5)
N(1)−Ru(1)−N(2)	90.4(2)	C(19)−N(2)−Ru(1)	119.7(5)
N(1)−Ru(1)−P(2)	94.76(18)	N(1)−C(3)−C(4)	122.2(7)
N(2)−Ru(1)−P(2)	80.88(17)	O(1)−C(3)−C(4)	120.0(6)
N(1)−Ru(1)−P(1)	79.97(16)	C(3)−C(4)−P(1)	105.2(5)
N(2)−Ru(1)−P(1)	169.57(17)	N(2)−C(19)−C(20)	122.9(7)
P(2)−Ru(1)−P(1)	103.67(9)	O(2)−C(19)−C(20)	119.4(7)

shorter 2.080(6) Å [2.067(5) Å] the N(1) atom *trans* to chlorine. The longer Ru−P bond distance, 2.292(2) Å [2.283(2) Å], is *trans* to nitrogen, and the shorter, 2.249(2) Å [2.2602) Å], is *trans* to chlorine. The Ru(1)−Cl(2) bond distance, 2.472(2) Å [2.472(2) Å], with Cl(2) *trans* to phosphorus is slightly longer than the Ru−Cl(1) distance, 2.452(2) Å [2.451(2) Å], with Cl(1) *trans* to nitrogen. This is consistent with the larger *trans* influence of phosphorus compared to nitrogen.[17,18] The three angles involving the coordinated atoms *trans* to one another, ranging from 169.27(8)° to 173.07(16)° [169.57(17)° to 171.90(16)°], indicate slight distortions from ideal octahedral geometry. The *P*,*N* bite angles of 78.75(17)° and 81.11(18)° [79.97(16)° and 80.88(17)°] are in accordance with other five-membered phosphorus, nitrogen chelates.[19] The double-bond character of N(1)−C(3) and N(2)−C(19) bonds is reflected in their lengths 1.300(9) and 1.239(9) Å [1.302(8) and 1.288(9) Å].

***trans,trans,trans*-[RuCl$_2$(PCH$_2$-oxazoline)$_2$] (2).** The reaction of 2 equiv of ligand **I** with 1 equiv of [RuCl$_2$(COD)]$_n$ in refluxing EtOH afforded two isomeric products. The major isomer, compound **1**, is soluble in EtOH while the minor one, **2**, precipitates in EtOH and was extracted with CH_2Cl_2 from unreacted [RuCl$_2$(COD)]$_n$ (eq 2, for clarity the front PCH$_2$-oxazoline ligand is drawn in bold). The elemental analysis of **2**



is in agreement with the formulation [RuCl$_2$(PCH$_2$-oxazoline)$_2$], and the mass spectrum contains an intense peak for the fragment [RuCl(PCH$_2$-oxazoline)$_2$]$^+$. While there are two *P*,*N* ligands in the molecule, the $^{31}P\{^1H\}$ NMR spectrum of **2** in $CDCl_3$ exhibits a singlet at δ 41.3. The ^1H NMR spectrum exhibits only three resonances for the six methylenic protons. There is therefore a mirror plane in the molecule which creates three pairs of enantiotopic protons. The only two possible structures for **3** are of types **D** and **E**, and to distinguish between them, we performed a 500 MHz ^1H ROESY NMR experiment in CD_2Cl_2. There are two key cross peaks: the first one is between the oxazoline NCH$_2$ protons at δ 3.90 and aryl protons, and the second is between the OCH$_2$ protons and aryl protons. This is not consistent with a *cis* arrangement of the *P*,*N* chelates, and only structure **E** can account for the existence of these cross peaks. Complex **2** should therefore be formulated as *trans,trans,trans*-[RuCl$_2$(PCH$_2$-oxazoline)$_2$]. Furthermore, the $^{13}C\{^1H\}$ and ^1H NMR spectra of **2** exhibit a broad virtual triplet for the PCH$_2$ carbon and protons, respectively, and the *ipso* carbon atoms of the four P-phenyl groups give rise to a well-resolved virtual triplet ($|^{1+3}J_{PC}| = 37.4$ Hz).[20−24] This is consistent with the pattern of an AXX′ (A = C; X = X′ = P) spin system where the $J_{XX'}$ coupling constant is large. These data confirm that the phosphorus atoms occupy mutually *trans* positions.

***cis,cis,trans*-[RuCl$_2$(PCH$_2$-oxazoline-Me$_2$)$_2$] (3).** In order to study the influence of the substituents α to the nitrogen atom of the oxazoline ring on the coordination properties of such ligands, we extended the procedure described for **2** to the ligand PCH$_2$-oxazoline-Me$_2$, and complex **3** was isolated in 55% yield after refluxing the reaction mixture for 3 h.

While with the PCH$_2$-oxazoline ligand two complexes were detected and isolated, the same procedure using PCH$_2$-oxazoline-Me$_2$ led to the formation of only complex **3**, of which the elemental analysis data indicate a composition [RuCl$_2$(PCH$_2$-oxazoline-Me$_2$)$_2$]. Its $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ exhibits a singlet at δ 40.9, indicative of a mirror plane or a C_2 axis for the molecule in solution. The ^1H NMR spectrum exhibits two singlets for the NC(CH$_3$)$_2$ protons and an AB spin system for

