Organometallics **2002,** *21,* 761−764

Notes

Asymmetric Induction and Configurational Stability at the Metal Center in Half-Sandwich (η^6-*p*-Cymene)ruthenium(II) and (η^5-Pentamethylcyclopentadienyl)rhodium(III) Complexes Containing Chiral Phosphito-N and Phosphonito-N Ligands

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Received June 25, 2001

Summary: The reactions of the complexes $[Ru(\eta^6\text{-}p\text{-}cymene)Cl_2]_2$ *and* $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ *with the ligands Phosphito-N ((S)-8-((3,5-dioxa-4-phosphacyclohepta[2,1-a;3,4-a′]dinaphthalen-4-yl)oxy)quinoline, (S)-**1**) and Phosphonito-N ((R)-8-(3,5-dioxa-4-phosphacyclohepta[2,1-a;3,4-a′]dinaphthalen-4-yl)quinoline, (R)-**2**) were investigated. The reactions of (S)-**1** with* $[Ru(\eta^6\text{-}p\text{-}cymene)Cl_2]_2$ *and* $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ *give the complexes* $[Ru(\eta^6\text{-}p\text{-}cymene)(S\text{-}\mathbf{1})Cl_2]$ *(**3**) and* $[Rh(\eta^5\text{-}C_5Me_5)(S\text{-}\mathbf{1})Cl_2]$ *(**5**). Treatment of **3** and **5** with* NH_4PF_6 *promoted the chelation process of the P-coordinated ligand (S)-**1**, affording the corresponding chelate complexes* $[Ru(\eta^6\text{-}p\text{-}cymene)(S\text{-}\mathbf{1})Cl]PF_6$ *(**4**) and* $[Rh(\eta^5\text{-}C_5Me_5)(S\text{-}\mathbf{1})Cl]PF_6$ *(**6**) with high stereoselectivity. The absolute configuration of the major diastereoisomer **6a** was determined by X-ray diffractometry. The reaction of (R)-**2** with* $[Ru(\eta^6\text{-}p\text{-}cymene)Cl_2]_2$ *and* $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ *afforded in one pot the chelate complexes* $[Ru(\eta^6\text{-}p\text{-}cymene)(R\text{-}\mathbf{2})Cl]Cl$ *(**7**) and* $[Rh(\eta^5\text{-}C_5Me_5)(R\text{-}\mathbf{2})Cl]Cl$ *(**8**); the latter was obtained as the only diastereoisomer. The asymmetric induction and the configurational stability at the metal center of the cationic half-sandwich ruthenium and rhodium diastereoisomers are considered.*

Introduction

Half-sandwich (η^6-arene)ruthenium(II) and (η^5-cyclopentadienyl)rhodium(III) complexes are isoelectronic species which exhibit a pseudotetrahedral geometry. This feature can be used as a powerful tool for examining the stereochemistry at the stereogenic metal center in the course of reactions such as ligand substitution or migratory insertion.[1] This information has important application in homogeneous asymmetric reactions catalyzed by transition-metal complexes. In particular, half-sandwich ruthenium(II) complexes are effective precursors for catalytic asymmetric hydrogenation,[2] whereas analogous half-sandwich rhodium(III) complexes have found little use as precatalysts for asymmetric reactions.

Several neutral and anionic chiral bidentate ligands have been employed to obtain half-sandwich diastereomeric ruthenium(II) and rhodium(III) species that differ in the configuration at the metal center.[3] Most of these optically active complexes are configurationally

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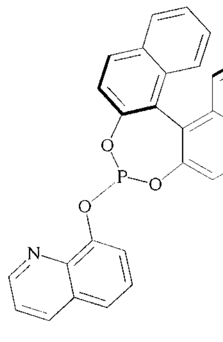
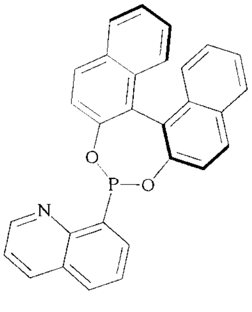
10.1021/om010563z CCC: $22.00
Publication on Web 01/25/2002

