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New chiral diphosphoramidite rhodium(I) complexes for asymmetric hydrogenation

Dario Drommi, Giuseppe Micalizzi and Carmela Grazia Arena*

Chiral 1,5-cyclooctadiene rhodium(I) cationic complexes with C_2-symmetric chelate diphosphoramidite ligands containing (*R*,*R*)-1,2-diaminocyclohexane as the backbone and two atropoisomeric biaryl units were easily synthesized and fully characterized by multinuclear one- and two-dimensional NMR spectroscopy and elemental analysis. These complexes were used as catalysts in the asymmetric hydrogenation of dimethyl itaconate, methyl 2-acetamidoacrylate and (*Z*)-methyl-2-acetamido-3-phenylacrylate. The rhodium complexes derived from diphosphoramidite ligands that contain two (*R*) or (*S*) BINOL (2,2′-dihydroxy-1,1′-binaphthyl) units proved to be efficient catalysts, giving complete conversion and very good enantioselectivity (up to 88% ee). An uncommon positive H_2 pressure effect on the enantioselectivity was observed in the hydrogenation of dimethyl itaconate catalyzed by Rh-complex with diphosphoramidite ligand that contains two (*S*)-binaphthol moieties. Copyright © 2014 John Wiley & Sons, Ltd.

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Keywords: diphosphoramidite; asymmetric hydrogenation; rhodium; hydrogen pressure

Introduction

The asymmetric hydrogenation of functionalized olefins catalyzed by homogeneous chiral transition metal complexes is one of the most efficient and reliable methods for the synthesis of enantiopure substances.[1] In recent years, industrial demand for enantiopure compounds in the production of chiral drugs, agrochemicals, flavor, fragrances and advanced materials has considerably increased.[2] Today, catalytic asymmetric reduction of prochiral unsaturated substrates has become a valuable and necessary tool in the industrial production of fine chemicals.[3] From an industrial point of view, catalytic enantioselective hydrogenation offers several advantages in the preparation of high value-added compounds such as high reactivity and selectivity, a broad application range and a minimal production of by-products.[4] Most of the catalysts used for the asymmetric hydrogenation of unsaturated compounds are complexes of iridium,[5] ruthenium[6] and rhodium[7] containing bidentate chiral ligands.

Among these, rhodium complexes bearing C_2-symmetric chiral diphosphines have led to excellent results in the enantioselective hydrogenation of functionalized olefins.[8] Over the years, requirements of cheaper chiral ligands and metal precursor easily available in technical quantities has prompted many researchers to develop new enantioselective rhodium complexes. Notably, research has been focused on the synthesis of cationic rhodium complexes containing chiral ligands derived from an inexpensive simple asymmetric source. In the last few years, phosphoramidites have emerged as highly versatile, modulable and readily available chiral ligands. Many monodentate phosphoramidites derived from the optically active group 1,1′-bi-2-naphtol (BINOL) have been successfully applied in asymmetric rhodium-catalyzed hydrogenation of functionalized olefin catalyzed by cationic rhodium complexes.[9] Conversely, C_2-symmetric diphosphoramidite ligands that are easily accessible from cheap achiral/chiral diamines have not been greatly used in catalytic asymmetric hydrogenation.[9,10]

Recently, we designed a series of C_2-symmetric chiral diphosphoramidites[11] containing a chiral diamine backbone which were synthesized starting from (*R*,*R*)-1,2-diaminocyclohexane, an inexpensive and commercially available chiral precursor (Fig. 1).

The ligands **L1** and **L2** are two diastereomers which differ in the configuration of the atropoisomeric group BINOL, R_a and S_a, respectively. In the case of the diphosporamidite **L3**, the presence of biphenol groups can give rise to three conformational diastereomers (R,R_a,R_a), (R,S_a,S_a), (R,R_a,S_a) which rapidly interconvert due to the low energy rotation barrier of the biaryl axis.[12]

This new family of C_2-symmetric diphosphoramidites has stereogenic different combinations that can play a crucial role in determining the sense and enantioselective value in hydrogenation reactions.

Herein we report on the synthesis and characterization of 1,5-cyclooctadiene rhodium(I) cationic complexes with diphosphoramidites **L1–L3** and their application as enantioselective catalysts in the hydrogenation of functionalized olefins.