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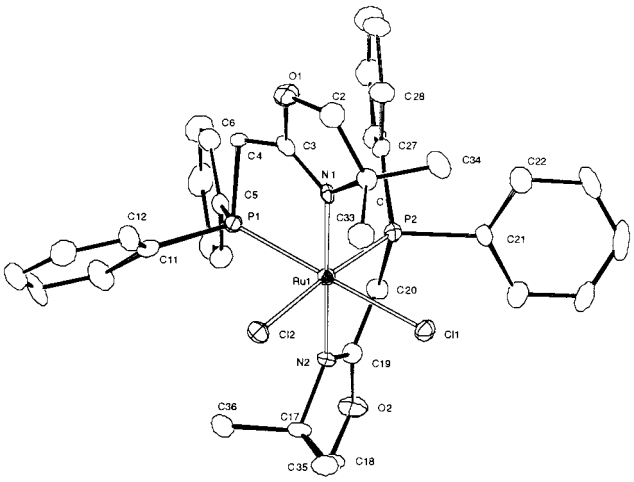
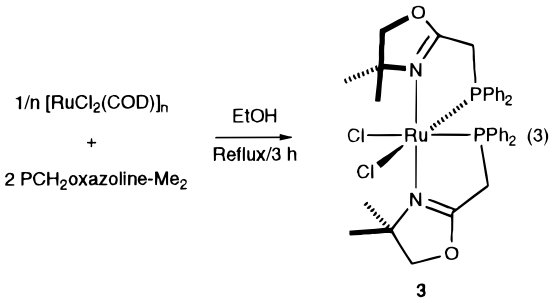


Figure 2. ORTEP view of the structure of the complex **3** together with the atomic numbering scheme. The ellipsoids for the atoms are drawn at the 30% probability level.



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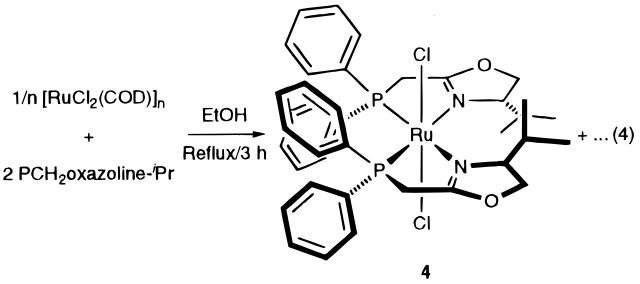
the methylenic OCH_2 protons, indicating their diastereotopic nature. There is therefore no mirror plane in the molecule, and the geometry of **3** cannot be described by structures of type **D** or **E**. At this stage, we are left with possibilities **B** or **C**. The PCH_2 protons exhibit in the ^1H NMR spectrum an ABX spin system of the "filled-in" type, consistent with a small *cis* $J_{PP'}$ coupling.[20,22] The $^2J_{HH}$ coupling was determined from the $^1H\{^{31}P\}$ NMR spectrum. Similarly, the PCH_2 carbons show in the $^{13}C\{^1H\}$ NMR spectrum a multiplet which has the appearance of a "filled-in" doublet. From this pattern, the $^2J_{PP'}$ coupling constant was extracted and found to be 31.3 Hz, which is in the expected range for two phosphorus atoms in *cis* position. The formulation of **3** as *cis,cis,trans*-[$RuCl_2$(PCH_2-oxazoline-Me_2)$_2$] has been also confirmed by an X-ray diffraction study on the crystals of its dichloromethane solvate. A view of the structure of **3** is shown in Figure 2 together with the atomic numbering system; selected bond distances and angles are given in Table 2. As expected from the mutual *trans* arrangement of the two nitrogen atoms, the Ru−N bond distances are similar, 2.122(6) and 2.133(6) Å. Although this molecule has no crystallographically imposed symmetry in the solid state, it shows an approximate C_2 symmetry with the pseudo-2-fold axis bisecting the Cl−Ru−Cl and P−Ru−P angles. The Ru−P bond distances, 2.267(3) and 2.290(2) Å, are similar whereas the Ru−Cl distances, 2.466(2) and 2.466(3) Å, involving chlorine atoms *trans* to phosphorus are identical. The three angles involving the coordinated atoms *trans* to one another, 175.77(9)°, 176.19(9)°, and 179.3(3)° indicate smaller distortions from ideal octahedral geometry than in complex **1**. The *P,N* bite angles are similar, 82.09(18)° and 81.3(2)°, and in accordance with those found in **1**. The double-bond character of the N(1)−C(3) and N(2)−C(19) bonds is reflected in their length, 1.283(10) and 1.288(10) Å, respectively.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3**·CH_2Cl_2

Bond Distances			
Ru(1)−N(2)	2.133(6)	Ru(1)−N(1)	2.122(6)
Ru(1)−P(2)	2.267(3)	Ru(1)−P(1)	2.290(2)
Ru(1)−Cl(2)	2.466(3)	Ru(1)−Cl(1)	2.466(2)
P(1)−C(5)	1.813(8)	P(2)−C(20)	1.877(8)
O(1)−C(3)	1.347(9)	O(1)−C(2)	1.438(9)
O(2)−C(19)	1.332(9)	O(2)−C(18)	1.458(10)
N(1)−C(1)	1.496(9)	N(2)−C(19)	1.288(10)
N(2)−C(17)	1.515(10)	C(1)−C(34)	1.519(11)
C(1)−C(33)	1.517(11)	C(1)−C(2)	1.544(11)
C(3)−C(4)	1.501(11)	C(17)−C(36)	1.554(11)
C(17)−C(35)	1.567(11)	C(17)−C(18)	1.553(11)
C(19)−C(20)	1.486(11)		

