Ruthenium(II) Complexes Containing Optically Active Hemilabile P,N,O-Tridentate Ligands. Synthesis and Evaluation in Catalytic Asymmetric Transfer Hydrogenation of Acetophenone by Propan-2-ol

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The trifunctional ligands (*R*)-1-(diphenylphosphino)-2-((1*R*,2*S*,5*R*)-menthoxy)-1-(2-pyridyl)-ethane (**2R**), (*S*)-1-(diphenylphosphino)-2-((1*R*,2*S*,5*R*)-menthoxy)-1-(2-pyridyl)ethane (**2S**), and (*S*)-(phenyl(2-anisyl)phosphino)(2-pyridyl)methane (**3**) have been synthesized, as well as the corresponding $RuCl_2(PPh_3)(L)$ complexes. The complexes $RuCl_2(PPh_3)$(**2R**) (**5**) and $RuCl_2(PPh_3)$(**2S**) (**6**) were isolated as mixtures of two isomers, **5a** and **5b** and **6a** and **6b**, respectively. In each of these isomers, the ligands **2** are η^3-(P,N,O) bound. They differ by the position of the triphenylphosphine, which is either in a trans position relative to the pyridyl ring (**5a** or **6a**) or in a trans position relative to the ether function (**5b** or **6b**). Variable temperature NMR experiments have shown that the hemilabile character in solution of the ligands **2** is through their pyridyl arm in the isomers **a** or their ether arm in **b**. The complexes **6b** and $RuCl_2(PPh_3)$(**3**) (**9**) were characterized by X-ray diffraction. The complexes **5**, **6**, and **9** are very active catalysts for the transfer hydrogenation of acetophenone by propan-2-ol in basic media, the higher activity being observed for **9** (turnovers frequency 48 900 h^{-1}). The enantioselectivity is modest and dependent on the reactions conditions. The best result has been observed for **5**, with an ee of 60%.

Introduction

In recent years, the design of so-called hemilabile ligands containing one functional group strongly bound to a late transition metal and another coordinatively labile has been of considerable interest and developed by several groups.[1−3] The weakly bound functional group plays the role of an intramolecular solvent molecule assuring the stability of the complex and possibly improving its stoichiometric reactivity[4−6] or catalytic activity.[7]

For our part, we have tried to apply this concept to tridentate ligands, which are expected to exert more control on the coordination sphere of a metal than bidentate ligands, with a possible effect on the catalytic properties of the resulting complexes.[8] This led us to synthesize the ligand 1-(diphenylphosphino)-2-ethoxy-1-(2-pyridyl)ethane (**1**), which associates phosphorus to a hard donor center, the oxygen of an ether function, and a quite soft donor center, the nitrogen of a pyridine cycle. We have previously shown that in the all *cis*-$RuCl_2(\mathbf{1})_2$ complex, the ligand **1** is P,N bonded. In polar solvent it evolves to $[RuCl(\mathbf{1})_2]^+Cl^-$, in which one of the ligands is P,N,O bonded, the ether arm being weakly bonded to ruthenium.[9] More recently, we have observed the easy formation of the complex $RuCl_2(PPh_3)$(**1**) by the reaction of 1 equiv of **1** with $RuCl_2(PPh_3)_3$. We have shown the later complex to be, to the best of our knowledge, the most efficient ruthenium-based catalyst for the transfer hydrogenation of ketones by propan-2-ol.[10]

This prompted us to investigate the asymmetric version of this reaction by using ruthenium complexes bearing optically active tridentate ligands with P,N,O donor atoms. In this paper, we report the synthesis of three ligands closely related to **1**, (*R*)-1-(diphenylphosphino)-2-((1*R*,2*S*,5*R*)-menthoxy)-1-(2-pyridyl)ethane (**2R**), (*S*)-1-(diphenylphosphino)-2-((1*R*,2*S*,5*R*)-menthoxy)-1-(2-pyridyl)ethane (**2S**), and a ligand in which the chiral center is the phosphorus atom, (*S*)-(phenyl(2-anisyl)-phosphino)(2-pyridyl)methane (**3**). These ligands have been coordinated to ruthenium in complexes of the type $RuCl_2(PPh_3)(L)$ (L = **1**, **2**, **3**). These complexes have been used as catalyst precursors for the transfer hydrogenation of acetophenone by propan-2-ol. A preliminary account of this work has been published.[10]

Results and Discussion

Synthesis of the Ligands. The synthesis of 1-(diphenylphosphino)-2-ethoxy-1-(2-pyridyl)ethane (**1**) from

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(1) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27.
(2) Lindner, E.; Haustein, M.; Mayer, H. A.; Gierling, K.; Fawzi, R.; Steimann, M. *Organometallics* **1995**, *14*, 2246 and references therein.
(3) Higgins, T. B.; Mirkin, C. A. *Inorg. Chim. Acta* **1995**, *240*, 347 and references therein.
(4) Chadwell, S. J.; Coles, S. J.; Edwards, P. G.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1995**, 3551 and references therein.
(5) Lindner, E.; Grepägs, M.; Gierling, K.; Fawzi, R.; Steimann, M. *Inorg. Chem.* **1995**, *34*, 6106.
(6) Werner, H.; Stark, A.; Steinert, P.; Grünwald, G.; Wolf, J. *Chem. Ber.* **1995**, *128*, 49.
(7) (a) Lindner, E.; Sickinger, A.; Wegner, P. *J. Organomet. Chem.* **1988**, *349*, 75. (b) Allgeier, A. M.; Singewald, E. T.; Mirkin, C. A.; Stern, C. L. *Organometallics* **1994**, *13*, 2928.
(8) Cotton, F. A.; Hong, B. *Prog. Inorg. Chem.* **1992**, *40*, 179.
(9) Alvarez, M.; Lugan, N.; Mathieu, R. *J. Chem. Soc., Dalton Trans.* **1994**, 2755.
(10) Yang, H.; Alvarez, M.; Lugan, N.; Mathieu, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1721.

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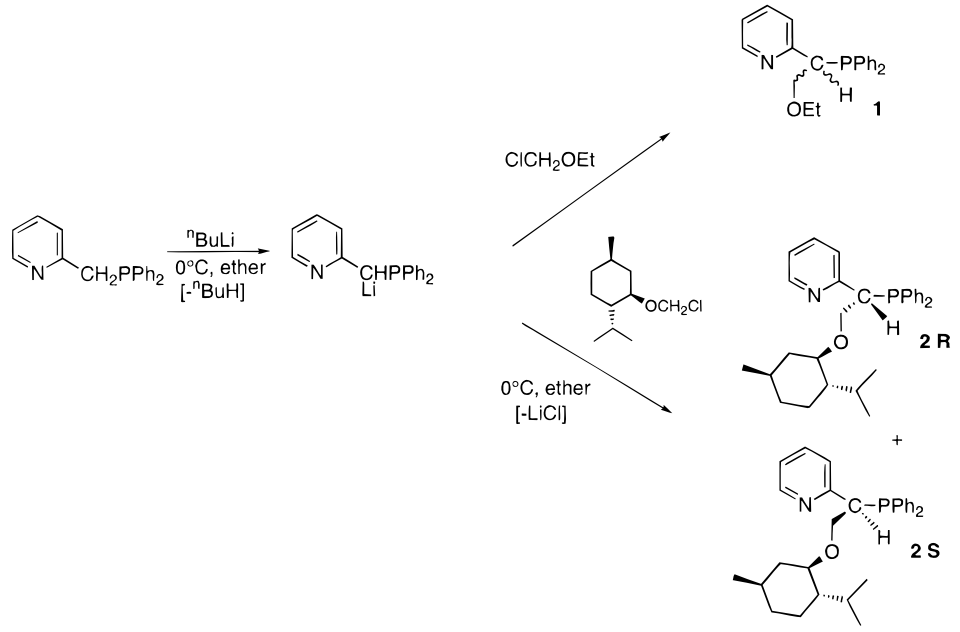
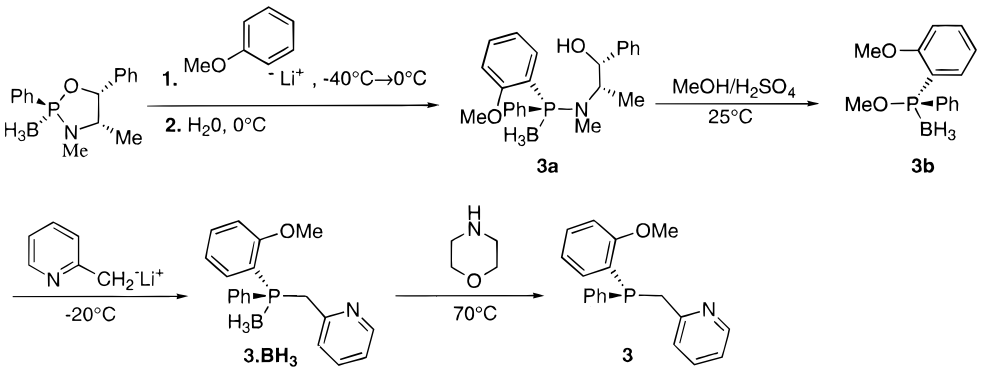
Scheme 1