Results and Discussion

Synthesis of Cationic Diphosphoramidite Rhodium(I) Complexes

The cationic Rh(I) complexes [Rh(cod)(P,P)]BF_4, **1–3**, (cod = 1,5-cyclooctadiene) containing the bidentate diphosphoramidite ligands [P,P = (R,R,R_a,R_a)-**L1**, (R,R,S,S_a)-**L2**, (*R*,*R*,)-**L3**] were synthesized at room temperature by reaction of the cationic

* *Correspondence to: Carmela Grazia Arena, Dipartimento di Scienze Chimiche-Università di Messina, Viale F. Stagno D'Alcontres 31, 98166, Messina, Italy. E-mail: arenac@unime.it*

Dipartimento di Scienze Chimiche-Università di Messina, 98166, Messina, Italy

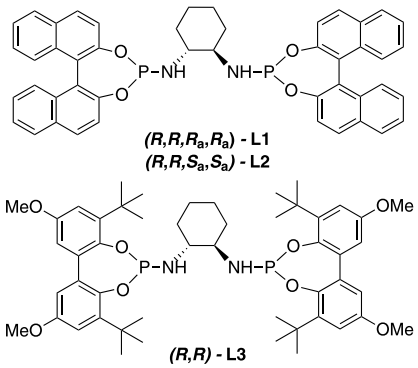


Figure 1. C_2-symmetric chiral diphosphoramidite ligands **L1–L3**.

complex $[Rh(cod)_2]BF_4$ with a slight excess of the corresponding P,P-ligand (1:1.1, as shown in the Scheme 1) in dichloromethane solution. The new compounds **1–3** were isolated as yellow solids that were found to be stable under an inert atmosphere and were fully characterized by elemental analysis and homo- and multinuclear 1D and 2D NMR spectroscopy.

In the $^{31}P\{^1H\}$ NMR spectrum, compound [Rh(cod)(**L1**)]BF_4 (**1**) shows a doublet at δ = 137.0 ppm with a coupling constant $^1J_{RhP}$ value of 235 Hz, in agreement with already reported values for similar complexes of rhodium with a *cis* arrangement of the two phosphorus atoms.[13] At a higher field position a doublet is present at δ = 128.0 ppm ($^1J_{RhP}$ = 261 Hz) belonging to a minor unidentified component (<5%). The ^1H NMR spectrum exhibits all expected signals relative to the diphosphoramidite **L1** and cyclooctadiene ligands chelated to the rhodium metal center. The $^{31}P,^1H$-HMBC correlation map allowed us to assign the broad signal at δ = 3.73 ppm present in the ^1H NMR spectrum to two overlapping resonances relative to the two NH protons and to the two 1,2-(*R*,*R*) methynic chiral protons of the cyclohexane ring.

The 2D COSY and NOESY experiments allowed us to completely assign all NMR signals of complex **1** and also to obtain useful information about the spatial arrangement of the coordinated ligands. Particularly, in the NOESY spectrum (Fig. 2), the presence of cross-peaks between the H_{ortho} proton (δ = 7.55 ppm) of the binaphthol group and the olefin protons (δ = 5.84 and 5.49 ppm) confirmed that the ligand **L1** is located close to the coordinated cyclooctadiene.

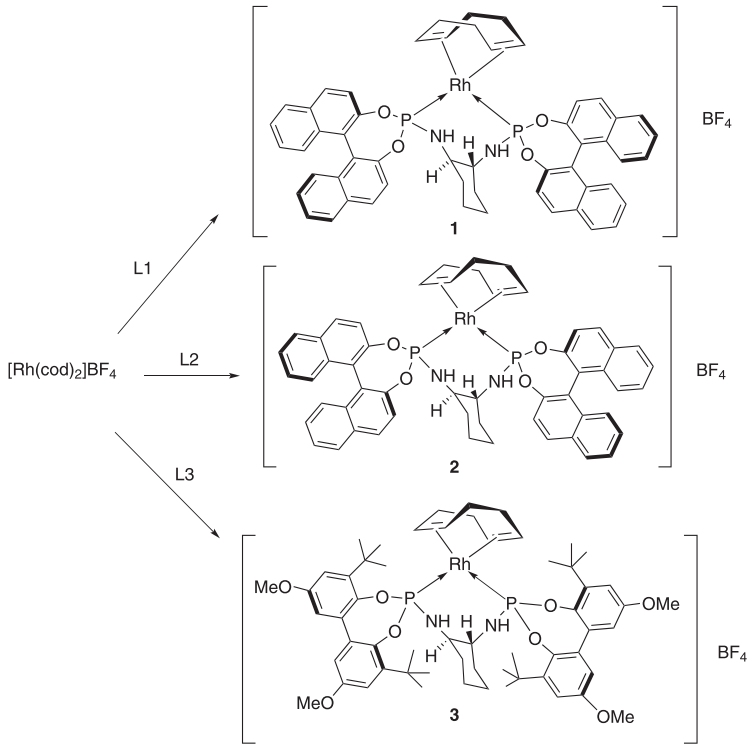
Moreover, this spatial proximity gave rise to a lower field shift of the *ortho*-hydrogen signals affected by double bond anisotropy. All carbon atom signals in compound **1** were assigned by $^{13}C,^1H$ HMQC correlation and $^{13}C,^1H$ HMBC long-range correlation experiments (see Experimental section).