Chart 1



(*S*)-1



(*R*)-2

unstable at the stereogenic metal center and epimerize on heating in protic solvents. Recently, we reported[4] the synthesis and characterization of configurationally stable (η^6-arene)ruthenium(II) complexes of the type [Ru(η^6-arene)(P-N*)Cl]Cl (P-N* = enantiomerically pure (β-aminoalkyl)phosphine or (β-aminoalkyl)phosphonite; arene = benzene, *p*-cymene, hexamethylbenzene). We also described the kinetics of the ring closure process that takes place in the complexes [Ru(η^6-arene)(P-N*)Cl$_2$], in which the P-N* ligand is monodentate P-bonded, affording the chelate [Ru(η^6-arene)(P-N*)Cl]Cl.

We report here the reactions between the ligands Phosphito-N ((*S*)-**1**) and Phosphonito-N ((*R*)-**2**) (based on 8-quinolines and (*S*)- or (*R*)-binaphthol) and the isoelectronic complexes [Ru(η^6-*p*-cymene)Cl$_2$]$_2$ and [Rh(η^5-C$_5$Me$_5$)Cl$_2$]$_2$, which lead to the expected pseudotetrahedral organometallic compounds. We discuss the asymmetric induction and the configurational stability at the metal center of the synthesized isoelectronic half-sandwich ruthenium and rhodium complexes. The absolute configuration at the rhodium center in the complex [Rh(η^5-C$_5$Me$_5$)(*S*-**1**)Cl]PF$_6$ (**6a**) was determined by X-ray diffractometry.

Rhodium(I), palladium(II), and platinum(II) complexes have previously been synthesized using the chiral ligands (*S*)-**1** and (*R*)-**2**.[5] These ligands have also been employed as chiral auxiliaries in the Cu-catalyzed enantioselective conjugate addition of diethylzinc to 2-cyclohexen-1-one.[6]

Results and Discussion

The syntheses of the ligands Phosphito-N ((*S*)-8-((3,5-dioxa-4-phosphacyclohepta[2,1-a;3,4-a′]dinaphthalen-4-yl)oxy)quinoline, (*S*)-**1**) and Phosphonito-N ((*R*)-8-(3,5-dioxa-4-phosphacyclohepta[2,1-a;3,4-a′]dinaphthalen-4-yl)quinoline, (*R*)-**2**) have been previously reported (Chart 1).[5,6] These ligands differ slightly in the electronic nature of the phosphorus donor atom and more substantially in the coordination properties.

In fact, on coordination to a metal center, (*S*)-**1** and (*R*)-**2** can form six- and five-membered chelate rings, respectively, and this feature strongly influences the outcome when they react with [Ru(η^6-*p*-cymene)Cl$_2$]$_2$ or [Rh(η^5-C$_5$Me$_5$)Cl$_2$]$_2$.

The reaction of (*S*)-**1** with [Ru(η^6-*p*-cymene)Cl$_2$]$_2$ in a 2:1 molar ratio in toluene afforded the complex [Ru(η^6-*p*-cymene)(*S*-**1**)Cl$_2$] (**3**), in which the (*S*)-**1** ligand is monodentate P-bonded to the ruthenium center. Acetone solutions of **3** are not conducting, indicating that **3** is a neutral species. The ^{31}P{^{1}H} NMR (C$_6$D$_6$) spectrum exhibits one singlet at δ 130.1 ppm. In the ^{1}H NMR spectrum no shift to lower field with respect to the free ligand was observed for the signal of the proton ortho to the nitrogen. The addition of NH$_4$PF$_6$ to a THF solution of **3** promoted the chelation process of the P-coordinated ligand (*S*)-**1**. After several days the cationic chelate complex [Ru(η^6-*p*-cymene)(*S*-**1**)Cl]PF$_6$ (**4**) was obtained as a pair of diastereoisomers differing in the configuration at the metal center. A ratio of 10:1 between the diastereoisomers **4a** and **4b** was estimated by integration of the singlets observed in the ^{31}P{^{1}H} NMR (C$_6$D$_6$) spectrum at δ 155.1 and 143.1 ppm, respectively. Unfortunately, we were unable to separate **4a** and **4b** by crystallization or chromatographic techniques, due to their low stability in solution over prolonged time or on silica. Moreover, mixtures of **4a** and **4b** in various solvents rapidly decompose on warming, thus preventing us from obtaining information about the configurational stability of the metal stereocenter.