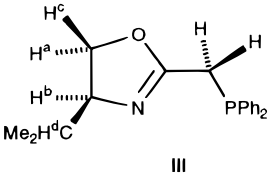
Bond Angles			
N(2)−Ru(1)−N(1)	179.3(3)	N(2)−Ru(1)−P(2)	81.3(2)
N(1)−Ru(1)−P(2)	98.07(19)	N(2)−Ru(1)−P(1)	98.31(19)
N(1)−Ru(1)−P(1)	82.09(18)	P(2)−Ru(1)−P(1)	93.78(9)
N(2)−Ru(1)−Cl(2)	95.5(2)	N(1)−Ru(1)−Cl(2)	85.09(19)
P(2)−Ru(1)−Cl(2)	175.77(9)	P(1)−Ru(1)−Cl(2)	89.43(9)
N(2)−Ru(1)−Cl(1)	85.02(19)	N(1)−Ru(1)−Cl(1)	94.61(18)
P(2)−Ru(1)−Cl(1)	88.55(9)	P(1)−Ru(1)−Cl(1)	176.19(9)
Cl(2)−Ru(1)−Cl(1)	88.39(8)	C(4)−P(1)−Ru(1)	102.6(3)
C(20)−P(2)−Ru(1)	103.0(3)	C(3)−N(1)−Ru(1)	120.1(5)
C(19)−N(2)−Ru(1)	120.6(5)	N(1)−C(3)−C(4)	123.9(7)
C(3)−C(4)−P(1)	107.7(5)	N(2)−C(19)−C(20)	123.4(7)
C(19)−C(20)−P(2)	106.7(6)		

***trans,cis,cis*-[$RuCl_2$(PCH_2-oxazoline-^{i}Pr)$_2$] (4).** The reaction of 2 equiv of enantiomerically pure ligand **III** with 1 equiv of $[RuCl_2(COD)]_n$ could lead to a maximum of eight stereoisomers (two diastereomers for each of structures **A**−**C** plus **D** and **E** in Scheme 1). The presence of at least four complexes was detected by $^{31}P\{^1H\}$ NMR spectroscopy where they exhibit singlets and AB spin systems in the range 40−54.5 ppm. Complex **4** was isolated by column chromatography in 27% yield (eq 4). The other products could not be isolated pure and



4

were retained on either alumina or silica gel. The $^{31}P\{^1H\}$ NMR spectrum of **4** in $CDCl_3$ exhibits a singlet at δ 54.5 indicative of a mirror plane or a C_2 axis in the molecule. All protons were assigned using ^1H homonuclear decoupling and $^1H\{^{31}P\}$ and 2D ^1H NMR experiments. As in the case of the free ligand, the methyl protons of the ^{i}Pr group appear in the ^1H NMR spectrum as a pair of doublets at similar chemical shifts. The PCH_2 protons were located at δ 3.20 and 3.85. Proton NCH^b could be easily distinguished by virtue of its complexity: it couples to H^a ($^3J_{H^aH^b_{cis}} = 10.3$ Hz), H^c ($^3J_{H^cH^b_{trans}} = 6.0$ Hz), H^d ($^3J_{H^dH^b} = 2.6$ Hz), and one proton of the PCH_2 moiety ($^5J_{HH} = 1.5$ Hz) (see **III**).



III

Table 3. Enantioselective Transfer Hydrogenation of Acetophenone in Propan-2-ol Catalyzed by Chiral Ru(II) Complexes[a]

catalyst	time (min)	yield (%)[b]	ee (%)/(confign)[c]	turnover freq (h^{-1})[d]
4	15	63	74 (*R*)	504
	60	90	73 (*R*)	180
	180	96	72 (*R*)	64
in situ[e]	15	97	68 (*R*)	776
	60	98	61 (*R*)	196

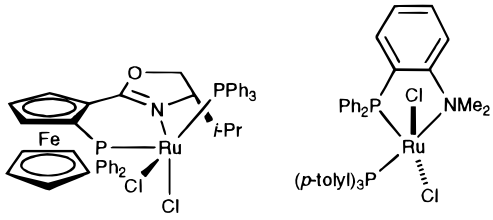
[a] Reactions were carried out in refluxing propan-2-ol using a 0.1 M substrate concentration, a 0.1 M solution of *i*-PrONa as a base, and a 1:200:5 Ru/ketone/base ratio. [b] Chemical yields determined by GC analysis on the crude reaction mixture at the reported time. [c] Determined by GC analysis (Lipodex A 25 m × 0.25 mm), absolute configurations were determined by comparing optical rotations of isolated 1-phenylethanol with literature data. [d] Given as a time-average. [e] See text for details.

This $^5J_{HH}$ coupling was also observed in related systems with phosphinooxazoline-type ligands.[8,25] The OCH_2 protons could be distinguished on the basis of the different magnitudes of their vicinal scalar couplings to H^b. In planar five-membered rings *cis*-vicinal couplings are greater than *trans*-vicinal couplings.[26] The $^{13}C\{^1H\}$ NMR spectrum of **4** is very helpful in the determination of the geometry of the molecule: the PCH_2 carbons exhibit an AXX′ spin system "filled-in" doublet at δ 33.5 of which the analysis allows the determination of $^2J_{PP'} =$ 38.9 Hz. This coupling constant is in the range found for two phosphorus atoms in *cis* position. Therefore among the possible structures of **4**, types **C** and **E** can be ruled out. To distinguish between **B** and **D** we recorded the 600 MHz ^1H NOESY spectrum in CD_2Cl_2. There are no cross peaks, neither between the NCH protons at 4.35 ppm and aryl protons nor between the OCH_2 protons at 4.45 and 4.55 ppm and aryl protons. Therefore complex **4** belongs to type **D** and is formulated as *trans*,*cis*,*cis*. Furthermore, this assignment is in agreement with the $^{31}P\{^1H\}$ NMR chemical shift of 54.5 ppm, downfield with respect to the expected chemical shift for a phosphorus *trans* to chloride, as would be the case for type **B** complex and as found in **3** (δ 40.9).[17,27,28] By comparison with the $^{31}P\{^1H\}$ NMR data collected in this study we conclude that the reaction mixture contains, among other products, the two possible diastereomeric structures of the type **A** observed by $^{31}P\{^1H\}$ NMR when we used the chiral PCH_2-oxazoline-^{i}Pr ligand. Another, chiral at phosphorus *P*,*N* ligand has recently been found to lead to a similar structure for its Ru(II) complex.[29]

Catalytic Transfer Hydrogenation of Acetophenone. As part of our interest in the reactivity of Ru complexes with multidentate heterotopic ligands that contain oxazoline unit(s) and a phosphorus donor atom,[25] we undertook a preliminary study on the asymmetric transfer hydrogenation of acetophenone in propan-2-ol catalyzed by **4** (see Discussion and Table 3 for results and details).