The $^{31}P\{^1H\}$ NMR spectrum of complex [Rh(cod)(**L2**)]BF_4 (**2**) shows a very broad doublet at δ = 136.7 ppm ($^1J_{RhP}$ = 220 Hz) together with a doublet at δ = 128.0 ppm ($^1J_{RhP}$ = 261Hz) belonging to a minor unidentified compound (<5%). The $^{31}P\{^1H\}$ and ^1H NMR analysis performed at a variable temperature in chloroform solution showed the coalescence of the broad doublet at 223 K; at 323 K the peaks sharpened. In the same temperature range no change of minor unidentified compound signal was observed. In the $^{31}P,^1H$ -HMBC NMR spectrum complex **2** displays two cross-peaks among the coordinate phosphorous, the NH groups and 1,2-(*R*,*R*) methynic chiral protons of the cyclohexane ring at δ = 3.99 and 3.85 ppm, respectively. In the 2D-NOESY spectrum the *ortho*-protons in the binaphthyl group (δ = 7.54 ppm) showed two selective cross-peaks with olefinic signals (δ = 6.00 and 5.07 ppm) while the NH proton showed a selective cross peak with the binaphtol aromatic proton H_{ar}. This confirms a different spatial arrangement of the chelated ligand **L2** from that observed for ligand **L1**. (Fig. 3).

The complex [Rh(cod)(**L3**)]BF_4 exhibits only one doublet at δ = 135.3 ppm ($^1J_{RhP}$ = 243 Hz) in the $^{31}P\{^1H\}$ NMR spectrum.

In the ^1H NMR spectrum, the *tert*-butyl and the –OMe groups appear as two pairs of singlets at δ = 1.63 and 1.60 ppm and δ = 3.86 and 3.84 ppm, respectively. For the aromatic biphenyl protons, four different doublets at δ = 7.10, 7.03, 6.71 and 6.65 ppm (J_{HH} = 3 Hz) were observed. Homo- and multinuclear 1D and 2D NMR experiments confirmed that **L3** is chelated to the metal center. In particular, the $^{31}P,^1H$ HMBC correlation spectrum showed a correlation of the phosphorus nuclei with the two NH (broad signal at δ = 3.25 ppm) and CH protons (δ = 3.11 ppm) of the 1,2-diaminocyclohexane moiety.

The structure of the complex [Rh(cod)(**L3**)]BF_4 and the mutual spatial arrangement of ligand **L3** and cyclooctadiene were elucidated by NOESY experiments. The NOESY spectra showed selective cross-peaks between H_{cod} and the two *tert*-butyl protons, confirming the expected spatial arrangement of the two biphenol fragments (Fig. 4).



Scheme 1. Synthesis of cationic diphosphoramidite rhodium(I) complexes **1–3**. Reaction conditions: Rh/L 1:1.1, solvent CH_2Cl_2, room temperature.

Asymmetric Hydrogenation of Functionalized Olefins

Hydrogenation of dimethyl itaconate

To assess the potential of cationic rhodium(I) complexes **1–3**, in the metal-catalyzed asymmetric

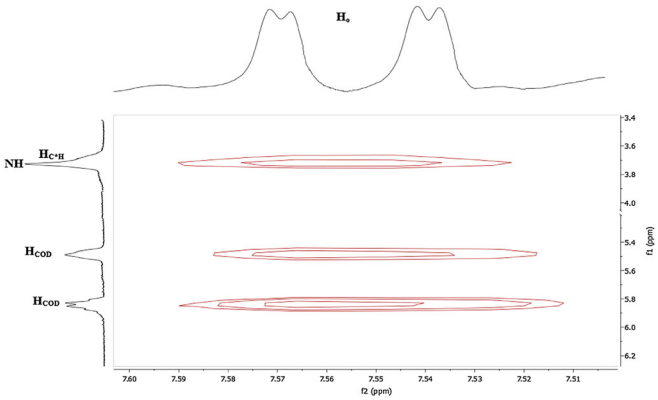


Figure 2. Section of 2D 1H-NOESY spectrum of [Rh(cod)(**L1**)]BF_4 **1** showing NOE contacts between the H_{ortho} proton of the binaphthol fragment and the olefinic protons of the cyclooctadiene.