Scheme 2



2-((diphenylphosphino)methyl)pyridine has been previously reported.[9] The parent 1-(diphenylphosphino)-2-(1*R*,2*S*,5*R*)-menthoxy)-1-(2-pyridyl)ethane (**2**) has been synthesized following the same strategy, as illustrated in Scheme 1. Successive addition of *n*-butyllithium and chloromethyl-(1*R*,2*S*,5*R*)-menthyl ether to 2-((diphenylphosphino)methyl)pyridine leads to **2** in a 70% yield as a mixture of two diastereoisomers in a 1:1 ratio. Only after complexation with borane could the two diastereomers **2R**·BH_3 and **2S**·BH_3 be separated by chromatography on silica gel. The free ligands (*R*)-1-(diphenylphosphino)-2-((1*R*,2*S*,5*R*)-menthoxy)-1-(2-pyridyl)-ethane (**2R**) and (*S*)-1-(diphenylphosphino)-2-((1*R*,2*S*,5*R*)-menthoxy)-1-(2-pyridyl)ethane (**2S**) have subsequently been liberated by reaction with morpholine at 70 °C and isolated in a 26% and 41% yield, respectively. The absolute configuration of these ligands has been deduced from the X-ray structure determination of $RuCl_2(PPh_3)$-(**2S**) (*vide infra*).

The enantiomerically pure (*S*)-(phenyl(2-anisyl)phosphino)(2-pyridyl)methane (**3**) has been synthesized following a procedure developed by Jugé *et al.*[11−14] In the first step, the addition of 2-anisyllithium to (2*R*,4*S*,5*R*)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine[12] affords the aminophosphine−borane complex **3a** (Scheme 2). A subsequent acidic methanolysis at room temperature gives the phosphinite−borane complex **3b**, and a final reaction with (2-pyridylmethyl)lithium at −20 °C leads to the phosphine borane complex **3**·BH_3. The ligand **3** is then liberated from its borane complex by morpholine at 70 °C. It has been isolated in a 70% overall yield.

Synthesis and Characterization of the $RuCl_2$-(PPh_3)(L) Complexes (L = 1, 2R, 2S, 3). The complexes $RuCl_2(PPh_3)$(L) (L = **1**, **2R**, **2S**, **3**) have been obtained by the addition at room temperature of 1 equiv of the ligand L to $RuCl_2(PPh_3)_2$ in dichloromethane solution, according to the general equation shown below.

$$RuCl_2(PPh_3)_3 + L \rightarrow RuCl_2(PPh_3)(L) + 2PPh_3$$

Characterization of the Complex $RuCl_2(PPh_3)$-(1) (4). The complex $RuCl_2(PPh_3)$(**1**) (**4**) has been isolated in a 73% yield as a yellow powder. It has been characterized by the usual spectroscopic techniques. $^{31}P\{^1H\}$ NMR in benzene solution shows an AB system (δ_A

(11) Jugé, S.; Genet, J.-P. *Tetrahedron Lett.* **1989**, *30*, 2783.
(12) Jugé S.; Wakselman, M.; Stephan, M.; Genet, J.-P. *Tetrahedron Lett.* **1990**, *31*, 4443.
(13) Jugé, S.; Stephan, M.; Lafitte, J.-A.; Genet, J.-P. *Tetrahedron Lett.* **1990**, *31*, 6357.
(14) Jugé, S.; Stephan, M.; Merdes, R.; Genet, J.-P.; Halut-Desportes, S. *J. Chem. Soc., Chem. Commun.* **1993**, 531.

= 63.3, δ_B = 61.2), and the J_{PP} coupling constant of 39 Hz indicates that the two phosphorus atoms are in a *cis* position. The room temperature ^{1}H NMR spectra in CD_2Cl_2 solution show the expected signals for the alkyl part of the ligand **1** (see Experimental Section). Noteworthy is the deshielding by 0.82 ppm of the resonance of the methylene group of the ethoxy group compared to that of the free ligand, which shows that the ether function is coordinated to ruthenium. The protons of the pyridyl group appear as a very broad resonance at 8 ppm. This suggests a fluxional process within the molecule, and variable temperature NMR experiments have been performed in CD_2Cl_2 solution. In this solvent, a single resonance is now observed at δ = 62.2 in the $^{31}P\{^1H\}$ spectrum and it is only by lowering the temperature to 203 K that an AB pattern is observed (δ_A = 66.7, δ_B = 64.7, J_{PP} = 39 Hz). In the same temperature range, the most salient feature in the ^{1}H NMR spectrum is in the 6−10 ppm area and, peculiarly, the replacement of the broad resonance observed at 8 ppm at 298 K by an ill-resolved triplet at 9.69 ppm, characteristic of the hydrogen in the 6-position on a coordinated pyridyl ring.[15] $^1H\{^{31}P\}$ NMR decoupling experiments transform this signal into a doublet. Taken altogether, these results indicate that the fluxionality of the molecule is certainly related to the reversible coordination of the pyridyl ring. This is a quite surprising observation as the ether function is a harder base than the pyridine and a reversible opening of the Ru−O was expected.

The structure of complex **4** will be presented later, along with the structure of the complexes $RuCl_2(PPh_3)$-(**2R**) (**5**) and $RuCl_2(PPh_3)$(**2S**) (**6**).

Characterization of the Complexes $RuCl_2(PPh_3)$-(2R) (5) and $RuCl_2(PPh_3)$(2S) (6). The reaction of **2R** or **2S** with $RuCl_2(PPh_3)_3$ leads to the formation of complexes $RuCl_2(PPh_3)$(**2R**) (**5**) and $RuCl_2(PPh_3)$(**2S**) (**6**), respectively. $^{31}P\{^1H\}$ NMR indicates that complexes **5** and **6** form as a mixture of two isomers, **5a** and **5b** and **6a** and **6b**. Each of the four complexes is characterized by an AB pattern in the $^{31}P\{^1H\}$ spectra, with a J_{PP} coupling constant characteristic of two phosphorus nuclei being in a *cis* position. In each reaction, the ratio between the two isomers varies when allowed to stand in solution, until **5b** or **6b** remains as the sole observable complex. The most significant features in the ^{1}H NMR spectra concern the resonances for the hydrogen in the 6-position on the pyridyl ring and in the 1-position on the menthyl group. At room temperature, the hydrogen in the 6-position on the pyridyl ring is observed as a broad signal at 8.45 and 8.39 ppm for the isomers **5a** and **6a**, respectively and as a thin doublet at 9.42 and 9.43 ppm for the isomers **5b** and **6b**, respectively. The hydrogen in the 1-position on the menthyl group appears as a complex multiplet at 4.41 and 4.50 ppm for **5a** and **6a** and at 2.79 and 2.91 ppm for **5b** and **6b**. First of all, these data indicate that **5a** and **6a** and **5b** and **6b** are diastereoisomers. Secondly, the comparison of the chemical shifts of the protons in the 6-position on the pyridyl ring, and in the 1-position on the menthyl group with the corresponding ones in the free ligand (8.49 and 2.89 ppm, respectively) suggests that the pyridyl group is not firmly coordinated to ruthenium in diastereoisomers **a** while the menthyl ether group does and that the reverse situation is occurring in diastereoisomers **b**. For **5a** and **6a**, a lowering of the temperature to 193 K induces the same type of changes as for **4** (*vide supra*). Indeed, the broad resonances observed at 8.45 and 8.39 ppm at 298 K shift to 9.73 and 9.74 ppm, respectively, and become ill-resolved triplets. These observations show that **5a** and **6a** experience the same fluxional process in solution as complex **4**, *i.e.*, a reversible opening of the Ru−N bond.

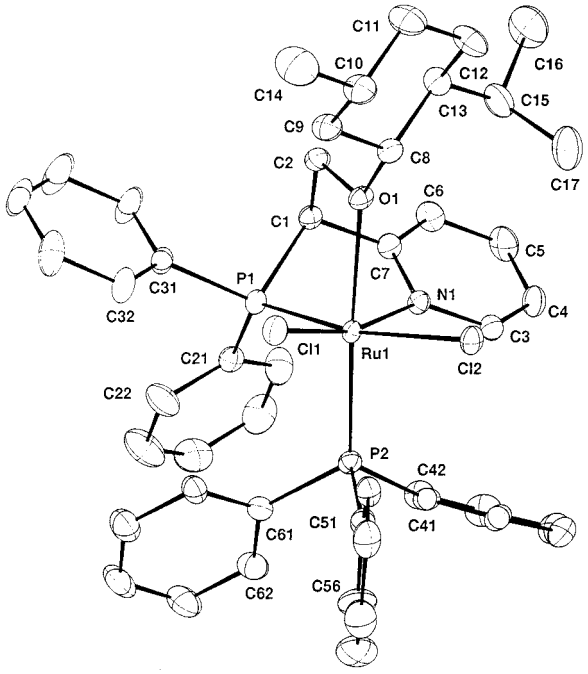


Figure 1. CAMERON drawing of compound **6b** with 50% thermal ellipsoids.