Discussion

Synthesis of the Ru Complexes. Reaction of 1 equiv of **I** with 1 equiv of $[RuCl_2(PPh_3)_3]$ in CH_2Cl_2 or toluene at room temperature led to the formation of a mixture of at least five complexes which gave rise in $^{31}P\{^1H\}$ NMR spectroscopy to doublets of doublets with cis $J_{P^AP^B}$ coupling constants. Upon addition of a second equivalent of *P*,*N* the orange solution turned yellow and a major complex formed at the expense of the others. When this reaction was repeated starting from a 2:1 ligand/Ru ratio, it led selectively to the formation of complex **1** in 90% isolated yield. The poor selectivity of the reaction when a 1:1 ligand/Ru ratio was used is surprising when compared to studies with other *P*,*N*-type ligands. For example, complexes **5** and **6** were prepared following similar procedures and gave high yields of a pentacoordinated complex with one bidentate *P*,*N* ligand.[13,15,19] Electronic and steric effects always play a crucial



5 **6**

role in coordination chemistry, and the latter govern the behavior of diphosphine ligands such as $Ph_2P(CH_2)_nPPh_2$ toward $[RuCl_2(PPh_3)_3]$.[28] This could account for the difference in reactivity between the six-membered-ring (phosphinoferrocenyl)oxazoline ligand in **5** and ligand **I**. Nevertheless the phosphinoamine ligand in **6** has a P−Ru−N bite angle (81.88(8)°) almost identical to that observed in the X-ray crystal structure of **1** (80.88(17)° and 79.97(16)° molecule B). It is likely that the electronic contribution of the tertiary phosphine is important to stabilize the 16-electron pentacoordinated complex **6** and that P(*p*-tolyl)$_3$ should be preferred to PPh_3. Using $[RuCl_2(COD)]_n$ as a metal precursor and a 1:1 *P*,*N*/Ru ratio led to the formation of complexes **1** and **2** which both have the chemical composition $[RuCl_2(PCH_2\text{-oxazoline})_2]$. These experiments suggested that there is a thermodynamic preference for the formation of bis(chelate) compounds of the type $[RuCl_2(PCH_2\text{-oxazoline})_2]$. As expected, an increased yield was observed for the reaction between *P*,*N* and $[RuCl_2(COD)]_n$ when a 2:1 ligand/Ru ratio was used. In complex **2** the *trans* arrangement of the phosphorus atoms is surprising since two donor atoms of high *trans* influence usually tend to occupy *cis* positions[17] as observed in the stable complexes *cis*-$[Pd(PCH_2\text{-oxazoline})_2](BF_4)_2$.[30] and *trans*,*cis*,*cis*-$[RuCl_2(P,O)_2]$ ($P,O = Ph_2PCH_2C(O)Ph$).[31] The low (ideally zero) dipolar moment of *trans*,*trans*,*trans*-$[RuCl_2(PCH_2\text{-oxazoline})_2]$ most likely explains the precipitation of the product in a polar solvent such as EtOH. This represents an obvious driving force for its formation. In a recent study, Otero *et al.* have succeeded in isolating complexes of the formula $[RuCl_2(COD)(N,N)]$ ($N,N =$ bis(pyrazol-1-yl)methane or bis(5-trimethylsilylpyrazol-1-yl)methane) upon reaction of $[RuCl_2(COD)]_n$ with *N*,*N* in a 1:1 molar ratio.[32] Interestingly, the subsequent addition of a second equivalent of ligand *N*,*N* led to *trans*-$[RuCl_2(N,N)_2]$ only in the case of bis(5-trimethylsilylpyrazol-1-yl)methane. No conclusive explanation was provided for this contrasting behavior. Obviously, subtle effects are at work, and,

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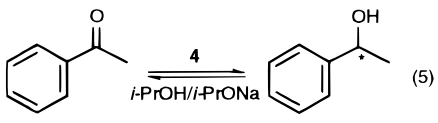
in order to evaluate the influence of the oxazoline substituents on the geometry of the complexes, we investigated the ligands PCH_2-oxazoline-Me_2 and PCH_2-oxazoline-^{i}Pr. All experiments were performed under similar conditions (1:2 Ru/ligand ratio, refluxing EtOH, 3 h).

The most selective reaction was obtained with PCH_2-oxazoline-Me_2 where only one complex, *cis,cis,trans*-[$RuCl_2$-(PCH_2-oxazoline-Me_2)$_2$], was detected. Despite their similar mode of preparation, the differences between the compounds obtained from **I** and **II** are surprising. They must be related to the nature of the substituents on each oxazoline. If two phosphinooxazoline ligands **II** were to coordinate in the equatorial plane, each pair of methyls would point toward another pair of methyls (as in structure **D**) or toward a pair of phenyls (as in structure **E**) and thus create in both cases an unfavorable steric clash. This is not the case with the smaller corresponding protons of **I**. Note that with PCH_2-oxazoline-Me_2 we failed to obtain a compound analogous to *cis*-[Pd(PCH_2-oxazoline)$_2$](BF_4)$_2$. Among the three possible structures **A**−**C** which avoid two coplanar PCH_2-oxazoline-Me_2 ligands, **B** is the only one where the two nitrogen atoms are in *trans* position, thus keeping further away the methyl substituents of the oxazolines.

