New Rhodium(I) and Iridium(I) Complexes of the Chiral 1,1′-Diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole Ligand − Synthesis and Applications to Catalytic Hydrogenation and Hydroformylation Reactions

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A convenient method for the synthesis of new racemic Rh^I and Ir^I complexes $[M(BIPHOS)(COD)]BF_4$ have been developed from the BIPHOS ligand and $[M(COD)Cl]_2$ precursors. These complexes have been tested as catalysts for hydrogenation and hydroformylation reactions. Excellent regioselectivities in branched aldehyde (98%) have been obtained in hydroformylation with the rhodium $[Rh(BIPHOS)(COD)]BF_4$ complex. The application of this convenient method to the synthesis of enantiomerically pure $[M(BIPHOS)(COD)]BF_4$ complexes has been investigated.

Introduction

Chiral diphosphane ligands, in particular those with C_2 symmetry,[1] have proved to be powerful auxiliaries in catalytic asymmetric processes.[2] We were interested in the possibilities offered by the 1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole (BIPHOS, **1**), first synthesized by Mathey et al. in 1986.[3] This diphosphane combines the axial chirality generated by the biphosphole framework with the central chirality of the phosphorus atoms. This implies the existence of six stereoisomers corresponding to three pairs of enantiomers (Figure 1). In a previous report,[4] we have shown that BIPHOS exists in solution as an equilibrium mixture of two diastereoisomers, **1a** and **1b**, because of the configurational instability of the central chirality of the phosphorus atoms and probably also because of the axial chirality. This stereolability does not exist in the solid state and the three diastereoisomers have been fully characterized by X-ray diffraction.[4] In solution in the presence of a transition metal, the equilibrium shifts to the most favorable configurations for chelating the metal $\{[a]^{S}_{RR}$ and $[a]^{R}_{SS}\}$. In this way, we have obtained numerous chiral complexes of Ni, Pd, Pt, Rh[5] and Ru,[6] as racemic mixtures. Recently, the enantiomerically pure palladium complex $[PdCl_2(BIPHOS)]$ was synthesized from the enantiomerically pure BIPHOS ligand **1** $\{[a]^{S}_{RR}$ or $[a]^{R}_{SS}\}$ obtained by spontaneous resolution upon crystallization. It proved to be active in catalytic asymmetric allylic substitution.[7]

Here, we report a convenient method for synthesizing new racemic rhodium(I) and iridium(I) complexes $[M(BIPHOS)(COD)]^+$, and their use in the catalytic hydrogenation and hydroformylation reactions. We have also investigated the synthesis of enantiomerically pure complexes $[M(BIPHOS)(COD)]^+$ from the enantiomerically pure BIPHOS ligand **1**.

Results and Discussion

Synthesis of $[M(BIPHOS)(COD)]BF_4$ Complexes in Racemic Form

In our previous work on 2,2′-biphosphole (BIPHOS), we have shown that this diphosphane is a rather good ligand for transition metals, as evidenced by the formation of bisbiphosphole complexes.[8] For example, under the conditions used with classical diphosphanes,[9] BIPHOS (1 equiv. per rhodium atom) reacted rapidly with $[Rh(COD)Cl]_2$ or $[Rh(COD)_2]BF_4$ at ambient temperature by displacement of the two labile COD ligands to afford $[Rh(BIPHOS)_2]^+$ (**2**)[5] instead of $[Rh(BIPHOS)(COD)]^+$ (**3**) (Scheme 1).

In order to prepare the monosubstituted biphosphole complex **3**, which could be an interesting catalyst precursor for hydrogenation[10] and hydroformylation,[10] we attempted to reduce the reactivity of BIPHOS towards the rhodium precursors by working at low temperature. At −78 °C with the $[Rh(COD)_2]BF_4$ precursor, the reaction proceeded rapidly in a dichloromethane solution and afforded a mixture of two complexes, **3** and **2′′**, in the ratio 75:25, which could not be separated.