Similarly, the reaction of [Rh(η^5-C$_5$Me$_5$)Cl$_2$]$_2$ with (*S*)-**1** afforded the compound [Rh(η^5-C$_5$Me$_5$)(*S*-**1**)Cl$_2$] (**5**) as an orange solid which is air-stable in the solid state for a long time. Complex **5** is not stable in chlorinated solvents and in methanol. The structure of **5** in which (*S*)-**1** is monodentate through phosphorus was confirmed by conductivity measurements in acetone, which showed the complex to be neutral. Furthermore, ^{1}H NMR exhibited no chemical shift difference between the proton ortho to the quinolinic nitrogen and the free ligand (*S*)-**1**.[7] When NH$_4$PF$_6$ was added to **5** in THF, the cationic chelate complex [Rh(η^5-C$_5$Me$_5$)(*S*-**1**)Cl]PF$_6$ (**6**) was formed, as confirmed by analytical, conductivity, and ^{1}H NMR spectroscopic data. Complex **6** was obtained as a pair of diastereoisomers, **6a** and **6b**, in the molar ratio 15:1, as estimated by the integration of the doublets respectively at δ 146.5 ($^1J_{\mathrm{RhP}}$ = 237 Hz) and δ 135.7 ppm ($^1J_{\mathrm{RhP}}$ = 217 Hz) in the ^{31}P{^{1}H} NMR (C$_6$D$_6$) spectrum. The diastereoisomers **6a** and **6b** have opposite configurations at rhodium. Since the molar ratio between the diastereoisomers does not change on refluxing for 36 h in methanol, we deduced that epimerization does not occur.

Crystallization of the diastereomeric mixture from dichloromethane–methanol afforded orange crystals after several days. These crystals corresponded to the major diastereoisomer **6a**, as was established by ^{31}P{^{1}H} NMR spectroscopy. An X-ray crystallographic study proved that the absolute configuration of this diastereoisomer is $S_{\mathrm{Rh}}S_{\mathrm{a}}$. We further confirmed that **6a** is configurationally stable in refluxing methanol over 24 h.

Dichloromethane solvation molecules were found in the crystals of complex **6a**. A view of the structure of **6a** is shown in Figure 1.

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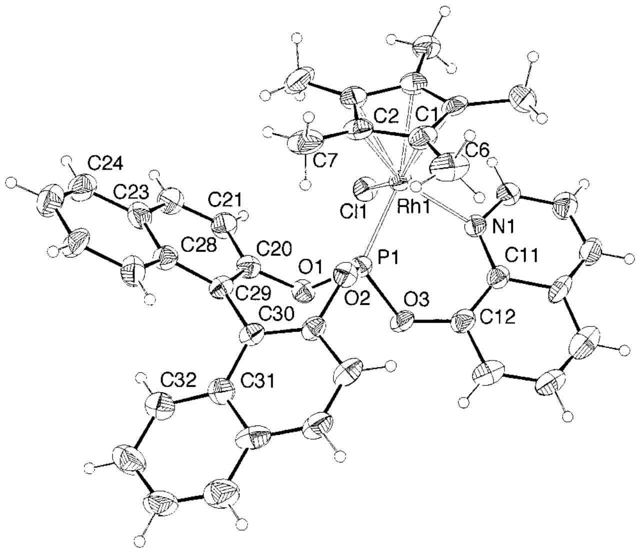

Figure 1. View of the molecular structure of the complex **6a** with the atomic numbering system. The ellipsoids are drawn at the 30% probability level.