Somewhat disappointingly, the reaction with the chiral ligand PCH_2-oxazoline-^{i}Pr was the least selective. From the reaction mixture, only compound *trans,cis,cis*-[$RuCl_2$(PCH_2-oxazoline-^{i}Pr)$_2$] **4** could be isolated pure. Its structure is different from those obtained with the ligands PCH_2-oxazoline and PCH_2-oxazoline-Me_2 and exhibits two phosphinooxazoline ligands coordinated to the metal in the equatorial plane, with the two phosphorus donor atoms in a *cis* arrangement. The bulky *i*-Pr substituents are not causing any steric clash when the two oxazoline rings are in close proximity since they point in opposite directions. The structure of **4** is to be compared with a recently reported X-ray crystallographic structure of a square-planar complex [Ni(*P,N*)$_2$](O_3SCF_3)$_2$ (*P,N* = (*S*)-^{i}Bu-phosphinoaryloxazoline) where the stereogenic carbons of the two oxazolines ring are in a pseudoaxial position relative to the P−Ni−N plane.[33] This study also showed that the *cis* arrangement of the phosphorus atoms is preferred to the *trans*.

Catalysis. The compound *trans,cis,cis*-[$RuCl_2$(PCH_2-oxazoline-^{i}Pr)$_2$] **4** exhibits a C_2 axis of symmetry and a structure related to those of **7** and **8**. Noyori *et al.* have shown that, despite their apparent similarity, complexes **7** and **8** exhibit very different reactivity for the catalytic transfer hydrogenation of acetophenone in propan-2-ol (**5**, 7% yield, 5% ee at 82 °C for 4 h; **8**, 93% yield, 97% ee at 45 °C for 7 h), a reaction of current interest.[34−39]



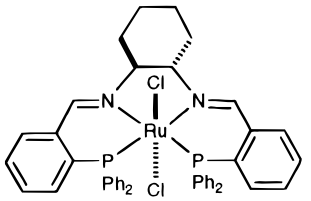
(5)

This difference between the diimine and the diamine complexes is due to the presence of the NH moiety in the diamine ligand, which is thought to be responsible for the stabilization of a six-membered transition state involving the Ru−H and the C=O fragment of the ketonic substrate.[35,40]

Table 4. Crystal Data and Structure Refinement for **1** and **3**·CH_2Cl_2

	1	**3**·CH_2Cl_2
formula	$C_{32}H_{32}Cl_2N_2O_2P_2Ru$	$C_{36}H_{40}Cl_2N_2O_2P_2Ru$·$CH_2Cl_2$
fw	710.51	851.54
temp (K)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	18.427(4)	15.757(5)
b (Å)	17.487(3)	12.212(4)
c (Å)	22.422(5)	11.390(3)
α (deg)		68.47(5)
β (deg)	113.44(6)	73.75(6)
γ (deg)		67.25(5)
vol (Å^3)	6629(2)	1856(1)
Z	8	2
density (calcd) (Mg/m^3)	1.424	1.524
abs coeff (cm^{-1})	0.761	0.833
final *R* indices [$I > 2\sigma(I)$][a]	R1 = 0.0673, wR2 = 0.1910	R1 = 0.0493, wR2 = 0.1392
R indices (all data)	R1 = 0.1599, wR2 = 0.2142	R1 = 0.1274, wR2 = 0.1639

[a] $R1 = \Sigma|F_o - F_c|/|\Sigma(F_o)$. $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.



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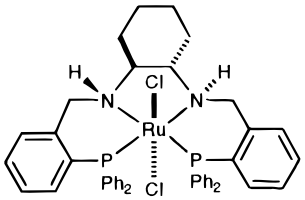

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Although complex **4** does not have any NH function, we obtained under standard reaction conditions a conversion up to 96% with 72% ee for this reaction (see Table 4). Reducing the amount of base from 24 to 5 equiv per Ru did not have any significant effect on either conversion or enantioselectivity. Whereas, in asymmetric transfer hydrogenation, long reaction times usually deteriorate the enantiomeric purity of the product, we found in our case that the enantioselectivity remains almost constant during the course of the reaction (up to 3 h). Since different isomeric complexes were formed with ligand **III** that could not be isolated pure, we decided to explore their catalytic potential *in situ* in order to examine the importance of different geometries on the catalysis. In a first experiment, the ruthenium complexes were prepared according to eq 4 but using propan-2-ol as a solvent for both their synthesis and catalysis. In a second set of experiments, the complex mixture of ruthenium complexes prepared according to eq 4 (in refluxing EtOH, 3 h) was taken to dryness and redissolved in propan-2-ol. In both cases, the catalytic results were identical: the conversion was 97% with 68% ee after 15 min. It is interesting that the crude mixture gives higher turnover frequency (TOF) than **4** alone with, however, a lower enantioselectivity. This indicates that

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the mixture contains other catalyst precursors than **4** and that the *trans,cis,cis* ligand arrangement may not be the optimum for catalysis. One can expect that a Ru−Cl bond *trans* to a P atom would be more reactive than a Ru−Cl bond *trans* to a chloride. It is difficult to comment on the slight decrease of enantioselectivity when starting from a mixture of two or more catalyst precursors. Nevertheless, the decrease of the enantiomeric purity with time when using the *in situ* catalyst mixture suggests that the reverse reaction becomes more significant, and this represents a clear disadvantage over the use of pure **4**. It is interesting to compare the activity of **4** with literature values for catalysts bearing only one chelating six-membered phosphinooxazoline, such as $[RuCl_2(PPh_3)(phosphinooxazoline)]$. Comparisons are not straightforward since reactions with the latter catalysts have not always been carried out under comparable conditions.[13,15,41] In transfer hydrogenation of ketones in propan-2-ol, a higher concentration of ketone gives a lower yield of alcohol,[42,43] while an increase of the amount of base can accelerate the reaction rate but may also deteriorate the enantioselectivity.[40] The best results were obtained with the complex $[RuCl_2(PPh_3)\{$(phosphinoaryl)oxazoline-^{i}Pr$\}]$ (80% yield, 78% ee, 3 min, 82 °C, [ketone] = 0.1 M, Ru:ketone:base = 1:1000:25),[15] $[RuCl_2(PPh_3)\{$(phosphinoferrocenyl)oxazoline-^{i}Pr$\}]$ (94% yield, >99% ee, 2 h, room temperature, [ketone] = 0.02 M, Ru:ketone:base = 1:200:4[13] and 77% yield, 48% ee, 5 min, 82 °C, [ketone] = 1 M, Ru:ketone:base = 1:1000:25[41]). Our preliminary results on complex **4** are encouraging and deserve further investigations on the optimization of the catalytic conditions. Further studies on the structure−reactivity relationship with metal complexes containing chiral ligands such as **III** are needed.