When the $[Rh(COD)Cl]_2$ precursor was used under the same conditions, a new rhodium complex **4** was observed by ^{31}P NMR spectroscopy ($\delta = 40.65$, $^{1}J_{P-Rh} = 137$ Hz) at −78 °C, along with the minor complex **2′** ($\delta = 46.10$, $^{1}J_{P-Rh} = 122$ Hz). This new complex slowly disappeared when the temperature increased, leading quantitatively to complex **2′** at room temperature. Complex **4**, which appears as an intermediate in the formation of complex **2′**, might

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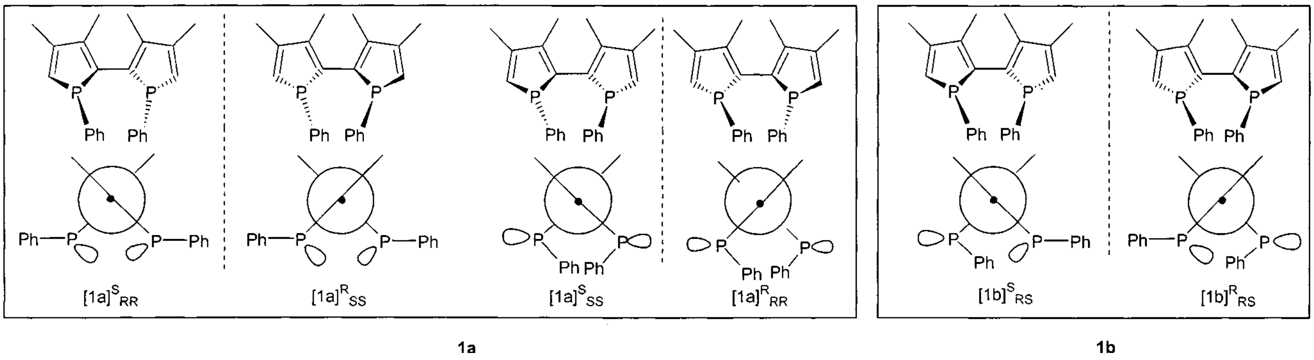
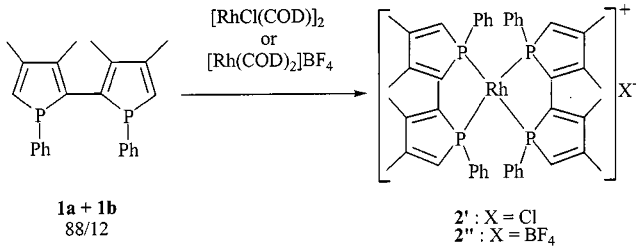
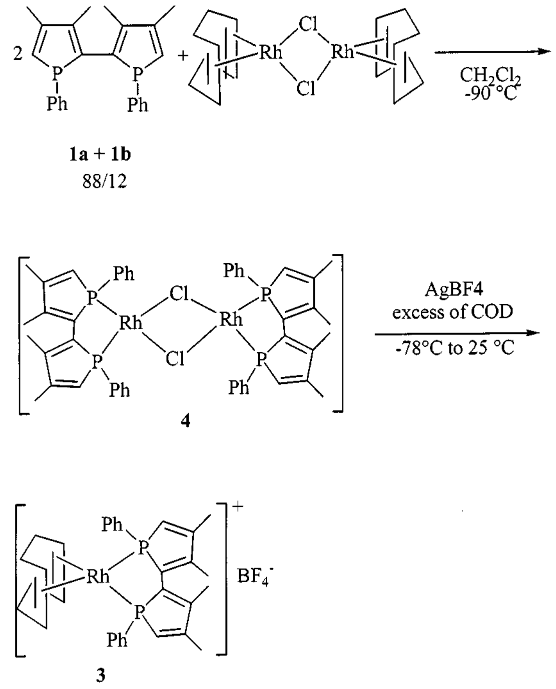


Figure 1. The different stereoisomers of BIPHOS (**1**) that possess two chiral centers and one chiral axis; each stereoisomer is also represented in a Newman projection along the axis of the C−C linking the phosphole rings; superscript refers to the axial chirality and subscript to the central chirality; the two diastereoisomers **1a** and **1b** observed in solution appear in this figure



Scheme 1

be the dinuclear complex [Rh(BIPHOS)Cl]$_2$.[11] Such an intermediate might allow the preparation of the desired complex [Rh(BIPHOS)(COD)]BF$_4$ by cleavage of the μ-Rh−Cl bonds and subsequent coordination of COD at the vacant rhodium site. Indeed, [Rh(BIPHOS)Cl]$_2$, quantitatively obtained by addition of two equivalents of a dichloromethane