The behavior in solution of diastereoisomers **5b** and **6b** is less clear. Indeed, the two resonances which could be sensitive to the mode of bonding of the N and O donating centers are not greatly affected. The most significant differences concern the resonance of the hydrogen bonded to the chiral carbon in the α-position relative to the phosphorus that moves by about 0.3 ppm to high field at 193 K. No clear conclusions about the mode of bonding of the ligands **2R** and **2S** in **5b** and **6b** could, however, be deduced.

Crystals of **6b** suitable for an X-ray structure determination have been obtained. A CAMERON perspective view of the complex is shown in Figure 1. Table 1 contains a selection of bond distances and angles of interest.

In complex **6b**, the ligand **2S** is P,N,O bound to ruthenium. The chlorine atoms are mutually cis and the triphenylphosphine ligand is in the trans position relative to the oxygen atom of the ether function. The geometry around the ruthenium atom is a distorted octahedron, due to the tridentate mode of bonding of **2S**. Bond distances illustrate the trans influence of the phosphorus ligands in this molecule. Indeed, the Ru(1)−Cl(2) bond (2.4634(8) Å) trans to P(1) is significantly longer than the Ru(1)−Cl(1) bond (2.4420(8) Å) trans to N(1). Moreover, the Ru(1)−O(1) bond trans to P(2) (2.311(2) Å) is one of the longest distances observed for ruthenium complexes with P,O ligands in which the oxygen atom is in a trans position to a phosphorus atom.[16−19] This last result suggests that the fluxionality

(15) Deeming, A. J.; Smith, M. B. *J. Chem. Soc., Chem. Commun.* **1993**, 844.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $RuCl_2(PPh_3)(2S)$ (6b), with Esd in Parentheses

Ru(1)−Cl(1)	2.4420(8)	C(1)−C(2)	1.515(5)
Ru(1)−Cl(2)	2.4634(8)	C(1)−C(7)	1.527(5)
Ru(1)−P(1)	2.2609(8)	C(3)−C(4)	1.378(5)
Ru(1)−P(2)	2.2437(9)	C(4)−C(5)	1.376(6)
Ru(1)−N(1)	2.125(3)	C(5)−C(6)	1.392(6)
Ru(1)−O(1)	2.311(2)	C(6)−C(7)	1.394(5)
P(1)−C(1)	1.858(4)	C(8)−C(9)	1.535(5)
P(1)−C(21)	1.836(4)	C(8)−C(13)	1.522(5)
P(1)−C(31)	1.855(3)	C(9)−C(10)	1.508(6)
P(2)−C(41)	1.860(4)	C(10)−C(11)	1.515(6)
P(2)−C(51)	1.851(4)	C(10)−C(14)	1.553(6)
P(2)−C(61)	1.835(4)	C(11)−C(12)	1.527(6)
N(1)−C(3)	1.366(4)	C(12)−C(13)	1.537(6)
N(1)−C(7)	1.360(4)	C(13)−C(15)	1.560(6)
O(1)−C(2)	1.439(4)	C(15)−C(16)	1.538(7)
O(1)−C(8)	1.459(4)	C(15)−C(17)	1.529(7)

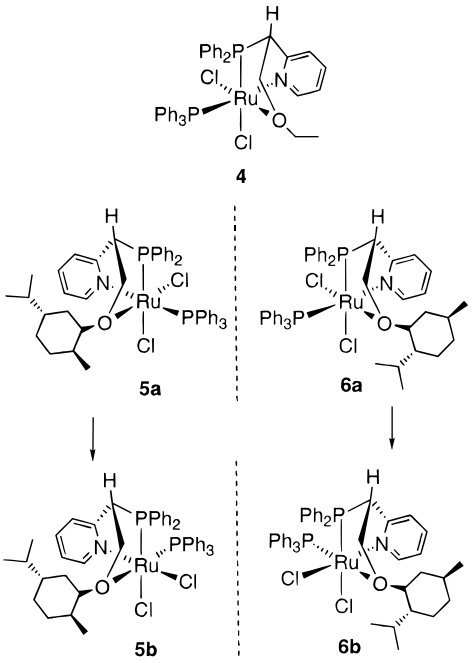
Cl(1)−Ru(1)−Cl(2)	91.48(3)	Cl(1)−Ru(1)−P(2)	93.35(3)
Cl(1)−Ru(1)−P(1)	97.29(3)	Cl(2)−Ru(1)−P(2)	89.21(3)
Cl(2)−Ru(1)−P(1)	166.88(3)	P(1)−Ru(1)−P(2)	99.96(3)
Cl(1)−Ru(1)−N(1)	165.83(8)	C(41)−P(2)−C(51)	102.6(2)
Cl(2)−Ru(1)−N(1)	87.94(8)	Ru(1)−P(2)−C(61)	117.8(1)
P(1)−Ru(1)−N(1)	81.16(7)	C(41)−P(2)−C(61)	107.2(2)
P(2)−Ru(1)−N(1)	100.80(8)	C(51)−P(2)−C(61)	95.5(2)
Cl(1)−Ru(1)−O(1)	90.07(6)	Ru(1)−N(1)−C(3)	127.4(2)
Cl(2)−Ru(1)−O(1)	89.14(5)	Ru(1)−N(1)−C(7)	115.4(2)
P(1)−Ru(1)−O(1)	81.14(5)	C(3)−N(1)−C(7)	116.7(3)
P(2)−Ru(1)−O(1)	176.24(6)	Ru(1)−O(1)−C(2)	113.6(2)
N(1)−Ru(1)−O(1)	75.8(1)	Ru(1)−O(1)−C(8)	126.9(2)
Ru(1)−P(1)−C(1)	91.3(1)	C(2)−O(1)−C(8)	117.9(2)
Ru(1)−P(1)−C(21)	124.7(1)	P(1)−C(1)−C(2)	107.2(2)
C(1)−P(1)−C(21)	104.9(2)	P(1)−C(1)−C(7)	107.2(2)
Ru(1)−P(1)−C(31)	125.8(1)	C(2)−C(1)−C(7)	110.4(3)
C(1)−P(1)−C(31)	103.5(2)	O(1)−C(2)−C(1)	105.8(3)
C(21)−P(1)−C(31)	101.6(2)	N(1)−C(7)−C(1)	114.7(3)
Ru(1)−P(2)−C(41)	111.9(1)		
Ru(1)−P(2)−C(51)	119.7(1)		

phenomenon observed by NMR for **5b** and **6b** could result from an easy reversible opening of the Ru−O bond, which is not totally frozen at the lowest temperature we have operated (193 K).

The solid state structure of **6b** has allowed us to deduce the relative arrangements of the ligands in **6a** (or **5a**) and **4**, as shown in Scheme 3. Indeed, the selective $^1H\{^{31}P\}$ NMR experiments run at 193 K show that the proton in the 6-position on the pyridyl in **6a**, **5a**, and **4** are coupled with the phosphorous atom of the triphenylphosphine ligand. So, the triphenylphosphine ligand is now in a trans position relative to the nitrogen atom of the pyridine ring in **6a** and its diastereoisomer **5a**. Since **5a** and **6a** experience the same type of fluxional process in solution as **4**, we propose the same type of structure for the latter. Note that in these structures, the triphenylphosphine is now in a cis position to the ether group. This could explains why **5a** and **6a** are less stable than **5b** and **6b**, where the bulky menthyl ether group is far away from the triphenylphosphine.

Finally, the behavior in solution of complexes **4**, **5**, and **6** show that the labile arm of the P,O,N ligands is the arm in a trans position to the triphenylphosphine ligand. This shows that the hemilabile character of this type of ligand is governed by the trans effect of the ancillary ligands bound to ruthenium.