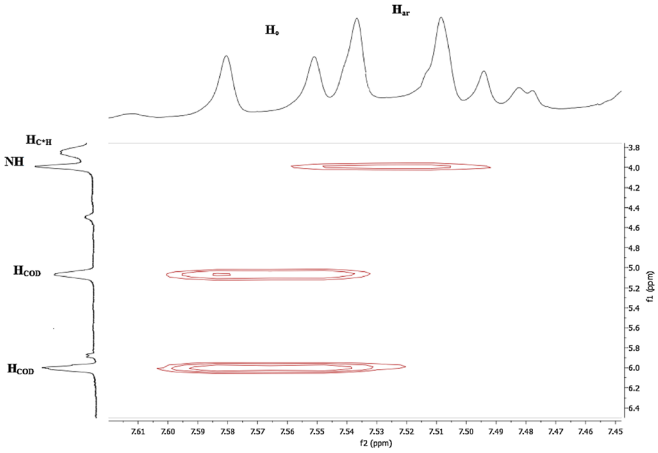


Figure 3. Section of 2D 1H-NOESY spectrum of [Rh(cod)(**L2**)]BF_4 **2** showing the NOE contacts between the H_{ortho} proton of the binaphthol fragment and the olefinic protons of the cyclooctadiene.

hydrogenation of functionalized olefins, we first performed a series of reactions using a model substrate such as dimethyl itaconate **4** (Scheme 2).

A first set of experiments was conducted under 1 bar of H_2 pressure in CH_2Cl_2 at room temperature for 20 h, with a substrate:[Rh] ratio of 1000:1. The results are reported in Table 1. Complete reduction of substrate **4** was achieved with complexes **1** and **2**. A low catalytic activity was observed when complex **3** was used.

Rhodium complexes **1** and **2** containing the two diastereomeric ligands (*R*,*R*,R_a,R_a)-**L1** and (*R*,*R*,S_a,S_a)-**L2** exhibited a very different stereoselectivity in the hydrogenation of dimethyl itaconate **4** (entries 1 and 5). The diphosphoramidite (*R*,*R*,R_a,R_a)-**L1** with two (*R*)-binaphthyl units proved to be the matched combination, affording (*R*)-**5** with an ee value of 85.5%. The mismatched ligand (*R*,*R*,S_a,S_a)-**L2** gave (*S*)-**5** with an ee value of only 48.7%.

These results also indicated that the sense of enantiodiscrimination depends on the configuration of the atropoisomeric binaphthyl unit.

Catalysts formed *in situ* ([$Rh(cod)_2$]BF_4:P,P = 1:1.1) were also tested. Similar conversion and ee values were obtained with *in situ* (*R*,*R*,R_a,R_a)-**L1**/Rh catalyst (entries 1–2). Instead, the *in situ* (*R*,*R*,S_a,S_a)-**L2**/Rh catalyst hydrogenated dimethyl itaconate **4** with slightly decreased enantioselectivity relative to that of the preformed catalyst (entries 5–6). The reason for these different outcomes is unclear. Dinuclear or oligomeric complexes which hydrogenate with lower selectivity were probably involved.

Rhodium complex **3** containing biphenol-derived diphosphoramidite (*R*,*R*)-**L3** showed very poor enantioselectivity (entries 11–12). In the case of ligand (*R*,*R*)-**L3** , the fluxional axially chiral biphenyl moieties should give rise to a mixture of three configurationally fluxional (*R*,*R*), (*R*,*S*), (*S*,*S*) diastereomeric rhodium complexes.

It is very likely that a rapid interconversion of diastereomeric catalysts is responsible for the poor enantioselectivity.

The catalytic performance of rhodium complex **1** was investigated in THF (aprotic solvent) and MeOH (protic solvent). The results, reported in Table 2, show that both solvents led to a drop in both rate and enantioselectivity.

The effect of the H_2 pressure on the stereoselectivity of hydrogenation was also examined (Table 1). With rhodium catalyst **1** a decrease in selectivity was noted at higher pressures; 85.5% ee (*R*) at 1 bar versus 80% ee (*R*) at 10 bar (entries 1 and 4). In contrast, a remarkable increase in enantiomeric excess at higher H_2 pressure was observed by using the compound [Rh(cod)(*R*,*R*,S_a,S_a)-**L2**] **2**. As shown in Fig. 5, the product enantiomeric excess rises from 48.7% (*S*) to 88% (*S*) by increasing the H_2 pressure from 1 to 60 bar.

Some significant beneficial H_2 pressure effects on enantioselectivity in the hydrogenation of dehydroamino acid derivatives have been reported in the literature but the origin of this phenomenon has not quantitative explained.[14,15] Recently, Heller[16] and de Bellefon[17] showed that an increase in enantioselectivity with rising hydrogen pressure can be explained both by the lock and key principle and major/minor principle. Moreover, Heller and co-workers[16] established that the pressure dependence of enantioselectivity alone is not sufficient to reveal the selectivity-determining pathway.