Scheme 2

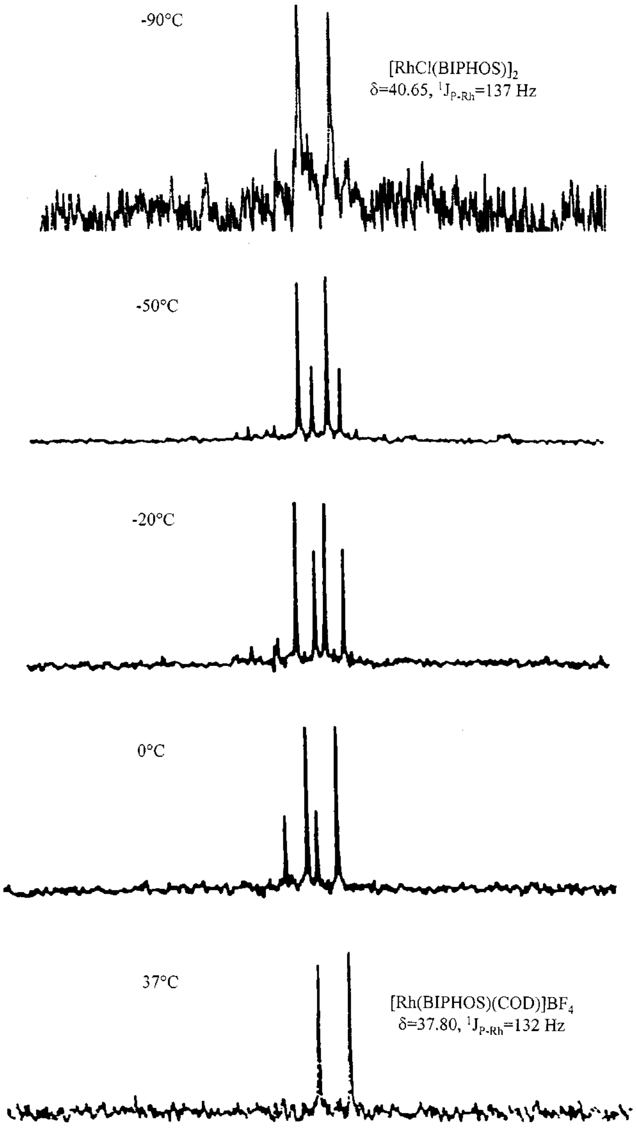
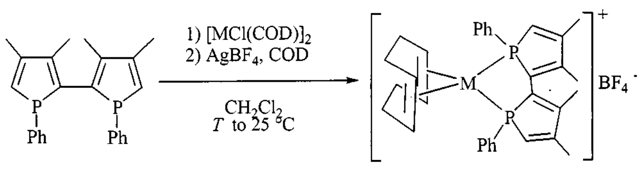


Figure 2. ^{31}P NMR studies from −90 °C to ambient temperature for the reaction of BIPHOS with [Rh(COD)Cl]$_2$

solution of BIPHOS to a dichloromethane solution of $[Rh(COD)Cl]_2$ precursor cooled to −90 °C, led to $[Rh(BIPHOS)(COD)]BF_4$ (**3**) after addition of four equivalents of $AgBF_4$ and an excess of cyclooctadiene at −78 °C (Scheme 2). This reaction was monitored by ^{31}P NMR spectroscopy from −78 °C to ambient temperature (Figure 2) showing the disappearance of complex **4** and the concomitant appearance of complex **3** ($\delta = 37.80$, $^1J_{P-Rh} = 132$ Hz). Complex **3** was isolated in 95% yield and characterized by multinuclear NMR spectroscopy, mass spectrometry and elemental analysis.

This method was then applied to the synthesis of an analogous iridium complex. Starting from $[Ir(COD)Cl]_2$ under similar conditions (Scheme 3), the ^{31}P NMR studies from −78 °C to ambient temperature revealed that the reaction was more complicated, since various intermediates were detected during the course of the reaction. However, the $[Ir(BIPHOS)(COD)]BF_4$ complex **5** was obtained quantitatively at room temperature, and was isolated in a pure form as a red solid, which was characterized by NMR spectroscopy, mass spectrometry and elemental analysis.