Experimental Section

All reactions were performed under purified nitrogen. Solvents were purified and dried under nitrogen by conventional methods. The ^{1}H NMR spectra were recorded at 300.13 MHz, $^{31}P\{^1H\}$ NMR spectra at 81.0 or 121.5 MHz, $^{13}C\{^1H\}$ NMR spectra at 75.4 MHz on a FT Bruker AC200 or AC300 instrument, IR spectra in the 4000−400 cm^{-1} range on a Bruker IFS66 FT spectrometer, far-IR spectra in the 500−90 cm^{-1} range on a Bruker ATS 83 spectrometer. The ligands PCH_2-oxazoline and PCH_2-oxazoline-Me_2 were prepared following a method described elsewhere.[8]

(2-Oxazolin-4-(*S*)-isopropyl-ylmethyl)diphenylphosphine (PCH_2-oxazoline-^{i}Pr, III). IR (CH_2Cl_2): ν(cm^{-1}) 1663 (C═N). ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 0.80 (d, 3 H, $^3J_{HH}$ = 8.1 Hz, CH(CH_3)(C*H*$_3$)), 0.85 (d, 3 H, $^3J_{HH}$ = 8.1 Hz, CH(C*H*$_3$)(CH_3)), 1.60 (sept, 1 H, $^3J_{HH}$ = 8.1 Hz, C*H*(CH_3)$_2$), AB spin system (A = B = H) δ_A 3.05 (1 H, $^2J_{HH}$ = 13.5 Hz, PC*H*H) and δ_B 3.10 (1 H, $^2J_{HH}$ = 13.5 Hz, PCH*H*), 3.80 (overlapping m, 2 H, NCH and OC*H*H), 4.10 (m, 1 H, OCH*H*), 7.10−7.40 (m, 10 H, aryl). $^{13}C\{^1H\}$ ($CDCl_3$, 75.5 MHz): δ 17.9 (s, CH(*C*H_3)(CH_3)), 18.5 (s, CH(CH_3)(*C*H_3)), 32.4 (s, *C*H(CH_3)$_2$), 28.3 (d, $^1J_{PC}$ = 18.5 Hz, PCH_2), 70.2 (s, NCH), 72.1 (s, OCH_2), 127.4 (d, *m*-aryl), 127.0−138.0 (m, aryl), 163.8 (d, $^2J_{PC}$ = 7.3 Hz, C═N). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ -17.2.

Ru(II) Complexes. All the complexes are air-stable for a short period of time but should be best kept under inert atmosphere. Yields of Ru complexes are given based on the phosphinooxazoline ligand. The compound $[RuCl_2(PPh_3)_3]$ and $[RuCl_2(COD)]_n$ were prepared according to literature procedures.[44,45]

***cis,cis,cis*-[$RuCl_2$(PCH_2-oxazoline)$_2$] (1).** In a 100 mL Schlenk flask were reacted ligand PCH_2-oxazoline (0.200 g, 0.745 mmol) and $[RuCl_2(PPh_3)_3]$ (0.340 g, 0.355 mmol) in CH_2Cl_2 (20 mL) The deep reddish solution quickly turned yellow and was stirred for 15 min. The solvent was removed under reduced pressure to afford a yellow solid, which was washed twice with a 1:3 mixture of toluene/hexane (2 × 15 mL) and Et_2O (2 × 10 mL). Compound **1** was obtained as a yellow powder (0.475 g, yield 90%). IR (KBr): ν (cm^{-1}) 1647, 1636 vs (C═N). ^{1}H NMR ($CDCl_3$, 300.16 MHz): δ 2.15 (m, 1 H), 3.05 (m, 1 H), 3.45, 3.45 (overlapping m, 2 H, PCH_2), 3.55 (overlapping m, 3 H), 4.00 (m, 1 H), 4.25 (m, 1 H), 4.45 (m, 1 H), 4.70 (m, 1 H), 4.80 (m, 1 H), 6.90−7.50 (m, 16 H), 8.20 (m, 4 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ AB spin system δ_A 52.4 (d, $^2J_{PP}$ = 30.5 Hz), δ_B 50.2 (δ, $^2J_{PP}$ = 30.5 Hz). Anal. Calcd for $C_{32}H_{32}Cl_2N_2O_2P_2Ru$: C, 54.09; H, 4.54. Found: C, 54.45; H, 4.84.