Thus we cannot explain the origin of the positive pressure effect observed with compound **2** without detailed mechanistic studies, which are in progress.

Hydrogenation of methyl 2-acetamido-acrylate derivatives

We then tested the cationic complexes of rhodium(I) **1–3** in the asymmetric hydrogenation of methyl 2-acetamidoacrylate **6** and (*Z*)-methyl-2-acetamido-3-phenylacrylate **7** (Scheme 3). The results are summarized in Table 3.

Complex **1** hydrogenated the methyl 2-acetamidoacrylate **6** almost quantitatively (99% conversion) at 1 bar pressure with an ee value of 76.6% (*R*) (entry 1). Rising hydrogen pressure increased catalytic activity with a slight decrease in the enantioselectivity (entry 2).

Using complex **2** a very low catalytic activity (<5% conversion) was observed at 1 bar (entry 3). Increasing H_2 pressure to 5 bar resulted in almost complete reduction of substrate **6** (99% conversion), with an ee value of 84.8% (*S*) (entry 4). At 20 bar, a small increase of the ee value to 87% (*S*) was obtained (entry 5). At 40 bar, metallic rhodium was formed in the reaction vessel.

The hydrogenation of (*Z*)-methyl-2-acetamido-3-phenylacrylate **7** catalyzed by complex **1** proceeded quantitatively at 1 bar and led to (*R*)-2-acetamido-3-phenylpropanoate methyl ester **9** with good enantioselectivity (77.8% ee (*R*)) (entry 7). Also, with substrate **7**

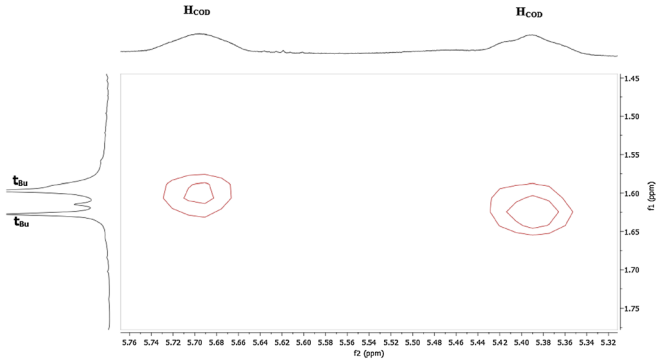
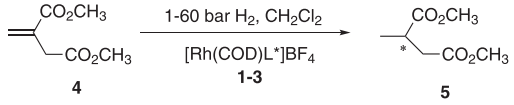


Figure 4. Section of 2D 1H-NOESY spectrum of [Rh(cod)(**L3**)]BF_4 **3** showing the NOE contacts between the two *tert*-butyl hydrogens of the biphenol fragment and the olefinic protons of the cyclooctadiene.



Scheme 2. Hydrogenation of dimethyl itaconate catalyzed by rhodium(I) complexes [Rh(cod)(*R*,*R*,R_a,R_a)-**L1**] **1**, [Rh(cod)(*R*,*R*,S_a,S_a)-**L2**] **2** and [Rh(cod)(*R*,*R*)-**L3**] **3**.

Table 1. Asymmetric hydrogenation results for dimethyl itaconate 4 with complexes [Rh(cod)(**L1**)]BF_4 **1**, [Rh(cod)(**L2**)]BF_4 **2** and [Rh(cod)(**L3**)]BF_4 **3**[a]

Entry	Catalyst	Pressure (bar)	Conversion (%)	ee (%)
1	1	1	100	85.5 (*R*)
2	Rh/L1	1	100	85.4 (*R*)
3	1	5	100	81.6 (*R*)
4	1	10	100	80.0 (*R*)
5	2	1	100	48.7 (*S*)
6	Rh/L2	1	100	47.5 (*S*)
7	2	5	100	70.1 (*S*)
8	2	20	100	74.8 (*S*)
9	2	40	100	80.0 (*S*)
10	2	60	100	88.0 (*S*)
11	3	1	62.5	12.9 (*R*)
12	3	5	100	raceme

[a]Substrate/Rh = 1000, 25°C, 20 h. Conversion and ee values were determined by GC.

Table 2. Asymmetric hydrogenation results for dimethyl itaconate **4** with complexes [Rh(cod)(**L1**)]BF_4 **1** in different solvents[a]

Entry	Solvent	Conversion (%)	ee (%)
1	CH_2Cl_2	100	85.5 (*R*)
2	THF	27.6	18.0 (*R*)
3	MeOH	46	19.7 (*R*)

[a]Substrate/Rh = 1000, 25°C, 20 h. Conversion and *ee* values were determined by GC.

increasing H_2 pressure decreased enantiomeric excess (72.1% ee (*R*)) at 20 bar (entry 8).