Scheme 3



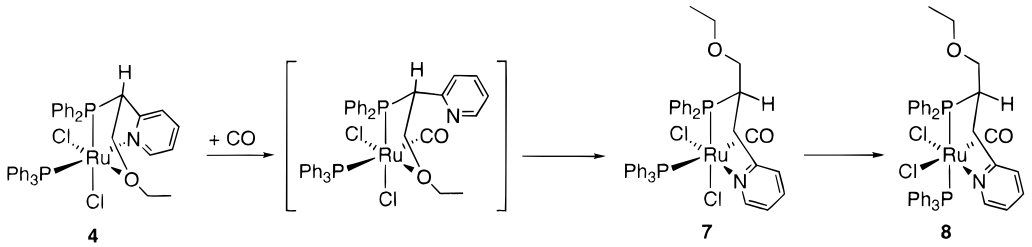
To evaluate the consequence of the lability of the various bonds in these complexes, we have investigated the reactivity of **4** toward carbon monoxide. At room temperature, the reaction is instantaneous and infrared spectroscopy shows a main absorption at 1980 cm^{-1} and another one at 1962 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum indicates that two complexes are formed. The most abundant one, **7**, is characterized by two doublets at 40.4 and 25.5 ppm (J_{PP} = 27.6 Hz) and the other, **8**, by two doublets at 61.2 and 18.8 ppm (J_{PP} = 354.5 Hz). When the complexes remain in solution, the ratio between the two complexes varies and after 1 h in the NMR tube, only **8** remains observable and, at this stage, only the absorption at 1962 cm^{-1} is noticed in the IR spectrum. This shows complex **7** to be the kinetic product of the reaction. As the $^{31}P\{^1H\}$ NMR data show that the two phosphine ligands are mutually cis and the ν(CO) value indicates the CO ligand is in a trans position to a phosphine ligand,[20] we propose the structure shown in Scheme 4 for **7**. It is very likely that the first step of the reaction is an opening of the Ru−N bond in **4**, in agreement with its observed labile character, which allows the coordination of CO. Subsequent intramolecular substitution of the pyridyl group for the ethoxy group would lead to **7**, the ligand **1** going from an η^2-(P,O) to an η^2-(P,N) coordination mode through the process (Scheme 4). This rearrangement is certainly the consequence of the increased soft character of the Ru center due to the coordination of CO.

The infrared spectrum of complex **8** shows two absorptions at 310 and 272 cm^{-1}, which is consistent with the cis position of the Ru−Cl bonds.[19] As the J_{pp} value indicates that the the two phosphorus atoms are mutually trans, we propose the structure shown in Scheme 4 for **8**.

Characterization of the Complex $RuCl_2(PPh_3)$-(3) (9). The complex $RuCl_2(PPh_3)$(**3**) (**9**) has been isolated in 90% yield as a yellow powder. Its $^{31}P\{^1H\}$

(16) Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1979**, *18*, 2658.
(17) Lindner, E.; Schober,U.; Fawzi, R.; Hiller, W.; Englert, U.; Wegner, P. *Chem. Ber.* **1987**, *120*, 1621.
(18) Lindner, E.; Möckel, A.; Mayer, H. A.; Fawzi, R. *Chem. Ber.* **1992**, *125*, 1363.
(19) Lindner, E.; Möckel, A.; Mayer, H. A.; Kühbauch, H.; Fawzi, R.; Steimann, M. *Inorg. Chem.* **1993**, *32*, 1266.
(20) Barnard, C. F. J.; Daniels, J. A.; Jeffery, J.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 1861.

Scheme 4



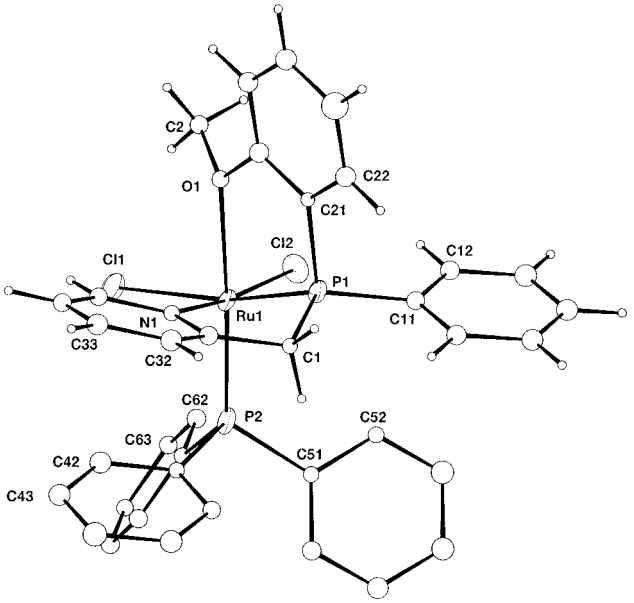


Figure 2. CAMERON drawing of compound **9** with 50% thermal ellipsoids.

NMR spectrum has an AB pattern ($\delta_A = 64.6$, $\delta_B = 62.9$, $J_{PP} = 37.5$ Hz), and its ^1H NMR spectrum indicates that **3** is P,N,O-bound. Indeed, the hydrogen in the 6-position on the pyridyl ring appears as a doublet at 9.61 ppm, while the methoxy group resonance is observed at 4.61 ppm, at lower field than the corresponding signals in the free ligand (8.44 and 3.66 ppm, respectively). As the $^1H\{^{31}P\}$ NMR experiment shows that the pyridyl ring is not in a trans position to any phosphorus atom, we propose a structure for **9** similar to that of **6b** in terms of the relative arrangement of the ligands. However, contrary to complexes **4**−**6**, no fluxional process has been evidenced in solution.

The solid state structure of complex **9** has been determined by X-ray diffraction. A CAMERON perspective view of the complex is shown in Figure 2. Bond distances and angles of interest are presented in Table 2. Though the crystals were of poor quality, this study confirms our hypothesis that triphenylphosphine is trans to the ether group.

When the complex **9** in dichloromethane solution is treated with carbon monoxide, the new complex $RuCl_2(CO)(PPh_3)$(**3**) (**10**) immediately forms. In the IR spectrum, there is a characteristic ν(CO) band at 1987 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum shows an AX spin system ($\delta_A = 44.9$, $\delta_X = 16.2$, $J_{PP} = 29.4$ Hz), and the ^1H NMR spectrum indicates that the ligand **3** is not O bound. Indeed, the methoxy resonance is observed at 3.24 ppm. As expected, carbon monoxide has replaced the coordinated ether arm of the ligand on ruthenium.

Catalytic Transfer Hydrogenation of Acetophenone. When this work was initiated, asymmetric transfer hydrogenation of ketones by ruthenium complexes containing optically active ligands met only moderate success.[21] In the last three years, however, considerable advancements have been reported, both in terms of activity and enantioselectivity.[22] Today, enantiomeric excesses up to 97% have been obtained with bi-[22e] or tetradentate ligands[22f] coordinating phosphorus and nitrogen atoms in ruthenium complexes. In these particularly efficient complexes, the ligands bear a chiral carbon atom in an α-position relative to the nitrogen binding site.

Our first experiments were performed under reaction conditions similar to those described by Bäckvall *et al.*, using $RuCl_2(PPh_3)_3$ as the catalyst precursor.[23] We have previously shown that in these conditions, the complex **4** is a very efficient catalyst, as a turnover frequency of 90 000 h^{-1} has been observed for the transfer hydrogenation of acetophenone.[10]

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $RuCl_2(PPh_3)$(3) (9), with Esd in Parentheses

Ru(1)−Cl(1)	2.461(7)	P(2)−C(51)	1.84(1)
Ru(1)−Cl(2)	2.405(7)	P(2)−C(66)	1.86(1)
Ru(1)−P(1)	2.207(8)	O(1)−C(2)	1.44(3)
Ru(1)−P(2)	2.248(8)	O(1)−C(26)	1.39(2)
Ru(1)−O(1)	2.25(2)	C(1)−C(31)	1.51(3)
Ru(1)−N(1)	2.10(2)	C(31)−N(1)	1.37(3)
P(1)−C(1)	1.79(2)	C(32)−C(33)	1.39(3)
P(1)−C(11)	1.82(2)	C(33)−C(34)	1.34(3)
P(1)−C(21)	1.82(2)	C(34)−C(35)	1.37(3)
P(2)−C(41)	1.83(1)	C(35)−N(1)	1.38(3)
Cl(1)−Ru(1)−Cl(2)	89.6(2)	Cl(1)−Ru(1)−N(1)	93.3(5)
Cl(1)−Ru(1)−P(1)	166.6(3)	Cl(2)−Ru(1)−N(1)	171.8(3)
Cl(2)−Ru(1)−P(1)	96.8(2)	P(1)−Ru(1)−N(1)	78.8(5)
Cl(1)−Ru(1)−P(2)	90.6(2)	P(2)−Ru(1)−N(1)	92.0(3)
Cl(2)−Ru(1)−P(2)	95.6(2)	O(1)−Ru(1)−N(1)	86.5(5)
P(1)−Ru(1)−P(2)	100.4(3)	Ru(1)−P(1)−C(1)	104.9(8)
Cl(1)−Ru(1)−O(1)	86.8(4)	Ru(1)−P(1)−C(11)	135.2(6)
Cl(2)−Ru(1)−O(1)	86.0(4)	C(1)−P(1)−C(11)	105.8(10)
P(1)−Ru(1)−O(1)	82.0(5)	Ru(1)−P(1)−C(21)	103.3(6)
P(2)−Ru(1)−O(1)	176.9(4)	C(1)−P(1)−C(21)	101.5(10)
C(11)−P(1)−C(21)	101.8(6)	C(1)−C(31)−N(1)	118.0(20)
Ru(1)−P(2)−C(41)	111.1(4)	Ru(1)−N(1)−C(31)	120.4(16)
Ru(1)−P(2)−C(51)	122.2(7)	Ru(1)−N(1)−C(35)	121.1(15)
Ru(1)−O(1)−C(2)	125.6(15)	P(1)−C(21)−C(22)	121.7(11)
Ru(1)−O(1)−C(26)	116.6(12)	P(1)−C(21)−C(26)	118.0(10)
C(2)−O(1)−C(26)	115.1(16)	C(22)−C(21)−C(26)	120.3(7)
P(1)−C(1)−C(31)	105.2(15)	O(1)−C(26)−C(21)	118.0(14)
C(1)−C(31)−C(32)	123.6(22)		

(21) Zassinovich, G.; Mestroni, G.; Gladiali, S. *Chem. Rev.* **1992**, *92*, 1051.