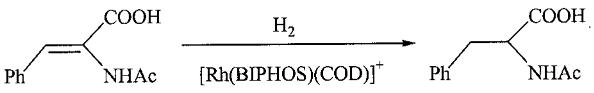
1a + 1b
88/12

3 : M = Rh, *T* = -90 °C
5 : M = Ir, *T* = -78 °C

Scheme 3

Catalysis

As a preliminary evaluation of the catalytic properties, these new rhodium and iridium complexes $[M(BIPHOS)(COD)]BF_4$ were tested in hydrogenation and hydroformylation reactions. Initial hydrogenation experiments were performed with the complexes **3** and **5** as precursor catalysts in the hydrogenation of α-acetoamidocinnamic acid. The rhodium complex $[Rh(BIPHOS)(COD)]BF_4$ (**3**) shows moderate activity for this hydrogenation in MeOH, THF or CH_2Cl_2 giving complete conversion over 20 h at 25 °C under 15 atm. of H_2 (Scheme 4, Table 1). Under the same conditions, the iridium complex $[Ir(BIPHOS)(COD)]BF_4$ (**5**) proved to be inactive. At higher pressure (150 atm.), very weak conversions, in the range 6−10%, were recorded (Table 1).



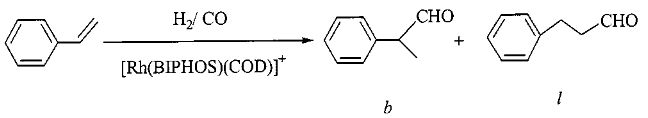
Scheme 4

Table 1. Hydrogenation of α-acetoamidocinnamic acid with $[M(BIPHOS)(COD)]BF_4$ [M = Rh (**3**) and M = Ir (**5**)][a]

Entry	Precursor	Solvent	P(Atm.)	Conv. (%)
1	**3**	MeOH	15	100
2	**3**	THF	15	100
3	**3**	CH_2Cl_2	15	100
4	**3**	Et_2O	15	45
5	**3**	CH_3CN	15	0
6	**5**	MeOH	150	10
7	**5**	THF	150	6
8	**5**	CH_2Cl_2	150	7

[a] Reaction conditions: $T = 25$ °C, $t = 20$ h, [cat]/[substrat] = 2:100.

To extend the utility of the $[Rh(BIPHOS)(COD)]BF_4$ catalyst precursor the hydroformylation of styrene was examined. The reaction was carried out at a temperature of 25 °C and a pressure of 150 atm. of CO/H_2 (1:1) (Scheme 5). High conversions of styrene were recorded, giving predominantly aldehydes with branched selectivities in CH_2Cl_2 (97%) or MeCN (98%) (Table 2). In MeOH, the regioselectivity towards the branched aldehyde regioisomer was lower, and the linear alcohol resulting from hydrogenation of the corresponding aldehyde was also formed in addition to the formyl regioisomer. Complex **4** proved to be a very regioselective catalyst in the hydroformylation of styrene.[12]



Scheme 5

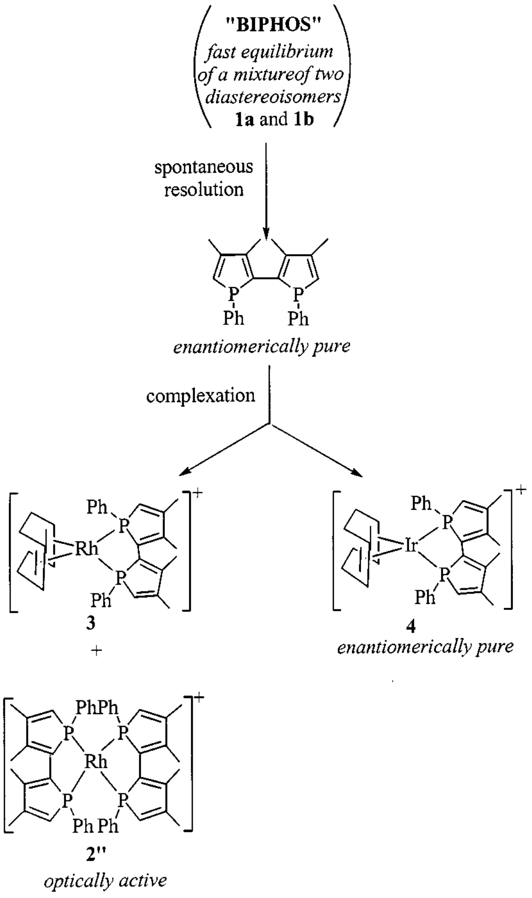
Table 2. Hydroformylation of styrene with $[Rh(BIPHOS)(COD)]BF_4$ (**3**)[a]