Catalyst **2** showed lower activity and enantioselectivity compared with **1** for the hydrogenation of **7** (entries 7 and 9). Moreover, the ee value was not much affected by hydrogen pressure (entries 9 and 10).

Hydrogenation reactions of **6** and **7** with rhodium complex **3** showed very low enantiomeric excesses and conversions (entries 6 and 11).

Experimental

Materials and Methods

All syntheses were performed under purified argon using standard Schlenk techniques. Solvents were dried by standard procedures and distilled under argon before use. NMR experiments were carried out with a Bruker AMX R300 spectrometer equipped with a probe *broadband* operating to the frequency of 300.13 MHz for ^{1}H NMR, 75.47 MHz for $^{13}C\{^1H\}$ NMR and 121.50 MHz for $^{31}P\{^1H\}$ NMR. The residual protiated resonance was used as an internal standard, but chemical shifts were reported with respect to tetramethylsilane (TMS). $^{31}P\{^1H\}$ NMR shifts are referenced to external 85% H_3PO_4. Standard pulse sequences were employed for phase-sensitive (TPPI method) 1H-2D NOESY, ^{13}C-^1H correlation (HMQC) and ^{13}C-^1H correlation long-range (HMBC) studies.[18] Unless otherwise indicated, all materials were commercially available and were used without further purification. Conversion and enantioselectivity of the catalytic reactions were determined by GC coupled to a mass spectrometer GCMS-QP 5000 Shimadzu and Fisons GC 8000 ThermoQuest, using helium as a carrier gas and a flame ionization detector (FID). For determination of hydrogenated products of dimethyl itaconate LIPODEX E was applied as a chromatographic column; Chirasil-Val was used for determination of hydrogenated products methyl 2-(acetylamino)propanoate and methyl (*Z*)-2-(acetylamino)-3-phenylpropanoate. The absolute configurations of the materials were determined by comparison with reported data.[19,20]

Synthesis of [Rh(cod)(P,P)]BF_4 Complexes

Diphosphoramidite ligand (0.1 mmol) was added to a solution of $[Rh(cod)_2]BF_4$ (40.6 mg, 0.1 mmol) in dichloromethane (4 ml). After 15 min., the solvent was reduced to ~2 ml and by addition

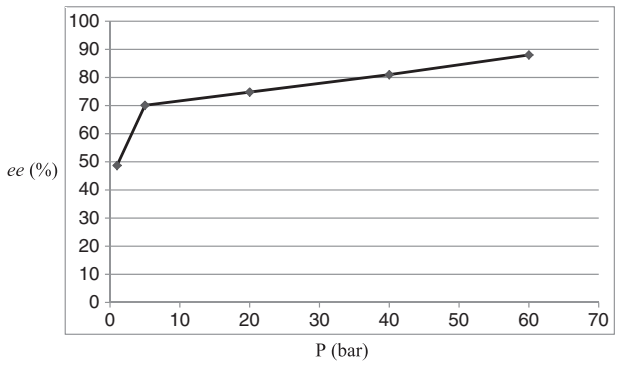
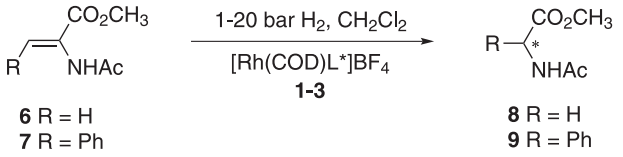


Figure 5. Effect of H_2 pressure on enantioselectivity in the hydrogenation of dimethyl itaconate catalyzed by ([Rh(cod)(*R*,*R*,S_a,S_a)-**L2**]BF_4 **2**.



6 R = H
7 R = Ph

8 R = H
9 R = Ph

Scheme 3. Hydrogenation of 2-methyl acetamidoacrylate derivatives catalyzed rhodium(I) complexes [Rh(cod)(*R,R,Ra,Ra*)-**L1**] **1**, [Rh(cod)(*R,R,Sa,Sa*)-**L2**] **2** and [Rh(cod)(*R,R*)-**L3**] **3**.

Table 3. Asymmetric hydrogenation results for methyl 2-acetamidoacrylate derivatives **6** and **7** with complexes [Rh(cod)(**L1**)]BF_4 **1**, [Rh(cod)(**L2**)]BF_4 **2** and [Rh(cod)(**L3**)]BF_4 **3**[a]

Entry	Catalyst	Pressure (bar)	Conversion (%)	ee (%)
Methyl 2-acetamidoacrylate				
1	1	1	99	76.6 (*R*)
2	1	20	100	74.7 (*R*)
3	2	1	<5	—
4	2	5	99	84.8 (*R*)
5	2	20	100	87.0 (*S*)
6	3	10	8	51.1 (*S*)
(Z)-Methyl 2-acetamido-3-phenylacrylate				
7	1	1	100	77.8 (*R*)
8	1	20	100	72.1 (*R*)
9	2	1	87	61.7 (*S*)
10	2	5	100	65.7 (*S*)
11	3	5	27	53.7 (*S*)

[a]Substrate/Rh = 1000, 25°C, 20 h. Conversion and ee values were determined by GC.

of hexane a yellow powder was obtained. It was filtered, washed with hexane and dried *in vacuo*.