(22) (a) Genêt, J-P.; Ratovelomanana-Vidal, V.; Pinel, C. *Synlett* **1993**, 478. (b) Hashiguchi, S.; Fujii, A.; Takehara, J.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 7562. (c) Takehara, J.; Hashiguchi, S.; Fujii, A.; Inoue, S.; Ikariya, T.; Noyori, R. *J. Chem. Soc., Chem. Commun*. **1996**, 233. (d) Jiang, Q.; Van Piew, D.; Murtuza, S.; Zhang, X. *Tetrahedron Lett*. **1996**, *37*, 797. (e) Langer, T.; Helmchen, G. *Tetrahedron Lett*. **1996**, *37*, 1381. (f) Gao, J. X.; Ikariya, T.; Noyori, R. *Organometallics* **1996**, *15*, 1087.

(23) Chowdhury, R. L.; Bäckvall, J. E. *J. Chem. Soc., Chem. Commun*. **1991**, 1063.

Table 3. Ruthenium-Catalyzed Asymmetric Transfer Hydrogenation of Acetophenone

catalyst	Substrate/Catalyst ratio	time (min)	base/catalyst ratio	temp (°C)	yield (%)	ee (%)	config
5	1000	20	240[a]	80	90	2	R
6	1000	20	240[a]	80	90	3	R
9	1000	1	240[a]	80	80	0	
9	1000	90	240[a]	50	24	10	R
9	500	90	240[a]	30	30	5	R
5	200	60	0.5[b]	45	50	60	R
5	200	5	1[b]	45	95	22	R
9	200	60	0.5[b]	45	2		
9	200	60	1[b]	45	30	12	R

[a] NaOH as base. [b] $(CH_3)_2CHOK$ as base.

The complexes **5** and **6** (used as mixtures of isomers **5a** and **5b** and **6a** and **6b**) are less active, and the enantiomeric excesses are very poor (Table 3). In both cases, the major enantiomer is *R*. Complex **9** is much more active and a turnover frequency of 48 900 h^{-1} has been obtained. To our disappointment, no enantiomeric excess is, however, detected. We have tried to improve the enantioselectivity of the system by lowering the reaction temperature. At 55 °C, the activity of the system notably decreases, but an enantiomeric excess of 10% is noticed (Table 3). At 30 °C and with a substrate/catalyst ratio of 1/500, a similar activity is observed but the stereoselectivity lowers.

In the last attempts to optimize the performance of our complexes, we have used the reaction conditions described by Noyori *et al.*, which allowed them to obtain the most efficient system to date for this catalytic reaction.[22f] The main differences between the later system and Bäckvall's system, besides the temperature of the runs (45 °C), reside in the use of a low concentration of potassium 2-propoxide as a base ($^1/_2$ equiv with respect to Ru) and a higher concentration of the complex (substrate/catalyst = 200). Under these conditions, complex **5** shows a lower activity, as the system deactivates after 1 h with a conversion of 53%. Nevertheless, a considerable increase of the enantiomeric excess of the reaction to 60% has been observed. For complex **9**, the result was disappointing as no significant activity could be noticed (Table 3). These results led us to slightly increase the base concentration to 1 equiv of potassium 2-propoxide per Ru. This induced a net increase of the activity for **5** but concurrently a net decrease in the enantioselectivity of the reaction. For complex **9**, some activity was then observed but the enantiomeric excess remained modest.

From these results it appears that with our catalyst precursors, an increase of the activity occurs with a decrease in the stereoselectivity. This suggests that contrary to the Noyori's catalysts,[22f] the reversibility of the transfer hydrogenation of acetophenone must be important in our case.

Experimental Section

All reactions were performed under a nitrogen atmosphere with the use of standard Schlenk techniques. Tetrahydrofuran and diethyl ether used for the syntheses were distilled under nitrogen from sodium benzophenone ketyl just before use. Other solvents were purified following the standard procedures and stored under nitrogen. NMR spectra were recorded on Bruker AC 200, WM 250, or AMX 400 instruments. Elemental analyses were performed in our laboratory on a Perkin-Elmer 2400 CHN analyzer. Optical rotations were measured with a Perkin Elmer 341 polarimeter using 10 cm cells. Chloromethyl-(1*R*,2*S*,5*R*)-menthyl ether,[24] 2-((diphenylphosphino)methyl)pyridine,[9] 1-(diphenylphosphino)-2-ethoxy-1-(2-pyridyl)-ethane,[9] and (2*R*,4*S*,5*R*)-3,4-dimethyl-1,3,2-oxazaphospholidine-2-borane[12] have been prepared according to published procedures.

Synthesis of (*R*)-1-(Diphenylphosphino)-2-((1*R*,2*S*,5*R*)-menthoxy)-1-(2-pyridyl)ethane (2R) and (*S*)-1-(Diphenylphosphino)-2-((1*R*,2*S*,5*R*)-menthoxy)-1-(2-pyridyl)-ethane (2S). To 2.77 g of 2-((diphenylphosphino)methyl)-pyridine (10 mmol) dissolved in 10 mL of diethyl ether cooled at 0 °C was slowly added 6.8 mL of a 1.6 M solution of *n*-BuLi in hexanes (10 mmol). The solution was stirred for 0.5 h at 0 °C. Then, 2.05 mL of chloromethyl (1*R*,2*S*,5*R*)-menthyl ether (10 mmol) was slowly added, and the solution was stirred for 3 h at 0 °C and then for 2 h at room temperature. The solvents were removed under vacuum, and the oily residue was dissolved in 50 mL of diethyl ether. The solution was washed with 2 × 50 mL of water, then dried over sodium sulfate. Evaporation of the solvent under vacuum left 4 g of a crude racemic mixture of 1-(diphenylphosphino)-2-((1*R*,2*S*,5*R*)-menthoxy)-1-(2-pyridyl)ethane (**2**) as a yellow oil (95% yield).

A crude racemic mixture of 1-(diphenylphosphino)-2-((1*R*,2*S*,5*R*)-menthoxy)-1-(2-pyridyl)ethane (1 g, 2.25 mmol) was dissolved in toluene (10 mL). To this was added 1.13 mL of a 2 M solution of $BH_3{\cdot}SMe_2$ in toluene (2.25 mmol), and the mixture was stirred for 4 h at room temperature. The toluene was removed under vacuum to leave the complex **2**·BH_3 as a white powder. The two diastereoisomers thus formed have been purified and separated by column chromatography on silica gel 60 using a CH_2Cl_2/hexanes (5:1) mixture as the eluant. Complexes **2R**·BH_3 and **2S**·BH_3 have been isolated in 29% and 43% yields, respectively, as white solids.

Each of the borane complexes **2R**·BH_3 and **2S**·BH_3 was dissolved in morpholine (5 mL) and the solution was heated at 70 °C for 2 h. Excess morpholine was eliminated under vacuum. The residue was treated by a mixture of diethyl ether (20 mL) and water (20 mL). The water phase, which contains most of the morpholine−borane complex, was discarded. The diethyl ether phase was evaporated under vacuum, and the residue was purified by filtration on a short column of silica gel using diethyl ether as the eluant. The phosphines **2R** and **2S** have been isolated as white powders (**2R**: 0.25 g, 26% yield (from **2·BH₃**). **2S**: 0.4 g, 41% yield (from **2·BH₃**)).

2R·BH₃. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.3 (m, 1H, C_5H_4N), 7.0−7.9 (m, 13H, 2 × C_6H_5 and C_5H_4N), 4.37 (m, 2H, CH_2), 3.80 (m, 1H, PCH_α), 2.95 (m, 1H, H_1 (menthyl)), 0.9−2.0 (m, 11H, CH and CH_2 (menthyl), BH_3), 0.79 (d, 3H, CH_3, J_{HH} = 6.6 Hz), 0.69 (d, 3H, CH_3, J_{HH} = 7.0 Hz), 0.57 (d, 3H, CH_3, J_{HH} = 7.0 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.01 MHz): δ 20.0 (br).