Entry	Solvents	Conversion	br/l
1	CH_2Cl_2	55	93:7
2	MeCN	72	98:2
3	EtOH	75	–[b]
4	MeOH	88	29:71[c]

[a] Reaction conditions: $T = 25$ °C, $t = 20$ h, p(CO) = p(H_2) = 150 atm., [cat]/[substrate] = 2:100. – [b] Not determined. – [c] In this case, the linear aldehyde was transformed into corresponding alcohol.

Synthesis of $[M(BIPHOS)(COD)]BF_4$ Complexes in Optically Active Form

In order to get an insight into asymmetric catalysis, we attempted to synthesize optically pure $[M(BIPHOS)(COD)]BF_4$ complexes. The present methods developed for the synthesis of racemic $[M(BIPHOS)(COD)]BF_4$ complexes, which require low temperature conditions, should be a convenient method for the synthesis of the optically pure complexes. Indeed, enantiomerically pure BIPHOS ligand **1** $\{[a]^{S}_{RR}$ or $[a]^{R}_{SS}\}$ was obtained by spontaneous resolution upon crystallization;[4] it racemizes in solution above −60 °C.[4] We investigated these syntheses with large single crystals (typically 50 to 150 mg) and the purity of each crystal was checked with polarized light before being used in the reaction. Using a slightly modified procedure that involved the addition of a single crystal of BIPHOS instead of a solution of BIPHOS, the reaction did not lead to complex **3** but quantitatively afforded complex **2′′**. Upon reverse addition, two problems arose. The first problem was to obtain a complete dissolution of the crystal at low temperature before addition of the metal precursor. For that, the solubilisation of one single crystal of **1** was carried out by stirring for 16 hours at −78 °C. Then, the solution was cooled to −90 °C before adding the solution of $[M(COD)Cl]_2$ precursor. However, this caused the second problem. During the addition, the ligand was always kept in excess with respect to the metal, and the formation of $[Rh(BIPHOS)_2]^+$ (**2**) could not be avoided, hence we obtained a mixture of complexes **2′′** and **3** in a 1:1 ratio at low temperature (Scheme 6). These two complexes could not be separated, as reported above for the racemic version. However, the optical rotation observed, $[\alpha]_D = 172$, proved that optically active complexes $[Rh(BIPHOS)_2]BF_4$ and/or [Rh(BIPHOS)-(COD)]BF_4 had been obtained.



Scheme 6

In contrast to the rhodium case, we were easily able to obtain the iridium complex **5** in an optically active form. In this case, the reaction was carried out by addition of one pure single crystal of BIPHOS to a dichloromethane solution of $[Ir(COD)Cl]_2$ cooled to −78 °C, followed by treatment with $AgBF_4$ in the presence of an excess of cyclooctadiene (Scheme 6). This complex was isolated as a red solid in 95% yield with $[\alpha]_{578} = -95$ ($c = 0.02$, CH_2Cl_2). The enantiomeric purity of complex **5** has not been evaluated; however, starting from different single crystals of BIPHOS, the same absolute value of [α] was obtained for complex **5**. Therefore, as in the case of the palladium complex,[7] we can consider that in dichloromethane at −78 °C, a single crystal of enantiomerically pure BIPHOS ligand reacts with $[Ir(COD)Cl]_2$ to give the enantiomerically pure complex [Ir-(BIPHOS)(COD)]BF_4.

Conclusions

We have developed a convenient route for the preparation of new racemic Rh^I and Ir^I complexes [M(BIPHOS)-(COD)]BF_4, and we have evaluated their catalytic properties in the hydrogenation and hydroformylation reactions. The efficiency of the rhodium complex was demonstrated in particular in hydroformylation, in which excellent regioselectivities (98%) in the branched aldehyde were obtained. In contrast, no specific efficiency was observed for the iridium complex.

This convenient synthetic method, when applied to the enantiomerically pure BIPHOS ligand, allows the synthesis of an enantiomerically pure iridium complex and an optically active mixture of the rhodium complexes **2′′** and **3**. Were are currently studying a method for the isolation of the rhodium complex in an optically pure form and hence carrying out studies of its use in asymmetric catalysis.