*[Rh(cod)(**L1**)]BF_4 **1***

Yield 95.7 mg, 92%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, ^3J = 9 Hz, H*ar*, 4H), 7.98 (d, ^3J = 8 Hz, H*ar*, 4H), 7.55 (d, ^3J = 9, H*o*, 4H), 7.53–7.51 (mbr, H*ar*, 4H), 7.41 (d, ^3J = 9 Hz, H*ar*, 4H), 7.32 (mbr, H*ar*, 4H), 5.89–5.80 (mbr, 2H, H_{cod}), 5.52–5.45 (mbr, 2H, H_{cod}), 3.73 (sbr, 2H, N*H*), 3.76–3.60 (mbr, 2H, $H^*_{cyclohex}$), 2.56–2.45 (mbr, 2H, H_{cod}), 2.34–2.29 (mbr, 2H, H_{cod}), 2.30–2.25 (mbr, 2H, H_{cod}), 2.25–2.21 (mbr, 2H, H_{cod}), 2.10–2.05 (mbr, 2H, $H_{cyclohex}$), 1.84–1.76 (mbr, 2H, $H_{cyclohex}$), 1.53–1.44 (mbr, 2H, $H_{cyclohex}$), 1.44–1.39 (mbr, 2H, $H_{cyclohex}$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 152.74 ($C_{ar(q)}$), 147.67 ($C_{ar(q)}$), 146.53 ($C_{ar(q)}$), 132.57 ($C_{ar(q)}$), 131.37 ($C_{ar(q)}$), 128.40 (C_{ar}), 127.36 (C_{ar}), 126.82 (C_{ar}), 125.81 (C_{ar}), 121.30 ($C_{ar(ortho)}$), 105.97 (C_{cod}), 105.51 (C_{cod}), 58.20 ($C^*_{cyclohex}$), 35.63 ($C_{cyclohex}$), 31.50 (C_{cod}), 28.70 (C_{cod}), 24.42 ($C_{cyclohex}$). $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$) δ 137.04 (d, $^1J_{RhP}$ = 235 Hz). Anal. Calcd for $C_{54}H_{48}BF_4N_2O_4P_2Rh$: calcd C 62.33; H 4.65; N 2.69; found: C, 62.43; H, 4.68; N, 2.74.

*[Rh(cod)(L2)]BF_4 **2***

Yield 92.6 mg, 89%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, ^3J = 9 Hz, H*ar*, 4H), 8.00 – 7.95 (mbr, H*ar*, 4H), 7.56–7.53 (mbr, H*o*, 4H), 7.52–7.49 (mbr, H*ar*, 4H), 7.40–7.36 (mbr, H*ar*, 4H), 7.33–7.30 (mbr, H*ar*, 4H), 6.03–5.97 (mbr, 2H, H_{cod}), 5.11–5.04 (mbr, 2H, H_{cod}), 3.99 (sbr, 2H, N*H*), 3.88–3.81 (mbr, 2H, $H^*_{cyclohex}$), 2.46–2.41 (mbr, 2H, H_{cod}), 2.34–2.30 (mbr, 2H, H_{cod}), 2.31–2.26 (mbr, 2H, $H_{cyclohex}$), 2.26–2.19 (mbr, 2H, H_{cod}), 1.96–1.90 (mbr, 2H, H_{cod}), 1.88–1.84 (mbr, 2H, $H_{cyclohex}$), 1.60–1.49 (mbr, 2H, $H_{cyclohex}$), 1.49–1.42 (mbr, 2H, $H_{cyclohex}$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 147.66 ($C_{ar(q)}$), 146.92 ($C_{ar(q)}$), 132.39 ($C_{ar(q)}$), 131.67 ($C_{ar(q)}$), 131.36 ($C_{ar(q)}$), 128.40 (C_{ar}), 126.93 (C_{ar}), 126.77 (C_{ar}), 125.91 (C_{ar}), 121.30 (C_{ar}), 105.71 (C_{cod}), 105.63 (C_{cod}), 58.90 ($C^*_{cyclohex}$), 36.12 ($C_{cyclohex}$), 31.06 (C_{cod}), 29.29 (C_{cod}), 25.05 ($C_{cyclohex}$). $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$) δ 136.66 (d, $^1J_{RhP}$ = 220 Hz). Anal. Calcd for $C_{54}H_{48}BF_4N_2O_4P_2Rh$: calcd C 62.33; H 4.65; N 2.69; found: C 62.42; H 4.69; N 2.75.