2S·BH₃. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.30 (m, 1H, C_5H_4N), 6.9−7.9 (m, 13H, 2 × C_6H_5 and C_5H_4N), 4.28 (m, 1H, CH_aH_b), 4.03 (m, 2H, CH_aH_b PCH_α), 2.82 (m, 1H, H_1 (menthyl)), 0.5−2.2 (m, 11H, CH and CH_2 (menthyl), BH_3), 0.77 (d, 3H, CH_3, J_{HH} = 6.5 Hz), 0.53 (d, 3H, CH_3, J_{HH} = 7.0 Hz), 0.18 (d, 3H, CH_3, J_{HH} = 7.0 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.01 MHz): δ 20.0 (br).

(24) Shatzmiller, S.; Dolithzky, B. Z.; Bahar, E. *Liebigs Ann. Chem.* **1991**, 375.

2R. $[\alpha]_D = +119.1°$ ($c = 0.96$, C_6H_6). ^1H NMR ($CDCl_3$, 200 MHz): δ 8.49 (m, 1H, C_5H_4N), 6.94−7.68 (m, 13H, 2 × C_6H_5 and C_5H_4N), 4.17 (ddd, 1H, CH_aH_b, $J_{H_aH_b} = 9.2$ Hz, $J_{H_aH_\alpha} = 3.3$ Hz, $J_{H_aP} = 9.2$ Hz), 3.96 (ddd, 1H, PCH_α, $J_{H_\alpha H_a} = 3.3$ Hz, $J_{H_\alpha H_b} = 4.6$ Hz, $J_{H_\alpha P} = 8.1$ Hz), 3.64 (ddd, 1H, CH_aH_b, $J_{H_bH_a} = 9.2$ Hz, $J_{H_bH_\alpha} = 4.6$ Hz, $J_{H_bP} = 6.9$ Hz), 2.89 (m, 1H, H_1 (menthyl)), 0.85−2.01 (m, 8H, C*H* and CH_2 (menthyl)), 0.78 (d, 3H, CH_3, $J_{HH} = 5.5$ Hz), 0.75 (d, 3H, CH_3, $J_{HH} = 6.9$ Hz), 0.58 (d, 3H, CH_3, $J_{HH} = 6.9$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.01 MHz): δ −7.6. Anal. Calcd for $C_{29}H_{36}NOP$: C, 78.16; H, 8.16; N, 3.14. Found: C, 77.36; H, 8.41; N, 3.40.

2S. $[\alpha]_D = -145.1°$ ($c = 0.94$, C_6H_6). ^1H NMR ($CDCl_3$, 200 MHz): δ 8.51 (m, 1H, C_5H_4N), 6.92−7.70 (m, 13H, 2 × C_6H_5 and C_5H_4N), 3.96 (m, 3H, PCH_α and CH_aH_b), 2.83 (m, 1H, H_1 (menthyl)), 0.87−1.97 (m, 8H, C*H* and CH_2 (menthyl)), 0.81 (d, 3H, CH_3, $J_{HH} = 6.5$ Hz), 0.60 (d, 3H, CH_3, $J_{HH} = 7.0$ Hz), 0.24 (d, 3H, CH_3, $J_{HH} = 6.9$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.01 MHz): δ −8.4. Anal. Calcd for $C_{29}H_{36}NOP$: C, 78.16; H, 8.16; N, 3.14. Found: C, 77.60; H, 8.61; N, 3.43.

Synthesis of (*S*)-(Phenyl(2-anisyl)phosphino)(2-pyridyl)methane (3). Synthesis of (*S*)-(Methyl[(1*R*,2*S*)-(1-hydroxy-2-methyl-1-phenyl-2-propyl)]amino)(*o*-anisyl)-phenylphosphine−borane (3a). To 5.54 mL of a 1.3 M solution of *s*-BuLi in cyclohexane (7.2 mmol) cooled at 0 °C was added 0.75 mL of 2-bromoanisole, and the reaction mixture was stirred for 0.5 h. To the solution of 2-(methoxyphenyl)lithium thus formed was added 2 mL of THF, and the mixture was slowly added to a solution containing 1.71 g (6 mmol) of (2*R*,4*S*,5*R*)-3,4-dimethyl-1,3,2-oxazaphospholidine-2-borane in THF (6 mL) cooled at −40 °C. Once the transfer was completed, the reaction medium was allowed to reach room temperature, stirred for an additional hour, and then hydrolyzed by the addition of water (0.1 mL). After elimination of the solvents, the residue was dissolved in dichloromethane and chromatographed on silica gel, using diethyl ether as the eluant. The ether was eliminated under vacuum to leave **3a** as a white solid (2.2 g, 93% yield).

3a. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.60−6.86 (m, 14H, 2 × C_6H_5 and C_6H_4), 4.88 (d, 1H, C*H*, $J_{HH} = 6.9$ Hz), 4.32 (m, 1H, C*H*), 3.57 (s, 3H, OCH_3), 2.54 (d, 3H, NCH_3, $J_{HP} = 8.1$ Hz), 1.22 (d, 3H, CH_3, $J_{HH} = 6.9$ Hz), 0.3−2.0 (m, 3H, BH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.01 MHz): δ 69.1 (bm).

Synthesis of Methyl (*R*)-(*o*-Anisyl)phenylphosphinite−Borane (3b). One molar equivalent of sulfuric acid (0.3 mL) was added to a solution of **3a** (2 g, 5.1 mmol) in anhydrous methanol (20 mL). After the mixture was stirred overnight, the solution was first filtered on a short column of silica gel to eliminate the acid in excess and then the methanol was evaporated under vacuum. The residue containing the phosphinite−borane complex **3b** was extracted by dichloromethane and purified by column chromatography on silica gel, using dichloromethane as the eluant. **3b** was isolated as a colorless liquid (1 g, 80% yield).

3b. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.84−6.84 (m, 9H, C_6H_5 and C_6H_4), 3.73 (d, 3H, OCH_3, $J_{HP} = 12$ Hz), 3.62 (s, 3H, CH_3), 1.8−0.2 (m, 3H, BH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.01 MHz): δ 106.2 (q, $J_{PB} = 81$ Hz). Anal. Calcd for $C_{14}H_{18}BO_2P$: C, 64.65; H, 6.98. Found: C, 64.94; H, 7.08.

Synthesis of (*S*)-(Phenyl(2-anisyl)phosphino)(2-pyridyl)methane−Borane (3·BH$_3$). To a solution containing 0.55 g of 2-picoline (5.94 mmol) in 3 mL of diethyl ether cooled at 0 °C was slowly added 3.7 mL of a 1.6 M solution of *n*-BuLi in hexane (5.94 mmol). The mixture was stirred at 0 °C for 1h and then added to a solution containing 0.8 g of **3b** (2.97 mmol) in THF (3 mL) cooled at −20 °C. Once the addition was completed, the reaction mixture was stirred for an additional 15 min at −20 °C and then for 1 h at 0 °C. The hydrolysis was performed at room temperature by adding a minimum amount of water. After the removal of the solvents under vacuum, the residue was purified by chromatography on silica gel using a diethyl ether/hexanes mixture as the eluant. Phosphine−borane **3·BH$_3$** was isolated as a yellow oil (0.7 g, 70% yield).

3c. ^1H NMR ($CDCl_3$, 200 MHz): δ 8.35 (m, 1H, C_5H_4N), 7.85−6.83 (m, 12H, C_6H_5, C_6H_4, and C_5H_4N), 4.01 (AB(X), 2H, PCH_2, $J_{H_aH_b} = 13.5$ Hz, $J_{H_aP} = 13.9$ Hz, $J_{H_bP} = 12.6$ Hz), 3.70 (s, 3H, CH_3), 2.1−0.2 (m, 3H, BH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.01 MHz): δ 17.0 (q, $J_{PB} = 52$ Hz).

(*S*)-(Phenyl(2-anisyl)phosphino)(2-pyridyl)methane (3). The phosphine−borane complex **3**·BH_3 (0.7 g, 2 mmol) was dissolved in 10 mL of morpholine, and the solution was heated at 70 °C for 2 h. Excess morpholine was eliminated under vacuum. The residue was treated by a mixture of diethyl ether (20 mL) and water (20 mL). The water phase, which contains most of the morpholine−borane complex, was discarded. The diethyl ether phase was evaporated under vacuum, and the residue was purified by filtration on a short column of silica gel using diethyl ether as the eluant. The phosphine **3** has been isolated as a white solid (0.6 g, 95% yield).

3 $[\alpha]_D = +61.4°$ ($c = 0.7$, C_6H_6). ^1H NMR ($CDCl_3$, 200 MHz): δ 8.44 (m, 1H, C_5H_4N), 6.78−7.49 (m, 12H, C_6H_5, C_6H_4, and C_5H_4N), 3.60 (AB, 2H, PCH_2, $J_{H_aH_b} = 13.2$ Hz), 3.66 (s, OCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.01 MHz): δ −19.2 (s). Anal. Calcd for $C_{19}H_{18}NOP$: C, 74.24; H, 5.92; N, 4.56. Found: C, 74.01; H, 5.97; N, 4.51.