Experimental Section

Instrumentation: All reactions were carried under an inert atmosphere of dry argon using Schlenk glassware and vacuum line techniques. The experiments requiring H_2 or H_2/CO pressure were carried out into a stainless steel high pressure reactor by "TOP-industrie". Floodgates for gas introduction and evacuation were fixed on the lid. A glass ampoule containing the reaction mixture was inserted into the reactor and stirring and heating were external.

^1H, $^{13}C\{^1H, ^{31}P\}$ and $^{31}P\ \{^1H\}$ NMR spectra were recorded on a Bruker WMX 400 instrument operating at 400, 100 or 162 MHz, respectively, or on a Bruker AM 250 instrument operating at 250, 63 or 101 MHz, respectively. Chemical shifts are reported in parts per million (ppm) relative to Me_4Si (^1H and ^{13}C) or 85% H_3PO_4 (^{31}P). Mass spectra were obtained on a Mermag R10−10 instrument. Elemental analyses were performed by the "Service d'Analyse du Laboratoire de Chimie de Coordination" at Toulouse, France. Optical rotations were measured on a Perkin−Elmer 241 polarimeter.

Chemicals: BIPHOS **1**[3] and the complexes **2′**[5] and **2′′**[5] were synthesised as previously described. $[Rh(COD)Cl]_2$ precursor was purchased from Aldrich Chemical Co. $[Ir(COD)Cl]_2$ precursor was purchased from Fluka. Solvents were freshly distilled from standard drying agents.

Preparation of Complex 3. Racemic Form: BIPHOS (**1**; 82 mg, 0.22 mmol) in dichloromethane (1.5 mL) at −90 °C was quickly added to a solution of (1,5-cyclooctadiene)rhodium(I) chloride dimer (54 mg, 0.11 mmol) in dichloromethane (4 mL) at −90 °C. The mixture was stirred for 20 min. and was then rapidly warmed to −78 °C. 1,5-Cyclooctadiene (0.107 mL, 0.88 mmol) was then slowly added followed by addition of silver tetrafluoroborate (42 mg, 0.22 mmol). The reaction mixture was warmed to 25 °C within 2 hours and filtered. The solvent was removed in vacuo and the resulting red solid was washed four times with diethyl ether (5 mL). The residue was dried in vacuo giving a brown solid (139 mg, 95%). − ^{1}H NMR (CD_2Cl_2): $\delta = 1.70$ (s, 6 H, CH_3), 2.21 (s, 6 H, CH_3), 2.12−2.54 [m, 8 H, CH_2 (COD)], 5.17 [m, 2 H, CH (COD)], 5.89 [m, 2 H, CH (COD)], 6.60 (d, $^2J_{H-P} = 32.6$ Hz, 2 H, CH-P), 7.37−7.63 (m, 10 H, Ph). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 159.8$ (s, $C{-}CH_3$), 145.6 (t, $J_{C-P} = 14.6$ Hz, $C{-}CH_3$), 136.8 (t, $J_{C-P} =$ 39.3 Hz, $C{=}C{-}CH_3$), 132.9 (t, $J_{C-P} = 6.2$ Hz, Ph), 131.8 (s, Ph), 129.7 (t, $J_{C-P} = 5.1$ Hz, Ph), 120.0 (m, CH-P), 99.2 [m, CH (COD)], 98.5 [m, CH (COD)], 30.2 [s, CH_2 (COD)], 30.0 [s, CH_2 (COD)], 18.9 (t, $J_{C-P} = 5.5$ Hz, CH_3), 15.2 (t, $J_{C-P} = 4.2$ Hz, CH_3). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 37.80$ (d, $^1J_{P-Rh} =$ 132.2 Hz). − FAB-MS (MNBA, CH_2Cl_2): *m/z* (%) = 585 (100) $[M - BF_4]^+$. − $C_{32}H_{36}BF_4P_2Rh$ (672.30): calcd. C 57.17, H 5.39; found C 56.82, H 5.09.