*[Rh(cod)(L3)]BF_4 **3***

Yield 111 mg, 94%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (d, ^4J = 3 Hz, H*ar*, 2H), 7.03 (d, ^4J = 3 Hz, H*ar*, 2H), 6.71 (d, ^4J = 3 Hz, H*ar*, 2H), 6.65 (d, ^4J = 3 Hz, H*ar*, 2H), 5.75 – 5.64 (mbr, 2H, H_{cod}), 5.43–5.35 (mbr, 2H, H_{cod}), 3.86 (s, 6H, OMe), 3.84 (s, 6H, OMe), 3.25 (sbr, N*H*, 2H), 3.12–3.08 (mbr, 2H, $H^*_{cyclohex}$), 2.39–2.21 (mbr, 4H, H_{cod}), 2.20–2.04 (mbr, 4H, H_{cod}), 1.63 (s, 18H, t_{Bu}), 1.60 (s, 18H, t_{Bu}), 1.58–1.53 (mbr, 2H, $H_{cyclohex}$), 1.52–1.46 (mbr, 2H, $H_{cyclohex}$), 1.12–1.07 (mbr, 2H, $H_{cyclohex}$), 1.05–1.00 (mbr, 2H, $H_{cyclohex}$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 157.47 ($C_{ar(q)}$), 156.63 ($C_{ar(q)}$), 156.46 ($C_{ar(q)}$), 141.67 ($C_{ar(q)}$), 141.58 ($C_{ar(q)}$), 132.68 ($C_{ar(q)}$), 132.25 ($C_{ar(q)}$), 131.82 ($C_{ar(q)}$), 115.63 (C_{ar}), 115.03 (C_{ar}), 114.59 (C_{ar}), 114.36 (C_{ar}), 107.73 (C_{cod}), 104.61 (C_{cod}), 60.64 ($C^*_{cyclohex}$), 55.99 (C_{OMe}), 55.91 (C_{OMe}), 35.76 (C_{tBuq}), 34.56 ($C_{cyclohex}$), 32.34 (C_{tBu}), 32.09 (C_{tBu}), 30.33 (C_{cod}), 29.91 (C_{cod}), 24.56 ($C_{cyclohex}$). $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$) δ 135.26 (d, $^1J_{RhP}$ = 243 Hz). Anal. Calcd for $C_{58}H_{80}BF_4N_2O_8P_2Rh$: calcd C 58.79; H 6.81; N 2.36; found: C 58.83; H 6.85; N 2.40.

General procedure for asymmetric hydrogenation

[Rh(cod)(P,P)]BF_4 **1–3**, (2×10^{-3} mmol) and 2 mmol of substrate was dissolved in CH_2Cl_2 (2.5–7.5 ml) under argon. The yellow solution was introduced with a syringe into a 100 ml glass-lined, stainless steel autoclave containing a magnetic stirring bar. Hydrogen was introduced to the desired pressure and the reaction mixture was stirred at 25°C for 20 h. Then, the hydrogen pressure was released and the solution was passed through a short pad of silica and analyzed by GC.

Conclusions

The cationic Rh(I) complexes [Rh(cod)(P,P)]BF_4 with C_2-symmetric chiral diphosphoramidite ligands containing a chiral diamine backbone and two atropoisomeric biaryl units have been easily prepared and fully characterized to be tested as catalysts in the asymmetric hydrogenation of prochiral benchmark substrates dimethyl itaconate, methyl 2-acetamidoacrylate and (*Z*)-methyl-2-acetamido-3-phenylacrylate.

The rhodium complexes derived from diastereomeric diphosphoramidite ligands (*R,R,R$_a$,R$_a$*)-**L1** and (*R,R,S$_a$,S$_a$*)-**L2**, which contain two BINOL (2,2′-dihydroxy-1,1′-binaphthyl) units, can be successfully applied to asymmetric olefin hydrogenation.

An uncommon positive H_2 pressure effect on the enantioselectivity was observed in the hydrogenation of dimethyl itaconate catalyzed by Rh-complex with diphosphoramidite ligand (*R,R,S$_a$,S$_a$*)-**L2**, which contains two (*S*)-binaphthol moieties.

The rhodium complex with ligand **L3** in which each BINOL unit was replaced by two fluxional axially chiral 3,3′-dimethoxy-5,5′-di-*tert*-butyldiphenol groups exhibited very low activity as well as poor asymmetric induction.

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