Synthesis of the Complexes 4, 5, 6, and 9. General Procedure. A dichloromethane solution (4 mL) of the appropriate phosphine (0.5 mmol) was added to a solution of 0.5 g of $RuCl_2(PPh_3)_3$ (0.5 mmol) in the same solvent (10 mL). The reaction medium was stirred overnight. The solvent was removed under vacuum, and the solid residue was washed with a toluene/hexanes mixture (1:3, 2 × 4 mL) to eliminate triphenylphosphine. The complexes have been purified by recrystallization from dichloromethane/hexane mixtures.

$RuCl_2(PPh_3)$(1) (4): yellow (73% yield). ^1H NMR (CD_2Cl_2, 303 K, 250 MHz): δ 8.48−6.20 (m, 29 H, C_6H_5, C_5H_4N), 4.30 (dt, $J_{HH} = 1.6$ Hz, $J_{PH} = 10.4$ Hz, 1H, $CH{-}CH_2{-}O{-}CH_2{-}CH_3$), 3.56, 3.55 (ABMX spin system (M = H, X = P), $J_{AB} = 7.8$ Hz, $J_{AH} = J_{BH} = 1.6$ Hz, $J_{PA} = 20$ Hz, $J_{PB} = 7.8$ Hz, 2H, $CH{-}CH_2{-}O{-}CH_2{-}CH_3$), 4.19, 4.18 ($J_{AB} = 5.1$ Hz, $J_{AH} = J_{BH} = 7$ Hz, 2H, $CH{-}CH_2{-}O{-}CH_2{-}CH_3$)), 1.07 (t, $J_{HH} = 7$ Hz, 3 H, $CH{-}CH_2{-}O{-}CH_2{-}CH_3$). ^1H NMR (CD_2Cl_2, 183 K, 250 MHz): δ 9.70 (bt, 1H, C_5H_4N), 8.28−6.19 (m, 28H, C_6H_5, C_5H_4N), 4.35 (d, $J_{PH} = 10.5$ Hz, 1H, $CH{-}CH_2{-}O{-}CH_2{-}CH_3$), 3.50 (m, 2H, $CH{-}CH_2{-}O{-}CH_2CH_3$), 4.18, 4.01 (bm, 2H, $CH{-}CH_2{-}O{-}CH_2{-}CH_3$)), 1.10 (bm, 3H, $CH{-}CH_2{-}O{-}CH_2CH_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 303 K, 32 MHz): δ 62.2. 183 K, $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 183 K, 101 MHz): δ 66.7, 64.7 ($J = 39$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 303 K, 32 MHz): δ 63.3, 61.2 ($J = 39$ Hz). IR (ν(Ru−Cl, CsI): 300, 275 cm^{-1}. Anal. Calcd for $C_{39}H_{37}Cl_2P_2ONRu$: C, 60.86; H, 4.85; N, 1,82. Found: C, 60.87; H, 5.17; N, 1.78.

$RuCl_2(PPh_3)$(2R) (5): yellow (64% yield).

5a (only significant NMR data are reported). ^1H NMR (CD_2Cl_2, 297 K, 400 MHz): δ 8.45 (b, 1H, C_5H_4N), 4.29 (d, $J_{PH} = 10.4$ Hz, 1H, $CH{-}CH_2{-}O{-}$menthyl), 3.51 (dd, $J_{HH} = 8$ Hz, $J_{PH} = 12.7$ Hz), 3.38 (d, $J_{HH} = 8$ Hz, $CH{-}CH_2{-}O{-}$menthyl), 4.41 (m, 1H, H_1 (menthyl)). ^1H NMR (CD_2Cl_2, 193 K): δ 9.73 (bt, 1H, C_5H_4N), 4.35 (d, $J_{PH} = 10$ Hz, 1H, $CH{-}CH_2{-}O{-}$menthyl), 3.46 (dd, $J_{HH} = 7$ Hz, $J_{PH} = 12$ Hz), 3.23 (d, $J_{HH} = 7$ Hz, $CH{-}CH_2{-}O{-}$menthyl), 4.26 (m, 1H, H_1 (menthyl)). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 297 K, 161.9 MHz): δ 62 (b), 66.4 (bd, $J = 38$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 193 K, 161.9 MHz): δ 62 (d), 66.8 (d, $J = 39$ Hz).

5b (only significant NMR data are reported). ^1H NMR (CD_2Cl_2, 297 K, 400 MHz): δ 9.42 (d, $J = 5.2$ Hz, 1H, C_5H_4N), 3.31 (dd, $J_{HH} = 8$ Hz, $J_{PH} = 12.3$ Hz, 1H, $CH{-}CH_2{-}O{-}$menthyl), 3.59 (t, $J_{HH} = 9$ Hz), 3.23 (t, $J_{HH} = J_{PH} = 9$ Hz, $CH{-}CH_2{-}O{-}$menthyl), 2.79 (m, 1H, H_1 (menthyl)). ^1H NMR (CD_2Cl_2, 193 K, 400 MHz): δ 9.44 (d, $J_{HH} = 4.9$ Hz, 1H, C_5H_4N), 3.06 (b, 1H, $CH{-}CH_2{-}O{-}$menthyl), 3.56, 2.78 (b, $CH{-}CH_2{-}O{-}$menthyl), 2.71 (b, 1H, H_1 (menthyl)). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 297 K, 161.9 MHz): δ 52 (b), 75.3 (b). $^{31}P\{^1H\}$ NMR (CD_2Cl_2,

Table 4. Crystal Data, Data Collection, and Refinement Parameters for 6b and 9

	6b	**9**·CH_2Cl_2
	Crystal Data	
chem formula	$C_{47}H_{51}Cl_2NOP_2Ru$	$C_{38}H_{35}Cl_4NOP_2Ru$
mol wt	879.85	826.53
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	10.020(2)	8.747(2)
b (Å)	16.746(2)	16.347(4)
c (Å)	25.711(4)	27.196(5)
V (Å^3)	4314(1)	3888(2)
Z	4	4
ρ_{calcd} (g·cm^{-3})	1.28	1.41
no. of reflns for cell params	25	25
range for cell params (deg)	12−14	12−14
μ (mm^{-1})	5.77	7.82
F_{000}	1820.31	1677.33
	Data Collection	
data collection method	$\omega/2\theta$	$\omega/2\theta$
no. of indep reflns	5707	3218
no. of obsd reflns	4933	1470
obs criterion	$F_o^2 > 3\sigma Fo^2$	$F_o^2 > 3\sigma Fo^2$
θ max (deg)	23	23
range of hkl	$0 \geq h \geq 11$, $0 \geq k \geq 18$, $-28 \geq l \geq 28$	$0 \geq h \geq 8$, $0 \geq k \geq 18$, $-26 \geq l \geq 26$
scan range θ (deg)	$0.8 + 0.35 \tan \theta$	$0.8 + 0.35 \tan \theta$
	Refinement	
R	0.0243	0.0765
R_w	0.0279	0.0844
abs corr	Ψ-scans	DIFABS
weighting scheme	Chebyshev	Chebyshev
coeff A_r	0.909, 0.2081, 0.688,	2.21, 0.110, 1.65
Flack's parameter		0.00(3)
GOF[a]	0.978	1.063
no. of reflns used	4933	1470
no. of params refined	488	224
residual electron density (e·Å^{-3})	−0.76 (min), 0.70 (max)	−1.01 (min), 2.33 (max)

[a] Goodness of Fit = $[\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{paras})]^{1/2}$.

193 K, 161.9 MHz): δ 53.2 (d), 74.5 (d, J = 32.5 Hz). Anal. Calcd for $C_{47}H_{51}Cl_2NOP_2Ru$: C, 64.15; H, 5.97; N, 1.59. Found: C, 62.94; H, 5.98; N, 1.60.

$RuCl_2(PPh_3)(2S)$ (6): yellow (79% yield).

6a (only significant NMR data are reported). ^{1}H NMR (CD_2Cl_2, 297 K, 400 MHz): δ 8.39 (b, 1H, C_5H_4N), 4.31 (d, J_{PH} = 10.7 Hz, 1H, CH−CH_2−O−menthyl), 3.57 (dd, J_{HH} = J_{PH} = 5.8 Hz), 3.39 (d, J_{HH} = 5.8 Hz, CH−CH_2−O−menthyl), 4.50 (m, 1H, H_1 (menthyl)). ^{1}H NMR (CD_2Cl_2, 193 K): δ 9.74 (b, 1H, C_5H_4N), 4.35 (m, 1H, CH−CH_2−O−menthyl), 3.48 (b), 3.23 (b, CH−CH_2−O−menthyl), 4.35 (b, 1H, H_1 (menthyl)). ^{31}P{^{1}H} NMR (CD_2Cl_2, 297 K, 161.9 MHz): δ 63.7 (d), 66.4 (d, J = 39 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, 193K, 161.9 MHz): δ 64.3 (d), 66.5 (J = 39 Hz).