The metal displays a three-legged piano-stool type of coordination involving an η^5-coordinated pentamethylcyclopentadienyl group (the five Rh−C bond distances are within the range 2.165(9)−2.252(9) Å), a Cl atom, and the P and N atoms of the phosphonito chelate (*S*)-**1** ligand. If the centroid of the Cp* ring is considered as a single site, the coordination geometry can also be described as pseudotetrahedral. The six-membered Rh(1)N(1)C1(1)C1(2)O(3)P(1) ring shows a roughly boat-shaped conformation (the O(3) and N(1) atoms are displaced by 0.408(6) and 0.519(7) Å, respectively, from the mean plane through the other four atoms) with a bite angle P(1)−Rh(1)−N(1) of 89.1(2)°. The Rh(1)−P(1), Rh(1)−Cl(1), and Rh(1)−N(1) bond distances are 2.209(2), 2.397(2), and 2.149(7) Å, respectively.

In the (*S*)-**1** ligand the quinoline moiety is almost planar, the P−O bond distances, 1.597(6), 1.598(5), and 1.604(6) Å, are practically identical, the O−P−O angles are within the range 94.8(3)−122.5(2)°, and the two naphthyl groups are planar and form a dihedral angle of 54.5(2)°.

Because of the lack of X-ray crystallographic characterization of the diastereoisomers **4a** and **4b**, a direct correlation between the asymmetric induction at the metal center in the isoelectronic half-sandwich complexes [Ru(η^6-*p*-cymene)(*S*-**1**)Cl]PF$_6$ (**4**) and [Rh(η^5-C$_5$Me$_5$)(*S*-**1**)Cl]PF$_6$ (**6**) is not possible. Besides, as pointed out by Brunner and co-workers,[9] the comparison of the CD spectra is not a certain method to establish the absolute configuration.

The reaction course of (*R*)-**2** with [Ru(η^6-*p*-cymene)Cl$_2$]$_2$ and [Rh(η^5-C$_5$Me$_5$)Cl$_2$]$_2$ is different from that observed with (*S*)-**1**.

The reaction of (*R*)-**2** with [Ru(η^6-*p*-cymene)Cl$_2$]$_2$, in a 2:1 molar ratio in toluene, afforded two compounds; the ^{31}P{^{1}H} NMR (C$_6$D$_6$) spectrum showed two signals at δ 194.2 and 182.5 ppm in a 16:1 ratio. Separation of these complexes by chromatography on an alumina column afforded only the product with a ^{31}P{^{1}H} chemical shift of 194.2 ppm. This compound is an orange solid, soluble in methanol, acetone, and chlorinated solvents. In methanol solution, it is a 1:1 electrolyte. Analytical, conductivity, and ^{1}H NMR spectroscopic data support [Ru(η^6-*p*-cymene)(*R*-**2**)Cl]Cl (**7a**) as the formula for this complex. All attempts to obtain **7a** in crystalline form suitable for X-ray analysis were not successful.

The reaction of [Rh(η^5-C$_5$Me$_5$)Cl$_2$]$_2$ with (*R*)-**2** in a 1:2 molar ratio in toluene gave the cationic chelate complex [Rh(η^5-C$_5$Me$_5$)(*R*-**2**)Cl]Cl (**8a**) as the only diastereomer. It is an air-stable orange solid; in acetone solution, it is a 1:1 electrolyte. As expected, the ^{31}P{^{1}H} NMR (C$_6$D$_6$) spectrum exhibits only one doublet centered at δ 180.5 ppm ($^1J_{\mathrm{RhP}} = 205$ Hz). In the ^{1}H NMR spectrum, the signal due to the proton in a position ortho to the nitrogen is significantly shifted to lower field of 0.73 ppm with respect to the free ligand.[7] Also, in this case, all attempts to obtain **8a** as crystals suitable for X-ray analysis failed.