Optically Active Form: A single crystal of BIPHOS was added to dichloromethane at −78 °C and the mixture was stirred overnight. After cooling to −90 °C, a dichloromethane solution of (1,5-cyclooctadiene)rhodium(I) chloride dimer was then added to the BIPHOS solution and the resulting mixture was stirred for only 5 min. The procedure is then the same as described above. The final product was a 1:1 mixture of $[Rh(BIPHOS)_2]BF_4$ (**2′′**) and $[Rh(BIPHOS)(COD)]BF_4$ (**3**). $[\alpha]_D = 172$ ($c = 0.3$, CH_2Cl_2).

Preparation of Complex 5. Racemic Form: BIPHOS (97 mg, 0.26 mmol) in dichloromethane (1.5 mL) at −78 °C was quickly added to a solution of(1,5-cyclooctadiene)iridium(I) chloride dimer (87 mg, 0.13 mmol) in dichloromethane (4 mL) at −78 °C. The mixture was stirred for 1 h at −78 °C. 1,5-Cyclooctadiene (0.130 mL, 1.03 mmol) was then slowly added followed by the addition of silver tetrafluoroborate (44 mg, 0.26 mmol). The reaction mixture was warmed to 25 °C within 2 hours and filtered. The solvent was removed in vacuo and the resulting purple solid was washed four times with *n*-pentane (5 mL). The residue was dried in vacuo giving a dark red solid (140 mg, 95%). − ^{1}H NMR (CD_2Cl_2): $\delta = 1.72$ (d, $^4J_{H-H} = 1$ Hz, 6 H, CH_3), 2.25 (s, 6 H, CH_3), 2.06−2.04 [m, 8 H, CH_2 (COD)], 4.73 [m, 2 H, CH (COD)], 5.43 [m, 2 H, CH (COD)], 6.67 (d, $^2J_{H-P} = 32.8$ Hz, 2 H, CH-P), 7.37−7.56 (10 H, m, Ph). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 159.7$ (s, $C{-}CH_3$), 145.8 (t, $J_{C-P} = 14.6$ Hz, $C{-}CH_3$), 136.5 (dd, $J_{C-P} = 55.1$ Hz, $J_{C-P} =$ 25.8 Hz, $C{=}C{-}CH_3$), 132.4 (d, $J_{C-P} = 9.7$ Hz, Ph), 131.7 (s, Ph), 129.5 (d, $J_{C-P} = 10.2$ Hz, Ph), 120.4 (d, $J_{C-P} = 44.4$ Hz, CH-P), 83.2 [m, CH (COD)], 32.8 [s, CH_2 (COD)], 31.3 [s, CH_2 (COD)], 18.9 (d, $J_{C-P} = 11.7$ Hz, CH_3), 15.9 (t, $J_{C-P} = 9.5$ Hz, CH_3). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 32.78$. − FAB-MS (MNBA, CH_2Cl_2): *m/z* (%) = 675 (100) $[M - BF_4]^+$. − $C_{32}H_{36}BF_4IrP_2$ (761.61): calcd. C 50.46, H 4.76; found C 49.90, H 4.66.

Optically Active Form: A single crystal of BIPHOS was added directly to a dichloromethane solution of(1,5-cyclooctadiene)iridium(I) chloride dimer at −78 °C and the resulting mixture was stirred overnight at −78 °C. The procedure was the same as described above. $[\alpha]_{578} = 95$ ($c = 0.02$, CH_2Cl_2).

Hydrogenation Experiments: In a typical experiment, a solution of 2×10^{-2} mmol of catalyst and substrate (50 equiv.) in 2 mL of the desired solvent was transferred under argon into a 3 mL glass ampoule. It was then placed into a stainless steel autoclave and stirred for 3 h with α-acetamidocinnamic acid. The reaction vessel was then pressurized to the required H_2 pressure and stirred for the desired time. After slow venting of the reactor, the mixture containing *N*-acetylphenylalanine was filtered through silica with ethyl acetate as eluent. The conversion was measured directly by integration of the CH_3 signals in the ^{1}H NMR spectrum.

Hydroformylation Experiments: The procedure was the same as described for hydrogenation. The mixture was stirred for 1 h before the autoclave was pressurized ($CO/H_2 = 1:1$). The conversion rate was measured directly by integration of the C*H*O and PhC*H*CH_2 signals in the ^{1}H NMR spectrum and the branched/linear value was given by integration of the C*H*O signals (branched: $\delta = 9.1$, linear: $\delta = 9.2$).

Acknowledgments

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