6b (only significant data are reported). ^{1}H NMR (CD_2Cl_2, 297 K, 400 MHz): δ 9.43 (d, J = 5.6 Hz, 1H, C_5H_4N), 3.26 (dd, J_{HH} = 9.1 Hz, J_{PH} = 7.7 Hz, 1H, CH−CH_2−O−menthyl), 3.70 (t, J_{HH} = J_{PH} = 9 Hz), 3.13 (b, CH−CH_2−O−menthyl), 2.91 (m, 1H, H_1 (menthyl)). ^{1}H NMR (CD_2Cl_2, 193 K): δ 9.38 (b, 1H, C_5H_4N), 2.90 (b, 1H, CH−CH_2−O−menthyl), 3.70, 3.07 (b, CH−CH_2−O−menthyl), 2.95 (b, 1H, H_1 (menthyl). ^{31}P{^{1}H} NMR (CD_2Cl_2, 297 K, 161.9 MHz): δ 53.2 (b), 74 (b). ^{31}P{^{1}H} NMR (CD_2Cl_2, 193 K, 161.9 MHz): δ 53.2 (d), 73.9 (d, J = 32.6 Hz). Anal. Calcd for $C_{47}H_{51}Cl_2NOP_2Ru$: C, 64.15; H, 5.97; N, 1.59. Found: C, 63.84; H, 5.68; N, 1.48.

$RuCl_2(PPh_3)(3)$ (9): yellow (91% yield). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 9.61 (d, 1H, C_5H_4N, J_{HH} = 5.4 Hz), 7.64−6.51 (m, 24H, 4 × C_6H_5, C_6H_4), 4.61 (s, 3H, OCH_3), 3.55 (AB(X), 2H, PCH_2, $J_{H_aH_b}$ = 15.9 Hz, J_{H_aP} =13.7 Hz, J_{H_bP} = 8.4 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 81.01 MHz): δ 64.5 (d), 62.9 (d, J_{PP} = 37.5 Hz). Anal. Calcd for $C_{37}H_{33}Cl_2NOP_2Ru$: C, 59.91; H, 4.49; N, 1.89. Found: C, 58.61; H, 4.51; N, 1.71.

Reactivity of 4 toward CO. Synthesis of 7. Carbon monoxide was bubbled through a solution of $RuCl_2(PPh_3)$(**1**) (**4**, 0.2 g) in dichloromethane (10 mL) for 10 min. The addition of hexanes (10 mL) induced the precipitation of **7**, which was isolated upon filtration as a pale yellow powder (0.15 g, 70% yield). IR (ν(CO), CH_2Cl_2): 1980 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 8.40−6.62 (29H, C_6H_5, C_5H_4N), 6.57 (dd, J_{HH} = 5.2 Hz, J_{PH} = 9.8 Hz, 1H, CH−CH_2−O−CH_2−CH_3), 4.16, 3.63 (m, 2H, CH−CH_2−O−CH_2−CH_3), 3.12 (m, 2H, CH−CH_2−O−CH_2−CH_3), 1.03 (t, J_{HH} = 7 Hz, 3H, CH−CH_2−O−CH_2−CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 81.01 MHz): δ 40.4 (d), 25.5 (d, J_{PP} = 27.6 Hz).

Synthesis of 8. Complex **7** (0.15 g) was dissolved in 5 mL of CH_2Cl_2, and the solution was stirred for 15 h at room temperature. The addition of 5 mL of hexanes induced the precipitation of 0.1 g (70% yield) of **8** as a pale yellow powder. IR (ν(CO), CH_2Cl_2): 1962 cm^{-1}; (ν(Ru−Cl), CsI) 310, 272 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 8.41−6.63 (m, 29H, C_6H_5, C_5H_4N), 5.91 (dd, J_{HH} = 7.8 Hz, J_{PH} = 14.3 Hz, 1H, CH−CH_2−O−CH_2−CH_3), 3.95 (m, 2H, CH−CH_2−O−CH_2−CH_3), 3.49 (m, 2H, CH−CH_2−O−CH_2−CH_3), 1.20 (t, J_{HH} = 7 Hz, 3H, CH−CH_2−O−CH_2−CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 81.01 MHz): 61.2 (d), 18.8 (d, J_{PP} = 354.5 Hz). Anal. Calcd for $C_{40}H_{37}Cl_2NO_2P_2Ru$: C, 60.23; H, 4.68; N, 1.76. Found: C, 60.45; H, 5.01; N, 2.02.

Reactivity of 9 toward CO. Synthesis of 10. Carbon monoxide was bubbled through a solution of $RuCl_2(PPh_3)$(**4**) (**9**, 0.1 g) in dichloromethane (10 mL) for 10 min. The addition of hexanes (10 mL) induced the precipitation of **10**, which was isolated upon filtration as a pale yellow powder (0.09 g, 43% yield). IR(ν(CO), CH_2Cl_2): 1987 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.40−6.20 (28H, C_6H_5, C_5H_4N), 4.92 (dd, J_{HH} = 16.8 Hz, J_{PH} = 10.9 Hz, 1H, CH_2), 4.34 (dd, J_{HH} = 16.8 Hz, J_{PH} = 12.2 Hz, 1H, CH_2), 3.25 (s, 3H, OCH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 81.01 MHz): 44.9 (d), 16.2 (d, J_{PP} = 29.4 Hz). Anal. Calcd for $C_{37}H_{31}Cl_2NO_2P_2Ru$: C, 58.82; H, 4.14; N, 1.85. Found: C, 58.56; H, 4.01; N, 1.92.

X-ray Diffraction Studies. Crystals of **6b** and **9** suitable for X-ray diffraction were obtained through recrystallization

at −20 °C from dichloromethane/hexane. Data were collected on an Enraf-Nonius CAD4 diffractometer at 22 °C. Cell constants were obtained by the least-squares refinement of the setting angles of 25 reflections in the range $24° < 2\theta(\text{Mo K}\alpha_1) < 28°$. The space group was determined by careful examination of systematic extinctions in the listing of the measured reflections.

All calculations were performed on a PC-compatible computer. Data reductions were carried out using the RC93 program.[25] Full crystallographic data are given in Table 4. The structures were solved by using the SIR92 program,[26] which revealed the positions of most of the non-hydrogen atoms. All remaining non-hydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses by using the CRYSTALS program.[27,28] Complex **9** was found to crystallize with 1 molecule of dichloromethane per unit cell. The least-square refinements were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and the calculated structure factors. The weighting scheme used in the last refinement cycles was $w = w'[1 - (\Delta F/6\sigma(F_o)^2]^2$, where $w' = 1/\sum_{n=1}{}^{n} A_r T_r(x)$ with a variable number of coefficients A_r for the Chebyshev polynomial $A_r T_r(x)$, where x was $F_c/F_c(\text{max})$.[29] Models reached convergence with $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)]^{1/2}$ having the values given in Table 4. Atomic scattering factors were taken from the usual tabulations.[30] Anomalous dispersion terms for the Ru atoms were included in F_c.[31] For the structure of **6b**, all non-hydrogen atoms were allowed to vibrate anisotropically. For the structure of **9**, owing to the poor quality of the monocrystal used, only Ru, P, and Cl atoms have been refined with anisotropic temperature factors. For both structures, all of the hydrogen atoms were set in idealized positions (C−H = 0.99 Å). The absolute configuration of **6b** was determined by refining the Flack's enantiopole parameter,[32] which is defined as: $F_o^2 = (1 - x)F(h)^2 + xF(-h)^2$. No attempts have been made to determine the absolute configuration of **9**.

Supporting Information Available: Tables giving final values of all refined atomic coordinates, calculated atomic coordinates, anisotropic thermal parameters, and all bond lengths and angles (14 pages). Ordering information is given on any current masthead page.

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(25) Watkin, D. J.; Prout, C. K.; de Q Lilley, P. M. *RC93*; Chemical Crystallography Laboratory: Oxford, U.K., 1994.
(26) Altomare, A.; Cascarano, G.; Giacovazzo, G.; Gualiardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. SIR92-A program for automatic solution of crystal structures by direct methods. *J. Appl. Crystallogr.* **1994**, *27*, 435.
(27) Watkin, D. J.; Prout, C. K.; Carruthers, R. J.; Betteridge, P. *CRYSTALS*, Issue 10; Chemical Crystallography Laboratory: Oxford, U.K., 1996.
(28) Watkin, D. J.; Prout, C. K.; Pearce, L. J. *CAMERON*; Chemical Crystallography Laboratory: Oxford, U.K., 1996.
(29) Carruthers, J. R.; Watkin, D. J. *Acta Crystallogr.* **1979**, *A35*, 698.
(30) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography;* Kynoch Press: Birmingham, England, **1974**; Vol. 4, Table 2.2B.
(31) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography;* Kynoch Press: Birmingham, England, **1974**; Vol. 4, Table 2.3.1.
(32) Flack, H. *Acta Crystallogr.* **1983**, *A39*, 876.