It is remarkable that the neutral species, namely [Ru(η^6-*p*-cymene)(*R*-**2**)Cl$_2$] and [Rh(η^5-C$_5$Me$_5$)(*R*-**2**)Cl$_2$], containing (*R*)-**2** as a monodentate P-bonded ligand, could not be observed. Similar results have been obtained also using the ligand (*S*)-**2** having opposite configuration at the binaphthol moiety. Thus, the ring closure process in these compounds, which can be considered as intermediates to the formation of **7** and **8**, is very fast. In contrast, the reactions of the analogous compounds containing (*S*)-**1** are very slow. Kinetic studies indicate that formation of a chelate five-membered ring occurs faster than a six-membered one.[10]

In a kinetic study[4] on the ring closure of P-N* ligands in the open-ring intermediates [Ru(η^6-arene)(P-N*)Cl$_2$], affording [Ru(η^6-arene)(P-N*)Cl]Cl (P-N* = enantiomerically pure (β-aminoalkyl)phosphines or (β-aminoalkyl)phosphonite), we found that Cl replacement occurs by a solvolytic bimolecular process in which k_{obs} is significant only when the nucleophile is an alcohol, particularly methanol. As a matter of fact, the chelate complexes [Ru(η^6-arene)(P-N*)Cl]Cl have been obtained by reacting [Ru(η^6-arene)Cl$_2$]$_2$ with P-N* in methanol or by adding a small amount of methanol to a chloroform solution of the open-ring intermediate [Ru(η^6-arene)(P-N*)Cl$_2$].[4] Unfortunately, complexes **3**−**5** are not stable in the presence of methanol.

The different behaviors of (*S*)-**1** and (*R*)-**2** in their reactions with [Ru(η^6-*p*-cymene)Cl$_2$]$_2$ and [Rh(η^5-C$_5$Me$_5$)Cl$_2$]$_2$ are certainly due to the size of the ring formed by chelation to the metal center. It should be noted that the distances of the binaphthol chiral moiety with respect to the metal center are the same in the chelate complexes formed by (*S*)-**1** and (*R*)-**2**. Nevertheless, the asymmetric induction at the metal center is higher for the formation of a five-membered chelate ring than for the six-membered ring. Moreover, the same ligand affords greater asymmetric induction in the rhodium substrate than in the ruthenium substrate.

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(8) Crystal data for **6a**·2CH$_2$Cl$_2$: formula, [C$_{39}$H$_{33}$ClNO$_3$PRh]PF$_6$·2CH$_2$Cl$_2$; crystal size, 0.23 × 0.33 × 0.41 mm; monoclinic; space group, $P2_1$; $a = 14.324(4)$ Å; $b = 8.562(3)$ Å; $c = 18.849(5)$ Å; $\beta = 108.70(5)°$; $V = 2190(1)$ Å^3, $Z = 2$, θ range 1.57−26.96°, $T = 293(2)$ K, 6679 reflections collected, 4652 independent reflections (R(int) = 0.0264), 3975 observed reflections, full-matrix least squares based on F_o^2, R1 = 0.0528, wR2 = 0.1392. Full details for the crystallographic analysis of **6a**·2CH$_2$Cl$_2$ are described in the Supporting Information.

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A comparison between the configurational stability at the metal center of the cationic half-sandwich ruthenium and rhodium diastereoisomers was hampered because of the instability of **4** in protic solvents, specifically methanol. However, experimental results indicate very high configurational stability for the complexes containing (*R*)-**2**, independently of the nature of the metal, and (*S*)-**1** for the rhodium species **6**. It is very likely that the five-membered chelate ring formed by (*R*)-**2** also induces high configurational stability to diastereomers. This assumption is in accord with our previous results.[4]

Experimental Section

Published methods were used to prepare the compounds 8-((3,5-dioxa-4-phosphacyclohepta[2,1-a;3,4-a′]dinaphthalen-4-yl)oxy)quinoline ((*S*)-**1**) and 8-(3,5-dioxa-4-phosphacyclohepta-[2,1-a;3,4-a′]dinaphthalen-4-yl)quinoline ((*R*)-**2**).[5,6] All other reagents were purchased from Sigma-Aldrich and used as supplied. Solvents were dried by standard procedures. All experiments were performed under a purified argon atmosphere and at room temperature. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AMX R300 instruments. ^{1}H NMR spectra were referenced to internal tetramethylsilane and ^{31}P-{^{1}H} spectra to external 85% H_3PO_4; positive chemical shifts for all nuclei are to higher frequency. Elemental analyses were performed by Redox snc, Monza, Milano, Italy.