***trans, trans, trans*-[$RuCl_2$(PCH_2-oxazoline)$_2$] (2).** In a 100 mL Schlenk flask fitted with a reflux condenser were reacted the ligand PCH_2-oxazoline (0.210 g, 0.780 mmol) and $[RuCl_2(COD)]_n$ (0.105 g, 0.390 mmol) in EtOH (20 mL). The brown suspension was heated under reflux for 3 h and then cooled to room temperature. The yellow solution containing pure *cis,cis,cis*-[$RuCl_2$(PCH_2-oxazoline)$_2$] **1** was separated from the brown suspension by means of a cannula fitted with a glass-fiber filter paper. The brown residue was treated with CH_2Cl_2 (20 mL), which extracted a yellow-orange solution, which was separated from the remaining solid with a cannula. This solution was concentrated to ca. 2 mL, and addition of pentane afforded a precipitate, which was further washed with pentane (2 × 10 mL). The product was obtained as a yellow-orange powder (0.055 g, yield 20%). IR (KBr): ν (cm^{-1}) 1631 vs (C═N). far-IR (polyethylene): ν (cm^{-1}) 391 s, 357 m, 271 m, 213 w. ^{1}H NMR ($CDCl_3$, 300.16 MHz): δ 3.70 (m with appearance of t, 4 H, PCH_2), 3.78 (t, 4 H, $^3J_{HH}$ = 9.5 Hz, NCH_2), 4.45 (t, 4 H, $^3J_{HH}$ = 9.5 Hz, OCH_2), 7.30−7.40 (m, 12 H, aryl), 7.70−7.80 (m, 8 H, aryl). $^{13}C\{^1H\}$ ($CDCl_3$, 125.7 MHz): δ 30.3 (m with appearance of t, PCH_2), 57.5 (s, NCH_2), 69.6 (s, OCH_2), 128.0 (m, *o*-aryl), 129.7 (s, *p*-aryl), 133.0 (virtual t, $^{1+3}J_{PC}$ = 37.4 Hz, *ipso*-aryl), 133.5 (m, *m*-aryl), 172.2 (br s, C═N). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 41.3 (s). Anal. Calcd for $C_{32}H_{32}Cl_2N_2O_2P_2Ru$: C, 54.09; H, 4.54; N, 3.94. Found: C, 54.13; H, 4.44; N, 3.90.

***cis,cis,trans*-[$RuCl_2$(PCH_2-oxazoline-Me_2)$_2$] (3).** In a 100 mL Schlenk flask fitted with a reflux condenser were reacted ligand **II** (0.855 g, 2.88 mmol) and $[RuCl_2(COD)]_n$ (0.405 g, 1.44 mmol) in EtOH (40 mL). The brown suspension was heated under reflux for 3 h and then cooled to room temperature. The yellow solution was separated from the brown suspension (unreacted $[RuCl_2(COD)]_n$) by means of a cannula fitted with a glass-fiber filter paper. The suspension was further washed with 15 mL of EtOH, the filtrates were collected together, and the solvent was evaporated under reduced pressure to approximately 5 mL. Addition of pentane (20 mL) afforded a yellow precipitate. This procedure was repeated to collect a second crop, and the solid fractions were washed with Et_2O (2 × 15 mL) to remove **II** and dried in vacuo. The product was isolated as a yellow powder (0.615 g, 55% yield). IR (KBr): ν (cm^{-1}) 1631 vs (C═N). far-IR (polyethylene): ν (cm^{-1}) 390 m, 366 w, 295 s, 267 w, 235 vs. ^{1}H NMR (CD_2Cl_2, 500.13 MHz): δ 1.25 (s, 6 H, NC(CH_3)(C*H*$_3$)), 1.75 (s, 6 H, NC(C*H*$_3$)(CH_3)$_2$), ABXX′ spin system (A = B = H; X = X′ = P) δ_A 3.15 ("filled-in d", 2 H, $^2J_{HH}$ = 18.1 Hz, $^{2+4}J_{PH}$ = 11.1 Hz, PC*H*H), δ_B 3.25 ("filled-in d", 2 H, $^2J_{HH}$ = 18.1 Hz, $^{2+4}J_{PH}$ = 8.5 Hz, PCH*H*), AB spin system δ_A 4.25 (d, 2 H, $^2J_{HH}$ = 8.1 Hz, OC*H*H), δ_B 4.30 (d, 2 H,$^2J_{HH}$ = 8.1 Hz, OCH*H*), 6.90 (m, 4 H, aryl), 7.15−7.30 (m, 14 H, aryl H), 7.50 (m, 2 H, aryl H). $^{13}C\{^1H\}$ ($CDCl_3$, 75.4 MHz): δ 28.0 (s, NC(*C*H_3)(CH_3)), 28.5 (s, NC(CH_3)(*C*H_3)$_2$), 32.0 ("filled-in d", $^2J_{XX'\ cis}$ = 31.3 Hz, $^1J_{AX}$ = 27.8 Hz, $^3J_{AX}$ = 1.2 Hz, PCH_2), 71.7 (s, N*C*(CH_3)$_2$), 83.5 (s, OCH_2), 126.8−133.5 (m, aryl H), 134.6 ("filled-in d", $^{1+3}J_{PC}$ = 43.2 Hz, *ipso*-aryl), 136.7 ("filled-in d", $^{1+3}J_{PC}$ = 41.3 Hz, *ipso*-aryl), 171.0 (m, C═N). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 40.9 (s). Anal. Calcd for $C_{36}H_{40}Cl_2N_2O_2P_2Ru$: C, 56.40; H, 5.26; N, 3.65. Found: C, 56.20; H, 5.27; N, 3.45.