[(η^6-*p*-cymene)Ru(*S*-1)Cl$_2$] (3). A solution of (*S*)-**1** (0.160 g, 0.348 mmol) in toluene (10 mL) was slowly added to a solution of [(η^6-*p*-cymene)RuCl$_2$]$_2$ (0.107 g, 0.174 mmol) in the same solvent (10 mL). After 1 h, the red-brown solution was reduced to ca. 5 mL, and by addition of 30 mL of *n*-hexane a light brown solid was obtained. The solid was collected, washed with *n*-hexane (3 × 10 mL), and dried in vacuo. Yield: 72% (0.191 g, 0.250 mmol). Anal. Calcd for $C_{39}H_{32}Cl_2NO_3PRu$: C, 61.18; H, 4.21; N, 1.83; Cl, 9.26. Found: C, 60.89; H, 4.53; N, 1.75; Cl, 9.29. ^{1}H NMR (C_6D_6): δ 8.64 (d, *o*-H, 1H), 7.44 (d, *ar*-H, 1H), 7.36 (m, *ar*-H, 6H), 5.74 (d, *ar*-H, 1H), 5.48 (d, *ar*-H, 1H), 5.36 (d, *ar*-H, 1H), 5.25 (d, *ar*-H, 1H), 3.05 (m, CH, 1H), 1.97 (s, CH_3, 3H), 0.87 (d, CH_3, 6H). ^{31}P{^{1}H} NMR (C_6D_6): δ 130.1 (s).

[(η^6-*p*-cymene)Ru(*S*-1)Cl]PF$_6$ (4). A solution of **3** (0.075 g, 0.096 mmol) in THF (13 mL) was treated with NH_4PF_6 (0.018 g, 0.117 mmol). The reaction mixture was vigorously stirred and monitored by ^{31}P NMR. After several days, the mixture was filtered off and the brown solution was reduced to ca. 5 mL. By addition of 30 mL of *n*-hexane a brown solid was obtained. The precipitate was collected, washed with *n*-hexane (3 × 10 mL), and dried in vacuo. Yield: 65% (0.055 g, 0.062 mmol). Anal. Calcd for $C_{39}H_{32}ClF_6NO_3P_2Ru$: C, 53.53; H, 3.69; N, 1.60; Cl, 4.05. Found: C, 53.42; H, 3.33; N, 1.54; Cl, 4.11. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 155.1 (s), 143.1 (s).

[(η^5-C$_5$Me$_5$)Rh(*S*-1)Cl$_2$] (5). A solution of (*S*)-**1** (0.148 g, 0.323 mmol) in toluene (5 mL) was added dropwise to a solution of [(η^5-C_5Me_5)RhCl$_2$]$_2$ (0.080 g, 0.129 mmol) in the same solvent (15 mL). After 4 h, the orange solution was reduced to ca. 5 mL, and by addition of *n*-hexane (20 mL) an orange solid was obtained. This solid was filtered, washed with *n*-hexane (3 × 10 mL), and dried in vacuo. Yield: 75% (0.743 g, 0.097 mmol). Anal. Calcd for $C_{39}H_{33}Cl_2NO_3PRh$: C, 60.95; H, 4.33; N, 1.82; Cl, 9.23. Found: C, 60.86; H, 4.34; N, 1.95; Cl, 9.13. ^{1}H NMR (C_6D_6): δ 8.68 (dd, *o*-H, 1H), 8.59 (d, *ar*-H, 1H), 8.37 (m, *ar*-H, 1H), 7.71 (d, *ar*-H, 1H), 7.56 (d, *ar*-H, 1H), 7.43 (dd, *ar*-H, 2H), 7.29 (m, *ar*-H, 3H), 7.36 (m, *ar*-H, 1H), 7.54 (m, *ar*-H, 3H), 6.78 (m, *ar*-H, 4H), 1.51 (d, CH_3, 15H). ^{31}P{^{1}H} NMR (C_6D_6): δ 134.10 (d, $J_{RhP} = 242$ Hz).