***trans, cis, cis*-[$RuCl_2$(PCH_2-oxazoline-^{i}Pr)$_2$] (4).** Following the procedure described for **3**, but starting from PCH_2-oxazoline-^{i}Pr (0.257 g, 0.825 mmol) and $[RuCl_2(COD)]_n$ (0.115 g, 0.412 mmol), the orange solid obtained was purified by filtration over silica (10 cm × 1 cm,

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THF). The first orange fraction was collected and the solvent removed under reduced pressure. The solid was dried in vacuo and isolated as an orange powder (0.090 g, 27% yield). IR (KBr): ν (cm^{-1}) 1637 vs (C═N). far-IR (polyethylene): ν (cm^{-1}) 398 s, broad absorptions in the range 340−280 w. ^{1}H NMR ($CDCl_3$, 600.22 MHz): δ 0.75 (d, 6 H, $^3J_{HH}$ = 6.6 Hz, CH(C*H*$_3$)(CH$_3$)), 0.90 (d, 6 H, $^3J_{HH}$ = 6.6 Hz, CH(CH$_3$)(C*H*$_3$)), 2.85 (sept. of d, 2 H, $^3J_{HH}$ = 6.6 Hz, $^3J_{H^dH^b}$ = 2.6 Hz, C*H*^{d}(CH$_3$)$_2$), ABXX′ spin system (A = B = H, X = X′ = P) δ_A 3.20 ("filled-in d", 2 H, $^2J_{HH}$ = 17.0 Hz, $^{2+4}J_{PH}$ = 11.2 Hz, PC*H*H), δ_B 3.85 ("filled-in d", 2 H, $^2J_{HH}$ = 17.0 Hz, $^{2+4}J_{PH}$ = 9.1 Hz, $^5J_{HH}$ = 1.5 Hz, PCH*H*), 4.35 (m, 2 H, $^3J_{H^bH^a\ cis}$ = 10.2 Hz, $^3J_{H^bH^c\ trans}$ = 6.0 Hz, $^3J_{H^bH^d}$ = 2.6 Hz, $^5J_{HH}$ = 1.5 Hz, NCH^b), 4.45 (dd, 2 H, $^2J_{H^cH^a}$ = 8.8 Hz, $^3J_{H^cH^b\ trans}$ = 6.0 Hz, OC*H*^{c}H), 4.55 (dd, 2H, $^3J_{H^aH^b\ cis}$ = 10.2 Hz, $^2J_{H^aH^c}$ = 8.8 Hz, OCH*H*^{a}), 7.00−7.55 (m, 20 H, aryl). ^{13}C{^{1}H} ($CDCl_3$, 150.9 MHz): δ 14.6 (s, CH(*C*H$_3$)(CH$_3$)), 19.8 (s, CH(CH$_3$)(*C*H$_3$)), 28.5 (s, *C*H(CH$_3$)$_2$), 33.5 ("filled-in d", $^2J_{XX'cis}$ = 38.9 Hz, $^1J_{AX}$ = 23.2 Hz, $^3J_{AX}$ = 4.3 Hz, PCH$_2$), 70.0 (s, NCH), 71.4 (s, OCH$_2$), 127.39 and 127.43 (two overlapping "filled-in d" with appearance of q, $^{3+5}J_{PC}$ = 10 Hz determined by a ^{13}C{^{31}P,^{1}H} experiment, *m*-aryl), 129.2 (s, *p*-aryl), 129.4 (s, *p*-aryl), 133.3 (AXX′ spin system with appearance of triplet, $^{2+4}J_{PC}$ = 9.0 Hz, *o*-aryl), 133.8 (AXX′ spin system with appearance of triplet, $^{2+4}J_{PC}$ = 10.0 Hz, *o*-aryl), 135.1 ("filled-in d", $^2J_{XX'cis}$ = 38.9 Hz, $^1J_{AX}$ = 41.7 Hz, $^3J_{AX'}$ = 5.6 Hz, *ipso*-aryl), 136.7 ("filled-in d", $^2J_{XX'cis}$ = 38.9 Hz, $^1J_{AX}$ = 34.9 Hz, $^3J_{AX'}$ = 3.6 Hz, *ipso*-aryl), 171.5 (AXX′ spin system with appearance of triplet, J_{PC} = 17.0 Hz, C═N). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 54.5. Anal. Calcd for $C_{38}H_{44}Cl_2N_2O_2P_2Ru$: C, 57.43; H, 5.53; N, 3.53 Found: C, 57.22; H, 5.52; N, 3.46.

Catalytic Transfer Hydrogenation. Typical procedure for catalytic transfer hydrogenation of acetophenone: **4** (0.0079 g, 0.01 mmol) was dissolved in 19.5 mL of ^{i}PrOH in a 50 mL two-neck round-bottom flask fitted with a reflux condenser. 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 0.5 mL (0.05 mmol) of a solution of ^{i}PrONa in ^{i}PrOH (0.1 M) was added. The volume of ^{i}PrOH was adjusted so that all catalytic runs were performed with an initial concentration in acetophenone of 0.1 M. The addition of ^{i}PrONa was considered as the starting time of the reaction. The extent of conversion was determined by gas chromatography using a Lipodex A 25 m × 0.25 mm column.

X-ray Structure Determination of 1 and 3•CH_2Cl_2. The intensity data of both complexes were collected at room temperature on a Siemens AED (**1**) and on a Philips PW 1100 (**3**·CH_2Cl_2) single-crystal diffractometer using graphite-monochromated Mo Kα radiation and the $\theta/2\theta$ scan technique. Crystallographic and experimental details for both structures are summarized in Table 4.

A correction for absorption was made for both complexes [maximum and minimum values for the transmission coefficient were 1.000 and 0.692 (**1**), 1.000 and 0.875 (**3**).[46,47] The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms.

In both structures the hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms. In the final cycles of refinement a weighting scheme $w = 1/[\sigma^2F_o^2 + (0.0916P)^2]$ (**1**) and $w = 1/[\sigma^2F_o^2 + (0.0677P)^2]$ (**3**•CH_2Cl_2) where $P = (F_o^2 + 2F_c^2)/3$ was used.

All calculations were carried out on the DIGITAL AlphaStation 255 computers of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, using the SHELX-97 systems of crystallographic computer programs.[47]

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Supporting Information Available: X-ray crystallographic files in CIF format of the structures of *cis,cis,cis*-[$RuCl_2$(PCH_2-oxazoline)$_2$] and *cis,cis,trans*-[$RuCl_2$(PCH_2-oxazoline-Me_2)$_2$]·CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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