[(η^5-C$_5$Me$_5$)Rh(*S*-1)Cl]PF$_6$ (6). NH_4PF_6 (0.025 g, 0.155 mmol) and **5** (0.099 g, 0.130 mmol), each dissolved in THF (5 mL), were mixed. An orange precipitate slowly formed; after 1 h the solid was filtered from the reaction mixture, washed with *n*-hexane (3 × 10 mL), and dried in vacuo. Yield: 81% (0.092 g, 0.105 mmol). Anal. Calcd for $C_{39}H_{33}ClF_6NO_3P_2Rh$: C, 53.35; H, 3.79; N, 1.60; Cl, 4.04. Found: C, 53.42; H, 3.78; N, 1.59; Cl, 4.02. ^{1}H NMR (C_6D_6): δ 9.25 (dd, *o*-H, 1H), 8.57 (d, *ar*-H, 1H), 8.25 (d, *ar*-H, 1H), 7.68 (m, *ar*-H, 15H), 1.33 (d, CH_3, 15H). ^{31}P{^{1}H} NMR (C_6D_6): δ 146.5 (d, $J_{RhP} = 237$ Hz), 135.7 (d, $J_{RhP} = 217$ Hz).

[(η^6-*p*-cymene)Ru(*R*-2)]Cl (7). A solution of (*R*)-**2** (0.162 g, 0.367 mmol) in toluene (10 mL) was added dropwise to a solution of [(η^6-*p*-cymene)RuCl$_2$]$_2$ (0.090 g, 0.147 mmol) in the same solvent (10 mL). The reaction mixture turned immediately purple, and a blue precipitate slowly formed. After the mixture stood for one night, the solid was collected, washed with *n*-hexane (3 × 10 mL), and dried. In the ^{31}P{^{1}H} NMR (C_6D_6) spectrum, the precipitate showed two different resonances. A basic alumina column has been used to separate the two products. Using dichloromethane as eluent, an uncharacterized unstable compound was separated; subsequently, using methanol as eluent, a brown solid was isolated. See Results and Discussion for product spectroscopic characterization.

[(η^5-C$_5$Me$_5$)Rh(*R*-2)Cl]Cl (8). A solution of (*R*)-**2** (0.143 g, 0.323 mmol) in toluene (5 mL) was added to a solution of [(η^5-C_5Me_5)RhCl$_2$]$_2$ (0.080 g, 0.129 mmol) in the same solvent (8 mL). The reaction mixture slowly turned orange-red, and gradually an orange precipitate formed. After 12 h, the solid was collected, washed with *n*-hexane (3 × 10 mL), and dried in vacuo. Yield: 70% (0.170 g, 0.226 mmol). Anal. Calcd for $C_{39}H_{33}Cl_2NO_2PRh$: C, 62.25; H, 4.42; N, 1.86; Cl, 9.42. Found: C, 63.18; H, 4.33; N, 1.74; Cl, 9.22. ^{1}H NMR (C_6D_6): δ 9.41 (d, *o*-H, 1H), 8.73 (d, *ar*-H, 1H), 8.35 (m, *ar*-H, 2H), 8.06 (m, *ar*-H, 5H), 7.61 (m, *ar*-H, 3H), 7.44 (m, *ar*-H, 4H), 7.20 (m, *ar*-H, 2H), 1.63 (d, CH_3, 15H). ^{31}P{^{1}H} NMR (C_6D_6): δ 180.5 (d, $J_{RhP} = 205$ Hz).

Acknowledgment. We thank the MURST for financial support.

Supporting Information Available: Tables giving data and details of the crystal structure determination of **6a**·2CH$_2$Cl$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010563Z